Synthesis and characterization of novel toughened thermosets derived from pendent amines on the backbone of poly(arylene ether sulphone)s*

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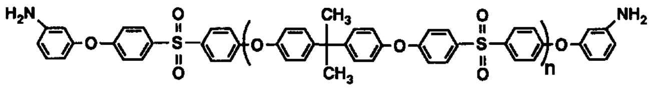
(Received 28 July 1992; revised 4 August 1992)

Random incorporation of pendent aryl amines on the backbone of poly(arylene ether sulphone)s was achieved by the copolymerization of a minor amount of a second activated aromatic dihalide, bis(4-fluorophenyl)-3-aminophenylphosphine oxide (amino DFTPPO), with 4,4′-dichlorodiphenylsulphone (DCDPS) and bisphenol A via aromatic nucleophilic substitution polymerization using *N*-methylpyrrolidone (NMP) as the solvent, toluene as the azeotroping agent and potassium carbonate as the base. The pendent amines were optionally chemically modified by conversion to maleimides and thermally cured to afford tough insoluble networks. Epoxy networks were also obtained by reacting the pendent amines with liquid epoxy resin and 4,4′-diaminodiphenylsulphone (DDS). The synthesis and characterization of these novel thermosetting materials were investigated, and it was demonstrated that selected compositions could significantly improve the fracture toughness of the epoxy networks. Two important variables identified were the weight or volume fraction of the thermoplastic modifier and, importantly, the concentration of the pendent aminophenyl 'cure' sites. In this research, about 2.5 mol% cure sites was the optimum concentration utilized, which produced tough multiphase systems. Higher aminophenyl concentrations resulted in more homogeneous morphologies and fracture toughness was about the same as the control.

(Keywords: poly(arylene ether)s; aminophenyl functionality; maleimide; epoxy; thermoset network; morphology; fracture toughness; synthesis; characterization)

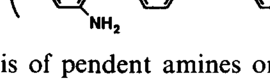
INTRODUCTION

Poly(arylene ether sulphone)s are engineering thermoplastics known for their good oxidative, thermal and hydrolytic stability as well as good mechanical properties[1–10]. Owing to the amorphous nature of the poly(arylene ether sulphone)s, they are readily soluble in common solvents such as chloroform, *N*-methylpyrrolidone (NMP) and tetrahydrofuran (THF). In order to obtain materials with better solvent resistance and thermal stability, introduction of functionalities that are capable of undergoing crosslinking reactions have been utilized. Most of these efforts have been concentrated on amine-terminated oligomers of polysulphones, which can be synthesized by adding stoichiometric amounts of an aminophenol as the end-capping agent[11–14]:



By using the Carothers equation, amine-terminated polysulphones of various controlled molecular weights can be synthesized. The amine functionality at the oligomer chain ends provides a reactive site for chemical modifications to other functionalities that are capable of undergoing chain extensions or crosslinking reactions. However, with this approach, as the molecular weight increases, the concentration of amine groups decreases, and hence lower crosslink densities are obtained. The amine-terminated polysulphones have been reacted with maleic anhydride to give maleimide-terminated polysulphones, which can be crosslinked by either a thermal or a microwave treatment[15]. The oligomeric amines can also be reacted with epoxy resins and diaminodiphenylsulphone (DDS) to afford toughened epoxy thermosets[12–14].

Recently, Naik *et al.*[16] reported on the preparation and properties of amination on the main chain of a copolymer of poly(ether sulphone) (PES) and poly(ether ether sulphone) (PEES) by nitrating the hydroquinone unit of the repeat unit with nitric acid and sulphuric acid with nitrobenzene as the solvent. The pendent nitro groups on the polymer chains were then reduced using sodium dithionate in dimethylformamide:



The synthesis of pendent amines on poly(ether ether ketone)s has also been studied in our laboratories by

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* Presented at 'Advances in Polymeric Matrix Composites', 5–10 April 1992, San Francisco, CA, USA

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0032-3861/93/040885-11

reacting a small mole percentage of 4,4′-difluoro(*N*-benzohydryl-*p*-aminoaniline) with difluorobenzophenone (DFB) and hydroquinone[17]. The pendent amines on the poly(ether ether ketone)s were then thermally cured and the pendent amines reacted with the carbonyls on the polymer backbone to generate reasonably stable ketimine crosslinks. Others have also reported on the synthesis of pendent maleimides on polyketones by reacting 5-maleimidoisophthaloyl chloride with various aromatic compounds using Friedel–Crafts polymerizations[18].

This paper describes recent investigations on the incorporation of pendent amines on the backbone of poly(arylene ether sulphone)s. Our efforts have been directed towards monomers that have the amine functionality, as well as the reactive difunctionality, which undergoes polymerization to afford a poly(arylene ether sulphone) backbone, with the incorporation of the pendent amines. Polymerization incorporating various mole percentages of the pendent amine monomer resulted in polymers with a predictable number of crosslinking sites along the polymer backbone. The pendent amines were, in some cases, further modified by reacting them with maleic anhydride to afford pendent maleimides, which were thermally crosslinked. The pendent amines were also reacted with epoxy resins and 4,4′-diaminodiphenylsulphone (DDS) to afford toughened thermosets. In contrast to amine-terminated polysulphones, the pendent amines are no longer restricted to be only on polymer chain ends. Therefore, the concentration of amines can be controlled independently of the molecular weight by varying the amount of the amine-containing monomer relative to the other monomers. The synthesis and characterization of thermosetting materials from modifications of pendent amines on the backbone of poly(arylene ether sulphone)s were investigated by this novel approach.

EXPERIMENTAL

Materials

Monomer-grade 4,4′-dichlorodiphenylsulphone (DCDPS) was provided by Amoco and was used without further purification. Bisphenol A was provided by Dow Chemical in a monomer grade and was also used as received. However, both the DCDPS and bisphenol A were dried in a vacuum oven at 80°C for 24 h prior to being used. Bis(4-fluorophenyl)phenylphosphine oxide (DFTPPO) was synthesized according to the procedure reported in the literature[19] and was purified by distillation. Epon 828 epoxy resin was supplied by Shell Chemical and was used as received. Maleic anhydride (Aldrich) was sublimed under vacuum at 60°C prior to use. Acetic anhydride (Aldrich) and *N*-methylpyrrolidone (NMP) (Fisher) were vacuum distilled from calcium hydride. Anhydrous potassium carbonate (Fisher), toluene (J. T. Baker), tin chloride dihydrate (Aldrich) and deuterated chloroform (Isotech Inc.) were all used as received.

