Synthesis, kinetic observations and characteristics of polyarylene ether sulphones prepared via a potassium carbonate DMAC process

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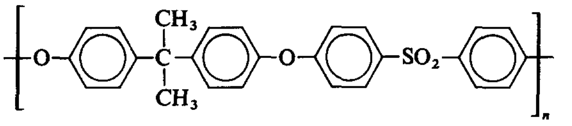
The classical route for the synthesis of this family of macromolecules is via nucleophilic aromatic substitution of 4,4′-dichlorodiphenyl sulphone with bisphenates using dimethylsulphoxide (DMSO) and aqueous sodium hydroxide. High molecular weight homopolymers can be synthesized in a relatively short time. However, hydrolytic side reactions can limit its scope for the synthesis of both homopolymers derived from insoluble bisphenates and for copolymers. An alternate route is discussed herein that uses potassium carbonate/dimethylacetamide as base and aprotic dipolar solvent, respectively, for the synthesis of several homopolymers and copolymers derived from various bisphenols. In this system, excess potassium carbonate, unlike aqueous caustic, does not prevent the synthesis of high molecular weight macromolecules. Investigations of the kinetics and mechanism of this process were conducted. These studies demonstrated that this route deviates from the relatively simple second order kinetics previously observed for the aqueous sodium hydroxide/DMSO system. This deviation has been rationalized as resulting from the partially heterogeneous nature of the potassium carbonate.

(Keywords: polysulphones; polymerization kinetics; poly(arylene ether sulphones); synthesis; bisphenols; heterogeneous reaction; K_2CO_3/DMAC process)

INTRODUCTION

In 1967, Johnson *et al.*[1] described the synthesis of a large number of high molecular weight poly(arylene ether sulphones) via step-growth condensation of bisphenates with activated aromatic dihalides. Additional papers by Rose[2] and Robeson *et al.*[3] are also pertinent. An important consequence of this work was the synthesis of 1, bisphenol-A polysulphone.



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This structure was derived from the disodium salt of bisphenol-A and 4-4′-dichlorodiphenylsulphone and is currently known as Udel polysulphone. The ether bond is thus formed via the displacement of the halide by the phenoxide. Although the bisphenol may also contain a sulphone group, this group forms an essential part of the dihalide. The electron withdrawing nature of the sulphone group activates the dihalide, thus facilitating displacement. Typically, the bisphenoxide is formed by reacting a DMSO solution of the bisphenol with a stoichiometric amount of aqueous sodium hydroxide, followed by careful removal of the water as an azeotrope with chlorobenzene. Precise, stoichiometric addition of 4,4′-dichlorodiphenylsulphone as a chlorobenzene solution to the solution of bisphenoxide in DMSO results in the formation of the polymer. An alternate route using anhydrous potassium carbonate/*N*,*N*′-dimethylacetamide as the base and aprotic solvent respectively was not believed to be significantly affected by excess anhydrous potassium carbonate. This process has received less attention compared with the DMSO/sodium hydroxide route. The literature available on this alternate process is mostly confined to patents[4,5].

Our interest in synthesis and study of copolymers[6,12] required the need for preparing and subsequently coupling well characterized oligomers. In addition we are also interested in crystallizable homopolymers. Although the DMSO/NaOH route does produce high molecular weight in a very short time, polymer hydrolysis and bisphenate insolubility pose a problem in these syntheses. It was of interest therefore to study the anhydrous potassium carbonate/*N*,*N*′-dimethylacetamide route for the preparation of these macromolecules.

EXPERIMENTAL

Monomer purification

Bisphenol-A (polymer grade, Union Carbide or Dow Chemical, USA) was recrystallized twice from hot toluene. The crystals were dried at 75°C for 12 h, cooled, well powdered and dried again for 12 h at 80°–90°C. This was essential to remove the last traces of solvent. 4,4′-Thiodiphenol (Bis-T; Crown Zellerbach Corp.) was recrystallized from aqueous methanol and dried at 75°C for

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12 h. 4,4'-Sulphonyldiphenol (Bis-S; Crown Zellerbach Corp.) was dissolved in 5% $NaHCO_3$ solution and reprecipitated by adjusting the pH to 5 with concentrated HCl. The precipitated monomer was recrystallized from aqueous methanol (50%) and dried at 100°C under reduced pressure for 24 h. Hydroquinone (Eastman Kodak) was purified in two steps. First, it was recrystallized from deoxygenated water and then sublimed under reduced pressure. The final product was white in colour and had a very sharp melting point (173°C). 4,4'-dichlorodiphenylsulphone (Union Carbide) was recrystallized three times from toluene and dried in a vacuum oven (150 Torr) at 100°C for 12 h.

Purification of solvents

The solvents used in the study were *N,N'*-dimethylacetamide (DMAC), *N*-methylprrolidone (NMP) and sulpholane. Methods for their purification are described below. All the solvents were vacuum distilled and stored under nitrogen over pretreated molecular sieves until use.

Molecular sieves (4 Å) were placed in a two necked round bottomed flask and heated under reduced pressure (5 Torr) to 50°C. In doing so, the moisture absorbed by the sieves condensed on the cooler sides of the round bottom flask. On heating for about 12 to 14 h, the molecular sieves were essentially dry. They were next cooled under reduced pressure and finally stored under dry nitrogen. These pretreated molecular sieves were then used to maintain the solvents after their purification.

N,N'-Dimethylacetamide (DMAC: Eastman Kodak) was stirred over phosphorous pentoxide for 24 h and distilled under reduced pressure in a nitrogen atmosphere. The constant boiling fraction (80°–82°C at 20 Torr) was collected at a reflux ratio of 1:1 and stored under nitrogen and over pretreated molecular sieves. Sulpholane (Technical grade, Phillips Petroleum Co.) was usually a solid at room temperature and was normally heated to first melt the material. To liquid sulpholane (500 ml) was added 5 g carbon and 15 g hiflo (filter aid from John Mansville Co.) followed by filtration. The filtrate was stirred overnight over sodium hydroxide pellets. The solvent was then vacuum distilled from a 3-necked round bottomed flask fitted with a six inch Vigreux column. The middle fraction was collected under a reduced pressure of nitrogen at 130°C. The whole process was repeated until the solvent showed the following positive test for purity. Equal volumes (e.g. 1 cc) of sulpholane and concentrated 100% sulphuric acid were mixed should remain colourless for at least 5 min[7]. Normally, two distillations are sufficient to produce such a polymer grade solvent. *N*-Methylpyrrolidone (NMP; GAF Corporation) was stirred over calcium hydride for 24 h. It was distilled under nitrogen at reduced pressure and stored over molecular sieves. Toluene (Fisher Chemicals) was used as an azeotroping solvent. It was stirred over calcium hydride for 24 h and distilled in a nitrogen atmosphere. The middle constant boiling fraction was stored under nitrogen over pretreated molecular sieves.

Synthesis of 4,4'-difluorodiphenyl sulphone from 4,4-dichlorodiphenyl sulphone and potassium fluoride

Finely divided (<350 mesh) anhydrous KF, 200 g (3.44 moles), was added to a reaction assembly which contained dry purified sulpholane (500 ml). The mixture was thoroughly stirred under nitrogen until a very fine dispersion was obtained. Next 4,4'-dichlorodiphenylsulphone, 49.36 g (0.17 moles) was added and a slow stream of dry nitrogen was maintained during subsequent heating. The mixture was refluxed for about 20–24 h. Upon cooling, the contents of the flask were poured into 100 ml water under vigorous stirring. The precipitated powder was washed with water and dried at 60°C for 2 h and then vacuum distilled at 5 mmHg. The main fraction was collected separately and recrystallized from toluene. The melting point of 98°C agrees with authentic samples. The overall yield was in the range of 70–78%.

