

Synthesis and Characterization of Phenylethynyl-terminated Polyimide Oligomers Derived from 2,3,3',4'-Diphenyl Ether Tetracarboxylic Acid Dianhydride and 3,4'-Oxydianiline*

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Abstract With the goal of improving processability of imide oligomers and achieving high toughness of thermosetting polyimides, a series of 4-phenylethynylphthalic anhydride (PEPA)-terminated imide oligomers prepared by the reaction of 2,3,3',4'-diphenyl ether tetracarboxylic acid dianhydride (a-ODPA) and 3,4'-oxydianiline (3,4'-ODA) with different molecular weights (degree of polymerization: $n = 1-9$) were formed. The resultant oligomers with different molecular weights were characterized for their chemical architecture, cure behavior, thermal properties, solubility in organic solvents and rheological characteristics. Besides, the thermal properties and tensile test of cured polyimide films were also evaluated. The imide oligomer (degree of polymerization: $n = 1$) has some somewhat crystalline phase, and imide oligomers (degree of polymerization: $n = 2-9$) showed excellent solubility (40 wt%) in *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc) at room temperature. Furthermore, the rheological properties of imide oligomers showed very low melt viscosity and wider processing window. The cured films exhibited good thermal properties with the glass transition temperatures of 282–373 °C and 5 wt% thermal decomposition temperatures higher than 551 °C in nitrogen atmosphere. The elongation at break of the prepared films was found to be high (almost > 9.3%).

Keywords: Polyimide; Imide oligomer; Processability; Film.

INTRODUCTION

Because of their outstanding mechanical properties, thermal stability, and chemical properties, aromatic polyimides are considered to be a typical well-established high-performance polymer with a wide range of applications over past 30 years^[1–3]. They can be widely used as structural adhesives, gas-separation membranes, thin films in electronic application, and advanced composites in aerospace industries, *etc.*^[4–7]. However, the paramount challenge in the pursuit of novel polyimides is the poor processability (high melt viscosity and limited solubility in organic solvents) in comparison with that of bismaleimides and epoxies, which has limited their widespread application^[8, 9]. It is highly desirable to search for strategy to improve the processability of aromatic polyimides while maintaining their excellent properties.

Owing to the practical demands from the aerospace industries and microelectronics, more and more emphases have been laid on addition-type polyimides which terminated with reactive groups. In the early 1970s, PMR-15 prepared from the reacting of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 4,4'-methylene dianiline with a nadic acid derivative for the reactive end cap is the first generation of PMR type polyimide

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developed by NASA Langley Research Center. PMR-15 is well known as a polyimide with cured glass transition temperature (T_g) > 300 °C, but the resin is brittle and the release of volatiles during processing can result in pin holes in the composites^[10, 11].

Ever since 1980s, more and more attention focused on the study of phenylethynyl terminated imide oligomers, because these oligomers possess favorable processability and no volatiles are formed during the curing reaction. Many researchers, especially in NASA Langley Research Center, have studied various kinds of phenylethynyl terminated imide oligomers^[12–15]. Among them, PETI-5 prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) and two diamines has high fracture toughness (elongation at break > 30%) and high thermo-oxidative stability. However, the high melt viscosity of PETI-5 oligomer and a relatively low T_g of 270 °C for cured resin have limited its application^[13].

Since 2000, Yokota *et al.* developed a novel 4-phenylethynylphthalic anhydride (PEPA)-terminated oligomer (TriA-PI) based on 2,3,3',4'-biphenyltetracarboxylic dianhydride (2,3,3',4'-BPDA) and 4,4'-oxydianiline (4,4'-ODA)^[16]. This oligomer exhibited higher T_g , improved solubility and reduced melt viscosity than those of symmetric 3,3',4,4'-BPDA, which are attributed to 2,3,3',4'-BPDA having asymmetric and non-planar structures. It is a pity that TriA-PI with the imide form is insufficiently soluble. However, when TriA-PI is fabricated by routing an amide acid solution prepreg, the evolution of water caused by the imidization of the amide acid oligomers during fabrication can create voids in the composites. Hence, to achieve the imide oligomers with high solubility in organic solvents in their fully imidized form and good processability, many research efforts have been devoted. Many efficient approaches have been taken to improve the processability, such as the incorporation of flexible links ($-O-$, $-CO-$, $-CH_2-$, $-S-$, *etc.*)^[17, 18], bulky pendent group^[19], branched^[20], noncoplanar and twisted monomers^[21, 22], and a hybrid organic-inorganic approach^[23]. Besides, the designation of geometrically asymmetric monomers in polyimide chain structure can improve processability^[24]. A lot of works also showed that the processability of uncured imide oligomers was critically dependent on the molecular weight of the system^[25, 26].

According to literatures, Gerber *et al.* first presented polyimides based on isomeric 2,2',3,3'-, 2,3,3',4'-, and 3,3',4,4'-oxydiphthalic dianhydrides (ODPA), the results showed that the polyimide from more asymmetric 2,3,3',4'-ODPA was more soluble than that from less asymmetric 3,3',4,4'-ODPA^[27]. Many works have found that polyimides based on 2,3,3',4'-BPDA exhibited better solubility, lower melt viscosity and higher T_g than the corresponding 3,3',4,4'-BPDA based polyimides^[6, 28]. In 2003, Fang and the coworkers also have found that polyimides prepared from 2,3,3',4'-benzophenonetetracarboxylic dianhydride (BTDA) had higher glass transition temperature and better solubility without sacrificing their thermal properties, lower melt viscosity and wider melt flow region compared with those from 3,3',4,4'-BTDA^[29]. Recently, 3-ethynylaniline (3-EA) terminated imide oligomers based on 2,3,3',4'-ODPA and 3,4'-ODA were developed in our group. These polyimide oligomers exhibited a high solubility, lower viscosity and excellent toughness after curing^[30]. However, the phenylethynyl terminated imide oligomers can offer a large processing window and good thermal stability.

