STUDIES ON POLY(DIPHENYLENE ETHER SULPHONES)

A Thesis presented to the University of Surrey for the degree of Doctor of Philosophy

by

Terence Edwin Attwood, A.R.I.C.

Exploratory Division
Research Department
Imperial Chemical Industries Limited
Plastics Division
Bessemer Road
Welwyn Garden City
Herts

July 1973
SUMMARY

A kinetic study has been made of the preparation of poly(diphenylene ether sulphone) from monomers containing fluorine and phenoxide end groups. The rate of reaction depends on the structure of the compound containing the end groups, for example fluorine and phenoxide end groups on polymer react 40 times as fast as these groups in the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone (monomer) under the same conditions. Phenoxide in a para position to sulphone reacts approximately 10 times as fast as phenoxide in the ortho position.

The rate of reaction between poly(diphenylene ether sulphone) and fluoride ion was also studied as well as the equilibrium between this polymer and fluoride ion, which was found not to obey a simple theory.

The rate of reaction between poly(diphenylene ether sulphone) and phenoxide end groups (ether exchange reaction) was measured. The rate of the polymerisation reaction, the fluoride cleavage reaction and the ether exchange reactions were shown to be similar at equilibrium.

The preparation and properties of poly(diphenylene ether sulphone) containing ortho links, meta links, branching, 1,5 dioxydiphenalene units, 1-oxy-4-sulphonyl naphthalene units and 4,4'-dioxydiphenyl units are described.

The polymers had similar glass transition temperatures (230°) with the exception of poly m,p' (diphenylene ether sulphone) which was lower (175°).
The ortho and meta links decrease impact strength and increase modulus and density. Branching also decreases impact strength. The 1,5-dioxynaphthalene and 1-oxo-4-sulphonyl naphthalene units decrease the impact strength and increase the modulus, while 4,4'-dioxydiphenyl increases the impact strength and decreases the modulus and density.

The results indicate that for aromatic polymers the best physical properties are to be expected with a linear, para polymer containing no bulky side groups.
ACKNOWLEDGEMENTS

I would like to thank my supervisors Dr J B Rose of ICI Plastics Division and Professor J A Elvidge of the University of Surrey for their advice and guidance given in the course of the work for this thesis.

I would also like to thank the other members of ICI Plastics Division who have given help in this work especially Miss A Turner-Jones for X-ray data, Mr P I Vincent and Mr S Turner for help with physical property measurements and Mr A Bunn for running some nmr spectra.

I would also like to thank Miss N Buikers for typing this thesis.
## CONTENTS

<p>| PART 1 | INTRODUCTION | 1 |
| PART 2 | SYNTHESIS OF POLYMER INTERMEDIATES AND MODEL COMPOUNDS | 29 |
| PART 3 | KINETICS OF POLYMERISATION REACTIONS | 36 |
| 1 | Polymerisation of the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone | 36 |
| 2 | Polymerisation of the potassium salt of 4-fluoro-2'-hydroxydiphenyl sulphone | 46 |
| 3 | Polymerisation of the potassium salt of 4-(4-fluorobenzene sulphonyl)4'-(4-hydroxybenzenesulphonyl) diphenyl ether | 49 |
| 4 | Rate of reaction of the potassium salt of 4(benzene-sulphonyl)-4'-(4-hydroxybenzenesulphonyl)diphenyl ether with 4(benzenesulphonyl)4'-(4-fluorobenzenesulphonyl) diphenyl ether | 53 |
| 5 | Rate of reaction of the dipotassium salt of 4,4'-dihydroxydiphenyl sulphone with 4,4'-difluorodiphenyl sulphone | 57 |
| 6 | Comparison of the three polymerisation systems | 63 |
| PART 4 | KINETICS OF THE ETHER EXCHANGE REACTION | 66 |
| PART 5 | POLYCONDENSATION EQUILIBRIUM AND CLEAVAGE OF POLY(DIPHENYLENE ETHER SULPHONE) BY FLUORIDE ION | 78 |
| 1 | Introduction | 78 |
| 2 | Measurement of the equilibrium constant | 87 |
| 3 | Polymerisation experiments | 88 |
| 4 | Cleavage experiments | 97 |
| 5 | Kinetics of the cleavage of poly(diphenylene ether sulphone) by fluoride ion | 102 |
| 6 | Cleavage using potassium fluoride | 104 |
| 7 | Cleavage of polymer with potassium fluoride in the presence of methyl chloride | 112 |</p>
<table>
<thead>
<tr>
<th>Page No</th>
<th>Section Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>114</td>
<td>Cleavage of poly(diphenylene ether sulphone) with potassium fluoride in the presence of 4,4'-difluoro-diphenyl sulphone</td>
</tr>
<tr>
<td>121</td>
<td>Calculation of K* from kinetic data</td>
</tr>
<tr>
<td>123</td>
<td>Cleavage experiments with soluble halides</td>
</tr>
<tr>
<td>130</td>
<td>Comparison of the rates of reactions occurring at equilibrium</td>
</tr>
<tr>
<td>132</td>
<td>PART 6 PREPARATION OF POLY(DIPHENYLENE ETHER SULPHONE) CONTAINING ORTHO, META AND PARA LINKAGES</td>
</tr>
<tr>
<td>151</td>
<td>PART 7 PREPARATION OF BRANCHED POLYMERS</td>
</tr>
<tr>
<td>158</td>
<td>PART 8 PREPARATION OF POLYMERS WITH OTHER STRUCTURAL VARIATIONS</td>
</tr>
<tr>
<td>162</td>
<td>PART 9 PHYSICAL PROPERTIES</td>
</tr>
<tr>
<td>162</td>
<td>1 Molecular weight</td>
</tr>
<tr>
<td>164</td>
<td>2 Molecular weight distribution</td>
</tr>
<tr>
<td>175</td>
<td>3 Crystallinity and glass transition temperature</td>
</tr>
<tr>
<td>181</td>
<td>4 Solution and melt viscosity</td>
</tr>
<tr>
<td>186</td>
<td>5 Impact strength</td>
</tr>
<tr>
<td>200</td>
<td>6 Flexural modulus</td>
</tr>
<tr>
<td>204</td>
<td>7 Tensile stress-strain testing</td>
</tr>
<tr>
<td>213</td>
<td>8 Density measurements</td>
</tr>
<tr>
<td>217</td>
<td>9 Dynamic mechanical properties</td>
</tr>
<tr>
<td>222</td>
<td>10 Brittle temperature testing</td>
</tr>
<tr>
<td>225</td>
<td>PART 10 DISCUSSION OF THE EFFECT OF STRUCTURE ON PROPERTIES</td>
</tr>
<tr>
<td>225</td>
<td>1 Repeat unit isomerization and chain branching</td>
</tr>
<tr>
<td>230</td>
<td>2 Other structural variations</td>
</tr>
<tr>
<td>Section</td>
<td>Page No</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>PART 11 EXPERIMENTAL</td>
<td>233</td>
</tr>
<tr>
<td>Preparation of polymer intermediates and model compounds</td>
<td>233</td>
</tr>
<tr>
<td>The kinetic experiments</td>
<td>265</td>
</tr>
<tr>
<td>1  Polymerisation experiments</td>
<td>265</td>
</tr>
<tr>
<td>2  Ether exchange reactions</td>
<td>282</td>
</tr>
<tr>
<td>3  Fluoride cleavage reactions</td>
<td>284</td>
</tr>
<tr>
<td>Physical properties</td>
<td>295</td>
</tr>
<tr>
<td>PART 12 APPENDIX</td>
<td>306</td>
</tr>
<tr>
<td>Computer programmes</td>
<td>306</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>311</td>
</tr>
</tbody>
</table>
Part 1 INTRODUCTION

1. Preparation of poly(arylene sulphones)

Poly(arylene sulphones) may be prepared by two main polycondensation reactions. A review of these and other methods is given in reference 1.

(1) \[ \text{ArH}_2 + \text{Ar}'(\text{SO}_2\text{Cl})_2 \rightarrow [\text{ArSO}_2 - \text{Ar}'\text{SO}_2] + 2\text{HCl} \]
(Ar and Ar' are arylene residues)

(2) \[ \text{Ar(OM)}_2 + \text{Ar'}X \rightarrow [\text{Ar} - \text{O} - \text{Ar'} - \text{O}] + 2\text{MX} \]
(M is an alkali metal, X a halogen, Ar' is an arylene residue containing sulphone)

Reaction (1) is an electrophilic aromatic substitution reaction in which a proton is displaced by some form of the sulphonylium cation, Ar'SO⁺, to form a sulphone.

The second reaction (2) is a nucleophilic substitution in which a halide is displaced by phenoxide ion to form an ether bond.

2. Preparation and structure of poly(arylene sulphones) by the electrophilic substitution reaction

The Friedel Crafts reaction (1) has been used to prepare many high molecular weight polysulphones in the melt and in suitable solvents e.g. nitrobenzene using \(\text{SbCl}_5\), \(\text{AlCl}_3\) or \(\text{FeCl}_3\) as catalyst (2-10).

The reaction has been carried out using more than 1 mole of Friedel Crafts catalyst (e.g., aluminium chloride) per mole of sulphonyl chloride (7-11).
Under these conditions, however, 1.2 to 1.5 times the theoretical amount of hydrogen chloride was evolved indicating that some reaction between aluminium chloride and the polymer chain had occurred. There is elemental analysis and nmr evidence that these side reactions introduce structural irregularities into the chain.

The polysulphonylation reaction may also be carried out using catalytic amounts of a suitable Friedel Crafts catalyst e.g. ferric chloride, antimony pentachloride, or indium chloride. Under these conditions the theoretical amount of hydrogen chloride is evolved. (8, 10, 12)

The structure of the reactants is important in determining whether high molecular weight polymer will be produced. High molecular weight polymers are not obtained from systems where the sulphonyl chloride is attacking a ring containing an electron withdrawing group such as -SO₂⁻ or -CO⁻. The highest polymers are obtained when attack is on a ring activated to electrophilic attack e.g. diphenyl ether. 8

The preparation of poly(diphenylene ether sulphone) (I) by polysulphonylation in the melt and in nitrobenzene solution has been studied in some detail. Three reactions were used to prepare the polymer:

\[
\begin{align*}
(3) & \quad \text{ClSO}_2\backslash\text{O-Cl} + \text{SO}_2\text{Cl} \quad \xrightarrow{-\text{HCl}} \quad \text{[-\text{O-Cl}]}_n \quad \text{I} \\
(4) & \quad \text{ClSO}_2\backslash\text{O-Cl} + \text{ClSO}_2\text{Cl} \quad \xrightarrow{-\text{HCl}} \quad \text{[-\text{O-Cl}]}_n \quad \text{II} \\
(5) & \quad \text{ClSO}_2\backslash\text{O-Cl} + \text{SO}_2\text{Cl} \quad \xrightarrow{-\text{HCl}} \quad \text{[-\text{O-Cl}]}_n \quad \text{II}
\end{align*}
\]

The melt polymerisations were carried out by melting the reactants under
a stream of nitrogen with the catalyst and then raising the temperature to about 200°. The reaction was completed by grinding up the cooled polymer and reheating to 250° under vacuum to remove the last traces of hydrogen chloride formed. (8).

The solution polymerisations were carried out in nitrobenzene solution at 120 - 140° using catalytic amounts of ferric chloride or antimony pentachloride as catalyst. (11, 13)

The melt polymers contained some insoluble polymer while polymer from solution polymerization was completely soluble. The insoluble polymer in the melt polymers was probably caused by decomposition of the sulphonyl chlorides at the higher temperature used, producing allyl radicals which attacked the polymer chain.

In the three reactions, (3), (4) and (5) there is the possibility of obtaining ortho(II) or branched (III) structures in the polymer as well as the all para structure (I). The structure of the polymers made by these three reactions in the melt and in solution has been investigated by nmr analysis of the product. (11, 12, 13)

The nmr spectrum of polymer from reaction (3) and (5) showed a normal AB quartet with chemical shifts 3.00 and 3.75T, indicating a structure with repeat units I containing two types of non-equivalent protons (ortho to sulphone and ortho to ether). The coupling constant (J value) of 8c/s confirms that the non-equivalent protons are ortho to each other i.e para substitution.

The nmr spectrum of polymers from reaction (4) were more complicated
with several additional peaks at the high field side of the main resonances. These additional peaks were assigned to the presence of ortho substituted structures (II) by comparison with the spectra of model compounds 4,4'-dinitro diphenyl ether and 2,4'-dinitro diphenyl ether. The spectra of 4,4'-dinitro diphenyl ether gave an AB quartet while a mixture with the 2,4'-isomer had additional peaks to high field. The mixture gave a spectrum analogous to the spectrum of polymer from reaction (4) (but with different chemical shifts).

The difference in the reactions is due to the structure of the reactants. In reactions (3) and (5) sulphone linkages are formed by substitution at rings linked via oxygen to rings containing sulphone or sulphonyl chloride substituents. These electron withdrawing groups orientate the substitution to the para position. The orientation to the para position could be due to the inductive effect of the sulphone which will deactivate ortho more than para, or to an effect of dipoles. The dipole of the sulphone may line up parallel with the transition state for ortho substitution and anti parallel for para substitution, thereby favouring para substitution. In reaction (4) 50% of the sulphone linkages are formed by substitution on diphenyl ether where there are no electron withdrawing groups so that some ortho substitution can occur.

Branched structures such as (III) in the polymer could be formed by attack of sulphonyl chloride on polymer chains, although this is less likely because the aromatic nuclei in the polymer chain are deactivated to electrophilic attack by the electron withdrawing effect of the sulphone groups. Model experiments have shown that this type of attack is possible, with substitution taking place ortho to the ether bond.
The reaction between 1 mole of diphenyl ether and 8 moles of diphenyl ether 4,4'-disulphonyl chloride was examined in nitrobenzene solution using ferric chloride catalyst. (11)

After 2.5 moles of hydrogen chloride had been evolved excess diethylamine was added to convert residual sulphonyl chloride groups to sulphonodiethyl amide. The nmr spectrum in deuterio chloroform showed minor peaks at 1.23 T and between 2 and 3.2 T. These peaks were assigned with reference to the spectrum of 2,4,4'-trinitrodiphenyl ether. The peak at 1.23 T was assigned to the proton HA and those between 2 and 3.2 to the protons HB and HC in a 2,4-disulphonyl phenoxy group (IV).

\[
\text{HC} \quad \text{HB} \\
\text{SO}_2^- \quad \text{SO}_2^- \\
\text{HA}
\]

IV

The use of accumulated nmr spectra and hydrogen chloride evolution versus time data has enabled the % of branching (III) and ortho para repeat units (II) in the polymers made by the reactions (3) and (5) to be estimated.(13)

A peak at 1.40 T on an accumulated nmr spectrum, recorded in dimethyl sulphone, of a polymer made by reaction (4) in nitrobenzene solution was assigned to the proton H_A in the branched structure (IV). The area of the band at 1.40 T was compared with the areas of the other resonances in the polymer. Calculation showed that the polymer (made by reaction (4)) had 1.7 branched units (IV) per hundred polymer repeat units.

Polymer prepared by reaction (3) in solution and reaction (5) in the melt were similarly examined. No resonance at 1.40 T was observed with polymer prepared by reaction (3) while polymer from reaction (5) had 0.4 to 0.7 of branched units (IV) per 100 polymer repeat units.

Reaction (4) has been shown to produce polymer with ortho sulphonyl
phenoxyl structures and it is likely that the para hydrogen in these is more reactive for steric reasons. The substitution reactions which could produce branching are shown below (reactions (6) and (7))

\[(6) \quad -\overset{\text{0}}{\text{Ph}} - \overset{\text{SO}_2^-}{\text{Cl}} \rightarrow -\overset{\text{0}}{\text{Ph}} \overset{\text{SO}_2^-}{\text{Cl}} \]

\[(7) \quad -\overset{\text{0}}{\text{Ph}} \overset{\text{SO}_2^-}{\text{Cl}} + -\overset{\text{SO}_2^-}{\text{Cl}} \rightarrow -\overset{\text{0}}{\text{Ph}} \overset{\text{SO}_2^-}{\text{Cl}} \]

Reaction (6) is faster than reaction (7) although both reactions are much slower than the monosulphonylation reactions. This explains why more branching is formed in reaction (4) (where ortho structures are present) than reactions (3) and (5) (where no ortho structures are present).

The % of ortho units II present in polymer from reaction (4) has been estimated by following the hydrogen chloride evolution with time graphs for reactions (3) and (4) carried out in nitrobenzene solution. In these experiments excess diphenyl ether-4,4'-disulphonyl chloride was added to the reactants. The reaction continues beyond 100% (corresponding to sulphonylation at phenoxyl groups) and the reaction is faster when ortho sulphonyl phenoxyl groups are present (reaction (6)). The reaction may be divided into three parts: an initial rapid reaction to 100% (sulphonylation at phenoxyl groups), an intermediate reaction (sulphonylation at ortho phenylene groups) and a final slow reaction (sulphonylation at para phenylene units). Reaction (3) showed virtually no intermediate reaction (no ortho phenylene groups present) while reaction (4) showed this intermediate reaction.

From the extent of this intermediate reaction in (4) the % of ortho sulphonyl phenoxyl groups present in polymer from reaction (4) was estimated at 11%. 
These hydrogen chloride evolution data and nmr data showed that polymer made by reaction (4) contains units (I), (II) and (III) in the approximate proportions 90:10:1.6, whereas polymers from reactions (3) and (5) consist essentially of the all para structure (I).

Preparation of poly(arylene sulphones) by the nucleophilic substitution reaction

Polysulphones have been prepared from the nucleophilic substitution reaction (2). (14, 15)

In this nucleophilic substitution reaction a halogen is displaced by a phenoxide to form an ether bond. The halogen is activated to nucleophilic attack by electron withdrawal by a sulphone group positioned para to the halogen. The displacement of the halogen is believed to occur via an intermediate complex as shown below.

\[
-\text{R}-O^- + \text{Cl}-\text{R}_2\text{SO} \to -\text{R}-O-\text{R}_2\text{S}=\text{O} + \text{Cl}^- 
\]

The electron withdrawing sulphone group aids reaction by stabilising the intermediate complex. Since formation of the complex is rate determining the kinetics are expected to be second order:

\[
\text{Rate} = k \left[ -\text{R}-O^- \right] \left[ \text{Cl}-\text{R}_2\text{SO} \right]
\]

The polymer (V) from the reaction of the dipotassium salt of Bisphenol A and 4,4'-dichlorodiphenyl sulphone (reaction 8) is a commercially available polymer manufactured by the Union Carbide Corporation.

\[
\text{n KO}-\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{OK} + \text{n Cl}-\text{C}_6\text{H}_4\text{SO}_2-\text{C}_6\text{H}_4-\text{Cl} \to -\text{[O-C}_6\text{H}_4\text{C}_6\text{H}_4\text{O-SO}_2-\text{C}_6\text{H}_4]}_{-}\text{n} + 2\text{nKCl}
\]
These reactions are carried out in dipolar aprotic solvents such as dimethyl sulfoxide or sulfolane which enhance the rates of nucleophilic substitution reactions. Dipolar aprotic solvents are defined as solvents with dielectric constant >15 which cannot donate suitably labile hydrogen atoms to form strong hydrogen bonds with a species. Examples are: N,N dimethylformamide, dimethyl sulfoxide, tetra methylene sulphone (sulfolane). Protic solvents are those which are hydrogen donors; examples are water, methanol, formamide.

Poly(diphenylene ether sulphone) may be prepared by a one or a two component system (17, 18) (reactions 9 and 10).

\[
\begin{align*}
(9) & \quad \text{n/2 } \text{Cl}-\text{SO}_2-\text{Cl} + \text{n/2 } \text{KO-SO}_2-\text{OK} \rightarrow \text{-[SO}_2-\text{O-}_{\text{n}}-\text{]} + \text{nKCl} \\
(10) & \quad \text{n } \text{Cl-SO}_2-\text{OK} \rightarrow \text{-[SO}_2-\text{O-}_{\text{n}}-\text{]} + \text{nKCl}
\end{align*}
\]

The polymer prepared by reaction (9) has been shown to have the all para structure indicated i.e no rearrangement occurs during the reaction. (12)

The nmr spectrum showed only a normal AB quartet with chemical shifts 2.99 ppm and 3.72 ppm. The coupling constant was 8 cps. This indicates 2 non equivalent types of proton positioned ortho to each other as occurs in the all para structure. The one component system has some advantages over the two component system: (i) both reactive groups are in the same molecule so that the stoichiometry is always correct (ii) the potassium salt is more soluble in the dipolar aprotic solvent than the bispotassium salt employed in the two component system. A disadvantage is that the reactivities of the functional groups are both reduced compared with those in the two component system. (19)
Nucleophilic cleavage of ether bonds in polysulphone

The ether bonds in polysulphone are known to be susceptible to cleavage by nucleophilic reagents such as sodium hydroxide and sodium phenate. This is as expected since the ether bonds are activated to nucleophilic attack by the electron withdrawing effect of the sulphone group. Johnson and Farnham could not find any evidence for cleavage of the ether bonds in the polysulphone (V) by fluoride ion in dimethyl sulphoxide at 150°. A polymerisation run in the presence of potassium fluoride showed no significant difference in reduced viscosity (RV) over a control experiment.

The reduced viscosity (RV) of polymer is related to the molecular weight of the polymer and may be defined as

\[
\eta_{\text{red}} = \frac{\eta - \eta_0}{\eta_0 \cdot C}
\]

where \(\eta_{\text{red}}\) = reduced viscosity (RV)
\(\eta\) = viscosity of polymer solution
\(\eta_0\) = viscosity of pure solvent
C = concentration of polymer in g/100 ml

The reduced viscosity is an easy measurement to make and enables a comparison of molecular weight for one particular polymer to be made: the higher the reduced viscosity the higher the molecular weight.

In this thesis the cleavage of poly(diphenylene ether sulphone) by fluoride ion is shown to occur in dipolar aprotic solvents. An equilibrium (11) is believed to exist between polymer and fluoride ion in solution.

\[
\text{Low polymer} \xrightarrow{\text{OK} + \text{F}^{-}} \text{High polymer} + \text{KF}
\]
Alkali metal fluorides are known to act as nucleophiles, particularly in dipolar aprotic solvents. The effectiveness of the fluorides in these reactions is:

$$\text{CsF} > \text{RbF} > \text{KF} > \text{NaF} > \text{LiF}$$

For example lithium fluoride and sodium fluoride do not react with 2,4-dinitro chlorobenzene after two hours at 195°, whereas potassium fluoride gives 51% rubidium fluoride 88% and caesium fluoride 98% of the 2,4-dinitrofluorobenzene.

\[
\begin{align*}
\text{Cl} & \quad \text{F}^- \quad \text{200°C} \\
\text{NO}_2 & \quad \text{NO}_2
\end{align*}
\]

The chlorine group in 2,4-dinitrochlorobenzene is strongly activated to nucleophilic attack by the electron withdrawal effect of the two nitro groups. The nitro group withdraws electrons by an inductive and a conjugative effect.

\[
\begin{align*}
\text{eg} & \\
\text{Cl} & \quad \text{N} & \quad \text{NO}_2 \\
\text{Cl} & \quad \text{N} & \quad \text{NO}_2
\end{align*}
\]

The reaction proceeds more readily in certain dipolar aprotic solvents. The reaction between potassium fluoride and 2,4-dinitro chlorobenzene goes at 200° in nitrobenzene $^{(24, 25)}$.

G C Finger and C W Knuse have found that the reaction will proceed at 100° in dimethyl sulfoxide and N,N dimethyl formamide $^{(26)}$. The chlorine in 4-nitro chlorobenzene may be replaced by fluorine using potassium fluoride if the reaction is carried out in dimethyl sulfoxide or N,N dimethyl formamide. The chlorine in this compound is only moderately activated to nucleophilic attack by the presence of the nitro group.
The halogen groups in hexachloro and hexabromo benzene have also been replaced by fluorine using potassium fluoride\(^{(27,28,29)}\).

In these compounds the halogen to carbon bond is activated to nucleophilic attack by the overall electron withdrawing effect of the other halogen substituents. The chlorine or bromine substituents in an aromatic system may withdraw electrons by an inductive effect due to their greater electronegativity but can also donate a lone pair of electrons (conjugative effect). The overall effect however is one of electron withdrawal\(^{(30)}\).

An example of the reaction is given by G G Yacobson and N E Minonova\(^{(29)}\). Hexabromobenzene was heated with potassium fluoride in an autoclave for ten hours at 380-390\(^{\circ}\)\(\text{C}\), followed by fifteen hours at 410-430\(^{\circ}\)\(\text{C}\). The products obtained were hexafluorobenzene (4%), pentafluorobromobenzene (23%), tetrafluorodibromobenzene (40%), trifluorotribromobenzene (20%), difluorotetra-benzene (2%).

This type of reaction may be carried out at much lower temperatures (<230\(^{\circ}\)\(\text{C}\)) if tetramethylene sulphone (sulpholane) is used as solvent\(^{(31,32)}\).

Hexafluorobenzene, pentafluorochlorobenzene and tetrafluorodichlorobenzene were prepared by heating mixtures of tri, tetra and penta - fluorochloro - benzenes with potassium fluoride in tetramethylene sulphone at less than 230\(^{\circ}\)\(\text{C}\).

In water ( a protic solvent) the nucleophilicity of the halides is\(^{(33,34)}\)

\[ \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^- \]

Values for the nucleophilic constant for these anions in water have been calculated by A B Ash, P Blumberg and C L Stevens\(^{(35)}\).

The values were \(\text{F}^- = 2.2\), \(\text{Cl}^- = 3.02\), \(\text{Br}^- = 3.89\), \(\text{I}^- = 5.05\), \(\text{OH}^- = 6.20\).
In dipolar aprotic solvents for example dimethyl sulfoxide the reverse order of nucleophilicity is found{33,36}.

\[ F^- >> Cl^- > Br^- > I^- \]

A. J. Parker has suggested that these differences are due to differences in ion solvation{16}.

In protic solvents anions are solvated by ion-dipole interactions together with a strong hydrogen bonding which is greater for small anions, so that solvation decreases in the series:

\[ OH^- F^- >> Cl^- > Br^- > I^- \]

In dipolar aprotic solvents anions are solvated by ion-dipole interaction together with an interaction due to the polarizability of the anions and the solvent molecules. This will be greater for large anions, so that solvation of anions by dipolar aprotic solvents decreases in the reverse order to that above for protic solvents. Fluoride ion is thus the most powerful nucleophile of the halides in dipolar aprotic solvents.

R. F. Rodewald and co-workers{36} have measured the solvation of chloride, bromide and iodide ions in dimethyl sulfoxide and water. They find the same order of solvation in the two solvents Cl^- > Br^- > I^- although the difference between the ions is much greater in water. They also found that rates of displacement on n-propyl tosylate by halides in aqueous dimethyl sulfoxide are in the order I^- > Br^- > Cl^- while in dimethyl sulfoxide the order was Cl^- > Br^- > I^-. They attribute the reversed order of nucleophilicity to the smaller difference in halide solvation in dimethyl sulfoxide than in water. They assume the nucleophilicities of the unsolvated halides to be Cl > Br > I and this order is not changed by solvation in dimethyl sulfoxide. In water, however, the extremely strong chloride
hydration decreases the reactivity of the ion to less than that of the weakly solvated iodide.

5 Equilibria in polymers prepared by polycondensation

An equilibrium of the type (11) between polysulphone and fluoride ion has not been reported in the literature.

An analogous equilibrium is known to exist with poly(ethylene terephthalate). Poly(ethylene terephthalate) is a condensation polymer of terephthalic acid and ethylene glycol:

\[
\text{HOOC-} \begin{array}{c}
\text{C} \\
\text{H}_2
\end{array} \text{COOH} + \text{HO-CH}_2\text{CH}_2\text{-OH} \rightarrow -[\text{-O-CH}_2\text{CH}_2\text{-O-}]_n
\]

The polymer may be prepared by this route but is more usually prepared by reaction (13) since direct esterification is usually slow.

\[
\text{CH}_3\text{-O-} \begin{array}{c}
\text{C} \\
\text{H}_2
\end{array} \text{OCH}_3 + 2\text{HO-CH}_2\text{CH}_2\text{-OH} \rightarrow
\]

\[
\text{HO-CH}_2\text{CH}_2\text{-O-} \begin{array}{c}
\text{C} \\
\text{H}_2
\end{array} \text{O-CH}_2\text{CH}_2\text{-OH} + 2\text{CH}_3\text{OH}
\]

\[
-\[\text{-O-CH}_2\text{CH}_2\text{-O-}]_n + \text{HO-CH}_2\text{CH}_2\text{OH}
\]

Dimethylterephthalate is reacted with 2 moles of ethylene glycol with elimination of methanol. This is followed by polycondensation to give poly(ethylene terephthalate) and ethylene glycol. The reaction is completed under reduced pressure to remove the ethylene glycol formed and achieve high molecular weight.

D A S Ravens and I M Ward have studied the equilibrium for the polyesterification reaction (14) in the solid phase.
In this equilibrium the back reaction (which corresponds to cleavage of ether bonds by fluoride in (11)) is hydrolysis of the ether linkages by water. This reaction would normally be prevented by removing the water under vacuum. The equilibrium (14) could not be established directly since two other reaction were important: oxidation and polycondensation. Polycondensation is defined by reaction (15)

\[
2 \sim \text{CH}_2\text{-CH}_2\text{-OH} \rightleftharpoons \sim \text{COO}^{-}\text{-CH}_2\text{-CH}_2\text{-OH} + \text{HO-CH}_2\text{-CH}_2\text{-OH}
\]
The effect of structure on physical properties of polymers

The effect of repeat unit isomerization in aromatic polymers such as poly(arylene sulphones) has not previously been reported in the literature.

It is known that a change in mechanical properties is often observed when structural changes are made to a polymer. For example, the impact strengths of the amorphous poly(alkyl methacrylates) (VI) are dependent on the nature of the side groups.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_2 \text{-COOR}
\end{array}
\]

VI

The impact strength of a polymer is a measure of its toughness or resistance to breakage. The test is performed under high speed conditions. It may be a tensile test in which case it is an extension of tensile stress versus strain measurements to high speeds. Other measures of impact strength are the Izod and Charpy testers which employ a pendulum weight to break the specimen. The Izod test uses a notched beam type of specimen which is struck on the free end, while the Charpy test uses a beam supported at two points near the ends which is struck in the centre by the pendulum.

The impact strength is dependent on the test conditions for example temperature. The impact strength also depends on the presence of a notch in the specimen. A notch increases the severity of the test by concentrating the applied stress. The impact strength of a polymer decreases as the notch tip radius is reduced. The dependence of impact strength on notch tip radius has been used to divide polymers into four main groups with respect to impact strength.
The four groups are shown below with some examples. The classification applies at 20°, at other temperatures some of the polymers may change group.

<table>
<thead>
<tr>
<th>Group</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>brittle when unnotched</td>
</tr>
<tr>
<td></td>
<td>Polymethylmethacrylate</td>
</tr>
<tr>
<td></td>
<td>Polystyrene</td>
</tr>
<tr>
<td>2</td>
<td>IS(2) &lt;20KJ/m²</td>
</tr>
<tr>
<td></td>
<td>Polypropylene</td>
</tr>
<tr>
<td></td>
<td>Polyethyleneterephthalate</td>
</tr>
<tr>
<td>3</td>
<td>IS(½) &lt;10KJ/m²</td>
</tr>
<tr>
<td></td>
<td>Polyvinyl chloride</td>
</tr>
<tr>
<td></td>
<td>Nylon</td>
</tr>
<tr>
<td></td>
<td>High density polyethylene</td>
</tr>
<tr>
<td>4</td>
<td>IS(½) &gt;10KJ/m²</td>
</tr>
<tr>
<td></td>
<td>Polycarbonate</td>
</tr>
<tr>
<td></td>
<td>Low density polyethylene</td>
</tr>
<tr>
<td></td>
<td>Poly(tetrafluoroethylene)</td>
</tr>
</tbody>
</table>

IS(2) refers to the impact strength with a 2 mm notch tip radius (blunt notch), IS(½) refers to the impact strength with a ½ mm notch tip radius (sharp notch). The test using a ½ mm notch radius is more severe than that with a 2 mm notch.

The impact strength of thermoplastics increases with temperature and, provided the test is severe enough, a sharp increase will occur near the glass transition temperature as the polymer becomes more rubber like. If the test is not severe enough this increase may occur well before the glass transition temperature and no further increase will be observed at the glass transition temperature.

For comparison purposes the test may be carried out at a particular temperature (e.g., room temperature) using either an unnotched specimen or a specified notch in the specimen.
The impact strength of crystalline polymers will depend on the per cent crystallinity. These polymers have high impact strength if their glass transition is below the test temperature. The impact strength decreases as the degree of crystallinity increases. High density polyethylene (crystallinity 70 to 80 per cent) has an impact strength of 2 ftlb/in while low density polyethylene (crystallinity approximately 50 per cent) has an impact strength greater than 10 ftlb/in.\(^4\)

Correlation of the impact strength of crystalline polymers with their chemical structure is more difficult for this reason.

The poly(alkylmethacrylates) are amorphous and their impact strengths may be compared. Poly(n propyl methacrylate) and poly(cyclo hexyl methacrylate) both have lower impact strengths than poly(methyl methacrylate). Poly(cyclo hexyl methacrylate) in particular is extremely brittle at room temperature\(^44\).

J Heijboer has given figures for the unnotched impact strength of these polymers\(^45\).

At 20°C the impact strength of poly(methyl methacrylate) was 15 kg f cm/cm\(^2\), poly(n-propyl methacrylate) 12 kg f cm/cm\(^2\) while for a 40:60 (wt %) copolymer of methyl methacrylate and cyclohexyl methacrylate it was 9 kg f cm/cm\(^2\). The difference in impact strength is presumably due to the size of the side group. The brittle poly(cyclohexyl methacrylate) having a very bulky side group.

Similarly polystyrene which has bulky phenyl groups along the main chain has a much lower impact strength than polyvinyl chloride.

Attempts have been made to correlate physical properties such as impact strength with dynamic mechanical properties\(^45\).
The main transition of amorphous polymers occurs at their softening point (glass transition temperature). At this temperature the polymer changes from a hard glass like solid to a soft rubber like material. A decrease in shear modulus (from $10^9$ to $10^6$ N/M$^2$) occurs on passing through the glass transition temperature, accompanied by a peak in the damping or mechanical loss of $\tan \delta > 1$.

The modulus of a polymer is a measure of its stiffness and is the slope of a stress versus strain graph for the polymer. A decrease in modulus of the polymer corresponds to a decrease in stiffness. When a sinusoidal stress is applied to a polymer the deformation is not completely in phase with the stress. The modulus may then be expressed as $E = E' + iE''$, where $E'$ is the in phase or real component, and $E''$ the out of phase or imaginary component. The damping or mechanical loss, $\tan \delta$ is then given by

$$\tan \delta = \frac{E''}{E'}$$

where the angle $\delta$, is the phase angle between the stress and the strain (41)

The changes in modulus and $\tan \delta$ on passing through the glass transition temperature are shown in the following diagram:
At the glass transition temperature (Tg) parts of the main chain are able to move freely. At temperatures below the main transition secondary transitions are often found. The damping peak reaches a tan δ of 0.01 to 0.1 for these transitions. Nielsen suggests that brittle polymers generally have no low temperature transitions or very weak ones, while the tougher amorphous polymers always have large secondary damping peaks below room temperature.

There are some examples where this holds: for example the amorphous polycarbonate of Bisphenol A (VII) which is very tough has a large secondary transition at -100°, the amorphous polysulphone (V) which is also tough has a secondary transition at -100°.

\[
[-\text{CH}_3\text{C}-\text{O}]-\text{O}-\text{C}-\text{O} \]_n

Polymethyl methacrylate (an amorphous polymer) which is brittle compared with polycarbonate or polysulphone does not show a secondary transition below room temperature.

The two partly crystalline polymers, high density polyethylene and poly(oxymethylene) both of which have high impact strengths in an unnotched test show pronounced secondary transitions below room temperature. For high density polyethylene this is at -120°, for poly(oxymethylene) it is at -70°. These transitions are presumably due to molecular movement of segments of the main chain and probably correspond to the glass transition temperature of the amorphous region of the polymer.

Heijboer points out several examples where there is no correlation between impact strength and the damping maxima below room temperature. Poly(n-propyl methacrylate) has a damping peak at -185°, although its impact strength is similar to poly(methyl methacrylate) which does not have this
peak. A copolymer of methyl methacrylate and cyclohexyl methacrylate which is very brittle compared with methyl methacrylate has a damping peak at -80°.

The damping peaks in these two polymers are attributed to movements of the side chain which do not in this case appear to influence the impact strength. For example the damping peaks in the cyclohexyl methacrylate polymer is due to the chair chair transitions of the cyclohexyl ring(45).

A copolymer of methyl methacrylate and acrylonitrile has a higher impact strength than poly(methyl methacrylate) but does not show any secondary transition with which this could be correlated.

Poly(2,6-dimethyl-p-phenylene oxide) (VIII) has a higher impact strength than polycarbonate and both polymers are much tougher than poly(methyl methacrylate)(45).

\[
\text{VIII}
\]

Poly(2,6-dimethyl-p phenylene oxide) however does not show a pronounced secondary transition below room temperature.

The presence of a secondary damping peak therefore does not always mean a polymer will be tough, and its absence does not always mean the polymer will be brittle.

Attempts have also been made to correlate physical properties with the number of bonds per unit area or volume (48,49).

For example P I Vincent has correlated critical tensile strength with the number of backbone bonds per nm². The critical tensile strength is the stress required to break a polymer sample in a tensile test at the temperature where the polymer changes from a tough to a brittle type fracture as illustrated over.
The molecular cross-sectional area perpendicular to the chain axis is given by:

\[
\text{Molecular cross-sectional area} = \frac{\text{Weight of repeat unit}}{\text{Sample density} \times \text{length of repeat unit}}
\]

The reciprocal of the molecular cross-sectional area is the number of bonds/nm^2 which is related to the effective strength of backbone bonds. A good correlation between critical tensile strength and bonds/nm^2 was obtained. The critical tensile strength is related to impact strength.

Polymers with high impact strength (and critical tensile strength) have the largest number of bonds per nm^2. For example polycarbonate 3.04 bonds/nm^2, poly(oxymethylene) 5.41. Polymers with low impact strength have a smaller number of bonds per nm^2: polymethyl methacrylate 1.50, polystyrene 1.35. The relationship explains some of the examples given by Heijboer where impact strength is not correlated with damping. The copolymer of methyl methacrylate and acrylonitrile will have more bonds per nm^2 than poly(methyl methacrylate). This is because polyacrylonitrile has 3.45 bonds/nm^2 compared with 1.50 for poly(methyl methacrylate). The higher impact strength of the acrylonitrile/methyl methacrylate copolymer is therefore explained.

Poly(cyclohexyl methacrylate) will have fewer bonds per nm^2 because of
the bulky side group, than polymethyl methacrylate. This explains its lower impact strength.

Some other results for example the higher impact strength of poly(2,6-dimethyl-p-phenylene oxide) compared with polycarbonate are not explained in these terms: both polymers have a similar number of bonds/nm².

L Halliday and W A Holmes-Walker relate the relative number of network bonds per unit volume (Ncr) to certain physical properties.

\[
Ncr = \frac{P \cdot X \cdot (CN)}{2y}
\]

P = density of polymer, X = number of network atoms in the repeat unit, y = molecular weight of repeat unit.

\[
CN = \text{average connection number} = \frac{2a + 3b + 4c}{a + b + c}
\]

a = number of 2-connected, b = number of 3-connected, and c = number of 4-connected atoms in repeat unit.

The relative number of network bonds per unit volume (Ncr) was shown to correlate fairly well with bulk modulus, Young's modulus, hardness and coefficient of expansion.

7. The effect of heat ageing on properties of polymers

The storage of moulded specimens of many thermoplastics at temperatures below the glass transition results in changes in mechanical properties.

Polycarbonate specimens held at 100 - 130° (glass transition temperature
142° undergo increases in flexural strength and tensile strength and a reduction in notched impact strength. (50)

Similarly on ageing the polysulphone (V) at 150° (glass transition temperature 195°) for one to three months the tensile yield strength increases from an initial 10,200 lb/in^2 to 13,000 lb/in^2 while tensile modulus increases from 360,000 to 400,000 lb/in^2. The tensile impact strength and the notched Izod impact strength decreases to about 60 per cent of the initial values. (51)

Various theories have been proposed to account for this effect of storage at high temperature on mechanical properties. T E Bugel has studied the effect of ageing at various temperatures on the properties of Union Carbide polysulphone (V).

Three properties of the polymer (tensile strength, tensile impact strength, notched impact strength) were measured on samples aged for various periods of time. The ageing temperatures were 150°, 160°, 170°, 180°, 190°, and 210°. The final value of the property was similar in each case but the rate at which this was reached increased with temperature. An Arrhenious plot was used to correlate the effect of time and temperature on thermal ageing.

Analysis of the polymer did not reveal any significant chemical change. Infra-red analysis showed no change in chemical structure of aged specimens, while weight loss below 500° in a thermogravimetric analysis was negligible. Viscosity measurements indicated a very small reduction in average molecular weight after 12 months at 165°.
Bugel attributes the ageing effect to oxidative cleavage at the isopropylidene linkage in the polymer. This would result in a concentration of low molecular weight material at the surface of the polymer specimen. The low molecular weight polymer would be brittle and could result in an overall embrittlement of the specimen. There is little experimental evidence to support this idea and it does not explain the changes in other properties for example the increase in modulus.

A more common theory is that a concentration of holes or voids are frozen into a polymer sample on cooling from above the glass transition temperature during specimen preparation. Storage of the specimen at temperatures below the glass transition temperature results in a gradual ordering of the polymer chains with a consequent reduction in the number of voids present in the polymer structure.

The ageing effect is shown by poly(vinyl chloride) and Illers has measured the variation in hole concentration on ageing the polymer.

The poly(vinyl chloride) used had a low crystallinity (5-10%). Measurements were made on annealed and unannealed specimens in a differential calorimeter which recorded heat given off or absorbed by the specimens as a function of temperature. As specimens were annealed an endothermal peak was observed superimposed on the $C_p$ step at the glass transition temperature on the specific heat versus temperature graphs.

This endothermal peak increased with increasing annealing time and was shown to be due to the change in the void concentration of the amorphous region and not to changes in crystallinity.

A very slight increase in density from 1.3743 to 1.3745 was observed on
annealing a specimen at 65°. The density was measured at 20° using the buoyancy method.

Diffusion and permeation measurements confirmed the reduction in hole concentration on annealing specimens at 65°, which is below the glass transition temperature for polyvinyl chloride of 70°. The rate of absorption of benzene and xylene by annealed specimens was much slower than with the unannealed specimens. This effect may also be attributed to a decrease in hole concentration in the annealed specimens.

The gas permeability of poly(vinyl chloride) was also dependent on annealing time. The permeation constants of hydrogen, helium, argon and methane were smaller for the annealed specimens. For example, the permeation constant of hydrogen was 1.93 for the unannealed specimen and 1.76 for a specimen annealed for 96 hours at 65°.

The mechanical properties of poly(vinyl chloride) were shown to be affected by the annealing process, the polymer becoming brittle.

Golden, Hammant and Hazell have studied the ageing effect in polycarbonate (poly[2,2 propane bis (4 phenyl carbonate)]) and conclude that the effect is due to an ordering of the polymer chains. Increases in tensile yield stress and flexural yield strength occur on ageing. The increase in strength occurred more rapidly at higher temperatures. The tensile impact strength was reduced by ageing.

No significant changes were observed in the infra-red spectra, X-ray powder photographs or density of the aged specimens compared with the unaged. A small secondary transition in the dynamic mechanical tan δ at 80° increased in sharpness on ageing at 132°.
Golden, Hammant and Hazell suggest that the chains are frozen into a disordered position on cooling specimens from the melt in preparation. On heating, the chains are able to move into more ordered positions without affecting the degree of crystallinity. This ordering of the polymer chains results in the observed changes in physical properties.

Further evidence for the ordering of the polymer chains in polycarbonate on heat ageing is given by Siegmann and Geil (55). They show electron micrographs which provide evidence for the presence of ordered regions in amorphous polycarbonate. These regions are affected by annealing above $80^\circ$ and below the glass transition temperature. The ordered regions or nodules were $60 - 110 \, \text{Å}$ in size in the unannealed specimens. On annealing for six days at $90^\circ$ the size increased to $200 \, \text{Å}$ and after seven days at $110^\circ$ the size was $350 \, \text{Å}$. These changes were not accompanied by any change in the X-ray diffraction pattern, so the degree of order introduced by annealing is relatively small.

Robeson (56) has shown that the addition of small amounts of antiplasticizers such as chlorinated biphenyls and terphenyls to polysulphone increases the tensile modulus and tensile strength and decreases the impact strength. Antiplasticizers are compounds which when added to a polymer have the opposite effect of a plasticizer. A plasticizer (57) is a compound which when added to a polymer reduces stiffness, hardness and brittleness. This is achieved by lowering the glass transition temperature below room temperature. An example is the addition of dioctyl phthalate to polyvinyl chloride. These effects were shown to be due to a filling of the free volume in the polymer. The apparent density of the antiplasticizer decreases as its content is increased. This indicates that the antiplasticizer initially fills the free volume in the polymer.
The addition of antiplasticizer also decreases the dynamic mechanical secondary loss transition. The permeability of the polymer to carbon dioxide is decreased by the addition of antiplasticizer as is the rate of water absorption. These results confirm that the free volume in the polymer is being taken up by the antiplasticizer.

It is apparent that a reduction in free volume in a polymer restricts the molecular motions resulting in the observed changes in mechanical properties: increase in modulus and tensile strength and a decrease in impact strength.

8. The works in this thesis

J B Rose and coworkers (unpublished work) have shown that poly(diphenylene ether sulphone) prepared by reaction between diphenyl ether and diphenyl ether disulphonyl chloride (reaction (4)) has poorer mechanical properties than the polymer from the other electrophilic substitution reactions (3) and (5). Unnotched specimens of polymer from reaction (4) break in an impact test while unnotched specimens of polymer from reactions (3) and (5) do not break in an impact test. The poorer impact properties of the polymer from reaction (4) were attributed to the branching and ortho substituted structures present in this polymer.

A knowledge of the effect of repeat unit isomerization and chain branching on properties is of fundamental importance in the field of aromatic polymers.

In this thesis the effect on properties of introducing ortho and meta links, and chain branching into poly(diphenylene ether sulphone) are described. The effect of some other structural variations, for example introducing 4,4-dioxydiphenyl and 1,5-naphthalene units into the polymer are also described.
The polymers were prepared by nucleophilic substitution so that defined structures were obtained.

The properties examined were: impact strength, tensile modulus, flexural modulus, solution viscosity, melt viscosity, crystallinity, glass transition temperature, density and molecular weight.

Some properties of the polysulphone made by the Union Carbide Company are included for comparison.

The kinetics of polymerisation of the fluorophenoxides eg (IX) used to prepare the polymers are also described.

\[ F-\text{SO}_2\text{-OK} \quad \text{IX} \]

The reaction between poly(diphenylene ether sulphone) and fluoride ion is also described and the consequent equilibrium (11) between polymer and fluoride ion studied.

\[(11) \quad \text{Low polymer} \quad \text{High polymer} \]

\[ \text{Low polymer} \quad \text{High polymer} \]
Synthesis of 4-fluoro-4'-hydroxydiphenyl sulphone

The route used to prepare 4-fluoro-4'-hydroxydiphenyl sulphone is shown in reactions (16) to (18).

\[
\begin{align*}
(16) \quad F-\text{Ar-SO}_2\text{Cl} + F-\text{Ar} & \xrightarrow{\text{AlCl}_3} F-\text{Ar-SO}_2\text{Ar}-F + \text{HCl} \\
(17) \quad F-\text{Ar-SO}_2\text{Ar}-F + 2\text{KOH} & \xrightarrow{} F-\text{Ar-SO}_2\text{Ar}-\text{OK} + \text{KF} + \text{H}_2\text{O} \\
(18) \quad F-\text{Ar-SO}_2\text{Ar}-\text{OK} + \text{HCl} & \xrightarrow{} F-\text{Ar-SO}_2\text{Ar}-\text{OH} + \text{KCl}
\end{align*}
\]

In reaction (16), the fluorine in fluorobenzene directs the electrophilic substitution mainly to the para position. In reaction (17) the first fluorine is displaced approximately 50 times as fast as the second so that the major reaction product is the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone as shown. In the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone the electron withdrawing effect of the sulphone (which activated the fluorines to nucleophilic attack) is reduced by donation of electrons by the negatively charged oxygen of the phenate group. This is represented in X.

\[
X
\]

This effect reduces the reactivity of the fluorine in the potassium salt of 4-Fluoro-4'-hydroxydiphenyl sulphone to nucleophilic attack.
Synthesis of 4-chloro-4'-hydroxydiphenyl sulphone

4-Chloro-4'-hydroxydiphenyl sulphone was prepared by hydrolysis of 4,4'-dichlorodiphenyl sulphone in dimethyl sulphoxide using two moles of aqueous potassium hydroxide.

\[(19) \quad \text{Cl}^-\text{SO}_2\text{Cl} \quad + \quad 2\text{KOH} \quad \rightarrow \quad \text{Cl}^-\text{SO}_2\text{OK} \quad + \quad \text{KCl} \quad + \quad \text{H}_2\text{O}\]

\[(20) \quad \text{Cl}^-\text{SO}_2\text{OK} \quad + \quad \text{HCl} \quad \rightarrow \quad \text{Cl}^-\text{SO}_2\text{OH} \quad + \quad \text{KCl}\]

Synthesis of 4-fluoro-2'-hydroxydiphenyl sulphone

4-Fluoro-2'-hydroxydiphenyl sulphone was prepared by a six stage route shown in reactions (21) to (26).

\[(21) \quad \text{F}^-\text{S} \quad + \quad 2\text{ClSO}_3\text{H} \quad \rightarrow \quad \text{F}^-\text{SO}_2\text{Cl} \quad + \quad \text{HCl} \quad + \quad \text{H}_2\text{SO}_4\]

\[(22) \quad \text{F}^-\text{SO}_2\text{Cl} \quad \xrightarrow{\text{reduce} \quad \text{Zn/H}_2\text{SO}_4} \quad \text{F}^-\text{SH}\]

\[(23) \quad \text{F}^-\text{SH} \quad \xrightarrow{\text{NaOCH}_2\text{H}_5} \quad \text{F}^-\text{SNa} \quad + \quad \text{C}_2\text{H}_5\text{OH} \quad \xrightarrow{\text{Cl}} \quad \text{F}^-\text{SNO}_2\text{NO}_2\]

\[(24) \quad \text{F}^-\text{SNO}_2\text{NO}_2 \quad \xrightarrow{\text{oxidise} \quad \text{H}_2\text{O}_2} \quad \text{F}^-\text{SO}_2\text{NO}_2\]

\[(25) \quad \text{F}^-\text{SO}_2\text{NO}_2 \quad \xrightarrow{\text{reduce}} \quad \text{F}^-\text{SO}_2\text{NH}_2\]

\[(26) \quad \text{F}^-\text{SO}_2\text{NH}_2 \quad \xrightarrow{\text{diazo} \quad \text{NaNO}_2/\text{HCl}} \quad \text{F}^-\text{SO}_2\text{Cl} \quad \xrightarrow{\text{heat in} \quad 50\% \text{H}_2\text{SO}_4} \quad \text{F}^-\text{SO}_2\text{OH}\]
The reduction step of reaction (25) was carried out using stannous chloride and hydrochloric acid in ethanol solution (reaction (27)). This method gave a better yield and a purer product than reduction using tin and hydrochloric acid.

\[
\text{(27)} \quad \text{ArNO}_2 + 3\text{SnCl}_2 + 6\text{HCl} \rightarrow \text{ArNH}_2 + 3\text{SnCl}_4 + 2\text{H}_2\text{O}
\]

The product was isolated as the free amine by pouring the ethanol solution onto ice. The expected tin complex (XI) of the amine did not appear to be formed under these conditions probably because of steric hindrance at the ortho position.

\[
2\text{ArNH}_2 + 2\text{HCl} + \text{SnCl}_4 \rightarrow [2\text{ArNH}_3]^+[\text{SnCl}_6]^{-}
\]

XI

4 Synthesis of 2,4,4'-trifluorodiphenyl sulphone

2,4,4'Trifluorodiphenyl sulphone was used to introduce branching into poly(diphenylene ether sulphone). The preparation was by Friedel Craft's reaction between meta-difluorobenzene and 4-fluorobenzenesulphonyl chloride (reaction (28)).

\[
\text{(28)} \quad \text{F-}[-\text{SO}_2\text{Cl} + \text{F-}[-\text{F} \rightarrow \text{F-}[-\text{SO}_2\text{F}[-\text{F}]
\]

The corresponding 2,4,4'trichlorodiphenyl sulphone was also prepared by reaction of meta-dichlorobenzene and 4-chlorobenzenesulphonyl chloride. The reactivity of the chlorines to nucleophilic attack is lower than fluorine and the more reactive fluoro derivative was used to prepare branched polymer.
Preparation of 4-methoxy-4'-hydroxydiphenyl sulphone

4-Methoxy-4'-hydroxydiphenyl sulphone was prepared from the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone as shown in reactions (29) to (31)

\[(29) \quad \text{F-SO}_2\text{OK} + \text{CH}_3\text{Cl} \rightarrow \text{F-SO}_2\text{OCH}_3 + \text{KCl}\]

\[(30) \quad \text{F-SO}_2\text{OCH}_3 + 2\text{KOH} \rightarrow \text{KO-SO}_2\text{OCH}_3 + \text{KF} + \text{H}_2\text{O}\]

\[(31) \quad \text{KO-SO}_2\text{OCH}_3 + \text{HCl} \rightarrow \text{HO-SO}_2\text{OCH}_3 + \text{KCl}\]

Preparation of 1-hydroxy-4-(4-fluorobenzenesulphonyl)naphthalene

This compound was prepared by the reaction scheme shown.

\[(32) \quad \text{N-OH} + (\text{O-CO})_2 \rightarrow \text{N-CO} + 2 \text{N-OH}\]

\[(33) \quad (\text{O-CO})_2 + 2\text{F-SO}_2\text{Cl} \rightarrow (\text{F-SO}_2\text{O})_2 \text{CO}\]

\[(34) \quad (\text{F-SO}_2\text{O})_2 \text{CO} + 4\text{KOH} \rightarrow 2\text{F-SO}_2\text{O} + \text{K}_2\text{CO}_3 + 2\text{H}_2\text{O}\]

\[(35) \quad \text{F-SO}_2\text{O} + \text{HCl} \rightarrow \text{F-SO}_2\text{OH} + \text{KCl}\]

In this reaction scheme the carbonate group acts as a protecting group for the phenol during the Friedel Crafts reaction.
Preparation of 4-(4-fluorobenzenesulphonyl)4'-4-hydroxybenzenesulphonyl)diphenyl ether

The route to this compound, which was used in a kinetic study of the polymerisation, is shown in reactions (36) to (39).

\[(36) \text{F-SO}_2\text{-} + \text{OK} \rightarrow \text{F-SO}_2\text{-O-} \]

\[(37) 2\text{F-SO}_2\text{-O-} + (\text{ClSO}_2\text{-O-})_2\text{CO} \rightarrow (\text{F-SO}_2\text{-O-ClSO}_2\text{-O-})_2\text{CO} + 2\text{HCl} \]

\[(38) (\text{F-SO}_2\text{-O-ClSO}_2\text{-O-})_2\text{CO} + 4\text{KOH} \rightarrow 2\text{F-SO}_2\text{-O-ClSO}_2\text{-OK} + \text{K}_2\text{CO}_3 + 2\text{H}_2\text{O} \]

\[(39) \text{F-SO}_2\text{-O-ClSO}_2\text{-OK} + \text{HCl} \rightarrow \text{F-SO}_2\text{-O-ClSO}_2\text{-OH} + \text{KCl} \]

In the first step a mixture of products is formed as shown. The mixture was separated by fractional distillation under reduced pressure to yield the required 4-fluoro-4'-phenoxydiphenyl sulphone.
8 **Preparation of 4-(benzenesulphonyl)4′-(4-hydroxybenzenesulphonyl)diphenyl ether**

4-(Benzenesulphonyl)4′-(4-hydroxybenzenesulphonyl)diphenyl ether was prepared by the route shown in reactions (40) to (44)

(40) \[ \text{F-SO}_2\text{Cl} + \text{C}_6\text{H}_5\text{O} \longrightarrow \text{F-SO}_2\text{C}_6\text{H}_5 + \text{HCl} \]

(41) \[ \text{F-SO}_2\text{C}_6\text{H}_5 + \text{K}_2\text{SO}_3 \longrightarrow \text{K}_2\text{SO}_3 + \text{H}_2\text{O} \]

(42) \[ 2\text{SO}_2\text{C}_6\text{H}_5\text{O} + (\text{ClSO}_2\text{C}_6\text{H}_5)\text{CO} \longrightarrow \]

\[ 2\text{SO}_2\text{C}_6\text{H}_5\text{O} + (\text{K}_2\text{SO}_3 + \text{H}_2\text{O}) \]

(43) \[ (\text{SO}_2\text{C}_6\text{H}_5\text{O} + (\text{SO}_2\text{C}_6\text{H}_5\text{O})\text{CO} + 4\text{KOH} \longrightarrow \]

\[ 2\text{K}_2\text{CO}_3 + 2\text{H}_2\text{O} \]

(44) \[ \text{SO}_2\text{C}_6\text{H}_5\text{O} + \text{HCl} \longrightarrow \]

\[ \text{SO}_2\text{C}_6\text{H}_5\text{OH} + \text{KCl} \]

9 **Preparation of 4-(benzenesulphonyl)4′-(4-fluorobenzensulphonyl)diphenyl ether**

This compound was prepared by two different routes.

(45) \[ \text{F-SO}_2\text{C}_6\text{H}_5\text{O} + \text{SO}_2\text{Cl} \longrightarrow \text{F-SO}_2\text{C}_6\text{H}_5\text{O} + \text{SO}_2\text{Cl} + \text{H} \]

(46) \[ \text{F-SO}_2\text{C}_6\text{H}_5\text{O} + 2\text{ClSO}_3\text{H} \longrightarrow \]

\[ \text{F-SO}_2\text{C}_6\text{H}_5\text{O} + \text{H}_2\text{SO}_4 + \text{HCl} \]
There is some chance of obtaining an ortho substituted product by the Friedel Crafts reaction (45). One sample made by this reaction did contain some ortho substituted product and this was observed in the nmr spectrum. The pure para product could be obtained with this reaction by purification by recrystallization.

