Synthesis, curing and physical behaviour of maleimide-terminated poly(ether ketones)

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Maleimide-terminated amorphous poly(arylene ether sulphones) and poly(arylene ether ketones) of controlled $\bar{M}_n$ (2000–10 000 or higher) were synthesized by nucleophilic aromatic substitution, step polymerization and bisphenol A phenolate with activated aromatic halides in the presence of *m*-aminophenol or 2,2′-(4-aminophenyl-4-hydroxyphenyl)propane. The amine-terminated oligomers of predictable molecular weight were then converted to maleimides. This 'two-step' method was accomplished by reacting the terminal amine with maleic anhydride in a co-solvent of *N*-methylpyrrolidone/*N*-cyclohexyl pyrrolidone (80/20). A second 'one-step' oligomer synthesis method employed either *m*-maleimidophenol or 2,2′-(4-maleimido-4′-hydroxyphenyl)propane as the 'monofunctional' end-capper. The oligomers were thermally crosslinked through a free-radical reaction of the maleimide end-groups. Curing at 250°C for 1 h produced networks which were 98% chloroform-insoluble. The influence of oligomer molecular weight on the thermal and mechanical properties of the solvent-resistant networks was investigated by differential scanning calorimetry, dynamic mechanical thermal analysis, flexural modulus and fracture toughness, K_{IC}. Very substantial increases in toughness were observed relative to simple bismaleimides and were a function of the molecular weight between crosslinks ($\bar{M}_c$) and the β-relaxation of the matrix.

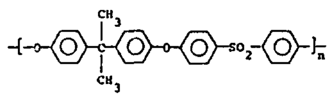
(Keywords: bismaleimides; poly(ether ketones); thermosets; functional oligomers; fracture toughness)

INTRODUCTION

Poly(arylene ether sulphones) and poly(arylene ether ketones) are classified as high-performance thermoplastics. The most familiar members of this class of materials are the linear amorphous polysulphones such as UDEL^R (**1**), Victrex (**2**), the semicrystalline PEEK^R (**3**) and more recently PEKK (**4**). Amorphous poly(arylene ether ketones) such as **5** and **6** may also be classified as high-performance thermoplastics. In general, amorphous systems such as **1**, **5** and **6** are soluble in a variety of solvents, which may limit utility.

However, with the appropriate terminal highly reactive functionalities, these ductile thermoplastics may also be transformed into tough solvent-resistant networks. Previous work in our laboratory has demonstrated the successful synthesis of amine-terminated oligomers of polysulphone[1], which were reacted with epoxy resin systems[2] or with bismaleimide via the Michael addition reaction[3] to form toughened networks. Several other groups have approached the problem of tough solvent-resistant networks by the use of maleimide-terminated oligomers[4–12]. The common theme throughout this work was to improve the fracture toughness of networks having both high crosslink densities and high T_g values.

Our objectives herein were to design solvent-induced



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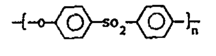

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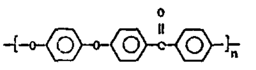

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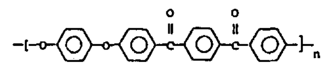

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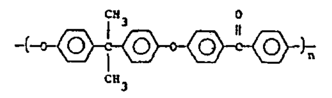

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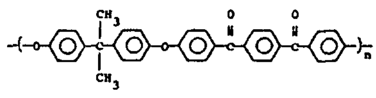

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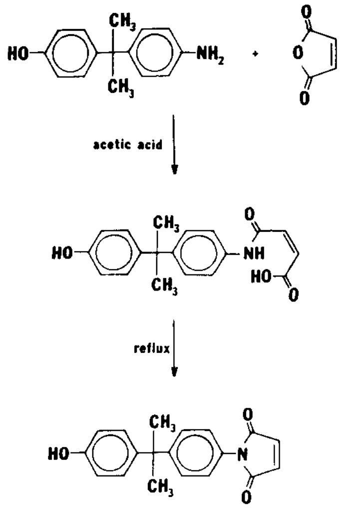


Scheme 1

stress-crack-resistant networks that exhibited high fracture toughness (K_{IC}) and to investigate the influence of crosslink density on these properties. Background knowledge of poly(ether sulphone) and poly(ether ketone) chemistry was utilized to design appropriate systems. For example, amine-terminated poly(ether ketones) were crosslinked thermally via the formation of ketamine crosslinks to afford an excellent combination of good solvent resistance and ductility[13,14]. Networks were also generated from the thermal or electromagnetic (microwave) activation of terminal maleimide groups[15]. Initial fracture toughness measurements showed that the linear bisphenol A based poly(arylene ether ketones) had very good values[16,17].

This paper describes the synthesis and characterization of these maleimide-terminated poly(ether ketones) by either a two-step or a one-step process.