On the basis of the above rationale, in this paper, phenylethynyl-terminated polyimide oligomers terminated with PEPA were synthesized using 2,3,3',4'-ODPA and 3,4'-ODA as the monomers. It was expected that the uncured oligomers with excellent processability could be obtained through the combination of flexible ether-bridge chain segments with geometrically asymmetric moieties. The polyimides from 2,3,3',4'-ODPA and 3,4'-ODA with different molecular weights have been investigated systematically in the literature. Molecular weights, chemical structure, crosslink characterization and crystallinity of the oligomers were investigated using gel permeation chromatography (GPC), Fourier transform infrared spectrometry (FTIR) and wide angle X-ray diffraction (WAXD). In addition, the effect of the oligomers with different molecular weights on thermal properties, solubility, melt viscosity was discussed in detail. Furthermore, dynamical mechanical properties, thermal properties and tensile properties of the cured films were also discussed in detail. The outstanding properties exhibited by 2,3,3',4'-ODPA based polyimides demonstrated a promising potential for future advanced composites and structural adhesives.

EXPERIMENTAL

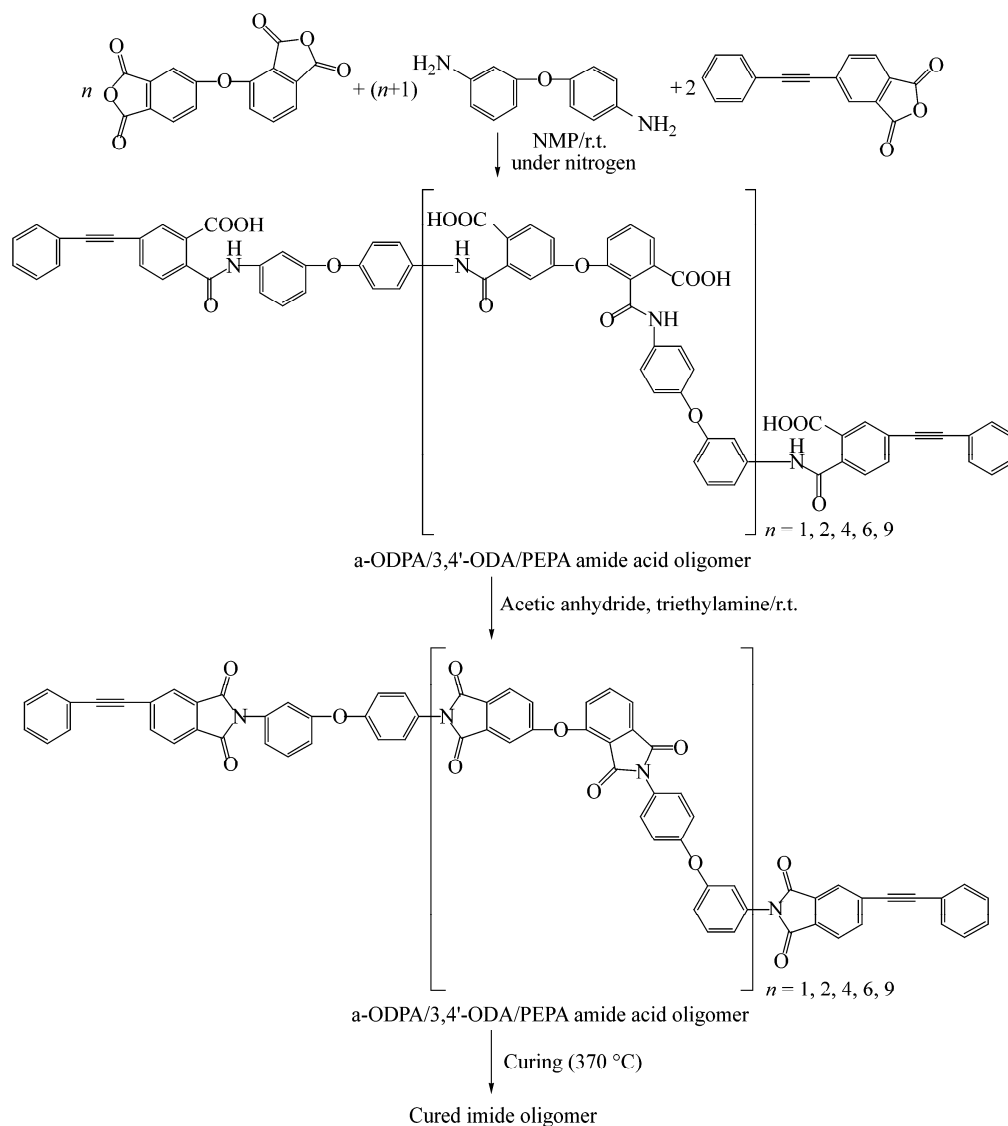
Materials

2,3,3',4'-Diphenyl ether tetracarboxylic acid dianhydride (a-ODPA, 99.64%), 3,4'-oxydianiline (3,4'-ODA, 99.92%) and 4-phenylethynylphthalic anhydride (PEPA, 99.94%) were obtained from Changzhou Sunlight Pharmaceutical Co., Ltd. (Changzhou China). Acetic anhydride (98.5%) and triethylamine (99%) were purchased from J&K Chemical Technology (Shanghai China). *N*-Methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc) were acquired from Ling Feng Chemicals Co., Ltd. (Shanghai China) and purified by vacuum distillation over P₂O₅ prior to use. Other solvents were all used as received from their respective vendors and without further purification.

Experimental Method

Synthesis of PEPA terminated oligomers

Scheme 1 represents the synthetic route used to prepare the oligomers and their cured polymers. The phenylethynyl terminated oligomers based on a-ODPA and 3,4'-ODA with different calculated molecular



Scheme 1 Polymerization of the imide oligomers and their crosslinkings

weights were synthesized by chemical imidization process. The nomenclature, monomer content and calculated molecular weight for the oligomers synthesized in this report are shown in Table 1. The PI-degree values 1, 2, 4, 6, 9 represent the the calculated polymerization degree of oligomers.

