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Phenylethynylnaphthalic endcapped imide oligomers with reduced cure temperatures

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ABSTRACT

A series of 4-(2-phenylethynyl)-1,8-naphthalic anhydride (PENA) endcapped imide oligomers with different chemical backbones and calculated number average molecular weights (Calc'd M_n) were successfully synthesized and characterized. The PENA-endcapped imide oligomers were mixtures of mono- and double-endcapped imide oligomers with polymerization degree (P_n) of 1–5 and number average molecular weights (M_n) of 2515–3851 g/mol. determined by GPC. Study on effect of chemical structures on the curing behaviors of two model compounds: PENA-m based on PENA and PEPA-m derived from 4-phenylethynylphthalic anhydride (PEPA) revealed that PENA-m showed the cure temperature of 50 °C lower than PEPA-m and the activity energy of thermal curing reaction for PENA-m was also lower than that of PEPA-m. The PENA-endcapped imide oligomers could be melt at temperatures of >250 °C with the minimum melt viscosity of 1.2–230 Pa s at 275–301 °C and the widen melt processing windows, along with 10–40 °C lower cure temperature than the PEPA-endcapped analogue.

The PENA-endcapped imide oligomers could be thermally cured at 350 °C/1 h to afford the thermally cured polyimides with good combined thermal and mechanical properties including T_g of 344–397 °C (DMA), T_d of 443–513 °C, tensile strength of as high as 54.7 MPa, flexural strength of as high as 126.1 MPa and modulus of as high as 2.3 GPa, respectively.

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1. Introduction

Phenylethynyl terminated imides oligomers (PETI) have recently received considerable attention due to its unique thermal curing process to generate network *via* chain extension and chain crosslinking to afford thermoset resin with outstanding mechanical strength and toughness [1,2]. The molecular weight-controlled PETI could be molten at <300 °C to give low viscous melt fluid with reasonable stability, which could then be thermally cured at higher temperature (370 °C) to produce thermoset polyimides with improved impact toughness and high mechanical strength. Hence, PETI has been employed as matrices to produce carbon fiber-reinforced composites for high temperature applications. For instance, PETI-5 [1], with Calc'd M_n of 5000, has been developed as matrix for autoclave process to produce high impact-resistance carbon fiber-reinforced composites. And PETIs with much lower Calc'd M_n (such as PETI-298, PETI-330 and PETI-375) were developed as matrix for RTM process to prepare carbon fiber composites [3–6]. However, the high cure temperature (370 °C) has always been considered the major drawback for PETI to expand its aerospace and aviation applications.

In recent years, a lot of efforts have been made to explore the possibility to reduce PETI's high cure temperature. Wright et al. [7–10] investigated the substituent effects of the ethynyl C–C triple bond on the thermal curing kinetics, revealing that some modified phenylethynyl endcapper such as 9-anthracenylethynylphthalic endcapper could effective lower the cure temperature (by about 80 °C) compared with the phenylethynyl analogue; McGrath and co-workers [11] noted that electron-withdrawing

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substituents on the backbone side of C–C triple bond (ethynyl) could accelerate thermal rates. In addition, the electron-withdrawing groups linked in the 4-position of the terminated phenyl ring could also accelerate the thermal curing of imide oligomers [12]. These data suggest the importance of stereoelectronic effects on the lowering thermal cure temperatures.

To explore the possibility of lowering the thermal cure temperature, a lot of new arylethynyl endcappers such as PENA, 4-(1-naphethlethynyl)phthalic anhydride, 9-anthracenylethynylphthalic anhydride and 3-phenylethynylphthalic anhydride have been reported [7–10,12–15]. It was noted that PENA exhibits much lower cure temperature than 4-phenylethynylphthalic anhydride (PEPA) [13]. To further understand the curing mechanism of PENA compared with PEPA, we have first synthesized two model compounds based on PENA and PEPA, *N*-phenyl-4-(2-phenylethynyl)-1,8-naphthalimide (PENA-m) and *N*-phenyl-4-phenylethynylphthalimide (PEPA-m), and compared their curing kinetic parameters. Then, a series of PENA-endcapped imide oligomers were prepared. The curing temperatures and melt processibility, thermal and mechanical properties of the PENA-endcapped imide oligomers as well as the thermally cured polyimides were systematically investigated.

2. Experimental section

2.1. Materials

2,3,3′,4′-biphenyltetracarboxylic dianhydride (α-BPDA, m.p.: 196–197 °C) and 4-phenylethynyl phthalic anhydride (4-PEPA, m.p.: 151–152 °C) were synthesized in this laboratory according to the reported methods [16,17]. 3,4′-Oxydianiline (3,4′-ODA, m.p.: 84–85 °C) was purchased from Shanghai Baicheng Chemicals Corp., China and recrystallized from ethanol/water (1:1) prior to use. 4-Bromonaphthalic anhydride was purchased from Liaoning Fuxin Sanbao Chemicals Corp., China and used as received. *N*-methyl-2-pyrrolidinone (NMP) was purchased from Beijing Beihua Fine Chemicals, China and purified by vacuum distillation over P_2O_5. Triethylamine was used after vacuum distillation in the presence of calcium hydride. Phenylacetylene was purchased from Beijing Bomi Chemicals Corp., China and used as received. All other reagents were commercially obtained from China National Medicines Corp., China and used as received.

