Synthesis and characterization of amine terminated poly(arylene ether sulphone) oligomers

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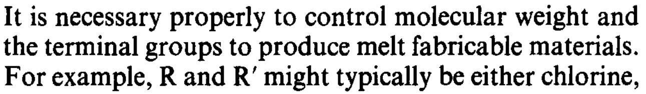
The nucleophilic aromatic substitution step polymerization route to poly(arylene ether sulphones) was investigated. Molecular weight control and/or endgroup functionalization can be achieved through simple stoichiometric control of monomers. The introduction of polymer endgroup functionality can also be accomplished through the use of an appropriate endcapping reagent. This paper describes the synthesis and characterization of poly(arylene ether sulphone) oligomers possessing terminal aromatic primary amine groups. A novel endcapping reagent, 2-*p*-aminophenyl-2-hydroxyphenylpropane or MBA, was synthesized for incorporation of the amine functionality. The use of MBA, together with a potassium carbonate, *N*-methyl-2-pyrrolidone reaction scheme affords a one-step synthesis yielding controlled molecular weight oligomers which are difunctional in nature. A second practical route using *m*-aminophenol was also demonstrated. The molecular weights, $\langle M_n \rangle$, of these amine terminated poly(arylene ether sulphone) oligomers (NH_2PSF) are predictable from stoichiometric considerations and were determined by a non-aqueous potentiometric titration of the amine endgroups. The materials were reproducibly synthesized in the range 3700–25 000 g mol^{-1} (Daltons). All oligomers were characterized with respect to their structure, molecular weight distribution and thermal properties. They have proved in other studies to be very useful for the synthesis of segmented poly(amide) and poly(imide) copolymers and for the toughening of epoxide and maleimide networks.

(Keywords: stoichiometry; Carothers equation; functionally terminated oligomers; endblocker; nucleophilic aromatic substitution)

INTRODUCTION

Poly(arylene ethers) such as the following have become important engineering thermoplastics and matrix resins for advanced polymeric composites in recent years[1–5]:



where:

$X = C(CH_3)_2$, SO_2 or a chemical bond;
$Y = SO_2$, C=O or a chemical bond;
$R = Cl, F, OH, OCH_3$; and
$R' = H, CH_3$.

It is necessary properly to control molecular weight and the terminal groups to produce melt fabricable materials. For example, R and R′ might typically be either chlorine, methoxy or methyl in most 'non-reactive' systems. It is also possible to produce 'reactive' endgroups such as hydroxyl, acetoxy[6,7] or carboxy[8,9] and amino[10–12].

A primary objective of molecular weight and endgroup control in polymers has historically been processability and cost. An 'infinite' molecular weight polymer would display high melt and solution viscosity and would be costly and/or impossible to process. Polymer properties are dependent on molecular weight and it is necessary to reach a 'plateau', which is often identified with the onset of chain entanglements. It becomes commercially desirable to limit molecular weight to the minimum value necessary for attainment of reasonable polymeric properties. Additionally, non-functional polymeric endgroups enhance polymer melt and lifetime stability.

A logical extension of molecular weight control/endgroup functionalization was the preparation of functionally terminated oligomers possessing reactive endgroups. A system can be defined for step-growth polymerizations with monomers A–A, B–B and B–C, where C is unreactive in the polymerization reaction toward A or B and A reacts only with B. Hence, the B–C monomer can be mathematically treated as a monofunctional reagent. Simplistically, a slight excess of A–A monomer is used, which consumes the B–B monomer, leaving a polymeric species with A endgroups. The B–C monomer reacts with the A endgroups, thus 'endcapping' the polymer chain. Oligomeric species can now be designed with predictable molecular weights containing endgroup functionalities different from those present in the initial polymer-forming reaction.

