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The influence of molecular weight on properties of melt-processable copolyimides derived from thioetherdiphthalic anhydride isomers

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Abstract A series of novel melt-processable copolyimides based on mixed thioetherdiphthalic anhydride (TDPA) isomers and 4,4′-oxydianiline (4,4′-ODA) were synthesized by a one-step polycondensation. Molecular weight of copolyimides was controlled with stoichiometric offsets in favor of 4,4′-ODA. All of the resulting polyimides (PIs) were amorphous and have nice solubility. With increase in molecular weight, the glass transition temperatures of copolyimides increased from 248 to ca. 270 °C based on DSC measurements. These copolyimides displayed excellent thermal and thermooxidative stability, as evidenced by thermogravimetric analysis in both air and nitrogen atmospheres. The melt processability, thermoplastic response, melt stability, and their dependence on molecular weight of the copolyimides have been investigated in terms of rheological measurements by monitoring the melt viscosity after residence at various times and temperatures.

Introduction

Aromatic polyimides (PIs), because of their excellent thermal stability, chemical resistance, mechanical properties, and low dielectric constants, are considered to be high-performance polymeric materials. Since they were developed in 1960s, PIs have found a variety of applications such as high-temperature insulators and dielectrics, coatings, adhesives, and matrices for high-performance composites [1–4]. However, most of aromatic PIs display a glass transition temperature ranging from 200 to 400 °C because of their stiff backbone structure, which has led to difficulties in melt processing. Traditional processing has often involved the solution casting of poly(amic acid) precursors into the desire shape, followed by thermal or chemical imidization into PIs. Nevertheless, melt processing is more desirable from both cost and environmental safety point of view, and therefore, the synthesis of melt-processable or thermoplastic PIs is of prime importance.

Melt-processable PIs are commonly applied in various industries because of ease in processing, handling, and storage. These applications require PIs to exhibit enhanced melt flow behavior at relatively low-processing temperatures. Meanwhile, thermal and melt stability is also a crucial factor in processing. Heretofore, there have been many commercial high-performance melt-processable PIs, such as ULTEM™ developed by General Electric Co. [5–7], AURUM™ developed by Mitsui Toatsu [8], and LARC™-IA developed by NASA Langley Research Center [9–11].

Many researchers used methods to modify polymer's melt flow behavior such as introduction of flexible linkages, fluorine-containing groups, meta linkages, bulky substituents, and noncoplanar moieties into PIs backbones [12–17]. Other methods include molecular weight controlled by end capping, and copolymerization or blend with PIs containing more flexible backbones to lower melt viscosity [18–21]. Among these methods, copolymerization is a usual but effective one to enhance the solubility or to improve melt processability of PIs. Since the addition of the third component generally disrupts the symmetry of recurrence regularity of the polymer chain, consequently weaken intermolecular interactions. Copolyimides from isomers of dianhydrides or diamines were an attractive field, and many isomeric monomers were used to synthesize copolyimides,

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such as biphenltetracarboxylic dianhydride (BPDA) isomers [22–27]. It is important to note that 2,3,3′,4′-BPDA used as a flexible blend component or a comonomer for copolymerization has improved the insufficient thermoplasticity of 3,4,3′,4′-BPDA-based homopolyimides without sacrificing the excellent properties of the homopolymer [20].

Thioetherdiphthalic anhydride (TDPA) has three isomers which are 3,3,4′,4′-diphenylthioether dianhydride (4,4′-TDPA), 2,3,3′,4′-diphenylthioether dianhydride (3,4′-TDPA), and 2,2′,3,3′-diphenylthioether dianhydride (3,3′-TDPA), respectively. Systematic study of the relationships between chemical structure and properties of PIs based on three TDPA isomers and its thermoplasticity was carried out by Zhang et al. [28] and Ding et al. [29]. Among these polymers, the PI derived from the unsymmetrical dianhydride, namely 3,4′-TDPA, possessed some attractive properties such as better solubility and lower melt viscosity. It has been proved that PI based on 3,4′-TDPA is a promising candidate for melt-processable PIs. As mentioned above, copolymerization with dianhydride isomers could offer the copolyimides some combined properties. However, little is known about copolyimides based on three isomers together.