EXPERIMENTAL

High-purity bisphenol A (Bis-A) obtained from Dow Chemical was dried at 60°C under vacuum prior to use. Similar, high-purity 4,4′-difluorobenzophenone was provided by ICI Americas (m.p. 98°C). Terephthaloyl chloride (TC, Fisher) was recrystallized from hexanes (m.p. 80–82°C). Maleic anhydride (MA, Fisher) was recrystallized from chloroform (m.p. 53–54°C). The *m*-aminophenol (MAP, Aldrich) was sublimed under vacuum at 120°C (m.p. 122–123°C). Anhydrous aluminium chloride (Fisher) was used as received. Anhydrous potassium carbonate (Fisher) was dried under vacuum at 100°C. Chlorobenzene, dimethylacetamide (DMAC, Fisher) and *N*-cyclohexylpyrrolidone (CHP, GAF) were distilled from calcium hydride under reduced pressure and stored in round-bottomed flasks sealed with rubber septa. The aminophenol, 2,2′-(4-hydroxyphenyl-4-aminophenyl)propane (MBA), was synthesized from bisphenol A and aniline hydrochloride as described previously[2]. Bis(4-chlorobenzoyl)benzene (CBB) was prepared by the Friedel–Crafts acylation reaction of terephthaloyl chloride and chlorobenzene[17].

Monomer synthesis

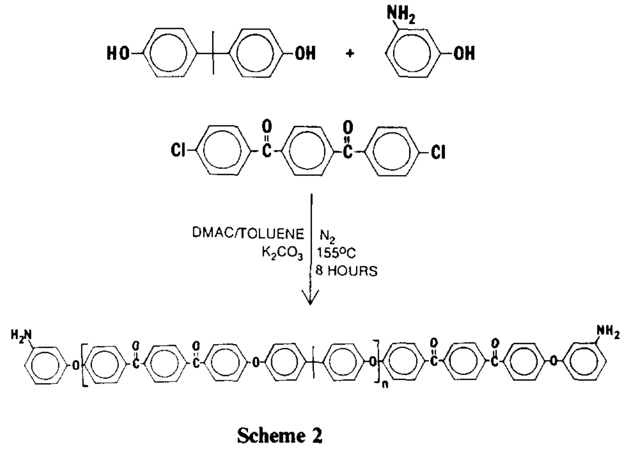
The end-blocking monomers were synthesized by the reaction of an amine with maleic anhydride to form the amic acid with subsequent cyclization to the maleimide (*Scheme 1*). The reaction was conducted using MBA (or *m*-aminophenol) in glacial acetic acid as a solvent. The maleic anhydride was added slowly and a yellow precipitate was immediately formed. The precipitate was confirmed to be a quantitative yield of the amic acid and upon heating to reflux slowly disappeared during the next 6 h. The disappearance of the amic acid could be followed via titration (see below) and was due to the cyclization to the maleimide. The product was precipitated in water and dried, dissolved in ether, filtered, and washed with sodium bicarbonate and finally distilled water. The final product was recrystallized from an ether–hexane mixture. The 2,2′-(4-maleimidophenyl-4-hydroxyphenyl)propane (MBAMI) formed yellow crystals (m.p. 162°C; yield 45%) and was confirmed by n.m.r. and *FT*i.r. The maleimide of *m*-aminophenol was prepared in a similar manner, but with lower yields (~20%).

Amine-terminated oligomers

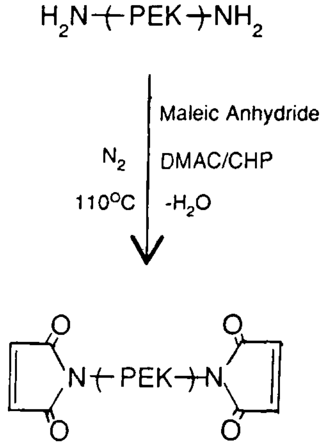
The stoichiometry of the reactants was varied according to the Carrothers equation to achieve the various molecular-weight oligomers. A typical polymerization procedure follows (*Scheme 2*). A four-neck round-bottomed flask was fitted with a Dean Stark trap, mechanical stirrer, thermometer and nitrogen inlet. The activated halide bis(4-chlorobenzoyl)benzene (CBB) (71.044 g) was added to the flask followed by bisphenol A (43.388 g) and *m*-aminophenol (MAP) (2.272 g), and the weighing pans were rinsed with DMAC to assure quantitative transfer of monomers. A total of 600 cm^3 of DMAC was added to the flask. Dried potassium carbonate (34 g) and toluene (150 cm^3) were added next and the reaction was refluxed at 145°C. After all the water had been removed from the reaction flask (~4 h), toluene was drawn from the Dean Stark trap until the temperature increased to 155°C. The reaction was allowed to proceed for 8 h, after which the solution was cooled and filtered to remove the inorganic salts, then coagulated in an excess of rapidly stirred methanol. The polymer was purified by redissolving in chloroform and coagulating in methanol again, prior to vacuum drying at 80°C to constant weight. A similar procedure was employed for the 4,4′-difluorobenzophenone systems.