An example that successfully illustrates this point is the reaction of an activated aromatic halide with a bisphenol and an endcapping reagent (*Figure 1*). This nucleophilic aromatic substitution reaction, in the

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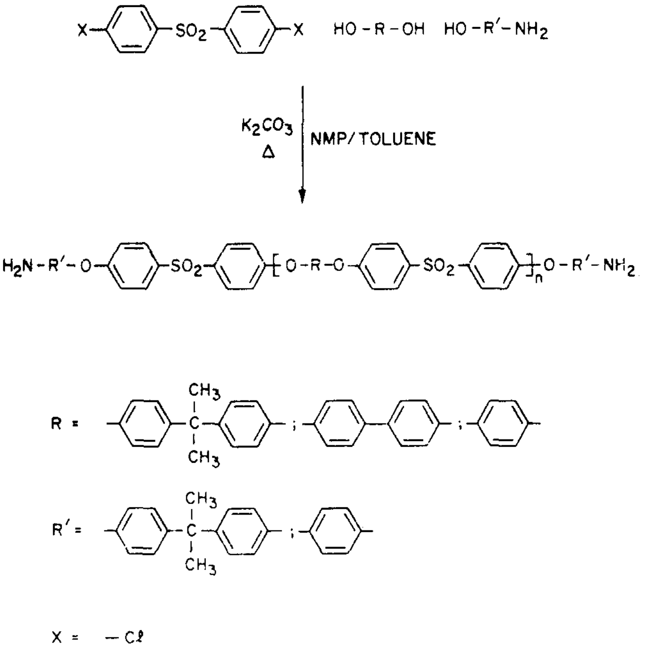


Figure 1 Synthesis of an amine terminated poly(arylene ether sulphone) oligomer

absence of the endblocker, is known to prepare linear, high molecular weight oligomers via proper stoichiometric control of the monomers[1–12]. The proper selection of an endblocking reagent which contains a non-reactive functional group during the polymerization was critical. The primary aromatic amine group derived from *p*-aminophenol was reported to be useful[10]. Identification of the monoamino derivative of bisphenol A (MBA) as the endblocking reagent resulted in the synthesis of more easily controlled poly(arylene ether sulphone) oligomers possessing terminal aromatic amine groups.

The number average molecular weights, $\langle M_n \rangle$, of these oligomers were readily determined via potentiometric titration of the endgroups; gel permeation chromatography (g.p.c.) and intrinsic viscosity values were also consistent. Once these functionalized oligomers had been synthesized and characterized, they served as reactive intermediates in block and segmented copolymer syntheses, as well as modifiers for epoxy and maleimide networks.

EXPERIMENTAL

Materials

Bisphenol A (Dow Parabis®) and 4,4′-dichlorodiphenylsulphone (Amoco), DCDPS, were recrystallized twice from hot toluene using decolourizing charcoal. *N*-methyl-2-pyrrolidone (Fisher Scientific) was vacuum distilled after drying over calcium hydride. Toluene (Fisher) and anhydrous potassium carbonate (Fisher) were used without further purification.

One endblocking reagent, 2-*p*-aminophenyl-2-hydroxyphenylpropane or MBA, was prepared by reacting bisphenol A (0.10 mol) with aniline hydrochloride (0.30 mol) in bulk at 180°C for 30 min (*Figure 2*)[12,13]. A rapid flow of argon was used to remove the phenol formed during the reaction. The reaction mixture was diluted with water and cooled to 25°C, and 50% NaOH was added until pH = 12. The aqueous layer was extracted twice with toluene and acidified with 10% HCl to pH = 6, whereupon the crude product precipitated. After water washing and two recrystallizations from an ethanol–water solution, white needles were obtained in 70% yield. Melting point = 192.0–192.5°C.

Synthesis

The polymerizations were carried out in a 1 litre 4 neck flask equipped with a mechanical stirrer, a Dean–Stark trap and condenser, a Y-tube for gas inlet and thermometer, and an addition funnel[1,2]. Calculated molar quantities of each monomer were charged and dissolved in *N*-methyl-2-pyrrolidone (NMP) to 15 wt% solids as described earlier[14]. Approximately 50 vol% toluene, based on NMP, was used as a dehydrating agent and finally a 40% molar excess[4] of K_2CO_3 was added. The reactions were run at 155°C for 2 h to complete dehydration of the system, followed by 8 h at 170°C. The polymer solution was filtered to remove inorganic salts and precipitated into a rapidly stirred methanol–water solution. After vacuum drying, the off-white powder was redissolved in methylene chloride, filtered, and precipitated in methanol–water. Recovered yields were ⩾95%. A specific example of an aminophenyl difunctional poly(arylene ether sulphone) follows.

