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New high-performance thermosetting polymer matrix material systems

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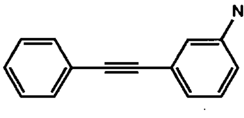
The synthesis of amorphous, soluble triarylphosphine oxide-containing imide oligomers and arylene ether sulfone triarylphosphine oxide copolymers is described. The imide oligomers were controlled-molecular-weight systems endcapped with 3-phenylethynyl aniline. The arylene ether copolymers were synthesized in high molecular weight with controlled amounts of a novel comonomer, which contained pendent aryl amino groups that were subsequently functionalized with 4-phenylethynylphthalic anhydride. The phenylethynyl groups were employed to afford a higher curing temperature (380–420°C), which widens the processing window between T_g and the cure temperature compared with the well studied ethynyl-endcapped systems. The polyimides were synthesized via solution imidization techniques, using the ester–acid derived from various dianhydrides and several aromatic diamines. The 'one-pot' procedure utilized *N*-methylpyrrolidinone as the primary solvent and *o*-dichlorobenzene as the azeotroping agent, and reproducibly produced fully imidized soluble polyimides. Thermally cured polymers displayed good solvent resistance and exhibited glass transition temperatures comparable to their high-molecular-weight linear analogues. These polyimides also showed excellent thermal stability as judged by dynamic thermogravimetric analysis (t.g.a.). The arylene ether phosphine oxide copolymers were synthesized by a nucleophilic aromatic substitution reaction of the activated aryl dihalides with various bisphenolates. The thermally cured polyimides also exhibit excellent solvent resistance. Both the triarylphosphine oxide-containing polyimides and the arylene ether copolymers exhibited very high char yields as determined by t.g.a., e.g. the polyimides displayed about 50% char at 700°C in air.

(Keywords: polyimides; arylene ether copolymers; phenylethynyl crosslink sites)

INTRODUCTION

Advances in thermosetting resins for functional and structural applications, which offer properties similar to those of thermoplastics but with improved solvent resistance and better high-temperature dimensional stability, are needed[1]. Thermoplastics and thermosets have both been widely used for high-performance composite applications. Thermoplastics have the advantages of minimal chemistry change during processing, as well as ductility, and may be recycled after the fabrication process. However, some amorphous thermoplastics have a major deficiency in solvent resistance. Thermosets, on the other hand, offer excellent solvent resistance and a large database. However, some of these resins may be too brittle[1] for certain applications and they are difficult to recycle once crosslinking has taken place. As a result, by combining the advantageous properties of both thermoplastics and thermosets into one material, one attempts to produce a material with good processability, mechanical performance and solvent resistance.

Thermoplastic polyimides can be designed to exhibit excellent thermal stability and mechanical properties. A number of polyimides have been developed that are useful as matrix resins, adhesives and coatings for high-performance applications in the aerospace and electronics industries[2–4]. However, as mentioned above, one major disadvantage of some thermoplastic systems is their poor solvent resistance. As a result, we have focused on the incorporation of 3-phenylethynyl aniline (**1**) as the endcapping agent for imide oligomers, which cures at ~380–420°C[5].



Phenylethynyl Aniline (1)

Hergenrother earlier reported that phenylethynyl groups randomly spaced along a quinoxaline backbone can undergo a thermally induced crosslinking reaction occurring at approximately 430–450°C[6]. With the use of this high-temperature curing endcap, polyimides may be utilized that exhibit T_g values in excess of 400°C after curing and still allow sufficient processing time at temperatures well above the oligomer's T_g before the system is fully cured. These reactive oligomers possess relatively low melt viscosities above their T_g and thermally cure without the evolution of volatile by-products.