Table 1. Oligomer nomenclature and equivalents of monomers used in each of their syntheses

Compounds	Cald. n	a-ODPA	3,4'-ODA	PEPA	Cald. M_n (g/mol)
PI-1	1	1	2	2	1130
PI-2	2	2	3	2	1610
PI-4	4	4	5	2	2560
PI-6	6	6	7	2	3500
PI-9	9	9	10	2	4930

In a typical experiment, PI-6 which has the polymerization degree of 6 was prepared in the following procedure. 3,4'-ODA (7 g, 0.035 mol) and 30 mL NMP were placed in a flame-dried 250 mL three necked round-bottom flask which was equipped with nitrogen inlet and magnetic stirrer. 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 6 h under a nitrogen atmosphere. PEPA (2.48 g, 0.01 mol) was added with additional NMP to adjust the reaction mixture with 20 wt% of solid content. The mixture was stirred at room temperature for another 24 h. Then acetic anhydride (0.105 mol, 10.7 g) and triethylamine (0.105 mol, 10.6 g) were added one by one with stirring during 5 h at 60 °C. 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 until the PH value of the filtrate reached about 7. At last, the product was dried under vacuum at 60 °C for 24 h, 150 °C for 6 h to obtain a light gray powder (yield: 16.64 g, 95%). The PEPA terminated oligomers PI-1, PI-2, PI-4 and PI-9 were synthesized with an analogous procedure described.

Films fabrication

As described in previous reports^[31], thin films (0.06–0.15 mm) were cast from imide oligomer solutions in NMP generally at 20 wt% solid content. The solutions were generally centrifuged, and the decantates were poured and spread onto level, clean, dry plate-glass and dried in a low-humidity air chamber overnight at room temperature. Then the films were stage-cured in a circulating air oven by heating for 1 h each at 100 °C, 150 °C, 230 °C, 350 °C, and 370 °C. In most cases, the thin films were removed from the glass by immersion in water. Finally, the dark red films were cut into specimens of 25 mm × 4 mm × 0.1 mm for thermal and mechanical testing.

Characterization methods

GPC measurements were performed using a Waters GPC system equipped with a Waters 515 high performance liquid chromatography (HPLC) pump, a Waters 2414 differential refractometer, and three Styragel columns (HT-3, HT-4, and HT-5) with dimethylformamide as the eluent at a flow rate of 1.0 mL/min at 35 °C.

FTIR were recorded on a Nicolet Nexus 8700 spectroscope with the range of 4000–400 cm⁻¹ to characterize the chemical structure of oligomers and monitor the crosslink characterization.

WAXD measurements were carried out using a Rigaku D-max-2550 diffractometer with Cu K α Radiation.

Imide oligomer PI-1 was dissolved in NMP and cast into about 0.25 mm film on glass cover slides by evaporating NMP at 150 °C. The films were then observed under crosspolarized light using an Olympus BX51-P optical microscope at 30 °C.

Differential scanning calorimetry (DSC) was performed on a TA DSC Q20 thermal analyzer with a cell nitrogen purge of 50 mL/min. Each oligomer was scanned twice. The sample powder sealed in an aluminum pan was heated to 500 °C at a heating rate of 20 K/min for the first scan run to observe its thermal curing behavior. After quenched to room temperature, the second scan run of the identical sample was carried out for measuring the T_g value of the cured resin from 30 °C to 500 °C at a heating rate of 20 K/min.

Inherent viscosity was measured in NMP at a concentration of 0.5 g/dL at 30 °C using a Ubbelohde viscosimeter.

Solubility of oligomer powder was determined by dissolving oligomer powder in NMP and DMAc with 40 wt% at room temperature for 24 h.

The rheological characteristics of the oligomers were performed on a HAAKE MARS III Rotational Rheometer, with a fixed strain of 5% and a fixed angular frequency of 10 rad/s. To prepare the sample specimen discs of 2.0 cm diameter and 1.5 mm thickness, 60 mg of each oligomer powder was consolidated in a circular mold of equivalent diameter in a pressure of 5 MPa with the mold cavity, at room temperature. Two different experiments were performed. First, melt viscosity of the oligomers was measured from 150 °C to 380 °C at a heating rate of 4 K/min under a continuous air flow to ascertain the temperature influence on viscosity. Subsequently, the isothermal viscosities of PI-4 were also measured at 280 °C, 300 °C and 320 °C.

The T_g of cured films was determined by dynamic mechanical analysis (DMA Q800). The specimens with the dimensions of 25 mm × 4 mm × 0.1 mm (length × width × thickness) were held by vertical clamps subjected to tensile modes. Measurements were conducted over a range of 50 °C to 400 °C at a heating rate of 5 K/min and a loading frequency of 1 Hz.

The mechanical properties such as the tensile strength, tensile modulus and elongation at break of the films 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%. All of the data were collected from testing at least five tests for each kind of specimens, and the averages were reported.

Thermogravimetric analysis (TGA) was conducted with a Netzsch TG 209 F1 Iris instrument carrying out on approximately 5 mg samples at a heating rate of 20 K/min under nitrogen and air atmosphere at a purge rate of 20 mL/min.

RESULTS AND DISCUSSION

Characterization of Imide Oligomers

GPC analyses were performed on a series of imide oligomers to assess the number average molecular weights (M_n), the weight average molecular weights (M_w), and polydispersities (M_w/M_n) with the data presented in Table 2. The number average molecular weights of the oligomers determined by GPC were in accordance with the trend of designed molecular weight but greater than the calculated number average molecular weights with polydispersities of 1.21–1.63.

