Novel acetylene-terminated polyimide oligomers with excellent processability and high toughness of films

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ABSTRACT: A series of acetylene-terminated imide oligomers based on 2,3,3′,4′-Diphenyl ether tetracarboxylic acid dianhydride (a-ODPA), 3,4′-Oxydianiline (3,4′-ODA), and 3-Ethynylaniline (3-EA) with different molecular weights were synthesized by using acetic anhydride and triethylamine as dehydrating agent. Their main structure was confirmed by Fourier transform infrared spectroscopy (FT-IR). Thermal curing processing was characterized by FT-IR and differential scanning calorimetry (DSC). All the uncured imide oligomers showed excellent solubility (more than 30 wt %) in organic solvent such as N,N-dimethylacetamide (DMAc) and N-methyl-2-pyrrolidone (NMP). These imide oligomers also possessed a very low viscosity, thus provided better processing window. These oligomers were formulated into thermosetting films by thermal crosslinking of the ethynyl groups. The properties of cured films were evaluated by dynamic mechanical thermal analysis (DMA), thermogravimetric analysis (TGA), and tensile measurement. The glass transition temperature (T_g) and elongation at break of the cured films were found to be almost >260°C and >9.2%, respectively. The cured films in air resulted in higher thermal stability than those under N_2 atmosphere. Experimental results suggested that the introduction of asymmetric and flexible ether-hinge with 3-EA in polyimide oligomers can improve the processability of the imide oligomers and the toughness for a cured sample without sacrificing their thermal-oxidative stability. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42537.

INTRODUCTION

Aromatic polyimides have gained tremendous attention over the last 30 years due to their outstanding mechanical properties, thermal stability, and chemical resistance, as well as electrical properties.[1–5] They are commonly utilized for advanced composites in aerospace industries, thin films in electronic application, structural adhesives, and gas-separation membranes, etc.[6–9] However, these materials typically exhibit poor solubility even in dipolar aprotic solvents as well as difficulties in melt processing, which limited their widespread application.[10] Therefore, a large amount of research was carried out to improve the processability of aromatic polyimides while maintaining their outstanding properties.[11–13]

Owing to the practical demands of aerospace industries and microelectronic, many imide oligomers terminated with reactive groups have been developed. Ever since 1980s, more and more attention has been focused on the study of the phenylethynyl terminated imide oligomers which possess good processability

without the evolution of volatiles during cure processes and excellent mechanical properties after cured.[14–17] Among 4-phenylethynyl terminated imide oligomers, PETI-5 prepared from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) and two diamines has good processability and excellent mechanical properties. Moreover, the melt viscosity of PETI-5 was still too high and the glass transition temperature (T_g) of cured PETI-5 was 270°C.[18–20] Since 2000, Yokota and coworkers found a new oligomer (TriA-PI) by replacing s-BPDA with asymmetric monomer 2,3,3′,4′-biphenyltetracarboxylic dianhydride (a-BPDA). This oligomer demonstrates higher T_g, good mechanical properties, in addition to low melt viscosity.[21–23]

Although the phenylethynyl terminated imide oligomers offer the significant advantages such as a large processing window and good thermal stability, the curing temperature of those is relatively high (>350°C) which require high performance devices and high cost during processing. Considering the curing temperature of acetylene group falls in the range of 180–250°C, thermosetting acetylene-terminated polyimides have been

studied extensively since 1970s. The synthesis of 3-ethynylaniline (3-EA) terminated imide oligomers were first completed by Norman Bilow et al. in 1974.[24] Landis and Naselow[25] also have made lots of the early research. After that, the crosslinking and isomerization reactions of acetylene-terminated polyisomide oligomers were studied by different methods, such as differential scanning calorimetry (DSC),[26] Fourier transform infrared (FT-IR),[27] nitrogen-15 solids Nuclear Magnetic Resonance (^{15}N-NMR),[28] and carbon-13 magic-angle spinning Nuclear Magnetic Resonance (^{13}C-NMR).[29] Among all the acetylene-terminated polyimides, thermid MC-600 (M_w=1099 g/mol), thermid IP-600 (M_w=1099 g/mol), and thermid FA-700 (M_w=1343 g/mol) which were produced by National Starch and Chemical Corp. have been as three commercially available products. The melting range of thermid MC-600, IP-600, and FA-700 were reported to be 190–210°C, 150–170°C, and 160–180°C, respectively.[30,31] As we can see, the processing window of those polyimide were not sufficient for the resin transfer molding (RTM). Because the imidization temperature is close to the crosslinking reaction of acetylene groups. Lots of efforts have been devoted to obtain polyimides by chemical imidization process which reacts at room temperature.[32,33]

The narrow processing window and low solubility even in dipolar aprotic solvents have limited their utilization severely. Therefore, the key technological to success for acetylene-terminated imide oligomers are broadening the processing window and improving the solubility in organic solvents. An effective approach to improve the solubility of the polyimides is the incorporation of flexible links (–O–, –CH$_2$–, –CO–, –S–, etc.),[34,35] bulky pendent group[36–40] or noncoplanar and twisted monomers.[41–43] The flexible links also can reduce the T_g of the oligomers. Besides, the designation of asymmetric monomers in polyimide chain structure can improve processability.[44–46] In addition, the low melt viscosity and low melting point can also be obtained by reducing the number average molecular weight (M_n) of polyimides.