Synthesis of bis(4-fluorophenyl)-3-nitrophenylphosphine oxide (nitro DFTPPO)

To a 500 ml four-necked round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, thermometer and addition funnel were added 22.79 g (0.0725 mol) of DFTPPO and 200 ml H_2SO_4. The contents in the flask were stirred at room temperature until a homogeneous solution was obtained. Then the flask was immersed in an ice–water bath until the temperature inside the flask reached approximately 5°C. At this point, a solution of 7.51 g (0.0834 mol) of HNO_3 and 28 ml H_2SO_4 in an addition funnel was introduced dropwise. When the addition was completed, the ice–water bath was removed and the contents inside the flask stirred for another 2 h. After 2 h, the reaction mixture was slowly poured into 3000 ml of water and ice. The precipitate was filtered and washed with a copious amount of water. It was then dissolved in chloroform and washed twice with water, once with a solution of sodium bicarbonate, and then finally with a saturated sodium chloride solution. The chloroform layer was separated and dried with magnesium sulphate and removal of the chloroform resulted in approximately 90% yield of the crude product, which was a yellow material with a melting point of 146–148°C. This material was used without further purification for the reduction of the nitro groups to the amines.

Synthesis of bis(4-fluorophenyl)-3-aminophenylphosphine oxide (amino DFTPPO)

Reduction of the nitro DFTPPO was carried out in 95% ethanol with tin chloride dihydrate and hydrochloric acid. To a 1000 ml four-necked round-bottomed flask equipped with a nitrogen inlet, mechanical stirrer, condenser and a thermometer were added 21.42 g (0.0596 mol) of nitro DFTPPO and 306 ml of ethanol. A heating mantle was used to induce a gentle reflux of the ethanol. Then, tin chloride dihydrate and the HCl were added in three portions, 18 g (0.0798 mol) of tin chloride dihydrate and 33 ml (0.3690 mol) of HCl in each addition. After the third addition, the solution was refluxed for another 2 h. The heating mantle was then removed and the solution was cooled to room temperature. The solution was transferred to a round-bottomed flask and the ethanol was removed under reduced pressure. The resulting solution was made alkaline using a solution of sodium hydroxide. The alkaline solution was poured into 3000 ml of water and ice. The resulting solid was filtered and washed with a copious amount of water and dried in a vacuum oven at 60°C overnight. After drying, 15.37 g (0.0467 mol) of the product was obtained, a yield of 78%. The product was purified by vacuum distillation, and the melting point of the resulting material was 157–159°C. ^{1}H n.m.r. (chloroform-d, ppm): 7.61 (m, 4H, *ortho* to P=O), 7.08 (m, 5H, four *ortho* to fluorine and one *para* to amine), 7.05 (d, 1H, *meta* to amine and P=O), 6.90 (m, 2H, *ortho* to amine), 4.00 (s, 2H, amine). I.r. (KBr pellet, cm^{-1}): NH_2 (3319, 3219), Ar–H (3056), aromatic C=C (1594, 1500), P–aromatic carbon (1434), P=O (1187), aromatic carbon–F (1162). Titration of the amine group yielded an average value of 327 g mol^{-1} (theoretical 329 g mol^{-1}) after three titrations.

Synthesis of pendent amino polysulphones

To a four-necked round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, thermometer and a Dean–Stark trap with a condenser were added the monomers, which were carefully weighed on Teflon-coated weighing pans. For the synthesis of a high-molecular-weight polysulphone with a 10% incorporation of amino DFTPPO monomer, 10 g (0.0438 mol) of bisphenol A, 11.3218 g (0.0394 mol) dichlorodiphenylsulphone and 1.4424 g (0.0044 mol) amino DFTPPO were transferred to the reaction flask along with 6.9627 g (0.0504 mol) of K_2CO_3 under a constant purge of nitrogen. A total of 114 ml of NMP and 57 ml of toluene was added. Initially, the polymerization was conducted at 145°C for approximately 4 h to azeotrope off the water. Then the temperature was raised to 165°C for an additional 16 h. The viscous brown solution was then filtered and coagulated into a large excess (5–10 times) of methanol and water 80:20). The polymer was filtered and washed with more methanol and dried in a vacuum oven at 80°C for 24 h. The dried polymer was redissolved in chloroform and coagulated into excess methanol and dried in a vacuum oven at 80°C.

Synthesis of pendent maleimide functional polysulphones

To a four-necked 500 ml round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, thermometer and condenser were added 13.8 g (0.0030 mol) of polysulphone (10% incorporation) along with 276 ml of chloroform. The contents were stirred at room temperature until a homogeneous yellow solution was obtained. Once homogeneous, 0.59 g (0.0060 mol) of maleic anhydride was added. This solution was stirred at room temperature for an additional 2 h. Then 5.19 ml (0.0550 mol) of acetic anhydride along with 0.45 g (0.0055 mol) of sodium acetate were added and refluxed for another 4 h. The clear homogeneous solution was then coagulated into excess methanol, filtered, washed with methanol and dried in a vacuum oven at 80°C overnight. Upon transformation of the amine groups to maleimides, a new peak corresponding to the olefin protons emerged as a singlet at 6.90 ppm on the proton n.m.r. spectra. Infra-red spectra showed the disappearance of amine absorptions at 3319 and 3219 cm^{-1} and the carbonyl absorptions from the maleimides emerged at 1719 and 1798 cm^{-1}.

Per cent gelation

The per cent gelation of cured maleimides was determined by extracting the samples in chloroform for four days. The samples were then dried until a constant weight was obtained. The per cent gelation was then calculated by using the following formula:

$$\text{gelation (\%)} = \frac{\text{initial weight} - \text{weight after extraction}}{\text{initial weight}} \times 100$$

Curing of pendent amines with epoxy resin

Epon 828 was added to the pendent amino polysulphones and allowed to react at 110°C until a homogeneous solution was obtained. Vacuum was applied throughout the process to degas the system. Then 4,4′-DDS was added and the temperature raised to 135°C until the mixture was homogeneous. The homogeneous solution was then poured into a preheated RTV silicone mould and cured in a convection oven at 190°C for 1.5 h and then post-cured at 235°C for an additional 1.5 h.

Fracture toughness

Fracture toughness measurements were performed in accordance with ASTM E399 with samples of approximate dimensions of 3.2 mm × 6.5 mm × 38 mm. A sharp crack was cryogenically initiated in each specimen and the load to failure was obtained on a three-point bend apparatus on an Instron (model 1123).

Morphology

The morphology of the fractured surfaces was studied by scanning electron microscopy (SEM) after the specimens were sputtered with gold.

Nuclear magnetic resonance

The proton n.m.r. spectra were obtained using a Varian Unity 400 MHz instrument. The samples were dissolved in chloroform that contained 0.05% tetramethylsilane (TMS) and all of the peaks were referenced relative to TMS peak at 0 ppm.

Differential scanning calorimetry

Measurements were made using a Perkin–Elmer DSC-7 at a heating rate of 10°C min^{-1}. The sample sizes were in the range of 10–20 mg.

Thermogravimetric analysis

Measurements were made using a Perkin–Elmer Thermogravimetric Analyzer TGA-7 at a heating rate of 10°C min^{-1} in air.

