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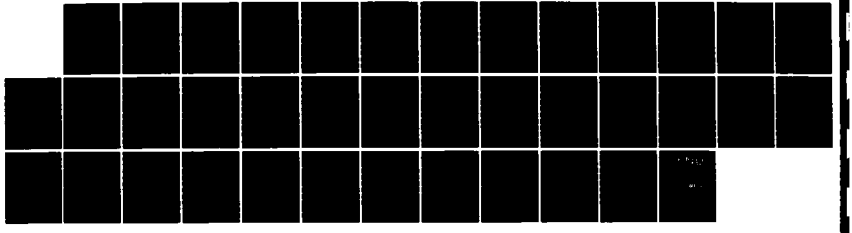

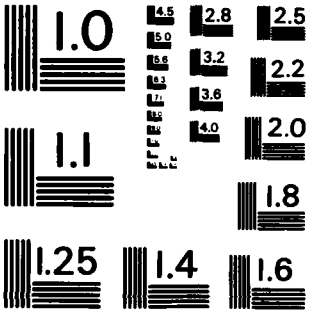

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SYNTHESIS OF HYDROPHOBIC, CROSSLINKABLE RESINS

SECOND ANNUAL REPORT

by

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THE SYNTHESIS OF HYDROPHOBIC, CROSSLINKABLE RESINS.

ABSTRACT.

This is the second annual report of progress in the synthesis of organic, crosslinkable polymers of low water absorption, for use as matrix materials in fiber composites and / or as coatings or adhesives. The approach has been to synthesize low molecular weight, chloromethyl terminated polyethers by the reaction of any of a number of bisphenols with the para or meta isomers of dichloroxylene. Various reaction conditions are described, and the polymers thus produced are discussed briefly.

The chloromethyl ends have in one case been converted to vinyl groups by the Wittig reaction, and the resultant unsaturated polymer crosslinked by heat alone without peroxide. Some properties of the crosslinked polymer have been briefly explored, and the low equilibrium water uptake of the product confirmed.

Further improvements are necessary in the control of molecular weight distribution and crosslink density before attention turns to fabrication and mechanical property determination. Original for Supplied Keywords Included

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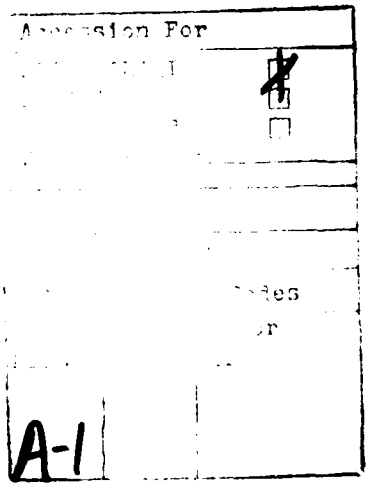
KEYWORDS.

Thermosetting, resin, matrix, moisture, water, synthesis, unsaturation, free radical, characterization, crosslinking.



CONTENTS.

SYNTHESIS OF HYDROPHOBIC CROSSLINKABLE RESINS.

Contract Number DAJA 45-84-C-0016.

AIM.

The project is concerned with the synthesis and evaluation of crosslinkable resins of low water absorption. It is intended that the resins should be suitable as organic matrix materials for high performance composites, but in addition the possibility of their application as coatings or structural adhesives has to be considered.

1.INTRODUCTION.

The previous annual report (December 1984) consisted mainly of a wide ranging literature survey covering the years from January 1974 to December 1983, and including references on new hydrophobic thermosets, crosslinking reactions, and hydrophobic polymer systems in general. In addition a brief outline of the intended synthetic route and preliminary experimental results were included.

The report outlined our objective, which was to produce polymers free of hydrophilic groups, with low equilibrium water absorption levels, thus resisting those hygrothermal degradation processes (whether physical or chemical), which cause lowering of modulus and Tg, hydrolysis, internal cracking, leaching etc.

The polymer would need the following characteristics :

1.A largely hydrocarbon backbone.

2.A low molecular weight for ease of fiber impregnation.

3.Mainchain stiffening groups .

4.No hydrophilic groups or volatile formation during cure.

5.No water soluble residues in the final product.

It was decided to utilise free radical curing reactions as this is a well established technology.

The conclusion of the literature survey was that the Wittig reaction was the most promising choice for producing unsaturated polymers, and two experimental procedures were outlined:

1.Condensation of excess α,α' dichloro p xylene (DCpX) with bisphenol A (BPA) and conversion of the resultant

chloromethyl polymers to vinyl polymers by the Wittig reaction.

2. Reaction of the mixed diphosphonium salts of DCpX and α, α′dichloro-m-xylene (DCmX) with terephthalaldehyde.

This second report concentrates on procedure 1, and modifications of it. It was thought that this procedure had more potential than procedure 2, which was hampered by the limited availability of any other suitable monomers, which would be required if the properties of the network were to be changed. Procedure 1, in which the Wittig reaction is used to introduce terminal styrene type unsaturation, could produce a wide range of new polymers, both di and polyfunctional, from commercially available reagents.

The scheme has resulted in a novel crosslinkable polymer, which has been characterised by a variety of techniques, and which cures rapidly on heating to produce a network polymer with extremely low equilibrium water uptake figures. A number of other chloromethyl polymers have been produced by using different bisphenols, and some polyfunctional systems are under review.

The literature survey has been updated to include some important new papers, and a variety of experimental details are included.

2. LITERATURE SURVEY: AN UPDATE .

Since the last annual report, the literature survey has been extended and updated.

A very important series of papers, closely related to the present work, has been published by Percec and Auman from Case Western Reserve University. Hydroxyl terminated polyether sulphones of varying number average molecular weight (Mn) were produced by reacting various ratios of the disodium salt of BPA with bis (4, chlorophenyl) sulphone (BCPS) [1]. These were then end capped quantitatively, under phase transfer conditions, with the commercially available m/p isomer mix of chloromethyl styrene, to produce vinyl terminated polyether sulphones, (see Fig. 1) which could be cured rapidly by heating [2].

In an extension of this work, a hydroxyl-terminated polyether sulphone was end capped with benzyl chloride, and then chloromethylated using 4,chloro butyl chloromethyl ether and stannic chloride in 1,1,2,2 tetrachloroethane. The chloromethyl groups were then converted to vinyl groups by the Wittig reaction, using triphenyl phosphine in 1,4 dioxane to produce the phosphonium salt, followed by a phase transfer reaction with aqueous formaldehyde for the final conversion (see Fig. 2). No hydrolysis of the phosphonium salts was

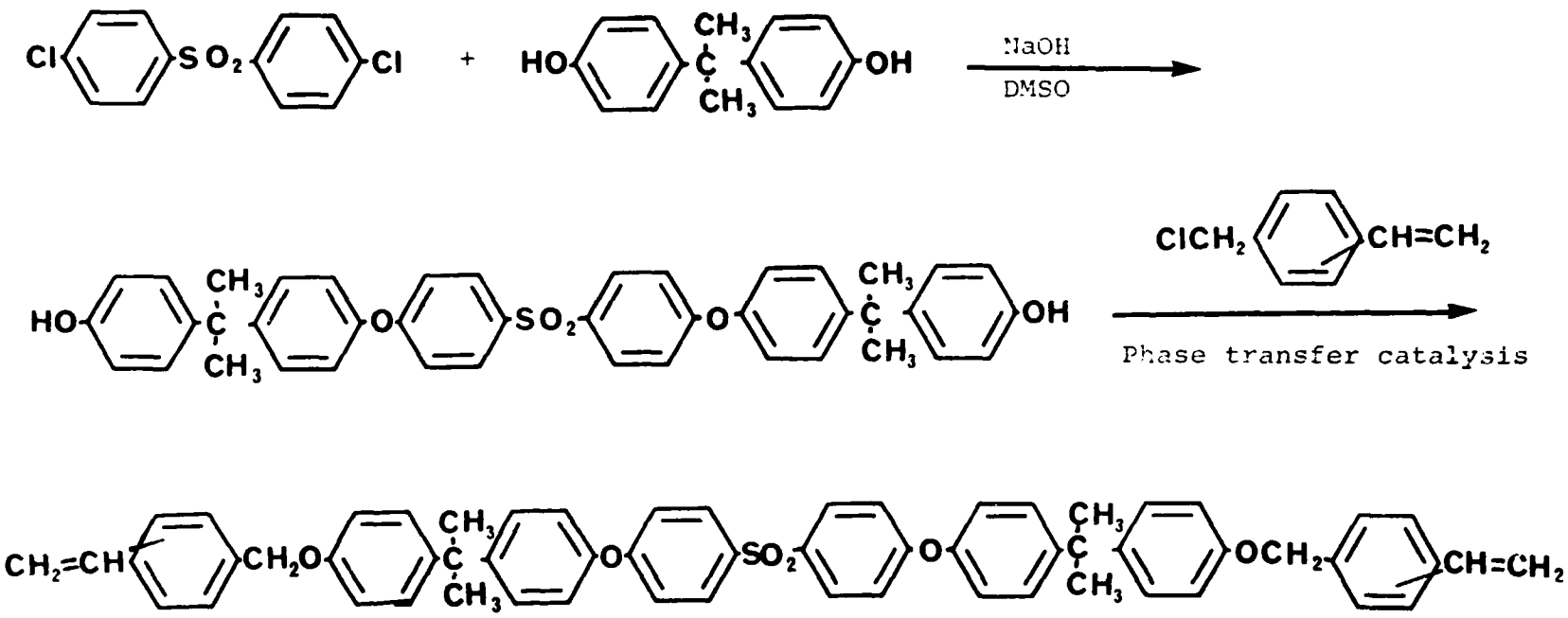


Fig 1. Synthesis of vinyl terminated polyether sulphones using m- and p- chloromethyl styrene.