Based on the above considerations, in this article, acetylene-terminated polyimide oligomers end-capped with 3-EA were synthesized using 2,3,3′,4′-diphenyl ether tetracarboxylic acid dianhydride (a-ODPA) and 3,4′-oxydianiline (3,4′-ODA) as the monomers, 3-EA as the end-capping reagent, acetic anhydride and triethylamine as the dehydrating agent, in order to obtain oligomers with excellent processability through the combination of flexible ether-bridge chain segment with asymmetric anhydride moieties. To our best knowledge, there is no report about this kind of polyimide. Chemical structure of the oligomers was investigated using Fourier transform infrared spectrometry (FT-IR) and wide angle X-ray diffraction (WAXD). Meanwhile, the effect of the oligomers with different M_n on thermal properties, solubility, and melt viscosity was discussed in detail. Furthermore, dynamical mechanical properties, tensile properties, and the thermal properties of the cured films were also discussed in detail.

EXPERIMENTAL

Materials

2,3,3′,4′-Diphenyl ether tetracarboxylic acid dianhydride (a-ODPA), 3,4′-oxydianiline (3,4′-ODA) and 3-ethynylaniline (3-EA) were

obtained from Changzhou Sunlight Pharmaceutical Co. (Changzhou, China). Acetic anhydride and triethylamine were purchased from J&K Chemical Technology (Shanghai, China). N,N-dimethylacetamide (DMAc) and N-methyl-2-pyrrolidone (NMP) were obtained from LingFeng Chemicals Co. (Shanghai, China) and then stored over 4 Å molecular sieves for at least 1 week. DMAc and NMP were distilled under reduced pressure before use. Alcohol (99.7%) was obtained from Yang Yuan Chemical Reagent Co.

Polyimide Synthesis

Synthesis of APA End-Capped Oligomers. The acetylene terminated oligomers based on a-ODPA, 3,4′-ODA, and 3-EA with different degree of polymerization were synthesized according to a published method were synthesized according to Scheme 1. The reaction mixture was reacted at ambient condition to yield acetylene terminated amic acid oligomer. The amide acid oligomers were synthesized by the reaction of calculated stoichiometric ratios of a-ODPA and 3,4′-ODA with acetylene endcapping agent and subsequently cyclodehydrated by chemical imidization with acetic anhydride and triethylamine to obtain acetylene terminated oligomers.

Many works have showed that reducing average molecular weight by changing the stoichiometry has a profound effect on the processability of the uncured oligomers and on the thermal stability after crosslinking.[37] In this article, the influence of molecular weight on the physical and film-forming properties was studied systematically. The 3-EA terminated oligomers which had the polymerization degree of 1, 2, 4, 6, and 9 were prepared.

In a typical experiment, PI-2 which has the polymerization degree of 2 was prepared in the following procedure. 3,4′-ODA (4 g, 0.02 mol) and 15 mL DMAc were placed in a flame-dried 100 mL three-necked round-bottom flask which was equipped with nitrogen inlet, mechanical stirrer, and drying tube. After the diamine was dissolved completely, a-ODPA (9.3 g, 0.03 mol) was added and the reaction mixture was stirred at room temperature for 2 h under a nitrogen atmosphere. 3-EA (2.34 g, 0.02 mol) was added with additional DMAc to adjust the solids' concentration to 30% (w/w). The mixture was stirred at room temperature for another 4 h. Then acetic anhydride (0.12 mol, 12.25 g) and triethylamine (0.06 mol, 6.07 g) were added one by one with stirring during 12 h at room temperature. Then the solution was poured into a large excess amount of deionized water. The precipitate was collected by filtration, washed thoroughly with deionized water for three times, and ethanol for one time. At last, the product was dried under vacuum at 80°C for several hours to obtain a light gray powder (yield:13.25 g, 91%). The acetylene terminated oligomers PI-1, PI-4, PI-6, and PI-9 (the PI-degree numbers 1, 4, 6, and 9 represent the degree of polymerization of oligomers) were synthesized with an analogous procedure as described.

