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Phenylmaleimide endcapped arylene ether imide oligomers

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High temperature cure sites for polyimides and related high performance thermosetting systems are important and it has been demonstrated now by several groups that 4-phenylethynylphthalic anhydride and/or 3-phenylethynylaniline are attractive endcappers for polyimides that have wide curing windows and afford solvent resistant networks after 30–90 min at 350–400°C. The present paper has investigated phenylmaleic anhydride (PMA) as an alternate system which is thermally and possibly electron beam curable. Thus, PMA has been successfully utilized as a high temperature crosslinking endgroup for several high performance amorphous polyimides and initial results are described in this paper. Imide oligomers of controlled molecular weights were successfully synthesized by conducting either chemical imidization or by employing a two-step amine-terminated oligomer route followed by endcapping with PMA at about 140°C or lower. The more conventional higher temperature process was complicated by side reactions which are discussed herein. The molecular weights of the oligomers were successfully controlled from 2000 to 15 000 g mol^{-1}. The materials exhibited about at 200°C curing window between oligomer T_g and cure exotherm. Glass transition temperatures increased by more than 50°C after curing and produced solvent resistant insoluble materials with about 85% gel content. Curing of the phenylmaleimide endgroups was most successful under a nitrogen atmosphere, but it appears that normal moulding operations are acceptable, wherein only moderate amounts of oxygen are introduced into the specimen. The thermosetting reaction appears to be more sensitive to radical initiation than the earlier studied phenylethynyl systems. Dynamic thermogravimetric analysis on the cured PMA functionalized oligomers showed good behaviour and 5% weight loss in air was only observed above 500°C. The systems are being evaluated as structural adhesives and matrix resins for composite materials and excellent titanium/titanium lapshear values of about 5000 psi (34 MPa) on the cured oligomers has been demonstrated. Copyright © 1996 Elsevier Science Ltd.

(Keywords: high temperature cure sites; phenylmaleic anhydride; polyimide thermosets)

INTRODUCTION

Polyimides endcapped with thermosetting groups are a major class of high performance network forming polymers. Acetylene endcapped polyimide oligomers have been developed for use as high performance, high temperature curing adhesive and matrix applications[1,2]. Polyimides have also been end-functionalized with benzocyclobutene[3], maleic anhydride[4] and nadic anhydride[5] (PMR-15 type). However, a major drawback in all of these systems is that the curing exotherm starts immediately after the glass transition of the polyimide has been reached and/or the development of a volatile by-product. This behaviour does not allow adequate flow to take place prior to curing. Recently, several groups have resolved this problem by synthesizing polyimides endcapped with phenylethynyl groups which raises the cure temperature from ~220°C to >350°C. The two most attractive endcapping agents are 4-phenylethynylphthalic anhydride, 1[6-10] or 3-phenylethynylaniline[12-15]. Polyimides endcapped with these monofunctional phenylethynyl groups exhibit heating rate dependent curing maximum exotherms of up to 420°C[9,10]; thereby allowing sufficient flow to occur before the curing reaction takes place. This allows for a desirably wide processing window between the glass transition temperature (T_g) and the curing temperature (T_{cure}). The literature demonstrates that the phenylethynyl systems have very attractive processing and mechanical behaviour characteristics[6-10]. These systems are very attractive, but may be somewhat expensive due to their costly starting materials and reaction catalysts[6-10]. Accordingly, we have explored the use of phenylsubstituted maleic anhydride[2] as an alternative high temperature endcapper. Maleimide-terminated high performance polymers, such as various poly(arylene ethers), are known to thermally cure at 230°C to produce crosslinked networks that afford high gel contents and resist stress cracking[16]. Analogous to the phenylethynyl systems, one of the olefinic protons in maleic anhydride has been replaced by a phenyl group and it was postulated that the curing temperature would be increased from that of the conventional maleimide sites, approximately 220°C, to well over 300°C. Furthermore, it seemed logical to expect that phenyl substitution of the maleimide would also improve stability as has been observed for the phenylethynyl systems.

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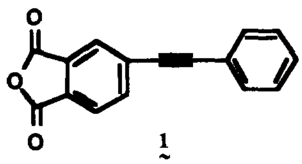

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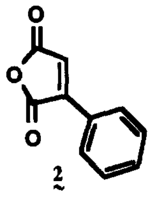

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Phenylmaleic anhydride (PMA) has been incorporated into polymer systems as a comonomer with styrene[17] in free radical processes via the olefinic carbon–carbon double bond to produce styrene-phenylmaleic anhydride high molecular weight copolymers. A second example employs the reaction of the anhydride functionality of PMA with various diols to prepare unsaturated polyesters. There are no reports of phenylmaleic anhydride being used as a high temperature curing monofunctional endcapping agent to subsequently form crosslinked networks with polyimides or other high performance polymers. The only reported use of a related compound in polyimide synthesis has been the reaction of 1,4-phenylenebis(phenylmaleic anhydride) with various aromatic diamines in our laboratory to form high molecular weight polyimides[18] or bismaleimides[19]. Moy *et al.* from our laboratory reported that polyimide films derived from 1,4-phenylenebis(phenylmaleic anhydride) could be thermally crosslinked at 350–360°C to form insoluble networks[18].

The reactive oligomers studied possess low melt viscosities and thermally cure without the evolution of volatile byproducts. The majority of polyimides have been prepared from hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride) (6FDA) and 4,4′-oxydianiline (ODA) and bisphenol A dianhydride (BPA-DA) and 1,3-phenylene diamine (*m*-PDA).

A major objective of our current research is to combine the desirable properties of processable amorphous polyimides and to utilize the phenylmaleic anhydride endcapping agent to develop high T_g, thermooxidative stable, solvent resistant networks of potential interest as structural adhesives and composite matrix resins. There may also be the possibility for electron beam (E-beam) curing which is of considerable current interest.

EXPERIMENTAL

Materials

N-Methylpyrrolidinone (NMP) was obtained from Fisher; vacuum distilled over P_2O_5 and stored under N_2. *N,N′*-Dimethylacetamide (DMAc), toluene, and acetic anhydride were obtained from Fisher and were vacuum distilled over calcium hydride and then stored under N_2 prior to use. 1,2-Dichlorobenzene (*o*-DCB) was also obtained from Fisher, and was used as received. Phenylsuccinic acid and selenium dioxide were obtained from Aldrich and were used as received. Hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride) (6FDA) was kindly donated by Hoechst Celanese. 6FDA was monomer grade material and was not further purified. 2,2′-Bis[4-(3,4-dicarboxyphenoxy) phenyl] propane dianhydride (BPA-DA) was donated by General Electric Company and was dried at 170°C under vacuum prior to use. 4,4′-Oxydianiline (ODA) was donated from the Ken Seika Corporation and was used as received. 1,3-Phenylenediamine (*m*-PDA) was obtained from Aldrich and was vacuum sublimed twice prior to use.

Synthesis of phenylmaleic anhydride

Phenylmaleic anhydride (PMA) was synthesized in our laboratory by a modification of the procedures reported by Hill[20] and Paquette *et al.*[21] by the reaction of phenylsuccinic acid with selenium dioxide using acetic anhydride as the solvent. For example 5.164×10^{-2} mol (10.028 g) of phenylsuccinic acid was charged to a 100 ml round bottom flask equipped with a condenser, N_2 purge, and a magnetic stir bar, and was washed in with 15 ml of acetic anhydride. Selenium dioxide (6.093×10^{-2} mol, 6.761 g) was then added followed by 16 ml of acetic anhydride. The reaction flask was immersed into an oil bath set at 155°C and the reaction was allowed to reflux ~9 h.

The reaction mixture was filtered hot to remove the selenium salts formed. Most of the acetic anhydride was removed under vacuum by a rotary evaporator. The solution was then allowed to sit overnight in a refrigerator, then poured into water and stirred. A dark yellow solid precipitated out of solution, which was filtered and dried *in vacuo* at 60°C for 12 h. The crude PMA was the sublimed under vacuum at ~100°C which afforded a light yellow solid. The proton n.m.r. spectra of the phenylmaleic anhydride are shown in *Figure 1*. Overall yield (8.27 g, 92%), mp 119–120°C, i.r. cm^{-1}: 1766, 1842 (anhydride, C-O), 3077 (aromatic C-H), 1508 (aromatic), C-C); ^{1}H n.m.r. (DMSO-d_6) 7.5–7.6 (*m*, 3H, aromatic), 7.75 (*s*, 1H, aromatic), 8.05 (*d*, 2H, aromatic); MS *m/z*(rel. int. %): 175 (M^+, 100).