Dynamic mechanical analysis

D.m.a. was carried out using a Perkin–Elmer DMA-7. The samples analysed using the extension mode from pressed samples had approximate dimensions of $0.6 \times 5 \times 6$ mm^3. The samples analysed using the three-point bend mode had approximate dimensions $2 \times 6 \times 15$ mm^3. A heating rate of 5°C min^{-1} and a frequency of 1 Hz were used.

Gel permeation chromatography

G.p.c. was performed using a Waters 150-C ALC/GPC with a differential refractive index and viscosity detectors. The concentration was 3 mg ml^{-1} in NMP. Permagel columns in the range of 100 to 10^6 Å were used as the separation system with a flow rate of 1 ml min^{-1} at 60°C.

Intrinsic viscosities

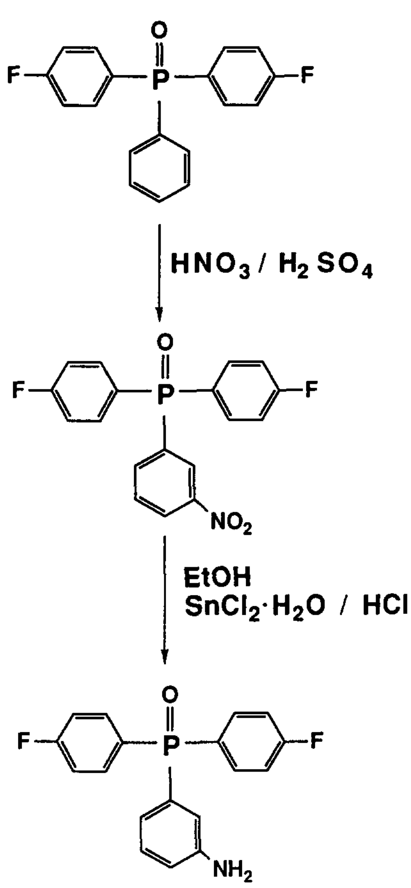
Intrinsic viscosities were measured at 25°C in Ubbelohde viscometers with chloroform as the solvent.

Titration

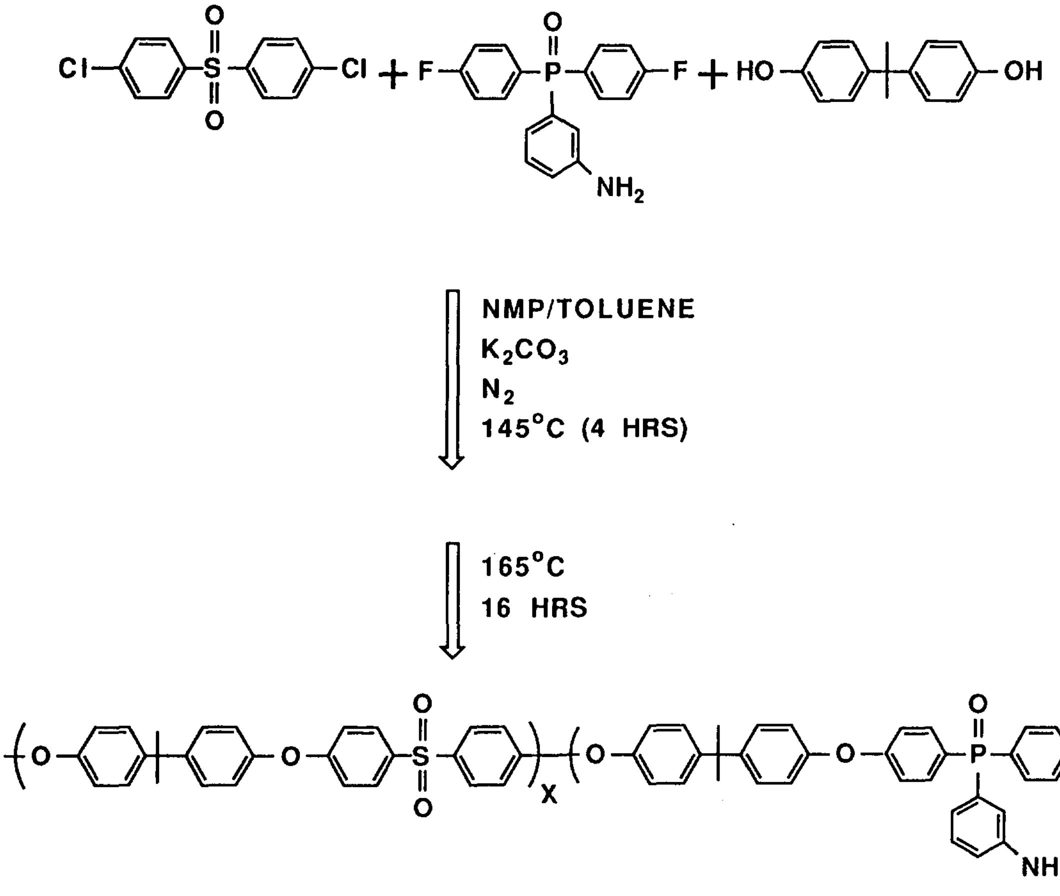
Potentiometric titrations for aromatic amines on both the monomer and polymers were performed using an MCI GT-05 automatic titrator. Samples were dissolved in 60 ml chloroform and 10 ml acetic acid and then titrated with HBr (0.025 N) in acetic acid as the titrant.

RESULTS AND DISCUSSION

It has been well established in our laboratory and elsewhere that *m*-aminophenol can be used as end-capper to give amine-terminated poly(arylene ether)s. Even though the end-capper contains both the amine functionality as well as the phenol, it is the phenolate that undergoes the aromatic nucleophilic substitution reaction, and the amine does not interfere with the polymerization under the conditions normally utilized[7]. Based on this chemistry, our rationale for the incorporation of amines on the backbone of poly(arylene ether sulphone)s was to synthesize a monomer with the amine functionality, as well as the activated dihalide, which can undergo polymerization. The monomer that we have synthesized to give pendent amines was bis(4-fluorophenyl)-3-aminophenylphosphine oxide (amino DFTPPO), which was synthesized by nitration of bis(4-fluorophenyl)phenylphosphine oxide followed by reduction of the nitro group to the amine as shown in *Scheme 1*. Owing to the electron-withdrawing nature of the phosphine oxide, nitration predominantly occurs in the *meta* position to the phosphine oxide on the pendent phenyl ring. The nitro group was then reduced to the amine using tin chloride dihydrate and hydrochloric acid to produce a yield of 78%. The proton n.m.r. spectra of amino DFTPPO is shown in *Figure 1*. The broad singlet at 3.9 ppm is assigned to the amine, and the experimental value of 6.7 was obtained for the ratio of the peak integrations of the amine to the aromatics as compared to 6.0 for the theoretical value. Titration was determined to be a better method for the characterization of the monomer. A molecular weight of 327 g mol^{-1} was obtained when the amino DFTPPO monomer was titrated for the amine as compared to the theoretical value of 329 g mol^{-1}, lending support to the fact that nitration results in one and only one nitro group per molecule. The copolymerizations of amino DFTPPO with DCDPS and bisphenol A were conducted according to the reaction conditions outlined in *Scheme 2*. The polymerizations were conducted to obtain high-molecular-weight polymers, and a 1:1 ratio of the activated dihalide monomers to the bisphenol A monomer was used. The proton n.m.r. spectrum of the polysulphone with 15 mol% of amino DFTPPO, 85 mol% of DCDPS and 100 mol% of bisphenol A is shown in *Figure 2*. The