The molecular weight of an engineering polymer has a profound effect on the mechanical properties and processability. Maintaining strength is a familiar issue for polymer design engineers while improving processability. It would be advantageous, therefore, if the researchers could optimize the macroscopic performance of materials by means of controlling molecular weight of polymers accurately. As well as other polymer, a variety of performance of PIs, such as mechanical strength [30], melt processability [18], and gas permeability [31], are closely affected by molecular weight of polymer.

Therefore, in this study, we synthesized a series of molecular weight controlled copolyimides derived from mixtures of TDPA isomers and 4,4′-oxydianiline (ODA) in terms of both processing and performance are intrinsically linked to the polymer's molecular weight. The dependence of polymer properties on molecular weight, especially the thermal properties and melt processability, was investigated systematically.

Experimental

Materials

3- and 4-Chlorophthalic anhydrides were obtained from Harbin Shidai Science and Technology Co., Ltd., and used as received. Anhydrous sodium sulfide was purchased from Inner Mongolia Lichuan Chemistry Co., Ltd., and used as received. PA was purified by sublimation before use. All of the other reagents were from the Sinopharm Chemical Reagent Co., Ltd., and were of analytical grade.

Characterization

The inherent viscosities were determined at 30 °C with an Ubbelohde viscometer, and the concentration was 0.5 g dL^{-1} in *N*-methyl-2-pyrrolidone (NMP). Number-average molecular weights (M_ns) and weight-average molecular weights (M_ws) were obtained via gel permeation chromatography (GPC) performed with a set of a Waters 515 high-performance liquid chromatography pump, a Waters 2414 differential refractometer. Fourier transform infrared (FTIR) spectra were obtained on a Thermo Nicolet 6700 FTIR spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AV/ANCE at 400 MHz using DMSO-d_6 as solvent and tetramethylsilane as an internal standard. The differential scanning calorimetry (DSC) was conducted on a Perkin-Elmer Diamond DSC system at a heating rate of 20 °C/min under a nitrogen atmosphere. The thermal stability of PIs was estimated using a Perkin-Elemer Diamond TG/DTA thermogravimetric analyzer at a heating rate of 10 °C/min in a nitrogen or an air atmosphere. Dynamic mechanical thermal analysis (DMA) was performed on a dynamic mechanical thermal analyzer (Mettler-Toledo, Inc., Switzerland) in a tensile mode at a heating rate of 3 °C/min from 30 to 300 °C and at a frequency of 1 Hz in air. The tensile measurements were carried out on an Instron model 5567 tensile tester at a crosshead speed of 5 mm/min at room temperature. The rheological measurements of PIs were conducted on a rotational Physica MCR 301 rheometer in an oscillation model. Sample discs of 25 mm diameter and 1 mm thickness were prepared by press-molding of the PIs powder at 80 °C under high pressure, which were then loaded in the rheometer fixture equipped with 25 mm diameter parallel plates. The complex viscosity η^* was measured as a function of temperature (T) or time (t) during each test hold.

Monomer synthesis

3,3′-TDPA and 4,4′-TDPA and the isomers mixture were synthesized as literature reported [32]. 3,4′-TDPA was synthesized by a method revealed by a Chinese Patent [33].

Polyimide synthesis

The molecular weight controlled copolyimides were synthesized via one-step polycondensation with *m*-cresol as the solvent. Stoichiometric imbalances, designated by percentage offsets, were controlled by adding an excess of the diamines with an appropriately reduced quantity of the dianhydrides. The synthesis of PI2 is used below as an example to illustrate the general synthetic route for the production of theses copolyimides: 4,4′-ODA (5.006 g, 25 mmol) and *m*-cresol (120 mL) were placed in a 250-mL three-necked flask fitted with a mechanical stirrer, a nitrogen inlet tube, and a Dean-Stark trap topped by a condenser. The reaction flask was purged with dry N_2, and the solution was heated to 100 °C. Then the TDPA mixture (7.790 g, 23.875 mmol), PA (0.333 g, 2.25 mmol), and several drops of isoquinoline were added successively. This mixture was stirred until the complete dissolution of solids, and then the temperature of an oil bath was gradually raised to 200 °C. The resulting homogeneous solution was stirred at these conditions for another 8 h under the steady flow of N_2. After it cooled to room temperature, the PI solution was diluted with *m*-cresol and slowly poured into a vigorously stirred solution of 95% ethanol (1 L). The precipitate was filtered off, washed thoroughly with boiling ethanol, and dried in vacuum at 200 °C to afford PIs powder in 97% yield. Other copolyimides were prepared by the same procedure as described above.

