The synthesis and characterization of vinyl-terminated oligomeric ethers

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Low-molecular-weight linear prepolymers have been prepared by three different methods, and crosslinked through their terminal vinyl end-groups, without added catalyst. The prepolymers were made in two stages: first, chloromethyl-terminated oligomers were synthesized by reacting 1,4-bis(chloromethyl)benzene with alkali-metal bisphenates; secondly, these products were subjected to a Wittig reaction to convert the chloromethyl end-groups to vinyl ones. The vinyl-terminated oligomers were characterized by ^{1}H nuclear magnetic resonance spectroscopy, infra-red spectroscopy, mass spectrometry, vapour-pressure osmometry, gel permeation chromatography and high-performance liquid chromatography, and found to be mixtures of oligomeric polyethers. On heating, insoluble products were obtained. The prepolymers could be used to impregnate glass-fibre woven fabrics.

(Keywords: oligomer; synthesis; vinyl; Wittig; crosslink; characterization; nuclear magnetic resonance spectroscopy; chromatography)

INTRODUCTION

Linear prepolymers can be crosslinked by several methods. It was one objective of this work to produce crosslinked polymers, of hydrophobic character, using crosslinking reactions that would not release volatile products liable to generate voids. One approach is the free-radical crosslinking of vinyl unsaturation. Vinyl unsaturation is more likely to be fully utilized in crosslinking reactions when terminally situated (as in vinyl ester resins) than when subject to possible steric restrictions by being centrally located within prepolymer molecules. This report describes one method of introducing terminal vinyl unsaturation and using it for crosslinking. Subsequent publications will discuss the electrical properties, water absorption and thermal stability of the crosslinked materials, and will consider the crosslinking process in more detail.

The synthesis was a two-stage one designed to exclude hydrophilic groups from the crosslinked network structure. The absence of groups such as ester, carbonyl and hydroxyl is known to reduce moisture absorption, although other factors, such as network free volume, also contribute. The first stage consists of the reaction of 1,4-bis(chloromethyl)benzene (BCMB) with a difunctional phenol to produce a chloromethyl-terminated prepolymer. The second stage involves conversion of the chloromethyl groups to vinyl ones by the Wittig reaction. An example of the intended reaction scheme is shown in *Figure 1*, using bisphenol A (BPA; 2,2′-bis(4-hydroxyphenyl)propane).

A similar prepolymer has been prepared[1] by end-capping BPA with vinyl benzyl chloride (VBC). If the VBC used had been the pure *para* isomer, the product would have been identical to the first oligomer from the product of our reaction illustrated in *Figure 1*. But because the VBC used was a mixture of *meta* and *para* isomers, the earlier product was a mixture of first oligomers. Also, a mixture of several chloromethyl-terminated oligomers was obtained in our case, as will be demonstrated. Thus the vinyl-terminated benzyl ethers described in this present report are of a higher molecular weight, and possess a broader molecular-weight distribution than those previously reported. They would be expected to give a lower crosslink density on crosslinking.

Percec and Auman[2] prepared hydroxy-terminated poly(ether sulphones) of varying molecular weights, and end-capped the products with VBC (mixed *meta* and *para* isomers). The properties of the products would be expected to differ from those of the vinyl-terminated prepolymers shown in *Figure 1* because poly(ether sulphone) promotes thermal stability rather than hydrophobic character.

EXPERIMENTAL

Preparation of chloromethyl-terminated prepolymers

Three methods were evaluated for preparing the chloromethyl-terminated intermediate from BCMB and BPA. The most suitable method was then employed to prepare similar oligomers, using other dihydroxy aromatic compounds instead of BPA.