Scheme 1 The synthesis of bis(4-fluorophenyl)-3-aminophenylphosphine oxide



Scheme 2 Synthesis of pendent amine-containing poly(arylene ether sulphone) copolymers

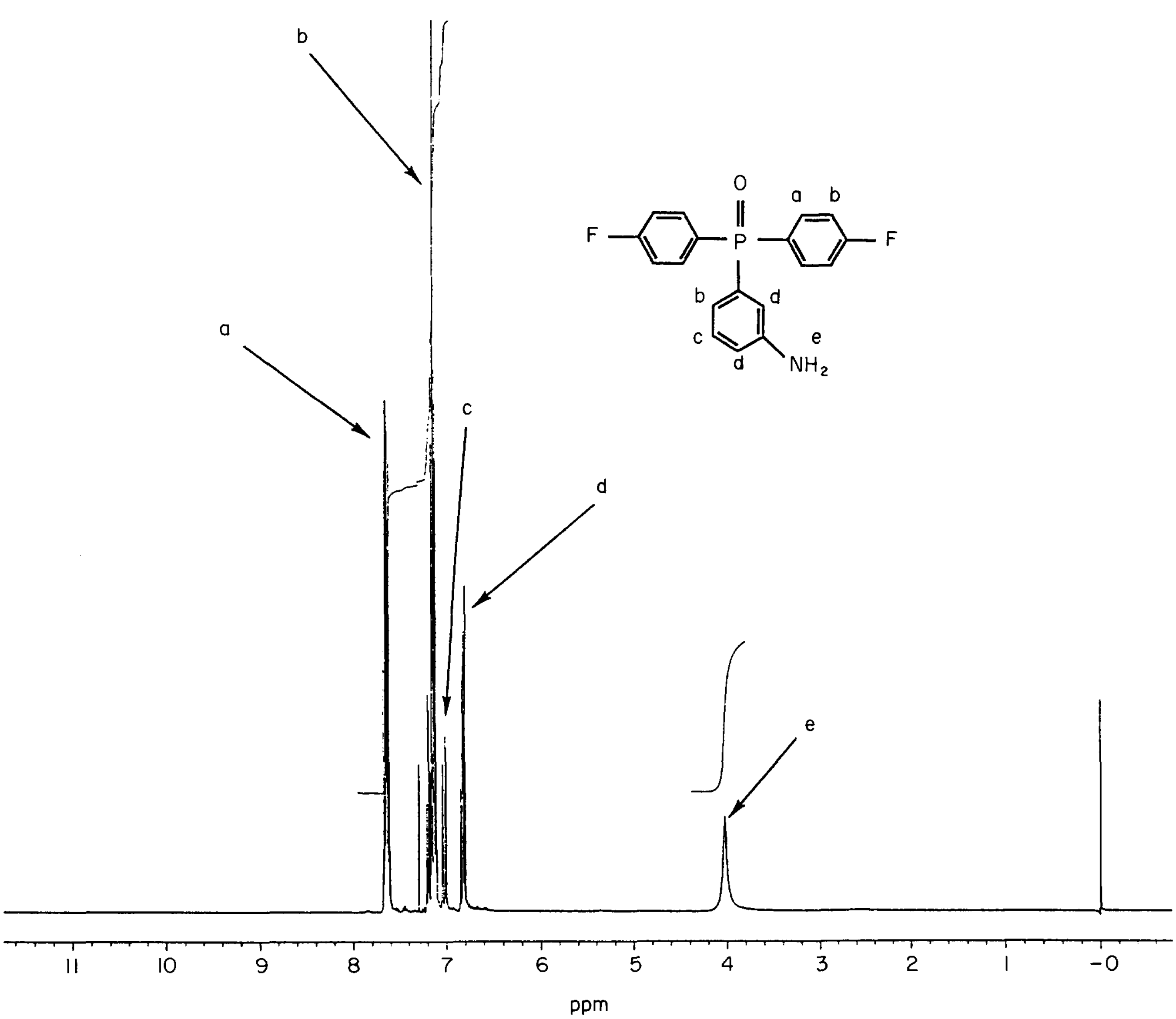


Figure 1 Proton n.m.r. spectrum of amino DFTPPO

peak corresponding to the amine is present at 3.9 ppm as well as the aromatic region from the amino DFTPPO monomer.

Titrations of the pendent amine polymers indicate a quantitative or nearly quantitative incorporation of the amine-containing monomers. Thus for the charged levels of 5, 10 and 15%, titration values of 5.0, 9.8 and 14.4% incorporation of the amino DFTPPO monomer were obtained. The intrinsic viscosity and g.p.c. data indicate that indeed high-molecular-weight polymers were synthesized, as shown in *Table 1*. The pendent amines show a slight increase in T_g as more of the amino DFTPPO is incorporated, which is probably due to the hydrogen bonding of the pendent amines with both the sulphones and the phosphine oxides. The increase in T_g could also be due to a higher T_g for the homopolymer of bis(4-fluorophenyl)phenylphosphine oxide and bisphenol A relative to the homopolymer of DCDPS and bisphenol A[20].

When the pendent amines are converted to maleimides, the amine peak disappeared and a new peak from the olefin protons on the maleimides emerged at 6.9 ppm, as shown in *Figure 3*. The pendent maleimides were then cured using a Pasedena Press at 250°C for 3 h and then post-cured at 280°C for an additional hour. The T_g values of the cured maleimides are higher than the T_g values of the pendent amines due to crosslinking of the maleimides. The T_g values of the crosslinked maleimides were higher as the concentration of the maleimides increased owing to the increase in the average crosslink density. Per cent gelation was higher for the 15% pendent maleimides than for the 5% pendent maleimides. Again, as the concentration of the pendent maleimides increases, more of the maleimides can undergo crosslinking reactions with other maleimides in the vicinity. For the 5% maleimides, per cent gelation of 89% was obtained as compared to 98% for the 15% maleimides; the lower value for the 5% may be due to the lower concentration of the maleimides, or perhaps to the possibility that not all of the maleimides actually reacted. Additional data to support the crosslinking of the pendent maleimides are given in *Figure 4*. Shown in *Figure 4* is a dynamic mechanical analysis (d.m.a.) of the control polysulphone. As the material is subjected to temperatures near the T_g, the modulus begins to decrease; after the T_g, the modulus continues to drop until the sample finally breaks. This is due to the lack of chemical bonds or crosslinked sites between the polymer chains. However, the d.m.a. of the