The PI powder obtained was dissolved in 1-methyl-2-pyrrolidone (NMP) at room temperature to afford about 15 wt% solution which was cast onto glass substrates. Wet films were placed in an oven at 80 °C for 12 h to release most of solvent. Then the films were gradually cured at 150 °C for 1 h, 200 °C for 1 h, 250 °C for 1 h, and finally 280 °C for 1 h to form 20–30 μm thick PI films.

Results and discussion

Monomer synthesis

As shown in Scheme 1, chloro-substituted phthimides were prepared using chlorophthalic anhydride and methylamine as starting materials. The chlorophthalic anhydride was a mixture of isomers, i.e., 3-chlorophthalic anhydride and 4-chlorophthalic anhydride. The ratio of these two isomers was 1:1. Afterward, a mixture of TDPA isomers was obtained by the aromatic nucleophilic substitution of chloro-substituted phthimides by sulfur anions, followed by alkaline hydrolysis and cyclodehydration to dianhydrides [32]. The composition of isomers in TDPA mixture was calculated according to ^{1}H NMR spectra as shown in Fig. 1. Figure 1 presents the ^{1}H NMR spectra of three isomers including characteristic peak assignments for each isomer. At the top of the figure is a typical spectrum of

Scheme 1 Synthesis of mixed TDPAs from chlorophthalic anhydrides

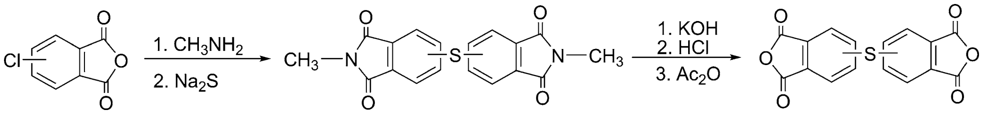
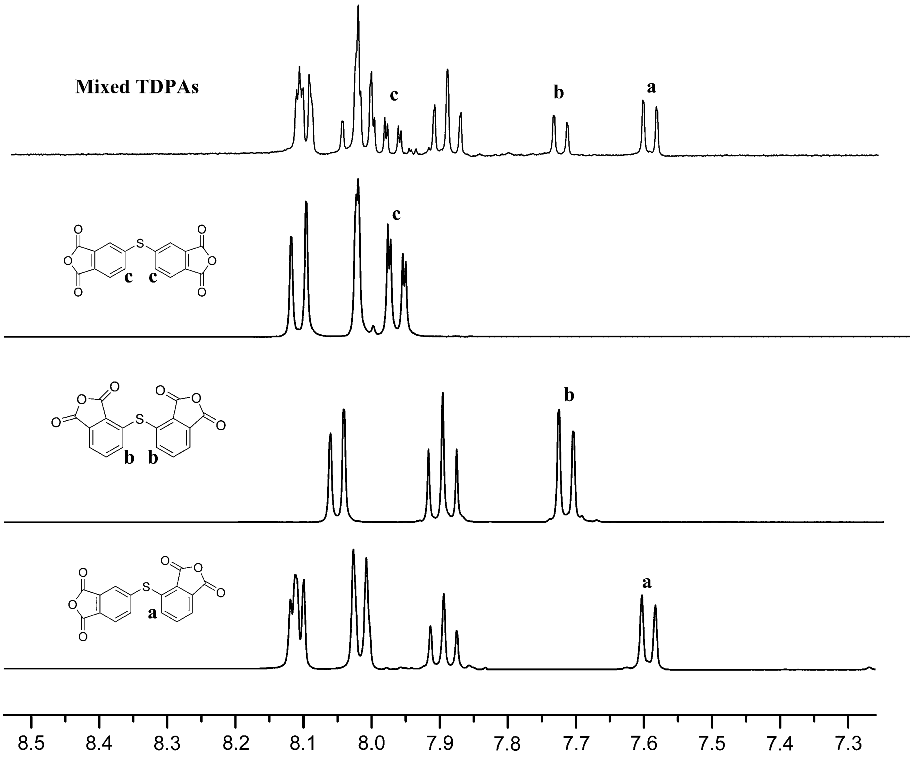