2.2. Measurements

Infrared spectra (IR) were obtained on a Perkin-Elmer 782 Fourier transform infrared (FT-IR) spectrometer. ^{1}H NMR spectra were measured on a Bruker AVANCE 400 spectrometer at frequencies of 400 MHz for samples dissolved in chloroform-*d*. Differential scanning calorimetry (DSC) was conducted on a TA-Q100 analyzer at a heating rate of 10 °C/min in a nitrogen atmosphere and at a flow rate of 50 cm^3/min. The glass transition temperature (T_g) was taken at the mid-point of the heat flow versus temperature curve. Thermogravimetric analysis (TGA) was performed on a TA-Q50 series thermal analysis system at a heating rate of 20 °C/min under a nitrogen atmosphere and at a flow rate of 80 cm^3/min. Complex viscosity was performed on a TA-AR 2000 rheometer using the test specimen disks with diameter of 25 mm and thickness of 1.2 mm, which were prepared by compression molding of the imide oligomers powders at room temperature. The compacted disk was subsequently loaded in the rheometer fixture with 25 mm diameter parallel plates. The top plate was oscillated at a fixed strain of 5% and a fixed angular frequency of 10 rad/s, whereas the lower plate was attached to a transducer, which was used to record the resultant torque. For the testing of dynamic thermal melt complex viscosity, the test specimens were scanned from 200 °C at a heating rate of 4 °C/min, in which the melt viscosity (η^*, complex viscosity as a function of time) was determined. Dynamic mechanical analysis (DMA) of the cured samples was performed on a TA instrument DMA Q800 at a heating rate of 5 °C/min and at a load frequency of 1 Hz in a nitrogen atmosphere. The peak on the tan δ as a function of temperature curve was regarded as T_g of the cured polyimide. Gel permeation chromatography (GPC) was performed on Waters system that was equipped with a model 1515 pump, a 2414 refractive index detector using NMP as the eluant at a flowing rate of 1.0 ml/min. The sample concentration was 1 mmol/ml and monodisperse polystyrene was employed as the standard sample. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were carried out with a Biflex III MALDI-TOF mass spectrometer (Bruker, Billerica, Germany) equipped with delayed extraction, a multisample probe, a time-of-flight reflection analyzer, a nitrogen laser with a wavelength of 337 nm and a pulse width of 3 ns, and a linear flight path length of 100 cm, in which the flight tube was evacuated to 1027 Pa. Measurements of the mechanical properties were performed with an Instron model 3365 universal tester at room temperature. The tensile strength, modulus, and the elongation at break were measured in according with GB/T16421-1996 at a strain rate of 2 mm/min.

2.3. Synthesis of 4-(2-phenylethynyl)-1,8-naphthalic anhydride (PENA)

4-(2-Phenylethynyl)-1,8-naphthalic anhydride was synthesized according to the literature [13] (yield: 71.3%). m.p. = 227–228 °C [determined by DSC]. ^{1}H NMR (chloroform-*d*, δ ppm): 8.99–8.96 (d, 1H), 8.68–8.66 (d, 2H), 8.60–8.58 (d, 1H), 8.17–8.15 (d, 1H), 8.09–8.05 (t, 1H), 7.82–7.80 (m, 2H), 7.54–7.52 (m, 3H). FT-IR (KBr cm^{-1}): 2199 (–C≡C–), 1729 (asym C=O str), 1770 (sym C=O str). Elem. Anal. Calc'd for $C_{20}H_{10}O_3$: C, 80.53%; H, 3.38%. Found: C, 80.60%; H, 3.41%.

2.4. Synthesis of the model compound

The model compound PENA-m was prepared by chemical cyclodehydration: 4-(2-phenylethynyl)-1,8-naphthalic anhydride (2.98 g, 0.01 mol), aniline (0.93 g, 0.01 mol) and 300 ml DMAc were placed in a 100 ml flask equipped with a water condenser and a mechanical stirrer. The reaction

solution was stirred at room temperature for 4 h and then chemically cyclodehydrated with acetic anhydride and pyridine (2:1, v/v) after stirring for 6 h. The resultant mixture was poured into 100 ml of ethanol to yield precipitate. The solid was collected by filtration, washed by ethanol twice, and recrystallized from acetic acid to afford an off-white solid (3.39 g, yield: 91.1%). m.p. = 193–194 °C. ^{1}H NMR (chloroform-*d*, δ ppm): 8.86–8.81 (m, 2H), 8.71–8.68 (m, 2H), 8.63–8.59 (m, 3H), 8.02–7.99 (m, 2H), 7.93–7.87 (m, 3H), 7.71–7.63 (m, 4H), 7.58–7.54 (m, 2H), 7.51 (d, 1H), 7.49–7.45 (m, 5H), 7.32–7.26 (d, 4H). FT-IR (KBr cm^{-1}): 2205 (–C≡C–), 1843 (asym C=O str), 1811 (sym C=O str), 1383 (imide C–N str). Elem. Anal. Calc'd for $C_{26}H_{15}NO_2$: C, 83.63%; H, 4.05%, N, 3.75%. Found: C, 83.60%; H, 4.02%; N, 3.67%.

The model compound PEPA-m as a comparative was prepared according to the method as described above except that PENA was replaced with 4-PEPA to afford off-white solid (30.98 g, yield: 95.8%). m.p. = 203–204 °C. ^{1}H NMR (chloroform-*d*, δ ppm): 8.12 (s, 1H), 8.01 (s, 2H), 8.00–7.93 (m, 2H), 7.89 (s, 1H), 7.54–7.50 (m, 2H), 7.45–7.41 (m, 3H). FT-IR (KBr cm^{-1}): 2117 (–C≡C–), 1853 (asym C=O str), 1820 (sym C=O str), 1392 (imide C–N str), 1147 (C–F). Elem. Anal. Calc'd for $C_{22}H_{13}NO_2$: C, 81.72%; H, 4.05%; N, 4.33%. Found: C, 81.84%; H, 4.13%; N, 4.21%.

2.5. Synthesis of the imide oligomers

Imide oligomers were prepared by the conventional two-stage polymerization and imidization process. In a typical experiment (PI-1), 3,4′-ODA (6.26 g, 58 mmol) and NMP (70 ml) was placed in a flask equipped with a water condenser, a mechanical stirrer, a Dean-Stark trap, a thermometer and a nitrogen inlet/outlet. After stirred for 30 min at room temperature to give a homogenous solution, a slurry of α-BPDA (11.17 g, 38 mmol), PENA (11.92 g, 40 mmol) and NMP (80 ml) was added. The reaction mixture was stirred at 110 °C for 8 h and 150 ml toluene was then added. The resultant solution was heated to reflux at 185 °C for 10 h., in which the water evolved in the thermal imidization was simultaneously removed from the reaction system by azeotropic distillation. After cooled down to about 120 °C, the hot solution was poured slowly into 100 ml of water. The solid was collected by filtration and washed with hot water three times, and then dried at 205 °C in vacuum for 10 h to give PI-1 as yellow powder (30.28 g, 96.6%).

Other imide oligomers including PI-2, PI-3, PI-4, PI-5, PI-5′ as well as the 4-PEPA derivatives PI-*comp* were prepared according to the similar procedure, in which the molar ratios of 3,4′-ODA, *a*-BPDA and PENA or 4-PEPA were listed in Table 2.

2.6. Preparation of the thermal-cured polyimides

The imide oligomer resin powders were placed in a die, which was then placed in a hot press preheated at 200 °C. The die temperature was increased gradually to 350 °C at a rate of 4 °C/min. After it was kept there for 10–25 min, the die was applied with a pressure of 1.0–3.5 MPa, and kept for 1 h at 350 °C. The die was then cooled with the applied pressure to less than 200 °C. The thermally cured polyimide sheet was removed from the die at room temperature and then cut to the desired sizes for thermal and mechanical testing. The cured PI-*comp* was prepared according to the same procedure except that the curing temperature was 370 °C.

