SOME STUDIES ON POLY(PHENYLENE ETHER KETONE)
AND COPOLY(PHENYLENE ETHER KETONE/SULPHONES)

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Two nucleophilic routes to poly (phenylene ether ketone) have been investigated and one of these was found to be more likely to lead to a structural aberration.

\[
\begin{align*}
X-\text{C}_6\text{H}_4-\text{CO-}\text{C}_6\text{H}_4-\text{OK} & \rightarrow (\text{C}_6\text{H}_4-\text{CO-}\text{C}_6\text{H}_4-\text{O})_n \\
X-\text{C}_6\text{H}_4-\text{CO-}\text{C}_6\text{H}_4-X & + \text{KO-}\text{C}_6\text{H}_4-\text{CO-}\text{C}_6\text{H}_4-\text{OK}
\end{align*}
\]

This non-ideal structure was found to be associated with an excess of the phenolate group during preparation and to give rise to red coloured sulphuric acid solutions of the polymer. The nature of this chromophore and the mechanism leading to its formation were both investigated but neither was fully elucidated.

The effect of reduced viscosity and gel on the toughness of poly (phenylene ether ketone) has been quantified for polymers containing up to 3% gel.

The relationship between intrinsic viscosity ([\eta]) and number average molecular weight (\(M_n\)) for poly (phenylene ether ketone) has been found to be

\[
[\eta] = 0.0215 (M_n) - 0.891
\]
The method used was to control molecular weight by adding an excess of functional groups to the polymerisation. The degree of polymerisation (and hence the number average molecular weight) is then calculable and can be related to the intrinsic viscosity.

The thermodynamic quantities characterising the fusion of poly (phenylene ether ketone) have been determined using the method of Flory.

Several copoly (phenylene ether ketone/sulphones) have been prepared by a nucleophilic route and have been shown to be random. The variation in several of the properties of these copolymers (e.g. density, crystal melting point and glass transition temperature etc) with changing composition has been studied.
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1 Preparation of Poly(Phenylene Ether Ketone)

This polymer may be prepared by two types of polycondensation reactions.

a) Electrophilic aromatic substitution in suitable diaryl ethers, such that the carbonyl function of the polymer repeat unit is thereby introduced.

b) Nucleophilic aromatic substitution in suitable diaryl ketones, so that the ether group is incorporated into the polymer repeat unit

These routes are analogous to those used for the preparation of poly(phenylene ether sulphone) (II)
where electrophilic polycondensation is used to introduce the sulphone function and nucleophilic polycondensation the ether linkage.1

1A) Preparation of Poly(Phenylene Ether Ketone) by Electrophilic Polycondensation

A variety of monomeric reactants, solvents and catalysts have been used to prepare this polymer by Friedel Crafts reactions\(^2,3,4\).

\(^1\)

\(^2\)

\(^3\)

\(^4\)

\(^3,4,5,6\)

Reaction temperatures are generally \(-70^\circ\) to room temperature depending on the reactants.

Reaction (4) has received the most study; the solvent here is liquid anhydrous hydrofluoric acid and the catalyst boron trifluoride/hydrofluoric acid. Polymerisation is carried out in the presence of a highly reactive end-capping agent (which should be more
than 150 times as reactive towards acylation as benzene, whose reactivity is taken as unity). The amount of end-capping agent used (diphenyl or diphenyl ether) controls molecular weight and also ensures that no potentially unstable acid chloride or carboxylic acid groups are left in the polymer. Work-up is effected by dilution of the polymerisation mass with liquid sulphur dioxide and subsequent spray-drying to yield an amorphous polymer of structure (III).

\[
\text{III}
\]

The polymer is then extracted with acetone which removes low molecular weight species. The extraction is possible only if the polymer 'as-made' is amorphous, because when it is in the crystalline state, it is so insoluble that nothing can be leached out. The removal of these low molecular weight species is claimed to be necessary if the polymer is to have the desired elongation properties. The use of too little end-capping agent produces very high molecular weight polymers whose subsequent high melt-viscosity precludes them from several applications.

In all four reactions (1), (2), (3) and (4), there is the possibility of structures other than the all para structure (I) being formed.

The ortho structure (IV)

\[
\text{IV}
\]
is one possibility, as is a branched structure (V)

\[ \text{Structures of this type are known to be formed during the electrophilic polycondensation route to poly(phenylene ether sulphone)(II) but their presence in poly(phenylene ether ketone) has not apparently been demonstrated.} \]

1B Preparation of Poly(Phenylene Ether Ketone) by Nucleophilic Polycondensation

Poly(phenylene ether ketone) has been prepared by nucleophilic polycondensation.

This reaction consists of displacement of halogen by phenoxide to form an ether linkage. The halogen is activated to nucleophilic displacement by electron withdrawal by a ketone group \textit{para} to the halogen.

\[
(5) \quad \text{\( \text{phenoxide} - \text{halogen} \)} + \text{\( \text{phenoxide} - \text{ether} \)} \rightarrow \text{\( \text{ether} \)} + \text{\( \text{halogen}^{-} \)}
\]

\((X = \text{halogen})\)

This type of reaction is carried out in dipolar aprotic solvents which enhance the rate of nucleophilic substitution reactions, typically, dimethyl sulphoxide and tetra methylene sulphone (sulpholane).
Poly(phenylene ether ketone) may be prepared by a one or a two 'monomer' system

\[ n \text{MO-}\begin{array}{c} \text{CO-} \end{array}\text{X} \rightarrow \left\{ \text{\begin{array}{c} \text{CO-} \end{array}} \right\}_n + n \text{MX} \]

\[ \frac{n}{2} \text{MO-}\begin{array}{c} \text{CO-} \end{array}\text{OM} + \frac{n}{2} \text{X-}\begin{array}{c} \text{CO-} \end{array}\text{X} \rightarrow \left\{ \text{\begin{array}{c} \text{CO-} \end{array}} \right\}_n + n \text{MX} \]

M = alkali metal, X = halogen

Both of these reactions should theoretically give the all para structure (I) for the polymer.

The one monomer system (reaction 6) has the advantage of intra molecular stoichiometric equivalence of reactive end groups, whereas the two monomer system (reaction (7)) has the advantage of the greater reactivity of the end groups.

The advantages and disadvantages of the relative solubilities of the two types of phenoxide (when the alkali metal is potassium) in the polymerisation solvents are not quite so straightforward and will be discussed in detail later.

Copolymers of (I) and (II) have also been prepared by nucleophilic polycondensation but the structure-property relationships of a series of these copolymers have not been investigated.

When crystalline, poly(phenylene ether ketone) is soluble only in strong acids (e.g., concentrated sulphuric acid and trichloro acetic acid) and has a crystalline melting point (Tm) of \( \sim 370^\circ \). Solutions of the all
para-structure (I) should give the pale yellow solutions in sulphuric acid typical of diaryl ketones and this was found to be the case for a sample of poly (phenylene ether ketone) prepared by the electrophilic route. This fact does not, of course, rule out the presence of such structures as (IV) or (V) in the polymer.

2) The Formation of Non-Ideal Structures in Polymers and their Effects on Properties

The phrase 'non-ideal structures' is taken to mean any structure other than the one the polymer chemist set out to make and in that context, it may be said, that all synthetically prepared polymers contain non-ideal structures. Their non-ideality may range from the superficial (eg slight differences between end-groups and idealised repeat units) to the more serious (eg large degrees of chain branching in some polyolefins).

These structural abnormalities usually arise as a result of some side-reaction taking place during the polymerisation process and their effect on properties becomes apparent at one of two stages;

i) During fabrication, when relatively high temperatures are involved and thermal or oxidative degradation may be brought about or accelerated by the abnormalities and

ii) During the working life of the polymer, which may be reduced because of degradative processes induced or accelerated by the defects.

This link between structural abnormalities and degradation is significant. Much of the work done on the elucidation of non-ideal structures in polymer systems has arisen from studies initially aimed at explaining degradative processes and behaviour (notably by Grassie).
It is convenient to divide structural abnormalities which are formed during the preparation of the polymer into two types.

i) Those occurring in end-groups and

ii) Those occurring 'in chain'.

End group abnormalities are most common in polymers prepared by addition methods (ie free radical polymerisation, anionic and cation polymerisation) and arise from the variety of termination and transfer reactions available to reactive species.

In polymers prepared by polycondensation, such end group abnormalities are rare, by the nature of the reaction. Aside from thermal degradation due to polymerisation at high temperatures, the only abnormality likely is the reactive end group itself. Thus, for example, in the Friedel Crafts preparation of poly (phenylene ether ketone) without the use of an end-capping agent, the end group of the polymer would be either a mono substituted benzene nuceleus or an acid chloride group

\[
\text{POLYMERISATION} \quad \text{[Chemical Structure]}
\]

Again, such end-group abnormalities are only likely to affect thermal or oxidative stability.

'In chain' abnormalities occur in both addition and condensation polymers but, as before, they are more common in addition polymers as they usually arise from side reactions of the highly reactive propagating species present in such reactions.
'In chain' abnormalities in polycondensation are rarer but do nevertheless occur. The main side reaction is ring formation$^{12}$ leading to relatively low molecular weights. Secondary reactions of the reactive end groups can also occur and may give rise to branching$^{13}$.

\[
\text{eg 8) } -\text{NH}(-\text{CH}_2\text{O})_2\text{NCHO}(-\text{CH}_2\text{O})_2\text{CO}^- + \text{ClCOCH}_2^- \\
\text{HCl} + -\text{NH}(-\text{CH}_2\text{O})_2\text{NCO}(-\text{CH}_2\text{O})_2\text{CO}^- \\
\text{COCH}_2^-
\]

Also noteworthy, are the structural isomers and branching formed during the electrophilic preparation of poly (phenylene ether sulphone)$^{1, 14}$

\[
\text{9) } \begin{array}{c}
\text{SO}_2^- \\
\text{SO}_2 \\
\text{SO}_2
\end{array}
\begin{array}{c}
\text{SO}_2^- \\
\text{SO}_2 \\
\text{SO}_2
\end{array}
\begin{array}{c}
\text{SO}_2^- \\
\text{SO}_2 \\
\text{SO}_2
\end{array}
\begin{array}{c}
\text{SO}_2^- \\
\text{SO}_2 \\
\text{SO}_2
\end{array}
\begin{array}{c}
\text{SO}_2^- \\
\text{SO}_2 \\
\text{SO}_2
\end{array}
\]

\[
\text{(structural isomer) } \text{(branching)}
\]

\[
\text{and } \begin{array}{c}
\text{SO}_2^- \\
\text{SO}_2 \\
\text{SO}_2
\end{array}
\begin{array}{c}
\text{SO}_2^- \\
\text{SO}_2 \\
\text{SO}_2
\end{array}
\]

\[
\text{(required structure)}
\]

The effects of structural abnormalities on polymer properties may be conveniently subdivided thus:

i) Their effect on thermal and oxidative stability

ii) Their effect on physical properties such as melt flow behaviour and crystallinity.
In the former category, the effects are due to chemical differences between the idealised and abnormal structures (e.g., the terminal double bonds on polyolefins) as well as to such non-ideal structures as branches. Grassie has studied these effects in detail and they will not be discussed further here.

In the latter category, the effects are due mainly to chain branching. The effects of chain branching on melt viscosity (itself molecular weight dependent) are variable and are usually explained in terms of the Bueche theory of chain entanglement. The theory predicts that melt viscosity will decrease as the proportion of chain branching increases. It has in fact been found that the melt viscosity of branched polymers may increase or decrease (relative to linear polymers of the same degree of polymerisation), apparently depending on the length of the branches. Thus Berry and Fox showed that for short chain (star) branched poly(butadiene) and poly(styrene), melt viscosity decreased relative to the linear polymers and Kraus and Gruver have shown that long chain branches increase the melt viscosity of poly(butadiene) relative to the linear polymer.

This type of phenomenon may be explained if the short chain branches do not cause sufficient further entanglements (further, that is, to those already experienced by the linear backbone of the chain) to compensate for their relatively smaller volume, i.e., melt viscosity is decreased. For the long chain branched polymers, the further entanglements caused by the branches lead to the observed increase in melt viscosity as the accompanying relative decrease in molecular volume is not sufficient compensation.
It is noteworthy that the type of investigations described above have been carried out on polymers whose repeat units have high degrees of rotational freedom (ie they are inherently flexible molecules) and the application of such theories to relatively 'stiff' polymers such as poly (phenylene ether ketone) may not be valid.

(Reference 21 was used for general background reading for this section).

The effect of chain branching on polymer crystallinity is discussed in the next section.

3 Polymer Crystallinity

The concept of crystallinity when applied to polymeric systems is more complex than when applied to 'simple' (ie monomeric) inorganic or organic systems.

Apart from lattice defects, simple organic and inorganic molecules are wholly (ie 100%) crystalline whereas in polymeric systems, this is almost never the case.

'Crystalline polymers' consist of two phases - a randomly arranged amorphous phase and a crystalline phase - the proportion of the polymer which is crystalline (ie its degree of crystallinity) can vary from as low as 10-15% (in the case of poly (vinyl chloride)) to as high as 80-90% (in the case of linear poly(ethylene)). These phases are not discrete; part of a polymer molecule may be incorporated into a crystalline region while another part of the same molecule is in the amorphous region. The result may be viewed as a complex of crystalline bodies linked by amorphous regions into a strong coherent solid.
The amorphous region may exist in one of two states, the liquid (or rubbery) state and the glassy state. The temperature at which the transition from one of these states into the other occurs is called the glass transition temperature (Tg). The crystalline regions have a crystal melting point (Tm) in the same way as simple organic and inorganic solids do.

The interrelationship between these two temperatures (Tg and Tm) and three states of matter of a crystalline polymer can be seen if one considers the transitions that take place when an amorphous sample of a crystallisable polymer is heated from below its Tg to some temperature at which it is completely molten. Below the Tg, no segmental motion of the polymer chains can occur, the amorphous region is in its glassy state, and no chain alignment (as a precursor to crystallisation) is occurring. At the Tg, segmental motion can occur within the amorphous region, chain ordering and alignment occurs in this region and crystallisation begins (possibly nucleated by the existing crystalline regions). As the temperature is increased and Tm is approached, the rate of crystallisation passes through a maximum until at Tm, the newly formed and the original crystalline regions melt and all order is lost. Cooling the molten polymer slowly will again give rise to the mixed amorphous/crystalline states below Tm but rapid cooling of the molten mass may, if the cooling rate were so fast that the temperature of the polymer dropped below the Tg before crystallisation had occurred, give rise to a totally amorphous polymer.

The requirements for a polymer to crystallise are, briefly, that the molecules of that polymer should be of such a shape and form that there is a minimum of difficulty in passing from the disordered state of a melt (or solution) to the precisely ordered arrangements required in the crystal.
Thus linear poly(ethylene), with no bulky side groups, crystallises rapidly and to a large extent whereas poly(vinyl carbazole) with its large bulky side groups randomly oriented, does not crystallise. Branching (such as is common in poly (ethylene)) is not conducive to crystallisation on two counts:

i) The branches act as bulky side groups so preventing the close packing necessary for crystallisation and

ii) The branches cause an increase in the number of chain entanglements in the amorphous region so that when above its $T_g$, the segmental motion of the chains is reduced, ordering and alignment of the chains is correspondingly reduced, and the tendency to crystallise is diminished.

Of course, the mere lack of bulky side groups or presence of a regular structural repeat unit does not guarantee crystallinity. Thus poly (phenylene ether sulphone), with its regular repeat unit (II) and essential lack of irregular structures cannot be crystallised (as cannot model compounds of this polymer equivalent to $n \geq 3$) whereas poly (phenylene ether ketone), which is structurally very similar to poly (phenylene ether sulphone) crystallises readily from the melt despite the probable presence of chain irregularities in this polymer.

The degree of crystallinity that a given sample of polymer possesses will depend not only on the structural consideration outlined above but also on the thermal history of that sample (eg the time that was allowed for it to crystallise and the temperature at which it was held) and, indeed, the term 'degree of crystallinity' itself requires qualifications before quantitative measurements can be quoted.
There is an inherent difficulty in posing a rigorous definition of 'degree of crystallinity' caused by the nature of crystallinity in polymers. The crystalline regions in a polymer are not definite entities with sharp boundaries or crystal faces separating them from the surrounding amorphous material. They are small regions in which segments of the polymer chains have a crystalline arrangement and which are connected to the amorphous region by segments of polymer chain in which there is a high degree of order. Thus the crystal/amorphous boundary is diffuse and contains ordered (though not crystalline) rather than randomly amorphous polymer. Even the crystalline portions themselves contain defects due to the difficulty of ordering long, entangled polymer chains. Thus, though the methods of determining degrees of crystallinity described below may give numerically comparable answers, these answers must be treated with a degree of caution.

All the methods of determining degrees of crystallinity contain the tacit assumption that the property of the two phases (ie crystalline and amorphous) being measured is additive and in proportion to the relative amounts of each phase present.

The most common method is that employing wide angle X-ray diffraction.

The X-ray diffraction pattern of a crystalline polymer consists of a series of sharply defined rings arising from the crystalline portion of the sample, superimposed on a diffuse halo arising from the amorphous region. The degree of crystallinity of a polymer sample may be obtained either by suitable integration of the intensities of the separate contributions to the X-ray diffraction pattern or by obtaining an X-ray diffraction pattern of a totally amorphous sample and estimating the degree of crystallinity by difference.
Density may also be used to determine the degree of crystallinity of a polymer sample. Density increases as the degree of crystallinity increases and the difference can be of the order of 10% between a totally amorphous and a highly crystalline sample of the same polymer. The weight fraction of material in the crystalline state ($\Theta$) may then be expressed as

\[
\Theta = \frac{V_a - V}{V_a - V_c}
\]

where:

- $V_a$ = density of totally amorphous polymer
- $V_c$ = density of totally crystalline polymer
- and $V$ = density of the sample

Obviously the difficulty here is obtaining a value for $V_c$; this is sometimes done from calculations based on the size of the unit cell obtained from X-ray diffraction studies.

Another well used method is that based on the heat of fusion of the crystalline regions. Here, the degree of crystallinity ($\Theta$) may be expressed as:

\[
\Theta = \frac{\Delta H}{\Delta H_v}
\]

where $\Delta H$ = heat of fusion of the partially crystalline polymer and

$\Delta H_v$ = heat of fusion of 100% crystalline polymer
The major problem associated with this method, is obtaining a reliable and accurate value of $\Delta H_v$. Flory has derived several equations enabling this value to be obtained either from a study of the depression of the melting points of a series of random copolymers (12) or from the depression of melting point by monomeric diluents (13).

\[ \frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_v} \ln \frac{X_A}{V_n} \]

where $T_m$ = melting point of the copolymer

$T_m^0$ = melting point of the crystalline homopolymer (both in °K)

$X_A$ = mole fraction of crystallisable units and

$R$ = gas constant

In the derivation of this equation it is assumed that the non-crystallisable co-units cannot enter the lattice of the crystallisable units.

\[ \frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_v} \left[ \frac{(Z/Z_s)(1-V_2)}{(1-V_2)^2} - \mu (1-V_2)^2 \right] \]

where $T_m$, $T_m^0$, $R$ and $\Delta H_v$ are as defined for equation (12) and

$Z/Z_s$ = the ratio of the molar volumes of the repeat unit and the diluent

$V_2$ = volume fraction of the polymer

$\mu$ = an energy of mixing parameter.

Again, the derivation assumes no inclusion of the diluent in the lattice.
The application of equation (12) is experimentally the simpler approach provided that copolymers which comply with Flory's requirements can be prepared (i.e., they must be of known composition, one unit must be crystallisable and the other not, and they should be random), however, the values of $\Delta H_v$ obtained by the use of this equation are subject to error. This arises from the need to determine the melting points of the copolymers accurately (i.e., the point at which the last traces of crystallinity disappear) and this is made difficult in the case of random copolymers by the increasing diffuseness of the melting process as the proportion of crystallisable units decreases. Failure to detect the last traces of crystallinity disappearing leads to a pseudo adherence to equation (12) (i.e., a plot of $\frac{1}{T_m} - \frac{1}{T_m^o}$ against $\ln X_A$ still gives a straight line, but the slope of the line alters) with subsequent low values of $\Delta H_v$. Mandelkern has shown by a model calculation that failure to detect the melting of the last 1% of the crystallinity in a series of copolymers (the homopolymers of the crystallisable units of which has a $T_m^o = 400^\circ$K and $\Delta H_v = 10^3$ cal/mole) gives a value of $\Delta H_v$ of 780 cal/mole. Flory et al. have shown this effect for poly(decamethylene sebacate) where the value of $\Delta H_v$ by the copolymer method was found to be 13.8 cal/g and by the diluent method 36 cal/g.

Good agreement between the two methods can be achieved however, the basic requirement for this being a sufficiently sensitive apparatus for detecting melting points. Flory et al. have obtained values of $\Delta H_v$ for poly(decamethylene sebacamide) of 23 cal/g and 24.5 cal/g by the copolymer and diluent methods respectively. In general, the diluent method is deemed the more accurate.
Another method of determining \( \Delta H_v \) is by study of the heat of fusion of model compounds. Examples of this type of approach are the use of \( \text{N,N'-n-propyladipamide} \) as a model compound for Nylon 66 and \( \text{dotriacontane} \) for poly(ethylene).

Nuclear magnetic resonance (nmr) can be used to determine degrees of crystallinity of certain polymers - the method being based on the different frequencies of the motions of the amorphous and crystalline regions. Similarly, infra-red spectroscopy can be used when the crystalline portion of a polymer has characteristic bands different from those of the amorphous region. This method is usually used to compare degrees of crystallinity in a series of samples of one polymer, because the intensities of the absorbances of the bands characteristic of wholly crystalline or wholly amorphous polymers are not known.

Despite the limitations and inherent uncertainties associated with all the described methods of determining degrees of crystallinity, when the values obtained for a single polymer sample by several methods have been compared, the agreement in the degree of crystallinity given by the different methods has been within \( \pm 5\% \).

The Work Described in this Thesis

The preparation of poly(phenylene ether ketone) by two nucleophilic routes is described. It was found that one of these routes gave rise to structurally non-ideal polymer; the qualitative causes for this are described as is the effect of this non-ideality on certain properties of the polymer. A structure which could account for this non-ideality has been postulated.
The solution viscosity/molecular weight relationship for poly(phenylene ether ketone) is described and the $K$ and $\eta$ values of the Mark-Houwink equation for poly(phenylene ether ketone) in 98% sulphuric acid at $25^\circ$ are quoted.

The thermodynamic quantities characterising the fusion of poly(phenylene ether ketone) have been determined and attempts made to use these to establish a method of determining the degrees of crystallinity of the polymer.

The preparation of copoly(phenylene ether ketone/phenylene ether sulphones) and the variations of their $T_m/T_g$, density, melt viscosity, and impact strength with copolymer composition are described.
The preparation of poly (phenylene ether ketone) by a nucleophilic route.