A 10 000 g mol^{-1} amine terminated poly(arylene ether sulphone) oligomer was prepared by charging a reaction flask with purified DCDPS (0.2000 mol, 57.4320 g), bisphenol A (0.1914 mol, 43.6908 g) and MBA (0.0177 mol, 4.0241 g) and dissolving in 800 ml NMP. Crushed K_2CO_3 (0.500 mol, 69.1050 g) was added to the colourless solution followed by 275 ml toluene. System dehydration was effected by heating to 155°C for 2 h. Toluene (≈250 ml) was removed from the reaction and the temperature was raised to 170°C for 8 h. The reaction mixture became viscous and dark green in colour. After cooling to 80°C, the reaction mixture was filtered to remove inorganic salts and coagulated into a methanol–water solution (80/20 v/v) acidified with glacial acetic acid. The oligomer was collected by filtration, washed with methanol and stirred in hot water (90°C) for 8 h to remove trapped salts. After drying, the tan powder was redissolved in methylene chloride, filtered, reprecipitated in methanol and dried under vacuum at 100°C for 15 h. Yield = 95%, titrated $\langle M_n \rangle$ = 9300 g mol^{-1}.

Characterization

The number average molecular weights, $\langle M_n \rangle$, of amine terminated poly(arylene ether sulphone) oligomers were determined by a non-aqueous potentiometric titration of the endgroups using a Fisher Automatic Titrimeter II. Bisphenol A based oligomers were dissolved in a 2:1 (v/v) ratio of dry chlorobenzene to

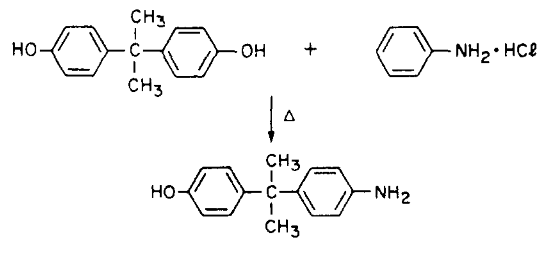


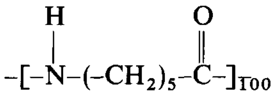
Figure 2 Synthesis of 2-*p*-aminophenyl-2-hydroxyphenylpropane or MBA

glacial acetic acid and titrated with 0.02N HBr in glacial acetic acid[15]. Proton nuclear magnetic resonance could also identify the isopropylidene group associated with the endgroup. The molecular weight distributions were determined in THF at 30°C relative to polystyrene standards. A Waters HPLC was used at a flow rate of $1\,\mathrm{ml\,min^{-1}}$ and detection was achieved by differential refractometry. Intrinsic viscosity measurements were run in chloroform at 25°C using a Cannon–Ubbelohde viscometer. Fourier transform infrared (*FT*i.r.) spectra were obtained on a Nicolet MX-1 from thin polymer films cast from methylene chloride directly onto NaCl windows. A Perkin–Elmer DSC-2 was used to determine the glass transition temperature for all oligomers and melting points of starting monomers. A scanning rate of $10^\circ\mathrm{C\,min^{-1}}$ and a sensitivity of $5\,\mathrm{mcal\,s^{-1}}$ were used*. Values reported are for the second scan after rapid cooling.

RESULTS AND DISCUSSION

Calculation of molecular weights and endgroups

An important aspect of step-growth polymerizations is the difference between $\langle X_n \rangle$, the number average degree of polymerization, and *DP*, the degree of polymerization. *DP* is defined as the average number of repeating units per polymer molecule. In an A–B system such as poly(ε-caprolactom) or nylon 6



$$-[-\overset{\text{H}}{\overset{|}{\text{N}}}-(-\text{CH}_2)_5-\overset{\text{O}}{\overset{\|}{\text{C}}}-]_{100}$$

both *DP* and $\langle X_n \rangle$ have the same value, 100. However, in the A–A/B–B two-component system, poly(hexamethylene adipamide) or nylon 6,6, *DP* and $\langle X_n \rangle$ are quite different. $\langle X_n \rangle$ is defined as 1.0 for each monomer, but *DP* in this case must be taken as the mean of the two (e.g. 100, if $\langle X_n \rangle = 200$). Hence, one would acknowledge the average degree of polymerization, $\langle X_n \rangle$, for the one-component system to be twice that for the two component system.