3. Results and discussion

3.1. Thermal curing behaviors of the model compounds

Prior to the imide oligomers and cured polyimides study, the model compound PENA-m and PEPA-m were synthesized and their thermal curing behaviors were compared. Fig. 1 depicts the DSC curves of PENA-m compared with PEPA-m, in which it can be seen that PENA-m showed lower melting points and lower thermal curing temperatures. The sharp endothermic peak of PEPA-m at 193 °C, assigned as the melt point (T_m), was 9 °C lower than that of PEPA-m (202 °C), and the wide exothermic peak in the range of 286–359 °C, attributed to the thermal-curing reactions of PENA-m, was obvious lower than that of PEPA-m (320–454 °C). The exothermal peak temperature of PENA-m (315 °C) was 61 °C lower than that of PEPA (377 °C), revealing that PENA-m exhibited much lower cure temperature than PEPA-m. Meanwhile, the exothermal enthalpy of PENA-m (ΔH = 421 J/g) was 81% of PEPA-m (ΔH = 516 J/g). This could be interpreted by the changes in electronic density of the C–C triple bond (ethynyl) in the end-capper by substituting phthalic group with naphthalic analogue, resulting in the ethynyl bond to be broken easier at lower temperature.

To further understand the curing behaviors of the model compounds, DSC at different heating rates was adopted to investigate the cure kinetics of PENA-m and PEPA-m. The exothermic peak temperatures (T_p) in DSC curves were shifted to higher temperatures with increasing of the heating rate (β) in the range of 2, 5, 10, 15 and 20 °C/min. The Kissinger's method has been employed to calculate the activation energy and the cure reaction order [18], and the thermal equation can be expressed as follows:

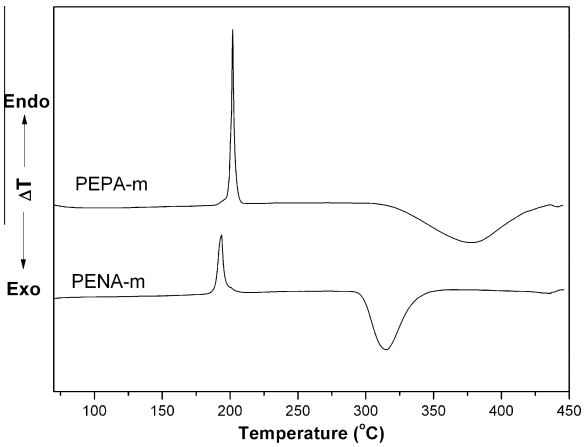


Fig. 1. DSC curves of the model compounds.

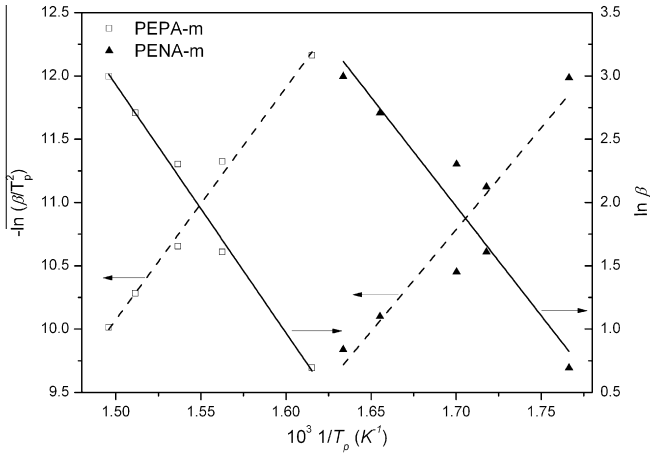


Fig. 2. Curing kinetic analysis and calculation of the thermal curing activation energy of the model compounds.

Table 1
Thermal data and kinetic parameters of the model compounds.

Sample	Endothermal temperature (°C)	Exothermal temperature (°C)			ΔH (J/g)	E (kJ/mol)	n	A
	Peak	Onset	Peak	End				
PEPA-m	202	320	377	434	516	152.9	0.94	8.1×10^{11}
PENA-m	193	286	315	359	421	143.6	0.89	1.2×10^{17}

$$-\ln(\beta/T_p^2) = \ln(E/R) - \ln(An) - (n-1)\ln(1-x)_p + E/RT_p$$

where E is the activation energy; R is the gas constant; A, n and x are the pre-exponential factor, the order of the cure reaction, and the extent of the cure action, respectively. The scatter graph of $-\ln(\beta/T_p^2)$ against T_p is shown in Fig. 2, in which the E was calculated as shown in Table 1. PENA-m has lower E value (143.6 kJ/mol) than PEPA (152.9 kJ/mol), implying that the activation energy might be an important factor for the lower cure temperature. If the E values are introduced into Crane's equation:

$$d(ln\beta)/d(1/T_p \approx -E/nR$$

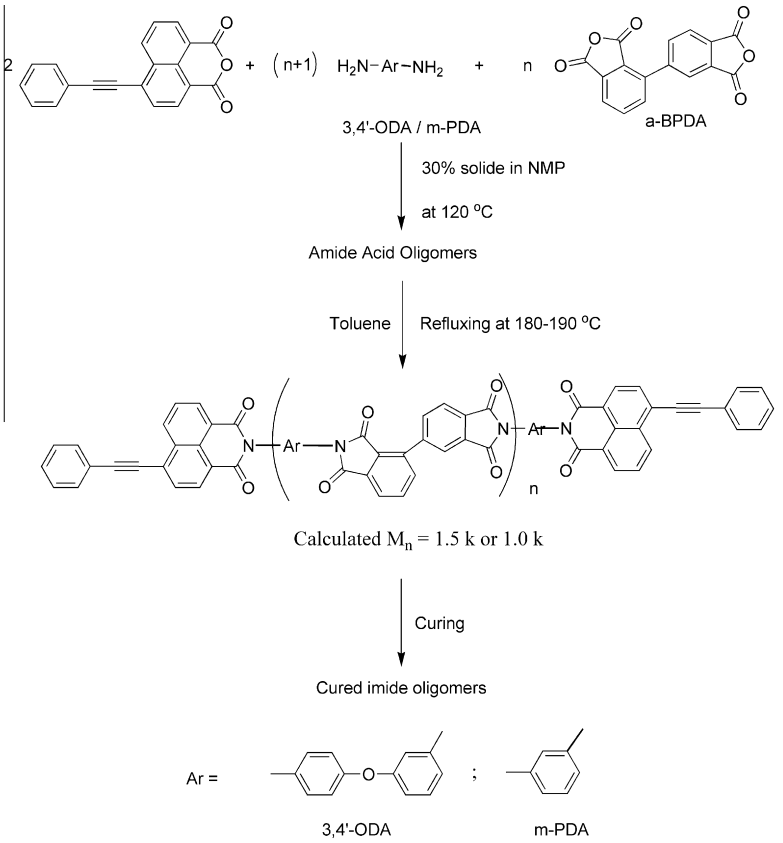
The scatter plot of $\ln(\beta)$ as a function of $1/T_p$ is also shown in Fig. 2, in which the reaction order n was calculated to be 0.89 for PENA-m and 0.94 for PEPA-m, respectively, implying that the thermal cure reaction of the model compounds follow the first-order kinetics reaction model. Moreover, pre-exponential factor (A) of PENA-m was 1.2×10^{17} which is much higher compared with that of PEPA-m (8.1×10^{11}). The higher value of A indicated that the valid collisions between C–C triple bonds (ethynyl) could occur more frequently during curing reaction of PENA-m at a certain temperature. So the different A values may be another main factor which leads to the lower curing temperature in PENA-m.