Method 1: use of potassium carbonate. The first method was adapted from that of Kaufmann[3]. A two-litre three-necked flask was provided with a mechanical stirrer, reflux condenser and nitrogen line. Then BPA (50 g, 0.22 mol) was added, followed by BCMB (77 g, 0.44 mol) and anhydrous potassium carbonate (80 g,

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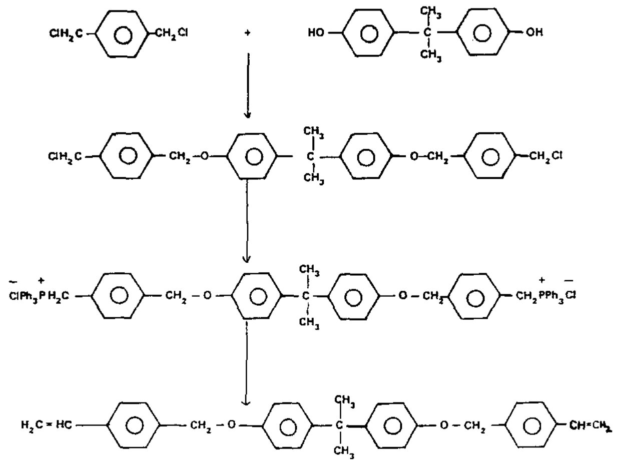

Figure 1 Reaction scheme showing the structure of the chloromethyl-terminated and vinyl-terminated products

0.58 mol) together with 400 cm^3 of dimethylacetamide (DMA). The mixture was vigorously stirred. The temperature was slowly raised to 87°C and maintained for 3 h. The hot reaction mixture was then precipitated by gradual addition to 2 litres of rapidly stirred distilled water, giving a granular product. The prepolymer was washed with hot water, filtered and washed repeatedly, before stirring in methanol to remove unreacted BCMB. The prepolymer was filtered again, washed with methanol, and dried under vacuum (2.7×10^{-5} bar) at 50°C for 5 h to remove last traces of solvents and BCMB. The yield was 87 g.

The prepolymer was a white solid, soluble in chlorinated organic solvents and in dimethylformamide. It became completely liquid at 130°C.

Method 2: reaction of the disodium salt of BPA with BCMB. Into a two-necked 250 cm^3 flask was placed BPA (10 g, 0.044 mol) and 100 cm^3 of methanol. When the BPA had dissolved, sodium hydroxide (3.67 g, 0.088 mol) was added and the mixture stirred until all the base had dissolved. The solvent and the water formed during the reaction were removed by means of a rotary evaporator, and the resulting white powder covered with dimethylformamide (DMF) (100 cm^3), followed by BCMB (15.35 g, 0.085 mol). The mixture was then heated at 90°C for 3 h, with vigorous stirring under a nitrogen atmosphere. Sodium chloride crystals began to form immediately.

The contents of the flask were poured slowly into 300 cm^3 of water, and the resulting precipitate filtered off and dried. It was then redissolved in 400 cm^3 of dichloromethane and dried over anhydrous sodium sulphate. The volume of the solution was reduced to 100 cm^3 before addition to three times this volume of methanol. The precipitate was filtered, dried at 70°C in an oven, and weighed. Some 13.8 g of product was obtained.

Method 3: preparation by phase-transfer-catalysed condensation. BPA (10 g, 0.044 mol) was dissolved in 50 cm^3 of water containing 5 g sodium hydroxide and a trace of benzyltriethylammonium chloride (BTEAC; 0.5 g, 0.0022 mol). Then BCMB (15.35 g, 0.085 mol) was added in 70 cm^3 toluene, followed by 30 cm^3 dimethylsulphoxide (DMSO). On vigorous stirring, a white suspension was formed, and the mixture was heated to 60°C for 2 h. The contents of the vessel were passed through a sintered funnel, giving two clear layers and a white residue. The white solid was extracted repeatedly with chloroform, and the two organic layers were combined for drying over anhydrous sodium sulphate. The solvents were removed by means of a rotary evaporator, and the crude prepolymer dissolved and reprecipitated from chloroform with 300 cm^3 methanol. The yield was 8.5 g.

Method 1 was used for other bisphenols as well as BPA. The following procedures are illustrative.

