The polycondensation of formaldehyde with phenyl ether - A model study

A Thesis presented for the Degree of Doctor of Philosophy
by
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For my parents -the best friends I’ve ever had.
Acknowledgements

Many people have played a part directly or indirectly in bringing this thesis to fruition, and I hope that I have mentioned most of them below.

My Ph.D. is likely to be the last academic qualification I achieve, and so this is an excellent time to formally acknowledge my enormous debt to my parents who have cajoled, helped and supported me through the ups and downs of my educational life, hence this culmination of all those efforts is dedicated to them.

I am naturally also very grateful to ICI for giving me this most unusual opportunity to carry out my Ph.D. whilst in full employment. I can only apologise to them for having taken over 2 years to complete the writing up (!) and to the typists who needed the patience of Job in carrying out my corrections as my thesis proceeded around the unusual Amsterdam, Runcorn, Guildford triangle. Within ICI I am particularly grateful to Mike Jones and Eric Nield for their guidance in overseeing the running of this project, and especially to John Carey with whom I shared a lab and office and who undertook the arduous and nigh impossible task of converting me to a half decent organic chemist. To Jim, Janice, Phil, Janet, Bill and Chim, and any other occupants of the strange, yellow lab. 721, thank you for making life so much more fun than it would otherwise have been. Together with John’s help I can honestly say you improved my ability to do the Guardian Quick Crossword no end.

The $^{13}$C NMR work done in this thesis was central to the whole project, and was only possible because Martin Kipps at Jealott’s Hill offered his services and those of his 400 MHz NMR despite already having a heavy work load from Plant Protection Division. Thank you, Martin.

It goes without saying that the unrivalled knowledge of my Prof., John Rose and all his experience in the field of aromatic polymers was essential to this project, and indeed to its writing up. If I have learned anything about writing scientifically, John must take the credit for it.

Finally I would like to thank Jill for all her support, moral and otherwise, and Fergus for not drawing trains on too many of my first copies. As his reward he gets the half a tonne of scrap paper that constitutes all my corrected versions.
Summary

Chapter One of this thesis describes the nature of the problem under investigation, viz an inability to control functionality number and type in phenylether-formaldehyde condensations, a review of the relevant literature, and the use of phenoxybenzyl monomers as a means to determine the reaction mechanism.

Chapter two describes the first syntheses and the syntheses used in this thesis of the phenoxybenzyl monomers used.

Chapter three contains an outline of the reaction techniques used and describes the analytical methods used in this thesis, namely gel permeation chromatography (GPC) and carbon-13 nuclear magnetic resonance (13C NMR).

In Chapter four the rates of oligomerisation of the hydroxy monomers under acid catalysis are measured, as is the rate when acetic acid is added as a reactive diluent. The effect of catalyst to monomer ratio is described, and the differences between the systems discussed with the aid of basicity data.
Chapter five commences with an assignment of the peaks observed in carbon-13 NMR spectra for the phenoxybenzyl monomers and of other species thought to be present during their oligomerisation reactions. It goes on to produce time-concentration profiles of the reactive intermediates (via 13C NMR measurements) present during the reaction discussed in chapter four. Important differences are seen when acetic acid diluent is present in terms of controlling functionality type.

Chapter 6 discusses attempts at controlling multi-substitution in polybenzyls before describing a technique useful in the phenoxybenzyl system for preventing this occurring. The same technique holds good when dihydroxy functional monomers are added, allowing control of the number of functional groups per oligomer chain.

Chapter 7 describes the use of GPC to assess the rate of monomer reactions in the systems researched in chapters four and five. Orders of reaction are determined and kinetic expressions derived.

The experimental methods and techniques used are described in detail in chapter 8, which concludes with references.
POLYCONDENSATION OF FORMALDEHYDE WITH PHENYL ETHER; A MODEL COMPOUND STUDY

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CHAPTER 1, INTRODUCTION

1.1 Problems in Controlling The Structure of Oligomers Made By Polycondensation of Formaldehyde With Phenyl Ether

Phenyl ether-formaldehyde oligomers, the approximate nature of which is depicted in the equation below, should offer a number of advantages over aromatic oligomers currently available.

They should be cheap, they should be very stable, impart good corrosion resistance when coated on metal and offer more flexibility, for instance in surface coatings (via the ether linkage) than other aromatic systems. In addition, a very wide range of chemistry should be possible, allowing oligomer structure to be tailored so as to give materials with specific properties to fit particular applications.

In reality however, only partial success in these features has been achieved\(^1\). With many potentially useful reactive functional groups, it has proved, so far, impossible to synthesise resins with the required number of these functional groups attached to the polymer molecules when reactions are carried out in one stage, as they must be in order to be commercially viable. Control of molecular weight is also poor, and gelation can be a problem.
Further experiments were carried out with other aromatics (e.g. naphthalene) and formaldehyde plus another reagent intended to provide a useful functional group for the resulting oligomer. However, none of these experiments resulted in oligomers with a sufficiently high functionality.

[Functionality can be defined in a number of ways, but is basically the average number of designated functional groups per polymer molecule. For the purpose of this thesis, the term oligomer is used to describe polymer molecules with an $M_n$ of less than 5000].

In the light of these failures, it was deemed necessary to try and comprehend more about the processes taking place during reaction to form the oligomer, in order to understand why a particular molecular structure results from a particular set of reaction conditions. Molecular structure, of course, is important in determining many of the final oligomer's properties, such as the melting point ($T_m$) and the glass transition temperature, $T_g$ ($T_g$ is defined as the temperature at which a polymer changes from a rigid, glassy condition to a flexible, rubbery state).

Whilst much work has been carried out on studying the kinetics and mechanism of the formation of phenol-formaldehyde resins, using just about every available analytical technique, relatively little such work has been carried out on resins from formaldehyde and phenyl ether. What has been done has tended to concentrate more on the effects of varying reaction conditions, and mechanistic schemes attributed to molecules such as phenyl ether have been taken
directly from those for phenol, with no rigid justification. The reason for the discrepancy in knowledge is, of course, that the phenolic resin business is a huge one, generating much profit, whilst resins based on phenyl ether have rarely had much impact, and so interest tended to be confined to the academic world. By the time the powerful analytical techniques of today were available, even this interest had died, leaving the problems unsolved. It is the aim of this study to try and and answer some of the questions and so address the aforementioned problems.

1.2 Reactions of Aqueous Formaldehyde with Aromatic Molecules

Before discussing the nature of the reaction it is important to emphasise that many of the difficulties associated with trying to unravel the mechanism of aromatic-formaldehyde oligomerisations are associated with the complexities of formaldehyde itself, and it is appropriate that these should be briefly discussed.

The definitive work on formaldehyde is a book by Walker², which is now 25 years old. Although the treatment of formaldehyde reactions with active aromatic hydrogens is not complete, the detail of formaldehyde chemistry is most extensive. Formaldehyde is very reactive and easily reacts with itself to give a large range of compounds, many of which are still capable of reacting with an aromatic molecule. Pure formaldehyde polymerises slowly at room temperature, to (CH₂O)ₙ the reaction being catalysed by water, acids and alcohols. However, the use of pure formaldehyde in oligomerisations would not be appropriate from a production viewpoint, and the most common sources are aqueous solutions. In such solutions formaldehyde monomer will only be present at levels of 0.1% or less.
Formaldehyde solutions have a pH of between 2.5 and 3.5 and are, in fact, composed of the monomeric hydrate as methylene glycol (although this has yet to be isolated) and various low molecular polymeric hydrates $\text{HO} \rightleftharpoons CH_2O \xrightarrow{n} \text{H}$ in equilibrium:

$$
\begin{align*}
\text{CH}_2\text{O} + \text{H}_2\text{O} & \rightleftharpoons \text{HOCH}_2\text{OH} \\
n\text{HOCH}_2\text{OH} & \rightleftharpoons \text{HO} \rightleftharpoons \text{CH}_2\text{O} \xrightarrow{n} \text{H} + (n-1)\text{H}_2\text{O} \\
\text{HO} \rightleftharpoons \text{CH}_2\text{O} \xrightarrow{n} \text{H} & + \text{HOCH}_2\text{OH} \rightleftharpoons \text{HO} \rightleftharpoons \text{CH}_2\text{O} \xrightarrow{n+1} \text{H} + \text{H}_2\text{O}
\end{align*}
$$

In many cases the most reactive form is the monohydrate, methylene glycol. The Cannizzaro reaction, producing methanol and methanoic acid is responsible for the low pH of aqueous formaldehyde solutions

$$
2\text{CH}_2\text{O} + \text{H}_2\text{O} \longrightarrow \text{HCOOH} + \text{CH}_3\text{OH}
$$

Naturally, these equilibria are affected by concentration, temperature, pH and the presence of other species. In any oligomerisation reaction all of the reaction conditions (except, perhaps, temperature) will be changing as reaction proceeds, giving rise to changing equilibria in the formaldehyde solution, and therefore changing the concentrations of various active species as the reaction proceeds. This makes the interpretation of reaction kinetics extraordinarily vague, because the concentration of one component is unknown, and the number of possible reaction products or intermediates is large. Thus when formaldehyde is one of the reagents, polymerisation kinetics are of limited value for elucidating reaction mechanisms.
As an example, the effect of an alteration in pH and concentration on the predominating equilibria is shown in Table 1.1\(^3\) for dilute solutions (\(\sim 2\%\) formaldehyde by weight).

<table>
<thead>
<tr>
<th>pH Ranges</th>
<th>Equilibria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below 2.6</td>
<td>(\text{H}_2\text{C(OH)}_2 \rightleftharpoons \text{CH}_2-\text{OH} + \text{OH}^-)</td>
</tr>
<tr>
<td>From 2.6 - 4.5</td>
<td>(\text{H}_2\text{C(OH)}_2 \rightleftharpoons \text{CH}_2-\text{O}^- + \text{H}_2\text{O})</td>
</tr>
<tr>
<td>Above 4.5</td>
<td>(\text{H}_2\text{C(OH)}_2 \rightleftharpoons \text{H}_2\text{C(OH)}\text{O}^- + \text{H}^+)</td>
</tr>
</tbody>
</table>

At greater concentrations:

<table>
<thead>
<tr>
<th>pH Ranges</th>
<th>Equilibria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below 2.6</td>
<td>(\text{HOCH}_2\text{OCH}_2\text{OCH}_2\text{OH} \rightleftharpoons \text{HOCH}_2\text{OCH}_2\text{OCH}_2\text{O}^- + \text{OH}^-)</td>
</tr>
<tr>
<td>From 2.6 - 4.5</td>
<td>(\text{HOCH}_2\text{OCH}_2\text{OCH}_2\text{OH} \rightleftharpoons \text{CH}_2\text{OCH}_2\text{OCH}_2\text{O}^- + \text{H}^+ + \text{OH}^-)</td>
</tr>
<tr>
<td>Above 4.5</td>
<td>(\text{HOCH}_2\text{OCH}_2\text{OCH}_2\text{OH} \rightleftharpoons \text{HOCH}_2\text{OCH}_2\text{OCH}_2\text{O}^- + \text{H}^+)</td>
</tr>
</tbody>
</table>

Thus during the condensation of an aromatic molecule with formaldehyde in moderately concentrated aqueous solution at a pH of less than 2.6, one of the initial species would be:

\[
\text{Ar-CH}_2\text{OCH}_2\text{OCH}_2\text{OH} \quad (1.1)
\]

where Ar denotes aromatic molecules

If subsequent polymerisation occurs, the formaldehyde trimer may eventually be incorporated into the polymer:

\[
\text{Ar-CH}_2\text{OCH}_2\text{OCH}_2-\text{Ar} \quad (1.2)
\]

However, this trimer is merely the predominant form under the conditions indicated - various other linkages - exemplified by some of the other equilibria in table 1.1 - will also form. In addition,
linkages such as in (1.2) can be broken and reformed in a different mode during reaction, given the appropriate conditions. Some of the reactions known to take place between phenol (denoted by ArOH) and formaldehyde solution at $3 \leq \text{pH} \leq 5$ are shown below (fig 1.2).

\[
\text{H}^+ + \text{HOCH}_2\text{OH} \rightleftharpoons \text{HOCH}^+_2\text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{CH}_2\text{OH}
\]

\[
\text{ArOH} + \text{CH}_2\text{OH} \rightleftharpoons \text{HOArCH}_2^+ + \text{H}_2\text{O}
\]

\[
\text{HOArCH}_2^+ + \text{OHArCH}_2\text{OH} \rightleftharpoons \text{HOArCH}_2\text{OCH}_2\text{ArOH} + \text{H}^+
\]

\[
\text{HOArCH}_2^+ + \text{HOCH}_2\text{OH} \rightleftharpoons \text{HOArCH}_2\text{OCH}_2\text{OH} + \text{H}^+
\]

\[
\text{HOArCH}_2^+ + \text{HOArCH}_2\text{OCH}_2\text{OH} \rightleftharpoons \text{HOArCH}_2\text{OCH}_2\text{OCH}_2\text{ArOH} + \text{H}^+
\]

\[
\text{HOArCH}_2 + \text{HOAr} \rightarrow \text{HOArCH}_2\text{ArOH} + \text{H}^+
\]

Figure 1.2 - Phenol-formaldehyde reactions in aqueous solution

Such a reaction is complex enough on its own, even before one tries to take into account the effect of the gradually changing concentration and pH as polymerisation proceeds. Given these circumstances, it was decided to use models to help gain an understanding of some of the more important processes involved in phenyl ether/formaldehyde reactions. These models will be discussed further at the end of the chapter.
Inevitably as the field of potential products from phenyl ether-formaldehyde resin enlarged other workers, particularly in academia, began to concern themselves with trying to gain a more detailed understanding of the chemical constitution and structure of these oligomers, in the hope that their properties might be controlled and influenced. First Japanese, and then Russian workers produced a number of papers between the mid-sixties and seventies before interest waned. Much of what they discovered was explained (without any rigorous basis for doing so) by resorting to the results and theories produced by the massive study around phenolic resins. Novolacs, the acid catalysed condensation product of phenol and formaldehyde had been extensively analysed for kinetics, structure and physical properties.

It is, therefore, suitable that a brief review of such research in phenol-formaldehyde chemistry be attempted.

The problem is immensely complex. In studying the intermediates formed during a reaction, the number of LINEAR oligomers that can be formed is large — by starting with phenol and formaldehyde, and assuming only methylene bridges link the phenol units in any or all of the ortho, meta or para positions the distribution of oligomers is illustrated in table 1.2.
Table 1.2

<table>
<thead>
<tr>
<th>No of Phenol-formaldehyde oligomers</th>
<th>No of Phenolic units in a molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 3 4 5 6 7 8 9 10</td>
</tr>
<tr>
<td></td>
<td>3 7 21 57 171 495 1485 4401 13203</td>
</tr>
</tbody>
</table>

Thus, by a molecular weight of 1070 [ten phenol units] there are, in theory, 13203 isomers. However, because of selectivity in the reactions forming methylene linkages [due to differences in the reactivity of ring positions] the number is less. Nevertheless, it is clear that any study of the reaction intermediates is going to be difficult. Many of the lower oligomers have now been synthesised to allow calibration of analytical instruments capable of separating the various molecular weight and isomeric fractions, and this makes progress much easier.

Before such sophisticated analytical techniques became available, workers in the field turned to kinetics and a tentative knowledge of the intermediates that existed, to help them. It is the aim of any kinetic study to determine how a reaction proceeds, but extreme difficulty was found in getting reliable, consistent data for phenol-formaldehyde condensations. Reaction conditions have a profound influence on the nature of the result - even down to the type of reaction vessel employed.
In Novolaks, it was determined that the first step in the reaction sequence is as shown in fig 1.3, producing a methylol phenol, the reaction rate constant being $k_1$.

The kinetics of this reaction have been examined by a number of workers \(^6,^7,^8\). They determined the reaction to be first order.

The next step in the formation of Novolaks is the reaction of the methylol phenol with more phenol to produce a dinuclear moiety, as shown in fig 1.4.

The overall order of this step was also determined to be first order, giving an order for the complete reaction of two (i.e., a repeat of the processes in figs 1.3 and 1.4 to form polynuclear compounds).

In addition to the methylene linkage shown above, a second possibility is the dimethylene ether species: (1.3)\[ \text{CH}_2\text{OCH}_2 \] formed by the reaction of two hydroxymethyl phenols, eliminating water. In fact, other more complex linkages are also possible resulting from the complicated nature of formaldehyde, but these have been briefly discussed previously.
The mechanism shown in figure 1.4, in which a benzyl cation is postulated, was by no means the only suggested route to the polymer. However, Rodia and Freeman provided indirect evidence that the benzyl cation was responsible for reaction in a Friedel-Crafts type process. Rodia and Freeman rejected other proposed possibilities, such as halomethyl species formed from the acid catalyst and quinone methide intermediates. (1.4)

\[
\begin{align*}
\text{phenol} + \text{formaldehyde} & \rightleftharpoons \text{resol} \\
\text{quinone methide} & \rightarrow \text{benzyl cation}
\end{align*}
\]

The halomethyl was rejected because they could not cause pre-synthesised phenols to self-condense with phenols in the absence of catalyst, and the quinone methides were found only to be appropriate in the formation of resols (the alkaline catalysed condensation product of phenol-formaldehyde). By using conditions favourable to the formation of the benzyl cation, Rodia and Freeman showed that catalysts producing the benzyl cation are also necessary for the reaction of the benzyl group with a vacant position on the aromatic ring. This also explains why reaction 2 in figure 1.5 (below) is faster than reaction one, because the reactivity of the benzyl cation is greater than that of "formaldehyde".

\[
\begin{align*}
\text{phenol} + \text{formaldehyde} & \rightleftharpoons \text{resol} \\
\text{quinone methide} & \rightarrow \text{benzyl cation}
\end{align*}
\]

Figure 1.5 - Formation of benzyl cations in phenolics
It should be stated that this proposition can also account for the formation of the methylene ether linkage, although in phenolic resins this does not normally occur at a pH of less than three (equation 3).

\[
2 \text{ OH} \quad \rightarrow \quad \text{HO-CH}_2\text{CH}_2\text{OH} \quad \cdots \quad 3
\]

By measuring the kinetics of reactions, workers such as Yeddanapalli and Kuriakose\(^8\) and Finn and James\(^{12}\) were able to establish the rates of the reactions shown in figure 1.6.

\[
\begin{align*}
F & = \text{Phenol} & \text{MP} & = \text{methylolphenol} \\
F & = \text{formaldehyde} & \text{DPM} & = \text{diphenolmethane}
\end{align*}
\]

![Diagram of reactions](attachment:image.png)

Figures 1.6 - Formation of dinuclear species in phenolics
Once the relative rates were known it was then possible to establish the relative proportions of isomers a, b and c. Similar work⁸,¹²,¹³ led to a knowledge of the relative reactivities of 2,6 and 4 sites in diphenolmethanes (i.e. two phenols linked by a methylene bridge) during the formation of triphenolmethanes, and hence to a qualitative idea of the molecular types present in the reaction. Little could be concluded quantitatively beyond "large, medium and small" quantities.

The introduction of first proton nuclear magnetic resonance (¹H NMR) and then carbon-13 nuclear magnetic resonance (¹³C-NMR) allowed the generation of considerably more data than it had previously been possible to access. Up to this point, skilled interpretation of IR spectra had allowed identification of the repeat unit, the presence of the relative amounts of 2,4;2,6; and 2,4,6 substituted phenolic aromatics and the functionalities present in the resin ¹⁴,¹⁵. ¹H NMR can provide a correlation of these observations, and was thought to be able to give a relative distribution of the methylene bridges between 2,6; 2,4 and 4,4 positions on the phenol ring, and a means of assessing Mn. Such studies are reported by Hirst et al¹⁶ and Szymanski and Blueule¹⁷.

In fact, proton NMR was unable to distinguish between a number of species because of overlap of peaks in the spectrum. In particular the work of Hirst¹⁶ et al and Szymanski and Blueule¹⁷ was later considered dubious by other workers¹⁸,¹⁹ who were unable to accurately resolve 2,6; 2,4 and 4,4 methylene bridge resonances²⁰. Various attempts to enhance resolution by using complexing agents have been made²¹ but it was the advent of ¹³C-NMR which allowed a
clear analysis of the structures involved. The first analytical study specifically aimed at phenol-formaldehyde resins was by de Breet and co-workers. By using a combination of the spectra of model compounds and Grant and Paul additivity relationships, workers were able to determine the relative concentrations of the different types of methylene bridges and successfully predict the spectrum achieved.

Pethrick and Thomson were able to provide a detailed analysis of the initial stages of novolak formation by carrying out the polymerisation in the carbon-13 NMR tube. They made a number of observations, detailed below:

1) Formalin retains its polymeric structure long into the reaction
2) Ortho methylol phenol (structure 1.5) and hemiformals (structure 1.6)
   
   \[
   \text{(1.5)} \quad \begin{array}{c}
   \text{HO} \\
   \text{CH}_2\text{OH}
   \end{array} \\
   \text{(1.6)} \quad \begin{array}{c}
   \text{HO} \\
   \text{CH}_2\text{OCH}_2\text{OH}
   \end{array}
   \]

   were formed before methylene bridges [4 methylol phenols and hemiformals were not observed, but their presence inferred. Lacking the additional hydrogen-bond stability imparted to 2,6 species [structure 1.7] they are not in existence long enough to be seen in the NMR].

   \[
   \text{(1.7)} \quad \begin{array}{c}
   \text{HO} \\
   \text{CH}_2\text{OH}
   \end{array}
   \]

3) 4,4 methylene-bridged species then appear (proof of the formation of 4 methylol before 2 methylol), followed by 2,4 methylene bridges and then 2,6 bridges.
Thus these analyses have provided clear evidence as to both the
time of appearance and the nature of particular molecules within
the resin by comparing the polymerisation spectra with those of
model compounds, and by using Grant and Paul additivity
calculations.

Overall, then, it may be said that considerable progress has been
made in understanding how phenol-formaldehyde oligomers are
formed.

1.4 Polymers Comprising Phenyl Ether Residues Linked by Methylene
Groups

The condensation of aromatic molecules with formaldehyde in the
presence of acid or base to yield polymer has been known for a long
time, with Baeyer\textsuperscript{31} especially studying phenol-aldehyde
condensations in 1872. At the time, the reaction could not be
controlled and the products were thus useless.

The potential of such work continued unfulfilled until L.H.
Baekeland filed his first patents on phenol-formaldehyde resins, in
which he recognised the importance of reactant ratios and the
catalytic role of the acid or base in controlling resin
formation\textsuperscript{32}. After this, various aromatics were condensed with
aldehydes, but it seems that the first in which the aromatic
molecule was phenyl ether, was synthesised by Brunner\textsuperscript{33} at I.G.
Farben. He condensed phenyl ether with formaldehyde and various
hydro-halogen acids to give "aromatic condensation products". He
does not mention polymer, which means that he may either not have
formed it, or not recognised its formation.
Then, in 1945, Reiff and Zech formed what they recognised as a plastic material when heating together chlorinated petroleum wax and phenyl ether in the presence of a Friedel-Crafts catalyst. The experiment was repeated by Reiff in 1947, but this time hexamethylenetetramine (a compound formed by reacting formaldehyde and ammonia) was added to cross-link the material to a rubber.

Then, in 1955, J.D. Doedens described polyaromatic ether compositions. His aim was to maintain the heat stability of phenyl ether in polymer form. He started with the chloro-methylated phenyl ether, (formed from a halomethylating agent such as methyl chloromethyl ether and phenyl ether), and then heated these to expel hydrogen chloride and form brittle polymers which exhibited high thermal stability.

Subsequent inventions made use of this stability - eg J.D. Doedens and H.P. Cordts produced a report in which foams and laminates produced from chloro-methylated phenyl ether exhibited impressive resistance, in particular to heat, but also to chemical reagents. At the time (1961) they expected such materials to find considerable utility, but, unlike the use of phenyl ether itself (in heat transfer agents) nothing ever came of it.

From the initial discovery of the ability to form thermoset resins in this way, other workers quickly moved into the field, producing resins first from halomethylated phenyl ether, and then from formaldehyde and phenyl ether itself, for applications in structures, surface coatings, antioxidants, lubricants and so
on. From here on, there was a steady stream of synthetic polymers based on or around phenyl ether which continues today. Its uses, though, are still limited to specialist applications in the fields of adhesives, electronics and dentistry**1.

1.5 Previous Investigations of The Reaction Between Formaldehyde and Phenyl Ether

1.5.1 Structure of the products

As a result of the large body of work available on phenol-formaldehyde oligomers, researchers into resins from phenylether turned to the interpretations obtained from such work (although at the time the NMR evidence was not available) to provide them with a basic framework around which to work.

