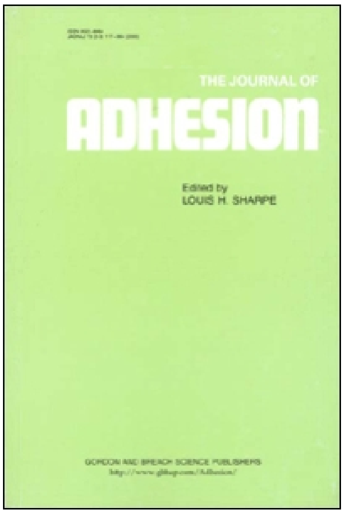

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Thermosetting Polyetherimides: The Influence of Reactive Endgroup Type and Oligomer Molecular Weight on Synthesis, Network Formation, Adhesion Strength and Thermal Properties

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Thermosetting Polyetherimides: The Influence of Reactive Endgroup Type and Oligomer Molecular Weight on Synthesis, Network Formation, Adhesion Strength and Thermal Properties*

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The influence of the reactive endgroup on the synthesis, cure behavior and network properties of thermosetting polyetherimides was investigated. Reactive phenylethynyl, ethynyl and maleimide terminated etherimide oligomers were prepared and characterized. Optimal reaction conditions were established to produce fully endcapped oligomers with imidized structures and controlled molecular weight. The phenylethynyl and ethynyl endcapped systems were synthesized by ester-acid methods. The maleimide endcapped system utilized an amic-acid route. Phenylethynyl endcapped oligomers had good processibility and were thermally cured at high temperatures (350–380°C). The networks exhibited good thermal and hydrolytic stability and good adhesion strength, and are candidates for "primary" bonding adhesives. In contrast, more reactive ethynyl and maleimide endcapped systems were prepared as "secondary" bonding materials, which could be cured at temperatures lower than that of the T_g of the primary structure. Lap shear test results obtained from NMP-cast/methanol-extracted scrim-cloth-supported

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precursors confirmed that good adhesion to titanium at both room temperature and at 177°C was achieved when cured at 250°C – 280°C. High glass transition temperatures and good thermal stability were achieved as determined by thermal analysis (DSC, TGA and DMA). Solvent extraction measurements confirmed that very high gel fractions were obtained, which is consistent with good chemical resistance.

The influence of molecular weight between crosslinks (Mc) on thermal and mechanical behavior was also investigated for 2, 3, 5, 7 and 10k initial $\overline{M_n}$ values. Lower molecular weight oligomers exhibited lower T_g and cure temperatures, but higher cured network crosslink densities afforded higher T_g and higher gel fractions, but with reduced toughness.

Keywords: Thermosetting polyimides; end caps; phenylethynyl; ethynyl; maleimide; structural adhesives; crosslink density

1. INTRODUCTION

Polyimides are well known to show excellent thermal, chemical, electrical, and high-temperature mechanical properties and are widely used as high temperature insulators, dielectrics, coatings, adhesives and advanced composite matrices [1 – 7]. Thermosetting polyimides are derived from low molecular weight oligomers or prepolymers with reactive terminal or pendant functional groups. The reactive groups can be thermally or catalytically cured to form crosslinked network structures [8 – 10]. The starting oligomers can display excellent processability, because of the low melt or solution viscosity and high solids content that can be employed. The melt processing window can be adjusted by using reactive groups which have different reactivities. Good adhesion to substrates is often achieved because of the low viscosity and, thus, excellent wetting ability of the short chain oligomers. With appropriate reactive groups, no cure volatiles are released if the oligomers are preimidized. The resulting cured polyimides typically exhibit high glass transition temperatures, good chemical resistance, high modulus and creep resistance. Some thermosetting polyimides are brittle, but toughness can be improved by increasing the oligomer molecular weight. Over the past 20 years considerable attention has been directed toward thermosetting polyimides because their superior properties [11 – 18].

The objective of this work was to explore the effects of the thermosetting polyimide endcapper type and the molecular weight between reactive endgroups on the performance of the cured materials. It was also of interest to develop thermosetting materials as primary and secondary adhesives for structural bonding as well as for composite matrix systems. A primary adhesive is to be used for the formation of

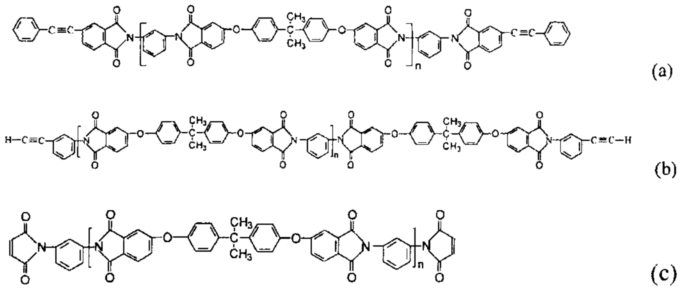


FIGURE 1 Phenylethynyl(a), ethynyl(b) and maleimide(c) endcapped poly(ether imide)s, $\overline{M}_n = 2\text{k}, 3\text{k}, 5\text{k}, 7\text{k}, 10\text{k}$(g/mole).

a primary structure and should exhibit good processibility. A secondary adhesive, however, is used for bonding performed primary bonding structures or for repair. The processing of secondary adhesives is done in the presence of primary adhesive and, therefore, cure temperatures should be low enough (250–280°C) not to adversely affect the performed primary bonded structures. Furthermore, both systems should display good thermal and mechanical properties, as well as good chemical resistance.

The oligomer selected has basically an Ultem® type poly(ether imide) backbone structure, because of ease of cyclization, low melt viscosity, excellent solubility *etc.*, as well as availability and potentially attractive economics. Phenylethynyl was selected as a primary adhesive because its high cure temperature allows a wide processing window as earlier reported by several workers [11–14, 16, 17]. Ethynyl and maleimide groups, on the other hand, were selected for endcapping secondary adhesives due to their more suitable lower cure temperatures. The structures of the three systems are shown in Figure 1. This research has focused on the synthesis and cure behavior of these oligomers, as well as on the adhesion strength and thermal properties of the cured networks.

2. EXPERIMENTAL

2.1. Materials

2,2′-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (bisphenol-A dianhydride or BPADA) was kindly donated by General

Electric Co. and purified by recrystallization from a mixture of toluene and acetic anhydride. 1,3-Phenylene diamine (*m*-PDA), maleic anhydride (MA) and phthalic anhydride (PA) were obtained from Aldrich and purified by sublimation under vacuum at ~80°C, ~60°C and ~120°C, respectively. 3-Ethynylaniline (*m*-aminophenylethynyl or *m*-APA) obtained from Acros was purified by distilling at ~90° and 50 millitorr prior to usage. 4-Phenylethynylphthalic anhydride (PEPA) was synthesized *via* the formerly-reported coupling reaction between 4-bromophthalic anhydride (4-BrPAN) and phenylethynyl catalyzed by bis(triphenylphosphine)palladium and cuprous dichloride [12, 13, 19]. 1-Methyl-2-pyrrolidone (NMP) was obtained from Fisher Scientific and was either used as received or vacuum distilled over phosphorus pentoxide. Acetic anhydride and chlorobenzene from Fisher Scientific were vacuum distilled over calcium hydride. Triethylamine obtained from Fisher Scientific, *o*-dichlorobenzene obtained from Aldrich and diethyl ether obtained from Mallinckrodt were used as received.