Maleimide-terminated oligomers

For the two-step procedure, the amine-terminated poly(ether ketone) oligomer was titrated to determine the number-average molecular weight ($\bar{M}_n$) before imid-



Scheme 2



Scheme 3

ization. For example, amine-terminated oligomer (21 g, $MW = 6850$) was added to a three-neck 500 cm^3 round-bottomed flask equipped with a nitrogen inlet, a mechanical stirrer and a Dean Stark trap (*Scheme 3*). The DMAC (200 cm^3) and CHP (40 cm^3) were added to the flask to dissolve the polymer. Chlorobenzene can also be used as the solvent and azeotropic media. Maleic anhydride (MA) (0.97 g) was added and the solution was stirred for 6 h. Subsequently, the nitrogen flow was increased, and the temperature was raised to 130°C and maintained at this temperature for up to 24 h. The polymer solution was coagulated at room temperature in water/methanol (30/70) and vacuum dried at 80°C to constant weight.

One-step maleimide oligomers

Oligomers of controlled molecular weight were prepared by aromatic nucleophilic substitution of the activated halide by the bisphenate in the presence of the maleimide monomer (*Scheme 4*). The reactions were conducted in the presence of excess potassium carbonate as the weak base, toluene as the dehydrating agent and DMAC as the dipolar aprotic solvent. The reaction was dehydrated at 140°C for 4 h then reacted at 155°C for 8 h. Oligomers were prepared from both 4,4′-difluorobenzophenone and bis(4-chlorobenzoyl)benzene. The reaction solutions were filtered to remove the salts, rapidly coagulated in methanol and dried to constant weight. Intrinsic viscosities were measured on the soluble materials in chloroform at 25°C. The oligomers were cured in a Pasadena Press at 250°C for 1 h. Other temperature/time variations were investigated to establish how reaction variables influenced the generation of the chloroform-insoluble solvent-resistant network.

Amic acid titrations

Both monomeric and oligomeric amic acids were analysed by an acid–base potentiometric titration. The titrant was a solution of tetramethylammonium hydroxide dissolved in absolute methanol. The samples were dissolved in either methanol or DMAC, depending upon their solubility. No indicators were necessary and all the endpoints were detected by the first derivative of the potential *versus* volume titration curve.

Differential scanning calorimetry

Glass transition temperatures were determined with a Perkin–Elmer model 2 differential scanning calorimeter (d.s.c.). The baseline was checked for flatness at each heating rate and temperature calibration was achieved by using indium, which has a melting point of 156.6°C and a known heat of fusion of 6.8 cal g^{-1}. The heating rate was maintained at 10 or 20 K min^{-1}.

Dynamic mechanical analysis

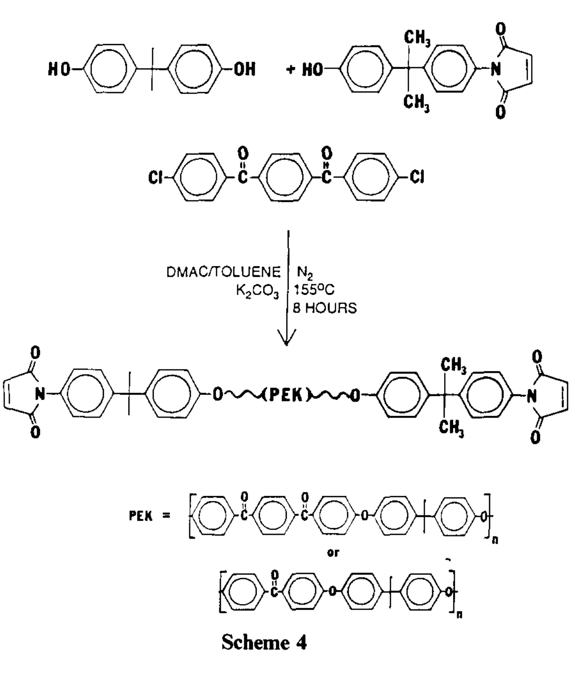
The dynamic mechanical behaviour (storage modulus ε' and tan δ) of the pre-cured and post-cured maleimide terminal oligomers were conducted on a Polymer Laboratories d.m.t.a. Samples (1.6 × 11.7 × 19 mm) cut from compression-moulded films were mounted on a dual cantilever clamp for the analyses, which were conducted at a heating rate of 4 K min^{-1} and at a frequency of 1 Hz.