Preparation of chloromethyl-terminated poly(ether sulphones)

In a flange pot, equipped as in method 1, were placed 30 g (0.12 mol) of bis(4-hydroxyphenyl)sulphone (BHPS), 42 g (0.24 mol) 1,4-BCMB, 42 g (0.30 mol) anhydrous potassium carbonate and 200 cm^3 of DMA. The mixture was stirred under nitrogen and heated at 80–90°C over a period of 3 h. When the mixture had cooled to room temperature, the crude product was precipitated with 600 cm^3 water, filtered and dried. It was then dissolved in 100 cm^3 hot DMF, filtered, and reprecipitated by pouring dropwise into 300 cm^3 vigorously stirred methanol. Some 44 g of product was obtained after drying in a vacuum oven at 70°C. The prepolymer was a white powder, soluble in DMF but partially insoluble in chlorinated organic solvents. It melted in the region 155–160°C.

Reaction of BCMB with other difunctional phenols

Chloromethyl-terminated prepolymers have also been prepared from the 1,3-isomer of BCMB, resorcinol and 2,2′-dihydroxybiphenyl. These systems gave reasonable yields of soluble chloromethyl-terminated prepolymers, which could potentially form vinyl-terminated analogues. Some of the bisphenols produced insoluble or partially soluble prepolymers by reactions that will be discussed elsewhere[4]. Examples include 1,5- and 2,7-dihydroxynaphthalene, 1,4-hydroquinone and 4,4′-thiodiphenol.

Conversion of chloromethyl end-groups to vinyl ones

BPA prepolymer. The Wittig reaction was carried out as follows. Chloromethyl-terminated prepolymer from the first procedure (50 g) outlined above were heated in 250 cm^3 dry dimethylformamide (DMF) to reflux and reacted with dry triphenylphosphine (50 g, 0.19 mol) for 3 h under nitrogen. The contents were cooled to 0°C and the flask then equipped with a long gas inlet and a dropping funnel containing 5 g of sodium hydroxide in 100 cm^3 of methanol. Gaseous formaldehyde, obtained by heating 10 g of paraformaldehyde at 180°C, was carried into the DMF solution in a nitrogen stream. When all the paraformaldehyde had decomposed, the solution was stirred and the base slowly added, with the temperature maintained at 0°C. The solution was then stirred for an hour and allowed to return to room temperature. The product was precipitated with 500 cm^3 of cold water while stirring vigorously.

The precipitate was washed three times with methanol, dried and dissolved in 300 cm^3 of dichloromethane, and the solution dried over anhydrous sodium sulphate. The volume of the solution was reduced to 100 cm^3; the product was precipitated with 300 cm^3 of methanol and dried at 50°C. The yield was 41.7 g of a product which became completely liquid over a range from 130 to 140°C. Further purification by reprecipitation from dichloromethane with methanol raised the melting range to 150°C.

BHPS prepolymer. Chloromethyl-terminated poly(ether sulphone) (30 g) was heated to reflux for 3 h with 30 g of triphenylphosphine in 300 cm^3 of dry DMF. The suspension of the phosphonium salts was then cooled to 0°C. Then 4.5 g of paraformaldehyde was thermally decomposed and passed into the reaction mixture. Sodium methoxide, made by dissolving 3 g sodium in 50 cm^3 methanol, was added dropwise, and the mixture was stirred for a further hour. The product was precipitated with 600 cm^3 of cold water and filtered. The fine white precipitate was stirred vigorously with three 500 cm^3 portions of hot water, filtered, extracted with three 300 cm^3 portions of methanol and dried in a vacuum oven at 70°C. The product was a white powder, soluble in hot DMF, and melting at 155–160°C. The yield was 27 g.

DISCUSSION

Characterization of the intermediates

BPA prepolymer. Figure 2 shows the ^{1}H n.m.r. spectrum of the BPA chloromethylated prepolymer in deuterochloroform, obtained by the first preparation above, using a Bruker Fourier Transform 80 MHz instrument. The peaks were assigned using model compounds, with results as in *Table 1*. The n.m.r. spectra of prepolymers obtained by the other two procedures were very similar, although the softening temperatures of the samples obtained by the second method were about 5°C lower.