3.2. Molecular structures of the PENA-endcapped imide oligomers

A series of PENA-endcapped imide oligomers with different chemical backbones and Calc'd M_n were synthesized as shown in Scheme 1. The chemical backbones of the imide oligomers could be controlled by carefully adjusting of the aromatic diamine compositions in the process of polycondensation, and the Calc'd M_n values were designed to be 1500 or 1000 by changing the molar ratios of aromatic dianhydride (α-BPDA) to aromatic diamines. The chemical compositions and the Calc'd M_n values of the imide oligomers were listed in Table 2.

The molecular weights of the synthesized imide oligomers determined by GPC using NMP as solvent, including the number average molecular weight (M_n), weight average molecular weight (M_w), and the molecular weight distribution (M_w/M_n) were also shown in Table 2. It can be seen that the measured molecular weights are much higher than the calculated ones due to the molecular weight distributions of the oligomers and the polarity difference of the testing samples compared to the GPC standard sample (polystyrene) [19]. For instance, PI-1 has the measured M_n of 2836 g/mol, compared with the Calc'd M_n (1500). The M_n values of the imide oligomers were measured in the range of 2515–3851 g/mol and the M_w values in the range of 4520–5991 g/mol, respectively. The molecular weight distributions M_w/M_n were calculated in the range of 1.59–2.67. The M_n and M_w values were reduced with lowering the Calc'd M_n. For instance, the imide oligomer with Calc'd M_n of 1000 (PI-5′) has M_n of 2372 g/mol and M_w of 2807 g/mol, respectively, compared to that with Calc'd M_n of 1500 (PI-5, M_n 3851 and M_w 5010, respectively). Hence, the GPC-measured molecular weight data are well accordance with the calculated ones.

Fig. 3 compares the MALDI-TOF mass spectra of the representative imide oligomers with different chemical



Scheme 1. Synthesis of PENA-endcapped imide oligomers and the thermally cured polyimides.

backbones and the fixed Calc'd M_n (1500). PI-1 derived from (α-BPDA-*m*-PDA-PENA), derived from α-BPDA as the aromatic dianhydride monomer, *m*-PDA as the aromatic diamine monomer and PENA as the reactive endcapper, was composed of a series of chemical species with different polymerization degree (P_n = 1, 2 and 3) and molecular weights, including three double-endcapped species with P_n = 1, 2 and 3 (*m/z*: 1057, 1423 and 1789), of which four mono-endcapped ones with P_n = 2–5 (*m/z*: 1143, 1509, 1875 and 2242) were detected (Table 3). The mono-endcapped species with P_n = 2 showed the 100% peak intensity. Meanwhile, PI-5 (α-BPDA-3,4′-ODA-PENA) showed seven chemical species, including five double-endcapped ones (P_n = 1–5: *m/z*: 1241, 1699, 2158, 2616 and 3074) and two mono-endcapped ones (P_n = 2 and 3: *m/z*: 1419 and 1877), of which the double-endcapped species with P_n = 1 showed the 100% peak intensity. PI-3 (α-BPDA-m-PDA/3,4′-ODA-PENA), derived from the mixed diamines (*m*-PDA:3,4′-ODA = 1:1), showed much complex chemical species than PI-1 and PI-5, including four

Table 2
Chemical compositions and molecular weights of the imide oligomers endcapped with PENA or PEPA.

Sample	Composition (mmol)				Calc'd M_n (g/mol)	M_n (g/mol)	M_w (g/mol)	M_w/M_n (g/mol)
	Diamines	*a*-BPDA	PENA	PEPA				
PI-1	*m*-PDA (58)	38	40	–	1500	2836	4520	2.46
PI-2	*m*-PDA (37.5) 3,4′-ODA (12.5)	30	40	–	1500	3740	5991	1.60
PI-3	*m*-PDA (25) 3,4′-ODA (25)	30	40	–	1500	2751	5392	2.67
PI-4	*m*-PDA (12.5) 3,4′-ODA (37.5)	30	40	–	1500	2515	4696	1.87
PI-5	3,4′-ODA (37)	17	40	–	1500	3851	5010	1.59
PI-5′	3,4′-ODA (22)	2	40	–	1000	2372	2807	1.23
PI-*comp*	3,4′-ODA (37)	17	–	40	1500	2153	4787	2.22