Fig. 1 ^{1}H NMR spectra of isomeric and mixed TDPAs



mixed TDPAs. In addition, each isomer which has the specific peaks assigning one or two H atoms which do not overlap with other peaks: Ha of 3,4′-TDPA, Hb of 3,3′-TDPA and Hc of 4,4′-TDPA. In the spectrum of TDPAs mixture, these peaks can be distinctly identified with almost the same shape and chemical shift with their isomeric counterparts. Therefore, relative content of each isomer was obtained from the integrals of the H peaks. The content of each isomer in the mixture was computed as follows: 23% (3,3′-TDPA), 20% (4,4′-TDPA), 57% (3,4′-TDPA).

Polyimide synthesis

The copolyimides were synthesized by the polycondensation of mixtures of TDPAs and 4,4′-ODA through a one-step polymerization. Seven PIs with stoichiometric offsets of 6.0, 4.5, 3.0, 1.6, 2.0, 1.0, and 0.1% in favor of 4,4′-ODA were synthesized, which were designated as PI1, PI2, PI3, PI4, PI5, PI6, and PI7, relatively. The reaction for a 2% stoichiometric offset version is shown in Scheme 2. Besides controlling molecular weight by established offsets, PA was used as an endcapper to terminate the reactive end groups of polymer. It has been proved that the end groups have an important effect on high-temperature stability of PIs. The reactive end groups, especially the amine end groups, were considered to be responsible for the chain extension/branching/cross-linking which reduced the thermal stability of PIs [34]. Therefore, even the PI7 was synthesized with a 0.1% stoichiometric offset for ensuring all the PIs have the thermal stability in a comparable level. The resulting seven copolyimides have the same backbone chemical structure but possess different molecular weight. Copolyimides, except PI1 and PI2 with a low-molecular weight, are able to form flexible films strong enough for DMA and tensile measurement. All the PIs exhibit characteristic imide group absorptions in FTIR spectra around 1,780 and 1,720 (imide carbonyl asymmetrical and symmetrical stretching), 1,380 (C–N stretching), and 730 cm^{-1} (imide ring deformation), indicating that the PIs structure were successfully obtained.

The inherent viscosity was measured with 0.5 g dL^{-1} NMP solution at 30 °C. Molecular weights were determined on the as-received PIs powders using gel permeation chromatography in chloroform ($CHCl_3$) solution. The theoretical average molecular weights (TMW) were calculated for a combination of stoichiometric offsets in favor of 4,4′-ODA. A summary of the results of molecular weight and inherent viscosity is summarized in Table 1.

It is noted that the number-average molecular weights, M_n, decreased as stoichiometric offsets increased. However, the measured M_ns were lower than the theoretical average molecular weights. PI7 cannot be measured by GPC because of its poor solubility in $CHCl_3$. The polydispersity values approximate 1.50 after the $\eta_{inh} > 0.40$ which represented that less low-molecular weight species are contained in polymer. Meanwhile, inherent viscosities and weight-average molecular weight decreased with increase of stoichiometric offset, as expected.

Solubility

As the homopolyimides synthesized from 3,3′-TDPA and 3,4′-TDPA show better solubility compared to PIs from

Scheme 2 Synthesis of copolyimide with a 2% stoichiometric offset

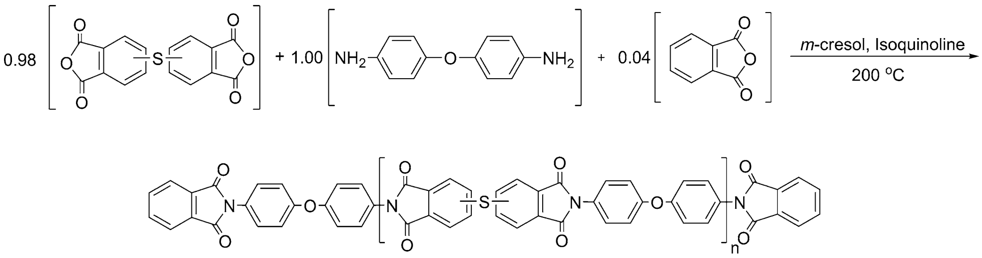


Table 1 Stoichiometric offsets, inherent viscosity (η_{inh}), and molecular weight of copolyimides