Polymer synthesis

Polymers endcapped with phenylmaleic anhydride were synthesized via three methods in order to study molecular weight control using PMA as the endcapping agent.

Ester-acid high temperature solution imidization The first method of polymerization utilized high temperature solution imidization through the ester–acid route[9,10]. A polymerization with a target number average molecular weight of $\bar{M}_n$) of 3000 g mol^{-1} as an example was conducted as follows: 4.9560 g (1.1156×10^{-2} mol) of 6FDA was charged to a 100 ml 3-neck round bottom flask heated in an oil bath equipped with an overhead stirrer, Dean–Stark trap, nitrogen purge and a condenser. The 6FDA was washed in with 20 ml of ethanol. The 0.9296 g (5.3378×10^{-3} mol) of PMA was washed in with an additional 20 ml of ethanol, and 3 ml of triethylamine was added and the solution refluxed at ~100°C until the ethanol was removed by distillation at which time the trap was drained. When the distillation of ethanol ceased, the trap was filled with *o*-DCB. Next, 2.7683 g (1.3825×10^{-2} mol) of ODA was added with 17 ml of NMP and 4 ml of *o*-DCB to make a 30% solution. The reaction mixture was then heated to 170–185°C for 20 h, after which time the polymer solution was coagulated by slowly dripping the polyimide solution into methanol in a high speed blender. The polymer was collected by suction filtration, washed with excess methanol and then excess anhydrous diethyl

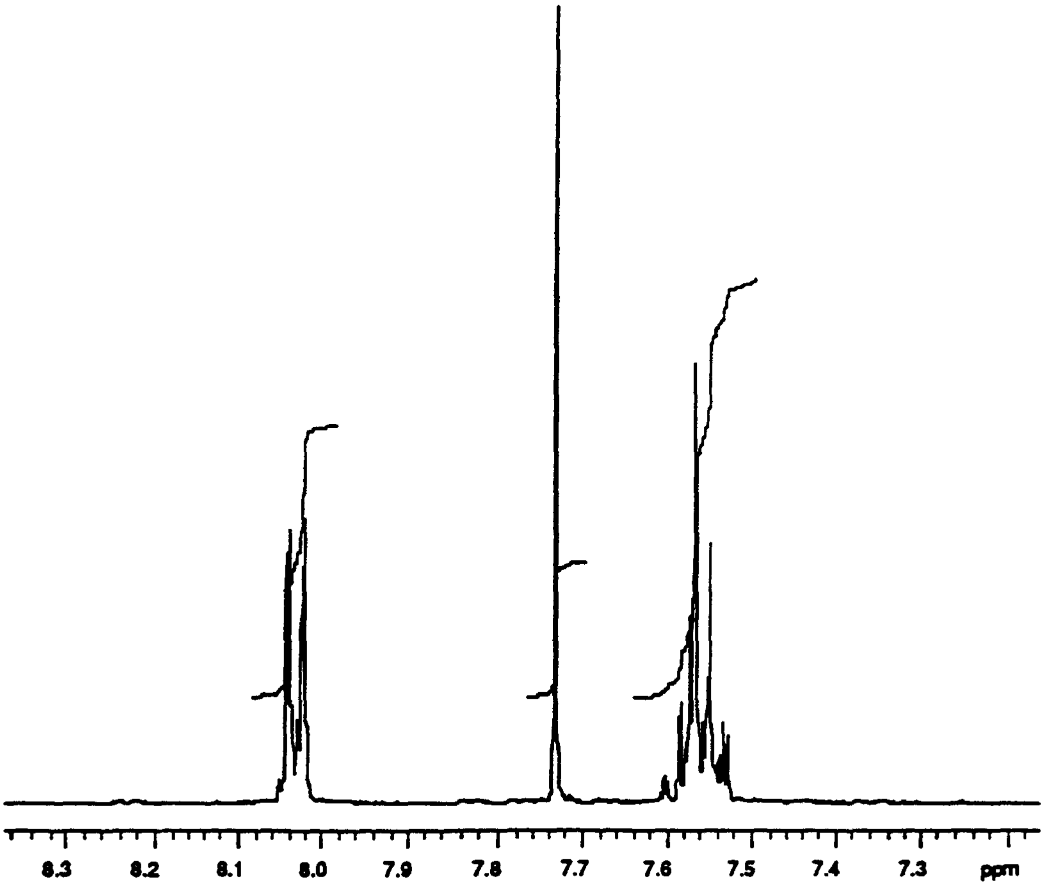


Figure 1 ^{1}H n.m.r. spectra of phenylmaleic anhydride in DMSO-d_6 (400 MHz)

ether. It was then air dried 6–8 h and vacuum dried at ~170°C for 24 h.

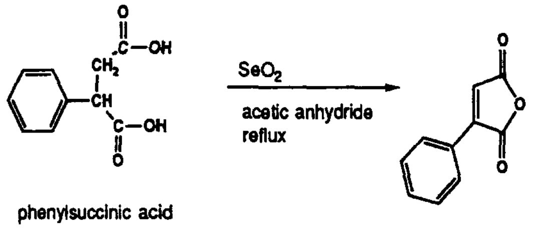
Amic acid chemical imidization The second method of polymerization employed chemical imidization of the amic acid precursor. A polymerization with a number average molecular weight ($\bar{M}_n$) of 3000 g mol^{-1} as an example was conducted as follows; 1.819 g (9.086×10^{-3} mol) of ODA was added with 8 ml of NMP to a 100 ml 3-neck round bottom flask heated in an oil bath and equipped with an overhead stirrer, Dean–Stark trap, nitrogen purge and a condenser. Next, 0.611 g (3.508×10^{-3} mol) of PMA was washed in with an additional 5 ml of NMP followed by addition of 3.257 g (7.332×10^{-3} mol) of 6FDA, which was washed in the vessel with 4 ml of NMP. The mixture was allowed to stir at room temperature for 3 h, after which 3.4 ml of acetic anhydride and 4.4 ml of triethylamine were charged to the flask. The reaction mixture was then heated to 60°C for 6 h and then coagulated by slowly dripping the polyimide solution into methanol in a high speed blender. The polymer was collected by suction filtration, washed with excess methanol and then excess anhydrous diethyl ether. The polymer was then air dried for 6–8 h and vacuum dried at ~170°C for 24 h.

Variable temperature solution imidization The third method of polymerization was a two-step method that involved forming an amine-terminated polyimide using the high temperature solution imidization ester-acid route, followed by endcapping the polyimide with PMA at a lower temperature. A polymerization with a targetted $\bar{M}_n$ of 3000 g mol^{-1} as an example was conducted by the same procedure reported in the ester–acid high temperature solution imidization section, *except the PMA was not initially charged to the reaction mixture*, which produced an amine-terminated imide oligomer. At this point the polymer was coagulated by slowly dripping the polyimide solution into methanol in a high speed blender. The polymer was collected by suction filtration, washed with excess methanol and then excess anhydrous diethyl ether and air dried for 6–8 h and vacuum dried at ~170°C for 24 h. The amine-terminated imide oligomer (2.022 g, 6.738×10^{-4} mol) was then redissolved in 2.1 ml of DMAc in the reaction setup previously described and 0.0235 g (1.348×10^{-3} mol) of PMA was added and washed in the flask with 2.1 ml of DMAc and 1.1 ml toluene. The reaction was heated in an oil bath to 140°C for 6 h, after which time the polymer solution was coagulated by slowly dripping the polyimide solution into methanol in a high speed blender, then isolated and dried as previously described. Alternatively, the polymer solution was lowered in temperature to 135°C by lowering the oil bath temperature and then the appropriate amount of PMA was added with NMP. The polymerization was allowed to proceed for 4–6 h after which time the polymer was precipitated and dried as described earlier.