A team of Japanese workers, principally Imoto and Ninagawa**2 were conducting research into resins from formaldehyde, and this work encompassed phenyl ether-formaldehyde oligomers. In a sense, they were going one step further back than the trend of the time in that they were NOT using (expensive) monomers which already "contained" formaldehyde in the form of the chloromethyl group (ie, chloromethyl phenyl ether) but starting from the basic constituents.

In their first paper phenyl ether formaldehyde condensations were carried out using a variety of catalysts, such as concentrated sulphuric acid or para-toluene sulphuric acid and solvents – eg,
1,4 dioxan, water, benzene, etc. Different sources of formaldehyde were also utilised, such as α-polyoxymethylene (1.8) as well as the

\[ \text{HO} + \overset{\text{CH}_2\text{O}}{\text{n}} \text{H} \]

(1.8)

more conventionally used formalin [formaldehyde dissolved in water]. The resulting resins were then fractionated by a series of solvent extractions and distillations, and the products identified.

A second paper\textsuperscript{4,3} identified further products previously not detected. The basic results are presented in table 1.3.

<table>
<thead>
<tr>
<th>Structure</th>
<th>melting point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>54-55</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>131-132</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td></td>
</tr>
<tr>
<td>n=0</td>
<td>68-68.5</td>
</tr>
<tr>
<td>n=1</td>
<td>116-117</td>
</tr>
<tr>
<td>n=2</td>
<td>145-147</td>
</tr>
<tr>
<td>n=3</td>
<td>163-164.5</td>
</tr>
</tbody>
</table>

Table 1.3 - Correlation of molecular structure with melting point

In addition to these species, products containing more than one hydroxy methyl \([\text{CH}_2\text{OH}]\) group per ring, and linkages of the methylene ether and acetal type (1.9) were inferred from a study.
of elemental analysis and molecular weight. The paper also attempts to explore the effects of solvent on resin properties, concluding that molecular weight is maximised in non-polar solvents. The reliance on phenolic resins is emphasised here by the comparison of resins produced in polar solvents (and containing hydroxy methyl groups), with Resols, and those from benzene (containing no hydroxy methyl groups), with Novolaks. This appears to infer two different mechanisms, but as will be shown later, this is not the case.

In further work however, this group synthesised resins which contained no linkages other than methylene bridges. In this case, the oligomers were produced using twenty-four times as much para toluene-sulphonic acid catalyst, and this seemed to produce a more uniform resin structure, ie one with mostly methylene bridge linkages.

The group then turned to considering the stereochemistry of their resins, ie the degree of linearity obtained. Using vapour phase chromatography, the level of 2 phenoxybenzyl was measured at only 2.6% that of the 4 derivative. They did not extend measurements further to look at the relative proportions of ortho and para linkages in the resin, for instance by infra-red spectroscopy (IR). They did, however, continue to build up their stock of model compounds by synthesising the mono hydroxymethyl derivatives of molecules containing both two and three phenyl ether units. Thus at this point, Ninagawa and co-workers claimed to have synthesised linear, structurally uniform oligomers. They were now in a good position to undertake more detailed mechanistic work, using their
stock of known intermediates, but do not appear to have pursued this.

Occasional interest in the resins had been shown by Soviet workers and in 1973 an IR study was undertaken by Kartseva in which most of the important oligomer peaks formed were identified (table 1.4).

<table>
<thead>
<tr>
<th>Band (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400-3300</td>
<td>- OH</td>
</tr>
<tr>
<td>3080-3020</td>
<td>Aromatic C-H</td>
</tr>
<tr>
<td>2920,2850</td>
<td>CH₂ methylene bridge (stretch)</td>
</tr>
<tr>
<td>1600,1500±10</td>
<td>Aromatic C-C stretch</td>
</tr>
<tr>
<td>1460-1420</td>
<td>CH₂ methylene bridge (deformation)</td>
</tr>
<tr>
<td>1245,1200</td>
<td>-O- ether linkage (asymmetric stretch)</td>
</tr>
<tr>
<td>875,800</td>
<td>-O- ether linkage (symmetric stretch)</td>
</tr>
<tr>
<td>830</td>
<td>Indicates para substituted ring</td>
</tr>
<tr>
<td>750-600</td>
<td>Aromatic C-H</td>
</tr>
</tbody>
</table>

Table 1.4 - Assignments for major IR bands in phenyl ether-formaldehyde oligomers

Again, little ortho substitution was detected. By measuring elemental composition they concluded that the oligomer was linked by methylene bridges and contained both hydroxymethyl and sulphonate functionality [The latter presumably arising because of the sulphuric acid catalyst]. It should be noted, however, that other workers concluded that the peaks in the 700-900 cm⁻¹ range were sufficiently broad to indicate considerable branching, that is tri-substitution.
the diluent and the ratio of the original components on yield and composition of phenyl ether-formaldehyde oligomers. Broadly, the conclusions were as follows:

a) Raising temperatures raises both yield and molecular weight
b) Increasing reaction time increases yield but reduces the hydroxymethyl and reactive diluent formed functionality of the resin
c) Increasing diluent concentration reduces molecular weight and yield but increases functionality arising from the diluent
d) Acid catalyst type and strength does not affect composition
e) Increasing the ratio of formaldehyde to phenyl ether at first increases molecular weight, then reduces it, and steadily increases hydroxymethyl functionality.

These trends are shown graphically in figure 1.7

Figure 1.7 - Effect of reaction conditions on oligomer properties
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Figure 1.7 - Effect of reaction conditions on oligomer properties
Once again, basic structure was resolved by IR and elemental analysis; a capping mechanism was proposed for the reduction in $M_n$ with increasing diluent concentration (figure 1.8).

Figure 1.8 - Capping/extension mechanism in the presence/absence of diluent.
1.5.2 Kinetics of the reaction

Again the first workers in this field were Ninagawa and his team\(^{50}\). They determined the overall rate equation, rate constants, activation energies and entropies for oligomerisations carried out in acetic acid.

Concentrations of phenyl ether were varied and that of formaldehyde (as formalin) held constant and only the first 15% of reaction was studied. Aliquots were periodically withdrawn and chemically analysed for unreacted formaldehyde.

They concluded that the reaction was second order overall, with a rate expression:

\[
\text{Rate} = -\frac{d[F]}{dt} = k_2[DPO][F]
\]

where \(k_2\) = second order rate constant, \([F]\) the concentration of formaldehyde, and \([DPO]\) the concentration of phenyl ether.

Other workers measured these overall rates of reaction \(^{6,7}\) but failed to measure the individual rates of reaction necessary to construct a reaction mechanism.

A comparison of the rate constants obtained by these workers is not strictly correct because they have used different conditions. However, the results and conditions are tabulated below (table 1.5).
<table>
<thead>
<tr>
<th>Ratio DPO:CH₂O</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Temperature °C</th>
<th>Rate Constant 1.mol.S⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>Acetic</td>
<td>Perchloric</td>
<td>50</td>
<td>0.000545</td>
<td>46</td>
</tr>
<tr>
<td>1:1</td>
<td>Acetic</td>
<td>Perchloric</td>
<td>30</td>
<td>0.000187</td>
<td>47</td>
</tr>
<tr>
<td>1:1.6</td>
<td>Acetic</td>
<td>Sulphuric</td>
<td>50</td>
<td>0.00013</td>
<td>48</td>
</tr>
<tr>
<td>1:1.6</td>
<td>Acetic</td>
<td>Sulphuric</td>
<td>60</td>
<td>0.00045</td>
<td>48</td>
</tr>
<tr>
<td>1:1.6</td>
<td>Acetic</td>
<td>Sulphuric</td>
<td>70</td>
<td>0.00082</td>
<td>48</td>
</tr>
<tr>
<td>1:1.6</td>
<td>Acetic</td>
<td>Sulphuric</td>
<td>80</td>
<td>0.000127</td>
<td>48</td>
</tr>
</tbody>
</table>

Table 1.5 Rate Constants For DPO/CH₂O Reactions Under Varying Conditions

The results are broadly in agreement - values varying between $1 \times 10^{-4} \text{ l.mol.S}^{-1}$ and $1 \times 10^{-3} \text{ l.mol.S}^{-1}$.

An excellent review paper on the kinetics and mechanism of aromatic-formaldehyde reactions is presented by Bayarstanova and Erdenova.

1.6 Objectives of The Present Study

To summarise, the work on phenyl ether-formaldehyde polymers went
through the initial developmental stage to produce thermally and chemically resistant cross-linked polymers. This was followed by investigations into the effect of varying reaction conditions on broad polymer properties and structure. Then some further work measured overall rates of reaction, but no mechanistic conclusions were drawn.

At this point then, people had a broad feeling for the conditions which controlled the oligomer's properties. In addition, some knowledge of the type of connecting linkage and of the type of molecules making up the oligomer was gained. A rather vague knowledge of the spatial arrangement of the molecules was also available. Little real progress had been made with the mechanistic side of matters, and as with phenol-formaldehyde resins, workers turned to kinetics to aid them, but with no success.

In this study, we were interested in trying to understand the fundamental oligomerisation processes, unobscured by all the additional complications from formaldehyde, and as a result the studies were conducted using model compounds. The models chosen had, therefore, to mirror the products of the initial Friedel-Crafts alkylation. Such a model would be of the form:

\[ \begin{align*} 
\text{ phenyl } & \text{-} \text{ o } \text{-} \text{ phenyl} \\
& \text{-} \text{ CH}_2 \text{X} 
\end{align*} \]  

(1.10)

Because the majority of linkages in the polymers formed are methylene bridges (not withstanding how they are formed) only this type of molecule was selected.
The nature of x was chosen according to the suspected intermediates in reactions of commercial importance. These dictate that x is hydroxyl, acetate or methyl ether, so that there are nine models in all, because all isomers were synthesised. They are illustrated below (figure 1.9).

One further model was chosen, 4,4' oxybisbenzyl alcohol:(1.11)

Reactions were carried out using these monomers, and in order to establish reaction profiles, aliquots were withdrawn at specific time intervals. The resins so obtained were analysed for molecular weight using gel permeation chromatography [GPC], and by carbon-13 nuclear magnetic resonance to determine the presence and substitution pattern of particular functional groups, and the rôle they play in the polymerisation.

Using GPC the resins were also studied to determine the kinetics of the depletion in monomer.

When brought together this knowledge allowed oligomer synthesis from the models in a more controlled fashion to produce gel free resins of a specified molecular weight, structure and hydroxy methyl or acetoxy methyl group content.
CHAPTER 2

SYNTHESIS OF THE MODEL COMPOUND MONOMERS

2.1 All the alcohols have been previously synthesized, the earliest syntheses available being those by Ninagawa and Imoto\(^2\), in 1966. They used the Ullman ether reaction to give the phenoxytoluene, followed by oxidation to the phenoxybenzoic acid, and finally reduction to the alcohol using lithium aluminium hydride [LiAlH\(_4\)] Figure 2.1.

\[
\text{HO-} + \text{NaOH} \rightarrow \text{ONa} + \text{H}_2\text{O}
\]

\[
\text{Cu(I)}
\]

\[
\text{ONa} + \text{Br} - \text{CH}_3 \rightarrow \text{O} - \text{CH}_3 + \text{NaBr}
\]

\[
\text{KMnO}_4
\]

\[
\text{O} - \text{CH}_3 \rightarrow \text{O} - \text{CO}_2\text{H}
\]

\[
\text{LiAlH}_4
\]

\[
\text{O} - \text{CO}_2\text{H} \rightarrow \text{O} - \text{CH}_2\text{OH}
\]

Fig 2.1: Synthesis of Phenoxybenzyl Alcohols

Reduction of the dicarboxy acid was more difficult owing to the complete insolubility of the substrate in ether. The reduction was therefore accomplished by conversion to the more soluble methyl ester first, followed by reduction.
In this study significant quantities of the monomers were used, and so starting materials as close as possible to the final product were selected, via the 3-phenoxybenzyl alcohol was commercially available as were the 2, the 4 and 4,4' acids. However, 4-phenoxybenzyl alcohol was initially synthesised as above on the grounds of the high cost of the parent acid. Because the procedure was very time consuming, we subsequently switched to the acid as starting material.

2.2 Phenoxybenzyl Acetates

Again, all three isomers have been synthesised previously. The earliest recorded synthesis of the 2 isomer is by the Sanko Chemical company in 1983. Using Co[OAc]₂ and acetic acid, they oxidised and esterified 2-phenoxy toluene to the ester.

3 phenoxybenzyl acetate was first synthesised in 1973 by Matsuo et al who synthesised the phenoxybenzyl alcohol and oxidised it.

The first synthesis of 4 phenoxybenzyl acetate was carried out by Torii et al of Kuraray Co Ltd in 1977, using electrolytic oxidation of 4 phenoxytoluene in the presence of various salts. In this study all the acetates were synthesised in the same way, namely by esterification of the relevant alcohol isomer with acetic anhydride in the presence of pyridine.

\[
\text{(CH}_3\text{CO})_2\text{O}^+ + \text{CH}_2\text{OH} + \text{Ar}^- \rightarrow \text{CH}_2\text{OCCH}_3 + \text{CH}_3\text{CO}^- + \text{H}_3\text{O}^+
\]
2.3 Phenoxybenzyl Methyl Ethers

Of the three methyl ether isomers, only one is reported in the literature; the 4 phenoxybenzyl methyl ether, synthesised by a catalytic hydrogenolysis of phenylether acetals, in a method reported by Fischer et al of Hoechst\textsuperscript{52}.

\[
\text{Catalyst} \quad \text{Co Carbonyl} \quad \text{H}_2 \quad \xrightarrow{\text{Catalyst}} \quad \text{Catalyst} \quad \text{H}_2 \quad \xrightarrow{\text{Catalyst}} \quad \text{Catalyst} \quad \text{H}_2 \quad \xrightarrow{\text{Catalyst}} \quad \text{Catalyst} \quad \text{H}_2
\]

In this thesis the ethers were synthesised from the corresponding alcohol and dimethyl sulphate by the technique known as Phase Transfer Catalysis [PTC] using an experimental method developed by A Merz\textsuperscript{56}.

This technique is also referred to as "extractive alkylation" and much of the developmental work was the responsibility of Brändstrom, Makosza and Starks\textsuperscript{57}. The technique utilises very mild conditions and allows reactions between heterogenous systems (either solid-liquid or liquid-liquid). In the liquid-liquid case this means that two substances which do not have a common solvent can be made to react very efficiently. This is achieved by addition of a catalytic amount of an agent which transfers one reactant across the liquid interface into the second solvent, where reaction can occur. Such phase transfer catalysts are often bulky onium ions, eg $R_4N^+$ or $P_4N^+$, or they may be crown ethers. The process is more easily understood if practically exemplified, and this will be done using the synthesis of phenoxybenzyl methyl ether.
The principle behind the ether synthesis is illustrated in the diagram below (fig 2.3.1) and is followed by the experimental description.

\[
\begin{align*}
\text{Aqueous layer} & : \quad (\text{Na}_2^2\text{SO}_4^{2-} + 2\text{R}_4\text{N}^+\text{OH}^- + 2\text{ArCH}_2\text{OH} \\
\text{Organic layer} & : \quad (\text{R}_4\text{N}^3\text{SO}_4^2-) + \text{ArCH}_2\text{OCH}_3 \\
& \quad + 2\text{Cl}^- \\
\end{align*}
\]

\[
2\text{ArCH}_2\text{O}^- \text{R}_4\text{N}^+ + 2\text{H}_2\text{O} \quad \rightarrow \quad 2\text{ArCH}_2\text{O}^- \text{R}_4\text{N}^3 + (\text{CH}_3)_2\text{SO}_4
\]

\[
\text{ArCH}_2\text{OH} = \begin{array}{c}
\text{CH}_3 \\
\text{CH}_2 \text{O} \\
\end{array}
\]

Figure 2.3.1 - Phase transfer mechanisms in the ether synthesis

Synthesis methyl ethers

0.1 moles (16gms) of the required isomer of phenoxy benzyl alcohol and 1gm of benzyl-tri-n-butyl ammonium chloride were dissolved in a two phase mixture containing 40mls of methylene chloride and 20.8mls 50% aqueous sodium hydroxide and the whole very vigorously stirred for 25 minutes, after which 27mls (0.18 moles) of dimethyl sulphate [care, suspected carcinogen] were added, dropwise, keeping the temperature below 45°C (to avoid destruction of the catalyst). Stirring was maintained for a further 150 minutes, before adding 3.0mls of 0.91 ammonia solution and stirring for a further 20 minutes to destroy any residual dimethyl sulphate. The mixture was then poured into water and the organic layer separated from the aqueous, washed and separated again and dried with 5A molecular sieve. The solvent was then removed on the rotary evaporator at 30°C to yield the ether, purified by distillation. Yield : 15.9gms.
3 POLYCONDENSATIONS; REACTION CONDITIONS AND ANALYSIS OF PRODUCTS

3.1 Reaction Conditions

3.1.1 Catalysts and solvents

Any solvent used must be inert under the reaction conditions utilised. This rules out any solvent which may participate in a Friedel-Crafts reaction, thereby upsetting the analysis. Such solvents include toluene and benzene. Also precluded are solvents which can react with the functional groups of the monomers, unless this is specifically desired.

Suitable solvents are the chlorinated alkanes. Reaction temperature was selected by convention - at ICI these reactions are typically carried out at about 80°C and so this was chosen. In addition, for the purposes of azeotroping, the reaction must be carried out under reflux. Such requirements limit the choice of solvent, and as such 1,2 dichloroethane was chosen: (fig 3.1).

![1,2 Dichloroethane](image)

\[
\text{Bpt: 84°C} \\
\text{BDH 'Analar' grade, dried over 4A molecular sieve.}
\]

The choice of catalyst is dictated by the need for a homogeneous solution, and so toluene-4 sulphonic acid monohydrate [PTSA] was used, as opposed to concentrated sulphuric acid, in order to avoid sulphonation and ensure homogeneity. Again, the reactant was supplied by BDH as the hydrated "Analar" grade.

Concentrations of monomer varied, but were always selected so as to
try not to affect the bulk properties of the solution, and so change reaction conditions as oligomerisation proceeded. Typically, concentrations would be between 0.01 and 0.2 molar. A typical reaction volume was 100mls, and was used for all kinetics experiments, but 1000mls was used for mechanistic investigation by NMR and 250mls in the attempts to control gelling.

3.1.2 Azeotropic distillation to remove water

A particular feature of the experimental technique used in all these investigations is azeotroping.

Because the reactions were all studied by withdrawing specific aliquots it is essential in all analyses that homogenous samples be withdrawn throughout the reaction to ensure reproducibility from sample to sample. Now, the condensation product is water, and this quickly develops a second phase; some of the oligomers will be more soluble in the aqueous layer than the organic layer, and as a result it is going to be more difficult to be sure that the sampling technique is reproducible.

When one begins to study kinetics, the situation becomes more serious. In kinetic studies it is important to maintain all things constant throughout the course of the reaction, except the variable under consideration. Now the acid catalyst will be far more soluble in the aqueous layer, and as a result will be progressively extracted into it from the organic layer. But the monomer and oligomer molecules will mostly reside in the organic layer, and as a result the effective acid catalyst concentration will fall as reaction proceeds. This makes any determination of kinetics prone to inaccuracy.
The answer to this problem was to try and remove the water as quickly as possible in order to minimise any inhomogeneity. This was achieved by running the reaction under vigorous reflux, and inserting an adaptor between flask and condenser which contained fresh molecular sieve supported on a porous plug of glass wool. As the azeotrope passes through the sieve, the water is trapped out, leaving pure solvent to return to the flask.

All oligomerisations were run under these conditions.

Temperatures were measured by means of a thermocouple connected to a digital thermometer, and are accurate to +0.1°C. The reaction flask was completely submersed in oil in an oil bath which was well lagged to ensure temperature consistency. Stirring was carried out magnetically, and all solutions were stirred at a rate of 300 revolutions per minute. The complete experimental set up is shown in Fig 3.2.
Fig 3.2 Apparatus for oligomerisation reactions.

It is essential that each set of conditions is reproduced as closely as possible. In particular, within each set of reactions in which comparisons are being made, it is important that the same glassware is used and that the flasks are thoroughly cleaned each time. Repeated reactions using different flasks can give markedly different results – an observation also made in phenolic resin chemistry\textsuperscript{14}.
3.2 Analysis for Functional Groups and Gel Content

3.2.1 Hydroxyl groups

By measuring concentrations of hydroxyl groups in oligomer samples, it is possible to get a measure of an oligomer's hydroxyl functionality.

Two methods were used, both involving acetylation of the OH followed by titration of residual acid. One was found to be unsuitable for measurements of OH on these resins because the perchloric acid catalyst caused cleavage of methylene ether groups present on the resin, producing a higher OH value than was appropriate. Both methods are from the American Society for testing and materials [ASTMS].

3.2.2 Acetate groups

Measurement of the level of acetate functionality in appropriately synthesised oligomers was carried out by infra red (IR) measurement of the absorption of the ester band at 1735cm\(^{-1}\) relative to that of chloroform at 2402cm\(^{-1}\) on a Perkin-Elmer 983G continuous wave machine which was calibrated using appropriate esters.

3.2.3 Gel content

The amount of gel produced during these oligomer syntheses was determined by filtering off the insoluble matter and taking its dry weight.

Because of the comparative nature of the experiments, very clean apparatus was used each time and experiments producing significant results were repeated three times to ensure reproduction of
results. Single results quoted are averages of the three values obtained. The accuracy of the method for determining gel was checked by running a blank reaction, in which every parameter was identical with other experiments except that the acid catalyst was omitted. Zero gel content was recorded.

3.3 Gel Permeation Chromatography

3.3.1 General theory

Gel permeation, or size separation, is a form of liquid chromatography in which the solute molecules are separated as a result of their permeation into a solvent-filled matrix of a porous gel. The pores vary in size, and whilst most molecules of the sample mixture can easily fit into at least some of the pores, and thus will diffuse into them, other molecules are too big to do so. The length of time a molecule spends in the column depends on its size, and so a separation, based on molecular volume, has been achieved.

In any system of columns there are experimentally determined size limits between which the separation occurs. Those molecules that fall outside the range of selective permeability of the column will all elute together, either at the same rate as the carrier solvent in the case of those molecules which are too big to be absorbed into any of the pores, or at the end of the chromatogram in the case of molecules that are of a minimum size sufficient to allow them to be absorbed onto all of the pores and thus take the longest time to diffuse through the matrix.
Close examination of the matrix shows that the gel particles — which are anything from lightly to heavily cross-linked polymers — are suspended in solvent. The channels between the gel particles are much larger than the pores inside the gels. Therefore, solvent flow occurs only in the interstitial space around the gel. Solute molecules permeate the gel pores only as fast as their size permits, and move, practically without restriction, in the solvent contained in the gel. Only very close to the network strands, where the gel segment density is high, does the diffusion rate drop sharply.

Under normal conditions molecules comparable in size to solvent molecules will distribute through the entire pore volume. Bigger molecules are excluded from the denser parts of the network, but they can diffuse freely through the more open passages. The larger a solute molecule the fewer apertures suitable for its size it will find. Finally, there may be molecules which are so big that they are excluded from the gel completely. As such they pass freely between the gel particles and elute quickly from the column.

Because the process is based on molecular volume, rather than, say adsorption, the process is reproducible between different polymers, irrespective of their polarised nature. Because of this, two polymers, of say molecular weight 5000 but completely different chemical constitution will elute at the same time. If the GPC is calibrated by a set of polymer samples of known molecular weight and narrow molecular weight distribution (see below) then GPC can be used for determining polymer molecular weights,

There is a proviso to this. Because of the reliance on molecular volume two molecules of the same weight can elute at different
times. For instance, a cyclic molecule will be eluted later than a molecule which has the same weight but is linear. Similarly, a "spikey" molecule, with many large side chains occupies a greater volume than a similar weight linear molecule, and will be eluted more quickly.

It would be appropriate here to briefly discuss the two different measures of molecular weight that are commonly used in polymer chemistry. Because a polymer consists of a whole range of discrete molecules, ranging from one repeat unit to many repeat units molecular weights when quoted are averages. \( \text{Mn} \), the number average molecular weight and \( \text{Mw} \) the weight average molecular weight are two averages compiled in different ways, and give different information on the polymer composition.