Measurement of mechanical properties

Samples for stress–strain measurements were cut from a 1.5 mm compression-moulded sheet of material using a die according to ASTM Standard D638-I. The specimens prepared at 250°C for both tensile and fracture measurements were formed from polymer powder which had first been pretreated either by heating it to 160°C under vacuum for 15–45 min or by drying under vacuum at 80°C for 12 h. The thickness of the sheets was controlled by a metal window insert. The sheets were cured under pressure at 270°C for 1.5–3 h and then quench-cooled to room temperature. Tests were performed using a model 1123 Instron Material Testing System at a rate of 5 mm min^{-1}.

Sample preparation and measurement of K_{IC}

Three-point bend specimens were cut out using a scrol saw from a 3 mm sheet of material (specimen dimensions were 36 × 9 × 3 mm). The K_{IC} samples were notched and then precracked by tapping a liquid-nitrogen-cooled razor blade into the notch. It was necessary to dip the specimen into the liquid nitrogen in order to start a precrack for the very ductile high-molecular-weight linear polymer. The measurements were performed on an

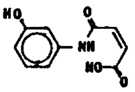
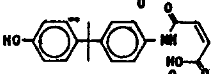
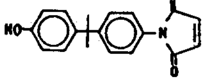


Scheme 4

Table 1 Intrinsic viscosities and glass transition temperatures of a series of poly(ether ketones) synthesized from CBB

Sample	25°C $[\eta]_{CHCl_3}$	T_g (olig) (°C)	$[\eta]_{CHCl_3}$ (capped olig)	Cured T_g (°C) (d.s.c.)
2500	0.13	119	0.18	177
5000	0.33	151	0.36	175
10 000	0.53	159	0.59	169
High *MW*	1.3	165		

Table 2 Titrations of amic acids

Sample	Solvent	Calc *MW*	Titration *MW*
	MeOH	208	207
	MeOH	325	323
	MeOH	307	No endpoint
Bisphenol A	MeOH	228	No endpoint
2500 PEKKEMI (two-step)	DMAC	3000	No endpoint

Instron Testing Machine using a strain rate of 50 mm min^{-1}. The relatively high rate was employed to match more closely 'plane strain', mode-I conditions in these toughened materials. By contrast, use of standard 2.5 mm min^{-1} rates produced pronounced crack growth deviations from a straight line.

RESULTS AND DISCUSSION

Polymerization to high molecular weights confirmed the high purity of the monomers used in these polymerizations. Bisphenol A was reacted with the ketone-containing monomer (either difluorobenzophenone, or bis(4-chlorobenzoyl)benzene) on an equimolar basis to yield high-molecular-weight materials with intrinsic viscosities over 1.0 dl g^{-1}. Functionally terminal oligomers, such as the amine-terminated poly(ether ketones) synthesized via *Scheme 2*, were characterized and then converted to the corresponding maleimide materials by solution imidization at moderate temperatures using a solvent/azeotroping agent system. DMAC was normally used as the solvent and CHP as the azeotroping agent. The role of the CHP was the efficient removal of water from the reaction solution. CHP is miscible with water only up to about 80°C and higher temperatures produce an efficient azeotroping system. It is also a strong dipolar aprotic solvent, which assists in the solvation of the amic acid. Moderate temperatures were necessary to achieve ring closure and also to prevent premature free-radical crosslinking from occurring (*Scheme 3*). Intrinsic viscosities were determined before and after imidization to assure that premature crosslinking had not occurred (*Table 1*). Previous work in our laboratories has shown that this solvent/azeotroping agent can assist in quantitatively converting polyamic acids to polyimides[18,19]. The maleimide-capped oligomers were analysed by *FT*i.r. and potentiometric titrations (*Table 2*) for residual amic acids. No endpoint for the amic acid titrations was detected in the case of samples judged to be fully imidized by *FT*i.r.

The thermal transition behaviour of poly(ether ketones) synthesized from CBB by the two-step process is provided in *Table 1*. The oligomers showed a significant rise in their T_g values between the first and second runs, which reflects the network formation. Exothermic enthalpy peaks at temperatures above T_g during dynamic d.s.c. temperature scans were observed. This higher value represents the T_g of the crosslinked network and was observed to be unchanged on subsequent scans. Dynamic mechanical behaviour was another even more sensitive method for characterizing the crosslinked material. The dynamic storage and loss moduli measured at low frequencies by the d.m.t.a. were very sensitive to changes in molecular mobility. The partially gelled system produced a much higher modulus as the crosslinking reaction proceeded. Another interesting feature of the d.m.t.a. plots was the presence of a large β-relaxation peak at -80°C. The presence and magnitude of the β-peak is proposed to be related to the very high fracture toughness of the poly(ether ketones), discussed in a later section. Typical dynamic mechanical behaviour is illustrated in *Figures 1* and *2*. The modulus behaviour above T_g reflects an increase in crosslink density.