Table 2. Molecular weight of the oligomers from a-ODPA/3,4'-ODA/PEPA with different Cald. M_n

Compounds	Cald. M_n (g/mol)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
PI-1	1130	4260	5420	1.27
PI-2	1610	4780	5770	1.21
PI-4	2560	5960	9080	1.52
PI-6	3500	9140	14870	1.63
PI-9	4930	10890	17630	1.62

The FTIR spectra of phenylethynyl terminated oligomers are shown in Fig. 1. It can be seen that all the oligomers with different molecular weights exhibited the similar absorptions. The strong band at 2212 cm^{-1} was associated with the terminated phenylethynyl $\text{C}\equiv\text{C}$. The appearances of characteristic imide carbonyl groups ($\text{C}=\text{O}$) at 1778 cm^{-1} (symmetric stretching vibration), 1717 cm^{-1} (asymmetric stretching vibration), and characteristic imide bands at 1373 cm^{-1} ($\text{C}-\text{N}$ stretching vibration), 743 cm^{-1} (bending vibration) were observed. In addition, the imidization process didn't produce the corresponding isoimide due to the absence of the characteristic peaks of isoimide around 1800 cm^{-1} (the $\text{C}=\text{O}$ in isoimide ring) and 905 cm^{-1} (the $\text{C}-\text{O}-\text{C}$ in isoimide ring) in FTIR spectra. Moreover, the absorption at 1600 cm^{-1} was assigned to aromatic $\text{C}=\text{C}$. The above information illustrates that the oligomers have the expected chemical structures.

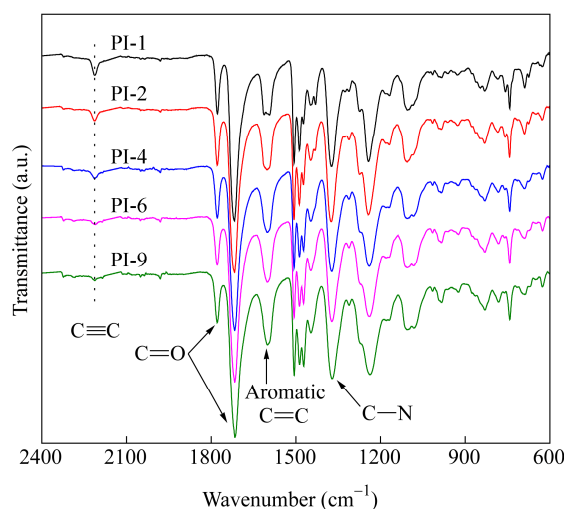


Fig. 1 FTIR spectra of phenylethynyl terminated oligomers

FTIR spectra were also used to compare the chemical structure changes upon curing. Figure 2 compares the crosslink reaction of phenylethynyl terminated group as illustrated by PI-2. It can be seen that the absorptions at about 2210 cm^{-1} assigned to the stretching vibrations of the terminated phenylethynyl $\text{C}\equiv\text{C}$ were decreased gradually and consumed totally within 60 min at $370\text{ }^{\circ}\text{C}$, implying the accomplishment of thermal cure reaction. The imide carbonyls at 1776 cm^{-1} and 1718 cm^{-1} remained constantly during the thermal cure process.

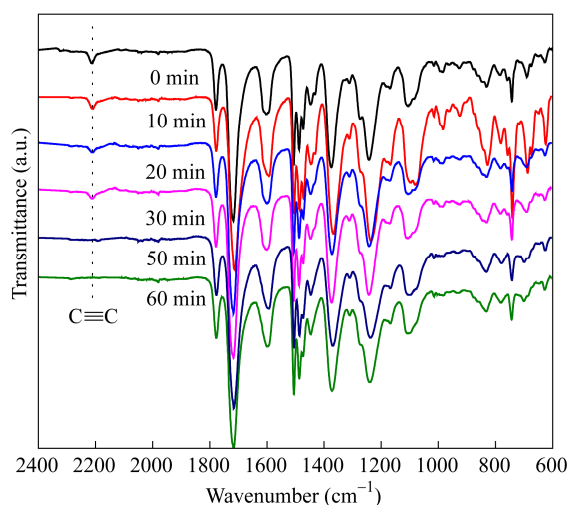


Fig. 2 Variations of FTIR spectra of PI-2 heat-treated at $370\text{ }^{\circ}\text{C}$

The WAXD patterns of the phenylethynyl terminated oligomers are shown in Fig. 3. There were no crystalline peaks observed in patterns of PI-2, PI-4, PI-6 and PI-9, which were attributed to the presence of the asymmetric monomers^[32]. While the pattern of PI-1 showed small amounts of sharp peaks in the 2θ angle of 18° – 30° . Furthermore, from the insert in Fig. 3, crystals of PI-1 imide oligomer film were observed at $30\text{ }^{\circ}\text{C}$ by optical microscope, which indicated somewhat crystalline phase in that oligomer^[33]. The semicrystalline behavior of PI-1 probably due to one unit of the imide oligomer and the flexibility of molecular chains^[34].

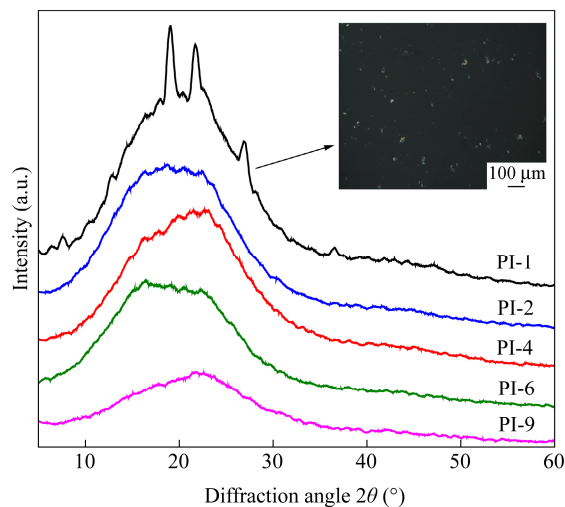


Fig. 3 Wide angle X-ray diffraction patterns of phenylethynyl terminated oligomers (The optical microscopy image of PI-1 imide oligomer film at 30 °C is observable in the inset.)