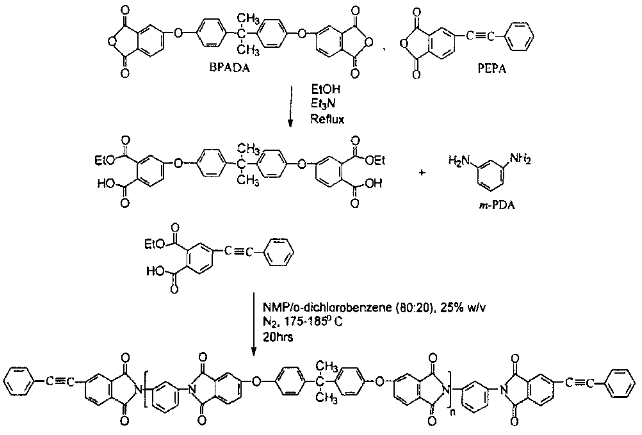
2.2. Polymer Synthesis

2.2.1. Phenylethynyl-Endcapped Thermosetting Poly(ether imide)s

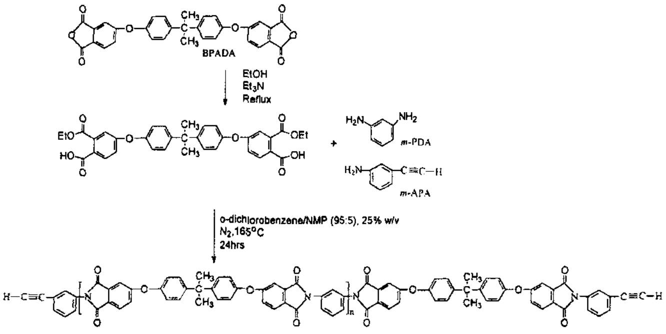
Phenylethynyl-endcapped Ultem® type poly(ether imide)s were synthesized employing the ester-acid synthetic route, which is frequently used for synthesizing soluble polyimides [20], as previously reported [11] (Scheme 1). 4-Phenylethynylphthalic anhydride (PEPA) was used to provide the imide oligomers with latent reactive endgroups. The stoichiometry of the monomers was varied according to the Carrothers equation to achieve the desired molecular weight oligomers with number average molecular weights varying from 2,000 to 10,000 ($\overline{M_n} = 2-10\text{k}$).

2.2.2. Ethynyl-Endcapped Thermosetting Poly(ether imide)s

Ethynyl-endcapped poly(ether imide)s were synthesized with controlled number average molecular weight from 2,000 to 10,000, using



SCHEME 1 Synthesis of phenylethynyl-endcapped poly(ether imide)s.

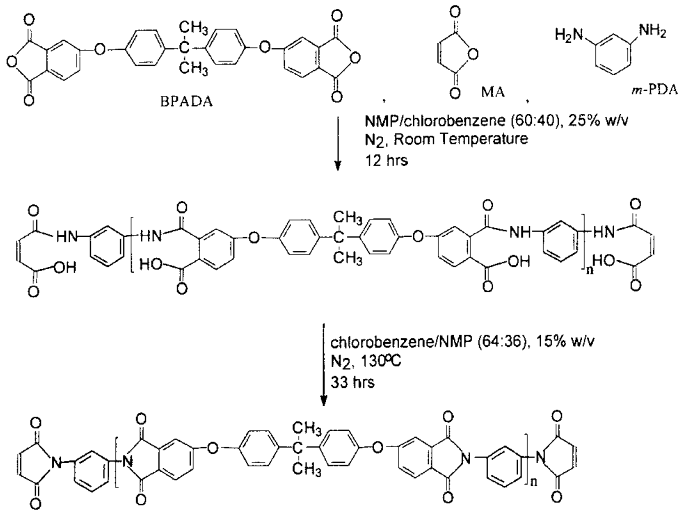


SCHEME 2 Synthesis of ethynyl-endcapped poly(ether imide)s.

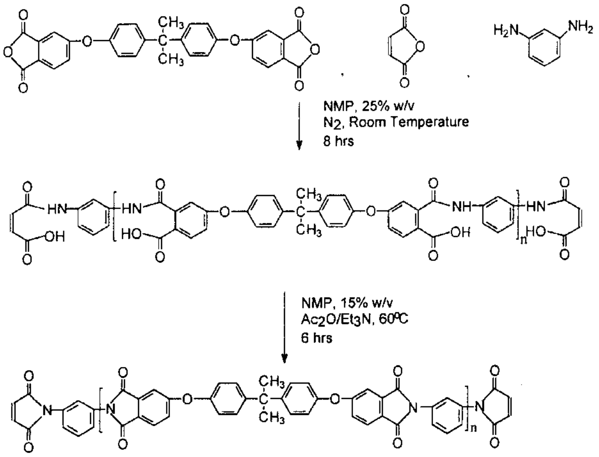
m-aminophenyl ethynyl (*m*-APA) as the endcapper. A procedure similar to the one described above was used, except that a lower imidization temperature and higher azeotropic agent (*o*-DCB) concentration were utilized, as shown in Scheme 2. The imidization temperature was lowered to eliminate possible premature reactions of the ethynyl endgroups.

2.2.3. Maleimide-Endcapped Poly(ether imide)s

Maleimide-endcapped etherimide oligomers were synthesized with controlled molecular weights *via* the amic-acid route using maleic



SCHEME 3 Synthesis of maleimide-endcapped poly(ether imide)s *via* amic acid intermediate followed by high temperature solution imidization.



SCHEME 4 Synthesis of maleimide-endcapped poly(ether imide)s by chemical imidization.

anhydride as endcapper. If the ester-acid method was used, it was anticipated that the maleic anhydride, its derivative and the amine might allow Michael addition to occur at high temperatures, which would be undesired. The solvents were all thoroughly dried and freshly distilled and the glassware was flame dried. The reaction sequence is shown in Scheme 3, which includes room temperature poly(amic acid) formation and high temperature solution imidization, which used chlorobenzene as a azeotropic agent.

A chemical imidization method was also used for preparing a maleimide-terminated oligomer with a target number average molecular weight of 5,000 g/mole. The reaction is shown in Scheme 4. Acetic anhydride and triethylamine were used as the imidizing agents.

2.3. Characterization Methods

2.3.1. Nuclear Magnetic Resonance (NMR) Spectroscopy

Proton and carbon 13 nuclear magnetic resonance (^{1}H, ^{13}C NMR) were used to obtain the chemical composition and molecular weight information of the polymers synthesized. Samples were dissolved in deuterated chloroform ($CDCl_3$) at concentrations of $\sim 2-10\%$ solid. NMR spectra were obtained on a Varian Unity Spectrometer operating at 400 MHz for proton and 100 MHz for carbon 13. The spectra were referred to tetramethylsilane (TMS) at 0 ppm.

Quantitative ^{1}H and ^{13}C NMR spectra were used to estimate accurately the molecular weight of the oligomers. The relaxation time was increased from 1 second for normal ^{1}H NMR to 6 seconds for quantitative ^{1}H NMR, to ensure that sufficient relaxation was allowed for each type of proton. For quantitative ^{13}C NMR, two changes were made. Firstly, an inverse gate decoupling was used to suppress the nuclear overhouser effect (NEO). Secondly, instead of 1 second, a relaxation time of 20 seconds was used, which provided adequate relaxation for all types of carbon [21].

2.3.2. Gel Permeation Chromatography (GPC)

GPC measurements were used to determine molecular weight and molecular weight distribution information. Chromatographs were obtained on a Waters 150C ALC/GPC instrument equipped with a differential refractive index detector and a Viscotek® Model 100 viscosity detector connected in parallel. NMP (HPLC grade), containing

$\sim$0.02 M P_2O_5, served as the mobile phase and the stationary phase was crosslinked polystyrene gel. The column compartment, lines and detectors were maintained at 60°C during the measurements. Number average molecular weight ($\overline{M_n}$), weight average molecular weight ($\overline{M_w}$) and polydispersity ($\overline{M_w}/\overline{M_n}$) were determined by the universal calibration generated with narrow molecular weight distribution polystyrene standards [22, 23].

2.3.3. Non-Aqueous Titration

Residual amic acid contents in the polymer were analyzed by non-aqueous acid-base potentiometric titration for the carboxylic acid group. The oligomers to be titrated were dissolved in chloroform and the titrant was a solution of tetramethylammonium hydroxide monohydrate (TMAH) in isopropanol. Titrations were performed using an MCI GT-05 (COSA Instruments Corp.) automatic potentiometric titrator, and the end-points were detected as the maximum of the first derivative for the potential *versus* volume of tetramethylammonium hydroxide (TMAH) titrant used. The percentage amount of residual amic acid (% AA) was calculated from:

$$\%\ \mathrm{AA} = \left[\frac{\mathrm{NV}}{10 \times \mathrm{SS}}\right] \times \mathrm{E}$$

where N = normal concentration of the TMAH, V = Volume of the TMAH consumed at the end point in ml, SS = sample size of polymer in g, and E = equivalent weight of repeat unit of amic acid in the polymer chain.