Coefficients of thermal expansion

The effect of crosslink density on the coefficient of thermal expansion (*CTE*) was also investigated. This property is of considerable importance in composite matrix resin and coatings systems. Decreases in the oligomer molecular weight of the cured networks resulted in lower *CTE* values (*Table 3*). Higher crosslink densities should result in more highly constrained networks, which no doubt influence the changes in free volume of the system as a function of temperature. The influence of oligomer molecular weight on *CTE* as determined by t.m.a. is shown in *Figure 3*.

One-step synthesis

The synthesis of the novel 'end-blocker' maleimidophenylisopropylidenephenol (MBAMI) was achieved in high crude yields. Isolation of the first-stage amic acid confirmed that this reaction was quantitative. Proton n.m.r. of the amic acid from the aminophenol (MBA) showed no by-products or unreacted MBA, and integration of its individual peaks matched the expected results. The amic acids were also titrated for carboxyl groups, and the experimental and theoretical molecular weights were equivalent (*Table 2*). Cyclization of the maleimide was essentially quantitative as judged by the disappearance of the insoluble amic acid. The purity of the maleimide monomers was confirmed by n.m.r. (*Figure 4*), by titration and by sharp melting points.

The one-step polymerization procedure employed basically the same aromatic nucleophilic substitution reaction as was used to make the amine-terminated oligomers (two-step process). The only change is the substitution of a maleimidophenol for an aminophenol as the end-capper. Of course, the reaction fails if the end-capper is not incorporated or if the maleimide group prematurely polymerizes. The incorporation of the maleimide end-group was demonstrated by *FT*i.r. spectroscopy. When one compares the *FT*i.r. spectra of

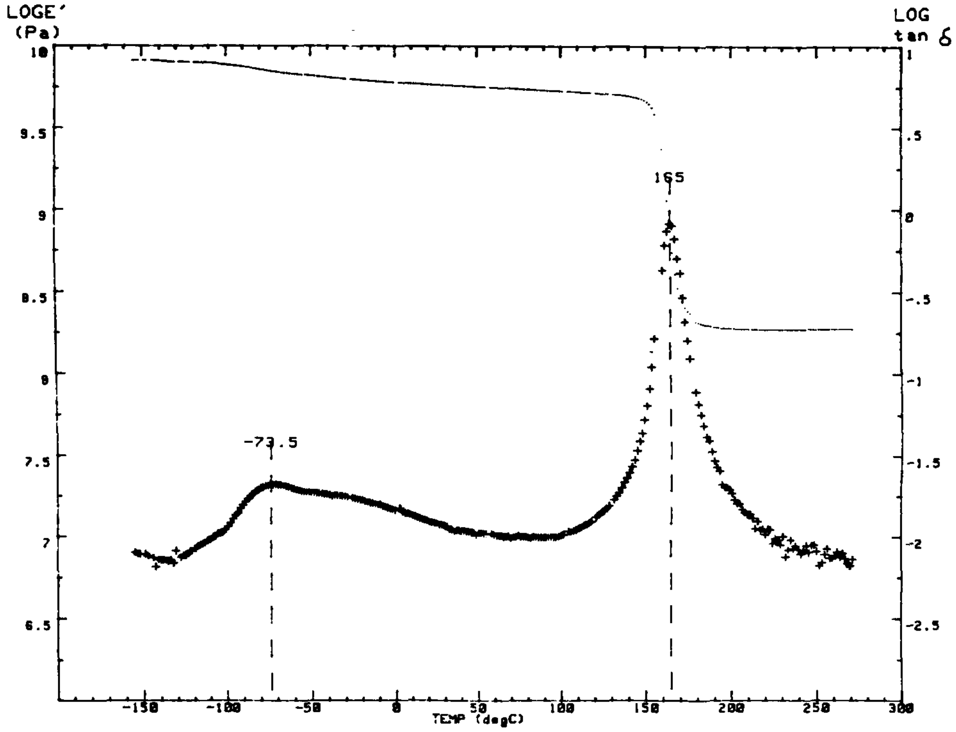


Figure 1 Dynamic mechanical behaviour (1 Hz) of a thermally cured bismaleimide functional 2500 $\bar{M}_n$ poly(arylene ether ketone)