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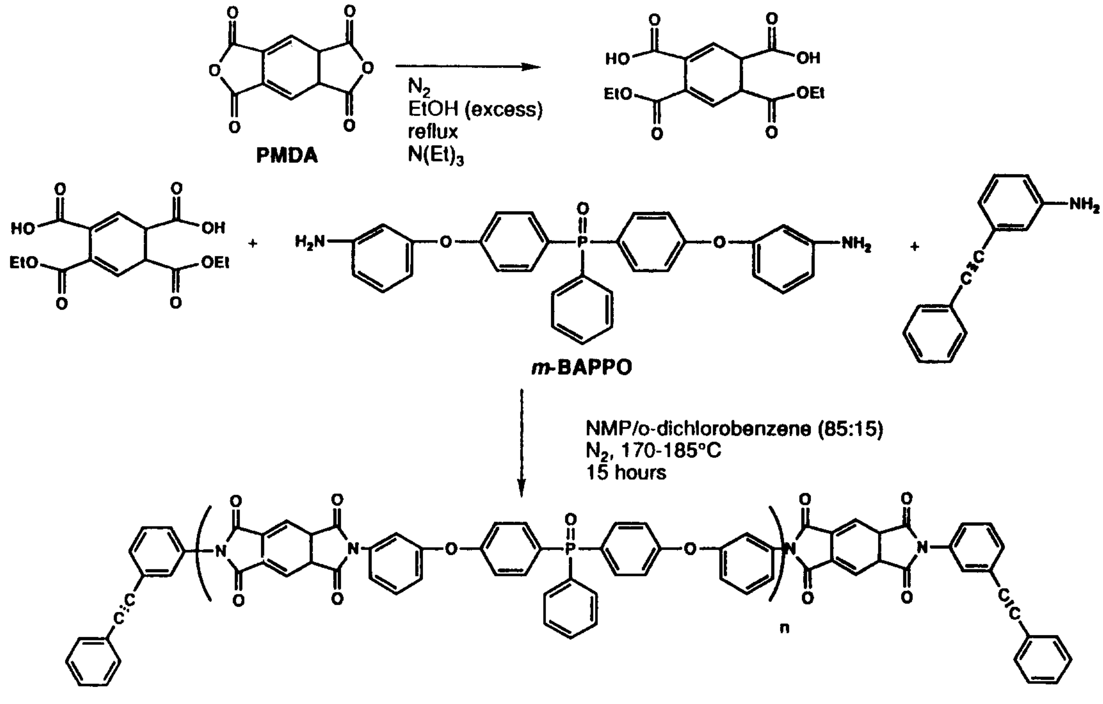
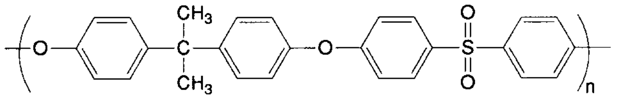


Scheme 1 Synthesis of phenylethynyl-terminated phosphine oxide polyimides

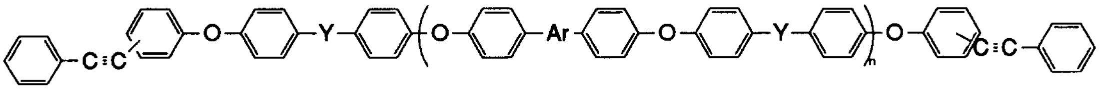


UDEL® (2)

Poly(arylene ether sulfone)s such as Udel^{R} (**2**) are excellent engineering thermoplastics, and are widely used in a variety of applications since they offer excellent mechanical properties, have relatively high T_g values and are hydrolytically and thermo-oxidatively stable. However, these materials are also solvent-sensitive, especially under stress, and undergo creep under load at elevated temperatures approaching T_g. Our group along with others have shown that phenylethynyl groups placed at the ends of arylene ether chains such as **3** or placed pendent along the chain backbone offer high T_g values, excellent solvent resistance and good mechanical properties[7,8].

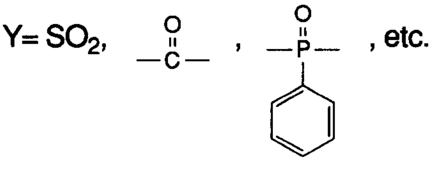
Jensen *et al.*[8] have synthesized phenylethynyl-containing monomers based on the 3F systems[9] that can be polymerized to afford the pendent acetylenic groups along the polymer backbone. In this paper, we describe a different approach where we have synthesized arylene ether copolymers that contain pendent aryl amine moieties. These pendent amines were then functionalized to afford maleimide[10] or 4-(phenylethynyl)phthalimide groups to give solvent-resistant, highly ductile arylene ether resins.