2.3.4. Differential Scanning Calorimetry (DSC)

DSC was used to determine the glass transition temperatures and the exothermic curing process of the uncured oligomers, as well as the glass transition temperatures of cured thermosetting polyimides. DSC was conducted on a Perkin Elmer DSC 7 instrument. Scans were run in nitrogen at a heating rate of 10°C/min. T_g values were determined as the midpoint of change on the baseline.

2.3.5. Thermogravimetric Analysis (TGA)

Dynamic TGA was performed to assess the relative thermal stability of the polymers. Thermograms were obtained using a Perkin Elmer TGA 7 thermogravimetric analyzer. Thin-film samples of $\sim 10\,\mathrm{mg}$ were placed in a platinum pan connected to an electric microbalance. The samples were heated at a rate of 10°C/min. in air or N_2. Weight losses of the samples were recorded as a function of temperature.

2.3.6. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to examine the structure of the polymers and to monitor the curing process of the reactive-functional-group-terminated thermosetting imide oligomers. Spectra were obtained with a Nicolet Impact 400 FTIR spectrometer. Oligomers were deposited on sodium chloride plates and each spectrum contained 32 scans with a resolution of $4\,\mathrm{cm}^{-1}$.

2.3.7. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis employed a Perkin Elmer DMA using the extension mode. A frequency of 1 Hz and heating rate of 5°C/min. were used. The samples were $\sim 0.5\,\mathrm{mm}$ thick, compression-molded films cured under the described conditions.

2.3.8. Solvent Extraction

Cured polyimides were extracted by chloroform to evaluate gel fractions and the influence of type of reactive endgroup on the oligomers, molecular weight between endgroups, and cure temperature on the chemical resistance. Films were formed either by cold pressing and then heating to the designated curing temperature for 90 minutes, or by melt pressing in a heat press at the designated curing temperature for 90 minutes. The films were then weighted and placed into a cellulose extraction thimble. Chloroform was selected because it is a solvent for the corresponding linear polyimide. The extraction was run for 5 days and the samples were first dried in the thimbles in air for

2 hours and in a vacuum oven at 120°C for 24 hours. They were then retrieved from the thimbles and dried at 250°C ($> T_g$) under vacuum for 2 hours. The gel fraction was calculated as the ratio of the dried insoluble gel weight to that of the initial sample weight.

2.3.9. Adhesive Strength by Single Lap Shear Test

The adhesion strength of the cured oligomers to titanium was examined *via* single lap shear adhesion tests according to ASTM-D1002. The adhesive tapes were prepared by coating 112 E-glass scrim cloth, finished with A1100 (aminopropyl triethoxy silane), with NMP solutions of the oligomers followed by drying in a vacuum oven. The amount of NMP was minimized to 1.25 – 1.7 times of the oligomer weight to be coated (85 wt% of the polymer for 15 wt% of the glass cloth). To facilitate efficient removal of NMP from the coated tape, the following procedure was adopted. The glass cloth was coated with the oligomer/NMP mixture, dried at 100°C in an air oven, then soaked in boiling methanol for one hour. The tape was then dried in a vacuum oven at a heating rate of 10°C/hour to a final temperature of 170 – 210°C for one hour depending on oligomer molecular weight. This procedure importantly reduced the residual NMP to 1 – 2% (by proton NMR), without inducing premature curing. The adherend, a titanium coupon (Ti, 6A1-4V), was surface anodized in chromic acid. Single lap shear specimens were fabricated in a hot press at 250°C (at a heating rate of 4°F/min) and held at this temperature for 1 hour at a constant load of 75 psi (0.52 MPa). The adhesion strength was measured with an Instron model 1123 at a crosshead speed of 1.25 mm/minute.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Oligomers

3.1.1. Phenylethynyl-Terminated System

Phenylethynyl-terminated etherimide oligomers were synthesized by a one-pot ester-acid procedure using 4-phenylethynylphthalic anhydride (PEPA) as the endcapping agent (shown in Scheme 1). The formation

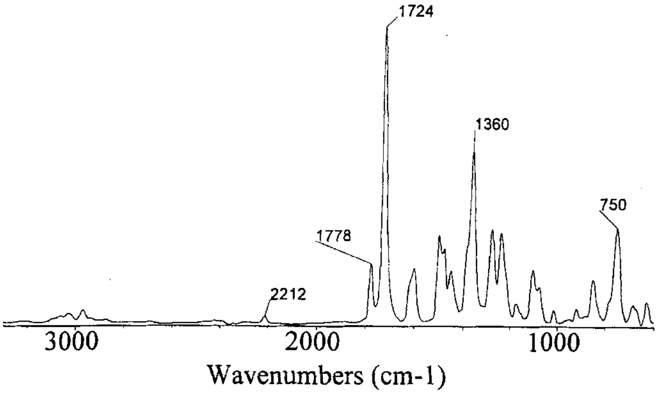


FIGURE 2 FTIR spectrum of a 2k phenylethynyl-terminated polyimide oligomer.

of the cyclodehydrated imide structure was confirmed by FTIR, NMR and non-aqueous titration [11].

The FTIR spectra for a 2k oligomer (Fig. 2) exhibited strong absorptions at 1778, 1724, 1360, 750 cm^{-1} and absence of 2900–3200, 1710, 1660, 1550 cm^{-1} absorptions, which suggests the formation of highly-imidized materials. The absorption around 2212 cm^{-1}, indicated on the figure, is due to the phenylethynyl groups; ^{1}H and ^{13}C NMR also demonstrated similar results. The amount of residual amic acid in the polymer structure was determined by titration with tertramethylammonium hydroxide and was less than 0.3%.

3.1.2. Ethynyl-Terminated System

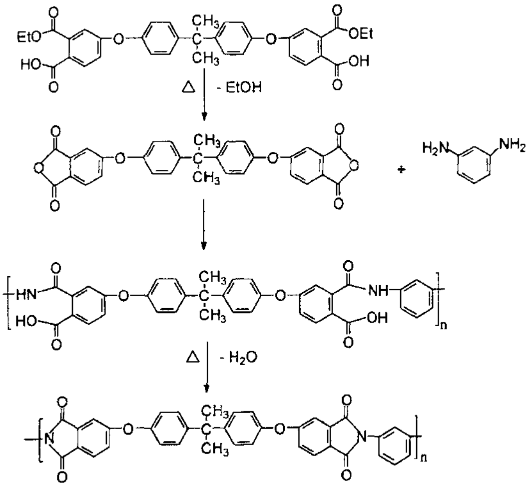
Ethynyl-endcapped etherimide oligomers were synthesized using *m*-aminophenylethynyl (*m*-APA) as the endcapping agent in conjunction with an excess of the BPADA. Initially, an attempt was made to synthesize ethynyl-terminated oligomers *via* the same procedure used to synthesize phenylethynyl-terminated oligomers. However, molecular characterization by GPC and intrinsic viscosity indicated that the observed molecular weight was more than twice the targeted molecular weight (Tab. I), possibly due to chain extension by the ethynyl endgroup. The latter might have occurred as a result of maintaining the reaction at the imidization temperature of 180°C for 20 hours.

TABLE I Molecular weight of an ethynyl oligomer determined by GPC and intrinsic viscosity after imidization at 180°C for 20 hours

Theoretical $\overline{M_n}$	$\overline{M_n}$ *by GPC*	$\overline{M_w}$ *by GPC*	$\overline{M_w}/\overline{M_n}$ *by GPC*	IV *in NMP (dl/g)* 25°*C*
3,000	7,150	12,100	1.7	0.185

Therefore, to avoid premature reactions of the endcapper, reaction conditions were modified by lowering imidization temperature to 165°C, which appeared to eliminate the problem.