Thermal Properties of PI oligomers

The typical DSC curves of a-ODPA/3,4'-ODA/PEPA uncured imide oligomers ($n = 1-9$) are shown in Fig. 4 and their thermal data are listed in Table 3. From the first DSC scan, it was found that all the oligomers exhibited an endothermic shift (T_g) in the range of 147–198 °C and a large exothermic peak with maximum around 383–447 °C which was attributed to the thermal curing of the phenylethynyl groups. Results showed that the imide oligomers of lower molecular weight have lower initial T_g and a large exothermic peak with maximum. Exothermic enthalpy (ΔH) increased as the content of phenylethynyl groups increased. In comparison, an endothermic peak of PI-1 at 214 °C was attributed to the melting of the oligomer, and other oligomers revealed no distinct melting peaks, which were consistent with the WAXD results. Meanwhile, the T_g values of a-ODPA/3,4'-ODA/PEPA imide oligomers were low, and they could melt at a low temperature. Exothermic enthalpy (ΔH) increased as the content of phenylethynyl groups increased. From the second DSC heating scan, it was found that all the exothermic peak of thermal curing disappeared, and each sample was fully cured. Meanwhile, the T_g values of cured polyimides were in the range of 265–319 °C. The T_g values determined in the second DSC heating scan was higher than those in the first scan.

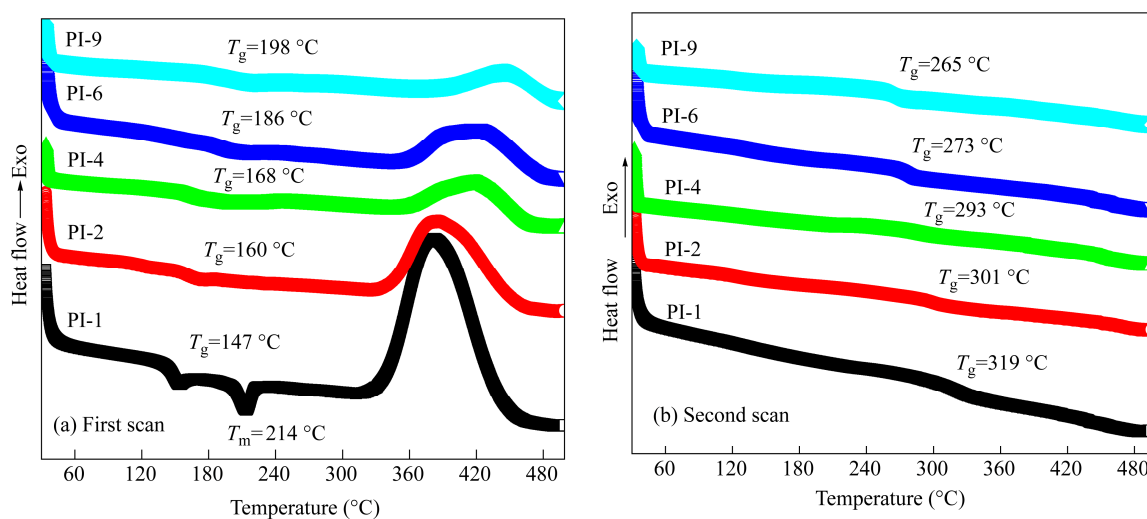


Fig. 4 DSC curves of phenylethynyl terminated oligomers: (a) first scan and (b) second scan

Table 3. Properties of the oligomers from a-ODPA/3,4'-ODA/PEPA

Table 1. Properties of the oligomers from A: CBTMS, B: CBTETA, C: CBTEPA										
Compounds	η_{inh} (dL/g)	Uncured powder							Cured T_{g2}^e (°C)	ΔT_g (K)
		Solubility (wt%)		DSC first run						
		NMP	DMAc	T_{g1}^a (°C)	T_m^b (°C)	T_{onset}^c (°C)	T_{exo}^d (°C)	ΔH (J/g)		
PI-1	0.064	< 3	< 3	147	214	339	383	298	319	172
PI-2	0.088	40	40	160	ND	344	388	155	300	140
PI-4	0.103	40	40	168	ND	356	423	133	293	125
PI-6	0.125	40	40	186	ND	363	423	97	273	87
PI-9	0.167	40	40	198	ND	390	447	55	265	67

^a Glass transition temperature of the oligomers determined on powdered sample by DSC in the first run; ^b The melting peak of oligomers; ^c Onset crosslink temperature of the oligomers; ^d The temperature of exothermic peaks on DSC curves; ^e glass transition temperature of the oligomers determined on powdered sample by DSC in the second run; $\Delta T_g = T_{g2} - T_{g1}$; ND: the data were not detected

Processability of Imide Oligomers

The data of inherent viscosity are listed in Table 3. The inherent viscosities of the imide oligomers were in the range of 0.064–0.167 dL/g. As expected, the inherent viscosities increased with the increase of molecular weights.

The solubility properties of the PI oligomers with different molecular weights were tested in NMP and DMAc with 40 wt%, which was placed and stirred for 24 h at room temperature, and the results were summarized in Table 3. It was found that PI-1 with a molecular weight 1134 g/mol had poor solubility, probably due to a certain crystalline phase originating from one unit of the imide oligomer and by-products of PEPA/3,4'-ODA, as proven by WAXD and DSC. In addition, PI-2, PI-4, PI-6 and PI-9 exhibited excellent solubility, which could be easily dissolved in NMP and DMAc with concentrations as high as 40 wt%. It is a steric hindrance due to the 2- and 3'-positions of the oxydiphthalic dianhydrides occupied by imide groups. The improved solubility of PI-2, PI-4, PI-6 and PI-9 were attributed to the decrease in the intermolecular interactions of the oligomers from a-ODPA and 3,4'-ODA which all have asymmetric architectures and the introduction of flexible links.