In addition to crosslinking the polyimide and poly(arylene ether)s to improve solvent resistance, we have also incorporated phosphorus into the backbone of these polymeric materials. Triarylphosphine oxide-containing polymers have also been shown in our laboratories to be excellent adhesives to metal substrates[11]. The good adhesive characteristics of these systems may be a function of the polar interaction of the phosphine oxide moiety with the surface of the metal substrate. In addition, phosphine oxide-containing polyimides and poly(arylene ether)s show excellent thermal stability, surpassing the thermal stability of more conventional aromatic-based systems such as polycarbonates or polyesters[12,13]. Even more desirable, phosphine oxide-based polymers are excellent flame-retardant materials owing to their self-extinguishing nature[14]. Therefore, we



(3)

Ar = bisphenol A, biphenol, etc.



$$Y = SO_2,\ -\overset{O}{\overset{\|}{C}}-,\ -\overset{O}{\overset{\|}{P}}(C_6H_5)-,\ \text{etc.}$$

have devoted considerable efforts towards developing processable, high-T_g thermosetting phosphine oxide-containing polymers having an attractive combination of properties.

EXPERIMENTAL

Materials

N-Methylpyrrolidinone (NMP) and *N,N'*-dimethylacetamide (DMAc) were obtained from Fisher and were vacuum distilled over P_2O_5 and stored under N_2 prior to use. 1,2-Dichlorobenzene (*o*-DCB) was also obtained from Fisher and was used as received. Toluene was obtained from Fisher, vacuum distilled over calcium hydride and stored under N_2 prior to use. Pyromellitic dianhydride (PMDA) was kindly donated by Allco. PMDA was polymer-grade material and was not further purified. *p*-Phenylenediamine (*p*-PDA) was obtained from Aldrich and was vacuum sublimed prior to use. *m*-Bis(aminophenoxy)phenylphosphine oxide (*m*-BAPPO) was synthesized as previously reported[15], and 3,3'4,4'-tetracarboxytriphenylphosphine oxide dianhydride (PPODA) was also synthesized as reported earlier[16]. 1,1-Bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3F diamine or 3FDAM) was synthesized by a modification of the formerly reported procedure[17]. 3-Phenylethynyl aniline (3-PEA) and 4-phenylethynylphthalic anhydride (4-PEPA) were prepared as previously reported[18,19]. Monomer-grade bisphenol A was provided by Dow Chemical and was also used as received. Bis(4-fluorophenyl)phenylphosphine oxide (DFTPPO) was synthesized according to a procedure reported in the literature[20] and was purified by vacuum distillation. Amino-DFTPPO was synthesized as previously reported[10].

Polyimide synthesis

Details of synthesis are provided elsewhere[15,16,18,19,21,22]. Polymers were synthesized via the previously described ester–acid route[18,21,22]. A representative polymerization conducted for the synthesis of a PMDA/*m*-BAPPO 9000 g mol^{-1} oligomer is provided as follows: PMDA (74.96 g, 3.4366×10^{-1} mol) was charged to a 2000 ml three-necked round-bottomed flask equipped with an overhead stirrer, nitrogen inlet, thermometer, reverse Dean–Stark trap and reflux condenser, and the reactor was heated with a silicone oil bath. Absolute ethanol (7–10 ml per gram of dianhydride) was then introduced. The mixture was then refluxed with stirring until a clear solution was obtained. When the distillation of ethanol ceased, the trap was filled with *o*-DCB. Next, 9.7943 g (5.0682×10^{-2} mol) of 3-phenylethynyl aniline was charged to endcap the oligomer as a solution in 100 ml of NMP. The diamine, *m*-BAPPO (156.74 g, 3.1825×10^{-1} mol), was then dissolved in 200 ml NMP and charged into the reaction vessel. An additional 280 ml of NMP was subsequently added to the reaction vessel. An azeotroping solvent, *o*-DCB (145 ml), was then added to provide a solids content of 25% wt/vol. The reaction mixture was then slowly heated to 170–185°C and held for ~15 h, after which time the viscous polymer solution was cooled to room temperature and coagulated by slowly dripping the polyimide solution into an excess of methanol in a high-speed blender. The polymer was collected by vacuum filtration, washed with excess methanol and excess anhydrous diethyl ether, air dried for 6–8 h and vacuum dried at ~170°C for 24 h.