Potential problems associated with a low imidization temperature can be considered by examining the reaction mechanism *via* the ester-acid route. As depicted in Scheme 5, the preparation of polyimides from diester-diacids and diamines involves three sequential reactions [24]. At high temperature, the diester-diacids are initially converted to dianhydrides through the elimination of alcohol. These dianhydrides then react with diamines to form poly(amic acid)s, which subsequently imidize with removal of water. Possible consequences associated with a low imidization temperature are: (1) in the first step, a decreased effectiveness of anhydride formation which could cause a decreased polymerization rate and lower molecular weight; and (2) in the third step, incomplete imidization might result in residual amic acid in the

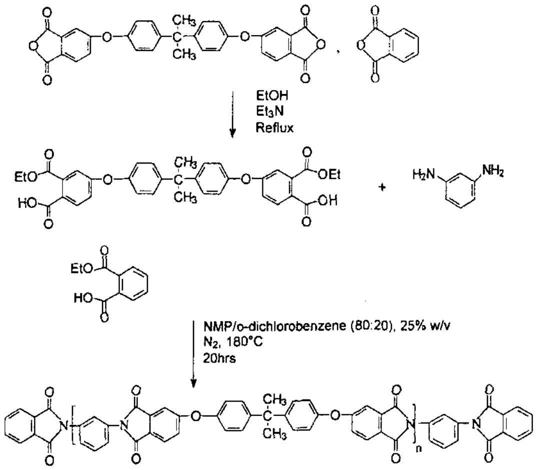


SCHEME 5 Imidization mechanism of polyimide *via* ester-acid route.

final structure. However, these possible effects can be mitigated by increasing the concentration of the azeotroping agent to ensure efficient alcohol and water removal. The amount of *o*-DCB was, therefore, increased from 20% to 95% v/v; a small amount of NMP allowed for homogeneous reaction. Moreover, the imidization time was increased to 24 hours. The synthesis of ethynyl-terminated polyimide oligomers under these revised conditions was shown in the Experimental section in Scheme 2.

A parallel reaction was conducted for a non-reactive phthalimide-endcapped poly(ether imide) using the "conventional" [19] reaction conditions at 180°C (Scheme 6) to validate these revised reaction conditions. The rate of polymerization and effectiveness of imidization were observed and compared for the two systems in terms of molecular weight increase rate, equilibrium molecular weight achieved, and residual amic acid concentration.

Molecular weight by GPC *vs.* imidization time for (A) the ethynyl-terminated system run under the revised conditions, and (B) the phthalimide-terminated system run under conventional conditions are compared in Figure 3, which shows that the weight average molecular weight, $\overline{M_w}$, increased at similar rates for both reactions. It was also observed that the molecular weight of both materials reached similar



SCHEME 6 Comparative synthesis of non-reactive phthalimide-terminated polyimides using the "conventional" reaction conditions.

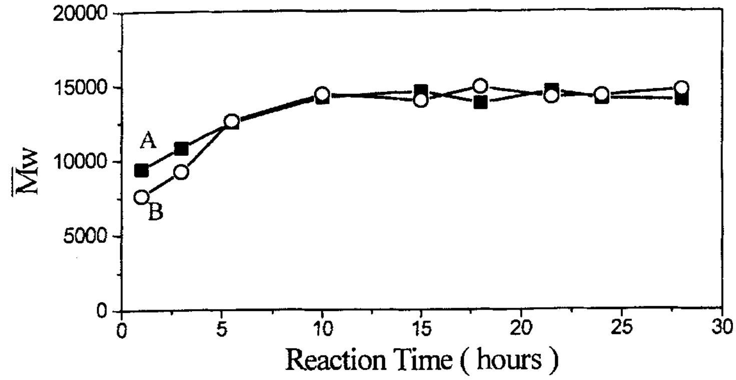


FIGURE 3 Weight average molecular weight, $\overline{M_w}$, *vs.* time for ethynyl-terminated polyetherimide synthesized @ 165°C (A) and phthalimide-endcapped polyetherimide synthesized @ 180°C (B), by GPC.

equilibrium values after 15 hours. In addition, there was no evidence of chain extension in the ethynyl-endcapped system under the revised conditions.

The residual amic acid contents for the oligomers prepared under both the revised and conventional conditions, as determined by titration with tetramethyl ammonium hydroxide, were 0.13 and 0.15%, respectively. The very low residual amic acid levels indicate that fully-imidized structures were achieved under both reaction conditions.

The FTIR spectra of the synthesized ethynyl-endcapped oligomers (Fig. 4) exhibited strong absorptions in the ranges 1778, 1724, 1360, 725 cm^{-1}, suggesting the formation of essentially imidized materials. The absorption shown at 3280 cm^{-1} indicates the existence of terminal ethynyl groups; ^{1}H and ^{13}C NMR also demonstrated similar results.

Therefore, it was established that the revised reaction conditions were as valid and effective as the conventional conditions, and ethynyl-terminated oligomers were synthesized in number average molecular weight of 2K, 3K, 5K, 7K and 10K using this modified method.

3.1.3. Maleimide-Terminated System

Maleimide endcapped oligomers were synthesized *via* the amic acid route to avoid the possible Michael reaction between maleic and amine groups at high temperature, which might have occurred if the

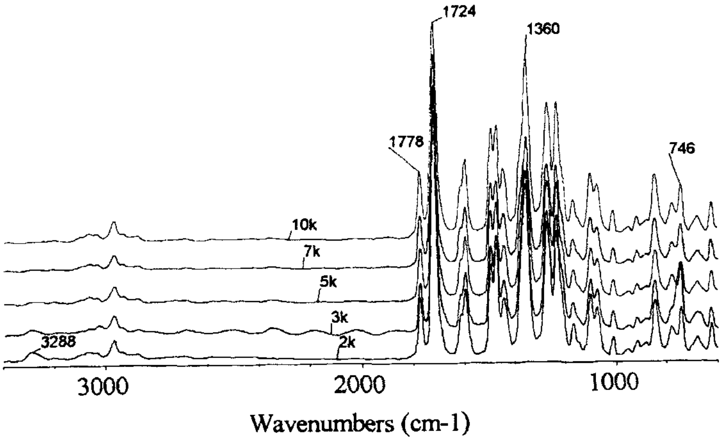


FIGURE 4 FTIR spectra of ethynyl-terminated polyimide oligomers of varying number average molecular weight ($\overline{M}_n$).

ester-acid method had been used. This synthetic route, shown in Scheme 3, consists of the room temperature formation of a poly(amic acid) between the anhydrides and the diamine, followed by a high-temperature solution imidization. The reaction time for the first stage was limited to 12 hours, based on the observation that the reaction mixture viscosity stabilized after 8 hours. The imidization temperature was determined by an experiment of endcapping an amine-terminated oligomer with a maleic anhydride. As shown by GPC in Figure 5, a temperature of 130°C was appropriate for endcapping, whereas a mere 5°C increase to 135°C resulted in an undesired chain extension, as shown by a lower elution volume and, hence, higher hydrodynamic volume than the original amine-termination oligomer. Therefore, imidization was conducted at 130°C for 33 hours, which was sufficient to reach the minimum residual amic acid plateau as demonstrated by titration (Fig. 6).

3.1.4. Molecular Weight Characterization

The molecular weights of phenylethynyl-terminated oligomers [11] were characterized by quantitative ^{13}C NMR and gel permeation chromatography (GPC) (Fig. 7). The number average molecular

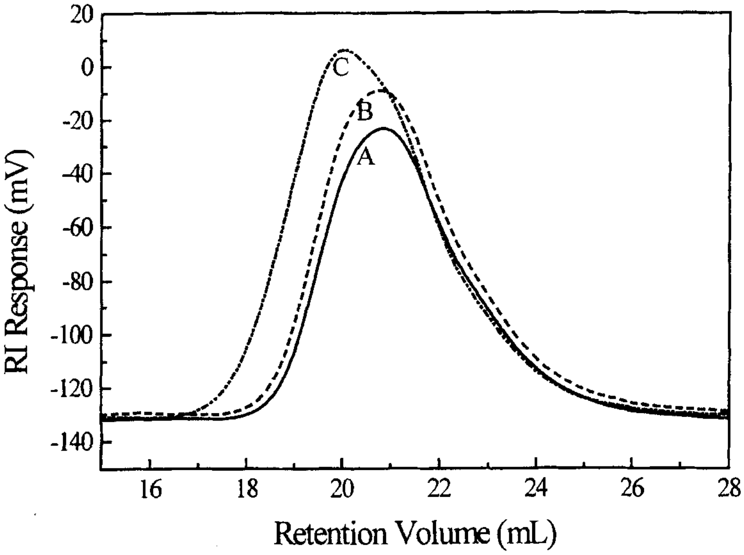


FIGURE 5 GPC chromatograms of original amine-terminated imide oligomer (A), maleimide-endcapped at 130°C (B) and maleimide-endcapped at 135°C (C).