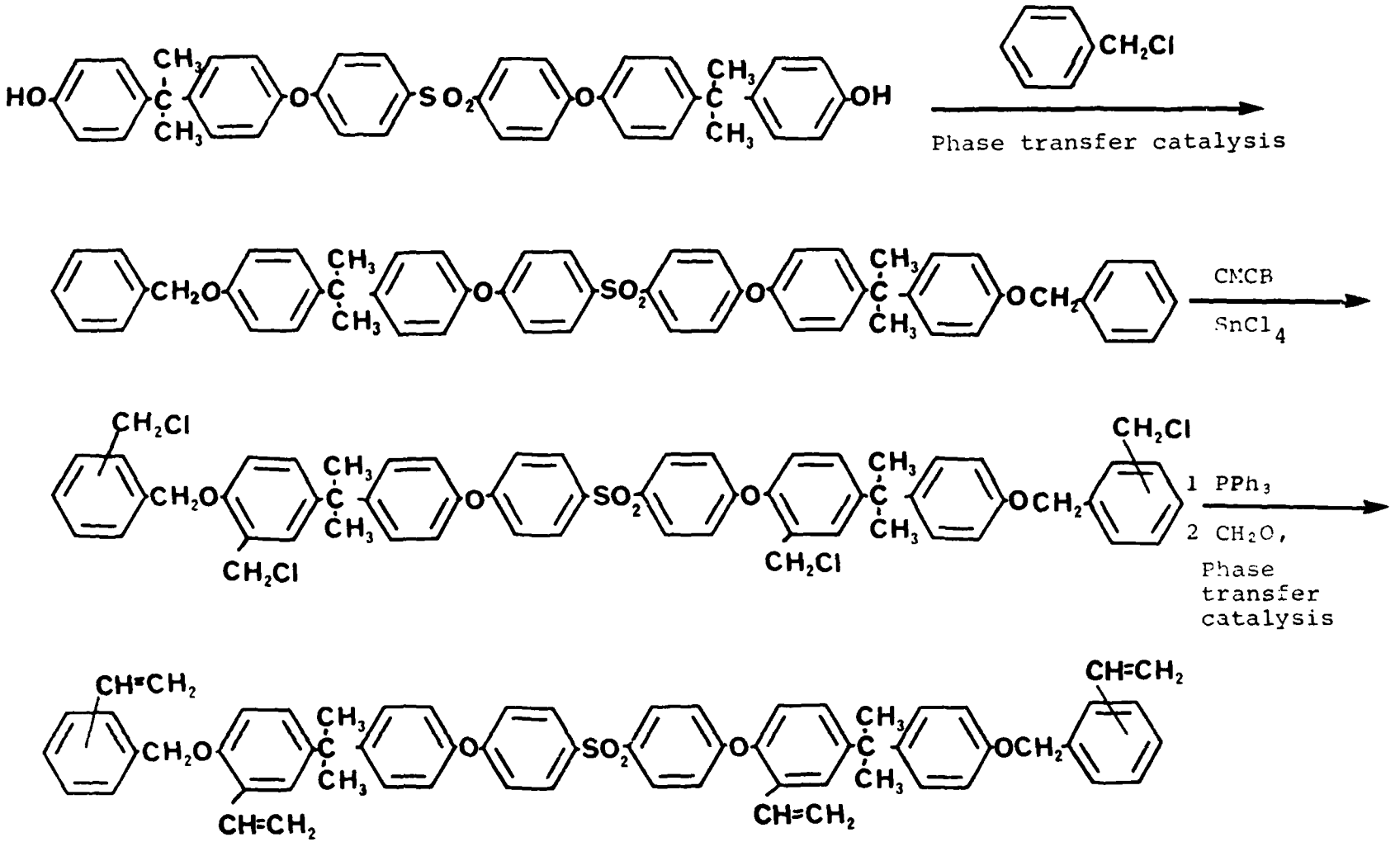


Fig. 2. Synthesis of polyether sulphones with pendant vinyl groups

Note 1. CMCB : (Chloromethyl) 4-chlorobutyl ether

observed [3]. Also detailed in the same paper was the bromination of the methyl side groups in a commercial sample of poly (oxy-2,6 -dimethyl -1,4-phenylene)(POP) using bromine in refluxing 1,1,2,2 tetra chloroethane, and the conversion of the product to the vinyl derivative by the Wittig reaction. A sample of POP was also chloromethylated and then converted to the vinyl derivative.

The polyether sulphones, with pendant vinyl groups as prepared above, were brominated with bromine in dichloromethane, and the dibromo products dehydrobrominated. This was again carried out under phase tranfer conditions to give the corresponding acetylene terminated polymers. The vinyl terminated polymers were found to cure much faster than the acetylene terminated polymers, and to give much more flexible networks. This was because the vinyl groups formed flexible aliphatic type units, while the acetylene groups formed very rigid polyphenylacetylene type units.

A further paper [4] concerned the synthesis of linear vinyl and acetylene terminated polyether sulphones, and again noted the much faster cure of the vinyl systems. A review of the new polymers with terminal or pendant styrene groups has now been published [5].

The concept of thermosetting polymers with terminal unsaturation is not new. The vinyl ester resins have been commercially available [6] for many years, and can be crosslinked with or without the normal styrene reactive diluent. The resins are more resistant to hydrolysis than unsaturated polyester resins but as they contain hydrophilic ester groups they were not mentioned in our earlier literature survey.

The papers published by Percec and Auman are the only references in the literature to thermosetting polymers containing styrene type unsaturation, except for the synthesis of a divinyl benzil end-capped phenylquinoxaline oligomer [7] as reported in the literature survey in the 1984 annual report.

Imai and Yamazaki [8] reported the phase transfer catalysed condensation of DCpX using the system THF-DMSO/50% aqueous NaOH/ benzyl triethyl ammonium chloride (BTEAC) which produced bright yellow, insoluble, infusible polymers. They were presumed to be poly (p-xylylidene), with some evidence for alpha chloro-p-xylylene units. When DCpX was used, the products were insoluble in common organic solvents, but if the ortho or meta isomers were used, the products of the reaction were soluble in N-methyl-2-pyrrolydone.

Phase transfer catalysed condensation of BPA and DCpX (1:2) using high base concentrations was attempted in this laboratory, but bright yellow, insoluble polymers were also produced.

3. DISCUSSION OF CURRENT PROGRESS.

3.1 POLYMERS BASED ON BPA and DCpX.

BPA has been reacted with DCpX to produce low molecular weight chloromethyl terminated polymers. Methods include :

1.Heating BPA, DCpX and potassium carbonate in dimethyl acetamide (see section 4.1).

2.Heating the disodium salt of BPA with DCpX in dimethyl formamide (DMF) (see section 4.2).

3.Phase transfer reactions (see section 4.3).

Methods 1 and 2 have proved the most effective, though both show signs of side reactions. These result in unidentified peaks in some of the products of method 2. Although method 1 is simple and convenient, it can result in bright yellow, insoluble and infusible products if the reaction is continued too long. The patent for high molecular weight polyaralkyl ethers by Kaufmann [9] notes that some solvent systems produce partially crosslinked products, but no explanation is offered. A variety of reactions are possible between bisphenols and DCpX, depending on the conditions. Xylylidene formation has been reported under basic conditions [8, 10] while certain bisphenols (notably resorcinol) are so reactive to DCpX that Friedel Crafts reactions will occur in the absence of the normal catalysts [11].

The phase transfer type of reaction is inhibited, because if high base concentrations are used then xylylidene formation is a competitive reaction, and at low base concentrations the DMSO is present mainly in the aqueous phase, and so cannot promote the reaction, which occurs in the organic phase.

Despite the problems noted above, suitable polymers have been produced, and method 3 has been adopted as the standard procedure. A 2:1 ratio of DCpX to BPA is used, and as expected this produces a range of low molecular weight polymers of the general structure as shown in Fig. 3, with some residual DCpX. The crude mixture, a portion precipitated with methanol from chloroform, and a portion soluble in the solvent mixture have been separated by gel permeation chromatography. The first oligomer is soluble in the methanolic portion, but the majority of it is precipitated out, along with some of the DCpX. These observations are supported by the NMR spectra.

HPLC, with THF/water mixtures as the mobile phase has

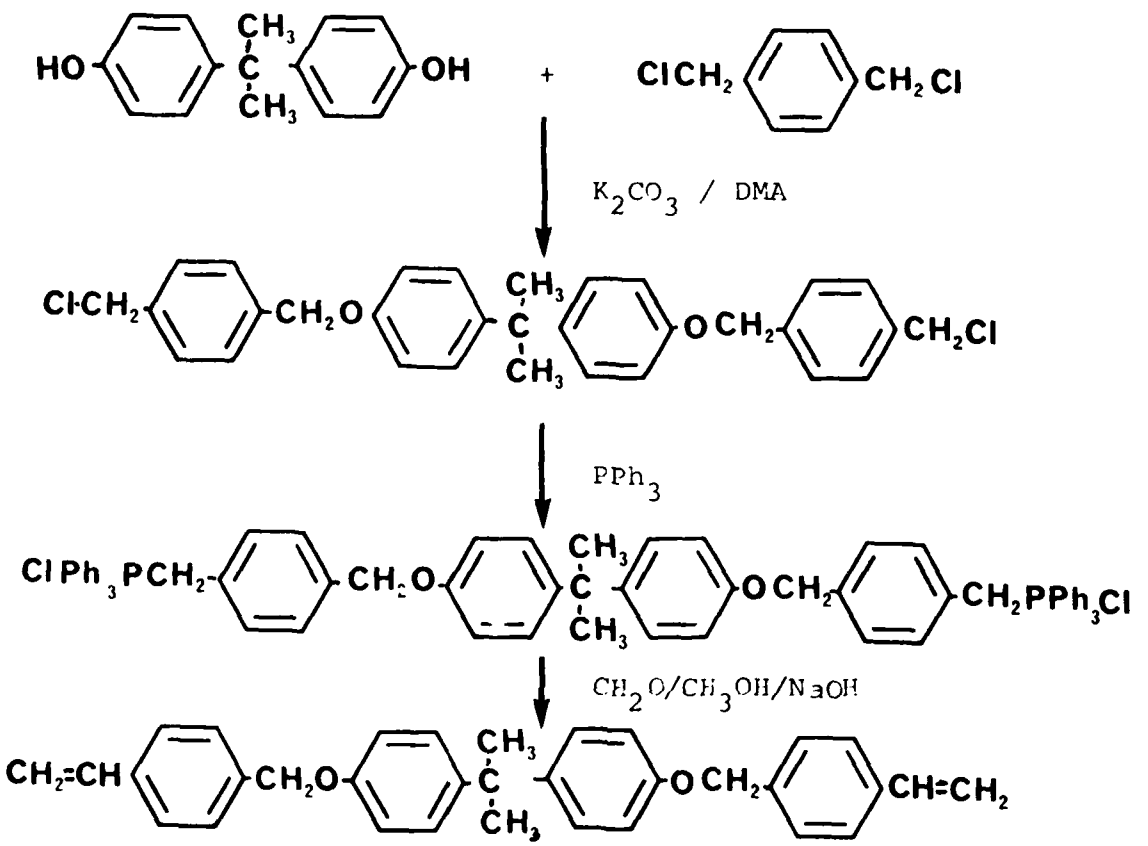


Fig. 3. Vinyl terminated polyethers from BPA and DCpX using the Wittig reaction.

been used to separate the oligomers in a similar manner to GPC.

The methanol insoluble mixture which contains the first five oligomers and some residual DCpX is used for the next stage - formation of the phosphonium salt, ylid generation with base and in-situ reaction with formaldehyde (see Fig.3).

In previous work 50% aqueous sodium hydroxide was used as the base, but as in all phase transfer catalysed Wittig reactions, some hydrolysis of the phosphonium salt occurs to give a very small peak in the NMR at d=2.3. This problem has been reduced by using sodium hydroxide in methanol as the base.

The polymer is precipitated from DMF with hot water, washed with methanol, and precipitated several times with methanol from dichloromethane. HPLC gives a good separation of the oligomers, using the same column and solvent mixture as for the chloromethyl terminated polymers. Because of the repeated precipitations to remove the excess triphenyl phosphine and the triphenyl phosphine oxide byproduct, all of the first oligomer is lost. This is a major problem, not only because it reduces the yields and increases the initial melting point, but it increases the average distance between crosslinks, thus reducing the crosslink density, and limiting the range of properties such as Tg, modulus and hardness.

The polymer is an off-white powder which melts at 150^{o}C (whereas the melting point of the chloromethyl polymer with some of the first oligomer present melts at ca.130^{o}C). The polymer was cured in open aluminium dishes at 200^{o}C to give reddish brown discs.

A sample of the polymer was ground up and extracted with dichloromethane. The percentage insolubility was 94.3%. The sol fraction was examined using HPLC and NMR, and the mixture is thought to consist mainly of polymer with unknown end groups and some byproducts from the Wittig reaction.