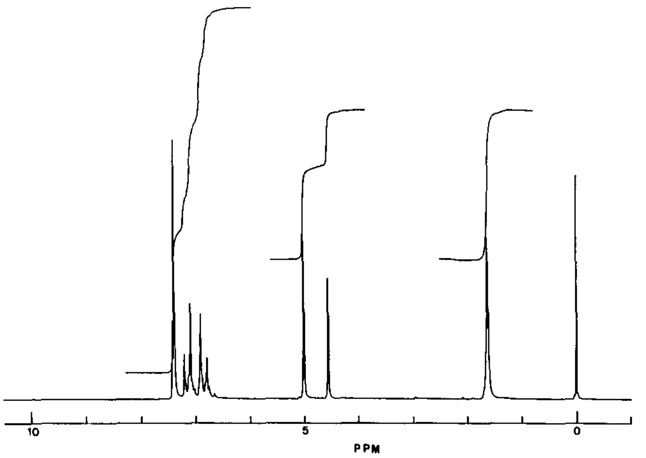

Figure 2 ^{1}H *FT*n.m.r. spectrum of the chloromethyl-terminated BPA prepolymer

Table 1 N.m.r. peak assignments for the chloromethyl-terminated BPA prepolymer

δ (ppm)	Peak type	Assignment
7.4	Singlet	Aromatic protons, BCMB residues
6.7–7.2	Quartet	Aromatic protons, BPA residues
5.0	Singlet	Methylene ether protons
4.55	Singlet	Chloromethyl protons
1.65	Singlet	Methyl protons, BPA residues

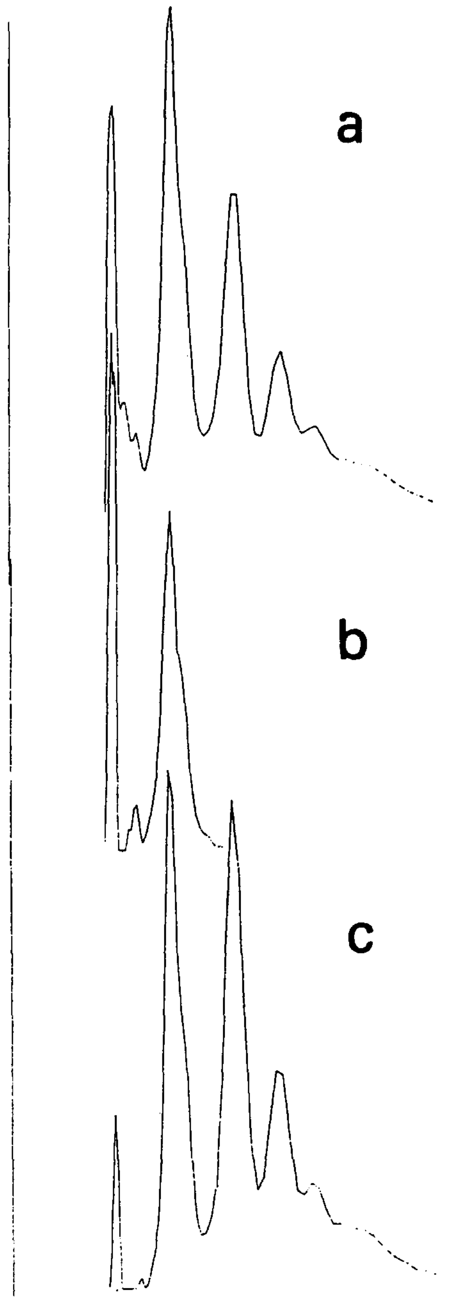

Figure 3 Gel permeation chromatogram of the chloromethyl-terminated BPA prepolymer: (a) crude chloromethyl polymer: (b) methanol-soluble portion; (c) methanol-insoluble portion

The ratio of the methylene ether to chloromethyl protons can provide an estimate of the chain length, assuming that all chain ends were chloromethyl. This appears reasonable since there was no sign of hydroxyl peaks in the infra-red spectrum. It would imply a number-average molecular weight (M_n) value of 716. The determination of M_n by means of a Knauer vapour-pressure osmometer gave a value of 632.