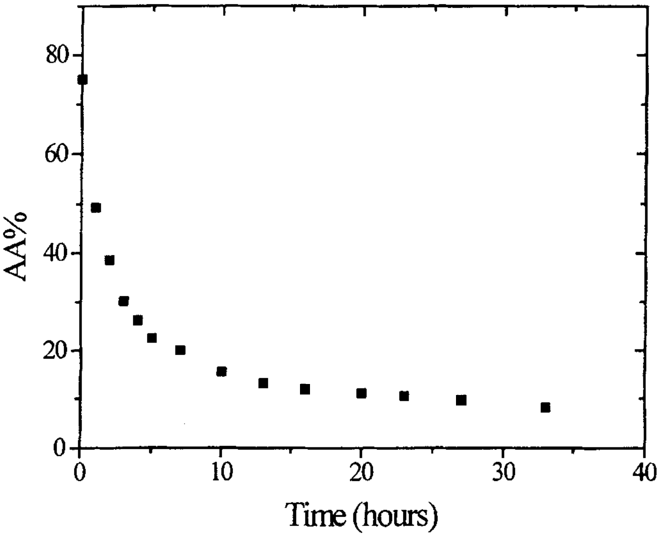


FIGURE 6 Residual amic acid concentration *vs.* imidization time at 130°C for maleimide-endcapped imide oligomers.

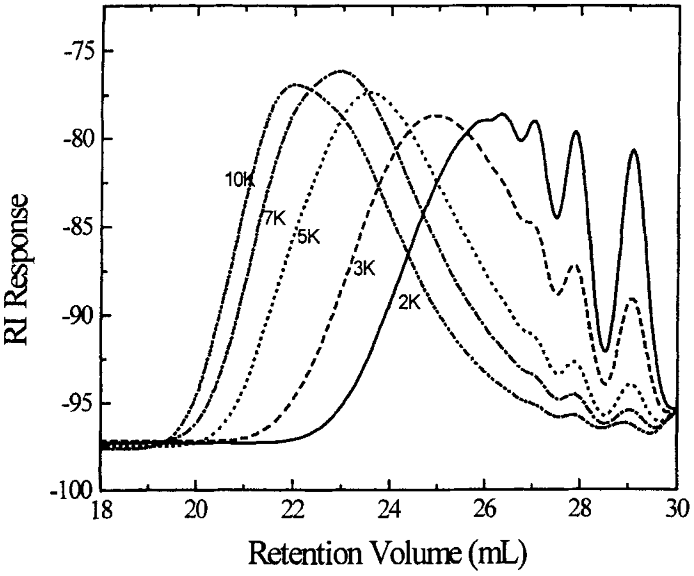


FIGURE 7 GPC chromatograms of phenylethynyl-terminated oligomers (in NMP, 60°C).

weight from ^{13}C NMR was calculated by comparing the ratio of the signal integrations for carbon in the backbone (—C(CH$_3$)$_2$, $\delta = 31$ and 43 ppm) with that of the endgroup (— C ≡ C —, $\delta = 88$ and 94 ppm). Molecular weights observed by ^{13}C NMR and GPC (Tab. II) are in fairly good agreement with the theoretical molecular weights, within experimental error. It has been observed in our laboratory that molecular weights obtained by GPC usually deviate to higher values for low molecular weight oligomers. The agreement between the molecular weights obtained by ^{13}C NMR and GPC suggested that the oligomers were fully endcapped.

TABLE II Molecular weights of phenylethynyl-endcapped etherimide oligomers

Target $\overline{M_n}$ (g/mole)	*$\overline{M_n}$ by GPC*	*$\overline{M_w}$ by GPC*	*$\overline{M_w}/\overline{M_n}$ by GPC*	*$\overline{M_n}$ by ^{13}C NMR*
2,000	3,800	4,600	1.2	2,100
3,000	4,400	6,200	1.4	3,000
5,000	6,600	10,500	1.6	5,000
7,000	7,200	14,200	2.0	6,100
10,000	9,600	18,300	1.9	9,400

TABLE III Molecular weights of ethynyl-terminated etherimide oligomers

Target $\overline{M_n}$ (g/mole)	$\overline{M_n}$ by GPC	$\overline{M_w}$ by GPC	$\overline{M_w}/\overline{M_n}$ by GPC	$\overline{M_n}$ by ^1H NMR
2,000	3,400	4,700	1.4	2,300
3,000	4,400	6,700	1.5	3,600
5,000	4,900	7,300	1.5	5,100
7,000	7,300	12,800	1.7	7,400
10,000	10,300	16,300	1.6	11,600

TABLE IV Molecular weights of maleimide-terminated etherimide oligomers

Target $\overline{M_n}$ (g/mole)	$\overline{M_n}$ by GPC	$\overline{M_w}$ by GPC	$\overline{M_w}/\overline{M_n}$ by GPC
2,000	4,100	6,100	1.5
3,000	5,100	7,400	1.5
5,000	5,200	9,400	1.8
7,000	6,400	11,100	1.7
10,000	9,000	16,700	1.9

The molecular weights of ethynyl-endcapped oligomers were determined by ^{1}H NMR and GPC. The number average molecular weights derived by comparing ^{1}H NMR signals of terminal ethynyl (3.1 ppm) and backbone isopropylidene (1.7 ppm), and number and weight average molecular weights obtained by GPC are listed in Table III. The molecular weights appear to be well controlled. The effectiveness of endcapping was demonstrated by the agreement between number average molecular weights determined by ^{1}H NMR and GPC.

Molecular weight control was demonstrated by GPC for the maleimide-terminated system (Tab. IV).

3.2. Curing Behavior

3.2.1. Phenylethynyl-Terminated System

Figure 8 depicts the DSC thermograms of phenylethynyl-terminated oligomers, each with a T_g and a cure exthotherm. As shown, both the T_g and the cure-onset temperatures increased systematically when the oligomer molecular weight increased. The cure-onset temperatures were generally high, ranging from 345°C to 370°C, resulting in a relatively large temperature gap between T_g and T_{cure}, and, thus, a wide processing window.

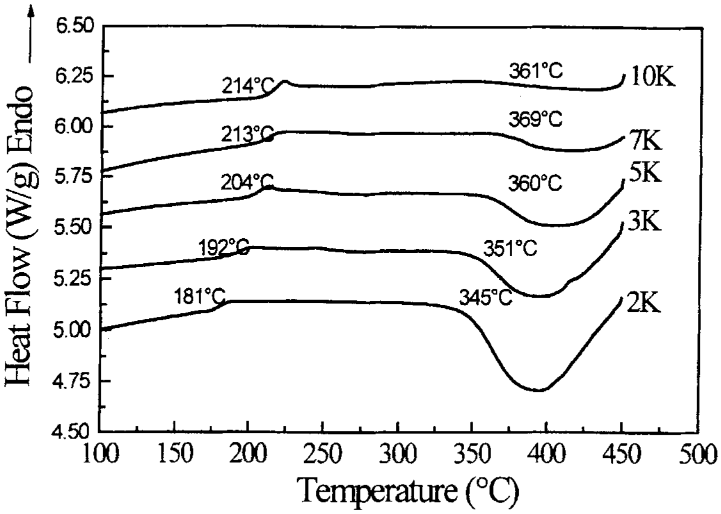


FIGURE 8 DSC thermographs of phenylethynyl-endcapped oligomers (in N_2, 10°C/min.) which show the oligomer T_g values and the cure exotherm onsets.