Three crosslinked discs have been evaluated for water absorption, and all gave maximum water uptakes between 0.3 and 0.43% with a diffusion coefficient in the order of 10^{-13} $m^2 s^{-1}$.

One sample, a disc measuring 4.5cm by 0.078cm was heated at 360^{o}C in air for twenty four hours during which time it turned very dark in colour, presumably as a result of oxidation, and lost 6.6% of its original weight.

The DSC curve of the polymer shows an endotherm in the region of 130^{o}C. With a heating rate of 16^{o}C per minute, the onset of cure is at 187^{o}C and the maximum exotherm is at 220^{o}C. Previous DSC runs have failed to indicate a value for the Tg.

3.2 NOVEL THERMOSETS BASED ON OTHER BISPHENOLS.

The loss of the first oligomer is a major problem. In an attempt to overcome it, a variety of chloromethyl terminated polymers have been produced. It was hoped to produce a polymer wholly insoluble in methanol, but unfortunately this has not been achieved. Methanol is preferred as the non solvent because it is completely miscible with DMF and water, and is a solvent for DCpX, triphenyl phosphine and triphenyl phosphine oxide. Its use would considerably reduce purification problems.

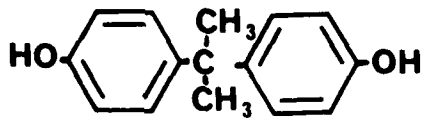
A wide variety of bisphenols are available, but some of these are prohibitively expensive (e.g dihydroxy diphenyl, dihydroxydiphenylmethane) so it was decided to concentrate on the following : 4,4 sulphonyl diphenol; 4,4 thiodiphenol; resorcinol; 1,5 and 2,7 dihydroxynaphthalenes (see Fig. 4).

Chloromethyl terminated polymers based on 4,4 sulphonyl diphenol (DHDPS) have been produced by methods 1 and 2 of the preceding section, with method 1 being the most successful. The yield of polymer suggests that the first oligomer from this reaction is much less soluble in methanol than the first oligomer from the BPA polymer, but NMR confirms that it is at least partially soluble. If the assumption is made that the solubilities of the chloromethyl polymer and the vinyl terminated polymers are the same or very similar, the next stage of the reaction will result in a further loss of the oligomer. The melting point of the polymer at 155-160^{O}C is very high. If more of the oligomer is lost, the melting point of the mixture can be expected to increase, which, given a short gel time, could adversely affect the "processing window" available.

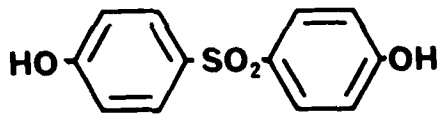
The above system produces high melting products so a modification would be to use DCmX or mixtures of DCmX and DCpX to decrease the stereoregularity and thus decrease the melting point. Another option is to use a mixture of bisphenols such as DHDPS/resorcinol or DHDPS/BPA etc., instead of a single bisphenol.

Chloromethyl polymers based on 4,4 thiodiphenol have been produced, but side reactions occur which produce a mixture of chloroform soluble and insoluble polymers. The reason for these side reactions, which occur with both systems (potassium carbonate/DMA, and the disodium salt of the bisphenol with DCpX), is not known, but they are a major restriction on the usefulness of this bisphenol.

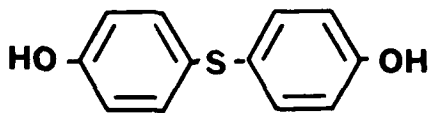
If resorcinol is used as the bisphenol the melting point of the polymer is expected to be much lower, which should mean easier fabrication. Chloromethyl terminated-polyethers based on resorcinol have been produced in reasonable yield



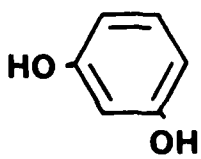
Bisphenol A



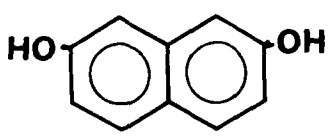
Bis (4,hydroxyphenyl)sulphone



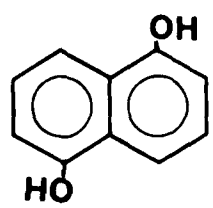
4,4' Thiodiphenol



Resorcinol



2,7 Dihydroxynaphthalene



1,5 Dihydroxynaphthalene

Fig. 4. Bisphenols used for the synthesis of chloromethyl terminated polyether.

and as expected the melting point is lower at 105-110°C than the corresponding BPA system.

If the reaction in section 3.1 is modified so that DCmX, or mixtures of DCmX and DCpX are used rather than DCpX, a polymer of lower melting point would be expected, for the same reasons as suggested for polymers based on DHDPS as noted above. BPA has been reacted with pure DCmX to produce low melting (110-115°C) chloromethyl terminated products. The reaction details can be found in the experimental section.

Several reactions have been attempted, under a variety of conditions, in order to produce soluble, fusible polymers from 1,5 and 2,7 dihydroxy naphthalenes, but each reaction produced polymers which appeared to be partially crosslinked.

3.3 POLYFUNCTIONAL SYSTEMS.

A drawback of the above-mentioned schemes is the crosslink density of the cured polymers. Besides the problem of losing the majority of the first oligomer, there are also expected to be some molecules with only one vinyl group per chain and possibly some with none. The Wittig reaction in this case gives a very good yield (there is only a very small aromatic methyl group in the FT NMR spectrum), but it would be useful to produce polymers with more than two potential reaction sites.

We have considered two approaches to this problem:

1. Introduction of chloromethyl groups to a polymer backbone.

2. Reaction of a polyfunctional phenol with DCpX.

The first approach can be implemented in a number of different ways. The first annual report of December 1984 commented on several, the most promising being (1) chlorination of aromatic methyl groups and (2), chloromethylation reactions.

Chloromethylation has been used successfully for the introduction of chloromethyl groups into polyethersulphones, as discussed in section 2.

Free radical halogenation of aromatic methyl groups could produce a wide variety of polyfunctional halomethyl compounds, which could be converted to vinyl groups by the Wittig reaction. One scheme under consideration involves the production of a low molecular weight tetramethyl sulphone from the condensation of 3,5 dimethyl phenol and BCPS. It is hoped that this can be chlorinated with chlorine and a peroxide in an inert solvent and the product used for the Wittig reaction (see Fig. 5). The preferred degree of

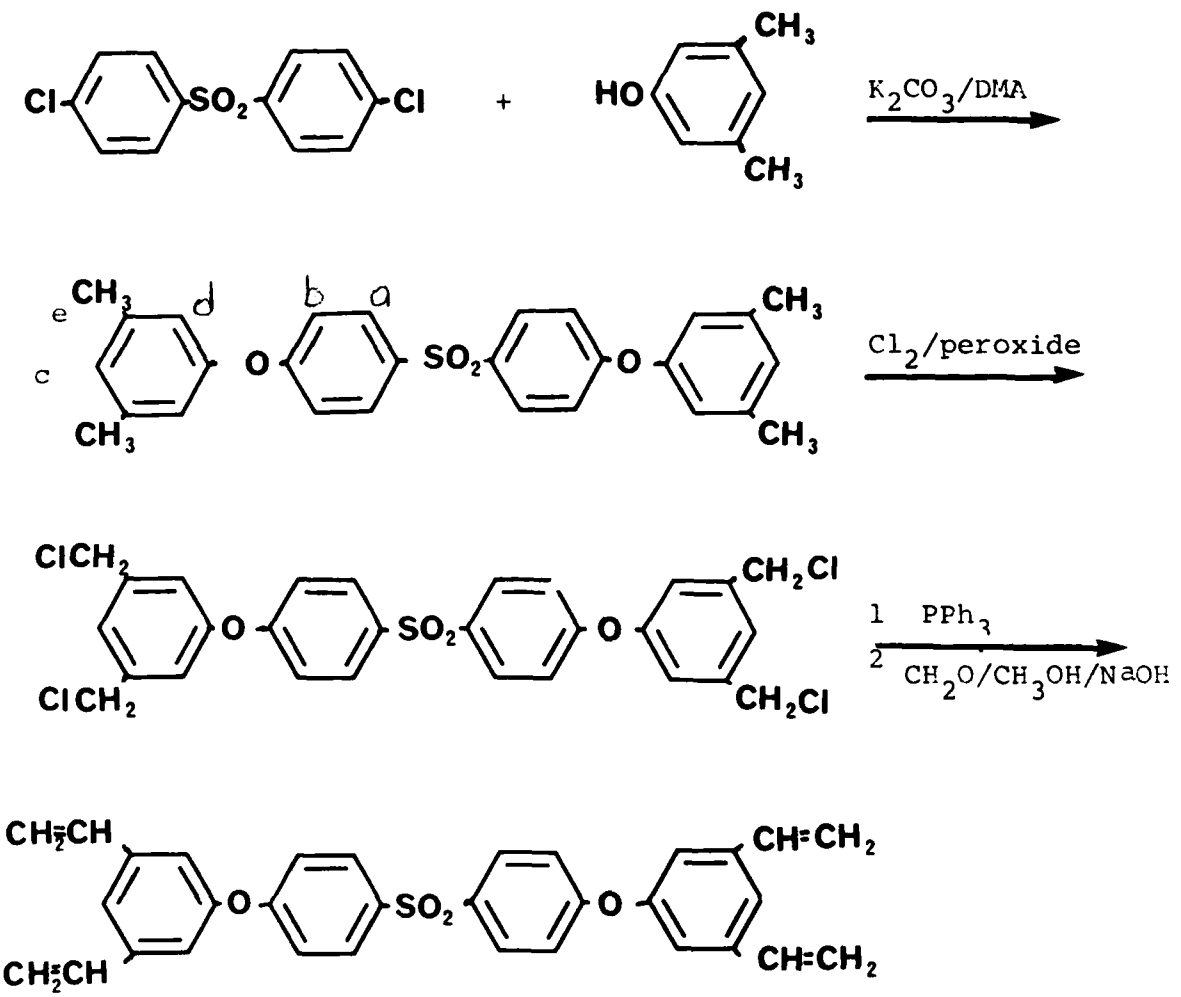


Fig. 5. Polyfunctional vinyl terminated oligomer based on bis (4, chlorophenyl) sulphone and 3, 5 dimethyl phenol.

chlorination is in the region of 50- 80 % of the methyl groups .

At present the tetra methyl compound has been produced in near quantitative yield to give crystals melting at 115°C. Chlorination of the product is in progress, but the high solubility of the product may be a problem in the next stage.

The second approach is limited by the availability of suitable poly functional phenols. One possible source is novolaks, but a number of commercially available polyfunctional phenols could also be used.

4.EXPERIMENTAL.

4.1 REACTION OF BPA AND DCpX IN DMA WITH POTASSIUM CARBONATE AS BASE.

In a two litre flange pot equipped with mechanical stirrer, reflux condenser and nitrogen inlet/exit were placed 50g BPA (0.22M), 77g of DCpX (0.44M), 80g (0.58M) anhydrous potassium carbonate and 400ml DMA. The mixture was stirred vigorously and nitrogen bubbled in. Over a period of two hours the temperature was slowly brought to reflux and then the heater was removed. While the mixture was stil hot 600ml of water was added with vigorous stirring to precipitate the crude polymer. The polymer was filtered and air dried, then dissolved in 500ml of chloroform and dried over anhydrous sodium sulphate. The volume of the solution was reduced by half and poured into 600ml of stirred methanol. The resultant white powder was filtered off, and dried overnight at 60°C to yield 74g of product.