\( \text{Mn} \) lies for most polymers near the peak of the weight distribution curve, ie it is the most probable molecular weight. Statistically, it can be defined as:

\[
\text{Mn} = \frac{\sum_{i=1}^{\infty} m_i N_i}{\sum_{i=1}^{\infty} N_i}
\]

Where \( \text{Mn} \) is the number average molecular mass

\( N_i \) is the number of molecules of the \( i^{th} \) kind in the sample

\( m_i \) is the mass of each \( i^{th} \) molecule

Multiplying by Avogadro's number gives the number average molecular weight:
In contrast, $M_w$ is defined as:

\[
\frac{\sum_{i=1}^{\infty} NiMi^2}{\sum_{i=1}^{\infty} NiMi}
\]

Thus each molecule contributes to $M_w$ in proportion to the square of its mass. This means that heavier molecules contribute more to $M_w$ than light molecules (The reverse is true for $M_n$). Thus $M_w$ is always bigger than $M_n$, and the ratio $M_w/M_n$, known as the dispersity, is a measure of the spread of molecular weights.
Fig. 3.3
Mol. wt./retention time calibration

Mol. wt. vs. Retention time mins.
3.3.2 Calibrations

In these studies GPC was used for two purposes: the first was in conventional measurement of molecular weight of the oligomers, the second to measure residual monomer levels in the reaction mixture at various time intervals.

Polymer molecular weights were determined by comparison with a calibration curve constructed using polystyrene samples (supplied by Polymer Labs) of a known Mn, and very narrow dispersivity. At the low molecule weight end phenyl ether and phenoxybenzyl alcohols were used. (See fig 3.3 opposite).

Residual monomer concentrations were determined via a calibration curve plotting GPC peak area (nominal units) against standard concentration solutions (Figure 3-4). The dedicated computer holds this data in its memory and provides a direct value of the monomer concentration of any partially polymerised sample analysed by the GPC.

3.4 Nuclear Magnetic Resonance Spectroscopy

3.4.1 General theory

The phenomenon of nuclear magnetic resonance (NMR) has been known since 1946. Briefly, the technique is used to detect the field strength at which particular nuclear transitions between magnetic levels occur. The magnetic levels are split by the application of a very powerful magnetic field. A second, oscillating radio frequency field is applied at a progressively varying strength, and a transition between the split levels occurs at resonance and this is detected. The resonances are characteristic for a particular atom in a particular electronic environment, and so allow qualitative
Figure 3.4
Calibration curve, [mon.] determination

log area under GPC curve

monomer concn. moles
analysis for molecules of those atoms with a nuclear spin of one half or greater. This includes nuclei such as $^1$H, $^{13}$C, $^{19}$F, but precludes those such as $^{12}$C and $^{16}$O.

The first nucleus for which suitable detection equipment was developed was $^1$H. This was by far and away the easiest - not only was it the most common isotope of hydrogen, but it has a large nuclear magnetic moment. In consequence, relatively small permanent magnetic fields only were required, and by today's standard a low radio frequency. A good spectrum was obtained by the "continuous wave" technique if exciting each type of hydrogen nucleus separately.

The technique of $^1$H NMR is now well known and has been in common usage in organic chemistry for many years. It has become established as the premier "bench top" analytical technique, largely replacing the old methods of wet chemistry.

The other common nucleus in organic chemistry is carbon. However, as previously noted carbon - 12 does not have a nuclear magnetic moment, and so cannot be detected by NMR. Fortunately though, carbon 13, an isotope with a natural concentration of 1.1% that of carbon 12 does have one, and so in theory is amenable to detection by magnetic resonance.

Because of the lower concentration of carbon -13 relative to the proton, detection equipment will have to be much more powerful. However, the situation is more awkward than this - the sensitivity of $^{13}$C is only $\frac{1}{4}$ that of hydrogen, so that effectively what is a
60MHz machine for 'H NMR is only a 15MHz machine for 13C NMR. The overall sensitivity of 13C is only $1.6 \times 10^{-9}$ that of the proton.

It would be impractical to build a spectrometer 16,000 times more powerful than the average proton machine, and so other solutions were sought. A more concentrated sample helps, but the real breakthrough was the development of Fourier Transform (FT), or pulsed NMR. In this case a very large number of spectra are accumulated, and superimposed on each other. This averaging process not only enhances the size of the peaks associated with carbon atoms but also suppresses random noise, and so a greatly improved signal-to-noise ratio results.

Again though, it would be impractical to collect each spectrum by scanning from zero parts per million (ppm) to two hundred ppm (a typical spread for carbon -13 as opposed to just 10ppm for the proton. In frequency terms on a 100MHz machine this is 1000Hz variation for the proton and 5000Hz for the carbon -13). If approximately 2000 frequency sweeps were required, each taking say, ten minutes, it would need approximately fourteen days to collect just one spectrum.

So instead of sweeping, a short pulse of radio frequency radiation covering the entire required frequency range is used. As soon as the nuclei have relaxed back to equilibrium, another pulse is applied, and the spectrum is now acquired in a few minutes. However, instead of now having all the resonances at discrete intervals, all the responses are mixed together giving an interferogram. They may be resolved into separate peaks by using the mathematical technique of Fourier transforms, a theory which
says that any complex waveform can be resolved into a number of simple waveforms - in this case one waveform for each resonance.

Carbon -13 NMR is an extremely powerful analytical tool, and some of the spectral features will now be described.

3.4.2 General methods of interpretation employed in this study

Unlike proton NMR carbon-13 shifts can go from a large negative shift up to about 230ppm. Such a large range means that peak overlap is very unlikely and this is part of the power of the technique. Identification of molecules which are only slightly different - impossible in 'H NMR because of peak overlap - now becomes much easier. For instance, a methylene group in the ortho position of a benzene ring has a different resonance position to a para methylene group.

Because $^{13}$C is at such low concentration it is unlikely (a probability of 1.1% x 1.1%) that two $^{13}$C nuclei will be adjacent. This means that $^{13}$C - $^{12}$C splitting rarely occurs.

However, $^{12}$C to proton coupling is large, and this does produce a very complex spectrum in which each multiplet is spread over a large range, making interpretation difficult. Such coupling can be prevented by applying a broad spectrum of radiation which time averages the field splitting effect of the protons, ie the nuclear magnets are flipped "up" and "down" so quickly that they average to zero on the NMR timescale. This leaves single peaks, each peak corresponding to one type of carbon. The technique also enhances
peak size by a phenomenon known as the Nuclear Overhauser Effect (NOE).

Such an application does however lose information. A halfway house is possible — off resonance decoupling, in which the irradiating frequency is just off proton resonance. This gives the multiplets, but in a collapsed form ie each multiplet is spread over a small frequency range, preventing the confusing overlapping seen in the coupled mode.

Carbon $^{13}$ spectra are not necessarily quantitative especially when operated in a decoupled form, and a separate check of each spectrum needs to be made before making qualitative measurements.

In the analyses used in this work, carbon spectra were completely decoupled, and were found to be quantitative. Because of time restrictions on machine use, integrals of the peak areas could not be run routinely and instead relative peak heights were used to give an approximate guide to the relative amounts of a particular carbon from sample to sample and so show changes in the concentration of a particular carbon atom with time. It is not an ideal method for comparing relative amounts of different carbons, although it may give some idea of this — but any firm conclusions should be supported with other evidence.
CHAPTER 4: CONVERSION OF MONOMERS TO OLIGOMERS: INVESTIGATION BY GEL PERMEATION CHROMATOGRAPHY

4.1 Procedure

The molecular weight of an oligomer is often an important factor in determining the way in which that oligomer may be manipulated, and as such it is important to have some knowledge of how to vary molecular weight in a controlled fashion.

For instance, in some applications high molecular weight oligomers with high solubility are of interest, spray paints being an example. Such a combination might be achieved by altering the reaction variables (time, temperature, catalyst, solvent and ratio of starting materials) to achieve an Mn of several thousand, but with a low dispersity. Since such an oligomer will have very few molecules of an extremely high molecular weight this will improve its solubility.

In this study, the variation of molecular weight with varying concentration of catalyst and reaction time was explored using gel permeation chromatography [GPC] to ascertain the change in both Mn and Mw with increasing conversion. Samples were withdrawn at regular intervals, worked up and analysis undertaken. Values quoted are the mean of three measurements from three separate experiments. All reactions were carried out under reflux with the azeotroping technique [See section 3.1.2] using as solvent 1,2 dichloroethane, or a mixture of this with acetic acid. The catalyst was toluene-4-sulphonic acid monohydrate [PTSA] and in all experiments, the solution of catalyst and solvent was heated under reflux to
remove water by the azeotroping technique described in 3.1.2 before
the monomers were added. The concentration of monomers employed
ranged from 0.01 mol/l to 0.4 and of catalyst from 0.053 mol/l to
0.315 mol/l. The reaction temperature, that of the refluxing
solvent was 83.3±0.4°C.

4.2 Polycondensation of 3 Phenoxybenzyl Alcohol

In these reactions the initial concentration of monomer ranged from
0.01 to 0.45 mol/l, while the catalyst concentration was held
constant at 0.105 mol/l. Thus the catalyst to monomer ratio ranged
from 0.23 to 10.5 to one. The data for these experiments is
presented in table 4.1, below and the data are also represented
graphically in figure 4.1. Typical gel phase chromatograms for
PL3228 are shown in Fig 4.2 opposite. It is seen from table 4.1
that at the two lower catalyst/monomer ratios the reaction is very
slow, and takes at least 2000 seconds to reach dimer (on average).
It requires higher catalyst/monomer ratios to give an Mn of greater
than 1000 in reasonable time.

<table>
<thead>
<tr>
<th>SAMPLE NO.</th>
<th>t secs</th>
<th>Mn</th>
<th>SAMPLE NO.</th>
<th>t secs</th>
<th>Mn</th>
<th>SAMPLE NO.</th>
<th>t secs</th>
<th>Mn</th>
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<td>4230</td>
<td>750</td>
<td>8</td>
<td>4240</td>
<td>1312</td>
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</table>

Table 4.1 - Molecular weight data and catalyst to monomer [c:m] ratios for 3-phenoxybenzyl alcohol oligomers.

RHD/P/PL1-370P
Fig. 4.1: Mol. wt./time plots for 3-PBA
Varying C/M ratios

mol. wt.

\[ t, \text{secs} \times 10^{-3} \]

- PL3237 C/M = 0.23
- PL3218 C/M = 0.42
- PL3228 C/M = 3.5
- PL3230 C/M = 10.5
Figure 4.2 GPC's for PL3228 at t=30, 1230, 2430 and 3630 seconds
4.3 Polycondensation of 4-Phenoxybenzyl Alcohol

The reactions with this isomer were run using a constant 0.15 mol/l concentration of 4 phenoxybenzyl alcohol and catalyst concentrations ranging from 1x10^{-3} mol/l to 0.1 mol/l. This gives a range of catalyst to monomer ratios of 6.67x10^{-3} to 0.67, to one. Relevant GPC plots for these experiments are shown opposite in figure 4.3, and the molecular weight data are represented graphically. [Fig 4.4]. Table 4.2 contains the exact values.

<table>
<thead>
<tr>
<th>t secs</th>
<th>PL1230 c/m = 0.0067</th>
<th>PL1231 c/m = 0.067</th>
<th>PL1229 c/m = 0.67</th>
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<td>372</td>
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<td>10800</td>
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<td>699</td>
<td>2.35</td>
</tr>
</tbody>
</table>

Table 4.2 - Molecular weight data for para phenoxybenzyl alcohol with varying catalyst to monomer [c:m] ratio
Figure 4.3 GPC's for PL1230 at t=40, 3600, 10800 secs and PL1229 at t=30, 900 and 2700.
Fig. 4.4: Mol. wt./time plots for 4-PBA
Varying C/M ratio

Mol. Wt.

0 1 2 3 4 5 6 7

0 200 400 600 800 1000 1200 1400 1600

t secs x 10^{-3}

- - PL1230 C/M=0.0067
- - PL1231 C/M=0.067
- - PL1229 C/M=0.067
From these two sets of data for the two isomers it is clear that the para isomer reacts much more rapidly than the meta isomer; with the para isomer, chain extension is complete after about 2000 seconds, but with the meta isomer the reaction is not complete after 2000 seconds with a C/M ratio of 10.5/1. The para isomer also shows the same dependence of conversion efficiency on catalyst, ie increasing catalyst concentration raises the rate of increase of Mn.

4.4 Polycondensation of 4-Phenoxybenzyl Alcohol in the Presence of Acetic Acid

Because of the similarity in conditions with a particular ICI process, a number of studies were carried out on oligomers synthesised in a solvent medium of 9 parts 1,2 dichloroethane and one part glacial acetic acid, by volume. NMR determinations [Chapter 5] show that this procedure converts the hydroxymethyl groups to acetate. In all experiments, the initial monomer concentration was 0.15 mol/l, and the catalyst concentration ranged between 0.053 mol/l to 0.315 mol/l. These give catalyst to monomer ratios ranging from 0.33 to 1.93.

The full data are presented in table 4.3. A graphical representation is given over, fig 4.5. Again, a dependance of rate on catalyst concentration is seen, and the overall rate is lower than for the para alcohol, but greater than for the meta alcohol.
Fig. 4.5: Mol. wt./time plots for 4-PBA plus AcOH: Varying C/M ratio

- C/M = 0.33
- C/M = 0.64
- C/M = 0.96
- C/M = 1.29
- C/M = 1.61
- C/M = 1.93
Figure 4. 6 GPC's for PL1221 at t=30, 2400 and 3400 secs.
Table 4.3 - Variations of molecular weight with catalyst to monomer ratio for 4 phenoxybenzyl alcohol oligomers in acetic acid/dichloroethane solvent
4.5 Conclusion and Reaction Mechanism

The plots of Mn versus time for the polycondensation of these monomers show clearly that these reactions are acid catalysed, and that rate of conversion is dependent upon the catalyst to monomer concentration ratio: the higher the ratio, the greater the rate of monomer consumption and the rate at which the degree of polymerisation increases.

Para phenoxybenzyl alcohol reacts far more rapidly than the meta isomer, for instance PL3228 with a [cat.]/[mon.] ratio of 3.5 takes 4000 seconds to reach an Mn of 700, whilst PL1229 with a [cat.]/[mon.] ratio of 0.67 reaches the same Mn in just 200 seconds. This can be explained by considering the relative stabilities of the phenoxybenzyl cations, illustrated by using the Wheland intermediates below, fig 4.7,

3 Isomer

\[ \begin{align*}
\text{3 Isomer} & \\
\text{4 Isomer} & \\
\end{align*} \]

Fig 4.7 Wheland intermediates for 3 and 4 isomers of phenoxybenzyl-cations
It is clear the para phenoxybenzyl cation will be much more stable than the meta isomer, because it alone can benefit from the delocalisation of the ether oxygen's lone pair. If we now further postulate that the formation of the cation is the rate determining step, then the relative rates are explained.

There is an assumption in this discussion that the catalyst delivers its proton to the alcohol. This is not the only possible choice - the ether oxygen is available too, and if this were protonated it would have important implications for the argument outlined above because a protonated oxygen could not stabilise the formation of a cation, and the ring would be deactivated.

Adequate reassurance that this is not the case can be found in tables of basicity data [see, for example refs 59, 60]. Para-toluene sulphonic acid is a moderately strong acid, and in the absence of water, will protonate the most basic species present in this system, ie, the alcohol, which has an approximate pKa of -2. Therefore there is a high equilibrium concentration of ArCH₂OH₂⁺ compared to the concentration of protonated bis aryl ether which will be vanishingly small in comparison, because such species are very weak bases with approximate pKa's of -7.

This data may be used further to provide information about the reaction mechanism. Using the pKa of -2 for the alcohols, we can say that the concentration of protonated species will be one hundred times less than that of the unprotonated alcohols.
The most nucleophilic species present is the hydroxyl group, so whilst these remain in the system they will react with the benzyl cations on monomers or chain ends to give phenoxybenzyl ethers. When most of the alcohols have reacted, the benzyl cations, from heterolysis of protonated phenoxybenzyl ethers (pKa $-2 \rightarrow -4$) will be free to react with the phenoxy rings, which due to their low basicity are scarcely protonated as discussed above. This is of particular significance because were protonation to occur to a much larger extent then the phenoxy ring would have a much lower reactivity towards electrophiles, due to the loss of the stabilisation provided by the aryl ether oxygen.

Turning to the reaction in acetic acid/1,2 dichloroethane the alcohol is shown both by proton and $^{13}$C NMR to undergo rapid esterification, and this is followed by polymerisation. The rate is slower than for 4-phenoxybenzyl alcohol in 1,2 dichloroethane only, but still much faster than for the 3 alcohol.

Basicity data indicate that phenoxybenzyl acetates (pKa $-6$ to $-8$) are less basic than the bis benzyl ethers (pKa for bis alkyl ethers is $-2$ to $-4$). Thus the acetates will provide a lower equilibrium concentration of protonated species than do the alcohols or ethers. Since heterolysis of the protonated species provides the benzyl cations this leads to reduced reactivity of 4 phenoxy benzyl alcohol in the presence of excess acetic acid.

Two final points deserve brief mention: One is the initial rise, and then fall in Mn in all the reactions (except PL3230) that occurs early in the reactions before a steady increase in Mn starts. The other is the low molecular weight reached by fast
reactions such as PL1229, which is contrary to Carothers equation:

\[ DP = \frac{1}{1-p} \]

where DP = degree of polymerisation, and p = the mole fraction of monomer converted.

Possible explanations for both these phenomena will be advanced when a mechanism is postulated in chapter 5.
CHAPTER 5: CONVERSION OF MONOMERS TO OLIGOMERS; INVESTIGATION BY $^{13}$C NMR

5.1 Procedure

The aim of the studies in this chapter was to try and obtain a more certain understanding of the reaction sequence unfolding in the oligomerisation of some of the selected phenoxybenzyl isomers. Initially, the hydroxymethyl functional only system was studied, before moving on to consider the more complex situation in which a reactive diluent (acetic acid) is added. The reactions to be studied clearly need to fulfil certain requirements regarding extent of reaction and the time taken to reach that point. To this end, a number of small scale reactions were run to determine (by GPC and proton NMR) that these requirements had been met, before running the reaction on the larger scale necessary to provide sufficient material for $^{13}$C NMR measurements. As with all other reactions, the azeotroping technique was used.

In more specific terms, these conditions are that all the chosen reactive group (for instance, the hydroxymethyl) has had sufficient time to completely react, plus some additional time to allow for other reactions (rearrangements etc) to occur. Such a time varies between 6000 and 12000 seconds, depending upon the isomer and the catalyst concentration.

Samples were withdrawn from the reaction flask by syringe at regular time intervals. The samples were rigorously neutralised, extracted and dried before solvent exchanging with deuterochloroform. In this way, it was hoped to produce a range of
5.2 Detailed Interpretation of The Spectra

Spectroscopic interpretation was carried out in a number of ways — by the use of the spectra obtained from the monomers, by calculation from similar compounds and by using previous ICI knowledge and the commercially available catalogues of data.

5.2.1 Assignment of the Peaks Shown by the Nine Monomers

The peaks arising from the aliphatic carbons were assigned by the use of standard tables, or in some cases by referring to actual reference spectra. Peaks from the aromatic region were assigned solely using commercially available tables.

The spectra of the nine monomers can each be divided into sections:

- 0-90 ppm (aliphatic carbons)
- 90-160 ppm (aromatic carbons)
- 160 ppm → (carboxylic carbons)

The aliphatic and carboxylic carbons are the most important in this study, and for the monomers at least are easily assigned. The aromatics are assigned by the use of tables and previously described compounds contained in the Bruker\textsuperscript{1} catalogue.

The assignments are as follows:
2-phenoxybenzyl alcohol [5.1]

These were assigned using a reference in the Bruker catalogue, but the peak positions are those observed in our spectra

$^{13}$C NMR

<table>
<thead>
<tr>
<th>Aromatic Carbons</th>
<th>Aliphatic Carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 = 153.8$ ppm</td>
<td>$1' = 157.0$ ppm</td>
</tr>
<tr>
<td>$4 = 131.9$ ppm</td>
<td>$2' = 117.0$ ppm</td>
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<td>$5 = 128.3$ ppm</td>
<td>$3' = 129.5$ ppm</td>
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<tr>
<td>$5 = 122.8$ ppm</td>
<td>$4' = 123.5$ ppm</td>
</tr>
<tr>
<td>$6 = 128.6$ ppm</td>
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</tr>
<tr>
<td>$6 = 118.4$ ppm</td>
<td>$6' = 117.9$ ppm</td>
</tr>
</tbody>
</table>
3-phenoxybenzyl alcohol [5.2]

Assigned with the aid of the spectrum from 2-phenoxybenzyl alcohol

$^{13}$C NMR:

<table>
<thead>
<tr>
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<tbody>
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<td>2 $\delta=117.4$ ppm</td>
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<td>4 $\delta=117.8$ ppm</td>
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</tbody>
</table>

![Chemical structure diagram](attachment:image)
4-phenoxybenzyl alcohol [5.3]

This was again assigned with the aid of the spectrum for the 2 isomer.

Aromatic Carbons

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<th>ppm</th>
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Aliphatic Carbons

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<td>129.6</td>
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<tr>
<td>6'</td>
<td>118.7</td>
</tr>
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[5.3]
2-phenoxybenzyl acetate [5.4]

The aromatic peaks were assigned by using positions and shifts from the spectrum for 2-phenoxybenzyl alcohol, and also a spectrum from the Bruker catalogue for 3 phenoxybenzyl acetate. This reference spectrum was also used to assign the aliphatic carbons.

$^{13}$C NMR:

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<td></td>
</tr>
<tr>
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<td>6' = 118.0 ppm</td>
<td></td>
</tr>
<tr>
<td>3 6 $\delta$ = 118.2 ppm</td>
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\[5.4\]
3 phenoxybenzyl acetate [5.5]

As mentioned above, this was assigned by using the Bruker reference spectrum.

Aromatic Carbons  

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</thead>
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Aliphatic Carbons  

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<td></td>
</tr>
<tr>
<td>2</td>
<td>180.1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>20.4</td>
<td></td>
</tr>
</tbody>
</table>

[5.5]
4 phenoxybenzyl acetate [5.6]

This was also assigned by reference to the Bruker example for the 3 isomer, and by using the spectrum of 4 phenoxybenzyl alcohol.

<table>
<thead>
<tr>
<th>Aromatic Carbons</th>
<th>Aliphatic Carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 ( \delta = 156.75 \text{ ppm} )</td>
<td>1' ( \delta = 156.25 \text{ ppm} )</td>
</tr>
<tr>
<td>5 ( \delta = 118.0 \text{ ppm} )</td>
<td>2' ( \delta = 118.7 \text{ ppm} )</td>
</tr>
<tr>
<td>6 ( \delta = 129.4 \text{ ppm} )</td>
<td>3' ( \delta = 129.5 \text{ ppm} )</td>
</tr>
<tr>
<td>1 ( \delta = 130.25 \text{ ppm} )</td>
<td>4' ( \delta = 123.0 \text{ ppm} )</td>
</tr>
<tr>
<td>2 ( \delta = 129.4 \text{ ppm} )</td>
<td>5' ( \delta = 129.5 \text{ ppm} )</td>
</tr>
<tr>
<td>3 ( \delta = 118.0 \text{ ppm} )</td>
<td>6' ( \delta = 118.7 \text{ ppm} )</td>
</tr>
</tbody>
</table>

[5.6]
2 phenoxybenzyl methyl ether [5.7]

No reference spectra could be found for any of these compounds, and so they were assigned by using the spectra of the other monomers (for the aromatic peaks) and by the use of tables (for the aliphatic peaks).