Code	Stoichiometric offset (%)	η_{inh} (dL g^{-1})	TMW (g mol^{-1})	M_n (g mol^{-1})	M_w (g mol^{-1})	M_w/M_n
PI1	6.0	0.30	8,383	3,996	14,465	3.62
PI2	4.5	0.36	11,105	5,996	17,364	2.90
PI3	3.0	0.41	16,549	16,909	26,310	1.56
PI4	2.0	0.45	24,716	20,365	30,126	1.48
PI5	1.6	0.50	30,841	20,366	34,313	1.68
PI6	1.0	0.59	49,216	24,899	37,259	1.50
PI7	0.1	0.71	490,216	–	–	–

Table 2 Solubility of copolyimides

Code	$CHCl_3$	DMF	DMAc	DMSO	NMP	*m*-cresol
PI1	++	++	++	+	++	++
PI2	++	++	++	+	++	++
PI3	++	++	++	+	++	++
PI4	++	+	++	+	++	++
PI5	++	+	++	+	++	++
PI6	++	±	++	+	++	++
PI7	±	±	++	+	++	++

Key: ++, fully soluble at room temperature; +, full soluble on heating; ±, partially soluble on heating

Table 3 Thermal properties of copolyimides

Code	T_g		$T_{5\%}$	
	DSC	DMA	N_2	Air
PI1	248	–	512	528
PI2	255	–	528	540
PI3	258	251	530	534
PI4	258	252	529	534
PI5	267	254	531	538
PI6	268	256	534	542
PI7	270	259	541	548

4,4′-TDPA in polar aprotic solvent [29], it is interesting to see whether the copolyimides containing 3,3′-TDPA and more than half content of 3,4′-TDPA exhibit good solubility as well. Solubility of all the copolyimides were measured quantitatively by dissolved 0.1 g polymer powder in 2 mL solvents and the results were summarized in Table 2. As can be seen in the table, copolyimides based on mixed TDPAs are easily soluble in polar aprotic solvent such as *N*,*N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and NMP in room temperature or on heating. In addition, all the copolyimides were soluble in phenol solvent. As mentioned above, the copolyimides are soluble in $CHCl_3$ except PI7 which cannot be measured by GPC. It is speculated that the molecular chains entanglement restrains the molecular chain mobility then weakens the solubility of polymer. Generally, the molecular weight greater than M_e is seen as the entanglements threshold of polymer, where M_e denotes the molecular weight between entanglements. As for the case in DMF, the solubility of copolyimides turns out from easily soluble in room temperature to soluble only on heating with the molecular weight increase, which might be attributed to the threshold of entanglements. It also explains that the PI7 with greatest molecular weight shows a poor solubility in $CHCl_3$. In general, copolymerization brings the copolyimides random distribution of three TDPA isomers in molecular backbone which exhibits a similar nonlinear molecular chain structure as PIs from 3,3′-TDPA. This kind of structure prevents intermolecular interactions and molecular chain packing thus enhanced solubility. However, the solubility may be affected by molecular weight in various solvents at different levels. As of result, copolyimides from TDPAs, especially the one with moderate molecular weight, have an excellent solubility in organic solvents.

Thermal properties

The glass transition temperatures (T_gs) measured using DMA and DSC are listed in Table 3. PI1 and PI2 were not able to form films strong enough to measure by DMA. It is shown that the T_gs (DSC) of copolyimides increase with the molecular weight but leveled off around 270 °C after the $\eta_{inh} > 0.5$. The results by DMA measurements show nearly the same trend of dependence of T_gs on molecular weight.

In relation to some commercial melt-processable PIs, the present copolyimides show higher T_g values compared to these PI as follows: Aurum$^{\text{TM}}$ (T_g: 250 °C) [8], LARC$^{\text{TM}}$-IA (T_g: 243 °C) [9], Ultem$^{\text{TM}}$1000 (T_g: 215 °C), and Ultem$^{\text{TM}}$5000 (T_g: 235 °C) [35]. Besides, none of the copolyimides exhibited a melt, clearly showing the amorphous nature of these polymers based on DSC results.