The polymer was highly soluble in dichloromethane, chloroform and DMF, and melted in the region of 130°C.

The NMR spectrum of the product (see Fig. 6) shows peaks at d=7.4 (singlet), d=6.7-7.2 (quartet), d=5 (singlet), d=4.55 (singlet), and d=1.65 (singlet). These can be attributed to aromatic protons from DCpX, aromatic protons from BPA, methylene ether protons, chloromethyl protons and the methyl groups from BPA respectively. The NMR spectrum of the chloroform/methanol mixture appeared to indicate mainly unreacted DCpX, together with oligomer and DMA.

The NMR spectrum suggests that the Mn of the polymer is 716, based on the ratio of methylene ether to chloromethyl groups.

4.2 REACTION OF DISODIUM SALT OF BPA WITH DCpX.

In a two necked 250ml flask was placed 10g of BPA (0.0439M) and 100 ml methanol. When the BPA had dissolved

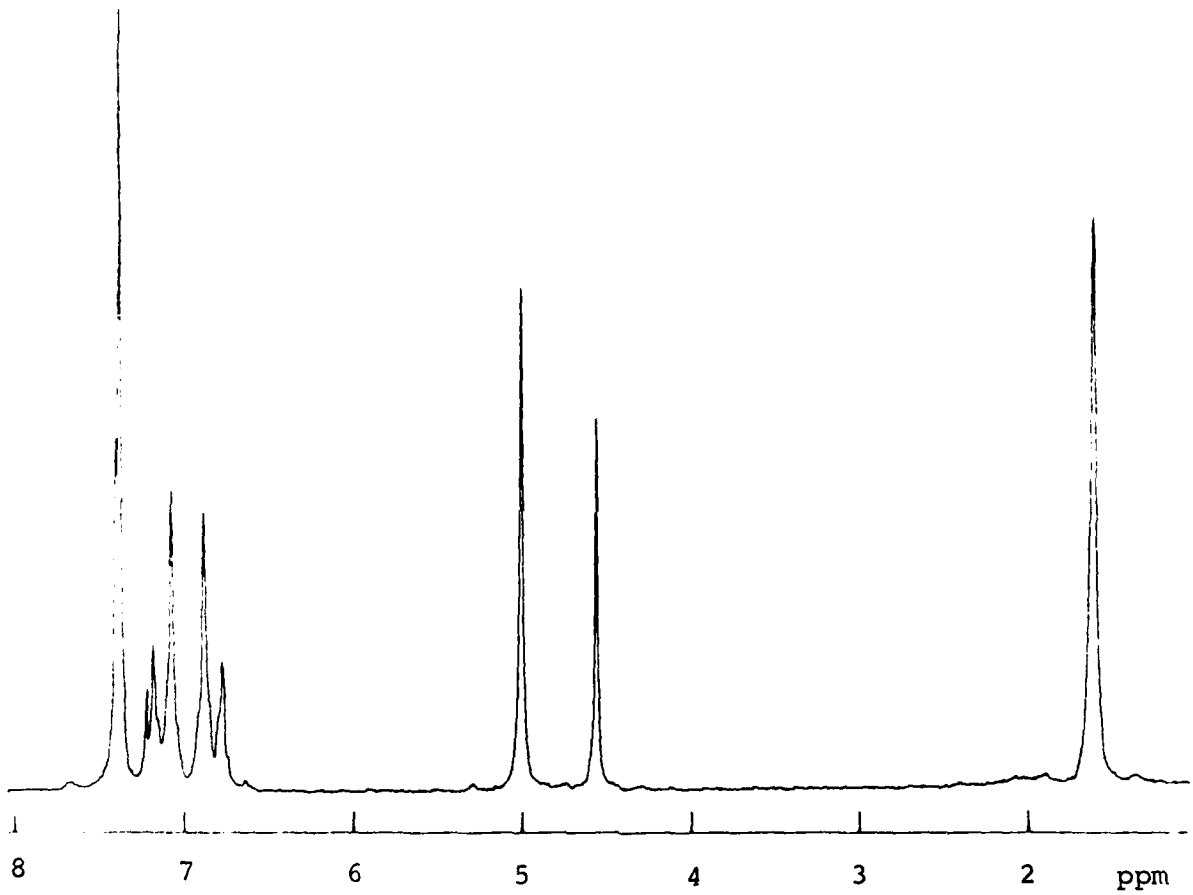


Fig 6. ^{1}H nmr spectrum of chloromethyl terminated polymer from BPA and DCpX

3.67g (0.88M) of sodium hydroxide was added and the mixture stirred until all the base had dissolved. The solvent and the water formed were removed on a rotary evaporator, and the resultant white powder was covered with 100 ml of DMF. 15.35g (0.085 M) of DCpX was added, and the mixture was heated to 90°C for three and a half hours with vigorous stirring. Sodium chloride crystals began to form immediately.

The contents of the flask were then poured into 300ml of water, and the resultant precipitate filtered off and dried in air overnight. The crude product was dissolved in 400 ml of chloroform, and dried over anhydrous sodium sulphate. The volume of the solution was reduced to less than 100ml, and the solution poured into 300 ml of methanol. On drying the resultant precipitate at 70°C in an oven, 13.8g of product was obtained. The melting point of the product was in the region of 125°C and the NMR spectrum was very similar to that obtained when the same reactants were polymerised with potassium carbonate in DMA.

4.3 PHASE TRANSFER CATALYSED POLYCONDENSATION OF BPA AND DCpX.

10g (0.0439 M) BPA was dissolved in 50ml of water containing 5g of sodium hydroxide and 0.5g (0.0022 M) of benzyl triethyl ammonium chloride (BTEAC) was added. DCpX, 15.35g (0.085) dissolved in 70ml toluene and 30ml DMSO were added. On vigorous stirring a white suspension was formed and the mixture was heated at 60°C for 2.5 hours.

The contents of the reaction vessel were poured through a sintered funnel, giving two clear layers and a white solid residue. The residue was extracted repeatedly with chloroform, and the two organic layers combined and dried over anhydrous sodium sulphate. The solvents were removed on a rotary evaporator and the crude polymer disssolved in 100ml of chloroform and precipitated with 300ml of methanol. The dried polymer was obtained in a yield of 8.5 g, and had a similar NMR spectrum and melting point to the DCX/BPA polymers prepared by other means.

4.4. PREPARATION OF LOW MOLECULAR WEIGHT CHLOROMETHYL TERMINATED POLYETHERSULPHONES.

In a flange pot equipped as in procedure 4.1 were placed 20g (0.08M) of DHDPS, 28g (0.16M) DCpX, 26g (0.19M) anhydrous potassium carbonate and 200ml of DMA. The mixture was stirred under nitrogen and brought to reflux over a period of 1.5 hours. When the mixture had cooled to less than 100°C the crude product was precipitated with 600ml water and the product filtered and air dried. It was then

dissolved in 100ml hot DMF, and precipitated by pouring into 300ml of stirred methanol. 35.2g of product was obtained after drying the precipitate in an oven at 70°C.

The polymer was a white powder, soluble in DMF but not wholely soluble in chloroform. It melted in the region of 155-160°C.

The NMR spectrum of the product showed peaks at d=7.9, 7.83, 7.23 and 7.13 from the aromatic sulphone, a peak at d= 7.45 from the aromatic DCpX protons, a peak at d=5.2 from the methylene ether protons, and a peak at d=4.74 from the chloromethyl protons.

The Mn value suggested from the NMR is 840 , based on the ratio of chloromethyl groups to methylene ether protons.

The residue soluble in methanol again consisted mainly of DCpX, with a small quantity of oligomer.

Similar results, though in poorer yield, were achieved when the disodium salt of the bisphenol was refluxed in DMF with DCpX. The salt was prepared in situ, from the bisphenol and aqueous sodium hydroxide, and the water was removed by azeotropic distillation using toluene.

4.5. REACTION OF 4,4´ THIODIPHENOL WITH DCpX.

10g (0.0459 M) of 4,4´thiodiphenol and 3.82g (0.0917 M) of sodium hydroxide (96%) were dissolved in 100ml of methanol and the contents of the flask were then dried using a rotary evaporator. The dry white solid was covered with 150ml of DMF and stirred and then 16g (0.091 M) of DCpX dissolved in 100ml of DMF was added. The mixture was heated and stirred for two hours at 90°C. On cooling, the mixture was diluted with 250ml of dichloromethane and the insoluble residue removed by filtration. The dichloromethane was removed on a rotary evaporator and the DMF solution was precipitated by pouring it into 500ml of methanol. The polymer was dried in an oven at 60°C. The yield of dichloromethane soluble/ methanol insoluble polymer was 7g and the melting point 125-130°C. The NMR spectrum contains peaks at d=7.35 (from DCpX), d=7.27, 7.19, 6.9, 6.8 (from the bisphenol), d=5 (methylene ether protons), and d=4.53 (chloromethyl protons). The methanol extract contained oligomer and DCpX.

The reaction above has been attempted a number of times, and each time, quantities of material insoluble in the highly polar reaction medium were obtained. When the DMA/potassium carbonate system was used, the products appeared to be partially crosslinked.

4.6. PREPARATION OF CHLOROMETHYL TERMINATED POLYETHERS FROM RESORCINOL AND DCpX.

30g (0.27M) of resorcinol, 95.5g (0.54M) of DCpX, 78g (0.57M) of potassium carbonate and 300ml DMA were brought slowly to reflux over two hours, and the product was then precipitated with 450ml water. It was washed with 500ml hot water,dried in the air, dissolved in 500ml chloroform, and dried over anhydrous sodium sulphate. The volume of solvent was reduced by half, and the product precipitated by pouring into 600ml of stirred methanol. The dried precipitate was obtained in 54.2g yield, and was a white powder soluble in chloroform and DMF, with a melting point in the region of 105-110^{o}C.

The NMR of the product showed the expected peaks and suggests that the Mn of the polymer is 635. The methanol soluble portion consists mainly of DCpX and oligomer.

4.7. PREPARATION OF CHLOROMETHYL TERMINATED POLYMERS FROM BPA AND DCmX.

In a similar reaction to those above, 32.5g, (0.14M) of BPA, 50g DCmX (0.28M) and 45g potassium carbonate were heated at 90^{o}C in 300ml of DMA, with vigorous stirring for six hours. After precipitation with water, drying, dissolving in chloroform and precipitating with methanol, 38g of polymer was obtained. The product was a white powder, melting at 110-115^{o}C.

The NMR spectrum of the product was very similar to that of polymers based on DCpX, except for the peaks from DCmX which appeared at d= 7.35-7.6. The methanol soluble portion again consisted mainly of DCmX, with some low molecular weight chloromethyl oligomers. The Mn from the NMR is approximately 752 .

4.8.REACTION OF DCpX WITH 2,7 DIHYDROXYNAPHTHALENE.

30g, (0.19 M) of 2,7DHN, 65g (0.37 M) of DCpX and 50g of potassium carbonate in 300ml DMA were slowly brought to reflux over a period of 2.5 hours, after which time the product was precipitated with 600ml water. The off white precipitate was crudely dried, and then stirred in 500ml methanol. The product was dried at 70^{o}C for 12 hours to give a 71g yield. The polymer appeared to be partly crosslinked as it was only partially soluble in DMF and did not melt.

4.9 .REACTION OF DCpX WITH 1,5 DIHYDROXYNAPHTHALENE.