Gel permeation chromatography (g.p.c.) was carried out by passing a 0.2% solution in tetrahydrofuran through 50 nm and 10 nm gel columns (Polymer Laboratories) at 30°C, using polystyrene as the calibration standard.

The crude mixture precipitated from solution in DMA appeared to contain five oligomers and BCMB (see *Figure 3*). When the mixture was separated by methanol precipitation, most of the BCMB was removed, together

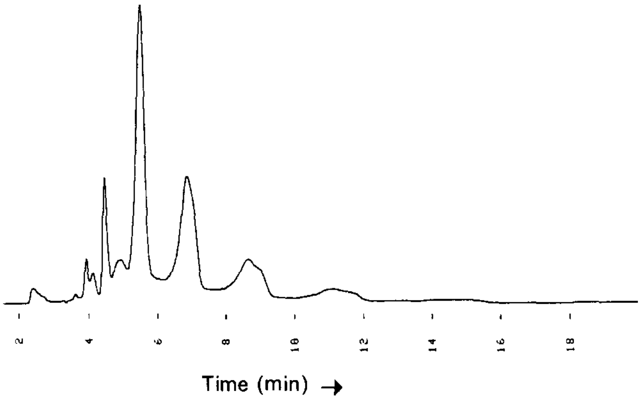

Figure 4 H.p.l.c. of the chloromethyl-terminated BPA prepolymer

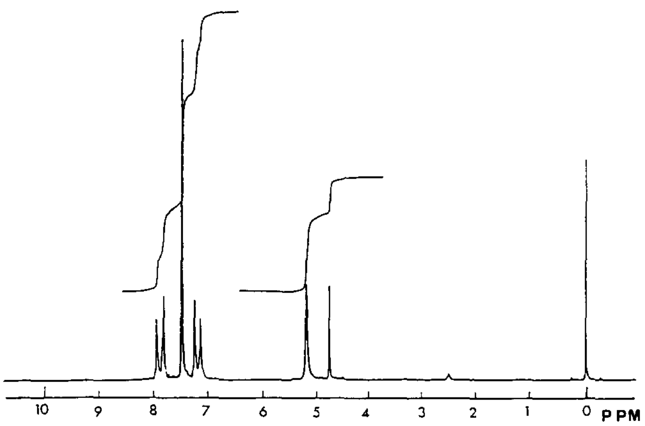

Figure 5 ^{1}H n.m.r. spectrum of the chloromethyl-terminated BHPS prepolymer

with some of the first oligomer, of molecular weight 505. The separation of oligomers was also carried out by an analytical high-performance liquid chromatograph (Spectrophysics HPLC) using tetrahydrofuran and water as the mobile phase. H.p.l.c. also indicated the presence of five oligomers (see *Figure 4*).

BHPS prepolymer. The ^{1}H n.m.r. spectrum was obtained from a sample in fully deuterated dimethylsulphoxide and is shown in *Figure 5*. The peak assignments are given in *Table 2*. The M_n value derived from the n.m.r. spectrum is 840, based on the ratio of chloromethyl groups to methylene ether protons.

Characterization of the Wittig product

BPA products. The ^{1}H *FT* n.m.r. spectrum of the product was obtained from a deuterochloroform solution (*Figure 6*). The peak previously assigned to chloromethyl protons was no longer present, but a series of new peaks at $\delta = 5.1$–5.9 and 6.7–7.5 ppm could be seen, which were consistent with the presence of vinyl groups. An additional, small peak at $\delta = 2.3$ ppm was observed and was indicative of the presence of methyl end-groups, resulting from the unintended hydrolysis of phosphonium salts.

When the Wittig reaction was carried out in methanolic sodium methoxide rather than sodium hydroxide, the peak at 2.3 ppm was very small.

Percec and Auman[5] claimed that no hydrolysis of phosphonium residues to methyl groups could be observed during a phase-transfer Wittig vinylation of a poly(ether sulphone) polymer, using aqueous formaldehyde. This contrasts with the findings of many other workers[6–9]. Some hydrolysis is to be expected, since the formaldehyde hydrate is extracted from aqueous formaldehyde into dichloromethane solvent. Our Wittig products were never entirely free from traces of hydrolysis, but after trying several procedures, it was possible to minimize the problem.