<table>
<thead>
<tr>
<th>Aromatic Carbons</th>
<th>Aliphatic Carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>A=153.98 ppm</td>
<td>1'=157.27 ppm</td>
</tr>
<tr>
<td>1 2=130.8 ppm</td>
<td>2'=117.79 ppm</td>
</tr>
<tr>
<td>3 3=128.57 ppm</td>
<td>3'=129.42 ppm</td>
</tr>
<tr>
<td>4 4=122.31 ppm</td>
<td>4'=123.31 ppm</td>
</tr>
<tr>
<td>5 5=129.22 ppm</td>
<td>5'=129.42 ppm</td>
</tr>
<tr>
<td>6 6=118.8 ppm</td>
<td>6'=117.9 ppm</td>
</tr>
</tbody>
</table>

[5.7]
3 phenoxylbenzyl methyl ether [5.8]

Aromatic Carbons

\[
\begin{array}{ccc}
3 & 1=158.0 \text{ ppm} & 1'=157.9 \text{ ppm} \\
4 & 2=118.3 \text{ ppm} & 2'=119.4 \text{ ppm} \\
5 & 3=141.7 \text{ ppm} & 3'=139.3 \text{ ppm} \\
6 & 4=122.8 \text{ ppm} & 4'=123.9 \text{ ppm} \\
7 & 5=130.1 \text{ ppm} & 5'=130.3 \text{ ppm} \\
8 & 6=122.8 \text{ ppm} & 6'=119.4 \text{ ppm} \\
\end{array}
\]

Aliphatic Carbons

\[
1=73.7 \text{ ppm} \\
2=57.5 \text{ ppm}
\]

[5.8]
4 Phenoxybenzyl methyl ether [5.9]

Aromatic Carbons

\[
\begin{align*}
4 & \delta=156.25 \text{ ppm} & 1' & =156.65 \text{ ppm} \\
5 & \delta=118.4 \text{ ppm} & 2' & =118.4 \text{ ppm} \\
6 & \delta=128.95 \text{ ppm} & 3' & =129.5 \text{ ppm} \\
1 & \delta=132.5 \text{ ppm} & 4' & =122.7 \text{ ppm} \\
2 & \delta=128.95 \text{ ppm} & 5' & =129.26 \text{ ppm} \\
3 & \delta=118.4 \text{ ppm} & 6' & =118.4 \text{ ppm}
\end{align*}
\]

Aliphatic Carbons

\[
\begin{align*}
1 & =73.7 \text{ ppm} \\
2 & =57.5 \text{ ppm}
\end{align*}
\]
5.2.2 Assignment of peaks by reference to the literature

Certain assignments can be made by using values found in the literature for related compounds. For higher molecular weight species, previous work on phenolic resin chemistry (see for example references 29,30) can be invaluable in helping to suggest which areas of the spectrum will correspond to particular parts of the resin molecule. The information gained can be quite detailed - including degree and position of aromatic ring substitution.

Such interpretation can be aided by comparing the spectra of simple molecules relevant to the expected resin structure, and the way in which resonances alter with varying substituents and their position.

Finally, there is a large body of work previously carried out in ICI on phenyl ether-formaldehyde resins, and this was frequently referred to.

More detailed information now follows:

Use was made of the work of Pethrick and Thomson\textsuperscript{29,30}. They used the \textsuperscript{13}C spectra of the vast number of synthesised versions of low molecular weight phenol-formaldehyde species to calculate the resonance positions for the species they expected to produce. Such calculations are very much more difficult in phenyl ether-formaldehyde work because the low molecular weight models have not been synthesised (to do so would be very difficult - perhaps the best way would be separation from a polymer mixture).
The main results are as follows:

ortho-ortho methylene bridges: 31-32ppm

ortho-para methylene bridges: 35-36ppm

para-para methylene bridges: 40-41ppm

Using their models they were also able to conclude that methyl groups could be used to reflect the change in chemical shifts caused by the variation in the substitution position of a benzyl group.

The following molecules were used as models [Solvent CDCl₃ unless otherwise stated]. Shifts are taken from the Bruker catalogue⁶¹.

A: benzyl ether

\[ \text{A: benzyl ether} \quad \begin{array}{c}
\text{[Diagram]}
\end{array} \]

1=72.0ppm

5.10

B: 3 phenoxytoluene

\[ \text{B: 3 phenoxytoluene} \quad \begin{array}{c}
\text{[Diagram]}
\end{array} \]

1=21.2ppm

5.11

C: 4 phenoxytoluene

\[ \text{C: 4 phenoxytoluene} \quad \begin{array}{c}
\text{[Diagram]}
\end{array} \]

1=20.6ppm

5.12

D: hydroxybenzyl methyl ether

\[ \text{D: hydroxybenzyl methyl ether} \quad \begin{array}{c}
\text{[Diagram]}
\end{array} \]

1=74.8ppm

2=57.6ppm

5.13

E: benzyl methyl ether

\[ \text{E: benzyl methyl ether} \quad \begin{array}{c}
\text{[Diagram]}
\end{array} \]

1=74.6ppm

2=57.8ppm

5.14
Diphenoxybenzyl ether was assigned by using these models. 'A' gave the approximate spectral position, 'E' and 'D' the effect of adding a phenoxy group to a benzene ring (this shifts the position downfield) and 'C' and 'B' to illustrate the difference between meta and para substitutions - m>p by 0.6 ppm.

The following assignments, based on previous ICI work were available:

\[ \text{p,p'phenoxybenzyl ether: } \text{ArOCH}_2\text{OCH}_2\text{OAr} \quad 1=71\text{ppm} \]
\[ \text{or } 71.6\text{ppm} \]

\[ \text{o,o'phenoxybenzyl ether } \quad 1=63.3\text{ppm} \]

\[ \text{o,o'methylene bridge } \quad 1=30.2\text{ppm} \]

\[ \text{p,p'methylene bridge } \quad 1=39.9\text{ppm} \]

\[ \text{o,p'methylene bridge } \quad (1)=34.2\text{ppm} \]

5.2.3 Assignment by Other Techniques

A number of minor peaks, especially in the spectra collected for the polymerisation of 3 phenoxybenzyl alcohol were assigned by using logical deduction and other information. The most important technique was the use of simultaneous appearance or disappearance.
of two or more peaks from different, but related sections of the spectrum.

<table>
<thead>
<tr>
<th>Spectrum No.</th>
<th>Appearing resonance</th>
<th>Disappearing resonance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>37.45 ppm and 71.4 ppm</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>72.2 ppm and 40.8 ppm</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>70.4 ppm and 36.2 ppm</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>31.6 ppm and 38.4 ppm</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>35.6 ppm</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>35.9 ppm, 38.4 ppm</td>
<td>72.2 ppm, 71.4 ppm, 70.4 ppm</td>
</tr>
<tr>
<td>8</td>
<td>31.6 ppm, 33.1 ppm</td>
<td>37.45 ppm, 36.2 ppm</td>
</tr>
</tbody>
</table>

Table 5.1 Order of appearance/disappearance of $^{13}$C resonances for 3 phenoxybenzyl alcohol.

It is not unreasonable to conclude that peaks appearing simultaneously may be connected, especially if they are from two different regions of the spectrum. Also, the apparent disappearance of methylene bridge resonances will not occur (methylene bridges are very stable), unless it is due to the gain or loss of a substituent which causes the displacement of the resonance to a different position.

Using this we can explain the peaks at 71.4 ppm, 70.4 ppm, 37.45 ppm and 36.2 ppm by suggesting that they correspond to two trimeric species containing both methylene ether and methylene links. The two species can be separated by noting that those at 71.4 and 37.45 appear first and achieve a greater magnitude, and so probably correspond to the 4-isomer, which should be formed faster than the ortho isomers.
The two molecules could be:

\[
\begin{align*}
\text{Q} & \quad \text{O} \\
\text{ml} & \quad \text{svH}
\end{align*}
\]

5.20

and

\[
\begin{align*}
\text{O} & \quad \text{ml} \\
\text{svH} & \quad \text{O}
\end{align*}
\]

5.21

It is worth pointing out that if the third phenoxybenzyl molecule were to go onto the terminal phenyl rings (i.e., those without methylene substituents), then only one methylene ether resonance would be seen, and the methylene bridge resonance would coincide with that of an all methylene bridge oligomer, as shown below. This point will be discussed further later.

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \\
70.4 & \quad 71.1
\end{align*}
\]

The disappearance of these two methylene bridge resonances at the same time as all peaks belonging to the related methylene ether peaks at 71.4 ppm and 70.4 ppm further exemplifies the connection between these two linkages. Since the other resonances listed below both remain and grow, it is reasonable to assume that these are part of a soluble oligomer containing only methylene bridges. Their relative sizes are:
40.8 > 38.4 (split) > (36.3, 35.6) > 36.4 > (31.2, 31.8, 33.0)

The peak at 40.8 ppm has already been assigned as a methylene linkage.

As indicated in section 5.2.2, peaks at around 35 ppm are normally associated with 4/2 methylene bridges in phenol-formaldehyde oligomers. In this case they are likely to be 3/2. There are three resonances, 35.6 ppm, 36.2 ppm and 36.4 ppm. That at 35.6 ppm is probably:

5.22

Those at 36.3 ppm and 36.4 ppm may well be:

5.23

36.3 ppm (the larger peak).

and:

5.24
Clearly, the two 2/3 isomers will be different because of the relatively different positions of the 3 alkyl moiety.

That corresponding to 36.4 ppm will be less important because of steric hindrance, appreciated more easily when Phenyl ether is drawn to show its 120° bond angle.

The region around 31 ppm is usually associated with 2/2 linkages [See section 5.2.2]. This would account for one of the peaks, but certainly not the peak at 33.0 ppm. Generally, these peaks are so small that it is preferable not to speculate on what their assignment might be.

This just leaves the large peak at 38.4 ppm, which is probably due to a methylene bridge on a 3/4 trisubstituted ring.

---

5.3 Polycondensation of 3 Phenoxybenzyl Alcohol

Polycondensation of 3 phenoxybenzyl alcohol in 1,2 dichloroethane was carried out as outlined in the procedure in section 5.1. The concentration of monomer was 1m, full details being given in 8.2.3.

5.3.1 Description of the samples' spectra and variation of these spectra with time

The assignments for the polymerisation spectra are summarised in table 5.2.
### Table 5.2: 3-Phenoxypyrazyl Aromatic Proton Assignments (ppm)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peak Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-cis</td>
<td>71.0</td>
</tr>
<tr>
<td>2,4-trans</td>
<td>71.7</td>
</tr>
<tr>
<td>3,4-cis</td>
<td>72.2</td>
</tr>
<tr>
<td>3,4-trans</td>
<td>72.8</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>73.6</td>
</tr>
<tr>
<td>3-hydroxy methyl [5.2]</td>
<td>74.9</td>
</tr>
<tr>
<td>3,4-dihydroxyphenyl-4-phenoxypyrazyl ether [5.2]</td>
<td>74.9</td>
</tr>
<tr>
<td>3,4-dihydroxyphenyl-3-phenoxypyrazyl ether [structure 5.20]</td>
<td>75.5</td>
</tr>
<tr>
<td>3-phenoxypyrazyl-4-phenoxypyrazyl ether [structure 5.15]</td>
<td>75.5</td>
</tr>
</tbody>
</table>

Notes: Numbers refer to molecules depicted.
Figure 5.1 $^{13}$C NMR spectra for m-phenoxybenzyl alcohol
Fig.5.2: Peak height/time variation for 3-phenoxybenzyl alcohol
Table 5.3 shows peak heights which are measured from the NMR spectrum in millimetres.

<table>
<thead>
<tr>
<th>Sample no</th>
<th>Time mins</th>
<th>Measured peak heights, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>3.9 84.5 0.0 0.0 0.0</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>7.3 34.9 0.0 0.0 0.0</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>11.9 25.4 0.0 0.0 0.0</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>15.0 19.6 0.75 0.0 0.0</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>22.1 13.2 2.5 1.3 1.3</td>
</tr>
<tr>
<td>6</td>
<td>75</td>
<td>22.6 11.7 2.8 1.6 1.6</td>
</tr>
<tr>
<td>7</td>
<td>90</td>
<td>29.4 0.5 10.1 2.9 3.0</td>
</tr>
<tr>
<td>8</td>
<td>105</td>
<td>5.4 0.0 13.0 4.8 5.4</td>
</tr>
<tr>
<td>9</td>
<td>135</td>
<td>0.0 0.0 14.0 4.7 4.5</td>
</tr>
<tr>
<td>10</td>
<td>165</td>
<td>0.0 0.0 14.3 4.6 5.7</td>
</tr>
</tbody>
</table>

* In trisubstituted ring

Table 5.3 PL3206 Heights of alkyl peaks for 3 phenoxybenzyl alcohol

Typical $^{13}$C NMR spectra are shown in Fig 5.1, and the peak height against time relationship is depicted in figure 5.2. It is important to remember that the plots only show the relative concentrations of particular groups, and not a particular molecule—thus the plot for hydroxymethyl includes both monomer and hydroxy-methyl functionalised oligomers. In addition, it would be wrong to make anything other than the crudest comparison of the relative levels of a particular group's peak. As an example, other experiments in which acetate functionality was involved showed three different peak heights for each of the carbons associated with the acetate group, and there was approximately 300% difference between the magnitudes of the three measurements.
Within these limitations however, a certain amount may be deduced, and a sequence of individual reaction steps proposed, although without measuring the rate constants for each reaction step, or having a definite quantitative knowledge of the relative amounts of an intermediate, little can be said regarding the actual course of the reaction except by recourse to experience.

5.3.2 Changes in Functional Group Content with Time

Each of the functional groups will be considered in turn.

Hydroxymethyl

This shows the behaviour one would expect in such a monohydroxy-functional system - a pretty rapid decline to give an oligomer which in the end has no side chain hydroxy functionality at all. The surprising part however is the reactions which are responsible for the removal of the hydroxymethyl - the vast majority is converted to the methylene ether:

\[
2 \text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{O} + H_2\text{O}
\]

Even allowing for a very wide error band in peak heights it is easy to see that the levels of the methylene ether linkage rise very high indeed, and this is clearly an important early reaction.

The other identifiable process by which hydroxymethyl functionality is used up is in the simple conversion to a methylene bridge. This does not appear to start happening to any extent until after about sixty minutes, and there are certainly no peaks observed in the
NMR until forty five minutes. By this time, half of the hydroxymethyl has gone, again underlining the importance of the conversion to the methylene ether linkage. All of the hydroxymethyl functionality has disappeared by 94 minutes reaction time.

The Methylene ether linkage
This exhibits a very rapid growth, and equally rapid reduction, peaking at approximately sixty minutes reaction time. As explained previously it is the product of the reaction of two hydroxymethyl groups. Its deterioration coincides with the steady increase in the methylene bridges, and it is reasonable to assume that in some way the ether is being ruptured to reform benzyl cation which attacks another phenyl ether molecule to give the methylene bridge:

\[
\begin{align*}
H \\
ArCH_2OCH_2Ar + H^+ &\rightarrow ArCH_2OCH_2Ar \\
+ \\
ArCH_2OCH_2Ar &\rightarrow Ar'CH_2 + ArCH_2OH \\
H &\rightarrow \ \\
Ar'CH_2 + ArCH_2OH &\rightarrow ArCH_2ArCH_2OH + H^+ \\
\end{align*}
\] 

(i) 
(ii) 
(iii)

In the mechanism depicted above, the most likely fate of a benzyl cation formed by reaction (ii) will be that it will reform the methylene ether by reacting with its nearest neighbour's hydroxymethyl - a reaction which is clearly faster than (iii). However, reaction (iii) is irreversible, and so there will be a steady decline in the concentration of the methylene ether after the initial peak.
The methylene ether linkage can be undesirable because it reduces some aspects of the final material's mechanical properties. Because the model studies here show that it is possible to remove the linkage if sufficient reaction time is allowed, it would presumably be possible to do the same commercially. However, because of the way such reactions are currently run, significant changes in the process would have to be undertaken.

The fundamental part of the mechanism then is a dynamic equilibrium between phenoxybenzyl alcohol and diphenoxybenzyl ether, with an irreversible reaction giving the methylene bridged species from the alcohol.

\[
2n\text{ArCH}_2\text{OH} \rightleftharpoons x\text{ArCH}_2\text{OCH}_2\text{Ar} \\
\downarrow \\
(n-x)y\text{ArCH}_2\text{ArCH}_2\text{OH}
\]

Methylene Bridges

The 4/3 methylene bridge is observed before the 2/3 bridge - but not by much. One might expect a greater period to elapse before the 2 - isomer appears in detectable quantities, given that the 4 position is between three and four times more reactive than the ortho position. (ref 62) There seems to be no good reason for this, and the eventual ratio of 4 to 2 isomer is approximately 3:1.
A mechanism can now be postulated as follows:

Abbreviations used are: Ar =

\[
\begin{align*}
D_1 &= \\
&= \\
\end{align*}
\]

All ring substitutions are 3 to the ether oxygen unless otherwise depicted.

i) \( H^+ + \text{ArCH}_2\text{OH} \xrightarrow{k_1} \text{ArCH}_2\text{O}^+\text{H}_2 \)

ii) \( \text{ArCH}_2\text{O}^+\text{H}_2 \xrightarrow{k_2} \text{ArCH}_2 + \text{H}_2\text{O} \)

iii) \( \text{Ar}^+\text{CH}_2 + \text{ArCH}_2\text{OH} \xrightarrow{k_3} \text{ArCH}_2\text{OCH}_2\text{Ar} + \text{H} \)

iv) \( D_1 + H^+ \xrightarrow{k_4} \text{ArCH}_2\text{OCH}_2\text{Ar} \xrightarrow{k_5} \text{Ar}^+\text{CH}_2 + \text{ArCH}_2\text{OH} \)

v) \( \text{ArCH}_2\text{OCH}_2\text{Ar} \xrightarrow{k_6} \text{Ar}^+\text{CH}_2 + \text{ArCH}_2\text{OH} \)

vi) \( D_1 + \text{Ar}^+\text{CH}_2 \xrightarrow{k_6} \text{ArCH}_2 + \text{CH}_2\text{OCH}_2\text{Ar} + H^+ \)

vii) \( D_1 + \text{Ar}^+\text{CH}_2 \xrightarrow{k_7} \text{CH}_2\text{AR} + \text{CH}_2\text{OCH}_2\text{Ar} + H^+ \)

RHDPD/PL1-370P
viii) \( \text{Ar}^*\text{CH}_2 + \text{ArCH}_2\text{OH} \xrightleftharpoons{\kappa_8} \text{ArCH}_2\text{O} + \text{H}^+ \)

ix) \( \text{Ar}^*\text{CH}_2 + \text{ArCH}_2\text{OH} \xrightleftharpoons{\kappa_9} \text{ArCH}_2\text{O} + \text{H}^+ \)

x) \( \text{ArCH}_2 + \text{D}_1 \xrightleftharpoons{\kappa_{10}} \text{ArCH}_2\text{O} + \text{H}^+ \)

xi) \( \text{ArCH}_2 + \text{ArCH}_2\text{OH} + \text{H}^+ \)

xii) \( \text{ArCH}_2 + (\text{para})\text{ArCH}_2\text{ArCH}_2\text{OH} + \text{H}^+ \)

It should be noted that this mechanism does not detail all the reactions taking place, but contains an example of the possible fates of the various reactive groups. As an example, the three unit species formed in reaction (vi) could break up at the methylene ether in the same way as for the dimer in reactions (iii) to (v). The rates, however, would be slightly different. The same can be said of the formation of polymer — any combination of \((\text{ArCH}_2)_n\text{OH}\) can react together, where \(n=1\) to approximately 6, giving polymer.
The rates for each different combination would be slightly different, and the reaction mechanism would run to several repetitive pages. Nevertheless, although the rate differences are small, there are occasions when it is important to bear them in mind.

Using the data from Chapter 4 regarding the increased rate with increasing catalyst to monomer concentration ratio, and the relative reactivities of meta and para isomers, it is possible to suggest that step (ii) is the rate limiting step; the rate of the reverse reaction would be reduced by azeotroping water away from the reaction. It is also possible to say that step (iii) is much faster than reactions which form a methylene bridge.

The mechanism is thus much as expected from phenol-formaldehyde with the exception of the considerable formation of the methylene ether linkage as an intermediate. In phenol-formaldehyde resins, this group is not observed at pH<3. Pethrick and Thomson’s $^{13}$C NMR studies illustrate that it is neither an intermediate or present in the final products at pH<3. Thus this would appear to be a peculiarity of Phenyl ether-formaldehyde resins, because the linkage is also present in the commercial product. It could be that this is an indication of a greater stability of the benzyl cation in phenol-formaldehyde systems.

5.4 Polycondensation of 4-Phenoxybenzyl Alcohol

Polycondensation of 4 phenoxybenzyl alcohol in 1,2 dichloroethane was carried out as outlined in section 5.1. Monomer concentration was 0.125m, full details being given in 8.2.3.
5.4.1 Spectra of the samples and variation of these spectra with sample time

The same comments as were made for the 3 isomer regarding spectral interpretation are also pertinent here. The peak positions are described in tables 5.4 and 5.5, using the same format as for the 3 isomer. Typical $^{13}\text{C}$ NMR spectra are shown in Fig 3.

Gel permeation chromatography was used to confirm that all monomers had reacted after approximately twenty minutes had elapsed.
<table>
<thead>
<tr>
<th>Order of Appearance</th>
<th>Peak Assignment (for 4-phenoxypyphenyl alcohol spectra)</th>
<th>Peak Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene-4-sulfonic acid (Bruker catalog)</td>
<td>11.4</td>
</tr>
<tr>
<td>1</td>
<td>1,4-dichloroethane</td>
<td>12.25</td>
</tr>
<tr>
<td>4</td>
<td>1,2-dichloroethane</td>
<td>21.25</td>
</tr>
<tr>
<td>4</td>
<td>4-methyl-4-phenoxypyphenyl ether</td>
<td>29.5</td>
</tr>
<tr>
<td>1</td>
<td>4-methyl-4-phenoxypyphenyl alcohol</td>
<td>35.25</td>
</tr>
<tr>
<td>1</td>
<td>4-methyl-4-phenoxypyphenyl alcohol</td>
<td>40.3</td>
</tr>
<tr>
<td>4</td>
<td>4-methyl-4-phenoxypyphenyl alcohol</td>
<td>42.75</td>
</tr>
<tr>
<td>1</td>
<td>4-phenoxypyphenyl methyl ether</td>
<td>42.75</td>
</tr>
<tr>
<td>1</td>
<td>4-phenoxopyphenyl alcohol</td>
<td>57.6</td>
</tr>
<tr>
<td>4</td>
<td>Unassigned</td>
<td>64.4</td>
</tr>
<tr>
<td>1</td>
<td>Unassigned</td>
<td>68.75</td>
</tr>
<tr>
<td>1</td>
<td>4-phenoxypyphenyl alcohol</td>
<td>71.5</td>
</tr>
<tr>
<td>1</td>
<td>4-phenoxypyphenyl alcohol</td>
<td>74.0</td>
</tr>
<tr>
<td>1</td>
<td>4-phenoxypyphenyl alcohol</td>
<td>74.0</td>
</tr>
</tbody>
</table>
Figure 5.3 $^{13}$C NMR spectra for 4-PBA
Table 5.5: $^{13}$C NMR peak heights for oligomerisation of 4-phenoxybenzyl alcohol
Fig. 5.4: Peak height/time variation for 4-phenoxybenzyl alcohol

Peak Heights mm

-CH₂OCH₃ - -CH₂OH - O-CH₃ [40.8]
-CH₂ [35.6] - O-CH₃ [38.4]
Peak profiles (height versus time graphs) were plotted out and are shown on figure 5.4. Again, each group will be discussed in turn, followed by a comparison of the 3 and 4 hydroxymethyl isomers.

5.4.2 Changes in functional group content with time

The hydroxymethyl Group

Concentration of the hydroxymethyl plummets to near-zero in seven minutes, before picking up again to over half the starting concentration, and then declining more steadily. From the graph it is clear that the initial decrease is due to an equally rapid formation of the methylene ether linkage. This tends to imply a rapid formation of benzyl cations, which quickly react with the available hydroxymethyl groups (then at high concentration) to give the methylene ether, which has a lower thermodynamic stability than the methylene bridge. Some 4 methylene bridge is also formed, but overall, this part of the reaction is clearly under kinetic rather than thermodynamic control.

The rate of increase in concentration of methylene ether groups slows, and then reverses as the chance of meeting another hydroxymethyl group falls. The decline in the concentration of methylene ether groups is matched by the steady rise in the concentration of hydroxymethyl groups due to the rupture of the methylene ether linkage to yield a methylene bridge and a hydroxymethyl group. Although the back reaction to yield the methylene ether is most likely immediately after rupture, once the benzyl cation and the hydroxymethyl break free from each other's influence a benzyl cation is statistically far more likely to react with an aromatic ring than a hydroxymethyl because the relative
concentration of the former is so much higher. Alternatively of course, we may propose the simultaneous reaction of benzyl cation with aromatic ring as methylene ether rupture occurs. This avoids the problems posed by bare benzyl cations! Eventually of course there is insufficient methylene ether linkage to sustain a rise in the overall concentration of hydroxymethyl, and the level of these begins to fall again, but gradually, matched by a steady increase in the concentrations of the two types of methylene bridges. It is worth pointing out that the fall-rise-fall behaviour of the hydroxymethyl functionality is matched by the molecular weight, which rises, falls and then rises again [See chapter 4]. This is clearly due to initial formation of polymers consisting of phenyl ethers linked by methylene ethers. When these start to break up at a rapid rate, molecular weight falls until polymers with methylene bridges reverse the trend again.