The fabrication of high-performance advanced composite materials is preferably by resin transfer molding (RTM), which requires a resin with low and stable melt viscosity during fabrication process. Low viscosity is a crucial character. The melt viscosity for a-ODPA/3,4'-ODA/PEPA imide oligomers as a function of temperature is displayed in Fig. 5. The data of temperature scale with $\eta^* < 10$ Pa·s and the minimum melt viscosities are listed in Table 4. It could be seen that the melt viscosity of all the oligomers declined and finally reach the minimum point with the rise in temperature at first, and then ascended sharply as the temperature increased. It was also found that imide oligomers could be melt in relatively low temperatures which reduced the demand of devices. The minimum melt viscosities of oligomers PI-1, PI-2, PI-4, PI-6 and PI-9 were as low as 0.18 Pa·s (268 °C), 0.36 Pa·s (273 °C), 0.99 Pa·s (305 °C), 4.2 Pa·s (316 °C) and 5.3 Pa·s (316 °C), respectively. Besides, it was found that all the minimum melt viscosities exhibited far lower than the reported oligomers, such as the minimum melt viscosity of PETI-5 was 60000 Pa·s at 371 °C and the minimum melt viscosity of TriA-PI was 1000 Pa·s at 320 °C. In contrast, PI-1 with the lowest molecular weight showed much lower melt viscosity and relatively higher melt processing window. From the data of temperature scale with $\eta^* < 10$ Pa·s in Table 4, it was found that the melt processing window of the oligomers increased as the degree of polymerization decreased, and PI-1 showed a much broad low viscosity range. In addition, the data of temperature scale with $\eta^* < 10$ Pa·s were considerable for oligomers, resulting in distinct improvements in the processability of thermosetting PI resin for fiber-reinforced composites. The low melt viscosity and wider processing window of the oligomers were the contribution of asymmetric monomers and flexible ether linkages in a-ODPA and 3,4'-ODA. The irregular structure based on a-ODPA reduces the efficiency of chain packing, and the flexible ether linkages improve the conformational freedom in the polyimide main chain. The low viscosity of oligomers provides them a distinct advantage in processing when they are used as structural adhesives and composites.

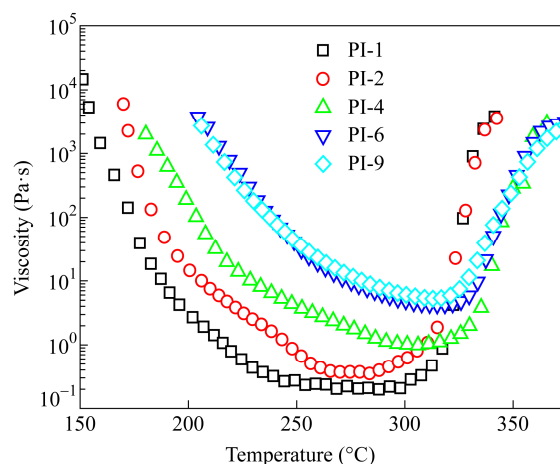


Fig. 5 Melt viscosity behaviors of imide oligomers

Table 4. The melt viscosity data of imide oligomers

Compounds	Temperature scale with $\eta^* < 10$ Pa·s	Minimum viscosity (Pa·s)
PI-1	135 K (188–323 °C)	0.18 (268 °C)
PI-2	115 K (206–321 °C)	0.36 (273 °C)
PI-4	109 K (229–338 °C)	0.99 (305 °C)
PI-6	60 K (274–334 °C)	4.2 (316 °C)
PI-9	47 K (281–328 °C)	5.3 (316 °C)

^{*}The melt viscosity of the oligomers.

The viscosity stability of oligomers has a great effect on the composite fabrication process. Figure 6 revealed the dependence of oligomer PI-4 viscosity on time at 280 °C, 300 °C and 320 °C, respectively. For each temperature, the material was held isothermally for 60 min. As can be seen in Fig. 6, the viscosities of the oligomers increased slowly at 280 °C and 300 °C with very low melt viscosity, whereas increased rapidly at 320 °C due to the thermal curing of imide oligomers. This phenomenon indicated that the low melt viscosity of oligomer PI-4 could remain stable at 280 °C. The novel imide oligomers based on a-ODPA exhibited good processability for advanced composite materials.

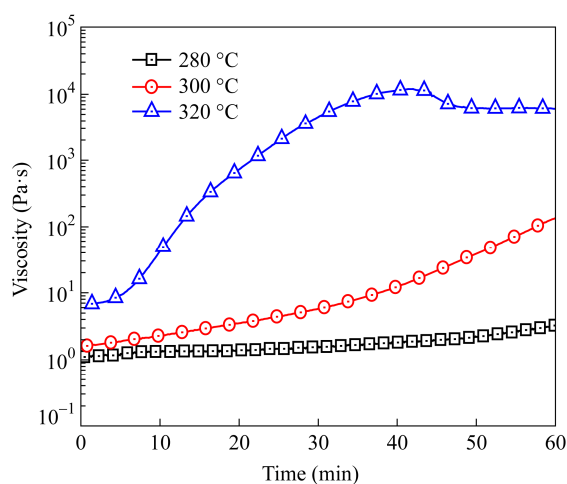


Fig. 6 Isothermal viscosity behaviors of PI-4 at 280 °C, 300 °C and 320 °C

Thermal and Mechanical Properties of Cured Films

Dynamical mechanical properties

The T_g values of prepared polyimide films were determined by DMA. The storage modulus, loss modulus and loss tangent ($\tan\delta$) as a function of temperature of cured polyimide films with different molecular weights are plotted in Figs. 7(a), 7(b) and 7(c), respectively. As can be seen in Table 5, the T_g values of the cured films based on the peak temperature of $\tan\delta$ were in the range of 282–373 °C, respectively. In addition, the T_g of the cured films decreased gradually with increasing the molecular weight because of lower crosslink density which resulted in the increase of free volume of the polyimide matrix. Regarding the peak temperature in the $\tan\delta$ curves as T_g , these imide oligomers exhibited $T_g > 300$ °C ($n = 1-6$). Although many ether bridges were incorporated into the main chains to improve processability, the polyimides had better T_g because a-ODPA possessed more bent chain structure and more restricted rotation.