Potassium carbonate, anhydrous grade, Baker Chemical Analytical, was granular and contained about 1% moisture as received. The following procedure was used to reduce the particle size and moisture content. Anhydrous potassium (about 40 g) carbonate was finely powdered using a mortar and pestle. The powdered K_2CO_3 was kept in a drying oven at 120°C for 12 h, repowdered in a Waring blender for about half an hour and passed through a standard sieve. Particle sizes less than 350 mesh were transferred into a large sublimator unit and heated to 100°C under reduced pressure (5 mmHg) for at least 24 h. The base was analysed as follows. A required amount of sample was dissolved in 250 ml 'carbon dioxide free' distilled water to give an approximately 0.05 N solution. This solution (50 ml) was potentiometrically titrated using a calibrated pH meter (Orion 601A) in conjunction with a glass electrode (Thomas, No. 4092-f15) and a calomel reference electrode (Thomas, No. 9090-B 15). The equivalent point was obtained from a plot of pH against volume of titrant.

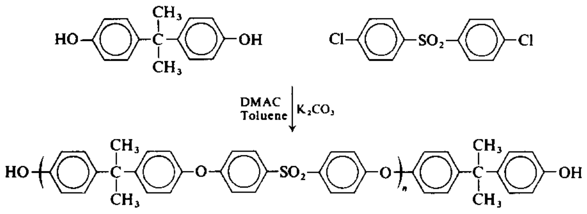
An alternate method employing a back titration was also performed as follows. To the sample solution (50 ml) 25 cc of 0.1 N HCl (solution should be acidic) was added. The resulting solution was boiled for 3–5 min to remove carbon dioxide, cooled and the excess acid titrated against standard base. The purity of the sample was found to be comparable to that found by the potentiometric titration method. Boiling and cooling the solution under nitrogen ensures reproducible values. This method is easier and faster than the potentiometric method but provides only the total base.

Study of the DMAC/toluene azeotrope

A three necked 250 ml round bottomed flask fitted with thermometer, inert gas inlet, stirring bar, a Vigreux column and a cold finger with an adjustable reflux return was used. To this apparatus was added 50 ml of DMAC and 50 ml of toluene and the mixture was heated to equilibrate the liquids. The temperature was noted and about 6.3 ml of the condensate were removed. The system was allowed to equilibrate to the new condition and again the temperature was noted and the condensate collected. This procedure was repeated until about 75% of the azeotrope was collected. The samples were analysed by gas liquid chromatography using a GOW-MAC instrument fitted with a column of 15% DC-200 on chromosorb-P. The flow rate of the carrier gas (He) was 40 ml/min coupled with a column temperature of 150°C gave good resolution of toluene and DMAC. The number of theoretical plates per column under these experimental conditions was calculated to be about 1600 plates/column. Quantitative analysis was done by measuring the area under the curves. The data were analysed by plotting the condensate and still reaction compositions against the respective temperatures.

Synthesis of polysulphone homopolymers

The polymers were usually synthesized by the nucleophilic displacement of 4,4'-dichlorodiphenylsulphone with one or more bisphenols (bisphenates). The type of functionality and molecular weight of the oligomers were controlled by the molar ratio of the monomers. A typical synthesis of a 5000 $\langle M_n \rangle$ molecular weight hydroxy terminated bisphenol-A polysulphone 2 is outlined below.



(1)

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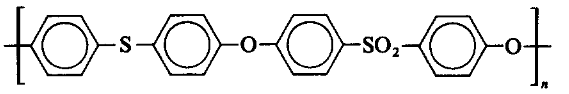
Procedure. The 500 ml reaction assembly was purged with nitrogen, then 150 ml of *N,N'*-dimethylacetamide (freshly purified) was added along with accurately weighed bisphenol-A (22.8 g, 0.1 mole) and DCDPS (23.88 g, 0.083 mole). The aluminium weighing pans and powder funnel were rinsed with 75 ml toluene. The reaction mixture was stirred vigorously with a constant purge of nitrogen and heated to reflux. It is maintained at reflux until no more water droplets from the reaction are observed. Toluene is removed continuously from the trap until the temperature rises to about 155°C. The reaction mixture appears lightly coloured and is maintained at this temperature for nearly 10–12 h. At this time the reaction is assumed to be complete. The reaction mixture is cooled to about 100°C and about 75 ml of chlorobenzene is added to dilute the solution and precipitate the inorganic salts. The mixture was filtered through a medium pore size sintered glass funnel. The filtrate was neutralized with acetic acid. The clear neutralized solution (in 25 ml portions) is coagulated in a blender containing 250 ml (1:1) water and methanol. The precipitate was filtered and washed with methanolic water and finally with water. Next, it was boiled in distilled water for 1 h to remove any trapped salts, filtered and dried in a vacuum oven at 100°C; yield was >90%. Other bisphenol-A oligomers were similarly prepared using the calculated ratios of bisphenol and dichlorodiphenyl sulphone.

Bis-T polysulphone

Structure:



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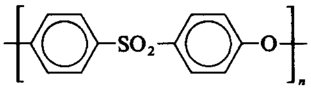
The bis-T oligomer 3 (10000 mol wt.) was similarly prepared using calculated amounts of the required monomers.

Bis-S polysulphone (cf. ref. 9)

Structure:



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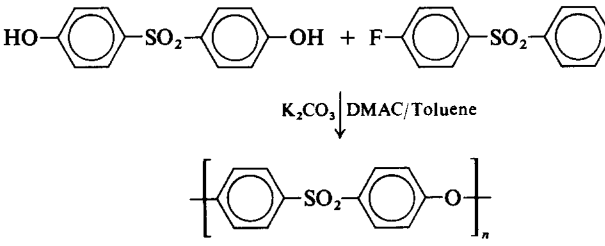
The bis-S polysulphone oligomers were generally prepared from 4,4'-difluorodiphenylsulphone and 4,4'-sulphonyldiphenol as shown below:



(2)

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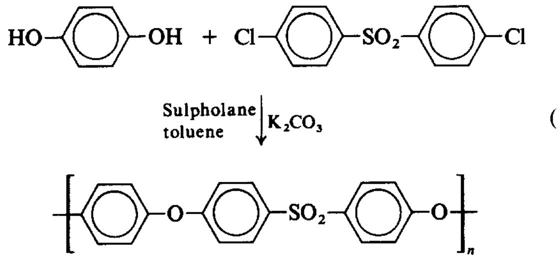
The bis-S oligomer was also synthesized from 4,4'-dichlorodiphenylsulphone and bis-S in sulpholane at 210°C for 8–10 h. Tetrachloroethane was used as a diluent.

Hydroquinone based polysulphone

The hydroquinone polysulphone, 5, was prepared in both *N*-methyl-1-pyrrolidone as well as in sulpholane at lower concentrations. The polymer had to be filtered hot to prevent crystallization. The reaction scheme is shown below.