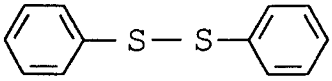
TABLE V Adhesive strength of phenylethynyl system as determined by single lap shear test

Sample	*Cure temp.*	*Cure time*	*Adhesive strength (PSI/MPa)*	*Failure mode*
PEPA 3K	370°C	1 hour	5300 ± 200/ 36.6 ± 1.5	Cohesive
PEPA 3K	280°C	8 hours	800 ± 200/ 5.5 ± 1.2	Cohesive
PEPA 3K	280°C	10 hours	1100 ± 200/ 7.7 ± 1.5	Cohesive

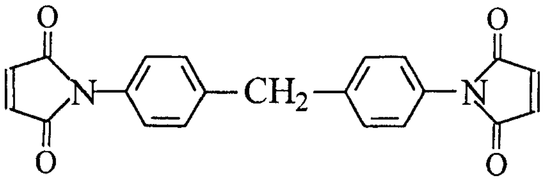
Single lap shear adhesion tests were performed for bonding to titanium (Ti, 6V-4Al) substrates. High adhesive strength was achieved when the materials were thermally cured at high temperature, *i.e.*, 370°C (Tab. V), suggesting that this system is a good candidate for a primary adhesive. However, when tested as a secondary adhesive, *i.e.*, thermally cured at 280°C even for a prolonged time of 8 and 10 hours, the system demonstrated poor adhesive strength, indicating the phenylethynyl-endcapped system is not efficiently reactive for secondary bonding.

3.2.2. Attempted Catalysis of the Phenylethynyl Curing Reaction

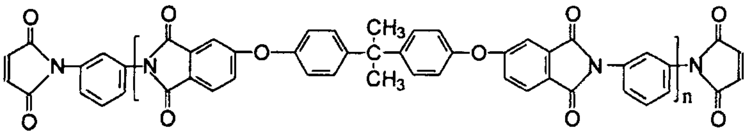
In order to study the potential of utilizing the phenylethynyl-terminated system as a secondary adhesive, research was conducted in an attempt to accelerate the cure at lower temperatures using free radical sources such as phenyl disulfide and bismaleimides (BMI) as initiators. The structures of the disulfide and BMI initiators used are shown in Figure 9. The nature of the phenylethynyl curing reaction is not fully understood yet, even though considerable research has



Phenyl disulfide



4,4' Bismaleimidodiphenyl methane (BMI)



Maleimide endcapped 3k etherimide oligomer (MI3k)

FIGURE 9 Initiators used for the attempted acceleration of phenylethynyl curing.

been conducted to understand better the thermal curing mechanism [14, 16, 17, 25–27]. It appears that the reaction involves chain extension and branching prior to the gel point, and is assumed to proceed by a free-radical mechanism. It was hypothesized that the production of free radicals from phenyl disulfide, and/or the occurrence of the free-radical reaction of BMI at relatively low temperatures, might initiate the curing process. Maleimide-endcapped Ultem® type oligomers were also examined because it was expected that compatibility due to the same backbone structures would increase the possibility of it functioning more effectively. A phenylethynyl-endcapped etherimide oligomer (2K) was cocured with these initiators in air and the cure reaction was monitored by FTIR. The disappearance of characteristic phenylethynyl absorption at 2212 cm^{-1} was used to follow the progress of the curing reaction. Using the backbone – CH_3 bond stretch (2968 cm^{-1}) as an internal reference, the percent conversion of the ethynyl group was calculated by its absorption intensity (Fig. 10). The initiators and phenylethynyl oligomers were dissolved in chloroform in the ratio described in Table VI and deposited on sodium chloride plates. Curing were conducted at 270°C and 280°C and results are listed in Table VI.

Compared with the neat phenylethynyl endcapped oligomer, the systems with the proposed initiators showed no increase in the extent of conversion as summarized in Table VI, suggesting that the reaction of the disulfide, BMI and maleimide endgroups did not favorably influence the cure process in air.

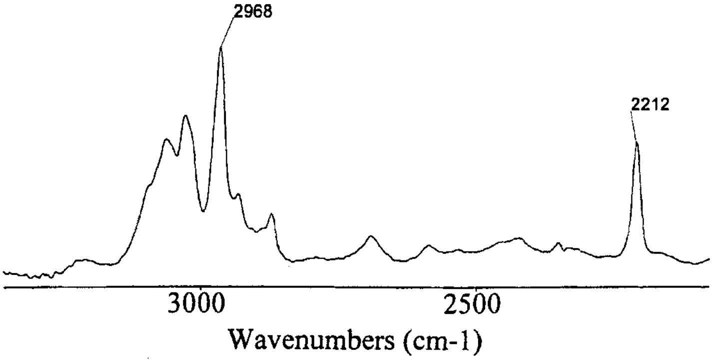


FIGURE 10 FTIR spectrum of 2k phenylethynyl-terminated oligomer.

TABLE VI Possible influence of radical sources on the conversion of the phenylethynyl group determined by FTIR

System	*270°C 8 hours*	*280°C 8 hours*
2k PEPA oligomer control	35%	60%
2k PEPA oligomer + 0.5% disulfide	35%	–
90% 2k PEPA oligomer + 10% BMI	–	65%
90% 2k PEPA oligomer + 10% MI3k	–	60%
50% 2k PEPA oligomer + 50% MI3k	–	60%

3.2.3. Ethynyl-Terminated System

The thermal transitions of the ethynyl-terminated oligomers were determined by DSC (Fig. 11). The glass transition temperatures of the ethynyl-terminated oligomers were similar to the phenylethynyl system, but the cure temperatures decreased significantly, possibly because of the reduced steric hindrance for endgroup mutual reactions. The position of the exothermic peaks showed that temperatures of 250°C to 280°C, the region desired for curing secondary adhesives, were sufficiently high for crosslinking and network formation to occur.

Single lap shear test results, listed in Table VII, indicated that high room temperature adhesive strengths were achieved when the materials were cured at 250°C, which suggests that this system is a good candidate for use as a secondary adhesive. In comparing the 3k and 7k oligomers, slightly higher values were recorded for the 7k system, while the highly crosslinked, more brittle, 3k system had lower shear strength. The mode of failure was observed to be exclusively cohesive when tested at room temperature, but 20–30% of adhesive failures (estimated visually) were observed when tested at 177°C.

Aging studies were carried out for APA-7K sample in air and in boiling water conditions and the results are listed in Table VIII. Aging at 177°C in air and in boiling water did not substantially reduce the adhesive strengths of these new secondary adhesives. These systems appear to be stable for moderate period of times under these conditions.

3.2.4. Maleimide-Terminated System

DSC thermograms of maleimide-terminated oligomers (Fig. 12) show that the T_g of this system was similar to the phenylethynyl- and ethynyl-terminated systems. It was also shown that the cure

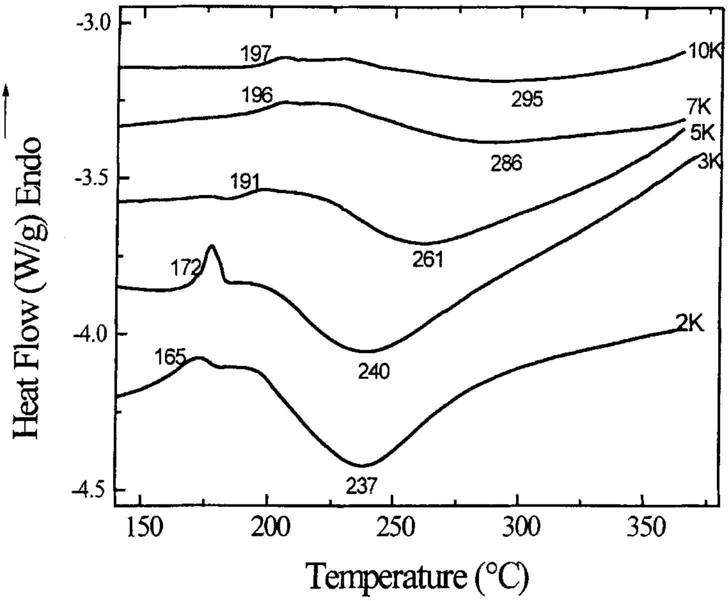


FIGURE 11 DSC thermograms of ethynyl-endcapped oligomers (in N_2, 10°C/min.).

TABLE VII Adhesive strength of ethynyl-terminated system by single lap shear test

Sample	*Drying condition*	*Residual solvent (wt%)**	*Adhesive strength (MPa)*	
			Tested @ RT	*Tested at* 177°*C*
APA-3K	130°C; 10 h	1.4	38.0 ± 3.1	17.0 ± 0.9
APA-7K	180°C; 1 h	1.8	48.6 ± 1.2	24.3 ± 1.8

* Proton NMR analysis.