In the second route (reaction (46) and (47)) ortho isomers could be formed in reaction (46) but this is less likely because chlorosulphonic acid appears to substitute almost exclusively in the para position. Once the para-sulphonyl chloride has been made there is no further chance of introducing ortho substituted product by reaction (47).

**Preparation of 2,4'-dihydroxydiphenyl sulphone**

2,4'-Dihydroxydiphenyl sulphone was prepared by hydrolysis of 4-fluoro-2'-hydroxydiphenyl sulphone as shown in reactions (48) and (49).

\[
\text{(48) } \text{F-} - \text{SO}_{2} - \text{OH} + 3\text{KOH} \rightarrow \text{K-} - \text{SO}_{2} - \text{O} + \text{KF} + 2\text{H}_{2}\text{O}
\]

\[
\text{(49) } \text{K-} - \text{SO}_{2} - \text{OH} + 2\text{HCl} \rightarrow \text{HO-} - \text{SO}_{2} - \text{OH} + 2\text{KCl}
\]
A kinetic study of the reactions used to synthesize poly(diphenylene ether sulphones) is described in this section. A knowledge of these rates was useful in predicting the possible structure of the copolymers made from the potassium salts of 4-fluoro-4'-hydroxydiphenyl sulphone and 4-fluoro-2'-hydroxydiphenyl sulphone. The rate constants obtained were also used in the study of the polycondensation equilibrium (see Part 5).

1 Polymerisation of the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone

\[
\begin{align*}
\text{F-} & \text{SO}_2\text{-OK} \rightarrow \text{[SO}_2\text{-O-]}_n^- + nKF \\
(\text{XII}) & \\
\end{align*}
\]

The rate of reaction of the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone was measured in sulfolane solution at temperatures between 140°-200°. Sulfolane (tetramethylene sulphone (XIII)) is a good solvent for the monomers used and for the polymers produced by their reaction.

\[
\begin{align*}
\text{CH}_2 & \text{CH}_2 \\
\text{CH}_2 & \text{CH}_2 \\
\text{SO}_2 & \\
(\text{XIII}) & \\
\end{align*}
\]

It is a liquid (mp 28°) with a high boiling point (285°) and is stable at the temperatures (up to 200°) used for these reactions (59).

Nucleophilic displacement reactions are known to proceed readily in dipolar aprotic solvents such as sulfolane.
Method

The reactions were carried out in a 3 necked flask equipped with stirrer, thermometer, nitrogen inlet and outlet, and rubber seal for sample removal with a syringe. The temperature of the flask contents was measured by means of a melting point thermometer (Gallenkamp, 30 mm immersion calibrated in 0.5°). The flask was heated by means of a thermostated silicone oil bath. The oil was heated by a 1500 watt cuff heater around the outside of the bath (controlled by a variable transformer ('Variac')) together with a 125 watt heater immersed in the bath. The second heater was switched by a contact thermometer wired to a relay box. The temperature control was ± 0.5°C.

The sulpholane was heated to the required temperature and then the dry potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone added and a stop watch started. The contents of the flask were generally 2-3° below the oil bath temperature, the difference was probably due to heat loss along the stirrer shaft and via the nitrogen flow. A slow stream of nitrogen was passed through the flask to prevent loss of phenoxide groups by reaction with water and carbon dioxide from the atmosphere.

Samples were removed at various times with a syringe and emptied into stoppered test tubes cooled in ice. The samples were kept cooled in ice until required for titration. The sample was then warmed to room temperature and filtered through a bed of 'Celite' (analytical filter aid supplied by BDH) on a Whatman No 1 filter paper to remove potassium fluoride. The removal of potassium fluoride was essential to prevent it interfering in the titration.
A weighed portion of the filtered sample was diluted to 100 ml with redistilled methanol and then titrated with 0.1N sulphuric acid using a pH meter (see experimental section). The titre for 10 g of each sample was then calculated and the first results extrapolated to zero time to obtain a zero time titre. The % reaction could then be calculated at each time:

\[
\% \text{ reaction} = \frac{To - Tt}{To} \times 100
\]

To = Titre for 10.000 g sample at zero time
Tt = Titre for 10.000 g sample at time t

The reaction is expected to follow second order kinetics:

\[
\frac{dx}{dt} = k(a - x)(b - x) \quad (1)
\]

In this case the initial concentration of reactants are equal, otherwise high molecular weight polymer could not be obtained, so that a = b.

\[
\frac{dx}{dt} = k(a - x)^2 \quad (2)
\]

Integrating (2)

\[
\frac{1}{a - x} = kt + I \quad (3)
\]

when \( t = 0 \), \( x = 0 \) so that \( I = \frac{1}{a} \)

\[
k t = \frac{x}{a(a - x)} \quad (4)
\]

\( a \) = initial concentration reactant
\( a - x \) = concentration of reactant at time \( t \)
\( x \) = concentration of product at time \( t \)
\( k \) = rate constant
A plot of \( \frac{1}{a - x} \) versus time should be a straight line of slope \( k \) if second order kinetics are obeyed. \( \frac{1}{a - x} \) was calculated in litre mole \(^{-1}\) using the density \( d \) of sulpholane from graph 1.

The concentration of OK end groups \((a-x)\) at time \( t \) is:

\[
\frac{T_t \times \frac{1}{10} \times \frac{d}{1000} \times 100}{10 \times 1000 \times 10} = \frac{T_t \times \frac{d}{100}}{100} \text{ moles litre}^{-1}
\]

\( T_t \) = titre \((\text{ml} \ N/10 \ H_2SO_4 \text{ for a 10.000 g sample})\).

A plot of % reaction versus time for the reaction of the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone in sulpholane at 158° is shown in graph 2 and \( \frac{1}{(a-x)} \) versus time in graph 3.

The % reaction scale on graph 3 was calculated from

\[
\% \text{ reaction } = 100 - \frac{100 - 100}{\frac{1}{a - x}} \frac{1}{\frac{1}{a}}
\]

From which \( \frac{1}{a - x} = \frac{100 \times \frac{1}{a}}{100 - \% \text{ reaction}} \)

Graph 3 would be a straight line if second order kinetics were obeyed. The curve obtained indicates that the reactivities of the functional groups increase with conversion. The sulphone group acts as an electron withdrawing group in the halogenated derivatives of diphenyl sulphone and so activates the halogen to nucleophilic attack. In the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone the negative charge of the phenoxide group reduces the electron withdrawing ability of the sulphone function and so reduces the reactivity of the fluorine to nucleophilic attack.
Graph 1: Density of Sulpholane.
Graph 2: Reaction of F-\( \text{SO}_3 \)-H\( \text{O} \) at 158°
Once dimer has been formed this effect is not expected to be transmitted to the fluorine so that the fluorine is more reactive and a faster rate pertains.

\[
\begin{align*}
F-\text{SO}_2-\text{OK} & \quad \xrightarrow{k_1} \quad F-\text{SO}_2-\text{O}-\text{SO}_2-\text{UK} \\
& \quad \downarrow k_2 \quad \text{Polymer}
\end{align*}
\]

\[k_2 > k_1.\]

\[k_1 \text{ may be calculated from the initial slope of the graph when the main reaction is dimerization} \]

\[
k_1 = \frac{1}{\frac{a-x}{t}} = \frac{4.541 - 4.243}{26 \times 60} = 1.91 \times 10^{-4} \text{ litre mole}^{-1} \text{ sec}^{-1}
\]

\[k_2 \text{ is not readily obtainable from the graph since the slope will only approximate to } k_2 \text{ at high conversions. This is because } k_2 > k_1, \text{ so that the dimer formed reacts more rapidly than monomer and at moderate conversions some of the phenoxide will be present as monomer. In the intermediate region other reactions than those indicated can occur eg reaction of phenoxide on monomer with fluorine on dimer.}\]
\( k_2 \) has been measured by using model compounds such as the dimer.

The results for polymerization experiments at 145.5°C, 158°, 168°, 177.5° and 196.5° are shown in Table 1

**TABLE 1**

*Polymerisation of \( F-\overline{SO_2-O}^-\overline{OK} \) in sulfolane*

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Concentration of ( F-\overline{SO_2-O}^-\overline{OK} )</th>
<th>Initial rate constant ( k_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>145.5°</td>
<td>2.77% ww</td>
<td>( 1.58 \times 10^{-4} ) litre mole(^{-1}) sec(^{-1} )</td>
</tr>
<tr>
<td>158°</td>
<td>6% ww</td>
<td>( 1.91 \times 10^{-4} ) &quot; &quot; &quot;</td>
</tr>
<tr>
<td>168°</td>
<td>6% ww</td>
<td>( 3.21 \times 10^{-4} ) &quot; &quot; &quot;</td>
</tr>
<tr>
<td>177.5°</td>
<td>6% ww</td>
<td>( 5.90 \times 10^{-4} ) &quot; &quot; &quot;</td>
</tr>
<tr>
<td>196.5°</td>
<td>6% ww</td>
<td>( 1.80 \times 10^{-3} ) &quot; &quot; &quot;</td>
</tr>
</tbody>
</table>

The data used to calculate these rate constants are shown in the experimental section. Since the rate constant is known at several temperatures the activation energy may be calculated using the Arrhenious expression:

\[
k = Ae^{\frac{-E}{RT}}
\]

\[
\log_e k = \frac{-E}{RT} + \text{constant}
\]

A plot of \( \log_{10} k \) against \( 1/T^oA \) should be a straight line with slope \(-E/2.303R\).

A graph of \( \log_{10} k \) versus \( 10^3/T^oA \) for the initial reaction of the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone is shown in graph 4, the data for this graph are shown in Table 2.
TABLE 2

Rate data for initial reaction of $F$-\(\text{\text{SO}}_2\text{-}\text{OK}\)

<table>
<thead>
<tr>
<th>Temperature (^{\circ}\text{C})</th>
<th>Temperature (^{\circ}\text{A})</th>
<th>(k) initial litre mole (^{-1}) sec (^{-1})</th>
<th>(\log_{10} k)</th>
<th>(\frac{10^3}{T^\circ\text{A}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>158</td>
<td>431.0</td>
<td>(1.94 \times 10^{-4})</td>
<td>(-3.7190)</td>
<td>(2.320186)</td>
</tr>
<tr>
<td>168</td>
<td>441.0</td>
<td>(3.21 \times 10^{-4})</td>
<td>(-3.4935)</td>
<td>(2.267574)</td>
</tr>
<tr>
<td>177.5</td>
<td>450.5</td>
<td>(5.90 \times 10^{-4})</td>
<td>(-3.2294)</td>
<td>(2.219756)</td>
</tr>
<tr>
<td>196.5</td>
<td>469.5</td>
<td>(1.80 \times 10^{-3})</td>
<td>(-2.7447)</td>
<td>(2.129925)</td>
</tr>
</tbody>
</table>

From the slope of the graph,

\[
\text{Energy of activation} = \frac{-2.303 \times 1.986 \times (-3.68) - (-3.765)}{(2.31 - 2.13)/1000}
\]

\[
= 23.25 \text{ K cals/mole}
\]

The straight line obtained in graph 4 is good evidence that the reaction obeys the Arrhenius law and that the values of rate constant are of good accuracy.

2 Polymerisation of the potassium salt of 4-fluoro-2'-hydroxydiphenyl sulphone

\[(51) \quad n \quad F-\text{\text{SO}}_2-\text{OK} \quad \longrightarrow \quad \text{[-\text{\text{SO}}_2-\text{OK}]n + n KF}\]

(XIV)

The rate of reaction of the potassium salt of 4-fluoro-2'-hydroxydiphenyl sulphone was measured at 200\(^{\circ}\text{C}\) in sulpholane. Graph 5 shows a plot of \(\frac{1}{n-x}\) against time. The graph is similar in shape to that obtained from the reaction of the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone. The ortho monomer also shows an increase in rate with \(\%\) conversion showing that the reactivity of the fluoro and phenoxide ends
is less than those in the corresponding polymer. Similar electronic effects are responsible for the reduced reactivity of this monomer to those found in the all para monomer (XII). The negative charge on the phenoxide can again be partly transferred to the sulphone. This reduces the electron withdrawing ability of the sulphone, so that the fluorine is not so susceptible to nucleophilic attack.

![Chemical structure](image)

The initial rate constant, $k_1$, may be calculated for the ortho-monomer as it was for the para-monomer. The slope of the graph over the first 23 mins was

$$\frac{4.752 - 4.456}{23 \times 60} = 2.15 \times 10^{-4} \text{ litre mole}^{-1} \text{ sec}^{-1}$$

This figure is approximately 1/10th of that for the potassium salt of 4-fluoro-2'-hydroxydiphenyl sulphone (at the same temperature) and reflects the reduced reactivity of phenoxide in the ortho-position. The reduced reactivity is probably largely a steric effect since electronic effects are expected to be similar in the two molecules.

A consequence of the reduced reactivity of the potassium salt of 4-fluoro-2'-hydroxydiphenyl sulphone is that polymers of high molecular weight will be more difficult to prepare from this monomer than from the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone.
Polymerization of the potassium salt of 4-(4-fluorobenzenesulphonyl) 4'- (4-hydroxybenzenesulphonyl) diphenyl ether

\[ \frac{1}{2} n \text{ F–C} = \text{SO}_2\text{–C} = \text{O–C} = \text{SO}_2\text{–C} = \text{OK} \rightarrow \left[ \text{C} = \text{SO}_2\text{–C} = \text{O} \right]_n + \frac{1}{2} n \text{KF} \]  

The rate of reaction of the potassium salt of 4-(4-fluorobenzene sulphonyl)-4'- (4-hydroxybenzenesulphonyl)diphenyl ether was measured to obtain values for the rate of the polymerization reaction, i.e. reaction between fluorine and phenoxide groups on the ends of polymer chains. This rate should equal the maximum rate obtained when polymerizing the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone.

The fluorophenoxy dimer (XV) is more reactive than the monomer (XII) and rate measurements were only made at temperatures up to 145.5°C. The method used to follow the reaction was the same as for the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone. The results obtained for a reaction at 124.5°C (see experimental section) are plotted in graph 6, as \( \frac{1}{a-x} \) versus time. A good straight line is obtained indicating that second order kinetics are obeyed.

The reactivity of the end groups in fluorophenoxy dimer (XV) is therefore expected to be approximately the same as end groups on polymer since no increase in reaction rate is observed with increasing % of conversion. The reactivity of one end group for example fluorine is apparently not affected by the other end group (phenoxide) as does occur in the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone.
Graph 6: Reaction of $F^{-}\text{SO}_3^-\text{Cl}^-\text{SO}_3^-\text{Cl}^-$ at 124.5 °C.
From the graph a value for the second order rate constant may be obtained.

\[ k = \frac{32.5 - 10}{(240-15)60} = 1.61 \times 10^{-3} \text{ litre.mole}^{-1}\text{sec}^{-1} \]

The reaction of the potassium salt of \(4(4\text{-fluorobenzenesulphonyl})\)
\(4'(4\text{-hydroxybenzenesulphonyl})\) diphenyl ether has also been measured at 135.5°C and 145.5°C. The results are shown in Table 3.

**TABLE 3**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Concentration of dimer</th>
<th>Rate Constant (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>124.5°C</td>
<td>6% w/w</td>
<td>1.61 \times 10^{-3}</td>
</tr>
<tr>
<td>135.5</td>
<td>6% w/w</td>
<td>3.33 \times 10^{-3}</td>
</tr>
<tr>
<td>145.5</td>
<td>6% w/w</td>
<td>5.98 \times 10^{-3}</td>
</tr>
</tbody>
</table>

The energy of activation may be calculated as for the initial reaction of the potassium salt of \(4\text{-fluoro-4'}\text{-hydroxydiphenyl sulphone}\). The data used are given in Table 4 and the Arrhenius plot of \(\log_{10}k\) against \(\frac{T}{T_A}\) is shown in graph 7. The graph also shows results obtained from a two component system (see following section).
TABLE 4

Activation energy data for F-\(\text{C}_{6}\text{H}_{4}\text{SO}_{2}\text{-}0\text{-C}_{6}\text{H}_{4}\text{SO}_{2}\text{-}\text{C}_{6}\text{H}_{4}\text{-}\text{OK}\)

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Temperature (\theta_A)</th>
<th>(k)</th>
<th>(\log_{10}k)</th>
<th>(\frac{10^3}{\theta_A})</th>
</tr>
</thead>
<tbody>
<tr>
<td>124.5</td>
<td>397.5</td>
<td>1.61 x 10^{-3}</td>
<td>-2.7932</td>
<td>2.51572</td>
</tr>
<tr>
<td>135.5</td>
<td>408.5</td>
<td>3.33 x 10^{-3}</td>
<td>-2.4776</td>
<td>2.44798</td>
</tr>
<tr>
<td>145.5</td>
<td>418.5</td>
<td>5.98 x 10^{-3}</td>
<td>-2.2233</td>
<td>2.38949</td>
</tr>
</tbody>
</table>

The slope of the graph is \((-2.81) - (-2.265) = -4541.67 \over (2.52-2.40)/1000\)

Hence the energy of activation for polymerization of fluoro phenoxy dimer (XV) is \(-2.303 \times 1.986 \times -4541.67 = 20.77\) K cals/mole.

The activation energy may be used to calculate a value for the rate constant at higher temperatures where direct measurement is very difficult because of the fast rate.

4 Rate of reaction of the potassium salt of 4(benzenesulphonyl)-4'-(4-hydroxybenzenesulphonyl) diphenyl ether with 4(benzenesulphonyl) 4'i(4-fluorobenzenesulphonyl) diphenyl ether

\((53)\) \(\text{C}_{6}\text{H}_{4}\text{SO}_{2}\text{-}0\text{-C}_{6}\text{H}_{4}\text{SO}_{2}\text{-}\text{C}_{6}\text{H}_{4}\text{-}\text{OK} + \text{C}_{6}\text{H}_{4}\text{SO}_{2}\text{-}0\text{-C}_{6}\text{H}_{4}\text{SO}_{2}\text{-}\text{C}_{6}\text{H}_{4}\text{-}\text{F}\rightarrow \text{C}_{6}\text{H}_{4}\text{SO}_{2}\text{-}0\text{-}(\text{C}_{6}\text{H}_{4}\text{SO}_{2}\text{-}0\text{-})\text{C}_{6}\text{H}_{4}\text{SO}_{2}\text{-}\text{C}_{6}\text{H}_{4}\text{-}\) (XVI) (XVII)
The model compounds (XVI) and (XVII) were prepared to simulate phenoxide and fluorine ends on polymer chains. The reaction (53) was followed as for the polymerization of monomer (XII) and dimer (XV) by removing samples and titrating unused base (phenoxide). In this case the solutions of the two reactants were prepared separately under nitrogen, and heated to the required temperature in the oil bath. The solution of phenoxide ended dimer (XVI) was added to the solution of fluorine ended dimer (XVII) to start the reaction. A little of the solution of phenoxide ended dimer was left in the flask used to prepare it, so that the concentration of the two reactants at the start were slightly different. To obtain the initial concentration of (XVI) accurately the concentration of phenoxide ends (expressed as ml 0.1N sulphuric acid) obtained over the initial reaction were extrapolated to zero time. Since the concentration of reactants are not equal the second order rate expression used was:

\[
\frac{dx}{dt} = k(a-x)(b-x)
\]

Integrating

\[
\frac{1}{a-b} \ln \frac{a-x}{b-x} = kt + I
\]

where \(a = \) initial concentration of fluorine ends (on dimer (XVII))

and \(b = \) initial concentration of phenoxide ends (on dimer (XVI))

A plot of \(\frac{1}{a-b} \ln \frac{a-x}{b-x}\) against time should be a straight line with slope \(k\) if second order kinetics are followed. The quantity \(\frac{1}{a-b} \ln \frac{a-x}{b-x}\) was evaluated using an IBM 360 computer with programme 1 (see Appendix) from the initial concentration of phenoxide and fluorine ends and the % reaction.
at each time. The results obtained at $135^\circ$ are shown in graph 8, as a plot of $\frac{1}{\text{a-b}} \ln \frac{\text{a-x}}{\text{b-x}}$ against time. A good straight line is obtained indicating that second order kinetics are obeyed. This result is expected since second order kinetics were obtained with the polymerization of the potassium salt of 4(4-fluorobenzencesulphonyl)-4$^-$(4-hydroxybenzenesulphonyl) diphenyl ether (XV).

From the graph a figure for the rate constant may be calculated:

$$k = \frac{46.0 - 11.5}{(190-30) \times 60} = 3.59 \times 10^{-3} \text{ litre mole.}^{-1} \text{sec.}^{-1}$$

The rate constants obtained for this system are summarized in Table 5.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Total Concentration of Reactants</th>
<th>Rate Constant litre mole.$^{-1}$ sec.$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$135^\circ$</td>
<td>13.40% ww</td>
<td>$3.59 \times 10^{-3}$</td>
</tr>
<tr>
<td>$148.5^\circ$</td>
<td>13.67% ww</td>
<td>$7.78 \times 10^{-3}$</td>
</tr>
<tr>
<td>$159^\circ$</td>
<td>20.1% ww</td>
<td>$8.39 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

The rate constants obtained may be compared with those from the polymerization of the dimer XV by means of an Arrhenious plot. The points for the 2 component dimer system are shown on graph 7, the data used being that shown in Table 6 (and may be compared with that in Table 4).
GRAPH 8

REACTION OF \((\text{SO}_2\text{O})\text{SO}_2\) AND \((\text{SO}_2\text{O})\text{SO}_2\) F

AT 135° IN SULPHOLANE.

\(\frac{1}{\alpha - b} \ln \frac{a - x}{b - x}\)

Time in min:

10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230
TABLE 6

Activation energy data for the reaction between

\[ \text{RSO}_2\text{C}_6\text{H}_4\text{O}^- + \text{SO}_2\text{C}_6\text{H}_4\text{F} \]

<table>
<thead>
<tr>
<th>Temperature ( ^\circ\text{C} )</th>
<th>Temperature ( ^\circ\text{A} )</th>
<th>( k )</th>
<th>( \log_{10}k )</th>
<th>( \frac{10^3}{k} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>135</td>
<td>408</td>
<td>3.59 x 10(^{-3})</td>
<td>-2.4449</td>
<td>2.450980</td>
</tr>
<tr>
<td>148.5</td>
<td>421.5</td>
<td>7.78 x 10(^{-3})</td>
<td>-2.1090</td>
<td>2.372479</td>
</tr>
<tr>
<td>159</td>
<td>432.0</td>
<td>8.39 x 10(^{-3})</td>
<td>-2.0762</td>
<td>2.314815</td>
</tr>
</tbody>
</table>

The graph shows that there is fairly good agreement between the two systems. This supports the conclusion that the reaction rate of dimer (XV) approximates to the rate of reaction between phenoxide and fluorine groups on the end of polymer chains.

5 Rate of reaction of the dipotassium salt of 4,4'-dihydroxydiphenyl sulphone with 4,4'-difluorodiphenyl sulphone

(54) \[ \frac{3}{2}\text{K} + \text{RSO}_2\text{C}_6\text{H}_4\text{O}^- + \frac{3}{2}\text{F} + \text{RSO}_2\text{C}_6\text{H}_4\text{F} \rightarrow \]

\[ \left[ \text{RSO}_2\text{C}_6\text{H}_4\text{O}^- \right]_n + \text{nKF} \]

The two component system (reaction (54)) gives another route to poly(diphenylene ether sulphone) and was studied for comparison with the one component system (reaction (50)). The kinetics of a similar reaction, that between the dipotassium salt of 2,2 bis(4-hydroxyphenyl) propane and 4,4'-dichlorodiphenyl sulphone (reaction (8)) has been studied in some detail by S R Schulze and A L Baron. This reaction is used to prepare the Union Carbide 'polysulphone'.

Reaction between the dipotassium salt of 4,4'-dihydroxydiphenyl sulphone and 4,4'-difluorodiphenyl sulphone was studied in sulpholane as for the other polymerization reactions. In this case the solutions of monomers were prepared separately and heated to reaction temperature in the oil bath. The dipotassium salt of 4,4'-dihydroxydiphenyl sulphone has a lower solubility than the other monomers used in dipolar aprotic solvents. At the concentrations (3% w/w) and temperatures (>124.5°C) used in the reactions complete solution in sulpholane was obtained. The solution of 4,4'-difluorodiphenyl sulphone was added to the stirred solution of the dipotassium salt of 4,4'-dihydroxydiphenyl sulphone and washed in with a known quantity of sulpholane. Samples were removed at known times and cooled in ice. The samples were warmed to room temperature as required, weighed, diluted with 75 ml of dimethyl sulphoxide and filtered to remove potassium fluoride. Dilution with dimethyl sulphoxide was necessary to keep the unreacted dipotassium salt of 4,4'-dihydroxydiphenyl sulphone in solution. The filtered solution was diluted with 25 ml of redistilled methanol and then titrated as before with 0.1N sulphuric acid.

The results for an experiment at 145.5°C are shown in graph 9 as a plot of \( \frac{1}{a-x} \) versus time. In these experiments equal concentrations of phenoxide and fluoro ends at the start of the reaction was ensured by careful washing in of the dipotassium salt of 4,4'-dihydroxydiphenyl sulphone. High molecular weight polymer could be achieved with the system, indicating that the concentrations were very nearly equal.
The reaction is fast at the start and then slows to a second rate. The rate constant for the initial and final rate may be calculated from the slope of the graph over the two sections. The initial rate is fast so that the rate constant obtained is not so accurate.

From graph 9:

\[ k_{\text{initial}} = \frac{13.7676 - 8.9959}{2 \times 60} = 3.97 \times 10^{-2} \text{ litre mole}^{-1} \text{ sec}^{-1} \]
\[ k_{\text{final}} = \frac{80 - 40}{(116 - 40) \times 60} = 8.77 \times 10^{-3} \text{ litre mole}^{-1} \text{ sec}^{-1} \]

The initial fast reaction corresponds to the formation of dimer:

\[
\text{KO-} \quad \text{SO}_2 \quad \text{OK} + \quad \text{F-} \quad \text{SO}_2 \quad \text{F} \quad \rightarrow \\
\text{KO-} \quad \text{SO}_2 \quad \text{O} \quad \text{-} \quad \text{SO}_2 \quad \text{F} + \quad \text{KF}
\]

The dimer formed is identical to the potassium salt of 4(4-fluorobenzene sulphonyl)-4'-(4-hydroxybenzenesulphonyl) diphenyl ether (XV), the reaction of which was found to follow second order kinetics. This corresponds to the second (slower) region of graph 9. The initial fast reaction (dimerization) is due to the enhanced reactivity of the end groups in the monomers. The phenoxide end in the dipotassium salt of 4,4'-dihydroxydiphenyl sulphone is more reactive than in the potassium salt of 4(4-fluorobenzenesulphonyl)-4'(4-hydroxybenzenesulphonyl) diphenyl ether because of electron donation by the phenoxide at the other end of the molecule:
Electron withdrawal by the sulphone is therefore reduced and
electron density at a phenoxide is higher (compared with dimer)
resulting in higher reactivity.

In 4,4'-difluorodiphenyl sulphone the fluorine withdraws electrons
from the sulphone by an inductive effect, thus increasing the
electron withdrawal by the sulphone group and so making the first
fluorine atom easier to substitute. The inductive effect for
fluorine is stronger than the opposite mesomeric effect in the ground
state.

These two effects combine to increase the reactivity of the two
monomer system.

Table 7 shows the rate constants obtained for the two monomer
system. The rate constants (k dimer) obtained for reaction of the
potassium salt of 4(4-fluorobenzenesulphonyl)-4'(4-hydroxybenzene
sulphonyl) diphenyl ether are also included for comparison with k
final obtained with the two monomer system.
TABLE 7

Rate constants for reaction of KO-\(\text{SO}_2\)-OK and F-\(\text{SO}_2\)-F

<table>
<thead>
<tr>
<th>Conc(^n) of Monomers % ww</th>
<th>Temp (^{\circ})C</th>
<th>(k_{\text{initial}}) (\text{litre mole}^{-1} \text{sec}^{-1})</th>
<th>(k_{\text{final}}) (\text{litre mole}^{-1} \text{sec}^{-1})</th>
<th>(k_{\text{dimer}}) (\text{litre mole}^{-1} \text{sec}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>6%</td>
<td>124.5</td>
<td>(1.03 \times 10^2)</td>
<td>(1.93 \times 10^{-3})</td>
<td>(1.61 \times 10^{-3})</td>
</tr>
<tr>
<td>2.8%</td>
<td>145.5</td>
<td>(3.97 \times 10^2)</td>
<td>(8.77 \times 10^{-3})</td>
<td>(5.98 \times 10^{-3})</td>
</tr>
<tr>
<td>6%</td>
<td>158</td>
<td>(2.08 \times 10^{-2})</td>
<td>(1.23 \times 10^{-2})</td>
<td>(1.24 \times 10^{-2})</td>
</tr>
</tbody>
</table>

The figure for \(k_{\text{dimer}}\) at 158° was calculated using the activation energy since direct measurement at 158° was not carried out.

\[
\log e k_1 = -\frac{E}{RT_1} + \text{const}
\]

\[
\log e k_2 = -\frac{E}{RT_2} + \text{const}
\]

\[
\log e k_1 - \log e k_2 = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)
\]

\[
\log_{10} k_2 = \frac{E}{R \cdot 2.303} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \log_{10} k_1
\]

\[
k_1 = 5.98 \times 10^3 \quad T_1 = (145.5 + 273)°A
\]

\[
k_2 = 1.24 \times 10^{-2} \text{ litre mole}^{-1} \text{sec}^{-1}
\]
Good agreement is obtained between \( k \) final for the two component system and \( k \) dimer for the dimeric fluorophenoxide system.

6 Comparison of the three polymerisation systems

A comparison of the three polymerisation systems (reactions (50), (52) and (54)) may be made by plotting \( \frac{1}{a-x} \) versus time.

\[
\text{(50)} \quad n \text{F-} \begin{array}{c} \text{SO}_2 \end{array} \text{OK} \rightarrow \begin{array}{c} \text{SO}_2 \end{array} \text{OK} + nKF
\]

\[
\text{(52)} \quad \frac{1}{2}n\text{F-} \begin{array}{c} \text{SO}_2 \end{array} \text{OK} \rightarrow \begin{array}{c} \text{SO}_2 \end{array} \text{OK} + \frac{1}{2}nKF
\]

\[
\text{(54)} \quad \frac{1}{2}n\text{KO-} \begin{array}{c} \text{SO}_2 \end{array} \text{OK} + \frac{1}{2}n\text{F-} \begin{array}{c} \text{SO}_2 \end{array} \text{F} \rightarrow \begin{array}{c} \text{SO}_2 \end{array} \text{OK} + nKF
\]

The plot is shown in graph 10. At the start there are considerable differences in rate: reaction (52) is approximately 40 times that of reaction (50), while (54) is approximately 6 times that of reaction (52). These differences are due to the different structures of the monomers concerned as discussed previously. At high conversions all three reactions have approximately the same rate, this corresponding to that of the dimeric fluorophenoxide (reaction 52).

Table 8 summarises the rate constants and activation energies measured for the polymerization reactions.
GRAPH 10. POLYMERIZATION REACTIONS IN
SULPHOLANE AT 145.5°C.
### TABLE 8

Rate constants and activation energies for polymerization reactions in sulfolane

<table>
<thead>
<tr>
<th>System</th>
<th>Concentration of Reactants %</th>
<th>Temp. °C</th>
<th>Second Order Rate Constant ( \text{litre mole}^{-1} \text{sec}^{-1} )</th>
<th>Activation Energy K cals/ mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} )</td>
<td>2.77</td>
<td>145.5</td>
<td>( 1.58 \times 10^{-4} )</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} )</td>
<td>6.0</td>
<td>158</td>
<td>( 1.91 \times 10^{-4} )</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} )</td>
<td>6.0</td>
<td>168</td>
<td>( 3.21 \times 10^{-4} )</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} )</td>
<td>6.0</td>
<td>177.5</td>
<td>( 5.90 \times 10^{-4} )</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} )</td>
<td>6.0</td>
<td>196.5</td>
<td>( 1.80 \times 10^{-3} )</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} )</td>
<td>6.0</td>
<td>200</td>
<td>( 2.15 \times 10^{-4} )</td>
<td>23.25</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} )</td>
<td>6.0</td>
<td>124.5</td>
<td>( 1.61 \times 10^{-3} )</td>
<td>20.77</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} )</td>
<td>6.0</td>
<td>135.5</td>
<td>( 3.33 \times 10^{-3} )</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} )</td>
<td>6.0</td>
<td>145.5</td>
<td>( 5.98 \times 10^{-3} )</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} )</td>
<td>13.40</td>
<td>135</td>
<td>( 3.59 \times 10^{-3} )</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} )</td>
<td>13.67</td>
<td>148.5</td>
<td>( 7.78 \times 10^{-3} )</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} )</td>
<td>20.10</td>
<td>159</td>
<td>( 8.39 \times 10^{-3} )</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} + \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 - \text{F} )</td>
<td>6.0</td>
<td>124.5</td>
<td>( k_1 1.03 \times 10^{-2} )</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} + \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 - \text{F} )</td>
<td>2.8</td>
<td>145.5</td>
<td>( k_2 1.93 \times 10^{-3} )</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} + \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 - \text{F} )</td>
<td>6.0</td>
<td>158</td>
<td>( k_1 3.97 \times 10^{-2} )</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} + \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 - \text{F} )</td>
<td>6.0</td>
<td>158</td>
<td>( k_2 8.77 \times 10^{-3} )</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} + \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 - \text{F} )</td>
<td>6.0</td>
<td>158</td>
<td>( k_1 2.08 \times 10^{-2} )</td>
<td>18.94</td>
</tr>
<tr>
<td>( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} + \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 - \text{F} )</td>
<td>6.0</td>
<td>158</td>
<td>( k_2 1.23 \times 10^{-2} )</td>
<td>18.94</td>
</tr>
</tbody>
</table>

**Notes**

1. The initial rate constant only is quoted for \( \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 \text{OK} \)
2. For the system \( \text{KO} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 - \text{OK} + \text{F} - \text{C}_2 \text{SO}_2 \text{C}_6 \text{H}_4 - \text{F} \)
   the initial and final rate constants are given.
PART 4 - KINETICS OF THE ETHER EXCHANGE REACTION

The ether linkages in poly(diphenylene ether sulphone) are activated to nucleophilic attack by the electron withdrawal of the sulphone group.

![Chemical structure diagram]

A possible reaction is then that between ether bonds and the phenoxide end groups of the polymer, the reaction being an ether exchange.

(55)  

\[ \text{A} - \text{O} - \text{B} - \text{SO}_2 - \text{C} \rightarrow \]

+ \[ \text{O} - \text{D} - \text{SO}_2 - \text{E} \rightarrow \]

\[ \text{A} - \text{O} - \text{D} - \text{SO}_2 - \text{E} \rightarrow \text{A} - \text{O} - \text{B} - \text{SO}_2 - \text{C} \rightarrow \text{O} - \text{B} - \text{SO}_2 - \text{C} \]
A kinetic study of this reaction is difficult because no loss of phenoxide end groups or ether linkages occurs.

The reaction has been studied by following the reaction between poly(diphenylene ether sulphone) and the potassium salt of 4-(4-benzenesulphonyl)-4'- (4-hydroxybenzenesulphonyl) diphenyl ether (XVI). The phenoxide groups in this compound are expected to be of very similar reactivity to phenoxide end groups. The overall reaction is shown below, using one mole of the phenoxide ended dimer (XVI) for every mole of ether bonds present in the polymer.

\[
\text{[\text{XVI}]_n + n \text{[XVI]} \rightarrow n \text{[XVI]}_n}
\]

There are still \(2n\) moles of ether linkages left at the end of this reaction and \(n\) moles of phenoxide end groups. The overall reaction is a redistribution of molecular weight in the system polymer and phenoxide ended dimer. The reaction proceeds stepwise with a gradual reduction in the molecular weight of the polymer. The reaction may be followed by removing samples and measuring their molecular weight. The samples are precipitated into water, and acidified to convert unreacted phenoxide groups to hydroxyl. The unreacted 4-(benzene sulphonyl)-4'- (4-hydroxybenzenesulphonyl) diphenyl ether may then be removed by extraction with hot methanol. The molecular weight of the remaining polymer may then be estimated as shown below.
Measurements of Molecular Weight of Polymer

The molecular weights of polymers are polydisperse, i.e. there is a distribution of molecular weight.

The molecular weight is usually measured as either weight average $\overline{M}_w$ or number average $\overline{M}_n$.

$$\overline{M}_w = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i}$$

$$\overline{M}_n = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i}$$

Where $N_i$ is the number and $M_i$ the molecular weight of the $i^{th}$ species.

Another method of expressing the molecular weight of a polymer is as degree of polymerization or DP, where $\overline{DP}$ is the average number of repeat units in a polymer chain. The degree of polymerization is related to the number average molecular weight by

$$\overline{M}_n = \overline{DP} \times \text{Molecular weight of a repeat unit.}$$
For a polycondensation the degree of polymerization is related to the % reaction by

$$\overline{DP} = \frac{100}{100 - %\;\text{reaction}}$$

The most easily measured parameter of a polymer which is proportional to molecular weight is reduced viscosity or RV. This was measured at 25° in a viscometer on a 1% wv solution of the polymer in N, N-dimethyl formamide and is defined by the following expression:

$$RV = \frac{ts - to}{cto}$$

$ts$ = flow time of polymer solution
$to$ = flow time of pure solvent
$c$ = concentration of polymer in g/100 ml

since $c = 1$ for a 1% wv solution the expression simplifies to

$$(RV)_{25°}^{1%} = \frac{ts}{to} - 1$$

A relationship between $(RV)_{25°}^{1%}$ and $\overline{DP}$ has been determined by T King.

$$(RV)_{25°}^{1%} = 0.0232 \overline{DP}^{0.663}$$

Rearranging

$$\overline{DP} = \left(\frac{(RV)_{25°}^{1%}}{0.0232}\right)^{\frac{1}{0.663}}$$

Using this expression the $(RV)_{25°}^{1%}$ of the samples removed may be converted to $\overline{DP}$ and this used to calculate the number of original polymer ether bonds remaining at any time.
A correction is applied to the DP to allow for the DP of the dimeric phenoxide used to cleave the polymer. In this way the cleavage of the ether bonds in the original polymer may be followed. The correction will range between 0 (at start of reaction) to 2 (at complete reaction). At complete reaction (see reaction (56)) the system will be comprised of polymer with DP 3, subtraction of 2 gives the DP of the polymer as 1 (i.e. monomer).

The corrected DP is given by:

$$\overline{DP_c} = \overline{DP_t} - \left(2 - \frac{2 \times \overline{DP_t}}{\overline{DP_o}}\right)$$

$\overline{DP}_c$ = DP corrected

$\overline{DP}_t$ = DP at time t from the (RV)\textsuperscript{1%} of the sample

$\overline{DP}_o$ = DP of the original polymer

The concentration of original polymer ether bonds is then given by:

Concentration of ether links = \(\frac{(\overline{DP}_c - 1)P}{\overline{DP}_c \times 232}\) moles/litre at time t

P = Concentration of polymer in g/litre.

The values of $\overline{DP}_t$, $\overline{DP}_c$ and concentration of ether links at time t were calculated from the (RV)\textsuperscript{1%} using an IBM 360 computer and programme 2. Since the (RV)\textsuperscript{1%} can only be measured accurately down to approximately 0.1, it is not essential to use equimolar amounts of polymer ether bonds and the potassium salt of 4(benzene sulphonyl)\textsuperscript{4'-}(4 hydroxybenzene - sulphonyl) diphenyl ether.
The data obtained by this method for a reaction at 146° is shown in Table 9. The experiment used poly(diphenylene ether sulphone) of (RV)\textsuperscript{1%} \textsubscript{25°} 0.72 (15 g); the potassium salt of 4-(benzenesulphonyl)-4'-
(4-hydroxybenzenesulphonyl) diphenyl ether (13.0383 g) and sulpholane
(439.26 g). The polymer concentration (P) was 3.21% = 37.075 g/litre
using the density from graph 1.

Graph 11 shows a plot of (RV)\textsuperscript{1%} \textsubscript{25°} and DP against time. The drop in
(RV)\textsuperscript{1%} \textsubscript{25°} and DP is quite fast with DP, falling from 179.0 to 15.0
in 3 hours.

The reaction between polymer ether links and phenoxide end groups
would normally be expected to follow second order kinetics:

\[
\frac{dx}{dt} = k(a-x)(b-x)
\]

In this case, however, the concentration of ether links and
phenoxide ends are held constant so that (a-x) and (b-x) are
constants (equal to a and b the initial concentration of reactants).
The reaction is then expected to follow pseudo zero order kinetics.

\[
\frac{dx}{dt} = k'
\]

Integrating: \( k't = (x) = a - (a-x) \)

where (x) = concentration of product at time t.

(a-x) = concentration of original polymer ether linkages at time t.
Graph II: Reaction of [R'NH]₃ with \( \text{SO}_2 \) in Sulfolane at 120°C.

- Reduced Viscosity, \( [\text{R'NH}]_\text{SO}_2 \).
- Degree of Polymerization, \( \overline{DP} \).

Time in Minutes: 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200.
TABLE 9

Reaction between \[\text{[\(\text{SO}_2\text{-O-}\text{-SO}_2\text{-OH}\)\]}\] and

\[\text{[\(\text{SO}_2\text{-O-}\text{-SO}_2\text{-OK}\)\]}\] at 146°

<table>
<thead>
<tr>
<th>Time (mins)</th>
<th>(RV)(_{25}^0)</th>
<th>(\overline{DF}_t)</th>
<th>(\overline{DF}_c)</th>
<th>Concentration of ether links in moles/litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.0</td>
<td>179.0</td>
<td>0.16015</td>
</tr>
<tr>
<td>2</td>
<td>0.663</td>
<td>157.1</td>
<td>156.8</td>
<td>0.16003</td>
</tr>
<tr>
<td>5</td>
<td>0.594</td>
<td>133.1</td>
<td>132.6</td>
<td>0.15984</td>
</tr>
<tr>
<td>10</td>
<td>0.514</td>
<td>107.0</td>
<td>106.2</td>
<td>0.15954</td>
</tr>
<tr>
<td>15</td>
<td>0.453</td>
<td>88.4</td>
<td>87.4</td>
<td>0.15921</td>
</tr>
<tr>
<td>20</td>
<td>0.403</td>
<td>74.1</td>
<td>73.0</td>
<td>0.15885</td>
</tr>
<tr>
<td>25</td>
<td>0.371</td>
<td>65.4</td>
<td>64.2</td>
<td>0.15854</td>
</tr>
<tr>
<td>30</td>
<td>0.353</td>
<td>60.7</td>
<td>59.4</td>
<td>0.15834</td>
</tr>
<tr>
<td>40</td>
<td>0.310</td>
<td>49.9</td>
<td>48.5</td>
<td>0.15773</td>
</tr>
<tr>
<td>60</td>
<td>0.253</td>
<td>36.7</td>
<td>35.1</td>
<td>0.15647</td>
</tr>
<tr>
<td>90</td>
<td>0.212</td>
<td>28.1</td>
<td>26.5</td>
<td>0.15496</td>
</tr>
<tr>
<td>120</td>
<td>0.184</td>
<td>22.7</td>
<td>21.0</td>
<td>0.15338</td>
</tr>
<tr>
<td>180</td>
<td>0.151</td>
<td>16.9</td>
<td>15.1</td>
<td>0.15035</td>
</tr>
<tr>
<td>272</td>
<td>0.128</td>
<td>13.1</td>
<td>11.3</td>
<td>0.14679</td>
</tr>
<tr>
<td>388</td>
<td>0.106</td>
<td>9.9</td>
<td>8.0</td>
<td>0.14092</td>
</tr>
</tbody>
</table>

A plot of concentration of original polymer ether linkages versus time should be a straight line with slope \(-k'\). Graph 12 shows a plot of concentration of original polymer ether linkages versus time. A straight line is obtained indicating that the kinetics are zero order.
Graph 12: Reaction of \( \left( \dfrac{\text{O-SO}}{\text{O}} \right)_n \) with \( \left( \dfrac{\text{O-SO}}{\text{O}} \right) \text{OK} \) in sulpholane at 146°C.

Concentration of Original Polymer Ether Links, \( \text{Moles/Litre} \):

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.161</td>
</tr>
<tr>
<td>20</td>
<td>0.160</td>
</tr>
<tr>
<td>30</td>
<td>0.159</td>
</tr>
<tr>
<td>40</td>
<td>0.158</td>
</tr>
<tr>
<td>50</td>
<td>0.157</td>
</tr>
<tr>
<td>60</td>
<td>0.156</td>
</tr>
<tr>
<td>70</td>
<td>0.155</td>
</tr>
<tr>
<td>80</td>
<td>0.154</td>
</tr>
<tr>
<td>90</td>
<td>0.153</td>
</tr>
<tr>
<td>100</td>
<td>0.152</td>
</tr>
<tr>
<td>110</td>
<td>0.151</td>
</tr>
<tr>
<td>120</td>
<td>0.150</td>
</tr>
<tr>
<td>130</td>
<td></td>
</tr>
<tr>
<td>140</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td></td>
</tr>
<tr>
<td>170</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td></td>
</tr>
<tr>
<td>190</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td></td>
</tr>
</tbody>
</table>
A zero order rate constant may be obtained from the graph

\[
k' \text{ (zero order)} = \frac{0.15950 - 0.15165}{(150-10).60} = 9.345 \times 10^{-7} \text{ mole litre}^{-1} \text{ sec}^{-1}
\]

The reaction has only been followed over about 6\% reaction in this case. The zero order rate constant incorporates the initial concentration of phenoxide groups and ether linkages. It may be converted to the second order rate constant by dividing by the two initial concentrations.

The initial concentration of polymer ether links is 0.16015 moles/litre and of phenoxide ends is 0.06436 moles/litre.

\[
\therefore k \text{ (second order)} = \frac{9.345 \times 10^{-7}}{0.16015 \times 0.06436} = 9.06 \times 10^{-5} \text{ litre mole}^{-1} \text{ sec}^{-1}
\]

Values for these rate constants at 156° and 174° were also measured using the same technique. The data is shown in the experimental section and a summary of results in Table 10.

### TABLE 10

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Zero order rate constant, m.l.\textsuperscript{-1}s.\textsuperscript{-1}</th>
<th>Concentration phenoxide ends, moles/litre</th>
<th>Concentration polymer ether links, moles/litre</th>
<th>Second order rate constant, l.m.\textsuperscript{-1}s.\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>146.0°</td>
<td>9.34 \times 10^{-7}</td>
<td>0.06436</td>
<td>0.16015</td>
<td>9.06 \times 10^{-5}</td>
</tr>
<tr>
<td>156.0°</td>
<td>1.61 \times 10^{-6}</td>
<td>0.06387</td>
<td>0.15891</td>
<td>1.59 \times 10^{-4}</td>
</tr>
<tr>
<td>174.0°</td>
<td>5.12 \times 10^{-6}</td>
<td>0.06298</td>
<td>0.15671</td>
<td>5.19 \times 10^{-4}</td>
</tr>
</tbody>
</table>
The activation energy for the ether exchange reaction (55) may be calculated using the Arrhenius expression. The data are shown in Table 11.

**TABLE 11**

 Activation energy for the ether exchange reaction

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Temperature °A</th>
<th>$10^3 \frac{T}{T^A}$</th>
<th>Second order rate constant k</th>
<th>$\log_{10} k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>146.0</td>
<td>419.0</td>
<td>2.38663</td>
<td>9.06 x 10^{-5}</td>
<td>-4.0429</td>
</tr>
<tr>
<td>156.0</td>
<td>429.0</td>
<td>2.33100</td>
<td>1.59 x 10^{-4}</td>
<td>-3.7986</td>
</tr>
<tr>
<td>174.0</td>
<td>447.0</td>
<td>2.23714</td>
<td>5.19 x 10^{-4}</td>
<td>-3.2851</td>
</tr>
</tbody>
</table>

The data are plotted in graph 13 as $\frac{T^3}{T^A}$ versus $\log_{10} k$. From the graph the energy of activation, $E_A$

$$E_A = 1.986 \times 2.303 \times \text{slope}$$

$$= 1.986 \times 2.303 \times \frac{-3.925 - (-3.305)}{(2.36-2.24)/1000}$$

$$= 23.6 \text{ K cals/mole}$$

The rate constant for the ether exchange reaction is about $\frac{1}{70}$ that of the rate constant for the polymerization reaction (see Part 2). At high % conversions however when the concentration of ether linkages is high compared with that of end groups, the rate of the ether exchange reaction will be significant compared with the polymerization reaction. The ether exchange reaction is probably fast enough to modify the structure of copolymers of poly(diphenylene ether sulphone).
PART 5: POLYCONDENSATION EQUILIBRIUM AND CLEAVAGE OF POLY(DIPHENYLENE -
ETHER SULPHONE) BY FLUORIDE ION

Introduction

This section describes the study of the polycondensation equilibrium
(11) which is set up between poly(diphenylene ether sulphone) and
potassium fluoride at high temperature in dipolar aprotic solvents
such as sulpholane.

(11) $\text{OK} + \text{F}^- \rightleftharpoons \text{KF}$

The effect of fluoride ion on polymerizations was first observed
when preparing $\omega,p'$ copolymers by polymerizing mixtures of the
potassium salt of 4-chloro-4'-hydroxydiphenyl sulphone or 4-fluoro -
4'-hydroxydiphenyl sulphone with the potassium salt of 4-fluoro 2' -
hydroxydiphenyl sulphone in dimethyl sulphone solution.

These reactions were normally carried out at high concentration
(approximately 70% ww) and temperature ($230^\circ$) in order to obtain high
molecular weight polymer. When the polymer had been prepared it was
necessary to convert any unreacted phenoxide end groups to methoxy by
reaction with methyl chloride. The 70% solution of polymer was very
viscous and was diluted with dimethyl sulphone to make it more mobile
so that methyl chloride could easily be passed through it. The
dilution was carried out at the polymerization temperature and caused
a rapid drop in ($RV\text{ }_{25^\circ}$) of the polymer.
For example a polymer was prepared from the potassium salt of 4-fluoro-2'-hydroxydiphenyl sulphone (20 mole%) and the potassium salt of 4-chloro-4'-hydroxydiphenyl sulphone (80 mole%). After polymerizing at 60% ww salt concentration in dimethyl sulphone for 24 hours at 230° a sample, A, was removed. The solution was then diluted to 30% ww and after 1 hour a sample, B, removed. A sample, C, was removed after a further 1 hour and the solution further diluted to 15%. Sample, D, was removed after 1 hour and methyl chloride passed through the remaining solution for 1 hour to give sample E. The samples were worked up for \( (RV)^{1\%}_{25} \) determination by dissolving in N,N-dimethylformamide solution, precipitating the solution into water and refluxing the polymer with water and methanol. The \( (RV)^{1\%}_{25} \) 's measured on the dry polymer samples were A = 0.47, B = 0.26, C = 0.28, D = 0.12, E = 0.11.

The observed drop in \( (RV)^{1\%}_{25} \) on dilution was thought to be due to cleavage of the polymer at the ether linkages by the fluoride ion produced by the original polymerization reaction. This cleavage by fluoride ion would result in an equilibrium (11) being set up between polymer and fluoride ion.

The change in \( (RV)^{1\%}_{25} \) on altering the polymer concentration is dependent on the potassium fluoride concentration remaining constant. During a polymerization the majority of the potassium fluoride formed is precipitated from the solution and so the concentration of potassium fluoride in solution is expected to be quite low. Since the solution is saturated with potassium fluoride and in contact with solid potassium fluoride the concentration of potassium fluoride should remain constant.
The rate of the forward or polymerisation reaction is then proportional to the \((\text{concentration of end groups})^2\) while the reverse reaction is proportional to the \((\text{concentration of ether linkages})\). At low polymer concentrations the equilibrium will therefore be to the left or low polymer side, and at high concentration to the right or high polymer side.

Some further indication that an equilibrium is responsible for determining the \([\text{RV}]_{25^\circ}^{1\%}\) at a given concentration is the effect on \([\text{RV}]_{25^\circ}^{1\%}\) of methyl chloride. A polymer was prepared from the potassium salt of 4-fluoro 4'-hydroxydiphenyl sulphone in dimethyl sulphone at 55% \(\text{ww}\) concentration and 230° for 6 hours. A sample A was removed from the polymer solution, and methyl chloride passed through the remaining solution for 1 hour at 230° to give sample B. The \([\text{RV}]_{25^\circ}^{1\%}\) obtained were \(A = 0.68\), \(B = 0.20\). This reduction in \([\text{RV}]_{25^\circ}^{1\%}\) is probably caused by the methyl chloride removing phenoxide ends by conversion to methoxy and the equilibrium moving to the left to compensate and so reducing the \([\text{RV}]_{25^\circ}^{1\%}\).

Some experiments were carried out to show that the polymer was being cleaved by fluoride ion and not by hydroxide which would be formed by reaction between potassium fluoride and any water in the system.

\[
\text{KF} + \text{H}_2\text{O} \rightleftharpoons \text{KOH} + \text{HF}
\]

A polymer of \([\text{RV}]_{25^\circ}^{1\%} 0.41\) was prepared by polymerising a mixture of the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone (0.1378 mole) with the dipotassium salt of 4,4'-dihydroxydiphenyl sulphone (0.000965 mole) in sulpholane at 40% \(\text{ww}\) concentration and 200° for 23 hours. The solution was cooled to 150° and methyl chloride passed through
the solution for 1 hour. At lower temperatures such as 150° in sulpholane, the effect of fluoride ion cleavage is very much reduced, and conversion of phenoxide end groups to methoxy by reaction with methyl chloride without any significant loss of [RV]$_{25°}$ is possible. A 2\% w/w concentration solution of this polymer in sulpholane was stirred with anhydrous potassium fluoride at 230° for 2 hours. Methyl chloride was then passed through the solution for 1 hour at 230°. The resulting polymer had [RV]$_{25°}$ 0.12

The OH content of the polymers was measured by IR, the OCH$_3$ by NMR. The fluorine content of the polymers was measured by heating a known weight of the polymer with a known weight of 0.141 molal sodium methoxide in dimethyl sulphoxide at 120° for 2 hours. The solution was poured into water and the remaining base titrated with 0.1N hydrochloric acid using a pH meter. The reactions occurring between the sodium methoxide and polymer are:

\[(57) ~ \text{O} + \text{NaOCH}_3 \rightarrow \text{ONa} + \text{CH}_3\text{O-} \]

\[(58) ~ \text{F} + \text{NaOCH}_3 \rightarrow \text{OCH}_3 + \text{NaF} \]

There is no loss of base in the reaction between polymer ether links and sodium methoxide, but base is lost in the reaction with fluorine end groups (reaction (58)). The amount of base lost is therefore equivalent to the number of fluorines present and so the number of fluorines per 100 repeat units of polymer may be calculated.

The average results obtained for the polymer of [RV]$_{25°}$ 0.41 (before fluoride cleavage) were <0.02 hydroxyl per 100 repeat units, 2.4 methoxyl per 100 repeat units, and 0.4 fluorines per 100 repeat units.
The cleaved polymer of \([RNV]_{25}^{12}\) had 4.6 methoxyl per 100 repeat units and 3.0 fluorines per 100 repeat units. The increase in methoxy end groups on cleavage is then 2.2 per 100 repeat units and of fluorine 2.6 per 100 repeat units. The figure for increase in methoxy end groups and that for fluorine end groups should be the same if cleavage has taken place by fluoride ion as shown in the equilibrium expression (11). The figures obtained are probably within the experimental error, since even if the fluorine results are accurate the accuracy of the nmr results is probably only \(\pm 10\%\).

In another experiment a polymer with methoxy end groups was prepared by polymerising the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone and the potassium salt of 4-methoxy-4'-hydroxydiphenyl sulphone (0.5 mole %) and 4-methoxy-4'-fluorodiphenyl sulphone (0.5 mole %) in sulpholane at 40\% ww rate concentration (polymer concentration 34.8\% ww) and 200\° for 24 hours.

A sample, A, was then removed and prepared for RV measurement. The solution was diluted to a polymer concentration of 9.4\% ww and a sample, B, removed after 1\%\% hours. A sample, C, was removed after a further 3 hours and the solution diluted to 2.4\% with more dry sulpholane and after 2 hours a sample, D, removed. After 18 hours a sample, E, was removed and the solution reconcentrated to 43\% ww polymer by distilling out some sulpholane under reduced pressure. After a further 18 hours at this concentration the solution was worked up to give sample F.
The RVs obtained were $A = 0.60$, $B = 0.41$, $C = 0.38$, $D = 0.21$, $E = 0.16$, $F = 0.63$. The sample, $A$, should have a DP of $\frac{100}{0.5} = 200$, corresponding to an $[RV]_{25^\circ}^{1\%}$ of 0.78. The failure of the polymer to reach this RV is probably due to some cleavage by fluoride ion in the concentration of solution used. The reduction in $[RV]_{25^\circ}^{1\%}$ on dilution, and subsequent increase on concentration does show that cleavage by fluoride is occurring. If cleavage by hydroxide had occurred there would be no fluorine ends available for reaction at the concentration stage. The experiment also demonstrates the reversibility of the fluoride cleavage reaction. The concentration of the solution when sample $F$ was taken is higher than the original polymer solution and this explains why sample $F$ has a higher $[RV]_{25^\circ}^{1\%}$ than sample $A$.

The cleavage of poly(diphenylene ether sulphone) by fluoride ion has been observed in several dipolar aprotic solvents: dimethyl sulfoxide, dimethyl sulphone, diphenyl sulphone, and sulpholane. Some results for cleavage in these solvents are shown in Table 12.