The first oligomer was isolated by extraction into methanol, in which it is sparingly soluble. Its identification was first confirmed by comparing the integral of the vinyl peak with the integral of the methylene ether peak on the n.m.r. spectrum. The ratio of terminal vinyl protons to methylene ether protons in the first oligomer is 6:4. But the two α protons of the vinyl groups are masked in the spectrum by adjacent benzene ring protons, and so the spectrum would be expected to reflect the ratio of β protons to methylene ether ones, i.e. 1:1. This is the case in practice, and further evidence was provided by mass spectrometry, using a VG Masslab Trio 2 instrument. The molecular ion of the powder appeared at $m/e = 460$. The major peaks in the mass spectrum have been assigned, and are summarized in *Table 3*.

H.p.l.c. analysis was performed on the product (*Figure 7*). The peak corresponding to the first oligomer was identified at a retention time of 5.6 min by using the isolated first oligomer as a standard. A total of five oligomers were observed.

BHPS product. The limited solubility of this material meant that an n.m.r. spectrum was not obtained. The i.r. spectrum was obtained using a Perkin–Elmer 782 and a KBr disc. It contained the expected absorptions from the vinyl group at 916, 990 and 1624 cm^{-1} and no obvious absorptions from the chloromethyl group.

Table 2 N.m.r. peak assignments for the chloromethyl-terminated BHPS prepolymer

δ (ppm)	Peak type	Assignment
7.9–7.14	Quartet	Aromatic protons, BHPS residues
7.45	Singlet	Aromatic protons, BCMB residues
5.2	Singlet	Methylene ether protons
4.74	Singlet	Chloromethyl protons

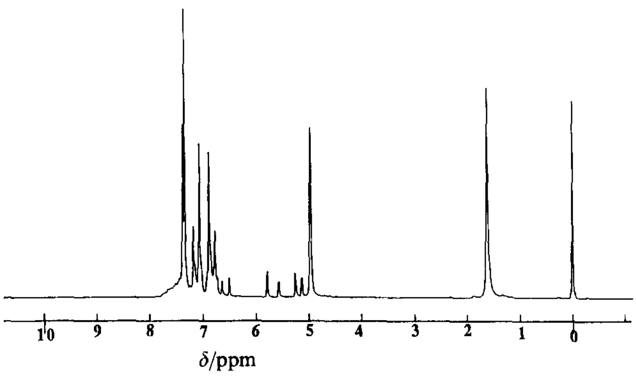

Figure 6 ^{1}H *FT* n.m.r. spectrum of the vinyl-terminated BPA product

Table 3 Mass spectrum of the first oligomer of the vinyl-terminated BPA product

m/e	Molecule/fragment cation
460	$CH_2{=}CH{-}Ph{-}CH_2{-}O{-}Ph{-}C(CH_3)_2{-}Ph{-}O{-}CH_2{-}Ph{-}CH{=}CH_2$
433	$CH_2{=}CH{-}Ph{-}CH_2{-}O{-}Ph{-}C(CH_3)_2{-}Ph{-}O{-}CH_2{-}Ph$
344	$CH_2{=}CH{-}Ph{-}CH_2{-}O{-}Ph{-}C(CH_3)_2{-}Ph{-}OH$
327	$CH_2{=}CH{-}Ph{-}CH_2{-}O{-}Ph{-}C(CH_3)_2{-}Ph$
277	$Ph{-}O{-}Ph{-}O{-}Ph{-}OH$
234	$CH_2{=}CH{-}Ph{-}CH_2{-}CH_2{-}Ph{-}CH{=}CH_2$
233	$CH_2{=}CH{-}Ph{-}CH_2{-}CH_2{-}Ph{-}CH{=}CH$
212	$HO{-}Ph{-}C(CH_3)_2{-}Ph$
183	$Ph{-}CH_2{-}O{-}Ph$
133	$CH_2{=}CH{-}Ph{-}CH_2{-}O$
118	$CH_2{=}CH{-}Ph{-}CH_3$
117	$CH_2{=}CH{-}Ph{-}CH_2$
107	$Ph{-}CH_2{-}O$
91	$Ph{-}CH_2$