As an example, the synthesis of a controlled molecular weight, functionally terminated oligomer of nylon 6,6 (molecular weight of repeat unit = $226.4\,\mathrm{g\,mol^{-1}}$) could be calculated[16,17], using $5000\,\mathrm{g\,mol^{-1}}$ as the oligomer block length:

$$DP = \frac{5000\,\mathrm{g\,mol^{-1}}}{226.4\,\mathrm{g\,mol^{-1}}} = 22.08 \qquad (1)$$

$$\langle X_n \rangle = 2(DP) = 44.16 \qquad (2)$$

As the degree of conversion approaches unity in a step growth polymerization, a relationship exists between $\langle X_n \rangle$ and *r*, the stoichiometric imbalance between monomers:

$$\langle X_n \rangle = \frac{1+r}{1-r} \qquad (3)$$

If perfect stoichiometry between monomers is maintained ($r = 1$), then in principle it should be possible to obtain a polymer chain of infinite molecular weight. However, if the value obtained in equation (2) is substituted in equation (3), a value of $r = 0.956$ is obtained. This implies that by maintaining a stoichiometric imbalance of monomers with the diamine present in excess (0.956 mol dicarboxylic acid and 1.000 mol diamine), a diamine terminated nylon 6,6 oligomer with $\langle M_n \rangle \cong 5000\,\mathrm{g\,mol^{-1}}$ will be produced.

This treatment can also be extended to molecular weight control via addition of a monofunctional reagent through use of the following equation[16,17]:

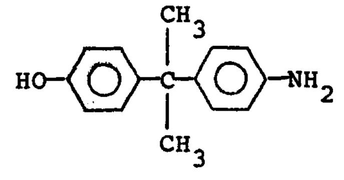
$$r = \frac{N_A}{N_B + 2N'_B} \qquad (4)$$

Here, N_A and N_B are the number of moles of monomers A and B, respectively, and $2N'_B$ is the number of moles of monofunctional reagent. The coefficient 2 is used since 2 mol of monofunctional reagent are necessary to maintain the same stoichiometric imbalance, *r*, as would 1 mol of difunctional monomer. If benzoic acid was used as the monofunctional reagent in the nylon 6,6 example, $2N'_B = 0.086$ mol would be necessary to maintain the same value of *r*. The result would again be a $5000\,\mathrm{g\,mol^{-1}}$ nylon 6,6 oligomer; however, benzamide endgroups would now be present at both chain ends. Thus if a system can be designed containing A–A, B–B and B–C (or A–C) and proceeds to essentially complete conversion, both molecular weight control and endgroup functionalization can be achieved.

Kawakami *et al.*[10] had earlier investigated the preparation of oligomeric diamines with poly(arylene ether sulphone) systems, but had not extended the work to oligomers with $\bar{M}_n > 2000\,\mathrm{g\,mol^{-1}}$. Their synthetic strategy utilized a bisphenol and *p*-aminophenol, as the endblocker, in a reaction with 50% sodium hydroxide solution in dimethyl sulphoxide to form the sodium phenates in a first step. The activated aromatic halide was added in a second step to prevent hydrolysis of the halide monomer. This approach necessitated the use of an excess of *p*-aminophenol since excess sodium hydroxide could further react in possible competing side reactions.

The use of a weak base such as K_2CO_3 essentially prevents this side reaction from occurring. Additionally, the reaction scheme can be simplified to a one-step procedure since hydrolysis will not be a factor[4]. Unfortunately, *p*-aminophenol did not easily function as a quantitative endcapping reagent due to the formation of a more stable (and less reactive) quinone type structure. Recent studies with *m*-aminophenol were much more reproducible[18,19].