30g (0.19M) of 1,5 DHN, 65g (0.37M) of DCpX and 50g of potassium carbonate were slowly brought to reflux, with stirring in 300ml DMA for four hours. The dark brown colour was maintained throughout the reaction. The product was precipitated with 600ml water, dried, and then stirred in methanol. Again, crosslinking reactions had taken place and the resultant polymer was only partially soluble in DMF, and decomposed before a melting point. The reaction was attempted at lower temperature (95^{o}C) but the result was the same. In a further attempt to prepare soluble fusible polymers from these reactants, the dry disodium salt of the bisphenol was prepared in DMSO using aqueous NaOH, then azeotropic distillation of the water with toluene. DCpX was then added, but on refluxing, the contents of the flask gelled.

4.10. REACTION OF BIS (4, CHLOROPHENYL) SULPHONE WITH 3,5 DIMETHYL PHENOL.

50g, (0.17M) of BCPS, 44g (0.36 M) of 3,5 dimethyl phenol, and 55g of potasssium carbonate were stirred under nitrogen in 300ml DMA. The mixture was refluxed strongly for eight hours to ensure complete reaction, and then precipitated with 500ml 5% aqueous sodium hydroxide, producing a gummy solid suspended in a red solution. The aqueous layer was decanted, and the solid washed with water, and then dissolved in diethyl ether. On standing, the red solution became cloudy, and white crystals were formed. The product was recrystallised from methylated spirits, to give a near quantitative yield of crystals melting at 115^{o}C.

The NMR spectrum of the product contains peaks at d= 7.7, 7.8, 6.95, 6.85 ppm (a and b on Fig 5) from the aromatic sulphone, d= 6.75, and 6.6 ppm (c and d on Fig 5) from the dimethyl phenol aromatic proton, and d= 2.28 ppm (e on Fig 5) from the methyl groups.

4.11. CONVERSION OF CHLOROMETHYL TERMINATED BPA POLYMER TO VINYL TERMINATED POLYMER.

50g of a chloromethyl terminated BPA polymer, as produced by the potassium carbonate DMA system (see section 4.1), was heated to reflux in 250ml dry DMF under nitrogen with 50g (0.01M) of triphenyl phosphine for 3 hours. The heater was removed and the contents allowed to cool. The flask was equipped with a long gas inlet and a dropping funnel containing 15g of sodium hydroxide dissolved in 100ml of methanol. 20g of paraformaldehyde was decomposed by strong heating, and the formaldehyde produced was passed as formed

into the DMF solution by a stream of nitrogen. When all the paraformaldehyde had decomposed, the solution was stirred and the base slowly added. The solution was stirred for a further hour, and then the product was precipitated out with 500ml of hot water whilst stirring vigorously. The precipitate was collected and washed with three 100ml portions of methanol, and then dried on a rotary evaporator. The polymer was dissolved in 300ml dichloromethane, and dried over anhydrous sodium sulphate. The volume of the solvent was reduced to c 100ml, and the product precipitated with 300ml of methanol and dried in an oven at 70°C to give 41.7g of polymer melting at 130-140°C. If the product is precipitated a further two times, the melting point rises to 150°C.

The NMR spectrum was consistent with that of a polyether with vinyl end groups (see Fig.7). The spectrum shows no peak due to chloromethyl protons but a series of new peaks at d=5.1-5.9 and 6.7-7.5 is indicative of vinyl groups. There is a very small peak at d=2.3 resulting from hydrolysis of phosphonium salts to aromatic methyl groups.

4.12. ESTIMATION OF SOLUBLE FRACTION.

2g quantities of the polymer, as prepared above, were placed in shallow 4.5cm diameter aluminium dishes and these were placed in an oven preheated to 200°C for three hours. The polymer melted rapidly to become a mobile liquid which then became a solid. Previous experiments indicate that the gel time at this temperature is in the region of seven minutes.

The products of the crosslinking reaction were clear brown coloured discs.

A number of the discs were ground crudely with a mortar and pestle, and 6.3045g was suspended in 30ml of dichloromethane for three weeks at room temperature. During this time the particles became swollen.

At the end of the three weeks the solid was filtered off using a fine sinter, washed repeatedly with dichloromethane and dried for three days at 100°C to give 5.9456g of insoluble product, and a percentage insolubility of 94.3%.

The dichloromethane solution of the sol portion was evaporated under vacuum, and the proton NMR spectrum recorded on a Bruker WP 80 SY Fourier Transform spectrometer. The spectrum as obtained was extremely complicated, especially in the aromatic region, so a portion of the mixture was extracted with methanol. The methanol soluble and methanol insoluble portions were separated and dried. The two spectra shown on Figs 8 and 9 indicate that the methanol soluble portion consists mainly of triphenyl phosphine oxide, and

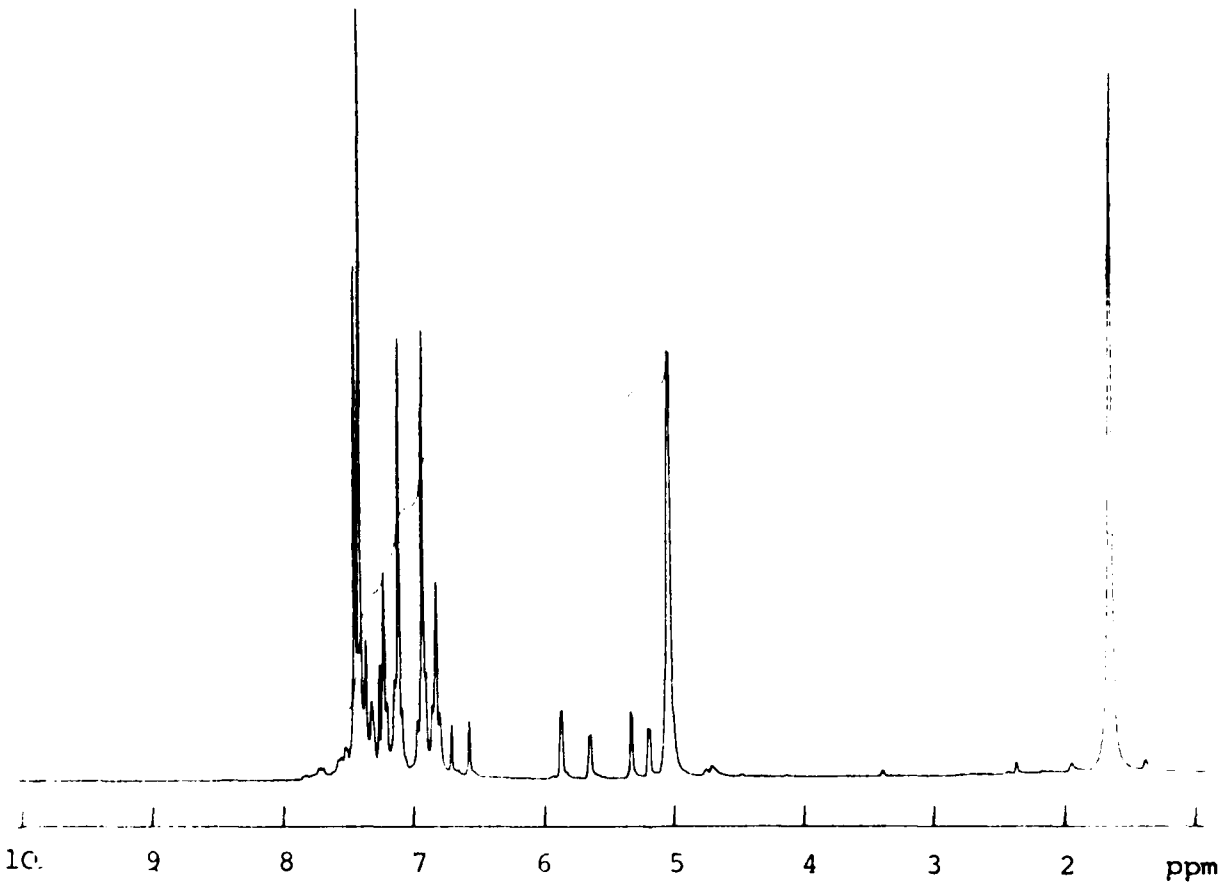


Fig. 7. ^{1}H NMR spectrum of vinyl terminated polymer from BPA and DCpX

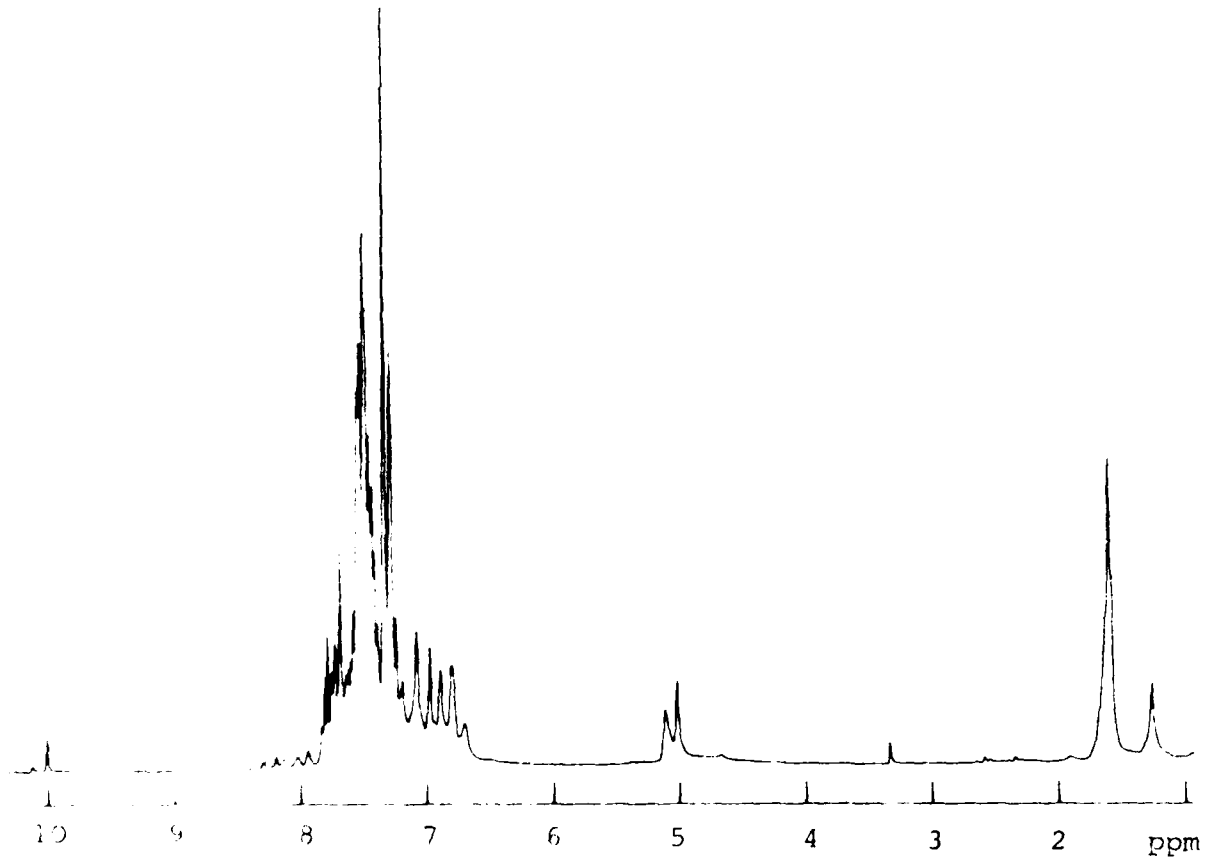


Fig. 8. ^{1}H NMR spectrum of CH_3OH soluble washings from crosslinked polymer.