(3)

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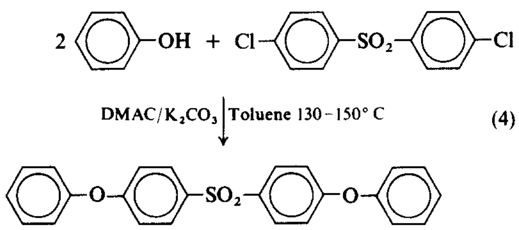
Synthesis of the model compound 4,4'-diphenoxydiphenylsulphone

Reaction:



(4)

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Procedure. To a 250 ml three necked round bottomed flask, fitted with a condenser, Dean Stark trap, nitrogen inlet, a magnetic stirring bar and an oil bath was added DMAC (50 ml), toluene (50 ml), 4,4'-dichlorodiphenylsulphone (2.87 g, 0.01 moles), phenol (2 g, 0.02 moles), and potassium carbonate. The mixture was first heated to 130°C and then to 150°C and maintained for 2 and 6 h, respectively. The reaction as checked by t.l.c. to demonstrate the absence of starting material. After 2 or more hours at 150°C it was concentrated by distilling off toluene. Finally it was cooled and coagulated in water. The precipitate was filtered, washed and dried. The product was crystallized from toluene in 85% yield with mp of 136°C. It was characterized in infra-red and ^{13}C n.m.r. (i.r. showed a C–O–C stretch at 1245 cm^{-1};

O=S=O stretch at 1295 cm^{-1}, and no –OH at 1320 cm^{-1}).

Kinetic studies

A five necked 1 litre round bottomed flask was equipped with a stirrer, nitrogen inlet sparge tube, thermometer, Dean Stark trap, water condenser with moisture trap, a silicone oil bath with magnetic stirring bar, thermometer and magnetic hot plate. High purity bisphenol-A (5.14 g, 0.0225 mole), 250 ml *N,N'*-dimethylacetamide (DMAC) and 100 ml of toluene were initially added. The Dean Stark trap was filled with toluene by gently heating the above mixture. The reactor was continuously purged with dry nitrogen and slowly heated to 130°–140°C to remove residual moisture. The reaction mixture was cooled to about 80°C and exactly 3.19 g (0.023 moles) of uniformly powdered, dry, anhydrous potassium carbonate was added under a constant purge of dry nitrogen. The reaction flask was then reheated to 140°C under nitrogen and good stirring. It was observed that the potassium carbonate particles formed a very fine dispersion in contrast to the monomers which had dissolved immediately. Good stirring was required to maintain a homogeneous dispersion. The temperature was maintained at 130°–140°C for 2 h or long enough until no further water distilled into the Dean Stark trap.

A sufficient amount of solvent was continuously distilled to increase the bath temperature to 150°C. When the temperature reached 150°C almost all of the water had already been removed and a very fine suspension of bisphenol-A dipotassium salt and/or excess potassium carbonate appeared. Then 4,4'-dichlorodiphenylsulphone (6.46 g, 0.0225 moles) was dissolved in dry DMAC (35 ml) and toluene (15 ml) and was heated to 140°–150°C. The toluene/DMAC mixture was continuously refluxed in order to maintain the reaction temperature 150°C ± 1°C. The resulting total volume was estimated to be about 300 ml. This figure was arrived at by estimating a 10% volume increase due to expansion from room temperature to 150°C. This allowed us to estimate the alkali concentration as 0.15 equivalent/litre.

Analytical samples

5.0 ml for analysis was withdrawn and emptied immediately into a 125 ml beaker containing 0.1 N HCl in DMAC. The acid reacted immediately with the base thus arresting the reaction. The excess HCl was back titrated with 0.0225 N KOH in methanol using a pH meter. The first derivative plot of $\Delta E/\Delta V$ vs. volume permitted the equivalent point to be measured.

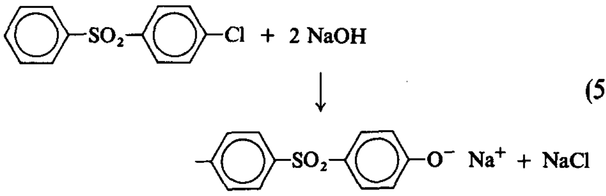
Hydrolysis study

It was of interest to study the possible hydrolytic side reactions of 4,4'-dichlorodiphenylsulphone (DCDPS) due to an excess of anhydrous potassium carbonate and bicarbonate. The reaction was studied under conditions of polymerization by reacting DCDPS (2.786 g, 0.01 mole) and bicarbonate (2 g, 0.02 moles), respectively. After 5 h in dry DMAC at 150°C the reaction mixture was cooled to room temperature and the product was analysed by thin layer chromatography (t.l.c.) and compared against DCDPS and bisphenol-S. The t.l.c. was developed using a benzene/ethyl acetate mixture (75:25) and showed no other product other than DCDPS. This was further confirmed by pouring the reaction mixture in water. Filtering and acidifying the filtrate pH showed no additional product. Analogous treatment of 4,4'-diphenoxydiphenylsulphone and high molecular weight methoxy capped polysulphone showed no change in infra-red spectra or intrinsic viscosities.

RESULTS AND DISCUSSION

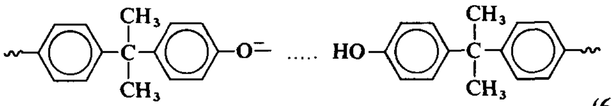
Kinetic and mechanistic aspects of the potassium carbonate/DMAC process

Hydrolytic side reactions. An established method for the synthesis of polyarylene ether sulphones is via the dimethyl sulphoxide/aqueous sodium hydroxide route[1]. This method is not without limitations since it requires the exact stoichiometric amount of sodium hydroxide. Even a modest 1% deviation of the base drastically decreased the reduce viscosity (*RV*) in chloroform at 25°C of the resultant polymer from 1.8 dl/g to 0.6 dl/g. Also, the effect of alkali deficiency on the reduced viscosity was greater than the corresponding excess. A decrease in viscosity in the presence of excess base has been attributed to the hydrolytic side reaction of dichlorodiphenylsulphone, to the relatively inactive phenoxide group[1], as shown in equation (5).



(5)

More recently[8], it has been reported that a deficiency of alkali not only disturbs the stoichiometry of the bisphenols but that unreacted phenol can hydrogen bond with an equivalent amount of sodium phenate, thereby reducing the nucleophilicity of the phenate by nearly one order of magnitude. The complex, 7, formed is believed to be:

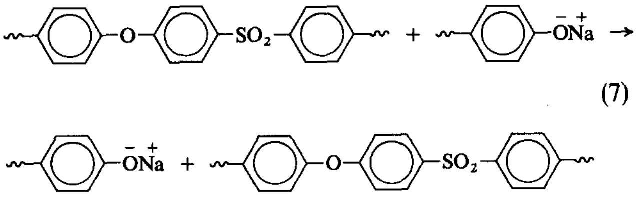


7 (6)

Hydrogen bonded complex

Thus, in the presence of excess alkali only half an equivalent in the halide is converted to the unreactive phenoxide while the lack of alkali renders more than an equivalent of the phenoxide unreactive. These data may rationalize the greater decrease of reduced viscosity when a lack of alkali is used.

Although the ether bond is relatively stable to hydrolysis, the presence of excess base under the reaction conditions can cleave the activated ether linkage[9]. The polymer hydrolysis is shown below:



(7)

curve was obtained from a plot of conversion *versus* time as provided in *Figure 7*.