Conversion of an arylene ether copolymer containing 10% pendent amines to phenylethynylphthalimides

To a four-necked round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, thermometer and a reverse Dean–Stark trap with a condenser was added 5.5000 g (1.2×10^{-3} mol) of the pendent amino(arylene ether phosphine oxide) copolymer[10] along with 55 ml (20 wt% solids) of NMP. The contents were allowed to stir at room temperature until a homogeneous solution was obtained. Then, 0.5770 g (2.0×10^{-3} mol) of phenylethynylphthalic anhydride was charged into the flask and allowed to stir at room temperature for an additional 4 h, after which 11 ml of *o*-DCB was added and the solution was heated to 180°C for 8 h. The resulting polymer with pendent phenylethynylphthalimides was cooled and then coagulated into excess methanol two times and dried in a vacuum oven at 100°C for 8 h.

Characterization

*FT*i.r. spectra obtained with a Nicolet MX-1 *FT*i.r. spectrometer were used to determine the presence of imide groups in the polymers. Proton n.m.r. spectra obtained with a Varian Unity 400 spectrometer were also used to confirm the polymer structure. Intrinsic viscosity measurements were performed in NMP at 25°C using a Canon–Ubbelohde viscometer. Gel permeation chromatography (g.p.c.) measurements were performed on a Waters 150-C ALC/GPC with a viscosity detector; $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ values for the polyimides were determined using universal calibration[23]. Potentiometric titrations were performed using a MCI GT-05 automatic titrator to determine the number-average molecular weight per amino group. The amine functionalities were titrated with HBr (0.025 N). Glass transition temperatures and cure exotherms were determined by differential scanning calorimetry (d.s.c.) using a Perkin Elmer DSC 7 differential scanning calorimeter. Scans were run at a heating rate of 10°C min^{-1}; reported glass transition values were obtained from a second heat after the first heating and quenching. Thermogravimetric analyses (t.g.a.) were performed on a Perkin Elmer TGA 7 at 10°C min^{-1} in air.

RESULTS AND DISCUSSION

Polyimides

The phenylethynyl-terminated phosphine oxide-containing polyimides have been synthesized using the ester–acid route in high yields and purity by a process previously described[7,15,16,18,19,21,22]. The oligomeric materials were based on PMDA, PPODA, *m*-BAPPO and *p*-PDA. The majority of polyimides were derived from the PMDA/*m*-BAPPO system where the resulting polyimides have been controlled to the targeted number-average molecular weight $\overline{M}_n$ of ~7000 and 10 000 g mol^{-1}. The intrinsic viscosities in NMP at 25°C were 0.17 and 0.20 dl g^{-1} respectively and $\overline{M}_n$, as determined by g.p.c., was 6700 g mol^{-1} for the 7000 g mol^{-1} sample. *Scheme 1* illustrates the general synthetic scheme for the phenylethynyl-terminated polyimides.