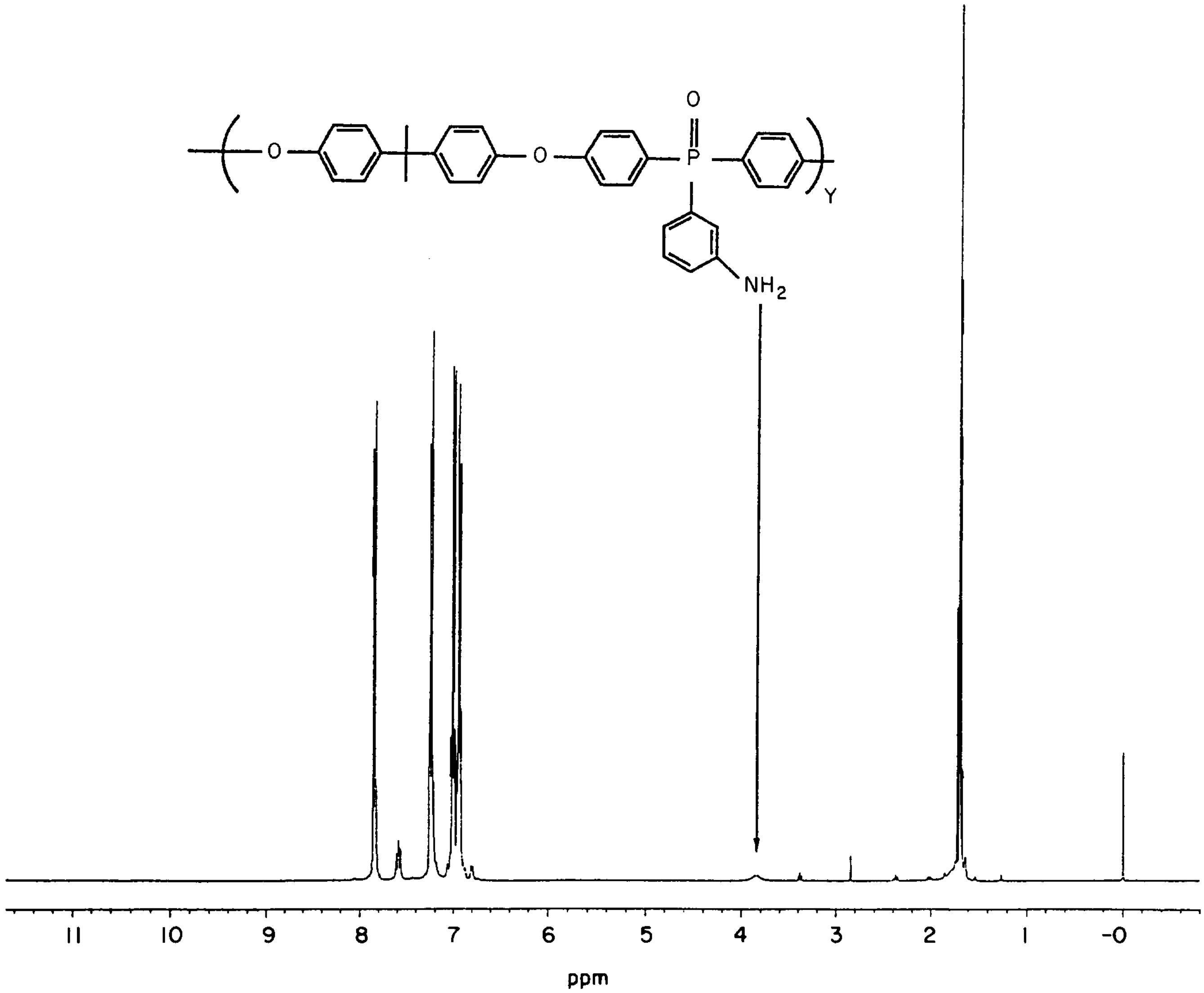


Figure 2 Proton n.m.r. spectrum of 15 mol% pendent amino DFTPPO incorporated polysulphone

Table 1 Characteristics of amine (linear) or maleimide (network) containing poly(arylene ether sulphone) copolymers

			D.s.c.		D.m.a.	
Amino DFTPPO (mol%)	$[\eta]^{25°C}_{CHCl_3}$ (dl g^{-1})	$\langle M_n \rangle^a$ (g mol^{-1})	T_g (amino) (°C)	T_g (maleimide) (°C)	T_g (°C)	Gelation^b (%)
0	0.89	56000	–	–	192	–
5	0.59	36000	194	199	197	89
10	0.51	31000	195	203	202	96
15	0.49	29000	198	211	213	98

[a] G.p.c., universal calibration

[b] After thermal cure at 250°C/3 h, 280°C/1 h

5% pendent maleimide system that has been crosslinked shows a relatively constant modulus above the T_g owing to the covalent chemical bonds between the polymer chains.

The effect of the incorporation of pendent amino-containing poly(arylene ether sulphone)s into epoxy networks was also investigated. The pendent amines were reacted with Epon 828 and 4,4'-DDS in an effort to improve the fracture toughness of modified epoxy thermosets. Amine-terminated polysulphones have been demonstrated to increase the fracture toughness of brittle epoxy thermosets[13]. One of the various factors that influence the fracture toughness of thermoplastic-modified epoxy thermosets is the molecular weight of the thermoplastic modifier. As the molecular weight of the amine-terminated polysulphones increased, the fracture toughness of the modified epoxy also increased. With the approach described in this paper, one can vary the concentration of amines on the backbone independently of the molecular weight. In this investigation, high-molecular-weight polysulphones with various amine concentrations on the polymer backbone were incorporated into the epoxy thermosets to determine if the fracture toughness can be improved. The characterization of