Since the expected second order plot was not obtained for both the polymerization and the model reaction at equal concentration of the reactants, it was reasoned that the reactive species (the phenoxide and the halide) were present in nonstoichiometric amounts in the reaction mixture. That is, the phenoxide ion concentration was far less than expected. To verify this, the concentration of total base in the reaction system at various temperatures was studied. A plot of total base as a function of temperature is shown in *Figure 8*. The concentration of total base shows a sixfold increase in solubility (from 0.01 to 0.065 g/litre) as the temperature increases from 130°C to 160°C. Also, the maximum base concentration is 0.07 g/litre at 160°C. As the kinetic study was performed at much higher concentrations than this, only a fraction of the total expected phenoxide was present. This could be due to the incomplete formation of the phenoxide caused by the poor solubility of the base under reaction conditions or the insolubility of the diphenoxide formed, or both. These possibilities are shown in the equation below:

$$K_2CO_3\ (\text{solid}) \rightleftharpoons K_2CO_3\ (\text{sol}^n) \qquad (11)$$

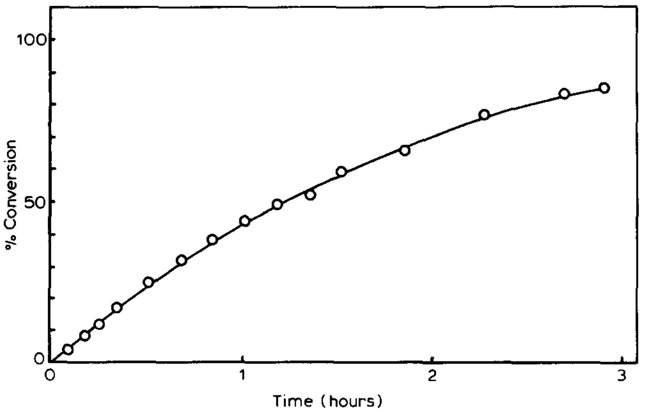


Figure 7 Kinetic plot of reaction of p(t-butyl) phenol with 4,4′-dichlorodiphenyl sulphone (conversion vs. time) at 150°C

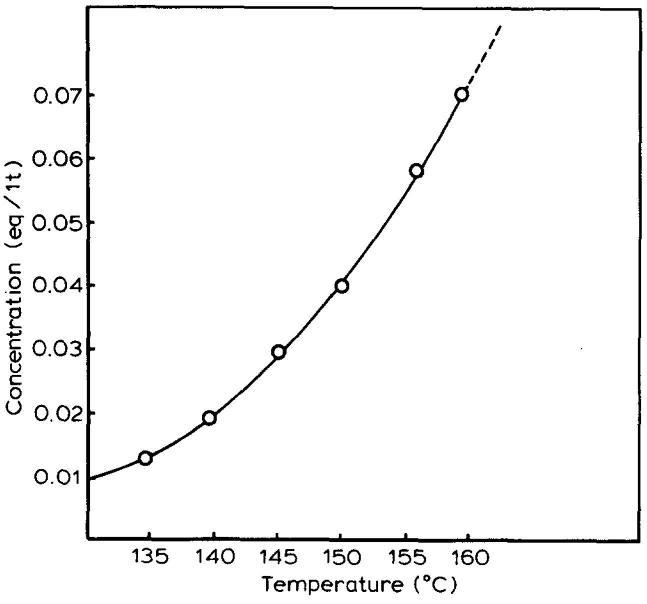


Figure 8 Concentration of total base as a function of temperature for the DMAC/toluene system

$$KHCO_3\ (\text{solid}) \rightleftharpoons KHCO_3\ (\text{sol}^n) \qquad (12)$$

$$\overset{+}{M}\overset{-}{O}\text{–Ar–}\overset{-}{O}\overset{+}{M} \rightleftharpoons \overset{+}{M}\overset{-}{O}\text{–Ar–}\overset{-}{O}\overset{+}{M} \qquad (13)$$

(solid) (solution)

Since DMAC has cation solvating power comparable to DMSO, one would expect much higher solubility of the bisphenate than observed. However, under reaction conditions, the azeotropic study shows the presence of the toluene cosolvent. This would no doubt significantly reduce the solubility of base in DMAC. In addition to the above reactions there should also be a rapid acid–base equilibria between phenols and carbonates. Bicarbonate formed by the reation of potassium carbonate and bisphenol can also react with phenol to form phenates. The reaction is accompanied by the evolution of carbon dioxide and formation of water.

$$K_2CO_3 + HO\text{–Ar–}OH \rightleftharpoons \overset{+}{K}\overset{-}{O}\text{–Ar–}OH + KHCO_3 \qquad (14)$$

$$K_2CO_3 + KO - \text{Ar–}OH \rightleftharpoons \overset{+}{K}\overset{-}{O}\text{–Ar–}\overset{-}{O}\overset{+}{K} + KHCO_3 \qquad (15)$$

The bicarbonate could also undergo decomposition to give carbonate, water and carbon dioxide. The carbonate formed from decomposition of bicarbonate can undergo the same cycle of reactions. The presence of toluene aids the removal of water formed by the reaction of bicarbonates, thus maintaining anhydrous conditions.

$$K_2CO_3 + HO\text{–Ar–}OH \rightleftharpoons \overset{+}{K}\overset{-}{O}\text{–Ar–}OH + KHCO_3 \qquad (16)$$

$$K_2CO_3 + KO\text{–Ar–}OH \rightleftharpoons \overset{+}{K}\overset{-}{O}\text{–Ar–}\overset{-}{O}\overset{+}{K} + H_2O + CO_2 \qquad (17)$$

$$2KHCO_3 \rightarrow K_2CO_3 + CO_2\uparrow + H_2O \qquad (18)$$

Phenoxides formed by the above reactions react with halides to form ether linkages. Due to the possible greater reactivity of monomers over dimers or oligomers, the following reactions may be envisaged.

$$\overset{+}{K}\overset{-}{O}\text{–Ar–}\overset{-}{O}\overset{+}{K} + X\text{–Ar–}X \xrightarrow{k_1} \overset{+}{K}\overset{-}{O}\text{–Ar–O–Ar–}X + KX\downarrow \qquad (19)$$

$$\overset{+}{K}\overset{-}{O}\text{–Ar–}\overset{-}{O}\overset{+}{K} + X\text{–Ar}\sim\sim \xrightarrow{k_2} \overset{+}{K}\overset{-}{O}\text{–Ar–O–Ar}\sim\sim + KX\downarrow \qquad (20)$$

$$\sim\sim\text{Ar–}\overset{-}{O}\overset{+}{K} + X\text{–Ar–}X \xrightarrow{k_3} \sim\sim ArOArX + KX \qquad (21)$$

$$\sim\sim Ar\overset{-}{O}\overset{+}{K} + X\text{–Ar}\sim\sim \xrightarrow{k_4} \sim\sim ArOAr\sim\sim + KX \qquad (22)$$

In the first two reactions the bisphenoxide reacts with monomeric dihalide and a reacted halide, respectively. Reaction (21) takes place between an oligomeric phenol and a dihalide. Reaction (22) between an oligomeric phenol and an oligomeric halide of course, truly represents the polymerization reaction. During the initial stages of the reaction, i.e. less than 50% extent of reaction, k_1, k_2 and k_3, will influence the overall observed kinetics. Beyond this point, k_4 is the predominant contributor to the observed rate constants. Although k_4 influences only after 50% extent of reaction, from a polymerization point of view, only dimers are formed at this stage and the polymerization process has just begun.

Compared to the DMSO/aqueous NaOH system, this alternate route appears to be nearly 10 times slower. The solubility and acid–base equilibria influence only the concentration of phenoxide and thereby the order of the reaction. The slower reaction rates may be due to hydrogen-bonding of the phenoxide with unreacted phenols, the lower dielectric constant of the reaction medium due to the presence of significant amounts of toluene or merely the initial heterogeneous nature of the K_2CO_3.