This section describes two methods of preparing poly (phenylene ether ketone) by nucleophilic routes. It was found that one of the routes was more likely to yield polymer with adverse properties than the other. The qualitative causes for this are discussed.

There are two possible routes to poly (phenylene ether ketone), the 'one monomer' route (14),

\[ \text{14) } n \text{-}X\text{-}
\begin{array}{c}
\text{C} \\
\text{O} \\
\text{C}
\end{array}
\text{-}
\begin{array}{c}
\text{C} \\
\text{O}
\end{array}
\text{-}O\text{K} \longrightarrow n \text{KX} + \left( \text{C} \text{-}
\begin{array}{c}
\text{C} \\
\text{O}
\end{array}
\right)_n
\]

and the 'two monomer' route,

\[ \text{15) } \frac{n}{2}X\text{-}
\begin{array}{c}
\text{C} \\
\text{O} \\
\text{C}
\end{array}
\text{-}
\begin{array}{c}
\text{C} \\
\text{O}
\end{array}
\text{-}X + \frac{n}{2} \text{K0-}
\begin{array}{c}
\text{C} \\
\text{O} \\
\text{C}
\end{array}
\text{-}\text{O}\text{K} \downarrow \left( \text{C} \text{-}
\begin{array}{c}
\text{C} \\
\text{O}
\end{array}
\right)_n \text{ + } n \text{KX}
\]

The one monomer route is apparently the more attractive from the point of view of preparing high molecular weight polymer, as the exact balance of reacting end-groups required is present within one molecule, whereas the two monomer route requires exact weighing to achieve the same stoichiometric balance.

Poly (phenylene ether ketone) is a crystalline polymer soluble in very few organic solvents. In order to prevent crystallisation of the polymer
during its preparation (so reduced mobility of the reacting end-groups and hence molecular weight), the polymer should be prepared at temperatures above its melting point of 370°. This very high temperature was not in fact needed because diphenyl sulphone was a sufficiently good solvent for the polymer that at dilutions of 50% or less, the polymerisation mass could be kept mobile at temperatures of 330-340°. However, very considerable thickening occurred towards the end of the reaction.

The one monomer route, used in early experiments, gave rise to the following observations:

(1) Molecular weight of polymer varied considerably from preparation to preparation (measured as reduced viscosity at 1% w/v in concentrated sulphuric acid).

(ii) These same solutions of the polymer tended to contain a gel fraction

(iii) 1% Solutions of the polymer in sulphuric acid were highly coloured, varying from a pale yellow/brown to a deep red/black.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Reduced viscosity (of the filtered solution)</th>
<th>% CONC in DPS*</th>
<th>gel</th>
<th>Colour of 1% solution in sulphuric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>F - C O - O K</td>
<td>2.04</td>
<td>50</td>
<td>+</td>
<td>gold</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.55</td>
<td>20</td>
<td>-</td>
<td>gold</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.13</td>
<td>50</td>
<td>+</td>
<td>brown</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.07</td>
<td>50</td>
<td>+</td>
<td>red</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.02</td>
<td>50</td>
<td>+</td>
<td>red/brown</td>
</tr>
</tbody>
</table>

*Diphenyl Sulphone, + gel fraction, - no gel fraction
Reaction times of ~15 mins were used for the 50% concentration runs (the time in which the reaction mass became unstirrable) and 4 hrs for the 20% run.

When compression moulded films (0.007" thick) of these polymers were prepared only the polymer of reduced viscosity 2.04 gave film which could be creased without cracking. All the other films were brittle.

Several different batches of 4-fluoro-4'-hydroxy benzophenone had been used for these experiments and it was thought that batch variation could be responsible for the irreproducibility of the reduced viscosities in that there may have been very small quantities of difunctional impurities (eg 4, 4'-dihydroxy benzophenone present which upset the stoichiometric balance of end groups).

Accordingly, a large batch of 4-fluoro-4'-hydroxybenzophenone was prepared and the potassium salt of this used to prepare a number of polymers, to which had been added (at the polymerisation stage) various quantities of difunctional monomers (Table 2).
### Table 2

The effect of added difunctional monomers on the polymerisation of the potassium salt of 4-fluoro-4'-hydroxybenzophenone

<table>
<thead>
<tr>
<th>Mole percent added</th>
<th>Reduced viscosity 1% in sulphuric acid (filtered)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>KO-(\text{C}_{2})-CO</td>
<td>F-(\text{C}_{2})-CO</td>
<td>Brittle film</td>
</tr>
<tr>
<td>0</td>
<td>0.2</td>
<td>1.02</td>
</tr>
<tr>
<td>0</td>
<td>0.4</td>
<td>1.40</td>
</tr>
<tr>
<td>0</td>
<td>0.6</td>
<td>1.67</td>
</tr>
<tr>
<td>0</td>
<td>1.0</td>
<td>2.09</td>
</tr>
<tr>
<td>0</td>
<td>1.2</td>
<td>4.66</td>
</tr>
<tr>
<td>0</td>
<td>1.5</td>
<td>2.17</td>
</tr>
<tr>
<td>0</td>
<td>1.7</td>
<td>1.95</td>
</tr>
<tr>
<td>0</td>
<td>2.0</td>
<td>1.29</td>
</tr>
<tr>
<td>0</td>
<td>2.5</td>
<td>1.10</td>
</tr>
<tr>
<td>0.2</td>
<td>0</td>
<td>1.02</td>
</tr>
<tr>
<td>0.4</td>
<td>0</td>
<td>1.09</td>
</tr>
<tr>
<td>1.0</td>
<td>0</td>
<td>0.99</td>
</tr>
</tbody>
</table>

All these polymers contained a gel fraction and their solutions in sulphuric acid (at 1%) tended to be red.

The above results show clearly that a 1.0 to 1.7 mole percent excess of 4,4'-difluorobenzophenone increases the reduced viscosity markedly and this in turn suggests an excess of hydroxyl end-groups in the original 4 fluoro-4'-hydroxybenzophenone. Although it is possible that some 4,4'-dihydroxybenzophenone had been formed during its preparation, this compound had been very carefully purified. The precise reason for the
apparent imbalance of end-groups in 4-fluoro-4'-hydroxybenzophenone has not been established but an exactly similar effect has been noted during the preparation of poly(phenylene ether sulphone) (II)

$$\left(\text{O}_2\text{SO}_2\text{O}\right)_n$$

from the potassium salt of 4-fluoro-4'-hydroxydiphenylsulphone.  

A further point to emerge from these results was confirmation of the earlier observation that reduced viscosities of $\eta > 2.0$ were required for the polymer to give film which could be creased, as opposed to brittle film which cracked on being creased. This simple creasing test was used as a quick and reproducible test of the toughness of the polymer (i.e., its resistance to breaking) and was carried out on bubble-free film, 0.007" thick at room temperature. A more rigorous test of the polymers toughness would have involved the preparation of much larger quantities of polymer, preparation of plaques and test specimens and this was not considered worthwhile at this stage of the work.

In view of the difficulties encountered in preparing poly(phenylene ether ketone) by the one monomer route (i.e., gel formation and the red colouration of sulphuric acid solutions of the polymers) it was decided to prepare the polymer by the two-monomer route.

It was hoped that an increased initial rate of polymerisation would be obtained (over that for the one-monomer system) and that this would significantly increase the proportion of gel-free polymer produced in the reaction. Table 3.
Table 3
Preparation of Poly(phenylene ether ketone)
By the Two-Monomer Route

<table>
<thead>
<tr>
<th>Experiment</th>
<th>System</th>
<th>Temperature °C</th>
<th>Time hrs</th>
<th>% Conc in DPS</th>
<th>([RV]^{1%}, 25^\circ\text{C} H_2SO_4)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A + C</td>
<td>325-335</td>
<td>(1\frac{1}{2})</td>
<td>50</td>
<td>1.0</td>
<td>Gold solution, trace of gel. Brittle film.</td>
</tr>
<tr>
<td>3</td>
<td>A + B</td>
<td>330-340</td>
<td>(1\frac{1}{2})</td>
<td>34</td>
<td>0.72</td>
<td>Gold solution, no gel. Brittle film.</td>
</tr>
<tr>
<td>4</td>
<td>A + B</td>
<td>330-340</td>
<td>(1\frac{1}{2})</td>
<td>45</td>
<td>0.53</td>
<td>Gold solution, no gel. Brittle film.</td>
</tr>
<tr>
<td>5</td>
<td>A + B</td>
<td>330-340</td>
<td>1</td>
<td>28</td>
<td>0.38</td>
<td>Gold solution, no gel. No film prepared</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&quot;&quot;&quot;&quot;&quot;&quot;Brittle film.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1(\frac{1}{2})</td>
<td>28</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>28</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>28</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6(\frac{1}{2})</td>
<td>28</td>
<td>0.63</td>
</tr>
<tr>
<td>6</td>
<td>A + B</td>
<td>330-340</td>
<td>(1\frac{1}{2})</td>
<td>50</td>
<td>0.70</td>
<td>Trace of gel, gold solution. Brittle film.</td>
</tr>
</tbody>
</table>

\(A = KO \quad \text{Cl} - \text{co} - \text{Cl}\) (anhydrous)
\(B = \text{Cl} - \text{co} - \text{Cl}\)
\(C = \text{F} - \text{co} - \text{F}\)
The results show that although gel formation had been considerably reduced, it had not been entirely eliminated. Two other facts emerged from these results.

i) That reduced viscosities of \( >0.73 \) cannot apparently be achieved using 4, 4'-dichlorobenzophenone as one 'co-monomer'.

ii) One experiment (experiment two) had given a polymer that was gel free, of reduced viscosity only 1.22, yet whose film was creaseable (compared to reduced viscosities of \( >2.0 \) required when the polymer contained gel).

Before investigations of these phenomena were continued, work was carried out to optimise the polymerisation conditions for the preparation of poly(phenylene ether ketone). Table 4.
### Table 4

Polycondensation of Difluorobenzophenone With the Anhydrous Bisphenoxide of Dihydroxy-Benzophenone

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time hours</th>
<th>Conc of soln %</th>
<th>[RV] 1%, 25°C CH₂SO₄</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.75</td>
<td>50</td>
<td>No gel 0.46</td>
<td>Reaction mass set solid after 0.75 hours. Film was almost white but fragile</td>
</tr>
<tr>
<td>2</td>
<td>3.25</td>
<td>20</td>
<td>No gel 1.49</td>
<td>Reaction mass was mobile throughout. Film was creaseable but of greyish/brown colour</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>35</td>
<td>No gel 1.82</td>
<td>Reaction mass just mobile after 3.0 hours. Film was creaseable but brownish in colour</td>
</tr>
<tr>
<td>4</td>
<td>0.50</td>
<td>50</td>
<td>No gel 0.62</td>
<td>Reaction mass set solid after 0.5 hours. Sample taken and mass allowed to stand for further 1.50 hours. Films fragile but of almost white colour</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>50</td>
<td>No gel 0.75</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.50</td>
<td>30</td>
<td>No gel 1.03</td>
<td>Reaction mass just mobile after 1.5 hours. Film of good colour but fragile</td>
</tr>
<tr>
<td>6</td>
<td>1.50</td>
<td>40</td>
<td>No gel 1.82</td>
<td>Reaction mass set solid after 1.5 hours. Film of good colour and creaseable</td>
</tr>
<tr>
<td>7</td>
<td>2.0</td>
<td>30</td>
<td>No gel 1.87</td>
<td>Reaction mass just mobile after 2.0 hours. Film of good colour and creaseable</td>
</tr>
</tbody>
</table>

All the experiments were carried out at 330-340° on a 1.724 x 10⁻⁴ M scale.

The results showed that 30% concentration in diphenyl sulphone at 330-340° gave acceptable polymer, also that polymers of reduced viscosities < 2.0 can give creaseable film if the polymer is gel free.

The results of the work so far may be summarised as follows:
i) The 'one-monomer' route to poly(phenylene ether ketone) gives rise to polymers whose solutions in sulphuric acid tend to be red and contain a gel fraction.

ii) The 'two-monomer' route gives polymers whose sulphuric acid solutions tend to be gold/yellow and do not contain a gel fraction. The use of 4,4'-dichlorobenzophenone appears to limit the reduced viscosities obtained but the causes for this last observation have not been fully investigated, and it may be that the polymerisation conditions could be altered so that higher reduced viscosities could be obtained using this system.

iii) Polymer containing a gel fraction requires a reduced viscosity of $\geq 2.0$ for compression moulded film to be creaseable.

iv) Gel free polymer only requires a reduced viscosity of $>1.2$ for film to be creaseable.

v) It has been tentatively suggested that the red colouration in sulphuric acid solutions of the polymers is due to some lightly branched but soluble species, the precursor of gel.

The differences in the polymers obtained by the two systems (ie one monomer and two monomer) may become clear when one examines the chemical and physical properties of the starting materials.

Thus considering the reactivity of the end-groups; the initial polymerisation step for the two monomer system (ie dimerisation) would be expected to proceed at a faster rate than for the one monomer system on the following grounds.

In 4,4'-difluorobenzophenone, one fluorine atom withdraws electrons from the carbonyl function by an inductive effect, thus increasing the electron
withdrawal by the carbonyl group from the second fluorine hence making it more susceptible to nucleophilic substitution.

\[
\begin{align*}
\text{F} & \quad \text{C} \\
& \quad \text{O} \\
& \quad \text{F}
\end{align*}
\]

In the potassium salt of 4-hydroxy-4′-fluoro benzophenone, however, the negative charge of the phenoxide end reduces the electron withdrawing ability of the carbonyl and hence reduces the reactivity of the fluorine to nucleophilic attack.

\[
\begin{align*}
\text{K} & \quad \text{O} \\
& \quad \text{C} \\
& \quad \text{F}
\end{align*}
\]

Again, comparing the phenoxide ends in the two systems, the phenoxide end in the bis-potassium salt of 4,4′-dihydroxybenzophenone will have increased electron density (hence greater reactivity) compared to the phenoxide end in 4-fluoro-4′-hydroxybenzophenone for the following reason.

In the bis-potassium salt of 4,4′-dihydroxybenzophenone, the electron withdrawing power of the carbonyl group is reduced by electron donation from one of the phenoxide ends,

\[
\begin{align*}
\text{K} & \quad \text{O} \\
& \quad \text{C} \\
& \quad \text{O}
\end{align*}
\]

whereas in the potassium salt of the 4-fluoro-4′-hydroxybenzophenone it is enhanced by the inductive effect of the fluorine (which is stronger than the opposite mesmeric effect in the ground state).
These factors combine to increase the reactivity of the two monomer system over the one monomer system. This effect has been shown to be the case in a kinetic study of the analogous system

\[
\begin{align*}
F & \quad \text{O} & \quad \text{SO}_2 & \quad \text{O} & \quad \text{OK} \quad \text{one monomer} \\
F & \quad \text{O} & \quad \text{SO}_2 & \quad \text{O} & \quad \text{F} \quad \text{two monomer} \\
\end{align*}
\]

for the nucleophilic preparation of poly(phenylene ether sulphone).

This increased initial rate for the two monomer system may not, however, be as important as the relative solubilities in the reaction medium of the two types of phenoxide in accounting for the formation of material which gives gel and a red colouration in sulphuric acid solutions of the polymers. Thus the potassium salt of 4-fluoro-4'-hydroxybenzophenone is soluble in diphenyl sulphone at the concentrations and temperatures used, whereas the bis-potassium salt of 4,4'-dihydroxybenzophenone is only 0.04% soluble at the same temperature.

This difference means that, in the one monomer system, phenoxide ends are in solution (therefore in contact with growing polymer chains) from the start of the polymerisation whereas, in the two monomer system, the bisphenoxide leaves the solid phase to come into contact with a very large excess of fluorine ends (the 4,4'-difluorobenzophenone being completely soluble in diphenyl sulphone at these concentrations and temperatures) presumably to form a fluoro ended trimer.

\[
\begin{align*}
&\quad \text{KO} - \text{CO} - \text{O} - \text{OK} + n \cdot F - \text{CO} - \text{O} - F \\
&\quad \text{F} - \text{CO} - \text{O} - \text{CO} - \text{O} - \text{CO} - \text{F} + n-2 \cdot F - \text{CO} - \text{O} - F \\
&\quad + 2n \cdot KF
\end{align*}
\]
Only at the end of the reaction, when the number of fluorine ends available for reaction, has been greatly reduced, will phenoxide ends be in solution and unreacted for any length of time.

These observations suggest that it is some non-ether forming reaction of the phenoxide ends which give rise to species, which cause gel and give rise to red coloured solutions in sulphuric acid during the preparation of poly(phenylene ether ketone).

Investigation of the Red Colour in Sulphuric Acid Solutions of Poly(Phenylene Ether Ketone)

Before this study could be undertaken, it was necessary to quantify the measurement of the degree of redness in polymer solutions.

Very dilute solutions of the polymers in sulphuric acid (0.0004-0.0012%) showed a single absorption at 430 nm, attributable to the carbonyl group. This absorption is in the ultra violet and indeed, the solutions were virtually colourless. When, however, 1% solutions of the polymer were examined, these showed an absorbance at ~550 nm which would not be expected for the ideal polymer.
The intensity of this absorption was shown to be directly related to the degree of redness of the polymer solution as observed by eye and in subsequent experiments, the value of this absorption was quoted to describe the intensity of the red colouration. (See appendix for typical examples).

It has been postulated that the product of some non-ether forming reaction of the penoxide ends might be responsible for the red colouration in sulphuric acid solutions of the polymers. Accordingly, experiments were carried out in which various amounts of the bis-potassium salt of 4,4'-dihydroxybenzophenone were added to polymerisation systems and the resulting polymers examined as sulphuric acid solutions. Table 5.
### Table 5

Ultra Violet and Visible Spectral Data of 1% Solutions of Poly(Phenylen Ether Ketone) in 98% Sulphuric Acid

<table>
<thead>
<tr>
<th>Code</th>
<th>Method of Preparation</th>
<th>M% Excess Monomer</th>
<th>Gel Content %</th>
<th>RV</th>
<th>Absorb max at max of λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>7188/7/8</td>
<td>F-OK⁺</td>
<td>KO-OK 1.0</td>
<td>0.36</td>
<td>0.99</td>
<td>&gt;2.0</td>
</tr>
<tr>
<td>7188/7/2</td>
<td>&quot;</td>
<td>&lt;0.04</td>
<td>1.09</td>
<td>&gt;2.0</td>
<td>?</td>
</tr>
<tr>
<td>7188/7/1</td>
<td>&quot;</td>
<td>0.72</td>
<td>1.02</td>
<td>&gt;2.0</td>
<td>?</td>
</tr>
<tr>
<td>7188/24G</td>
<td>&quot;</td>
<td>None</td>
<td>0.08</td>
<td>1.30</td>
<td>just &gt;2.0</td>
</tr>
<tr>
<td>7188/7/3</td>
<td>&quot;</td>
<td>1.56</td>
<td>1.07</td>
<td>&gt;2.0</td>
<td>?</td>
</tr>
<tr>
<td>7188/14/1</td>
<td>&quot;</td>
<td>0.44</td>
<td>1.02</td>
<td>&gt;2.0</td>
<td>?</td>
</tr>
<tr>
<td>7188/7/4</td>
<td>&quot; F-F</td>
<td>0.20</td>
<td>1.16</td>
<td>1.04</td>
<td>1.85</td>
</tr>
<tr>
<td>7188/7/5</td>
<td>&quot; F-F</td>
<td>0.4</td>
<td>1.64</td>
<td>1.4</td>
<td>&gt;2.0</td>
</tr>
<tr>
<td>7188/7/6</td>
<td>&quot; F-F</td>
<td>0.6</td>
<td>1.04</td>
<td>1.67</td>
<td>1.63</td>
</tr>
<tr>
<td>7188/14/2</td>
<td>&quot;</td>
<td>1.0</td>
<td>0.20</td>
<td>1.82</td>
<td>1.55</td>
</tr>
<tr>
<td>7188/7/7</td>
<td>&quot;</td>
<td>1.0</td>
<td>1.12</td>
<td>2.09</td>
<td>1.22</td>
</tr>
<tr>
<td>7188/14/3</td>
<td>&quot;</td>
<td>1.5</td>
<td>0.32</td>
<td>1.64</td>
<td>1.24</td>
</tr>
<tr>
<td>7188/16/3</td>
<td>&quot;</td>
<td>1.5</td>
<td>1.08</td>
<td>2.17</td>
<td>0.98</td>
</tr>
<tr>
<td>7188/14/5</td>
<td>&quot;</td>
<td>2.5</td>
<td>0.92</td>
<td>1.29</td>
<td>1.0</td>
</tr>
<tr>
<td>7188/14/6</td>
<td>&quot;</td>
<td>2.5</td>
<td>1.24</td>
<td>1.1</td>
<td>0.86</td>
</tr>
<tr>
<td>7424/70</td>
<td>KO-OK + F-F⁻</td>
<td>KO-KO 2.5</td>
<td>None</td>
<td>0.77</td>
<td>0.77</td>
</tr>
<tr>
<td>7424/64</td>
<td>&quot;</td>
<td>1.0</td>
<td>0.57</td>
<td>1.02</td>
<td>546</td>
</tr>
<tr>
<td>7297/32</td>
<td>&quot;</td>
<td>None</td>
<td>1.82</td>
<td>0.25</td>
<td>544</td>
</tr>
<tr>
<td>7297/37</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1.03</td>
<td>0.25</td>
<td>~550</td>
</tr>
<tr>
<td>7297/64</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.63</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>7424/63</td>
<td>&quot;</td>
<td>F-F</td>
<td>1.60</td>
<td>0.21</td>
<td>~555</td>
</tr>
<tr>
<td>7424/65</td>
<td>&quot;</td>
<td>F-F</td>
<td>0.93</td>
<td>0.18</td>
<td>~555</td>
</tr>
<tr>
<td>7424/59</td>
<td>&quot;</td>
<td>F-F</td>
<td>1.53</td>
<td>0.29</td>
<td>~550</td>
</tr>
<tr>
<td>7424/67</td>
<td>&quot;</td>
<td>F-F</td>
<td>0.67</td>
<td>0.20</td>
<td>~555</td>
</tr>
<tr>
<td>7424/60</td>
<td>&quot;</td>
<td>F-F</td>
<td>0.55</td>
<td>0.23</td>
<td>~550</td>
</tr>
<tr>
<td>7424/19</td>
<td>&quot;</td>
<td>F-F</td>
<td>0.37</td>
<td>0.18</td>
<td>~550</td>
</tr>
<tr>
<td>7424/18</td>
<td>&quot;</td>
<td>F-F</td>
<td>0.14</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>7424/51</td>
<td>&quot;</td>
<td>F-F</td>
<td>0.11</td>
<td>None</td>
<td></td>
</tr>
</tbody>
</table>

F-⁻ CO-⁻ OK⁺ F⁻ CO-⁻ F⁻ KO-⁻ CO-⁻ OK⁻
The gel contents of the polymers were also measured.