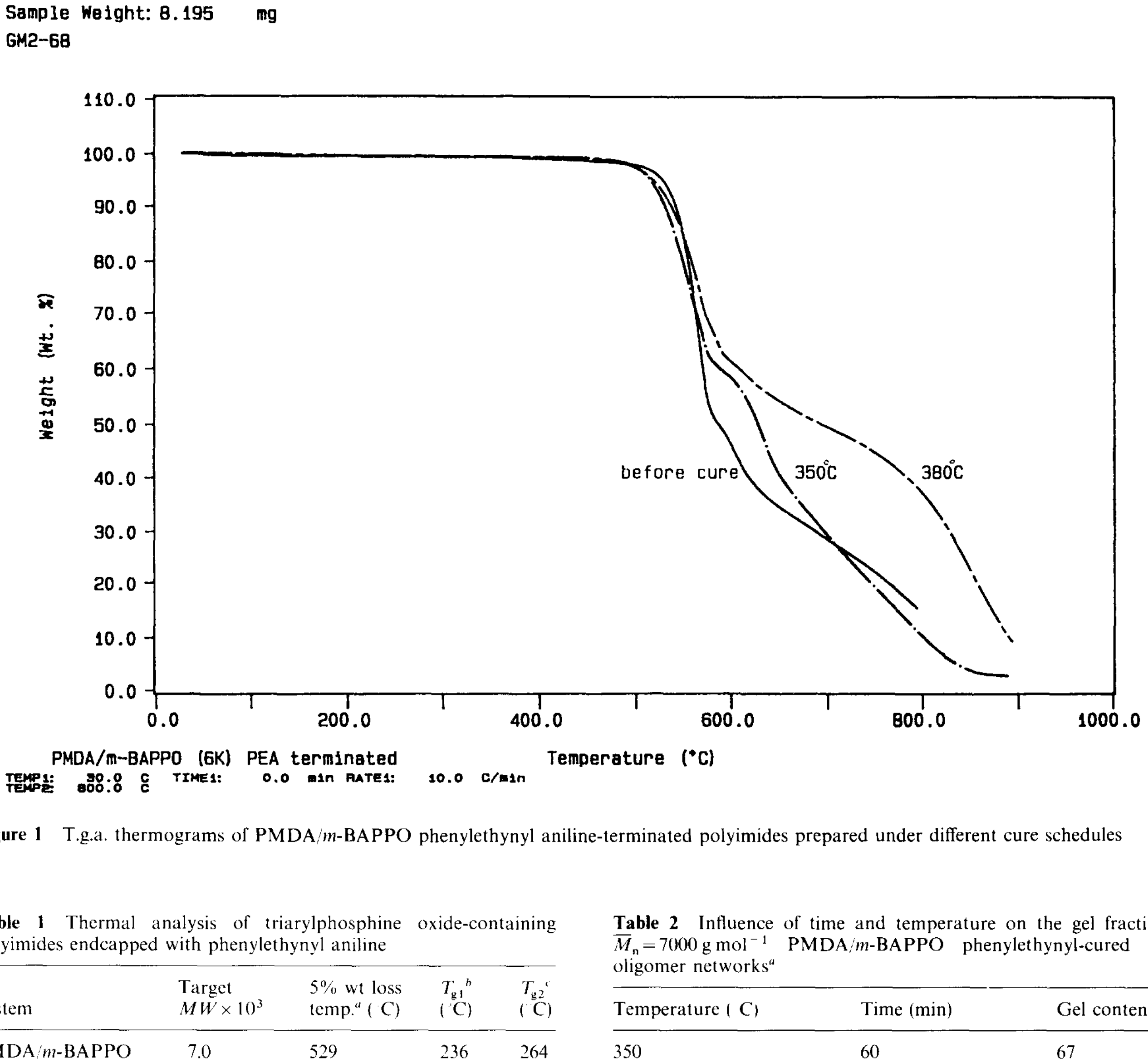


Figure 1 T.g.a. thermograms of PMDA/*m*-BAPPO phenylethynyl aniline-terminated polyimides prepared under different cure schedules

Table 1 Thermal analysis of triarylphosphine oxide-containing polyimides endcapped with phenylethynyl aniline

System	Target $MW \times 10^3$	5% wt loss temp.[a] (°C)	T_{g1}[b] (°C)	T_{g2}[c] (°C)
PMDA/*m*-BAPPO	7.0	529	236	264
	10.0	517	239	255
PPODA/*p*-PDA	3.0	492	–	360
PPODA/3FDAM	3.0	531	–	379

[a] Heating rate of 10°C min^{-1} in air, t.g.a. of the *in situ* cured oligomer
[b] T_g before cure, heating rate of 10°C min^{-1} in nitrogen
[c] T_g after cure, heating rate of 10°C min^{-1} in nitrogen

Table 2 Influence of time and temperature on the gel fraction of $\bar{M}_n = 7000$ g mol^{-1} PMDA/*m*-BAPPO phenylethynyl-cured imide oligomer networks[a]

Temperature (°C)	Time (min)	Gel content (%)
350	60	67
350	90	89
380	30	90
380	60	94
380	90	98

[a] Solvent extraction experiments — each sample was extracted with chloroform for 5 days, and then dried 5 days at 100°C under vacuum

The T_g values of the polyimides were determined by d.s.c. before and after network formation, as shown in *Table 1*. The T_g of the 7000 g mol^{-1} polymer before curing on the first scan was 240°C. Curing the polyimide for 90 min at 380°C increased the T_g to 264°C. The thermal stability was also investigated by thermogravimetric analysis (t.g.a.) in air by comparing the polymer before cure, after 90 min at 350°C and after 90 min at 380°C. As seen in *Figure 1*, the initial weight loss is unchanged by the thermal treatment. However, the char yield (which is often correlated with flame resistance) determined at 700°C for each of the three curing schedules was influenced. The char yield after curing for 90 min at 380°C increased substantially to 49 wt%. These initial results suggest that the polymer network exhibited better char formation when cured for 90 min at 380°C.