Finally, it is worth noting that for a short time there is still hydroxymethyl functionality remaining when all the methylene ether linkage has gone. This fact could be of significance to a polymer chemist, because as pointed out previously it can be desirable to remove all methylene ether groups. However, it is useful in many cases to have residual functionality as well, and it is clear that in this case a window exists in which both can be attained.
Methylene ether

Many of the relevant points concerning this linkage have been discussed under the hydroxymethyl linkage, but it is interesting to note the shape of the curve—the very rapid rise demonstrating the kinetic control, the much steadier decline an indication that an equilibrium has been established.

Methylene linkage

The growth in both 4 and 2 linkages is near linear, the first 2 linkages appearing after about five minutes, whilst under the conditions used 4 linkages are formed within the first 30 seconds. Without quantitative data it is impossible to be sure of the 4/2 ratio, but it could be as large as 7:1.

Other Spectral Features

The spectra are remarkably simple, but prominent amongst the unlooked for peaks are two which appear simultaneously at 74.0 ppm and 57.6 ppm. These are assigned to the methylene and methyl groups respectively of 4 phenoxybenzyl methyl ether, or an oligomer containing it. Assignment was achieved by comparison with the spectrum of the pure compound.

It is difficult to explain the formation of this without postulating the release of free formaldehyde. The literature indicates that such a reaction can occur, although it has never been seen to a great extent. Any of the hydroxymethyl or methylene ether species can theoretically undergo the process, e.g:
To check for the presence of formaldehyde, the condensate in the molecular sieve trap was subjected to the silver mirror test, and found to give a positive result.

Using this information, a possible reaction responsible for the methyl ether is:

1. \( H_2O + 2CH_2O \rightarrow \text{HCO}_2H + CH_3OH \)

2. \( \text{ArCH}_2 + CH_3OH \rightarrow \text{ArCH}_2\text{OCH}_3 + H^+ \)

The ether functionality does not survive the reaction - it maintains an equilibrium concentration until all the methylene ether linkage has gone, when it too disappears, presumable polymerising via the benzyl cation.

Free formaldehyde is capable of undergoing a number of reactions in such a system, and this will be discussed further later.

Overall reaction mechanism

Abbreviation used is \( \text{Ar} = \)

All ring substitutions are 4 to the ether oxygen unless otherwise depicted.

i) \( \text{ArCH}_2\text{OH} + H^+ \rightarrow \text{ArCH}_2 + \text{H}_2\text{O} \)

\[ k_1 \]

ii) \( \text{Ar}^+\text{CH}_2 + \text{ArCH}_2\text{OH} \rightarrow \text{ArCH}_2\text{OCH}_2\text{Ar} + H^+ \)

\[ k_2 \]
iii) \[ \text{ArCH}_2\text{OCH}_2\text{Ar} + \text{H}^+ \rightarrow \text{ArCH}_2\text{OHCH}_2\text{Ar} \]

iv) \[ \text{ArCH}_2\text{OHCH}_2\text{Ar} \rightarrow \text{Ar}^+\text{CH}_2 + \text{ArCH}_2\text{OH} \]

v) \[ \text{Ar}^+\text{CH}_2 + \text{ArCH}_2\text{OCH}_2\text{Ar} \rightarrow \text{ArCH}_2\text{ArCH}_2\text{OCH}_2\text{Ar} + \text{H}^+ \]

vi) \[ \text{Ar}^+\text{CH}_2 + \text{ArCH}_2\text{OCH}_2\text{Ar} \rightarrow Q \text{ArCH}_2\text{ArCH}_2\text{OCH}_2\text{Ar} + \text{H}^+ \]

vii) \[ \text{Ar}^+\text{CH}_2 + \text{ArCH}_2\text{OH} \rightarrow \text{ArCH}_2\text{ArCH}_2\text{OH} + \text{H}^+ \]

viii) \[ \text{ArCH}_2 + \text{ArCH}_2\text{OH} \rightarrow Q \text{ArCH}_2\text{ArCH}_2\text{OH} + \text{H}^+ \]

ix) \[ \text{Ar}^+\text{CH}_2 + \text{ArCH}_2\text{OCH}_2\text{Ar} \rightarrow \text{ArCH}_2\text{ArCH}_2\text{OCH}_2\text{Ar} \]

x) \[ \text{ArCH}_2\text{OCH}_2\text{Ar} + \text{Ar}^+\text{CH}_2 + \text{CH}_2\text{O} + \text{ArH} \]

xi) \[ \text{ArCH}_2\text{OH} + \text{ArH} + \text{CH}_2\text{OH} \]

xii) \[ \text{H}_2\text{O} + 2\text{CH}_2\text{O} \rightarrow \text{HCO}_2\text{H} + \text{CH}_2\text{OH} \]

xiii) \[ \text{ArCH}_2 + \text{CH}_3\text{OH} \rightarrow \text{ArCH}_2\text{OCH}_3 + \text{H}^+ \]
As with the 3 isomer, this mechanism does not depict all the reactions of different rates, but contains an example of every possible fate observed for a particular reactive group. Rates of the reaction will vary with the oligomer size, and this should be kept in mind.

Implications

Again, as with the 3 isomer the concentration reached by the methylene ether group is totally unexpected when compared to the results gained from phenol-formaldehyde investigations, and the same points apply here as for the 3 isomer.
Here, the most interesting feature is the release of free formaldehyde which has implications for cross-linking and gelling of the polymer because formaldehyde gains dihydroxy functionality in acidic solution. These will be considered under the chapter on functionality control.

The apparently high 4/2 methylene bridge ratio is interesting - it may be simply because the starting molecule is 4 substituted or there may be some reason such as loss of formaldehyde from the 2 position. Again, this will be discussed later.

Finally, the point at which residual hydroxyl functionality remained even after methylene ether links had disappeared has possible implications for the combined mechanical and chemical properties of the final oligomer. Strictly quantitative NMR data of the concentration of each linkage and functionality together with molecular weight data will allow the synthesis of oligomers of tightly controlled characteristics.

5.4.3 Comparison of 3 and 4 spectra

Here each group will be considered in turn before comparing some of the finer spectral detail.
Comparison of the two plots shows radical differences here - the 3 isomer displays a fairly rapid but steady decline, whilst the 4 isomers exhibits an initial precipitous decline followed by a more steady increase and decline. There is clearly a much greater desire on the part of the 4 isomers to form the benzyl cation, which can then go on and react further. This was also seen in chapter 4. This implies that the 4 cation is more stable than the 3 isomer. This can be demonstrated using Wheland intermediates as follows.

3 Isomer

In the case of the 3 isomer, none of the additional stability provided by the ether oxygen's lone pair can be devolved onto the cation to provide charge stabilisation. With the 4 isomer this is possible, as demonstrated by intermediate (iii).

It is also noticeable that whereas all the hydroxymethyl functionality disappears first in the 3 isomer, it follows after all methylene ether linkage has gone in the case of the 4, with the possibilities already discussed.
Methylene ether linkage

Here it is interesting to compare the curve shapes (figs 5.2 & 5.4) - in the case of the much slower 3 phenoxy benzyl alcohol reaction the equilibrium between hydroxymethyl and methylene ether is clearly established early - the curve has a Gaussian form with a line of reflection passing vertically through its peak. In the 4 case the linkage only settles into equilibrium once it has reached peak concentration in very rapid fashion.

Methylene bridge

The only differences here lie in (a) the types of bridge as regards substitution pattern, and (b) the relative quantities of 2 and 4 linkages. If we compare the relative numbers of 2 and 4 in di-substituted rings only, then it is clear that the difference in the 4/2 ratio is large. However, as will be discussed shortly, there is a far greater range of linkage substitution in the 3 isomer, and this makes it more difficult to be sure of the relative ratios.

Nevertheless the 4 isomer does seem to provide a much higher 4/2 ratio.
A comparison of the two sets of spectra shows instantly that the situation arising from the 3 isomer is far more complex, as is illustrated from the attempts to assign the 3 spectrum.

The reason lies in the apparent ability of the 3 isomer to accept substituents on the disubstituted ring to a much greater extent than is the case with the 4 isomer.

This is likely to be due to the fact that the ring containing a meta substituent still has all its highly reactive para and ortho sites available for substitution — whereas in a para isomer the most reactive position is blocked, encouraging a further substitution to go on a ring with a free para position.
Whereas 4-phenoxybenzyl methyl ether, or oligomers containing it, is quite an important species in the 4 isomer's spectrum, such ethers do not appear at all in the 3 isomer's oligomerisation. As discussed previously, they are probably the result of the liberation of free formaldehyde, but the 3 isomer should be more inclined to lose it than the 4 because it has no stabilisation for its protonated alcohol.

Stabilisation is only afforded to such substituents in the 4 and 2,6 positions. Therefore, the loss of formaldehyde from these positions is relatively encouraged:

The most likely explanation for not observing methyl ether is that the formaldehyde reacts in other ways — perhaps to give the 4 phenoxybenzyl alcohol. This could be easily envisaged, as such a reaction could occur whilst the just liberated formaldehyde is still in the same solvent envelope as the phenyl ether.
5.5 Polycondensation of 4 Phenoxybenzyl Alcohol in the Presence of Acetic Acid

This experiment was carried out in a solution of 90% 1,2 dichloroethane and 10% acetic acid by volume. Concentrations of 0.125 molar PPBA and 0.026 molar PTSA were employed. Total reaction time was 260 minutes with samples being extracted at regular intervals and worked up before NMR analysis.

5.5.1 Spectra of the samples and variation of these spectra with time

Peak assignment is not too difficult, the peaks mostly corresponding to those seen previously or in model compounds. The assignments are presented in Table 5.6. Typical $^{13}$C NMR spectra are shown in Fig 5.5.

<table>
<thead>
<tr>
<th>PEAK POSITION (ppm)</th>
<th>PROBABLE PEAK ASSIGNMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>170.2</td>
<td>Carbonyl from ester</td>
</tr>
<tr>
<td>71.2</td>
<td>4/4 dibenzyl ether</td>
</tr>
<tr>
<td>62.25</td>
<td>methylene in ester: $\text{Ar-CH}_2\text{CO}_2\text{CH}_3$</td>
</tr>
<tr>
<td>64.3</td>
<td>4-phenoxybenzyl alcohol</td>
</tr>
<tr>
<td>40.8</td>
<td>4/4- methylene benzyl</td>
</tr>
<tr>
<td>35.5</td>
<td>4/2 methylene bridge</td>
</tr>
<tr>
<td>29.5</td>
<td>2/2 methylene bridge</td>
</tr>
<tr>
<td>20.5</td>
<td>methyl from acetate $\text{CH}_2\text{CO}_2\text{CH}_3$</td>
</tr>
</tbody>
</table>

Table 5.6 Peak positions and assignments for PL1235

The most interesting feature here is the appearance of acetate functionality; the extent of the formation of acetate, and the profiles of other groups is presented in Table 5.7, and plotted out in figure 5.6.
### Table 5.7 Variation of peak heights with time for PL1235

<table>
<thead>
<tr>
<th>SAMPLE No</th>
<th>TIME mins</th>
<th>Peak Heights, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>62.25ppm CH₂C</td>
</tr>
<tr>
<td>1</td>
<td>1.20</td>
<td>75.0</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>90.0</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>90.0</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>66.5</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>38.0</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>26.0</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>17.0</td>
</tr>
<tr>
<td>8</td>
<td>70</td>
<td>10.0</td>
</tr>
<tr>
<td>9</td>
<td>77</td>
<td>9.0</td>
</tr>
<tr>
<td>10</td>
<td>80</td>
<td>7.0</td>
</tr>
<tr>
<td>11</td>
<td>85</td>
<td>5.5</td>
</tr>
<tr>
<td>12</td>
<td>90</td>
<td>4.5</td>
</tr>
<tr>
<td>13</td>
<td>97</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Although reaction was continued until some 260 minutes, carbon -13 NMR shows that all polymerisable groups have reacted by 130 minutes, with the corresponding small change in methylene bridge concentrations. No change whatsoever is observed thereafter.

**5.5.2 Changes in Functional Group Content with Time**

The general polymerisation proceeds here much as expected - a reactive group - the acetate - decays in concentration at a steady rate forming methylene bridges in the 2 and 4 positions.
Fig. 5.6: Peak height/time variation for 4-phenoxybenzyl alcohol plus AcOH
Figure 5.5 $^{13}$C NMR for 4 PBA in acetic acid
The most interesting feature is that the polymerisable group appears to be an acetate, and not the hydroxymethyl - Comparison of the two \( \text{CH}_2\text{OH} \) curves shows that the rate of formation of the acetate, relative to the polymerisation rate is huge, so that even at a concentration of only 10% acetic acid in the solvent mixture, hydroxymethyl concentration is negligible from the start and zero after forty minutes. However, one might argue that in fact it is the hydroxymethyl only that oligomerises, via the alcohol/ester equilibrium, and this is in accordance with the pKa data presented in Chapter 4, which indicate that due to its greater basicity the alcohol is far more easily protonated than the ester.

As a consequence of the very low hydroxymethyl concentration, methylene ether linkages scarcely figure, and only then for a very short time. The implication from this is that oligomers synthesised under conditions in which esterfication is the fastest reaction will not have the generally undesirable methylene ether linkage.

A more important conclusion arising from this pre-oligomerisation conversion of functionality is that control of functionality concentration is now possible. If it is a general rule that conversion of a particular monomer to a desired functionality is much quicker than oligomerisation, then it will be possible to achieve functionality control by stopping reaction once the required concentration/molecular weight has been reached. The alternative - a slower or comparable rate of conversion and oligomerisation would result in an oligomer at best containing a mixed functionality. In order to complete the conversion, reaction would have to be continued, but this would result in a lower functionality as the end groups were lost in the process of molecular weight growth.
However, this is not the whole story, because a system containing a monomer which is monofunctional only in a chosen reactive group is not suitable for the achievement of a useful concentration of that functionality at a useable degree of polymerisation; to achieve a more suitable level, multifunctional monomers must be introduced, but these produce their own problems in that they can lose their additional functionality by bringing about cross linking between oligomer chains to such an extent that an insoluble and useless gel results. How this problem may be overcome is dealt with later.

Turning again to the profiles in figure 5.6, it is interesting to note that the concentration of the acetate group is still at approximately 50% of the maximum achieved when no further growth in methylene linkage is observed. It is pertinent to ask what happens to the remaining acetate after this.

A little growth in the resonance associated with 2,6 tri-substituted products is observed, but nothing like enough to use up the available acetate. There can only be one other possible explanation, and that is that formaldehyde is being liberated.

5.5.3 Gel formation

It was an observation with experiments carried out in this solvent medium that gelling was occurring to a significant extent, and that the higher the concentration of acetic acid, the worse was the extent of gelling. (This is separate from the problem of the lower solubility of oligomeric products in acetic acid rich solvent mixtures). It is more than likely that this gelling is caused by the significant release of formaldehyde from the substituted phenyl
ether molecules. Because formaldehyde is difunctional, it can link two oligomer chains in the manner shown in figure 5.7:

Thus the cross-link has turned two oligomers of molecular weight x into one of approximate weight 2X. Such a drastic rise in molecular weight is accompanied by a similar fall in solubility, and if cross-linking occurs to such an extent that the reaction mixture consists of just a few very large molecules, then a completely insoluble gel precipitates out.

Although formaldehyde was tested for in the molecular sieve trap by the silver mirror test in the same manner as previously, and found, there is one other cause of gelling which could also be in operation and that is oligomer disproportionation, in which a monofunctional species breaks up to give two smaller molecules, one non-functionalised and the other of functionality two.

At its simplest this may be represented as:
The difunctional molecule is now capable of causing cross-linking just as formaldehyde is. Such disproportionation is characterised by a gel permeation chromatogram in which two peaks develop from the single peak, one of lower molecular weight than the previous peak maximum and one of higher molecular weight, the process being illustrated in figure 5.8.

![Diagram](image)

**Fig. 5.8 Development of disproportionation during oligomerisation**

Using duplicate conditions to that used for $^{13}$C NMR an experiment was attempted to try and establish if such a phenomenon was occurring. The experiment was run for a total of nine hours, and gel permeation chromatographs recorded at regular intervals. Those taken at 3, 6 and 9 hours are shown in figure 5.9 below, and it is clear that there is no evidence of disproportionation taking place.
Fig 5.9 Gel phase chromatograms for polymerisation of 4 phenoxybenzyl alcohol in acetic acid/dichloroethane.

From this it was concluded that the only factor contributing to gelling was the release of formaldehyde.

To return to the extent of this release it is relevant to question why the acetate functionlised oligomer, or an oligomer in acetic acid is so much more prone to formaldehyde evolution.

If we consider deformylation of the acetate:

$$\text{Ph}-\text{O} \quad \text{CH}_2\text{COCH}_3 \rightarrow \text{Ph}-\text{O} \quad \text{COCH}_2 + \text{CH}_2\text{O}$$

then this will clearly be more extensive than deformylation of alcohol or methylene ether, because it is not reversible.
Thus deformylation is going to be seen to a greater extent in acetic acid media.

The greatest significance of the observation that acetate functionality is still present when oligomer growth stops is that an oligomer has been synthesised of suitable molecular weight with a moderate level of acetate functionality - and from a monofunctional monomer. It would be a simple matter to stop reaction at this point - or at any other point along the functionality curve as desired. However, a higher functionality may still be desired, and so experiments with the addition of difunctional monomer will also be explored.
CHAPTER 6: CONTROL OF GELLING IN THE SYNTHESIS OF OLGOMERS CONTAINING HYDROXYLMETHYL OR ACETOXYMETHYL

6.1 Introduction

It was previously outlined in the NMR section on acetate functionalised resin how the fact that the first stage in the reaction of phenoxybenzyl alcohol in an acetic acid/dichloroethane solvent is esterification, and although hydrolysis probably occurs prior to oligomerisation, the equilibrium constant for esterification is such that ester is the only observed functional group. This offered the opportunity to control the concentration of acetate end groups and molecular weight at the same time. To achieve a useful concentration though a dihydroxymethyl species had to be introduced, and this required that a control on gel formation be established, because adding such a monomer could cause cross-linking. Gelling was known to occur anyway to a small extent with the mono hydroxymethyl monomers because of the release of formaldehyde, but deliberately adding a dihydroxymethyl monomer could make this much worse. This left two problems to be solved: (a) Controlling gel in the monohydroxymethyl system and (b) Do the same in a system containing both the monohydroxymethyl monomer - 4 phenoxybenzyl alcohol and the dihydroxymethyl monomer - 4, 4'-oxybisbenzyl alcohol.

Gelation is a result of crosslinking, the joining of oligomer chains with a suitable "crosslinker" molecule to give a bigger molecule. It occurs in these systems by electrophilic attack at the 2, 6 positions, the 4 positions having been utilised in growing the
oligomer in a linear fashion. Attack at the 2, 6 positions is already disadvantageous relative to the 4 positions, and if it can be made more so then crosslinking will be significantly reduced.

In order to achieve this the relevant literature has been reviewed. The most useful work for condensation polymers lies in the considerable amount of effort made to synthesise linear polybenzyls. Linearity is achieved by preventing multisubstitution, and so bears considerable relation to the problems outlined above. Polybenzyls have a "star" structure in which a single benzene ring is multisubstituted to form the centre of the star. This occurs because each successive substitution makes the ring electronically more attractive to being substituted again. In order to prevent this, and so obtain polymers with good mechanical properties, all sorts of variations on reaction conditions were tried, one group of workers going so far as to carry out polymerisation at -130°C. This was at first thought to have been successful, the theory being that the initially "linear" and crystalline small polymer molecules encouraged other molecules to grow in this way because molecular movement at this temperature was restricted. However, subsequent x-ray studies by Montaudo and co-workers showed that only some of these samples exhibited crystallinity, and these were of low molecular weight.

In order to make the ring less attractive to multi-substitution Kuo and Lenz carried out polymerisations in the presence of sulphur dioxide, which was known to form Pi complexes with the benzene ring, thus reducing the ring's electron density and attractiveness to electrophilic attack. This did lead to an apparently significant
reduction in multisubstitution, but this was not mirrored in the physical properties of the polybenzyl so produced.

It was an experimental observation that during work to establish the appropriate reaction conditions for a suitable rate of polymerisation, there were indications that gel formation was much greater at lower concentration of acid catalyst than at higher. This was rather contrary to what might have been expected, but it was decided to try and put this observation on a more certain basis before trying some of the more exotic work attempted by workers in the polybenzyl field.

6.2 Polycondensation of 4-Phenoxybenzyl Alcohol

6.2.1 Effect of catalyst to monomer ratio on gelling
A series of polymerisation reactions were set up, in which catalyst monomer ratios ranged from nothing - a blank test - to parity. The number of moles of 4 phenoxybenzyl alcohol was kept at 0.0250 with constant reaction volume throughout. Significant results, namely PL1244 and PL1246 were repeated three times and averaged. The results are presented in table 6.1.
### Table 6.1 - Molecular weight and gel data for oligomers from 4 phenoxybenzyl alcohol [PPBA]

<table>
<thead>
<tr>
<th>Expt.</th>
<th>[ArCH₂OH] moles</th>
<th>[PTSA] mols</th>
<th>[PTSA] [ArCH₂OH]</th>
<th>Gel produced gms</th>
<th>Mn</th>
<th>Mw</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0250</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>230</td>
<td>305</td>
<td>1.33</td>
</tr>
<tr>
<td>PL1242</td>
<td>0.0250</td>
<td>1.053x10⁻³</td>
<td>0.0421</td>
<td>1.1699</td>
<td>190</td>
<td>4500</td>
<td>23.7</td>
</tr>
<tr>
<td>PL1243</td>
<td>0.0250</td>
<td>3.158x10⁻³</td>
<td>0.1263</td>
<td>0.6470</td>
<td>477</td>
<td>4087</td>
<td>8.57</td>
</tr>
<tr>
<td>PL1244</td>
<td>0.0250</td>
<td>6.316x10⁻³</td>
<td>0.2526</td>
<td>0.0667</td>
<td>939</td>
<td>2819</td>
<td>3.00</td>
</tr>
<tr>
<td>PL1245</td>
<td>0.0250</td>
<td>0.0126</td>
<td>0.5040</td>
<td>0.0411</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PL1246</td>
<td>0.0250</td>
<td>0.0253</td>
<td>1.0120</td>
<td>0.0000</td>
<td>1567</td>
<td>3697</td>
<td>2.36</td>
</tr>
</tbody>
</table>

Key
- N/A = not available
- PTSA = toluene-4-sulphonic acid

Each reaction was run under azeotroping conditions for 105 minutes using 5.000gms of 4-phenoxybenzyl alcohol in 200.0mls of 1,2 dichloroethane and using between zero and 4.8gms of catalyst. In this series of gel experiments, sufficient reaction time was available such that each sample (with the exception of PL1242) was able to reach a value for degree of polymerisation beyond which further molecular weight growth was slow. The results substantiate the previous casual observation of the relationship between gel levels and catalyst concentration, and are graphically represented in figure 6.1.

Considering each result in turn; the blank was run to ensure that the method of measuring gel contents was appropriate. No gel was produced, though a small amount of polymerisation does occur (perhaps due to acid end groups on the reaction glassware).
Regardless of this, the lack of any gel when none would be expected indicates that the method is suitable.

PL1242 uses a catalyst to monomer ratio of 0.042 and gives an Mn approximately the same as that of the monomer. Mw, however, is large in comparison, giving a very high dispersity of 23.7. The high Mw indicates the formation of highly branched molecules, indicating crosslinking caused by formaldehyde released. Many molecules eventually form a gel, whose weight of 1.17 gms represents over 20% of the initial monomer concentration.