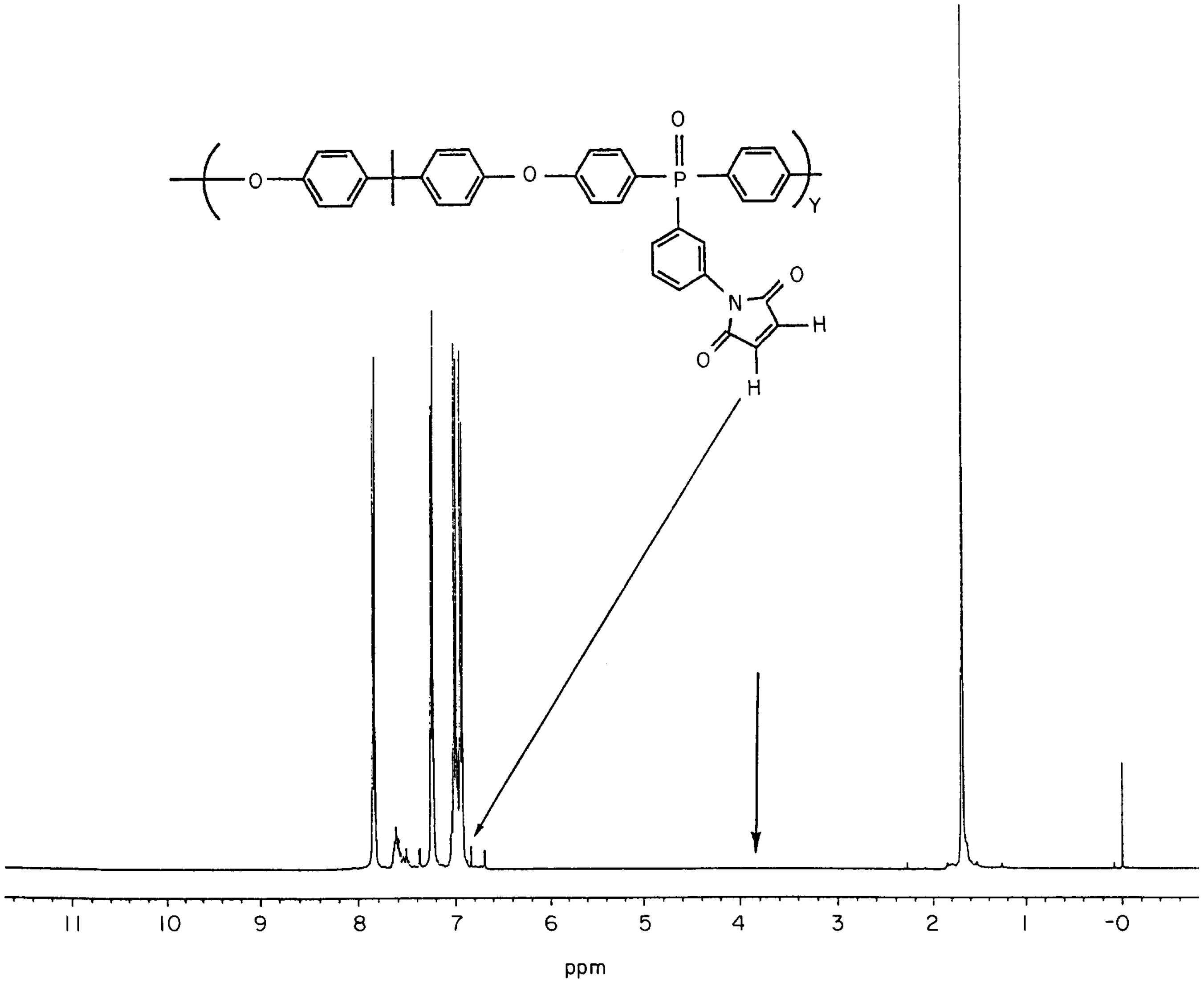


Figure 3 Proton n.m.r. spectrum of 15 mol% pendent maleimide-containing polysulphone units

various pendent amino poly(arylene ether sulphone)s utilized in this investigation is shown in *Table 2*. From titration and g.p.c. data, one may estimate the *average* molecular sequence between amine functionalities. *Figure 5* shows a two-phase morphology that is generated as a result of the incorporation of 15 wt% of commercial Udel polysulphone into the epoxy thermoset. The non-reactive commercial bisphenol A based poly(arylene ether sulphone) is initially soluble in the epoxy resin. However, as the cure progresses, it phase separates from the epoxy matrix and forms discrete particles. It is widely believed that these discrete particles enhance the fracture toughness of the modified epoxy thermosets, although chemical resistance is impaired. In the case with Udel, even though a two-phase morphology was obtained, only a slight improvement in the fracture toughness was observed[21]. This may be due to poor adhesion between the phase-separated particles and the epoxy matrix. By incorporating reactive amine-terminated polysulphones into epoxies, we have reported a similar two-phase morphology and a dramatic increase in the fracture toughness[13]. The increase in the fracture toughness was attributed to the good adhesion between the polysulphone particles and the epoxy matrix as a result of the reaction of the amines with the epoxy resin. The fracture toughness of epoxy thermosets that have been modified with high-molecular-weight polysulphones with various amine contents on the backbone is shown in *Table 3*. Concentrations of 2.5, 5, 10, 20 and 30 mol% cure sites were investigated. Interestingly, a noticeable increase in the fracture toughness was observed only when amino DFTPPO monomer concentration was 2.5%. In this case, the fracture toughness increased as a function of the concentration of the poly(arylene ether sulphone) copolymer that was incorporated into the epoxy thermoset. For the 25% loading, a three-fold increase in the fracture toughness was observed over that of the control. The d.m.a. showing the tan δ behaviour for the control and the 25% loading of the polysulphone with 2.5% amino DFTPPO monomer is shown in *Figure 6*. For the control, only a single transition was observed at 215°C, which corresponded to the T_g of the epoxy. However, for the 25% loading two transitions were observed, one for the T_g of the polysulphone at 193°C and the other at 215°C for the T_g of the epoxy. The SEM micrographs of the fractured surfaces are shown in *Figure 7*.

A two-phase morphology was observed with a uniform distribution of polysulphone particles in the epoxy matrix at lower levels of loadings. Around 15% loading, a phase