The thermal properties of the other phosphine oxide-based systems have also been examined. The phosphine oxide dianhydride-based polyimides exhibit even higher T_g values and higher thermo-oxidative stability than the *m*-BAPPO systems. Thus, the T_g values range from 360 to 379°C and the temperatures of 5% weight loss range from 492 to 531°C for the cured systems.

Preliminary studies to examine the gel fraction of the cured samples have also been performed. Films cured at various times and temperatures were extracted with chloroform (which is a solvent for the linear material) for 5 days. They were then dried for 5 days at 100°C under vacuum. As *Table 2* shows, the sample cured at 380°C for 90 min had the highest gel fraction at 98%. By contrast, samples cured for 90 min at 350°C exhibited a high, but significantly lower, gel fraction of 89%.

Table 3 Tensile behaviour of cured polyimide networks[a]

Modulus (ksi) (MPa)	403 (2780)
Yield stress (ksi) (MPa)	11.1 (76.5)
Yield strain (%)	4.0

[a] Samples were cured at 350°C for 90 min

Table 4 Mechanical testing of PMDA/*m*-BAPPO phenylethynyl-terminated polyimide 7000 g mol^{-1} $\overline{M}_n$ oligomer[a]

(a) Ti/Ti tensile shear strength (cure conditions of 1 h at 350°C)

Test temperature	Strength (psi) (MPa)
RT	4760 (32.8)
177°C	3930 (27.1)

(b) IM-7 unidirectional composite flexural properties

Test temperature	Flexural strength (ksi) (MPa)	Modulus (Msi) (MPa)	Compression strength (ksi)
RT	219 (1510)	21.4 (148 000)	182
177°C	143 (986)	18.2 (125 000)	

[a] Data courtesy of NASA Langley/William and Mary

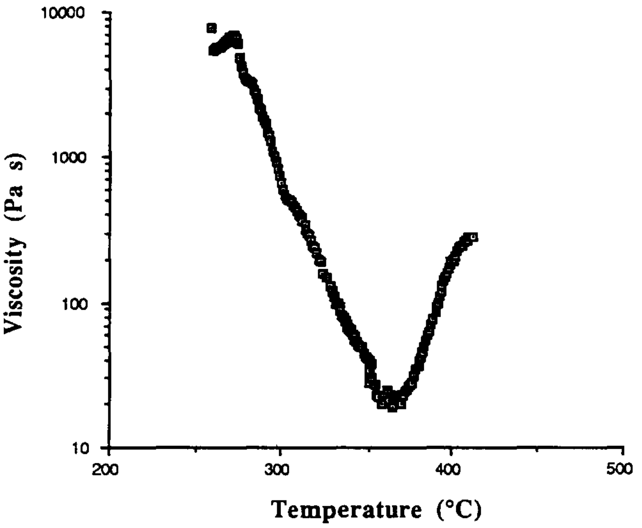


Figure 2 Viscosity vs. temperature profile of PMDA/*m*-BAPPO phenylethynyl aniline-terminated polyimide

Mechanical testing has also been initiated to measure the tensile properties of the cured polyimide. Some data based on samples cured at 350°C for 90 min are in the general range expected for polyimides, and are shown in *Table 3*. Furthermore, initial evaluation of the composite materials based on this polyimide system have been provided by NASA Langley, and these results are shown in *Table 4*.

The flow properties and cure window, defined as the interval between T_g and T_{gel}, have been examined by rheological parallel-plate studies. The viscosity–temperature behaviour and the real and imaginary shear moduli have been plotted against temperature as shown in *Figures 2* and *3*. The gel point may be established to be ~380°C as judged from the crossover point of the real and imaginary (storage and loss) moduli, G' and G''.