### Table 12

<table>
<thead>
<tr>
<th>$[RV]_{25^\circ}^{1%}$ of starting polymer</th>
<th>Solvent</th>
<th>Polymer conc % ww</th>
<th>Salt</th>
<th>Temp</th>
<th>Reaction Time</th>
<th>$[RV]_{25^\circ}^{1%}$ of final polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>Dimethyl sulphone</td>
<td>10</td>
<td>-</td>
<td>230°</td>
<td>1 hr</td>
<td>0.52</td>
</tr>
<tr>
<td>0.50</td>
<td>Dimethyl sulphone</td>
<td>10</td>
<td>KCl</td>
<td>230°</td>
<td>1 hr</td>
<td>0.51</td>
</tr>
<tr>
<td>0.50</td>
<td>Sulpholane</td>
<td>10</td>
<td>KF</td>
<td>230°</td>
<td>1 hr</td>
<td>0.17</td>
</tr>
<tr>
<td>0.61</td>
<td>Dimethyl sulphone</td>
<td>10</td>
<td>KF</td>
<td>230°</td>
<td>1 1/2 hrs</td>
<td>0.26</td>
</tr>
<tr>
<td>0.61</td>
<td>Sulpholane</td>
<td>10</td>
<td>KF</td>
<td>220°</td>
<td>3 hrs</td>
<td>0.33</td>
</tr>
<tr>
<td>0.61</td>
<td>Diphenyl sulphone</td>
<td>10</td>
<td>KF</td>
<td>260°</td>
<td>2 hrs</td>
<td>0.50</td>
</tr>
<tr>
<td>0.61</td>
<td>Diphenyl sulphone</td>
<td>10</td>
<td>KCl</td>
<td>260°</td>
<td>17 1/2 hrs</td>
<td>0.58</td>
</tr>
<tr>
<td>0.61</td>
<td>Dimethyl sulphoxide</td>
<td>10</td>
<td>KF</td>
<td>150°</td>
<td>3 hrs</td>
<td>0.29</td>
</tr>
<tr>
<td>0.72</td>
<td>Sulpholane</td>
<td>5</td>
<td>KF</td>
<td>200°</td>
<td>24 hrs</td>
<td>0.22</td>
</tr>
</tbody>
</table>
In all these experiments except the last one shown (at 5% w/w concentration in sulfolane) methyl chloride was passed through the solution for 1 hour after reaction for the time indicated.

The extent of cleavage by fluoride depends on the solvent used, for example more cleavage takes place in dimethyl sulphone than diphenyl sulphone. The solubility of potassium fluoride is probably different in each solvent and this would explain the different amounts of cleavage.

The solubility of a salt in a solvent will depend on the degree of cation and anion solvation and on the dielectric constant of the solvent. A salt such as potassium fluoride will have a high solubility in water which has a high dielectric constant (78.30) and where strong anion and cation solvation can take place.

In dimethyl sulfoxide (dielectric constant 46.70) and sulfolane (dielectric constant 44.0) solubilities are expected to be less because of the lower dielectric constant and lower amounts of ion solvation.

The cleavage of poly(diphenylene ether sulphone) by chloride ion is very much less than by fluoride. This is in agreement with the expected nucleophilicities of the halides in dipolar aprotic solvents.
The results of some cleavage experiments with lithium, potassium and caesium fluorides on poly(diphenylene ether sulphone) I and the polysulphone V from 4,4' dichlorodiphenyl sulphone and the dipotassium salt of 2,2 bis (4-hydroxy phenyl) propane are shown in Table 13.

### TABLE 13

Cleavage by alkali metal fluorides in sulpholane at 200°

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Fluoride</th>
<th>[RV]1% at start</th>
<th>[RV]1% after 25 hours</th>
<th>[RV]1% after 48 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Polymer Image]</td>
<td>KF</td>
<td>0.47</td>
<td>0.505</td>
<td>0.480</td>
</tr>
<tr>
<td>![Polymer Image]</td>
<td>CsF</td>
<td>0.47</td>
<td>0.255</td>
<td>0.205</td>
</tr>
<tr>
<td>![Polymer Image]</td>
<td>None</td>
<td>0.723</td>
<td>0.725</td>
<td>0.718</td>
</tr>
<tr>
<td>![Polymer Image]</td>
<td>LiF</td>
<td>0.723</td>
<td>0.718</td>
<td>0.678</td>
</tr>
<tr>
<td>![Polymer Image]</td>
<td>KF</td>
<td>0.723</td>
<td>0.250</td>
<td>0.240</td>
</tr>
<tr>
<td>![Polymer Image]</td>
<td>CsF</td>
<td>0.723</td>
<td>0.090</td>
<td>0.084</td>
</tr>
</tbody>
</table>

The experiments were all carried out at 200° with a 5% ww solution of the polymer in sulpholane. The reactions were carried out under nitrogen and samples removed after 25 and 48 hours.

There is a trend of increasing amount of cleavage with increasing size of cation. This effect is probably due to an increase in solubility of the salt as the cation size is increased. The increase in solubility probably results from an increased amount of cation solvation with the larger cation.
Another feature of Table 13 is the smaller amount of cleavage with the polysulphone V compared with poly(diphenylene ether sulphone) under the same conditions. The polysulphone V undergoes very little cleavage by potassium fluoride but is cleaved by caesium fluoride. This reflects the decreased reactivity of the ether bonds in the polysulphone V towards nucleophilic reagents. In this polymer the sulphone groups decrease electron density at the ether bonds by an inductive and conjugative effect while the isopropylidene group tends to increase the electron density at the ether bonds by an inductive effect.

\[
\text{Structure of Polysulphone V}
\]

The ether bonds are still activated to nucleophilic attack because the overall effect is expected to be electron withdrawal, but less so than for poly(diphenylene ether sulphone) where stronger electron withdrawal can take place.

\[
\text{Structure of Polysulphone V}
\]

The reduced reactivity of ether bonds in the polysulphone (V) results in a slower cleavage reaction so that the equilibrium for this polymer tends to lie over to the high polymer side. The phenoxide end groups formed by fluoride cleavage are also more reactive for the polysulphone (V) than for the poly(diphenylene ether sulphone) (I) since the phenoxide is adjacent to the electron donating isopropylidene group:

\[
\begin{align*}
\text{Polysulphone V} + F^- & \rightleftharpoons \text{Phenoxide + Polysulphone V} - F^- \\
\text{Phenoxide + Polysulphone V} - F^- & + \text{Isopropylidene group}
\end{align*}
\]
The increased reactivity tends to increase the rate of the forward reaction and this also will make the equilibrium lie on the high polymer side.

2 Measurement of the equilibrium constant

If the system poly(diphenylene ether sulphone) and potassium fluoride is described by the equation (11) it should have an equilibrium constant $K$ defined as

$$\text{(11)} \quad \text{ether linkages} + \text{fluorine end groups} + \text{phenoxide end groups} \rightleftharpoons \text{polymer} + KF$$

$$K = \frac{[\text{ether linkages}][KF]}{[\text{OK ends}][\text{F ends}]}$$

In order to measure this equilibrium constant, it is necessary to know the concentration of ether linkages, fluorine end groups, phenoxide end groups, and potassium fluoride at equilibrium.

It has not been possible to obtain an accurate figure for the concentration of potassium fluoride in sulpholane solutions. Some results are shown for the kinetic experiments in this part where the concentration of fluoride varied from 0.0019 to 0.1017 moles litre$^{-1}$ in 5% polymer solutions in sulpholane at 200°. Measurements were also made in pure sulpholane.

Anhydrous potassium fluoride was stirred in sulpholane at 200° under dry nitrogen. The solution was allowed to stand so that excess potassium fluoride settled out and samples of the supernatant liquid were removed and analysed for potassium and fluoride. The results obtained were potassium 105 ppm ww, fluoride 7 ppm ww. A repeat experiment gave
the results potassium 47 ppm ww, fluoride 20 ppm ww. These fluoride results correspond to 0.0004 and 0.0012 moles litre\(^{-1}\) respectively which is of the same order as found in the polymer solutions, but not accurate enough to include in the equilibrium expression.

If the potassium fluoride concentration is constant but unknown a constant \( K^* \) can be measured.

\[
K^* = \frac{K}{[KF]} = \frac{[\text{ether linkages}]}{[\text{OK ends}][\text{F ends}]}
\]

The concentrations of ether links and end groups may be calculated from the DP at equilibrium which is known from the equilibrium \([RV]^{1%}_{25^\circ}\).

The constant \( K^* \) has been measured at 200\(^\circ\) in sulpholane by approaching the equilibrium either by polymerising the potassium salt of 4-fluoro-4\'-hydroxydiphenyl sulphone or by cleavage of a polymer. The measurements were made in sulpholane as this is the most convenient solvent in which to study the equilibrium. More cleavage occurs in sulpholane than diphenyl sulphone and dimethyl sulfoxide. The amount of cleavage in dimethyl sulphone is probably more than in sulpholane but dimethyl sulphone is a poorer solvent for polymer. Attempts to dissolve high polymer in dimethyl sulphone often resulted in the production of a 2 phase system.

3 Polymerisation experiments

The potassium salt of 4-fluoro-4\'-hydroxydiphenyl sulphone has been polymerised at several concentrations in sulpholane at 200\(^\circ\). To obtain the maximum possible \([RV]^{1%}_{25^\circ}\) at a given concentration it was necessary
to add small amounts of 4,4'-difluorodiphenyl sulphone to the polymerisation. This is most probably because the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone contains a little of the dipotassium salt of 4,4'-dihydroxydiphenyl sulphone impurity and the added 4,4'-difluorodiphenyl sulphone is necessary to ensure a perfect balance of end groups. The 4-fluoro-4'-hydroxydiphenyl sulphone could contain a little 4,4'-dihydroxydiphenyl sulphone if this were not completely removed at the synthesis stage.

Each batch of 4-fluoro-4'-hydroxydiphenyl sulphone used in the polymerisation to equilibrium experiments was calibrated to find the amount of 4,4'-difluorodiphenyl sulphone to add. The calibration was carried out by polymerising samples of the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone in sulpholane at 200° and 40% ww concentration with added amounts of 4,4'-difluorodiphenyl sulphone or the dipotassium salt of 4,4'-dihydroxydiphenyl sulphone. The polymerisation was run for 24 hours to ensure that maximum [RV]_{25}^{1\%} was reached in each case. The results for one calibration experiment are shown in Table 14.

**TABLE 14**

<table>
<thead>
<tr>
<th>Additive</th>
<th>[RV]_{25}^{1%}</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>1.23</td>
</tr>
<tr>
<td>0.5 mole % KO-$\text{SO}_2$-$\text{OK}$</td>
<td>0.59</td>
</tr>
<tr>
<td>1.0 mole % KO-$\text{SO}_2$-$\text{OK}$</td>
<td>0.43</td>
</tr>
<tr>
<td>0.25 mole % F-$\text{SO}_2$-$\text{F}$</td>
<td>1.27</td>
</tr>
<tr>
<td>0.50 mole % F-$\text{SO}_2$-$\text{F}$</td>
<td>1.01</td>
</tr>
<tr>
<td>1.0 mole % F-$\text{SO}_2$-$\text{F}$</td>
<td>0.66</td>
</tr>
</tbody>
</table>
A plot of \([RV]_{25^\circ}^1\%\) versus mole % additive is shown in graph 14. The curves intercept at 0.12 mole % added 4,4'-difluorodiphenyl sulphone and this quantity of 4,4'-difluorodiphenyl sulphone was added to the potassium salt of this batch of 4-fluoro 4'-hydroxydiphenyl sulphone to obtain the maximum \([RV]_{25^\circ}^1\%\). In this case at 40% concentration the maximum \([RV]_{25^\circ}^1\%\) obtainable is 1.42. With other batches of 4-fluoro 4'-hydroxydiphenyl sulphone a different amount of 4,4'-difluorodiphenyl sulphone had to be added for maximum \([RV]_{25^\circ}^1\%\), but at 40% concentration the maximum \([RV]_{25^\circ}^1\%\) was always approximately 1.4.

The potassium salt of 4-fluoro 4'-hydroxydiphenyl sulphone was polymerised at 200° and concentrations from 1% to 70% ww with the required amount of 4,4'-difluorodiphenyl sulphone in each case. The polymerisations were run to equilibrium in each experiment as shown by no further increase in \([RV]_{25^\circ}^1\%\). The results are given in Table 15. The \([RV]_{25^\circ}^1\%\) of monomer is 0.027 and this figure is taken as the \([RV]_{25^\circ}^1\%\) for 0% concentration.

**TABLE 15**

*Polymerisation of F \(\text{SO}_2 \text{C} \equiv \text{O} \text{K} \) at 200° in dry sulphalone*

<table>
<thead>
<tr>
<th>Concentration of F (\text{SO}_2 \text{C} \equiv \text{O} \text{K} )</th>
<th>RV at 24 hrs</th>
<th>RV at 49 hrs</th>
<th>RV at 71 hrs</th>
<th>RV at 144 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% ww</td>
<td>0.063</td>
<td>0.063</td>
<td>0.062</td>
<td>0.066</td>
</tr>
<tr>
<td>2% ww</td>
<td>0.104</td>
<td>0.102</td>
<td>0.103</td>
<td>0.107</td>
</tr>
<tr>
<td>5% ww</td>
<td>0.236</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8% ww</td>
<td>0.337</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RV at 2hrs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RV at 19(\frac{1}{2}) hrs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% ww</td>
<td>0.42</td>
<td>0.44</td>
<td>0.45</td>
<td>0.44</td>
</tr>
<tr>
<td>30% ww</td>
<td>1.00</td>
<td>1.22</td>
<td>1.23</td>
<td>1.14</td>
</tr>
<tr>
<td>40% ww</td>
<td>1.42</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50% ww</td>
<td>1.93</td>
<td>-</td>
<td>1.99</td>
<td>-</td>
</tr>
<tr>
<td>70% ww</td>
<td>2.22</td>
<td>-</td>
<td>3.56</td>
<td>-</td>
</tr>
</tbody>
</table>
The DP at equilibrium may be obtained from the $[RV]^{1\%}_{25^\circ}$ at equilibrium using the expression

$$\text{DP} = \left( \frac{[RV]^{1\%}_{25^\circ}}{0.0232} \right)^{\frac{1}{0.663}}$$

The % reaction can be calculated from the DP since

$$\% \text{ reaction} = 100 - \frac{100}{\text{DP}}$$

The constant $K^*$ may be calculated from the DP as shown below in an example for a polymerisation of the potassium salt of 4-fluoro 4'-hydroxydiphenyl sulphone at 2% salt concentration.

Polymer concentration was 1.6062% ww = 17.995 g/litre

(Using density of solution = 1.12 from graph 15)

The $[RV]^{1\%}_{25^\circ}$ at equilibrium was 0.104, and DP was 9.61

Concentration of ether links was $(\text{DP} - 1) \times \text{polymer concentration} \div \text{DP} \times \text{Mol Wt of a repeat unit}$

$$= \frac{9.51 \times 17.9975}{9.61 \times 232} = 0.069503 \text{ moles/litre}$$

Concentration of F and OK end groups was $\frac{1 \times \text{polymer concentration}}{\text{DP} \times \text{Mol Wt of a repeat unit}}$

$$= \frac{1 \times 17.9975}{9.61 \times 232} = 0.008072 \text{ moles/litre}$$

$$K^* = \frac{[\text{ether links}]}{[\text{OK ends}][\text{F ends}]} = \frac{0.069503}{(0.008072)^2} = 1.07 \times 10^3 \text{ litre mole}^{-1}$$

The results for the polymerisation experiments are summarised in Table 16.
GRAPH 15

DENSITY OF POLY P, P' (DIPHENYLENE ETHER SULPHONE) SOLUTIONS IN SULPHOLANE AT 200°
TABLE 16

<table>
<thead>
<tr>
<th>Conc% of salt % ww</th>
<th>Polymer conc% ww</th>
<th>[RV]% 25° at equilibrium</th>
<th>DP at equilibrium</th>
<th>% reaction</th>
<th>K* litre mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.8015</td>
<td>0.063</td>
<td>4.51</td>
<td>77.83</td>
<td>0.41 x 10^3</td>
</tr>
<tr>
<td>2</td>
<td>1.6062</td>
<td>0.104</td>
<td>9.61</td>
<td>89.59</td>
<td>1.07 x 10^3</td>
</tr>
<tr>
<td>5</td>
<td>4.0399</td>
<td>0.236</td>
<td>33.07</td>
<td>96.98</td>
<td>5.41 x 10^3</td>
</tr>
<tr>
<td>8</td>
<td>6.5033</td>
<td>0.337</td>
<td>56.60</td>
<td>98.23</td>
<td>9.91 x 10^3</td>
</tr>
<tr>
<td>10</td>
<td>8.1531</td>
<td>0.44</td>
<td>84.63</td>
<td>98.82</td>
<td>17.72 x 10^3</td>
</tr>
<tr>
<td>30</td>
<td>25.530</td>
<td>1.0</td>
<td>291.96</td>
<td>99.66</td>
<td>66.1 x 10^3</td>
</tr>
<tr>
<td>40</td>
<td>34.780</td>
<td>1.42</td>
<td>495.47</td>
<td>99.80</td>
<td>135.7 x 10^3</td>
</tr>
<tr>
<td>50</td>
<td>44.4415</td>
<td>1.95</td>
<td>799.4</td>
<td>99.87</td>
<td>272.2 x 10^3</td>
</tr>
</tbody>
</table>

A plot of [RV]1% 25° and % reaction against salt concentration is shown in graph 16. The constant K* versus polymer concentration is shown in graph 17. This graph shows that a rapid increase in K* with polymer concentration occurs.

The increase in K* may be due to a change in the concentration of potassium fluoride. If the concentration of potassium fluoride falls with increasing polymer concentration then K* would be expected to increase. Under these conditions the true equilibrium constant, K, (K* [KF]) should be calculated but this has not been done since the concentration of potassium fluoride is not known.

A drop in concentration of potassium fluoride with increasing polymer concentration is not unexpected since there is a large change in the solvent medium. The dielectric constant will be less at the higher polymer concentration since the dielectric constant of sulpholane is 44.059 whilst that of poly(diphenylene ether sulphone) is only 3.515.
GRAPH 16 POLYMERIZATION OF F-O-SO₂-O-HOK IN DRY SULPHOLANE AT 200°C.
GRAPH 17

\[ K^* \] FOR POLYMERIZATION OF F-\( \text{C} \)-SO\(_2\)-\( \text{C} \)-OK

IN DRY SULPHOLANE AT 200°C.

\[ K^* \] LITRE MOLE\(^{-1}\)

\[ X = VALUE \ OF \ K^* \ CALCULATED \ FROM \ KINETIC \ DATA. \]

\[ 10, 20, 30, 40 \]

POLYMER CONC
\%

\[ 100 \times 10^3, 200 \times 10^3, 300 \times 10^3 \]
Other possible explanations for the change in $K^*$ with concentration are a change in reactivity of the fluoride or ether links. The fluoride reactivity may change if ion pairing takes place or due to a lower mobility in the more viscous polymer solution at higher concentration. The ether link reactivity may be different in the higher concentration because of coiling of the polymer molecules.

4 Cleavage experiments

The equilibrium (11) has also been approached by cleaving polymers of known [RV]$_{25}^{12}$ with anhydrous potassium fluoride in dry sulpholane solution at various concentrations. The polymers used had fluoro, chloro, or methoxy end groups. The fluoro end groups on the original polymer were included in the calculation of $K^*$, the chloro and methoxy end groups were assumed to be unreactive.

There is a possibility of chloro end groups being replaced by fluorine either by direct reaction with fluoride or indirectly by reaction with phenoxide ends, followed by cleavage of the ether bonds formed by fluoride. If some replacement occurs a different $K^*$ would result.

The concentration of ether links in the original polymer and polymer at equilibrium were calculated from the [RV]$_{25}^{12}$ and $\overline{DP}$.

Concentration of ether links was

$$\frac{(\overline{DP}) \times \text{Polymer concentration (g/l)}}{\overline{DP} \times 232}$$

The concentration of fluorine and phenoxide ends produced by cleavage then equals the initial concentration of ether links minus the concentration of ether links at equilibrium.
In the case of the fluorine ended polymers some extra fluorine ends are present from the original polymer. The concentration of these are calculated from:

\[
\text{Concentration of original fluorine end groups was } \frac{2 \times \text{Polymer concentration}}{\overline{DPs} \times 232}
\]

where DPs is the degree of polymerisation of the original polymer.

This figure is added to the fluorines produced by cleavage to give the total concentration of fluorine end groups in the fluorine ended polymer after cleavage to equilibrium.

The constant \( K^* \) was then calculated as before from the expression

\[
K^* = \frac{[\text{ether links}]}{[\text{OK ends}] [\text{F ends}]}
\]

The results obtained in these experiments are shown in Table 17.
TABLE 17

*K* from equilibrium reached by cleavage at 200°

<table>
<thead>
<tr>
<th>Polymer concn % ww</th>
<th>End groups of starting polymer</th>
<th>[RV]_{25°}^1% starting polymer</th>
<th>\overline{DP} of starting polymer</th>
<th>[RV]_{25°}^1% equilibrium polymer</th>
<th>\overline{DP} of equilibrium polymer</th>
<th>K* litre-mole^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>OCH$_3$</td>
<td>1.36</td>
<td>464.2</td>
<td>0.26</td>
<td>38.28</td>
<td>6.87 x 10^3</td>
</tr>
<tr>
<td>0.5%</td>
<td>Cl</td>
<td>0.723</td>
<td>179.0</td>
<td>0.062</td>
<td>4.40</td>
<td>0.65 x 10^3</td>
</tr>
<tr>
<td>1.0%</td>
<td>Cl</td>
<td>0.723</td>
<td>179.0</td>
<td>0.080</td>
<td>6.47</td>
<td>0.79 x 10^3</td>
</tr>
<tr>
<td>5%</td>
<td>Cl</td>
<td>0.723</td>
<td>179.0</td>
<td>0.23</td>
<td>29.96</td>
<td>5.19 x 10^3</td>
</tr>
<tr>
<td>5%</td>
<td>Cl</td>
<td>0.723</td>
<td>179.0</td>
<td>0.24</td>
<td>33.92</td>
<td>7.05 x 10^3</td>
</tr>
<tr>
<td>7.5%</td>
<td>Cl</td>
<td>0.723</td>
<td>179.0</td>
<td>0.287</td>
<td>44.43</td>
<td>9.35 x 10^3</td>
</tr>
<tr>
<td>15%</td>
<td>Cl</td>
<td>0.723</td>
<td>179.0</td>
<td>0.394</td>
<td>71.65</td>
<td>18.96 x 10^3</td>
</tr>
<tr>
<td>20%</td>
<td>Cl</td>
<td>0.723</td>
<td>179.0</td>
<td>0.441</td>
<td>84.92</td>
<td>25.8 x 10^3</td>
</tr>
<tr>
<td>30%</td>
<td>Cl</td>
<td>0.723</td>
<td>179.0</td>
<td>0.551</td>
<td>118.82</td>
<td>81.23 x 10^3</td>
</tr>
<tr>
<td>40%</td>
<td>Cl</td>
<td>0.723</td>
<td>179.0</td>
<td>0.629</td>
<td>145.09</td>
<td>280 x 10^3</td>
</tr>
<tr>
<td>1%</td>
<td>F</td>
<td>0.728</td>
<td>180.9</td>
<td>0.086</td>
<td>7.21</td>
<td>0.93 x 10^3</td>
</tr>
<tr>
<td>5%</td>
<td>F</td>
<td>0.728</td>
<td>180.9</td>
<td>0.269</td>
<td>40.29</td>
<td>6.86 x 10^3</td>
</tr>
<tr>
<td>5%</td>
<td>F</td>
<td>0.84</td>
<td>224.4</td>
<td>0.28</td>
<td>42.80</td>
<td>7.43 x 10^3</td>
</tr>
<tr>
<td>5%</td>
<td>F</td>
<td>0.84</td>
<td>224.4</td>
<td>0.29</td>
<td>45.13</td>
<td>8.33 x 10^3</td>
</tr>
<tr>
<td>7.5%</td>
<td>F</td>
<td>0.728</td>
<td>180.9</td>
<td>0.354</td>
<td>60.97</td>
<td>11.27 x 10^3</td>
</tr>
<tr>
<td>10%</td>
<td>F</td>
<td>0.728</td>
<td>180.9</td>
<td>0.441</td>
<td>84.92</td>
<td>18.7 x 10^3</td>
</tr>
<tr>
<td>15%</td>
<td>F</td>
<td>0.728</td>
<td>180.9</td>
<td>0.532</td>
<td>112.7</td>
<td>27.7 x 10^3</td>
</tr>
<tr>
<td>20%</td>
<td>F</td>
<td>0.728</td>
<td>180.9</td>
<td>0.670</td>
<td>159.59</td>
<td>114 x 10^3</td>
</tr>
</tbody>
</table>

Graph 18 shows the [RV]$_{25°}^1$ versus concentration of polymer for the experiments using Cl ended polymer. The RV approaches that of the starting polymer (0.723) with increasing concentration.

A plot of K* versus concentration is shown in graph 19 for the chlorine and fluorine ended polymers.
Graph 19. $K^*$ for cleavage of Cl and F ended poly(dimethylene ether sulphone) at 200°C in sulpholane with KF.

$K^*$

LITRE MOLE$^{-1}$

$10 	imes 10$

$20 	imes 10$

$30 	imes 10$

$40 	imes 10$

$50 	imes 10$

$60 	imes 10$

$70 	imes 10$

$10^3$

$10^4$

$10^5$

$10^6$

$K^*$

$\times 10$

$10^3$

$10^4$

$10^5$

$10^6$

$\times 10$

$10^3$

$10^4$

$10^5$

$10^6$

$X = F$ ended

$.$ = Cl ended.

POLYMER CONC$^a$

% WW
A similar trend of increasing $K^*$ with increasing polymer concentration is observed with these experiments in which equilibrium is approached by cleavage of high polymer. At low concentrations the $K^*$ obtained are very similar to those obtained in the polymerisation experiments. At high concentrations the $K^*$ obtained by cleavage of high polymer are lower.

Kinetics of the cleavage of poly(diphenylene ether sulphone) by fluoride ion

The phenoxides used to cleave poly(diphenylene ether sulphone) at the ether bonds are fairly powerful nucleophiles. The halides: fluoride, chloride, bromide and iodide are much less powerful and would not be expected to react with poly(diphenylene ether sulphone). It was found that in dipolar aprotic solvents such as sulpholane, at the high temperatures used for polymerisation (approximately 200°C), that fluoride is a sufficiently strong nucleophile to attack the activated ether bonds in poly(diphenylene ether sulphone). In dipolar aprotic solvents, fluoride is the strongest nucleophile of the halides, their nucleophilicity being in the order $F\gg Cl>Br>I$. The reasons for this order are believed to be differences in the degree of solvation (see Introduction).

Attack of ether bonds in poly(diphenylene ether sulphone) by fluoride ion corresponds to a depolymerisation reaction.

\[
(59) \quad \begin{array}{c}
\begin{array}{c}
\text{polymer}
\end{array}
\end{array} + KF \rightarrow \begin{array}{c}
\begin{array}{c}
\text{polymer}
\end{array}
\end{array} + F^{-} + \text{OK}
\]

The reaction of the potassium salt of 4-fluoro 4'-hydroxydiphenyl sulphone to form polymer is therefore a reversible reaction and an equilibrium (11) can be set up between polymer and fluoride ion.

\[
(11) \quad \text{\begin{tikzpicture}[baseline = -0.5ex]
    \node at (0,0) {\Huge \text{O}};
    \filldraw[black] (-0.5,0) circle (1ex);
    \filldraw[black] (0.5,0) circle (1ex);
    \filldraw[black] (0,1) circle (1ex);
    \filldraw[black] (0,0) circle (1ex);
    \node at (0,-0.5) {\text{OK}};
\end{tikzpicture}} + \text{\begin{tikzpicture}[baseline = -0.5ex]
    \node at (0,0) {\Huge \text{F}};
    \filldraw[black] (-0.5,0) circle (1ex);
    \filldraw[black] (0.5,0) circle (1ex);
    \filldraw[black] (0,1) circle (1ex);
    \filldraw[black] (0,0) circle (1ex);
    \node at (0,-0.5) {\text{\Huge \text{O}}};
\end{tikzpicture}} \rightleftharpoons \text{\begin{tikzpicture}[baseline = -0.5ex]
    \node at (0,0) {\Huge \text{O}};
    \filldraw[black] (-0.5,0) circle (1ex);
    \filldraw[black] (0.5,0) circle (1ex);
    \filldraw[black] (0,1) circle (1ex);
    \filldraw[black] (0,0) circle (1ex);
    \node at (0,-0.5) {\text{KF}};
\end{tikzpicture}} + \text{\begin{tikzpicture}[baseline = -0.5ex]
    \node at (0,0) {\Huge \text{O}};
    \filldraw[black] (-0.5,0) circle (1ex);
    \filldraw[black] (0.5,0) circle (1ex);
    \filldraw[black] (0,1) circle (1ex);
    \filldraw[black] (0,0) circle (1ex);
    \node at (0,-0.5) {\text{\Huge \text{O}}};
\end{tikzpicture}}
\]

During the polymerisation of the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone the majority of the potassium fluoride formed is precipitated from the solution, so that the solution is saturated with potassium fluoride. The amount of potassium fluoride dissolved in the polymerisation solvent is expected to be quite small but as the solution is saturated it should remain constant.

The equilibrium (11) lies over to the right under normal conditions otherwise high polymer would not be formed. For example a polymer of 100 repeat units corresponds to a 99% reaction

\[
\overline{DP} = \frac{100}{100 - \% \text{ reaction}}
\]

\[
\therefore \% \text{ reaction} = 100 - \frac{100}{\overline{DP}}
\]

\[
\% \text{ reaction for } \overline{DP} = 100 = 100 - \frac{100}{100} = 99\%
\]

The amount of cleavage under normal polymerisation conditions is therefore quite small.

Over the last few % reaction the \(\overline{DP}\) and hence \([RV]_{25^\circ}\) increase rapidly as shown below.
Clearly a small amount of ether bond cleavage will result in a large drop in $\overline{DP}$ and $[RV]_{25}^{1\%}$. The small amount of cleavage can then be followed by measuring the much larger change in $[RV]_{25}^{1\%}$.

6 Cleavage using Potassium Fluoride

The first attempts to measure the rate of reaction between polymer ether links and fluoride ion were made by reaction between a high molecular weight poly(diphenylene ether sulphone) and potassium fluoride in sulfolane at a polymer concentration of about 5\% \text{ w/w}. All the reactions were carried out at 200$^\circ$C, this being a typical temperature used for polymer preparation.

The polymers used in these experiments were prepared with halogen or methoxy end groups. A polymer with mainly chloro ends of $[RV]_{25}^{1\%} = 0.723$ was prepared by polymerizing the potassium salt of 4-chloro-4'-hydroxydiphenyl sulphone with 4,4'-dichlorodiphenyl sulphone. A polymer with fluoro ends and of $[RV]_{25}^{1\%} = 0.84$ was prepared similarly from the potassium salt of 4 fluoro 4'-hydroxydiphenyl sulphone and 4,4' difluorodiphenyl sulphone. A polymer with methoxy ends was prepared by polymerising a mixture of the potassium salt of 4-fluoro 4'-hydroxydiphenyl sulphone, with 0.25 mole \% dipotassium salt of 4,4'-dihydroxydiphenyl sulphone, in sulfolane. When polymerisation was complete,
methyl chloride was passed through the solution to convert phenoxide ends to methoxy:

\[(\text{phenoxide}) + \text{CH}_2\text{Cl} \rightarrow (\text{methoxy}) + \text{KCl}\]

The polymer from this reaction had an \([\text{RV}]_{25^\circ}^{1%} = 1.36\]

All of these polymers had very low hydroxyl end group concentrations: less than 1 hydroxyl per 1000 repeat units as measured by ir.

A solution of the polymer in sulpholane was prepared at 200°C under nitrogen. A saturated solution of potassium fluoride was also prepared under these conditions, sufficient potassium fluoride was employed to react with all the ether bonds present in the polymer. The polymer solution was then added to the stirred saturated solution of potassium fluoride in sulpholane. Samples (10ml containing approximately 0.5g of polymer) were removed at various times and worked up for \([\text{RV}]_{25^\circ}^{1%}\) determination by extracting the solvent and potassium fluoride. The samples were precipitated into water and the resulting polymer boiled once with distilled water acidified with acetic acid and again boiled with distilled water. After drying, the \([\text{RV}]_{25^\circ}^{1%}\) of the sample was measured as a 1% w/v solution in N,N-dimethyl formamide.

Additional samples were removed towards the end of the reaction, precipitated into water and filtered to remove polymer. The solutions were made up to 100 ml and analysed for fluoride.
The [RV]$_{25^\circ}$ were converted to degree of polymerisation using the formula

$$\overline{DP} = \frac{[RV]_{25^\circ} \frac{1}{0.663}}{0.0232}$$

The concentration of ether links at each time was then calculated from:

$$\text{Concentration of ether links} = \frac{(\overline{DP} - 1) \times P}{\overline{DP} \times 232} \text{ moles/litre}$$

P = Polymer concentration g/litre

232 = Molecular weight of a repeat unit.

The polymer concentration is known from the experiment in % ww and may be converted to g/litre by using the density of polymer solution at 200°C from graph 15.

The density of polymer solution was measured by filling a weighed 25ml volumetric flask with the polymer solution placing in the thermostated oil bath at 200°C, and levelling to mark once the temperature had been reached. The flask was reweighed to obtain the weight of solution and the density calculated (weight/volume). The measurements were made on pure sulpholane and 5 and 10% ww polymer solution. The flask used was calibrated at 20°C and so there will be an error in volume at 200°C. The density volumes for pure sulpholane however were very close to literature values.

The $\overline{DP}$ and concentration of ether links were calculated at each time from the formula shown above using the computer programme 3. The results obtained using a polymer with chlorine ends and of initial [RV]$_{25^\circ}$ = 0.723 are shown in Table 18. The final column of Table 18 shows % fission of ether linkages, which is calculated from the concentration of ether linkages at each time.
TABLE 18

Reaction of \(-\left(\begin{array}{c}\text{O} \\ \text{SO}_2 \text{O} - \text{O}\end{array}\right)_n\) with KF in sulphonylone at 200°C and 4.95% vv concentrations

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>[RV] (_{25^\circ})</th>
<th>DP</th>
<th>Concentration of ether links moles/litre</th>
<th>% fission of ether links</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.0</td>
<td>0.239858</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.651</td>
<td>152.8</td>
<td>0.239627</td>
<td>0.096</td>
</tr>
<tr>
<td>6</td>
<td>0.595</td>
<td>133.4</td>
<td>0.239398</td>
<td>0.192</td>
</tr>
<tr>
<td>9</td>
<td>0.553</td>
<td>119.5</td>
<td>0.239187</td>
<td>0.280</td>
</tr>
<tr>
<td>12</td>
<td>0.522</td>
<td>109.5</td>
<td>0.239003</td>
<td>0.356</td>
</tr>
<tr>
<td>15</td>
<td>0.493</td>
<td>100.5</td>
<td>0.238805</td>
<td>0.439</td>
</tr>
<tr>
<td>20</td>
<td>0.444</td>
<td>85.8</td>
<td>0.238394</td>
<td>0.610</td>
</tr>
<tr>
<td>30</td>
<td>0.405</td>
<td>74.7</td>
<td>0.237976</td>
<td>0.785</td>
</tr>
<tr>
<td>60</td>
<td>0.328</td>
<td>54.3</td>
<td>0.236767</td>
<td>1.290</td>
</tr>
<tr>
<td>120</td>
<td>0.284</td>
<td>43.7</td>
<td>0.235690</td>
<td>1.728</td>
</tr>
<tr>
<td>180</td>
<td>0.264</td>
<td>39.2</td>
<td>0.235047</td>
<td>2.006</td>
</tr>
<tr>
<td>1140</td>
<td>0.230</td>
<td>31.8</td>
<td>0.233624</td>
<td>2.599</td>
</tr>
<tr>
<td>1440</td>
<td>0.225</td>
<td>30.8</td>
<td>0.233368</td>
<td>2.706</td>
</tr>
<tr>
<td>3060</td>
<td>0.221</td>
<td>30.0</td>
<td>0.233154</td>
<td>2.795</td>
</tr>
</tbody>
</table>

In graph \(\widetilde{D}P\) plots of RV, DP and % fission of ether linkages against time are shown. The DP decreases quickly at first but as the polymerisation reaction becomes important, the rate of decrease in DP drops and finally comes to a constant level (approximately 30 in this case). At this point the rate of cleavage of ether linkages by fluoride equals the rate of formation of ether linkages by the polymerisation reaction, ie equilibrium as represented by reaction (11) has been reached. The total cleavage reaction corresponds to only about 2.8% reaction of the available ether linkages.
Graph 2.0 Reaction of \( \left( \mathbf{\cdot \cdot \cdot} \mathbf{\cdot \cdot \cdot} \mathbf{\cdot \cdot \cdot} \right) \) with KF in Sulpholane

At 200° and 4.95% w/w concentration.

\[ \square = \left[ \text{R.V.} \right]_{x5} \%
\]

\[ x = \text{D.P.} \]

\[ r = \% \text{ Fission of Ether Linkages} \]

% Fission of Ether Linkages

\[ \uparrow \text{Time in Minute} \]
Only over the initial part of the reaction can the rate of cleavage be measured. As the reaction proceeds the rate is affected by the polymerisation reaction which restores ether bonds. In order to obtain a value for the rate constant values were calculated over short time increments at the beginning of the reaction. The reaction would normally be expected to follow second order kinetics, but the potassium fluoride concentration is held constant since the solution is saturated and in contact with solid potassium fluoride which can dissolve up as the reaction proceeds. Under these conditions pseudo first order kinetics are expected:

\[
\frac{dx}{dt} = k' (a-x)(b-x)
\]

\[(b-x) \text{ is constant}\]

\[
\therefore \quad \frac{dx}{dt} = k(a-x)
\]

This first order rate expression is integrated between \(t_2\) and \(t_1\) so that rate constants over a small part of the reaction may be calculated.
Where \((a-x)^*\) is concentration of ether links in moles/litre at time \(t^*\),

Values for the first order rate constant were calculated over the initial part of the reaction, from this formula using computer programme 4.

The results obtained for the reaction in Table 18 are shown in Table 19.
TABLE 19

First order rate constants for reactions of $[-\left(\text{SO}_2\right)\left(\text{O}^{-}\right)]_{n}$ with KF at 200°C in sulpholane

<table>
<thead>
<tr>
<th>$t_1$</th>
<th>$t_2$</th>
<th>$(a-x)_1$</th>
<th>$(a-x)_2$</th>
<th>First order rate constant $\text{sec}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>180</td>
<td>0.23986</td>
<td>0.23963</td>
<td>$5.33 \times 10^{-6}$</td>
</tr>
<tr>
<td>180</td>
<td>360</td>
<td>0.23963</td>
<td>0.23942</td>
<td>$4.87 \times 10^{-6}$</td>
</tr>
<tr>
<td>360</td>
<td>540</td>
<td>0.23942</td>
<td>0.23921</td>
<td>$4.87 \times 10^{-6}$</td>
</tr>
<tr>
<td>540</td>
<td>720</td>
<td>0.23921</td>
<td>0.23899</td>
<td>$5.11 \times 10^{-6}$</td>
</tr>
<tr>
<td>720</td>
<td>900</td>
<td>0.23899</td>
<td>0.23879</td>
<td>$4.65 \times 10^{-6}$</td>
</tr>
<tr>
<td>900</td>
<td>1200</td>
<td>0.23879</td>
<td>0.23849</td>
<td>$4.10 \times 10^{-6}$</td>
</tr>
<tr>
<td>1200</td>
<td>1800</td>
<td>0.23849</td>
<td>0.23795</td>
<td>$3.78 \times 10^{-6}$</td>
</tr>
<tr>
<td>1800</td>
<td>2700</td>
<td>0.23795</td>
<td>0.23729</td>
<td>$3.08 \times 10^{-6}$</td>
</tr>
<tr>
<td>2700</td>
<td>3600</td>
<td>0.23729</td>
<td>0.23680</td>
<td>$2.30 \times 10^{-6}$</td>
</tr>
<tr>
<td>3600</td>
<td>7200</td>
<td>0.23680</td>
<td>0.23570</td>
<td>$1.29 \times 10^{-6}$</td>
</tr>
<tr>
<td>7200</td>
<td>10800</td>
<td>0.23570</td>
<td>0.23505</td>
<td>$7.67 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

The rate constant decreases as the reaction proceeds towards equilibrium but an average value may be obtained over the first two results $= 5.1 \times 10^{-6}$ sec$^{-1}$.

Measurements of first order rate constants for cleavage of polymer ether linkages with fluoride were made on several polymers, with different initial [RV]s and end groups. A summary of results is given in Table 20 and the data for these results are given in the experimental section.
First order rate constants for reaction of polymer ether linkages with potassium fluoride in sulphonylone at 200°

<table>
<thead>
<tr>
<th>End groups of starting polymer</th>
<th>Polymer conc n</th>
<th>[RV]1% of starting polymer</th>
<th>Fluoride ion conc n by analysis moles/litre (Duplicates)</th>
<th>first order rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>4.95% ww</td>
<td>0.72</td>
<td>0.0019</td>
<td>5.10x10^-6 sec^-1</td>
</tr>
<tr>
<td>OCH₃</td>
<td>4.98% &quot;</td>
<td>1.36</td>
<td>0.0032</td>
<td>4.24x10^-6 sec^-1</td>
</tr>
<tr>
<td>F</td>
<td>5.10% &quot;</td>
<td>0.84</td>
<td>0.0068</td>
<td>3.33x10^-6 sec^-1</td>
</tr>
<tr>
<td>F</td>
<td>5.12% &quot;</td>
<td>0.84</td>
<td>0.0107</td>
<td>2.74x10^-6 sec^-1</td>
</tr>
</tbody>
</table>

There is some variation in the value for the rate constant in the different experiments. This could be due to the small % reaction which was followed or to a variation in fluoride ion concentration. The fluoride analysis is not accurate enough to give a completely reliable value.

7 Cleavage of polymer with potassium fluoride in the presence of methyl chloride

In an attempt to increase the extent of the cleavage reaction, an experiment was carried out with potassium fluoride in the presence of methyl chloride. Methyl chloride should react rapidly with the phenoxide ends formed by cleavage. This should prevent the polymerisation reaction.

\[
\text{Cleavage: } \quad \text{CH}_3\text{Cl} \rightarrow \text{CH}_3\text{O}\text{CH}_3 + \text{KCl}
\]
The experiment was carried out as before using a 5% w/w solution of the polymer in sulpholane at 200° and sufficient potassium fluoride to react with all the ether linkages present. The reaction was slower than the normal reaction and only went a little lower in [RV]₁% as shown in Table 21.

TABLE 21

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>[RV]₁% 25°</th>
<th>DP</th>
<th>Concentration of ether links moles/litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.0</td>
<td>0.239371</td>
</tr>
<tr>
<td>5</td>
<td>0.700</td>
<td>170.5</td>
<td>0.239304</td>
</tr>
<tr>
<td>17</td>
<td>0.624</td>
<td>143.4</td>
<td>0.239036</td>
</tr>
<tr>
<td>35</td>
<td>0.566</td>
<td>123.7</td>
<td>0.238770</td>
</tr>
<tr>
<td>70</td>
<td>0.491</td>
<td>99.9</td>
<td>0.238305</td>
</tr>
<tr>
<td>90</td>
<td>0.452</td>
<td>88.1</td>
<td>0.237984</td>
</tr>
<tr>
<td>121</td>
<td>0.413</td>
<td>76.9</td>
<td>0.237586</td>
</tr>
<tr>
<td>180</td>
<td>0.374</td>
<td>66.2</td>
<td>0.237081</td>
</tr>
<tr>
<td>270</td>
<td>0.328</td>
<td>54.3</td>
<td>0.236286</td>
</tr>
<tr>
<td>350</td>
<td>0.298</td>
<td>47.0</td>
<td>0.235596</td>
</tr>
<tr>
<td>1350</td>
<td>0.211</td>
<td>27.9</td>
<td>0.232099</td>
</tr>
<tr>
<td>1530</td>
<td>0.217</td>
<td>29.1</td>
<td>0.232455</td>
</tr>
</tbody>
</table>

It is possible that the potassium chloride formed by reaction of phenoxide ends with methyl chloride interferes and prevents further reaction of fluoride with polymer. This would be due to a common ion effect or to a physical coating of the undissolved potassium fluoride. Another explanation is that the methyl chloride reacts with the fluoride in solution therefore reducing its concentration.
Cleavage of poly(diphenylene ether sulphone) with potassium fluoride in presence of 4,4'-difluorodiphenyl sulphone

An alternative method of removing phenoxide end groups is by reaction with 4,4'-difluorodiphenyl sulphone (reaction (63)).

\[
\begin{align*}
\text{(62)} & \quad \text{CH}_3\text{Cl} + \text{KF} \rightarrow \text{CH}_3\text{F} + \text{KCl} \\
\end{align*}
\]

In this case potassium fluoride is formed in the end stopping reaction and this cannot interfere in the reaction of fluoride with polymer. The reaction was carried out at 200° by adding a solution of polymer in sulpholane to a solution of 4,4'-difluorodiphenyl sulphone in sulpholane saturated with potassium fluoride. Two moles of 4,4'-difluorodiphenyl sulphone were used for 1 mole of polymer ether linkages to ensure rapid reaction of phenoxide ends.

Samples containing 0.5g of polymer were removed as before, precipitated into water and refluxed twice with methanol (to remove unreacted 4,4'-difluorodiphenyl sulphone), once with distilled water, and then dried at 120° under vacuum. The \([\text{RV}]_{25°}^{1%}\) s of the samples were then measured.
In the reaction (63) there is no overall loss of ether linkages and if the potassium fluoride concentration remains constant then the reaction should follow pseudo zero order kinetics. The reaction may be followed by converting the $[RV]_{25^\circ}^{1\%}$ to DP and applying a correction to allow for the 4-fluorodiphenyl sulphone ends. The concentration of original polymer ether bonds remaining may then be calculated.

$$\bar{DP}_c = \bar{DP}_t - (1 - \frac{\bar{DP}_t}{\bar{DP}_o})$$

Where $\bar{DP}_c = \bar{DP}$ corrected for $-\text{O}-\overset{\text{SO}}{-}\overset{\text{F}}{-}$ ends

$\bar{DP}_t = \bar{DP}$ at time t from the $[RV]_{25^\circ}^{1\%}$

$\bar{DP}_o = \bar{DP}$ of the original polymer.

The concentration of ether links at time $t$

$$= \frac{(\bar{DP}_o - 1) \times P}{\bar{DP}_o \times 232} \text{ moles/litre}$$

$P = \text{concentration of polymer in g/litre}$

The concentration of polymer ($P$) was calculated from the % ww concentration using the density from graph 21 which shows density of polymer/4,4'-difluorodiphenyl sulphone solutions in sulpholane at 200°.

The results for an experiment at 2.47% ww polymer concentration are shown in Table 22 and graph 22 as RV and DP against time and ether link concentration against time. Calculations were made with the IBM 360 computer and programme 5.
TABLE 22

Reaction of \(\text{SO}_2\)-alkyl-0-]_n - with KF in sulfolane with added
\(\text{F-SO}_2\)-alkyl-0-F

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>[\text{RV}]%</th>
<th>(\overline{DP}_t)</th>
<th>(\overline{DP}_c)</th>
<th>Concentration of ether links moles/litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.0</td>
<td>179.0</td>
<td>0.119231</td>
</tr>
<tr>
<td>3</td>
<td>0.667</td>
<td>158.5</td>
<td>158.4</td>
<td>0.119144</td>
</tr>
<tr>
<td>5</td>
<td>0.622</td>
<td>142.7</td>
<td>142.5</td>
<td>0.119059</td>
</tr>
<tr>
<td>10</td>
<td>0.563</td>
<td>122.7</td>
<td>122.4</td>
<td>0.118922</td>
</tr>
<tr>
<td>15</td>
<td>0.484</td>
<td>97.7</td>
<td>97.3</td>
<td>0.118668</td>
</tr>
<tr>
<td>20</td>
<td>0.456</td>
<td>89.3</td>
<td>88.8</td>
<td>0.118551</td>
</tr>
<tr>
<td>30</td>
<td>0.433</td>
<td>82.6</td>
<td>82.1</td>
<td>0.118440</td>
</tr>
<tr>
<td>40</td>
<td>0.379</td>
<td>67.6</td>
<td>66.9</td>
<td>0.118110</td>
</tr>
<tr>
<td>60</td>
<td>0.304</td>
<td>48.5</td>
<td>47.7</td>
<td>0.117389</td>
</tr>
<tr>
<td>120</td>
<td>0.218</td>
<td>29.3</td>
<td>28.5</td>
<td>0.115695</td>
</tr>
<tr>
<td>180</td>
<td>0.169</td>
<td>20.0</td>
<td>19.1</td>
<td>0.113623</td>
</tr>
<tr>
<td>270</td>
<td>0.123</td>
<td>12.4</td>
<td>11.4</td>
<td>0.109426</td>
</tr>
<tr>
<td>360</td>
<td>0.110</td>
<td>10.5</td>
<td>9.5</td>
<td>0.107302</td>
</tr>
<tr>
<td>1320</td>
<td>0.054</td>
<td>3.6</td>
<td>2.6</td>
<td>0.073714</td>
</tr>
</tbody>
</table>

The reaction follows pseudo zero order kinetics up to 38% reaction.

From the graph a zero order rate constant may be obtained.

\[
k = \frac{a - (a-x)}{t} = \frac{0.119231 - 0.073714}{22 \times 60 \times 60}
\]

\[
= 5.7 \times 10^{-7} \text{ mole litre}^{-1} \text{ sec}^{-1}
\]
The zero order rate constants were measured for several polymer concentrations between 2.47 and 7.76 % ww. A summary of the rate constants obtained is shown in Table 23. and the data used is given in the experimental section. The same polymer was used for all these experiments.

The polymer had chlorine end groups and $[\text{RV}]_{25^\circ} = 0.723$

**TABLE 23**

Zero order rate constants for reaction of $\text{KF}$ in sulpholane/$\text{F}^{-}$ at $200^\circ$

<table>
<thead>
<tr>
<th>Polymer concentration % ww</th>
<th>Initial ether links conc. moles/litre</th>
<th>Zero order rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.47</td>
<td>0.119231</td>
<td>$5.7 \times 10^{-7}$ mole litre$^{-1}$ sec$^{-1}$</td>
</tr>
<tr>
<td>3.47</td>
<td>0.168112</td>
<td>$9.7 \times 10^{-7}$</td>
</tr>
<tr>
<td>4.46</td>
<td>0.217104</td>
<td>$1.64 \times 10^{-6}$</td>
</tr>
<tr>
<td>4.95</td>
<td>0.240622</td>
<td>$1.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>7.32</td>
<td>0.359446</td>
<td>$9.1 \times 10^{-7}$</td>
</tr>
<tr>
<td>5.95</td>
<td>0.290892</td>
<td>$1.6 \times 10^{-6}$</td>
</tr>
<tr>
<td>7.76</td>
<td>0.381842</td>
<td>$1.95 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

A graph of $k'$ versus the ether link concentration is shown in graph 23. A fairly good straight line is obtained passing through the origin. The graph indicates that the reaction is first order in ether linkages as expected, since doubling the concentration of ether links, doubles the pseudo zero order rate constant.

A value for the first order rate constant may be obtained from the graph.
k first order = \frac{k 	ext{ zero order}}{\text{concentration of ether links}}

= 5.55 \times 10^{-6} \text{ sec}^{-1}

This value agrees quite well with that obtained using poly(diphenylene ether sulphone) and potassium fluoride alone in sulpholane, when the reaction should initially obey first order kinetics. The figure for this polymer (see table 19) was 5.10 \times 10^{-6} \text{ sec}^{-1}.

The rate constant for the reaction between poly(diphenylene ether sulphone) and potassium fluoride in the presence of 4,4'-difluorodiphenyl sulphone was also measured at a polymer concentration of 25% w/w. A first order rate constant of 2.40 \times 10^{-6} \text{ sec}^{-1} was obtained. This figure is lower than that obtained in the concentration range 2.47 to 7.76% w/w. The difference could be due to difference in fluoride ion concentration. The low level of fluoride ion concentration in these experiments has made accurate determination difficult.

9 Calculation of K* from Kinetic Data

The constant K* may be calculated from the rate constants for the polymerisation reaction (kp) and that for cleavage (kc)

\[
\begin{align*}
\text{Rate of polymerisation reaction} & = kp [OK \text{ ends}] [F \text{ ends}] \\
\text{Rate of cleavage reaction} & = kc [\text{ether linkages}] (\text{assuming KF concentration is constant}).
\end{align*}
\]
At equilibrium rate of polymerisation equals rate of cleavage.

\[ \frac{k_c}{[\text{ether linkages}]} = \frac{k_p}{[\text{OK ends}][\text{F ends}]} \]

\[ \therefore k_p = \frac{[\text{ether linkages}]}{k_c [\text{OK ends}][\text{F ends}]} = K^* \]

The value of \( k_c \) obtained at approximately 5% polymer concentration was \( 5.55 \times 10^{-6} \) sec\(^{-1}\). Extrapolation of the rate constants obtained for the polymerisation of dimer (see part 3) to 200° gives a value for \( kp \), the polymerisation rate constant, of \( 9.016 \times 10^2 \) litres mole\(^{-1}\) sec\(^{-1}\).

Substituting these values

\[ K^* = \frac{9.016 \times 10^{-2}}{5.55 \times 10^{-6}} = 16.2 \times 10^3 \text{ litre mole}^{-1} \]

This value for \( K^* \) is in fair agreement with that obtained at approximately 6% polymer concentration by polymerising the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone and is shown in graph 17.

A figure of \( 2.40 \times 10^{-6} \) sec\(^{-1}\) was obtained for \( k_c \) at 25% concentration. Using this a figure for \( K^* \) at 25% concentration may be calculated assuming the same polymerisation rate constant, \( kp \) applies

\[ K^* = \frac{9.016 \times 10^{-2}}{2.40 \times 10^{-6}} = 37.6 \times 10^3 \text{ litre mole}^{-1} \]

This is higher than the \( K^* \) found at 6% polymer concentration but not as high as that found in practice at 25% concentration, \( 65.4 \times 10^3 \) litre mole\(^{-1}\).
This slower rate of cleavage at 25% concentration does suggest that it could be a decrease in fluoride ion concentration or reactivity which is causing the increase in $K^*$. 

Cleavage experiments with soluble halides

Some experiments were carried out with tetra-ethyl ammonium halides in sulpholane. These compounds are completely soluble in sulpholane and their concentration may be obtained more easily by analysis.

Table 24 shows the results of some qualitative experiments using the soluble halides and a poly(diphenylene ether sulphone)- 1 mole of halide was used for each mole of ether linkages except for the fluoride when accurate weighing was difficult due to the hygroscopic nature of this compound.

TABLE 24

<table>
<thead>
<tr>
<th>Polymer concentration</th>
<th>Tetra ethyl ammonium halide</th>
<th>$[R_{UV}]^%$ after reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5%</td>
<td>$-$</td>
<td>1.23</td>
</tr>
<tr>
<td>2.5%</td>
<td>I$^-$</td>
<td>1.16</td>
</tr>
<tr>
<td>2.5%</td>
<td>Br$^-$</td>
<td>1.01</td>
</tr>
<tr>
<td>2.5%</td>
<td>Cl$^-$</td>
<td>0.97</td>
</tr>
<tr>
<td>2.5%</td>
<td>F$^-$</td>
<td>0.18</td>
</tr>
<tr>
<td>30%</td>
<td>F$^-$</td>
<td>0.15</td>
</tr>
</tbody>
</table>
These reactions were carried out for 4.5 hours at 200°. A trend of increasing nucleophility is seen along the halide series with fluoride being much the stronger $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$. 

**Reaction between poly(diphenylene ether sulphone) and tetra ethyl ammonium fluoride in sulpholane**

Three reactions were carried out between poly(diphenylene ether sulphone) and tetra ethyl ammonium fluoride in sulpholane at 200°. Tetra ethyl ammonium fluoride is completely soluble in sulpholane and its concentration may be measured more accurately than potassium fluoride.

Tetra ethyl ammonium fluoride is difficult to handle because it is very hygroscopic (much more so than potassium fluoride). For this reason its concentration in solution is best measured by analysis rather than direct weighing.

In these experiments the concentration of poly(diphenylene ether sulphone) was kept at approximately 5% ww and the concentration of tetra ethyl ammonium fluoride changed in each experiment. The method used was the same as for the reactions employing potassium fluoride. The polymer solution at 200° was added to the stirred solution of tetra ethyl ammonium fluoride in sulpholane at 200°. Samples were removed and worked up for $[\text{RV}]_{25}^{1%}$. The $\overline{DP}$ and concentration of ether links were then calculated at each time using computer programme 3. The results for an experiment using 2.0g of tetra ethyl ammonium fluoride in 400g of solution containing 20 g of polymer are shown in Table 25 and graph 24 as a plot of concentration of ether links against time.
TABLE 25

Reaction of $\left[ \begin{array}{c} \text{SO}_2 \text{O} \\ \end{array} \right]_n$ with $(\text{C}_2\text{H}_5)_4\text{NF}$ in sulphonylam at 200°

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>[RV]$_{250}$</th>
<th>DF</th>
<th>Concentration of ether links moles/litre</th>
<th>Second order rate constants litre mole$^{-1}$ sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.0</td>
<td>0.238629</td>
<td>...</td>
</tr>
<tr>
<td>1.5</td>
<td>0.678</td>
<td>162.5</td>
<td>0.238493</td>
<td>2.97 x 10$^{-4}$</td>
</tr>
<tr>
<td>3</td>
<td>0.646</td>
<td>151.0</td>
<td>0.238381</td>
<td>2.45 x 10$^{-4}$</td>
</tr>
<tr>
<td>6</td>
<td>0.564</td>
<td>123.1</td>
<td>0.238020</td>
<td>2.78 x 10$^{-4}$</td>
</tr>
<tr>
<td>9</td>
<td>0.520</td>
<td>108.9</td>
<td>0.237766</td>
<td>2.84 x 10$^{-4}$</td>
</tr>
<tr>
<td>12</td>
<td>0.477</td>
<td>95.6</td>
<td>0.237460</td>
<td>2.96 x 10$^{-4}$</td>
</tr>
<tr>
<td>15</td>
<td>0.442</td>
<td>85.2</td>
<td>0.237154</td>
<td>2.91 x 10$^{-4}$</td>
</tr>
<tr>
<td>18</td>
<td>0.418</td>
<td>78.3</td>
<td>0.236906</td>
<td>3.11 x 10$^{-4}$</td>
</tr>
<tr>
<td>21</td>
<td>0.406</td>
<td>75.0</td>
<td>0.236769</td>
<td>2.73 x 10$^{-4}$</td>
</tr>
<tr>
<td>25</td>
<td>0.390</td>
<td>70.6</td>
<td>0.236569</td>
<td>2.68 x 10$^{-4}$</td>
</tr>
<tr>
<td>30</td>
<td>0.366</td>
<td>64.1</td>
<td>0.236227</td>
<td>2.27 x 10$^{-4}$</td>
</tr>
<tr>
<td>45</td>
<td>0.333</td>
<td>55.6</td>
<td>0.235653</td>
<td>1.88 x 10$^{-4}$</td>
</tr>
<tr>
<td>60</td>
<td>0.314</td>
<td>50.9</td>
<td>0.235254</td>
<td>...</td>
</tr>
<tr>
<td>120</td>
<td>0.309</td>
<td>49.7</td>
<td>0.235138</td>
<td>...</td>
</tr>
<tr>
<td>180</td>
<td>0.301</td>
<td>47.7</td>
<td>0.234943</td>
<td>...</td>
</tr>
<tr>
<td>1140</td>
<td>0.303</td>
<td>48.2</td>
<td>0.234993</td>
<td>...</td>
</tr>
<tr>
<td>1440</td>
<td>0.304</td>
<td>48.5</td>
<td>0.235018</td>
<td>...</td>
</tr>
<tr>
<td>2580</td>
<td>0.308</td>
<td>49.4</td>
<td>0.235114</td>
<td>...</td>
</tr>
</tbody>
</table>

The reaction is similar to that using potassium fluoride, the cleavage being fast at the start and then slowing up as equilibrium is approached.