From a more practical point of view, we have studied the reaction by an *in situ* method. Here, both the monomers and the base were added to the reaction solvent, i.e. the phenoxide was formed *in situ*. The reaction kinetics were studied at three different temperatures, 140°C, 150°C and 157°C, respectively. Plots of conversion *versus* time are shown in *Figure 9*. Qualitatively, one observes that the time taken for 50% extent of reaction to be completed is about 130 min, 45 min and 25 min at 140°C, 150°C and 157°C, respectively. At the end of 10 h under the above conditions, the reaction carried out at 157°C produced high molecular weight polymers while the one at 140°C yielded only trimers and oligomers. In these cases, too, the reactions were of fractional order (see *Figure 10*).

Synthesis of polysulphone oligomers

During the course of investigation, several homopolymers of polysulphone were synthesized by the K_2CO_3/DMAC route as described in the Experimental section. Results and discussions of their characteristics are given in this section.

Various number average molecular weight polysulphone oligomers derived from bisphenol-A, bisphenol-T, bisphenol-S and hydroquinone were prepared by using calculated monomer mole ratios. These ratios used were such that the oligomers were always phenol terminated. This aspect simplified the characterization of oligomers and also in subsequent reactions for the synthesis of block copolymers since we could utilize our previously published titration procedure[13]. The use of a modest excess (10–20%) of anhydrous potassium carbonate did not reduce the intrinsic viscosity of the resultant bis-A polysulphone. *Figure 11* shows a plot of intrinsic viscosity (at 25°C in methylene chloride) as a function of mole per cent of anhydrous potassium carbonate. Reduction in the intrinsic viscosity due to lack of alkali results in less than the calculated amount of phenoxide being formed, thereby allowing only the formation of lower molecular weight oligomers.

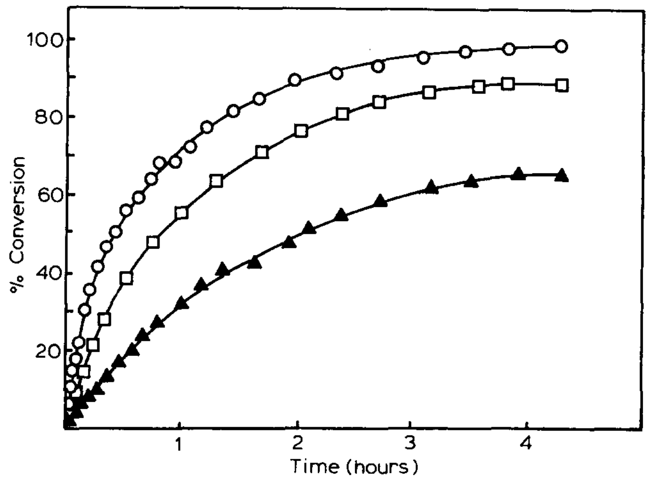


Figure 9 Kinetics of the *in situ* polymerization reaction. (○) 157°C, (□) 150°C, (△) 147°C of conversion vs. time

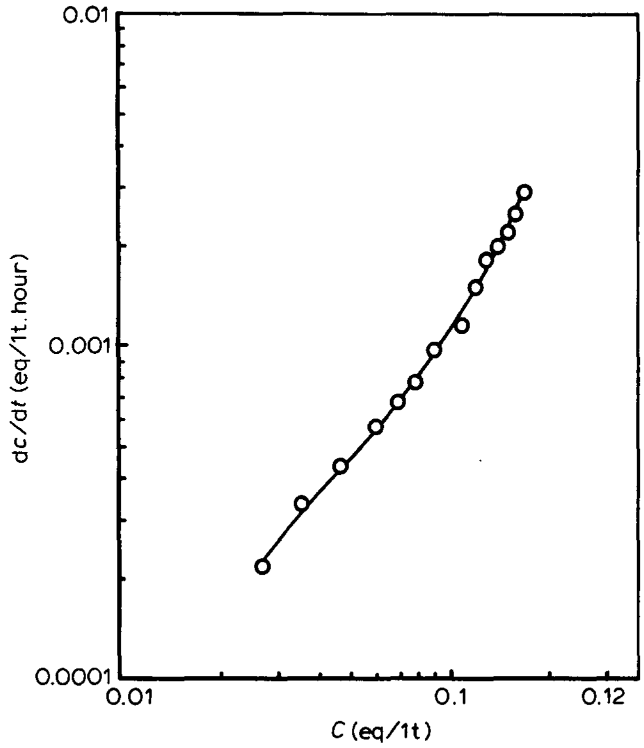


Figure 10 Order of polymerization reaction for the *in situ* process at 150°C. [(d*c*/d*t*) vs. *c*]

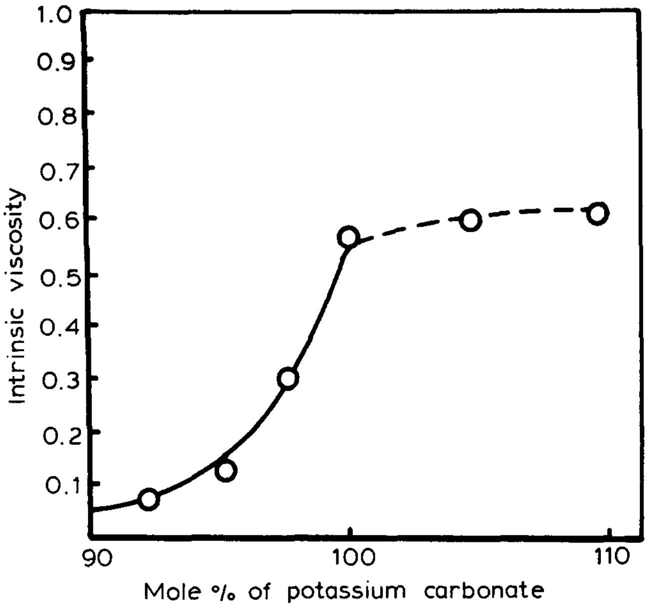
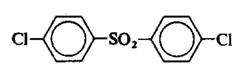


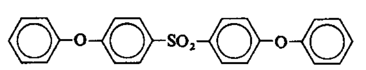
Figure 11 Intrinsic viscosity of bisphenol A polysulphone as a function of the mole% potassium carbonate relative to bisphenol-A

The i.r. spectra of all polymers showed peaks at 1245 cm^{-1} characteristic of C–O–C stretching of aryl ether group. Also, doublets in the region 1280–1320 cm^{-1} resulting from asymmetric O=S=O stretching were observed. Aromatic ring vibrations at 1010 cm^{-1} were consistent with *para* substituted products. Absorption bands were not found in the regions characteristic of *ortho* or *meta* substituted products. *Figure 12* shows a typical i.r. trace of bis-A polysulphone, obtained via the DMAC/ K_2CO_3 route.

This hydrolysis reaction and related phenate interchange limits the potential direct synthesis of block copolymers.

The effect of a modest excess of anhydrous potassium carbonate on the hydrolytic side reactions of the dihalide, diphenoxydiphenylsulphone and methoxy terminated polysulphone **8** were studied, as outlined in the Experimental section.





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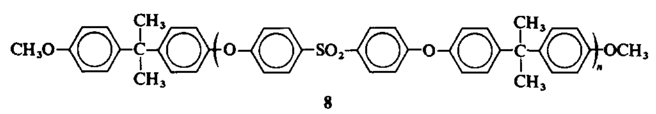
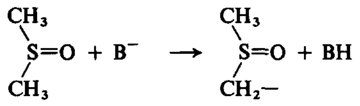


8

These studies show no significant hydrolysis of the halide or the polymer in presence of anhydrous potassium carbonate after 5 h in DMAC at 150°C.