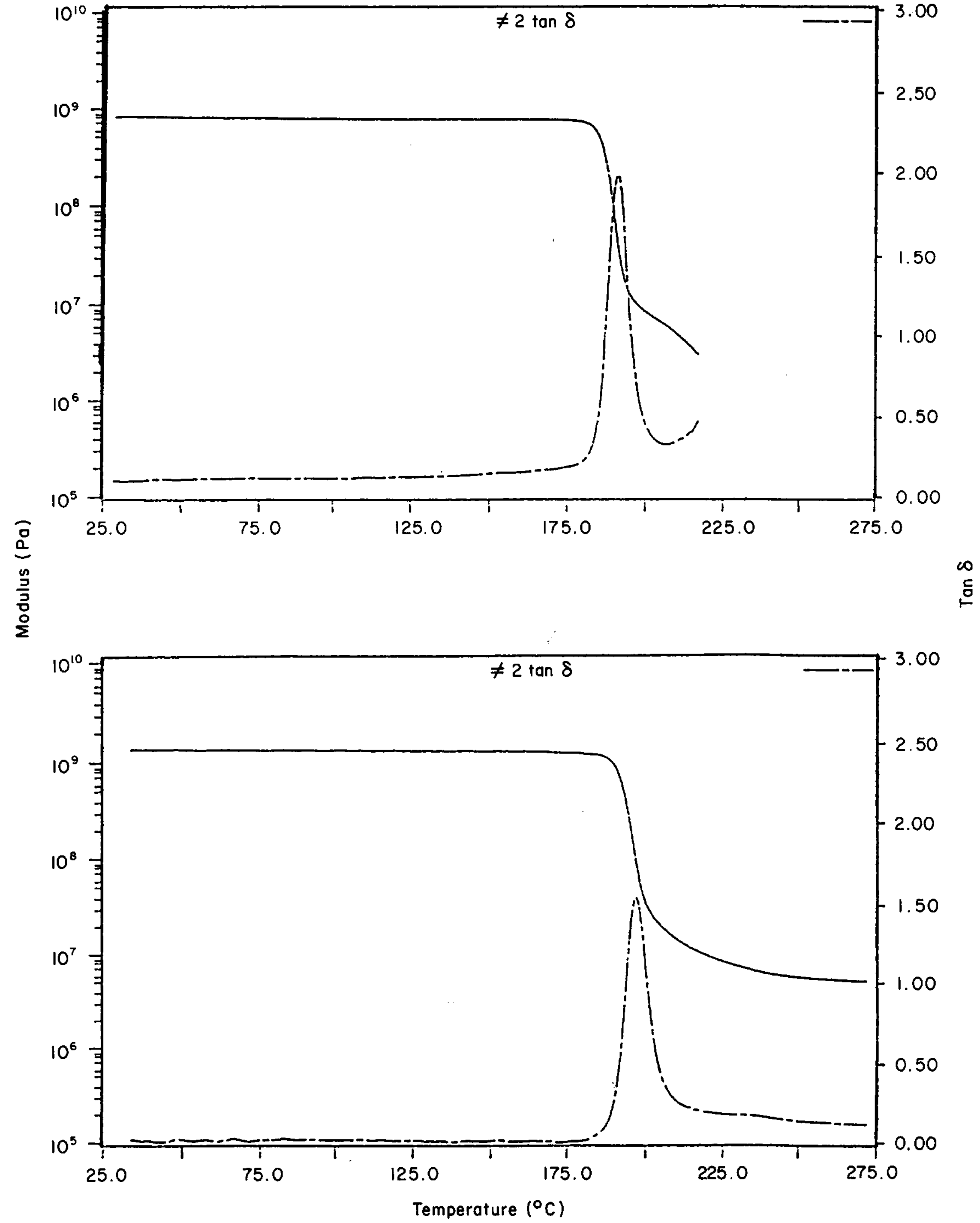


Figure 4 D.m.a. of control linear polysulphone (top) and crosslinked (5 mol% pendent maleimide) polysulphone (bottom)

Table 2 Characterizations of pendent amino poly(arylene ether sulphone)s with various concentrations of amine groups utilized for modification of epoxy–DDS networks

Samples	$[\eta]^{25°C}_{CHCl_3}$ (dl g^{-1})	D.s.c. T_g (°C)	Average molecular weight/amine[a] (g mol^{-1})
Control	–	–	–
2.5% Amino PSF	0.45	191	16 699
5.0% Amino PSF	1.00	197	9324
10% Amino PSF	0.61	193	4965
20% Amino PSF	0.45	196	2525
30% Amino PSF	0.41	199	1566

[a] An estimate from titration and g.p.c. data of the number-average distance between reactive amine groups

inversion began to occur, and for the 20 and 25% loading, the thermoplastic became the continuous phase and the epoxy was now the discrete phase. Also, a honeycomb type of morphology was observed after phase inversion, which was similar to the morphology reported in instances where relatively high-molecular-weight amine-terminated oligomers of polysulphones were used for modifications of epoxy thermosets[22].

CONCLUSIONS

Bis(4-fluorophenyl)-3-aminophenylphosphine oxide (amino DFTPPO) was synthesized and successfully copolymerized with DCDPS and bisphenol A for the synthesis of random pendent amines on the backbone of polysulphones. A unique feature of the pendent amino polysulphones that were synthesized was that molecular weight was controlled independently of the concentration of the amines. As with the amine-terminated polysulphones, the pendent amino polysulphones were also converted to maleimides and cured to give crosslinked materials. The pendent amines were also utilized to modify epoxy thermosets. For high-molecular-weight polysulphones, the concentration of amine groups on the backbone was an important variable in determining multiphase character and the fracture toughness of modified epoxy thermosets. As the incorporation of amino DFTPPO monomer into polysulphones increased, the polysulphone appears to be less able to phase separate from the epoxy network. Therefore, only a very slight or no improvement in the fracture toughness was observed; in particular, a 2.5 mol% crosslink site copolymer was very efficient in developing multiphase highly toughened resin networks. For the higher concentrations of the curing site (e.g. >2.5 mol%), the reactive thermoplastic toughener appears to be much more miscible with the epoxy network and relatively little improvement in plane strain fracture toughness was observed.

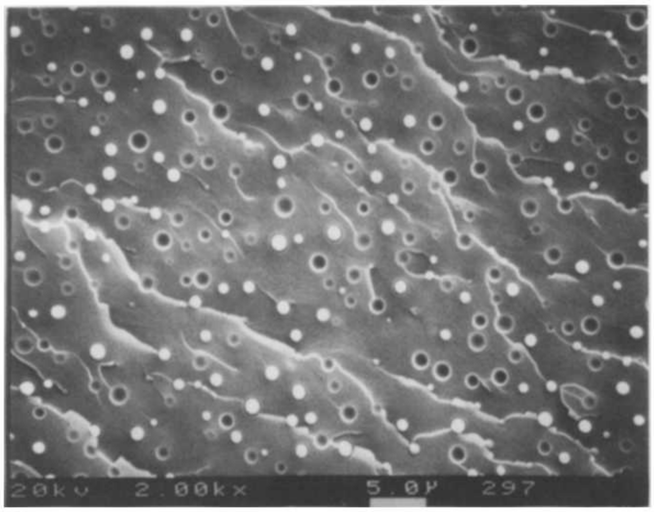


Figure 5 SEM micrograph of 15 wt% incorporation of Udel into epoxy–DDS network

Table 3 Influence of cure site and thermoplastic concentration on the fracture toughness enhancement of epoxy–DDS networks

Samples	Cure site (mol%)	Reactive thermoplastic (wt%)	Fracture toughness (MN m$^{-3/2}$)
Control (Udel)	–	–	0.75±0.08
		10	0.84±0.08
Amino PSF	2.5	5	0.86±0.08
		10	0.92±0.06
		15	1.19±0.10
		20	2.05±0.17
		25	2.28±0.43
Amino PSF	5.0	5	0.96±0.06
		10	1.11±0.21
Amino PSF	10.0	5	0.75±0.06
		10	0.84±0.12
		15	0.85±0.04
		20	0.89±0.06
Amino PSF	20.0	5	0.85±0.06
		10	0.88±0.01
		15	0.88±0.12
Amino PSF	30.0	5	0.75±0.07
		10	0.66±0.05
		15	0.65±0.16