Characterization

*FT*i.r. spectra were obtained with a Nicolet Impact 400 *FT*i.r. spectrometer. ^{1}H n.m.r. spectra were obtained with a Varian Unity 400 spectrometer. Titration (MCI titrator) was used to analyse endgroups of the polyimide oligomers. Titrations for residual amine endgroups were performed using HCl as the titrant. The

0.04 N HCl solution was standardized with sodium carbonate (0.1 mmol) in deionized water (70 ml). Polyimide samples (0.1 mmol) were dissolved in NMP (70 ml) and titrated three times each with 12 ml of titrant. Intrinsic viscosity measurements gave an indication of the molecular weights attained and were performed in NMP at 25°C using a Canon-Ubbelohde viscometer. Absolute molecular weight values were also determined using a Waters GPC/ALC 150C with a viscosity detector that allowed the use of universal calibration[23,24]. Glass transition temperatures and cure exotherms were determined using a Perkin Elmer DSC 7 differential scanning calorimeter. Scans were run at a heating rate of 10°C min^{-1} and reported values were obtained from a second heat after quick cooling. Weight loss behaviour utilized a Perkin Elmer TGA 7 thermogravimetric analyser at 10°C min^{-1} in air for dynamic scans. A Bohlin rheometer was used to determine the melt viscosities and was operated at 3°C min^{-1} and 0.1 Hz in nitrogen for dynamic scans. Mechanical behaviour was investigated with a Perkin Elmer dynamic mechanical analyser (DMA) and an Instron model 1123. Adhesive properties of the two series were evaluated using Ti/Ti lap shear specimens conforming to ASTM-D1002 methods. The Ti (6Al-4V) coupons of dimensions $5 \times 1 \times 0.64$ in^3 were first degreased, grit blasted with aluminium oxide and washed with cold water. After drying at room temperature they were treated with a mixture of chromic and nitric acid using Pasa Jell-107 (Courtaulds, Inc.) for 30 min and cleaned in cool running water. The coupons were dried at room temperature and then in a vacuum oven at 120°C for 1 h to remove any moisture. They were then primed with polymer solution to prevent any surface oxide layer degradation and dried in a vacuum oven at 160–180°C for 6 h. Lap shear specimens were prepared by coating 112-E glass scrim cloth with the resin dissolved in chloroform. The glass cloth was coated several times with the 15 wt% polymer solution to provide an adhesive tape with a 10–12 mil thickness. The Ti coupons were bonded in a tetrahedron press with pressures of 75 psi and a temperature ramp of 10°C min^{-1} from 25 to 380°C where they were held isothermally for up to 90 min and then cooled to 200°C at 10°C min^{-1}



Scheme 1 Synthesis of phenylmaleic anhydride

RESULTS AND DISCUSSION

Phenylmaleic anhydride (PMA) was successfully synthesized in our laboratory by refluxing phenylsuccinic acid anhydride in the presence of selenium dioxide for 9 h as shown in *Scheme 1*. The crude product can be easily sublimed under vacuum to yield pure PMA in yields of 92% or higher. Note that PMA can also be prepared industrially from biphenyl without the use of selenium as reported by Shier[22].

6FDA/ODA PMA endcapped polyimides

The monomers and the monofunctional endcapping agent used in the polyimide synthesis is shown in *Figure 2*. The phenylmaleic anhydride terminated polyimide matrix resins based on 6FDA and ODA have been synthesized using three routes all of which were targeted to a number average molecular weight of 3000 g mol^{-1}. The first route employed involved using the ester–acid route[9] in which the ester–acid of the dianhydride and in some cases the ester–acid of PMA was formed first, followed by the addition of the diamine with NMP and *o*-DCB and subsequent heating of the solution to 175–

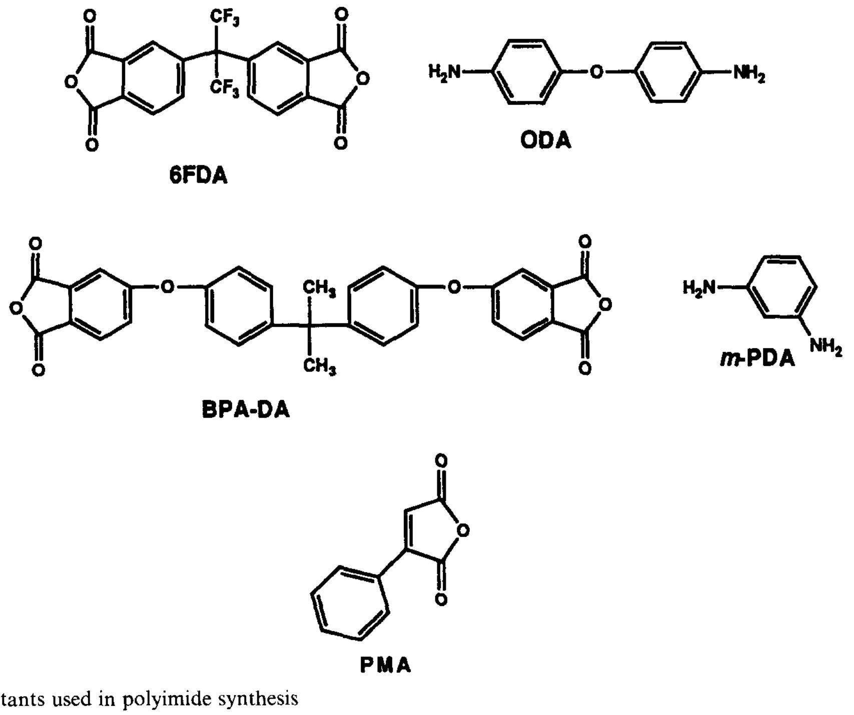


Figure 2 Monomeric reactants used in polyimide synthesis

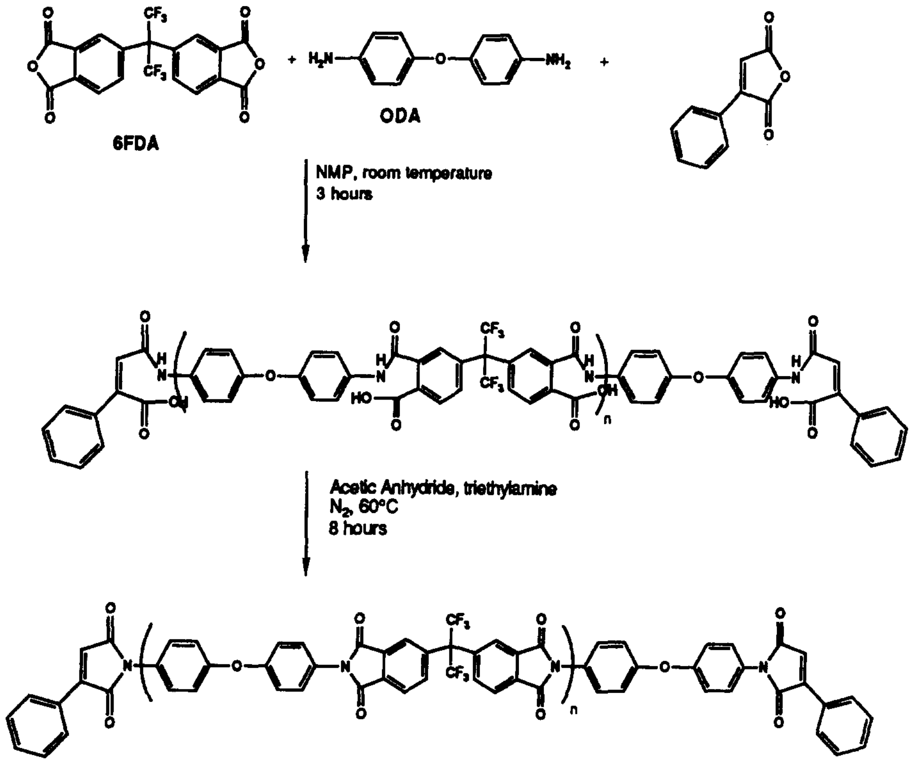
180°C for 12–24 h. This procedure surprisingly resulted in high molecular weight, fibrous, creasable film forming polymer upon workup that exhibited intrinsic viscosity values of 0.46–0.57 dl g^{-1} or higher. Many variations were executed by varying the sequence of monomer and endcapper addition. However, in all cases, the molecular weight was not controlled to 3000 g mol^{-1} as evidenced by the high intrinsic viscosity values. Some possible explanations for this behaviour are discussed later (see phenylmaleic imide study). The T_g values determined by d.s.c. of 291 and 303°C also indicated high molecular weight polymer since the T_g reported for high molecular weight 6FDA/ODA polyimide is ~300°C. These polymers exhibited 5% weight loss values in air of 548 and 551°C, attesting to the thermal stability of polymers.