An endcapping reagent in which the phenolic and amine functional groups were electronically isolated, but which also possessed a similar reactivity to the bisphenol was used. A derivative of bisphenol A, 2-*p*-aminophenyl-2-hydroxyphenylpropane (MBA), was prepared which appeared to satisfy both these requirements:



The synthesis of a series of α,ω-amino terminated poly(arylene ether sulphone) oligomers was accomplished via stoichiometric control of a bisphenol, an activated aromatic halide and the endcapping reagent (*Figure 1*) in accordance with calculations and example presented earlier. Typical results for bisphenol A based oligomers

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* 1 cal = 4.184 J

Table 1 Characterization of bisphenol-A amine terminated poly(arylene ether sulphone) oligomers

Theoretical $\langle M_n \rangle$	Endgroup analysis	T_g (°C)	*MWD*
4000	3700	140	1.9
5000	5300	155	2.0
7500	7100	162	2.1
9000	8800	165	2.0
10000	9300	168	1.9
12000	11300	169	1.8
14000	13300	172	1.9
16000	15600	175	2.0
18000	17000	178	2.0
20000	19500	184	2.1
22000	21400	189	2.0
25000	24600	194	1.9
28000	27700	194	2.1

can be seen in *Table 1*. Endgroup analysis yielded $\langle M_n \rangle$ values in close agreement with calculated theoretical values. The T_g increased with $\langle M_n \rangle$ and at 25 000 g mol^{-1} exhibited values close to those of a commercial high molecular weight poly(arylene ether sulphone) (UDEL P-1700 polysulphone, $T_g = 195$°C).

This range of $\langle M_n \rangle$ could be obtained routinely and oligomers with molecular weights in this range were most frequently used in post-polymerization reactions. Below $\approx$4000 g mol^{-1} polymer isolation was difficult and above 25 000 g mol^{-1} the molar concentrations of endgroups were extremely low for use in subsequent copolymerizations.

The molecular weight distributions (*MWD*) for all oligomers were monomodal and close to the most probable distribution of 2.0 (*Table 1, Figure 3*). This was a good indication that only one reaction mechanism operated and that it proceeded to essentially complete conversions.

Although theoretical and experimental $\langle M_n \rangle$ values were in close agreement and the *MWD* were $\approx$2, oligomer difunctionality remained an unknown. Bisphenol A based phenolic hydroxyl terminated poly(arylene ether sulphone) oligomers possessing known difunctionality[6,11,13] were synthesized and compared with the amine terminated oligomers. Intrinsic viscosity measurements of comparable $\langle M_n \rangle$ oligomers should be very close to one another since the only difference in polymer structure was the endgroups (<2% by weight). This comparison can be seen in *Table 2* and, indeed, the values were in close agreement with all molecular weights examined.

An additional important indirect test of difunctionality is the ability to produce linear, high molecular weight polymers when reacted with an appropriate difunctional reagent. A post-reaction of an oligomeric diamine with a diacid chloride was chosen to accomplish this; dianhydrides are another good example. A 5100 g mol^{-1} amine terminated poly(arylene ether sulphone) oligomer was dissolved in dry NMP and triethylamine was added as an acid acceptor. An equimolar quantity of pure terephthaloyl chloride was added dropwise as a 10% solution in NMP. A white fibrous polymer was obtained which had an extremely high $\langle M_n \rangle = 199\,000$ g mol^{-1} as measured by g.p.c. (*Figure 4*). This value corresponds to >99% conversion, indicating that highly difunctional monomers were used and that the amine terminated poly(arylene ether sulphone) oligomers prepared by this method were difunctional in nature.

As final verification of oligomer structure, *FT*i.r. spectra of a low molecular weight amine terminated oligomer and a high molecular weight poly(arylene ether sulphone) were obtained (*Figure 5*). The only difference between the two materials is in the N–H stretching region, 3400 cm^{-1}, which contains two small peaks corresponding to the terminal amine groups of the oligomer. No indication of ester or other possible functionalities could be observed.

Once these amine terminated poly(arylene ether sulphone) oligomers had been synthesized and characterized, the utility of the amine group in subsequent copolymerizations was realized. *Figure 6* shows the range of successful post-reactions available with these thermoplastic oligomeric diamines.