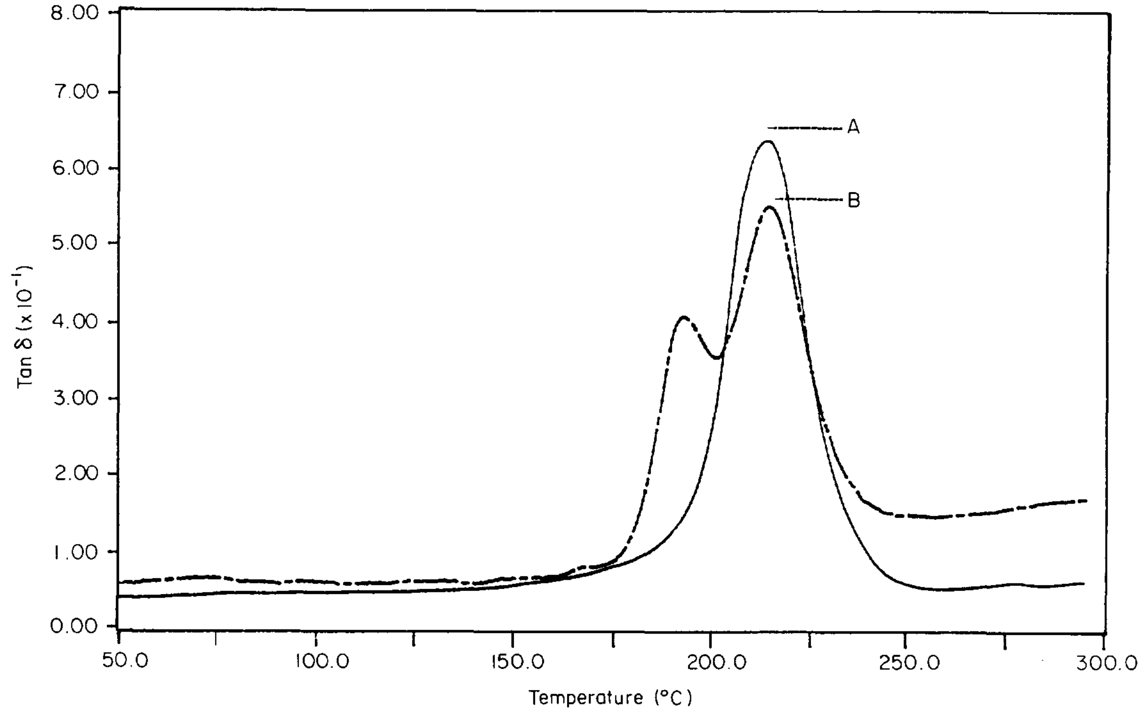


Figure 6 D.m.a. showing the tan δ behaviour of control (A) and 25 wt% loading of 2.5 mol% pendent amino polysulphone (B) modified epoxy–DDS network

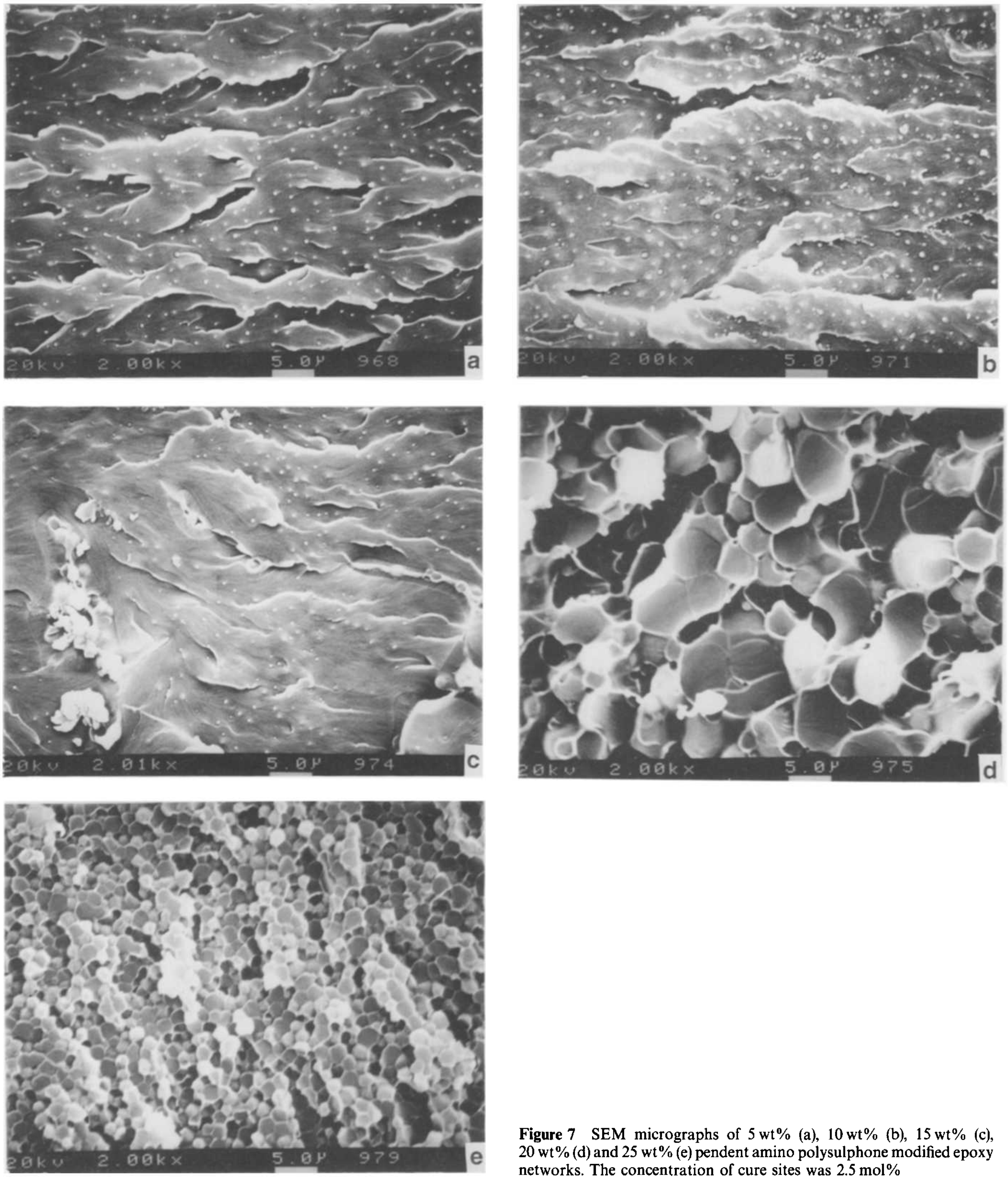


Figure 7 SEM micrographs of 5 wt% (a), 10 wt% (b), 15 wt% (c), 20 wt% (d) and 25 wt% (e) pendent amino polysulphone modified epoxy networks. The concentration of cure sites was 2.5 mol%

ACKNOWLEDGEMENTS

The authors would like to acknowledge the National Science Foundation Science and Technology Center for support under contract DMR-912004.

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