The viscoelastic behaviors of copolyimides (PI3–PI7) were analyzed by DMA measurements, and the storage modulus and tan δ curves versus temperature are shown in Figs. 2 and 3, respectively. The maximum tan δ values for the copolyimides were taken to represent T_gs. All of the copolyimides exhibit an initial storage modulus around 1,100 MPa then the storage modulus drop rapidly after the T_g with no platform which represents the copolyimides are totally amorphous. From the tan δ curves, two relaxation

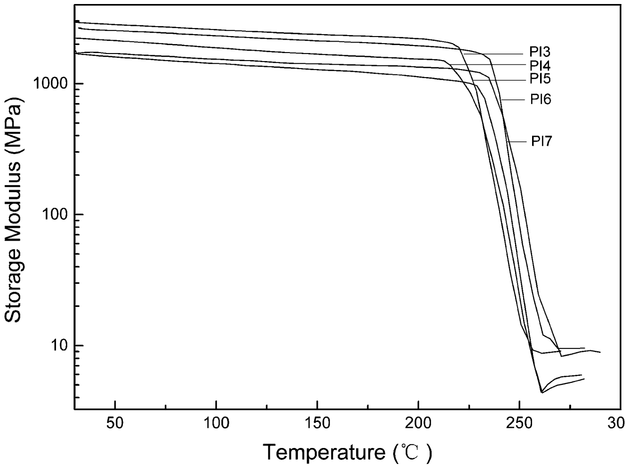


Fig. 2 Storage modulus of copolyimides films curves as a function of temperature

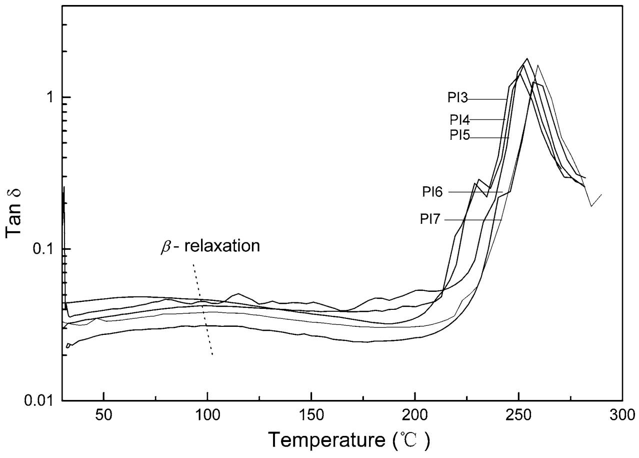


Fig. 3 Tan δ of copolyimides curves as a function of temperature

processes can be observed above room temperature of these copolyimides. Besides the glass transition, the β-relaxation is observed from ca. 90 to 110 °C varied with the increase of molecular weight.

The thermal stability of PTEIs has been probed with traditional TGA analysis to evaluate the degradation occurring via weight loss. Representative TGA curves for PI2 are shown in Fig. 4. Very small weight losses were detected below 500 °C both in air and N_2. Other TGA curves of PI samples were not showed because the results would be similar. The thermal and thermo-oxidative stability were represented using the onset temperatures corresponding to 5% weight loss ($T_{5\%}$) in both nitrogen and air atmospheres, which are summarized in Table 3. In TGA measurements with a heating rate of 10 °C/min, the copolyimides undergo 5% weight loss within 512–541 °C in nitrogen and within 528–548 °C in air. The onset temperatures show same increasing dependence with increase of molecular weight in both atmospheres. It is worthwhile to note that the $T_{5\%}$ of these copolyimides in air is higher than that in nitrogen which is just contrary to a majority of PIs. This phenomenon has been found in the other sulfur-containing polymers, which are ascribed to the different degradation mechanisms in various atmospheres [36, 37].