These results strongly suggest that phenoxide end groups are in some way responsible for the formation of the species with an absorbance at ~550 nm.

Thus, when the phenoxide end group is soluble (as in the one monomer system), the absorbance of the polymer solutions are much higher than when the polymers were prepared from the relatively insoluble bis-phenoxide of the two monomer system. Further, within say the one monomer set of results, addition of excess 4,4'-difluorobenzophenone reduces the absorption as more excess difluoride is added. A similar effect is noticeable within the set of results for the two monomer system.

Having demonstrated that excess phenoxide end groups cause the resulting polymers to have red colourations in sulphuric acid solution, it was now decided to investigate the nature of the chromophore absorbing at ~550 nm and the mechanism of the reaction leading to it. In doing so, however, two things had to be borne in mind, firstly that the side reaction of the phenoxide should give some functional group which would absorb at ~550 nm when dissolved in sulphuric acid and secondly that this reaction should be associated with the formation of a branch point as would be the case if the red colouration were due to a soluble precursor of gel.

Attempts to Identify the Chromophore
There are several possible sites of attack on the polymer repeat unit (and its precursors) for phenoxide.

\[
\begin{align*}
  &\text{Attack on carbon atom 1 leads to ether interchange} \\
  &\text{carbon atom 1 leads to ether interchange}
\end{align*}
\]

with no overall change in the polymer structure having taken place.
Attack on carbon atom 2 leads to a branch point.

(cf the preparation of ortho nitrophenol from nitrobenzene and potassium hydroxide)

This reaction does not seem likely for two reasons. Firstly, elimination of the hydride ion would only be expected where an oxidising agent was present to convert it to the more stable hydroxyl ion and secondly, although the reaction outlined above does give rise to a branch point, the resulting structure would not be expected to give a red colouration in sulphuric acid.

It is known that substitution patterns in diaryl ketones can affect the position of $\lambda_{\text{max}}$ for the protonated carbonyl group but values of $\lambda_{\text{max}}$ greater than 400 nm are rare and this wavelength would only give rise to a yellow solution.

Extensive conjugation does, however, give rise to red colouration in acid solutions of ketones.

The model compound (XIV), corresponding to the branch structure (X), was
prepared and found to have $\lambda_{\text{max}} = 413$ nm in sulphuric acid.

\[
\text{XIV}
\]

This is in good agreement with the literature value of $\lambda_{\text{max}} = 412$ nm for the analogous 2,4,4'-trimethoxybenzophenone. From this evidence, attack of phenoxide on the carbon atom \textit{ortho} to carbonyl in the poly(phenylene ether ketone) repeat unit does not appear to be the side reaction that occurs.

Attack on carbon atom 4 is most likely to occur before the halogen atom has been displaced, further reaction would then give rise to a branched polymeric structure.

\[
\text{XV}
\]

\(X = \text{Halo-}en\)
Again for the reasons outlined previously, this structure would not appear the likely cause of the red colouration. Nevertheless, the corresponding model compound (XVI) was prepared and its absorption in sulphuric acid solution determined.

![Chemical Structure]

The position of the maximum, at 380 nm (yellow solution) was again at too short a wavelength.

Attack of the phenoxide at carbon atom 3 would give rise to several possibilities and attack here would appear to be most likely in view of the slight polarisation of the carbonyl group.

![Reaction Scheme]

Attack of phenoxide on the carbonyl could, by one mechanism, give rise to an alcohol of the type

![Alcohol Structure]

by the following reaction scheme
However, the protonation of such a group (as would occur in sulphuric acid solution) would give rise to the carbonium ion

which is partly analogous to an intermediate in the acid hydrolysis of ketals and acetals which is known\(^3\) to rapidly decompose.

\[
\text{R}_2C(\text{OR'})_2 + \text{H}^+ \xrightarrow{\text{FAST}} \left[ \begin{array}{c} \text{R}_2C \\ \text{OR'} \\ \text{OR'} \end{array} \right] \xrightarrow{\text{SLOW}} \text{R}_2C = \text{O} + \text{ROH} + \text{H}_3\text{O}^+ \\
\text{R}_2C = \text{OR'} + \text{ROH} \]

Such a simple mechanism for the attack of phenoxide on the carbonyl
function is not the only possibility however, Swan describes the formation of triphenyl carbinol when benzophenone is attacked by potassium tert-butoxide in an ethereal solution containing water, by the following mechanism

\[
\begin{align*}
\text{22)} & \quad \overset{\text{O} - \text{t} - \text{O}}{\text{C}} \quad \overset{\text{O} - \text{f} - \text{G}}{\text{C}} = 0 - 1 \\
\text{C-(CH}_3)_3 & \quad \overset{\text{C-(CH}_3)_3}{\text{C}} \\
\text{O} & \quad \overset{\text{f} ? \ ,}{\text{ft}} \\
\text{\&} & \quad w
\end{align*}
\]

although he states that potassium phenoxide did not give the reaction when used in place of the potassium tert-butoxide. Gassman et al refined the mechanism, indicating that an intermediate dianion is formed

\[
\begin{align*}
\text{23)} & \quad \overset{\text{O} - \text{t} - \text{O}}{\text{C}} \quad \overset{\text{O} - \text{f} - \text{G}}{\text{C}} = 0 - 1 \\
\text{C} \quad \overset{(\text{C})_3}{\text{C} \quad \text{OH}}
\end{align*}
\]

but again confirming the formation of triphenyl carbinol by the Swan mechanism.
Despite the facts that Swan found that potassium phenoxide did not cleave the ketone and that the Gassman et al mechanism requires the presence of water, these two investigations are of relevance to the present work. Both workers carried out their experiments at $30^\circ$ whereas polymerisation temperatures for the preparation of poly(phenylene ether ketone) are $330^\circ$ and both found triphenyl carbinol as a product.

It is possible, that even under our anhydrous conditions, the rather high temperature might cause ketone cleavage by phenoxide of the type described by Swan.

\[\text{The phenanion so formed could then attack a carbonyl to yield a triphenyl carbinol type structure}\]

\[\text{XVII}\]
This last reaction is of particular interest for the following reasons:

i) The triphenyl carbinol type structure formed is a branch point.

ii) Such structures, when dissolved in sulphuric acid, give highly coloured carbonium ions.

Triaryl carbonium ions absorb in the general range 400-600 nm depending on their substituents, and show extinction coefficients of the order $10^5$ (in sulphuric acid solution). This very high extinction value is important because it is noticeable that even polymers whose sulphuric acid solutions have very high absorbances show no gross loss in bulk properties (ie provided their reduced viscosity is sufficiently high, they can be moulded into creaseable film) which suggests that the non-ideal chromophoric structure present in the polymer chains is present in only small amounts.

These combined factors are strong indications that some triphenyl carbonium-like ion is responsible for the red colour in sulphuric acid solutions of poly(phenylene ether ketone). Structural defects of this type in poly(arylene ketones) have been previously reported. Kutner postulates the presence of di-para-phenoxy triphenylcarbonium ion in sulphuric acid solutions of a polymer prepared by electrophilic condensation of diphenyl
ether with terephthaloyl chloride as the cause of the red colour.

The precise nature of the triphenyl carbonium ion (ie its substituents and substitution pattern) in poly(phenylene ether ketone) is, however, not immediately apparent nor easy to predict.

Attempts to identify the chromophoric structure by conventional methods (eg n m r) would not be likely to succeed as calculation shows that a chromophoric group with an extinction coefficient of $10^5$ present in a polymer whose absorbance as a 1% solution in sulphuric acid was 0.38 would be present at the 0.01% level (see appendix).

Model compound synthesis would appear to be the best approach to the problem, but even this method is not without its drawbacks, for even if a model carbonium ion with $\lambda_{\text{max}}$ at 550 nm were prepared, it might still be difficult to establish identity with the unknown. This is partly because the chromophoric group in the polymer would be incorporated into the polymer chain, possibly altering somewhat the position and the extinction of the maximum.

Application of a Swan type mechanism to attack by phenoxide on a poly(phenylene ether ketone) repeat unit leads to the carbinol (XX) as follows:

\[ \text{(polymer chain)} \rightarrow \text{carbinol (XX)} \]
for which a realistic model compound would be 4,4',4''-triphenoxypiphenyl carbinol (XIX).
The position of $\lambda_{\text{max}}$ for the corresponding carbonium ion of this compound is $433$ nm, so unless further substitution corresponding to that which would be present in polymer chains radically alters the position of $\lambda_{\text{max}}$, this is not the correct structure for the carbonium ion.

A search of the literature failed to find a triphenyl carbonium ion which had a $\lambda_{\text{max}}$ of $550$ nm whose structure was mechanistically attainable with the precursors present in the polymerisation system. The only compound that gave a carbonium ion whose $\lambda_{\text{max}}$ was within $20$ nm of that observed in polymer solutions was 4,4'-dimethoxy-4''-benzoyl triphenyl carbinol.

Dilthey's evidence shows that substitution of a methoxy group for a phenoxy group has very little or no effect on the position of $\lambda_{\text{max}}$ in the carbonium ions derived from substituted triphenyl carbinols
so this model compound (XXIII) should be an adequate molecular representation of the model compound 4,4'-diphenoxo-4''-benzoyltriphenyl methanol.

The position of λ<sub>max</sub> of the carbonium ion

in sulphuric acid was 530 nm (λ<sub>max</sub> of the chromophore in poly(phenylene ether ketone) is ~550 nm).

This position of λ<sub>max</sub> is quite close to that observed in polymer solutions but the structure it corresponds to in the polymer chain

is

is not easy to account for mechanistically. Thus, such a structure formed by a Swan type mechanism, would involve formation of the
intermediate phenanion

\[
\begin{align*}
\text{Intermediate Phenanion} & \\
\text{\begin{minipage}[c]{.5\textwidth}
which could then attack the carbonyl function in the linear polymer chain thus
\end{minipage}} & \\
\end{align*}
\]

The difficulty is accounting for the formation of the 4-benzoylphenanion.

The high polymerisation temperatures required for the preparation of poly(phenylene ether ketone) could lead to radical formation. E s r has shown the presence of radicals in the polymerisation system but no attempt was made to elucidate their structures. The initially formed radicals could in turn lead to a number of possible irregular structures within the polymer chains.

Thus it is known that benzophenone as a solution in isopropanol forms benzopinacol when irradiated with light, the intermediate being the radical

\[
\begin{align*}
\text{Benzophenone} & \\
\text{\begin{minipage}[c]{.5\textwidth}
benzopinacol & \\
\end{minipage}} & \\
\end{align*}
\]

In conclusion it may be stated that the available evidence suggests that the chromophoric group causing the red colourations in sulphuric acid solutions of poly(phenylene ether ketone) is a substituted triphenyl carbinol structure. Its detailed structure and mechanism of formation are
not, however, known nor is it suggested that the formation of such a structure is the only side reaction occurring.

The Effect of Reduced Viscosity/Gel on the Toughness of Poly(Phenylene Ether Ketone)

In early experiments, it had been noticed that gel free polymer required a substantially lower reduced viscosity than gelled polymer for film prepared from the polymers to be creaseable. This effect was quantified for polymers containing up to 3% gel. The method employed to test the polymers was a simple creasing or flex test. Specimens of the polymers were compression moulded under standard conditions to give 0.007" thick film. The films were tested by first creasing the film in one direction then flexing along the crease line through 180°, six times. This procedure was repeated using a new crease line crossing the first at 90°. A pass (P) shows the film could be treated in this way without any visible cracking, a fail (F) indication that the film cracked when first creased. Failure during flexing is shown by an F with a subscript number indicating the number of flexes before failure.

This test would not be expected to show anything but gross differences between polymer samples - a more rigorous and quantitative type of toughness testing (eg impact testing), would demand larger quantities of polymer, more sophisticated specimen preparation and, in this case, a knowledge of the degree of crystallinity of the polymer samples as impact strength varies with degree of crystallinity.46,47 It was hoped that the standard method of preparation of the films used in the creasing test would confer approximately equal degrees of crystallinity on the samples (as far as was intrinsically possible) and that given this, the creasing test would show up large differences in behaviour of the samples.
Table 6

Flex Test Results and Gel Contents for Various Samples of Poly(Phenylene Ether Ketone)

<table>
<thead>
<tr>
<th>Code</th>
<th>RV</th>
<th>C\textsubscript{H\textsubscript{2}}\textsubscript{SO\textsubscript{4}}</th>
<th>% Gel</th>
<th>Flex Test</th>
<th>Code</th>
<th>RV</th>
<th>C\textsubscript{H\textsubscript{2}}\textsubscript{SO\textsubscript{4}}</th>
<th>Flex Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>7188/7/10</td>
<td>6.0</td>
<td></td>
<td>2.97</td>
<td>P</td>
<td>7297/35</td>
<td>1.87</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>7188/7/9</td>
<td>4.66</td>
<td></td>
<td>1.97</td>
<td>P</td>
<td>7297/17</td>
<td>1.82</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>7188/16/3</td>
<td>2.17</td>
<td></td>
<td>1.08</td>
<td>P</td>
<td>7297/32</td>
<td>1.82</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>7188/7/7</td>
<td>2.09</td>
<td></td>
<td>1.12</td>
<td>P</td>
<td>7297/14</td>
<td>1.49</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>7035/52</td>
<td>2.04</td>
<td></td>
<td>1.79</td>
<td>P</td>
<td>7188/68</td>
<td>1.22</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>7188/16/4</td>
<td>1.95</td>
<td></td>
<td>1.16</td>
<td>P</td>
<td>7297/41</td>
<td>1.16</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>7188/14/2</td>
<td>1.82</td>
<td></td>
<td>0.20</td>
<td>F\textsubscript{4}</td>
<td>7297/37</td>
<td>1.03</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>7188/7/6</td>
<td>1.67</td>
<td></td>
<td>0.04</td>
<td>F</td>
<td>7297/31</td>
<td>1.03</td>
<td></td>
<td>F\textsubscript{2}</td>
</tr>
<tr>
<td>7188/14/3</td>
<td>1.64</td>
<td></td>
<td>0.32</td>
<td>+</td>
<td>7188/61</td>
<td>1.00</td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>7188/7/5</td>
<td>1.40</td>
<td></td>
<td>1.64</td>
<td>F</td>
<td>7297/29</td>
<td>0.75</td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>7188/24G</td>
<td>1.30</td>
<td></td>
<td>0.08</td>
<td>F</td>
<td>7188/72</td>
<td>0.72</td>
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<td>F</td>
</tr>
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<td>7188/24/8</td>
<td>1.29</td>
<td></td>
<td>0.12</td>
<td>F</td>
<td>7297/64</td>
<td>0.63</td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>7188/14/5</td>
<td>1.29</td>
<td></td>
<td>0.92</td>
<td>F</td>
<td>7188/41</td>
<td>0.61</td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>7188/7/2</td>
<td>1.09</td>
<td>&lt;0.04</td>
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<td>0.53</td>
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<td>F</td>
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<td>7188/7/3</td>
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<td>1.56</td>
<td>F</td>
<td>7297/13</td>
<td>0.46</td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>7188/7/4</td>
<td>1.04</td>
<td></td>
<td>1.16</td>
<td>F</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7188/7/1</td>
<td>1.02</td>
<td></td>
<td>0.72</td>
<td>F</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

+Film not homogeneous, parts failed, others passed.

Several points emerged from these results;

i) Gelled polymer requires a reduced viscosity of \(\geq 2.0\) for compression moulded film to be creaseable.

ii) Gel free film only requires a reduced viscosity of \(\geq 1.20\) for compression moulded film to be creaseable.

iii) It is not the actual gel content of a polymer which causes brittleness.
in film prepared from that polymer but the presence of gel is an indication of branching and this branching causes brittleness, eg 7188/7/6 has a reduced viscosity of 1.67 (well above the limit of 1.20 observed for gel free polymers) but even the very small gel content of <0.04% is apparently enough to induce brittle behaviour in film prepared from it.

A fourth point to emerge was that gel content did not relate to the absorption at 550 nm of a 1% solution in sulphuric acid, even for polymers of the same reduced viscosity.

Initial attempts to demonstrate that branched but soluble species caused brittleness in poly(phenylene ether ketone) films were unsuccessful as the method employed was to attempt to filter gel from a sulphuric acid of a polymer who reduced viscosity was >1.20 but <2.0, to reprecipitate the soluble polymer, mould into film and retest. This necessitated using quite large quantities of polymer (~20 g) and subsequent filtration was slow. The filtered polymer solution was added slowly to water and the precipitated polymer was washed repeatedly with dilute sodium bicarbonate solution and then distilled water. Drying the polymer and subsequent moulding gave brittle but black film, and it was uncertain whether the brittleness of the film was an effect of soluble branched species (as was hoped) or of some degradative process initiated by lengthy exposure to sulphuric acid at the filtration stage, or even of decomposition (due to residual sulphuric acid) that had taken place during moulding.

This line of approach was abandoned and it was decided to introduce, artificially, branch units into the polymer structure.
This was done by incorporating a trifunctional monomer into the polymerisation system - usually 2,4,4'-trifluorobenzophenone.

\[
\begin{align*}
&\text{F} \begin{array}{c}
\text{C} \\
\text{O}
\end{array} \begin{array}{c}
\text{F} \\
\text{F}
\end{array} \ = \\
&\text{XXVI}
\end{align*}
\]

This gives a branch point of structure

\[
\begin{array}{c}
\text{O} \\
\text{C} \begin{array}{c}
\text{C} \\
\text{O}
\end{array} \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \ =
\end{array}
\]

These branched polymers were made from the two monomer system using both 4,4'difluorobenzophenone and 4,4'dichlorobenzophenone as bishalogeno monomers.

\[
\begin{align*}
30) & \quad \text{F} \begin{array}{c}
\text{C} \\
\text{O}
\end{array} \begin{array}{c}
\text{F} \\
\text{F}
\end{array} + \text{KO} \begin{array}{c}
\text{C} \\
\text{O}
\end{array} \begin{array}{c}
\text{C} \\
\text{O}
\end{array} \text{OK} + \text{F} \begin{array}{c}
\text{C} \\
\text{O}
\end{array} \begin{array}{c}
\text{C} \\
\text{F}
\end{array} \\
\downarrow & \quad \left( \begin{array}{c}
\text{C} \\
\text{O}
\end{array} \begin{array}{c}
\text{C} \\
\text{O}
\end{array} \text{O} \right) \left( \begin{array}{c}
\text{C} \\
\text{O}
\end{array} \begin{array}{c}
\text{C} \\
\text{O}
\end{array} \text{O} \right) \\
& \quad 0.995 \ln n \quad 0.005 \ln n
\end{align*}
\]

\[
\begin{align*}
31) & \quad \text{C} \begin{array}{c}
\text{C} \\
\text{C}
\end{array} \begin{array}{c}
\text{C} \\
\text{C}
\end{array} \text{C} + \text{KO} \begin{array}{c}
\text{C} \\
\text{C}
\end{array} \begin{array}{c}
\text{C} \\
\text{C}
\end{array} \text{OK} + \text{F} \begin{array}{c}
\text{C} \\
\text{C}
\end{array} \begin{array}{c}
\text{C} \\
\text{F}
\end{array} \\
\end{align*}
\]

The trifunctional monomer was introduced in sufficient quantities to give 0.5 % of the branch unit overall. The quantities of the bis potassium salt of 4,4'-dihydroxybenzophenone were adjusted to keep the end groups in balance.
Several initial attempts to prepare such branched polymers resulted in highly gelled polymers (demonstrating that the 2,4,4′-triphenxoybenzophenone unit is incorporated into the chains) which were nevertheless a pale gold colour in sulphuric acid. Eventually, however, two polymers were prepared with reduced viscosities in the desired range (ie 1.20 to 2.0) which were gel free. Compression moulded films of both of these polymers (reduced viscosities of 1.29 and 1.32) were brittle, confirming that soluble but branched species can cause brittleness in poly(phenylene ether ketone) film.

The type of branching point that was artificially introduced was not, of course, of the same type as is normally present in the polymers. However, as it is the branching which causes the effect, this should not matter.

The effect of branching on the toughness of polymers is complex when the polymer is crystalline.

For crystalline polymers whose glass transition is below the test temperature (in this case room temperature), toughness (as measured by impact strength) decreases with increasing crystallinity. This is because the relatively disordered amorphous regions absorb the energy of the applied load by molecular motion so any decrease in the proportion of amorphous polymer (as happens when crystallinity increases) decreases the polymer's resistance to breakage. For polymers whose glass transition (Tg) is above the test temperature, as is the case with poly(phenylene ether ketone) of Tg 140-150, the effect will not be so marked. This is because an increase in crystallinity leads to a decrease in the proportion of amorphous polymer. The amorphous polymer is below its glass transition temperature so that segmental motion of the chains is greatly reduced and
the energy of a high speed impact is less easily absorbed.

In poly(phenylene ether ketone), the branching would be expected to reduce the degree of crystallinity ultimately attainable by the polymer as the presence of branches would be expected to prevent close packing of the chains. This should lead to a slight increase in the proportion of amorphous polymer and hence greater resistance to breaking. This effect appears to be more than offset, however, by the effect of the branches on the amorphous regions.

Below the glass transition temperature, the amorphous polymer chains can only undergo slow segmental motion. Branching in these chains, and hence interchain entanglements would further reduce segmental motion and hence further reduce the resistance of the polymer to breakage.

Thus in the series of gelled polymers, those with the highest proportion of soluble branched precursors of gel, require a higher overall molecular weight (as measured by reduced viscosity) to resist breakage compared with the ungelled series. The resulting fall in the chance of brittle failure with increasing molecular weight is known.48,49

It is worth pointing out at this point that the use of reduced viscosity as a method of comparing molecular weights between gelled and ungelled polymers is valid. The reduced viscosities of the gelled polymers were measured after filtration and the effect of the branched but soluble species would be, if anything, to reduce the values of reduced viscosity for a given molecular weight. Thus it is known that short chain branching has little effect on solution viscosity50 and long chain branching reduces dilute solution viscosity because, for a given degree of polymerisation,
a branched molecule has a smaller hydrodynamic volume than a linear one.

The Molecular Weight/Solution Viscosity Relationship for Poly(Phenylene Ether Ketone)

The coefficient of viscosity of any solution is the ratio of the shear stress to the rate of shear. If this ratio is constant for different rates of shear, the solution is said to be Newtonian. For polymer solutions, Newtonian behaviour is usually observed at polymer concentrations of \(<1\%\) (exceptions to this general rule are observed for dilute solutions of polyelectrolytes).