Since the concentration of ether links and fluoride ion changes as the reaction proceeds, second order kinetics should be followed at the start of the reaction when the effect of approach to equilibrium can be ignored.
\[ \frac{dx}{dt} = k(a-x)(b-x) \]

Integrating between time \( t \) and \( 0 \)

\[ kt = \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} \]

The rate constant may be calculated from this expression over the initial part of the reaction. The concentration of ether links at each time \((a-x)\) is known from \([RV]\) and the concentration of fluoride \((b-x)\) at each time may be calculated, knowing the concentration at the start.

The concentration of fluoride at the start was calculated from the known concentration at the end of the reaction (from analytical results).

Values of the rate constant were calculated at each time using computer programme 5. An average value over the first few results was taken.

The results for the three experiments are shown in Table 26.

**TABLE 26**

**Reaction of \([\bigcirc] - \text{SO}_2 - \bigcirc - 0 - )_n \text{ with } (C_2H_5)_4NF \text{ in sulphonale at } 200^\circ**

<table>
<thead>
<tr>
<th>Initial concentration of ether links moles/litre</th>
<th>Initial concentration fluoride moles/litre</th>
<th>Second order rate constant ( \text{litre mole}^{-1} \text{ sec}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.24034</td>
<td>0.01187</td>
<td>( 3.3 \times 10^{-4} )</td>
</tr>
<tr>
<td>0.23863</td>
<td>0.02202</td>
<td>( 2.8 \times 10^{-4} )</td>
</tr>
<tr>
<td>0.24252</td>
<td>0.06468</td>
<td>( 8.3 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

The first two results are in good agreement. In the third experiment the initial reaction was very rapid, the \([RV]\) falling from 0.723 to 0.212 in 60 seconds. An accurate result under these conditions is not expected.
If it is assumed that the fluoride in tetra ethyl ammonium fluoride has
the same reactivity as in potassium fluoride an estimate of the concentration
of potassium fluoride in 3% polymer solution may be made. The first
order rate constant, \( k_1 \), for cleavage by potassium fluoride is in fact
\( k_2 [KF] \) where \( k_2 \) is the second order rate constant and \([KF]\) is the
(constant) concentration of potassium fluoride.

\[
\therefore [KF] = \frac{k_1}{k_2} = \frac{5.55 \times 10^{-6}}{3.0 \times 10^{-4}} = 0.0185 \text{ moles/litre}
\]

The result is of the same order as that found by analysis (see table 20).
This figure will not be valid if the reactivities of the fluoride in
the two compounds is different. The reactivities could be different,
if for example, some ion pair formation takes place.

These cleavage experiments were run to equilibrium and the concentration
of soluble fluoride at equilibrium measured by analysis. In this case
the true equilibrium constant, \( K \), for the system poly(diphenylene
ether sulphone) and tetra ethyl ammonium fluoride may be measured.

\[
K = \frac{[\text{ether links}][F^-]}{[O \text{ ends}][F \text{ ends}]}
\]

The concentration of ether links, phenoxide end groups and fluorine
end groups were obtained from the \([RV]^{18}\% \) at equilibrium as before.

The results obtained are shown in Table 27.
Equilibrium constants for reaction between $-[-\left(\begin{array}{c} S \end{array}\right)_{2} \left(\begin{array}{c} O \end{array}\right)-0]_n -$ and $(C_{2}H_{5})NF$ in sulfolane at 200°.

<table>
<thead>
<tr>
<th>[RV]% at equilibrium</th>
<th>Concentration of polymer</th>
<th>Concentration $(C_{2}H_{5})NF$</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.407</td>
<td>4.96% ww</td>
<td>0.010 moles/litre</td>
<td>0.68 x 10³</td>
</tr>
<tr>
<td>0.308</td>
<td>4.92% ww</td>
<td>0.0184 &quot;</td>
<td>0.33 x 10³</td>
</tr>
<tr>
<td>0.154</td>
<td>5.01% ww</td>
<td>-0.52 &quot;</td>
<td>0.068 x 10³</td>
</tr>
</tbody>
</table>

The reason for the decrease in equilibrium constant with increasing concentration of tetra ethyl ammonium fluoride is not known. Tetra ethyl ammonium fluoride is known to decompose to some extent on heating:

$$(C_{2}H_{5})_{4}NF\rightarrow (C_{2}H_{5})_{3}NHF + CH_{2}CH_{2}$$

It may be that some unreactive ends are introduced into the polymer chain so that further cleavage takes place. This effect would probably be more severe with a higher concentration of tetra ethyl ammonium fluoride.

The average second order rate constant for reaction between poly(diphenylene ether sulphone) and tetra ethyl ammonium fluoride was $3.00 \times 10^{-4}$ litre mole$^{-1}$ sec$^{-1}$. Assuming the same polymerisation rate constant applies for phenoxide ends with a tetra ethyl ammonium cation as with a potassium cation, an equilibrium constant may be calculated from the kinetic data.
This value is in good agreement with the equilibrium constant obtained in the experiment using a concentration of tetra ethyl ammonium fluoride of 0.0184 mole/litre (see table 27).

\[
K = \frac{k_p}{k_c} = \frac{9.016 \times 10^{-2}}{3.00 \times 10^{-4}} = 0.30 \times 10^3
\]

Comparison of the rates of reactions occurring at equilibrium

The concentration of fluorine ends, phenoxide ends and ether links, are known at equilibrium from the DP at equilibrium. Using these figures the actual rates of the three reactions occurring at equilibrium may be calculated from the relevant rate constants. The three reactions occurring at equilibrium are chain extension, chain cleavage by fluoride and chain cleavage by phenoxide ends. The rates are calculated below for the polymerisation of the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone at 200° and 10% w/w concentration in sulpholane (see table 16).

At equilibrium \([RV]^{19\%}_{25^\circ} = 0.44, \text{DP} = 84.6\)

\[-F \text{ ends} = [OK \text{ ends}] = 0.00472 \text{ moles litre}^{-1}\]

\[[\text{ether linkages}] = 0.3947 \text{ moles litre}^{-1}\]

**Chain extension**

\[
\text{\[F - \] + KO-\[O\] + KF}
\]

\[
k = 9.0 \times 10^{-2} \text{ litre mole}^{-1} \text{ sec}^{-1}
\]

\[
\text{rate} = 9.0 \times 10^{-2} \times (4.72 \times 10^{-3})^2 = 2.00 \times 10^{-6} \text{ mole litre}^{-1} \text{ sec}^{-1}
\]
Chain cleavage by fluoride

\[
\text{\[
\begin{array}{c}
\text{\textbullet} \text{\textbullet} \text{\textbullet} \text{\textbullet} \\
\text{\textbullet} \text{\textbullet} \text{\textbullet} \text{\textbullet} \\
\text{\textbullet} \text{\textbullet} \text{\textbullet} \text{\textbullet} \\
\text{\textbullet} \text{\textbullet} \text{\textbullet} \text{\textbullet}
\end{array}
\]}
\text{ + KF} \rightarrow \text{\[
\begin{array}{c}
\text{\textbullet} \text{\textbullet} \text{\textbullet} \text{\textbullet} \\
\text{\textbullet} \text{\textbullet} \text{\textbullet} \text{\textbullet} \\
\text{\textbullet} \text{\textbullet} \text{\textbullet} \text{\textbullet} \\
\text{\textbullet} \text{\textbullet} \text{\textbullet} \text{\textbullet}
\end{array}
\]
\text{F} + \text{KO-\[
\begin{array}{c}
\text{\textbullet} \text{\textbullet} \text{\textbullet} \text{\textbullet} \\
\text{\textbullet} \text{\textbullet} \text{\textbullet} \text{\textbullet} \\
\text{\textbullet} \text{\textbullet} \text{\textbullet} \text{\textbullet} \\
\text{\textbullet} \text{\textbullet} \text{\textbullet} \text{\textbullet}
\end{array}
\]}}
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
\]
PART 6 PREPARATION OF POLY(DIPHENYLENE ETHER SULPHONE) CONTAINING
ORHO, META AND PARA LINKAGES

Poly(diphenylene ether sulphone)s containing the three possible isomeric
repeat units shown below were prepared in order to determine the effect
on physical properties of ortho and meta linkages in these polymers.

\[
\text{(XVIII)} \quad \text{P,P'} \text{- repeat unit}
\]

\[
\text{(XIX)} \quad \text{O,P'} \text{- repeat unit}
\]

\[
\text{(XX)} \quad \text{M,P'} \text{- repeat unit}
\]

The polymers made were homopolymers consisting entirely of these repeat
units as well as copolymers comprised of the units (XVIII) with (XIX)
and (XX).

For measurement of physical properties, approximately 100g of each
polymer was required. The reduced viscosity of the polymer measured
as a 1% wv solution in N,N dimethyl formamide \([\text{RV}_{25^\circ}]^{1\%}\) must be \(>0.38\)
for the measurement of physical properties to be practicable. Polymers
of lower \([\text{RV}]^{1\%}_{25^\circ}\) than 0.38 are brittle and mouldings of the polymer are
usually cracked and not suitable for measurement of physical properties.
An $[\text{RV}]_{25^\circ}^\%$ of, for example, 0.40 corresponds to a degree of polymerisation of 73 repeat units, which is a number average molecular weight ($M_n$) of approximately 17,000. To achieve an $[\text{RV}]_{25^\circ}^\%$ of 0.40 the % reaction must be 98.6%:

$$\%\text{ reaction} = \frac{100 - 100}{\text{DP}} = \frac{100 - 100}{73} = 98.6\%$$

In order to obtain % reaction of this order the monomers used must be of high purity and the reaction has to proceed cleanly without loss of end groups by side reactions.

The polymers were prepared by the nucleophilic substitution reaction which is known to be a clean reaction producing polymers of defined structure depending on the monomers used. There are two possible methods of preparing the polymer by nucleophilic substitution: a two component system (eg reaction (54)) or a one component system (eg reaction 50)).

\begin{align*}
4) & \quad \frac{3}{2}n \text{ KO} - \text{SO}_2 - \text{O}^- \quad \text{OK} + \frac{3}{2}n \text{ F} - \text{SO}_2 - \text{O}^- \quad \text{F} \quad \rightarrow \\
& \quad \left[ - \sigma \text{ SO}_2 - \text{O}^- \right]_n^- \quad + \quad n \text{ KF} \\
6) & \quad n \text{ F} - \text{SO}_2 - \text{O}^- \quad \text{OK} \quad \rightarrow \quad \left[ - \sigma \text{ SO}_2 - \text{O}^- \right]_n^- \quad + \quad n \text{ KF}
\end{align*}

Of these two alternatives the one component system was chosen because the correct stoichiometry is easier to achieve. The monomer used is self balancing in phenoxide and fluorine end groups, provided the monomer is pure. With the two component system errors in stoichiometry are
easily introduced by errors in weighing or losses during addition. A small error in stoichiometry (~1%) is enough to prevent the production of high polymer. The disadvantage of the one component system compared with the two component system is its lower reactivity (see Part 3 Kinetics of polymerisation reactions). The lower reactivity means that temperatures in excess of 180° are needed to produce high molecular weight polymer.

The polymerisation may be carried out in a suitable solvent or preferably in the melt for example at 280° for 45 minutes when the highest \([RV]_{25^\circ}\) value is obtained. The reaction under these conditions is a useful test for the purity of the monomer used. If high \([RV]_{25^\circ}\) polymer is produced the monomer is of high purity. When heated the monomeric salt melts but very quickly solidification occurs as polymer is produced. The melt polymerisation technique is not suitable for making copolymers since adequate mixing of the monomers cannot take place. Control of \([RV]_{25^\circ}\) is not possible because the reaction is so rapid.

Polymerisation in solution is carried out in a suitable solvent such as dimethyl sulphone (mp 109°, bp 238°) or sulpholane (mp 28°, bp 285°). Both solvents are dipolar aprotic solvents and are expected to enhance the rate of nucleophilic substitution reactions. These solvents are good solvents for the monomer and polymer produced and are stable at the temperatures (180–235°) used for the polymerisations.
Method

The potassium salt of the phenol was prepared by reaction with potassium hydroxide in aqueous methanol solution. Approximately 4N – potassium hydroxide was prepared by diluting a standard concentrated volumetric solution with redistilled methanol. This solution was standardised against a sample of the pure phenol to be used, by potentiometric titration (see experimental section). The potassium salt was then prepared by adding the required amount of 4N potassium hydroxide solution to the phenol dissolved in methanol. The neutralisation proceeds with formation of water eg

$$\text{F-SO}_2\text{-OH} + \text{KOH} \rightarrow \text{F-SO}_2\text{-OK} + \text{H}_2\text{O}$$

A 0.25% deficiency of potassium hydroxide was used in preparing the salt as this was found to produce the best salt. A series of salts were prepared from 4-chloro-4'-hydroxydiphenyl sulphone and potassium hydroxide solution with different stoichiometries. The salts were dried and then melt polymerised at 280° for 45 minutes with the results shown in Table 28.
TABLE 28

Melt Polymerisation of Cl-$$\text{SO}_2$$-$$\text{OH}$$-OK

<table>
<thead>
<tr>
<th>Stoichiometry used to prepare salt</th>
<th>[RV]$_{25%}$ of the melt polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 mole % excess KOH</td>
<td>0.66</td>
</tr>
<tr>
<td>Equimolar</td>
<td>0.82</td>
</tr>
<tr>
<td>0.25 mole % excess Cl-$$\text{SO}_2$$-$$\text{OH}$$</td>
<td>0.84</td>
</tr>
<tr>
<td>0.50 mole % excess Cl-$$\text{SO}_2$$-$$\text{OH}$$</td>
<td>0.82</td>
</tr>
<tr>
<td>0.75 mole % excess Cl-$$\text{SO}_2$$-$$\text{OH}$$</td>
<td>0.71</td>
</tr>
</tbody>
</table>

The results show that the best salt is obtained using approximately 0.25 mole % excess phenol. The excess phenol probably sublimes out of the salt during drying leaving the pure potassium salt behind. A 0.25 mole % deficiency of potassium hydroxide was adopted as standard when preparing the potassium salts.

The solution of the potassium salt after preparation was evaporated to dryness in a rotary evaporator, and the potassium salt obtained further dried to remove the last traces of water. This water is difficult to remove and drying was carried out at approximately 120° under high vacuum (<0.001 mm pressure).

Polymerisation of the dry salt was effected by stirring under nitrogen in the chosen solvent in a flask suspended in a thermostated oil bath. Reaction was usually carried out for 24 hours at temperatures of about 200°. When reaction was complete methyl chloride was passed through the solution in order to convert unreacted phenoxide end groups to methoxyl.
If this is not done the phenoxide end groups are converted into hydroxyl during work up. It has been shown that the presence of hydroxyl end groups on the polymer makes the polymer unstable at high temperatures (>350°).

The instability is probably caused by a branching or cross linking reaction and results in an increase in the melt viscosity of the polymer. If the polymer has methoxyl, fluorine or chlorine ends the polymer is stable at these temperatures. One property of the polymers which was examined was melt viscosity at high temperature so it was essential to convert unreacted phenoxide groups to methoxyl.

The polymer was worked up by cooling the solution to room temperature, dissolving in N,N-dimethylformamide or dimethyl sulphoxide and precipitating into methanol in a macerator. The resulting fine polymer powder was refluxed twice with methanol, once with water acidified with acetic acid, twice with distilled water, and once with methanol/acetone (90:10). The resulting polymer which was substantially free of solvent and potassium halide was dried for 18 hours at approximately 140° under vacuum.

**Poly p.p' (diphenylene ether sulphone)**

Samples of the poly(diphenylene ether sulphone) with all para repeat units (VIII) and with [RV]<sub>175</sub> up to 0.61 were available in ICI Plastics Division and had been prepared by polymerisation of the potassium salt of 4-chloro-4' hydroxydiphenyl sulphone. These polymers were subjected
to a further work up to ensure freedom from polymerisation solvent and potassium halide. Samples with \[ \text{RV}_{25^\circ} \] 1.17 and 1.71 were prepared by melt polymerising the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone at 280° for 1 hour.

Samples of poly(diphenylene ether sulphone) were also prepared by the reaction between 4,4'-difluorodiphenyl sulphone and the dipotassium salt of 4,4'-dihydroxydiphenyl sulphone (reaction 54). With this system a lower temperature of 160° could be used because of the greater reactivity of the monomers. Dimethyl sulfoxide (bp 189°) was the solvent, instead of sulfolane, and polymer samples with RVs up to 0.80 were obtained.

**Poly(diphenylene ether sulphone) with ortho linkages**

Poly(diphenylene ether sulphone) containing o,p' repeat units (XIX) were prepared using the potassium salt of 4-fluoro-2'-hydroxydiphenyl sulphone. This monomer is less reactive than the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone (see Part 3: Kinetics of polymerisation) mainly because of the lower reactivity of phenoxide in the ortho position. This had also been shown by an approximate kinetic study in dimethyl sulfoxide. The potassium salt of 4-chloro-4'-hydroxy diphenyl sulphone (1 mole) or the potassium salt of 4-fluoro-2'-hydroxy diphenyl sulphone (1 mole) was reacted with 4,4' difluorodiphenyl sulphone (2 moles) in dimethyl sulfoxide at 80° for various times. Percentage reaction was measured by titrating unused base (phenate) with 0.1N-sulphuric acid using a pH meter. The results are shown in Table 29.
TABLE 29

Reaction of Cl-SO₂⁻-OK and F-SO₂⁻-OK with F-SO₂⁻-F

<table>
<thead>
<tr>
<th>Cl-SO₂⁻-OK</th>
<th>F-SO₂⁻-OK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>% reaction</td>
</tr>
<tr>
<td>0 hours</td>
<td>1.2</td>
</tr>
<tr>
<td>1/4 &quot;</td>
<td>7.2</td>
</tr>
<tr>
<td>1/2 &quot;</td>
<td>13.4</td>
</tr>
<tr>
<td>1 &quot;</td>
<td>24.4</td>
</tr>
<tr>
<td>1 1/2 &quot;</td>
<td>37.6</td>
</tr>
</tbody>
</table>

A phenoxide O⁻ group in the para- position to sulphone reacts approximately 8 times as fast as phenoxide in the ortho- position. This factor is similar to that found in the polymerisation experiments (see Part 3).

The homopolymer (XXI) of the potassium salt of 4-fluoro-2'-hydroxy diphenyl sulphone was prepared by melt polymerisation at 280° under reduced pressure for up to 3 hours.

\[
[-\text{SO}_2^-\text{O}]_n \quad (XXI)
\]

The polymer was crystalline to X-rays and insoluble in solvents such as dimethyl sulphoxide and N,N-dimethyl formamide and was converted to an amorphous form by dissolution in cold concentrated sulphuric acid and then precipitation into water. The highest [RV]²⁵⁰ value for the amorphous polymer thus obtained was 0.39. A sample of this polymer, pressed into film at 320° under 20 tons pressure for 5 minutes was
extremely brittle and so this homopolymer of 4-fluoro 2'-hydroxydiphenyl sulphone was not prepared on a large scale.

Polymers containing ortho para'- repeat units were prepared using mixtures of the potassium salt of 4-chloro-4'-hydroxydiphenyl sulphone and the potassium salt of 4-fluoro-2'-hydroxydiphenyl sulphone in dimethyl sulphone. With this system however, it was difficult to obtain high [RV]$\%_{25^\circ}$ polymer. Using mixtures of the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone and the potassium salt of 4-fluoro-2'-hydroxydiphenyl sulphone polymers of higher [RV]$\%_{25^\circ}$ could be obtained as shown in Table 30. This system is more reactive because ether bonds are formed by displacement of fluorine only and not by displacement of chlorine.

**TABLE 30**

Copolymerisation of F-\(\overset{\circ}{\text{O}}\)SO\(_2\) in dimethyl sulphone

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Polymerisation Conditions</th>
<th>[RV]$%_{25^\circ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl (\overset{\circ}{\text{O}})SO(_2)OK (0.08 mole) 230°, 70% w.w</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Cl (\overset{\circ}{\text{O}})SO(_2)OK (0.08 mole) + F-(\overset{\circ}{\text{O}})SO(_2) (0.02 mole) solution, 230°, 70% w.w, 24 hours</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>Cl (\overset{\circ}{\text{O}})SO(_2)OK (0.08 mole) + F-(\overset{\circ}{\text{O}})SO(_2) (0.02 mole)</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>Cl (\overset{\circ}{\text{O}})SO(_2)OK (0.02 mole) + F-(\overset{\circ}{\text{O}})SO(_2) (0.005 mole)</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>Cl (\overset{\circ}{\text{O}})SO(_2)OK (0.02 mole) + F-(\overset{\circ}{\text{O}})SO(_2) (0.005 mole)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In experiments 1 and 2 the solution was diluted to 40% with dimethyl sulphone after 24 hours and methyl chloride passed through for 1 hour.

As shown in part 5, dilution of the polymer solution with the polymerisation solvent after reaction was complete, in order to pass methyl chloride through, resulted in a drop in $[\text{RV}]_{25^\circ}^{1\%}$ due to fluoride cleavage of the polymer. Two methods of polymer preparation and end stopping were tried to overcome this problem.

In the first method a high $[\text{RV}]_{25^\circ}^{1\%}$ polymer ($>0.55$) was prepared in dimethyl sulphone at 60-70% ww concentration and $230^\circ$ for 24 hours. The polymer was worked up without end stopping with methyl chloride so that the polymer had fluorine and hydroxyl end groups. The polymer was then dissolved in dimethyl sulphoxide under nitrogen at $120^\circ$ and small weighed amounts of approximately 0.4 M sodium methoxide in dimethyl sulphoxide were added. After each addition, the solution was stirred under nitrogen at $120^\circ$ for 2 hours. A sample was then removed and prepared for RV determination. Two reactions occur with sodium methoxide, first conversion of hydroxyl end groups to phenoxide:

$$\sim\left(\begin{array}{c} \text{OH} \\ \text{OH} \end{array}\right) + \text{NaOCH}_3 \rightarrow \sim\left(\begin{array}{c} \text{ONa} \\ \text{ONa} \end{array}\right) + \text{CH}_3\text{OH}$$

and secondly cleavage of ether bonds:

$$\sim\left(\begin{array}{c} \text{O} \\ \text{O} \end{array}\right) + \text{NaOCH}_3 \rightarrow \sim\left(\begin{array}{c} \text{ONa} \\ \text{ONa} \end{array}\right) + \text{CH}_3\text{O-CH}_3$$

The second reaction reduces the molecular weight and so provides a method of controlling the $[\text{RV}]_{25^\circ}^{1\%}$. By adding small increments of sodium methoxide the $[\text{RV}]_{25^\circ}^{1\%}$ value could be lowered to any required level.
When the required $[RV]_{25^\circ}^{1\%}$ value had been reached, methyl chloride was passed through the solution to convert phenoxide end groups to methoxy phenyl so that the polymer would be stable when molten. Polymers containing 10 and 20 mole \% ortho-para repeat units (XIX) and of $[RV]_{25^\circ}^{1\%}$ 0.40 0.55 were thus prepared.

In the second method the polymer was prepared from a mixture of the potassium salts of 4-fluoro-4'-hydroxydiphenyl sulphone and 4-fluoro-2'-hydroxydiphenyl sulphone in sulpholane at 200° and 40-50\% concentration. After polymerisation for the required time the solution was cooled to 150° and methyl chloride passed through the solution to convert unreacted phenoxide groups to methoxyl. At this temperature and concentration in sulpholane there is very little cleavage of ether links by the fluoride also formed. Polymer with 10-50 mole \% of the ortho-para' repeat unit were prepared by this method, the RV value being controlled by the reaction time, 24 hours at 200° usually being adequate.

As the mole \% of the potassium salt of 4-fluoro-2'-hydroxydiphenyl sulphone is increased it becomes progressively more difficult to make high $[RV]_{25^\circ}^{1\%}$ polymer due to the lower reactivity of this monomer.

The addition of small amounts of 4,4'-difluorodiphenyl sulphone on the dipotassium salt of 4,4'-dihydroxydiphenyl sulphone to the polymerisation in sulpholane did not significantly increase the $[RV]_{25^\circ}^{1\%}$ as shown in Table 31.
TABLE 31

Effect of Stoichiometry on Polymerisation of F-SO₂-F and F-SO₂-OK (50 mole %) and F-SO₂-OK (50 mole %)

<table>
<thead>
<tr>
<th>Mole % added F-SO₂-F</th>
<th>Temp</th>
<th>Conc</th>
<th>Time</th>
<th>[RV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>220°</td>
<td>40%</td>
<td>24 hours</td>
<td>0.31</td>
</tr>
<tr>
<td>1.0</td>
<td>220°</td>
<td>''</td>
<td>''</td>
<td>0.32</td>
</tr>
<tr>
<td>0</td>
<td>200°</td>
<td>''</td>
<td>''</td>
<td>0.30</td>
</tr>
<tr>
<td>0</td>
<td>180°</td>
<td>''</td>
<td>''</td>
<td>0.39</td>
</tr>
<tr>
<td>0.5</td>
<td>180°</td>
<td>''</td>
<td>''</td>
<td>0.40</td>
</tr>
<tr>
<td>1.0</td>
<td>180°</td>
<td>''</td>
<td>''</td>
<td>0.32</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mole % added KO-SO₂-OK</th>
<th>Temp</th>
<th>Conc</th>
<th>Time</th>
<th>[RV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>180°</td>
<td>40%</td>
<td>24 hours</td>
<td>0.29</td>
</tr>
<tr>
<td>1.0</td>
<td>180°</td>
<td>''</td>
<td>''</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The best conditions for the polymerisation here are 40% concentration and 180° with no added 4,4'-difluorodiphenyl sulphone or dipotassium salt of 4,4' dihydroxydiphenyl sulphone. At temperatures higher than 200° the RV is probably limited by fluoride ion cleavage. A 50 mole % copolymerisation at 180° for 48 hours is shown in Table 32.
TABLE 32

Copolymerisation of \( \text{F} - \overset{\text{SO}_2}{\text{O}} \text{OK} \) (50 mole %) and \( \text{F} - \overset{\text{SO}_2}{\text{O}} \text{OK} \) (30 mole %) in sulpholane

<table>
<thead>
<tr>
<th>Reaction Time</th>
<th>([\text{RV}]_{25^\circ}^{100})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 hours</td>
<td>0.08</td>
</tr>
<tr>
<td>3 &quot;</td>
<td>0.10</td>
</tr>
<tr>
<td>5 &quot;</td>
<td>0.11</td>
</tr>
<tr>
<td>8 &quot;</td>
<td>0.12</td>
</tr>
<tr>
<td>16 &quot;</td>
<td>0.25</td>
</tr>
<tr>
<td>21 &quot;</td>
<td>0.31</td>
</tr>
<tr>
<td>24 &quot;</td>
<td>0.36</td>
</tr>
<tr>
<td>32 &quot;</td>
<td>0.48</td>
</tr>
<tr>
<td>48 &quot;</td>
<td>0.53</td>
</tr>
</tbody>
</table>

A 50 mole % ortho-para repeat unit polymer of RV 0.51 was prepared by polymerisation at 180° for 44.5 hours.

A further difficulty encountered when preparing copolymers with more than 30 mole % of the potassium salt of 4-fluoro-2'-hydroxydiphenyl sulphone was the production of some insoluble material. The polymers after a normal extraction procedure to remove polymerisation solvent and potassium fluoride still contained some material which was insoluble in N,N dimethyl formamide. N,N dimethyl formamide is normally a good solvent for poly(diphenylene ether sulphone) and reduced viscosities are normally measured in it. The solubility, in N,N dimethyl formamide, of some polymers prepared in concentrated solution (60-70 % w/w monomer) in dimethyl sulphone are shown in Table 33.
TABLE 33

Solubility of Copolymers in N,N Dimethyl Formamide

<table>
<thead>
<tr>
<th>Mole % F-(\text{SO}_2)</th>
<th>Mole % F-(\text{SO}_2)</th>
<th>% insoluble material</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>60</td>
<td>2.25</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>4.95</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>5.46</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>75.86</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>92.65</td>
</tr>
</tbody>
</table>

The insoluble material has been identified as the cyclic dimer (XXII):

\[
\text{\(\begin{array}{c}
\text{O} - \text{\(\text{SO}_2\)} - \text{\(\text{SO}_2\)} - \\
\text{\(\text{SO}_2\)} - \text{\(\text{SO}_2\)} - \text{\(\text{SO}_2\)}
\end{array}\)}
\]

(XXII)

Mass spectrometry gave m/e 464 which being double the molecular weight (232) of the polymer repeat unit, is therefore consistent with structure (XXII). The elemental analysis shown below, supported this conclusion.

<table>
<thead>
<tr>
<th>Found %</th>
<th>Theory %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>62.9</td>
</tr>
<tr>
<td>H</td>
<td>3.54</td>
</tr>
<tr>
<td>S</td>
<td>13.60</td>
</tr>
</tbody>
</table>

In agreement, cleavage of the material with sodium methoxide in dimethyl sulfoxide followed by methylation with methyl chloride gave 2,4'-dimethoxydiphenyl sulphone. Moreover, the nmr of the dimer in trichloroacetic acid solution showed peaks characteristic of the constituent ortho- and para phenylene moieties in a ratio of 1:1. The ir spectrum
showed very sharp bands whereas high polymer has broadened bands. The evidence, then, firmly identified the dimer (XXII), as the material insoluble in dimethyl formamide.

The use of more dilute solution (50\% ww) in sulpholane reduced the amount of this insoluble material (in the case of the 70 mole \% ortho para-polymer down to approximately 11\%). Polymer with more than 50 mole \% ortho-para- repeat units was not prepared on a large scale because of the difficulties of obtaining sufficiently high molecular weight and formation of insoluble dimer. A polymerisation was carried out with 70 mole \% of the potassium salt of 4-fluoro-2'-hydroxydiphenyl sulphone and 30 mole \% of the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone in sulpholane at 200\° and 40\% ww concentration for 30 hours. Methyl chloride was then passed through the solution at 150\° for 1 hour. The polymer obtained had RV 0.22 and contained 11\% insoluble material. A similar reaction was carried out in sulpholane at 220\° and 50\% concentration. Samples removed after 24 hours, 40 hours and 48 hours had RVs 0.18, 0.18 and 0.17,

Details of the polymers containing ortho-para- repeat units prepared for physical testing are shown in Table 34.
TABLE 34

Ortho-para Copolymers

<table>
<thead>
<tr>
<th>Mole % A</th>
<th>Mole % B</th>
<th>Solvent</th>
<th>Temp</th>
<th>Conc %</th>
<th>Polym Time (hours)</th>
<th>After treatment of polymer</th>
<th>Final [RV] % IMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>10</td>
<td>dimethyl sulphone</td>
<td>230°</td>
<td>70%</td>
<td>24</td>
<td>Polymer worked up then cleaved to required RV with MaOMe in DMSO</td>
<td>0.38</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.43</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.53</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.41</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.46</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.54</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>&quot;</td>
<td>230°</td>
<td>70%</td>
<td>&quot;</td>
<td>Insoluble dimer removed</td>
<td>0.50</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>Sulpholane</td>
<td>200°</td>
<td>50%</td>
<td>24</td>
<td>&quot;</td>
<td>0.76</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.70</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.53</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Insoluble dimer removed</td>
<td>0.45</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>44.5</td>
<td>&quot;</td>
<td>0.51</td>
</tr>
</tbody>
</table>

A \( \text{-SO}_2 \text{OK} \) \hspace{1cm} B \( \text{F-SO}_2 \text{OK} \)

The insoluble dimer was removed from those polymers (40 and 50 mole % \( \text{o, p'} \)-repeat units) which contained it by filtration of an N,N-dimethyl formamide solution of the polymer. These polymers will therefore have rather less mole % \( \text{o, p'} \)-repeat units than shown in the table. The actual compositions are 38.6 and 47.4 mole % \( \text{o, p'} \)-repeat units respectively (based on the solubility measurements of table 33).
The polymers, with the exception of the 50 mole % made in dimethyl sulphone, were reacted with methyl chloride after polymerisation to convert phenoxide ends to methoxyl.

**Polymer Structure**

The randomness of the copolymers is determined by the reactivities of the monomers and by the extent of any rearrangement of the polymer by cleavage reactions at the ether bonds. When polymerising mixtures of the potassium salt of 4-fluoro 4'-hydroxydiphenyl sulphone with the potassium salt of 4-fluoro-2'-hydroxydiphenyl sulphone the first step will be mainly reaction of para phenoxide with fluorine. When this occurs the *ortho* phenoxide will react last so that the *ortho-para-* repeat units are spaced out along the polymer chain. The *ortho-* phenoxide group can react with fluorine in the potassium salt of 4-fluoro-2'-hydroxydiphenyl sulphone to produce some *ortho-para* repeat units adjacent to each other as in (XXIII)

![Chemical Structure](image)

(XXIII)

An alternative route to the *ortho-para-* copolymer, was therefore examined in which there was less chance of the adjacent units (XXIII) being present.
This comprised treating the potassium salt of 4-fluoro 4'-hydroxydiphenyl sulphone (5 moles) with 4,4'-difluorodiphenyl sulphone to produce a polymer with degree of polymerisation (DP) 6. This polymer was then reacted with 2,4'-dihydroxydiphenyl sulphone to produce high polymer of [RV]_25^\circ \text{D} M F 0.39 in which the ortho para repeat units should be evenly spaced out. The second stage in the reaction relies on the potassium fluoride formed in the first step acting as a base and converting hydroxyl end groups (in 2,4'-dihydroxydiphenyl sulphone) to phenoxide for reaction with fluorine ends. The structure shown in (XXIV) may be altered by chain cleavage at the ether bonds by either fluoride or phenoxide, followed by further reaction.

**Polymers containing meta para repeat units**

Polymers containing meta-para repeat units were prepared by L R J Hoy of ICI Plastics Division using the potassium salt of 4-fluoro-3' hydroxydiphenyl sulphone (XXV).
The effect of cleavage by fluoride ion was greater with the meta-para polymer than for the all para- polymer or the ortho-para-copolymers. The monomer is more reactive, however, and a lower temperature for polymerisation could be used thereby eliminating or reducing the effect of cleavage. The polymers were prepared at 40% concentration in sulphonolane at 150°. Methyl chloride was passed through at 100° to convert phenoxide to methoxyl since reaction at higher temperature resulted in a reduction in the RV of the polymer.
Two types of branched polymer with structures (XXVI) and (XXVII) have been prepared.

\[
\text{(XXVI)} \quad \text{(XXVII)}
\]

The trifunctional monomer 2,4,4'-trifluorodiphenyl sulphone was used to introduce the branching. A low molecular weight polymer with one phenoxide end group and one methoxyl end group was prepared by polymerising a mixture of the potassium salts of 4-fluoro-4'-hydroxydiphenyl sulphone and 4-hydroxy-4'-methoxydiphenyl sulphone. A sample, A, was removed and the amount of 2,4,4'-trifluorodiphenyl sulphone required to react with the remaining phenoxide end groups was added.

Polymerisation was continued to give the final polymer sample, B. The idealized reaction scheme is shown below.
The initial low polymer was prepared with about 40 repeat units by polymerising the salts in the ratio 1 mole of the potassium salt of 4-hydroxy-4'-methoxydiphenyl sulphone to 40 moles of the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone. This should produce a polymer of [RV]_{25}^{1\% \text{ DMF}} 0.26 with 2.44 hydroxyl end groups and 2.44 methoxyl end groups per 100 repeat units. The final polymer would have 1 branch point in 120 repeat units if the second stage in the reaction went to completion.

The reaction was followed by measuring the [RV]_{25}^{1\% \text{ DMF}} of the samples and by measuring the number of hydroxyl end groups per 100 repeat units of the polymer. An infra red method was used to measure the number of hydroxyl end groups per 100 polymer repeat units. The theoretical hydroxyl figure for the A sample is readily calculated from the mole % of the potassium salt of 4-hydroxy-4'-methoxydiphenyl sulphone used in the first step. The hydroxyl figure for the B sample would be zero if the reaction had gone to completion. Some results for polymers made by this route are shown in table 35.
### Branched polymers of type XXVI

<table>
<thead>
<tr>
<th>Example</th>
<th>[RV]_{1% DMF}^{25^\circ}</th>
<th>OH/100 repeat units</th>
<th>OCH_{2}/100 repeat units</th>
<th>% reaction of OK end groups</th>
<th>% branched polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A  B</td>
<td>A  B</td>
<td>A  B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.26 0.43</td>
<td>2.6 0.5</td>
<td>2.0</td>
<td>79</td>
<td>37</td>
</tr>
<tr>
<td>2</td>
<td>0.26 0.59</td>
<td>4.2 0.3</td>
<td>2.2 1.9</td>
<td>93</td>
<td>79</td>
</tr>
<tr>
<td>3</td>
<td>0.26 0.48</td>
<td>3.6 0.7</td>
<td>- -</td>
<td>79</td>
<td>37</td>
</tr>
<tr>
<td>4</td>
<td>0.26 0.51</td>
<td>2.9 0.3</td>
<td>- -</td>
<td>89</td>
<td>67</td>
</tr>
</tbody>
</table>

The results for number of methoxyl end groups per 100 repeat units were determined by nmr measurements. The hydroxyl figure for the A sample was higher than expected in examples 2 and 3 (table 35). It was known that when polymerising the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone in solution a maximum [RV]_{1\% DMF}^{25^\circ} was often obtained by the addition of a small mole % of 4,4'-difluorodiphenyl sulphone to the polymerisation. The potassium salt of 4-fluoro 4'-hydroxydiphenyl sulphone (batch used in example 3) was polymerised with added amounts of 4,4'-difluorodiphenyl sulphone at 50% concentration for 18 hours at 200°. The results shown in table 36 indicate that maximum [RV]_{1\% DMF}^{25^\circ} may be obtained with approximately 0.4 mole % added 4,4'-difluorodiphenyl sulphone.
This may be due to the presence of an impurity, for example the dipotassium salt of 4,4'-dihydroxydiphenyl sulphone, in the salt providing excess phenoxide end groups.

The branched polymer experiment was repeated using this mole % added 4,4'-difluorodiphenyl sulphone in the first step to give the improved results of example 4 in table 35.*

An estimate of the amount of branching may be made by calculating the percentage reaction of the available phenoxide groups with the 2,4,4'-trifluorodiphenyl sulphone from the hydroxyl figures. For example 4 the percentage reaction of the phenoxide groups present in the low polymer of sample A is

\[
\frac{2.9 - 0.3}{2.9} = 89\% \text{ reaction}
\]

the ortho-fluoride in 2,4,4'-trifluorodiphenyl sulphone is less reactive than the two para- fluorines. Assuming that the two para- fluorines react first then 66.6% reaction is needed to displace these, the
remaining 33.3% reaction displacing the ortho fluorine and producing the branched polymer. The proportion of branched polymer may be calculated on this basis. In example 4 of table 35, 89% reaction of phenoxide end groups corresponds to

\[
\frac{89 - 66.6}{33.3} \times 100 = 67\% \text{ reaction}
\]

of ortho-fluorine. Therefore the amount of branched polymer of the type (XXVI) is 67% the remainder being linear polymer.

The polymer of type (XXVII) was prepared to increase the amount of branching in the polymer. This polymer was made by preparing a reaction mixture consisting of 4 parts polymer chains with one phenoxide group and one methoxyl end group and one part polymer chains with two phenoxide end groups. After removing a sample A, the required amount of 2,4,4-trifluorodiphenyl sulphone was added to react with the remaining phenoxide end groups and polymerisation continued. The idealized reaction scheme is shown below.

\[
(69) \quad \text{F-} - \text{SO}_2 - \text{OK (200 moles)} + \text{CH}_3 - \text{SO}_2 - \text{OK (4 moles)} + \text{KO-SO}_2 - \text{OK (1 mole)} \rightarrow \text{CH}_3 - \text{SO}_2 - \text{O}_4^+ \quad \text{K 4 parts}
\]

\[
\text{KO-SO}_2 - \text{O}_4^+ \quad \text{K 1 part}
\]
The theoretical number of branches in this polymer if the reaction went to completion is 1 in 100 repeat units. Samples were taken during the polymerisation and the [RV]s obtained were A = 0.28, B = 0.83. The hydroxyl figures by infra red were A = 4.27, B = 0.07 per 100 repeat units. The theoretical hydroxyl figure for the A sample is 3.00. If the hydroxyl content of A was in fact 4.27 per 100 repeat units then the figure for B should have been higher. Calculations of percentage reactions from the hydroxyl figures as before gives results of 98% for reaction of phenoxide end groups corresponding to 97% branched polymer.

The difference between theoretical and measured hydroxyl figures is probably due in part to the inaccuracy of the hydroxyl determination by infra red. Any error in these results would also produce an error in the calculation of the amounts of branched polymer present.
Another measure of the amount of branched polymer present in these polymers was made by gel permeation chromatography measurements of the molecular weight distribution. The results are reported in the physical properties section.

Further increases in the extent of branching by the methods shown above are not possible without introducing cross linking. Other methods also tend to produce cross linked polymer rather than just branched. A polymer was produced by polymerising the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone with 2,4,4'-trifluorodiphenyl sulphone and the dipotassium salt of 4,4'-dihydroxydiphenyl sulphone in the ratio 18 moles : 1 mole : 1 mole. The resulting polymer contained 54% of N,N-dimethyl formamide insoluble polymer and was probably highly crosslinked.
Polymers containing the naphthalene and diphenyl units shown below have been prepared in order to investigate the effect of these structures on the properties of poly(diphenylene ether sulphone)

\[
\begin{align*}
\text{(XXVIII)} & \quad \text{(XXIX)} & \quad \text{(XXX)} \\
\end{align*}
\]

Preparation of polymers from the potassium salt of \(1-(4\text{-fluorobenzenesulphonyl})-4\text{-hydroxynaphthalene}\)

The homopolymers (XXXI) was prepared by melt polymerisation of the potassium salt of \(1-(4\text{-fluorobenzenesulphonyl})-4\text{-hydroxynaphthalene}\) (XXXII)

\[
\begin{align*}
\text{XXXI} & \quad \text{XXXII} \\
\end{align*}
\]

A solution polymerisation of the potassium salt (XXXII) at 50% concentration in sulpholane at 200° for 18.5 hours yielded a polymer which was incompletely soluble in \(N,N\)-dimethyl formamide. This polymer was shown to be crystalline by x-ray examination. The homopolymer (XXXI) was also prepared by melt polymerisation of the potassium salt (XXXII) at 280°. Two polymers were prepared with \([\eta]_{25^\circ}^{\text{DMF}}\) 0.60 and 0.49.
These homopolymers were amorphous. The difference in crystallinity is probably due to the difference in temperatures of the two polymerisations. The polymer made in the melt at 280° was probably amorphous at this temperature and did not crystallize on the subsequent rapid cooling to room temperature. At 200° the polymer was able to crystallize during preparation as this is much further below the crystalline melting point for this polymer (see physical properties section).

Copolymers of the potassium salt of 1-(4-fluorobenzenesulphonyl) 4-hydroxynaphthalene with the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone (XII) were also prepared. These copolymers were prepared by polymerising mixtures of the two salts in sulpholane solution at 200°. These copolymers were amorphous to x-rays and were soluble in N,N-dimethyl formamide. A summary of the polymers prepared from the potassium salt of 1-(4-fluorobenzenesulphonyl)-4 hydroxynaphthalene, is shown in Table 37.

TABLE 37
Polymers from F-\(\text{SO}_2\)-OH

<table>
<thead>
<tr>
<th>Mole % A</th>
<th>Mole % B</th>
<th>Polymerisation conditions</th>
<th>[(\text{RV})]_{25°}^{1%}</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>Melt 0.75 hour 280°</td>
<td>0.60</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>Melt 1 hour 280°</td>
<td>0.49</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>50% soln in sulpholane 18.5 hours 200°</td>
<td>0.89</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>30% soln in sulpholane 20 hours 200°</td>
<td>0.37</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>50% soln in sulpholane 20 hours 200°</td>
<td>0.63</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>60% soln in sulpholane 27 hours 200°</td>
<td>0.61</td>
</tr>
</tbody>
</table>

A F-\(\text{SO}_2\)-OH \(\text{OK}\)  B F-\(\text{SO}_2\)-OH \(\text{OK}\)
Preparation of polymers from 1,5 dihydroxynaphthalene

Copolymers of 1,5 dihydroxynaphthalene with probable structure (XXXIII) have been prepared by the following route

\[
\begin{align*}
(71) \quad & n \text{ F} \begin{array}{c}
\text{SO}_2\text{-}O\text{-}\text{OK} + \text{ F} \begin{array}{c}
\text{SO}_2\text{-}F
\end{array} \\
\end{array} \rightarrow \\
\text{F} \begin{array}{c}
\text{SO}_2\text{-}O\text{-}\text{OK} \rightarrow n \text{ F} \begin{array}{c}
\text{SO}_2\text{-}F
\end{array} + n \text{ KF}
\end{array}
\end{align*}
\]

\[
(72) \quad \text{F} \begin{array}{c}
\text{SO}_2\text{-}O\text{-}n \text{ F} \begin{array}{c}
\text{SO}_2\text{-}F
\end{array} + \text{OH}
\end{array} \rightarrow \text{[-OH-]}_m
\]

In the first step (reaction (71)) the potassium salt of 4-fluoro-4' hydroxydiphenyl sulphone was polymerized with 4,4'-difluorodiphenyl sulphone to produce a low molecular weight polymer with fluorine end groups. The stoichiometric amount of 1,5-dihydroxynaphthalene to react with all the fluorine end groups was added and polymerisation continued (reaction (72)). In reaction (72) the potassium fluoride formed by reaction (71) acts as base to convert the hydroxyl groups of 1,5 dihydroxynaphthalene to phenoxide prior to their reaction with fluorine end groups on the polymer. 

Polymers were prepared containing 20 mole % 1,5-dihydroxynaphthalene (n = 3 in XXXIII) of [RV]^{1\%}_{25^\circ} DMF 0.42 and 14 mole % 1,5 dihydroxynaphthalene of [RV]^{1\%}_{25^\circ} DMF 1.39 [n = 5 in (XXXIII)].
Preparation of polymers from 4,4'-dihydroxydiphenyl

Polymers of probable structure (XXXIV) were prepared from 4,4'-dihydroxydiphenyl. The route used was similar to that used to prepare polymers from 1,5 dihydroxynaphthalene. A low polymer with fluorine end groups was prepared by reaction (71). The stoichiometric amount of 4,4'-dihydroxydiphenyl to react with all the fluorine end groups was then added and polymerisation continued in the presence of potassium fluoride formed by the initial reaction.

\[
\text{(73)} \quad \text{F} + \text{HO-SO}_2\text{-OR} + \left[\text{SO}_2\text{-OR}\right]_n \rightarrow \text{HO-SO}_2\text{-OR} + \left[\text{SO}_2\text{-OR}\right]_n \text{F} + \text{HO-SO}_2\text{-OR}
\]

Polymers containing 20 mole % dioxydiphenyl units \([n = 3 \text{ in (XXXIV)}]\) of \([\text{RV}]^{2\text{% DMF}}_{25^\circ} 0.51\) and with 5 mole % dioxydiphenyl units \([n = 18 \text{ in (XXXIV)}]\) of \([\text{RV}]^{1\text{%}}_{25^\circ} 0.47\) were prepared by this route.

The regular structures shown in (XXXIII) and (XXXIV) are those which are expected to be formed by the polymerisation reactions. Cleavage of the polymer by phenoxide end groups or fluoride ion (see parts 4 and 5) however, would result in a rearrangement of the structure shown to produce a more random distribution of the 4,4'-dioxydiphenyl or 1,5-dioxynaphthalene units.
PART 9 PHYSICAL PROPERTIES

Molecular Weight

The physical properties, for example notched impact strength and modulus, of a polymer with a given structure are dependent on the molecular weight. A comparison of the physical properties of polymers with different structures is best done with polymers of similar molecular weight. This ensures that any differences observed in the properties are due to structure and not molecular weight.

The number average molecular weight, $\bar{M}_n$, and weight average molecular weight, $\bar{M}_w$, were measured for some of the polymers used for physical testing.

The number average molecular weight is defined as:

$$\bar{M}_n = \frac{\sum_{i=1}^{N} N_i M_i}{\sum_{i=1}^{N} N_i}$$

and weight average molecular weight as

$$\bar{M}_w = \frac{\sum_{i=1}^{N} N_i M_i^2}{\sum_{i=1}^{N} N_i M_i}$$

Where $N_i$ is the number of molecules of and $M_i$ the molecular weight of the $i^{th}$ species.
The number average molecular weights were measured by osmometry, the weight average by light scattering. The results are shown in Table 38.

**TABLE 38**

**Number and Weight Average Molecular Weights of Polymers**

<table>
<thead>
<tr>
<th>Polymer Structure</th>
<th>$[\text{RV}^{1% \text{ DMF}}]_{25^\circ}$</th>
<th>$\overline{M_n}$</th>
<th>$\overline{M_w}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[-\left(-\text{SO}_2-\text{O}\right)_n]$</td>
<td>0.99</td>
<td>70,900</td>
<td>$2.59 \times 10^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.72</td>
<td>43,000</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>0.61</td>
<td>33,600</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>0.54</td>
<td>25,200</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>0.48</td>
<td>&lt;23,000</td>
<td></td>
</tr>
<tr>
<td>o,p' copolymers:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mole % A</td>
<td>mole % B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>0.76</td>
<td>49,000</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>0.70</td>
<td>46,000</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>0.50</td>
<td>51,000</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>0.75</td>
<td>approx</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>0.45</td>
<td>60,000-</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>0.62</td>
<td>70,000</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>Branched polymer type XXVII</td>
<td>0.83</td>
<td>49,000</td>
<td>$3.7 \times 10^5$</td>
</tr>
</tbody>
</table>

$$A = [-\text{SO}_2-\text{O}]_n \quad B = [-\text{SO}_2-\text{O}]_n$$
The results for number average molecular weights of the polymers containing ortho-para-repeat units are only approximate due to permeation of the membrane by some low molecular weight material but they do indicate that the molecular weights of o,p' copolymers and the p,p' homopolymer are comparable. There is an indication that the o,p' copolymers are of slightly higher molecular weight for the same \([RV]_{25^\circ}^{10\% DMF}\), but the accuracy of the results is not high enough to be certain of this. The molecular weights of these polymers with the same \([RV]_{25^\circ}^{10\% DMF}\) are close enough to enable a valid comparison of their properties to be made.

Molecular Weight Distribution

The molecular weight distribution of several polymer samples was examined by gel permeation chromatography. In this technique a solution of the polymer is passed through a column containing polystyrene beads. The beads contain pores or voids into which the polymer molecules can pass. The effect is to slow up the passage of polymer molecules through the column. The smaller molecules are retained most as there are more suitably sized pores into which these molecules can pass. The polymer is thus fractionated, the larger molecules coming off first, the smaller last. The passage of fractions coming off the column are measured by a detector, which usually measures the refractive index of the solution compared with the pure solvent. A plot of \(\Delta RI\) (representing amount of polymer) versus elution volume may be made. A typical result is shown in graph 25 for a poly p,p'(diphenylene ether sulphone) of RV 0.72.

The graph is equivalent to a plot of the number of molecules versus molecular weight. No monodisperse samples of poly(diphenylene ether sulphone) were available so that the graphs could not be calibrated for
molecular weight. A comparison of the polymers may still be made however.

Graph 25 consists of a main distribution with a smaller secondary distribution on the high molecular weight side. In graph 26 the plot for one of the branched polymers of type (XXVI) and $[RV]_{25}^{7\%\text{DMF}}$ 0.51 is shown. This has a much larger secondary distribution, indicating that this is due to branched polymer. It is possible that branched polymer occupies a larger volume for its molecular weight than does linear polymer. This would cause it to be retained for a shorter time on the column and behave as though it were of a very high molecular weight.

An alternative explanation, that the secondary distribution is due to very high molecular weight is less likely, because a sample of a branched polymer, when examined by light scattering showed no evidence for the presence of a very high molecular weight fraction. The molecular weights for this polymer are given in Table 38, while its molecular weight distribution is shown in graph 27. This polymer (XXVII) should have 2 branches per chain. Graphs 28, 29, and 30 show the gel permeation chromatography results for polymers containing o,p' repeat units and m,p' repeat units.

The o,p' copolymers and m,p' polymers have a similar distribution of molecular weight to the p,p' homopolymer and the peak of the main distribution comes at a similar position indicating that they are all of similar molecular weight. The 50 mole % o,p' copolymer has its peak (graph 29) at a slightly higher molecular weight than expected for the $[RV]$, confirming the results found by molecular weight measurements.
GRAPH 28. G.P.C. FOR COPOLYMER OF $\text{[SO}_2\text{-]}_2$ 20 MOLE% + $\text{[SO}_2\text{-]}_2$ 90 MOLE% [R.V.] 0.70

ΔRI

0.05

0.04

0.03

0.02

230 220 210 200 190 180 170 160 150 140 130 120

ELUTION VOLUME.
GRAPH 29  G.P.C. FOR COPOLYMER OF \[
\text{[content of graphic]}\] 50 MOLE% +

\[
\text{[content of graphic]}\] 50 MOLE%, R.V._{25^\circ}

ΔRI

0.04

0.03

0.02

0.01

230  220  210  200  190  180  170  160  150  140  130  120

ELUTION VOLUME.
GRAPH 30  GPC FOR m, p'- Homopolymer \( \left( \begin{array}{c} \text{C} \\ \text{S} \end{array} \right) \}_{n} \) [R.V.] \( 1\% \text{DMF} \) 25°C 0.74.
Branching could arise in a normal polymerisation by the reaction of a trifunctional impurity with the polymer, or by a side reaction such as substitution of a hydrogen in the polymer chain by a phenoxide end group.

A polymer made by reaction between the dipotassium salt of 4,4'-dihydroxydiphenyl sulphone and 4,4'-difluorodiphenyl sulphone at 160° in dimethyl sulphoxide had the molecular weight distribution shown in graph 31. The secondary peak for this polymer is very small indicating the presence of very little branching. Side reactions are likely to be reduced in this more reactive system where a lower temperature can be used for the polymerisation.

The amount of branched polymer, as a percentage by weight may be estimated from the area under the graph and Table 39 shows a summary of these results. This figure does not give the percentage of repeat units which are branched. This is a much smaller figure, for example the branched polymer of type XXVII has a maximum of 1 branch in 100 repeat units (see part 7).
GRAPH 31  G.P.C. FOR HOMOPOLYMER \{(-\text{SO}_2-\text{O})_n\} PREPARED BY

2 COMPONENT ROUTE. [R.I.]% DMF 0.44.
TABLE 39

Gel Permeation Chromatography Results for Poly(diphenylene ether sulphone)s

<table>
<thead>
<tr>
<th>Polymer Structure</th>
<th>[RV]$^\circ_{25^\circ}$</th>
<th>% branched polymer</th>
<th>Position of peak of main distribution elution volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[-\begin{array}{c}S!!O_2\end{array}\begin{array}{c}O!!S\end{array}<em>{\begin{array}{c}0!!S\end{array}}</em>{\begin{array}{c}n\end{array}}\begin{array}{c}-\end{array}]$</td>
<td>0.72</td>
<td>14</td>
<td>187</td>
</tr>
<tr>
<td></td>
<td>0.43</td>
<td>1.8</td>
<td>(140)</td>
</tr>
<tr>
<td></td>
<td>0.44</td>
<td>1.0</td>
<td>(140)</td>
</tr>
<tr>
<td></td>
<td>0.37</td>
<td>2.5</td>
<td>(142)</td>
</tr>
<tr>
<td>$o,p'$ copolymers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mole % A</td>
<td>mole % B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>0.76</td>
<td>3.9</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>0.70</td>
<td>5.7</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>0.50</td>
<td>9.5</td>
</tr>
<tr>
<td>$[-\begin{array}{c}S!!O_2\end{array}\begin{array}{c}O!!S\end{array}<em>{\begin{array}{c}0!!S\end{array}}</em>{\begin{array}{c}n\end{array}}\begin{array}{c}-\end{array}]$</td>
<td>0.74</td>
<td>7%</td>
<td>185</td>
</tr>
<tr>
<td>Branched polymer type (XXVI)</td>
<td>0.51</td>
<td>34%</td>
<td>192</td>
</tr>
<tr>
<td>Branched polymer type (XXVII)</td>
<td>0.83</td>
<td>39%</td>
<td>190</td>
</tr>
</tbody>
</table>

* 1 component route $+$ 2 component route

$A = [-\begin{array}{c}S\!\!O_2\end{array}\begin{array}{c}O\!\!S\end{array}_{\begin{array}{c}0\!\!S\end{array}}_{\begin{array}{c}n\end{array}}\begin{array}{c}-\end{array}]$ $B = [-\begin{array}{c}S\!\!O_2\end{array}\begin{array}{c}O\!\!S\end{array}_{\begin{array}{c}0\!\!S\end{array}}_{\begin{array}{c}n\end{array}}\begin{array}{c}-\end{array}]$
The samples of poly p,p' (diphenylene ether sulphone) made by the two component route were run with different columns on the apparatus so that the position of the main distribution peak cannot be compared with the other results.