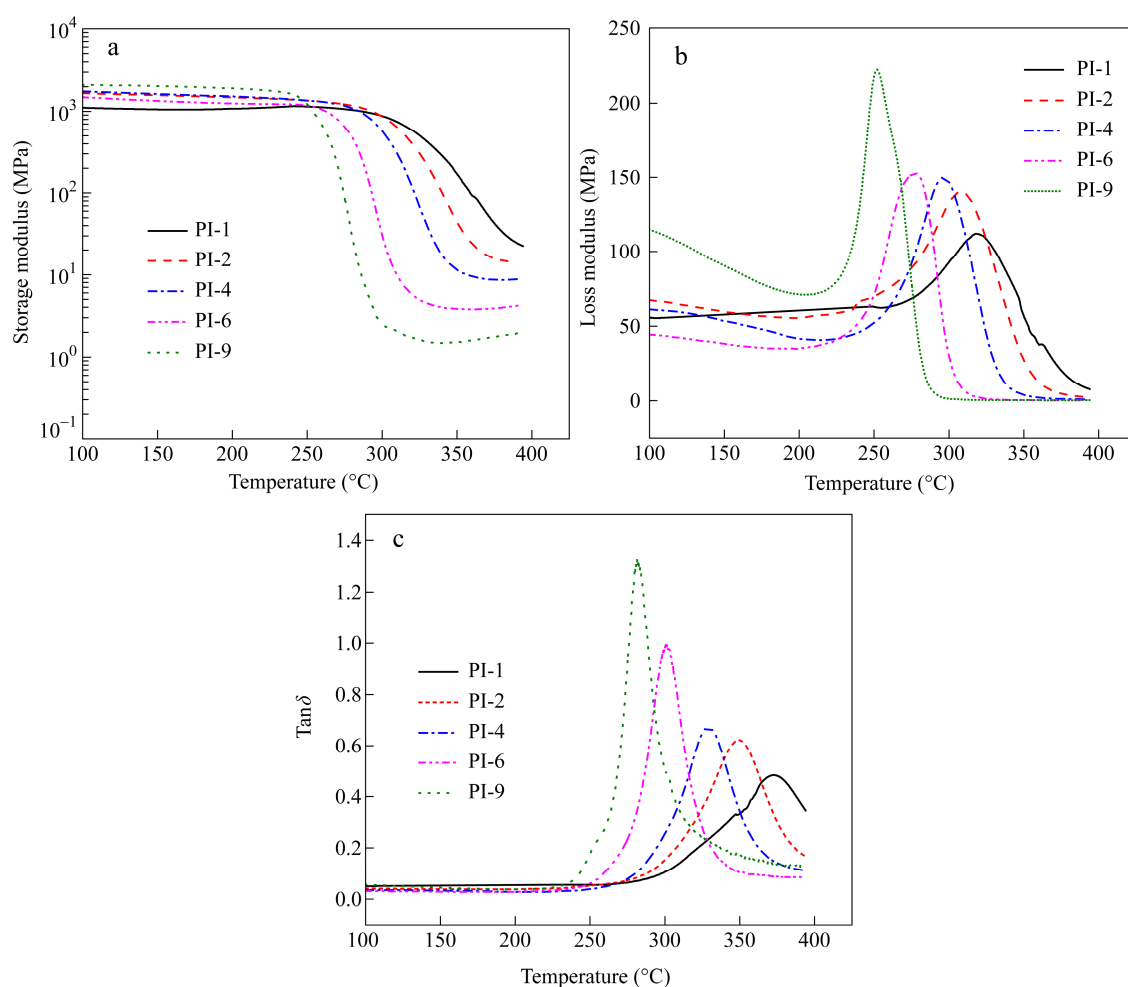


Fig. 7 DMA properties of cured PI oligomer ($n = 1, 2, 4, 6, 9$) films: (a) the storage modulus, (b) the loss modulus and (c) the loss tangent ($\tan\delta$) as a function of temperature

Thermal stability

The thermal stabilities of prepared polyimide films were evaluated by TGA in both inert (N_2) and oxidizing (air) atmospheres at a scan rate of 20 K/min. The thermal data of the cured films are summarized in Table 5, the thermal stability curves of films ($n = 1-9$) are plotted in Fig. 8. The variance of thermal stabilities was possibly caused by molecular weights and crosslinking density. The 5 wt% thermal decomposition temperatures (T_{d5}) of

these polyimide films were around 555 °C in N₂ and 548 °C in air. Surprisingly, as can be seen the typical curves of cured PI-6 films in Figs. 8(c) and 8(d), the thermal degradation in air exhibited an additionally subsequent fast degradation stage compared with the thermal degradation in nitrogen. Oxygen was apparently involved in the thermal degradation of the films. In this case, stable oxidation products could form at high temperatures, causing much higher T_d measured in air than that in nitrogen. In addition, the 10 wt% thermal decomposition temperatures (T_{d10}) of all the cured films based on a-ODPA and 3,4'-ODA in air were excellent which probably caused by thermal-oxidative crosslinking. A similar phenomenon has also been found in the previous reported literatures^[12, 35, 36]. Besides, the char yields reported at 800 °C in N₂ atmosphere were all above 61%. It was found that the cured films exhibited excellent thermal stability.