Poly(arylene ether)s

Phenylethynylphthalic anhydride was also successfully reacted with pendent aryl amines on copolymers of arylene ether phosphine oxides to produce pendent phenylethynylphthalimides. The latter was subsequently thermally cured to afford networks with an increase of T_g up to 17°C, as shown in *Table 5*. *Scheme 2* illustrates the general synthetic scheme for the arylene ether phosphine oxide copolymers as was reported earlier[10] and *Scheme 3* illustrates the general synthetic scheme for the conversion of the amino groups of poly(arylene ether phosphine oxide)s to pendent phenylethynylphthalimides. The pendent amines prior to conversion were characterized as also shown in *Table 5*. The intrinsic viscosity values indicate that high-molecular-weight polymers were indeed synthesized. The T_g of the pendent amine polymers increased slightly as the concentration of the amines on the backbone increased, which is probably due to the hydrogen bonding between the amines and the phosphine oxides. Results from the titration of the amines along the polymer backbone show that, as the concentration of the amines increases, the average molecular weight per amine decreased, as expected.

Upon curing these polymers in flowing air at 350°C for 30 min, results from the gelation studies show that the phenylethynyl groups react nicely to afford networks with increased solvent resistance.

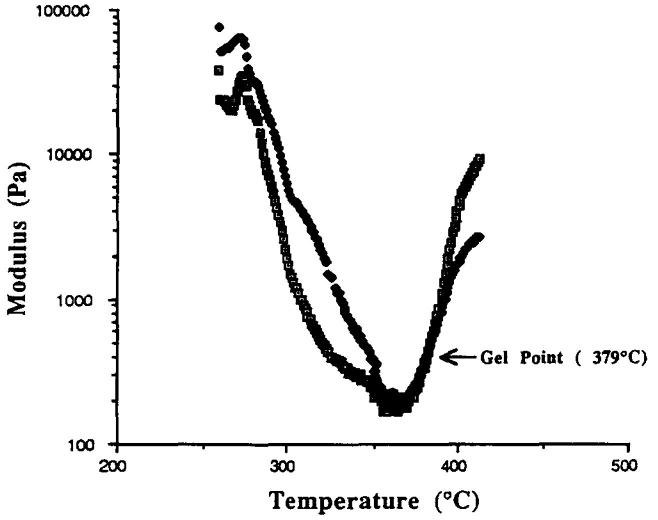
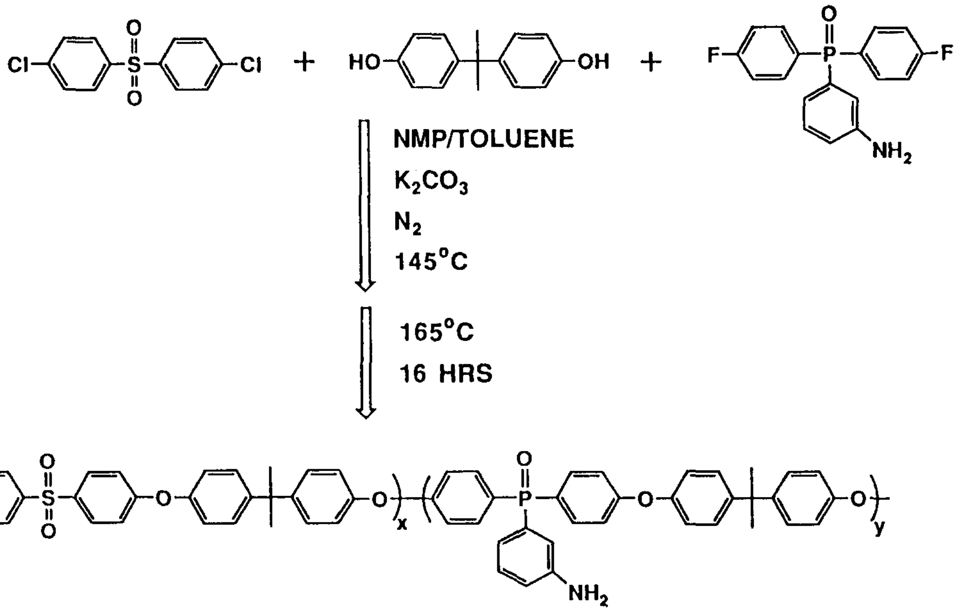


Figure 3 Influence of temperature on the storage and loss moduli, G' (□) and G'' (◆)