Subsequent oligomers in which the PTSA concentration is gradually increased shows the Mn rising and dispersity and gel quantities falling. At PL1246 no gel whatsoever is produced and a dispersity of 2.36 is reached. This reduction in the amount of gel produced could be a result of the protonation of in chain aryl ether linkages. Although protonation of these is not easy, the rise in acidity as the concentration of PTSA increased could facilitate this. The result would be a deactivation of the adjacent phenylenes, and hence a reduction in the likelihood of ortho trisubstitution, as indicated below.

\[
\begin{align*}
\ce{CH2} &\rightarrow\ce{CH2} \\
\ce{H} &\rightarrow\ce{H}
\end{align*}
\]
A further reason for the reduction in gel contents could lie in a steric argument. It is an experimental observation\textsuperscript{70} that with phenyl ether polymerisations, different ratios of 2, 6; 4 substitution occur depending upon the nature of the electrophile. For instance:

\[
\begin{align*}
\text{"CH}_2\text{O"} & \quad \rightarrow \text{Ratio } \frac{p}{o} = 3:1 \\
\text{H}^+ & \\
\text{CF}_3\text{CHO} & \rightarrow \text{Exclusively para} \\
\text{CCl}_3\text{CHO}
\end{align*}
\]

Fig 6.2

A reasonable explanation of this observation is that steric effects play an important role in determining the ratio of ortho/para substitution. It is possible to envisage how the association of the electrophile with the relatively bulky PTSA would strongly discourage 2,6 substitution in the concave side of the phenyl ether, and how only one of the 2 positions would be accessible to attack. Once one 2 substitution had occurred, it could hinder attack at the other 2 position (fig 6.3):

\[
\begin{align*}
\text{CH}_2 & \\
\text{H} & \\
\text{H} & \\
\end{align*}
\]

Fig 6.3 Steric hindrance in phenyl ether oligomers

H = hindered
Fig. 6.1: Relationship between gel quantity and C/M ratio
6.3 Polycondensation of 4-Phenoxybenzyl Alcohol [PPBA] and 4,4’ Oxybisbenzyl Alcohol [OXBBA]

Having established how gel could be controlled in a mono hydroxymethyl system, the next stage is to add a dihydroxy methyl monomer in order to synthesise an oligomer molecule with residual hydroxymethyl groups.

Gel formation will again have to be prevented, the functionality measured, and a correlation, if any, established between final number of hydroxymethyl groups per oligomer molecule and the number of these functional groups available at the start of the reaction.

6.3.1 Effect of catalyst/monomer ratio on molecular weight and gel content

A series of reactions were run under azeotroping conditions in which the volume of 1,2 dichloroethane (20mls), the number of moles of PPBA (1.96x10⁻³) and the number of moles of PTSA (2.73x10⁻³) were held constant. OXBBA concentrations were varied between 2.8x10⁻⁴ mols and 8.7x10⁻⁴ mols. Reactions were run for as long as was required to remove all monomer (analysed by GPC).

The results of these experiments are given in table 6.2.
Table 6.2 - Reaction conditions and gel quantity produced for oligomers synthesized from PPBA and OXBBA.

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>Freezing Point (°C)</th>
<th>Reaction Time (sec)</th>
<th>[OH] \text{ mol} \times 10^{-3}</th>
<th>[PTSA]</th>
<th>[OXBHA]</th>
<th>[PPBA]</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>P11273</td>
<td>73</td>
<td>6.7</td>
<td>2.73</td>
<td>0.965</td>
<td>0.096</td>
<td>0.006</td>
<td>0.00606 g. gel.</td>
</tr>
<tr>
<td>P11272</td>
<td>74</td>
<td>6.7</td>
<td>2.74</td>
<td>0.965</td>
<td>0.096</td>
<td>0.006</td>
<td>0.00606 g. gel.</td>
</tr>
<tr>
<td>P11271</td>
<td>75</td>
<td>6.7</td>
<td>2.75</td>
<td>0.965</td>
<td>0.096</td>
<td>0.006</td>
<td>0.00606 g. gel.</td>
</tr>
<tr>
<td>P11270</td>
<td>76</td>
<td>6.7</td>
<td>2.76</td>
<td>0.965</td>
<td>0.096</td>
<td>0.006</td>
<td>0.00606 g. gel.</td>
</tr>
<tr>
<td>P11269</td>
<td>77</td>
<td>6.7</td>
<td>2.77</td>
<td>0.965</td>
<td>0.096</td>
<td>0.006</td>
<td>0.00606 g. gel.</td>
</tr>
<tr>
<td>P11268</td>
<td>78</td>
<td>6.7</td>
<td>2.78</td>
<td>0.965</td>
<td>0.096</td>
<td>0.006</td>
<td>0.00606 g. gel.</td>
</tr>
<tr>
<td>P11267</td>
<td>79</td>
<td>6.7</td>
<td>2.79</td>
<td>0.965</td>
<td>0.096</td>
<td>0.006</td>
<td>0.00606 g. gel.</td>
</tr>
<tr>
<td>P11266</td>
<td>80</td>
<td>6.7</td>
<td>2.80</td>
<td>0.965</td>
<td>0.096</td>
<td>0.006</td>
<td>0.00606 g. gel.</td>
</tr>
<tr>
<td>P11265</td>
<td>81</td>
<td>6.7</td>
<td>2.81</td>
<td>0.965</td>
<td>0.096</td>
<td>0.006</td>
<td>0.00606 g. gel.</td>
</tr>
<tr>
<td>P11264</td>
<td>82</td>
<td>6.7</td>
<td>2.82</td>
<td>0.965</td>
<td>0.096</td>
<td>0.006</td>
<td>0.00606 g. gel.</td>
</tr>
<tr>
<td>P11263</td>
<td>83</td>
<td>6.7</td>
<td>2.83</td>
<td>0.965</td>
<td>0.096</td>
<td>0.006</td>
<td>0.00606 g. gel.</td>
</tr>
<tr>
<td>P11262</td>
<td>84</td>
<td>6.7</td>
<td>2.84</td>
<td>0.965</td>
<td>0.096</td>
<td>0.006</td>
<td>0.00606 g. gel.</td>
</tr>
<tr>
<td>P11261</td>
<td>85</td>
<td>6.7</td>
<td>2.85</td>
<td>0.965</td>
<td>0.096</td>
<td>0.006</td>
<td>0.00606 g. gel.</td>
</tr>
<tr>
<td>P11260</td>
<td>86</td>
<td>6.7</td>
<td>2.86</td>
<td>0.965</td>
<td>0.096</td>
<td>0.006</td>
<td>0.00606 g. gel.</td>
</tr>
</tbody>
</table>

Comments:
- Very little gel.
- Some gel resulting from solvent loss.
- Constant cone peak in GPC at M270.
- Persistent acid cat contamination.
- No extra comments.
In most cases, an immeasurably small amount of gel was produced (although it could be seen on the walls of the reaction vessel). In the two cases where [PTSA]<[Phenyl ether] a measurable amount of gel was produced, amounting to about 1% of the total monomer weight. It should be noted that PL1262-PL1267 were run until no monomer was present in the reaction solution [GPC]. PL1268-PL1273 were run at a constant time of 2 hours to achieve greater consistency. The conclusions that can be drawn are, however, identical.

The first of these experiments, PL1262, was run for 540 minutes because of a peak in the gel permeation chromatogram at an approximate Mn of 270. Because GPC molecular weights can be a little inaccurate this was at first assumed to be OXBBBA. However, "spiking" the analysis solutions with both of the monomers showed that this was not the case. By more careful calibration of the GPC at this low molecular weight end, an Mn of 260 was found to be more appropriate. It is very difficult to propose an unreactive molecule of this weight and the peak, which appeared in all these determinations remains an unexplained anomaly. However, its stability means that it is unlikely to contain hydroxyl functionality, and so would not interfere with subsequent end-group analysis.

The molecular weight measurements show that a higher molecular weight is obtained than with the all mono hydroxy functional system, and that gel control is not quite as efficient, although, as discussed above, the quantities formed are still very small. The increase in gel with reduced [PTSA]:[MONOMER] ratios is further evidence for the explanation discussed in the previous section.
The reason why gel control is less efficient, and indeed how 4,4' OXBBA polymerises at all given that both 4 positions are already substituted should be explored further.

There are fewer ways in which OXBBA can be incorporated into the growing oligomer chain than there are for PPBA because OXBBA cannot itself be attacked at a 4 or 4' position. If we consider its incorporation into the oligomer via reaction with the vacant 4' position on PPBA then an oligomer of the form shown below will be formed [6.4]

\[
\begin{align*}
\text{HOCH}_2 & \quad \text{O} & \quad \text{CH}_2 & \quad \text{O} & \quad \text{CH}_2 & \quad \text{O} & \quad \text{CH}_2 \text{OH} \\
\text{PPBA} & \quad \text{OXBBA} & \quad \text{PPBA}
\end{align*}
\]

Fig 6.4 PPBA/OXBBA Oligomers

Once this trimer has been reached, the chain can only keep growing by the formation of methylene ethers, or by 2,6 attack. Loss of formaldehyde from the methylene ether linkage would result in the methylene, but the formaldehyde would then have to go on and attack at the 2 or 6 position. Only when small concentrations of OXBBA were used relative to PPBA, could 2,6 attack be avoided. It is clear from above that one OXBBA unit per oligomer chain could be incorporated and maintain linearity. However, this would give oligomers of similar Mn to those obtained with PPBA only. This is not the case. In addition, OXBBA has already been shown to be capable of self-condensation, and so 2 or 6 attack is the only satisfactory way of explaining the continuation of reaction when the situation illustrated above has been reached.
This, at first sight, seems contrary to the argument for why gelling is prevented in the first place but, as was suggested before, one such substitution per phenyl ether residue could occur, which should not give gel formation.

If we allow this, then an oligomer formed by the self condensation of 4,4' oxybisbenzyl alcohol will be unlike the linear 4,4' linked chains resulting from 4 phenoxybenzyl alcohol, the oligomer forms somewhat of a zig-zag shape, and almost every phenyl ether unit will have at least one residual hydroxymethyl group, as shown in figure 6.5.

[6.5]

If this logic is extended to the situation with a mixture of mono and difunctional monomers, then we could envisage molecules such as shown in figure 6.6.
[6.6] is, of course, not the only permutation, (in the case of a high monofunctional:difunctional ratio linear oligomers capped by hydroxymethyl groups from the difunctional monomers are likely,) but all that needs to be recognised is that (a) gel will not be a problem and (b) residual functionality will be present.

Thus the aim of this experiment has been achieved.

6.3.2 Hydroxymethyl group content of the oligomers

These measurements were carried out as described in sections 3.2.1 and 8.3.1

Oligomers PL1245 and PL1246

These two oligomers both used 4-phenoxymethyl alcohol (PPBA) as their only monomer. The purpose of evaluating such resins was as a
double check on the hydroxyl analysis method chosen. Neither of these two oligomers showed any CH₂OH present in their \(^{13}\text{C}\) NMR spectra, nor any di-methylene ether linkage, and so chemical analysis should show that no hydroxyl groups are present, which was the case. The data are presented in table 8.3, section 8.3.1.

Within experimental errors these results confirm that the analytical method is appropriate — OH analysis and \(^{13}\text{C}\) NMR both concur. As a result other synthesised oligomers were measured in the same way.

Oligomers PL1266→PL1273
Determinations were carried out on these oligomers as indicated in sections 3.2.1 and 8.3.1. Because varying proportions of the 4,4' oxybisbenzyl alcohol (OXBBA) were used, hydroxyl functionalities may be found. PL1266 → PL1268 had longer reaction times than PL1269 → PL1273, and consequently have a lower final functionality.

The results are presented in table 6.3 below, and functionalities are quoted both as numbers of moles of OH per mole of resin, and as a "hydroxy number." The two are related by the molecular weight of the resin and the relation is:

\[
\text{Functionality(moles)} \times 56.1 = \text{OH number} \quad \frac{M_n}{\text{M}}
\]

The origin of the number lies in the "wet" analysis of such resins. After acetylation such a sample would be titrated against potassium hydroxide solution, and the OH number is a measure of the quantity of titrant needed.
The 56.1 is the molecular weight of potassium hydroxide. The advantage of the OH number over the normally quoted functionality – i.e. number of moles of a functional group per mole of resin – is that it is not affected by molecular weight, and so is a better parameter for resin to resin comparison.
<table>
<thead>
<tr>
<th>Sample no</th>
<th>Molar Ratio [OXBBA]</th>
<th>OH Functionality mgs/gm</th>
<th>OH/mol resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL1245</td>
<td>-</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>PL1246</td>
<td>-</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>PL1266</td>
<td>0.111</td>
<td>56.1</td>
<td>2.3</td>
</tr>
<tr>
<td>PL1267</td>
<td>0.222</td>
<td>79.0</td>
<td>3.5</td>
</tr>
<tr>
<td>PL1268</td>
<td>0.333</td>
<td>98.6</td>
<td>6.3</td>
</tr>
<tr>
<td>PL1269</td>
<td>0.111</td>
<td>62.0</td>
<td>3.7</td>
</tr>
<tr>
<td>PL1270</td>
<td>0.222</td>
<td>85.0</td>
<td>5.7</td>
</tr>
<tr>
<td>PL1271</td>
<td>0.222</td>
<td>86.0</td>
<td>5.9</td>
</tr>
<tr>
<td>PL1272</td>
<td>0.333</td>
<td>106.0</td>
<td>6.7</td>
</tr>
<tr>
<td>PL1273</td>
<td>0.444</td>
<td>106.0</td>
<td>9.9</td>
</tr>
<tr>
<td>Blank</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Blank</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.3: Hydroxyl functionalities of oligomers synthesised from 4 phenoxy benzyl alcohol (PPBA) and 4,4' oxybisbenzyl alcohol (OXBBA)

Toluene-4-sulphonic acid content was constant at 2.73x10⁻³ mols.

OH number = number of mgs KOH per gm of resin.
Before going on to discuss these results, it is interesting to compare them with those obtained from theory as follows.

The functionality of an oligomer, \( \overline{N}_E \) is given by:

\[
\overline{N}_E = \bar{x}_N [f_0 - 2] + 2
\]

where \( \bar{x}_N \) is the number average degree of oligomerisation, i.e. the average number of phenyl ether units in the oligomer.

\( f_0 \) is the average functionality of the initial monomer mixture.

\( f_0 \) is given by \( \sum N_i f_i / \sum N_i \)

Where \( N_i \) is the number of molecules of functionality \( f_i \). In calculating \( f_i \), it is important to remember that the positions of attack on the benzene ring are also a functional group. In the case of PPBA only oligomerisations we can assume that at sufficient acid strengths such functional groups are limited (more or less) to the 4' position. In the case of OXBBA/PPBA reactions, however, we know that this cannot be the case. If we allow for an additional ring functionality per OXBBA molecule then this does not seem unreasonable. Of course, this does not mean that only OXBBA has vacant ortho position, only that an additional ortho substitution will occur for each OXBBA molecule present.

\( \bar{x}_N \) is obtained by dividing the Mn obtained from GPC by the molecular weight of a phenoxybenzyl unit.
The functionality thus obtained also includes vacant ring positions:

In any oligomer, the functionality calculated in this way must be reduced by one in order to obtain the hydroxyl functionality.

<table>
<thead>
<tr>
<th>Resin no</th>
<th>$f_0$</th>
<th>$\bar{x}_n$</th>
<th>$\bar{N}_e$</th>
<th>$\bar{N}_e$ corrected to OH only</th>
<th>Actual $N_E$</th>
<th>Theoretical OH number, mg KOH/gm</th>
<th>Actual OH No. mg KOH/gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL1266</td>
<td>2.098</td>
<td>12.32</td>
<td>3.2</td>
<td>2.2</td>
<td>2.3</td>
<td>54.7</td>
<td>56.1</td>
</tr>
<tr>
<td>PL1267</td>
<td>2.178</td>
<td>13.7</td>
<td>4.4</td>
<td>3.4</td>
<td>3.5</td>
<td>76.0</td>
<td>79.0</td>
</tr>
<tr>
<td>PL1268</td>
<td>2.25</td>
<td>19.5</td>
<td>6.9</td>
<td>5.9</td>
<td>6.3</td>
<td>93.0</td>
<td>98.6</td>
</tr>
<tr>
<td>PL1269</td>
<td>2.098</td>
<td>18.48</td>
<td>3.8</td>
<td>2.8</td>
<td>3.7</td>
<td>46.4</td>
<td>62.0</td>
</tr>
<tr>
<td>PL1270</td>
<td>2.178</td>
<td>20.63</td>
<td>5.7</td>
<td>4.7</td>
<td>5.7</td>
<td>70.0</td>
<td>85.0</td>
</tr>
<tr>
<td>PL1271</td>
<td>2.178</td>
<td>21.15</td>
<td>5.8</td>
<td>4.8</td>
<td>5.9</td>
<td>69.0</td>
<td>86.0</td>
</tr>
<tr>
<td>PL1272</td>
<td>2.25</td>
<td>19.27</td>
<td>6.8</td>
<td>5.8</td>
<td>6.7</td>
<td>92.3</td>
<td>106</td>
</tr>
<tr>
<td>PL1273</td>
<td>2.30</td>
<td>28.65</td>
<td>10.6</td>
<td>9.6</td>
<td>9.9</td>
<td>103</td>
<td>106</td>
</tr>
</tbody>
</table>

Table 6.4 Comparison of Actual and Theoretical Functionalities, Resins PL1266→PL1273

There is reasonable agreement between the results, theoretical and actual, with the exception of PL1272, which is very high. Generally, all the actual values are higher than theory predicts; why is not immediately obvious unless there is still some problem
Fig. 6.7 Measured fn OH against monomer composition.
with the splitting of dimethylene ether linkage by the acetylation technique used for determination [see chapter 3].

Turning to consider the trend in functionality for the measured OH values there is a steady trend of increasing functionality with increasing content of the difunctional monomer, as would be expected. Again PL1272 is abnormally high, and it would seem that this result should be treated as suspect. The trend of the values against monomer ratio is shown in figure 6.7.

This result is most encouraging - although the figures seem a little high the most important feature is that increasing the proportion of dihydroxymethyl monomer in the initial reaction mixture increases the final hydroxyl functionality on the oligomer in a progressive manner. In this observation lies the key to controlling functionality at least with these model monomers in the case of hydroxyl functionality.
6.4 Polycondensation of 4 Phenoxybenzyl Alcohol with 4,4' Oxybisbenzyl Alcohol in the Presence of Acetic Acid

6.4.1 Effect of catalyst to monomer ratio on gelling

Introduction

Previous experiments in which acetic acid was a component of the solvent mixture [see chapter on $^{13}$C NMR] had suffered more difficulty with gelling than those with a solvent of dichloroethane only. Such gelling had been put down to an irreversible release of formaldehyde under these condition, but there was no reason to suppose that in this situation the measures taken to prevent gelling would be any less effective.

The results are presented in table 6.5.

<table>
<thead>
<tr>
<th>Resin No</th>
<th>OXBBA gms</th>
<th>PPBA gms</th>
<th>PTSA gms</th>
<th>Mn</th>
<th>Mw</th>
<th>Mw/Mn</th>
<th>Quantity gel gms</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL1283</td>
<td>2.70</td>
<td>3.91</td>
<td>6.00</td>
<td>4372</td>
<td>14754</td>
<td>3.38</td>
<td>0.00</td>
</tr>
<tr>
<td>PL1284</td>
<td>0.50</td>
<td>3.91</td>
<td>6.00</td>
<td>3570</td>
<td>11653</td>
<td>3.3</td>
<td>0.00</td>
</tr>
<tr>
<td>PL1285</td>
<td>1.00</td>
<td>3.91</td>
<td>6.00</td>
<td>4261</td>
<td>15063</td>
<td>3.5</td>
<td>0.00</td>
</tr>
<tr>
<td>PL1286</td>
<td>1.50</td>
<td>3.91</td>
<td>6.00</td>
<td>3726</td>
<td>14963</td>
<td>4.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 6.5 - Molecular Weight and Gel Data for Varying Quantities of OXBBA
Clearly, fulfilling the requirement for more toluene-4-sulphonic acid molecules than phenyl ether has again been successful in preventing gel formation. $M_n$ is highest with the largest quantity of OXBBA and lowest with the smallest quantity. Once again, no obvious trend is apparent with $M_w$. Dispersities are all rather high—in the region of 3-4.

6.4.2 Acetoxymethyl group content of the oligomers

To see if the control could be extended to the oligomers synthesised in the presence of acetic acid, (see section on gel control) acetate analysis was carried out in the manner described previously, i.e. using the intensity of the infra-red absorption of the acetate peak.

The results are presented in table 6.6 below

<table>
<thead>
<tr>
<th>Resin No.</th>
<th>Wt OXBBA gms</th>
<th>Wt PPBA gms</th>
<th>Wt PTSA gms</th>
<th>Mn</th>
<th>$M_w$</th>
<th>Functionality mols acetate per mole of resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL1283</td>
<td>2.70</td>
<td>3.91</td>
<td>6.00</td>
<td>4372</td>
<td>14754</td>
<td>4.0</td>
</tr>
<tr>
<td>PL1284</td>
<td>0.50</td>
<td>3.91</td>
<td>6.00</td>
<td>3570</td>
<td>11653</td>
<td>0.65</td>
</tr>
<tr>
<td>PL1285</td>
<td>1.00</td>
<td>3.91</td>
<td>6.00</td>
<td>4261</td>
<td>15063</td>
<td>1.4</td>
</tr>
<tr>
<td>PL1286</td>
<td>1.50</td>
<td>3.91</td>
<td>6.00</td>
<td>3726</td>
<td>14936</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 6.6 Acetate functionalities in resins PL1283→PL1286

These functionalities are plotted out as a function of the ratio of the two monomers, figure 6.8. Again, functionality steadily
Fig. 6.8: Acetate functionality against monomer composition
increases with an increasing weight percentage of 4,4' oxybisbenzyl alcohol.

6.5 Conclusions

From the results for these two sets of oligomers - OH and acetate functional - it seems reasonable to conclude that functionality control is possible within these model systems. Of course, the industrial situation is far more complex, but nevertheless an extension of these ideas and results could be attempted.
7.1 Introduction

When this project was started, a kinetic approach was conceived as being the definitive way, in association with qualitative methods of determining reaction mechanisms precisely. That is, not only the species that are present but also the rates of which they are formed and react. In the event however, and as will now be described, this proved to be too difficult, and, as with so many previous attempts to use the kinetics of aromatic - formaldehyde reactions in this way, the hope foundered.

The basic method proposed for measuring the kinetics was to withdraw homogeneous samples from the reaction mixture at equal intervals, isolate the polymeric produce and subject it to molecular weight analysis to determine the progress of the reaction with time. The first experiments carried out in these investigations were to establish the appropriate reaction conditions for the kinetic measurement method used. That is, the reaction had to be slow enough to allow sufficient aliquots to be taken from the reaction mixture to enable a profile of the reaction's progress to be produced. At the same time it had to be sufficiently swift such that the experiment would take no more than a few hours to react all the monomers.

Subsequently, the kinetic method was gradually refined until very little variation in the reaction parameters occurred, either during an experiment, or from analysis to analysis (see sections 8.2.1,
8.2.5 and chapter 3 for full descriptions). Consequently, consistent results became possible, allowing legitimate comparison of different reactions to be made.

7.2 Reactions with 3-Phenoxybenzyl Alcohol

3-phenoxybenzyl alcohol (MPBA) was subjected to kinetic analysis during oligomer reactions run in which:

(a) The initial concentration of monomer and acid catalyst (Para toluene sulphonic acid, PTSA) was kept constant at 0.01 moldm$^{-3}$ to observe consistency of results. [Experiments PL3220, PL3223, PL3224 and PL3225]

(b) The concentration of MPBA was varied whilst catalyst levels were kept constant at 0.01moldm$^{-3}$. [Experiments PL3235, PL3237 and PL3238].

The results are tabulated below (table 7.1). Table 7.2 shows the conditions used in each reaction.
<table>
<thead>
<tr>
<th>SAMPLE NO</th>
<th>TIME ELAPSED secs</th>
<th>[MPBA] mols</th>
<th>SAMPLE NO</th>
<th>TIME ELAPSED secs</th>
<th>[MPBA] mols x 10^-3</th>
<th>SAMPLE NO</th>
<th>TIME ELAPSED secs</th>
<th>[MPBA] mols x 10^-4</th>
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</thead>
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</tbody>
</table>

Table 7.1 Kinetic data for depletion of 3-phenoxybenzyl alcohol [MPBA] during oligomerisation

<table>
<thead>
<tr>
<th>SAMPLE NO</th>
<th>TIME ELAPSED secs</th>
<th>[MPBA] mols x 10^-4</th>
</tr>
</thead>
<tbody>
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<td>0.4</td>
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<td>9</td>
<td>4800</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>5460</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 7.2 Concentration of PTSA and MPBA used for reactions in table 7.1
Fig. 7.1: consistency curves for reaction of 3-phenoxybenzyl alcohol
The concentration versus time plots for the consistency experiments as above) are shown in Fig 7.1. All the curves are characterised by an initial sharp, parabolic decline before a uniform straight line depletion sets in. Average rate of reaction was 1.72 \times 10^{-6} \text{moldm}^3\text{s}^{-1} (calculated from the slope of the curves in 7.1), and the similarity in the plots indicates that the experimental technique is consistent. The uniform decrease in concentration with time led to the conclusion that (although first order behaviour was expected), pseudo zeroth order seems to occur. It was speculated that this could be due to the rate of formation of the phenoxybenzyl cation being much slower than the rate of conversion of the cation to higher molecular weight materials.