The bisphenol A based oligomers were initially studied because of their ease of characterization, good solubility and amorphous behaviour. Even greater possibilities exist for copolymer synthesis and matrix resin modifications if oligomers are prepared possessing higher T_g and/or potentially liquid crystalline behaviour. Amine terminated poly(arylene ether sulphone) oligomers based on hydroquinone (HQ), bisphenol (BP) or 50/50 molar mixtures of the two bisphenols were prepared. *Table 3*

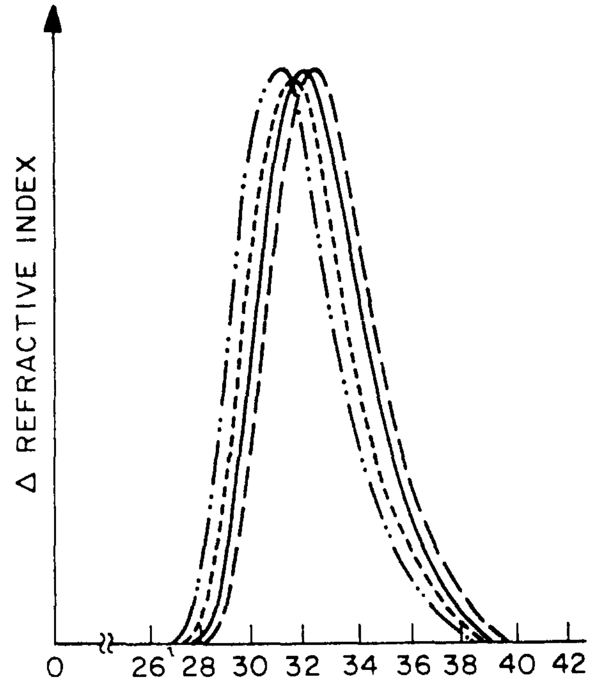

Figure 3 Gel permeation chromatography traces of bisphenol A based amine terminated poly(arylene ether sulphone) oligomers run in THF at 30°C and 1 ml min^{-1}: ——, 4600 g mol^{-1}; ——, 8800 g mol^{-1}; ----, 15 600 g mol^{-1}; —·—, 27 700 g mol^{-1}

Table 2 Intrinsic viscosity measurements for phenolic hydroxyl and amine terminated bisphenol A poly(arylene ether sulphone) oligomers

HO– terminated $\langle M_n \rangle$	$[\eta]_{\mathrm{CHCl_3}}$(25°C)	–NH$_2$ terminated $\langle M_n \rangle^a$	$[\eta]_{\mathrm{CHCl_3}}$(25°C)
5000	0.10	5100	0.11
8200	0.13	8800	0.14
14600	0.22	15600	0.22
20500	0.26	21400	0.27

[a] Determined by endgroup analysis

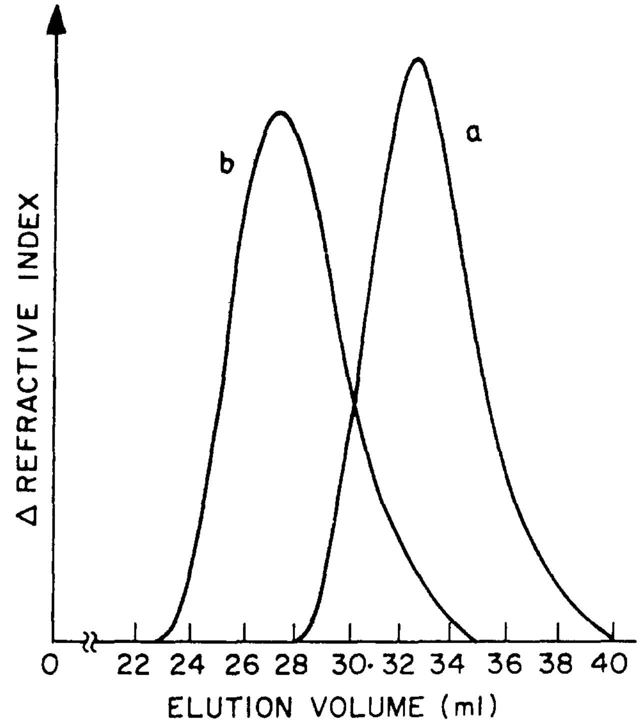

Figure 4 Gel permeation chromatography traces of: (a) 5100 g mol^{-1} bisphenol A based amine terminated poly(arylene ether sulphone) oligomer, *MWD* = 2.1; and (b) the same oligomer after chain extension with terephthaloyl chloride, *MWD* = 2.4. Run in THF at 30°C and 1 ml min^{-1}