Preparation of the Cured Films. Thin films (0.025–0.1 mm) were cast from imide oligomer solutions in DMAc generally at 25% (w/w) solids content. The solutions were generally centrifuged, and the decantate was poured into clean, dry plate-glass and dried in a low-humidity air chamber overnight at room
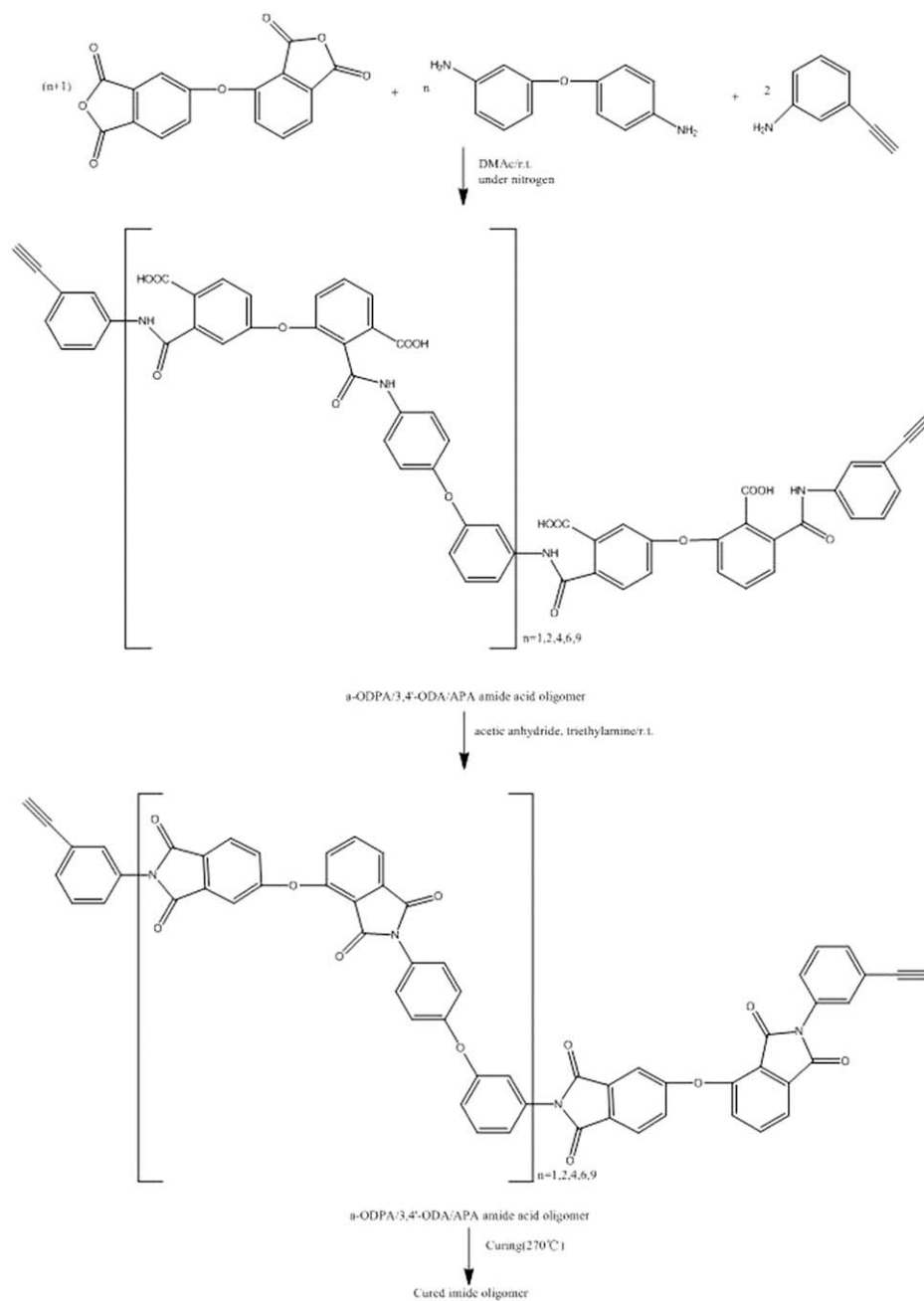
Scheme 1. Polymerization of the PI oligomers and their crosslinkings.

temperature. Then the films were stage-cured in Muffle furnace by heating for 1 h each at 80°C, 100°C, 120°C, 150°C, 180°C, 200°C, 220°C, 250°C, and 270°C. In most cases, the thin films were removed from the glass by immersion in water. Finally, the brown-colored films were cut into the specimens of $20 \times 5 \times 0.05$ mm^3.

Measurement. FT-IR (ATR) spectra were recorded on a Nicolet Nexus 8700 spectroscope with the range of 4000–400 cm^{-1}. Differential scanning calorimetry (DSC) was performed on a TA DSC Q20 at a scan rate of 20°C/min in flowing nitrogen. TGA was conducted with a Netzsch TG 209 F1 Iris carrying out on approximately 5 mg samples at a heating rate of 20°C/min