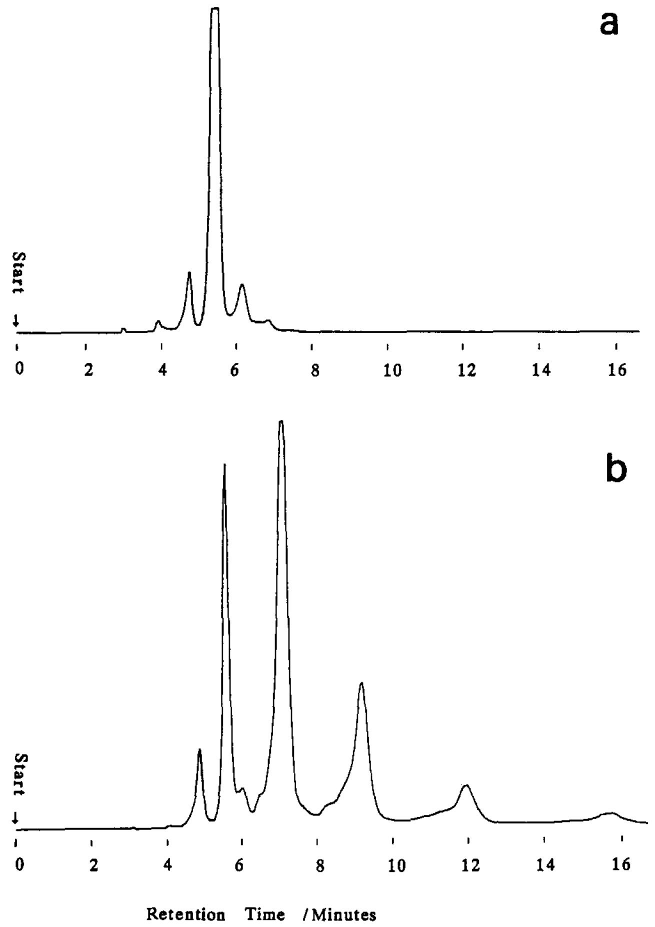

Figure 7 H.p.l.c. of the vinyl-terminated BPA product: (a) first oligomer of vinyl-terminated product; (b) vinyl-terminated product

Crosslinking

Samples of the Wittig BPA product were heated at temperatures in the range 170–200°C for periods from 15 to 60 min. The solubility of the crosslinked product in dichloromethane was determined and found to be between 5 and 7%. Woven glass fabric was impregnated, and the composite was cured in a compression press. Optical microscopic examination showed no sign of significant fibre debonding after boiling the cured laminate for 2 h in distilled water.

Comparison between the three methods of preparation of the chloromethyl prepolymer

The first procedure proved the most satisfactory of the three methods tried for the synthesis of the chloromethyl intermediate. It gave the best yield, produced prepolymers that were soluble in the reaction medium, involved no prior formation of the disodium salt and did not require an exact amount of base. Moreover the isolation procedure was relatively straightforward.

However, it was noticed that prolonging the reaction, or raising the temperature above 90°C, resulted in the formation of a yellow, insoluble and infusible product. Kaufmann[3] reported that the preparation of high-molecular-weight poly(aralkyl ethers) can lead to partially crosslinked products in some solvents, but no explanation was offered. A variety of reactions can occur between BPA and BCMB, depending on the conditions[10,11]. A bright yellow colour is attributed to the formation of xylylidene units under basic conditions. This was confirmed by Dunnavant and Marckle, who homopolymerized BCMB to form insoluble poly(*p*-xylylidene)[11]. Imai and Yamakazi[12] suggest that xylylidene formation can be suppressed by using dimethylsulphoxide as solvent. In this present study we confirmed that the formation of poly(*p*-xylylidene) can be a troublesome side-reaction when using the potassium carbonate system. The infra-red spectrum of one product is shown in *Figure 8* and is consistent with poly(*p*-xylylidene) formation. The problem of self-condensation is greatly reduced by maintaining the reaction temperature between 80 and 90°C and using short reaction times.