A film cast from chloroform of the polymer exhibited a T_g of 291°C. After thermally curing at 350°C for 1 h, the T_g increased to ~305°C and the 5% weight loss temperature was 570°C, indicating that some crosslinking had taken place even in these high molecular weight polyimides.

The second route employed in the synthesis of PMA endcapped polyimides involved chemical imidization techniques. *Scheme 2* illustrates the general synthetic scheme for phenylmaleic anhydride terminated polyimides.

Molecular weight control was achieved utilizing phenylmaleic anhydride as an endcapping agent and chemical imidization techniques. This route afforded an intrinsic viscosity value of 0.18 dl g^{-1} that corresponded very well with 3000 g mol^{-1} 6FDA/ODA polyimide systems. Glass transition temperatures increased from 245°C before curing to 290°C after curing at 350°C for 45 min, which is consistent with the T_g of the high molecular weight linear systems. A curing study was performed at various temperatures and times in a convection oven. After curing for 30 min at 310°C in a nitrogen atmosphere, the system was completely soluble in chloroform. After 30 min at 350°C the system was mostly insoluble, but still had a soluble portion. However, when cured at 350°C for 45 min, the system was completely (>99%) insoluble. The 5% weight loss at 526°C before curing, and at 558°C after cure indicated good thermal stability. The thermal stability of the 3000 g mol^{-1} oligomer synthesized by chemical imidization was subjected to an isothermal t.g.a. scan in air at 350°C for 6 h. Importantly, only 0.36% weight was lost, indicating no volatiles were released during the curing process. Furthermore, to compare the relative thermo-oxidative stability of the PMA endcapped oligomers to the phenylethynyl endcapped systems, a dynamic t.g.a. scan was performed on three 6FDA/ODA 3000 g mol^{-1} oligomers. The oligomers were all cured at 380°C for 90 min under nitrogen; the only differences were the endcapping agents employed. As seen in *Figure 3*, the 3-phenylethynylaniline and 4-phenylethynylphthalic anhydride endcapped oligomers were moderately more thermooxidately stable than the PMA endcapped oligomer above 550°C; however, below 550°C there was no difference.

The third route employed to synthesize PMA terminated polyimides was a two-step route where an amine-terminated polyimide was first formed and then subsequently functionalized with PMA. The amine-terminated imide oligomer in some cases was isolated in methanol, dried *in vacuo* and redissolved in DMAc and toluene which permits imidization to take place at lower temperature (~145°C) than in NMP/*o*-DCB and was then allowed to react with the calculated amount of PMA. The intrinsic viscosity values for the amine-terminated oligomer and the PMA capped oligomer were 0.18 and 0.22 dl g^{-1}, respectively, indicating that molecular weight was controlled in both steps. Alternatively, the amine-terminated oligomer was formed in NMP/*o*-DCB at ~180°C, the



Scheme 2 Synthesis of phenylmaleic anhydride-terminated polyimides by chemical imidization

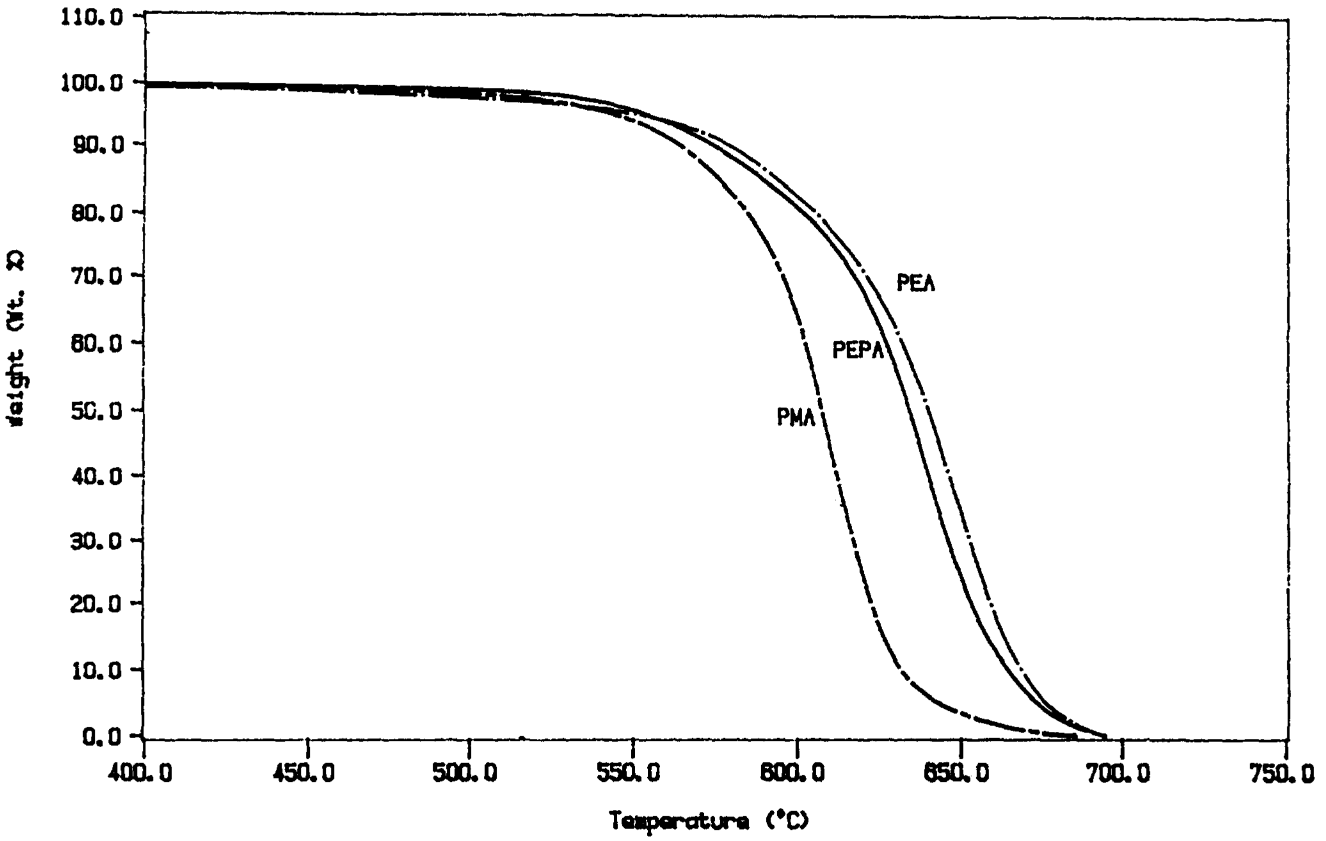


Figure 3 Dynamic t.g.a. comparison of cured 6FDA/ODA (3000 g mol^{-1}) imide oligomers endcapped with different endcapping agents