under nitrogen or air atmosphere. X-ray diffraction (XRD) measurements were carried out using a Rigaku D-max-2550 diffractometer with Cu K$_\alpha$ Radiation. Inherent viscosity was measured in DMAc at a concentration of 0.5 g/dL at 30°C using an Ubbelohde viscosimeter. Complex viscosity measurements were performed on a HAAKE MARS III Rotational Rheometer, with a fixed strain of 5% and a fixed angular frequency of 10 rad/s. Sample specimen discs of 2.0 cm diameter and 1 mm thickness were prepared by press molding the oligomer powders at $T_g - 10°C$. Complex viscosity (η^*) was measured from 100 to 270°C at a heating rate of 4°C/min under a continuous nitrogen flow. Dynamic mechanical analysis (DMA) was performed on thin film specimens ($20 \times 5 \times 0.05$ mm^3) on a dynamic
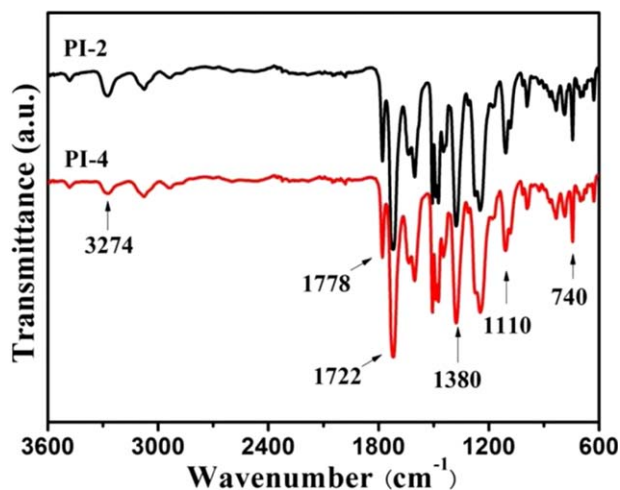
Figure 1. FT-IR spectra of acetylene terminated oligomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. Wide angle X-ray diffraction patterns of acetylene terminated oligomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mechanical analyzer (TA Q800, USA) at a heating rate of 5°C/min and a loading frequency of 1 Hz. The mechanical properties such as the tensile strength, tensile modulus, and elongation of the films at break were tested through an Instron 5567 tensile testing machine. The stress–strain curves were gathered at a cross-head speed of 50 mm/min at room temperature with the humidity set at about 50% and all of the data were collected from testing at least five tests for each kind of specimens.

RESULTS AND DISCUSSION

Characterization by IR and XRD

The FT-IR spectra of PI-2 and PI-4 were analyzed as a representative example in Figure 1. As shown in Figure 1, the strong band at 3274 cm^{-1} was associated with the acetylenic C–H stretch, and the absorptions of imide carbonyl groups (C=O) at 1778 cm^{-1} (symmetric stretching vibration), 1722 cm^{-1} (asymmetric stretching vibration), and 740 cm^{-1} (bending vibration). The absorption at 1380 cm^{-1} was assigned to C–N stretching vibration of imides rings. Moreover, the absorption at 1600 cm^{-1} was assigned to aromatic C=C. Furthermore, no peaks can be found around 1800 cm^{-1} (the C=O in isoimide ring) and 905 cm^{-1} (the C–O–C in isoimide ring), which demonstrated the imidization process didn't produce the corresponding isoimide. The above information illustrated that PI-2 and PI-4 were synthesized successfully. IR spectra of the other oligomers were similar.

The crystallinity of oligomers was examined by wide angle X-ray diffraction (WAXD). As shown in Figure 2, in which it can be seen that all oligomers were amorphous according to no crystalline peaks were observed. The non-crystallizability of these PI oligomers probably originates from the presence of the asymmetric monomers.[47]

Properties of PI Oligomers

Thermal Properties of PI Oligomers. The typical DSC curves of all uncured oligomers with different molecular weights were illustrated in Figure 3 and their thermal data were listed in Table I. All of PI oligomers had similar thermal behavior. From the first DSC scan, all the oligomers exhibited an endothermic
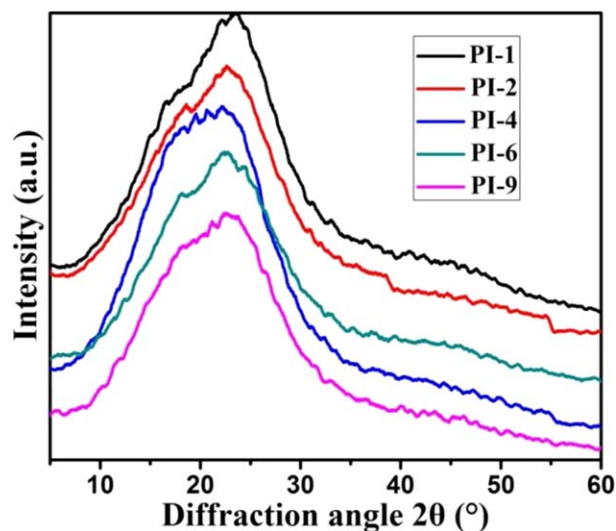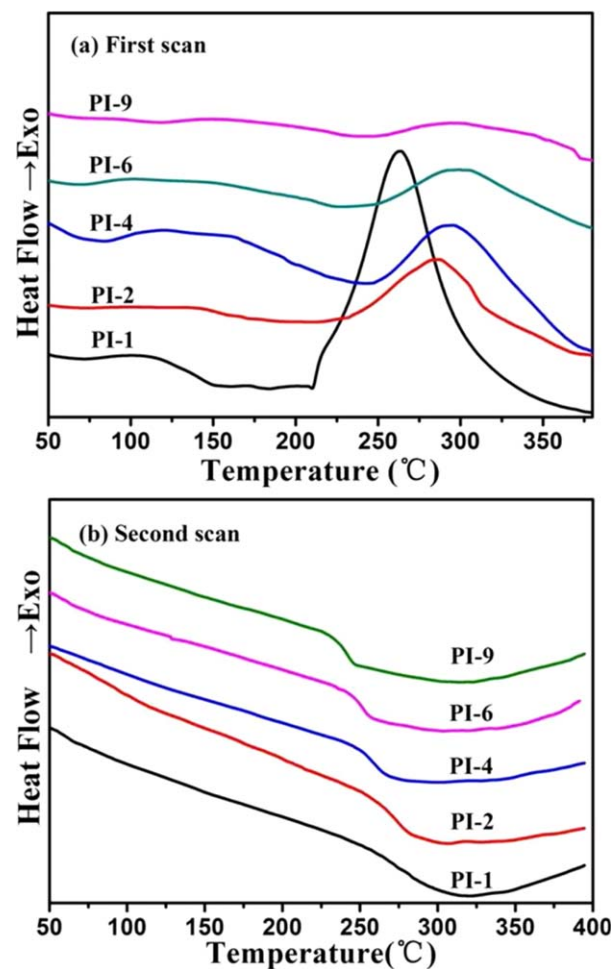
Figure 3. DSC curves of the PI oligomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Properties of PI Oligomers