Comparison of dilute polymer solution viscosities with pure solvent viscosities can be made in several ways:

The ratio of the viscosity of a solution (\(\eta\)) to the viscosity of the pure solvent (\(\eta_0\)) is called the viscosity ratio, \(\eta_r\)

\[
(3.1) \quad \eta_r = \frac{\eta}{\eta_0}
\]

the relative increase of the viscosity is called the specific viscosity (\(\eta_{sp}\))

\[
(33) \quad \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1
\]

and the specific viscosity divided by the concentration is the viscosity number or reduced viscosity (\(\eta_c\))

\[
(34) \quad \eta_c = \frac{\eta_{sp}}{c} = \frac{1}{c} \left( \eta_r - 1 \right)
\]

The value of the reduced viscosity at infinite dilution is called the intrinsic viscosity (\([\eta]\))

\[
(35) \quad [\eta] = \lim_{c \to 0} \eta_c = \lim_{c \to 0} \frac{1}{c} \left( \eta_r - 1 \right)
\]
Thus a plot of $\eta_{SP/C}$ against $C$ will give the value of $[\eta]$ ie the value of $\eta_{SP/C}$ at $C = 0$.

This plot is a straight line whose slope is related to the Huggin's constant $k'$ by the equation

\[ \eta_{SP/C} = [\eta] + k' [\eta]^2 C \]

Staudinger proposed that the molecular weight, $(M)$, of a polymer was related to its solution viscosity by the equation

\[ [\eta] = KM \]

where $K$ was a constant.

This purely empirical equation was later refined by Kuhn and Mark to

\[ [\eta] = KM^\lambda \]

where $K$ and $\lambda$ are constants.

The relationship was shown to hold for a number of polymers by Houwink and the equation is generally called the Mark-Houwink equation.

The values of $K$ and $\lambda$, as well as depending on the polymer, depend on the solvent used and the temperature.

This method of determining molecular weight is widely used because the method is quick and the apparatus required is simple (a thermostated bath and a suitable viscometer). However, the values of $K$ and $\lambda$ in the Mark-Houwink equation must first be determined before the equation can be applied to a polymer of unknown molecular weight.

Polymers have a range of molecular weights (i.e., a distribution of molecular
weights) so any method which determines 'molecular weight' gives in fact some form of average molecular weight.

The two most common molecular weight averages that are determined are weight average molecular weight ($\bar{M}_w$) and number average molecular weight ($\bar{M}_n$). These averages may be expressed mathematically, thus

\[
\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}
\]

and

\[
\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}
\]

where

- $N_i$ = number of the $i^{th}$ species
- $M_i$ = the molecular weight of the $i^{th}$ species

Generally any molecular weight average ($\bar{M}$) may be expressed

\[
\bar{M} = \sum_{i=1}^{\infty} \frac{N_i M_i^a}{\sum_{i=1}^{\infty} N_i M_i^{a-1}}
\]

where $N_i$ and $M_i$ are as defined above and $a$ = an index having any real value.

thus when $a = 2$, $\bar{M} = \bar{M}_w$ etc

The type of molecular weight average obtained by any method will depend on how that method is affected by the distribution of molecular weights within the sample under study.
Thus if the method 'counts' the molecules irrespective of their size, the average obtained will be the statistical mean ie the number average molecular weight. This then will be true for all studies based on colligative properties (eg elevation of boiling point, depression of freezing point and osmometry), whereas a study based on molecular size (eg light scattering) will give a weight average molecular weight.

It can be seen from this, that if the values of $K$ and $\alpha$ in the Mark-Houwink equation are to be determined by solution viscosity studies of a polymer of known molecular weight, the values will be altered depending on whether the molecular weight of the polymer was calculated as a weight or number average. This problem may be overcome if a polymer sample can be obtained which is homodisperse (ie each molecule in the sample is exactly the same molecular weight as the next). In this case $\bar{M}_n = \bar{M}_w$.

It is, however, exceedingly difficult to prepare such polymers and the usual method of obtaining as near homodisperse samples as is possible is to fractionate a heterodisperse sample. This is done by very slowly adding a non-solvent to a polymer solution and filtering off the precipitated fractions. With great care, these fractions can be obtained nearly homodisperse, when

\[ \bar{M}_n \propto \bar{M}_w \]  \hspace{1cm} (42)

Now $K$ and $\alpha$ can be determined by calculating the average molecular weight of the fraction and using this value as $M$ in the equation,

\[ [\eta] = K M^\alpha \]  \hspace{1cm} (38)

the intrinsic viscosity of the fraction is obtained.
This now gives $K$ and $\alpha$ for a particular polymer, at a particular temperature, in a particular solvent.

If these values are used on a different, heterodisperse (ie with a distribution of molecular weights) sample of the same polymer with the same solvent and at the same temperature, the molecular weight of this sample is obtained - this average is called the viscosity average molecular weight ($M_v$) and lies, numerically, between weight average and number average.

In the light of what has been said, poly(phenylene ether ketone) presents a number of problems when a quantitative study of its solution viscosity/molecular weight relationship is undertaken.

The polymer is crystalline as made and has only one useful solvent- concentrated sulphuric acid - and whilst fractionation of a sample of the polymer is theoretically possible, it is doubtful whether the polymer repeat unit would survive such a procedure without becoming chemically changed. This is because in order to achieve satisfactory fractionation it is usual, after adding a small quantity of non-solvent (in this case water), and precipitating a fraction, to heat the solution until the fraction has redissolved. The solution is then allowed to cool slowly to precipitate the fraction once again. This ensures that equilibrium is achieved and the procedure is repeated for each fraction. In the case of poly(phenylene ether ketone), this would involve heating quite strong sulphuric acid solutions of the polymer several times, and sulphonation might occur.

In view of this, it was decided to prepare samples of poly(phenylene ether
ketone) of known number average molecular weight and use these to
determine values of $K$ and $\alpha$ in the Mark-Houwink equation.

This would mean, of course, that the values of $K$ and $\alpha$ so obtained
would give a value of number average molecular weight and not viscosity
average molecular weight when used subsequently to analyse a sample of
polymer of unknown molecular weight. It is possible to prepare samples
of poly(phenylene ether ketone) of any desired number average degree of
polymerisation ($\overline{DP}_n$) by adjusting the ratio of end-groups. This may be
demonstrated thus:

Consider the polymerisation of 4-fluoro-4'-hydroxybenzophenone (as the
potassium salt).

\[ \text{(43)} \quad n \text{F} - \text{O} - \text{O} \text{K} \rightarrow \text{(O} - \text{O} - \text{O})_n + n \text{KF} \]

Let $p$, be the extent of reaction, which may be defined as the ratio of
the number of ether links formed to the total number of reactive end
groups originally present,

and $\overline{DP}_n$ be the number average degree of polymerisation which may be
defined as the ratio of the original number of molecules, $N_0$, to the
number of molecules, $N$, present at any time $t$

\[ \text{(44)} \quad \text{ie} \quad \overline{DP}_n = \frac{N_0}{N} \]

Thus by definition,

\[ \text{(45)} \quad N = N_0 - p N_0 \]

and $\frac{N}{N_0} = 1 - p$
Now consider the reaction between \( x \) molecules of \( \text{F-CO-OK} \) and 1 molecule of \( \text{F-CO-0-F} \) going to completion. Now \( p \) may be defined (with respect to the excess end-groups) as the ratio of the number of reacted end-groups to the initial number of reactive end-groups.

In this case the number of reactive end groups is \( 2x + 2 \) and the number reacted is \( 2x + 2 - 2 \).

\[
p = \frac{2x + 2 - 2}{2x + 2} = \frac{x}{x+1}
\]

\[
\frac{\text{DP}_n}{1-p} = \frac{1}{1- \frac{x}{x+1}} = \frac{1}{\frac{x+1-x}{x+1}} = x+1
\]

Therefore, for example, to prepare a fluoro ended sample of poly(phenylene ether ketone) of number average degree of polymerisation, say, ten requires the following stoichiometry.

\[
9 \text{F-CO-OK} + \text{F-CO-F}
\]

Alternatively this may be stated as a ratio of eleven fluoro ends to nine phenoxide ends and hence applied to the two monomer system of preparation of poly(phenylene ether ketone).

Fluoro ended oligomers of various number average degrees of polymerisation were prepared by the two monomer route and their intrinsic viscosities
measured. The fluoro end was used as the excess reactive end-group and not phenoxide to ensure freedom from side reactions. As all the end-groups on the oligomers were fluoro, elemental analysis for fluorine was used to check that the calculated number average degree of polymerisation had been achieved. The model used for this calculation was

\[ F-\begin{array}{c}
\text{\text{C}}
\end{array}-CO\left(\begin{array}{c}
\text{\text{C}}
\end{array}-O-\begin{array}{c}
\text{\text{C}}
\end{array}-CO\right)_n-F \]

XXVII

The value of \( n \) being calculated from the analysis results should be one less than the calculated number average degree of polymerisation aimed for.

Analysis was only attempted for oligomers of \( \overline{DP}_n \leq 20 \) as the very low fluorine content of higher oligomers would probably render the results inaccurate.

**Table 7**

<table>
<thead>
<tr>
<th>Calculated ( DP_n )</th>
<th>Actual ( \overline{DP}_n ) by Fluorine analysis</th>
<th>( [\eta] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4.1</td>
<td>0.10</td>
</tr>
<tr>
<td>5</td>
<td>5.16</td>
<td>0.10</td>
</tr>
<tr>
<td>7</td>
<td>7.07</td>
<td>0.12</td>
</tr>
<tr>
<td>10</td>
<td>10.20</td>
<td>0.21</td>
</tr>
<tr>
<td>15</td>
<td>15.65</td>
<td>0.23</td>
</tr>
<tr>
<td>20</td>
<td>21.43</td>
<td>0.36</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>0.49</td>
</tr>
<tr>
<td>40</td>
<td>-</td>
<td>0.63</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>0.93</td>
</tr>
</tbody>
</table>
Plotting these values on log/log paper, indicated that they were related linearly.

The best straight line through the points was determined using the method of least squares and the values of $K$ and $\alpha$ calculated from the intercept and slope. The errors in the value of these constants were also calculated. (See experimental section for details).

The values obtained were

$$K = 0.0215 \pm 0.0034$$

$$\alpha = 0.891 \pm 0.0023$$

These values apply for solutions of poly(phenylene ether ketone) in concentrated (98%) sulphuric acid at 25° and will give a number average molecular weight. ($\overline{DP}_n \times$ Molecular weight of the repeat unit = $\overline{M}_n$).

The molecular weight range was \( \sim 1000 - \sim 10,000 \).

The value of $\alpha$ obtained, may be interpreted in terms of the configuration of the polymer molecules in solution.\(^56\)

The constant $\alpha$ generally lies in the range 0.5-0.8, its value increasing over this range as the solvent power increases. This is because a better solvent for the polymer (ie one where polymer/solvent interactions tend to be preferred to polymer/polymer or solvent/solvent interactions) increases the size of the polymer molecules by encouraging them to expand to their fullest extent. This causes the value of the intrinsic viscosity to rise; hence $\alpha$ rises. The value of 0.8 is usually the upper limit for polymers with a high degree of flexibility in the chain.
MARK-HOUWINK PLOT FOR

\[ \bar{D} \bar{P}_n \] for \( \{\theta\}-co-\{\theta\}-o \) in 93% SULPHURIC
ACID AT 25°.
For stiffer molecules in good solvents, $\alpha$ lies between 0.8 and 1.0. The value of $\alpha$ of 0.891 for poly(phenylene ether ketone) in sulphuric acid at $25^\circ$ fits well with this theory. The repeat unit of the polymer with its two benzene nuclei is relatively inflexible and sulphuric acid would be expected to protonate the carbonyl group causing interchain repulsions.

The Preparation and Structure of Copoly(Phenylene Ether Ketones/Sulphones)

The phenylene ether sulphone repeat unit

\[
-\left(\text{phenylene} \right) - \text{SO}_2 - \left(\text{phenylene} \right) - \text{O-}
\]

may easily be incorporated into the poly(phenylene ether ketone) chains by using the appropriate precursors to polycondensation.

Thus a mixture of the following

\[
\text{Cl}-\left(\text{phenylene} \right) - \text{SO}_2 - \left(\text{phenylene} \right) - \text{Cl}
\]

\[
\text{Cl}-\left(\text{phenylene} \right) - \text{CO} - \left(\text{phenylene} \right) - \text{Cl}
\]

and

\[
\text{KO}-\left(\text{phenylene} \right) - \text{CO} - \left(\text{phenylene} \right) - \text{OK}
\]

will lead to a copolymer containing both

\[
-\left(\text{phenylene} \right) - \text{SO}_2 - \left(\text{phenylene} \right) - \text{O-}
\]

and

\[
-\left(\text{phenylene} \right) - \text{CO} - \left(\text{phenylene} \right) - \text{O-}
\]

units.

Adjustment of the various amounts of these three components can be made
to lead to any desired copolymer compositions down to 50 M% of the phenylene ether ketone repeat unit. Copolymers containing less than 50 M% of this unit would necessitate using at least some of the bispotassium salt of 4,4'-dihydroxydiphenyl sulphone. The use of this compound was in fact avoided because the most favourable combination of end-group reactivities is obtained using the combination of components already outlined, i.e., the chlorines in 4,4'-dichlorodiphenyl sulphone should be more susceptible to nucleophilic displacement than those in 4,4'-dichlorobenzophenone due to the greater electron withdrawing power of sulphone compared to ketone.\(^{57}\) It may be similarly argued, therefore, that the charge density will be greater on the phenoxide end from the benzophenone derivative than from the diphenylsulphone derivative when comparing the bis potassium salts of 4,4'-dihydroxybenzophenone and 4,4'-dihydroxydiphenylsulphone. The range of copolymer compositions investigated was restricted to those containing greater than 50 M% of the phenylene ether ketone repeat unit for this reason.

The precise details of experimental procedure for the preparation of these copolymers is set out in the experimental section but it is worthy of mention at this stage that the required amounts of 4,4'-dichlorobenzophenone and 4,4'-dichlorodiphenyl sulphone were added to the polymerisation mixture at the same time and for the purposes of further discussion this technique will be called a "one step addition".

Thus, if a copolymer containing 80 Mole% of phenylene ether ketone repeat units were desired, the following stoichiometry would be observed.

\[
\begin{align*}
\text{KO-} & \quad \text{CO-} & \quad \text{OK} & \quad 0.5 \text{ mole} \\
\text{Cl-} & \quad \text{CO-} & \quad \text{-CL} & \quad 0.3 \text{ mole} \\
\text{Cl-} & \quad \text{-SO}_2- & \quad \text{-CL} & \quad 0.2 \text{ mole}
\end{align*}
\]
The bisphenoxide would be added first, followed by a mixture of the two bishalageno compounds. Complete polymerisation would then lead to a copolymer of overall composition.

\[
\left( \text{\includegraphics[width=0.3\textwidth]{structure1}} \right)_{0.8n} \left( \text{\includegraphics[width=0.3\textwidth]{structure2}} \right)_{0.2n}
\]

XXVIII

The melting points of these one step addition copolymers are shown in Graph 2.

What is not clear from this method of preparation, however, is the arrangement with respect to one another of the two types of repeat unit within a polymer chain, ie the copolymer could be, block, random, or, to some extent, alternating.

It might, for instance, be thought that the difference in reactivity of the end-groups of the starting materials could give rise to some ordering of repeat units within a polymer chain.

As has been discussed, the chlorine end-groups in 4,4'-dichlorodiphenyl sulphone should be more susceptible to nucleophilic attack than those in 4,4'-dichlorobenzophenone. If this difference in reactivity were large enough, it is possible that all the 4,4'-dichlorodiphenyl sulphone would react with the bisphenoxide before any of the 4,4'-dichlorobenzophenone did so. Polymerisation to completion with no other reactions taking place, would then lead, for a copolymer containing 80 mole % phenylene ether ketone repeat unit, to the structure (XXIX).

\[
\left( \text{\includegraphics[width=0.3\textwidth]{structure1}} \right)_{0.4n} \left( \text{\includegraphics[width=0.3\textwidth]{structure2}} \right)_{0.6n}
\]

XXIX
CHANGE IN CRYSTALLINE MELTING POINT (Tm) WITH CHANGING COPOLYMER COMPOSITION.

Mole % (10 50 - 10 0 ) in (10 50 - 10 0 ) (10 0 - 10 0 ) / an bn
The little kinetic data available suggests, however, that such ordered block copolymers would not in fact be formed.

Table 8

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Second Order Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_6\text{H}_4\text{SO}_2-\text{C}_6\text{H}_4\text{-Cl} )</td>
<td>( 3.0245 \times 10^{-5} \text{ mole}^{-1} \text{ sec}^{-1} )</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_4\text{CO-}\text{C}_6\text{H}_4\text{-Cl} )</td>
<td>( 6.29 \times 10^{-5} \text{ mole}^{-1} \text{ sec}^{-1} )</td>
</tr>
</tbody>
</table>

The chloro group in the ketone is 4.8 times less reactive than that in the corresponding sulphone.

In order to demonstrate the degree to which ordering took place during the build up of polymer chains, the following experiments were carried out.

A series of copolymerisations were carried out to yield polymer of composition 80 Mole % phenylene ether ketone units and 20 Mole % phenylene ether sulphone units.

These polymerisations were stopped (by removing the reaction vessel from the heat bath, so setting the polymerisation mass solid) at various conversions. The extent of conversion was determined by titration of unreacted phenoxide end-groups.

Now, if the polyetherification process were completely random ie there
were no difference whatever between the reactivities of the chloro group on the ketone containing substrate and the chloro group on the sulphone containing substrate, the proportion of phenylene ether sulphone units incorporated into the oligomers should be 20 mole % (ie the same as the overall ratio of phenylene ether sulphone dictated by the ratio of starting materials). If, however, all the 4,4'-dichlorodiphenyl sulphone reacted before any of the 4,4'-dichloro benzophenone did so, at conversions of less than 40%, the proportion of phenylene ether sulphone repeat units in the oligomers should be 50 mole %. At conversions of greater than 40%, the proportion of phenylene ether sulphone repeat units would then be expected to gradually decrease to a limit of 20 mole % at high conversions.

Examination of the oligomers by n m r gave the following results.

Table 9

<table>
<thead>
<tr>
<th>Experiment</th>
<th>% Conversion (by residual base titration)</th>
<th>Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30.0</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>52.6</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>61.4</td>
<td>29</td>
</tr>
<tr>
<td>4</td>
<td>68.6</td>
<td>24</td>
</tr>
</tbody>
</table>

(A polymerisation taken to 91% conversion gave an oligomer which was insoluble in most common organic solvents and was not therefore examined by n m r).
The n m r analysis was carried out in dimethyl sulphoxide solution at 200°, and the relative concentrations of the phenylene ether ketone and phenylene ether sulphone units were calculated from measurements of the areas of the appropriate resonances in the n m r spectrum. These resonances were assigned with reference to the spectra of the polymers

\[
\left\{ \begin{array}{c}
\text{XXX}
\end{array} \right\}_n
\]

\[
\left\{ \begin{array}{c}
\text{XXXI}
\end{array} \right\}_n
\]

\( \delta \ 8.07 \text{ (d } H_c), \ 7.94 \text{ (d } H_B), \ 7.30 \text{ (complex } H_A) \)

(XXX) and (XXXI) for which

\( \delta (H_c) = 8.07 \text{ (d)}, \delta (H_B) = 7.94 \text{ (d)} \) and \( \delta (H_A) = 7.30 \text{ (complex)} \)

Reference polymers of known phenylene ether ketone to phenylene ether sulphone ratios were also used to check the accuracy of the quantitative determinations.

The results show a fairly constant proportion of phenylene ether sulphone repeat units of 24-29 mole %. This value is higher than the 20 mole % expected for completely random reaction of chloro end-groups, and neither is it in agreement with the predicted range of mole percentages consistent
with completely separate reaction of the two types of dichloride. The figures, in fact, show what might be expected from the kinetic data (Table 8), that is that the slightly greater reactivity of the chloro group para to sulphone compared to that para to ketone causes slightly preferential inclusion of phenylene ether sulphone units in the copolymer chains during the early part of the reaction, but this increased reactivity is not sufficient to render the arrangement completely ordered.

Further evidence of the random nature of the copolymers is apparent in their melting behaviour.

Inclusion of phenylene ether sulphone units into the chain of phenylene ether ketone units causes a marked drop in crystalline melting point (Tm) (Graph 2). This drop (some 11° for each 5 Mole % phenylene ether sulphone) is consistent with the copolymers being random, for if they were blocked, no such marked drop in Tm would be expected. Theil and Mandelkern have shown that for a blocked copolymer consisting of one unit that was crystallisable and another that was not, the melting point was the same as for the crystalline homopolymer, even for low concentrations of this unit. This is because the blocks of crystallisable units in a block copolymer behave similarly to the corresponding homopolymer and it is known that the Tm for a crystalline polymer is essentially independent of the degree of polymerisation. This has been demonstrated for poly(poly phenylene ether ketone) (Graph 3), where it was found that chain lengths above approximately nine repeat units had essentially the same Tm of 370-380°.

Mandelkern has also shown by model calculation that for a random copolymer containing 80 mole % of crystallisable units and 20 mole % non-
THE VARIATION IN CRYSTALLINE MELTING POINT WITH DEGREE OF POLYMERISATION FOR \((\bigcirc-\text{co-}\bigcirc-\text{o})_n\)

\[ T_m \text{ °C} \]

Symbols:
- \(\bigcirc\) = Model Compounds
- \(\times\) = Floreo Ended Oligomers
- \(\oplus\) = Polymer

\(n\) in \((\bigcirc-\text{co-}\bigcirc-\text{o})_n\)
crystallisable units, the depression of $T_m$ should be about $50^\circ$. The copolymers of phenylene ether sulphone and phenylene ether ketone units containing 80 mole $\%$ of phenylene ether ketone has a $T_m$ 47$^\circ$ below that for homopoly(phenylene ether ketone), which is in good agreement with Mandelkern's figure.

As well as this evidence, there is a further factor which would lead to randomisation of the two types of unit in the copolymers.

It is known that suitably activated ether links are susceptible to nucleophilic cleavage:

\[ \text{A1) } \text{[Diagram]} \]

In the context of the copolymer system, the nucleophile would initially be phenoxide para to ketone, but cleavage would give rise to phenoxide para to sulphone and hence would lead to complete randomisation of the two types of unit.

\[ \text{A2) } \text{[Diagram]} \]
To demonstrate that ether cleavage does in fact take place, the following experiments were carried out.

Two copolymers of the following compositions were prepared; 80 mole % phenylene ether ketone/20 mole % phenylene ether sulphone and 95 mole % phenylene ether ketone/5 mole % phenylene ether sulphone, but by a two step addition process as opposed to the usual one step addition.