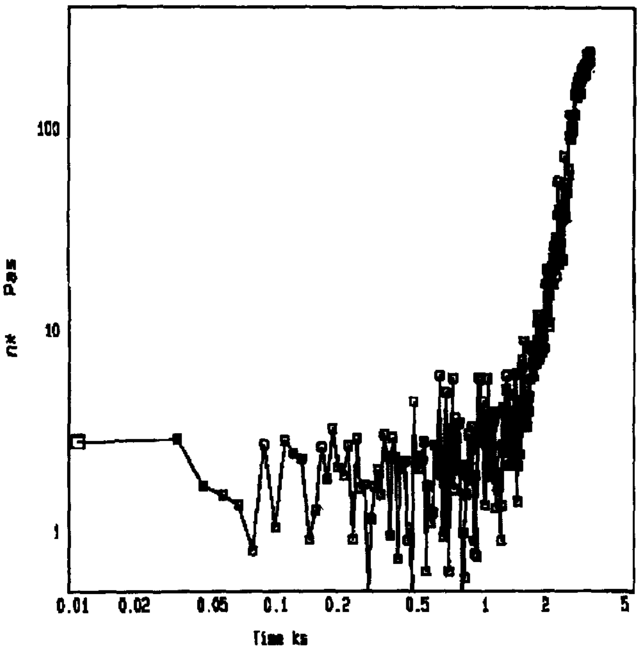


Figure 4 Isothermal melt viscosity of 3000 g mol^{-1} 6FDA/ODA/PMA (3000) polyimide held at 350°C under nitrogen

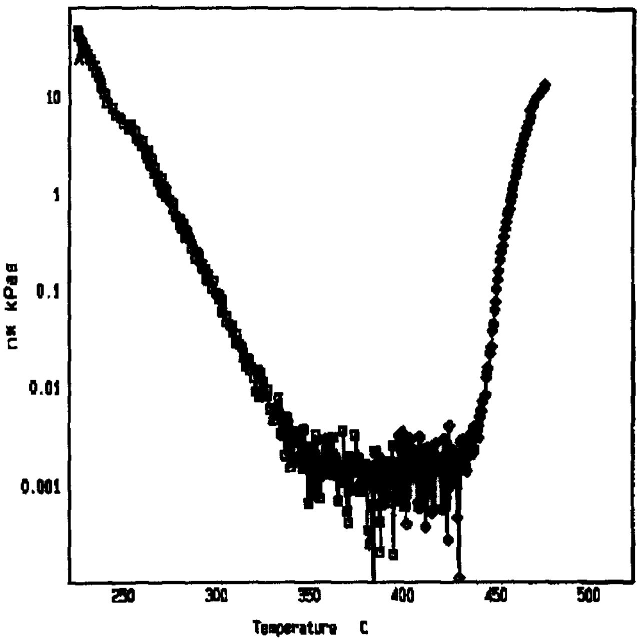


Figure 5 Influence of temperature of melt viscosity of 6FDA/ODA/PMA (3000) polyimide

Table 1 Characterization of BPA-DA/*m*-PDA PMA endcapped polyimides synthesized by two-temperature route

Target M_n (g mol^{-1})	$[\eta]_{25^\circ C, NMP}$	$T_{g(uncured)}$(°C)[a]	$T_{g(cured)}$(°C)[a]	5% wt loss (°C)[b]
2000	0.18	200	227	504
7000	0.24	208	219	522
10 000	0.26	212	219	524
15 000	0.34	213	221	525

[a] T_g's were run under nitrogen at heating rate of 10°C min^{-1} and values were taken from the second heat after quench cooling
[b] T.g.a.'s were run in air at a heating rate of 10°C min^{-1}

Table 2 Molecular weight characterization of BPA-DA/*m*-PDA PMA endcapped polyimides synthesized by two-temperature route

Target M_n (g mol^{-1})	$[\eta]_{25^\circ\mathrm{C,NMP}}$	M_n by g.p.c.Δ^a	M_n by ^{1}H n.m.r.
2000	0.12	1700	2400
7000	0.38	6300	6600
10 000	0.54	8500	10 200

^{a} Δ = Absolute number average molecular weights were determined using universal calibration methods[23]

reaction temperature was lowered to 135°C and the PMA was added and allowed to react for 6 h. Again, the intrinsic viscosity value of 0.18 dl g^{-1} supports the point that the desired molecular weight was achieved. ^{1}H n.m.r. showed the reaction to be essentially complete after 3 h, and that no unimidized carboxylic groups remained. This suggested complete imidization of the end cap.

The melt flow properties of these systems were also examined by parallel plate rheology studies. The imide oligomer held isothermally at 350°C under a nitrogen atmosphere exhibited a melt viscosity below 5.0 PaS for approximately 30 min at which point the viscosity began to rapidly increase indicating curing or network formation (*Figure 4*). A dynamic scan from 225 to 470°C at 3°C min^{-1} also showed that after the T_g, the viscosity dropped to below 10 Pa s and at approximately 440°C, the viscosity began to increase indicating the onset of curing (*Figure 5*). These measurements indicate a wide curing window of ~200°C.

BPA-DA/m-PDA PMA endcapped polyimides

Two series (A and B) of polyimides based on BPA-DA/*m*-PDA (Ultem-like) endcapped with PMA were synthesized to controlled molecular weights ranging from 2000 to 15 000 g mol^{-1}. The second series was prepared to confirm that complete endcapping and molecular weight control had been achieved. A third

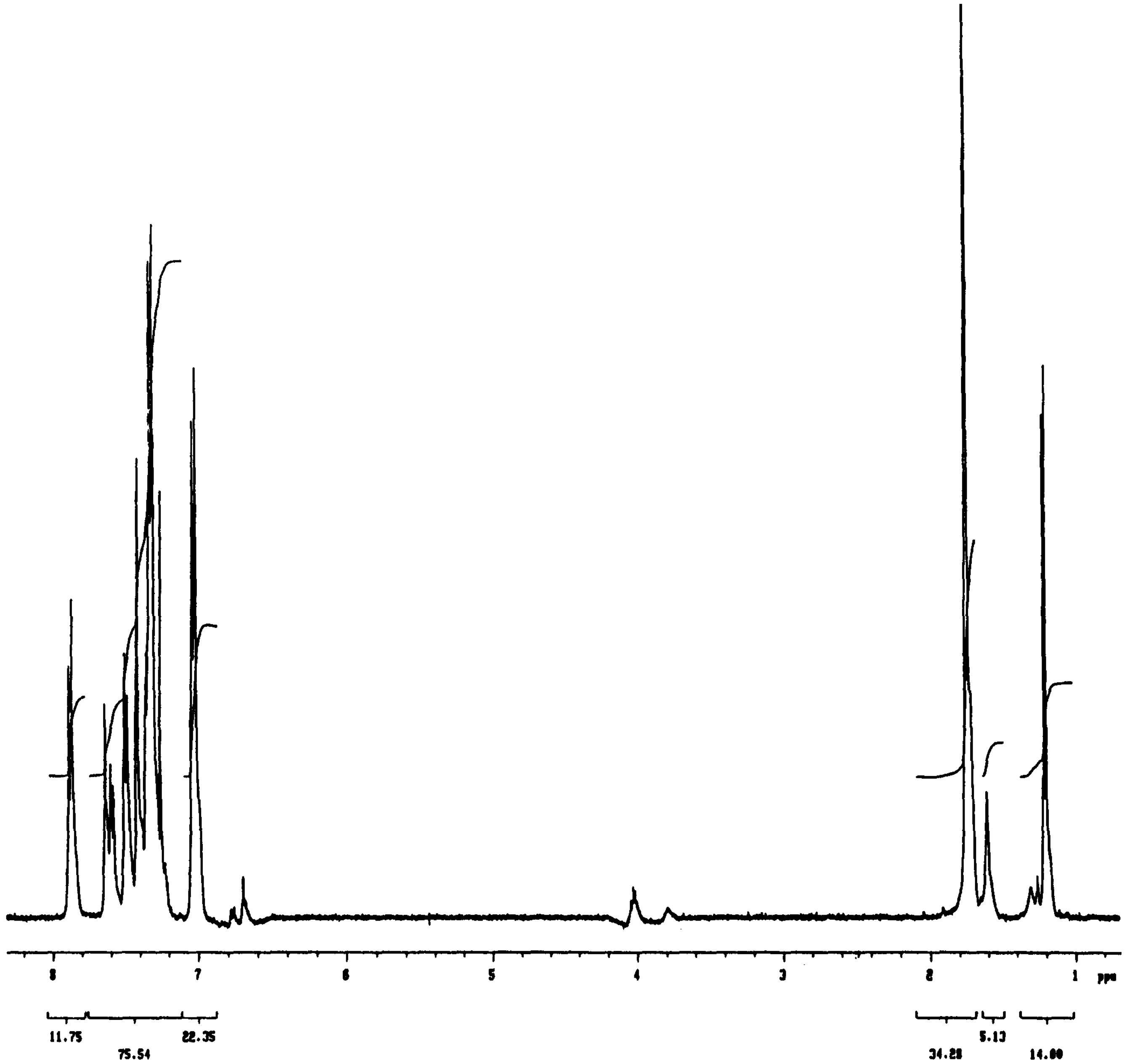


Figure 6 ^{1}H n.m.r. spectra of 7000 g mol^{-1} amine terminated BPADA/*m*-PDA polyimide in $CDCl_3$ (400 MHz)