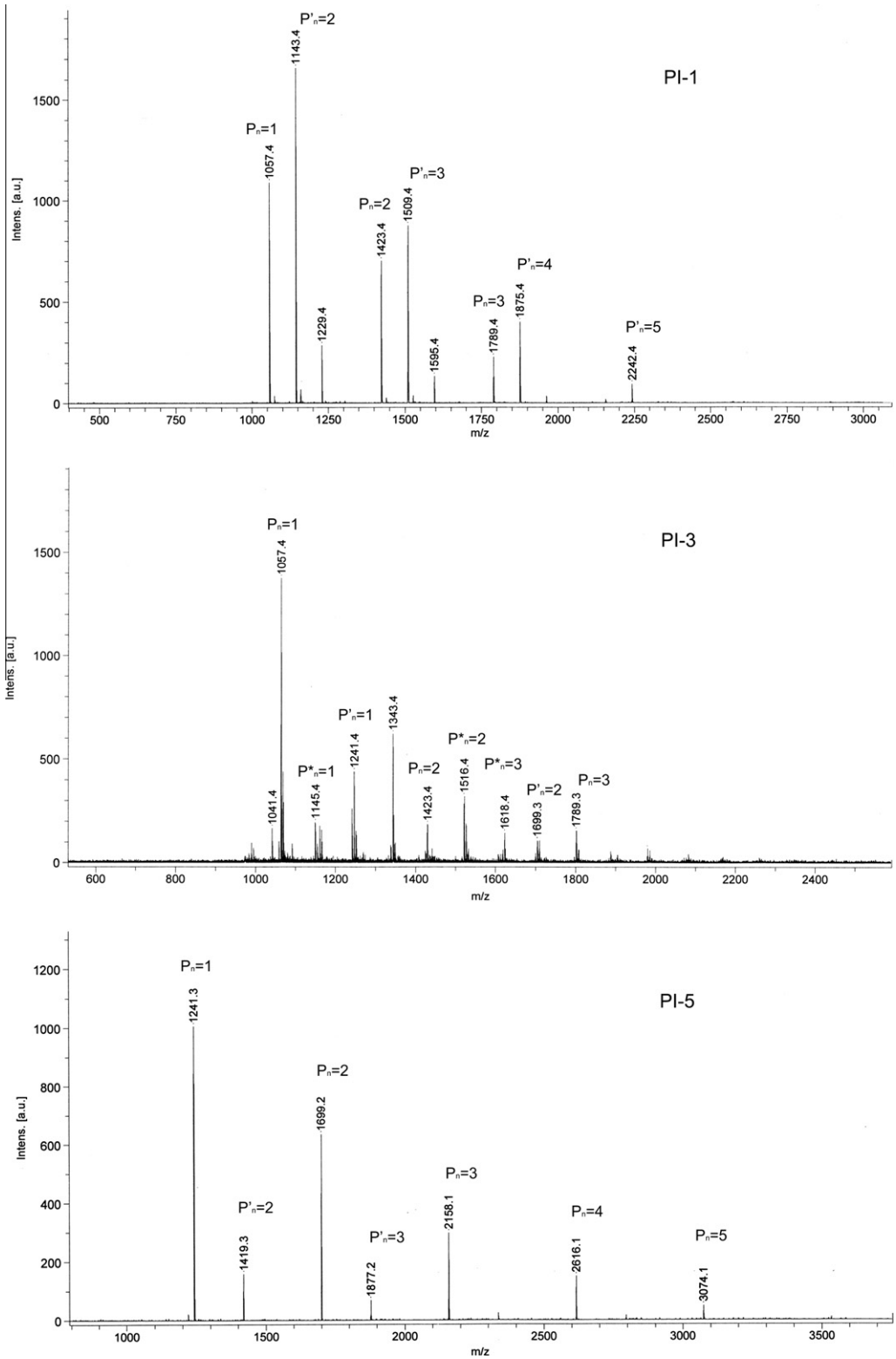
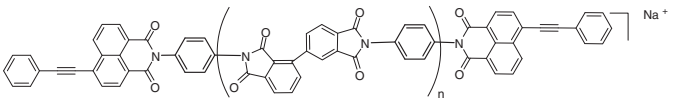
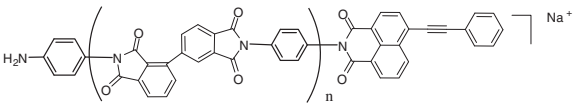
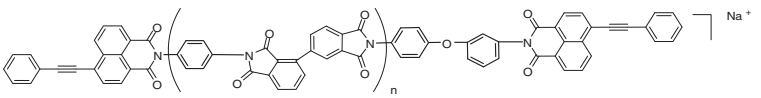
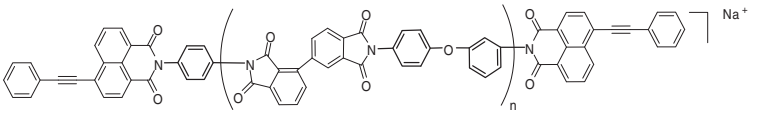
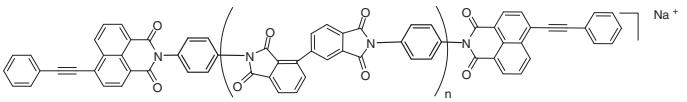
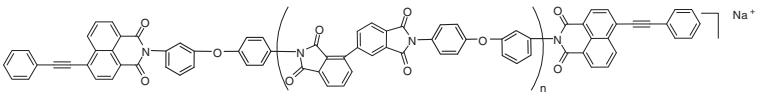
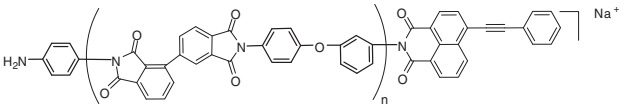
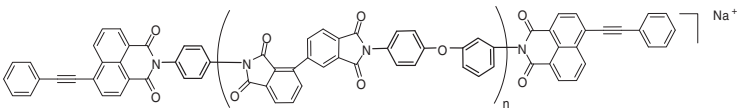
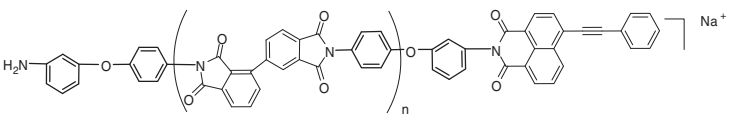


Fig. 3. MODI-TOF mass spectra of PENA-endcapped imide oligomers.

Table 3
Molecular structures of the chemical species detected by MODI-TOF for PENA-endcapped imide oligomers.

Sample	Chemical structure of the molecular species	P_n	Mass (m/z)	Intensity (%)
PI-1		1	1057	65.6
		2	1423	41.9
		3	1789	8.6
		2	1143	100
		3	1509	52.7
		4	1875	24.7
		5	2242	5.4
		1	1145	14.1
		2	1516	23.1
		2	1618	10.3
PI-3		1	1057	100
		2	1423	12.8
		3	1789	11.5
		1	1241	12.8
		2	1699	7.7
		2	1343	44.9
PI-5		1	1241	100
		2	1699	63.0
		3	2158	30.0
		4	2616	8.6
		5	3074	4.9
		2	1419	16.0
		3	1877	9.8

double-endcapped chemical species with different chemical backbones and P_n values, and one mono-endcapped species with $P_n = 2$ (m/z: 1343, 44.9%). PI-3 contains not only the same species as detected in PI-1 (m/z: 1057, 1423 and 1789) and PI-5 (m/z: 1241 and 1699), but also some new species with different chemical backbones (m/z: 1145, 1516 and 1618). One of the double-endcapped species detected in PI-1 (α-BPDA-m-PDA-PENA, $P_n = 1$) showed the 100% peak intensity, revealing that *m*-PDA showed stronger reaction ability than 3,4′-ODA. Obviously, the imide oligomers were an oligomer mixture of various chemical species. The chemical structures of the oligomer mixture could be changed by adjusting the chemical compositions in the polycondensation.