However, certain bisphenols are reported to undergo Friedel–Crafts reactions with BCMB, even in the absence of added Friedel–Crafts catalyst[13], resulting in the formation of undesirable polymeric products. We observed that when BPA and 1,4-BCMB are heated together in the melt, a rapid evolution of hydrogen chloride occurs, and a highly insoluble polymer is formed. It is probable that Friedel–Crafts alkylation occurs by dissociation of the C–Cl bond to give the benzyl cation, which then reacts with the activated bisphenol at the position *ortho* to the bisphenol hydroxyl group. In solution, it is more likely that crosslinking reactions occur by alkylation of a carbon instead of the preferred alkylation of the oxygen atom of the phenolate ion. The situation is analogous to the reaction between sodium

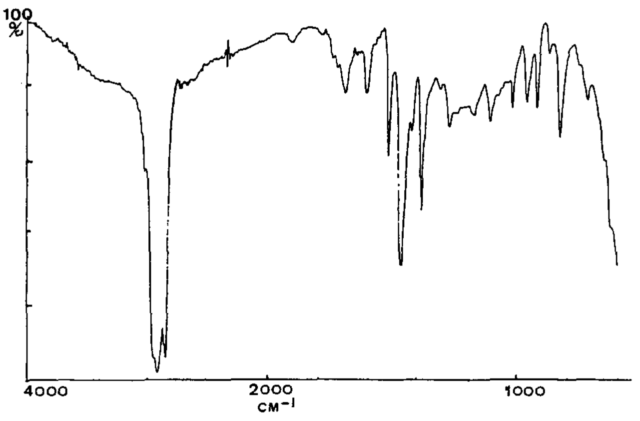

Figure 8 Infra-red spectrum of the xylylidene compound, obtained using the potassium carbonate method

phenoxide and allyl chloride, which gives a mixture of allyl phenyl ether and 2-propenylphenol. A highly polar solvent favours the former, and thus in our case would discourage crosslinking.

In the second method the number of moles of sodium hydroxide used must be exactly equal to the number of moles of phenolic hydroxy groups present. This is because an excess of sodium hydroxide hydrolyses the chloromethyl groups to form benzyl-alcohol-terminated molecules, while insufficient would leave phenolic end-groups in the product. The benzyl alcohol end-groups would be expected to undergo a Williamson etherification, forming dibenzyl ethers. During the preparation of high-molecular-weight poly(ether sulphones), it is found that small variations in the amount of base have a considerable effect on the reaction stoichiometry[14]. A further problem is the low solubility of BPA in DMF, which necessitates a high reaction temperature. When methanol was used as the solvent, the reaction proceeded well, with good yield of the prepolymer intermediate. Nevertheless, methoxymethyl end-groups were detected in the ^1H n.m.r. spectrum, suggesting nucleophilic substitution by methanol. The same end-groups were detected when BCMB was refluxed in methanol. As a result, the second procedure was eliminated.

The third procedure was also abandoned because of xylylidene formation when high base concentrations were used. At low ($<40\%$) base concentrations, the DMSO was present mainly in the aqueous phase, whereas it was intended to promote the reaction in the organic phase. The phase-transfer reaction also led to some hydrolysis of the chloromethyl end-groups, and premature precipitation of reactant.

Despite some problems, the first method produced suitable chloromethyl-terminated prepolymers of the structure shown in *Figure 1*, and was adopted as the standard procedure. The first oligomer was soluble to some extent in methanol, but the majority was precipitated.

CONCLUSIONS

Vinyl-terminated oligomeric ethers have been prepared by three two-stage methods. In each case the second stage was the same. The first of the three methods was preferred. The structure of the intermediate-stage prepolymers and of the final product were studied by n.m.r. spectroscopy, h.p.l.c. and g.p.c. The vinyl-terminated oligomers were crosslinked without catalyst to form insoluble products, and could be reinforced with glass fibres to form laminates.

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