series (C) was prepared with molecular weights ranging from 2000 to 10 000 g mol^{-1}. Series A and B were synthesized using the two-temperature route where the amine-terminated polyimide was formed at 180°C in NMP/*o*-DCB and then the reaction temperature was lowered to 135°C, at which point the PMA was added to the flask to endcap the polyimide chains. Again, molecular weight control was achieved as judged by the progressive increase in intrinsic viscosity values in *Table 1*. The intrinsic viscosity values for Series A increased from 0.18 dl g^{-1} for the 2000 g mol^{-1} polyimide up to 0.34 dl g^{-1} for the 15 000 g mol^{-1} polymer. Molecular weight control was reconfirmed in the Series B of Ultem-like PMA endcapped oligomers as seen in the progressive increase of intrinsic viscosity values found in *Table 2*. Absolute number average molecular weights were also found for Series B using GPC via universal calibration fitted with a viscosity detector[23,24]. The number average molecular weights agreed very closely with the targeted values as illustrated in *Table 2*. Molecular weight distributions ($\bar{M}_w/\bar{M}_n$) were all close to 2.0 by g.p.c. analysis. Quantitative ^{13}C n.m.r. spectrometry was also used to determine molecular weight control. Integration of the chemical shifts occurring at 113 and 115 ppm which correspond to the PMA olefinic carbons were compared to the integration of the quaternary carbon peak at 42 ppm, corresponding to the isopropylidene group of the bisphenol A dianhydride moiety. The number average molecular weights calculated using the integration of the three peaks specified above are listed in *Table 2* and correspond closely to the targeted values. ^{1}H n.m.r. was not used to determine molecular weight, because the olefinic proton of the PMA endgroup was hidden in the aromatic region at approximately 7.0 ppm which hindered quantitative integration.

Titration with HCl was utilized to confirm complete endcapping of all amine endgroup functionalities and no endpoint was observed in any of the PMA endcapped polyimides. Proton n.m.r. was also used to support the assumption that the imide oligomers were fully endcapped. An amine terminated polyimide with an Ultem-type backbone[9,10] exhibits a peak at 4.0 ppm corresponding to aromatic amine protons in the proton n.m.r. spectra as shown in *Figure 6*. This peak is absent in the spectrum of

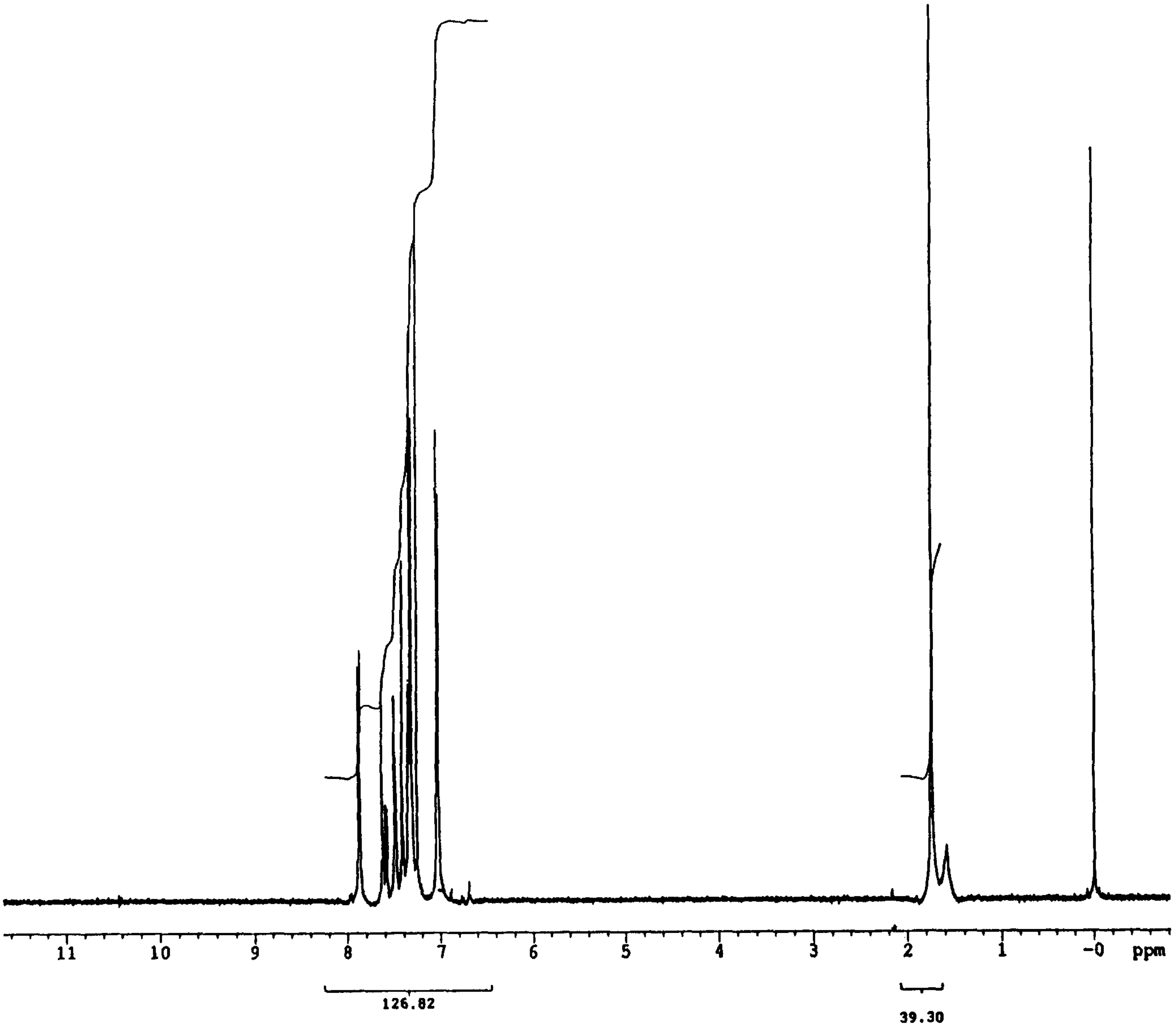


Figure 7 ^{1}H n.m.r. spectra of 7000 g mol^{-1} PMA terminated BPADA/*m*-PDA polyimide in chloroform (400 MHz)

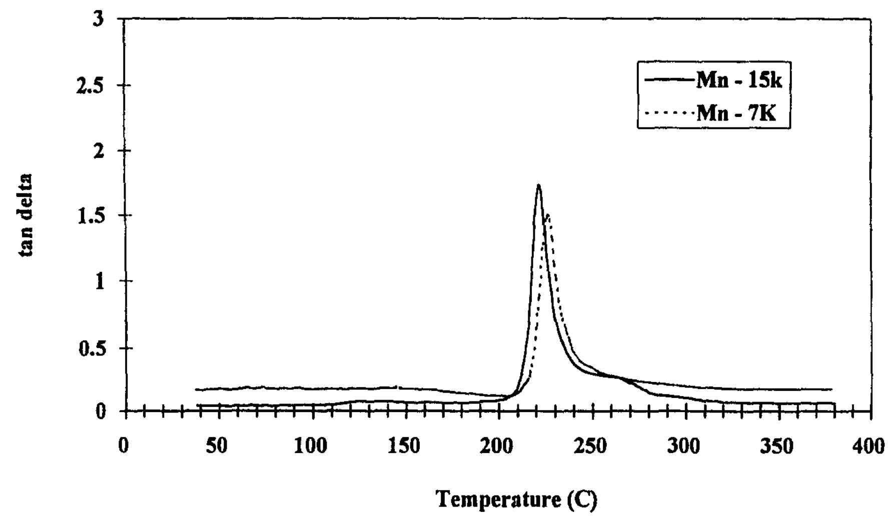


Figure 8 Tan delta (d.m.a.) curves of BPADA/*m*-PDA PMA endcapped imide oligomers (7000 and 15 000 g mol^{-1}) cured at 380°C for 90 min