3.3. Melt processability of the PENA-endcapped imide oligomers

Fig. 4 showed the typical viscosity–temperature curves of the imide oligomers, in which the melt viscosities decreased gradually with increasing of temperature scanned at >200 °C, down to a valley stage where the viscosity reached the lowest point, and then went up with further increasing of temperature due to the thermal curing of the phenylethynyl groups [20–23]. The complex melt viscosities at different temperatures, the minimum melt viscosities were all compiled in Table 4. Obviously, the temperatures at which the imide oligomer had the minimum melt viscosities decreased with increasing of 3,4′-ODA loading. The minimum melt viscosity decreased from 230 Pa s (301 °C) for PI-1 (α-BPDA-*m*-PDA-PENA) to 1.2 Pa s (284 °C) for PI-4 (α-BPDA-*m*-PDA/3,4′-ODA (1:1)-PENA), revealing that the flexible segment (–O–) in the imide backbones could low the melt viscosity efficiently. However, when the diamine employed was pure 3,4′-ODA (PI-5), the minimum melt viscosity increased up to 8.2 Pa s (329 °C). This might be the result of high steric regularity of the imide backbone. Furthermore, by reducing PI-5′s Calc'd M_n (1500) to 1000 g/mol (PI-5′), the minimum melt viscosity went down to 1.9 Pa s (292 °C). Meanwhile,

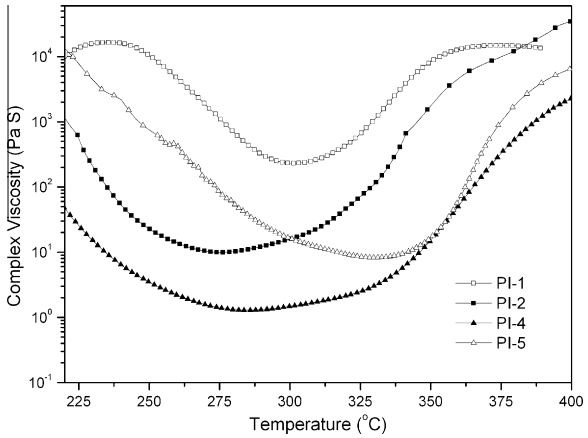


Fig. 4. Dynamic rheological behaviors of PENA-endcapped imide oligomers with different chemical backbones.

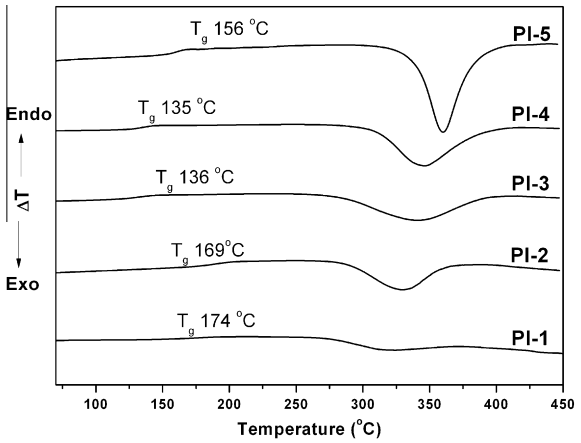


Fig. 5. DSC curves of PENA-endcapped imide oligomers with different chemical backbones.

the imide oligomers exhibited wider melt processing windows with the increase of 3,4′-ODA used in the oligomer synthesis.

In comparison, PI-5 showed higher melt viscosity than PI-comp which has the same Calc'd M_n and same chemical composition except that PEPA instead of PENA was used as the endcapper. For instance, the minimum melt viscosity of PI-5 was 8.2 Pa s at 329 °C, compared to 0.8 Pa s at 320 °C for PI-*comp*. In addition, PI-5 also exhibited narrower melt processing window than PI-*comp*, which showed much lower melt viscosity than the PENA-endcapped ones at temperatures of 350–370 °C, indicating that PENA-endcapped imide oligomers showed reduced melt processability than the corresponding PEPA-endcapped ones. This might be interpreted by the contribution of the stronger steric hindrance of the phenylethynylnaphthalimide groups in the imide oligomers, which resulted in the retardence of the imide chain mobility. Probably due to the lower cure temperature, PENA-endcapped imide oligomers showed rapid increases in melt viscosity at >350 °C caused by the imide chain crosslinking and extension reaction.

3.4. Thermal curing of the PENA-endcapped imide oligomers

Fig. 5 compares the DSC curves of the representative PENA-endcapped imide oligomers with the same Calc'd M_n (1500) and Table 5 summarizes the thermal data. The PENA-endcapped imide oligomers showed T_gs in the range of 135–156 °C. In comparison, the imide oligomers derived from the *m*-PDA/3,4′-ODA mixtures (PI-2, PI-3 and PI-4) showed decreases in T_gs with increasing of 3,4′-ODA loadings. PI-2 has the T_g of 169 °C, 33–34 °C higher than PI-3 (136 °C) and PI-4 (135 °C), respectively. However, the imide oligomers derived from the pure diamines (PI-1 with *m*-PDA, and PI-5 with 3,4′-ODA) showed higher T_gs than those derived from the diamine mixtures (PI-1: 174 °C and PI-5: 156 °C, respectively). This might be interpreted that the mono-diamine based polymer has more rigid backbones than the multi-diamine based ones, resulting in the higher T_gs.

The thermal curing exothermal peaks were observed for the PENA-endcapped imide oligomers, in which the curing

Table 5
Thermal curing behaviors of PENA-endcapped imide oligomers with different chemical backbones and Calc'd M_n.

Sample	T_g (°C)	T_{onset} (°C)	T_{exo} (°C)	T_{end} (°C)	ΔH (J/g)
PI-1	174	268	305	376	192.6
PI-2	169	257	329	384	174.7
PI-3	136	245	340	410	240.1
PI-4	135	243	364	416	139.1
PI-5	156	336	367	418	109.6
PI-5′	145	317	352	403	178.5
PI-*comp*	134	343	393	431	249.6

Table 4
Complex melt viscosities of PENA-endcapped imide oligomers.