The amount of branched polymer present in the polymers of type (XXVI) and (XXVII) as measured by gel permeation chromatography is lower than that found by hydroxyl end group analysis. If correct this indicates that some cleavage by fluoride ion, and rearrangement of the polymer structure has occurred. Both of these polymers do contain, as expected, a significantly greater degree of branching than the normal poly-p,p' (diphenylene ether sulphone).

Crystallinity and Glass Transition Temperature

Polymers of the structure made for physical testing have been examined by x-rays and differential scanning calorimetry (DSC). X-ray examination has shown whether the polymers are crystalline or amorphous. The presence of crystallinity in the polymers would be expected to affect various physical properties (see part 1), such as solubility in solvents, impact strength and modulus. The polymers as made were, in general, amorphous so that a study of impact strength and other properties versus chemical structure could be made. The glass transition temperature, Tg, of the amorphous polymers and the crystalline melting point, Tp, of the crystalline polymers were measured by DSC. The Tg is shown as a change in baseline on the DSC and is caused by an increase in specific heat of the material. The Tp is shown as a more pronounced peak.
The glass transition temperature or softening point (see part 1) is an important polymer property as it determines the upper working temperature of the polymer and also its processing temperature. Poly p,p' (diphenylene ether sulphone) is amorphous to X-rays and the glass transition temperatures for samples with various RVs are shown in Table 40. The polymers were prepared by solution and melt polymerisation of the potassium salt of 4-chloro-and-fluoro-4'-hydroxydiphenyl sulphone.

### TABLE 40

<table>
<thead>
<tr>
<th>[RV]₁₀₀₀</th>
<th>Tg°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
<td>226 reheat 231</td>
</tr>
<tr>
<td>1.71</td>
<td>232 reheat 238</td>
</tr>
<tr>
<td>1.28</td>
<td>238 reheat 237</td>
</tr>
<tr>
<td>0.98</td>
<td>232 reheat 233</td>
</tr>
<tr>
<td>0.83</td>
<td>239 repeat 242</td>
</tr>
<tr>
<td>0.60</td>
<td>227</td>
</tr>
<tr>
<td>0.51</td>
<td>231</td>
</tr>
<tr>
<td>0.45</td>
<td>227 reheat 225</td>
</tr>
<tr>
<td>0.42</td>
<td>220</td>
</tr>
<tr>
<td>0.29</td>
<td>225 repeat 226</td>
</tr>
<tr>
<td>0.14</td>
<td>197 repeat 202</td>
</tr>
</tbody>
</table>

There is an increase in Tg with RV up to a limit of about 238°C for poly p,p' (diphenylene ether sulphone). The DSC scans were made with a heating rate of 16°C/minute. The reheat Tgs were found by cooling the sample used in the first Tg determination to below the glass transition temperature and then reheating.

The X-ray and DSC data on poly o,p' (diphenylene ether sulphone) are shown in Table 41.
TABLE 41

X-ray and DSC data on the Homopolymer -

<table>
<thead>
<tr>
<th>Sample</th>
<th>Details</th>
<th>X-ray crystalline form</th>
<th>DSC Heating rate 16°/min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tg°</td>
</tr>
<tr>
<td>1</td>
<td>Melt polymerised</td>
<td>α(+)φ</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>Heated to 363° and cooled 16°/min</td>
<td>Practically amorphous</td>
<td>212°</td>
</tr>
<tr>
<td>1</td>
<td>Heated to 376° and cooled 16°/min</td>
<td>Amorphous</td>
<td>201°</td>
</tr>
<tr>
<td>2</td>
<td>Original sample 1 precipitated into water from sulphuric acid solution</td>
<td>Amorphous</td>
<td>220°</td>
</tr>
<tr>
<td>3</td>
<td>Melt polymerised</td>
<td>α(+)φ</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>DMF soluble fraction</td>
<td>Some D form + paracrystallinity</td>
<td>213°</td>
</tr>
<tr>
<td>3</td>
<td>DMF insoluble fraction</td>
<td>α(+)φ</td>
<td></td>
</tr>
</tbody>
</table>

Two samples of the poly-o,p'(diphenylene ether sulphone) were examined. The polymers were crystalline as made with double melting points (Tp) of 355° and 368°. Two crystalline forms (α and φ) appear to be present, although it may be that α converts to φ during the heating process.

The polymer can be made amorphous by melting and cooling or by precipitating into water from sulphuric acid solution. It has not been possible to reconvert the amorphous poly-o,p'(diphenylene ether sulphone) back to the crystalline form. The polymer is probably crystalline when first made because the chains take up a regular steric conformation during the polymerisation. The homopolymer contains small amount of material
soluble in N,N'-dimethylformamide. This has a different crystalline form and is probably low molecular weight material, for example dimer or trimer.

Table 42 shows the Tg by DSC and X-ray data for copolymers containing 10-70 mole % of the o,p'-repeat unit.

The amorphous polymers containing o,p'-repeat units have essentially the same Tg as the o,p'-homopolymers.

The copolymers with more than 30 mole % of o,p' repeat units contained some crystalline material which was insoluble in N,N'-dimethylformamide and showed the same type of crystallinity to that of the D type crystallinity (i.e., low molecular weight) observed in the o,p' homopolymer.

This crystalline material has been identified as a cyclic dimer (XXII) as described in part 6.

Table 43 shows the DSC and X-ray data for the m,p'-homopolymer. This polymer has a much lower Tg (maximum of 175°) than either the poly-p,p' (diphenylene ether sulphone) or the o,p'-copolymer.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole % A</th>
<th>Mole % B</th>
<th>[RV]1% DMF</th>
<th>DSC heating rate 16°/min</th>
<th>X-ray crystallinity</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>90</td>
<td>0.71</td>
<td>233 234</td>
<td>Amorphous</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>90</td>
<td>0.43</td>
<td>230 226</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>90</td>
<td>0.38</td>
<td>226 226</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>90</td>
<td>0.32</td>
<td>233 223</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>80</td>
<td>0.79</td>
<td>229 233</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>80</td>
<td>0.54</td>
<td>230 231</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>80</td>
<td>0.46</td>
<td>227 227</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>20</td>
<td>80</td>
<td>0.41</td>
<td>223 223</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>80</td>
<td>0.18</td>
<td>211 211</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>70</td>
<td>0.63</td>
<td>226 224</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>40</td>
<td>60</td>
<td>0.51</td>
<td>230 227</td>
<td>Small amounts</td>
<td>Contain small</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>of crystallinity</td>
<td>amounts of</td>
</tr>
<tr>
<td>12</td>
<td>40</td>
<td>60</td>
<td>0.78</td>
<td>226 227</td>
<td></td>
<td>DMF insoluble</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>material</td>
</tr>
<tr>
<td>13</td>
<td>50</td>
<td>50</td>
<td>0.58</td>
<td>227 227</td>
<td></td>
<td>Insoluble</td>
</tr>
<tr>
<td>14</td>
<td>50</td>
<td>50</td>
<td>0.50</td>
<td>217 225</td>
<td>Amorphous</td>
<td>Material removed</td>
</tr>
<tr>
<td>15 DMF</td>
<td>60</td>
<td>40</td>
<td>0.38</td>
<td>219 224</td>
<td>Amorphous</td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>Mole % A</td>
<td>Mole % B</td>
<td>[RV] (1% \text{DMF} ) (25^\circ)</td>
<td>DSC Heating rate (16^\circ/\min)</td>
<td>X-ray crystallinity</td>
<td>Remarks</td>
</tr>
<tr>
<td>-------------------------</td>
<td>----------</td>
<td>----------</td>
<td>-------------------------------------</td>
<td>----------------------------------</td>
<td>---------------------</td>
<td>---------</td>
</tr>
<tr>
<td>15 DMF Insoluble fraction</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>crystalline</td>
<td>8.6% insoluble</td>
</tr>
<tr>
<td>16 DMF soluble fraction</td>
<td>70</td>
<td>30</td>
<td>0.35</td>
<td>224</td>
<td>Amorphous</td>
<td>13.1% insoluble</td>
</tr>
<tr>
<td>16 DMF Insoluble fraction</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Crystalline</td>
<td></td>
</tr>
</tbody>
</table>

A \(\text{F-} \begin{array}{c} \text{SO}_2 \end{array} \begin{array}{c} \text{OK} \end{array}\) B \(\text{F-} \begin{array}{c} \text{SO}_2 \end{array} \begin{array}{c} \text{OK} \end{array}\)
TABLE 43

DSC and X-ray data on Homopolymer

<table>
<thead>
<tr>
<th>RV</th>
<th>X-ray crystallinity</th>
<th>Tg by DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.64</td>
<td>Amorphous</td>
<td>172°</td>
</tr>
<tr>
<td>1.0</td>
<td>&quot;</td>
<td>175°</td>
</tr>
<tr>
<td>0.71</td>
<td>&quot;</td>
<td>159°</td>
</tr>
<tr>
<td>0.61</td>
<td>&quot;</td>
<td>169°</td>
</tr>
<tr>
<td>0.52</td>
<td>&quot;</td>
<td>150°</td>
</tr>
<tr>
<td>0.34</td>
<td>&quot;</td>
<td>144°</td>
</tr>
<tr>
<td>0.21</td>
<td>&quot;</td>
<td>142°</td>
</tr>
</tbody>
</table>

The X-ray and DSC results for polymers containing the naphthalene and diphenyl units described in part 8 are shown in table 44, page 182.

The units shown in table 44: 4,4'-dioxydiphenyl, 1,5-dioxynaphthalene and 1-oxy-4-benzenesulphonyl naphthalene do not make any significant difference to the glass transition temperature which remains approximately 230° as for poly p,p'(diphenylene ether sulphone). The polymer prepared by solution polymerisation of 1-(4-fluorobenzenesulphonyl)4-hydroxy-naphthalene (XXXII) was crystalline to X-rays, whereas the melt polymer was amorphous.

4 Solution and Melt Viscosity

The intrinsic viscosity (ηI) of poly p,p'(Diphenylene ether sulphone) and of copolymers containing 10 and 20 mole % of p,p' repeat units were measured in N,N'-dimethyl formamide solution. The results are shown in Table 45. A plot of intrinsic viscosity versus reduced viscosity
<table>
<thead>
<tr>
<th>Structure</th>
<th>[RV] 1% DMF at 25°C</th>
<th>X-ray</th>
<th>DSC Heating rate 16°/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>[-O-][O-O]5-O(-SO2-O)5-SO2-[-]n</td>
<td>0.97</td>
<td>Amorphous</td>
<td>231.5°</td>
</tr>
<tr>
<td>[-O-][O-O]5-O(-SO2-O)5-SO2-[-]n</td>
<td>1.39</td>
<td>&quot;</td>
<td>234.5°</td>
</tr>
<tr>
<td>[-SO2-0-]n - melt polymerisation</td>
<td>0.60</td>
<td>&quot;</td>
<td>238° 237°</td>
</tr>
<tr>
<td>[-SO2-SO2-O-]n - solution polymerisation</td>
<td>-</td>
<td>Crystalline</td>
<td>Tp = 367°</td>
</tr>
<tr>
<td>[-SO2-SO2-O-]n 20 mole % +</td>
<td>0.89</td>
<td>Amorphous</td>
<td>211° 210°</td>
</tr>
<tr>
<td>[-SO2-SO2-O-]n 80 mole %</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(graph 32) does not reveal any significant difference in solution viscosity behaviour between the \( \alpha, \beta' \)-homopolymer and the \( \alpha, \beta' \)-copolymers.

**TABLE 45**

Intrinsic Viscosities

<table>
<thead>
<tr>
<th>Sample</th>
<th>( [\text{RV}]_{25^\circ} )</th>
<th>DMF</th>
<th>( \eta_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-[-\text{SO}_2\text{-O-}]_n) ( \alpha, \beta' )</td>
<td>1.28</td>
<td>0.825</td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta' )</td>
<td>0.98</td>
<td>0.714</td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta' )</td>
<td>0.83</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta' )</td>
<td>0.58</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta' )</td>
<td>0.43</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta' )</td>
<td>0.43</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta' )</td>
<td>0.24</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta' )</td>
<td>0.145</td>
<td>0.137</td>
<td></td>
</tr>
<tr>
<td>(-[-\text{SO}_2\text{-O-}]_n) 10 mole % + (-[-\text{SO}_2\text{-O-}]_n) 90 mole %</td>
<td>0.71</td>
<td>0.543</td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta' )</td>
<td>0.436</td>
<td>0.326</td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta' )</td>
<td>0.36</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta' )</td>
<td>0.32</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>(-[-\text{SO}_2\text{-O-}]_n) 20 mole % + (-[-\text{SO}_2\text{-O-}]_n) 80 mole %</td>
<td>0.765</td>
<td>0.565</td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta' )</td>
<td>0.53</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta' )</td>
<td>0.46</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta' )</td>
<td>0.40</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta' )</td>
<td>0.18</td>
<td>0.13</td>
<td></td>
</tr>
</tbody>
</table>

The melt viscosity of poly \( \alpha, \beta' \)-(diphenylene ether sulphone) and copolymers containing \( \alpha, \beta' \)-repeat units have been measured at 350\(^\circ\) with a shear rate of 1000 sec\(^{-1}\) in a 1cm diameter ram extruder. The measurements were carried out at 350\(^\circ\) to avoid any problems associated with melt instability. At higher temperatures eg 380\(^\circ\) the melt viscosity
is lower but the polymers may be unstable particularly if hydroxyl end groups are present on the polymer. This instability would result in an increase in melt viscosity with time in the ram extruder.

Attempts to measure the melt viscosity at 350° of a poly-$m,p'$ (diphenylene ether sulphone) and a copolymer containing 10 mole % of $m,p'$-repeat units and 80 mole % of $p,p'$-repeat units were unsuccessful as both the polymers were unstable at this temperature, possibly due to the presence of the meta linkages.

Table 46 shows the melt viscosity of the $p,p'$- homopolymer and $o,p'$ copolymers which were measured.

**TABLE 46**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>[RV]% 1%</th>
<th>Melt viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[-\left(-\left[\begin{array}{c}S\end{array}\right]_{n}\right]-$</td>
<td>0.40</td>
<td>0.54 KNsm$^{-2}$</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.44</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.48</td>
<td>&quot;</td>
</tr>
<tr>
<td>mole % $[-\left(-\left[\begin{array}{c}S\end{array}\right]_{n}\right]-$</td>
<td>mole % $[-\left(-\left[\begin{array}{c}S\end{array}\right]_{n}\right]-$</td>
<td>0.53</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>0.54</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>0.53</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>0.54</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>0.44</td>
</tr>
</tbody>
</table>

There is some scatter in the results but there does not appear to be any significant difference between the melt viscosity of the $p,p'$ homopolymer and the $o,p'$-copolymers.
The impact strength of a polymer is a useful measure of its toughness or resistance to breakage. The impact strength of the polymer was measured using a form of the charpy test in which a specimen supported at two points near the ends is struck by a pendulum. Some of the measurements were carried out with unnotched specimens but in the remainder the specimens were made with a 2 mm (0.080") notch. The latter is a more severe form of the test (see part 1). The poly-p,p'-diphenylene ether sulphone is in class 3 of the fourfold classification given in part 1; i.e., the impact strength with a 2 mm notch (IS2) is greater than 20 KJ/m² while impact strength with a 1/2 mm notch (IS2) is less than 10 KJ/m². Using the 2 mm notch test the greatest variation in impact strength could be observed with the different polymers.

The impact strength of poly-p,p'-diphenylene ether sulphone was measured on both injection mouldings and compression mouldings. The compression mouldings were prepared from fine powder and a technique for moulding was developed which ensured bubble-free mouldings (see experimental section).

The impact strength was measured at room temperature (approx 20°) using specimens with a 2 mm notch cut in them. Some specimens were placed in an oven at 150° and the impact strength (at room temperature) of the specimens measured after periods of 1 day, 1 week, and 1 month, in order to study the effect of storage at high temperature on impact strength.

The results are shown in Table 47 and graphs 33 (notched impact strength versus storage time for compression mouldings), 34 (notched impact strength
versus storage time for injection mouldings) and 35 (impact strength versus RV).

TABLE 47

Notched (2mm) Impact Strength of Homopolymer $[-\text{SO}_2\text{-}]_n$

<table>
<thead>
<tr>
<th>Sample</th>
<th>[RV]$_{1%}$ DMF $^{25^\circ}$</th>
<th>Notched impact strength (kJ/m$^2$) with storage time at $150^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Compression moulding</td>
<td>1.71</td>
<td>66.0</td>
</tr>
<tr>
<td></td>
<td>1.17</td>
<td>66.1</td>
</tr>
<tr>
<td></td>
<td>0.61</td>
<td>56.3</td>
</tr>
<tr>
<td></td>
<td>0.48</td>
<td>47.2</td>
</tr>
<tr>
<td></td>
<td>0.44</td>
<td>44.5</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>35.5</td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>31.7</td>
</tr>
<tr>
<td>Injection moulding</td>
<td>0.48</td>
<td>80.2</td>
</tr>
<tr>
<td></td>
<td>0.44</td>
<td>58.2</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>40.7</td>
</tr>
</tbody>
</table>

* Aged for 1 week + Aged for 2 weeks

Inspection of the results shows that (i) the increase in impact strength with RV levels off at about [RV]$_{1%}$ DMF $^{25^\circ}$ = 1.0; (ii) the impact strength of injection mouldings are higher than compression mouldings of the same RV but after storage at $150^\circ$ (ageing) the impact strengths are very similar. All the polymers show a decrease in impact strength after storing the impact specimens at $150^\circ$ for periods up to 1 month.
The ageing effect is not a permanent change in the polymer since on remoulding the aged specimens and preparing new specimens, the impact strength returns to that found before ageing. The effect of storage at 150° is not due to drying out of water, as shown by the absence of recovery in impact strengths of aged specimens when left in the air to absorb water. These results are shown below for a polymer of RV 0.41 which showed an unusually large decrease in impact strength on storage at 150°.

<table>
<thead>
<tr>
<th>Storage time at 150°</th>
<th>0</th>
<th>2 hours</th>
<th>24 hours</th>
<th>48 hours</th>
<th>1 week</th>
</tr>
</thead>
<tbody>
<tr>
<td>Notched (2mm) impact strength KJ/m²</td>
<td>40.5</td>
<td>37.8</td>
<td>4.6</td>
<td>7.5</td>
<td>9.2</td>
</tr>
<tr>
<td>2 weeks</td>
<td>8.8</td>
<td>6.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 weeks</td>
<td>8.8</td>
<td>6.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Specimens of the polymer which had been stored for 2 days at 150° were left in the air at room temperature for 5 days. The notched impact strength, was measured as 7.6 KJ/m². Some broken specimens which had been stored for 1 month at 150°, were remoulded. The notched (2mm) impact strength was 42 KJ/m².

Samples of low RV poly p,p' (diphenylene ether sulphone) were tested to find at what RV the polymer was brittle when unnotched. Specimens of polymer with RV 0.41 and 0.39 did not break in an unnotched impact test even after storage at 150° for 2 weeks. With polymer of RV 0.34 50% of the specimens broke. Mouldings of polymer with RV lower than 0.34 had cracks in them and it was not possible to prepare specimens for testing. The polymer is probably brittle unnotched when the RV is below about 0.34,
The notched (2mm) impact strengths of injection and compression mouldings of the polysulphone of structure (V) made by the Union Carbide Corporation are shown in table 48.

**TABLE 48**

<table>
<thead>
<tr>
<th>Sample</th>
<th>[RV]_{1%}^{25^\circ}</th>
<th>Notched impact strength in KJ/m² with storage time at 150°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>P. 1700 injection moulding</td>
<td>0.38</td>
<td>37.8</td>
</tr>
<tr>
<td>P.3500 injection moulding</td>
<td>0.45</td>
<td>34.0</td>
</tr>
<tr>
<td>P. 2300 injection moulding</td>
<td>0.47</td>
<td>46.6</td>
</tr>
<tr>
<td>P. 1700 compression moulding</td>
<td>0.38</td>
<td>35.7</td>
</tr>
<tr>
<td>P.3500 compression moulding</td>
<td>0.45</td>
<td>31.1</td>
</tr>
<tr>
<td>P. 2300 compression moulding</td>
<td>0.47</td>
<td>42.4</td>
</tr>
</tbody>
</table>

The impact strength of this polymer increases with [RV]_{1\%}^{25^\circ} as did poly(diphenylene ether sulphone) and decreases to a limiting value after storage at 150°. Poly(diphenylene ether sulphone) shows better impact strength than the Union Carbide polysulphone (V), and this is particularly noticeable after storage at 150°.
The notched (2mm) impact strength of polymers containing the o,p'-repeat units (XIX) are summarised in table 49. The impact measurements were made on specimens prepared from compression mouldings. The measurements were made at room temperature, and some specimens were stored at 150° for a period and then cooled to room temperature before measurement.

**TABLE 49**

**Notched (2mm) Impact Strength of Polymers containing o,p'-repeat units**

<table>
<thead>
<tr>
<th>Polymer Structure</th>
<th>[RV]_{25^o}^{1% DMF}</th>
<th>Notched impact strength KJ/m² with storage time at 150°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>mole % A mole % B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 90</td>
<td>0.38</td>
<td>22.2</td>
</tr>
<tr>
<td>10 90</td>
<td>0.43</td>
<td>22.0</td>
</tr>
<tr>
<td>10 90</td>
<td>0.53</td>
<td>23.9</td>
</tr>
<tr>
<td>10 90</td>
<td>0.76</td>
<td>22.9</td>
</tr>
<tr>
<td>20 80</td>
<td>0.41</td>
<td>9.2</td>
</tr>
<tr>
<td>20 80</td>
<td>0.46</td>
<td>10.3</td>
</tr>
<tr>
<td>20 80</td>
<td>0.54</td>
<td>17.6</td>
</tr>
<tr>
<td>20 80</td>
<td>0.70</td>
<td>16.0</td>
</tr>
<tr>
<td>30 70</td>
<td>0.53</td>
<td>7.8</td>
</tr>
<tr>
<td>40 60</td>
<td>0.44</td>
<td>5.9</td>
</tr>
</tbody>
</table>

\[ A = \left[ \begin{array}{c} -O- \end{array} \right] \left[ \begin{array}{c} -SO_2- \end{array} \right] \left[ \begin{array}{c} -O- \end{array} \right] \]

\[ B = \left[ \begin{array}{c} -O- \end{array} \right] \left[ \begin{array}{c} -SO_2- \end{array} \right] \left[ \begin{array}{c} -O- \end{array} \right] \]
TABLE 50

Unnotched Impact Strength of Polymers Containing $o,p'$ Repeat Units

<table>
<thead>
<tr>
<th>Polymer Structure</th>
<th>[RV] $1%$ DMF $25^\circ$</th>
<th>Unnotched impact strength KJ/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mole $%$ A mole $%$ B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 90</td>
<td>0.53</td>
<td>Did not break</td>
</tr>
<tr>
<td>20 80</td>
<td>0.54</td>
<td>36.5</td>
</tr>
<tr>
<td>30 70</td>
<td>0.53</td>
<td>32.1</td>
</tr>
<tr>
<td>40 60</td>
<td>0.44</td>
<td>20.1</td>
</tr>
<tr>
<td>50 50</td>
<td>0.50</td>
<td>16.0</td>
</tr>
</tbody>
</table>

$A = [-\left(\text{SO}_2\text{O}\right)_{n}]_{0-}$  $B = [-\left(\text{SO}_2\text{O}\right)_{n}]_{0-}$

The data in table 49 may be compared directly with that in table 47. A clear trend of lower impact strength with increasing $o,p'$ repeat units of the polymer may be seen for the samples before and after storage at $150^\circ$. The impact strength does not change so much with RV for the polymers containing $o,p'$ repeat units but there is similar reduction in impact strength on storage at $150^\circ$. The results are shown in graph 36 as plots of impact strength versus mole $\%$ $o,p'$-repeat units for two RV ranges.

The impact data for polymers containing $m,p'$-repeat units are shown in table 51. The presence of $m,p'$-repeat units in the polymer reduces the impact strength. The effect is not as severe as with $o,p'$ repeat units although an exact comparison is difficult because of the scatter in these results.
Graph 36: Impact Strength of \(D_2\) Copolymers

\[\left(\text{[C-H]-SO}_2\text{-CH}_{\text{CH}_2}\text{-SO}-\text{C-H]}\right)\]

- \(\pm 2\) mm notch.
- \(X\) = Unnotched.
- R.V. \(0.46-0.54\)
- R.V. \(0.41-0.43\)

Impact Strength \(\text{kJ/m}^2\):

- 60
- 50
- 40
- 30
- 20
- 10

Mole % \(D_2\) Repeat Unit
### TABLE 51

*Impact Data for Polymers Containing m,p' Repeat Units*

<table>
<thead>
<tr>
<th>Structure</th>
<th>RV</th>
<th>Notch</th>
<th>Impact Strength in KJ/m² with storage time at 150°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>mole % A</td>
<td>mole % B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0.61</td>
<td>None</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0.28</td>
<td>None</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>0.63</td>
<td>None</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>0.63</td>
<td>2 mm</td>
</tr>
</tbody>
</table>

A = [-\(\text{-SO}_2\text{-O-}\)]  B = [-\(\text{-SO}_2\text{-O-}\)]

The presence of o,p' or m,p' linkages in the polymer in great enough quantity can cause the polymer to be brittle unnotched. This represents a large difference in strength since the polymers are now in a different class for impact behaviour. (see fourfold classification in part 1).

The 2 mm notched impact strengths of branched polymers together with the maximum number of branches which could be present (see part 7) are shown in Table 52.
TABLE 52

Notched Impact Strength of Branched Polymers

<table>
<thead>
<tr>
<th>Branched polymer type</th>
<th>[RV]1% DMF25°C</th>
<th>Maximum number of branches</th>
<th>Notched impact strength KJ/m² with storage time at 150°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>XXVI</td>
<td>0.51</td>
<td>1 in 120 repeat units</td>
<td>27.5</td>
</tr>
<tr>
<td>XXVI</td>
<td>0.48</td>
<td>1 in 120 repeat units</td>
<td>36.7</td>
</tr>
<tr>
<td>XXVII</td>
<td>0.83</td>
<td>1 in 100 repeat units</td>
<td>38.6</td>
</tr>
</tbody>
</table>

The presence of branching in poly(diphenylene ether sulphone) reduces the notched impact strength. Storage of the specimens at 150°C produces a greater drop in impact strength than was found for the normal poly E,E′-(diphenylene ether sulphone) which is much lower in branching.

In table 53 the impact strengths of polymer prepared from the dipotassium salt of 4,4′-dihydroxydiphenyl sulphone and 4,4′-difluorodiphenyl sulphone. Polymer prepared by this route shows a much smaller secondary peak in the gel permeation chromatography graph and is believed to contain a lower amount of branched polymer than the polymer made by the one monomer route.
The impact strengths before storage at 150° are a little lower than those found for poly-\(P-P'-(\text{diphenylene ether sulphone})\) made by a 1 monomer route. After storage at 150°, however, the impact strength is very close to that expected (see table 47). The amount of branching in these polymers appears to be too small to make a significant difference to the impact strength.

In table 54 the notched impact strength of polymers containing diphenyl and naphthalene units are shown.
TABLE 54
Notched Impact Strength of Polymers Containing Diphenyl and Naphthalene Units

<table>
<thead>
<tr>
<th>Polymer Structure</th>
<th>[RV]_{25^\circ}^{1%}</th>
<th>0</th>
<th>3 days</th>
<th>1 week</th>
<th>4 weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[-[O(\text{phenyl})_3\text{SO}_2\text{-naphthalene}]_n]^-</td>
<td>0.57</td>
<td>133.8</td>
<td>108.6</td>
<td>95.1</td>
<td>70.8</td>
</tr>
<tr>
<td>[-[O(\text{phenyl})_3\text{SO}_2\text{-naphthalene}]_n]^-</td>
<td>0.47</td>
<td>72.0</td>
<td>42.2</td>
<td>37.6</td>
<td>18.1</td>
</tr>
<tr>
<td>[-[O(\text{phenyl})_3\text{SO}_2\text{-naphthalene}]_n]^-</td>
<td>0.42</td>
<td>29.4</td>
<td>11.8</td>
<td>8.8</td>
<td>7.1</td>
</tr>
<tr>
<td>[-[\text{phenyl}\text{-SO}_2\text{-naphthalene}]]^- 20 mole %</td>
<td>0.37</td>
<td>9.4</td>
<td>-</td>
<td>5.0</td>
<td>4.9</td>
</tr>
<tr>
<td>[-[\text{phenyl}\text{-SO}_2\text{-naphthalene}]]^- 80 mole %</td>
<td>0.63</td>
<td>33.3</td>
<td>-</td>
<td>12.5</td>
<td>15.7</td>
</tr>
<tr>
<td>[-[\text{phenyl}\text{-SO}_2\text{-naphthalene}]]^- 50 mole % +</td>
<td>0.61</td>
<td>7.89</td>
<td>-</td>
<td>-</td>
<td>7.22</td>
</tr>
<tr>
<td>[-[\text{phenyl}\text{-SO}_2\text{-naphthalene}]]^- 50 mole %</td>
<td>0.49</td>
<td>14.0*</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Unnotched impact strength
The introduction of 4,4'-dioxyphephenyl units into poly(diphenylene ether sulphone) produces a substantial increase in impact strength. The effect is particularly noticeable on the specimens which were not stored at 150°. With 20 mole % 4,4'-dioxyphephenyl units the impact strength is approximately 2.5 times that of poly(diphenylene ether sulphone) of the same RV and with 5 mole % 4,4'-dioxyphephenyl units the impact strength is approximately 1.5 times the impact strength of poly(diphenylene ether sulphone).

The units 1,5 dioxynaphthalene and 1-oxy-4-(benzene sulphonyl)naphthalene both cause a lowering of the impact strength. These units do not cause as big a drop in impact strength as the same mole % of o,p' repeat units. Thus the higher impact strength measured with 20 mole % o,p' repeat units was 17.6 KJ/m² while with 20 mole % 1,5 dioxyphephenyl units the impact strength was 29.4 KJ/m² (RV = 0.42) and with 20 mole % 1-oxy-4-(benzene sulphonyl)naphthalene units the impact strength was 33.3 KJ/m² (RV = 0.63). The homopolymer containing 1-oxy 4-(benzene sulphonyl) naphthalene groups was brittle unnotched showing a change of class for impact behaviour as was observed with >20 mole % o,p' repeat units.

6 Flexural Modulus

The modulus of a polymer is an important property, being a measure of its stiffness. The polymers made were tested in flexure and some in tension (see next section). The modulus may be defined as the slope of the stress versus strain graph.

\[ E = \frac{\text{stress}}{\text{strain}} \]
When a load is applied to a polymer sample the sample creeps, that is the strain increases with time. This means that the reading of strain (or deflection) for each load must be made after a set time. Provided the strain does not exceed a certain level the sample will recover after a time when the load is removed and the deflection returns to zero.

The flexural modulus measured was a 100 second creep modulus; readings of deflection were taken 100 seconds after applying the load. The method was a 3 point loading method, the specimen being supported at two points 10cm apart and the load applied in the centre as shown.

The loads applied were such as not to exceed a 1 mm deflection at the centre of the specimen. The specimen was allowed to recover for 400 seconds before applying further loads.

The results obtained for the repeat unit isomers of poly(diphenylene ether sulphone) are shown in table 55 and the results for the other structural variations are in table 56.
TABLE 55

Flexural Modulus at 20° for Repeat Unit Isomers of Poly(diphenylene ether sulphone)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>[RV] \textsuperscript{1%} DMF</th>
<th>Flexural Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-[-\text{SO}_2-\text{O}-]_n)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>0.40</td>
<td>(2.63 \times 10^9 \text{N/m}^2)</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>0.48</td>
<td>(2.56 \times 10^9 )</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>0.61</td>
<td>(2.54 \times 10^9 )</td>
</tr>
<tr>
<td>&quot; After storing at 150° for 5 weeks</td>
<td>0.40</td>
<td>(2.79 \times 10^9 )</td>
</tr>
</tbody>
</table>

\(o,p'\) copolymers

<table>
<thead>
<tr>
<th>Mole % A</th>
<th>Mole % B</th>
<th>[RV] \textsuperscript{1%} DMF</th>
<th>Flexural Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>90</td>
<td>0.53</td>
<td>(2.63 \times 10^9 \text{N/m}^2)</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>0.54</td>
<td>(2.77 \times 10^9 )</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>0.53</td>
<td>(2.85 \times 10^9 )</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>0.44</td>
<td>(2.90 \times 10^9 )</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>0.49</td>
<td>(3.07 \times 10^9 )</td>
</tr>
<tr>
<td>(-[-\text{SO}_2-\text{O}-]_n)</td>
<td>0.74</td>
<td>(3.44 \times 10^9 \text{N/m}^2)</td>
<td></td>
</tr>
</tbody>
</table>

A = \(-[-\text{SO}_2-\text{O}-]\) \quad B = \(-[-\text{SO}_2-\text{O}-]\)
TABLE 56

Flexural Modulus at 20° for Polymers Containing Diphenyl and Naphthalene Units

<table>
<thead>
<tr>
<th>Structure</th>
<th>[RV]_{25°}^{1% DMF}</th>
<th>Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>([-\text{\begin{array}{c} \text{\includegraphics[width=0.05\textwidth]{structure1}} \ \text{\includegraphics[width=0.05\textwidth]{structure2}} \ \text{\includegraphics[width=0.05\textwidth]{structure3}} \end{array}}\text{_}_n] -</td>
<td>0.51</td>
<td>2.39 x 10^9 N/m²</td>
</tr>
<tr>
<td>([-\text{\begin{array}{c} \text{\includegraphics[width=0.05\textwidth]{structure4}} \ \text{\includegraphics[width=0.05\textwidth]{structure5}} \ \text{\includegraphics[width=0.05\textwidth]{structure6}} \end{array}}\text{_}_n] -</td>
<td>0.47</td>
<td>2.56 x 10^9 N/m²</td>
</tr>
<tr>
<td>([-\text{\begin{array}{c} \text{\includegraphics[width=0.05\textwidth]{structure7}} \ \text{\includegraphics[width=0.05\textwidth]{structure8}} \ \text{\includegraphics[width=0.05\textwidth]{structure9}} \end{array}}\text{_}_n] -</td>
<td>0.42</td>
<td>2.87 x 10^9 N/m²</td>
</tr>
<tr>
<td>([-\text{\begin{array}{c} \text{\includegraphics[width=0.05\textwidth]{structure10}} \ \text{\includegraphics[width=0.05\textwidth]{structure11}} \end{array}}\text{_}\text{ 20 mole % }] +</td>
<td>0.37</td>
<td>2.92 x 10^9 N/m²</td>
</tr>
<tr>
<td>([-\text{\begin{array}{c} \text{\includegraphics[width=0.05\textwidth]{structure12}} \ \text{\includegraphics[width=0.05\textwidth]{structure13}} \end{array}}\text{_}\text{ 80 mole % }] \ &quot;</td>
<td>0.63</td>
<td>2.81 x 10^9 N/m²</td>
</tr>
<tr>
<td>([-\text{\begin{array}{c} \text{\includegraphics[width=0.05\textwidth]{structure14}} \ \text{\includegraphics[width=0.05\textwidth]{structure15}} \end{array}}\text{_}\text{ 50 mole % }] +</td>
<td>0.61</td>
<td>3.12 x 10^9 N/m²</td>
</tr>
<tr>
<td>([-\text{\begin{array}{c} \text{\includegraphics[width=0.05\textwidth]{structure16}} \ \text{\includegraphics[width=0.05\textwidth]{structure17}} \end{array}}\text{_}\text{ 50 mole % }]</td>
<td>0.49</td>
<td>3.54 x 10^9 N/m²</td>
</tr>
</tbody>
</table>
The flexural modulus correlates well with impact strength. For poly-
(diphenylene ether sulphone) the modulus decreases with increasing 
RV while the impact strength increases. The modulus of the sample of 
homopolymer stored at 150° had increased from 2.63 to 2.79 x 10^9 N/m². 
This correlates with the lower impact strength of the aged specimens.

The flexural modulus increases as the mole % o,p'-repeat units in the 
polymers increases while the impact strength decreases. This is also 
shown for the poly-m,p'- (diphenylene ether sulphone) which has a higher 
flexural modulus and is more brittle than poly-p,p'- (diphenylene ether 
sulphone). Graph 37 shows a plot of modulus against mole % o,p'-
repeat units.

The polymers containing 1,5 -dioxynaphthalene units or 1-oxy 4-(benzene 
sulphonyl)naphthalene units have a higher modulus than poly-p,p'-
(diphenylene ether sulphone) and both of these units make the polymer 
more brittle.

The polymer containing 4,4'-dioxyphephenyl units which are the only 
polymer studied which had a higher impact strength than poly-p,p'-
(diphenylene ether sulphone) have a lower modulus than the poly-p,p'-
(diphenylene ether sulphone).

7 Tensile Stress-Strain Testing

Tensile stress-strain testing was carried out on a specimen with a 10 
cm parallel sided section of approximate thickness 3.25 mm and width 
5.5 mm and with splayed ends. The specimen was subjected to a load 
along its own axis and the resulting strain measured by means of an 
optical extensometer.
Isochronous stress-strain measurements were carried out for polymers containing 10 and 50 mole % o,p'-repeat units after 1 hour, 1 day, 7 days and 12 days at 150°. The strain was measured 100 seconds after applying the load and the specimen was allowed to recover for 400 seconds between readings. The strain was limited to 0.4% for the first three experiments, on the 12th day a full 100 second isochronous experiment was carried out (ie until the specimen broke). The results are shown in graphs 38 and 39 and may be compared with the results for poly-p,p'- (diphenylene ether sulphone) which are also shown in graph 39.

The behaviour of the o,p' polymer is similar to poly-p,p'- (diphenylene ether sulphone) but the higher modulus of the o,p' polymers is apparent. The modulus of poly-p,p'- (diphenylene ether sulphone) after 1 hour at 150° is 2.50 x 10^9 N/m^2 while for the 10 mole % o,p' -copolymer it is 2.60 x 10^9 N/m^2 and for 50 mole % o,p' copolymer it is 2.87 x 10^9 N/m^2. The modulus figures found in tension are very similar to those found in flexure. This is expected as the same type of modulus (Young's modulus) is being measured.

On storage at 150° smaller strains were obtained for the same stress so that the stress-strain line is moved up as shown in the graphs 38 and 39. This corresponds to an increase in modulus. Thus the modulus of the 10 mole % o,p' -polymer increases from 2.60 to 2.75 x 10^9 N/m^2 and that of 50 mole % o,p' -polymer increases from 2.87 to 3.10 x 10^9 N/m^2 after 12 days at 150°. During this time the modulus of poly-p,p' - (diphenylene ether sulphone) increases from 2.50 to 2.65 x 10^9 N/m^2. These results are in agreement with the flexural modulus behavior.
Graph 38: Isochronous Stress-Strain Relationship

For experiment [○○○] 100 mole% +

[○○○] 20 mole% R.V. 0.53

Temperature 180°

Stress (N/m²)

Strain (at 100 sec)

0.01  0.001  0.0001

12 days

7 days

30 minutes
GRAPH 39. ISOCRONS STRESS STRAIN RELATIONSHIP

FOR HOMOPOLYMER \( \left\langle \frac{2}{2} \cdot \frac{3}{3} \cdot \frac{4}{4} \right\rangle \) AND FOR THE COPOLYMER \( \left\langle \frac{2}{2} \cdot \frac{3}{3} \cdot \frac{4}{4} \right\rangle \) 50 MOLE % I

\( \left\langle \frac{2}{2} \cdot \frac{3}{3} \cdot \frac{4}{4} \right\rangle \) 30 MOLE % C

TEMPERATURE 50°C

50 mol% \( \left\langle \frac{2}{2} \cdot \frac{3}{3} \cdot \frac{4}{4} \right\rangle \) copolymer
R.V. 0.149

12 days
7 days
15 days
1 day
1 hour

homopolymer. R.V. 0.49

STRAIN (at 100 sec)

STRESS (N/m²)
The lower strength properties of the \( o_o \), \( p' \) - copolymers are also apparent from the full isochronous line in the graphs. The 50 mole % \( o_o \), \( p' \) - copolymer has failed (X) at a stress of \( 3.5 \times 10^7 \) N/m\(^2\), the 10 mole % \( o_o \), \( p' \) - copolymer at \( 3.8 \times 10^7 \) N/m\(^2\) while the \( p, p' \) - homopolymer failed at \( 4.6 \times 10^7 \) N/m\(^2\).

Graph 40 shows tensile creep experiments for a 50 mole % \( o_o \), \( p' \) - copolymer and a \( p, p' \) - homopolymer. The polymers were stored at 150° for 12 days before applying a stress of \( 2.0 \times 10^7 \) N/m\(^2\). The extension of the specimen and hence strain with time at this constant stress was then followed as shown on the graph. The 50 mole % \( o_o \), \( p' \) - copolymer shows a smaller strain than the homopolymer after 10 seconds (due to its higher modulus). The copolymer fails after 1.75 hours at this stress with only a small increase in strain. The homopolymer does not fail until >1 month at this stress and the strain has increased markedly (ie the polymer has yielded). The experiment confirms the brittle nature of the 50 mole % \( o_o \), \( p' \) - copolymer.

An attempt to measure the creep of a 50 mole % \( o_o \), \( p' \) - copolymer at 20° and with a stress of \( 5.0 \times 10^7 \) N/m\(^2\) was not successful as the specimen broke almost immediately the load was applied.

Graph 41 shows isochronous stress-strain data at 20° for the 50 mole % \( o_o \), \( p' \) - copolymer and a \( p, p' \) - homopolymer. In this case the specimen failed (X) at a stress of \( 4 \times 10^7 \) N/m\(^2\) and strain 0.013 while the homopolymer did not fail up to a stress of \( 7.8 \times 10^7 \) N/m\(^2\) and strain 0.053.

A summary of some of the isochronous stress-strain data is shown in table 57.
GRAPH 40 CREEP IN TENSION FOR THE HOMOPOLYMER \( \left[ \begin{array}{c} \text{C} \\ \text{SO}_2 \\ \text{C} \end{array} \right]_n \) AND THE COPOLYMER \( \left[ \begin{array}{c} \text{C} \\ \text{SO}_2 \\ \text{C} \end{array} \right] \) 50 MOLE% + \( \left[ \begin{array}{c} \text{C} \\ \text{SO}_2 \\ \text{C} \end{array} \right] \) 50 MOLE%.

TEMPERATURE \( = 150^\circ \), STRESS \( = 2.0 \times 10^7 \text{ N/m}^2 \).

STRAIN

TIME (SEC)
Graph 4: Isochronous stress strain relationship

For the homopolymer \( \text{[monomer]} \) and for the copolymer \( \text{[monomer]} \)

Sacrifice \% \[ (\text{monomer}) \] \( 50 \text{ mole}\% \).

Temperature \( 20^\circ \text{C} \)

\begin{align*}
\text{STRESS (N/m²)} \\
\text{STRAIN (AT 100 SEC)}
\end{align*}
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temp</th>
<th>Storage time at this temp</th>
<th>Modulus at 0.002 strain (N/m²)</th>
<th>Stress at break (N/m²)</th>
<th>Strain at break</th>
</tr>
</thead>
<tbody>
<tr>
<td>-[-SO₂-0-]ₙ</td>
<td>20°</td>
<td>-</td>
<td>2.6 x 10⁹</td>
<td>&gt;7.8 x 10⁷</td>
<td>&gt;0.053</td>
</tr>
<tr>
<td>&quot;</td>
<td>150°</td>
<td>1 hour</td>
<td>2.45 x 10⁹</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>&quot;</td>
<td>1 day</td>
<td>2.55 x 10⁹</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>&quot; (RV 0.48)</td>
<td></td>
<td>13 days</td>
<td>2.70 x 10⁹</td>
<td>4.55 x 10⁷</td>
<td>0.0195</td>
</tr>
<tr>
<td>[SO₂-0-]ₙ</td>
<td>20°</td>
<td>-</td>
<td>3.5 x 10⁹</td>
<td>4.0 x 10⁷</td>
<td>0.013</td>
</tr>
<tr>
<td>&quot;</td>
<td>150°</td>
<td>1 hour</td>
<td>2.9 x 10⁹</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>&quot;</td>
<td>1 day</td>
<td>3.0 x 10⁹</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>&quot; (RV 0.49)</td>
<td></td>
<td>12 days</td>
<td>3.1 x 10⁹</td>
<td>3.5 x 10⁷</td>
<td>0.012</td>
</tr>
<tr>
<td>-[-SO₂-0-]ₙ</td>
<td>150°</td>
<td>1 hour</td>
<td>2.6 x 10⁹</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>&quot;</td>
<td>1 day</td>
<td>2.65 x 10⁹</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>&quot; (RV 0.53)</td>
<td></td>
<td>12 days</td>
<td>2.80 x 10⁹</td>
<td>4.0 x 10⁷</td>
<td>0.0155</td>
</tr>
</tbody>
</table>
Density Measurements

The density of the polymers have been measured by the buoyancy method. Early work showed that careful exclusion of water from the samples was necessary in order to obtain accurate densities. Examples where water was not carefully excluded are shown in table 58, using samples cut from a compression moulding.

TABLE 58

<table>
<thead>
<tr>
<th>Sample</th>
<th>[RV]_{25\degree}</th>
<th>Weight of sample</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.61</td>
<td>1.3004</td>
<td>1.3684 g/cc</td>
</tr>
<tr>
<td>B</td>
<td>0.61</td>
<td>1.3234</td>
<td>1.3689 &quot;</td>
</tr>
<tr>
<td>A stored for 9 days at 150\degree</td>
<td>0.61</td>
<td>1.2963</td>
<td>1.3667 &quot;</td>
</tr>
<tr>
<td>B &quot; &quot; &quot; &quot; &quot; &quot;</td>
<td>0.61</td>
<td>1.3191</td>
<td>1.3668 &quot;</td>
</tr>
<tr>
<td>A The aged samples after</td>
<td>0.61</td>
<td>1.3049</td>
<td>1.3725 &quot;</td>
</tr>
<tr>
<td>B keeping in air for 3 weeks</td>
<td>0.61</td>
<td>1.3278</td>
<td>1.3723 &quot;</td>
</tr>
<tr>
<td>C</td>
<td>0.41</td>
<td>1.9083</td>
<td>1.3690 &quot;</td>
</tr>
<tr>
<td>C after ageing for 7 days at 150\degree</td>
<td>0.41</td>
<td>1.9040</td>
<td>1.3677 &quot;</td>
</tr>
<tr>
<td>C The aged sample after storing in air for 3 weeks</td>
<td>0.41</td>
<td>1.9165</td>
<td>1.3735 &quot;</td>
</tr>
</tbody>
</table>

The results indicate that the unaged samples contain some water (the weight loss on ageing is approximately 0.004 g in these samples). On storing at 150\degree this water is lost resulting in a loss in weight and a decrease in density. A decrease in density is probably observed because the unaged specimens contains water in voids or pores in the polymer structure. The loss of this water by heating creates a structure with some voids resulting in a less dense material. On storing the aged samples in air at 20\degree the density and weight increase, probably due to water uptake.
The problem of water in the specimens was largely eliminated by a technique of moulding dry film directly into density samples and then cooling these from 150° to room temperature in a vacuum dessicator over phosphorus pentoxide. The density was then measured as rapidly as possible. The results obtained with these samples are shown in table 59 for the repeat unit isomers of poly(diphenylene ether sulphone) and table 60 for the other structural variations.

**TABLE 59**

**Density at Room Temperature of Repeat Unit Isomers of Poly(diphenylene ether sulphone)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>[RV]_{25^\circ}^{12% DMF}</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>[-\text{-SO}_2\text{-O-}]_n\</td>
<td>0.44</td>
<td>1.3658 g/cc</td>
</tr>
<tr>
<td>[-\text{-SO}_2\text{-O-}]_n\</td>
<td>0.44</td>
<td>1.3672 &quot;</td>
</tr>
<tr>
<td>[-\text{-SO}_2\text{-O-}]_n\</td>
<td>0.28</td>
<td>1.3872 &quot;</td>
</tr>
<tr>
<td>[-\text{-SO}_2\text{-O-}]_n\</td>
<td>0.31</td>
<td>1.3839 &quot;</td>
</tr>
<tr>
<td>[-\text{-SO}_2\text{-O-}]_n\</td>
<td>0.45</td>
<td>1.3846 &quot;</td>
</tr>
<tr>
<td>[-\text{-SO}_2\text{-O-}]_n\</td>
<td>0.61</td>
<td>1.3844 &quot;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mole % A</th>
<th>Mole % B</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>90</td>
<td>1.3656  &quot;</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>1.3669  &quot;</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>1.3678  &quot;</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1.3691  &quot;</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>1.3698  &quot;</td>
</tr>
</tbody>
</table>

* Aged for 3 days at 150°

\[ A = [-\text{-SO}_2\text{-O-}]_n \quad B = [-\text{-SO}_2\text{-O-}]_n \]
TABLE 60

Density of Polymers Containing Diphenyl and Naphthalene Units

<table>
<thead>
<tr>
<th>Structure</th>
<th>[RV]_{25^\circ}</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>-[O-O-O-SO_2-O-O-SO_2-O-O-SO_2-O-O-SO_2-]_n</td>
<td>0.51</td>
<td>1.3353 g/cc</td>
</tr>
<tr>
<td>-[O-O-O-SO_2-O-O-SO_2-O-O-SO_2-O-O-SO_2-]_n</td>
<td>0.47</td>
<td>1.3586</td>
</tr>
<tr>
<td>-[O-O-O-SO_2-O-O-SO_2-O-O-SO_2-O-O-SO_2-]_n</td>
<td>0.42</td>
<td>1.3477</td>
</tr>
<tr>
<td>[-O-SO_2-O-O-O-SO_2-O-O-SO_2-O-O-SO_2-O-O-SO_2-]_20 moles % +</td>
<td>0.37</td>
<td>1.3620</td>
</tr>
<tr>
<td>[-O-SO_2-O-O-O-SO_2-O-O-SO_2-O-O-SO_2-]_80 moles %</td>
<td>0.63</td>
<td>1.3514</td>
</tr>
<tr>
<td>[-O-SO_2-O-O-O-SO_2-O-O-SO_2-O-O-SO_2-]_50 moles % +</td>
<td>0.61</td>
<td>1.3569</td>
</tr>
<tr>
<td>[-O-SO_2-O-O-O-SO_2-O-O-SO_2-O-O-SO_2-]_50 moles %</td>
<td>0.49</td>
<td>1.3499</td>
</tr>
</tbody>
</table>

The densities shown are an average of two determinations. The weight loss on storing the samples of the poly-\textsubscript{p,p}\textsuperscript{1}(diphenyl ether sulphone) at 150° was very small (0.0005 g) so that the original samples contained very little water. On these very dry samples there was a small increase in density on storage at 150°.

The weight loss on storing the density samples of \textsubscript{o,p}\textsuperscript{1}-copolymers was 0.0005 - 0.001 g so that the samples of these polymers contained very little water (the sample weight is approximately 1.4 g). The density of these copolymers increases with increasing \textsubscript{o,p}\textsuperscript{1} repeat unit content (see graph 42). The increase though small is consistent and follows the increase in modulus with \textsubscript{o,p}\textsuperscript{1} repeat unit content.
A decrease in density may be observed with the polymers containing 4,4'-dioxydiphenyl units, in agreement with their lower modulus. The polymers containing 1-oxy-4-(benzene sulphonyl)naphthalene units and 1,5dioxynaphthalene units have a lower density than poly p,p'-(diphenylene ether sulphone) although in this case their modulus is higher.

The literature value for the density of the polysulphone (V) made by the Union Carbide Corporation is 1.24 g/ml which is lower than poly p,p'-(diphenylene ether sulphone).

Dynamic Mechanical Properties

The dynamic mechanical properties of the poly p,p'-(diphenylene ether sulphone) and o,p' copolymers were measured to see if there was any correlation between physical properties and the damping processes, as has been observed with some other polymers (see Introduction).

Dynamic mechanical tests measure the deformation of a material under a varying force. The force and deformation usually vary sinusoidally with time.

A dynamic modulus and a mechanical damping term may be obtained from the results of the tests. In the case of the vibrating reed apparatus which was used for these measurements the modulus obtained is a Young's modulus (as obtained by the flexural and tensile tests). The mechanical damping is obtained in the form tan δ where δ is the phase angle between the stress and the strain.
\[ \delta = w \Delta t \] where \( w \) is the angular frequency and \( \Delta t \) is the time shift between the peaks of the stress and strain curves.

\[ \sigma \text{ (stress)} \quad \xi \text{ (strain)} \]

Measurements were made at temperatures between +20° and -120° using a manually operated vibrating reed apparatus. At each temperature the frequency of the vibration applied to the reed was increased until resonance was reached (amplitude of free end of reed reaches a maximum at resonance). The modulus was then calculated from the resonance frequency and the damping from the sharpness of the resonance peak.

Measurements were made on a \( p, p' \)-homopolymer of RV 0.61 before and after storing at 150° for 1 week. The results are shown in graph 43. There was no significant difference in \( \tan \delta \) or the modulus although the impact strength falls from 56.3 to 40.5 KJ/m² in this time. Similarly, measurements were made on a copolymer containing 50 mole % \( o,p' \)-repeat units and of RV 0.50. The results are shown in graph 44. The low temperature \( \tan \delta \) peak (at approximately -50°) is still observed for this polymer which has a much lower impact strength than poly \( p,p' \) (diphenylene ether sulphone).

The higher modulus of the 50 mole % \( o,p' \) copolymer (3.25 x 10⁹ N/m² at 20°) compared with the \( p,p' \)-homopolymer (2.60 x 10⁹ N/m² at 20°) may be seen from graphs 43 and 44. The modulus figures are in quite good agreement with those obtained by flexure (see table 55) and tension.
GRAPH 43  DYNAMIC MODULUS AND TAN S FOR A

POLY p,p' (DIPHENYLENE ETHER SULPHONE) OF R.V. 0.61.
GRAPH 4.4  DYNAMIC MODULUS AND TAN δ FOR A
CO-POLYMER \{(\text{-})3\text{-}0\text{-}0\}\ 50\text{ MOLE}\% + \{(\text{0})3\text{-}0\text{-}0\}\ 50\text{ MOLE}\%
GRAPH 45 Tan δ versus temperature at 4°/min

For the copolymer \[ \begin{align*}
\text{50 mole}\% \\
\text{50 mole}\% \\
\end{align*} \]
Measurements were also made on an automatic dynamic mechanical apparatus at a heating rate of 4°/minute. The results are shown in graph 45. The low temperature peak in tan δ is still observed although at a different temperature (approximately -75°), than when using the manual apparatus. There does not appear to be any definite correlation between the impact strength of these polymers and the low temperature damping peak. The o,p'- copolymers which are much more brittle than the p,p'- homopolymer still have a significant low temperature damping peak.

Brittle Temperature Testing

The 50 mole % o,p'- copolymer, which is brittle at room temperature, has been tested to see if a transition from brittle to yielding type failure occurs at some temperature in a tensile test.

The two types of failure are shown below

![Diagram showing brittle and yield failure](#)

The test consisted of producing a load versus extension graph for each specimen and temperature in a short time (the test speed was 5 or 500 mm/minute). Measurements were made up to 220°. At this temperature the stress at breaking was 20 MN/m² (brittle stress) and the polymer still showed a brittle type failure. The results are shown in graph 46 together with results for poly-p,p'- (diphenylene ether sulphone)\(^7\). Poly-p,p'
GRAPH 46  BRITTLE STRENGTH FOR 50 MOLE% o,p' COPOLYMER AND YIELD STRESS FOR p,p' HOME POLYMER VERSUS TEMPERATURE.

\[ x = \left( \begin{array}{c} \text{p,p'} \text{ copolymer} \\ \text{o,p'} \text{ copolymer} \end{array} \right) \]

\[ y = \left( \begin{array}{c} 50 \text{ mole}\% \text{ p,p'} \\ 50 \text{ mole}\% \text{ o,p'} \end{array} \right) \]
(diphenylene ether sulphone) shows a yielding type failure at these
temperatures and down to -180°, when it shows a brittle failure. The
maximum yield stress for poly-$\text{P,P'}$- (diphenylene ether sulphone) is
148 MN/m$^2$ (at -180°) whereas for the 50 mole % $\text{a,P'}$- copolymer it is <
20MN/m$^2$ at >220° indicating a large difference in behaviour between
the two polymers.
Repeat Unit Isomerization and Chain Branching

The polymers containing the ortho-para repeat units (XIX), meta para repeat units (XX) and para-para repeat units (XVIII) were amorphous with the exception of poly-o,p'-(diphenylene ether sulphone) which was crystalline as made but could be converted to an amorphous form which could not be reconverted to a crystalline form.

![Chemical structure](image)

The glass transition temperature of the poly-o,p'-(diphenylene ether sulphone) and polymers containing ortho-para repeat units were very similar (approximately 230°) but that of the poly-m,p'-(diphenylene ether sulphone) was lower (approximately 170°).

The solution and melt viscosity behaviour of the poly-o,p'-(diphenylene ether sulphone) and the ortho-para - copolymers was very similar.

The molecular weight and molecular weight distribution of the polymers was very similar at the same [RV], but branched polymer had a larger secondary peak in the molecular weight distribution.

There was no marked difference in dynamic mechanical behaviour of the poly-o,p'-(diphenylene ether sulphone) and a 50 mole % ortho-para copolymer.
The bulk properties of the isomeric poly(diphenylene ether sulphones) are very different. The introduction of ortho-para repeat units or meta-para - repeat units into poly(diphenylene ether sulphone) causes a decrease in impact strength and an increase in flexural modulus and density. The tensile data also showed that the ortho-para - copolymers had a higher modulus and broke at a smaller stress and strain in an isochronous test than poly-p,p'-(diphenylene ether sulphone). In a creep test the brittle behaviour of a 50 mole % o,p' - copolymer was shown by its failure after a shorter time and much lower strain than a p,p' - homopolymer. The 50 mole % ortho-para - copolymer had a much lower initial tensile strength than the poly-p,p' - (diphenylene ether sulphone).