That is, the stoichiometrically required amount of 4,4'-dichlorodiphenyl sulphone was added to the bisphenoxide and reaction was allowed to proceed to completion (1 hour at ≈330°C was sufficient for this - a check was carried out by running a blank experiment which was stopped after this one hour period and the unreacted bisphenoxide titrated to confirm that complete reaction of the 4,4'-dichlorodiphenyl sulphone had taken place). The required amount of 4,4'-dichlorobenzophenone was then added. Polymerisation was completed in the normal way.

In the absence of ether cleavage, this type of copolymerisation should have yielded copolymers of the following type

\[
\left( \begin{array}{c}
\text{Ph} \text{-SO}_2\text{-Ph} \\
\text{Ph} \text{-CO-Ph}
\end{array} \right)_{\text{a,n}} \left( \begin{array}{c}
\text{Ph} \text{-SO}_2\text{-Ph} \\
\text{Ph} \text{-CO-Ph}
\end{array} \right)_{\text{b,n}}
\]

where a = 0.4, b = 0.6

and a = 0.1, b = 0.9

respectively for the two copolymers.

The Tm's of these two copolymers should in theory be the same as homopoly (phenylene ether ketone). In fact they showed the same depression of melting point as was observed for copolymers prepared by the one step addition process (Graph 4). This means that the ordered structures postulated for the two step addition copolymers were not in fact formed,
COMPARISON OF $T_m$ FOR COPOLYMERS PREPARED BY "ONE-STEP ADDITION" (LINE) TO THOSE PREPARED BY "TWO-STEP ADDITION".
and that ether cleavage had taken place to randomise the two structural repeat units.

One further point to emerge from the n m r study of the oligomers was that they were all chloro ended; undoubtedly a consequence of the very low solubility of the bis potassium salt of 4,4'-dihydroxybenzophenone in diphenyl sulphone.

Further evidence for ether cleavage was obtained when it was found that a mixture of poly(phenylene ether ketone) and poly(phenylene ether sulphone) formed a copolymer when heated together at normal polymerisation temperature in the presence of a little phenoxide. Reaction for 20 h gave a copolymer with quite a large melting range (290-330°) consistent with that of a copolymer of 20-30 mole % sulphone units.

The Effect on Properties of Changing Copolymer Composition

Tm (Crystalline Melting Point)

The homopolymer, poly(phenylene ether ketone), is crystalline with a crystalline melting point (Tm) of 365-370° (depending on the sample) and introduction into this chain of the non-crystallisable phenylene ether sulphone units would be expected to yield copolymers with different Tm's. Examination of a range of such copolymers, varying from 50 to 95 mole % phenylene ether ketone units, by differential thermal analysis, has shown that copolymers containing less than ~70 mole% of the phenylene ether ketone repeat unit are not crystalline and that above this level, Tm increases with increasing phenylene ether ketone content. These observations were confirmed by x-ray examination of the same copolymers.
Heating rates of $10^\circ / \text{min}$ were used for these measurements and the $T_m$ was taken as the 'point' of the endothermic peak on the thermogram.

Graph 2 shows that $T_m$ falls $11^\circ$ for each 5 mole % phenylene ether sulphone units added.

Parallel with this observation is a corresponding increase in the glass transition temperature ($T_g$) as the mole percentage of the phenylene ether sulphone unit increases.

<table>
<thead>
<tr>
<th>Mole % $\big{\text{ phenylene ether sulphone unit }\big}$</th>
<th>$T_g$ (Differential Scanning Calorimetry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>145</td>
</tr>
<tr>
<td>10</td>
<td>150</td>
</tr>
<tr>
<td>20</td>
<td>169</td>
</tr>
<tr>
<td>25</td>
<td>174</td>
</tr>
<tr>
<td>30</td>
<td>175</td>
</tr>
<tr>
<td>40</td>
<td>180</td>
</tr>
</tbody>
</table>

Density

A similar change in property with changing composition of the copolymers can be observed in the densities of rapidly quenched samples of the copolymer. Graph 5.
Change in density with changing copolymer composition.

(for amorphous copolymers)
Extrapolation of the line to 100% phenylene ether sulphone units gives a value of 1.385 for homopoly (phenylene ether sulphone) which is in fair agreement with the value of 1.37 obtained for compression moulded film of this material. 31

Measurements were made on a density column.
Melt Viscosity

The melt viscosity ($\eta_c$) is an important parameter of any thermoplastic as almost all fabrication techniques involve melt flow.

The melt viscosity characteristics of several copoly (phenylene ether ketone/sulphones) were measured to see if they changed with changing composition of the copolymers. Measurements were made in a ram extruder at a temperature of $400^\circ$ and at a sheer rate $125$ sec$^{-1}$.

$400^\circ$ represents a compromise between a temperature high enough to enable melt flow to take place and low enough to prevent thermal degradation of the polymer. Even so, thermal degradation may have occurred.

Melt viscosity may be defined as the ratio of the sheer stress ($s$) to the rate of sheer ($\dot{\gamma}$).

$$\eta_c = \frac{s}{\dot{\gamma}}$$

If the melt viscosity is independent of the rate of sheer the melt is said to be Newtonian.

Polymer melts behave in a Newtonian manner if the sheer stress needed to make them flow is of the order of $10^2 - 10^3$ dynes / cm$^2$. When large shear stresses are required, however ($>10^5$ dynes / cm$^2$), their behaviour is Non-Newtonian.

Melt viscosity is molecular weight dependent, being related to the weight average molecular weight by the following equations.

$$\eta_c = K_1 \bar{M}_w^a$$  
$$\eta_0 = K_2 \bar{M}_w^b$$

where $a$ lies between 1 and 2 and $b$ has a value of 3.4. The changeover from dependence of equation 50 to equation 51 takes
takes place at a critical molecular weight $M_c$.

These equations apply only to Newtonian melts. Non-Newtonian melts display a relationship

$$(52) \quad \eta_0 = k_3 \frac{M}{w}^c$$

where $c$ is usually of the order of 4, but the relationship, particularly the value of $c$, is less precise. The shear stresses used in the measurements of melt viscosity of the copoly (phenylene ether ketone/sulphones) were of the order of $10^7$ dynes/cm$^2$, well within the non-Newtonian region.

In order to plot melt viscosity against some function of molecular weight for the copolymer, it was necessary to derive an empirical relationship between an easily measured function of molecular weight and molecular weight for the copolymers.

The Mark-Houwink equation

$$[\eta] = kM^d$$

relates intrinsic viscosity to molecular weight, and intrinsic viscosity is related to reduced viscosity by the Huggins equation,

$$\eta_{sp} = \text{reduced viscosity} = (\eta_0) + k_1 (\eta_0)^2 c$$

It was found, however, that reduced viscosity could replace intrinsic viscosity in the Mark-Houwink equation as there was found to be linear relationship between reduced viscosity and intrinsic viscosity for poly (phenylene ether ketone) (Graph 6). Although this substitution is not strictly correct, the Mark-Houwink equation is itself empirical, and the result gave the desired, easily measured, function of molecular weight (i.e. $RV$).
The empirical relationship between intrinsic viscosity $[\eta]$ and reduced viscosity for $\left[\left(\text{cis-1,4}\right)\text{-cyclooctatetraene}\right]_n$ in sulfuric acid.
Thus \( R V = K ( \bar{M}_n )^\alpha \)

For ideal polycondensation \( \bar{M}_n = \frac{M_w}{2} \)

\[ \therefore R V = K \left( \frac{\bar{M}_n}{2} \right)^\alpha \]

Taking logs

\[ \log_{10} R V = \log_{10} K + \alpha \log_{10} \bar{M}_n - \alpha \log_{10} 2 \]

(54) \[ \therefore \log_{10} \bar{M}_w = \frac{\log_{10} R V - \log_{10} K + \log_{10} 2}{\alpha} \]

Now

\[ \dot{\lambda}_c = K_3 \left( \frac{\bar{M}_w}{2} \right)^C \]

Taking logs

(55) \[ \log_{10} \dot{\lambda}_c = \log_{10} K_3 + C \log_{10} \bar{M}_w \]

Substituting for \( \log_{10} \bar{M}_w \) we have

(56) \[ \log_{10} \dot{\lambda}_c = \log_{10} K_3 + C \left( \frac{\log_{10} R V - \log_{10} K + \log_{10} 2}{\alpha} \right) \]

Let \( \log_{10} K_3 - \frac{C}{\alpha} \log_{10} K + C \log_{10} 2 = \log_{10} K_4 \)

(ie collecting the constants)

then

(57) \[ \log_{10} \dot{\lambda}_c = \log_{10} K_4 + \frac{C}{\alpha} \log_{10} R V \]

Thus a plot of \( \log_{10} \dot{\lambda}_c \) against \( \log_{10} R V \) should give a straight line of slope \( \frac{C}{\alpha} \) where the value of \( \alpha \) may be taken as \( \sim 0.9 \) (from section 9).
Measurements of melt viscosity were made on four types of polymer (all made from the two-monomer route). Stoichiometries are given in parenthesis.

Set 1  A copolymer comprising 90 mole% phenylene ether ketone units (prepared from 0.5 moles A, 0.4 moles B, 0.1 moles C).

Set 2  A copolymer comprising 95 mole% phenylene ether ketone units (prepared from 0.5 moles A, 0.45 moles B, 0.05 moles C).

Set 3  Homopoly (phenylene ether ketone) (Prepared from 0.5 moles A, 0.5 moles B).

Set 4  Homopoly (phenylene ether ketone) (prepared from 0.5 moles A, 0.5 moles D).

A = bis potassium salt of 4,4' - dihydroxy benzophenone
B = 4, 4' dichloro benzophenone
C = 4, 4' dichlordiphenyl sulphone
D = 4, 4' difluoro benzophenone
The Melt Viscosity ($\eta_m$)/Reduced Viscosity (RV) Data for Homopoly (phenylene ether ketone) and Copoly (phenylene ether ketone/sulphones) (See Graph 7)

<table>
<thead>
<tr>
<th>Set Number</th>
<th>$\eta_m/KNs/m^2$</th>
<th>RV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.42</td>
<td>1.69</td>
</tr>
<tr>
<td>1</td>
<td>3.74</td>
<td>1.62</td>
</tr>
<tr>
<td>1</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>1</td>
<td>1.04</td>
<td>1.33</td>
</tr>
<tr>
<td>1</td>
<td>0.7</td>
<td>1.46</td>
</tr>
<tr>
<td>1</td>
<td>11.4</td>
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</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>0.94</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>1.07</td>
</tr>
<tr>
<td>2</td>
<td>0.44</td>
<td>1.15</td>
</tr>
<tr>
<td>2</td>
<td>0.53</td>
<td>1.25</td>
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<td>2</td>
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<td>1.45</td>
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<td>2</td>
<td>1.35</td>
<td>1.65</td>
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<tr>
<td>2</td>
<td>3.2</td>
<td>1.95</td>
</tr>
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<td>2</td>
<td>12.1</td>
<td>2.05</td>
</tr>
<tr>
<td>3</td>
<td>0.15</td>
<td>0.77</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>1.14</td>
</tr>
<tr>
<td>3</td>
<td>0.62</td>
<td>1.02</td>
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<tr>
<td>3</td>
<td>0.56</td>
<td>1.22</td>
</tr>
<tr>
<td>3</td>
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<tr>
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<td>1.45</td>
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<tr>
<td>3</td>
<td>1.20</td>
<td>1.45</td>
</tr>
<tr>
<td>3</td>
<td>1.35</td>
<td>1.35</td>
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<tr>
<td>3</td>
<td>1.45</td>
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<td>3</td>
<td>20</td>
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</tr>
<tr>
<td>4</td>
<td>0.014</td>
<td>0.67</td>
</tr>
<tr>
<td>4</td>
<td>0.046</td>
<td>0.80</td>
</tr>
<tr>
<td>4</td>
<td>0.065</td>
<td>0.90</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>1.02</td>
</tr>
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</table>

Continued...
<table>
<thead>
<tr>
<th>Set Number</th>
<th>$h_0$ KNs/m$^2$</th>
<th>RV</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.16</td>
<td>1.02</td>
</tr>
<tr>
<td>4</td>
<td>0.27</td>
<td>1.22</td>
</tr>
<tr>
<td>4</td>
<td>0.35</td>
<td>1.49</td>
</tr>
<tr>
<td>4</td>
<td>0.36</td>
<td>1.51*</td>
</tr>
<tr>
<td>4</td>
<td>0.48</td>
<td>1.46</td>
</tr>
<tr>
<td>4</td>
<td>0.51</td>
<td>1.73</td>
</tr>
<tr>
<td>4</td>
<td>3.6</td>
<td>3.21</td>
</tr>
<tr>
<td>4</td>
<td>4.6</td>
<td>3.7</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>2.75</td>
</tr>
</tbody>
</table>

*This polymer was prepared by an electrophilic route.

The four sets of data were examined to find the best straight lines and also the significance of any difference between them.

Computer analysis gave the following results:

Sets 1 and 3 showed no significant difference from one another, both having the equation

$$(59) \quad \log_{10} h_0 = -0.451 + 4.405 \log_{10} RV$$

Set 2 differed from these two only at the 4% significance level, its equation being

$$(59) \quad \log_{10} h_0 = -0.654 + 4.405 \log_{10} RV$$

The value of the slope in both these equations (4.405) gives a value of $C$ of 3.96.

Set 4 differed from all the previous sets, its equation being

$$(60) \quad \log_{10} h_0 = -0.988 + 3.481 \log_{10} RV$$

This gives a value of $C$ of 3.12 (see Graph 8).

No attempt was made to interpret these data in terms of rheological
THE MELT VISCOSITY / MOLECULAR WEIGHT
RELATIONSHIP FOR \( \text{f(SO}_2 \text{O}_3 \text{CO}_2 \text{O}) \)
WHERE \( \alpha = 0.1, 0.05, \) AND 0.0

\( \text{SET 1} \)
\( \text{SET 2} \)
\( \text{SET 3} \)
\( \text{SET 4} \)
theory, the results obtained being complicated by the fact that the polymers were crystalline. Crystalline polymers which are subjected to melt flow under high pressures at temperatures only slightly above their crystalline melting points (as was the case here) may be subject to a type of melt ordering leading to erroneously high melt viscosities. Although this phenomenon may invalidate the results with respect to rheological theory, the results are nevertheless those observed and are therefore of use at the empirical level.

The significance of the results is twofold. Firstly, the melt viscosities of the two high phenylene ether ketone unit content copolymers and the homopoly(phenylene ether ketone) prepared from 4,4'-dichlorobenzophenone showed essentially the same relationship with reduced viscosity, although this might have been expected considering that the highest phenylene ether sulphone content was only 10 mole %.

Secondly, and more importantly, is the significantly lower melt viscosity for a given reduced viscosity observed for poly(phenylene ether ketone) prepared from 4,4'-difluorobenzophenone. This reduction in melt viscosity appears to be a function of the large initial rate of polymerisation afforded by the difluorobenzophenone which in turn, it is tentatively suggested, leads to a lower degree of branching. Branching may increase or decrease melt viscosity depending on the length of the branch units and the flexibility of the repeat unit. If the repeat unit is inflexible then branching may lead to an increase in melt viscosity as the branches cause interchain entanglements and hence reduce the flow or slippage of polymer chains past one another.

An attempt to demonstrate that branching caused an increase in melt viscosity
by the introduction of deliberately branched units into the chain gave
inconclusive results however.

**Impact Strength**

The impact strengths of two copoly(phenylene ether ketone/sulphones)
have been measured. Measurements were restricted to non-crystallisable
copolymers as the degree of crystallinity can affect impact strength.

The tests were carried out using a form of the Charpy test in which the
specimen is supported at two points (near the ends) and is struck by a
pendulum. All measurements were made on specimens having a 0.080" notch,
and the impact strength as a function of ageing at 150° was plotted.

A typical example of compression moulded poly(phenylene ether sulphone)
is shown for comparison (Graph 9).

**The Determination of the Thermodynamic Quantities**

**Characterising the Fusion of Poly(Phenylene Ether Ketone) and the Use of Them in Determining Degrees of Crystallinity**

The well known equation (61) relates the melting point of a crystalline
material (Tm) with its heat of fusion (ΔHu) and entropy of fusion

\[ Tm = \frac{ΔHu}{ΔSu} \]

The value of ΔHu for a '100% crystalline' polymer can be used to determine
the degree of crystallinity of a partially crystalline polymer comprised
of the same repeat units.

Flory\(^{23}\) has derived an equation which relates the heat of fusion of a
'100% crystalline' polymer to the melting points of copolymers of this
crystalline unit with non-crystallisable units.

\[
12) \quad \frac{1}{T_m} - \frac{1}{T_m^0} = - \frac{R \ln X_A}{\Delta H_u}
\]

(See introduction)

The use of this equation (12) to determine the values of \( \Delta H_u \) and \( \Delta S_u \) for poly(phenylene ether ketone) was convenient, as a series of copolymers conforming to Flory's requirements has already been prepared in another context. These copolymers comprised units of phenylene ether ketone (I) and phenylene ether sulphone, the ketone-containing repeat unit being the crystallisable unit (the mol fraction of which, \( X_A \), appears in equation (12)) and the sulphone containing unit being the non-crystallisable one. Details of the preparation and structure of these copolymers is given in Section 10.

The melting points of these copolymers were determined using differential thermal analysis (D.T.A.). The apparatus and the experimental procedure are detailed in the experimental section, but it is worthwhile summarising the basis of the method at this point.

The sample under study and a completely inert substance (e.g. sand or glass beads) are supplied with the same, constant amount of heat. Thermocouples are used to monitor the temperature rises in both the sample and reference and the outputs of these thermocouples are constantly compared.

Below the melting point of the sample, both sample and reference increase in temperature by the same amount and at the same rate. At the crystal
melting point \( T_m \) of the sample, the reference continues to rise in temperature as before but the sample stays at a constant temperature while sufficient heat to melt the crystal lattice is absorbed. This change in the relative temperatures of the reference and sample is recorded by the thermocouple outputs and is translated into a visual display (a D.T.A. thermogram), giving a highly sensitive and accurate record of the melting processes that have taken place within the sample.

Having obtained the melting points of the copolymers by this method, a graph of \( \frac{1}{T_m} - \frac{1}{T_m^0} \) against \( \ln \kappa_A \) was constructed. (Graph 10).

The slope of this line is related to the heat of fusion of 100% crystalline poly(phenylene ether ketone).

\[
\text{Slope} = \frac{-R}{\Delta H_u} \quad \text{(from equation (12))}
\]

From the graph:

\[
\frac{10.7 \times 10^{-5}}{-0.2} = \frac{-R}{\Delta H_u}
\]

\[\therefore \Delta H_u = 15.54 \times 10^3 \text{ joules mol}^{-1}\]
\[= 19 \text{ cal g}^{-1}\]

Substituting in equation (61) we have:

\[
643 = \frac{19}{\Delta S_u}
\]

\[\therefore \Delta S_u = 5.8 \text{ cal deg}^{-1} \text{ mol}^{-1}\]

Table 12 shows how these values compare with those of some other polymers.
THE APPLICATION OF FLORY'S EQUATION

\[ \frac{1}{T_m} - \frac{1}{T_m^0} = -R \frac{\ln x_A}{\Delta H_u} \]

TO DETERMINE

\[ \Delta H_u \]
### Thermodynamic Quantities Characterising the Fusion of Various Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_m$ in °C</th>
<th>$\Delta H_u$ cal mol$^{-1}$</th>
<th>$\Delta H_u$ cal g$^{-1}$</th>
<th>$\Delta S_u$ cal deg$^{-1}$ mol$^{-1}$</th>
<th>Method of Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(phenylene ether ketone)</td>
<td>367</td>
<td>3,714</td>
<td>18.95</td>
<td>5.8</td>
<td>Copolymer equation</td>
</tr>
<tr>
<td>Poly(ethylene)</td>
<td>138.5</td>
<td>960</td>
<td>68.5</td>
<td>2.34</td>
<td>Depression of melting point by monomeric diluents</td>
</tr>
<tr>
<td>Poly(styrene)</td>
<td>239</td>
<td>2,000</td>
<td>19.2</td>
<td>3.9</td>
<td>&quot;</td>
</tr>
<tr>
<td>Poly(decamethylene terephthalate)</td>
<td>138</td>
<td>11,000</td>
<td>36</td>
<td>27</td>
<td>&quot;</td>
</tr>
<tr>
<td>Collagen</td>
<td>145</td>
<td>2,250</td>
<td>24</td>
<td>5.85</td>
<td>&quot;</td>
</tr>
<tr>
<td>Poly(tetrafluoroethylene)</td>
<td>330</td>
<td>1,460</td>
<td>14.6</td>
<td>2.9</td>
<td>Variation of melting point with applied hydrostatic pressure</td>
</tr>
</tbody>
</table>

Mandelkern\(^4\) has discussed the possibility of a relationship existing between these thermodynamic quantities ($\Delta S_u$ and $\Delta H_u$) and structure for all polymers, but without arriving at any definite conclusion.

Some trends are apparent within groups of polymers whose structures are similar (e.g. polyesters and polyanhydrides) and the heats of fusion for polymers generally lie in one of two groups: one with heats of fusion of 10,000-12,000 cal mol$^{-1}$ (Mandelkern quotes eight examples) and another with heats of fusion of 1000-4,000 cal mol$^{-1}$ (sixteen examples). Poly(phenylene ether ketone) apparently falls into the latter group - although it should be stated that there are eight examples of other polymers whose heats of fusion are in the range 4000-10,000 cal mol$^{-1}$ and no comment is passed on these.
In view of the error which the copolymer equation method of determining $\Delta H_w$ is subject to (see introduction), it was decided to obtain a comparative value by a study of the fusion of suitable model compounds.

This work necessitates the use of quantitative D.T.A. and before this could be carried out, it was necessary both to calibrate the apparatus and to check its accuracy.

The heat of fusion of a crystalline compound (monomeric or polymeric) may be determined by comparing the area under the melting peak of a known weight of that compound in the D.T.A. thermogram with the similar area of a known weight of a compound of known heat of fusion.65

When using this method, however, account must be taken of the changing heat capacity of the block (used to heat the samples) with changing temperature. A calibration curve for a particular block may be prepared by plotting temperature against cal/unit (e.g., cal/sq mm or cal/g of chart paper) over the desired temperature range.

Before this calibration was done, it was thought worthwhile to check the accuracy and reproducibility of the results obtained from the apparatus by comparing the results obtained for several compounds of known heat of fusion.

Kirshenbaum et al66 recommended the use of silver nitrate as a D.T.A. calibrant instead of the more commonly used benzoic acid. This latter compound has a tendency to sublime as it passes through its melting point, giving rise to error. When silver nitrate was used, however, it was found
to show two endothermic processes, a small one at $168^\circ$ and a larger one at the quoted melting point of $210^\circ$. Purification of this reagent by conventional methods failed to remove this extraneous process at $168^\circ$ and in view of this, silver nitrate was abandoned in favour of benzoic acid. The heat of fusion of benzoic acid was taken as $33.9 \text{ cal g}^{-1}$ and this compound was used to calculate the heats of fusion of several compounds (Table 13), from the area under their melting points as measured on our apparatus.