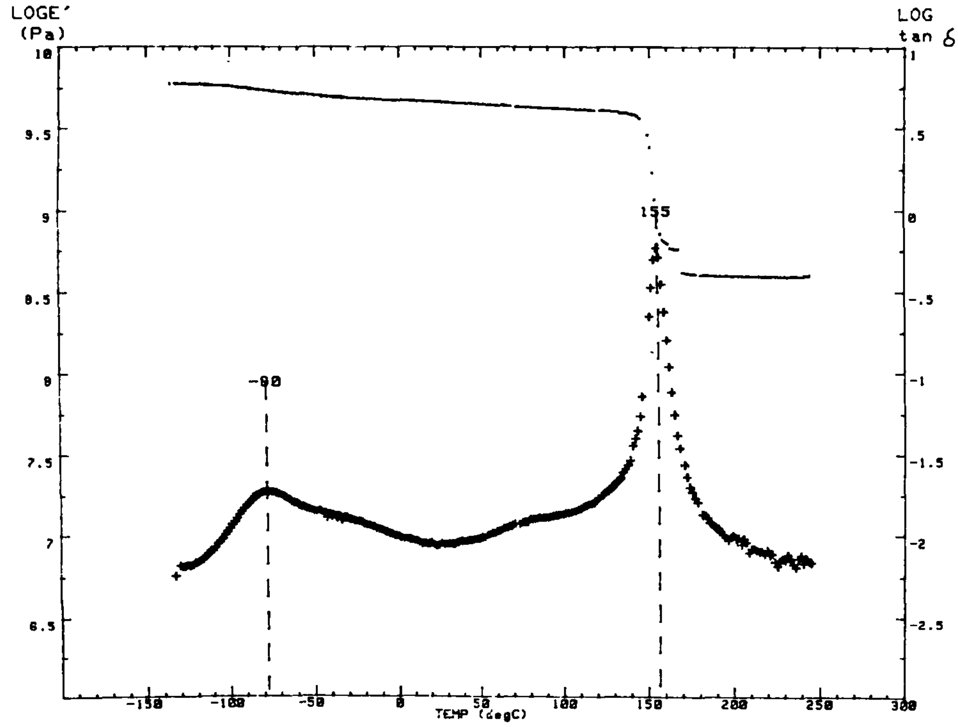


Figure 2 Dynamic mechanical behaviour (1 Hz) of a thermally cured bismaleimide functional 10000 $\bar{M}_n$ poly(arylene ether ketone)

an amine-terminated 3000 *MW* oligomer to that of a maleimide-terminated 3000 *MW* oligomer synthesized by the 'one-step' method, the only differences observed were the absence of the amine stretching band at ~3300 cm^{-1} and the appearance of an imide carbonyl band at 1712 cm^{-1} (*Figure 5*). Comparison with model compounds and the maleimide monomers confirmed that the 1712 cm^{-1} peak was a strong imide band. The weaker imide peaks were not anticipated to be observable since imide carbonyls were present only at the chain ends. A similar maleimide oligomer synthesized by the 'two-step' method had an identical *FT*i.r. spectrum, demonstrating that both methods yielded essentially the same results.

Ring opening of the maleimide during the oligomerization reaction must be considered as a possible side-reaction. If this side-reaction was significant, a peak corresponding to a carboxylic acid should appear in the *FT*i.r., particularly at low molecular weights. In fact, no

Table 3 Linear thermal expansion coefficients of cured bismaleimide-terminated poly(ether ketones)

$\bar{M}_n$	$\alpha \times 10^5$ (°C^{-1})	T_g (°C)		
		T.m.a.	D.s.c.	D.m.t.a.
2500	3.92	173	177	165
5000	4.75	172	175	160
10000	5.93	170	169	155
High *MW*	6.12	166	165	150

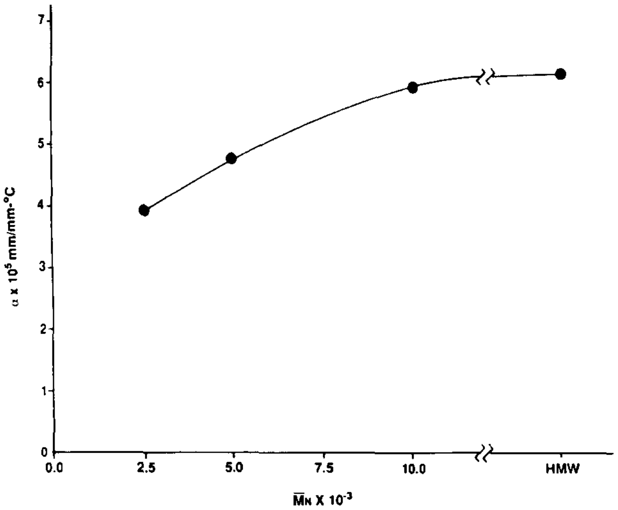


Figure 3 Effect of oligomer $\bar{M}_n$ on linear thermal expansion coefficients of thermally cured bismaleimide functional poly(arylene ether ketones)