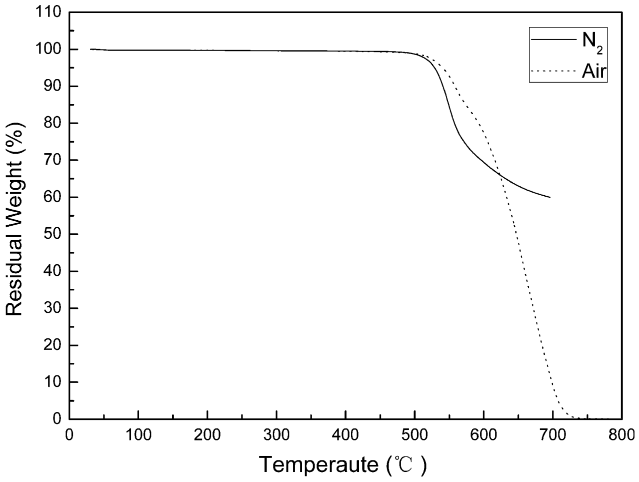


Fig. 4 TGA curves for PI2 at a heating rate of 10 °C/min under N_2 and air

Mechanical properties

PI1 and PI2 were not able to form creasable films by solution casting as mentioned above. Films from other samples were subjected to a tensile test, and their mechanical properties are summarized in Table 4. The copolyimides had tensile strengths at break of 110–125 MPa, elongations at break of 6–8%, and moduli of 3.0–3.5 GPa. Besides, the tensile strength increase slightly when molecular weight are higher, it is worth noting that yield points were emerged from the stress–strain curves after $\eta_{\text{inh}} > 0.5$ (PI5–PI7). It is known that the strength and elongation of polymer with a molecular weight above M_e will increase dramatically thus toward a limiting value at high molecular weight [38, 39]. Therefore, it is speculated that the molecular weight of copolyimides greater than ca. 20,000 g mol^{-1} of M_w at which PIs were able to form manageable films have exceeded the M_e. Moreover, the fracture behavior of copolyimides underwent a transition from brittle to ductile fashion upon moving toward increasing molecular weight. The critical molecular weight at which the transition was observed occurs at $\eta_{\text{inh}} > 0.5$ dL g^{-1} or the M_w of $\sim 3.4 \times 10^4$ g mol^{-1} in our copolyimides. Nicholson found that a similar critical molecular weight of another glassy PIs (LaRC$^{\text{TM}}$-SI) was at M_w of $\sim 2.2 \times 10^4$ g mol^{-1} [30]. It seems then that the beginning of entanglement of molecular chains leads the polymer a pronounced increase in tensile strength and more entanglements per chain length by higher molecular weight bring the polymer a ductile fracture behavior. The variation of soluble behavior of copolyimides mentioned above demonstrated the increasing entanglement extent of polymers as well. Often, M_e and the concentrations of entanglement loci are determined from rheological experiments. The speculation above, accordingly, still needs further demonstration.

Melt processability

Rheological measurements for copolyimide powders were conducted from 300 to 420 °C, and the melt viscosity as a function of time for four samples with moderate molecular weight was plotted in Fig. 5. As shown in the figure, the complex viscosity of all the samples tested declined with temperature rising then show lowest melt viscosity around 400 °C. Copolyimides with higher molecular weight exhibit relatively greater melt viscosity at the same

Table 4 Tensile properties of copolyimide films

Code	Tensile strength at break (MPa)	Yield strength (MPa)	Young's modulus (GPa)	Elongation at yield (%)	Elongation at break (%)
PI3	111.2	–	3.0	–	8.4
PI4	115.5	–	3.2	–	6.4
PI5	122.9	126.0	3.0	7.6	7.8
PI6	118.6	120.5	3.2	7.2	7.6
PI7	125.9	127.3	3.5	6.9	7.1

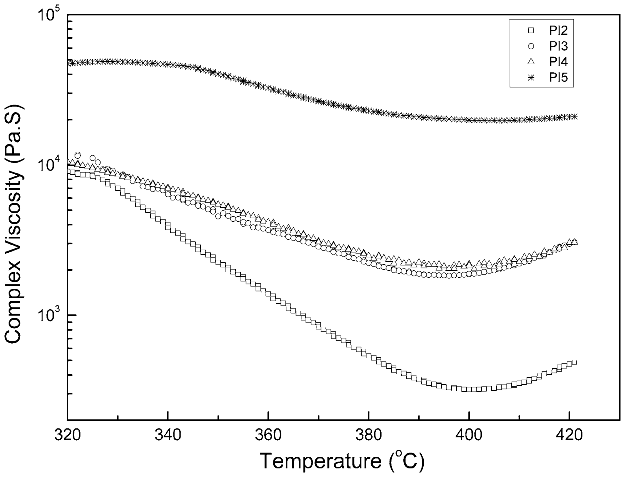


Fig. 5 The melt viscosities as a function of temperature for PI2, PI3, PI4, and PI5

temperature. Actually, our samples with greater molecular weight such as PI6 and PI7 were not melt flowable obviously during the scope of testing temperature and exhibited over high melt viscosity. This is due to the fact that in general the melt viscosity of polymer depends strongly on the extent of entanglement between polymer chains. PI3 and PI4 have nearly same value and variation trend of melt viscosity which might be able to be explained by the very close molecular weight of these two samples.