Table 3 Glass transition temperatures of BPA-DA/*m*-PDA PMA endcapped polyimides synthesized by two-temperature route

Target M_n (g mol^{-1})	$T_{g(uncured)}$(°C)^a	$T_{g(cured\ in\ air)}$(°C)^a	$T_{g(cured\ in\ nitrogen)}$(°C)^a
2000	176	213	229
7000	210	217	222
10 000	203	225	222

[a] T_g's were run under nitrogen at a heating rate of 10°C min^{-1} and values were taken from the second heat after quench cooling

Table 4 Glass transition temperatures of BPA-DA/*m*-PDA 4-phenylethynylphthalic anhydride endcapped polyimides

Target M_n (g mol^{-1})	$T_{g(uncured)}$(°C)^a	$T_{g(cured)}$(°C)^a
3000	192	233
7000	205	227
30 000	218	218

[a] T_g's were run under nitrogen at a heating rate of 10°C min^{-1}, cured for 60 min at 350°C and values were taken from the second heat after quench cooling

the PMA endcapped polyimides, indicating the chains were completely PMA endcapped. A proton n.m.r. spectrum of the 7000 g mol^{-1} PMA endcapped oligomer is shown in *Figure 7*.

The glass transition temperatures for these polyimides before curing ranged from 200°C for the 2000 g mol^{-1} oligomer to 213°C for the 15 000 g mol^{-1} as shown in *Table 1*. After curing the oligomers at 380°C for 90 min under *nitrogen* in a convection oven, the T_g values increased substantially to as high as 227°C for the 2000 g mol^{-1} oligomer. Dynamic mechanical analysis (d.m.a.) was also used to confirm the T_g of the cured films. The T_g values from the 7000 and 15 000 g mol^{-1} cured oligomers were 220°C and 222°C as shown in *Figure 8*. Glass transition values of the uncured oligomers for Series B increased for the 2000 to the 7000 g mol^{-1}, but the 10 000 g mol^{-1} was slightly lower than the 7000 g mol^{-1} as illustrated in *Table 3*.

Oxygen may have a significant role in the curing mechanism of the PMA functionalized imide oligomers, probably by altering the concentration of the presumed, but unconfirmed at this point, free radical species. Glass transition values of oligomers endcapped with 4-phenylethynylphthalic anhydride controls are given in *Table 4* as a comparison[11]. The T_g values of the PMA endcapped sample were comparable to those values of phenylethynylphthalic anhydride endcapped polyimide samples. These systems showed good stability demonstrated by the 5% weight loss values by t.g.a. in air ranging from 504 to 525°C. Cured films displayed good mechanical integrity even for the 2000 g mol^{-1} system, which implies that significant chain extension occurred prior to the gel point.

BPA-DA/*m*-PDA polyimides were also synthesized using chemical imidization to imidize the poly(amic acid) at 60°C in NMP using acetic anhydride and triethylamine, which provided a direct comparison with the imide oligomers obtained by the two-temperature route described previously. Again, molecular weight control was achieved as judged by the progressive increase in intrinsic viscosity values in *Table 5*. The intrinsic viscosity values increased from 0.18 dl g^{-1} for the 2000 g mol^{-1} polyimide up to 0.40 dl g^{-1} for the 15 000 g mol^{-1} polymer. The glass transition temperatures for the polyimides before curing ranged from 192°C for the 2000 g mol^{-1} oligomer to

Table 5 Characterization of BPA-Da/*m*-PDA PMA endcapped polyimides synthesized by chemical imidization

Target M_n (g mol^{-1})	$[\eta]_{25°C,NMP}$	$T_{g(uncured)}$(°C)^a	$T_{g(cured)}$(°C)^a	5% wt loss (°C)^b
2000	0.18	192	223	522
7000	0.21	205	215	518
10 000	0.35	205	221	525
15 000	0.40	205	220	515

[a] T_g's were run under nitrogen at heating rate of 10°C min^{-1} and values were taken from the second heat after quench cooling

[b] T.g.a.'s were run in air at a heating rate of 10°C min^{-1}

Table 6 Gel content of cured BPA-DA/*m*-PDA/PMA polyimides

System	Target $\langle M_n \rangle$ (g mol^{-1})	% gel content
BPA-DA/*m*-PDA	2000	85
	7000	80
	10000	77
	15000	75

Samples were refluxed in chloroform for 5 days and then dried *in vacuo* for 5 days ~100°C

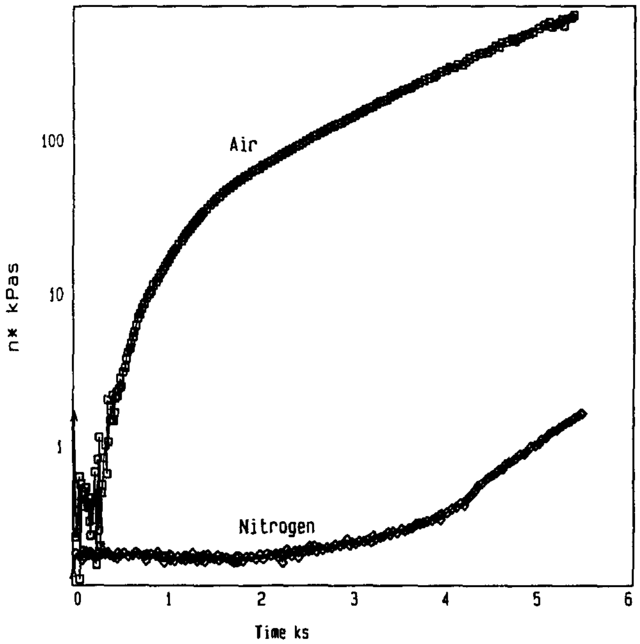


Figure 9 Isothermal melt viscosity of BPA-DA/*m*-PDA/PMA (2000) imide oligomer at 350°C in nitrogen and air

205°C for the 15000 g mol^{-1} as shown in *Table 5*. T_g values increased upon curing at 380°C for 90 min as was expected, as shown in *Table 5*. These systems showed good 5% weight loss values (>500°C) by t.g.a. in air.

Refluxing Soxhlet extractions in chloroform were also performed on the cured PMA functionalized polymers to evaluate their gel content and solvent resistance. Thermally cured samples displayed moderate solvent resistance as shown in *Table 6*, and moderately high (>85%) gel fractions were obtained upon thermally curing the phenylmaleic anhydride-terminated poly(ether imide)s. These values were significantly lower (e.g. 98–99%) than those obtained from poly(ether imides) endcapped with 4-PEPA[11].

The melt flow properties of these PMA endcapped systems were also examined by parallel plate rheology studies. A detailed study was performed using the BPA-DA/*m*-PDA/PMA(2000) imide oligomer synthesized by the two-temperature method. Isothermal scans were conducted at 350 and 380°C under both *air* and *nitrogen* atmosphere. At 380°C under a *nitrogen* purge, a melt viscosity below 100 Pa s was observed for ~25 min before crosslinking began. However, at 380°C under an *air* purge, crosslinking started almost immediately as illustrated by the sharp rise in melt viscosity from the onset of the experiment. Moreover, a sample held at 350°C under a *nitrogen* atmosphere displayed a melt viscosity of ~200 Pa s for ~42 min before a rise in melt viscosity was observed. Lowering the scan temperature 30°C resulted in an increase of melt stability before gelation of ~17 min. Nevertheless, when the sample was exposed to an *air* atmosphere, again a sharp increase in melt viscosity was observed immediately upon starting the scan. The results obtained at 350°C are overlaid in *Figure 9*. A dynamic scan was performed in air from ~190–450°C and showed a significant window (~200°C) between T_g and T_{cure}. These measurements indicate that in an *inert atmosphere* such as nitrogen, a wide processing window of ~30–40 min can be achieved. Differences in air and nitrogen melt viscosity behaviour may indicate that oxygen plays a significant role in the presumed free radical curing mechanism of the PMA endcapped polyimides. Nevertheless, conventional compression moulding appears to be successful.