				Uncured powder						
				Solubility (wt %)		DSC first run			Cured	
Samples	n	Calculated. M_n (g mol^{-1})	η_{inh} (dL/g)	DMAc	NMP	T_{g1} (°C)	T_{exo} (°C)	ΔH (kJ/mol)	T_{g2} (°C)	ΔT_g (°C)
PI-1	1	982	0.258	>30	>30	140.8	264	316.2	285	144.2
PI-2	2	1456	0.405	>30	>30	168.3	287.5	349.4	275	106.7
PI-4	4	2404	0.473	>30	>30	194.4	297.2	254.8	260	65.6
PI-6	6	3352	0.482	>30	>30	210	305.6	318.4	252	42
PI-9	9	4774	0.579	>30	>30	220	299	367.6	242	22

T_{g1}: glass transition temperature of the oligomers determined on powdered sample by DSC at a heating rate of 20°C/min in the first run. T_{g2}: glass transition temperature of the oligomers determined on powdered sample by DSC at a heating rate of 20°C/min in the second run. T_{exo}: the temperature of exothermic peaks on DSC curves. $\Delta T_g = T_{g2} - T_{g1}$. η_{inh}: measured at a concentration of 0.5 g/L in DMAc at 30°C.

shift (T_g) in the range of 140–220°C and a large exothermic peak with maximum around 264–306°C which attributed to the thermal curing of the ethynyl groups. Meanwhile, the rate of crosslinking was very fast. PI-6 and PI-9 did not show obvious exothermal absorptions as PI-1, PI-2, and PI-4, probably because of the low concentrations of the acetylene-terminated groups in the oligomers. From the second DSC heating scan, a higher glass transition temperature (T_g) ranging from 242°C to 285°C was observed, and the exothermic peak of thermal curing was disappeared. With the molecular weight increasing, the uncured oligomers showed an increasing trend in T_g, but the cured oligomers showed a decreasing trend in T_g. ΔT_g ($T_{g2}-T_{g1}$) varied from 22–145°C according to the polymerization degree and the content of ethynyl groups. It was found that PI-1 and PI-2 provided a wide processing temperature window between T_g and the cure exothermal. There was no melt endothermic peak observed, implying that amorphous nature of the oligomers. This conclusion was consistent with the XRD results.

Processability of Imide Oligomers

The data of intrinsic viscosity were listed in Table I. The intrinsic viscosities of the imide oligomers were in the range of 0.25–0.58 dL/g. The solubility properties of the imide oligomers were

Figure 4. Complex melt viscosity of imide oligomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

investigated by dissolving 0.3 g oligomer powder in 0.7 g organic solvent. The results can be seen in Table I, all oligomers were completely soluble in NMP or DMAc solution with high concentration even at room temperature (>30 wt %). These data were attributed to the decrease in the intermolecular interactions of the oligomers from a-ODPA and 3,4′-ODA which all have helical chains and the introduction of flexible links. The good solubility of oligomers played an important role in processing.