To check that zeroth order was definitely being observed, a set of experiments were undertaken in which the initial monomer concentration was varied whilst maintaining the same catalyst concentration (b, above). If rate of reaction is truly independant of the monomer concentration then the same rates of reaction should be observed as before, ie 1.72\times10^{-6} \text{moldm}^3\text{s}^{-1}.

The data, [see tables 7.1 and 7.2] when plotted out in figures 7.2-7.4 shows curves of the same characteristic shape but also that rates alter with the varying monomer concentration - the values are summarised in table 7.3 below.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Rate constant [\text{moldm}^3\text{s}^{-1}]</th>
<th>[MPBA]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average of PL3220, PL3223, PL3224, PL3225.</td>
<td>1.72\times10^{-6}</td>
<td>0.015</td>
</tr>
<tr>
<td>PL3235 (average of 2 expts)</td>
<td>3.35\times10^{-6}</td>
<td>0.003</td>
</tr>
<tr>
<td>PL3237 (average of 2 expts)</td>
<td>6.5 \times 10^{-7}</td>
<td>0.0003</td>
</tr>
<tr>
<td>PL3238 (average of 2 expts)</td>
<td>2.6\times10^{-7}</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

Table 7.3 Variation of rate with concentration of MPBA
Fig. 7.2:
Concn./time plot for PL3235
Fig. 7.3: 
Concentration/time plot PL3237

[MPBA] (1E-4)

0 1 2 3 4 5 6

0 5 10 15 20 25 30 35

t, secs (Thousands)
Fig. 7.4: Concentration/time plot PL3238
This anomaly, namely depletion curves that are mainly straight lines indicating apparently no dependance on monomer concentration, when such a dependance is found to exist seemed to be an insoluble problem. To aid in unravelling it a full theoretical kinetic analysis was undertaken. The mechanism used is rather simpler than that shown to be the case by $^{13}$C NMR studies, but nevertheless contains all the important features of the complete picture.

**Mechanism of the oligomerisation of 3-phenoxybenzyl alcohol**

\[ M = \text{Chain terminator} \]

**Definitions**

\[ \begin{align*}
\text{Ar} &= C_6H_5OC_6H_5 \\
D_1 &= \text{ArCH}_2\text{OCH}_2\text{Ar} \quad (3,3 \text{ substitution}) \\
D_2 &= \text{ArCH}_2\text{ArCH}_2\text{OH} \quad (3,4' \text{ substitution}) \\
T &= \text{ArCH}_2\text{ArCH}_2\text{ArCH}_2\text{OH} \quad (3,4' \text{ substitution}) \\
Q_1 &= \text{ArCH}_2\text{ArCH}_2\text{ArCH}_2\text{OH} \quad (3,4' \text{ substitution}) \\
Q_2 &= \text{ArCH}_2\text{ArCH}_2\text{ArCH}_2\text{OH} \quad (\text{Di substituted ring - } 4',2')
\end{align*} \]

\[ \begin{align*}
\text{(i)} & \quad \text{H}^+ + \text{ArCH}_2\text{OH} \xrightarrow{k_1} + \text{ArCH}_2 + \text{H}_2\text{O} \\
\text{(ii)} & \quad \text{ArCH}_2 + \text{H}_2\text{O} \xrightarrow{k_2} \text{ArCH}_2\text{OH} + \text{H}^+ \\
\text{(iii)} & \quad \text{ArCH}_2 + \text{ArCH}_2\text{OH} \xrightarrow{k_3} \text{ArCH}_2\text{OCH}_2\text{Ar} \quad (\text{=}D_1) + \text{H}^+ \\
\text{(iv)} & \quad D_1 + \text{H}^+ \xrightarrow{k_4} D_1\text{H}^+ \\
\text{(v)} & \quad D_1\text{H}^+ \xrightarrow{k_5} \text{ArCH}_2 + \text{ArCH}_2\text{OH} \\
\text{(vi)} & \quad \text{ArCH}_2 + \text{ArCH}_2\text{OH} \xrightarrow{k_6} \text{ArCH}_2\text{ArCH}_2\text{OH} \quad (\text{=}D_2) + \text{H}^+ \\
\text{(vii)} & \quad D_2 + \text{ArCH}_2 \xrightarrow{k_7} D_2\text{CH}_2\text{Ar} \quad [\text{=}T] + \text{H}^+ \\
\text{(viii)} & \quad T + \text{ArCH}_2\text{OH} \xrightarrow{k_8} \text{ArCH}_2\text{ArCH}_2\text{ArCH}_2\text{OH} \quad [\text{=}Q_1] + \text{H}^+
\end{align*} \]
Whilst there are many more possible reactions, this mechanism includes all possible reactions in the early stages of the reaction, and all the major ones later in the reaction.

**Kinetic Analysis**

**Assumptions:**
(i) \([\text{ArCH}_2]\) has a steady state (ss) concentration.
(ii) Creation is positive.
(iii) Chain terminator \(\text{M}\) may be a low level impurity or catalyst.

\[
\frac{d[\text{ArCH}_2^*]}{dt} = k_1[H^+][\text{ArCH}_2\text{OH}] + k_5[D_1][H^+] - k_2[\text{ArCH}_2^*][H_2O] - k_3[\text{ArCH}_2^*][\text{ArCH}_2\text{OH}] - k_6[\text{ArCH}_2^*][\text{ArCH}_2\text{OH}] - k_7[D_2][\text{ArCH}_2^*] - k_8[T][\text{ArCH}_2^*] - k_9[T][\text{ArCH}_2^*] - k_{10}[\text{ArCH}_2^*][\text{M}]
\]

But at equilibrium \(\frac{d[\text{ArCH}_2^*]}{dt} = 0\)

\[
=> k_1[H^+][\text{ArCH}_2\text{OH}] + k_5[D_1][H^+] = [\text{ArCH}_2^*] \{ k_2[H_2O] + (k_3+k_6)[\text{ArCH}_2\text{OH}] + k_7[D_2] + (k_8+k_9)[T] + k_{10}[\text{M}] \}
\]

\[
=> [\text{ArCH}_2] = \frac{k_1[H^+][\text{ArCH}_2\text{OH}] + k_5[D_1][H^+]}{k_2[H_2O] + (k_3+k_6)[\text{ArCH}_2\text{OH}] + k_7[D_2] + (k_8+k_9)[T] + k_{10}[\text{M}]}
\]
If the denominator is denoted as \( N \) then
\[
[\text{ArCH}_2] = \frac{k_1[H^+][\text{ArCH}_2\text{OH}] + k_6[D_1][H^+]}{N}
\]

Now: \( d[\text{ArCH}_2\text{OH}] \) is given by:
\[
dt[\text{ArCH}_2\text{OH}] = k_2[\text{ArCH}_2][\text{H}_2\text{O}] + k_1[D_1][H^+] - k_3[\text{ArCH}_2\text{OH}][\text{ArCH}_2]
\]
\[
- k_6[\text{ArCH}_2\text{OH}][\text{ArCH}_2] - k_4[\text{ArCH}_2\text{OH}][H^+] - k_1[\text{ArCH}_2\text{OH}]
\]

\[=> d[\text{ArCH}_2\text{OH}] = [\text{ArCH}_2](k_2[H_2O] - (k_3 + k_6)[\text{ArCH}_2\text{OH}] + [H^+](k_4[D_1] - k_1[\text{ArCH}_2\text{OH}])
\]

Substituting for \( [\text{ArCH}_2] \) gives:
\[
d[\text{ArCH}_2\text{OH}] =
\]
\[
\frac{(k_1[H^+][\text{ArCH}_2\text{OH}] + k_4[D_1][H^+])(k_2[H_2O] - (k_3 + k_6)[\text{ArCH}_2\text{OH}])}{k_6}[H^+](k_4[D_1] - k_1[\text{ArCH}_2\text{OH}])
\]

This is the full equation. By common sense it is possible to say that certain concentrations will be negligible at particular times in the reaction. Furthermore, GPC measurements can be used to determine approximately the relative importance of other concentrations at various times. Table 7.4 opposite shows the level of \( D \) and all other oligomeric products with time for four of the hydroxymethyl oligomers, expressed as percentages of the total oligomeric product. The data obtained from the integration of the molecular weight profiles are plotted out for PL3224 on figure 7.5.
Fig 7.5: Percentage ratios of oligomeric reaction products

- Concentration vs. time (t, secs x 10)
- Graph showing changes in concentration over time for monomer, dimer, and polymer.
Table 7.4

<table>
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<th>TIME secs</th>
<th>M</th>
<th>D</th>
<th>P</th>
</tr>
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<td>0</td>
<td>0</td>
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<td>86</td>
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</tr>
<tr>
<td>5440</td>
<td>21</td>
<td>23</td>
<td>56</td>
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</tbody>
</table>

Percentage ratios of: 3-phenoxy benzyl alcohol [M] : Combined isomers of phenoxy benzyl ether [D] : all other polymeric products [P]

In the first 30 seconds of reaction there will be little water produced. Theoretically water should not play a part in the analysis at all, because of the azeotroping technique. However, as is discussed later there were doubts as to how efficient the process is, and so its presence is taken into account. Regardless of this, its concentration in the first 30 seconds will be negligible when compared to that of the monomer, and so the \( H_2O \) term may be dropped.

Also of negligible concentration at this stage will be \( D_1, D_2, T \) and \( CH_3O \).

If we operate under very clean conditions and using the absence of sulphonate ester resonances in the NMR we can also claim that \( M \) is too small to take into account.
So we have:

\[ [\text{H}_2\text{O}] = [D_1] = [D_2] = [T] = [M] \ll [\text{ArCH}_2\text{OH}] \]

Thus:

\[
\frac{d[\text{ArCH}_2\text{OH}]}{dt} = -k_1[H^+][\text{ArCH}_2\text{OH}] - \frac{k_1(k_3 + k_4)[\text{ArCH}_2\text{OH}][H^+]}{[k_3 + k_4][\text{ArCH}_2\text{OH}]} \\
\Rightarrow d[\text{ArCH}_2\text{OH}] = -2k_1[\text{ArCH}_2\text{OH}][H^+] 
\]

i.e. first order in both acid catalyst concentration and monomer concentration.

Between t=30 and t=1500 seconds, \( D_1 \) constitutes more than 10% of the products, and the water concentration could also be significant, depending upon the azeotroping efficiency. A rather more complex equation is now relevant therefore, as follows:

\[
d[\text{ArCH}_2\text{OH}] = k_1[H^+][\text{ArCH}_2\text{OH}][k_2[H_2O] - (k_3 + k_4)[\text{ArCH}_2\text{OH}]] \\
+ [H^+][k_4[D_1] - k_1[\text{ArCH}_2\text{OH}]]
\]

From this equation it is clear that the appearance of the methylene ether bridged dimer slows down the rate of depletion. Any water present will have the same effect. The result of this is that the curve on the monomer depletion/time plot will be raised, or straightened, as shown below (fig 7.6).
This is exactly what is observed, and it appears to be appropriate.

The hypothesis can be partially tested. Although we cannot produce a situation in which (a) no methylene ether is formed and (b) all water produced is instantaneously removed, we can do the opposite. By adding water to the initial reaction mixture, it should be possible to produce a complete straight line plot, providing that azeotroping is also dispensed with.

The results of such a test is shown in table 7.5, as an average over 3 experiments. The amount of water added was chosen to be approximately a 10% excess over the amount produced during the curved part of the plot – approximately 40% depletion.

<table>
<thead>
<tr>
<th>Sample No.PL3240</th>
<th>t, secs.</th>
<th>[MPBA] mols</th>
</tr>
</thead>
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<td>0.0 3</td>
</tr>
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<td>60</td>
<td>0.0 276</td>
</tr>
<tr>
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<td>300</td>
<td>0.0 27</td>
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<td>0.0 186</td>
</tr>
<tr>
<td>10</td>
<td>4800</td>
<td>0.0 168</td>
</tr>
</tbody>
</table>

Table 7.5 – Rate of consumption MPBA in aqueous solution without azeotroping.
Fig 7.7 concentration/time plot for MPBA without azeotroping
The results are plotted out on figure 7.7. The graph is a uniformly straight line, which is predicted by the hypothesis above.

So it would seem reasonable to conclude that the reaction of 3-phenoxybenzyl alcohol to give a methylene bridged oligomer is first order in the alcohol, but that reaction byproducts and intermediates alter the kinetic equation to give a much more complicated form.

7.3 Reaction of 4-Phenoxybenzyl Alcohol in the Presence of Acetic Acid

Further kinetic studies have been made on the reaction of 4-phenoxybenzyl alcohol (PPBA) in the presence of a solvent containing 10% acetic acid. A constant concentration of PPBA (0.15molar) was used, whilst the catalyst concentration was varied between 0.053m and 0.315molar. The initial esterification is very rapid, and if we assume instantaneous conversion of alcohol to acetate then the ester concentration can be determined in the same way as for the alcohol, using GPC. The results are presented in table 7.6 and plotted out on figure 7.8.
Fig 7.8 Concentration/Time Curves for PPBA in the Presence of Acetic Acid
### Table 7.6: Affect of Catalyst Concentration on Rate in Acetate Functionalised Oligomers

<table>
<thead>
<tr>
<th>Catalyst Concentration</th>
<th>Rate (Moles x 10^-3)</th>
<th>Reaction Time (Secs)</th>
</tr>
</thead>
<tbody>
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<td>0.60</td>
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<tr>
<td>2.50</td>
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<tr>
<td>3.00</td>
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<td>10</td>
</tr>
<tr>
<td>4.00</td>
<td>0.10</td>
<td>10</td>
</tr>
</tbody>
</table>

Summary of Conditions: Resin [TPSA]
It is clear here that the kinetics are yet more complicated than in the case of the alcohol only system. A number of different reactions (eg esterification as well as oligomerisation) are operating in unison and simultaneously, and unless their rate constants are very different so as to produce a clear rate determining step, then the rate curves will not show a definite order. As an example, most of the curves have been plotted as concentration versus time (appropriate for order zero) and also as log concentration versus time (appropriate for first order) Fig. 7.9. From these it is clear that the order is not zero, but neither can it be claimed that it is first order. PL1223 was plotted out as the reciprocal concentration versus time to examine the possibility of 2nd order (figure 7.10), but it is clearly very difficult to choose between first or second order kinetics. Trying to rationalise these, it is easier to understand the second order option because this is probably due to esterification, which will be manifesting itself in the first part of the curve. Esterification here is fast and so could be expected to be the dominating factor in any kinetic equation at this stage.

However, in our opinion this is not a suitable explanation for the whole curve - the majority of the esterification occurs too quickly. In addition, the first order curves seem marginally more appropriate. First order kinetics are more difficult to explain, than when observed in the solvent of dichlorethane only. If we consider the first few stages in the reaction:

(i) \[ \text{ArCH}_2\text{OH} + \text{CH}_3\text{CO}_2\text{H} \xrightarrow{\text{H}^+} \text{ArCH}_2\text{CO}_2\text{CH}_3 + \text{H}_2\text{O} \]
FIG. 7.9. LOG CONCENTRATION/TIME CURVES FOR PPBA IN THE PRESENCE OF ACETIC ACID
Fig 7.10: Reciprocal concn./time plot for PL1223
(ii) \[ \text{ArCH}_2\text{CO}_2\text{CH}_3 \leftrightarrow \text{ArCH}_2^+ + \text{CH}_3\text{CO}_2\text{H} \]

(iii) \[ \text{ArCH}_2 + \text{ArCH}_2\text{CO}_2\text{CH}_3 \rightarrow \text{ArCH}_2\text{Ar} \ldots \text{etc} \]

The crucial reaction is probably reaction (ii) where the reaction by-product (acetic acid) could again be complicating otherwise simple kinetics. In a way, the reaction is similar to that run in aqueous solution mentioned previously, where water was produced as well as being present at the start. Here acetic acid is produced from ester in forming the cation as well as being in the solution.

If the two situations were exactly comparable, we should observe a straight line depletion curve. However, this is not the case, and probably indicates that it is step (iii) (which would probably be first order) that is the rds. Unfortunately, it is not overwhelmingly so, hence the complicated depletion curves.

Kinetic analysis of the acetate can also, therefore, be said to have revealed very little about the mechanism.

7.4 Conclusions

A reasonably plausible explanation has been advanced for the apparently anomalous behaviour of the depletion curve of 3-phenoxybenzyl alcohol in pure dichloroethane, and a more tenuous explanation for the behaviour observed in dichloroethane/acetic acid.

Whilst an explanation has been advanced, the kinetics have proved to be too complex to aid in understanding the mechanistic processes occurring.
CHAPTER 8, EXPERIMENTAL

8.1 Monomer Synthesis

8.1.1 Phenoxybenzyl alcohols

2-Phenoxybenzyl Alcohol

300ccs of previously distilled 1,4 dioxan and 0.5 grams of lithium aluminium hydride [LiAlH₄] were vigorously mixed with an air driven stirrer for thirty minutes to ensure complete dryness of the 1,4 dioxan. A further 9.5gms of LiAlH₄ were then added and the whole slurried together for a further thirty minutes.

50gms of dry ortho phenoxybenzoic acid were then added as a solution in 350mls dry 1,4 dioxan dropwise. No reaction occurs at first, but after approximately 120mls have been added, an exotherm occurs, which must be controlled by rapid stirring and an ice bath. Once the exotherm has subsided, steady addition of the acid solution maintains a reaction temperature of approximately 50°C. Once addition is complete, steady stirring is undertaken for a further 60 minutes allowing the reaction temperature to subside to room temperature. Excess LiAlH₄ is then destroyed by the very careful dropwise addition of just sufficient ice-cold water, ensuring good venting of hydrogen produced and keeping the flask at room temperature with an ice bath. The grey sludge produced is then filtered off from the solvent at the tap with a number two sinter, and repeated if necessary to clarify the solution. The solution is then dried with 5A molecular sieve and the dioxan stripped on the rotary evaporator at 50°C to yield a clear, viscous liquid.
The grey sludge is then repeatedly extracted with chloroform, to yield more of the viscous liquid, and these fractions combined and purified by vacuum distillation:

Yield 43.9g (94%)

Boiling Point: 128.1-8°C lit value  127.5-8°C

Analysis: Calc % C : 77.96 Found % C : 78.34
Calc % H : 6.05 Found % H : 6.05
Calc % O : 15.99 Found % O : 15.61

'H NMR : 2.68ppm [OH]
       : 4.78ppm [CH₂]
       : 6.84-7.6ppm [Aromatic hydrogens]

Carbon-13 NMR data have already been reported [Section 5.2.1].

IR 3600cm⁻¹(s) Free OH.
3460cm⁻¹(a) weak intermolecular H-bond.
1035cm⁻¹  C-O (alcohol) stretch.
3-Phenoxybenzyl Alcohol

This compound is supplied by Aldrich at 98% purity. This was purified by distillation to 100%.

Boiling point \text{1.0mmHg} 133.0^\circ \text{C} \ [\text{Lit b.pt} \text{1.2mmHg} 134^\circ \text{C}]

Analysis:

\begin{align*}
\text{Calc} \ % \ C & : 77.96 & \text{Found} \ % \ C & : 78.45 \\
\text{Calc} \ % \ O & : 15.99 & \text{Found} \ % \ O & : 15.45 \\
\text{Calc} \ % \ H & : 6.05 & \text{Found} \ % \ H & : 6.10 \\
\end{align*}

\text{H NMR} \ 2.2\text{ppm} \ [\text{OH}]

\begin{align*}
4.6\text{ppm} \ [\text{CH}_2] \\
6.8\text{ppm} \to 7.5\text{ppm} \ [\text{Aromatic hydrogens}] \\
\end{align*}

See section 5.2.1 for \text{\textsuperscript{13}} \text{C NMR data}

\text{IR:} \ 3600\text{cm}^{-1}(s) : \text{Free OH}

\begin{align*}
3460\text{cm}^{-1}(m) : \text{Intermolecular H-bond (weak)} \\
1035\text{cm}^{-1}(m) : \text{C-O alcohol stretch} \\
\end{align*}

4 Phenoxybenzyl Alcohol

This is synthesised via phenoxytoluene, which is oxidised to phenoxybenzoic acid and then reduced to phenoxybenzyl alcohol.
Synthesis of 4-Phenoxytoluene\textsuperscript{71}

A three necked flask, fitted with an air stirrer, reflux condenser and thermometer was charged with 116gms of phenol and 68gms of powdered potassium hydroxide. They were dissolved in 350mls of dimethylsulphoxide [DMSO] under a nitrogen atmosphere and stirred overnight. The mixture was then steadily heated on an oil bath until distillation commenced. Heating was continued until the still-head temperature reached 145°C, when the solution was cooled to allow a still-head temperature of 120°C. 211gms of para-bromo-toluene dissolved in 50mls of DMSO were then added in a single batch, followed by 1.0gm of powdered copper (I) oxide. Reaction temperature immediately rose to give a still-head temperature of 150°C, which was maintained without heating until the initial exotherm had passed. Reaction at 150°C was continued for 24 hours. The mixture was then cooled, filtered and poured into two litres of cold water, and then extracted with five batches of 150ml of chloroform. The extracts were combined, washed with water, dried with 5A molecular sieve and the solvent removed on the rotary evaporator. The residue was then distilled at 18mm pressure, collecting the fraction boiling at between 128°C and 155°C. This fraction was then redistilled at 23mmHg, the fraction collected being at a still-head temperature of 142.3-144°C. The product was confirmed by 'H NMR, using the methyl peak at 2.2ppm. Yield:57.4gms

Oxidation of 4-Phenoxytoluene to 4-Phenoxybenzoic Acid

The 57.4gms of para phenoxy toluene from above, 48mls of pyridine and 80 mls of distilled water were heated on an oil bath at 100°C, and 138gms of potassium manganate (VII) were added in portions over two hours. Heating was maintained for a further ninety minutes
before the warm solution was filtered and acidified with dilute hydrochloric acid. This gave a white precipitate which was filtered, water washed and dried. This was recrystallised from methanol and thoroughly dried at 70°C in a vacuum oven at 0.1mmHG for 48 hours. The acid was confirmed by infra red (absorption at 1690cm⁻¹). Yield:51.5gms. Melting point 159-+160°C (lit melting point 160°C)₁³.

Reduction of 4 Phenoxybenzoic Acid

This reduction can be carried out as for the ortho isomer, but the exotherm in the case of the para isomer proved to be too dangerous. Experiments with different solvents eventually showed diethylether [sodium dried] to be the safest, reaction then proceeds slowly. The procedure is as follows:

A thoroughly dried three necked two litre flask with reflux condenser, air stirrer, dropping funnel and thermocouple for a digital thermometer was flushed with nitrogen for five minutes to remove the residual moisture. 300mls of sodium dried diethyl ether and 0.5gms of fresh lithium aluminium hydride [LiAlH₄] were then introduced (some effervescence) and stirred for 15 minutes (to remove any remaining water) before a further 9.5gms of fresh LiAlH₄ were added. A slurry of 50gms of 4 phenoxybenzoic acid was then prepared in 400mls of sodium dried ether, and constantly stirred during the course of the reaction (The acid is barely soluble in ether, and must be added as a slurry). Addition is carried out by transferring sufficiently small amounts in suspension to the dropping funnel, thus preventing the clogging of the funnel. Addition should be completed in one hour, a rate sufficient to
maintain reflux. Stirring is then continued for a further hour before bringing the solution to reflux for 24 hours.

On cooling, any LiAlH₄ residues are carefully destroyed with ice cold water, maintaining a low temperature in the reaction vessel with an ice cold bath. The grey sludge is then filtered off at the tap with a number 2 sinter, until a clear solution is obtained. This is transferred to a separatory funnel to allow separation from any residual water, and the ether is then stripped on the rotary evaporator at 30°C, to give a white crystalline solid.

As for the ortho isomer, the sludge is repeatedly extracted with chloroform, which is then dried, and taken off on the rotary evaporator at 50°C to give more white crystalline product.

The fractions are combined and recrystallised from aqueous methanol to give white needles. Yield: 42gms (90%).

Melting point: 53.5-54°C [Lit melting point 54-55°C]

Analysis: Calc % C : 77.96   Found % C : 77.54
Calc % H : 6.05     Found % H : 5.98
Calc % O : 15.99    Found % O : 16.28

'H NMR : 1.78ppm - OH
4.20ppm - CH₂
7.02-7.50ppm - [Aromatic Hydrogens]

See 5.2.1 for ¹³C NMR data
Attempts to produce this compound by direct reduction of 4,4' oxybisbenzoic acid were unsuccessful: solubility of the acid in even 1,4 dioxan is so low that yields were in the 5% region, even after prolonged refluxing of the reaction mixture. On this basis, the methyl ester was first synthesised, and then reduced.