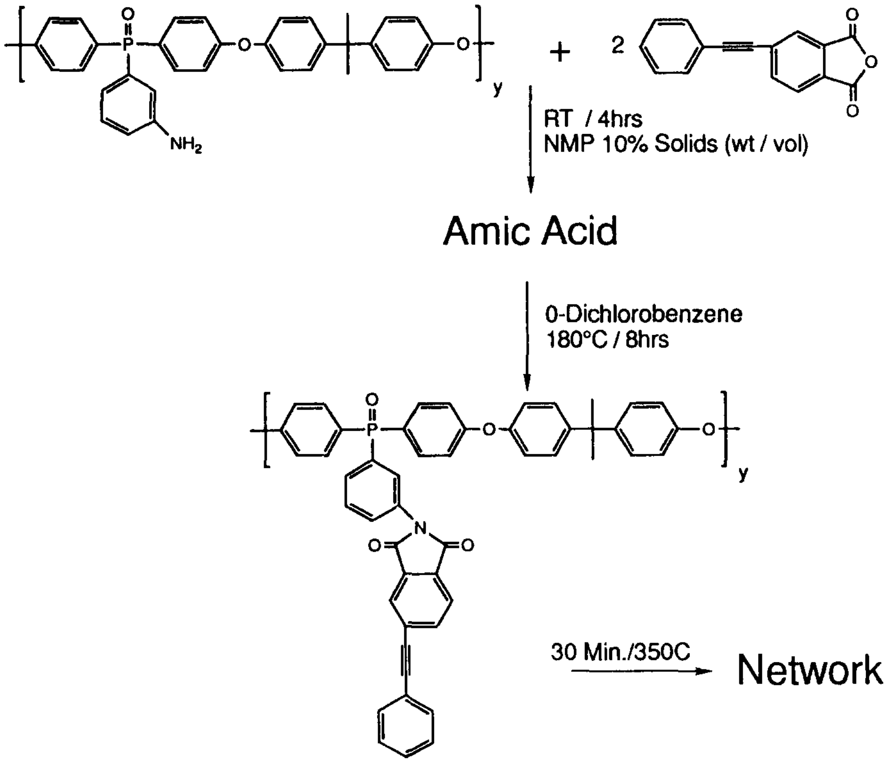
Table 5 Characterization of poly(arylene ether) containing pendent phenylethynylphthalimides

Polymer	$[\eta]^{25}_{CHCl_3}$ (dl g^{-1})	$\overline{M}_n$ amine (g mol^{-1})	T_g (°C) uncured	T_g (°C) cured	Gel fraction[a] (%)
PEPO control	1.09	–	–	–	0
5% amino PEPO	1.01	9700	201	201	93
10% amino PEPO	0.99	4700	201	207	98
20% amino PEPO	0.81	2500	201	218	99

[a] Soxhlet extraction in chloroform for 3 days



Scheme 2 Synthesis of arylene ether phosphine oxide copolymer with pendent amines



Scheme 3 Conversion of pendent amino groups on arylene ether phosphine oxide copolymer to 4-(phenylethynyl)phthalimides

CURRENT AND FUTURE STUDIES

Efforts are currently directed at the synthesis of additional 4-phenylethynylphthalic anhydride-terminated polyimide systems. In addition, further studies aimed at elucidating the network formation and cure chemistry using solid-state magic-angle ^{13}C nuclear magnetic resonance are ongoing. Fabrication of structural adhesives for metal and polymer matrix carbon fibre composites is also in progress.

CONCLUSIONS

Triarylphosphine oxide imide oligomers endcapped with phenylethynyl aniline were synthesized via a 'one-pot' solution imidization involving ester–acid and diamine monomers to yield highly imidized, controlled-molecular-weight phenylethynyl-functionalized polyimides, which had a desirably wide processing window. Upon curing, insoluble, highly crosslinked films with high T_g values were obtained that exhibited excellent thermo-oxidative stability and high char yields. Also, phenylethynylphthalimides pendent to the backbone of poly(arylene ether phosphine oxide)s were synthesized by reaction of phenylethynylphthalic anhydride with precursor pendent aryl amines. The resulting polymer was thermally cured to afford tough networks, which displayed increased T_g values and greatly improved solvent resistance.

ACKNOWLEDGEMENTS

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