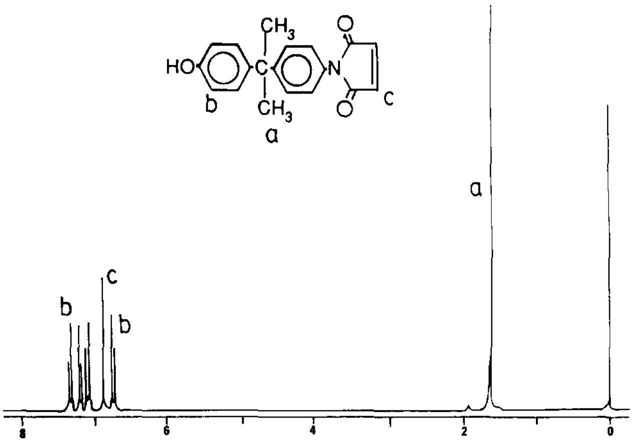


Figure 4 ^{1}H n.m.r. of 2,2'-(4-maleimidophenyl-4-hydroxyphenyl)propane

such absorptions were observed and no amic acid could be detected by titration. It was thus concluded that the ring was stable under the anhydrous polymerization reaction conditions. This was not too surprising since the reaction conditions were anhydrous and water is necessary to hydrolyse the maleimide ring. Another possible side-reaction could be the premature free-radical crosslinking of the maleimides in solution. Premature crosslinking would result in large increases in branching, molecular weight and possible gel formation. Crosslinking could be detectable by comparing the intrinsic viscosities of the 'one-step' oligomers with the values for 'two-step' oligomers of similar molecular weight. The oligomers prepared by both methods should be essentially identical and similar molecular weights should of course have the same intrinsic viscosity in the absence of chain extension or crosslinking. Under the reaction conditions reported, the amount of crosslinking was apparently negligible. However, if the reaction temperature exceeded 155°C or if the reaction time was increased, the viscosity of the 'one-step' oligomer was much higher than expected. In one reaction, the oligomer actually gelled in the flask! Since it has been reported that maleimides crosslink via a free-radical addition reaction and that phenols can inhibit radical polymerizations, it is suggested that the phenolic monomers used could effectively inhibit the crosslinking until all the phenol groups were consumed and the polymerization was completed. The crosslinking reaction appears to be slow even at 150°C and was unimportant if the polymerization was terminated soon after completion.

Network formation behaviour

The purified and dried oligomers were thermally crosslinked under press cure conditions as a function of temperatures and cure times (*Figure 6*). *Figure 6*

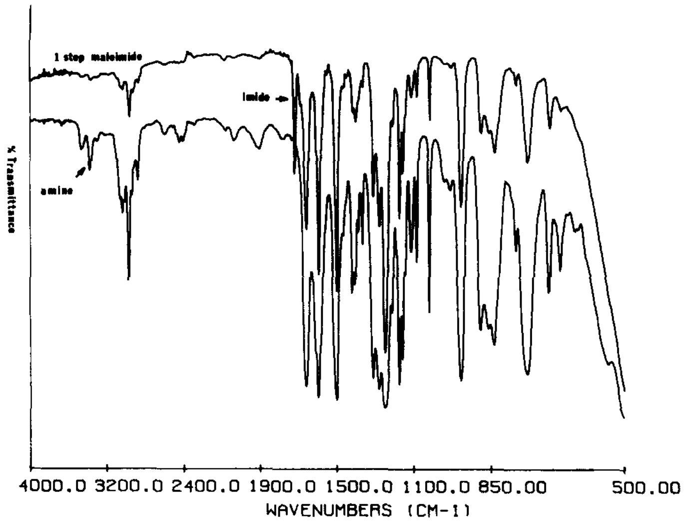


Figure 5 *FT*i.r. spectra of 2500 $\bar{M}_n$ amine-terminated poly(ether ketone) and a one-step 2500 $\bar{M}_n$ maleimide-terminated poly(ether ketone)

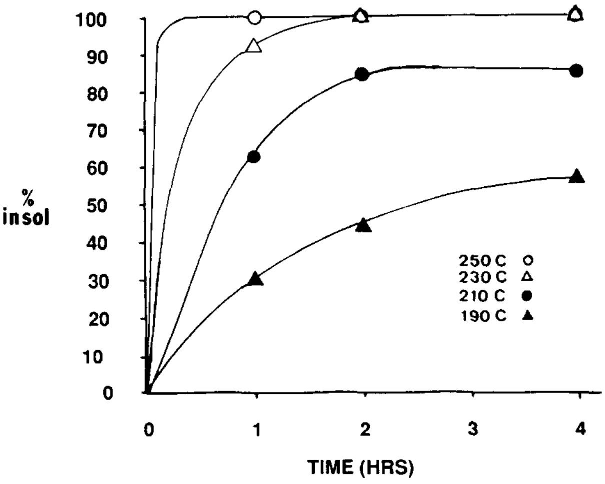


Figure 6 Chloroform insoluble fraction of cured maleimide networks for various curing times and temperatures

Table 4 Mechanical properties of maleimide-terminated poly(ether ketone) networks