For the RTM, the complex melt viscosity of imide oligomers must be low. Melt viscosity measurements of the oligomers were carried out, the viscosity-temperature curves of the oligomers were displayed in Figure 4. The minimum melt viscosity of imide oligomers was listed in Table II. As can be seen, the oligomers initially showed the viscosity decrease until the minimum, and then increased continuously with the temperature increasing because of the crosslinking reaction of acetylene groups. Furthermore, all the minimum melt viscosities were much lower than the reported oligomers, such as the minimum melt viscosity of PETI-5 was 60,000 Pas at 371°C and the minimum melt viscosity of TriA-PI was 1000 Pas at 320°C. In particular, the melt viscosity of PI-1 was below 10 Pas in the range 130–182°C with minimum only 0.6 Pas at 159°C, resulting in distinct improvements in the processability of thermosetting PI resin for molding fiber-reinforced composites. The flexible ether linkages in a-ODPA and 3,4′-ODA possess improved conformational freedom in the polyimide maintain and contribute to a reduction in viscosity. The asymmetric monomers of a-ODPA and 3,4′-ODA reduces the efficiency of chain packing also leading to reduced viscosity at the processing temperature.[48] The low-weight oligomers made positive contribution towards achieving a low-melt viscosity, it will provide a broader processing window. a-ODPA/3,4′-ODA/3-EA oligomers displayed excellent low-melt viscosity was conceivably attributed to the much
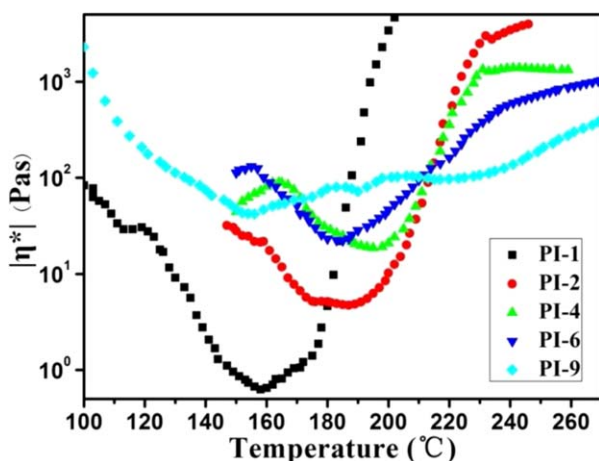
Table II. Minimum Melt Viscosity of PI Oligomers

| Oligomer	PI-1	PI-2	PI-4	PI-6	PI-9
η^*_{min}/T (Pas/°C)	0.6 at 159	4.77 at 186	18.81 at 195	22.1 at 185	41.3 at 153
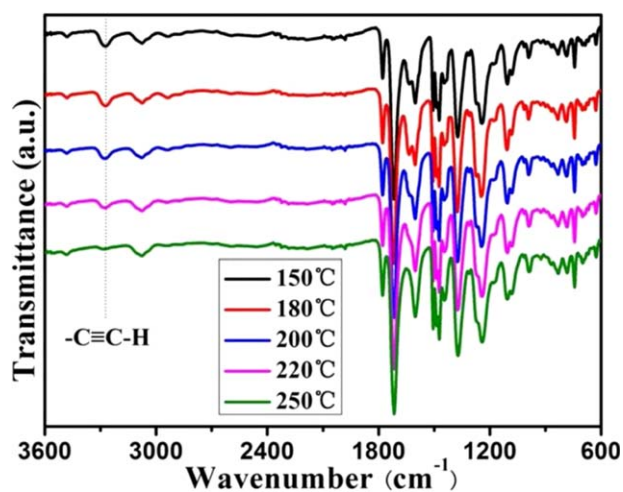
Figure 5. FT-IR spectra of PI-2 oligomer at different temperatures for 1 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

weak intermolecular interaction by the incorporation of asymmetric monomers and aryl ether structures.

In summary, a-ODPA/3,4′-ODA/3-EA oligomer had a high solubility in dipolar aprotic solvents such as DMAc and NMP and a low melt viscosity attributable to its asymmetric and flexible structures. The result had made a positive effect on using RTM which required wetting and good flow.