DMAC/toluene azeotrope study. DMSO is sensitive to acidic or basic moieties. In the presence of oxygen and excess alkali or alkaline solution (e.g. potassium hydroxide or potassium t-butoxide), DMSO is subject to autoxidation. This is likely to be due to the deprotonation of DMSO to form a methyl–sulphinyl carbanion, **9**[1]. Acidic substitution substances such as phenol may also slowly react with DMSO.



$$\mathrm{(CH_3)_2S{=}O} + \mathrm{B^-} \longrightarrow \mathrm{(CH_3)(CH_2^-)S{=}O} + \mathrm{BH} \qquad (8)$$

9

The anhydrous potassium carbonate/*N,N'*-dimethylacetamide route was studied to reduce the requirement for an exact amount of alkali. Although this solvent has perhaps a comparable cation solvating power to DMSO, it appears to be not significantly affected by excess anhydrous potassium carbonate. The success of the polymerization reaction using bisphenate and an activated halide is critically dependent on the ability of the solvent to homogenize both the phenate and the growing polymer end under anhydrous conditions. The solvent composition during the reaction also influences the kinetics or the rate of reaction. Since azeotropic data was not available under the experimental conditions, the DMAC/toluene azeotrope was studied as outlined in the Experimental section. *Figure 1* shows the gas chromatography (g.l.c.) trace of the condensate composition at various temperatures. Using the results obtained from the data, the condensate and reactor compositions were calculated and plotted for a series of temperatures as shown in *Figure 2.* At all times during the distillation the reactor temperature was, of course, higher than the condensate temperature. However, at any given temperature, the condensate contained more toluene than the reactor still as one might predict. At 150°C, which was often the temperature used for the polymerization reaction, the reactor composition was found to be 85:15, DMAC:toluene as indicated in *Figure 2.*

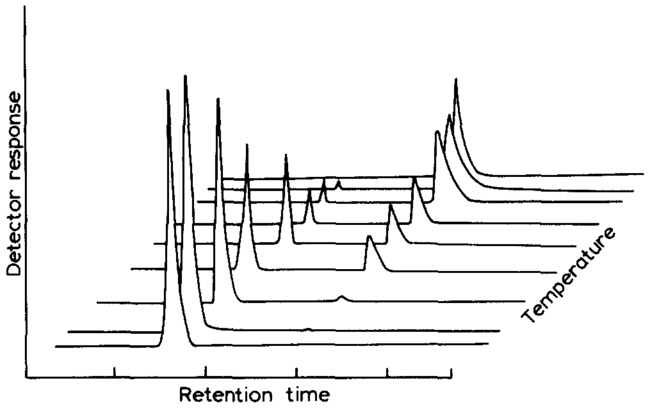


Figure 1 Gas chromatography trace of condensate composition as a function of temperature. Column 15% DC 200 on chromosorp P. Temperature 150°C. Flow rate 40 ml/min. Sample size 25 μl. Chart speed 1 inch/min

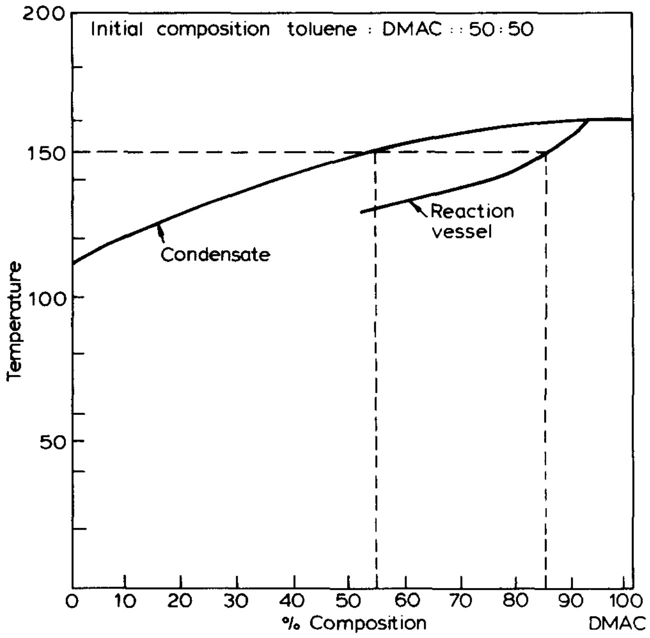


Figure 2 Plot of composition of condensate and reactor as a function of temperature

Kinetics of bis-A phenoxide with 4,4'-dichlorodiphenyl sulphone in DMAC/toluene

Both n.m.r. and infra-red spectroscopy of model compounds and polymers obtained by reacting 4,4'- dichlorodiphenylsulphone (DCDPS) with monophenols and bisphenols via the DMAC/K_2CO_3 were consistent with all *para* products, i.e. not *meta* or *ortho* products were observed, ruling out the possibility of the benzyne mechanism. This is, of course, analogous to the DMSO/aqueous sodium hydroxide procedure[1]. The formation of the orange yellow colour upon the addition of the sulphone to the phenoxide has been reported to be possible formation of the Meisenheimer type sigma complex formed by the reactants. It is thus likely that the formation of the ether linkage occurs exclusively via a bimolecular process.

The polymer forming reaction between difunctional bisphenate and DCDPS groups has been shown to be second order in DMSO with respect to the concentration of the functional groups[11]. The equation representing the rate of reaction is expressed as follows:

$$-\frac{d[ArO^-]}{dt}=k[ArO^-][ArX] \qquad (9)$$

where $[ArO^-]$ and $[ArX]$ represent the concentrations of the phenoxide ion and the activated halide. The integrated form of the above equation for equal initial concentrations of the monomers is then,

$$\frac{1}{C}=\frac{1}{C_0}+kt \qquad (10)$$

where C_0 and C are the concentrations of the phenoxide ion at $t=0$ and at any given 't'. Thus a plot of $1/c$ vs. t should yield a straight line with a slope equal to 'k', the apparent reaction rate constant. Schulze and Baron[12] studied the reaction of bisphenol-A with 4,4'-dichlorodiphenylsulphone in the DMSO/aqueous NaOH process. They observed an initial curvature in the plot and rationalized it to the greater reactivity of one halide in the DCDPS monomer. By comparison, the reaction of bis-A phenoxide with 4,4'-dichlorodiphenylsulphone via the DMAC/K_2CO_3 route showed identical initial behaviour (*Figure 3*). However, in this case, it was not possible to reproduce their results completely. The plots derived from K_2CO_3/DMAC do not show any portion of completely linear behaviour (*Figure 4*). The non-linear nature of the plot suggests that it may not be a second order reaction where $C_A=C_B$. A more meaningful interpretation was sought by plotting C vs. T and taking the slope at various points to obtain the expected differential, dc/dt. The order of the reaction was then obtained by plotting dc/dt vs. C on a log–log scale. The slope of the curve at various C yielded the order of the reaction at the respective concentration C. The apparent 'order' of the reaction for preformed phenoxide for various initial concentrations varied from 0.85 to 1.35 as indicated in *Figure 5*.