Sample	Complex melt viscosity (Pa s) at different temperature					Minimum melt viscosity (Pa s/°C)
	250 °C	280 °C	310 °C	340 °C	370 °C	
PI-1	9930	690.9	266.4	3641	14,680	230.1 at 301 °C
PI-2	22.5	10.2	23.8	555.7	7753	9.9 at 275 °C
PI-3	5.7	6.8	13.7	58.7	677.5	5.3 at 320 °C
PI-4	3.4	1.3	1.8	5.7	195	1.2 at 284 °C
PI-5	742	54	11.8	9.5	477	8.2 at 329 °C
PI-5′	17.7	2.3	2.0	5.3	3712	1.9 at 292 °C
PI-*comp*	2.3	1.2	0.8	0.9	11.7	0.8 at 320 °C

Table 6
Characteristic curing temperatures of the representative PENA-endcapped imide oligomers (PI-5) at different heating rates.

β (°C/min)	T_{onset} (°C)	T_{exo} (°C)	T_{end} (°C)
2.5	316	344	397
5	325	353	411
10	336	367	418
15	346	376	435
20	350	381	441
0 (extrapolated)	314	342	395

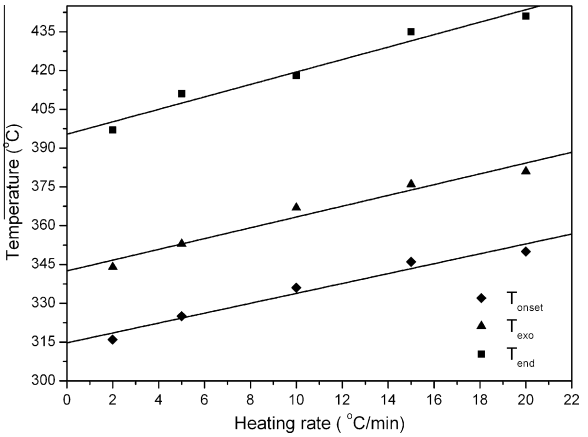


Fig. 6. DSC analysis at different heating rates of the representative PENA-endcapped imide oligomers (PI-5).

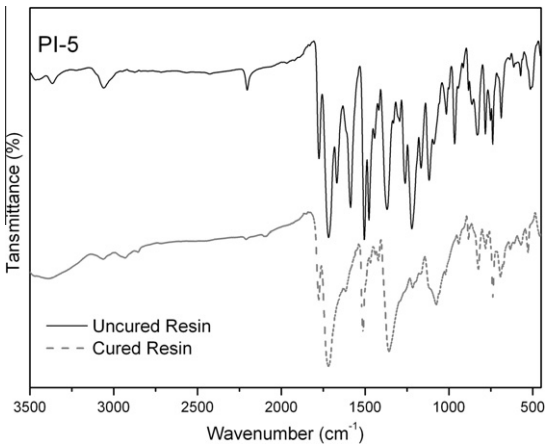


Fig. 7. FT-IR spectra of the representative PENA-endcapped imide oligomers (PI-5) before and after thermal-cured at 350 °C/1 h.

onset temperatures (T_{onset}) were measured at 243–336 °C, the exothermic peaks (T_{exo}) at 305–367 °C and exothermic ends (T_{end}) at 376–418 °C, respectively. Generally, T_{exo} values of the imide oligomers were decreased with decreasing of 3,4′-ODA loadings. For instance, PI-2 showed T_{exo} of 329 °C, 11 °C lower than PI-3 (340 °C) and 35 °C lower than PI-4 (364 °C), respectively. Additionally, PI-1 showed T_{exo} of 305 °C, 62 °C lower than PI-5 (367 °C). It was demonstrated that the chemical backbones of the imide oligomers could affect profoundly on the curing temperatures of the phenylethynylnaphthalimide groups, in which the ether bond (–O–) in the polymer backbone has to some degree retarding impacts on the phenylethynyl curing reaction. PI-4, which has the highest –O– loading, exhibited the highest curing temperature (364 °C), but still being much lower than the PEPA-endcapped analogue (PI-*comp*, 393 °C). The normalized heat enthalpy (ΔH) was calculated at 109.6–240.1 J/g, lower than the PEPA-endcapped analogue (PI-*comp*, 249.6 J/g).

In order to investigate the curing process of the PENA-endcapped imide oligomers, the non-isothermal DSC curves scanned at different heating rates of 2.5, 5, 10, 15 and 20 °C/min, respectively, were measured. Table 6 summaries the characteristic curing temperatures, including T_{onset}, T_{exo} and T_{end} of the representative imide oligomer (PI-5). It can be seen that the thermal curing data were shifted into higher temperatures with increase of heating rate (β).

The intrinsic data of T_{onset}, T_{exo} and T_{end} were determined to be 314, 342 and 395 °C, respectively, by extrapolating the characteristic curing temperatures at different heating rates to 0 °C/min (Fig. 6). Accordingly, the curing temperature of the PENA-endcapped imide oligomers was measured at around 342–344 °C.

3.5. Thermal properties of the thermally cured polyimides

Fig. 7 compares the FT-IR spectra of the representative PENA-endcapped imide oligomer before and after thermally cured (PI-5). It can be seen that asymmetric and symmetric stretching absorptions at 1798 and 1765 cm^{-1} assigned to the imide groups in the polymer backbone of the imide oligomer, the absorption at 2220 cm^{-1} assigned to the stretching vibrations of the ethynyl groups (–C≡C–) in PI-5, were observed in the uncured resin in Fig. 7, which were then almost disappeared after thermally cured at 350 °C for 1 h in the cured resin, implying that the phenylethynyl groups in the imide oligomer have been mostly converted into thermoset polyimide by chemical reactions such as chain extension and crosslinking. Fig. 8 shows the DMA curves of some representative thermoset polyimides including PI-1, PI-3 and PI-5.The thermoset polyimides showed tan δ (T_g) in the range of 334–397 °C, which was decreased with increasing of the –O– segments in the polyimide backbones. For instance, PI-1 showed T_g value of 397 °C, 53 °C higher than PI-5 (344 °C). The onset temperature at which the storage modulus was dropdown rapidly was 389 °C for PI-1, 27 °C higher than PI-3 (362 °C) and 54 °C higher than PI-5 (335 °C), respectively, implying that the thermal properties of the thermally cured polyimides were improved by increasing of the *m*-PDA loadings in the imide oligomers. In comparison, the PENA-endcapped imide oligomer (PI-5) showed similar thermal stability to the PEPA-endcapped analogue (PI-*comp*). For instance, PI-5 showed T_g of 344 °C, compared to 343 °C for PI-*comp*.