Crosslink Characterization

The crosslink reaction of acetylene end group was monitored by spectroscopy as illustrated by PI-2. FT-IR spectra of PI-2 oligomer before and after thermally cured at different temperatures for 1 h were shown in Figure 5. FT-IR spectra of PI-2 oligomer before and after thermally cured at different time in 250°C were shown in Figure 6. When cured in 250°C, the
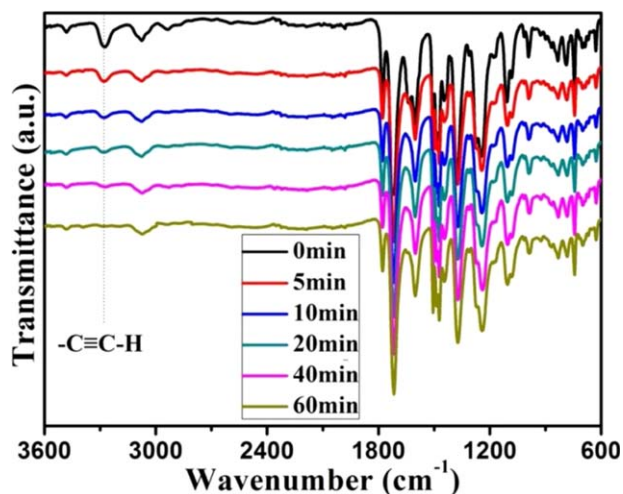
Figure 6. FT-IR spectra of PI-2 oligomer at different time with 250°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
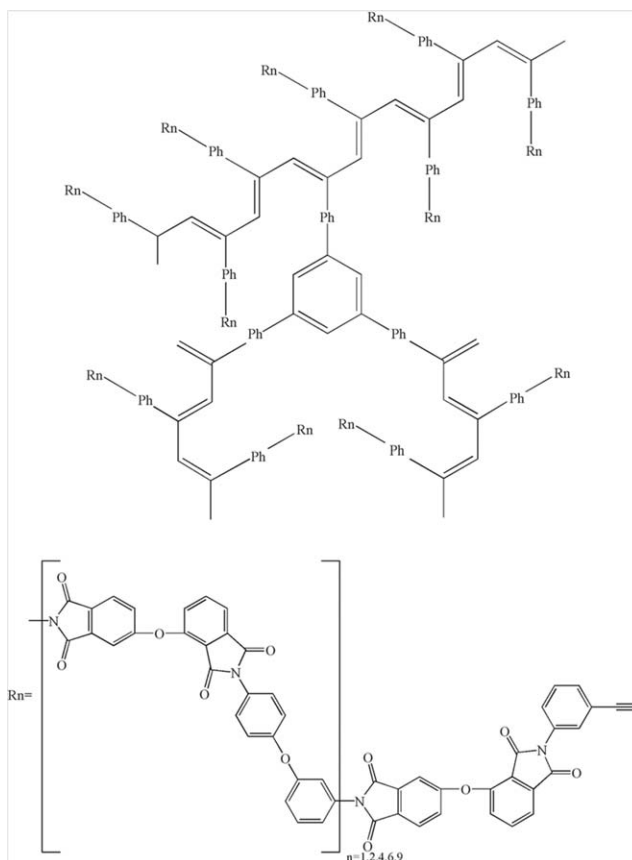
Scheme 2. Proposed chemical structure of partially cured polyimide.

absorption of the C–H in ethynyl group at 3274 cm^{-1} decreased gradually and almost disappeared after 60 min, which demonstrated the accomplishment of thermal cure reaction and the rate of crosslinking was very fast. As can be seen from Scheme 2, the major reaction was the simple ethynyl to ethynyl reaction to form cured polyene structures, branched structures, and partial benzene ring structures.

Thermal and Mechanical Properties of Cured Films

Dynamical Mechanical Properties. The T_g values of the cured films were evaluated by DMA. The peak temperatures of the tan δ were considered as the T_g values of the cured films, and the data were summarized in Table III. The DMA curves of the cured PI-1 film as a function of temperature were showed as a representative example in Figure 7. Figure 8 shows the DMA curves (modulus as a function of temperature) of cured PI (n=1, 2, 4, 6, and 9) films. Moreover, the T_g values of cured oligomer films decreased gradually with the increasing molecular weight because of lower crosslink density. The result was similar with that obtained by DSC curves. The film prepared by PI-9 gave the T_g of 252°C, which was 73°C lower than that for PI-1, probably because the content of ethynyl groups in PI-9 were much lower than that in PI-1.

Tensile Properties. The room temperature tensile properties of cured oligomer films were presented in Table III. All data were obtained from the homogeneous brown-colored films. All cured

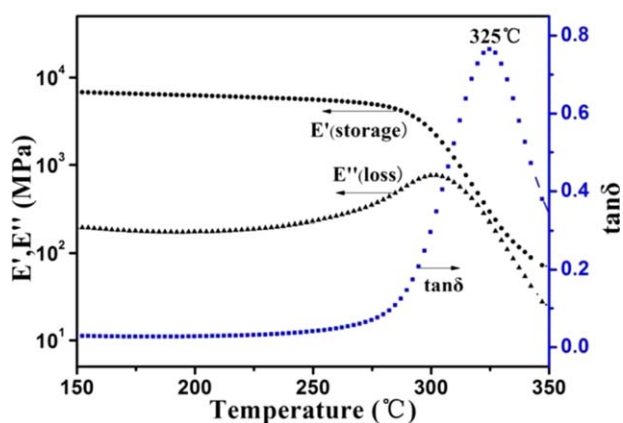**Table III.** Properties of the Cured Films from Oligomers

		Cured film properties									
	DMA	TGA(N_2)				TGA(air)			Tensile properties		
Samples	T_{g3} (°C)	T_d	T_{d5} (°C)	T_{d10} (°C)	R_w (%)	T_d	T_{d5} (°C)	T_{d10} (°C)	Strength (MPa)	Modulus (GPa)	Elongation (%)
PI-1	325	472	468	512	62.9	587	436	524	25	2.11	2.8
PI-2	293	508	497	535	59.1	571	491	550	51	2.39	9.2
PI-4	270	502	493	532	56.5	574	487	539	66	2.12	12.8
PI-6	262	494	505	534	54.1	566	503	547	97	2.35	14.9
PI-9	252	478	490	523	54.8	561	491	542	47	1.9	13.5