The branched polymers have a lower impact strength than the poly-p,p' - (diphenylene ether sulphone).

The similarity in glass transition temperature of the ortho-para and para-para polymers suggests that the chain flexibilities of the two types of polymer are very similar. The higher glass transition temperature of the ortho-para and para-para polymers compared with meta-para may be due to a stiffening of the main chain bonds by the formation of resonance structures.
With the o-, p' and p,p' polymers all the linkages between benzene rings may be stiffened in this way. The resultant restriction of rotation by the double bond character increases the glass transition temperature of the polymers. In the m,p' polymers only half the linkages may be stiffened by this type of resonance, hence its lower glass transition temperature.

The reasons for the different mechanical properties (impact strength, density and modulus) of the o-, p' and m,p' polymers compared with the p,p' polymer are not known for certain.
There are two possible explanations of the different properties of the repeat unit isomers of poly(diphenylene ether sulphone). The first is that the difference is due to a different number of bonds per unit area. P I Vincent has shown that the number of bonds per unit area correlates well with critical tensile strength for a wide range of polymers including poly(diphenylene ether sulphone). The length of repeat unit along the chain, which is used to calculate the molecular cross sectional area and hence number bonds /nm$^2$ (1/molecular cross sectional area) is not known for certain for the o,p' polymers. The length of the repeat unit was estimated by using the most extended form of the Courtauld's model. The results of the calculation are shown below.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Length of repeat unit</th>
<th>Molecular cross sectional area x 10$^{-20}$ m$^2$</th>
<th>Bonds/nm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{[-} \text{O} \text{-SO}_2 \text{-O} \text{-]}_n$</td>
<td>10.4 Å</td>
<td>27.2</td>
<td>3.68</td>
</tr>
<tr>
<td>$\text{[-} \text{O} \text{-SO}_2 \text{-O} \text{]}_n$</td>
<td>8.75 Å</td>
<td>32.4</td>
<td>3.09</td>
</tr>
<tr>
<td>$\text{[-} \text{O} \text{-SO}_2 \text{-O} \text{]}_n$  50 mole % +</td>
<td>9.58 Å</td>
<td>29.6</td>
<td>3.39</td>
</tr>
<tr>
<td>$\text{[-} \text{O} \text{-SO}_2 \text{-O} \text{-]}_n$  50 mole %</td>
<td>9.58 Å</td>
<td>29.6</td>
<td>3.39</td>
</tr>
</tbody>
</table>

The differences in number of bonds per unit area for the polymers is quite small although the difference in properties is large. The critical tensile strength equals:

$$\text{number bonds/nm}^2 \times 36.8$$

The predicted value for the 50 mole % o,p'- copolymer is 107/Mn/m$^2$. 

The experimental value is much lower (<20 MN/m²). For this theory to explain the observed properties, therefore, it is necessary to assume that the polymer chains are very folded or spiralled resulting in a reduction in the effective length of the repeat units along the chain. While such folding or spiralling can occur, as demonstrated by models, a complete explanation in these terms seems unlikely.

Another possible explanation is that closer packing of the chains occurs in the ortho-para and meta-para polymers. The closer packing of the polymer chains would result in a reduction in the number of voids or free volume present in the structure. The poly o,p'(diphenylene ether sulphone) as made is crystalline to X-rays ie there is considerable order in the arrangement of the polymer chains. When copolymerising the ortho-para monomer with para-para monomer it is possible that some degree of order in the arrangement of the polymer chains occurs. While this is not enough to make the polymer crystalline to X-rays it may be sufficient to cause a closer packing of the polymer chains. The reduction in number of voids or free volume in the polymer could cause a lowering of impact strength by restricting the movement of the polymer chains when impact occurs. Support for this theory is given by the higher density and modulus of the ortho-para and meta-para polymers compared with poly-p,p'(diphenylene ether sulphone). The increased density is presumably caused by a closer packed structure and the higher modulus by a more restricted movement of the polymer chains in the closer packed structure.
Other Structural Variations

The introduction of the 1,5-dioxynaphthalene unit (XXIX) and \(1(\text{benzene sulphonyl})_4\)-oxy naphthalene unit (XXVIII) into poly(diphenylene ether sulphone) cause a decrease in notched impact strength, an increase in modulus and a decrease in density.

\[
\text{(XXIX) } \quad \text{(XXVIII)}
\]

The glass transition temperature of the polymer remains unaffected by the presence of these units, however, indicating that the flexibility of the polymer chains is similar to that in poly(diphenylene ether sulphone).

The explanation of the different properties of these polymers may be the same as for the polymers containing ortho-para and meta-para - repeat units ie some ordering of the polymer chains may take place resulting in a reduction in voids in the polymer structure. The homo-polymer containing the \(1(\text{benzene sulphonyl})_4\) oxy naphthalene units can be made in a crystalline form by polymerizing the potassium salt of \(1(4\text{-fluorobenzene sulphonyl})_4\) hydroxy naphthalene in solution. This indicates that the polymer can take up an ordered structure and some degree of order could be present in the amorphous polymers and copolymers from this salt. A reduction in voids would explain the lower impact strength and higher modulus of these polymers but not the density which is less than poly(diphenylene ether sulphone) and not more as would be expected on the basis of closer packing. Density depends on the actual density of the polymer chains as well as the presence of voids.
and it may be that in this case the chains themselves have a lower
density, so that although the structure may have less free volume the
overall density is less.

The introduction of 4,4'-dioxydiphenyl units (XXX) into poly(diphenylene
ether sulphone) increases the notched impact strength, and decreases
the density and modulus. The effect of the 4,4'-dioxydiphenyl unit
is thus the opposite of the \textit{ortho-para} repeat unit.

\begin{center}
\begin{tikzpicture}
\draw[thick,black] (-1,0) -- (0,0) -- (1,0);
\draw[thick,black] (0,0) -- (0,-1);
\draw[thick,black] (0,0) -- (0,1);
\end{tikzpicture}
\end{center}

(XXX)

The glass transition temperature of the polymers containing the 4,4'-
dioxydiphenyl unit is the same as for poly(diphenylene ether sulphone,
indicating that the overall chain flexibility is similar. The improved
impact strength of these polymers may be due to the structure having
more free volume than poly(diphenylene ether sulphone). This would be
consistent with the lower density and modulus.

\textbf{Effect of Storage at High Temperature on Properties}

The notched impact strength of all the polymers examined was decreased
by storage at 150°. This is a common effect with thermoplastics (see
Introduction). Measurements on poly E.E'- (diphenylene ether sulphone)
indicate that the decrease in impact strength on storing at 150° is
accompanied by a small increase in modulus and density for dry specimens.
These facts may be explained in terms of the void theory. The presence of voids in poly \( \text{p,p}'-(\text{diphenylene ether sulphone}) \) was indicated by the density measurements. The density of samples of the polymer increased on storage in air at room temperature. The density increase was accompanied by an increase in weight. The density increase may be explained by uptake of water into voids which previously contained air. Storage of these samples at 150\(^\circ\) resulted in a weight loss and a decrease in density, presumably due to loss of water from the voids.

On storage of dry polymer samples at 150\(^\circ\) some reorientation of the polymer molecules to partially fill the voids probably occurs. This would account for the observed changes in physical properties.

**Conclusion**

The physical testing of these poly(arylene sulphones) indicate that any deviation from a linear, para- structure including the presence of ortho- links, meta- links, branching or bulky side groups, for example naphthalene, will result in a decrease in impact strength and an increase in modulus. The presence of ortho- and meta- linkages will cause an increase in density compared with the para- structure. These observations will probably apply to other aromatic polymer systems.
PART 11 EXPERIMENTAL

PREPARATION OF POLYMER INTERMEDIATES AND MODEL COMPOUNDS

The thermometer used in determining the melting points quoted in the following sections was checked and found correct by using some reference compounds.

Infra red spectra (Nujol mulls or KBr discs) were measured with a Perkin Elmer 157 spectrophotometer with sodium chloride prism.

Nmr measurements were made with a Varian A-60D (60 MHz), a Varian HA 100 (100 MHz) or a Varian HR 220 (220 MHz) spectrometer and chemical shifts are recorded as 5 ppm from tetramethyl silane.

Preparation of 4-fluorobenzenesulphonyl chloride

Chlorosulphonic acid (80 moles, 5180 ml, 6980 g) was charged to a 10 litre flanged flask equipped with stirrer, condenser and thermometer. The contents of the flask were cooled to -5° by immersing the flask in a "Drikold"/methanol bath. Redistilled fluorobenzene (20 moles, 1920 ml) was added to the stirred chlorosulphonic acid over a period of 5½ hours, maintaining the reaction mixture at -5 to -2°. The mixture was stirred overnight at room temperature and then poured onto ice (50 Kg). The resulting aqueous mixture was extracted with carbon tetrachloride (8 litres) in batches. The carbon tetrachloride extracts were washed three times with water and then dried over anhydrous sodium sulphate. The dried solution was filtered and the carbon tetrachloride removed by distillation. During the distillation the temperature was kept below 95° by using reduced pressure. The residue was then distilled under nitrogen using an 18" column packed with glass helices, to yield
4-fluorobenzensulphonyl chloride (3,170 g, 81%) bp 79°/0.9mm.

The product had mp 34-36° (literature 75.76 values 33, 35-36°).

\[ \text{ir } \lambda 3.25 \text{ (aromatic C-H stretch); } 5.22, 5.62 \text{ (overtones characteristic of para-substitution); } 6.28, 6.70 \text{ (aromatic C-C multiple bond stretch); } 7.28, 8.45 \text{ (S=O stretch in sulphonyl chloride) } \mu. \]

\[ \text{nmr } (60 \text{ MHz}) \]

\[ F-\begin{array}{c}
\text{H}_A \\
\text{H}_B \\
\text{SO}_2\text{Cl}
\end{array} \]

\[ 6 \text{ (acetone) } 8.08 \text{ (q, } 2\text{H}_B, J_{AB} 9 \text{ Hz, } J_{FB} 5 \text{ Hz), } 7.41 \text{ (t, } 2\text{H}_A, J_{FA} 9 \text{ Hz) } \text{ppm} \]

Preparation of 4,4'-difluorodiphenyl sulphone (reaction (16))

4-Fluorobenzensulphonyl chloride (1000g, 5.15 moles) was added to fluorobenzene (480 g, 5.00 moles) in a 5 litre flanged flask equipped with condenser. Anhydrous aluminium chloride (1000 g, 7.5 moles) was added to this solution over 2 hours. The addition was begun at room temperature but when 400 g of aluminium chloride had been added the solution was heated to 45° to speed the reaction up. When addition was complete the mixture was heated at 95° for 2 hours. The hot reaction mixture was poured onto ice (5 Kg) and allowed to stand overnight. The product was filtered off, washed well with water and dried. The product was recrystallized from ethanol (3,000 ml) using activated charcoal to decolourize the hot solution which was filtered using 'Celite' filter aid. The product was dried at 65° in a vacuum oven. The yield was 1129 g (89%) mp 98.9-99.6 (literature 78.79 value 98°).
\[ \text{nmr (60 MHz)} \]
\[
\begin{array}{c}
\text{F} \\
\text{H}_A \\
\text{H}_B \\
\text{SO}_2 \\
\text{F}
\end{array}
\]

6 (acetone) 8.02 (q, 4H, J_AB 9Hz, J_FB 5Hz); 7.29 (t, 4H, J_FB 9Hz)ppm

Preparation of 4-fluoro-4'-hydroxydiphenyl sulphone (reactions (17) and (18))

4,4'-Difluorodiphenyl sulphone (1017 g, 4 moles), 50% aqueous potassium hydroxide (918.1 g, 8 moles) and dimethyl sulphoxide (4 litres) were charged to a stainless steel vessel equipped with efficient stirrer, condenser and nitrogen inlet and outlet. The reaction mixture was stirred under nitrogen at 60° for 24 hours. The vessel was heated by means of a water bath. The resulting hydrolysate was poured into 10 litres of ice/water and then filtered to remove unreacted 4,4'-difluorodiphenyl sulphone. The filtered solution was acidified with concentrated hydrochloric acid to yield an oily product which crystallized on standing. The product was filtered off and washed with water in a laboratory blender. The product was dissolved in methanol (3,000 ml) at 60° treated with activated charcoal and filtered using 'Celite' filter aid then poured into ice/water. The crude product was filtered off and dried.
The crude 4-fluoro-4'-hydroxydiphenyl sulphone was distilled under nitrogen at reduced pressure (bp 242°/0.2 mm). The still flask was equipped with an anti-splash head to prevent any crude product splashing over with the vapours. The yield of redistilled 4-fluoro-4'-hydroxydiphenyl sulphone was 812 g. The redistilled product was ground up and dissolved in methanol (3,000 ml) and the solution treated with activated charcoal, filtered and poured into ice/water. The product was filtered off, dried and recrystallized from toluene (3,500 ml) to give 712 g (70%) of product with mp 154-155° (literature mp 157-158°).

**Elemental Analysis**

Calculated for C12H9FO3S:  C, 57.1%; H, 3.6%; F, 7.5%; S, 12.7%.  
Found:  C, 58.7%; H 3.6%; F, 7.8%; S, 12.6%

The mass spectrum was consistent with a fluorohydroxydiphenyl sulphone.

**ir**  λ 2.92 (OH stretch); 3.27 (aromatic C-H stretch); 5.25, 5.63 (overtones characteristic of para substitution); 6.25 (aromatic C-C multiple bond stretch); 8.68 (S=O stretch in sulphofte) μ.

**nmr** (60 MHz)  
\[
\begin{align*}
&\text{F-} \begin{array}{c}
\text{SO}_2- \\
\text{H}_A & \text{H}_B & \text{H}_C & \text{H}_D
\end{array} \\
&\text{OH}
\end{align*}
\]

δ (dimethyl sulphoxide) 7.92 (q, 2H_B, J_AB 9Hz, J_FB 5 Hz), 7.74 and 6.89 (AB, 2H_C, 2H_D, J_CD 8 Hz), 7.34 (t, 2H_A, J_FA 9Hz).
Preparation of 4-chloro-4'-hydroxydiphenyl sulphone (reactions (19) and (20))

4,4'-Dichlorodiphenyl sulphone (573 g, 2.0 moles) 50% aqueous potassium hydroxide (461 g, 4.0 moles) and dimethyl sulphoxide (2,000 ml) were charged to a 5l stainless steel vessel equipped with stirrer, thermometer and nitrogen inlet and outlet. The mixture was stirred at 110° for 21 hours under nitrogen. The hydrolysate was filtered to remove potassium chloride and diluted with 5 litres of ice/water. The mixture was extracted with ether to remove a small amount of white precipitate (unreacted 4,4'-dichlorodiphenyl sulphone or low polymer). The aqueous solution was acidified with concentrated hydrochloric acid (200 ml) and extracted with ether. The ether extract was washed twice with water and then dried over anhydrous sodium sulphate. Evaporation of the ether yielded the crude 4-chloro-4'-hydroxydiphenyl sulphone (454 g).

The crude 4-chloro-4'-hydroxydiphenyl was distilled under vacuum using a nitrogen bleed (bp 220-230°/0.09 - 0.12 mm). The product was melted and poured into water in a laboratory blender, filtered off and washed with water. The yield after drying was 400 g (mp 148-150°).

The dried product was recrystallized from toluene (2,000 ml) and dried at 100° in a vacuum oven to give 386 g (72%) of 4-chloro-4'-hydroxydiphenyl sulphone mp 149-150°. (literature melting point 147.5 - 149°).
Elemental Analysis Calculated for C_{12}H_{9}ClO_{5}S: C, 53.6%; H, 3.4%; S, 11.9%; Cl, 13.2%.
Found: C, 53.8%; H, 3.4%; S, 10.7%; Cl, 13.2%

5 Preparation of 4-fluorobenzene thiol (reaction (22))

Concentrated sulphuric acid (1300 ml, 2,400 g, 23.4 moles) and ice (6 Kg) were charged to a 10 litre flanged flask equipped with a very efficient stirrer, condenser and thermometer. The mixture was cooled to −5° by immersing the flask in a "Drikold"/methanol bath and molten 4-fluorobenzenesulphonyl chloride added slowly from a dropping funnel to give a fine suspension in the aqueous solution. Zinc dust (1200 g, 12.6 moles) was then added over 2 hours keeping the temperature between −5° and 0°. The mixture was then stirred overnight, heated to reflux to dissolve the unreacted zinc and then steam distilled to obtain the product. The product (4-fluorobenzene thiol) was separated, dried over anhydrous calcium chloride and filtered. The yield was 374 g (86%) of clear liquid.

6 Preparation of 4-fluoro-2'-nitrodiphenyl sulphide (reaction (23))

Sodium (142 g, 6.18 moles) was dissolved in absolute ethanol (5,000 ml) in a 10 litre flanged flask equipped with stirrer and condenser. 4-Fluorobenzene thiol (6.18 moles, 791 g) was added followed by ortho-chloronitrobenzene (6.18 moles, 973 g). The solution was stirred overnight at 75-80°, then cooled and poured into ice/water. The product was filtered off and washed with water and 1 litre of methanol, then dried at 70° in a vacuum oven. The yield was 1467 g (97%) and mp 112-113.5° (literature mp 111-112°).
Elemental Analysis  Calculated for C₁₂H₈FNO₂S:  C, 57.7%;  H, 3.2%;
S, 12.9%;  N, 5.6%;  F, 7.6%.
Found:  C, 58.3%;  H, 3.2%;  S, 12.8%;  N, 5.3%;  F, 7.5%;

IR  3.28 (aromatic C-H stretch), 6.28, 6.39, 6.68, 6.72 (aromatic
C-C multiple band stretch), 7.51 (aromatic C-NO₂ stretch).

nmr  (60 MHz)  F'  S  H  H_D  H_C
H_A  H_B  NO₂  H_F

δ  (dimethyl sulfoxide)  8.15  (dd  H_F,  J_EF  8 Hz, J_DF  2 Hz), 7.60 (t,
H_D, J_DE  9 Hz, J_CD  9 Hz), 7.50 (t, 2H_A, J_AB  9 Hz, J_FA  9 Hz) 7.42 (q,
2H_B, J_AB  9 Hz, J_FB  6 Hz) 7.31 (t, H_E), 6.80 (dd, H_C, H_CD  9 Hz, J_CE  2 Hz) ppm

Preparation of 4-fluoro-2'-nitrodiphenyl sulphone (reaction (24))

The oxidation of sulphide to sulphone was carried out using hydrogen
peroxide and sodium tungstate catalyst.

4-Fluoro-2'-nitrodiphenyl sulphide (1513 g, 6.08 moles) was dissolved
in glacial acetic acid (6,000 ml) at 70° in a 10 litre flanged flask
equipped with stirrer, thermometer and condenser. Sodium tungstate
(6.0g) was added followed by hydrogen peroxide. The hydrogen peroxide
(1516 ml, 1700 g of 30%, 15 moles) was added at such a rate as to bring
the mixture to reflux. When the hydrogen peroxide had been added the
mixture was stirred overnight while cooling and then poured onto 5
litres of ice/water. The product was filtered off, washed with water
until acid free and then with a little methanol, and then dried at 70°
in a vacuum oven. The yield was 1609 g (94%) and mp 141-142°.
**Elemental Analysis**  Calculated for C_{12}H_{8}FNO_{4}S:  C, 51.2%; H, 2.8%;
S, 11.4%;  F, 6.8%;  N, 5.0%;

Found:  C, 50.9%; H, 2.8%;  S, 10.8%;  F, 6.0%;  N, 4.8%;

IR  $\lambda$ 3.27 (aromatic C-H stretch), 6.28 (aromatic C-C multiple bond stretch),
6.48 (aromatic C-NO$_2$ stretch), 6.70, 6.95 (aromatic C-C multiple bond
stretch), 7.58 (aromatic C NO$_2$ stretch), 8.63 (S=O stretch in sulphone)

**nmr** (220 MHz)

5 (CDCl$_3$) 8.25 (t, H$_F$), 7.95 (q, H$_B$, $J_{AB}$ 9Hz, $J_{FB}$ 5 Hz) 7.71 (multiplet
H$_C$, H$_D$, H$_E$), 7.18 (t, H$_A$, $J_{FA}$ 9Hz) ppm.

**Preparation of 4-fluoro-2'-aminodiphenyl sulphone (reaction (25))**

4-Fluoro-2' nitrodiphenyl sulphone (400 g, 1.42 moles) was dissolved
in ethanol (5,500 ml) at 70° in a 10 litre flanged flask equipped with
stirrer, thermometer and condenser. A solution of stannous chloride
dihydrate (5.68 moles, 1280 g) in ethanol (1500 ml) was added in portions
to the solution. Concentrated hydrochloric acid (1890 ml, 22.72 moles)
was added in portions at the same time. The addition of stannous chloride
and hydrochloric acid was carried out over about 1 hour, during which
time the heat of reaction maintained the solution at reflux. When
addition was complete the solution was refluxed for a further 2 hours
and then cooled overnight. The solution was poured onto ice and the
white product filtered off, then washed with water and dried at 70°
in a vacuum oven. The yield of 4-fluoro-2'-aminodiphenyl sulphone was
346 g (97%), mp 122°-123°.
Elemental Analysis  Calculated for $C_{12}H_{10}FNO_S$:  C, 57.4%;  H, 4.0%;  N, 5.6%;  F, 7.6%;  S, 12.8%.

Found:  C, 57.3% H, 3.9% N, 5.5%;  F, 7.2% S, 12.0%.

ir  $\tilde{\nu}$ 2.84, 2.91 (N-H stretch amine), 3.30 (aromatic C-H stretch), 6.12
6.25, 6.35, 6.72 (aromatic C C multiple bond stretch), 8.80 (S=O stretch
in sulphone). $\mu$.

nmr (100 MHz)

Preparation of 4-fluoro-2'-hydroxydiphenyl sulphone

4-Fluoro-2'-aminodiphenyl sulphone (450 g, 1.79 moles) was dissolved
in acetic acid (2,500 ml) in a 5 litre beaker equipped with mechanical
stirrer. Concentrated sulphuric acid (270 ml) in water (800 ml) was
added. The solution was cooled to 4° and sodium nitrite (30 g, 1.85
moles) in water (200 ml) was added slowly, keeping the temperature at
0-5°. A clear red solution of the diazonium salt was obtained. The
cold diazonium salt solution was run slowly into a refluxing mixture
of concentrated sulphuric acid (2,000 ml) and distilled water (4,000
ml). The solution was cooled overnight and then poured onto ice. The
orange coloured product was filtered off, washed with water in a
laboratory blender and dried overnight at 70° in a vacuum oven. The
yield of crude product was 429 g (95%) mp 109-112°.

The crude product was distilled under nitrogen from a 500 ml 3 necked flask using an 8" Vigreaux column (bp 155°/0.8 mm). The yield of distilled product was 394 g (92% of crude yield).

The redistilled 4-fluoro 2'-hydroxydiphenyl sulphone was sublimed at approximately 0.1 mm /100° (water vapour in jacket of sublimator) in 100 g batches. The yield from the sublimation (which took 24 hours) was 95%.

The resublimed product was recrystallised as follows. The 4-fluoro 2'-hydroxydiphenyl sulphone (100g) was dissolved in boiling benzene (150 ml) Petroleum ether (400 ml of 60-80) at 70° was added to the benzene solution. The solution was stirred until homogenous and then allowed to cool. The white crystalline product was filtered off and dried at 70° in a vacuum oven. The yield was 95% on recrystallisation, mp 113-114°. (Overall yield is approximately 79%).

**Elemental Analysis** Calculated for C_{12}H_{9}FO_{3}S: C, 57.1%; H, 3.6%; S, 12.7%; F, 7.5%.

Found: C, 57.4%; H, 3.9%; S, 13.0%; F, 7.8%.

**ir** λ3.0 (O-H stretch, phenol), 3.22 (aromatic C-H stretch), 5-6 (overtones characteristic of ortho substitution), 6.70 (aromatic C=C multiple bond stretch), 8.65 (S=O stretch sulphone) μ.
nmr (100 MHz)

\[
\begin{align*}
\text{F'} & \quad \text{SO}_2 \\
\text{H}_A & \quad \text{H}_B & \quad \text{H}_C & \quad \text{H}_D & \quad \text{H}_E & \quad \text{H}_F
\end{align*}
\]

5 (CDCl\(_3\)) 9.12 (s, H\(_G\)), 7.94 (q, 2H\(_B\), \(J_{AB} \) 9 Hz, \(J_{BF} \) 5 Hz), 7.67 (dd, H\(_D\), \(J_{CD} \) 8.5 Hz, \(J_{CE} \) 1.5 Hz), 7.41 (t, H\(_B\), \(J_{DE} \) 8 Hz, \(J_{EF} \) 8 Hz), 7.10 (t, 2H\(_A\), \(J_{AF} \) 8.5 Hz), 6.95 (d, H\(_F\)), 6.90 (td, \(J_{DF} \) 1.5 Hz).

**Preparation of 2,4,4'-trifluorodiphenyl sulphone (reaction 28)**

4 Fluorobenzenesulphonyl chloride (38.9 g, 0.2 mole) was dissolved in meta-difluorobenzene (23 g, 0.2 mole) in a 250 ml 3 neck flask equipped with stirrer, thermometer and nitrogen inlet and outlet. The solution was heated to 70-80° and aluminium chloride (40 g, 0.3 mole) gradually added. The reaction was carried out for 6 hours when it was 93% complete (according to titration of evolved hydrogen chloride). The mixture was then poured onto ice and the crude product filtered off. The yield of crude product was 39 g (72%). The crude solid was dissolved in hot ethanol (250 ml) and the solution was treated with activated charcoal, filtered, concentrated to 120 ml and allowed to crystallize. The white crystals were dried and recrystallized from ethanol (80 ml). The yield was 21 g, mp 122-123.5°.

**Elemental Analysis** Calculated for C\(_{12}\)H\(_7\)F\(_3\)O\(_S\): C, 52.9%; H, 2.6%; S, 11.8%; F, 20.9%.

Found: C, 53.7%; H, 2.9%; S, 12.3%; F, 19.8%.
ir λ 3.20 (aromatic C-H stretch), 5.20, 5.60 (overtones characteristic of para substitution), 6.24, 6.70, 6.80, 7.00 (aromatic C-C multiple bond stretch), 8.65 (S=O stretch, sulphone), μ.

nmr (220 MHz)

\[
\begin{array}{c}
\text{H}_A \quad \text{H}_B \quad \text{H}_C \quad \text{H}_D \\
\text{F}_1 \quad \text{SO}_2 \quad \text{F}_2 \\
\text{H}_E
\end{array}
\]

5 (CDCl₃) 8.12 (sextet, H₉, J_CD 9 Hz, J_CF₂ 9 Hz, J_CF₃ 6 Hz) 8.00 (qd, H_B, J_AB 9 Hz, J_BF₁ 5 Hz, J_BB 1 Hz), 7.19 (t, H_A, J_AF₁ 9 Hz), 6.88 (t, H_E, J_EF₂ 9 Hz, J_EF₃ 9 Hz) ppm.

11 Preparation of 4 fluoro-4' methoxydiphenyl sulphone (reaction (29))

The potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone (100g) was dissolved in dimethyl sulphoxide (500 ml) and methyl chloride was passed through the stirred solution at 100°C for 3 hours. The solution was then cooled and poured onto ice. The product was filtered off, washed well with water and dried at 50°C in a vacuum oven. The crude yield was 87g. This product was recrystallized from methanol (300 ml) to give 79 g (86%) of product, mp 107-108.5°C (literature 80 mp 100-102°C).

ir λ 3.20 (aromatic C-H stretch), 3.48 (aliphatic C-H stretch, alkane), 5.20, 5.60 (overtones characteristic of para substitution), 6.25, 6.68. 6.89 (aromatic C-C multiple bond stretch), 7.11 (C-O stretch, ether), 8.65 (S=O stretch, sulphone), μ.
12 Preparation of 4-hydroxy-4'-methoxydiphenyl sulphone (reactions 30 and 31)

4-Fluoro-4'-methoxydiphenyl sulphone (92 g, 0.346 mole), dimethyl sulfoxide (250 ml) and 50% aqueous potassium hydroxide (81.6 g, 0.69 mole) were stirred together at 100° under nitrogen in a stainless steel vessel for 24 hours. The hydrolysate was poured onto ice and the aqueous mixture extracted with ether to remove unreacted starting material. The aqueous solution was acidified with concentrated hydrochloric acid and the product extracted with ether. This ether solution was washed twice with water and dried over anhydrous sodium sulphate. The ether was removed by distillation to yield an oily product which slowly crystallized (yield, 85 g).

The crude product together with 18 g from another hydrolysis was distilled under nitrogen (bp 255°/0.7 mm) to yield 85 g of glassy solid. The distilled product was dissolved in boiling benzene (1500 ml). The solution was filtered and then allowed to crystallize. The crystalline product was dried carefully in a drying pistol under high vacuum, the temperature being gradually increased (over 24 hours) from room temperature to 70°. The yield was 77 g, mp 127-128° (literature mp 126-127°).
Elemental Analysis

Calculated for C\textsubscript{13}H\textsubscript{13}O\textsubscript{3}S: C, 59.1%; H, 4.6%; S, 12.1%

Found: C, 61.5%; H, 4.7%; S, 11.6%.

\text{I}r\ \lambda\ 2.98 (O-H stretch), 3.20 (aromatic C-H stretch), 3.48 (aliphatic C-H stretch) 5.20, 5.50 (overtones characteristic of \textit{para} substitution), 6.25, 6.65, 6.90 (aromatic C-C multiple bond stretch), 8.10 (C-O stretch, ether), 8.72 (S=O stretch sulphone), \nu.

\text{nmr (60 MHz)}

\begin{align*}
\text{H} & \quad \text{H} \\
\text{H-C} & \quad \text{SO}_2 \\
\text{H} & \quad \text{OH} \\
\text{H}_E & \quad 
\end{align*}

5 (dimethyl sulphoxide) 7.75 and 7.03 (ABq, 2H\textsubscript{B}, 2H\textsubscript{A}, J\textsubscript{AB} 9 Hz) 7.66
and 6.86 (ABq, 2H\textsubscript{C}, 2H\textsubscript{D}, J\textsubscript{CD} 9Hz), 3.75 (s, 3H\textsubscript{E}) ppm

13 \textbf{Preparation of di(1 naphthyl) carbonate (reaction 32)}

Diphenyl carbonate (321.3 g, 1.5 moles) and 1-naphthol (432.5 g, 3 moles) were charged to a 1 litre 3 neck flask. The flask was equipped with a vigreux column leading to a condenser and distillation take off. The contents of the flask were heated to 80°, a trace of sodium hydride was added and the apparatus evacuated by means of an oil pump to 50 mm pressure. The flask temperature was increased to 140° when phenol began to distil off. The phenol was distilled off over 2 hours, the temperature being increased gradually over this time to 185° and the pressure reduced to 9 mm. The yield of phenol was 283.5 g (98%).

The di(1 naphthyl) carbonate product was poured out and allowed to cool.
The yield was 459.7 g (97.5%) mp 112-123°C. The crude product was recrystallized twice from isopropanol (3.5 litres) using activated charcoal to decolorize the first solution. The yield of white product was 336 g (71%) mp 128.5-129.5°C (literature mp 130°).

14 Preparation of bis 4,4'- (4-fluorobenzene sulphonyl)di(1-naphthyl) carbonate (reaction (33))

Di(1-naphthyl) carbonate (0.5 mole, 157g) 4-fluorobenzene sulphonyl chloride (1.0 mole, 194.6g) and nitrobenzene (140 ml) were charged to a 1 litre 3 necked flask equipped with stirrer, thermometer, nitrogen inlet and outlet. The nitrogen outlet was led into a beaker of water containing indicator so that hydrogen chloride evolved during the reaction could be estimated by titration with 4N-potassium hydroxide solution. Ferric chloride (2g) was added to the reaction mixture and the temperature increased to 115°C. Reaction was continued at this temperature for 2.5 hours when 90% of the theoretical hydrogen chloride had been evolved. The reaction mixture was cooled, washed twice with methanol in a laboratory blender to obtain a solid product. This product was boiled with dilute hydrochloric acid to remove iron and dried. The yield of crude product was 220g (70%). The crude product was recrystallized from toluene (4,000 ml) to give 76 g (24%) of white crystals mp 233-236°C.

15 Preparation of 1-hydroxy 4-(4-fluorobenzene sulphonyl)naphthalene (reaction (34) and (35))

Bis 4,4'- (4-fluorobenzene sulphonyl)di(1 naphthyl) carbonate (76 g, 0.12 mole) was slurried in methanol (1500 ml). Potassium hydroxide solution (120 ml, 0.48 mole) was added at room temperature and the solution stirred for 10 minutes. The resulting pale yellow solution
was filtered and diluted with ice/water. This solution was acidified to pH 1 with hydrochloric acid to yield a white solid which was filtered off and dried (71 g yield). The product was sublimed at 0.001 mm using bromobenzene (bp 155°) in the vapour jacket of the sublimator. The yield of sublimed product was 60 g (83%) mp 148-151°. The product was recrystallized from methanol to give a product with mp 152.5-154°.

Elemental Analysis Calculated for C₁₆H₁₁FO₃S: C, 63.6%; H, 3.7%; F, 6.3%; S, 10.6%

Found: C, 63.3%; H, 3.3%; F, 5.8%; S, 10.2%.

The mass spectrum was consistent with a fluorophenyl-hydroxynaphthyl sulphone and no impurities were detected.

**ir** 3.298 (OH stretch), 3.22 (aromatic C-H stretch), 6.28, 6.23, 6.58, 6.69, 6.83, (aromatic C-C multiple bond stretch), 8.70 (S=O stretch, sulphone). μ,

**nmr** (220 MHz)

δ (CDCl₃) 8.59 (dd, H₅, JGH 8.5 Hz, JFH 1.5 Hz) 8.41 (d, H₆, JCH 8.5 Hz), 8.31 (dd, H₆, JEF 8 Hz, JEG 1.5 Hz), 7.95 (q, 2H₅, JAB 9 Hz, JF'B 5 Hz), 7.58 (td, H₃ and H₂, JGF 9 Hz) 7.08 (t, 2H₄, JF'A 9 Hz) 6.88 (d, H₁) ppm.
Preparation of 4-fluoro-4'-phenoxydiphenyl sulphone (reaction (36))

Phenol (1 mole, 94.1 g), 50% potassium hydroxide solution (1 mole) benzene (150 ml) and dimethyl sulphoxide (800 ml) were charged to a 2 litre 3 neck flask. The potassium hydroxide was washed in with 50 ml of water. The flask was equipped with stirrer and apparatus for azeotroping off water. The contents were maintained under a slow stream of nitrogen and the flask heated by means of an oil bath. The water was azeotroped out with the benzene, the oil bath temperature being 110°-130°. When all the water had been removed (14 hours) the oil bath was cooled to 60° and 4,4'-difluorodiphenyl sulphone (254.2g, 1 mole) was washed into the flask with dimethyl sulphoxide (100 ml). Reaction between the potassium phenate and the 4,4'-difluorodiphenyl sulphone was carried out at 60° for 24 hours at which time the reaction was shown to be almost complete by titrating a sample with 0.1N-sulphuric acid.

The reaction solution was filtered and poured onto ice/water. The product was extracted with ether. The ether solution was washed with water, dried and the ether was removed by distillation to yield a yellow oil which crystallized on standing. This product was recrystallized from a mixture of ethanol (1300 ml) and water (500 ml). The product was dried at 60-70° in a vacuum oven. The product was distilled under nitrogen at 0.5 mm pressure to yield 3 fractions. The first fraction (27 g) had bp 141-153°/0.5mm. A sample was recrystallised from ethanol when it had mp 92.5-98° and an nmr spectrum consistent with 4,4'-difluorodiphenyl sulphone.
The second fraction (132 g) had bp 215º/0.5 mm and was recrystallized from ethanol (300 ml) to give 4-fluoro 4'-phenoxydiphenyl sulphone (128 g, 39%) mp 112-113º.

The third fraction was left as a residue in the distillation flask and is probably 4,4'-diphenoxydiphenyl sulphone which has a known bp of 250º/0.07 mm.

The structure of the 4-fluoro-4'-phenoxydiphenyl sulphone was confirmed as shown.

**Elemental Analysis**

Calculated for C_{18}H_{13}FO_{2}S: C, 65.8%; H, 4.0%; S, 9.8%; F, 5.8%.

Found: C, 67.2%; H, 4.0%; S, 9.7%; F, 4.8%.

**IR**

5.20, 5.60 (overtones characteristic of _para_ substitution), 6.27, 6.70 (aromatic C-C multiple bond stretch), 8.10 (C-O stretch, ether), 8.65 (S=O stretch sulphone) μ.

**NMR** (100 MHz)

δ (CDCl₃) 7.93 (q, 2Hₕ, J_{AB} 9 Hz, J_{FB} 5 Hz) 7.82 (d, 2Hₗ, J_{CD} 9 Hz), 7.29 (t, 2Hₕ, J_{EF} 8 Hz, J_{FG} 8 Hz), 7.17 (d, Hₗ), 7.01 (t, 2Hₜ, J_{AB} 9 Hz, J_{FB} 9 Hz), 7.00 (d, 2Hₗ), 6.99 (d, 2Hₜ) ppm.
Preparation of 4-(4-fluorobenzenesulphonyl)4''-(4 hydroxybenzene sulphonyl) diphenyl ether (reactions 37, 38 and 39)

4-Fluoro-4''-phenoxydiphenyl sulphone (164.2 g, 0.5 mole), diphenyl carbonate 4,4''-disulphonyl chloride (102.7 g, 0.25 mole) and nitrobenzene (250 ml) were charged to a 1 litre 3 neck flask. The flask was equipped with stirrer, condenser and nitrogen inlet and outlet. The nitrogen outlet was led into a beaker of water so that the evolved hydrogen chloride could be titrated with 4N-potassium hydroxide using screened methyl orange indicator.

Ferric chloride (1 g) was added and the temperature of the reaction mixture raised to 100°. Hydrogen chloride evolution began after 50 minutes. The reaction was carried out at 100-114° for 23 hours when it was 82% complete as measured by hydrogen chloride evolution. The reaction mixture was then cooled and stirred with methanol in a laboratory blender until a solid product was obtained.

The product was slurried in methanol (2000 ml) at room temperature and 50% potassium hydroxide (1.0 mole) added. The resulting solution was filtered, ice was added and the solution acidified to pH1 with concentrated hydrochloric acid. The product was filtered off and dissolved in boiling acetic acid (2000 ml). The solution (A) was treated with activated charcoal twice and then allowed to crystallize to give 88 g of product. The main part of this (70 g) was dissolved in ethanol, treated with charcoal and the solution poured onto ice and filtered to give 62 g of product. This was recrystallized again from acetic acid to give 50 g pale yellow crystals mp 225-228.5 after careful drying.
The original acetic acid solution (A) was precipitated onto ice. The product was dissolved in ethanol and treated with activated charcoal, then poured onto ice and filtered. This product was recrystallized twice from acetic acid to give 31 g of product mp 224.5-228°. The total yield of purified product was 81 g (33%).

**Elemental Analysis**

Calculated for C_{24}H_{17}F_6O_{14}S_2: C, 59.5%; H, 3.5%; S, 13.2%; F, 3.9%;

Found: C, 58.6%; H, 3.5%; S, 12.4%; F, 3.8%.

**ir** λ 2.92 (O-H stretch) 6.30, 6.70, 6.92, (aromatic C=C multiple bond stretch) 8.06 (O-O stretch, ether), 8.65 (S=O stretch, sulphone).

**nmr** (60 MHz)

\[
\begin{array}{cc}
\text{F'}- & \text{SO}_2- \\
\text{H}_A & \text{H}_B \\
\text{H}_C & \text{H}_D \\
\text{H}_E & \text{H}_F \\
\text{H}_G & \text{H}_H \\
\end{array}
\]

δ (dimethyl sulfoxide) 7.99 (q, 2H_B, J_{AB} 8 Hz, J_{F'B} 5 Hz), 7.95 and 7.18 (ABq, 2H_C, 2H_D, J_{CD} 8.5 Hz), 7.91 and 7.18 (ABq, 2H_F, 2H_E, J_{EF} 8.5 Hz), 7.77 and 6.93 (ABq, 2H_G, 2H_H, J_{GH} 9 Hz), 7.34 (t, 2H_A, J_{F'A} 8 Hz) ppm.
Preparation of 4-fluorodiphenyl sulphone (reaction (40))

Benzene (1.5 mole, 133.5 ml) and 4-fluorobenzene sulphonyl chloride (1.5 mole, 294 g) were heated to 46° in a 700 ml flanged flask equipped with stirrer and condenser. Anhydrous aluminium chloride (1.65 mole 219 g) was added to the reaction mixture over 2 hours, maintaining the temperature at approximately 50°. The mixture was then heated for 2.5 hours at 80° and then poured out onto ice. The product was filtered, stirred with water in a laboratory blender and dried. This product was dissolved in hot ethanol, treated with activated charcoal and then filtered hot using "Celite" filter aid. The solution was allowed to crystallize, yielding the 4-fluorodiphenyl sulphone (286 g, 83%), mp 112-113° (literature 85 mp 113°).

Elemental Analysis Calculated for C_{12}H_{9}F_{2}S: C, 60.9%; H, 3.8%; S, 13.6%; F, 8.0%.

Found: C, 59.9%; H, 3.8%; S, 13.3%; F, 6.3%.

IR \( \nu \) 3.22 (aromatic C-H stretch), 6.25, 6.65 6.88 (aromatic C-C multiple bond stretch), 8.60 (S=O stretch in sulphone). m

NMR (100 MHz)

\[
\begin{array}{c}
\text{F} \\
\text{H}_A \\
\text{H}_B \\
\text{H}_C \\
\text{H}_D \\
\text{SO}_2 \\
\text{H}_E
\end{array}
\]

5 (CDCl₃) 8.00 (6 peaks, 2Hₐ, 2 Hₜ), 7.48 (4 peaks, 2Hₖ, Hₜ), 7.14 (t, 2Hₐ, Jₐₕ 9 Hz, Jₕₐ 9 Hz) ppm.
Preparation of 4-phenoxydiphenylsulphone (reaction (41))

Potassium phenate (1 mole, 132.3 g), 4-fluorodiphenyl sulphone (1 mole, 236 g) and dimethyl sulfoxide (1 litre) were stirred under nitrogen in a glass flask in an oil bath at 100° for 6 hours. At this stage a sample of the solution after filtration to remove potassium fluoride had pH 6.8, which indicated that the reaction was complete. The solution was cooled, filtered to remove potassium fluoride and precipitated onto ice. The product obtained crystallized on standing. The solid was filtered off, stirred with water in a laboratory blender, filtered and dried.

The crude product was dissolved in boiling ethanol, treated with activated charcoal and filtered using "Celite" filter aid. The solution was allowed to crystallize, yielding 4 phenoxydiphenyl sulphone (265 g, 85%) mp 86.5-88° (literature mp 86-87°).

Elemental Analysis Calculated for C_{18}H_{14}O_{3}S: C, 69.7%; H, 4.6%; S, 10.3%. Found: C, 70.1%; H, 4.7%; S, 10.0%.

\[ \text{ir } \nu 6.28, 6.70 \text{ (aromatic C-C multiple bond stretch), 8.01 (C-O stretch ether), 8.65 (S=O stretch, sulphone)} ]

\[ \text{nmr (220 MHz)} \]

\[ \delta (\text{CDCl}_3) \] 7.85 (dd, H$_C$, $J_{BC}$ 8 Hz, $J_{AC}$ 2 Hz), 7.80 (d, H$_D$, $J_{DE}$ 9 Hz), 7.44 (t, H$_A$, H$_B$), 7.31 (t, H$_G$, $J_{FG}$ 8 Hz $J_{GH}$ 8 Hz), 7.18 (d, H$_H$, $J_{GH}$ 8 Hz), 6.99 (dd, 2 H$_F$, $J_{FG}$ 8 Hz $J_{FH}$ 1.5 Hz) 6.93 (d, 2H$_E$). ppm
Preparation of 4-(benzenesulphonyl),4'-(4-hydroxybenzenesulphonyl)diphenyl ether (reactions (42), (43), and (44))

4-Phenoxydiphenyl sulphone (0.3 mole, 93.1 g), diphenyl carbonate 4,4'-disulphonyl chloride (0.15 mole, 61.6 g) and nitrobenzene (130 ml) were charged to a 500 ml 3 necked flask equipped with stirrer, thermometer, nitrogen inlet and outlet. The nitrogen outlet was led into water so that the acid gases evolved could be titrated with 2 N potassium hydroxide. The reaction mixture was heated to 70°, ferric chloride (1 g) was added, and the temperature raised to 110°. Hydrogen chloride evolution began after approximately 40 minutes. The reaction was continued at this temperature for 24 hours, when it was 91% complete as measured by hydrogen chloride evolution. The reaction mixture was then cooled and poured into methanol. After stirring twice with methanol in a laboratory blender a solid product was obtained.

The product was slurried in methanol (1500 ml), cooled to 5° and 50% potassium hydroxide (71 g, 0.60 mole) added. The solution obtained was diluted to 2 litres with water and filtered. This solution was poured onto ice and acidified with concentrated hydrochloric acid. The product was filtered off, dried at 75° in a vacuum oven (yield 123 g), and recrystallized from a triple mixture. The solid was dissolved in hot isopropanol (190 ml), the solution treated with activated charcoal and filtered using "Celite" filter aid. Benzene (1500 ml) and petroleum spirit (bp 60-80°) (900 ml) were added slowly, keeping the solution hot. The resulting hazy solution was treated with charcoal and filtered. The clear yellow solution was allowed to cool yielding an amorphous looking solid, 61 g mp 158-164°. The product was recrystallized again from isopropanol (94 ml) benzene (740 ml) and petroleum spirit (bp 60-80°), (30°C). The yield of product was 56.5 g, mp 165-167°.
Elemental Analysis  Calculated for C$_{24}$H$_{18}$O$_2$S$_2$:  C, 61.8%; H, 3.9%;  
S, 13.8%.

Found: C, 62.0%, H, 3.8%; S, 13.9%.

ir  λ 2.91 (O-H stretch), 6.29 , 6.70, 6.90 (aromatic C-C multiple 
    bond stretch), 7.95 (C-O stretch, ether), 8.68 (S=O stretch sulphone).μ.

nmr (60 MHz) 

5 (dimethyl sulphoxide ) 7.94 (d, 2 H$_G$, 2H$_B$, J$_{AB}$ 8.5 Hz, J$_{GH}$ 8.5 Hz) 
7.88 (d, 2 H$_C$, 2H$_F$, J$_{CD}$ 9 Hz, J$_{EF}$, 9 Hz), 7.60 (t, 2 H$_H$, H$_{IH}$ 7.0 Hz), 
7.56 (d, H$_I$, J$_{IH}$ 8 Hz). 7.17 (d, 2 H$_E$, 2H$_D$, J$_{FE}$, 8.5 Hz, J$_{CD}$ 8.5 Hz), 
6.90 (d, H$_A$, J$_{AB}$ 8.5 Hz) ppm.

Preparation of 4-(benzenesulphonyl),4'--(4 fluoro-benzenesulphonyl)diphenyl 
ether (reactions (45), (46), and (47))

This compound was prepared by two routes.

(a) Reaction (47)

4-(4 Fluorobenzenesulphonyl)diphenyl ether-4'-sulphonyl chloride (0.225 
mole, 96 g) and benzene (200 ml, excess as solvent) were charged to 
a 500 ml 3 necked flask. The flask was equipped with stirrer, condenser 
and nitrogen inlet and outlet. Ferric chloride was added and the reaction 
was carried out at reflux (82°) for 48 hours, when >72% of the hydrogen 
chloride had been evolved (estimated by titration with 2N-potassium 
hydroxide). The reaction mixture was then boiled with dilute hydrochloric 
acid to remove iron, the excess benzene evaporating off. The product 
after filtration was dried at 70° to give 97 g of product (92%)
mp 133-143°. The product was dissolved in a mixture of boiling methanol (2,000 ml) and acetone (300 ml). The solution was evaporated to 1800 ml and allowed to crystallize to give (60 g of product mp 148-150.5°). A second crop (17 g, mp 147-150.5°) was obtained by concentrating the solution and allowing it to crystallize. Further crystallization of these samples from methanol and acetone mixture (8:1) gave 55 g of product with mp 153.6-155°.

Careful drying under very high vacuum was necessary to completely remove the methanol. If incompletely removed a lower melting product was obtained which showed a small peak at 3.3 ppm in the nmr probably due to methanol.

(b) Preparation by reaction (45)

4-Fluoro-4'-phenoxydiphenyl sulphone (0.6 mole, 197 g), benzene sulphonyl chloride (0.6 mole, 106 g) and nitrobenzene (300 ml) were charged to a 1 litre flask. Ferric chloride (1 g) was added and the temperature raised to 100°.

The hydrogen chloride evolved was led into water and titrated with 2N-potassium hydroxide. The reaction was carried out at 100-110° for 7 hours when it was 95% complete. The nitrobenzene was removed by steam distillation and the residual solution stirred with methanol in a laboratory blender to give 196 g of product. The methanol was evaporated to give a further 65 g of product. The product was recrystallized from methanol to give 238 g of product. This was dissolved in boiling methanol (4,000 ml) filtered to give 28 g of the product and then allowed to crystallize to give 171 g product. The 28 g was recrystallized from acetic acid (78 ml) and then from methanol/acetone to give 17 g mp
151.5-152.5 (sample A). The 171 g was recrystallized from methanol/acetonic, then from benzene to give 130 g and finally from methanol/acetone to give 85 g of product, mp 152-156° (sample B).

Both samples (A and B) were shown by nmr to be the required 4-(benzene-sulphonyl)4'-4-fluorobenzenesulphonyldiphenyl ether containing a little methanol impurity. Both samples were redried to remove the methanol.

**Elemental Analysis**

Calculated for C₂₄H₁₇FO₅S₂: C, 61.5%; H, 3.7%; S, 13.7%; F, 4.0%.

Found: C, 60.4%; H, 3.6%; S, 13.4%; F, 3.0%.

**IR**

3.22 (aromatic C-H stretch), 6.31 (aromatic C-C multiple bond stretch), 8.10 (C=O stretch, ether), 8.69 (S=O stretch, sulphone).

**NMR**

(220 Mhz) 6 (CDCl₃) 7.85 (4 peaks, H₂B, H₂G), 7.83 (d, 2H₆, 2H₉, JCD 9 Hz, JEF 9 Hz), 7.44 (t, 2H₈, H₇), 7.09 (t, 2H₆, JAB 9 Hz, JAF 9 Hz), 6.98 (d, 2H₉, 2H₈) ppm.

**Preparation of 2,4'-dihydroxydiphenyl sulphone (reactions (48) and (49))**

4-Fluoro-2'-hydroxydiphenyl sulphone (126 g, 0.5 mole) was stirred with 50% aqueous potassium hydroxide (177 g, 1.5 mole) in dimethyl sulphoxide (500 ml) in a stainless steel vessel for 22 hours at 120° under nitrogen. The yellow hydrolysate was poured onto ice/water to give a yellow solution. This solution was filtered and then acidified with
concentrated hydrochloric acid. The solution was extracted twice with ether. The ether extracts were washed with distilled water, then dried over anhydrous sodium sulphate. The ether solution was filtered and distilled to dryness. The product was sublimed at 0.02 mm pressure using ortho-dichlorobenzene (bp 177-181°) in the vapour jacket of the sublimator. This product was recrystallized from a mixture of 900 ml of water and 370 ml of methanol to yield white crystals 95g, mp 184-186° (literature 88,89 mp 184-185°, 186°).

**Elemental Analysis**

Calculated for C$_{12}$H$_{10}$O$_4$: C, 57.6%; H, 4.0%; S, 12.8%.

Found: C, 57.2%; H, 4.0%; S, 11.8%.

IR λ 2.95 (O-H stretch), 3.20 (aromatic C-H stretch), 6.25, 6.65 (aromatic C-C multiple bond stretch), 8.70 (aromatic S=O stretch, sulphone)$\mu$.

**NMR (60 MHz)**

δ (dimethyl sulphoxide ) 7.83 (dd H$_C$, $J_{CD}$ 7.5 Hz, $J_{CE}$ 2 Hz) 7.70 and 6.85 (ABq, 2H$_B$, 2H$_A$, $J_{AB}$ 8.5 Hz), 7.40 (td, H$_D$, $J_{DF}$ 2 Hz), 6.90 (t, H$_E$, $J_{DE}$, 7 Hz, $J_{CE}$ 1.5 Hz), 6.84 (d, H$_F$, $J_{EF}$ 7 Hz) ppm.
Purification of 4,4'-dihydroxydiphenyl

4,4'-dihydroxydiphenyl (50g) ex BDH was recrystallized from ethanol (600 ml) using activated charcoal to decolorize the hot solution. Yield 20g mp 278.5-280.5 (literature mp 274-275°).

Purification of 1,5 dihydroxynaphthalene

1,5 Dihydroxynaphthalene (100 g) ex Koch Light was dissolved in boiling ethanol (600 ml) the solution was treated with activated charcoal, filtered and allowed to crystallize giving 72 g of brown crystals. The crystals were dissolved in a hot mixture of water (200 ml) and methanol (300 ml). A little sodium sulphite and concentrated hydrochloric acid was added to the brown solution. The solution was then treated with activated charcoal and filtered to give a pale yellow solution which gave pale yellow crystals, mp 261-264° (literature mp 265°).

Purification of sulpholane

Method (a) The sulpholane (ex Koch Light) was dried over Linde type 4A molecular sieve and then distilled from sodium hydroxide pellets under reduced pressure using a nitrogen bleed. A 12" silvered column packed with Raschig rings was used. The distillation was carried out at 0.5 mm pressure with a distillation flask temperature of 110°, the vapour temperature was 88-90. After 3 distillations the product was water white and had freezing point 28.47° (literature mp 28.37°).

The sulpholane was stored at 60° between distillations. A further distillation from calcium hydride did not improve the freezing point any more (28.43°).
As well as having a good f.p. the pure sulpholane did not discolour on storing at 60° and gave no colouration on heating with potassium fluoride. Less pure sulpholane (eg after 1 distillation) became slightly brown on storage at 60° and gave a purple colouration on heating with potassium fluoride.

Method (b) The sulpholane was dried over Linde type 4A molecular sieve and then 1800 ml was stirred in a 2 litre 3 necked flask under a fast stream of nitrogen with potassium fluoride (10g) and poly(diphenylene ether sulphone) (20g) in an oil bath at 210° for 18 hours. The polymer and potassium fluoride probably act as base and render some impurities involatile. Other impurities are blown off at this stage. The sulpholane was then cooled to 70° and poured into the distillation flask. The sulpholane was then distilled under vacuum using a nitrogen bleed and 12" column packed with Raschig rings. Typical temperatures and pressure were: distillation 108°, stillhead 81°, pressure 0.4mm. A forerun of 100ml was taken followed by the main fraction of 1200 ml. The distilled sulpholane was kept in the stoppered receiver (2 litre 3 necked flask) at 60° in a hot cabinet until required. The sulpholane obtained by this technique which required only 1 distillation had freezing points in the range 28.61 to 28.78° for several batches and is of similar purity to that obtained by method (a) which required 3 distillations.

Purification of dimethyl sulphone

Dimethyl sulphone (ex Crown Zellerbach) was distilled through a Vigreux column. A forerun of about 10% was taken, followed by the main fraction of 340g bp 162-172°/70 80mm.
Purification of dimethyl sulphoxide

Dimethyl sulphoxide (151) was charged to a 20l flask with sodium chloride (100g) and some calcium hydride. The sodium chloride stabilizes the dimethyl sulphoxide during distillation. The dimethyl sulphoxide was distilled under reduced pressure using a nitrogen bleed and a column packed with glass helices. A forerun was taken followed by the main fraction, bp 77°/15 mm pressure. The main fraction was stored over 4A molecular sieve to remove water present.

Purification of fluorobenzene

Fluorobenzene (ex Koch Light) 2.5 Kg, was distilled at atmospheric pressure using an 18" column packed with glass helices. A forerun of 200 ml was taken followed by the main fraction which had bp 85.0°. The redistilled fluorobenzene had <0.01% ww chlorobenzene by glc and no other volatile impurities could be detected. The original sample (ex Koch Light) had 0.3 % ww chlorobenzene and 0.3% ww of a second high boiling impurity.

Preparation of potassium salts of the phenols

The dry potassium salts were prepared as described below for the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone.

An approximately 4N solution of potassium hydroxide was prepared by diluting a standard volumetric solution concentrate ("Convol" ex Hopkin and Williams) to 250 ml with redistilled methanol. The resulting aqueous methanolic potassium hydroxide was standardised against 8.000g of 4 fluoro-4'-hydroxydiphenyl sulphone. The titration was carried out potentiometrically using a glass electrode and a sodium sulphate or calomel reference electrode with an EIL model 23A pH meter. Small equal
volume increments (0.2 ml) of potassium hydroxide were added near the end point. The end point was calculated using the method described by J J Lingane.93

An example of a titration and calculation is shown below.

<table>
<thead>
<tr>
<th>ml of KOH (V)</th>
<th>mv (E)</th>
<th>ΔE/ΔV (mv/0.2 ml)</th>
<th>Δ²E/ΔV²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>190</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>447</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>482</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>508</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>528</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>547</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>567</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>590</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.2</td>
<td>598</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>7.4</td>
<td>608</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>7.6</td>
<td>620</td>
<td>12</td>
<td>+9</td>
</tr>
<tr>
<td>7.8</td>
<td>641</td>
<td>21</td>
<td>+28</td>
</tr>
<tr>
<td>8.0</td>
<td>690</td>
<td>49</td>
<td>-16</td>
</tr>
<tr>
<td>8.2</td>
<td>723</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>8.4</td>
<td>739</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>8.6</td>
<td>748</td>
<td>9</td>
<td></td>
</tr>
</tbody>
</table>

The end point (for 8.000 g of 4-fluoro-4'-hydroxydiphenyl sulphone) is

\[ 7.8 + \left(0.2 \times \frac{28}{28 + 16}\right) = 7.93 \text{ ml} \]
From the standardisation the amount of potassium hydroxide solution to use for the salt preparation was calculated (a 0.25% deficiency of potassium hydroxide was used).