Adhesive properties of the two series were evaluated using Ti/Ti lap shear specimens conforming to ASTM-D1002 methods. *Table 7* shows that commercial Ultem 1000® exhibited an average value of 4420 ± 300 psi which was comparable to a phenylethynyl controlled imide oligomer of 3000 mol. wt. The PMA endcapped samples exhibited values which depended on $\langle \bar{M}_n \rangle$ ranging from 3330 to 5070 psi (22.9 to 34.9 MPa). All of the samples failed cohesively, except for the 15000 g mol^{-1} sample which failed at the Ti/scrim cloth interface (adhesive failure). The optimal lap shear adhesive properties were obtained at 7000–10000 g mol^{-1} as shown in *Table 7*.

Phenylmaleimide model study

A model study was performed in order to elucidate why molecular weight control was unsuccessful during the polymerization of imide oligomers directly endcapped with phenylmaleic anhydride at temperatures above ~150°C. A model compound based on PMA and aniline was synthesized by first forming the amic acid at room temperature and subsequently imidizing at high temperatures (~180°C) using NMP/*o*-DCB as the reaction solvents. The ^{1}H n.m.r. of the amic acid compound formed at room temperature is shown in *Figure 10*. The protons observed at 12.8 ppm due to the carboxylic acid, at 10.2 ppm corresponding to the amide linkage and the olefinic protons at 6.3 and 6.5 ppm as well as the aromatic protons confirmed the formation of the amic acid in its two expected isomeric forms.

Table 7 Ti/Ti lap shear adhesive data for BPA-DA/*m*-PDA/PMA polyimides

Polyimide	$\langle M_n \rangle$ (g mol^{-1})	Ti/Ti lap shear (psi) (MPa)
Commercial Ultem	20000	4420 ± 300 (30.5 ± 2)
PMA Capped Ultem-Like	2000	4420 ± 320 (30.5 ± 2)
	7000	5070 ± 580 (34.9 ± 4)
	10000	4750 ± 590 (32.7 ± 4)
	15000	3330 ± 180 (22.9 ± 1)

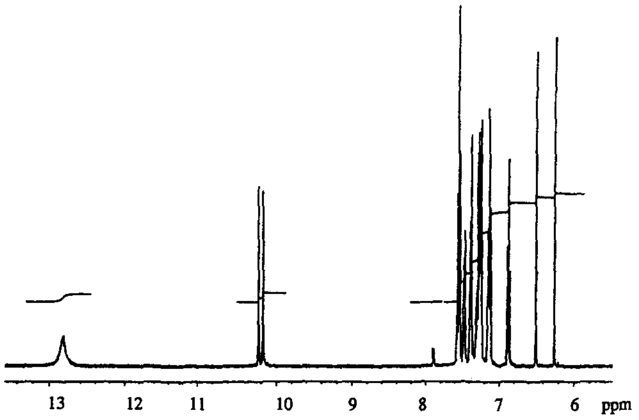


Figure 10 ^{1}H n.m.r. spectrum of PMA/An amic acid in DMSO-d_6 (400 MHz)

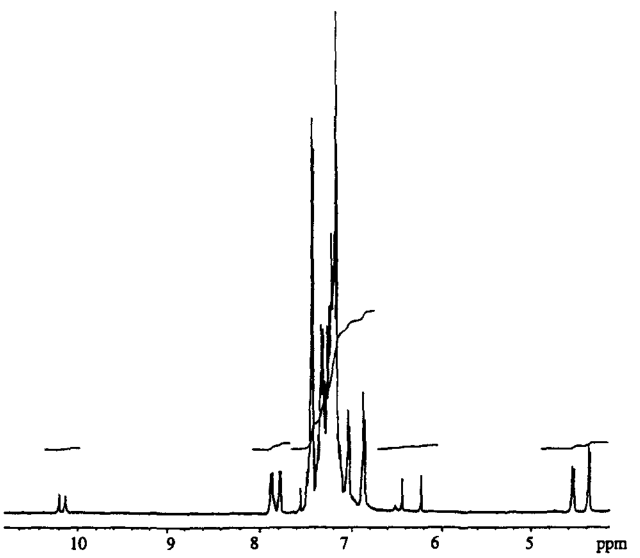


Figure 11 ^{1}H n.m.r. spectrum of PMA/An after 30 min imidization at 180°C (DMSO-d_6, 400 MHz)

Therefore, room temperature formation of the amic acid is not affected by the presence of the phenylmaleic anhydride groups. However, as the reaction is heated to ~180°C, unexpected peaks appear in the ^{1}H n.m.r. spectra.

Aliquots taken from the reaction solution at various times clearly reveal the formation of two doublets at 4.4 and 4.6 ppm, as early as 30 min into the reaction time and a significant reduction in the olefinic protons relative to the aromatic protons as illustrated in *Figure 11*. ^{13}C n.m.r. results also indicate significant formation of signals occurring at 131.7 and at 35.4, 39.9, 50.6 and 57.6 ppm. Based on heteronuclear chemical shift correlation (HETCOR), heteronuclear multiple quantum coherence (HMBC) and distortionless enhancement by polarization transfer (DEPT) n.m.r. analysis, the carbon at 131.7 ppm is correlated to the proton occurring at 8.0 ppm indicating that a protonated nitrogen is attached to the carbon arising from the olefinic bond. In addition, the aliphatic protons occurring at 4.4 ppm are correlated only to two carbons at 50.6 and 35.4 ppm and the protons at 4.6 ppm are correlated to three carbons occurring at 57.6, 39.9 and 35.4 ppm. Furthermore, protonated carbons are only observed at 35.4, 39.9 and 50.6 ppm indicating that a quaternary carbon is present. This seems highly unlikely since a reaction would have to be occurring at the phenyl substituted olefinic carbon which is highly hindered. A proposed pathway of the reaction may be attack of the arylamine on the olefinic bond followed by coupling through another olefinic bond. These results seem to suggest that the amic acid structure is partially hydrolysed to yield free terminal amine and carboxylic acid groups as Kim *et al.*[25] have proposed for polyimide formation from polyamic acid. The free amine groups may act a nucleophile and add to the carbon–carbon dioxide double bond through a Michael addition instead of recombining to form imide. This Michael addition process is well known to occur with bismaleimides and is even a method for formation of high molecular weight step-growth polymers[26]. Even arylamines can add rapidly and quantitatively to maleimides in solution (>60°C)[20]. It is suggested that phenylmaleimide systems impose more steric barrier due to the phenyl moiety and as a result, higher reaction temperatures are needed to cause this Michael-type addition. Therefore, it is likely that at polymerization temperatures above ~150°C, polyamides endcapped with phenylmaleic anhydride may undergo this side reaction to produce high molecular weight polymer. However, one should caution that the model compound work serves only as a guide and may not have a direct correlation to the products formed from the polymerization of phenylmaleimide anhydride terminated imide oligomers.

CONCLUSIONS

Polyimide controlled molecular weight oligomers endcapped with potentially inexpensive phenylmaleic anhydride can be synthesized via chemical imidization or a two-step amine-terminated lower temperature imidization route followed by endcapping at ≤140°C. Upon curing, insoluble, crosslinked films were obtained that exhibited good thermooxidative stability and good adhesion to titanium. However, the gel fractions were lower and the cured networks were slightly less thermooxidatively stable at very high temperatures (>550°C) than those observed with control phenylethynyl endcapped imide systems. These oligomers are easily processable (low melt viscosities) and have a wide curing window of ~ 200°C, indicating that phenylmaleic anhydride appears to be a viable candidate for attractive thermosetting polyimides. Further studies to better elucidate the curing mechanisms, the role of atmosphere (e.g. nitrogen vs air) and applicability of *E*-beam curing are continuing.

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