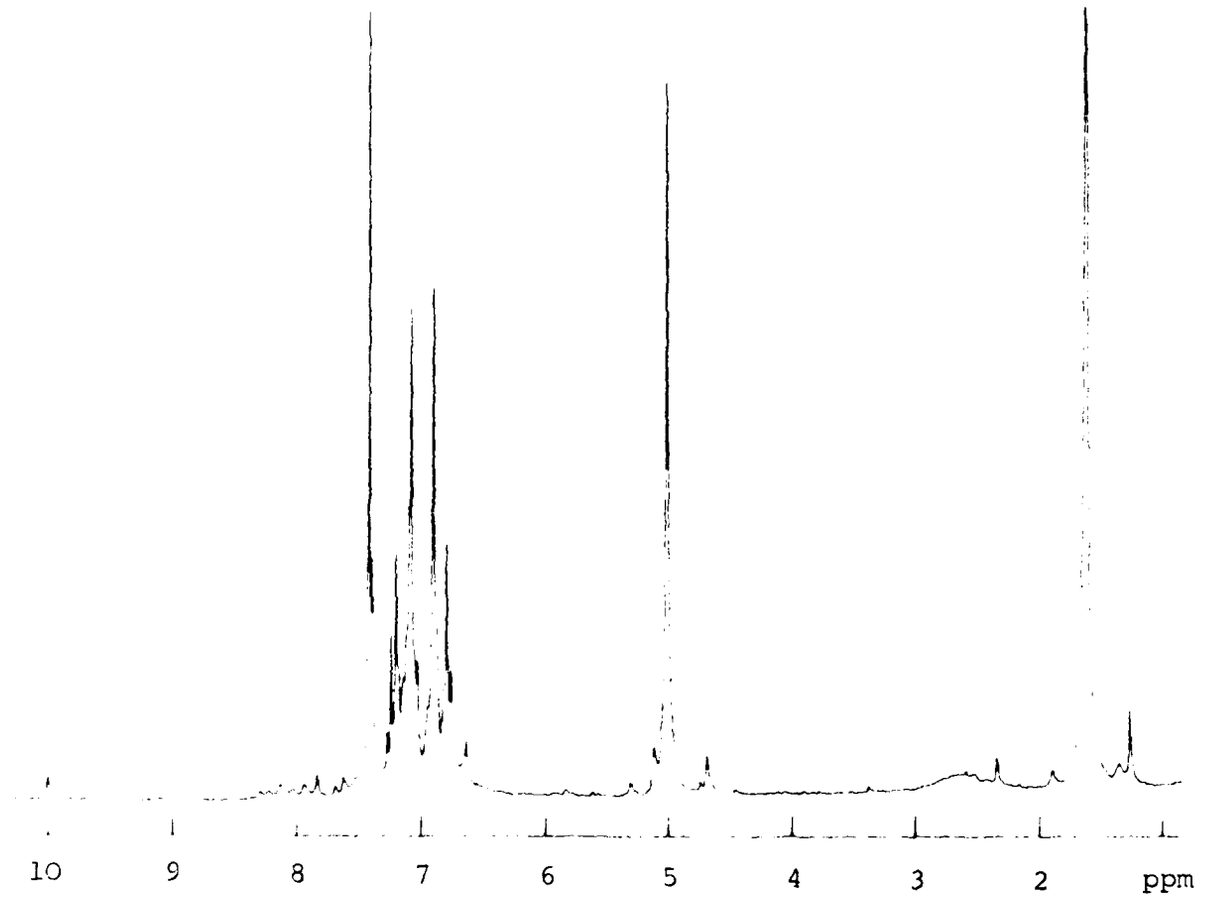


Fig. 9. ^{1}H NMR spectrum of CH_3OH insoluble washings from crosslinked polymer.

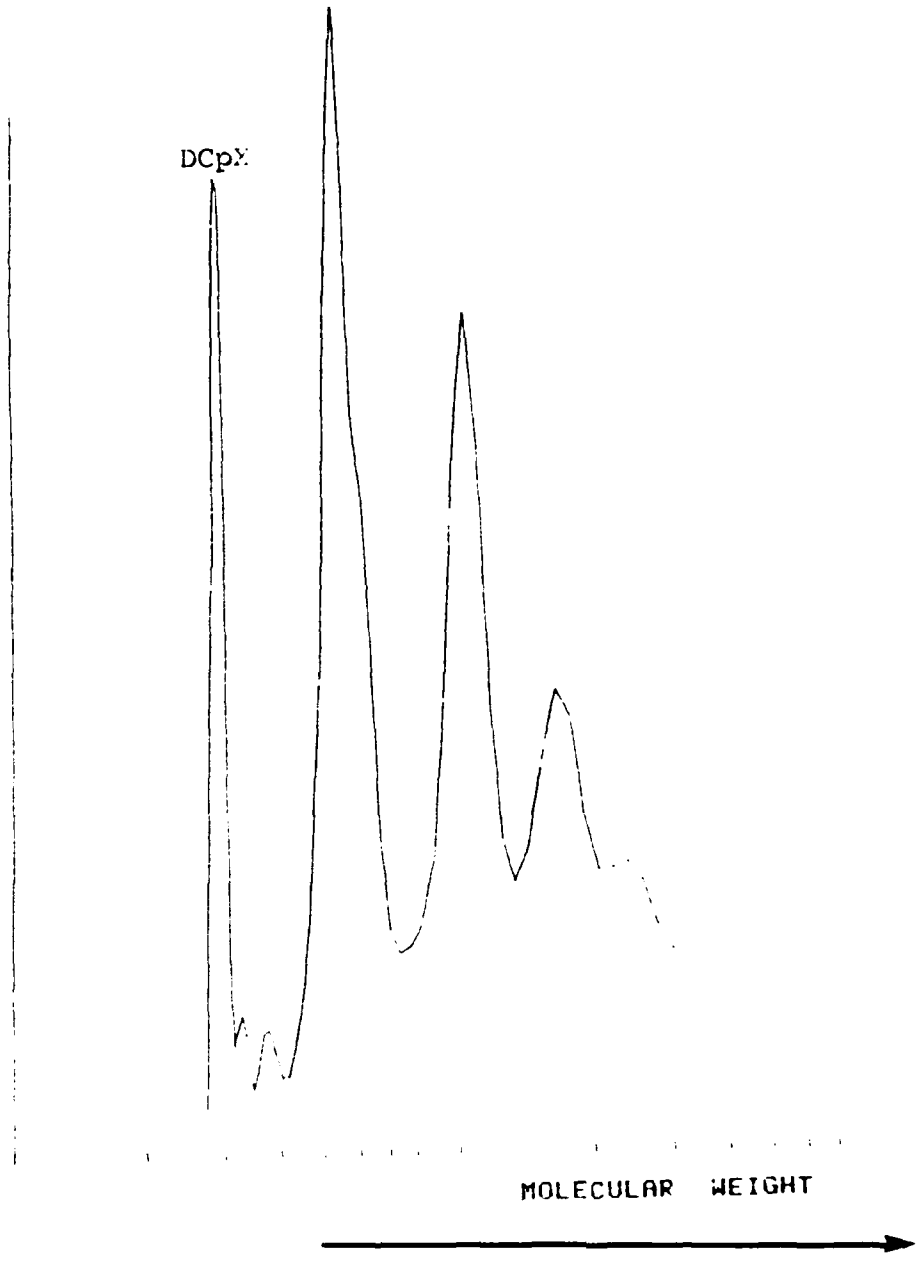


Fig. 10. Gel permeation chromatogram of crude chloromethyl polymer as precipitated from DMF with water.

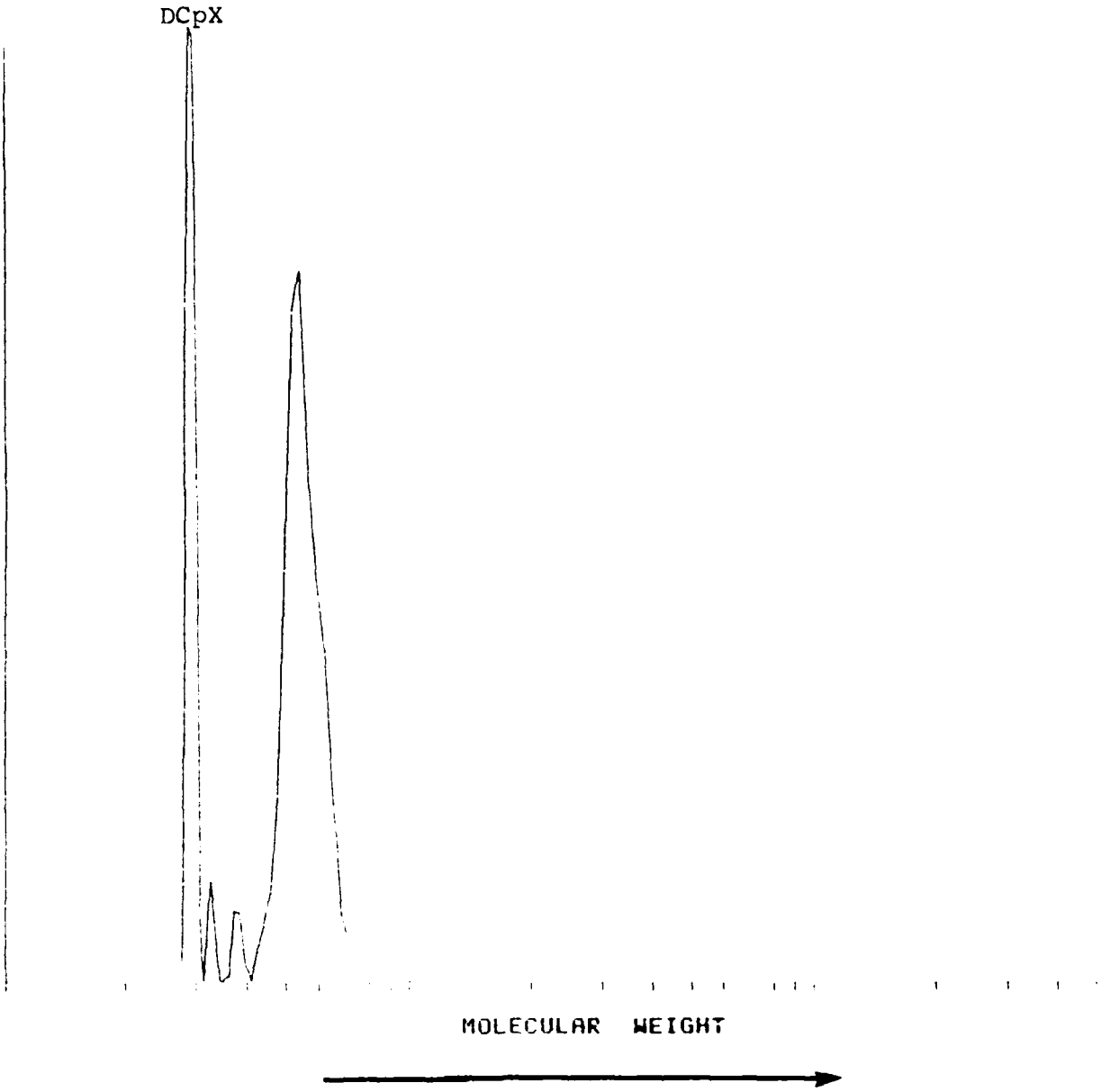


Fig. 11. Gel permeation chromatogram of CH_3OH soluble portion of chloromethyl terminated polymer.