Sample	Tensile strength (MPa)	Yield elongation (%)	Ultimate elongation (%)	K_{IC} ($10^{-6}\,N\,m^{-3/2}$)
Polycarbonate	–	–	–	3.8 ± 0.5
2500 M_n	70	9	10	1.8 ± 0.2
5000 M_n	70	10	11	2.0 ± 0.2
10 000 M_n	70	11	21	3.3 ± 0.1
Linear high M_n control	63	13	110	4.0 ± 0.5

demonstrates that the films must be cured at a minimum of 230°C to achieve 100% gelation. At lower temperatures, the decreasing mobility of the macromolecular chains due to network formation may prevent complete curing of the network. The experiments demonstrated that 1 h at 250°C was sufficient to cure the films fully into highly solvent-resistant networks (>98% chloroform-insoluble).

Stress–strain behaviour

Variation of the molecular weight of the starting oligomer correlates well with the observed stress–strain behaviour of the final crosslinked network (*Table 4*). Thus, as the number-average molecular weight ($\bar{M}_n$) increased from 2500 to 10 000, the yield and ultimate elongation increased significantly. The 10 000 crosslinked oligomeric network even showed the formation and subsequent drawing of shear bands before fracture. The latter behaviour was not unexpected, since the molecular mobility of the final cured network should *increase* with increasing molecular weight of the starting oligomers (increasing $\bar{M}_c$). Therefore, the ductility should be greatest for the higher-molecular-weight oligomer. On the other hand, the swelling behaviour of the networks increased with $\bar{M}_c$. The control was a linear, tough high-molecular-weight thermoplastic polymer and exhibited extensive amounts of plastic deformation. In this sense, its behaviour appeared similar to the well known commercially available thermoplastic polycarbonates based on bisphenol A. However, the poly(arylene ether ketone) would, of course, show greatly enhanced hydrolytic stability.

Fracture toughness behaviour

The critical stress intensity factor for mode-I loading, K_{IC}, was used as the measure of fracture toughness for these materials. K_{IC} values were obtained from fracture tests on three-point bend specimens and were calculated using the equation:

$$k = \frac{PS}{BW^{3/2}}\left[2.9\left(\frac{a}{w}\right)^{1/2} - 4.6\left(\frac{a}{w}\right)^{3/2} + 21.8\left(\frac{a}{w}\right)^{5/2} - 37.6\left(\frac{a}{w}\right)^{7/2} + 38.7\left(\frac{a}{w}\right)^{9/2}\right]$$

where P is maximum load, S is sample length, B is sample thickness, W is sample width and a is initial crack length. The margin of error for the K_{IC} values was determined using a 90% confidence level. A minimum of 10 specimens were utilized.

The K_{IC} values (*Table 4*) showed that fracture toughness increases with the molecular weight of the oligomer used in the network. This was in agreement with the stress–strain behaviour, which showed the greatest amount of plastic deformation (strain at break) for the 10 000 oligomeric network. Furthermore, the high-molecular-weight polymer showed the highest toughness of the systems tested and was comparable to Bis-A based thermoplastic polycarbonate, as mentioned earlier.

Fracture toughness values presented here should, perhaps, be considered only semiquantitative, since difficulties encountered in fabricating thick sheets (6 mm or greater) required a specimen whose thickness did not precisely meet requirements for plane strain fracture toughness testing. A high testing strain rate, 50 mm min^{-1}, was used to reduce plastic deformation. Even though this procedure did produce less ductile behaviour than in the samples tested at slower strain rates, yielding was still observed in a number of our samples, as well as in the polycarbonate control. Nevertheless, it may be concluded that the crosslinked networks clearly showed excellent toughness.

CONCLUSIONS

Amorphous poly(arylene ether ketones) functionalized with maleimide end-groups could be synthesized at controlled molecular weights by nucleophilic step-growth polymerization of bisphenol A phenolates with activated halides at about 150°C. Either 4,4'-difluorobenzophenone or bis(4-chlorobenzoyl)benzene was used as desired. The maleimides were synthesized either by the conversion of terminal amine groups or by directly end-capping with appropriate maleimide phenol derivatives of bisphenol A or *m*-aminophenol. The properties of the resulting cured polymer networks were essentially the same regardless of the method of synthesis. Thermal curing could be monitored by d.s.c. and d.m.t.a. and showed d.s.c. T_g values of 145–175°C, with modulus above the T_g proportional to crosslink density. The cured networks were insoluble in common solvents such as chloroform. Fracture toughness K_{IC} values showed the materials to be very ductile. Toughness increased with molecular weight and approached values observed for linear high-molecular-weight control and a polycarbonate control. The coefficient of thermal expansion was shown to vary with oligomer molecular weight, probably as a result of increased network constraint at higher crosslink densities. The materials are currently also being evaluated for processing with electromagnetic radiation, and these results will be reported later.

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