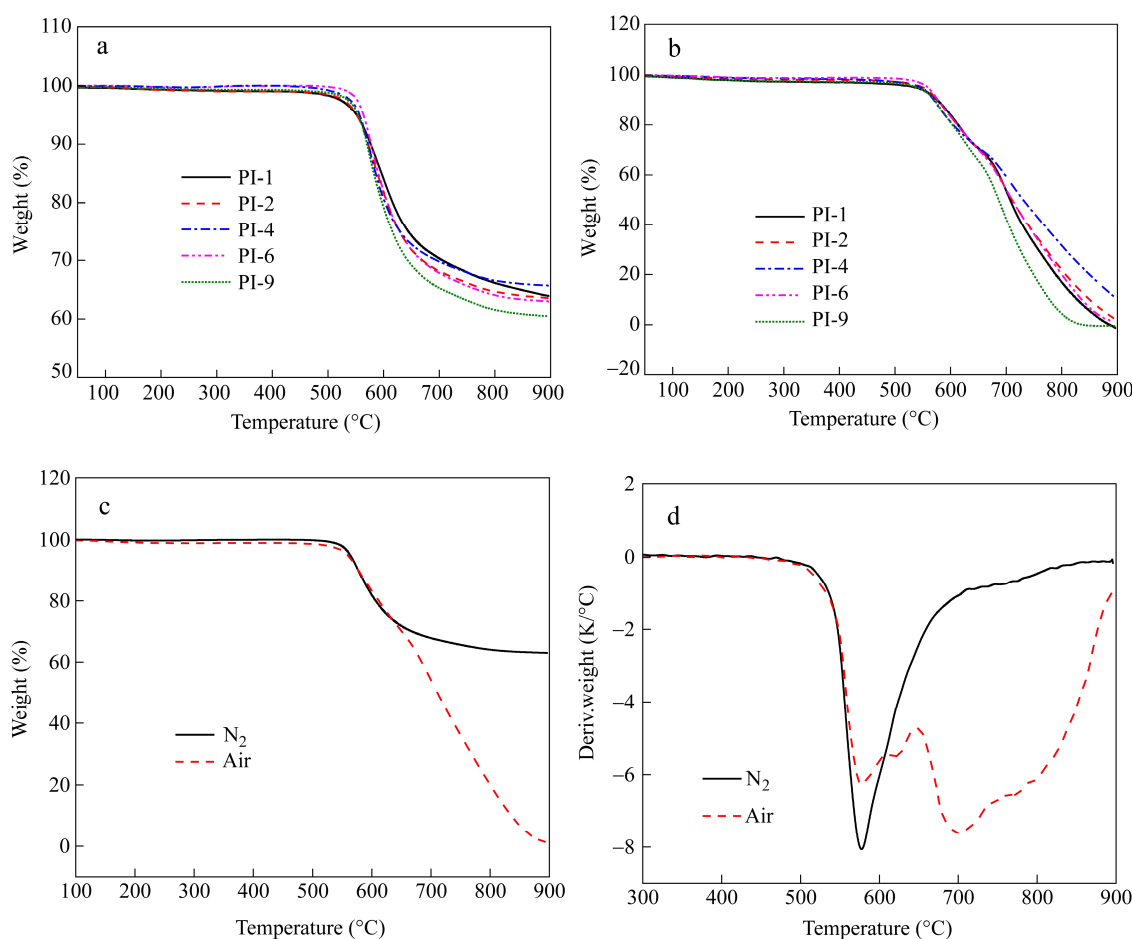


Fig. 8 (a) TGA curves of the fully cured polyimide films in N₂ atmosphere; (b) TGA curves of the fully cured polyimide films in air atmosphere; (c) TGA curves of the fully cured PI-6 film in N₂ and air atmosphere; (d) DTG curves of the fully cured PI-6 film in N₂ and air atmosphere

Tensile properties

The mechanical properties of the prepared films were evaluated by tensile test at room temperature. The resulted Young's modulus, tensile strength and elongation at break are listed in Table 5. All data were obtained from the homogeneous brown-colored films. All cured films exhibited a relatively lower tensile strength (35.7–98.1 MPa), and the Young's modulus was in the range of 2.09–2.58 GPa. It was expected that the values of elongation at break were more than 9.3% except PI-1, indicating that the cured films exhibited excellent fracture toughness. This could be explained in terms of the introduction of ether bridges into main chains. This

result also agreed with the reaction mechanism of the PEPA which was mainly by chain extension rather than cyclization^[14, 37]. The film prepared by PI-1 was brittle due to its high crosslink density. Overall, it would make sense the cured polyimide films prepared by PI-6 possessed the best tensile properties, with a tensile strength of 98.1 MPa and a Young's modulus of 2.58 GPa, and elongation at break 15.1%. This result also agrees well with the previous report^[25].

Table 5. Properties of the cured films from oligomers

Samples	Cured film properties										
	DMA	TGA(N ₂)				TGA(air)			Tensile properties		
	T_{g3}^g (°C)	T_d^h (°C)	T_{d5}^i (°C)	T_{d10}^j (°C)	R_w^k (%)	T_d (°C)	T_{d5} (°C)	T_{d10} (°C)	Strength (MPa)	Modulus (GPa)	Elongation (%)
PI-1	373	543	551	577	66.2	619	539	576	35.7 ± 4.5	2.09 ± 0.11	6.2 ± 0.7
PI-2	350	543	552	572	66.7	582	551	577	51.3 ± 3.7	2.10 ± 0.10	9.3 ± 0.5
PI-4	329	544	557	572	66.6	580	548	570	94.5 ± 3.9	2.41 ± 0.15	12.9 ± 0.6
PI-6	302	550	564	577	64.1	581	560	578	98.1 ± 4.2	2.58 ± 0.18	15.1 ± 0.6
PI-9	282	545	555	570	61.2	583	541	571	75.3 ± 4.1	2.22 ± 0.13	13.6 ± 0.4

^g Glass transition temperature of the oligomers determined on cured film by DMA; ^h the onset decomposition temperature in N₂ or air atmosphere; ⁱ 5% weight loss temperature in N₂ or air atmosphere; ^j 10% weight loss temperature in N₂ or air atmosphere; ^k residual weight retention at 800 °C

CONCLUSIONS

In the present paper, as confirmed by FTIR spectra, novel PEPA-terminated oligomers based on a-ODPA and 3,4'-ODA with different molecular weights were successfully synthesized and they could be converted to cured resins after curing at 370 °C for 1 h. We discovered that oligomer PI-1 exhibited the melting point and very low solubility in organic solvents. According to the introduction of geometrically asymmetric architecture and flexible ether-bridge backbone structures, all the oligomers possessed very low melt viscosity and wider processing window. Oligomers ($n = 2-9$) were found to have high solubility (40 wt%) in NMP and DMAc to afford homogeneous and stable solutions at room temperature. Low melt viscosity and high solubility are highly desired for the fabrication of high quality composites. Moreover, thermosetting polyimide films gave better T_g , high thermal stabilities in N₂ and air, and high toughness. In addition, PI-6 offered the best value of tensile strength and elongation at break. In summary, the imide oligomers developed in this article exhibited remarkable processability and mechanical properties of cured resins without sacrificing thermal properties. It was moderate and uncomplicated for the whole preparation process, and suitable for industrialized mass production. We believe this novel a-ODPA/3,4'-ODA/PEPA oligomers have great potential in preparing the high performance resin-based composite materials by RTM and structural adhesives.

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