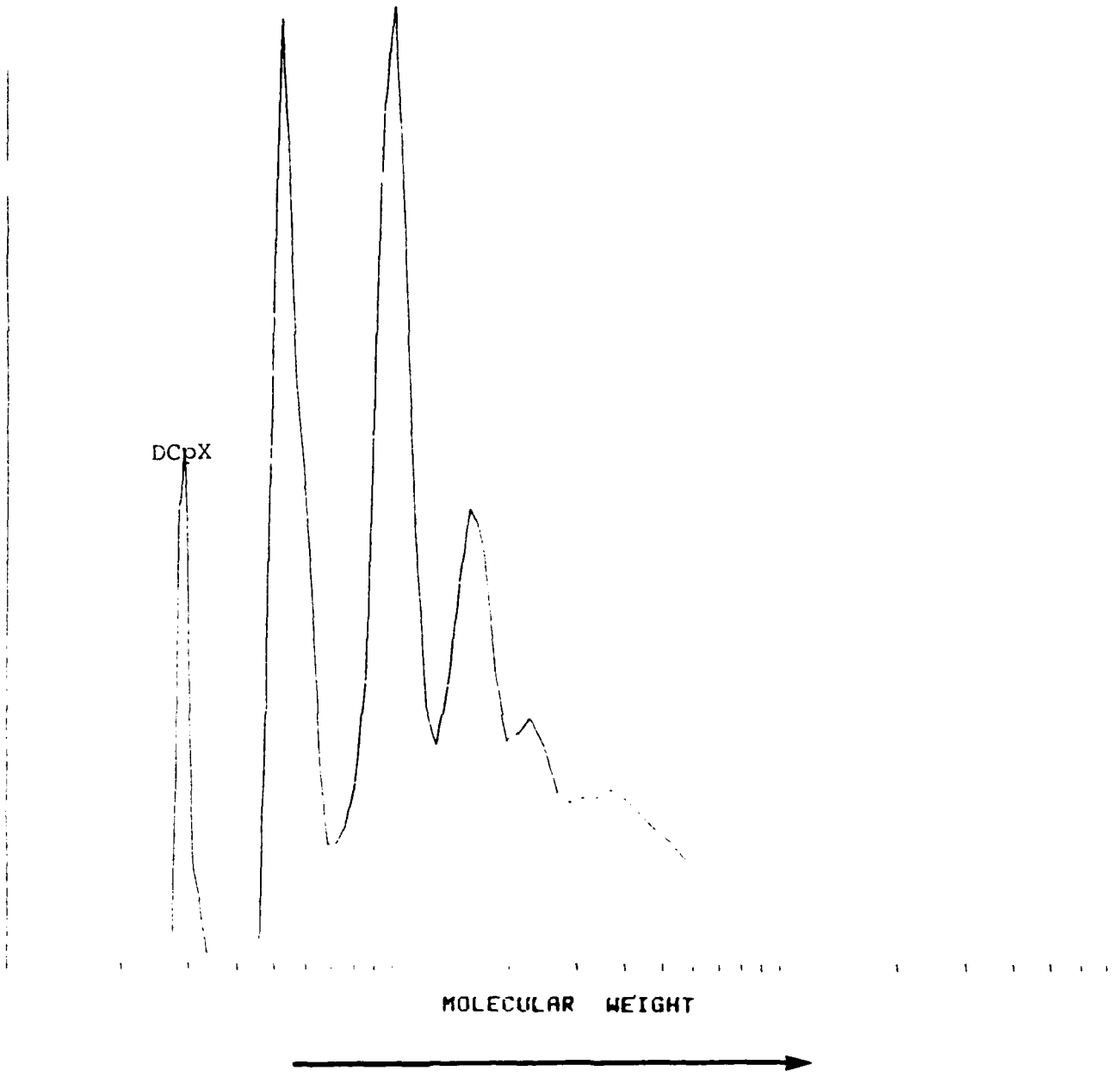


Fig. 12. Gel permeation chromatogram of CH_3OH insoluble portion of chloromethyl terminated polymer.

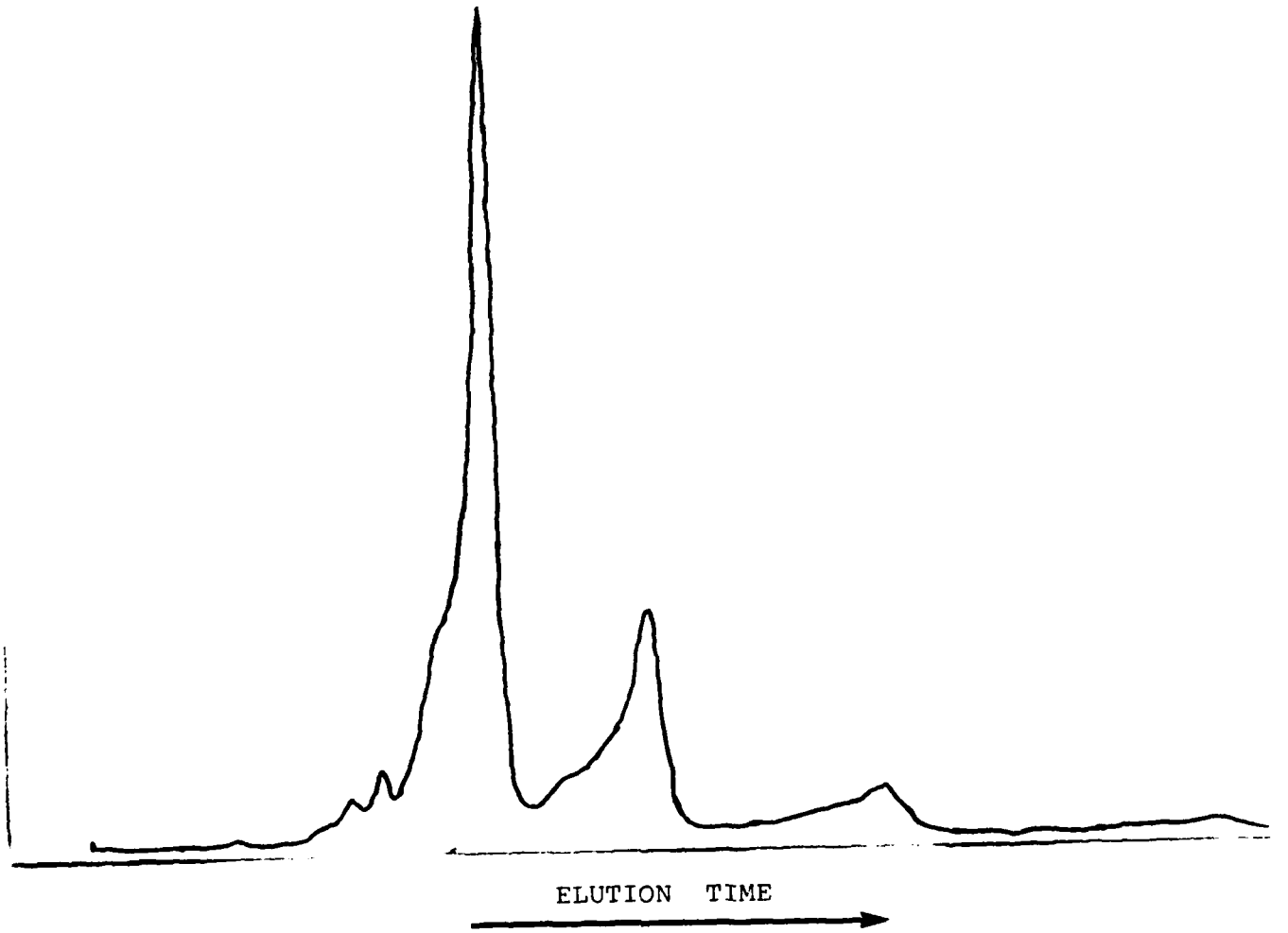


Fig.13. HPLC of vinyl terminated polyether.

possibly triphenyl phosphine, along with a small quantity of methanol soluble polymer. The methanol insoluble portion consists almost entirely of the polymer with as yet unidentified end groups, though in the spectrum there is evidence of a methyl peak at d=2.3, and possibly some unreacted vinyl groups. The absence of discernible end groups may suggest the presence of cyclic structures.

4.13. CHROMATOGRAPHIC SEPARATION OF BPA/DCX OLIGOMER.

The reaction products of the potassium carbonate/DMA polymerisation have been characterised by GPC and HPLC, and a good separation of the products was obtained with both methods. The crude mixture precipitated from the DMA contains the first five oligomers and DCX, as shown by the GPC in Fig.10. When this mixture is separated by methanol precipitation most of the DCX is removed along with some of the first oligomer (of molecular weight 505) as shown in Figs. 11 and 12 .

The GPC curves illustrated were provided by the RAPRA consultancy organisation. Our own HPLC facilities have resolved the oligomers in a similar way by using a 10cm C18 column with THF/water mixtures as the mobile phase, and a UV detector. The separation was virtually identical to that obtained by GPC . The HPLC of the vinyl terminated polymer (see Fig 13) shows that after purification of the product by methanol precipitation the majority of the first oligomer was lost.

4.14 DIFFERENTIAL SCANNING CALORIMETRY.

The DSC trace of a typical vinyl terminated polymer is shown on Fig. 14. There is a broad endotherm commencing at 130^{o}C when the polymer starts to melt. With a heating rate of 16^{o}C per minute the onset of cure is at 187^{o}C and the maximum exotherm is at 220^{o}C. It is not possible to decide on a value for the Tg of the cured polymer from the DSC traces obtained to date. Preliminary studies using an automated torsional pendulum indicate that the Tg of the crosslinked polymer is over 130^{o}C.