Table 13

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calculated $\Delta H_u$ cal g$^{-1}$</th>
<th>Lit Value of $\Delta H_u$ cal g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Napthalene</td>
<td>29.6, 29.5</td>
<td>33.68</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>17.7, 17.3</td>
<td>22.29</td>
</tr>
<tr>
<td>Polyox WSR-205</td>
<td>30.3</td>
<td>33.69</td>
</tr>
</tbody>
</table>

The results show an error of $\sim 10\%$ in the heats of fusion of two of the materials and a slightly large error in the other — the results are however consistent.

This error did not change when sodium nitrate was used as a standard and it therefore appears inherent to the apparatus and method. This error was considered acceptable and the block was calibrated using the compounds indicated in Table 14.
Table 14
Compounds Used to Calibrate the D.T.A. Block

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tm °C</th>
<th>Heat of Fusion Cal mol$^{-1}$</th>
<th>cal g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>47</td>
<td>4,200</td>
<td>22.9</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>80</td>
<td>4,300</td>
<td>33.67</td>
</tr>
<tr>
<td>Potassium thiocyanate</td>
<td>177</td>
<td>2,500</td>
<td>25.73</td>
</tr>
<tr>
<td>Silver nitrate</td>
<td>210</td>
<td>3,000</td>
<td>17.7</td>
</tr>
<tr>
<td>Sodium nitrate</td>
<td>310</td>
<td>3,800</td>
<td>44.70</td>
</tr>
<tr>
<td>Potassium nitrate</td>
<td>337</td>
<td>2,800</td>
<td>27.69</td>
</tr>
</tbody>
</table>

The calibration curve is shown in Graph 11.

This calibration curve was then used to calculate the heats of fusion of some model compounds of poly(phenylene ether ketone).

This was done by measuring the area under the melting process peak for a known weight of the model compound, reading off from Graph 11 the cal/sq mm at the melting temperature and hence obtaining a value for the heat of fusion of that compound.

Table 15
Heats of Fusion of Model Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔHu cal g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-3CO-F+</td>
<td>22.8</td>
</tr>
<tr>
<td>((\text{C}_6\text{H}_5))_2 (\text{O}) = 0</td>
<td>24.4</td>
</tr>
<tr>
<td>((\text{C}_6\text{H}_5))_2 (\text{O}) = 0</td>
<td>22.29 (Lit value)</td>
</tr>
<tr>
<td>+F- (\text{C}_6\text{H}_5)-CO-(\text{C}_6\text{H}_5)-O= (\text{C}_6\text{H}_5)-CO-(\text{C}_6\text{H}_5)-O= (\text{C}_6\text{H}_5)-CO-(\text{C}_6\text{H}_5)-F</td>
<td>XXXII</td>
</tr>
</tbody>
</table>
Calibration plot for the differential thermal analysis block.
These values compare quite well with the value of 19 cal g\(^{-1}\) obtained for poly(phenylene ether ketone) by the copolymer equation method.

The higher value for \(\Delta H_u\) for the repeat unit (I) obtained by D.T.A. of model compounds over that obtained from the copolymer equation is expected from the errors to which this latter method is subject (see introduction).

![Diagram](https://example.com/diagram.png)

I

from the errors to which this latter method is subject (see introduction).

Taking the model compound (XXXII) as the most representative model compound, it appears that a value of \(\sim 21\) cal g\(^{-1}\) for \(\Delta H_u\) of poly(phenylene ether ketone) is a reasonable estimate (hence \(\Delta S_u\) has a value of \(\sim 6.4\) cal deg\(^{-1}\) mol\(^{-1}\)).

The aim of this line of work was to establish a method of determining degrees of crystallinity of poly(phenylene ether ketone) samples. Having obtained a value for the heat of fusion of '100% crystalline' polymer it was now necessary to establish a technique to yield the heat of fusion of partially crystalline polymer (the ratio of these two values being the degree of crystallinity of the partially crystalline sample).

There are several major factors which can affect quantitative determinations of heats of fusion of partially crystalline polymer by D.T.A.\(^{65, 66, 70}\) These include, the thermal history of the sample, sample-sensor contact, heating rate and apparatus design.

Sample-sensor contact was the first of these factors to be examined.
The apparatus available utilised thermocouples embedded in the centre of a small sample of the powdered polymer, itself encased in a small glass sample tube. It was quickly established that this type of sample could give rise to poor results as it was observed that as soon as melting (of the sample) began, the polymer tended to shrink away from the thermocouple. This, of course, would result in the thermocouple failing to monitor correctly the bulk temperature changes within the sample. The use of powdered polymer was unsatisfactory from another viewpoint, in that the air trapped between the polymer particles would be likely to lead to poor heat transfer across the sample.

These two combined problems were overcome in the following way. A small quantity of polymer in a sample tube was melted, a pre-weighed thermocouple was embedded in the melt and the whole was rapidly cooled. This process shattered the glass around the now solid plug of polymer which was then re-weighed (with the thermocouple attached), given any desired thermal treatment and slipped back into a new sample tube for D.T.A. These polymer 'plugs' with their attached thermocouples were annealed to give the maximum degree of crystallinity available before being examined. This was done because during the D.T.A. the sample is heated above its Tg and, if not completely annealed, could therefore change its degree of crystallinity during the measurement. The annealing process gives samples of maximum crystallinity only.

Despite the use of these two techniques, very variable results were obtained for poly(phenylene ether ketone) crystallinity. Some samples showed very poor crystallinity ($< 10\%$) others were $\sim 50\%$ crystalline. It seems unlikely that this variation was due to sample differences (ie that one sample was only capable of attaining $10\%$ crystallinity while
another was capable of attaining 50%). More likely causes were poor sample-sensor contact and apparatus design.

The use of the sample 'plug' (as used above) gave the best available sensor-sample contact with the available apparatus but it did not guarantee that shrinkage away from the thermocouple did not occur during analysis. Other workers \(^{66, 70}\) have used an apparatus in which the sample under study is placed in a small copper cup, this cup itself being a thermocouple junction, and heating is carried out by means of an air oven. This type of apparatus appears superior when quantitative D.T.A. is undertaken; the type used for the experiments described (ie a metal block as heat source and sample tubes as sample holders) above only seems adequate for qualitative D.T.A.

If the D.T.A. method of determining poly(phenylene ether ketone) crystallinity is to be continued, the apparatus should be redesigned with quantitative measurements in mind.
EXPERIMENTAL

The thermometer used in determining the melting points quoted in the following sections was checked against various reference compounds and found to be correct.

Infra red spectra (Nujol mulls or KBr discs) were measured on a Perkin Elmer 157 spectrophotometer.
i) Preparation of 4,4'-difluorobenzophenone

Redistilled fluorobenzene (96 g, 1.0 M) and carbon tetrachloride (500 g) were stirred in a 1 litre three necked flask fitted with a thermometer, aqueous hydrogen chloride trap and condenser. The flask was cooled in an ice/salt bath to 10° and anhydrous aluminium chloride (94 g added slowly so that the exothermic reaction maintained the reaction mass at 15°. When hydrogen chloride evolution had ceased (1.5 h) the bright red slurry was allowed to warm to room temperature and left to stand for 18 h. Distilled water was slowly added (with cooling) until the slurry was pale yellow, then the excess of carbon tetrachloride was distilled out. The resulting two phase system was ether extracted three times to yield (on evaporation of the ether) a brown oil. Cooling of this oil gave buff crystals which were crystallised from low boiling petroleum ether containing a little decolourising charcoal. After being dried at 80° under reduced pressure, the product formed white plates (57.2 g, 47.7%), m.p. 105 - 106° (Lit 102 - 103° and 107.5 - 108.5°).

Elemental analysis gave:

Found: C, 73.3; H, 3.6; F, 16.9. Calc. for C13H8F2O: C, 71.55; H, 3.7; F, 17.4%; i.r. (maximum) 5.14, 5.55 (substitution), and 6.02 µ (>C=O).

ii) Preparation of 4,4'-(4-fluorobenzoyl) diphenyl ether

Diphenyl ether (17.0 g, 0.1 M), 4-fluorobenzoyl chloride (31.7 g 0.2 M), anhydrous aluminium chloride (27.0 g, 0.21 M) and nitrobenzene (25 ml) were placed in a 250 ml three-necked flask fitted with stirrer, thermometer, nitrogen inlet/outlet and aqueous hydrogen chloride trap. Hydrogen chloride evolution began
immediately with the temperature self maintaining in the range 50 - 60°.

Heating to 100° was necessary to increase hydrogen chloride evolution to 99% of theory (total reaction time 2 h). The reaction mass was allowed to cool to room temperature, when the 'pasty' solid was slurried with methanol (400 ml) and filtered. The pale pink powder was crystallised from chloroform/low boiling petroleum ether containing a little active charcoal, then vacuum dried at 130° (27.4 g, 66%), m.p. 214 - 215°. (Found: C, 76.9; H, 3.7; F, 9.5, C_{26}H_{16}F_{2}O_{2} requires C, 75.35; H, 3.8; F, 9.2%), i.r. (maximum) 5.2 and 5.6 (substitution), 6.0 μ (>C = 0).

iii) Preparation of Bis-4,4'-(4-fluorobenzoyl-4-phenoxy)benzophenone

(a) Preparation of the intermediate 4,4'-diphenoxynbenzophenone

4,4'-Difluorobenzophenone (21.8 g, 0.1 M) and potassium phenate (26.4 g, 0.2 M) were heated in dimethylsulphoxide (200 ml) at 160 - 165° for 6 h with stirring.

The cooled slurry was filtered, washed several times with boiling water and dried under reduced pressure at 100° (35.7 g, 98%). The off-white powder was crystallised from a benzene/petroleum ether mixture (85 parts/15 parts by volume) to yield (after vacuum drying) off-white crystalline plates (31.0 g, 86%, m.p. 143.5 - 144° (Lit 147°), i.r. (maximum) 5.1 - 5.8 mono and di-p-substitution), 6.05 μ (>C=0)

(b) Preparation of Bis 4,4'-(4-fluorobenzoyl-4-phenoxy) benzophenone

4,4'-Diphenoxynbenzophenone (18.2 g, 0.05 M), 4-fluorobenzoylchloride (15.9 g, 0.1M), anhydrous aluminium chloride (25 g) and nitrobenzene (100 ml) were stirred in a 250 ml, three-necked flask fitted with nitrogen inlet/outlet, thermometer and aqueous hydrogen chloride trap at 75 - 85° for 4 h. The cooled reaction mass was poured into 1 litre of methanol and the 'milky' suspension filtered, washed with methanol several times, and finally vacuum dried at 120° (29.3 g, 96%). The dried off-white powder was crystallised from 1,2-dichlorobenzene to yield a buff, crystalline product (27.1 g, 88.8%), m.p. 274 - 276°

(Found: C, 77.4; H, 4.0; F, 5.7; C_{39} H_{24} F_{2} O_{5} requires
iv) Preparation of Bis-4,4'-(4-fluorobenzoyl-4-phenoxy-4-benzoyl)diphenyl ether

(a) Preparation of the intermediate 4-phenoxy-4-fluorobenzophenone

Diphenyl ether (80 g, 0.45 M), 4-fluorobenzoyl chloride (51.7 g, 0.2 M), anhydrous aluminium chloride (18.5 g) and nitrobenzene (75 ml) were heated in a 250 ml three-necked flask fitted with a stirrer, thermometer, nitrogen inlet/outlet and aqueous hydrogen chloride trap at 60 - 90° for 1 h. The hot reaction mass was poured into methanol (500 ml) and then filtered to yield pale purple plates (41.8 g, 71.6%) m.p. 80 - 90°. The crude product was repeatedly crystallised from petroleum ether, finally being dried under reduced pressure at 60° (25.3 g, 43.4%), m.p. 94 - 96°.

(b) Preparation of the intermediate di acid chloride of 4,4'-dicarboxydiphenylether

4,4'-Dicarboxydiphenylether (258 g, 1.0 M), thionyl chloride (350 g, an excess), low boiling petroleum ether (1 litre) and N,N-dimethyl formamide (1 ml) were refluxed for 3 h. Petroleum ether and unreacted thionyl chloride were then distilled off, a higher boiling petroleum ether being slowly added. The cooled suspension was filtered and the white product crystallised from a high boiling petroleum ether containing a little active charcoal. The product was vacuum dried at 60° (168 g, 57%), m.p. 86 - 88° (Lit² 82 - 83°); i.r. (maximum) 5.6 μ (acyl halide).

(c) Preparation of Bis-4,4'-(4-fluorobenzoyl-4-phenoxy-4-benzoyl) diphenyl ether

4-Phenoxy-4'-fluorobenzophenone (14.6 g, 0.025 M), the diacid chloride of 4,4'-dicarboxydiphenylether (7.35 g, 0.025 M), anhydrous aluminium chloride (15 g) and nitrobenzene (50 ml) were heated at 60 - 80° for 1 h in a 250 ml flask fitted with stirrer, thermometer, nitrogen inlet/outlet and aqueous hydrogen chloride trap. The cooled, bright red reaction mass was poured into methanol (500 ml), filtered, washed several times with methanol, boiled with petroleum ether (b.p. 80 - 100°) and filtered while hot. The vacuum dried product was a pale pink powder (13.1 g, 65%, m.p. 310°).
The product was crystallised with difficulty from N-methyl-2-pyrrolidone, washed with methanol and vacuum dried (m.p. 308 - 310°).

v) Preparation of 4-(4-fluorobenzoyl)-4'-carboxydiphenylether

4-Hydroxybenzoic acid (69 g, 0.5 M), aqueous potassium hydroxide (113 g, 1.0 M), dimethylsulphoxide (150 ml) and dry benzene (50 ml) were heated at 100° in a 500 ml flask fitted with a stirrer, nitrogen inlet/outlet and a Dean and Stark apparatus. After 1.25h when approximately 0.25 of the available water had been azeotroped off, 4-4'-difluorobenzophenone (109 g, 0.5 M) was added and the reaction left stirring under a fast stream of nitrogen for a further 19.5h. The cooled reaction mass was poured into water (2 l) filtered, washed with water and then vacuum dried at 140° (170.0 g), m.p. 230 - 300°.

The product (which was insoluble in aqueous alkali) was crystallised from glacial acetic acid and vacuum dried at 150° (152.0 g, 90.5%), m.p. 240°,

(Found: C, 69.5; H, 3.5; F, 5.4. C_{20}H_{13}F_4O requires C, 71.4; H, 3.9; F, 5.65%).

i.r. (maximum). 3.1 - 3.8 (bonded OH), 5.2 and 5.6 (p-substitution), 5.87 (> C = 0), 6.02 μ (> C = 0, diaryl ketone).

vi) Preparation of 4-fluoro-4'-hydroxybenzophenone

(a) Preparation of the intermediate 4,4'-bis(4-fluorobenzoyl) diphenylcarbonate

Diphenyl carbonate (107 g, 0.5 M), 4-fluorobenzoyl chloride (165.7 g, 1.0 M), anhydrous ferric chloride (10.3 g) and nitrobenzene (200 ml) were heated in a 1 litre three-necked flask fitted with a stirrer, thermometer, nitrogen inlet/outlet and aqueous hydrogen chloride trap, at 130° for 24 h. Acetyl acetone (30 ml) and methanol (500 ml) were added to the hot reaction mass which was stirred for a short time. The product was filtered off, washed several times with methanol and vacuum dried at 110° (123.1 g, 54%), m.p. 193 - 195°. The crude product was crystallised from 1,2-dichlorobenzene to yield off-white crystals (119.2 g, 52%), m.p. 193 - 194° (Found: C, 69.9; H, 3.4; F, 8.0;

C_{27}H_{16}F_2O requires C, 70.7; H, 3.5; F, 8.3%).
Basic cleavage of the intermediate carbonate

4,4'-Bis-(4-fluorobenzoyl)diphenylcarbonate (114.5 g, 0.25 M) was slurried in methanol (700 ml) in a 2 l beaker. Aqueous potassium hydroxide (113.4 g, 1.0 M) was slowly added to yield a clear orange solution. This was filtered, then carefully acidified (HCl) to yield an off-white solid, this was filtered and washed several times with water, and finally vacuum dried (103.0 g, 95.4%), m.p. 167 - 169°. The crude material was dissolved in warm methanol (1 l) and treated several times with decolourising charcoal, then precipitated by addition of an excess of water and, (after being dried) was repeatedly crystallised from xylene (Yield, 95.3 g, 88%) m.p. 169 - 171°. Found: C, 72.4; H, 4.2; F, 8.5; \( \text{C}_{13} \text{H}_{9} \text{FO}_2 \) requires C, 72.2; H, 4.2; F, 8.8%). i.r. (maximum) 3.1 (OH), 6.07 μ (> C ≈ O).

Preparation of the anhydrous potassium salt of 4-fluoro-4'-hydroxybenzophenone

A small quantity of the phenol (accurately weighed) was dissolved in methanol and then titrated potentiometrically with 4N-potassium hydroxide prepared by dilution of a portion of 50% aqueous potassium hydroxide solution with methanol. The end-point was calculated and the result used for the exact neutralisation of a methanolic solution of the bulk of the phenol (XIV). The solution was rotary evaporated and the last traces of water were removed from the bright yellow potassium salt using a vacuum drying pistol at 80 - 90° < 0.01 mmHg. The potassium salt did not melt up to 360° but darkened at temperatures greater than 270°. The anhydrous salt was stored in a vacuum dessicator over phosphorus pentoxide.

Preparation of 4,4'-dihydroxybenzophenone

4-Hydroxybenzoic acid (30 g, 0.2173 M), phenol (20.4 g, 0.2167 M), anhydrous zinc chloride (68 g, 0.4912 M) and orthophosphoric acid [317 g, 3.2 M, taken from a solution of phosphorus pentoxide (125 g) in commercial orthophosphoric acid (317 g)] were stirred in a 1 litre three-necked flask fitted with a stirrer, condenser, thermometer and dropping funnel. Phosphorus trichloride (38 g, 0.2763 M) was slowly added to the reaction mixture over 1.25 hours with
the temperature at approx 50°. When addition was complete the now clear, viscous, yellow solution was heated to 60° and left stirring at this temperature for 0.5 hours. The temperature was then raised to 70 - 76° and the solution left stirring for 1 hour, after which liquid had solidified. The bright orange solid was slurried with distilled water (1 l) and the orange crystals filtered off (40 g, 90%), m.p. 210° - 214°. The crystals were sublimed at <0.01 mmHg, using 1,2-dichlorobenzene in the vapour jacket and then crystallised from methanol/water to yield very pale yellow crystals, m.p. 217 - 219°). (Lit. 210 – 212°). i.r. (max) 2.95 (–O–), 5.2 and 5.6-substitution), 6-10 μ (C = 0). The anhydrous bis potassium salt of this compound was prepared analogously to that of 4-fluoro-4'-hydroxybenzophenone (above).

Preparation of the hydrated bis potassium salt of 4,4'-dihydroxybenzophenone

4,4'-Dihydroxybenzophenone (20.19 g, 0.09425 M), 4 N-potassium hydroxide (47.12 ml, 0.1885 M) and just sufficient methanol to dissolve the whole were placed in a rotary evaporator flask and shaken until the pale yellow solution was clear. The methanol/water was then removed by rotary evaporation under reduced pressure for several hours. The pale yellow cake was then scrapped from the flask and ground until it passed through a 500 μ sieve. Two samples of the salt were then titrated against 0.1N sulphuric acid (Found: purity, 91.65, 91.7%).

Preparation of the acid chloride of 4-(4-fluorobenzoyl)-4'-carboxydiphenylether

4-(4-Fluorobenzoyl)-4'-carboxydiphenylether (67.2 g, 0.2 M), thionyl chloride (200 g, excess), N,N-Dimethylformamide (1 ml) and petroleum ether (300 ml; b.p. 40 - 60° were refluxed for 2½ hours in a 1 litre, three-necked flask fitted with stirrer, condenser, thermometer and hydrogen chloride trap. The apparatus was then set up for distillation and the excess of thionyl chloride and low boiling petroleum were distilled off, whilst petroleum ether (b.p. 100 - 120°) gradually added. The brown crystals were recrystallised (charcoal) from petroleum ether (b.p. 100 - 120°) to give water-white crystals (59.0 g, 83%), m.p. 138 - 140°.
iv) Preparation of 2,4,4'-trichlorobenzophenone

1,3-Dichlorobenzene (77.0 g, 0.5 M + 5% excess), 4-chlorobenzoylchloride (87.5 g, 0.5 M) and anhydrous aluminium chloride (80 g, 0.6 M) were placed in 500 ml flask fitted with stirrer, thermometer, condenser, nitrogen inlet and outlet and aqueous hydrogen chloride trap. The flask was slowly heated to 140° over 5½ hours, during which time 92% of the theoretical hydrogen chloride was evolved. The bright red solution was poured on to ice and the resulting mauve solid was crushed, washed with water, filtered, sucked dry at the pump, and then dissolved in ~ 750 ml of acetone to yield a dark mauve solution. This was treated with active charcoal and the solid precipitated by the addition of water. The off-white solid was collected and crystallised from hexane (active charcoal) (Yield of pure white crystals 103.8 g, 73%) and then had m.p. 61.5 - 62° (Lit 64 - 64.5°).

x) Preparation of 3,4,4'-trichlorobenzophenone

This compound was prepared in an analogous manner to the 2,4,4'-isomer except that 1,2-dichlorobenzene was used in place of the 1,3-dichlorobenzene. The crude product was crystallised from ethanol (active charcoal). (Yield 72.4 g, 50.7%) and then had m.p. 110 - 113°. (Found: C 54.8; H 2.5; Cl 37.0. C₁₃H₇Cl₃O requires C 54.64; H 2.45; Cl 37.30.

xi) Preparation of 2,4,4'-triphenoxybenzophenone

2,4,4'-Trichlorobenzophenone (57.10 g, 0.2 M), potassium phenate (79.2 g, 0.6 M) and dry dimethyl sulphoxide (219 g) were placed in a 500 ml flask fitted with a stirrer and nitrogen inlet/outlet. The flask was heated in an oil bath at 100 - 140° for 77 hours, cooled to 100° and the contents poured on to ice. The product, precipitated as a sticky solid, was washed several times with water and then dissolved in boiling ethanol. After treatment with active charcoal the solution was allowed to cool, when the product precipitated partly as an oil and partly as pale yellow crystals. The crystals were physically separated from the oil and the extraction with ethanol repeated. A second crop of crystals proved identical to the first (by mixed m.p. and i.r.) and
The yield of pale yellow crystals was 15.4 g (16.8%), m.p. 103.5 - 104°.
(Found: C 81.1; H 4.80. $C_{31}H_{22}O_{4}$ requires C 81.22, H 4.80.)

xii) Preparation of 3,4,4′-trihydroxybenzophenone

1,2-Dihydroxybenzene (55.0 g, 0.5 M) 4-hydroxybenzoic acid (69 g, 0.5 M),
granular zinc chloride (136 g, 1.0 M) and ~ 100% ortho phosphoric acid
(884 g) were placed in a 1 l vessel fitted with stirrer, dropping funnel,
condenser, nitrogen inlet/outlet and aqueous hydrogen chloride trap. The
flask was stirred at 40° whilst phosphorus trichloride (75 g, 0.5 M + 10%) was slowly added over 3 h. The yellow slurry was stirred at 40° for 60 h and then poured into water to yield a white solid. From methanol/water, very pale pink crystals were obtained. (78.0 g, 68%), m.p. 185 - 187°.
(Found: C, 67.8; H, 4.3. Calc. for $C_{15}H_{10}O_{4}$: C, 67.8; H 4.3%).

xiii) Preparation of 2,4,4′-Trihydroxybenzophenone

This compound was prepared in an exactly analogous manner to the 3,4,4′-
isomer except that 1,3-dihydroxybenzene was used in place of the 1,2-isomer.