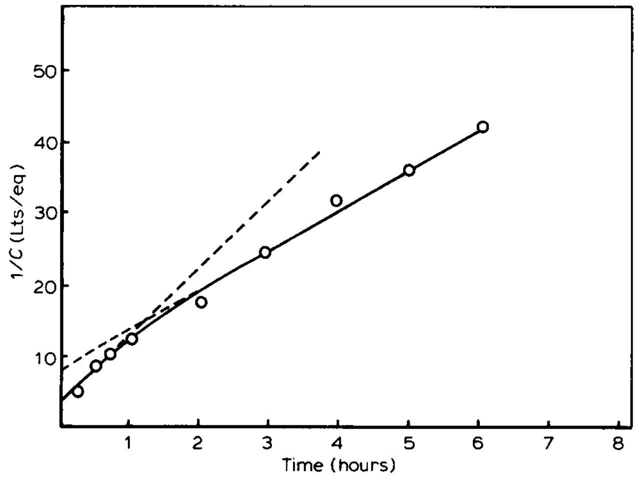


Figure 3 Kinetic plot of polymerization reaction of bis-A and 4,4 dichlorodiphenyl sulphone (1/$c$vs. time). $C_0 \simeq 0.25$ eq/lts (Expected second order plot)

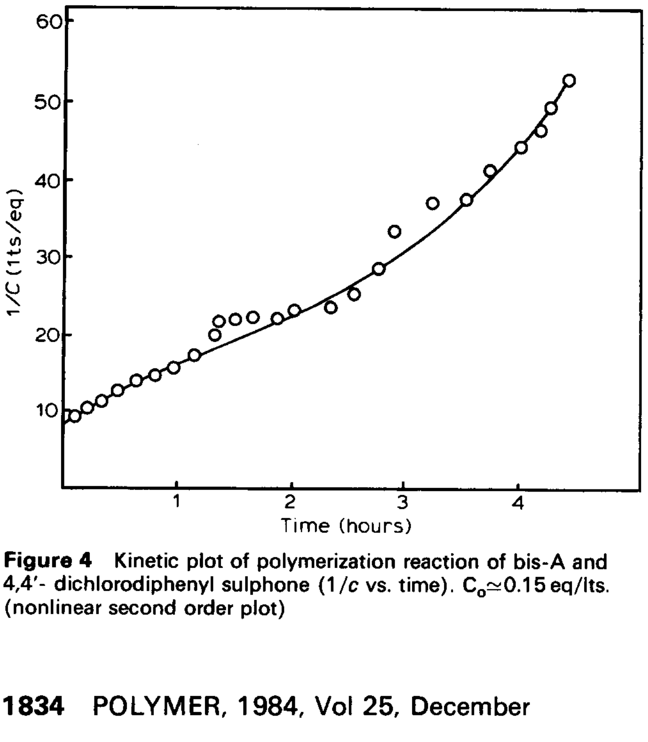


Figure 4 Kinetic plot of polymerization reaction of bis-A and 4,4'- dichlorodiphenyl sulphone (1/c vs. time). $C_0 \simeq 0.15$ eq/lts. (nonlinear second order plot)

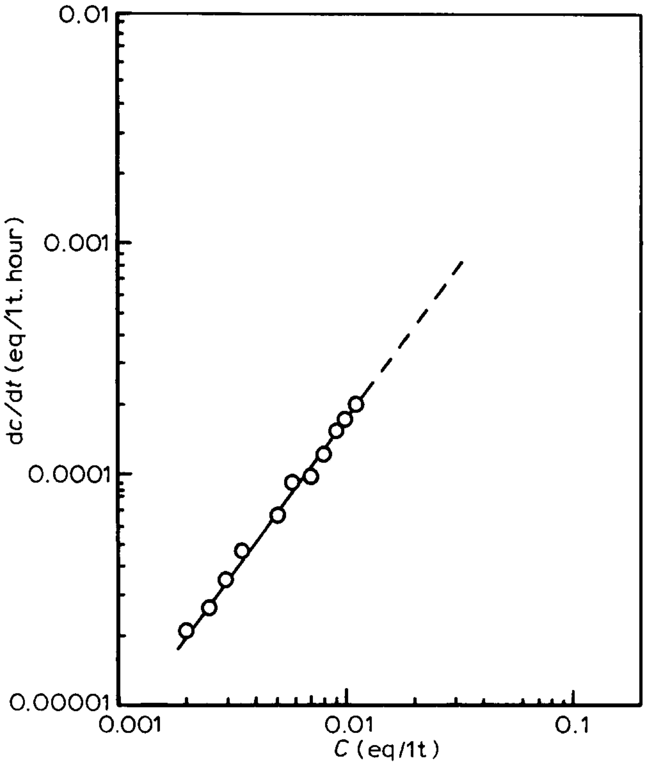


Figure 5 Apparent order of polymerization reaction in the presence of preformed phenoxide at 150°C (n=1.36 for $C_0 \simeq 0.015$)

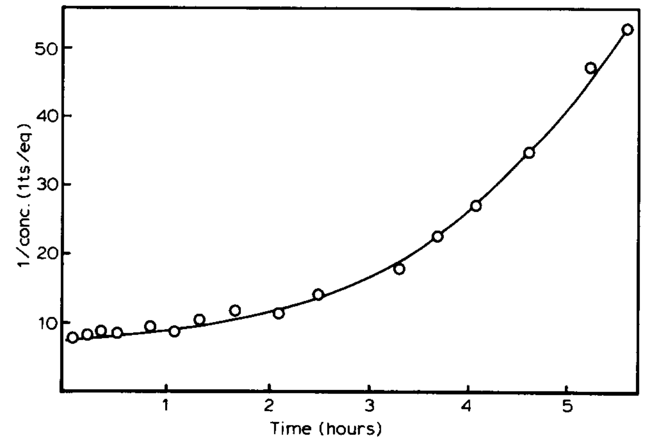


Figure 6 Kinetic plot of the reaction of *p*-(t-butyl) phenol and 4,4'- dichlorophenyl sulphone (1/conc. vs. time), at 150°C

As the nature of the reaction seemed complex, a model reaction of *p*-(t-butyl)phenol, an example of a model monofunctional phenol with dichlorodiphenylsulphone was performed. A second order plot of $1/C$ *versus* 't' again did not yield a straight line (*Figure 6*). However, a smooth

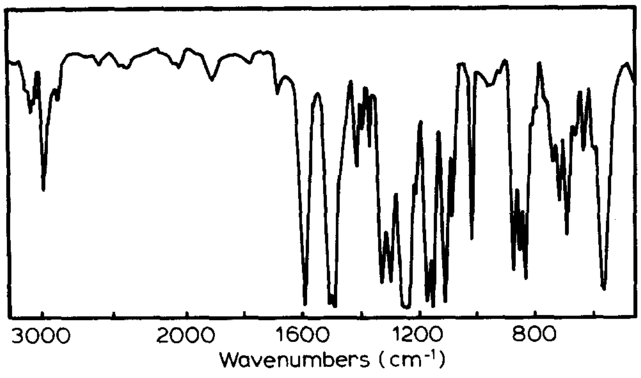


Figure 12 I.R. spectra of bis-A polysulphone obtained by the DMAC/K_2CO_3 process

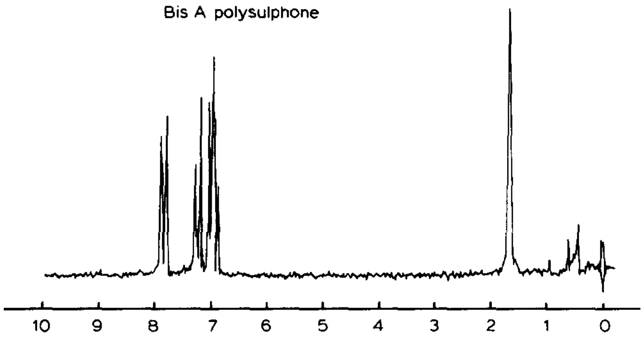


Figure 13 N.m.r. spectra of bis-A polysulphone

The n.m.r. spectra of bis-A polysulphone is shown in *Figure 13*. The protons at 1.7 ppm (TMS = 0) are due to the aliphatic protons from the isopropylidene group in bisphenol-A. The remaining proton signals are observed in the aromatic region (6–7.8 ppm). For clarity, an expanded aromatic region is shown in *Figure 14*. The spectrum shows a series of doublets arising from non-equivalent *ortho* protons as indicated by a typical coupling constant (*J* value) of 8.2–8.14 Hz. The most downshifted doublet centred around 7.85 ppm (H_a) is due to protons *ortho* to sulphone. The doublet around 7.25 ppm (H_c) is due to protons *ortho* to isopropylidene group and *meta* to ether linkage. Doublets around 7.00 ppm and 6.92 ppm have been assigned to H_b protons (*ortho* to ether and *meta* to sulphone) and H_d protons (*ortho* to ether and *meta* to isopropylidene). It is clear from both i.r. and n.m.r. that the polymer obtained by DMSO/aqueous NaOH and DMAC/K_2CO_3 are identical.