The 4-fluoro-4'-hydroxydiphenyl sulphone (40.00 g) was dissolved in methanol (300 ml) in a 1 litre rotary evaporator flask. Potassium hydroxide solution (39.55 ml) was added from a burette. The resulting solution was evaporated to dryness on a rotary evaporator on water pump vacuum. The flask was heated by a water bath, the temperature being gradually increased to 100°. The salt was left in the evaporator for approximately 2 hours. The salt was then removed, ground up and placed in a bottle wrapped with aluminium foil. The mouth of the bottle was covered with a perforated piece of aluminium foil and the salt dried overnight in an electrically heated drying pistol to remove the last traces of water. The pistol was evacuated by means of an oil or mercury diffusion pump system. The system had a trap, cooled by a mixture of methanol and solid carbon dioxide ("Drikold"), between the pistol and the pumping system. The pressure in the system between the pistol and the trap was measured by a Pirani gauge. When the salt was dry the pressure fell to <0.001 mm. The dry salt was stored in the tightly capped foil wrapped bottle in a vacuum dessicator over phosphorous pentoxide.
Polymerisation Experiments

The technique used in the polymerisation experiments is described in Part 3.

An example of a titration and calculation for a sample from the reaction of the potassium salt of 4-fluoro-4'-hydroxydiphenyl sulphone is shown below.

Time = 92 minutes. Sample weight (after filtration) = 11.395 g

Sample diluted with 100 ml methanol and titrated with 0.1N sulphuric acid.

<table>
<thead>
<tr>
<th>ml 0.1N H₂SO₄</th>
<th>mv E</th>
<th>Δ E/Δ V</th>
<th>Δ²E/ΔV²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>602</td>
<td>13</td>
<td>+8</td>
</tr>
<tr>
<td>10</td>
<td>469</td>
<td>21</td>
<td>+8</td>
</tr>
<tr>
<td>11</td>
<td>455</td>
<td>29</td>
<td>-10</td>
</tr>
<tr>
<td>12</td>
<td>440</td>
<td>19</td>
<td>-7</td>
</tr>
<tr>
<td>13</td>
<td>420</td>
<td>12</td>
<td>-10</td>
</tr>
<tr>
<td>14.0</td>
<td>391</td>
<td>13</td>
<td>+8</td>
</tr>
<tr>
<td>14.2</td>
<td>385</td>
<td>21</td>
<td>+8</td>
</tr>
<tr>
<td>14.4</td>
<td>372</td>
<td>29</td>
<td>-10</td>
</tr>
<tr>
<td>14.6</td>
<td>359</td>
<td>19</td>
<td>-7</td>
</tr>
<tr>
<td>14.8</td>
<td>338</td>
<td>12</td>
<td>-10</td>
</tr>
<tr>
<td>15.0</td>
<td>309</td>
<td>12</td>
<td>-7</td>
</tr>
<tr>
<td>15.2</td>
<td>290</td>
<td>12</td>
<td>-7</td>
</tr>
<tr>
<td>15.4</td>
<td>278</td>
<td>12</td>
<td>-7</td>
</tr>
<tr>
<td>15.6</td>
<td>265</td>
<td>12</td>
<td>-7</td>
</tr>
<tr>
<td>15.8</td>
<td>258</td>
<td>12</td>
<td>-7</td>
</tr>
</tbody>
</table>
End point = 14.8 + (0.2 x \( \frac{8}{8 + 20} \)) = 14.89 ml of 0.1N \( \text{H}_2\text{SO}_4 \)

Titre for a 10.000 g sample (\( T_t \)) = 13.11 ml of 0.1N \( \text{H}_2\text{SO}_4 \)

Concentration of phenoxide ends is :

\[
\frac{T_t \times D}{100} = \frac{13.11 \times 1.153}{100} = 0.1512 \text{ moles litre}^{-1}
\]

\[
\frac{1}{a - x} = \frac{1}{0.1512} = 6.614 \text{ litre mole}^{-1}
\]

\( D \) is the density of the solution.

The results for the polymerisation experiments are given below. The amount of salt weighed out is given, the quantity in the solution was slightly less due to losses during addition and is given by the titration.
Polymerisation of F-[\(\text{SO}_2\)]-[\(\text{OK}\) (0.05 mole) at 158° in sulphonate (277.4g)

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample weight, g</th>
<th>Titre (ml 0.1N H(_2)SO(_4))</th>
<th>Titre for 10.000g</th>
<th>% reaction</th>
<th>Conc(^n) of OK ends moles litre(^{-1})</th>
<th>(\frac{1}{a-x}) litre mole(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>20.43</td>
<td>0</td>
<td>0.2357</td>
<td>4.243</td>
</tr>
<tr>
<td>3</td>
<td>11.9814</td>
<td>24.31</td>
<td>20.29</td>
<td>0.69</td>
<td>0.2341</td>
<td>4.272</td>
</tr>
<tr>
<td>6</td>
<td>11.4897</td>
<td>23.14</td>
<td>20.14</td>
<td>1.42</td>
<td>0.2323</td>
<td>4.305</td>
</tr>
<tr>
<td>10</td>
<td>14.8953</td>
<td>29.80</td>
<td>20.01</td>
<td>2.06</td>
<td>0.2308</td>
<td>4.333</td>
</tr>
<tr>
<td>26</td>
<td>11.8560</td>
<td>22.63</td>
<td>19.09</td>
<td>6.56</td>
<td>0.2202</td>
<td>4.541</td>
</tr>
<tr>
<td>48</td>
<td>11.0657</td>
<td>19.26</td>
<td>17.40</td>
<td>14.83</td>
<td>0.2007</td>
<td>4.982</td>
</tr>
<tr>
<td>68</td>
<td>8.2047</td>
<td>12.46</td>
<td>15.19</td>
<td>25.65</td>
<td>0.1752</td>
<td>5.708</td>
</tr>
<tr>
<td>92</td>
<td>11.3595</td>
<td>14.89</td>
<td>13.11</td>
<td>35.83</td>
<td>0.1512</td>
<td>6.614</td>
</tr>
<tr>
<td>124</td>
<td>8.5240</td>
<td>8.60</td>
<td>10.09</td>
<td>50.61</td>
<td>0.1164</td>
<td>8.591</td>
</tr>
<tr>
<td>136</td>
<td>10.1067</td>
<td>9.12</td>
<td>9.02</td>
<td>55.85</td>
<td>0.1041</td>
<td>9.606</td>
</tr>
<tr>
<td>156</td>
<td>7.7062</td>
<td>6.05</td>
<td>7.85</td>
<td>61.58</td>
<td>0.0905</td>
<td>11.049</td>
</tr>
<tr>
<td>209</td>
<td>7.1586</td>
<td>3.55</td>
<td>4.96</td>
<td>75.72</td>
<td>0.0572</td>
<td>17.48</td>
</tr>
<tr>
<td>248</td>
<td>5.0944</td>
<td>1.69</td>
<td>3.32</td>
<td>83.75</td>
<td>0.0383</td>
<td>26.11</td>
</tr>
<tr>
<td>438</td>
<td>5.2118</td>
<td>0.564</td>
<td>1.08</td>
<td>94.71</td>
<td>0.0125</td>
<td>80.00</td>
</tr>
<tr>
<td>1405</td>
<td>32.1832</td>
<td>0.92</td>
<td>0.29</td>
<td>98.6</td>
<td>0.0033</td>
<td>30.3</td>
</tr>
</tbody>
</table>

These results are shown in graphs 2 and 3 (see part 3).
Polymerisation of $F\overset{\cdot}{\bigcirc}SO_2\overset{\cdot}{\bigcirc}OK$ (0.03818 mole) in sulpholane (388.9 g) at 145.5°

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample weight g</th>
<th>Titre ml 0.1N H$_2$SO$_4$</th>
<th>Titre for 10,000g</th>
<th>% reaction</th>
<th>Conc$^n$ of OK ends moles litre$^{-1}$</th>
<th>$\frac{1}{a-x}$ litre mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>8.92</td>
<td>0</td>
<td>0.1038</td>
<td>9.631</td>
</tr>
<tr>
<td>5</td>
<td>13.1872</td>
<td>11.73</td>
<td>8.89</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>12.1833</td>
<td>10.89</td>
<td>8.93</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>12.6363</td>
<td>11.27</td>
<td>8.91</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>11.9032</td>
<td>10.13</td>
<td>8.51</td>
<td>4.60</td>
<td>0.0990</td>
<td>10.095</td>
</tr>
<tr>
<td>60</td>
<td>13.9079</td>
<td>11.71</td>
<td>8.42</td>
<td>5.60</td>
<td>0.0980</td>
<td>10.202</td>
</tr>
<tr>
<td>91</td>
<td>11.1164</td>
<td>9.50</td>
<td>7.97</td>
<td>10.65</td>
<td>0.0928</td>
<td>10.779</td>
</tr>
<tr>
<td>148</td>
<td>13.4478</td>
<td>9.90</td>
<td>7.36</td>
<td>17.49</td>
<td>0.0857</td>
<td>11.673</td>
</tr>
<tr>
<td>190</td>
<td>12.9960</td>
<td>8.89</td>
<td>6.84</td>
<td>23.32</td>
<td>0.0796</td>
<td>12.560</td>
</tr>
<tr>
<td>240</td>
<td>11.6321</td>
<td>7.12</td>
<td>6.12</td>
<td>31.39</td>
<td>0.0712</td>
<td>14.037</td>
</tr>
<tr>
<td>300</td>
<td>12.1170</td>
<td>6.51</td>
<td>5.37</td>
<td>39.80</td>
<td>0.0625</td>
<td>15.998</td>
</tr>
<tr>
<td>364</td>
<td>11.4587</td>
<td>5.33</td>
<td>4.65</td>
<td>47.87</td>
<td>0.0541</td>
<td>18.475</td>
</tr>
<tr>
<td>428</td>
<td>12.4033</td>
<td>4.91</td>
<td>3.96</td>
<td>55.60</td>
<td>0.0461</td>
<td>21.691</td>
</tr>
<tr>
<td>578</td>
<td>9.8241</td>
<td>2.74</td>
<td>2.79</td>
<td>68.72</td>
<td>0.0325</td>
<td>30.790</td>
</tr>
<tr>
<td>638</td>
<td>11.4249</td>
<td>2.72</td>
<td>2.38</td>
<td>73.32</td>
<td>0.0277</td>
<td>36.100</td>
</tr>
<tr>
<td>700</td>
<td>10.3431</td>
<td>2.12</td>
<td>2.05</td>
<td>77.02</td>
<td>0.0239</td>
<td>41.910</td>
</tr>
<tr>
<td>1363</td>
<td>18.2274</td>
<td>0.91</td>
<td>0.50</td>
<td>94.39</td>
<td>0.0058</td>
<td>171.674</td>
</tr>
<tr>
<td>1589</td>
<td>17.1311</td>
<td>0.50</td>
<td>0.29</td>
<td>96.75</td>
<td>0.0034</td>
<td>296.38</td>
</tr>
<tr>
<td>1868</td>
<td>18.7379</td>
<td>0.36</td>
<td>0.19</td>
<td>97.85</td>
<td>0.0022</td>
<td>448.02</td>
</tr>
</tbody>
</table>

$k_1 = \frac{10.202 - 9.631}{60 \times 60} = 1.58 \times 10^{-4}$ litre mole$^{-1}$ sec$^{-1}$
Polymerisation of $\text{F-}^\neq\text{SO}_2\text{OK}$ (0.05 mole) in sulfolane (227.4g) at 168°

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample weight g</th>
<th>Titre ml 0.1N $\text{H}_2\text{SO}_4$</th>
<th>Titre for 10.000g</th>
<th>% reaction</th>
<th>Conc$^n$ of OK ends moles litre$^{-1}$</th>
<th>$\frac{1}{a - x}$ litre mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>20.46</td>
<td>0</td>
<td>0.2343</td>
<td>4.268</td>
</tr>
<tr>
<td>2</td>
<td>10.4503</td>
<td>21.23</td>
<td>20.31</td>
<td>0.7</td>
<td>0.2326</td>
<td>4.298</td>
</tr>
<tr>
<td>4</td>
<td>11.2110</td>
<td>22.60</td>
<td>20.16</td>
<td>1.47</td>
<td>0.2308</td>
<td>4.332</td>
</tr>
<tr>
<td>6</td>
<td>11.5484</td>
<td>23.04</td>
<td>19.95</td>
<td>2.49</td>
<td>0.2285</td>
<td>4.377</td>
</tr>
<tr>
<td>12</td>
<td>11.2875</td>
<td>21.91</td>
<td>19.41</td>
<td>5.13</td>
<td>0.2223</td>
<td>4.499</td>
</tr>
<tr>
<td>22</td>
<td>8.9391</td>
<td>15.88</td>
<td>17.76</td>
<td>13.2</td>
<td>0.2034</td>
<td>4.917</td>
</tr>
<tr>
<td>38</td>
<td>7.7026</td>
<td>11.44</td>
<td>14.85</td>
<td>27.42</td>
<td>0.1700</td>
<td>5.818</td>
</tr>
<tr>
<td>46</td>
<td>7.5377</td>
<td>10.28</td>
<td>13.64</td>
<td>33.33</td>
<td>0.1562</td>
<td>6.402</td>
</tr>
<tr>
<td>60</td>
<td>7.2613</td>
<td>7.89</td>
<td>10.86</td>
<td>46.92</td>
<td>0.1244</td>
<td>8.041</td>
</tr>
<tr>
<td>80</td>
<td>5.8928</td>
<td>4.70</td>
<td>7.97</td>
<td>61.05</td>
<td>0.0913</td>
<td>10.958</td>
</tr>
<tr>
<td>100</td>
<td>5.9491</td>
<td>3.60</td>
<td>6.05</td>
<td>70.42</td>
<td>0.0693</td>
<td>14.434</td>
</tr>
<tr>
<td>130</td>
<td>5.0932</td>
<td>1.92</td>
<td>3.77</td>
<td>81.57</td>
<td>0.0432</td>
<td>23.159</td>
</tr>
<tr>
<td>160</td>
<td>5.8202</td>
<td>1.34</td>
<td>2.30</td>
<td>88.76</td>
<td>0.0263</td>
<td>37.979</td>
</tr>
<tr>
<td>203</td>
<td>6.4734</td>
<td>0.73</td>
<td>1.13</td>
<td>94.48</td>
<td>0.0129</td>
<td>77.339</td>
</tr>
<tr>
<td>259</td>
<td>7.7198</td>
<td>0.47</td>
<td>0.61</td>
<td>97.04</td>
<td>0.0069</td>
<td>144.300</td>
</tr>
<tr>
<td>1370</td>
<td>18.1885</td>
<td>0.69</td>
<td>0.38</td>
<td>98.10</td>
<td>0.0044</td>
<td>224.72</td>
</tr>
</tbody>
</table>

$k_1 = \frac{4.499 - 4.268}{12 \times 60} = 3.21 \times 10^{-4}$ litre mole$^{-1}$ sec$^{-1}$
Polymerisation of $\mathrm{F-\bigcirc-SO_2-\bigcirc-OK}$ (0.05 mole) in sulpholane (227.4 g) at 177.5° C

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample Weight g</th>
<th>Titre ml 0.1N $\text{H}_2\text{SO}_4$</th>
<th>Titre for 10,000g</th>
<th>% Reaction</th>
<th>Conc$^2$ of OK</th>
<th>$\frac{1}{a-x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>20.32</td>
<td>0</td>
<td>0.2310</td>
<td>4.328</td>
</tr>
<tr>
<td>2</td>
<td>9.8303</td>
<td>19.72</td>
<td>20.06</td>
<td>1.28</td>
<td>0.2281</td>
<td>4.384</td>
</tr>
<tr>
<td>4</td>
<td>9.8249</td>
<td>19.46</td>
<td>19.81</td>
<td>2.51</td>
<td>0.2252</td>
<td>4.440</td>
</tr>
<tr>
<td>6</td>
<td>9.9751</td>
<td>19.32</td>
<td>19.37</td>
<td>4.68</td>
<td>0.2202</td>
<td>5.541</td>
</tr>
<tr>
<td>10</td>
<td>6.6200</td>
<td>11.68</td>
<td>17.64</td>
<td>13.19</td>
<td>0.2006</td>
<td>4.986</td>
</tr>
<tr>
<td>14</td>
<td>5.0417</td>
<td>8.31</td>
<td>16.48</td>
<td>18.90</td>
<td>0.1874</td>
<td>5.337</td>
</tr>
<tr>
<td>20</td>
<td>5.2188</td>
<td>7.68</td>
<td>14.72</td>
<td>27.56</td>
<td>0.1674</td>
<td>5.975</td>
</tr>
<tr>
<td>30</td>
<td>5.9482</td>
<td>6.83</td>
<td>11.48</td>
<td>43.50</td>
<td>0.1305</td>
<td>7.661</td>
</tr>
<tr>
<td>41</td>
<td>8.1466</td>
<td>6.75</td>
<td>8.29</td>
<td>59.2</td>
<td>0.0943</td>
<td>10.609</td>
</tr>
<tr>
<td>61</td>
<td>8.3587</td>
<td>4.03</td>
<td>4.82</td>
<td>76.30</td>
<td>0.0547</td>
<td>18.265</td>
</tr>
<tr>
<td>84</td>
<td>4.9891</td>
<td>1.11</td>
<td>2.22</td>
<td>89.10</td>
<td>0.0252</td>
<td>39.714</td>
</tr>
<tr>
<td>103</td>
<td>8.0942</td>
<td>1.32</td>
<td>1.63</td>
<td>92.0</td>
<td>0.0185</td>
<td>54.142</td>
</tr>
<tr>
<td>122</td>
<td>8.2496</td>
<td>0.94</td>
<td>1.13</td>
<td>94.44</td>
<td>0.0128</td>
<td>77.882</td>
</tr>
<tr>
<td>162</td>
<td>7.5322</td>
<td>0.50</td>
<td>0.66</td>
<td>96.75</td>
<td>0.0075</td>
<td>133.156</td>
</tr>
<tr>
<td>1423</td>
<td>47.1497</td>
<td>1.49</td>
<td>0.32</td>
<td>98.40</td>
<td>0.0037</td>
<td>270.270</td>
</tr>
</tbody>
</table>

\[
k_1 = \frac{4.51 - 4.328}{6 \times 60} = 5.90 \times 10^{-4} \text{ litre mole}^{-1} \text{ sec}^{-1}
\]
Polymerisation of \( F-\overset{\text{+}}{\text{O}}\overset{\text{S}}{\text{O}}\overset{\text{-}}{\text{OK}} \) (0.05 mole) in Sulpholane (227.4g) at 196.5°

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample Weight g</th>
<th>Titre ml 0.1N H( _2 )SO( _4 )</th>
<th>Titre for 10.000g</th>
<th>% Reaction</th>
<th>Conc(^{\text{\text{II}}}) of OK ends moles litre(^{-1})</th>
<th>( \frac{1}{a-x} ) litre mole(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>20.14</td>
<td>0</td>
<td>0.2256</td>
<td>4.433</td>
</tr>
<tr>
<td>1</td>
<td>8.9145</td>
<td>17.54</td>
<td>19.67</td>
<td>2.33</td>
<td>0.2203</td>
<td>4.539</td>
</tr>
<tr>
<td>2</td>
<td>10.1068</td>
<td>19.40</td>
<td>19.19</td>
<td>4.72</td>
<td>0.2149</td>
<td>4.653</td>
</tr>
<tr>
<td>3</td>
<td>5.4181</td>
<td>9.70</td>
<td>17.90</td>
<td>11.12</td>
<td>0.2005</td>
<td>4.988</td>
</tr>
<tr>
<td>5</td>
<td>6.8342</td>
<td>11.55</td>
<td>16.90</td>
<td>16.09</td>
<td>0.1893</td>
<td>5.283</td>
</tr>
<tr>
<td>7</td>
<td>6.3491</td>
<td>9.64</td>
<td>15.18</td>
<td>24.63</td>
<td>0.1700</td>
<td>5.882</td>
</tr>
<tr>
<td>10</td>
<td>9.2435</td>
<td>11.77</td>
<td>12.73</td>
<td>36.79</td>
<td>0.1426</td>
<td>7.014</td>
</tr>
<tr>
<td>15</td>
<td>8.3762</td>
<td>7.47</td>
<td>8.92</td>
<td>55.71</td>
<td>0.0999</td>
<td>10.010</td>
</tr>
<tr>
<td>20</td>
<td>8.3202</td>
<td>5.11</td>
<td>6.14</td>
<td>69.50</td>
<td>0.0688</td>
<td>14.535</td>
</tr>
<tr>
<td>30</td>
<td>8.3448</td>
<td>2.46</td>
<td>2.95</td>
<td>85.35</td>
<td>0.0330</td>
<td>30.257</td>
</tr>
<tr>
<td>40</td>
<td>10.2695</td>
<td>1.72</td>
<td>1.67</td>
<td>91.71</td>
<td>0.0187</td>
<td>53.476</td>
</tr>
<tr>
<td>52</td>
<td>11.8200</td>
<td>1.13</td>
<td>0.96</td>
<td>95.25</td>
<td>0.0107</td>
<td>93.371</td>
</tr>
<tr>
<td>61</td>
<td>12.3935</td>
<td>0.91</td>
<td>0.73</td>
<td>96.38</td>
<td>0.0082</td>
<td>122.399</td>
</tr>
<tr>
<td>80</td>
<td>14.9846</td>
<td>0.86</td>
<td>0.57</td>
<td>97.17</td>
<td>0.0064</td>
<td>156.740</td>
</tr>
<tr>
<td>420</td>
<td>26.6112</td>
<td>0.88</td>
<td>0.33</td>
<td>98.36</td>
<td>0.0037</td>
<td>270.270</td>
</tr>
<tr>
<td>1395</td>
<td>24.0019</td>
<td>0.90</td>
<td>0.37</td>
<td>98.16</td>
<td>0.0041</td>
<td>240.96</td>
</tr>
</tbody>
</table>

\[ K_1 = 1.8 \times 10^{-3} \text{ litre mole}^{-1} \text{ sec}^{-1} \]
Polymerisation of \( \text{H} \) \( \text{SO}_2 \) \( \text{OK} \) (0.05 mole) in Sulpholane (227.4g) at 200°

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample Weight g</th>
<th>Titre ml 0.1N ( \text{H}_2\text{SO}_4 )</th>
<th>Titre for 10.000g</th>
<th>% Reaction</th>
<th>Conc ( n ) of OK ends moles litre(^{-1} )</th>
<th>( \frac{1}{a-x} ) litre mole(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0.2244</td>
<td>4.456</td>
</tr>
<tr>
<td>2</td>
<td>11.0297</td>
<td>22.09</td>
<td>20.03</td>
<td>0.15</td>
<td>0.2241</td>
<td>4.463</td>
</tr>
<tr>
<td>4</td>
<td>10.8270</td>
<td>21.65</td>
<td>20.00</td>
<td>0.30</td>
<td>0.2237</td>
<td>4.469</td>
</tr>
<tr>
<td>6</td>
<td>10.8272</td>
<td>21.51</td>
<td>19.87</td>
<td>0.95</td>
<td>0.2223</td>
<td>4.499</td>
</tr>
<tr>
<td>12</td>
<td>9.5399</td>
<td>18.66</td>
<td>19.56</td>
<td>2.48</td>
<td>0.2188</td>
<td>4.570</td>
</tr>
<tr>
<td>23</td>
<td>10.1587</td>
<td>19.11</td>
<td>18.81</td>
<td>6.23</td>
<td>0.2104</td>
<td>4.752</td>
</tr>
<tr>
<td>40</td>
<td>7.6023</td>
<td>13.36</td>
<td>17.57</td>
<td>12.41</td>
<td>0.1966</td>
<td>5.087</td>
</tr>
<tr>
<td>54</td>
<td>9.7055</td>
<td>16.30</td>
<td>16.79</td>
<td>16.30</td>
<td>0.1878</td>
<td>5.324</td>
</tr>
<tr>
<td>96</td>
<td>8.5455</td>
<td>12.37</td>
<td>14.47</td>
<td>27.87</td>
<td>0.1619</td>
<td>6.178</td>
</tr>
<tr>
<td>121</td>
<td>7.9460</td>
<td>10.33</td>
<td>13.00</td>
<td>35.19</td>
<td>0.1454</td>
<td>6.876</td>
</tr>
<tr>
<td>163</td>
<td>6.0464</td>
<td>6.70</td>
<td>11.08</td>
<td>44.76</td>
<td>0.1239</td>
<td>8.067</td>
</tr>
<tr>
<td>210</td>
<td>8.4705</td>
<td>7.51</td>
<td>8.87</td>
<td>55.78</td>
<td>0.0992</td>
<td>10.077</td>
</tr>
<tr>
<td>276</td>
<td>2.8960</td>
<td>4.94</td>
<td>6.25</td>
<td>68.84</td>
<td>0.0699</td>
<td>14.300</td>
</tr>
<tr>
<td>346</td>
<td>6.2987</td>
<td>2.71</td>
<td>4.30</td>
<td>78.56</td>
<td>0.0481</td>
<td>20.786</td>
</tr>
<tr>
<td>420</td>
<td>8.4377</td>
<td>2.49</td>
<td>2.95</td>
<td>85.29</td>
<td>0.0330</td>
<td>30.294</td>
</tr>
<tr>
<td>1440</td>
<td>46.0416</td>
<td>1.10</td>
<td>0.24</td>
<td>98.80</td>
<td>0.0027</td>
<td>371.75</td>
</tr>
</tbody>
</table>

\[ k_1 = 2.15 \times 10^{-4} \text{ litre mole}^{-1} \text{ sec}^{-1} \]

These results are shown in graph 5.
Polymerisation of $F-SO_2-O-SO_2-O-K$ (0.045 mole)
in Sulpholane (368.3 g) at 135.5°

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample Weight g</th>
<th>Titre ml 0.1N H$_2$SO$_4$</th>
<th>Titre for 10.000g</th>
<th>% Reaction</th>
<th>Conc$^n$ of OK ends moles litre$^{-1}$</th>
<th>$\frac{1}{a-x}$ litre mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>14.3938</td>
<td>12.70</td>
<td>8.82</td>
<td>12.67</td>
<td>0.1035</td>
<td>9.662</td>
</tr>
<tr>
<td>5</td>
<td>10.3539</td>
<td>8.35</td>
<td>8.06</td>
<td>20.20</td>
<td>0.0945</td>
<td>10.582</td>
</tr>
<tr>
<td>10</td>
<td>10.9289</td>
<td>8.32</td>
<td>7.61</td>
<td>24.65</td>
<td>0.0893</td>
<td>11.202</td>
</tr>
<tr>
<td>15</td>
<td>11.0041</td>
<td>7.89</td>
<td>7.11</td>
<td>29.01</td>
<td>0.0841</td>
<td>11.891</td>
</tr>
<tr>
<td>20</td>
<td>11.2515</td>
<td>7.51</td>
<td>6.67</td>
<td>33.96</td>
<td>0.0782</td>
<td>12.781</td>
</tr>
<tr>
<td>30</td>
<td>10.0653</td>
<td>5.91</td>
<td>5.87</td>
<td>41.88</td>
<td>0.0688</td>
<td>14.524</td>
</tr>
<tr>
<td>40</td>
<td>10.1924</td>
<td>5.32</td>
<td>5.22</td>
<td>48.32</td>
<td>0.0612</td>
<td>16.332</td>
</tr>
<tr>
<td>60</td>
<td>10.0186</td>
<td>4.13</td>
<td>4.12</td>
<td>59.21</td>
<td>0.0483</td>
<td>20.691</td>
</tr>
<tr>
<td>85</td>
<td>11.1277</td>
<td>3.72</td>
<td>3.34</td>
<td>66.93</td>
<td>0.0392</td>
<td>25.523</td>
</tr>
<tr>
<td>108</td>
<td>13.1055</td>
<td>3.67</td>
<td>2.80</td>
<td>72.28</td>
<td>0.0328</td>
<td>30.451</td>
</tr>
<tr>
<td>134</td>
<td>11.3057</td>
<td>2.71</td>
<td>2.40</td>
<td>76.24</td>
<td>0.0281</td>
<td>35.524</td>
</tr>
<tr>
<td>180</td>
<td>9.7323</td>
<td>1.70</td>
<td>1.75</td>
<td>82.67</td>
<td>0.0205</td>
<td>48.709</td>
</tr>
<tr>
<td>210</td>
<td>9.9352</td>
<td>1.52</td>
<td>1.53</td>
<td>84.85</td>
<td>0.0179</td>
<td>55.710</td>
</tr>
<tr>
<td>307</td>
<td>12.6742</td>
<td>1.73</td>
<td>1.36</td>
<td>86.53</td>
<td>0.0159</td>
<td>62.696</td>
</tr>
<tr>
<td>425</td>
<td>12.8767</td>
<td>1.68</td>
<td>1.30</td>
<td>87.00</td>
<td>0.0153</td>
<td>65.574</td>
</tr>
<tr>
<td>451</td>
<td>53.4193</td>
<td>5.96</td>
<td>1.12</td>
<td>88.91</td>
<td>0.0131</td>
<td>76.103</td>
</tr>
</tbody>
</table>

From a graphical plot $k = 3.33 \times 10^{-3}$ litre mole$^{-1}$ sec$^{-1}$
Polymerisation of \( \text{F-} \overset{\text{O}}{\text{S}}_{2} \text{O-} \overset{\text{O}}{\text{S}} \overset{\text{O}}{\text{S}} \text{OK} \) (0.040 mole) in sulphonane (327.4 g) at 145.5°

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample weight g</th>
<th>Titre ml 0.1N ( \text{H}<em>{2}\text{SO}</em>{4} )</th>
<th>Titre for ( \text{10.000g} )</th>
<th>% reaction</th>
<th>Conc(^n) of OK ends moles litre(^{-1})</th>
<th>( \frac{1}{a-x} ) litre mole(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1111</td>
<td>9.00</td>
</tr>
<tr>
<td>3</td>
<td>9.2415</td>
<td>7.50</td>
<td>8.11</td>
<td>15.04</td>
<td>0.0944</td>
<td>10.593</td>
</tr>
<tr>
<td>5</td>
<td>10.4698</td>
<td>8.10</td>
<td>7.74</td>
<td>18.91</td>
<td>0.0901</td>
<td>11.100</td>
</tr>
<tr>
<td>10</td>
<td>12.0828</td>
<td>9.37</td>
<td>6.93</td>
<td>27.36</td>
<td>0.0807</td>
<td>12.398</td>
</tr>
<tr>
<td>15</td>
<td>10.9812</td>
<td>6.89</td>
<td>6.27</td>
<td>34.13</td>
<td>0.0730</td>
<td>13.702</td>
</tr>
<tr>
<td>20</td>
<td>11.3707</td>
<td>6.31</td>
<td>5.55</td>
<td>41.88</td>
<td>0.0646</td>
<td>15.480</td>
</tr>
<tr>
<td>30</td>
<td>11.9135</td>
<td>5.33</td>
<td>4.47</td>
<td>53.2</td>
<td>0.0520</td>
<td>19.220</td>
</tr>
<tr>
<td>40</td>
<td>10.7590</td>
<td>3.94</td>
<td>3.66</td>
<td>61.68</td>
<td>0.0426</td>
<td>23.474</td>
</tr>
<tr>
<td>60</td>
<td>10.9623</td>
<td>3.12</td>
<td>2.85</td>
<td>70.10</td>
<td>0.0332</td>
<td>30.147</td>
</tr>
<tr>
<td>80</td>
<td>12.4480</td>
<td>2.84</td>
<td>2.28</td>
<td>76.20</td>
<td>0.0265</td>
<td>37.679</td>
</tr>
<tr>
<td>120</td>
<td>13.1894</td>
<td>2.11</td>
<td>1.60</td>
<td>83.30</td>
<td>0.0186</td>
<td>53.706</td>
</tr>
<tr>
<td>150</td>
<td>9.7902</td>
<td>1.33</td>
<td>1.36</td>
<td>85.80</td>
<td>0.0158</td>
<td>63.171</td>
</tr>
</tbody>
</table>

From the graphical plot \( \frac{1}{a-x} \) versus time the rate constant:

\[
k = 5.98 \times 10^{-3} \text{ litre mole}^{-1} \text{ sec}^{-1}
\]
Polymerisation of \( \text{F-} \left( -\overset{\text{S}}{-}\overset{\text{O}}{2} \right) \left( -\overset{\text{O}}{2} \right) \left( -\overset{\text{O}}{2} \right) \text{OK} \) (0.045 mole) in
sulpholane (368.32 g) at 124.5°

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample weight g</th>
<th>Titre ml 0.1N ( \text{H}_2\text{SO}_4 )</th>
<th>Titre for 10.000g</th>
<th>% reaction</th>
<th>Conc° of OK ends moles litre(^{-1})</th>
<th>( \frac{1}{a-x} ) litre mole(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>11.7729</td>
<td>10.09</td>
<td>8.57</td>
<td>-</td>
<td>0.1013</td>
<td>9.868</td>
</tr>
<tr>
<td>7</td>
<td>9.2048</td>
<td>7.75</td>
<td>8.42</td>
<td>-</td>
<td>0.0996</td>
<td>10.043</td>
</tr>
<tr>
<td>9</td>
<td>9.8207</td>
<td>8.51</td>
<td>8.66</td>
<td>12.96</td>
<td>0.1024</td>
<td>9.766</td>
</tr>
<tr>
<td>12</td>
<td>14.2614</td>
<td>12.26</td>
<td>8.60</td>
<td>13.57</td>
<td>0.1017</td>
<td>9.834</td>
</tr>
<tr>
<td>15</td>
<td>13.6655</td>
<td>11.48</td>
<td>8.40</td>
<td>15.58</td>
<td>0.0993</td>
<td>10.067</td>
</tr>
<tr>
<td>20</td>
<td>13.2675</td>
<td>10.72</td>
<td>8.08</td>
<td>18.79</td>
<td>0.0956</td>
<td>10.466</td>
</tr>
<tr>
<td>30</td>
<td>12.9871</td>
<td>9.72</td>
<td>7.48</td>
<td>24.82</td>
<td>0.0885</td>
<td>11.306</td>
</tr>
<tr>
<td>43</td>
<td>13.9412</td>
<td>9.65</td>
<td>6.92</td>
<td>30.45</td>
<td>0.0818</td>
<td>12.220</td>
</tr>
<tr>
<td>60</td>
<td>14.8054</td>
<td>9.09</td>
<td>6.14</td>
<td>38.29</td>
<td>0.0726</td>
<td>13.774</td>
</tr>
<tr>
<td>100</td>
<td>15.5383</td>
<td>7.51</td>
<td>4.83</td>
<td>51.46</td>
<td>0.0571</td>
<td>17.510</td>
</tr>
<tr>
<td>146</td>
<td>13.7746</td>
<td>5.16</td>
<td>3.74</td>
<td>62.41</td>
<td>0.0442</td>
<td>22.614</td>
</tr>
<tr>
<td>203</td>
<td>14.8346</td>
<td>4.30</td>
<td>2.90</td>
<td>70.85</td>
<td>0.0343</td>
<td>29.163</td>
</tr>
<tr>
<td>252</td>
<td>13.3428</td>
<td>3.27</td>
<td>2.45</td>
<td>75.37</td>
<td>0.0290</td>
<td>34.518</td>
</tr>
<tr>
<td>301</td>
<td>15.4051</td>
<td>3.08</td>
<td>2.00</td>
<td>79.90</td>
<td>0.0236</td>
<td>42.283</td>
</tr>
<tr>
<td>410</td>
<td>15.0641</td>
<td>2.71</td>
<td>1.80</td>
<td>81.91</td>
<td>0.0213</td>
<td>46.992</td>
</tr>
<tr>
<td>1404</td>
<td>34.7668</td>
<td>3.84</td>
<td>1.10</td>
<td>88.94</td>
<td>0.0130</td>
<td>76.864</td>
</tr>
</tbody>
</table>

These results are shown in graph 6.

From graph 6, \( k = \frac{32.5-10}{(240-15) \cdot 60} = 1.61 \times 10^{-3} \) litre mole\(^{-1}\) sec\(^{-1}\)
Reaction of $\text{SO}_2\text{O-SO}_2\text{O}$ with $\text{SO}_2\text{F}$ in sulpholane (308 g) at 135°

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample weight g</th>
<th>Titre ml 0.1N H$_2$SO$_4$</th>
<th>Titre for 10000g</th>
<th>% reaction</th>
<th>Conc$^n$ of OK ends moles litre$^{-1}$</th>
<th>Conc$^n$ of F ends moles litre$^{-1}$</th>
<th>$\frac{1}{a-b\ln(b-x)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0.1595</td>
<td>0.1648</td>
<td>6.166</td>
</tr>
<tr>
<td>5</td>
<td>13.0842</td>
<td>16.55</td>
<td>12.65</td>
<td>6.78</td>
<td>0.1487</td>
<td>0.1540</td>
<td>6.607</td>
</tr>
<tr>
<td>8</td>
<td>12.4246</td>
<td>15.02</td>
<td>12.09</td>
<td>10.91</td>
<td>0.1421</td>
<td>0.1474</td>
<td>6.908</td>
</tr>
<tr>
<td>10</td>
<td>12.4373</td>
<td>14.35</td>
<td>11.54</td>
<td>14.96</td>
<td>0.1357</td>
<td>0.1410</td>
<td>7.231</td>
</tr>
<tr>
<td>15</td>
<td>7.0067</td>
<td>6.90</td>
<td>9.85</td>
<td>27.41</td>
<td>0.1158</td>
<td>0.1211</td>
<td>8.444</td>
</tr>
<tr>
<td>20</td>
<td>7.6203</td>
<td>6.94</td>
<td>9.11</td>
<td>32.87</td>
<td>0.1071</td>
<td>0.1124</td>
<td>9.114</td>
</tr>
<tr>
<td>25</td>
<td>8.3158</td>
<td>6.91</td>
<td>8.31</td>
<td>38.76</td>
<td>0.0997</td>
<td>0.1030</td>
<td>9.968</td>
</tr>
<tr>
<td>30</td>
<td>7.6184</td>
<td>5.90</td>
<td>7.74</td>
<td>42.96</td>
<td>0.0910</td>
<td>0.0963</td>
<td>10.68</td>
</tr>
<tr>
<td>40</td>
<td>8.8384</td>
<td>5.87</td>
<td>6.64</td>
<td>51.07</td>
<td>0.0781</td>
<td>0.0833</td>
<td>12.39</td>
</tr>
<tr>
<td>60</td>
<td>10.9319</td>
<td>5.59</td>
<td>5.11</td>
<td>62.34</td>
<td>0.0601</td>
<td>0.0654</td>
<td>15.95</td>
</tr>
<tr>
<td>80</td>
<td>9.8509</td>
<td>3.87</td>
<td>3.93</td>
<td>71.04</td>
<td>0.0402</td>
<td>0.0515</td>
<td>20.49</td>
</tr>
<tr>
<td>102</td>
<td>9.3876</td>
<td>2.88</td>
<td>3.07</td>
<td>77.38</td>
<td>0.0361</td>
<td>0.0414</td>
<td>25.86</td>
</tr>
<tr>
<td>120</td>
<td>10.2163</td>
<td>2.67</td>
<td>2.61</td>
<td>80.77</td>
<td>0.0307</td>
<td>0.0360</td>
<td>30.08</td>
</tr>
<tr>
<td>160</td>
<td>9.0543</td>
<td>1.70</td>
<td>1.88</td>
<td>86.15</td>
<td>0.0221</td>
<td>0.0274</td>
<td>40.58</td>
</tr>
<tr>
<td>191</td>
<td>10.7213</td>
<td>1.71</td>
<td>1.59</td>
<td>88.28</td>
<td>0.0187</td>
<td>0.0240</td>
<td>47.11</td>
</tr>
<tr>
<td>250</td>
<td>11.3274</td>
<td>1.14</td>
<td>1.01</td>
<td>92.56</td>
<td>0.0119</td>
<td>0.0171</td>
<td>69.71</td>
</tr>
<tr>
<td>323</td>
<td>12.3940</td>
<td>0.93</td>
<td>0.75</td>
<td>94.47</td>
<td>0.0088</td>
<td>0.141</td>
<td>88.86</td>
</tr>
<tr>
<td>381</td>
<td>33.3255</td>
<td>2.30</td>
<td>0.69</td>
<td>94.92</td>
<td>0.0081</td>
<td>0.0134</td>
<td>95.05</td>
</tr>
</tbody>
</table>

These results are shown in graph 8.

\[ k = 3.59 \times 10^{-3} \text{ litre mole}^{-1} \text{ sec}^{-1} \]
Reaction of \(\text{SO}_2-\text{O}-\text{SO}_2\text{-OK}(0.042\text{ mole})\) and \(\text{SO}_2-\text{O}-\text{SO}_2\text{-F}(0.042\text{ mole})\) in sulpholane (269g) at 148.5\(^\circ\)

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample weight g</th>
<th>Titre ml 0.1N (H_2SO_4)</th>
<th>Titre for 10.000g</th>
<th>% reaction</th>
<th>Conc(^n) of OK ends moles litre(^{-1})</th>
<th>Conc(^n) of F ends moles litre(^{-1})</th>
<th>(\frac{1}{a-b}\ln a-x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0.1605</td>
<td>0.1664</td>
<td>6.119</td>
</tr>
<tr>
<td>2</td>
<td>9.5503</td>
<td>12.13</td>
<td>12.70</td>
<td>5.99</td>
<td>0.1509</td>
<td>0.1567</td>
<td>6.501</td>
</tr>
<tr>
<td>3</td>
<td>10.0348</td>
<td>12.33</td>
<td>12.29</td>
<td>9.03</td>
<td>0.1460</td>
<td>0.1519</td>
<td>6.714</td>
</tr>
<tr>
<td>5</td>
<td>5.5929</td>
<td>6.07</td>
<td>10.85</td>
<td>19.69</td>
<td>0.1289</td>
<td>0.1347</td>
<td>7.586</td>
</tr>
<tr>
<td>12</td>
<td>8.0643</td>
<td>6.78</td>
<td>8.41</td>
<td>37.75</td>
<td>0.0999</td>
<td>0.1058</td>
<td>9.726</td>
</tr>
<tr>
<td>20</td>
<td>9.4581</td>
<td>6.09</td>
<td>6.44</td>
<td>52.33</td>
<td>0.0765</td>
<td>0.0823</td>
<td>12.59</td>
</tr>
<tr>
<td>40</td>
<td>9.8331</td>
<td>3.69</td>
<td>3.75</td>
<td>72.24</td>
<td>0.0446</td>
<td>0.0504</td>
<td>21.09</td>
</tr>
<tr>
<td>60</td>
<td>10.4606</td>
<td>2.56</td>
<td>2.45</td>
<td>81.86</td>
<td>0.0291</td>
<td>0.0349</td>
<td>31.30</td>
</tr>
<tr>
<td>80</td>
<td>8.8811</td>
<td>1.50</td>
<td>1.69</td>
<td>87.49</td>
<td>0.0201</td>
<td>0.0259</td>
<td>43.72</td>
</tr>
<tr>
<td>121</td>
<td>8.4297</td>
<td>0.74</td>
<td>0.87</td>
<td>93.55</td>
<td>0.0104</td>
<td>0.0162</td>
<td>76.63</td>
</tr>
<tr>
<td>190</td>
<td>11.2432</td>
<td>0.63</td>
<td>0.56</td>
<td>95.85</td>
<td>0.0067</td>
<td>0.0125</td>
<td>107.88</td>
</tr>
<tr>
<td>294</td>
<td>11.2168</td>
<td>0.43</td>
<td>0.38</td>
<td>97.16</td>
<td>0.0046</td>
<td>0.0104</td>
<td>414.35</td>
</tr>
<tr>
<td>403</td>
<td>46.1895</td>
<td>1.42</td>
<td>0.31</td>
<td>97.70</td>
<td>0.0037</td>
<td>0.0095</td>
<td>162.60</td>
</tr>
</tbody>
</table>

\(k = 7.78 \times 10^{-3} \text{ litre mole}^{-1} \text{ sec}^{-1}\)
Reaction of $\text{SO}_2^-$-$\text{SO}_2^-$-$\text{O}^-$-$\text{SO}_2^-$ $\text{OK}$ (0.05 mole) and $\text{SO}_2^-$-$\text{SO}_2^-$-$\text{O}^-$-$\text{SO}_2^-$-$\text{F}$ (0.05 mole) in sulpholane (193.3 g) at 150°C

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample weight g</th>
<th>Titre ml 0.1N H$_2$SO$_4$</th>
<th>Titre for 10.000g</th>
<th>% reaction</th>
<th>Conc$^n$ of OK ends moles litre$^{-1}$</th>
<th>Conc$^n$ of F ends moles litre$^{-1}$</th>
<th>$\frac{1}{\ln(a-x)}(a-b)(b-x)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0.2296</td>
<td>0.2472</td>
<td>4.197</td>
</tr>
<tr>
<td>2</td>
<td>7.3884</td>
<td>12.53</td>
<td>19.96</td>
<td>11.62</td>
<td>0.2029</td>
<td>0.2205</td>
<td>4.726</td>
</tr>
<tr>
<td>3</td>
<td>7.6154</td>
<td>12.08</td>
<td>15.86</td>
<td>17.35</td>
<td>0.1897</td>
<td>0.2073</td>
<td>5.040</td>
</tr>
<tr>
<td>5</td>
<td>7.2560</td>
<td>9.72</td>
<td>13.40</td>
<td>30.17</td>
<td>0.1603</td>
<td>0.1779</td>
<td>5.919</td>
</tr>
<tr>
<td>7</td>
<td>7.1854</td>
<td>8.30</td>
<td>11.55</td>
<td>39.81</td>
<td>0.1382</td>
<td>0.1558</td>
<td>6.812</td>
</tr>
<tr>
<td>10</td>
<td>4.8722</td>
<td>4.55</td>
<td>9.34</td>
<td>51.33</td>
<td>0.1117</td>
<td>0.1293</td>
<td>8.311</td>
</tr>
<tr>
<td>15</td>
<td>6.6044</td>
<td>4.59</td>
<td>6.95</td>
<td>63.78</td>
<td>0.0832</td>
<td>0.1007</td>
<td>10.909</td>
</tr>
<tr>
<td>20</td>
<td>6.7341</td>
<td>3.56</td>
<td>5.29</td>
<td>72.43</td>
<td>0.0633</td>
<td>0.0809</td>
<td>13.941</td>
</tr>
<tr>
<td>30</td>
<td>6.7953</td>
<td>2.30</td>
<td>3.38</td>
<td>82.39</td>
<td>0.0404</td>
<td>0.0580</td>
<td>20.536</td>
</tr>
<tr>
<td>50</td>
<td>6.6887</td>
<td>1.36</td>
<td>2.03</td>
<td>89.42</td>
<td>0.0243</td>
<td>0.0419</td>
<td>30.969</td>
</tr>
<tr>
<td>95</td>
<td>6.7586</td>
<td>0.69</td>
<td>1.02</td>
<td>94.68</td>
<td>0.0122</td>
<td>0.0298</td>
<td>50.715</td>
</tr>
<tr>
<td>214</td>
<td>9.5779</td>
<td>0.32</td>
<td>0.334</td>
<td>98.26</td>
<td>0.0040</td>
<td>0.0216</td>
<td>95.908</td>
</tr>
</tbody>
</table>

$k = 8.39 \times 10^{-3}$ litre mole$^{-1}$ sec$^{-1}$
Reaction of $\text{K} - \text{SO}_2 - \text{OK}$ (0.025 mole) with $\text{F} - \text{SO}_2 - \text{F}$ (0.025 mole) in sulphotane (227.4g) at 124.5°

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample weight g</th>
<th>Titre ml 0.1N H$_2$SO$_4$</th>
<th>Titre for 0.000g</th>
<th>% reaction</th>
<th>Conc$^n$ of OK ends moles litre$^{-1}$</th>
<th>$\frac{1}{a-x}$ litre mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>12.3536</td>
<td>21.52</td>
<td>20.67</td>
<td>0</td>
<td>0.2383</td>
<td>4.196</td>
</tr>
<tr>
<td>2</td>
<td>12.4766</td>
<td>19.90</td>
<td>17.42</td>
<td>15.72</td>
<td>0.2009</td>
<td>4.979</td>
</tr>
<tr>
<td>3</td>
<td>12.9439</td>
<td>19.65</td>
<td>15.95</td>
<td>22.83</td>
<td>0.1839</td>
<td>5.438</td>
</tr>
<tr>
<td>6</td>
<td>12.9911</td>
<td>18.96</td>
<td>15.18</td>
<td>26.56</td>
<td>0.1750</td>
<td>5.713</td>
</tr>
<tr>
<td>10</td>
<td>12.2393</td>
<td>16.28</td>
<td>14.59</td>
<td>29.41</td>
<td>0.1682</td>
<td>5.944</td>
</tr>
<tr>
<td>15</td>
<td>12.1220</td>
<td>14.88</td>
<td>13.30</td>
<td>35.66</td>
<td>0.1533</td>
<td>6.521</td>
</tr>
<tr>
<td>20</td>
<td>13.0303</td>
<td>14.73</td>
<td>12.27</td>
<td>40.64</td>
<td>0.1415</td>
<td>7.068</td>
</tr>
<tr>
<td>30</td>
<td>12.5434</td>
<td>12.37</td>
<td>11.30</td>
<td>45.33</td>
<td>0.1303</td>
<td>7.675</td>
</tr>
<tr>
<td>40</td>
<td>12.0923</td>
<td>10.88</td>
<td>9.86</td>
<td>52.3</td>
<td>0.1137</td>
<td>8.976</td>
</tr>
<tr>
<td>60</td>
<td>12.3934</td>
<td>7.91</td>
<td>6.38</td>
<td>69.13</td>
<td>0.0736</td>
<td>13.594</td>
</tr>
<tr>
<td>82</td>
<td>11.6889</td>
<td>5.91</td>
<td>5.06</td>
<td>75.52</td>
<td>0.0583</td>
<td>17.140</td>
</tr>
<tr>
<td>117</td>
<td>12.7188</td>
<td>5.63</td>
<td>4.43</td>
<td>78.57</td>
<td>0.0511</td>
<td>19.578</td>
</tr>
<tr>
<td>205</td>
<td>10.4976</td>
<td>3.16</td>
<td>3.01</td>
<td>85.44</td>
<td>0.0347</td>
<td>28.814</td>
</tr>
<tr>
<td>286</td>
<td>11.6588</td>
<td>2.48</td>
<td>2.13</td>
<td>89.70</td>
<td>0.0266</td>
<td>40.718</td>
</tr>
<tr>
<td>362</td>
<td>12.4974</td>
<td>2.09</td>
<td>1.67</td>
<td>91.92</td>
<td>0.0193</td>
<td>50.0134</td>
</tr>
<tr>
<td>420</td>
<td>12.9322</td>
<td>1.90</td>
<td>1.47</td>
<td>92.89</td>
<td>0.0169</td>
<td>59.000</td>
</tr>
</tbody>
</table>

$k_1 = 1.03 \times 10^{-2}$ litre mole$^{-1}$ sec$^{-1}$

$k_2 = 1.93 \times 10^{-3}$ litre mole$^{-1}$ sec$^{-1}$
Reaction of KO$\cdot$SO$_2$$\cdot$OK (0.01909 mole) with F$\cdot$SO$_2$$\cdot$F (0.01909 mole) in sulphonol (388.9g) at 145.5°

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample weight g</th>
<th>Titre ml 0.1N H$_2$SO$_4$</th>
<th>% reaction</th>
<th>Conc$^n$ of OK ends moles litre$^{-1}$</th>
<th>$\frac{1}{a-x}$ litre mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0.1112</td>
<td>8.996</td>
</tr>
<tr>
<td>2</td>
<td>16.664</td>
<td>10.40</td>
<td>6.24</td>
<td>34.66</td>
<td>0.0726</td>
</tr>
<tr>
<td>3</td>
<td>16.034</td>
<td>9.16</td>
<td>5.71</td>
<td>40.21</td>
<td>0.0665</td>
</tr>
<tr>
<td>4</td>
<td>16.671</td>
<td>9.07</td>
<td>5.44</td>
<td>43.04</td>
<td>0.0633</td>
</tr>
<tr>
<td>5</td>
<td>16.108</td>
<td>7.87</td>
<td>4.88</td>
<td>48.90</td>
<td>0.0568</td>
</tr>
<tr>
<td>7</td>
<td>16.399</td>
<td>7.26</td>
<td>4.43</td>
<td>53.61</td>
<td>0.0516</td>
</tr>
<tr>
<td>10</td>
<td>17.723</td>
<td>7.20</td>
<td>4.06</td>
<td>57.49</td>
<td>0.0473</td>
</tr>
<tr>
<td>15</td>
<td>17.973</td>
<td>6.27</td>
<td>3.49</td>
<td>63.47</td>
<td>0.0406</td>
</tr>
<tr>
<td>20</td>
<td>18.212</td>
<td>5.91</td>
<td>3.24</td>
<td>66.07</td>
<td>0.0377</td>
</tr>
<tr>
<td>30</td>
<td>18.885</td>
<td>5.17</td>
<td>2.74</td>
<td>71.31</td>
<td>0.0319</td>
</tr>
<tr>
<td>40</td>
<td>17.796</td>
<td>4.29</td>
<td>2.41</td>
<td>74.76</td>
<td>0.0280</td>
</tr>
<tr>
<td>62</td>
<td>18.025</td>
<td>3.30</td>
<td>1.83</td>
<td>80.84</td>
<td>0.0213</td>
</tr>
<tr>
<td>80</td>
<td>18.149</td>
<td>2.73</td>
<td>1.50</td>
<td>84.29</td>
<td>0.0175</td>
</tr>
<tr>
<td>120</td>
<td>18.212</td>
<td>2.00</td>
<td>1.10</td>
<td>88.48</td>
<td>0.0128</td>
</tr>
<tr>
<td>172</td>
<td>19.669</td>
<td>1.49</td>
<td>0.76</td>
<td>92.04</td>
<td>0.0088</td>
</tr>
</tbody>
</table>

These results are shown in graph 9.