4.15. WATER ABSORPTION : METHOD AND RESULTS.

Several discs were prepared, and cured as detailed in section 4.12. The discs were ground on emery paper till they were flat with even surfaces. The thickness of the discs was then measured repeatedly with a micrometer, and the values averaged. The discs had thicknesses between .0.55 and 0.85 mm

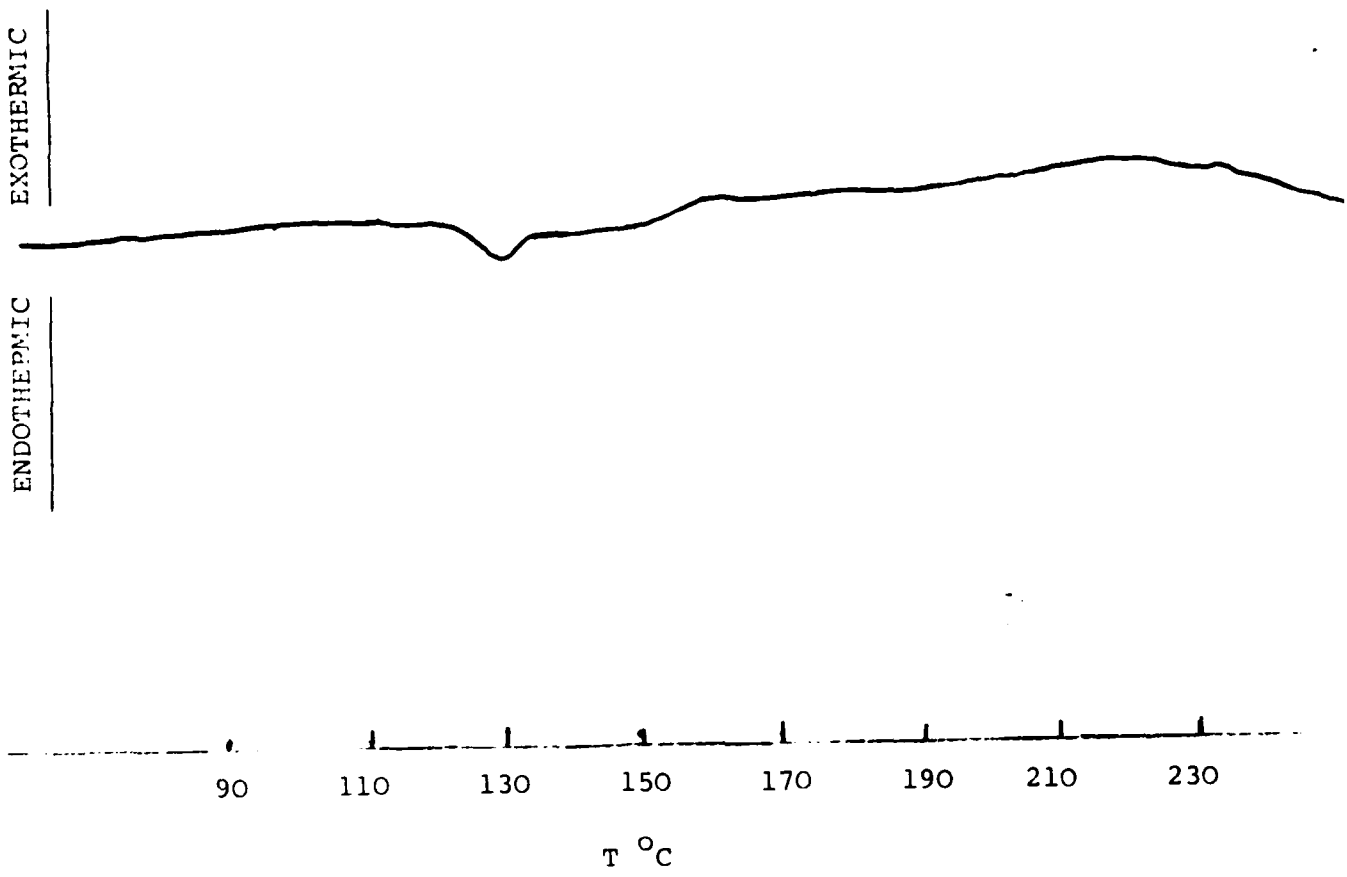


Fig. 14 DSC of vinyl terminated polyether.

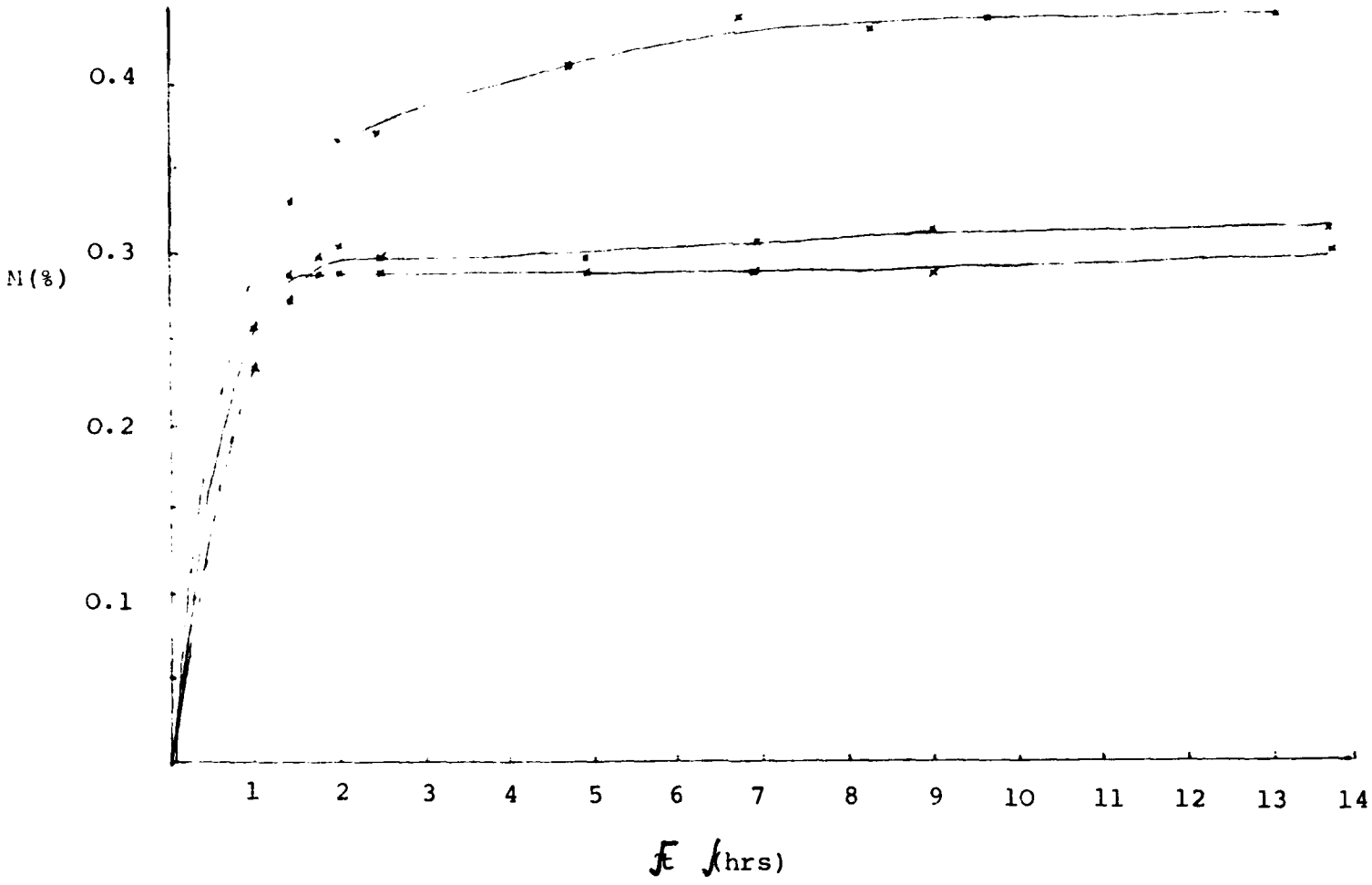


Fig. 15. Water absorption of a crosslinked bisphenol A polymer at 70°C

with initial weights between 0.93 and 1.42g. The discs were dried at 105°C for 48 hrs and cooled in a dessicator, then, at time t=0 they were weighed on a balance to within 0.1 mg. The discs were then immersed in a desiccator containing 200ml of distilled water which had been preheated to 70°C, and placed in a humidity chamber at the same temperature. The discs were removed at short intervals during the first eight hours, dried with an absorbent cloth and weighed. A plot of the % weight increase (M) against the square route of time is given in Fig 15 . The discs absorbed water very rapidly in the first hour, but very little increase occurred after forty eight hours. The weight had long been constant after one hundred and seventy hours. The three discs evaluated each gave maximum water uptake figures (Mmax) of between 0.3 and 0.43 %, the figure varying with the quality of the specimen.

The diffusion coefficient was obtained by using the expression:

$$D = \pi\left(\frac{h}{4\ Mmax}\right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}\right)$$

where D = diffusion coefficient ($m^2 s^{-1}$)
h = thickness (m)
t_1, t_2 = times 1 and 2 (s)
m_1, m_2 = % weight increases at t_1 and t_2

and gave a value of the order of 10^{-13} $m^2 s^{-1}$. This is comparable with the diffusivity of epoxies, suggesting that the small quantity of water sorbed is able is able to diffuse in without hindrance.

5. CONCLUSIONS.

Low molecular weight chloromethyl terminated polyethers have been produced by the reaction of a bisphenol and either DCpX or DCmX. The reaction has been attempted under a variety of conditions, and those involving (a.) DMA/potassium carbonate and (b.) the dry disodium salt of the bisphenol in DMF have been the most useful. The second stage of the reaction involves precipitation of the product from chloroform with methanol, so methanol insolubility is a preferred characteristic of the products. Unfortunately, all the systems tried which gave soluble products produced a first oligomer which was at least partially soluble in methanol, and this reduces the yields. It also poses a problem when physical properties are evaluated. Those systems based on 4,4 thiodiphenol gave partially insoluble products and so are of little interest. The methanol insoluble

reaction product of dihydroxydiphenyl sulphone and DCpX is very high melting, and problems could occur when processing the vinyl terminated product, given the rapid cure of these systems. Those systems still of interest are vinyl polymers derived from:
a. BPA/ DCpX.

b. BPA/ DCmX.

c. Resorcinol / DCpX.

d. and possibly the sulphone system noted above.

To date, only chloromethyl polymers derived from BPA and DCpX have been converted to the vinyl derivatives. The reaction products have been characterised by NMR, GPC and HPLC and the NMR evidence suggests a very high conversion rate. The polymers have been cured thermally, and need no peroxide. The soluble fraction has been determined, and examined by NMR. Water absorption characteristics of the polymer have been determined, and as expected the maximum water uptake is very low - much lower than that of any of the thermosets commonly in use at present.

In an attempt at producing a highly crosslinked system, 3,5 dimethyl phenol was condensed successfully with bis (4 chlorophenyl) sulphone to give a tetramethyl substituted methyl compound. It is hoped that the product can be halogenated, and then converted to the vinyl derivative by the Wittig reaction or a variation of it. Other polyfunctional systems using polyfunctional phenols are at present under evaluation.

Future work involves: firstly, carrying out the Wittig reaction on the above mentioned bis (chloromethyl) polymers and a brief characterisation of the products, ie by NMR, HPLC, melting point, soluble fraction estimation etc., and if suitable products result, determination of their water absorption characteristics. The same procedures will be followed if any of the polyfunctional systems are of interest.

In an attempt to decrease the purification problems associated with the Wittig step, two different approaches will be tried. The first involves precipitating the phosphonium salt with ether, to remove excess triphenyl phosphine, and then removing the triphenyl phosphine oxide byproduct from the Wittig reaction, with methanol/water mixtures. The second approach is to use the Wadsworth Emmons variation of the Wittig reaction [12]. In this reaction, base is added to a diethyl phosphonate, to form an anion which reacts with the aldehyde to form the olefin, and water

soluble diethyl phosphates, enabling water to be used in the purification steps. The diethyl phosphonates are readily prepared by heating triethyl phosphite with the chloromethyl compound, and distilling out the ethyl chloride thus produced - see for example the synthesis of divinyl benzene compounds [13].

It is hoped that soon the range of alternative syntheses will be greatly reduced, and that one or possibly two of particular interest will be examined in greater depth. Larger quantities of the polymers will be produced, and a significant amount of time will be devoted to producing specimens so that the physical properties of the polymers can be evaluated.

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