TABLE VIII Adhesive strengths of the aged samples of APA-7K samples in air and in boiling water

Aging condition	*Time*	*Adhesive strength (MPa)*	
		Tested at RT	*Tested at* 177°*C*
Control (unaged)	–	48.6 ± 1.2	24.3 ± 1.8
Aged at 177°C	2 weeks	43.4 ± 1.5	25.5 ± 1.4
Aged in boiling water	1 week	40.2 ± 2.9	–

temperature range was comparable with the ethynyl system, although slightly wider. Moreover, the positions of the exothermic peaks showed that 250°C to 280°C was appropriate for the curing process.

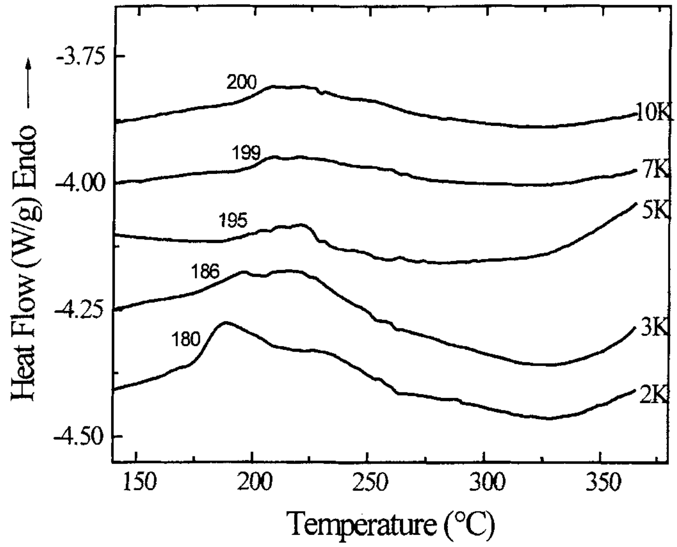


FIGURE 12 DSC thermograms of maleimide-endcapped oligomers (in N_2, 10°C/min.).

The adhesive strengths of the maleimide terminated oligomers are given in Table IX. The maleimide-terminated systems also exhibited high adhesive strengths when tested at room temperature. In practical autoclave systems, when a large part is being cured, the temperature ramp may need to be low to achieve uniform curing. It must be noted that, in the present study, the adhesive strengths were high even when the samples were bonded at such a slow heating rate (4°F/min). The adhesive strength of the higher molecular weight oligomer (10K) exhibited reduced adhesive strength compared with 5K and 7K counterparts, possibly due to reduced flow properties. The adhesive strengths of these systems were quite respectable even when tested at 177°C.

TABLE IX Adhesive strength at 25°C of cured maleimide-terminated imide oligomers to titanium by single lap shear test

Sample	*Drying condition*	*Residual solvent (wt%)*	*Adhesive strength (MPa)* Tested @ RT	*Adhesive strength (MPa)* Tested at 177°C
MI-5K	180°C; 1 h	1.5	50.2 ± 3.0	23.2 ± 1.9
MI-7K	180°C; 1 h	1.2	47.6 ± 1.5	23.7 ± 1.3
MI-10K	210°C; 1 h	1.7	36.9 ± 1.5	23.6 ± 1.4

TABLE X Adhesive strengths of the aged samples of MI-5K samples in air and in boiling water

Aging condition	*Aging Time*	*Adhesive strength (MPa)*	
		Tested at RT	*Tested at* 177°*C*
Control (unaged)	–	50.2 ± 3.0	23.2 ± 1.9
Aged at 177°C	2 weeks	42.3 ± 2.4	27.3 ± 2.0
Aged at 177°C	1 month	41.9 ± 2.5	26.3 ± 1.3
Aged in boiling water	1 week	40.5 ± 2.0	–
Aged in boiling water	1 month	35.4 ± 1.5	19.8 ± 1.2

Aging tests indicated that the drop in adhesive strength from the unaged sample, when aged at 177°C in air or when aged in boiling water, is small (Tab. X). These results suggested that maleimide-endcapped oligomers are good candidates for use as secondary adhesives.

Chemically-imidized 5k maleimide-endcapped polyimide oligomers were also characterized for their utility as secondary adhesives. The chloroform-cast samples were thermally cured at 250°C for 2 hours and single lap shear strength values of 3480 ± 560 PSI (24 ± 3.9 MPa) were observed, which is significantly lower than the analogous high temperature solution imidized sample (5998 ± 405 PSI) (41.4 ± 2.8 MPa). Possibly this might be attributed to structural isoimide defects, which have been reported for chemically-imidized polyimides [28].

3.3. Properties of the Cured Polyimide Networks

3.3.1. Phenylethynyl-Terminated System

The cured oligomers formed fully-crosslinked structures and demonstrated excellent solvent resistance as judged by gel fraction. Gel fraction was defined as the portion of a material not soluble in solvents. The non-reactive endcapped linear polymers were totally soluble in chloroform as shown in Table XI, whereas all the thermally-cured phenylethynyl-endcapped oligomers displayed nearly 100% gel fractions and were unaffected by the solvent, as reported earlier [11].

The cured material exhibited good weight loss retention and high glass transition temperatures as indicated by dynamic TGA and DSC (Tab. XII). Initial thermal decomposition temperatures determined by

TABLE XI Gel fraction of cured phenylethynyl-endcapped oligomers* by Soxhlet extraction with chloroform for 5 days

Oligomer, $\overline{M_n}$	*Gel fraction*
2k	99
3k	100
5k	100
7k	98
10k	99
Non-reactive phthalimide endcapped 20k	0

*Samples cured at 380°C for 90 minutes.

TABLE XII Summary of thermal properties of cured phenylethynyl-endcapped poly(ether imide)s

Oligomer $\overline{M_n}$	*5% Wt. loss temp. in air, TGA (°C)*	*5% Wt. loss temp. in* N_2*, TGA (°C)*	T_g*(°C), DSC*
2K	574	578	253
3K	577	579	240
5K	581	575	228
7K	581	581	224
10K	581	582	220

dynamic thermogravimetric analysis (both in air and nitrogen) were high (570–580°C). Glass transition temperatures as determined by DSC ranged from 220°C to 253°C, depending on the molecular weight of the original oligomer. Lower oligomer molecular weight produced higher crosslink density and higher T_g values.

3.3.2. Ethynyl-Terminated System

The cured ethynyl-terminated oligomer systems also exhibited good chemical resistance. Gel fractions, determined by chloroform extraction, are shown in Table XIII. Nearly 100% gel fractions were

TABLE XIII Gel fractions of cured ethynyl-endcapped oligomers determined by Soxhlet extraction

Oligomer, $\overline{M_n}$	*Cured at 280°C for 90 min.*	*Cured at 250°C for 90 min.*
2k	100	99
3k	100	100
5k	95	92
7k	93	90
10k	84	77

observed for the cured low molecular weight oligomers. For higher molecular weight oligomers, the gel fractions were 77% to 95%. Compared with the phenylethynyl-endcapped system, the relatively lower gel fraction (especially at high molecular weight) can possibly be attributed to diffusion-limited curing. It can be observed from the DSC thermograms that the curing occurred shortly after the glass transition temperatures of the oligomers was reached, where they may not have had sufficient mobility to advance the cure.

DSC analysis revealed high glass transition temperatures for the cured materials, as listed in Table XIV. Glass transition temperatures increased when the initial oligomer molecular weights decreased, probably due to the higher crosslink density formed. These T_g values also indicate that a slightly higher extent of crosslinking was achieved when the cure was performed at 280°C as opposed to 250°C. In addition, the cured materials were found to exhibit good thermal stability, as determined by dynamic TGA (Tab. XV).

The dynamic mechanical analysis (DMA) of some representative cured materials are shown in Figure 13. They generally exhibited behavior typical of a crosslinked network structure. The elastic modulus was high below the glass transition temperature and a significant value was maintained above T_g.

TABLE XIV T_g (°C) of cured ethynyl-terminated oligomers by DSC

Oligomer, $\overline{M_n}$	*Cured at 280°C for 90 min.*	*Cured at 250°C for 90 min.*
2k	251	248
3k	231	227
5k	229	224
7k	222	219
10k	217	213

TABLE XV Thermal stability of cured ethynyl-endcapped poly(ether imide)s by dynamic TGA (10°C/min.)