$k_1 = 3.97 \times 10^{-2}$ litre mole$^{-1}$ sec$^{-1}$

$k_2 = 8.77 \times 10^{-3}$ litre mole$^{-1}$ sec$^{-1}$
Reaction of $\text{KO} \cdot \text{SO}_2 \cdot \text{OK}$ (0.025 mole) and $\text{F} \cdot \text{SO}_2 \cdot \text{F}$ (0.025 mole) in sulpholane (227.4g) at 158°

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Sample weight g</th>
<th>Titre ml 0.1N $\text{H}_2\text{SO}_4$</th>
<th>Titre for 10.000g</th>
<th>% reaction</th>
<th>Conc$^n$ of OK ends moles litre$^{-1}$</th>
<th>$\frac{1}{a-x}$ litre mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>20.67</td>
<td>0</td>
<td>0</td>
<td>0.2383</td>
<td>4.196</td>
</tr>
<tr>
<td>1</td>
<td>12.4551</td>
<td>17.65</td>
<td>14.17</td>
<td>31.4</td>
<td>0.1634</td>
<td>6.122</td>
</tr>
<tr>
<td>2</td>
<td>12.4289</td>
<td>14.29</td>
<td>11.50</td>
<td>44.36</td>
<td>0.1326</td>
<td>7.542</td>
</tr>
<tr>
<td>3</td>
<td>11.4099</td>
<td>11.49</td>
<td>10.07</td>
<td>51.28</td>
<td>0.1161</td>
<td>8.163</td>
</tr>
<tr>
<td>4</td>
<td>10.9789</td>
<td>9.67</td>
<td>8.81</td>
<td>57.38</td>
<td>0.1016</td>
<td>9.844</td>
</tr>
<tr>
<td>5</td>
<td>11.1380</td>
<td>8.69</td>
<td>7.80</td>
<td>62.26</td>
<td>0.0899</td>
<td>11.119</td>
</tr>
<tr>
<td>7</td>
<td>11.2831</td>
<td>7.75</td>
<td>6.87</td>
<td>66.76</td>
<td>0.0792</td>
<td>12.624</td>
</tr>
<tr>
<td>10</td>
<td>10.3359</td>
<td>5.84</td>
<td>5.65</td>
<td>72.66</td>
<td>0.0651</td>
<td>15.350</td>
</tr>
<tr>
<td>15</td>
<td>11.8870</td>
<td>5.72</td>
<td>4.81</td>
<td>76.73</td>
<td>0.0555</td>
<td>18.031</td>
</tr>
<tr>
<td>20</td>
<td>12.1757</td>
<td>4.68</td>
<td>3.84</td>
<td>81.42</td>
<td>0.0443</td>
<td>22.586</td>
</tr>
<tr>
<td>30</td>
<td>11.7760</td>
<td>3.34</td>
<td>2.84</td>
<td>86.26</td>
<td>0.0327</td>
<td>30.359</td>
</tr>
<tr>
<td>40</td>
<td>12.3644</td>
<td>3.08</td>
<td>2.49</td>
<td>87.95</td>
<td>0.0287</td>
<td>34.831</td>
</tr>
<tr>
<td>62</td>
<td>11.3232</td>
<td>2.28</td>
<td>2.01</td>
<td>90.27</td>
<td>0.0232</td>
<td>43.450</td>
</tr>
<tr>
<td>81</td>
<td>10.9461</td>
<td>1.40</td>
<td>1.28</td>
<td>93.81</td>
<td>0.0148</td>
<td>67.759</td>
</tr>
<tr>
<td>104</td>
<td>11.7355</td>
<td>2.28</td>
<td>1.94</td>
<td>90.60</td>
<td>0.0224</td>
<td>44.707</td>
</tr>
</tbody>
</table>

$k_1 = 2.08 \times 10^{-2}$ litre mole$^{-1}$ sec$^{-1}$

$k_2 = 1.23 \times 10^{-2}$ litre mole$^{-1}$ sec$^{-1}$
Ether Exchange Reactions

Reaction between \([-\underset{SO_2}{\text{O}}\underset{\text{O}}{\text{O}}}\) \(_n\) (15g) and
\([\underset{\text{O}}{\text{O}}}S\text{O}_2\text{O}\cdot\underset{\text{O}}{\text{O}}\text{S}_2\text{O}\cdot\underset{\text{O}}{\text{O}}\) \((-\text{OK})\) (13.038 g) in sulpholane (439.3g) at 156°

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>([\text{RV}]) (_{25^\circ})</th>
<th>(\frac{\text{DP}}{t})</th>
<th>(\frac{\text{DP}}{c})</th>
<th>Conc(_n) of ether links (_1) moles litre (^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.00</td>
<td>179.00</td>
<td>0.15891</td>
</tr>
<tr>
<td>2</td>
<td>0.620</td>
<td>141.97</td>
<td>141.55</td>
<td>0.15868</td>
</tr>
<tr>
<td>4</td>
<td>0.562</td>
<td>122.42</td>
<td>121.79</td>
<td>0.15849</td>
</tr>
<tr>
<td>6</td>
<td>0.499</td>
<td>102.32</td>
<td>101.47</td>
<td>0.15823</td>
</tr>
<tr>
<td>8</td>
<td>0.458</td>
<td>89.91</td>
<td>88.92</td>
<td>0.15801</td>
</tr>
<tr>
<td>10</td>
<td>0.427</td>
<td>80.89</td>
<td>79.80</td>
<td>0.15780</td>
</tr>
<tr>
<td>13</td>
<td>0.387</td>
<td>69.74</td>
<td>68.52</td>
<td>0.15747</td>
</tr>
<tr>
<td>15</td>
<td>0.368</td>
<td>64.64</td>
<td>63.36</td>
<td>0.15728</td>
</tr>
<tr>
<td>20</td>
<td>0.332</td>
<td>55.34</td>
<td>53.96</td>
<td>0.15684</td>
</tr>
<tr>
<td>35</td>
<td>0.244</td>
<td>34.78</td>
<td>33.17</td>
<td>0.15499</td>
</tr>
<tr>
<td>53</td>
<td>0.205</td>
<td>26.75</td>
<td>25.04</td>
<td>0.15342</td>
</tr>
<tr>
<td>82</td>
<td>0.173</td>
<td>20.70</td>
<td>18.94</td>
<td>0.15137</td>
</tr>
<tr>
<td>170</td>
<td>0.119</td>
<td>11.78</td>
<td>9.91</td>
<td>0.14367</td>
</tr>
</tbody>
</table>

Density of solution = 1.155 g/ml
Concentration of polymer = 3.21% \(\text{ww}\) = 37.075 g/litre
\(k\) (zero order) = \(1.61 \times 10^{-6}\) mole litre \(^{-1}\) sec \(^{-1}\)
Conc\(_n\) OK dimer = 0.02584 mole in 467.29 g (404.59 ml)

\[\text{Conc}_n \text{ OK dimer} = 0.063868 \text{ moles/litre}\]

\[\text{Conc}_n \text{ ether links} = 0.15891 \text{ moles/litre}\]

\[\therefore k\) (second order) = \(\frac{1.61 \times 10^{-6}}{0.063868 \times 0.15891} = 1.59 \times 10^{-4}\) litre mole \(^{-1}\) sec \(^{-1}\)\]
Reaction between \( [\text{O} - \text{SO}_2 - \text{O}]_0 n \) (15\%) and \( [\text{O} - \text{SO}_2 - \text{O} - \text{SO}_2 - \text{O}]_0 \text{OK} \) (13.0383) in sulfolane (439.3 g) at 174°

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>([RV]_{25^\circ} ) % DMF</th>
<th>(\overline{DP}_t)</th>
<th>(\overline{DP}_c)</th>
<th>Conc(^n) of ether links, moles litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.00</td>
<td>179.00</td>
<td>0.15671</td>
</tr>
<tr>
<td>2</td>
<td>0.529</td>
<td>111.74</td>
<td>110.99</td>
<td>0.15617</td>
</tr>
<tr>
<td>4</td>
<td>0.421</td>
<td>79.18</td>
<td>78.07</td>
<td>0.15558</td>
</tr>
<tr>
<td>6</td>
<td>0.357</td>
<td>61.75</td>
<td>60.44</td>
<td>0.15499</td>
</tr>
<tr>
<td>8</td>
<td>0.308</td>
<td>49.42</td>
<td>47.97</td>
<td>0.15431</td>
</tr>
<tr>
<td>10</td>
<td>0.288</td>
<td>44.66</td>
<td>43.16</td>
<td>0.15394</td>
</tr>
<tr>
<td>12</td>
<td>0.260</td>
<td>38.28</td>
<td>36.70</td>
<td>0.15330</td>
</tr>
<tr>
<td>15</td>
<td>0.223</td>
<td>30.37</td>
<td>28.70</td>
<td>0.15210</td>
</tr>
<tr>
<td>20</td>
<td>0.196</td>
<td>24.99</td>
<td>23.27</td>
<td>0.15082</td>
</tr>
<tr>
<td>35</td>
<td>0.141</td>
<td>15.21</td>
<td>13.38</td>
<td>0.14581</td>
</tr>
<tr>
<td>50</td>
<td>0.127</td>
<td>12.99</td>
<td>11.13</td>
<td>0.14344</td>
</tr>
<tr>
<td>81</td>
<td>0.109</td>
<td>10.32</td>
<td>8.43</td>
<td>0.13890</td>
</tr>
<tr>
<td>180</td>
<td>0.079</td>
<td>6.35</td>
<td>4.42</td>
<td>0.12193</td>
</tr>
</tbody>
</table>

Density of solution = 1.139 g/ml

Polymer concentration = 3.21 % w/w = 36.562 g/litre

\( k \) (zero order) = \( 5.12 \times 10^{-6} \) mole litre\(^{-1}\) sec\(^{-1}\)

\( \text{Conc}^n \) OK end groups = 0.02584 mole in 467.3 g (410.3 ml) = 0.06298 mole/litre

\( \text{Conc}^n \) ether links = 0.15671 mole/litre

\( k \) (second order) = \( \frac{5.12 \times 10^{-6}}{0.06298 \times 0.15671} = 5.19 \times 10^4 \) litre mole\(^{-1}\) sec\(^{-1}\)
Fluoride Cleavage Reactions

Reaction of [-\(\text{SO}_2\text{O}^-\)]\(\_\) with KF (2.5 g) in sulpholane (175.5 g) at 200°

The actual polymer concentration (some polymer solution was not added to the sulpholane/KF solution saturated solution) was 4.98% ww. Taking the density as 1.1305 g/ml the polymer concentration is 56.2989 g/litre.
The polymer used in this experiment had methoxyl end groups and \([\text{RV}]^{1\%}_{25^\circ} = 1.36\). \(\overline{DP}\) and concentration of ether links were calculated using computer programme 3.

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>([\text{RV}]^{1%}_{25^\circ})</th>
<th>(\overline{DP})</th>
<th>Conc^n of ether links</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.36</td>
<td>464.24</td>
<td>0.24215</td>
</tr>
<tr>
<td>3</td>
<td>1.09</td>
<td>332.49</td>
<td>0.24194</td>
</tr>
<tr>
<td>6</td>
<td>0.96</td>
<td>274.53</td>
<td>0.24178</td>
</tr>
<tr>
<td>9</td>
<td>0.84</td>
<td>224.45</td>
<td>0.24159</td>
</tr>
<tr>
<td>12</td>
<td>0.76</td>
<td>193.00</td>
<td>0.24141</td>
</tr>
<tr>
<td>15</td>
<td>0.69</td>
<td>166.83</td>
<td>0.24121</td>
</tr>
<tr>
<td>20</td>
<td>0.61</td>
<td>138.53</td>
<td>0.24092</td>
</tr>
<tr>
<td>30</td>
<td>0.50</td>
<td>102.63</td>
<td>0.24030</td>
</tr>
<tr>
<td>45</td>
<td>0.41</td>
<td>76.08</td>
<td>0.23948</td>
</tr>
<tr>
<td>60</td>
<td>0.38</td>
<td>67.84</td>
<td>0.23909</td>
</tr>
<tr>
<td>180</td>
<td>0.33</td>
<td>54.84</td>
<td>0.23824</td>
</tr>
<tr>
<td>1440</td>
<td>0.26</td>
<td>38.28</td>
<td>0.23633</td>
</tr>
<tr>
<td>3165</td>
<td>0.26</td>
<td>38.28</td>
<td>0.23633</td>
</tr>
</tbody>
</table>

Evaluation of the first order rate constant over the initial reaction using computer programme 4 (see Part 5) gives an average value of \(k = 4.24 \times 10^{-6} \text{ sec}^{-1}\).
Reaction of \(-\overset{\cdot}\text{C}=-\overset{\cdot}\text{SO}_2\overset{\cdot}\text{C}=-\overset{\cdot}\text{O}\) (14g) with KF (3.5g) in sulpholane (258g) at 200°

The polymer used had fluorine end groups and the actual concentration was 5.10 % ww. Taking density of 1.1305 g/l the concentration is 57.720 g/litre. The DP and concentration of ether links were calculated using computer programme 3.

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>[RV](_{25\degree})%</th>
<th>DP</th>
<th>Conc(<em>{1}) of ether links (</em>{1}) moles litre(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.841</td>
<td>224.85</td>
<td>0.24769</td>
</tr>
<tr>
<td>4</td>
<td>0.778</td>
<td>199.94</td>
<td>0.24755</td>
</tr>
<tr>
<td>6</td>
<td>0.740</td>
<td>185.39</td>
<td>0.24745</td>
</tr>
<tr>
<td>9</td>
<td>0.686</td>
<td>165.37</td>
<td>0.24729</td>
</tr>
<tr>
<td>12</td>
<td>0.637</td>
<td>147.88</td>
<td>0.24711</td>
</tr>
<tr>
<td>15</td>
<td>0.610</td>
<td>138.53</td>
<td>0.24699</td>
</tr>
<tr>
<td>20</td>
<td>0.555</td>
<td>120.13</td>
<td>0.24672</td>
</tr>
<tr>
<td>30</td>
<td>0.487</td>
<td>98.63</td>
<td>0.24627</td>
</tr>
<tr>
<td>45</td>
<td>0.448</td>
<td>86.97</td>
<td>0.23593</td>
</tr>
<tr>
<td>60</td>
<td>0.411</td>
<td>76.36</td>
<td>0.24553</td>
</tr>
<tr>
<td>120</td>
<td>0.358</td>
<td>62.01</td>
<td>0.24478</td>
</tr>
<tr>
<td>180</td>
<td>0.339</td>
<td>57.11</td>
<td>0.24444</td>
</tr>
<tr>
<td>1440</td>
<td>0.287</td>
<td>45.13</td>
<td>0.24329</td>
</tr>
<tr>
<td>3060</td>
<td>0.293</td>
<td>45.13</td>
<td>0.24328</td>
</tr>
</tbody>
</table>

Average first order rate constant over initial reaction is \(k = 3.33 \times 10^{-6} \text{ sec}^{-1}\)
Reaction of \(-[-(\mathrm{SO}_2-\mathrm{O})_n-]-(11g)\) with KF (2.5g) in sulpholane (200g) at 200°.

Concentration of fluorine ended polymer was actually 5.12 % ww. Taking density as 1.1305 g/ml the polymer concentration was 57.881 g/litre.

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>[RV] 1% 25°</th>
<th>DF</th>
<th>Conc(^n) of ether links(^1) moles litre(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.84</td>
<td>224.85</td>
<td>0.24838</td>
</tr>
<tr>
<td>5</td>
<td>0.76</td>
<td>193.00</td>
<td>0.24819</td>
</tr>
<tr>
<td>10</td>
<td>0.70</td>
<td>170.49</td>
<td>0.24802</td>
</tr>
<tr>
<td>15</td>
<td>0.64</td>
<td>148.93</td>
<td>0.24781</td>
</tr>
<tr>
<td>20</td>
<td>0.59</td>
<td>131.74</td>
<td>0.24759</td>
</tr>
<tr>
<td>30</td>
<td>0.53</td>
<td>112.06</td>
<td>0.24726</td>
</tr>
<tr>
<td>60</td>
<td>0.42</td>
<td>78.90</td>
<td>0.24632</td>
</tr>
<tr>
<td>135</td>
<td>0.35</td>
<td>59.93</td>
<td>0.24532</td>
</tr>
<tr>
<td>300</td>
<td>0.32</td>
<td>52.35</td>
<td>0.24472</td>
</tr>
<tr>
<td>1290</td>
<td>0.29</td>
<td>45.13</td>
<td>0.24396</td>
</tr>
<tr>
<td>1440</td>
<td>0.28</td>
<td>42.80</td>
<td>0.24366</td>
</tr>
<tr>
<td>3704</td>
<td>0.28</td>
<td>42.80</td>
<td>0.24366</td>
</tr>
</tbody>
</table>

Average first order rate constant over the initial reaction is 2.74 x 10\(^{-6}\) sec\(^{-1}\).
Reaction of \(-\left(\text{CF}_{2}\text{CF}_{2}\right)_{n} 0\) \((20g, 0.0862\) mole) with KF \((5g)\) in sulpholane \((507.4g)\) with \(\text{CF}_{2}\text{CF}_{2}\text{SO}_{2}\text{CF}_{2}\) \((44 g, 0.172\) mole) at \(200^\circ\)

The polymer used had chlorine end groups. Polymer concentration was 3.47 \% \text{ww}, which corresponds to 39.221 \text{g/litre} taking density as 1.1304 \text{g/cc}. (graph 21).

\(\overline{DP_t}, \overline{DP_c}\) and concentration of ether links were evaluated using computer programme 5 (see Part 5 and Appendix).

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>[RV] (^{1}%_{25^\circ})</th>
<th>(\overline{DP_t})</th>
<th>(\overline{DP_c})</th>
<th>Conc(^n) of ether links \text{moles litre} (^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.00</td>
<td>179.00</td>
<td>0.16811</td>
</tr>
<tr>
<td>15</td>
<td>0.489</td>
<td>99.25</td>
<td>98.80</td>
<td>0.16734</td>
</tr>
<tr>
<td>30</td>
<td>0.375</td>
<td>66.50</td>
<td>65.87</td>
<td>0.16649</td>
</tr>
<tr>
<td>45</td>
<td>0.301</td>
<td>47.74</td>
<td>47.00</td>
<td>0.16546</td>
</tr>
<tr>
<td>60</td>
<td>0.262</td>
<td>38.72</td>
<td>37.94</td>
<td>0.16460</td>
</tr>
<tr>
<td>120</td>
<td>0.173</td>
<td>20.70</td>
<td>19.82</td>
<td>0.16053</td>
</tr>
<tr>
<td>180</td>
<td>0.135</td>
<td>14.24</td>
<td>13.32</td>
<td>0.15637</td>
</tr>
<tr>
<td>300</td>
<td>0.107</td>
<td>10.03</td>
<td>9.09</td>
<td>0.15045</td>
</tr>
<tr>
<td>390</td>
<td>0.093</td>
<td>8.12</td>
<td>7.16</td>
<td>0.14546</td>
</tr>
<tr>
<td>1324</td>
<td>0.061</td>
<td>4.30</td>
<td>3.32</td>
<td>0.11816</td>
</tr>
<tr>
<td>1822</td>
<td>0.055</td>
<td>3.68</td>
<td>2.70</td>
<td>0.10637</td>
</tr>
</tbody>
</table>

From the graph (time versus concentration of ether links) the zero order rate constant is

\(k = 0.97 \times 10^{-6} \text{ mole litre}^{-1} \text{sec}^{-1}\)
Reaction of \([-\{-\{\text{SO}_2\}-\{\text{O}\} \}_{n}\] with KF (5.0 g) in sulfolane (380 g) with F-\{-\{\text{SO}_2\}-\{\text{O}\} \}_{2}\text{F} (44 g) at 200°C

Polymer concentration was actually 4.465 % ww which is equal to 50.65 g/litre taking density as 1.1344 g/ml

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>([\text{RV}]^{1%}_{25^\circ})</th>
<th>(\overline{\text{DP}}_t)</th>
<th>(\overline{\text{DP}}_c)</th>
<th>Conc:(n) of ether links(^{1}) moles litre(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.00</td>
<td>179.00</td>
<td>0.21710</td>
</tr>
<tr>
<td>3</td>
<td>0.662</td>
<td>156.72</td>
<td>156.60</td>
<td>0.21693</td>
</tr>
<tr>
<td>5</td>
<td>0.603</td>
<td>136.14</td>
<td>135.90</td>
<td>0.21672</td>
</tr>
<tr>
<td>15</td>
<td>0.427</td>
<td>80.89</td>
<td>80.34</td>
<td>0.21561</td>
</tr>
<tr>
<td>20</td>
<td>0.381</td>
<td>68.11</td>
<td>67.49</td>
<td>0.21509</td>
</tr>
<tr>
<td>30</td>
<td>0.311</td>
<td>50.15</td>
<td>49.43</td>
<td>0.21391</td>
</tr>
<tr>
<td>40</td>
<td>0.264</td>
<td>39.17</td>
<td>38.39</td>
<td>0.21264</td>
</tr>
<tr>
<td>60</td>
<td>0.211</td>
<td>27.93</td>
<td>27.09</td>
<td>0.21026</td>
</tr>
<tr>
<td>91</td>
<td>0.161</td>
<td>18.58</td>
<td>17.68</td>
<td>0.20598</td>
</tr>
<tr>
<td>130</td>
<td>0.143</td>
<td>15.54</td>
<td>14.62</td>
<td>0.20339</td>
</tr>
<tr>
<td>180</td>
<td>0.117</td>
<td>11.48</td>
<td>10.54</td>
<td>0.19671</td>
</tr>
<tr>
<td>360</td>
<td>0.081</td>
<td>6.59</td>
<td>5.63</td>
<td>0.17954</td>
</tr>
<tr>
<td>1320</td>
<td>0.054</td>
<td>3.58</td>
<td>2.60</td>
<td>0.13422</td>
</tr>
</tbody>
</table>

From a graphical plot \(k\) (zero order) =

\[1.64 \times 10^{-6} \text{ mole litre}^{-1} \text{ sec}^{-1}\]
Reaction of \([ -\left\{ \begin{array}{c}
\text{SO}_2 - \text{O} \\
\text{SO}_2 \\
\end{array} \right\} _n \] \text{O} - \] \text{K}^+ \text{F}^- (20g) with \text{KF} (5g) in sulphotane (336g) with \text{F}^+ - \text{SO}_2 - \text{F}^- (44g) at 200° C.

The actual polymer concentration was 4.94% ww which corresponds to 56.138 g/litre taking the density of the solution as 1.1364 g/ml.

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>[RV] \text{1%}^{25^0}</th>
<th>DP_t</th>
<th>DP_c</th>
<th>Conc^n of ether link$^a$ mole litre$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.00</td>
<td>179.00</td>
<td>0.24062</td>
</tr>
<tr>
<td>15</td>
<td>0.467</td>
<td>92.54</td>
<td>92.11</td>
<td>0.23935</td>
</tr>
<tr>
<td>30</td>
<td>0.329</td>
<td>54.59</td>
<td>53.90</td>
<td>0.23748</td>
</tr>
<tr>
<td>45</td>
<td>0.276</td>
<td>41.88</td>
<td>41.12</td>
<td>0.23609</td>
</tr>
<tr>
<td>60</td>
<td>0.231</td>
<td>32.02</td>
<td>31.20</td>
<td>0.23422</td>
</tr>
<tr>
<td>120</td>
<td>0.163</td>
<td>18.93</td>
<td>18.03</td>
<td>0.22856</td>
</tr>
<tr>
<td>180</td>
<td>0.124</td>
<td>12.53</td>
<td>11.60</td>
<td>0.22111</td>
</tr>
<tr>
<td>240</td>
<td>0.110</td>
<td>10.46</td>
<td>9.52</td>
<td>0.21655</td>
</tr>
<tr>
<td>300</td>
<td>0.102</td>
<td>9.33</td>
<td>8.38</td>
<td>0.21311</td>
</tr>
<tr>
<td>379</td>
<td>0.095</td>
<td>8.38</td>
<td>7.43</td>
<td>0.20941</td>
</tr>
<tr>
<td>1326</td>
<td>0.052</td>
<td>3.38</td>
<td>2.40</td>
<td>0.14103</td>
</tr>
<tr>
<td>1735</td>
<td>0.050</td>
<td>3.18</td>
<td>2.20</td>
<td>0.13208</td>
</tr>
</tbody>
</table>

From the graph $k = 1.48 \times 10^{-6}$ mole litre$^{-1}$ sec$^{-1}$
Reaction of \([-\left(\begin{array}{c} \circ \end{array}\right)_n - \text{SO}_2 - \left(\begin{array}{c} \circ \end{array}\right)_n - 0\text{-}]\) with KF (5g) in sulpholane (269.3 g) with F-\(\left(\begin{array}{c} \circ \end{array}\right)\text{SO}_2 \left(\begin{array}{c} \circ \end{array}\right)\text{-F}\) (44g) at 200°

The actual polymer concentration was 5.95% w/w which corresponds to 67.866 g/litre taking the density as 1.1406 g/ml

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>[RV] 25°</th>
<th>DP_t</th>
<th>DP_c</th>
<th>Conc^n of ether links moles litre^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.00</td>
<td>179.00</td>
<td>0.29089</td>
</tr>
<tr>
<td>15</td>
<td>0.520</td>
<td>108.89</td>
<td>108.50</td>
<td>0.28983</td>
</tr>
<tr>
<td>30</td>
<td>0.391</td>
<td>70.83</td>
<td>70.22</td>
<td>0.28836</td>
</tr>
<tr>
<td>45</td>
<td>0.316</td>
<td>51.37</td>
<td>50.66</td>
<td>0.28675</td>
</tr>
<tr>
<td>68</td>
<td>0.248</td>
<td>35.64</td>
<td>34.86</td>
<td>0.28413</td>
</tr>
<tr>
<td>120</td>
<td>0.183</td>
<td>22.54</td>
<td>21.66</td>
<td>0.27902</td>
</tr>
<tr>
<td>180</td>
<td>0.145</td>
<td>15.86</td>
<td>14.95</td>
<td>0.27296</td>
</tr>
<tr>
<td>240</td>
<td>0.122</td>
<td>12.23</td>
<td>11.29</td>
<td>0.26663</td>
</tr>
<tr>
<td>300</td>
<td>0.109</td>
<td>10.32</td>
<td>9.37</td>
<td>0.26132</td>
</tr>
<tr>
<td>390</td>
<td>0.095</td>
<td>8.38</td>
<td>7.43</td>
<td>0.25316</td>
</tr>
<tr>
<td>1324</td>
<td>0.054</td>
<td>3.58</td>
<td>2.60</td>
<td>0.17984</td>
</tr>
<tr>
<td>1818</td>
<td>0.052</td>
<td>3.38</td>
<td>2.40</td>
<td>0.17049</td>
</tr>
</tbody>
</table>

From the graph \(k = 1.61 \times 10^{-6} \text{ mole litre}^{-1} \text{ sec}^{-1}\)
Reaction of \(-\left[\begin{array}{c} \text{S} \end{array}\right]_{n}-\text{O}-\left(20g\right)\) with KF (5g) in sulfolane (206.7 g) with \(\text{F}-\left[\begin{array}{c} \text{SO}_2 \end{array}\right]-\text{F}\) (44g) at 200°

Actual polymer concentration was 7.32 %wt which corresponds to 83.860 g/litre taking density as 1.1461 g/ml

| Time in minutes | [RV] \(1{\%}\) 
25\textdegree | \(\overline{DF}_T\) | \(\overline{DF}_C\) | Conc\(^n\) of ether links
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.00</td>
<td>179.00</td>
</tr>
<tr>
<td>5</td>
<td>0.670</td>
<td>159.59</td>
<td>159.48</td>
</tr>
<tr>
<td>10</td>
<td>0.592</td>
<td>132.41</td>
<td>132.15</td>
</tr>
<tr>
<td>15</td>
<td>0.573</td>
<td>126.05</td>
<td>125.76</td>
</tr>
<tr>
<td>20</td>
<td>0.532</td>
<td>112.70</td>
<td>112.33</td>
</tr>
<tr>
<td>31</td>
<td>0.485</td>
<td>98.02</td>
<td>97.57</td>
</tr>
<tr>
<td>40</td>
<td>0.438</td>
<td>84.05</td>
<td>83.52</td>
</tr>
<tr>
<td>60</td>
<td>0.382</td>
<td>68.38</td>
<td>67.77</td>
</tr>
<tr>
<td>120</td>
<td>0.297</td>
<td>46.78</td>
<td>46.04</td>
</tr>
<tr>
<td>210</td>
<td>0.207</td>
<td>27.14</td>
<td>26.29</td>
</tr>
<tr>
<td>300</td>
<td>0.169</td>
<td>19.99</td>
<td>19.10</td>
</tr>
<tr>
<td>390</td>
<td>0.148</td>
<td>16.36</td>
<td>15.45</td>
</tr>
<tr>
<td>1336</td>
<td>0.079</td>
<td>6.35</td>
<td>5.38</td>
</tr>
<tr>
<td>1548</td>
<td>0.072</td>
<td>5.52</td>
<td>4.55</td>
</tr>
<tr>
<td>1821</td>
<td>0.060</td>
<td>4.19</td>
<td>3.22</td>
</tr>
</tbody>
</table>

From the graph the zero order rate constant is \(9.1 \times 10^{-7}\) mole litre\(^{-1}\) sec\(^{-1}\)
The actual polymer concentration was 7.76% ww which corresponds to 89.085 g/litre taking the density as 1.148 g/ml

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>$[^{13}]^{25\circ}$</th>
<th>$D\bar{F}_t$</th>
<th>$D\bar{F}_c$</th>
<th>Conc. of ether links, moles litre$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.00</td>
<td>179.00</td>
<td>0.38184</td>
</tr>
<tr>
<td>15</td>
<td>0.638</td>
<td>148.23</td>
<td>148.06</td>
<td>0.38139</td>
</tr>
<tr>
<td>30</td>
<td>0.452</td>
<td>88.14</td>
<td>87.63</td>
<td>0.37960</td>
</tr>
<tr>
<td>45</td>
<td>0.359</td>
<td>62.27</td>
<td>61.62</td>
<td>0.37776</td>
</tr>
<tr>
<td>60</td>
<td>0.292</td>
<td>45.60</td>
<td>44.85</td>
<td>0.37543</td>
</tr>
<tr>
<td>120</td>
<td>0.199</td>
<td>25.57</td>
<td>24.72</td>
<td>0.36845</td>
</tr>
<tr>
<td>194</td>
<td>0.145</td>
<td>15.86</td>
<td>14.95</td>
<td>0.35831</td>
</tr>
<tr>
<td>240</td>
<td>0.131</td>
<td>13.61</td>
<td>12.69</td>
<td>0.35372</td>
</tr>
<tr>
<td>300</td>
<td>0.111</td>
<td>10.60</td>
<td>9.66</td>
<td>0.34424</td>
</tr>
<tr>
<td>383</td>
<td>0.107</td>
<td>10.03</td>
<td>9.09</td>
<td>0.34173</td>
</tr>
<tr>
<td>1329</td>
<td>0.055</td>
<td>3.68</td>
<td>2.70</td>
<td>0.24161</td>
</tr>
<tr>
<td>1739</td>
<td>0.058</td>
<td>3.98</td>
<td>3.01</td>
<td>0.25621</td>
</tr>
</tbody>
</table>

From the graph of time versus concentration of ether links the zero order rate constant is $k = 19.5 \times 10^{-7}$ mole litre$^{-1}$ sec$^{-1}$
The concentration of fluoride ion at the end of the experiment was 0.010 moles/litre (by analysis). Initial concentration was 0.010 + 0.00187 = 0.1187 moles/litre, where 0.00187 was the change in ether link concentration during the reaction as calculated from the RV measurements.

The $\overline{DF}$ and ether link concentration at each time was calculated from the RV using programme 3; and second order rate constant using programme 6.

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>$[RV]_{25^\circ}$</th>
<th>$\overline{DF}$</th>
<th>Concentration of ether links $[n]$</th>
<th>Second order rate constant $k_2$ (litre mole$^{-1}$ sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.00</td>
<td>0.24034</td>
<td></td>
</tr>
<tr>
<td>1 $\frac{1}{2}$</td>
<td>0.688</td>
<td>166.10</td>
<td>0.24024</td>
<td>$3.13 \times 10^{-4}$</td>
</tr>
<tr>
<td>3</td>
<td>0.665</td>
<td>157.79</td>
<td>0.24016</td>
<td>$3.53 \times 10^{-4}$</td>
</tr>
<tr>
<td>6</td>
<td>0.608</td>
<td>137.84</td>
<td>0.23994</td>
<td>$3.36 \times 10^{-4}$</td>
</tr>
<tr>
<td>9</td>
<td>0.591</td>
<td>132.07</td>
<td>0.23986</td>
<td>$3.18 \times 10^{-4}$</td>
</tr>
<tr>
<td>12</td>
<td>0.564</td>
<td>123.08</td>
<td>0.23973</td>
<td>$3.10 \times 10^{-4}$</td>
</tr>
<tr>
<td>15</td>
<td>0.552</td>
<td>119.15</td>
<td>0.23966</td>
<td>$3.06 \times 10^{-4}$</td>
</tr>
<tr>
<td>18</td>
<td>0.532</td>
<td>112.70</td>
<td>0.23955</td>
<td>$2.97 \times 10^{-4}$</td>
</tr>
<tr>
<td>21</td>
<td>0.502</td>
<td>103.25</td>
<td>0.23935</td>
<td>$2.88 \times 10^{-4}$</td>
</tr>
<tr>
<td>25</td>
<td>0.484</td>
<td>97.72</td>
<td>0.23922</td>
<td>$2.81 \times 10^{-4}$</td>
</tr>
<tr>
<td>30</td>
<td>0.464</td>
<td>92.89</td>
<td>0.23909</td>
<td>$2.69 \times 10^{-4}$</td>
</tr>
<tr>
<td>45</td>
<td>0.424</td>
<td>80.04</td>
<td>0.23867</td>
<td>$2.24 \times 10^{-4}$</td>
</tr>
<tr>
<td>60</td>
<td>0.418</td>
<td>78.33</td>
<td>0.23860</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.418</td>
<td>78.33</td>
<td>0.23860</td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>0.416</td>
<td>77.77</td>
<td>0.23858</td>
<td></td>
</tr>
<tr>
<td>360</td>
<td>0.407</td>
<td>75.25</td>
<td>0.23848</td>
<td></td>
</tr>
<tr>
<td>1440</td>
<td>0.406</td>
<td>74.97</td>
<td>0.23847</td>
<td></td>
</tr>
</tbody>
</table>
Reaction of \( \left( \frac{\text{SO}_2}{\text{O}} \right)_n \) with \((\text{C}_2\text{H}_5)\text{NF (5 g)}\) in sulphonate (374 g) at 200°.

Concentration of fluoride ion at end of reaction (by analysis) was 0.052 moles/litre. The concentration at the start was 0.052 + 0.01268 = 0.06468 moles/litre.

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>[RV]_{250} %</th>
<th>DF</th>
<th>Conc of ether links moles/litre</th>
<th>Second order rate constant litre mole (^{-1}) sec(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.723</td>
<td>179.00</td>
<td>0.24252</td>
<td>8.36 \times 10^{-3}</td>
</tr>
<tr>
<td>1</td>
<td>0.212</td>
<td>28.13</td>
<td>0.23522</td>
<td>4.77 \times 10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>0.198</td>
<td>25.38</td>
<td>0.23427</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.187</td>
<td>23.28</td>
<td>0.23341</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>0.185</td>
<td>22.91</td>
<td>0.23324</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.171</td>
<td>20.35</td>
<td>0.23189</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.170</td>
<td>20.17</td>
<td>0.23179</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.169</td>
<td>19.99</td>
<td>0.23168</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.162</td>
<td>18.75</td>
<td>0.23088</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.150</td>
<td>16.70</td>
<td>0.22928</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>0.154</td>
<td>17.37</td>
<td>0.22984</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>0.150</td>
<td>16.70</td>
<td>0.22928</td>
<td></td>
</tr>
<tr>
<td>1140</td>
<td>0.154</td>
<td>17.37</td>
<td>0.22984</td>
<td></td>
</tr>
<tr>
<td>1440</td>
<td>0.154</td>
<td>17.37</td>
<td>0.22984</td>
<td></td>
</tr>
<tr>
<td>1560</td>
<td>0.156</td>
<td>17.37</td>
<td>0.22984</td>
<td></td>
</tr>
</tbody>
</table>
PHYSICAL PROPERTIES

Preparation of Mouldings

The following technique was used to give bubble free mouldings.

The required amount of dry polymer powder (28 g for a 4" x 2" x 1/8" moulding) was pressed into film at 300° between sheets of 0.010" aluminium foil. The pressing was carried out at 20 tons pressure in an electrically heated press. After 3 minutes the film was cooled to 150° in the press. The film was removed from the press and cut up into pieces to fit the template. The film pieces were freed of dust by means of compressed air and then redried overnight. The drying was either in a pistol at 140° under high vacuum (<0.001 mm) or in an oven at 160° at 0.5 mm. The film was then placed in a template between stainless steel or chromium plated glazing plates and pressed at 320°. The pressure was raised to 5 tons for 2 minutes (preheat), released, raised to 10 tons, released raised to 15 tons, released and finally raised to 20 tons and kept there for 5 minutes. This allows any air bubbles to be released from the moulding. The moulding was cooled to 150° in the press (at 20 tons pressure) and then removed.

Density measurements

Two density samples (1" x 3/4" x 1/8") were prepared as described above using 1.7 g of film for each moulding. The samples were cooled to 150° in the press and then removed rapidly from the template and cooled further to room temperature in a vacuum dessicator over phosphorous pentoxide.
The samples were then weighed in air and then in water. The weighings in water were carried out by suspending the sample from a preweighed 44 SWG wire. The density was then calculated as shown on the next page. The temperature of the water was measured by means of a 0-40° thermometer.

The average figure for this polymer (10 mole % 0, p' copolymer) was then 1.3656 g/cc.

Measurement of intrinsic viscosity

Intrinsic viscosity was measured by determining reduced viscosity, RV, and inherent viscosity, \( \eta_I \) at 4 concentrations up to 1g/100ml in N,N-dimethyl formamide solution. The RV and \( \eta_I \) were then plotted against polymer concentration and the line extrapolated to zero concentration. The 2 intercepts were averaged to give a figure for the intrinsic viscosity, \( \langle \eta \rangle \). Definitions of the terms used are shown below.

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative viscosity</td>
<td>( \eta_{\text{rel}} )</td>
<td>( \frac{\eta_s}{\eta_o} = \frac{\tau_s}{\tau_o} )</td>
</tr>
<tr>
<td>Specific viscosity</td>
<td>( \eta_{\text{sp}} )</td>
<td>( \frac{\eta_s - \eta_o}{\eta_o} = \frac{\tau_s - \tau_o}{\tau_o} = \eta_{\text{rel}}^{-1} )</td>
</tr>
<tr>
<td>Reduced viscosity</td>
<td>( \eta_{\text{rel}} ) (or RV)</td>
<td>( \frac{\eta_{\text{sp}}}{C} = \frac{\tau_s - \tau_o}{\tau_o} )</td>
</tr>
<tr>
<td>Inherent viscosity</td>
<td>( \eta_I )</td>
<td>( \frac{2 \cdot 303}{C} \log_{10} \eta_{\text{rel}} )</td>
</tr>
<tr>
<td>Intrinsic viscosity</td>
<td>( \langle \eta \rangle )</td>
<td>( \lim_{C \to 0} \frac{\eta_{\text{rel}}}{C} )</td>
</tr>
</tbody>
</table>

\( \eta_s = \) Viscosity of the polymer solution

\( \eta_o = \) Viscosity of the pure solvent

\( C = \) Polymer concentration in g/100ml

\( \tau_s = \) Flow time of polymer solution

\( \tau_o = \) Flow time of pure solvent
<table>
<thead>
<tr>
<th>(1) Weight in air</th>
<th>(2) Weight in water</th>
<th>(3) Weight of wire</th>
<th>(4) (2)-(3) true weight in water</th>
<th>(5) (1)-(4) loss in weight</th>
<th>(6) 5/7 density water</th>
<th>(7) 1/6 density water</th>
<th>(8) Temp water</th>
<th>(9) Density water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4029g</td>
<td>0.3838g</td>
<td>0.0062g</td>
<td>0.3776g</td>
<td>1.0253g</td>
<td>1.0273g</td>
<td>1.3656 g/cc</td>
<td>20.8°</td>
<td>0.9980</td>
</tr>
<tr>
<td>1.3813g</td>
<td>0.3778g</td>
<td>0.0060g</td>
<td>0.3718g</td>
<td>1.0095g</td>
<td>1.0115g</td>
<td>1.3655 g/cc</td>
<td>20.8°</td>
<td>0.9980</td>
</tr>
</tbody>
</table>
Example (\([\text{SO}_2-\text{O-}]_n\) of [RV]_{25\degree}^{1\%} 0.58)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt of polymer in 25ml</td>
<td>0.0697g</td>
<td>0.1220g</td>
<td>0.1892g</td>
<td>0.2395g</td>
</tr>
<tr>
<td>Conc^n g/100ml (%v)</td>
<td>0.2788</td>
<td>0.4880</td>
<td>0.7568</td>
<td>0.9580</td>
</tr>
<tr>
<td>Viscometer No</td>
<td>338</td>
<td>628</td>
<td>696</td>
<td>746</td>
</tr>
<tr>
<td>t o (secs)</td>
<td>261.4</td>
<td>269.8</td>
<td>251.6</td>
<td>255.0</td>
</tr>
<tr>
<td>ts (secs)</td>
<td>296.3</td>
<td>336.3</td>
<td>356.1</td>
<td>395.6</td>
</tr>
<tr>
<td>(\eta_{rel})</td>
<td>1.134</td>
<td>1.247</td>
<td>1.416</td>
<td>1.55</td>
</tr>
<tr>
<td>(\eta_{red})</td>
<td>0.481</td>
<td>0.506</td>
<td>0.550</td>
<td>0.574</td>
</tr>
<tr>
<td>(\eta_1)</td>
<td>0.451</td>
<td>0.453</td>
<td>0.460</td>
<td>0.458</td>
</tr>
</tbody>
</table>

From graph \((\eta) = 0.44\)

Impact Strength Measurements

Notched impact strength was measured on specimens as shown below.

The specimens were tested on a Hounsfield Impact Tester, which is a Charpy type test.
Using this tester the specimens are supported at 2 points 1.5" apart and struck at 2 points equidistant from the notch (points X on diagram) on the edge opposite the notch by a pendulum dropping from a height of 1 foot. From the residual energy of the pendulum the energy required to break the specimen was calculated. The pendulum weight (1/32lb - 2lb) was selected so that a reading of 0.2 to 0.8 was obtained on the tester.

Notched impact strength = \( \frac{R \times w}{d \times t} \times 2.1 \text{ KJ/m}^2 \)

- \( R \) = reading on tester
- \( w \) = pendulum weight used (in lb)
- \( d \) = depth under notch (inches)
- \( t \) = thickness (inches)

2.1 is the conversion factor from ftlb/in² to KJ/m².

Five or six specimens were tested to obtain each impact strength, the median value being taken. An example of the results is shown below.

<table>
<thead>
<tr>
<th>Notch radius</th>
<th>d (inches)</th>
<th>t (inches)</th>
<th>Pendulum weight</th>
<th>Reading</th>
<th>Notched impact strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.080&quot; (2mm)</td>
<td>0.142</td>
<td>0.133</td>
<td>1lb</td>
<td>0.40</td>
<td>44.5</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.138</td>
<td>0.131</td>
<td>&quot;</td>
<td>0.38</td>
<td>44.1</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.140</td>
<td>0.130</td>
<td>&quot;</td>
<td>0.39</td>
<td>45.0</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.135</td>
<td>0.129</td>
<td>&quot;</td>
<td>0.37</td>
<td>44.6</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.141</td>
<td>0.131</td>
<td>&quot;</td>
<td>0.38</td>
<td>43.2</td>
</tr>
</tbody>
</table>
The median value (2 highest and 2 lowest values discarded) is 44.5 KJ/m².

The unnotched impact strength was measured on specimens of the same shape but without the notch. The unnotched specimens were struck on the wide (0.25") face.

**Flexural Modulus Measurements**

Measurements were made on a compression moulded bar of length 12-15cm (length between supports on apparatus is 10 cm) and width 5.5 or 13mm, and thickness 3.2 mm. An example of the load and deflections obtained for a poly(diphenylene ether sulphone) of [RV]_{25}^1{\%} = 0.48 are shown below. The deflections were measured by a drum micrometer which lowered a probe on to the centre of the specimen before and 100 seconds after applying the load. Contact between the probe and specimen was shown by an electronic gauge. The difference in micrometer readings before and 100 seconds after applying the load is the 100 second deflection (δ).

<table>
<thead>
<tr>
<th>Initial reading on micrometer</th>
<th>100 sec reading on micrometer</th>
<th>100 sec deflection (\delta)</th>
<th>Load</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.667 mm</td>
<td>5.942 mm</td>
<td>0.275 mm</td>
<td>50g</td>
<td>20.60°</td>
</tr>
<tr>
<td>5.668 mm</td>
<td>6.217 mm</td>
<td>0.549 mm</td>
<td>100g</td>
<td>20.55°</td>
</tr>
<tr>
<td>5.668 mm</td>
<td>6.329 mm</td>
<td>0.661 mm</td>
<td>120g</td>
<td>20.65°</td>
</tr>
<tr>
<td>5.670 mm</td>
<td>6.496 mm</td>
<td>0.826 mm</td>
<td>150g</td>
<td>20.65°</td>
</tr>
<tr>
<td>5.671 mm</td>
<td>6.635 mm</td>
<td>0.963 mm</td>
<td>175g</td>
<td>20.50°</td>
</tr>
</tbody>
</table>

These measurements were made in a constant temperature laboratory at 20° ± 1°.
The results were calculated using a computer and programme designed to give the best line through the points (correlation coefficient in the above example was \(0.999995\)) and allow for the specimen shape. The specimen was measured for thickness \((b)\) and width \((a)\) at 10 points along the 10 in span used in measurement.

The modulus is given by\(^{94}\)

\[
E = \frac{FL^3}{4ab^3\delta} \quad \text{N/m}^2
\]

Where \(F\) is the force in Newtons (\(=\) load \((W)\) in Kg \(\times 9.81\))

\(L_0\) is original length of specimen between supports (10 cm \(= \) 0.1 metre)

\(\delta\) is deflection in metres

\(a\) is width and \(b\) the thickness of the specimen in metres.

For the sample above the load for a deflection of 1mm was 181.4g and average thickness 3.1738 mm and width 5.4724mm. Substituting gives the mean modulus as:

\[
E = \frac{0.1814 \times 9.81 \times (10^{-1})^3}{4 \times 5.4724 \times 10^{-3} \times (3.1738 \times 10^{-3})^2 \times 10^{-3}} = 2.54 \times 10^9 \text{ N/m}^2
\]

\((2.54 \text{ GN/m}^2)\).

The computer also gives a corrected modulus which weights the widths and thicknesses. The corrected value for this polymer was \(2.56 \times 10^9 \text{ N/m}^2\).

**Tensile Measurements**

An account of uniaxial tensile creep testing is given in references 95 and 71.
The measurements were made on a specimen as shown prepared by cutting and routing from a 6" x 1" x 1/8" compression moulding.

```
5.5 mm
Thickness 3.2 mm

10 cm
```

The deflection was measured by means of an optical extensometer. The stress was applied by means of a lever type apparatus, incorporating the scale for the image from the optical extensometer. An example of the measurements obtained for an isochronous stress-strain experiment are shown below for a 50 mole % o,p' copolymer after 1 hour at 150°.

The stress was given by:

\[
\text{Stress (N/m}^2\text{)} = \text{load (Kg) x load conversion constant.}
\]

Load conversion constant \(= \frac{\text{lever arm ratio x 9.81}}{\text{thickness (metres) x width (metres)}}\)

\[
= \frac{4.96 \times 9.81}{3.219 \times 10^{-3} \times 5.488 \times 10^{-3}} = 2.77 \times 10^6 \text{ N/m}^2 \text{ Kg}
\]

The strain was given by:

\[
\text{strain} = \text{deflection x strain constant}
\]

The strain constant was a constant for the apparatus used, in this case the strain constant was 0.000781 cm\(^{-1}\).
<table>
<thead>
<tr>
<th>Load (Kg)</th>
<th>Stress $\sigma$ (N/m$^2$)</th>
<th>Strain $\varepsilon$</th>
<th>100 sec deflection (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>$1.384 \times 10^6$</td>
<td>0.000453</td>
<td>0.58</td>
</tr>
<tr>
<td>1.3</td>
<td>$3.60 \times 10^6$</td>
<td>0.00123</td>
<td>1.58</td>
</tr>
<tr>
<td>1.807</td>
<td>$5.0 \times 10^6$</td>
<td>0.001726</td>
<td>2.21</td>
</tr>
<tr>
<td>2.40</td>
<td>$6.64 \times 10^6$</td>
<td>0.00233</td>
<td>2.98</td>
</tr>
<tr>
<td>3.10</td>
<td>$8.58 \times 10^6$</td>
<td>0.00303</td>
<td>3.88</td>
</tr>
<tr>
<td>3.613</td>
<td>$1.0 \times 10^7$</td>
<td>0.00353</td>
<td>4.52</td>
</tr>
</tbody>
</table>

These results are shown in graph 38. A modulus may be calculated directly from the slope of the graph.

**Dynamic Mechanical Measurements**

An account of dynamic mechanical testing is given in ref 73.

The reed used was 3cm long, 0.030" thick and 0.050" wide and was cut from a 2" x 2" x 1/8" compression moulding. The reed was made to vibrate by applying a varying stress to one end and the movement of the free end was observed by a photo cell and light. The reed was brought to the fundamental resonance and measurements of frequency, $f_1$ and $f_2$ were taken at two points where the amplitude was $\frac{h}{\sqrt{2}}$, where $h$ is the amplitude at resonance as shown.

$f_0$ = resonant frequency. $\Delta f = f_2 - f_1$  
$f_1 + \frac{1}{2} \Delta f = f_0$
Calculation of $\tan \delta$

The width of this resonant frequency curve measured at $\frac{h}{\sqrt{2}}$ of the maximum amplitude is related to the mechanical losses in the material of the reed by the expression:

$$\tan \delta = \frac{\Delta f}{f_0}$$

Dynamic Modulus

For the fundamental resonance

$$E' = \frac{5.940 \cdot 1^4 \cdot d \cdot f_0^2}{t^2}$$

where $E'$ = Young's modulus in dynes/cm$^2$

- $l$ = length of reed in cm
- $d$ = density of reed in g/cc
- $t$ = thickness of reed in inches
  (measured in place of vibration)

The modulus in N/m$^2$ is given by multiplying by $10^{-1}$. An example of the results obtained for a poly(diphenylene ether sulphone) of RV 0.61 is shown below. The temperature of the reed was measured by a thermocouple; the mv readings are shown in the first column. The reed was 3.0005 cm long, 0.033" thick and its density was 1.377 g/cc.
**Dynamic Mechanical Results**

\[
\begin{array}{|c|c|c|c|c|c|c|c|}
\hline
mV & Temperature & f_1 (Hz) & f_2 (Hz) & \Delta f (Hz) & f_0 (Hz) & \tan \delta & E' (GN/m^2) \\
\hline
0.805 & 20.1° & 199.6 & 201.5 & 1.9 & 200.5 & 0.0094 & 2.67 \\
0.443 & 11.0° & 200.7 & 202.5 & 1.8 & 201.6 & 0.0089 & 2.69 \\
0.025 & 1.5° & 202.3 & 205.2 & 2.9 & 203.7 & 0.0142 & 2.75 \\
-0.468 & -11.4° & 204.0 & 207.2 & 3.2 & 205.6 & 0.0155 & 2.80 \\
-0.784 & -20.9° & 205.5 & 209.9 & 4.4 & 207.7 & 0.0211 & 2.86 \\
-1.10 & -29.2° & 206.9 & 211.7 & 4.8 & 209.3 & 0.0229 & 2.90 \\
-1.48 & -39.8° & 209.8 & 214.0 & 4.2 & 211.9 & 0.0198 & 2.98 \\
-1.786 & -48.1° & 211.2 & 217.2 & 6.0 & 214.2 & 0.0280 & 3.04 \\
-2.164 & -59.0° & 214.5 & 220.5 & 6.0 & 217.5 & 0.0275 & 3.14 \\
-2.51 & -69.6° & 218.0 & 223.0 & 5.0 & 220.5 & 0.0226 & 3.22 \\
-2.85 & -80.0° & 222.0 & 225.8 & 3.8 & 223.9 & 0.0169 & 3.32 \\
-3.15 & -89.8° & 224.2 & 227.5 & 3.3 & 225.8 & 0.0146 & 3.38 \\
-3.38 & -97.6° & 226.6 & 229.5 & 2.9 & 228.1 & 0.0127 & 3.45 \\
-3.77 & -110.1° & 229.6 & 232.0 & 2.4 & 230.8 & 0.0103 & 3.53 \\
\hline
\end{array}
\]

These results are shown in graph 42.
Computer Programmes

The following programmes were used in the evaluation of some of the kinetic data shown in Parts 3, 4 and 5 of this thesis. The programmes are written in the BASIC language and were used on an IBM 360 computer.

Programme 1

This programme was used to calculate second order rate data where the initial concentrations of reactants were different. The programme gives the concentration of fluorine end groups, concentration of phenoxide end groups and \( \frac{1}{(a - b)\ln(b - x)} \) at each time \( T \) (in minutes). The data fed in at line 500 are \( F \) (initial concentration of fluorine ends in moles/litre), \( K \) (initial concentration of phenoxide ends in moles/litre), followed by a series of \( T \) (time in minutes) and \( R \) (% reaction). Zero time and zero % reaction are included.

```
10 CONC F ENDS CONC F ENDS TIME 1/(A-P)!!(A-X)/(B-X)
11 MOLES/L MOLES/L MINS
20 #,### #,### #,### #,###!!!
25 PRINT USING 10
26 PRINT USING 11
30 READ F,K
40 READ T,R
50 K1 = ((K*(100-R))/100)
60 F1 = (K1 + (F-K))
70 Q = ((1/(T-K))*(LOG(F1/K1)))
80 PRINT USING 20, K1, F1, T, Q
100 GO TO 40
500 DATA
900 END
```
Programme 2

This programme was used to calculate $\overline{DP}_t$, $\overline{DP}_c$, and the concentration of ether links (in moles/litre) at time $T$ for the ether exchange reaction (ie reaction of poly(diphenylene ether sulphone) with the potassium salt of 4-(benzene sulphonyl)4'-(4-hydroxybenzenesulphonyl) diphenyl ether).

The data fed in is the polymer concentration in g/litre ($P$) at line 40 and a series of time in minutes ($T$) and RV ($R$) at line 500.

```
10:   TIME (MIN)   DP   DP(CORRECTED)   CONC ETHER LINKS MOLES/LITRE
20:   #   #   #   #   #   #   #   
25:   PRINT USING 10
40:   LET $P = 
50:   READ $T_1$, $R_1$
60:   $D_1 = ((R_1/0.0232)*(1/0.003))$
70:   $A_1 = (((D_1-1)*P)/(01*232))$
75:   PRINT USING 20, $T_1$, $R_1$, $D_1$, $A_1$
80:   READ $T_2$, $R_2$
90:   $D_2 = ((R_2/0.0232)*(1/0.003))$
100: $D_3 = (D_2-(2-(2*(D_2/D_1))))$
200: $A_2 = (((T_2-1)*P)/(03*232))$
500: PRINT USING 20, $T_2$, $D_2$, $D_3$, $A_2$
320: GO TO 80
500: DATA
900: END
```
Programme 3

This programme was used to calculate $\bar{DP}$ and concentration of ether links (in moles/litre) at time, $T$, for the cleavage of polymer by potassium fluoride experiments.

The data fed in was the polymer concentration in g/litre ($P$) at line 40 and the RVs ($R$) at each time at line 500.

```
10: DP
15 PRINT USING 10
20: #######
40 LET $P =$
50 READ $R$
100 $D = ((R/0.0232)^(1/0.663))$
200 $A = (((D-1)*P)/(D*232))$
300 PRINT USING 20, $D$, $A$
320 GO TO 40
500 DATA
990 END
```

Programme 4

This programme was used to calculate the first order rate constant for the cleavage of poly(diphenylene ether sulphone) by potassium fluoride. The data was fed in at line 500 as the concentration of ether links in moles/litre ($A$) at each time ($T$) thus: $A_1$, $T_1$, $A_2$, $T_2$, $A_3$, $T_3$ ....

The rate constant was calculated using this programme between two consecutive sets of time ie between $T_1$ and $T_2$, then between $T_2$ and $T_3$ etc.
Programme 5

This programme was used to calculate $DP_t$, $DP_c$ and the concentration of ether links (in moles/litre) for the experiments in which poly(diphenylene ether sulphone) was reacted with potassium fluoride in the presence of 4,4'-difluorodiphenyl sulphone. The data fed in at line 500 was the RVs at each time thus: $R_1$, $R_2$, $R_3$, $R_4$, ....

```
10:  DP
20:  DP CORRECTED
30:  CONC. ETHER LINKS. MOLES PER LITRE
```

```
10:  DP
20:  DP CORRECTED
30:  CONC. ETHER LINKS. MOLES PER LITRE
```

Programme 5

This programme was used to calculate $DP_t$, $DP_c$ and the concentration of ether links (in moles/litre) for the experiments in which poly(diphenylene ether sulphone) was reacted with potassium fluoride in the presence of 4,4'-difluorodiphenyl sulphone. The data fed in at line 500 was the RVs at each time thus: $R_1$, $R_2$, $R_3$, $R_4$, ....

```
10:  DP
20:  DP CORRECTED
30:  CONC. ETHER LINKS. MOLES PER LITRE
```

```
10:  DP
20:  DP CORRECTED
30:  CONC. ETHER LINKS. MOLES PER LITRE
```
Programme 6

This programme was used to calculate the second order rate constant for the reaction of poly(diphenylene ether sulphone) with tetraethyl ammonium fluoride. It also gives the concentration of ether links (a-x) and fluoride, (b-x), at each time. The data fed in at line 500 are the initial concentration of ether links (moles/litre), and the initial concentration of fluoride ion, followed by a series of ether link concentrations and times.

```plaintext
10: TIME (A-X) (B-X)          SECOND ORDER RATE CONSTANT
11: (SECONDS) M/LITRE M/LITRE LITRE/MOLE/SEC
12: #.### #.##### #.##### #.##### #.#####
15 PRINT USING 10
16 PRINT USING 11
20 READ A1, B1
25 READ A2, T
30 B2 = (B1 - (A1 - A2))
100 PRINT USING 12, T, A2, B2, K
200 GO TO 25
500 DATA
300 END
```
REFERENCES


3. ICI Belgium Patent 639 634 (Chem. Abstr., 1965, 63, 700f)


5. 3M's British Patent 1, 060 546 (1967)


12. M E A Cudby, R G Feasy, B E Jennings, M E B Jones and J B Rose, Polymer, 1965, 6, 589

312

14 R N Johnson and A G Farnham, British Patent 1 078 234


16 A J Parker, Quart. Reviews, 1962, 16, 163

17 J B Rose and D A Barr, British Patent 1 153 035

18 R A Clendinning, British Patent 1 177 183

19 A B Newton and J B Rose, Polymer, 1972, 13, 465


22 R Stephens and J C Tatlow, Quart. Reviews, 1962, 16, 44


24 J F Bunnett and R E Zahler, Chem. Reviews, 1951, 49, 273


32  H C Fielding, British Patent 1 086 595 (Chem. Abstr., 1968, 68 77947a)


34  S Winstein, Tetrahedron Letters, 1960, No 9, 24


38  J R Whinfield, Nature, 1946, 158, 930

39  J R Whinfield and J T Dickson, British Patent 578 079


42  'Engineering Properties of Thermoplastics', Ed. R M Ogorkiewicz

43  P I Vincent, 'Impact Tests and Service Performance of Thermoplastics',
The Plastics Institute, London, 1971, p 46
44 P I Vincent, *Polymer*, 1960, 1, 425


51 H M Clayton and A E Thornton, *Plastics*, 1968, 32, 76

52 T E Bugel, *SPE Journal*, 1968, 24, 52

53 W Retting, *Die Angewandte Makromolekulare Chemie*, 1969, 8, 87


56 L M Robeson, *Polymer Eng. and Science*, 1969, 9, 277


58 J B Rose and coworkers, unpublished work

59 'The Properties of Shell Sulpholane', Shell Technical Bulletin


62 T King and J B Rose, unpublished work


64 W T Miller, J H Fried and H Goldwhite, J. Amer. Chem. Soc. 1960, 82, 3091

65 J B Rose and coworkers, unpublished work

66 J B Rose and coworkers, unpublished work

67 T King and J B Rose, unpublished work

68 Measurements made by Physical Chemistry Division, Imperial Chemical Industries Limited, Plastics Division

69 Measurements made by Miss A Turner-Jones and coworkers, Physics Division, Imperial Chemical Industries Limited, Plastics Division


72 Data for poly pp'(diphenylene ether sulphone) was supplied by Physics Division, Imperial Chemical Industries Limited, Plastics Division.

76 E H Huntress and F H Carten, J. Amer. Chem. Soc., 1940, 62, 511
77 H Beckurts and R Otto, Ber., 1878, 11, 2066
78 H Zahn and H Zuber, Ber., 1953, 86, 172
79 H L Bradley and C A Vanderwerf, J. Amer. Chem. Soc., 1948, 70, 654
80 H H Szmant and G Sud, J. Amer. Chem. Soc., 1956, 78, 3400
A H Blatt, John Wiley and Sons London 1941, p504
1965, 48, 336 (Chem Abstr., 1965, 62, 14681h)
83 US Patent 3 006 963
84 F Reverdin, Ber., 1889, 27, 3459
318
1959, 52, 10101b)
87 A Campagnini, N Marziano, Ricerca Sci., 1959, 29, 2339 (Chem Abstr
1961, 55, 19848b)
88  J Huismann, German Patent 745 127, 1943 (Chem Abstr., 1946, 40 1176)


94  L E Nielsen, 'Mechanical Properties of Polymers', Van Nostrand Reinhold, New York, 1962, p 4