While bis-T polysulphone could be made in a similar way to bis-A polysulphone, synthesis of bis-S[9] and hydroquinone polysulphone had to be modified. The more acidic bis-S phenol results in a lower nucleophilicity of the resulting phenates. Thus to achieve the desired molecular weight in a reasonable time required the use of relatively higher reaction temperatures or a more reactive dihalide. Sulpholane was used as a high boiling solvent, however, base-contact time was kept short due to a slow base consuming side reactions. The reaction could be carried out without much modification by using the more reactive 4,4'-difluorodiphenyl-sulphone instead of the dichloro derivative. More recently, NMP has been successfully utilized in our laboratory[14].

Hydroquinone polysulphone was crystalline as prepared and often precipitated out of the solvent under experimental conditions. To overcome this problem, the reaction was carried out at a lower concentration (10% wt/vol) in *N*-methyl-pyrolidone at 180°C and filtered hot after completion of reaction.

Since a slight excess of anhydrous potassium carbonate was used for the synthesis, the coagulated polymer was boiled in hot distilled water for two hours. This minimized the amount of inorganic salts trapped in the polymer.

Glass transition temperatures (T_g) and molecular weight of the oligomers are given in *Table 2*. T_g values ranged

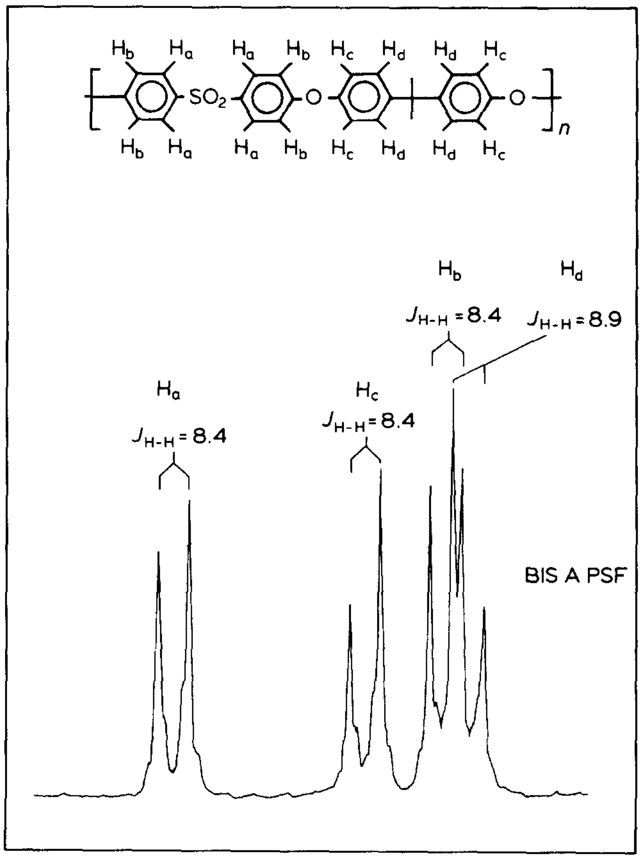


Figure 14 Proton n.m.r. spectra of bis-A polysulphone (aromatic region only)

Table 1 Molecular weight (M_n) of polysulphone oligomers by end group analysis

Polymer type	Molecular weight Calculated	Obtained
Bis-A polysulphone	2500	2400 ± 100
	5000	4250 ± 170
	10000	9000 ± 300
	25000	25750 ± 500
Bis-T polysulphone	10000	10250 ± 50
Bis-S polysulphone	5000	4800 ± 200
	10000	10250 ± 200
Bis-A/Hq polysulphone	20000	17000 ± 300

Table 2 Glass transition temperature of various polysulphones

Oligomer	T_g (°C)*
Bis A PSF	190
Bis S PSF	231
Bis T PSF	180
Hq PSF	210**

* From Rheovibron at 3.5 Hz
** From d.s.c. (40°C/minute), T_m at 310°C also observed

from 180°C for bis-T homopolymer to 231°C for bis-S homopolymer. The thioether in bis-T homopolymer linkage imparts greater chain flexibility compared to the aliphatic carbons of bisphenol-A. The polymer consequently has a lower T_g than bis-A polysulphone. However, the rigid polar sulphone linkage in bis-S polysulphone increases the glass transition temperature of the homopolymers. Only hydroquinone homopolymer shows a crystalline melting point peak at around 310°C. Additional physical characterization studies on these systems will be reported shortly. Some preliminary results have already been published[14].

REFERENCES

1 Johnson, R. N. *et al. J. Polym. Sci. A-1* 1967, **5**(9), 2375

2 Goethals, E. J. 'Reviews in Macromolecular Chemistry', Vol. 2, p. 73–144, (1968)

3 Robeson, L. M., Farnham, A. G. and McGrath, J. E. *Appl. Polym. Symp.* 1975, **26**, 373

4 Imperial Chemical Industries U.S. Ger. Pat. 2 635 101. Chem. Abst. 86-156203e (1977), Taylor, I. C. (Imperical Chemical Industries Ltd.) Ger. Pat. 2 733 905. Chem. Abst. 88-137183y (1978), Imperial Chemical Industries Ltd. Jap. Pat. 78 12991. Chem. Abst. 89-444111b (1978)

5 Gerd, B. and Claus, C. (BASF A-G), Ger. Pat. 2 749 645. Chem. Abst. 91-40110w

6 Ward, T. C., Shchori, E., Wnuk, A. J., Viswanathan, R. and McGrath, J. E. 'Multiphase Polymers', (Eds. S. Cooper and G. Estes), ACS Symposium Series, 1979, p. 289

7 Fieser, L. F. and Fieser, M. 'Reagents for Organic Synthesis', Vol. 2, John Wiley Press (1979)

8 Storozhuk, I. P. *et al. Vysokomol, Soed.* 1977, **A19**, 8 (800-06)

9 Rose, J. B. *Polymer* 1974, **15**, 456

10 Martin, D. and Hauthal, H. G. 'Dimethyl Sulfoxide', John Wiley and Sons, New York (1975), p. 330

11 Schulze, S. R. and Baron, A. L. *Adv. Chem. Ser.* 1969, **91**, 689

12 Webster, D. C. and McGrath, J. E. 'Poly(Aryl Ether)-Poly(Aryl Ester) Block Copolymers I. Polysulfone-Polybisphenol-A Terephthalates', Contemporary Topics in Polymer Science, Volume 4, (Ed. W. J. Bailey), Plenum Press, 1983

13 Wnuk, A. J., Davidson, T. F. and McGrath, J. E. *J. Appl. Polym. Sci., Appl. Polym. Symp.* 1978, **34**, 89

14 Mohanty, D. K., Hedrick, J. L., Johnson, B. C. and McGrath, J. E., to be published

15 McGrath, J. E., Ward, T. C., Viswanathan, R. and Webster, D. C., 12th National SAMPE Technical Conference, pp. 305–319 (1980)