Oligomer,	*Cured at 280°C for 90 min.*		*Cured at 250°C for 90 min.*	
$\overline{M_n}$	*5% Wt. loss in Air (°C)*	*5% Wt. loss in N_2 (°C)*	*5% Wt. loss in Air (°C)*	*5% Wt. loss in N_2 (°C)*
2k	578	579	578	581
3k	576	581	572	581
5k	581	575	580	579
7k	584	577	574	574
10k	580	576	577	576

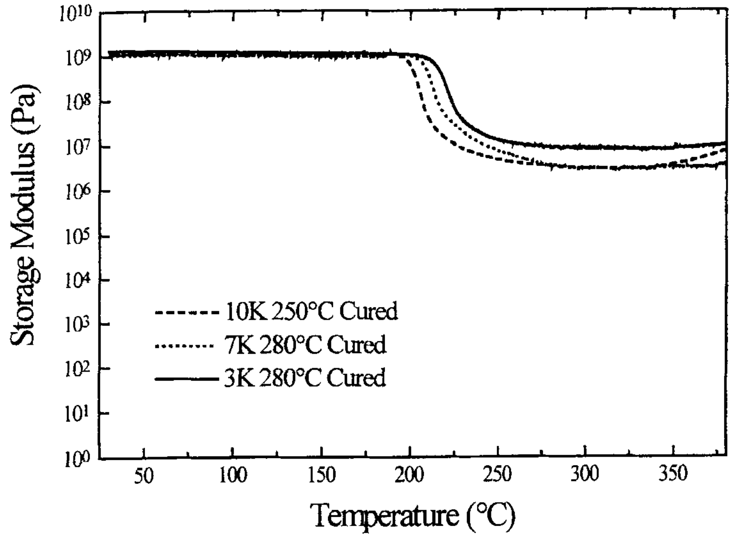


FIGURE 13 Representative DMA spectra of cured ethynyl-endcapped polyimides (5°C/min., 1 Hz, in N_2).

3.3.3. Maleimide-Terminated System

The gel fractions of cured maleimide-endcapped oligomers, as determined by Soxhlet extraction, were lower than the phenylethynyl- and ethynyl-terminated systems (see Tab. XVI). Little flow was observed during the cure process of this system. Limited diffusion might be the cause of the reduced extent of crosslinking.

Figures 14 and 15 depict the behavior of the three cured thermosetting systems along with the thermoplastic Ultem 1000® control, as demonstrated by representative dynamic TGA traces in air and nitrogen atmosphere. The three thermosetting systems all show better

TABLE XVI Gel fractions of cured maleimide-endcapped oligomers determined by Soxhlet extraction

Oligomer, $\overline{M_n}$	*Cured at* 280°*C for* 90 *min.*	*Cured at* 250°*C for* 90 *min.*
2k	98	92
3k	93	74
5k	91	48
7k	74	40
10k	57	32

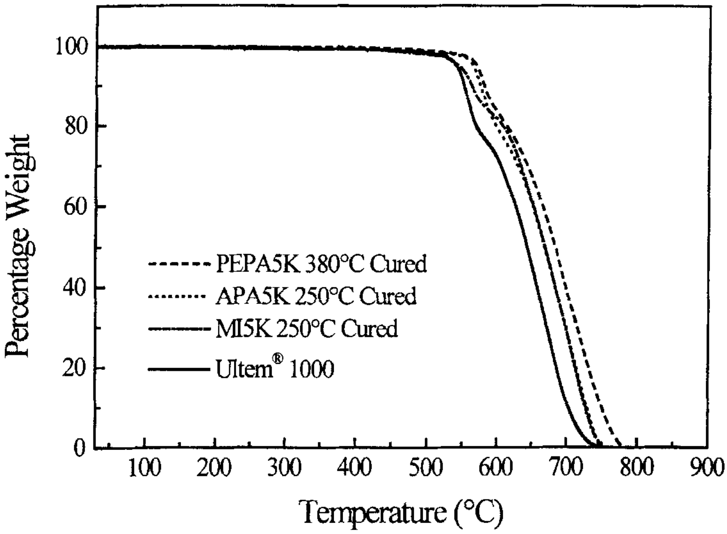


FIGURE 14 Dynamic TGA thermograms of linear and cured thermosetting polyetherimides in air (10°C min.).

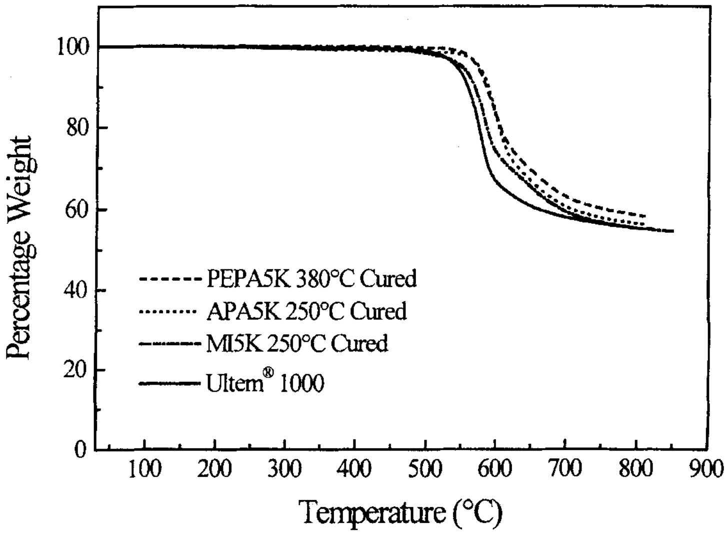


FIGURE 15 Dynamic TGA thermograms of linear and cured thermosetting polyetherimides in N_2 (10°C min.).

TABLE XVII Weight loss behavior of cured maleimide-endcapped poly(ether imide)s by dynamic TGA (10°C/min.)

Oligomer,	*Cured at 280°C for 90 min.*		*Cured at 250°C for 90 min.*	
$\overline{M_n}$	*5% Wt. loss in Air (°C)*	*5% Wt. loss in in N_2 (°C)*	*5% Wt. loss in Air (°C)*	*5% Wt. loss in N_2 (°C)*
2k	560	559	554	555
3k	556	561	552	560
5k	559	555	550	549
7k	554	557	554	549
10k	554	555	547	550

TABLE XVIII T_g (°C) of cured maleimide-terminated oligomers by DSC (10°C/min., N_2)

Oligomer, $\overline{M_n}$	*Cured at 280°C for 90 min.*	*Cured at 250°C for 90 min.*
2k	240	226
3k	232	223
5k	229	222
7k	227	219
10k	225	219

weight retention than the thermoplastic analogue. Among these thermosets, the maleimide endcapped system was slightly lower in initial thermal degradation temperature as summarized in Table XVII.

The glass transition temperatures of the cured maleimide-terminated oligomers, listed in Table XVIII, are similar to those observed for the phenylethynyl- and ethynyl-terminated systems. Glass transition temperature increased with decreased oligomer molecular weight, and samples cured at higher temperature demonstrated a higher degree of crosslinking.

4. CONCLUSIONS

Phenylethynyl-, ethynyl- and maleimide-terminated etherimide oligomers were successfully synthesized to controlled molecular weight under appropriate reaction conditions. The phenylethynyl system was synthesized using an ester-acid method; the ethynyl system was prepared *via* an ester-acid route using modified conditions; and the maleimide system was made *via* an amic-acid method. Fully-endcapped oligomers with essentially imidized structures and well-controlled molecular weights were achieved.

The lower molecular weight oligomers exhibited low T_gs and cure temperatures, and the resulting cured materials showed increased T_gs and higher gel fractions, but reduced toughness due to higher crosslink density.

The phenylethynyl-terminated oligomers demonstrated high cure temperatures, good melt processability and high adhesive strength suitable for application as primary adhesives. However, this system was not sufficiently reactive at moderately low temperatures ($\leq 280°C$) in neat form or even in the presence of radical initiators. In contrast, the ethynyl- and maleimide-terminated systems exhibited relatively low cure temperatures and afforded materials with high room temperature and good 177°C adhesive strength values when cured at 250°C. Thus, they are candidates for use as secondary adhesives. All cured materials investigated showed high glass transition temperatures, good short-term and thermo-oxidative stability with good solvent resistance, as judged by very high gel fractions.

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