The product was isolated as a pale yellow solid and crystallised from water.
Yield, 101.8 g (88%), m.p. 201 - 202°. (Lit. 203.4 - 204°). Elemental
analysis gave: (Found: C, 67.3; H, 4.5. Calc. for $C_{13}H_{10}O_{4}$: C, 67.8, H 4.3%).

xiv) Preparation of 4-fluorobenzophenone

Benzoyl chloride (140.5 g, 1.0 M), redistilled fluorobenzene (101 g, 1.0 M;
5% excess) and anhydrous aluminium chloride (150 g, 1.131 M) were placed in
a 1 l flask fitted with stirrer, condenser, nitrogen inlet/outlet and aqueous hydrogen chloride trap. The flask was gradually heated to 130° over 3 h, then cooled to ca 100° and poured on to ice. The crude product was crushed, washed with water and then crystallised (2x) from petroleum ether. (b.p. 60-80°) Yield of pale yellow plates, 123 g (61.5%), m.p. 44 - 45° (Lit. m.p. 60 - 80°).
xv) Preparation of 3,4,4'-tris(4-benzoylphenoxy)benzophenone

3,4,4'-Trihydroxybenzophenone (11.5 g, 0.05 M) was dissolved in 100 ml of dimethyl sulphoxide and the solution purged with nitrogen. The purged solution was placed in a 500 ml nitrogen purged flask fitted with stirrer and Dean and Stark apparatus, and aqueous potassium hydroxide solution (previously nitrogen purged 17.19 g, 0.15 M) was added. Nitrogen purged benzene (50 ml) was added and the solution azeotroped at 140°. When 25% of the available water had been removed, the 4-fluorobenzophenone dissolved in 100 ml of nitrogen purged dimethyl sulphoxide, was run in. A precipitate immediately formed and azeotroping was continued until 90% of the available water had been removed. The reaction mixture was stirred for 22 h at 140°; it was then cooled and poured on to ice. The crude product precipitated as a sticky pale buff solid which was washed with water and was then boiled with acetone (ca 400 ml). This gave a buff solution plus a fine white crystalline solid which was filtered off. This solid was insoluble in most common organic solvents but could be crystallised from dimethyl formamide and dimethyl sulphoxide. Yield, 10.6 g (27.5%), m.p. 38 - 40° by differention thermal analysis). i.r. (maximum): 6.01 μ (> C=O) and no OH absorption.

The thermogram obtained for this compound showed a very sharp melting process, typical of a pure compound. Examination by Mass spectroscopy proved impossible as the sample would not volatilise. The nmr spectrum was very complex and was not interpreted.

xvi) Preparation of 2,4,4'-trifluorobenzophenone

4-Fluorobenzoyl chloride (35.0 g, 0.22 M), 1,3-difluorobenzene (22.8 g, 0.2 M) and anhydrous aluminium chloride (31 g, 0.23 M) were placed in a 250 ml flask fitted with a stirrer, condenser, thermometer, nitrogen inlet/outlet and an aqueous hydrogen chloride trap. The flask was heated at 90 - 110° for 5 h, when 84% of the theoretical hydrogen chloride had been liberated. The liquid product was then slowly poured on to ice and allowed to stand for 24 h. The buff product was filtered, washed with water and then crystallised from petroleum ether (m.p. 100 - 120°; 500 ml) (charcoal). An initial crop
of 4-fluorobenzoic acid was discarded. Repeated crystallisation of second crop material gave pale yellow crystals of 2,4,4'-trifluorobenzophenone, m.p. 41 - 42°. Found: C, 66.1; H, 2.8; F, 23.8. C₁₃H₇F₃O requires C, 66.6; H 3.0; F, 24.15%.

xvii) Preparation of 4-hydroxybenzophenone
Benzoic acid (61 g, 0.5 M), phenol (47 g, 0.5 M), granular zinc chloride (13.6 g, 1.0 M) and ca 100% phosphoric acid (884 g) were slurried in a 2 l flask fitted with stirrer, dropping funnel, condenser, nitrogen inlet/outlet and aqueous hydrogen chloride trap. The flask was placed in an oil bath at 40 - 45° and phosphorus trichloride (75 g, 0.69 M) slowly added to the flask via a dropping funnel over 3 h. When addition was complete, the reaction mass was stirred at 40 - 45° for 48 h and then poured into a large volume of water. The solid was filtered, crystallised from methanol/water (charcoal) and then dried. The orange product was dissolved in concentrated aqueous potassium hydroxide, filtered, and then reprecipitated with aqueous acid. The product (still orange) was sublimed at <0.1 mmHg using a water vapour jacket to yield 18.2 g (18%) of creamy crystals of 4-hydroxy benzoic acid, m.p. 132.5° (Lit. 135 - 138°). (Found: C, 78.8; H, 4.8. Calc. for C₁₃H₁₀O₂: C, 78.8, H, 5.0%).

xviii) Preparation of 4,4'-((4-benzoylphenoxy)benzophenone
4,4'-Difluorobenzophenone (0.4618 g, 0.0021 M), the anhydrous potassium salt of 4-hydroxybenzophenone (1.000 g, 0.0042 M) and dried dimethyl sulphoxide (30 ml) were placed in a 100 ml round bottomed flask fitted with a stirrer, condenser and nitrogen inlet/outlet. The flask was heated at 140° (+ 5°) (73.5 h) and then allowed to cool under nitrogen. The product was slurried in water, filtered, washed several times with water, and finally it was washed with methanol and vacuum dried (Yield: 1.02 g (85% m.p. 233 - 240°). The white product was crystallised from toluene (200 ml) and again dried. (Yield, 0.90 g), m.p. 234 - 237°. (Found: C, 80.9; H, 4.4. C₃₈H₂₆O₅ requires C, 81.5; H, 4.5%).
Preparation of dichlorodiphenylmethane

Anhydrous aluminium chloride (135 g, 1 M) and carbon tetrachloride (500 ml; excess) were phased in to a 2 l flanged flask, fitted with a stirrer and thermometer and the whole was cooled in an ice bath to 10°. Benzene (156 g, 2M) was added slowly over 1.5h with the temperature being maintained at 10 - 20°. After the addition, the mixture was left to warm gradually to room temperature before being shaken with 5 l of ice. The organic layer was separated and dried (CaCl₂) before the carbon tetrachloride was distilled off. The residue was vacuum distilled to give a water white liquid, b.p. 120° at 1.0 mmHg. Yield, 60 g (25%).

Preparation of dimethoxydiphenylmethane

Pyridine (anhydrous, 23.7 g, 0.3 M) and methanol (anhydrous, 9.6 g, 0.3 M) were cooled to 0° in a nitrogen purged, 100 ml, stirred flask. Dichlorodiphenylmethane (previously cooled to 0°) was added slowly to the flask, and then the stirring was continued for 5 h at 0° under a stream of nitrogen. The flask was allowed to warm to room temperature under a fast stream of nitrogen. After 2 h, crystals formed in the system. These were filtered off and recrystallised from methanol. Yield, 11.0 g (48%), m.p. 104 - 106°. (Lit. 107 - 108°.)

Preparation of 4,4'-diphenoxybenzhydrol

4,4'-Diphenoxybenzophenone (9.15 g, 0.025 M), sodium borohydride (4.0 g; a large excess) and ethanol (75 ml) were stirred in a 100 ml flask and warmed to ca 40°. After 0.5h, a white 'crusty' solid had formed; the clear liquid was decanted, cooled in an ice bath, and the resulting solid treated with acetic acid until frothing ceased. This mixture was then drowned with water, filtered, and the solid crystallised from ethanol/water. Yield, 7.1 g (77%), m.p. 93.5 - 94°. (Found: C, 81.4; H, 5.3; C₁₂H₂₀O₃ requires C, 81.5; H, 5.4%).
xxii) Preparation of 4-methylbenzophenone

Toluene (350 g) and anhydrous aluminium chloride (300 g) were slurried in a 1 l flask fitted with a stirrer, thermometer, condenser, dropping funnel, nitrogen inlet/outlet and aqueous hydrogen chloride trap. Benzoyl chloride (281 g, 2.0 M) was run slowly into the flask over 3 h, the flask temperature being self-maintained at 55 - 60°. Hydrogen chloride evolution was steady. When the addition was complete, the flask contents were heated to 90° (> 90% reaction was attained, as shown by titration of the hydrogen chloride). The flask was cooled and the dark brown liquid poured on to ice. After standing for several hours, the organic layer was separated off and the excess of toluene distilled. The resulting black liquid was allowed to crystallise and the crystals were taken up in boiling methanol (charcoal). Cooling the clarified solution caused the product to crystallise (68%), m.p. 36 - 37° (Lit. 37°).

xxiii) Preparation of 4-(trichloromethyl)benzophenone

4-Methylbenzophenone (98 g, 0.5 M) was dissolved in refluxing 1,2-dichlorobenzene in a 1 l three necked flask fitted with condenser, dip leg and hydrogen chloride trap. Chlorine was passed into the system until no further gain in weight was recorded (ca 48 h). The contents of the flask were cooled and the resulting crystals filtered, washed with cold methanol and crystallised from methanol. Yield, 54.6 g (36%), m.p. 111 - 112°. (Lit. 111.5°).

xxiv) Preparation of 4-benzoyl-4',4''-dimethoxytriphenylmethanol

4-Trichloromethyl benzophenone (30 g, 0.1 M), anisole (25 g, 21.6 g = 0.2 M) and anhydrous aluminium chloride (15 g, 0.114 M) were warmed to 60° in a 100 ml three necked flask fitted with a stirrer, thermometer, nitrogen inlet/outlet and aqueous hydrogen chloride trap. The reaction mass became self maintaining at 65 - 75° and the reaction was complete (by hydrogen chloride titration) in 1 h. The product was poured on to water and the crude mass boiled for 0.5 h and then allowed to cool.
dissolved in boiling methanol, (charcoal) cooling of the clarified solution caused the product to precipitate. Attempts to crystallise the products from petroleum ether/toluene and methanol gave only oil. After being vacuum dried and cooled, the product set to a pale red/orange glass (Found: C, 77.1; H, 5.6. \( \text{C}_{28}\text{H}_{24}\text{O}_4 \) requires C, 79.2, H, 5.7%). The n.m.r. spectrum showed the presence of the methyl ether of this compound (presumably formed during work-up).

xxv)  The reaction between 4,4'-difluorobenzophenone and the anhydrous potassium salt of 4-hydroxybenzophenone

4,4'-Difluorobenzophenone (1.09 g, 0.005 M), the anhydrous potassium salt of 4-hydroxybenzophenone (3.54 g = 0.015 M) and a solvent (as used for polymerisation reactions) were allowed to react for 3 h at 330 - 40° in a 100 ml, three necked flask fitted with a stirrer, air condenser and nitrogen inlet/outlet. Initially, the reactants formed a pale orange slurry, which gradually darkened to a deep red over the course of the reaction.

The product was cooled under nitrogen then ground to a powder, treated with dilute aqueous hydrochloric acid, filtered, and washed with distilled water. The brown solid was then boiled with methanol and the insoluble portion (0.63 g) dried. This product gave a deep red solution in sulphuric acid but attempts to purify it failed.

xxvi)  The reaction between gel free poly(phenylene ether ketone) and the anhydrous potassium salt of 4-hydroxybenzophenone

Poly(phenylene ether ketone) (2.0 g) (7297/32 [RV]1% 25° \( \text{C}_{28}\text{H}_{24}\text{O}_4 \) = 1.82: the anhydrous potassium salt of 4-hydroxybenzophenone (2.0 g) and diphenyl sulphone as solvent were allowed to react in at 330 - 40° for 3 h in a 100 ml round bottomed flask fitted with a stirrer, air condenser and nitrogen inlet/outlet. The product was cooled under nitrogen, ground to a powder, treated with dilute aqueous hydrochloric acid, filtered and washed with water.
portion being soluble in hot N,N-dimethyl formamide, cold dimethyl sulphoxide and cold concentrated sulphuric acid (to give a deep red solution.)

14 Preparation of Polymers

Polymerisations were carried out in 100 ml, 3 necked, round-bottomed glass flasks fitted with stirrers, nitrogen inlet/outlets and air condensers.

Temperature control was achieved by immersing the flask in a bath of molten solder ("Tinman's C", m.p. ca 230°) heated by a 1.5 kw cuff heater and thermostatically controlled via a "Mini ether" controller. Temperature control was generally ±3°.

i) Preparation of poly(phenylene ether ketone) using the "one monomer" route i.e.

\[ n X - \overset{\text{O}}{\text{C}} - \overset{\text{O}}{\text{K}} \rightarrow \overset{\text{O}}{\text{C}} - \overset{\text{O}}{\text{K}} - n \ (X = \text{Cl or F}) \]

The anhydrous potassium salt was placed in the flask together with sufficient diphenyl sulphone (as solvent) to give the desired concentration (generally 30 - 50% by weight of polymer) and the flask was heated at 335° (± 3°) with stirring for the desired length of time (usually 2 - 3 h.) At the end of this time, the flask was removed from the bath and the contents allowed to cool to room temperature under a stream of nitrogen. The flask was then broken and the solid cake removed.

The polymer cake was first ground to a fine dust in a hammer mill (fitted with 1 mm screen) and then extracted (3x each) with boiling methanol, boiling water, and methanol again. The polymer was dried in a vacuum oven at 140° overnight. Yields of polymers were usually >98%.
The bis potassium salt in the above equation was used in either the hydrated (Section 13) or the fully dehydrated form (as for the potassium salt of 4-fluoro-4'-hydroxybenzophenone in section 13). The hydrated form was preferred, being more stable to storage; moreover the percentage of water was easily established by titration (Section 13 of Experimental Section).

(a) Exactly equivalent molar quantities of the anhydrous bis potassium salt of 4,4'-dihydroxybenzophenone and the 4,4' bis halogeno benzophenone were transferred to the flask with the solvent. Polymerisation and work-up were then exactly as for the 'one-monomer' system.

With the hydrated salt, the desired quantity was washed into the reaction flask using ca 0.5 of the total amount of diphenyl sulphone required for the final reaction mixture. The flask was then immersed in the metal bath (set at 240°) and, without stirring, the pressure was reduced to ca 60 mmHg. When all the water had been removed, the other reactant(s) and remaining solvent were added, the bath temperature was raised to the required level and polymerisation and work-up were carried out as previously described.
The copolymers were prepared using the 'two-monomer' system. The nucleophile used was the bis potassium of 4,4'-dihydroxybenzophenone and the quantities of the 4,4'-dihalogenobenzophenone and diphenyl sulphone were adjusted to give:

(a) exact stoichiometry
(b) the desired copolymer composition, e.g.

\[
\begin{align*}
&\text{KO-} \begin{array}{c} \text{CO} \end{array} \begin{array}{c} \text{OK} \end{array} & 0.5 \text{ M} \\
&\begin{array}{c} \text{X-} \end{array} \begin{array}{c} \text{CO} \end{array} \begin{array}{c} \text{X} \end{array} & 0.4 \text{ M} \\
&\begin{array}{c} \text{X-} \end{array} \begin{array}{c} \text{SO}_2 \end{array} \begin{array}{c} \text{X} \end{array} & 0.1 \text{ M}
\end{align*}
\]

(\(X = \text{Cl or F}\))

to give a copolymer of composition

\[
\begin{array}{c}
\text{CO} \begin{array}{c} \text{O} \end{array} \begin{array}{c} \text{SO}_2 \end{array} \begin{array}{c} \text{O} \end{array} \\
\begin{array}{c} \text{n} \end{array}
\end{array}
\]

- generally called a 90/10 copolymer. The Experimental procedure was as described for 14 ii a using the hydrated bis potassium salt of 4,4'-dihydroxybenzophenone.

iv) Preparation of oligomer of poly(phenylene ether ketone)

Typically, 4,4'-difluorobenzophenone (3.27 g, 0.015 M), the anhydrous bis potassium salt of 4,4'-dihydroxybenzophenone (2.90 g, 0.01 M) and a suitable solvent were allowed to react for 1 h at 330 - 340° in a nitrogen-purged glass vessel as previously described. This stoichiometry gives a fluoro ended oligomer of \(M_n = 5\). The oligomer was worked up as described for poly(phenylene ether ketone) except that the methanol was replaced by 80:20 methanol water in order to avoid leaching out low molecular weight species.
v) Preparation of deliberately branched poly(phenylene ether ketone)

The anhydrous bis potassium salt of 4,4'-dihydroxybenzophenone (2.9870 g, 0.0103 M), 4,4'-difluorobenzophenone (2.18 g, 0.001M), 2,4,4'-trifluorobenzophenone (0.0472 g, 0.0002M) and a suitable solvent were allowed to react in a nitrogen purged, stirred glass vessel at 330 - 340°C for 35 min (the reaction mixture could no longer be stirred.) The mass was allowed to cool under nitrogen and was worked-up in the manner previously described.

The above stoichiometry should have given a polymer of the following composition:

The pale buff polymer had a gel content of 3.5% and $[\text{RV}]_{25^\circ}^{1%, \text{C}_2\text{H}_6\text{SO}_4} = 3.58$

Preparation of deliberately branched poly(phenylene ether ketone)

The hydrated bis potassium salt of 4,4'-dihydroxybenzophenone (8.843 g, 0.03045 M) and diphenyl sulphone (15 g) were placed in a 100 ml three-necked round bottomed flask fitted with a stirrer, air condenser, nitrogen inlet and vacuum line. The vessel was immersed in a metal bath at ~ 230°C and reduced pressure (~ 30 mmHg) applied. The pale yellow paste in the reaction was stirred until dehydration of the bis potassium salt was complete (~ 45 min). Nitrogen was then let into the apparatus. The 4,4'-dichlorobenzophenone (7.5333 g, 0.03 M), 2,4,4'-trifluorobenzophenone (0.0709 g, 0.0003 M) and the remaining diphenyl sulphone (12.9 g: to give a 30% solution of polymer) were then added and the reaction mixture stirred under nitrogen whilst the temperature of the bath was increased to 330 - 340°C.

After 27 h at this temperature, the polymerisation product was allowed to cool under nitrogen, and then worked-up in the manner previously described.
vi) Preparation of an 80 : 20 ketone : sulphone copolymer taken to low conversion: a typical example

The hydrated bis potassium salt of 4,4'-dihydroxybenzophenone (15.8217 g, 0.05 M) and diphenyl sulphone (27 g) were dehydrated in the manner described in Section 13. 4,4'-Dichlorobenzophenone (7.5333 g, 0.03 M), 4,4'-dichlorodiphenyl sulphone (5.7432 g, 0.02 M) and diphenyl sulphone (20.46 g: total to give a 30% solution of polymer) were then added and the polymerisation allowed to proceed for 3 hours at 300° before being cooled under nitrogen. The cold polymer cake was ground to a fine dust and two aliquots (~4 g) of this were titrated potentiometrically against 0.1 N-sulphuric acid. A typical analysis is given below:

<table>
<thead>
<tr>
<th>ml of 0.1 N-HCl</th>
<th>m V</th>
<th>Δm V</th>
<th>Δ²m V</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>459</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>442</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>420</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>370</td>
<td>50</td>
<td>+60</td>
</tr>
<tr>
<td>5.0</td>
<td>260</td>
<td>-63</td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>213</td>
<td>47</td>
<td></td>
</tr>
</tbody>
</table>

\[
\text{Titer} = 4.8 + 0.2 \times \frac{63}{123} = 4.8976 \text{ ml}
\]

This titer corresponds to \(4.8976 \times 10^{-4}\) M phenate end groups.

This was contained in 4.0658 g of polymer.

\[
\text{In 76.56 g (total weight of solids in the reaction) there are}
\]

\[
\frac{4.8976 \times 76.56 \times 10^{-4}}{4.0658} = 0.0092 \text{ M phenate end groups}
\]

Moles of phenate end groups at the start was 0.05 x 2, i.e. 0.1 M

\[
\text{Consumed end groups} = 0.1 - 0.0092 = 0.0908
\]

\(= 90.8\% \text{ reaction.}
\]

The other aliquot gave 91.1% reaction.

A further sample of the cake was worked-up in the normal way and examined by nmr as a dimethyl sulphoxide solution.
addition process

This was performed in exactly the same way as 14 vi except that after dehydration of the bis potassium salt, only the 4,4'-dichlorodiphenyl sulphone was added and allowed to react for 1 h before the 4,4'-dichlorobenzophenone was added. A blank reaction was also carried out in which no 4,4'-dichlorobenzophenone was added at all and the 'polymer' cooled after 1 h's reaction with the 4,4'-dichlorodiphenyl sulphone.

The cake was ground to a dust and analysed as in 4vi. (Found: 40.4, 40.6%. Calc. 40.0%). The results show the reaction is complete in 1 h.

vii) Preparation of a copoly(phenylene ether ketone/sulphone) by ether interchange

Poly(phenylene ether sulphone) (11.0 g), poly(phenylene ether ketone) (9.8 g), the potassium salt of 4-chloro-4'-hydroxydiphenyl sulphone (0.6 g) and diphenyl sulphone (75.6 g) were placed in a standard polymerisation system and heated at 330° for 54 h.

The above stoichiometry gives 0.05 M of each polymer repeat unit as a 20% solution in diphenyl sulphone.

Samples of the polymerisation mixture were withdrawn at intervals by way of a side neck on the flask using a 'Pro-pippette'.

The samples (when cooled and solidified) and final polymer were worked-up in the manner previously described.

EXPERIMENTAL TECHNIQUES

i) Determination of the gel content of samples of poly(phenylene ether ketone)

0.2500 g of the polymer was accurately weighed into a 25 ml volumetric flask and 98% sulphuric acid (~15 ml) added.