T_{g3}: glass transition temperature of the oligomers determined on cured film by DMA. T_d: the onset decomposition temperature in N_2 or air atmosphere. T_{d5}: 5% weight loss temperature in N_2 or air atmosphere. T_{d10}: 10% weight loss temperature in N_2 or air atmosphere. R_w: residual weight retention at 800°C.
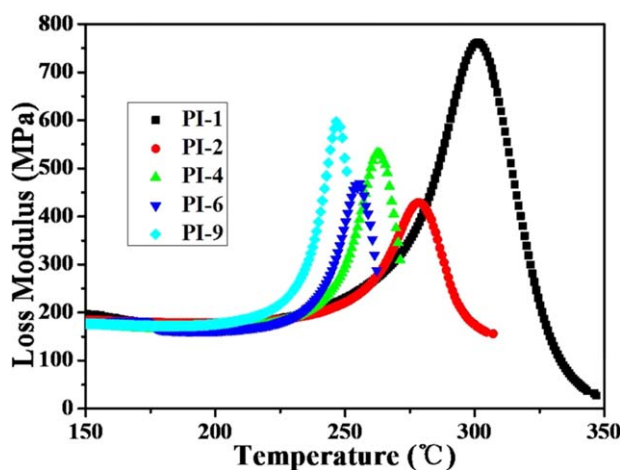
3-EA end-capped oligomer films possessed relatively lower tensile strength at break (25–97 MPa), but the modulus values were always more than 2.0 GPa. Surprisingly, the values of

Figure 7. DMA curves of cured PI-1 film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

elongation at break were more than 9.2% except PI-1, indicating that the cured films exhibited excellent fracture toughness. The excellent fracture toughness of cured films was clearly attributed to the introduction of ether structures into oligomers. Because the film prepared by PI-1 with lower molecular weight had higher crosslink density, it was easy to break. These data showed that the cured films prepared by PI-6 possessed the best tensile properties, with a tensile strength of 97 MPa and a modulus of 2.35 GPa, and elongation 14.9%.

Thermal Stability. The thermal and thermal-oxidative stability of cured films were measured by TGA under N_2 and air atmosphere. The thermal data of the cured films were summarized in Table III and the thermal stability behavior was illustrated by PI-6 in Figure 9. The temperatures of 5% weight loss in N_2 atmosphere were all above 468°C, the char yields reported at 800°C in N_2 atmosphere were all above 54%. Surprisingly, the T_d and T_{d10} value of all the cured films in N_2 were much lower than in air which may caused by the unreacted ethynyl moieties were oxidized and made crosslinks.[38,49,50] Therefore, the cured films exhibited better thermal stability, especially thermal-oxidative stability.

Figure 8. DMA curves of PI oligomer (n=1,2,4,6,9) films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]
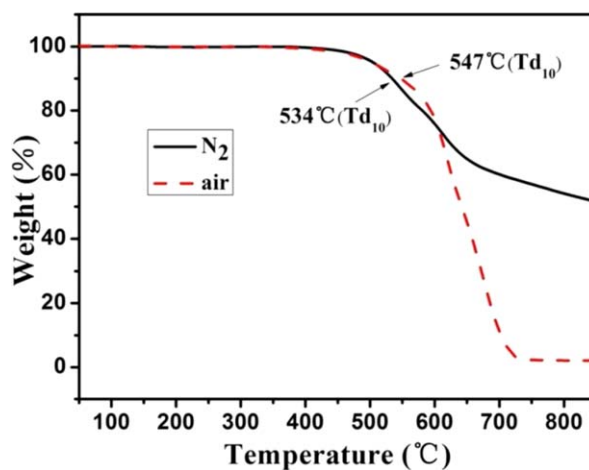
Figure 9. TGA curves of the fully cured PI-6 film in N_2 and air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conclusions

In this work, a series of acetylene-terminated polyimide oligomers based on a-ODPA and 3,4′-ODA were successfully synthesized. As a result of introduction of asymmetric monomers and flexible ether-bridge structures, the polyimide oligomers exhibited a high solubility, lower viscosity, and excellent toughness after cured. All the oligomers can be easily dissolved in DMAc or NMP with concentration as high as 30% (w/w), which greatly facilitated the processing of wetting prepreg. Rheometer study showed the minimum melt viscosity of PI-1 and PI-2 was very low. Low-melt viscosity is highly desired for high quality composites fabrication. Furthermore, as confirmed by FT-IR spectra, the accomplishment of thermal cure process needed 60 min. All the polyimide oligomers can be made into films and the films possessed better thermal stability and tensile properties. Meanwhile, PI-6 offered the best value of elongation at break. Moreover, the onset decomposition temperature and 10% weight loss temperature of all the cured films were much higher in air than that in N_2. We believe that these excellent properties of a-ODPA/3,4′-ODA/3-EA oligomers suggest promising potential for application to be used as low-temperature curing but high-temperature using composites or adhesive.

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