Fig. 9 depicts the thermal stabilities of the cured polyimides. The temperatures at 5% (T_5) and 10% (T_{10}) of original weight losses were measured at >457 and >508 °C, respectively (Table 7). The initial decomposition temperatures

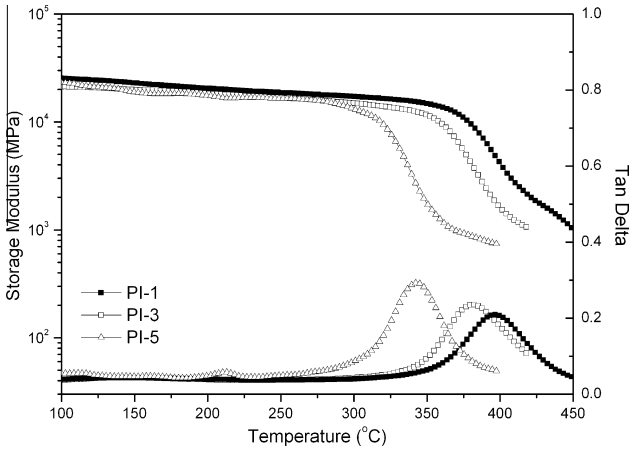


Fig. 8. DMA curves of the representative thermoset polyimides cured at 350 °C for 1 h.

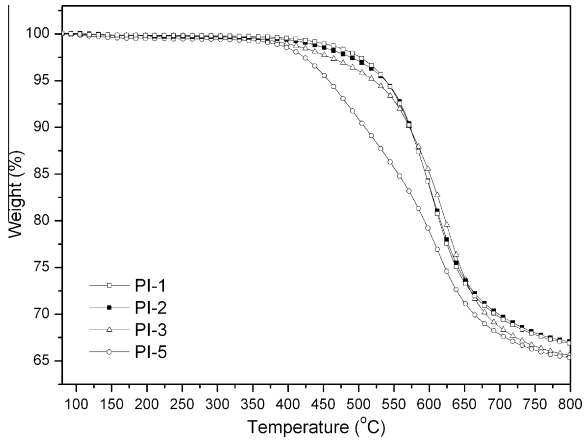


Fig. 9. TGA curves of the thermoset polyimides cured at 350 °C for 1 h.

(T_d) were over 443 °C and the char yields at 800 °C was >65%. It can be seen that the thermal stability of the cured polyimides were deteriorated by increasing of the flexible segment (–O–) in the imide oligomers. For instance, PI-1 has T_d and T_5 of 513 and 538 °C, respectively, 70–81 °C higher than PI-5 (T_d: 443 °C and T_5: 457 °C). The lower Calc'd M_n PI-5′ showed relatively higher T_g and better thermo stability than PI-5 probably due to the higher crosslinking density resulted from the higher content of the curable endcapper in the imide oligomer. Additionally, PENA-endcapped imide oligomer (PI-5) showed some lower thermal stability (T_d and T_5) than the PEPA-endcapped analogue (PI-*comp*).

3.6. Mechanical properties of the thermally cured polyimides

Table 8 summarizes the mechanical properties of the thermally cured polyimides. After thermally cured at

Table 7
Thermal properties of the thermoset polyimides cured at 350 °C/1 h.

Sample	G' (MPa)	tan δ (°C)	T_d (°C)	T_5 (°C)	T_{10} (°C)	Char at 800 °C (%)
PI-1	389	397	513	538	572	66.8
PI-2	377	386	510	537	573	67.0
PI-3	362	380	503	521	572	65.6
PI-4	349	357	456	468	537	65.4
PI-5	335	344	443	457	508	65.3
PI-5′	354	362	512	541	576	67.8
PI-*comp*[a]	329	343	543	557	578	70.1

[a] Cured at 370 °C for 1 h.

Table 8
Mechanical properties of the thermally cured polyimides.

Sample	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at breakage (%)	Flexural strength (MPa)	Flexural modulus (GPa)
PI-1	Brittle	Brittle	Brittle	Brittle	Brittle
PI-2	26.7	0.5	1.2	82.4	1.1
PI-3	41.1	0.8	3.1	118.6	1.2
PI-4	46.7	1.1	2.9	108.3	2.5
PI-5	54.7	1.2	3.0	126.1	2.3
PI-5′	51.5	1.3	1.9	108.9	1.7
PI-*comp*	57.1	1.3	4.7	147.2	1.6

350 °C for 1 h, the resulted thermoset polyimides exhibited good combined mechanical properties except that PI-1 is too brittle to obtain the mechanical properties, probably due to its very rigid backbone. Tensile strength of the thermally cured polyimides was improved by increasing of the flexible segment (–O–) loadings in the polyimide backbone. For instance, PI-3, PI-4 and PI-5 showed tensile strengths of 41.1–54.7 MPa, much higher than PI-2 (26.7 MPa). Additionally, all of the 3,4′-ODA-based polyimides (PI-5, PI-5′ and PI-comp) showed the highest tensile strength. In comparison, PI-*comp* showed better mechanical properties than the PENA-endcapped polyimides probably due to the different properties of the endcappers or the higher curing temperature. In addition, the post-cure at higher temperature could further improve the mechanical properties of the PENA-endcapped polyimides.

4. Conclusion

A series of phenylethynylnaphthalic anhydride (PENA) endcapped imide oligomers with different chemical backbones and calculated number average molecular weights (Calc'd M_n) have been synthesized, which were the mixtures of mono- and double-endcapped imide oligomers with polymerization degree (P_n) of 1–5 and number average molecular weights (M_n) of 2515–3851 g/mol determined by GPC. The PENA-endcapped imide oligomers could be melt at temperatures of >250 °C with the minimum melt viscosity of 1.2–230 Pa s at 275–301 °C and the widen melt processing windows, along with 10–40 °C lower cure temperature than the PEPA-endcapped analogue. The PENA-endcapped imide oligomers could be thermally cured at 350 °C/1 h to afford the thermally cured polyimides with good combined thermal and mechanical properties including T_g of 344–397 °C (DMA), T_d of 443–513 °C, tensile strength of as high as 54.7 MPa, flexural strength of as high as 126.1 MPa and modulus of as high as 2.3 GPa, respectively. The PI-4 exhibited the best combination of melt processibility, curing temperature, thermal properties and mechanical properties.

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