The stoppered flask was allowed to stand for 24 h with occasional stirring and then made up to the mark with 98% sulphuric acid. The solution was then
was stoppered). A 35 mm No 1 porosity glass sinter was prepared by washing with water then acetone and drying in an air oven for several hours at 140° before being accurately weighed. The polymer solution was filtered through this sinter under gravity, using a watch glass to cover the sinter while filtration took place. The flask was washed out with 4 x 25 ml portions of pure 98% sulphuric acid and these were used to wash the collected gel. When all the gel had been collected and washed with acid, it was washed repeatedly with distilled water. Then the sinter was dried to constant weight in a vacuum oven at 100°. The weight of gel was expressed as a percentage of the original 0.25 g of polymer.

<table>
<thead>
<tr>
<th>Wt of sinter</th>
<th>Wt of sinter + gel</th>
<th>.gel</th>
<th>% gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>34.1896</td>
<td>a) 34.1923 g</td>
<td>0.0028 g</td>
<td>1.12%</td>
</tr>
<tr>
<td></td>
<td>b) 34.1925 g</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**The determination of the density of poly(phenylene ether ketone) and copoly(phenylene ether ketone/sulphones)**

The polymer was first compression moulded into bubble free film. This was done by placing a small quantity of the dried polymer in a template made from 0.007" thick aluminium foil and placing this between sheets of the same foil. The polymer was then compressed in an electrically heated press at 20 tons pressure (on a 4" diameter ram) at the appropriate temperature (this was 410° for poly(phenylene ether ketone), 400° for the 95/5 copolymer and proportionately lower as the sulphone content of the copolymer increased). The film was allowed to cool slowly in the press to ~100° before being taken out. Amorphous samples of the film were prepared by heating small squares of the film in aluminium foil trays over a metal bath at > 420° and when the film had become clear and soft, the tray was transferred as quickly as possible to an ice bath. The clear polymer film was then peeled off the
Measurement of density of poly(phenylene ether ketone and poly(phenylene ether ketone sulphones)

Densities were measured by placing small samples of bubble free amorphous film in a density column. This column consists of a 'mixture' of two liquids of differing density (in this case calcium nitrate solution and methanol) in a temperature regulated column. The two liquids are added carefully to the column such that a density gradient is obtained along its length. The column is calibrated using small glass 'pips' of known density and a graph of density against column length is plotted; in this way the depth to which a polymer sample drops into the column can be read off directly as a density.

This method is not as accurate as the Archimedes method when large samples are available but when only very small samples of polymer are available the density column method is preferred, as small samples lead to weighing errors in the Archimedes method.

Measurement of the density of copoly(phenylene ether ketone/sulphones)

by the Archimedes Method

The polymer was compression moulded into small plaques (approx 1 cm x 1 cm), great care being taken to ensure that the plaques were free from bubbles of trapped air. The plaques were then accurately weighed in air, then in water (by suspending the sample from a wire of known weight) and the following calculations made:

1 = Wt in air
2 = Wt in water
3 = Wt of wire
2-3 = True wt in water = 4
1-4 = Difference in wt in water and air = 5
5 ÷ = Density of water (at the temperature the experiment was carried out at) = 6
1 ÷ 6 = Density of the sample.
in 98% sulphuric acid

Solutions of the polymer were made up at four different concentrations in 98% sulphuric acid. The reduced and inherent viscosities of these solutions were then determined using the equations:

Reduced viscosity (RV) = \( \frac{1}{c} \times \frac{(t_{\text{soln}} - t_{\text{solvent}})}{(t_{\text{solvent}})} \)

and

Inherent viscosity = \( \frac{1}{c} \times \log_{e} \frac{t_{\text{soln}}}{t_{\text{solvent}}} \)

Where:
- \( c \) = concentration of the polymer solution
- \( t_{\text{soln}} \) = flow time of the polymer solution through a Grade C Ostwald viscometer at 25° and
- \( t_{\text{solvent}} \) = flow time of pure solvent through the same Ostwald viscometer at 25°

Both reduced and inherent viscosities were then plotted against concentration and the viscosity at zero concentration (i.e. the intrinsic viscosity) obtained for that polymer.

Measurements were carried out at 25° (± 0.05°) in a thermostatically controlled water bath.

A typical example is shown in Graph 12.

The value of reduced viscosity at 1% concentration was used to compare polymers of one type – thus for, say, poly(phenylene ether ketone), the higher the reduced viscosity, the higher the molecular weight.
Measurement of melt-viscosity

Sample Preparation

Samples of polymer were cold compacted into bars (0.9 cm x 3") using a stainless steel mould with a pressure of 10 tons (on a 4" diameter ram). These bars were then vacuum dried for 1 - 2 h at -120° just prior to the measurement being made.

APPARATUS

The measurements were carried out in a rain extruder, a sketch of which is shown:

![Diagram of extruder]

The speed of the motor driving the ram downwards has been adjusted such that the shear rate is 1000 sec$^{-1}$ when a die of hole size 0.5 mm diameter x 1/8" depth is used (thus 125 sec$^{-1}$ when a die of hole size 1.0 mm x 1/4" depth.) The gauge shows pressure which is related to the shear stress by a constant factor. This factor was 0.013 for the gauge used.
Thus shear stress = Pressure reading x factor and therefore melt viscosity
= Pressure x factor Nsn T (for the small die).

Typical Melt - Viscosity Measurement

<table>
<thead>
<tr>
<th>Polymer 7767/73</th>
<th>T = 400°</th>
<th>Shear rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>RV = 1.53</td>
<td>Die</td>
<td>125 cm⁻¹</td>
</tr>
<tr>
<td>Gauge factor</td>
<td>1.0 mm x 0.25 ins</td>
<td>Operator : L Hoy</td>
</tr>
<tr>
<td>0.013</td>
<td></td>
<td>Date : 4/2/74</td>
</tr>
<tr>
<td>Time (min)</td>
<td>Pressure reading</td>
<td>Viscosity (KNS/m²)</td>
</tr>
<tr>
<td>0 (3 min preheat)</td>
<td>24</td>
<td>2.5</td>
</tr>
<tr>
<td>5</td>
<td>21</td>
<td>2.18</td>
</tr>
<tr>
<td>10</td>
<td>21</td>
<td>2.18</td>
</tr>
<tr>
<td>15</td>
<td>21</td>
<td>2.18</td>
</tr>
<tr>
<td>20</td>
<td>21</td>
<td>2.18</td>
</tr>
<tr>
<td>25</td>
<td>21</td>
<td>2.18</td>
</tr>
<tr>
<td>30</td>
<td>21</td>
<td>2.18</td>
</tr>
<tr>
<td>35</td>
<td>21</td>
<td>2.18</td>
</tr>
<tr>
<td>40</td>
<td>21</td>
<td>2.18</td>
</tr>
<tr>
<td>45</td>
<td>22</td>
<td>2.29</td>
</tr>
<tr>
<td>50</td>
<td>22</td>
<td>2.29</td>
</tr>
<tr>
<td>60</td>
<td>23</td>
<td>2.39</td>
</tr>
</tbody>
</table>

The constant value of 2.18 K Ns/m² was taken.

v) The recording of ultra-violet/visible spectra

The recordings were made on a Unicam SP 800 B Ultraviolet Spectrophotometer
using 1 cm quartz cells, over the range 300 to 800 mp. When 98% sulphuric
acid was placed in both reference and sample beams, no absorption was
detected - the samples were run using 98% sulphuric acid in the reference
beam.
Sample preparation for ultra violet and visible spectroscopy

0.2500 g of the compound to be examined was accurately weighed into a 25 ml volumetric flask and made up to mark with 98% sulphuric acid (if the sample was gelled polymer, the gel was filtered off at this stage). 1.00 ml of this solution was diluted to 50 ml in a volumetric flask with 98% sulphuric acid and this 0.02% stock solution was used to prepare more dilute solution, e.g. 1.000 ml diluted to 25 ml gives 0.0008% solution etc.

All flasks and pipettes used for these operations were carefully washed and dried before use. Operations involving transfer of the sulphuric acid solutions were carried out as quickly as possible and all solutions were carefully stoppered when not in use.

vi) Differential thermal analyser

The apparatus consists of a cylindrical aluminium block heated with a 55 w cartridge heater placed in its centre. The sample and reference cells (1.5 mm glass tubes : Du Pont, Part No 900302) are placed in holes drilled in the top of the cylinder. The material under study is placed in the sample cell (the reference consisting of glass powder) and thermocouples (which are a flush fit for the glass tube) are pushed into both this and the reference (thermocouples are butt welded: Du Pont, Part No 900329). This whole assembly is encased in a glass dome to prevent external temperature changes affecting the measurements. The block itself can be cooled by way of an air jacket (nitrogen is used if cooling is ever required). The signals from the thermocouples are amplified and then recorded on a Hewlett Packard 7035B X-Y recorder with $\Delta T$ on the Y axis and $T$ (sample temperature) on the X axis.

The heating assembly is controlled such that any heating rate from $< 1^\circ/\text{min}$ to $49^\circ/\text{min}$ can be achieved. The apparatus can also be made to achieve any desired constant temperature. Temperature display is given
on a digital voltmeter in millivolts (a conversion chart is used to convert to °C). Heating rates of 10°/min were used throughout the experiments.

The thermocouples detect temperature changes within both the sample and the reference (which should be inert in all senses, over the temperature range being used). If the sample is a crystalline solid and it is heated through its melting point, it will absorb heat (to break down the lattice) as it melts, this will appear on the X-Y recorder as an endothermic 'peak' because the temperature of the sample (during the melting process) stayed constant whereas the reference continued to heat up (see diagram).

Typical DTA Thermogram

\[ \Delta T \]

\[ T \]

The melting range is taken from the point at which the plot of \( \Delta T \) against \( T \) first deviates from the base-line to the tip of the endothermic peak (the melting point). The area under this peak is related to the heat of fusion of the sample.

Sample preparation

Samples were ground up (if monomeric) or sieved (if polymeric). The samples were packed into the glass tubes to a depth just sufficient to cover the exposed thermocouple wires (usually \( \frac{1}{4}'' \)) - this gave 1 - 5 mg depending on the density of the sample.
Calibration of the D T A Block

Small quantities (3 - 10 mg) of the standard compounds were accurately weighed into the melting point tubes and the thermograms of these compounds measured in the usual way. The area under each melting point process (as shown in the thermogram) was measured by triangulation and from this together with the weight of the sample and the known heat of fusion, a value of cal/sq mm was calculated. These values were then plotted against the melting points of the compounds.

Annealing of polymer samples

Early annealing experiments were carried out by heating a small (~1 g) polymer sample in a nitrogen flushed test tube immersed in a metal bath at the required temperature. This was thought, however, to partly degrade the polymer and also cause the smaller polymer particles to agglomerate, making good contact with the thermocouples in the D T A impossible. Accordingly, the following procedure was adopted.

A thermocouple was weighed then pushed into a glass tube containing the polymer as powder. The tube was then immersed in a metal bath at a higher temperature than its melting point for 1.5 - 2 min before being plunged quickly into ice/water (below its glass transition temperature). The glass tube was then removed and the whole assembly reweighed. The thermocouple plus polymer 'plug' was then annealed in a test tube at the required temperature before being slid back into a new glass tube for D T A.

vii) Mathematical treatment of data

The method of least squares was used to determine the best straight lines through a series of points, when such treatment was necessary, as e.g. for the plot of intrinsic viscosity against number average degree of polymerisation for poly(phenylene ether ketone) to obtain K and \( \lambda \) values.
in the Mark - Houwink equation.

The Mark - Houwink equation is:

\[ [\eta] = K (M)^{\alpha} \]

where \([\eta]\) = intrinsic viscosity

\(M\) = a molecular weight average and \(K\) and \(\alpha\) are constants.

This equation can be obtained in the form \(y = mx + c\) (i.e. the equation of a straight line) by taking logs, thus:

\[ \log ([\eta]) = \log K + \alpha \log M \]

The following data were obtained relating intrinsic viscosity and molecular weight for poly(phenylene ether ketone):

\[
\overline{DF}_n \times \text{Molecular weight of repeat unit} = \overline{M}_n
\]

<table>
<thead>
<tr>
<th>(\overline{DF}_n)</th>
<th>([\eta])</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.10</td>
</tr>
<tr>
<td>5</td>
<td>0.10</td>
</tr>
<tr>
<td>7</td>
<td>0.12</td>
</tr>
<tr>
<td>10</td>
<td>0.21</td>
</tr>
<tr>
<td>15</td>
<td>0.23</td>
</tr>
<tr>
<td>20</td>
<td>0.36</td>
</tr>
<tr>
<td>30</td>
<td>0.49</td>
</tr>
<tr>
<td>40</td>
<td>0.63</td>
</tr>
<tr>
<td>50</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Taking logs of each set and letting \(\log \overline{DF}_n = x\) and \(\log ([\eta]) = y\) we obtain:
\[
\begin{array}{cccc}
 x & y & x \cdot y & x \cdot x \\
 0.6021 & -1.0 & -0.6021 & 0.3625 \\
 0.6990 & -1.0 & -0.6990 & 0.4886 \\
 0.8451 & -0.9208 & -0.7782 & 0.7142 \\
 1.000 & -0.6778 & -0.6778 & 1.0000 \\
 1.1761 & -0.6383 & -0.7507 & 1.3832 \\
 1.3010 & -0.4437 & -0.5773 & 1.6926 \\
 1.4771 & -0.3098 & -0.4576 & 2.1818 \\
 1.6021 & -0.2007 & -0.3215 & 2.5667 \\
 1.6990 & -0.0315 & -0.0535 & 2.8866 \\
\end{array}
\]

\[
\begin{align*}
\overline{x} &= 10.4015 \quad \overline{y} = -5.226 \quad \overline{x \cdot y} = -4.9177 \quad \overline{x \cdot x} = 13.2762
\end{align*}
\]

From which \( n \) (the number of points) = 9

Now: by the method of least squares, \( m \) (the slope) = \[
\frac{n \sum xy - (\sum x \cdot \sum y)}{n \sum x^2 - (\sum x)^2}
\]

\[
\therefore \quad m = \frac{9(-4.9177) - (10.4015 \cdot -5.226)}{9(13.2762) - (10.4015)^2}
\]

\[
\therefore \quad m = 10.0636
\]

\[
\therefore \quad m = 11.2946
\]

\[
\therefore \quad m = 0.891009
\]

And \( c \) (the intercept)

\[
\begin{align*}
\log K &= \frac{\sum xy \cdot \sum x - \sum x \cdot \sum xy}{n \sum x^2 - (\sum x)^2} \\
&= \frac{(-3.2226 \cdot 13.2762) - (10.4015 \cdot (-4.9177))}{11.2946}
\end{align*}
\]

\[
\therefore \quad \log K = \frac{-18.1846}{11.2946}
\]

\[
\therefore \quad \log K = -1.61
\]

\[
\therefore \quad K = 0.02147
\]
The errors in these values of K and d were also determined.

First, a straight line was constructed using the values of K and d obtained by the above calculation, the values of y (i.e. log [ y ] ) were then compared to the values obtained experimentally, thus:

<table>
<thead>
<tr>
<th>Actual value of y (by experiment)</th>
<th>y from construction of the line</th>
<th>difference d</th>
<th>d.d</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.0</td>
<td>-1.0655</td>
<td>0.0655</td>
<td>0.0043</td>
</tr>
<tr>
<td>-1.0</td>
<td>-0.9747</td>
<td>0.0253</td>
<td>0.0006</td>
</tr>
<tr>
<td>-0.9208</td>
<td>-0.8539</td>
<td>0.0669</td>
<td>0.0049</td>
</tr>
<tr>
<td>-0.6778</td>
<td>-0.7122</td>
<td>0.0344</td>
<td>0.0012</td>
</tr>
<tr>
<td>-0.6383</td>
<td>-0.5686</td>
<td>0.0697</td>
<td>0.0049</td>
</tr>
<tr>
<td>-0.4437</td>
<td>-0.4437</td>
<td>0.0</td>
<td>0</td>
</tr>
<tr>
<td>-0.3098</td>
<td>-0.2924</td>
<td>0.0174</td>
<td>0.0003</td>
</tr>
<tr>
<td>-0.2007</td>
<td>-0.805</td>
<td>0.0202</td>
<td>0.0004</td>
</tr>
<tr>
<td>-0.0315</td>
<td>-0.0969</td>
<td>0.0654</td>
<td>0.0043</td>
</tr>
</tbody>
</table>

\[ \sum_{dd} = 0.0209 \]

Now, error in slope = \( \chi_a \)

and error in intercept = \( \chi_b \)

\[
\chi_a/n = \chi_b/\chi_{xx} = \chi_1 \Delta
\]

where \( \chi_1 = \sum_{dd}/n-2 \)

and \( \Delta = n \chi_{xx} - (\chi_x)^2 \)

thus \( \chi_1 = 0.0209 \)

and \( \Delta = 11.2946 \)
\[ \frac{\alpha^2_{a/n}}{\alpha^2_b} = \frac{13.2762 \times 0.0029}{11.2946} \]
\[ = \frac{9 \times 0.0029}{11.2946} \]
\[ = 0.0023 \]
and \[ \alpha^2_b = \frac{13.2762 \times 0.0023}{9} \]
\[ = 0.0034 \]

Thus we have finally;

\[ = 0.891 \pm 0.0023 \]

and \[ K = 0.0215 \pm 0.0034 \]

viii) 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. The specimens were supported at two points 1.5" apart and struck at two points equidistant from the notch (points X on the diagram) on the edge opposite the notch by a pendulum dropped from a height of one foot. From the residual energy of the pendulum, the energy required to break the specimen was calculated. The pendulum weight was selected from a range of \(\frac{1}{32}\) lb - 2 lb such that a reading 0.2 to 0.8 was obtained on the tester scale (this was the most accurate
Then Notched impact strength $= \frac{R \times W}{d \times t}$ ft lb/in$^2$

$= \frac{R \times W}{d \times t} \times 2.1$ KJ/m$^2$

where $R =$ reading in the tester
$W =$ weight used on the pendulum (lb)
$d =$ notch depth (ins)
$t =$ thickness on specimen (ins)

Five or six specimens were tested to obtain each impact strength and the median value was calculated. An example is shown below.

<table>
<thead>
<tr>
<th>Notch Radius</th>
<th>d (in)</th>
<th>+ (in)</th>
<th>Pendulum Weight</th>
<th>Reading</th>
<th>Notched Impact Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.080&quot;</td>
<td>0.152</td>
<td>0.132</td>
<td>1.0 lb</td>
<td>0.61</td>
<td>30.4</td>
</tr>
<tr>
<td></td>
<td>0.150</td>
<td>0.133</td>
<td></td>
<td>0.74</td>
<td>37.1</td>
</tr>
<tr>
<td></td>
<td>0.151</td>
<td>0.140</td>
<td></td>
<td>0.72</td>
<td>34.1</td>
</tr>
<tr>
<td></td>
<td>0.160</td>
<td>0.132</td>
<td></td>
<td>0.60</td>
<td>28.4</td>
</tr>
<tr>
<td></td>
<td>0.162</td>
<td>0.128</td>
<td></td>
<td>0.80</td>
<td>38.6</td>
</tr>
</tbody>
</table>

Thus the values 30.4, 28.4, 38.6 and 37.1 ft lb/in$^2$ are discarded and the median value 34.1 ft lb/in$^2$ (71.2 KJ/m$^2$) is taken.
Purification of Reagents

i) Diphenyl sulphone

The diphenyl sulphone used was Fluka 'A' material, crystallised from methanol or isopropanol containing a little active charcoal.

mp 126 - 126.5

ii) Sulphuric acid

Fisons 'Analytical Reagent' 98% sulphuric acid was used without further purification.

iii) Potassium hydroxide

Hopkin and Williams 'Convol' solutions were used without further purification. These solutions contain 40% w/w of potassium hydroxide.
Examples of the ultra-violet/visible spectra of poly (phenylene ether ketones), showing in Graph 13, a very dilute polymer solution (absorption due to the carbonyl group) and in Graph 14, polymer solutions at 1% showing the absorbance due to the chromophore.
ULTRA-VIOLET \( \leftrightarrow \) UV SPECTRUM OF \( \left[ \left( \text{O} \cdot \text{CO} \cdot \text{O} \cdot \text{O} \right) \right]_n \)

AT 0.0008 N/\% IN SULPHURIC ACID (SULPHURIC ACID AS REF)

POLYMER 7188 7/3
ULTRA-VIOLET/VISIBLE SPECTRA OF 1% SOLUTIONS
OF $\left(\text{C}=\text{O}^{\text{3}}\right)\text{-CO}_{\text{4}}^{\text{4}} \text{O}^{\text{4}}_{\text{4}}$ IN SULPHURIC ACID SHOWING
TYPICAL ABSORBANCES AT ~550 nm

GRAPH 14

450 500 550 600 WAVELENGTH (nm)
The Calculation of the Extinction Coefficient for the Carbonium Ion Derived from 4,4'-diphenyloxy benzhydrol

Four solutions of different dilutions were made of 4,4'-diphenyloxy benzhydrol in 98% sulphuric acid and the absorbances of these solutions measured at 505 nm.

The values obtained were then plotted against concentration. The resulting straight line shows that at these concentrations, the carbonium ion in solution obeys Beer's Law

\[ \text{absorbance} = \varepsilon \cdot l \cdot c \]

where \( \varepsilon \) = extinction coefficient, \( c \) = concentration (moles/lit) and \( l \) = path length (cm).

From the graph, at an absorbance of 0.38 the concentration of carbonium ion = \( 1 \times 10^{-4} \) g/100 ml soln.

\[ \% \text{carbonium ion in the polymer} = 1 \times 10^{-4} \times 100 \]

\[ = 0.01\% \]

The molar extinction coefficient for the carbonium ion \( \varepsilon = \frac{\text{absorbance}}{l \times c} \)

\[ = \frac{0.38 \times 351}{1 \times 1 \times 10^{-4} \times 10} = 1.32 \times 10^5 \]
**Beer's Law Plot**

For:

\[ |\text{o} - |\text{o}^2| - \frac{e}{\Theta} - |\text{o} - |\text{o}^2| \]

in Sulphuric Acid

Absorbance vs. \( \text{C}_{\text{H}_2\text{SO}_4} \times 10^4 \)


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(36) A Macoll, Quart Rev, 1947, 1, 16.


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(49) G Bier, Polymer, 1974, 15, 8.


(51) Huggins, J Am Chem Soc, 1942, 64, 2716.

(52) Kuhn, Kolloidzschr, 1934, 68, 2.

(53) H Mark, Der Feste Korper, Leipzig, 1938, 103.


(58) A B Newton, unpublished work.


(69) A poly(ethylene oxide), Mn = 600,000, ~ 95% crystalline. Data from the manufacturers trade pamphlet.


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