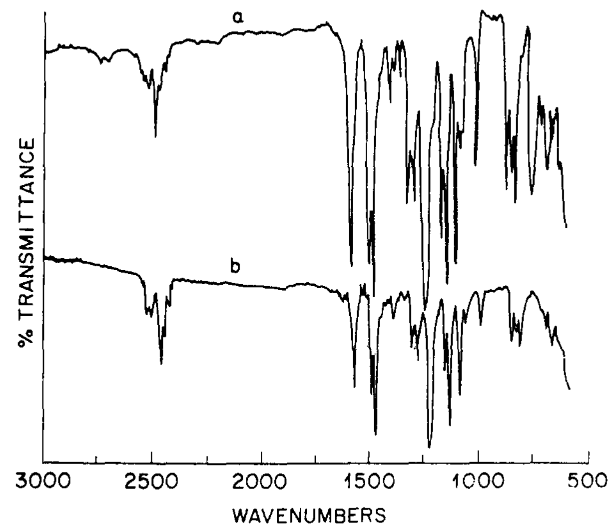

Figure 5 *FT*i.r. spectra of: (a) 5100 g mol^{-1} bisphenol A based poly(arylene ether sulphone) oligomer; and (b) a high molecular weight poly(arylene ether sulphone)

Table 3 Hydroquinone and biphenol based amine terminated poly(arylene ether sulphone) oligomers

Theoretical $\langle M_n \rangle$	Endgroup analysis	$[\eta]_{CHCl_3}$(25°C)	T_g (°C)	*MWD*
5 000^a	5 400	0.20	196	2.0
5 000^b	7 100	0.34	170	1.9
10 000^b	9 700	0.50	187	2.1
7 500^c	6 500	0.31	191	2.2
15 000^c	14 400	0.44	204	2.1
20 000^c	19 200	0.73	213	2.0

^{a} Biphenol
^{b} Hydroquinone
^{c} 50/50 Molar ratio of hydroquinone and biphenol

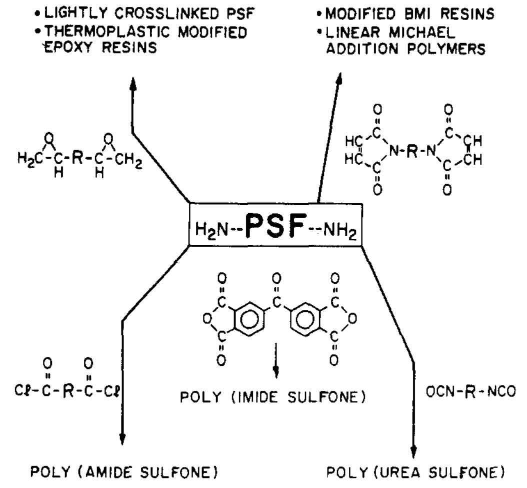

Figure 6 Post-polymerizations available using amine terminated poly(arylene ether sulphone) oligomers

lists the results for these syntheses. As with the bisphenol A based oligomers, endgroup analysis yielded values in close agreement to those predicted by the Carothers equation. High molecular weight poly(arylene ether sulphones) based on hydroquinone and bisphenol are known to possess T_g which are 20–30°C higher than those of bisphenol A based polymers[14]. It was expected that oligomers prepared using these bisphenols would also exhibit higher T_g than bisphenol A based oligomers.

This synthetic approach to functional termination has also been extended to include acetoxy or carboxy[8,9] and maleimide[18,19] endgroups and, more recently, to amine terminated poly(arylene ether ketone) oligomers[18,19].

CONCLUSIONS

Proper modification of the Carothers equation was practically applied for the preparation of aminophenyl functionally terminated poly(arylene ether sulphone) oligomers of predictable molecular weights. A quantitative endgroup functionalization with primary aromatic amine groups via a novel endcapping reagent, 2-*p*-aminophenyl-2-hydroxyphenylpropane in a one-step synthesis was shown. These oligomeric diamines were characterized with respect to molecular weight and structure and have shown utility in block copolymer syntheses in addition to matrix resin modification.

FUTURE STUDIES

Utilization of the terminal aminophenyl difunctional poly(arylene ether sulphones) is being extended to segmented poly(amide), poly(amide–imide) polyimide and 'ketimine' chain extended copolymers. Several examples of the use of these thermoplastic functionalized oligomers as toughening agents for epoxide and maleimide networks have already been demonstrated[20,21].

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