10mls of concentrated sulphuric acid were dissolved in 100mls of ice cold methanol with vigorous stirring. 10gms of 4,4' oxybisbenzoic acid in 15mls of methanol were then gradually added, and the mixture refluxed on an oil bath for 1 hour. During this time the ester precipitates out as fine white crystals. These are filtered off, dissolved in chloroform, and washed with water to neutral. The product was dried in the oven at 70°C for 48 hours at a pressure of 0.1mmHg. Product confirmed by CH₃ peak at 3.9ppm in the 'H NMR spectrum. Yield : 10 gms (88%).

Reduction of the Ester

To 70mls of dry tetrahydrofuran (THF) in a one litre flask fitted with an air stirrer, reflux condenser, dropping funnel and thermocouple for a digital thermometer was added 0.5gms of fresh LiAlH₄ and the mixture stirred for ten minutes to ensure the solvent was dry. A further 2.5gms of LiAlH₄ were then added and the solution stirred for a further 30 minutes. A slurry of 4,4' oxybisbenzyl methanoate (10gms) in 150mls of dry THF were then added using the same procedures as for the reduction of 4 phenoxybenzoic acid. On completing the addition the mixture was stirred for a further thirty minutes, before bringing to reflux.
for 24 hours. After cooling, water was very carefully added to destroy residual LiAlH₄, whilst cooling the flask in an ice bath. The sludge was filtered off and extracted with five 100ml portions of chloroform, the fractions collected together and dried with 5A molecular sieve. The solvent was then removed on the rotary evaporator to yield a white solid. The THF layer filtered off from the sludge was also dried with 5A molecular sieve and the solvent similarly removed.

Product recrystallised from aqueous methanol. Yield : 8.0gms (97%)
mpt 131.2°C (Lit ¹ 131.5 → 132°C)

Analysis

<table>
<thead>
<tr>
<th>Found %</th>
<th>Calc %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C : 73.14</td>
<td>73.01</td>
</tr>
<tr>
<td>H : 6.17</td>
<td>6.13</td>
</tr>
<tr>
<td>O : 20.69</td>
<td>20.85</td>
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</table>

'H NMR

4.05ppm [OH]
4.60ppm [CH₂]
6.85→7.45 [Aromatic, symmetric arrangement of four peaks characteristic of 4,4' substituted bis aromatics]
8.1.2 Phenoxybenzyl acetates

Synthesis of All Isomers

0.1 moles of phenoxybenzyl alcohol (20gms) were placed in a two-necked flask, (previously flushed with nitrogen) with 13.5mls of acetic anhydride and 150mls of dry pyridine. These were magnetically stirred for 18 hours under a nitrogen atmosphere. Addition of 250mls of water precipitates the white ester, and the mixture was extracted with 4x100mls of diethyl ether. The combined ether extracts were then acidified with dilute hydrochloric acid, the ether layer separated, and then made alkaline with one tenth normal sodium hydroxide. The layers were again separated, and the ether removed at 30°C on the rotary evaporator. The crude product was then distilled. Yield: 22.9gms (95%).

Boiling points: 2 phenoxybenzyl acetate : 150°C 1 mmHg
3 phenoxybenzyl acetate : 140°C 1 mmHg
4 phenoxybenzyl acetate : 185°C 1 mmHg

<table>
<thead>
<tr>
<th>Analysis:</th>
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<th>H</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found, % 2</td>
<td>74.93</td>
<td>5.64</td>
<td>19.44</td>
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<td>3</td>
<td>74.65</td>
<td>5.88</td>
<td>19.47</td>
</tr>
<tr>
<td>4</td>
<td>74.61</td>
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<tr>
<td>Calc %</td>
<td>74.35</td>
<td>5.83</td>
<td>19.83</td>
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'\text{H NMR}

\begin{center}
\begin{tabular}{|c|c|c|c|}
\hline
& O & CH$_2$ & Aromatic protons \\
\hline
O-C-CH$_3$ & 2.12ppm & 5.25ppm & 7.05-7.55ppm \\
\hline
C & 3.12ppm & 5.15ppm & 7.0-7.54ppm \\
\hline
O & 4.05ppm & 5.05ppm & 6.85-7.4 ppm \\
\hline
\end{tabular}
\end{center}

See section 5.2.1 for $^{13}$C NMR data

\text{Infra Red (Neat Film)}

1745cm$^{-1}$(s) C=O

1380cm$^{-1}$(s) C-C=CH$_3$

8.1.3 \text{Phenoxybenzyl methyl ether}

\text{All Isomers}

0.1 moles (16gms) of the required isomers of phenoxybenzyl alcohol and 1gm of benzyl-tri-n-butyl ammonium chloride were dissolved in a two phase mixture containing 40mls of methylene chloride and 20.8mls 50% aqueous sodium hydroxide and the whole very vigorously stirred for 25 minutes, after which 27mls (0.18 moles) of dimethyl sulphate [care, suspected carcinogen] were added, dropwise, keeping the temperature below 45°C (to avoid destruction of the catalyst). Stirring was maintained for a further 150 minutes, before adding 3.0mls of 0.91 ammonia solution and stirring for a further 20 minutes to destroy any residual dimethyl sulphate. The mixture was then poured into water and the organic layer separated from the aqueous, washed and separated again and dried with 5A molecular sieve. The solvent was then removed on the rotary evaporator at 30°C to yield the ether, purified by distillation. Yield: 15.9gms.
Boiling points: 2 - phenoxybenzyl methyl ether: 121.5° 10mmHg
3 - phenoxybenzyl methyl ether: 125.0° 10mmHg
4 - phenoxybenzyl methyl ether: 132.0° 10mmHg

Analysis:

<table>
<thead>
<tr>
<th></th>
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<th>O</th>
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<tr>
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<td>78.77</td>
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<td>14.67</td>
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<tr>
<td>Found %</td>
<td>78.96</td>
<td>6.56</td>
<td>14.48</td>
</tr>
<tr>
<td>4</td>
<td>78.66</td>
<td>6.59</td>
<td>14.94</td>
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<tr>
<td>Calc %</td>
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<td>6.59</td>
<td>14.95</td>
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</tbody>
</table>

'\text{H NMR}

<table>
<thead>
<tr>
<th></th>
<th>\text{OCH}_3</th>
<th>\text{CH}_3</th>
<th>\text{Aromatic}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.36ppm</td>
<td>4.50ppm</td>
<td>6.57-7.55ppm</td>
</tr>
<tr>
<td>Isomer</td>
<td>3.35ppm</td>
<td>4.40ppm</td>
<td>6.75-7.50ppm</td>
</tr>
<tr>
<td>4</td>
<td>3.35ppm</td>
<td>4.38ppm</td>
<td>6.8-7.4 ppm</td>
</tr>
</tbody>
</table>

See section 5.2.1 for $^{13}$C NMR data

\text{Infra Red}

\text{C-H stretch from methyl at 2825 cm}^{-1} (m)

8.2 Synthesis of Oligomers Used in Investigations

8.2.1 General Work up procedure

Work up of the isolated polymer samples is identical in all cases. The sample is washed with 2N ammonia solution, separated and washed again with distilled water. The organic layer is again separated and the solvent stripped to dryness on the Buchi at 40°C.

8.2.2 Molecular weight determinations

Acetate functionalised oligomers - PL1220, PL1221, PL1222, PL1223, PL1224, PL1225.

80mls of 1,2 dichloroethane, 10mls of acetic acid and the required
quantity of para toluene sulphonic acid (between 1 and 6gms) were refluxed together for 30 minutes in 250ml flask. To this was added 3 gms of 4-phenoxybenzyl alcohol in 10 mls of 1,2 dichloroethane. This solution was preheated to 70°C and added via syringe through a rubber suba seal. Reflux was re-established within a minute at 83.6°C and samples were withdrawn by syringe at the intervals discussed previously. Work-up was as indicated in 8.2.1.

Hydroxymethyl functionalised oligomer PL1229, PL1230, PL1231 90 mls of 1,2 dichloroethane and the required quantity of para toluene sulphonic acid (between 0.019gms and 1.9gms) were refluxed together for 30 minutes in a 250ml flask. To this was added 3gms of 4-phenoxybenzyl alcohol in 10mls of 1,2 dichloroethane. This solution is preheated to 70°C and added via a syringe through a rubber "Suba" seal. Reflux was re-established within a minute at 82.9°C, and samples withdrawn by syringe through the "Suba" seal at the time intervals previously discussed. Work-up was as indicated in 8.2.1.

Polymerisation of 4,4' oxybisbenzyl alcohol

0.220gms of para toluene sulphonic acid were refluxed in 30mls of 1,2 dichloroethane for 30 minutes. A slurry of 0.220gms of 4,4' oxybisbenzyl alcohol in 5mls of 1,2 dichloroethane were then added and the reaction run at reflux for one hour. Samples were taken at 35 minutes and 60 minutes for GPC analysis. Each sample was worked up as described in 8.2.1.
8.2.3 Carbon 13 NMR studies

3-Phenoxybenzyl alcohol

25mls of 1,2 dichloroethane in which were dissolved 3gms of para toluene sulphonic acid were brought to reflux at 82.9°C for 30 minutes before the addition of a solution of 6gms 3-phenoxybenzyl alcohol in 5mls of 1,2 dichloroethane using a syringe through a rubber "Suba" seal. Aliquots were then withdrawn by syringe at the intervals previously discussed. Work-up was as indicated in 8.2.1.

4-Phenoxybenzyl alcohol (PL1208)

A solution of 5gms para toluene sulphonic acid in 950mls of 1,2 dichloroethane was brought to reflux for 30 minutes in a two litre flask. A solution of 25gms 4-phenoxybenzyl alcohol in 50mls of 1,2 dichloroethane was warmed to 70°C before being added by syringe through a "Suba" seal to the acid solution refluxing at 82.9°C. Aliquots were then withdrawn as discussed previously. Work-up was as indicated in 8.2.1.

4-Phenoxybenzyl alcohol/acetic acid (PL1219)

A solution of 60gms para toluene sulphonic acid in 850mls of 1,2 dichloroethane and 100mls of acetic acid was brought to reflux for thirty minutes in a two litre flask. A solution of 23.5gms of 4-phenoxybenzyl alcohol in 50mls of 1,2 dichloroethane, previously heated to 70°C was then added by syringe via the "Suba" seal. Equilibrium was quickly re-established at 83.6°C and samples were withdrawn at the time intervals discussed previously. Work-up was as indicated in 8.2.1.
8.2.4 Gel determinations and functional group content

Gel determinations PL1242 - PL1246

A 500ml flask was thoroughly cleaned with methylene chloride, acetone and water before being rinsed with concentrated nitric acid. This was followed by a wash in the detergent bath and rinsing with water and acetone before drying in the vacuum oven at 80°C and 1mmHg pressure for ten minutes. In addition, a number 3 sinter funnel was washed with methylene chloride, acetone, detergent, water and finally acetone again before drying at 80°C and 1mmHg pressure.

The required weight of para toluene sulphonic acid was then dissolved in 180.0mls of 1,2 dichloroethane and brought to reflux at 82.9°C, 5.00gms of 4-phenoxybenzyl alcohol were then dissolved in 20.0mls of 1,2 dichloroethane and this solution added to the reaction vessel. Reaction was then continued for 105 minutes for samples PL1242 to PL1246. Gel permeation chromatography on a small sample withdrawn at thirty minute intervals was used to check that there was no residual monomer after 90 minutes reaction time.

The contents of the flask were then passed through the previously weighed sinter. The flask was well washed out with chloroform, acetone and water, and the filtrate was well washed with these solvents as well. The gel in the funnel was sucked dry, and the funnel transferred to the vacuum oven where it was thoroughly dried for one hour at 80°C and 1mmHg. Once the sinter had cooled it was weighed and the gel content deduced by subtracting the weight of the clean funnel.
The mother liquor was washed with 2M ammonia solution and then twice with distilled water before being dried with 5A sieve, and the solvent removed on the rotary evaporator. The resin was dried at 40°C and 1mmHg pressure, and set aside for subsequent hydroxyl group analysis.

Gel determinations: PL1262 - PL1268

The same procedures were followed for cleaning the apparatus as were used in the gel determination for oligomers PL1242 - PL1246. 0.4510gms of para toluene sulphonie acid were dissolved in 18.0mls of 1,2 dichloroethane and the solution refluxed for 30 minutes before the addition of a slurry 0.390gms 4-phenoxybenzyl alcohol and the desired amount of 4,4' oxybisbenzyl alcohol in 2.0 mls of 1,2 dichloroethane. A slurry rather than a solution was used because of the low solubility of the monomers at this concentration and room temperature. Reaction was carried out until aliquots withdrawn for GPC analysis showed no residual monomer present. The actual period of reaction for PL1263 - 68 is considerably longer than is necessary to remove all monomer by reaction. This is because the reaction was checked for absence of monomer by taking two GPC samples. As each one takes 20 minutes to execute, the absence of monomer was confirmed some 40 minutes after it had occurred. The reaction was then stopped, and any gel formed collected by filtering on the sinter funnel as for the 4-phenoxybenzyl alcohol above. The mother liquor was washed with 2M ammonia solution and twice with distilled water before drying the organic fraction with a grade 5A molecular sieve. The solvent was then removed on the rotary evaporator at 40°C and the resin dried in the vacuum oven at 40°C and 1mmHg pressure before being set aside for hydroxyl group analysis.
Exactly the same procedure was followed as with PL1262 - PL1267, except that a constant reaction time of 150 minutes was used. Each sample was checked to ensure that there was no residual monomer remaining.

Gel determinations with mixed monomers and an acetic acid/1.2 dichloroethane solvent: PL1283 - PL1286

Again, all glassware was cleaned as for PL1242 - PL1246 determinations. 6.00gms of para toluene sulphonic acid, 70mLs of 1,2 dichloroethane and 10mLs of acetic acid were refluxed together for 30 minutes. A solution of 3.910gms of 4-phenoxybenzyl alcohol and the required amount of 4,4' oxybisbenzyl alcohol (between 0.500 gms and 2.700gms) was added to this and the reaction brought back to reflux at 83.6°C for one hour. Reaction was then stopped and the reaction contents passed through the previously prepared sinter to ascertain the weight of any gel as before. The solution was then washed with 2M ammonia solution and twice with distilled water before drying the organic layer with 5A molecular sieve. The solvent was then removed on the rotary evaporator at 40°C and the resin dried at 40°C and 1mmHg pressure.
<table>
<thead>
<tr>
<th>Expt No.</th>
<th>(OXBBA)</th>
<th>Reaction Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gms</td>
<td>mols</td>
</tr>
<tr>
<td>PL1262</td>
<td>0.15</td>
<td>6.52 x 10^{-4}</td>
</tr>
<tr>
<td>PL1263</td>
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<td>8.7 x 10^{-4}</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>PL1267</td>
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<td>PL1273</td>
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<td>8.7 x 10^{-4}</td>
</tr>
</tbody>
</table>

Table 8.1 Chemical Data for polymers of para phenoxy benzyl alcohol (PPBA) and dihydroxymethyl phenyl ether (OXBBA)

Conditions fixed are: Concentration PPBA = 0.391g, 1.956 x 10^{-3} moles
Concentration para toluene sulphonic acid = 0.451g, 2.374 moles
Reaction carried out in 20 ccs, 1,2 dichloroethane at reflux (83.6°C) with azeotroping

Table 8.1 contains experimental values for the hydroxyl determinations
8.2.5 Kinetic studies

Kinetic studies followed the standard reaction procedure described before. The quantities utilised are described below in Table 8.2.

<table>
<thead>
<tr>
<th>EXPT NO</th>
<th>MONOMER</th>
<th>AMOUNT</th>
<th>AMOUNT</th>
<th>SOLVENT VOLUME (mls)</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL-X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3220</td>
<td>3-PPBA</td>
<td>3.000</td>
<td>1.900</td>
<td>-</td>
<td>100.0</td>
</tr>
<tr>
<td>3223</td>
<td>3-PPBA</td>
<td>3.000</td>
<td>1.900</td>
<td>-</td>
<td>100.0</td>
</tr>
<tr>
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<td>3-PPBA</td>
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<td>1.900</td>
<td>-</td>
<td>100.0</td>
</tr>
<tr>
<td>3225</td>
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<td>1.900</td>
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<td>1220</td>
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<td>90.0</td>
<td>No azeotroping</td>
</tr>
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<td>90.0</td>
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<tr>
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<td>10.0</td>
<td>90.0</td>
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</tr>
<tr>
<td>1225</td>
<td>4-PPBA</td>
<td>3.000</td>
<td>10.0</td>
<td>90.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 8.2 Experimental conditions used in kinetic studies.

8.3 Analytical Procedures

8.3.1 Hydroxyl and acetate analysis

Hydroxyl analysis was carried out according to the American Society Testing Materials Standards (ASTMS) test number E222-B as follows.
Method (1) - Using Perchloric Acid

The sample is acetylated at room temperature with a solution of acetic anhydride and perchloric acid in 1,2 dichloroethane. The excess reagent is hydrolysed with aqueous DMF-pyridine and the resulting acetic acid is titrated with standard NaOH solution. The OH value is calculated by the difference between the blank and the sample solutions.

Acetyling reagent - a 1 m solution of acetic anhydride in 1,2 dichloroethane with perchloric acid (0.15N). Made up of 3 mls 72% perchloric acid, 27.5 mls acetic anhydride and 219.5 mls 1,2 dichloroethane.

Aqueous DMF-Pyridine - Mix water, DMF and pyridine 1:6:3.
Indicator - mixture of 0.1% methanolic thymol blue and cresol red (neutralised) in the ratio 3:1.

Titrant - methanolic sodium hydroxide [0.5N]. From BDH, standardised against 0.5N HCl.

All chemicals BDH "Analar".

Add 20 mls of the acetylating reagent to 0.5 gms sample, and also two blanks. Stopper the flasks, swirl until resin dissolved and leave for exactly 30 minutes. Add 35 mls aqueous DMF-pyridine, leave to stand 10 minutes. Add 0.5 mls indicator and titrate immediately.
To calculate the OH number:

\[
\text{Hydroxyl no.} = \frac{[(A-B) \times N_t \times 56.1]}{W}
\]

- **A** = Vol. solution required for blank.
- **B** = Vol. solution for sample
- **N_t** = Normality of titrant : **W** = weight resin used.

To correct for free acid contamination: To 20 mls 1,2 dichloroethane add 35 mls aqueous DMF-pyridine, add 1 ml indicator and titrate. To this add 0.5 gms sample, mix and re-titrate. Calculate the correction by using:

\[
(A-B) = \text{Vol. used in second titration}
\]

- **N_t** = Normality
- **W** = Weight of sample

Method 2, Using Para Toluene Sulphonic Acid at 50°C is as follows:

Acetylating reagent: 2m in acetic anhydride. Contains 14.4g PTSA, 360 mls 1,2-dichloroethane and 120 mls acetic anhydride. Hydrolysing solution - aqueous pyridine containing pyridine:water at ratio 3:1.

Indicator - as for first method.
Weigh the quantity of resin (typically 0.5g) used. Add 5 mls of the acetylating reagent. Record the weight of this. Do the same for two blanks. Swirl the flasks (stoppered) to dissolve the resin and place in a water bath at 50°C ± 1°C. Raise the stopper to release excess pressure and leave for 20 minutes. Remove the flask. Add 2.0 mls water and shake thoroughly. Add 10.0 mls aqueous pyridine, swirl and leave for 5 minutes. Add 1.0 ml indicator and titrate against methanolic NaOH [0.5].

Calculate the hydroxyl value from:

\[
\frac{T_c \times E_t - T_t \times N \times 56.1}{E_c W}
\]

Where

- \( T_c \) = vol. used for blank titration
- \( T_t \) = vol. used for sample titration
- \( E_c \) = Wt. acetylating reagent used in blank
- \( E_t \) = Wt. acetylating reagent used in sample
- \( W \) = Weight of resin

Correct for free acid as before.

Experimental determinations were carried out using the quantities detailed in table 8.3.
<table>
<thead>
<tr>
<th>Sample no</th>
<th>Wt PPBA gms</th>
<th>Wt OXBBA gms</th>
<th>Molar Ratio [OXBBA]</th>
<th>Wt Resin used in determination gms</th>
<th>Et gms</th>
<th>Vol0.56N used mls</th>
<th>OH functionality mgs/gm mol resin</th>
<th>OH/mol</th>
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</thead>
<tbody>
<tr>
<td>Blank</td>
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<td>-</td>
<td>-</td>
<td>0.500</td>
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<td>4.76</td>
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<td>4.76</td>
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<td>PL1246b</td>
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<td>0.500</td>
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</tbody>
</table>

Table 8.3: Hydroxyl functionalities of oligomers synthesised from 4 phenoxy benzyl alcohol (PPBA) and 4.4' oxybisbenxyl alcohol (OXBBA).

Toluene-4-sulphonic acid content was constant at 2.73x10\(^{-3}\) mols. \(E_t\) = weight of acetylation solution used.

OH number = number of mgs KOH per gm of resin.
Acetate Analysis

Oligomer acetate functionality was measured by infra red [IR] in the absorption mode. The absorption of the ester band at 1735cm\(^{-1}\) relative to that of chloroform at 2402cm\(^{-1}\) was measured. Calibration curves were then used to calculate the acetate functionality.

To check the reproducibility of the method whilst varying the functional group attached to the acetate two calibration curves [fig 8.1] were constructed for ethyl acetate and benzyl acetate. Their similarity was taken as an indication that phenoxybenzyl acetate could be used to calibrate the IR for the measurement of the concentration of acetate functionality in phenyl ether oligomers. The calibration curve is shown in figure 8.2.

Samples were prepared as dilute solutions in chloroform

All measurements were carried out on a Perkin Elmer 983G continuous wave infra red spectrometer.
Fig. 8.1 IR Calibration curves for benzyl acetate and ethyl acetate

[absorption C=O]

---

**gms acetate/ml of CHCl₃ soln. x10**

- Ethyl acetate
- Benzyl acetate
Fig. 8.2: Calibration curve for para phenoxybenzyl acetate

(absorption C=O)
8.3.2 Calibration of the GPC

The GPC was calibrated using 2\% (by weight) solutions of polystyrene of varying molecular weights. Each sample (supplied by Polymer Labs) has a narrow dispersity and hence closely defined Mn and Mw. For the very low molecular weight end (where many of the studies were carried out) phenyl ether and phenoxy benzyl alcohol were used.

GPC's were carried out on a fully automated equipment from Waters. Columns were of the "Ultrastyragel" type using pore sizes of 100\Å or 500\Å depending on the molecular weights of interest. Rate of solvent flow was 0.8 mls a minute, using an in column time of 15 minutes maximum.

8.3.3 'H and $^{13}$C NMR

Proton NMR was carried out on a Hitachi Perkin Elmer 60MHz machine with deuterochloroform as the solvent in 5mm OD tubes and tetramethylsilane (TMS) as a reference.

Carbon-13 NMR was carried out on a Jeol GX400 machine. Although there was occasional variation in the operating conditions those described below are typical.
<table>
<thead>
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<th>Instrument</th>
<th>JOEL GX400</th>
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</thead>
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<tr>
<td>Operating Frequency</td>
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</tr>
<tr>
<td>Spectral Width</td>
<td>25KHz 250ppm</td>
</tr>
<tr>
<td>Accumulations</td>
<td>Typically 1800</td>
</tr>
<tr>
<td>Pulse Width/Flip angle</td>
<td>4.7 usec 45 deg</td>
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<tr>
<td>Data Points</td>
<td>32K Acquired Zero filled to 64K</td>
</tr>
<tr>
<td>Repetition rate</td>
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</tr>
<tr>
<td>Solvent</td>
<td>CDCL3 (+d6 DMSO if required)</td>
</tr>
<tr>
<td>Tube O D</td>
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</tr>
<tr>
<td>Sample Volume</td>
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</tr>
<tr>
<td>Concentration</td>
<td>ca 100 - 200mg/ml</td>
</tr>
<tr>
<td>Experiment Type</td>
<td>Single Pulse Quadrature Detection</td>
</tr>
<tr>
<td>Proton Decoupling</td>
<td>Broad Band Pulsed</td>
</tr>
<tr>
<td>Temperature</td>
<td>Ambient (ca 23°C)</td>
</tr>
<tr>
<td>Reference</td>
<td>TMS (0ppm) or CDCL3 (77ppm)</td>
</tr>
<tr>
<td>Line Broadening</td>
<td>1Hz</td>
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</table>
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