Semicrystalline PIs offer advantages of increased solvent resistance and retention of mechanical properties above the glass transition temperature. However, semicrystalline PIs generally have a high melting temperature around 400 °C. While the amorphous PIs, such as ULTEM, have a relatively lower processing temperature (about 3,000 Poise at 350 °C), the copolyimides we synthesized by TDPA isomers and ODA were totally amorphous polymer with no T_m value. Therefore, the melt viscosity will decrease dramatically after the temperature higher than T_g. PI3 and PI4 showed a complex viscosity of 5,000 Pa S around 350 °C. Even though, its melt-flowability looked inferior to that of ULTEM. Above 400 °C the melt viscosity increase with temperature raised up continuously. This is speculated to occur due to chain extension/crosslinking reactions in the melt.

In order to evaluate the melt processability of copolyimides, the rheological measurements for PI2, PI3, PI4, and PI5 powder were also conducted isothermally at 340 °C. Melt viscosity as a function of time (*t*) for four resins was plotted in Fig. 6 and the loss tangent (tan δ) versus *t* in Fig. 7.

As seen in Fig. 6, the increasing molecular weight leads to an increase in the melt complex viscosity of copolyimides. Meanwhile, the melt viscosity increases after

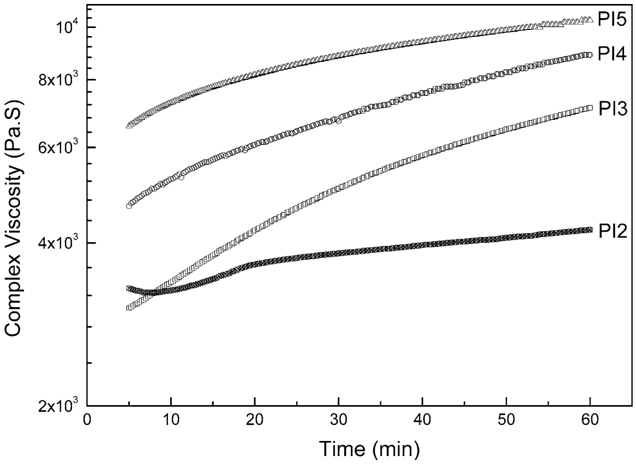


Fig. 6 Complex viscosity of PI2, PI3, PI4, and PI5 in air as a function of time at 340 °C

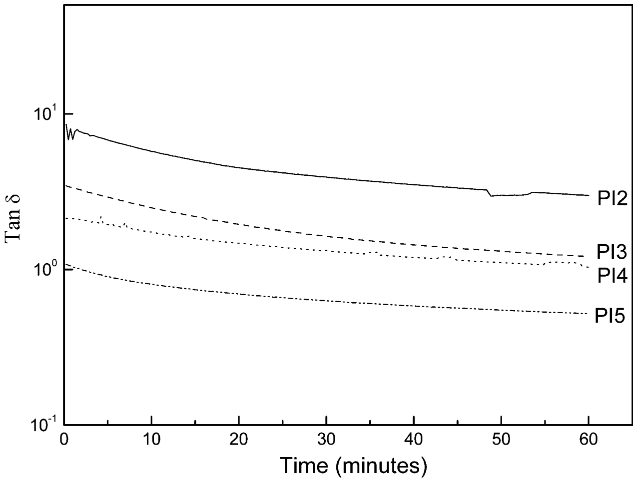


Fig. 7 Tan δ curves of PI2, PI3, PI4, and PI5 versus time

60 min hold as expected. Tan δ is the ratio of the loss (dissipation, G″) and the storage (elastic, G′) moduli for a test specimen deformed under frequency ω at time t and temperature T. It has been observed that PIs with tan $\delta > 1$, the specimen exhibits viscoelastic liquid-like behavior; when tan $\delta < 1$, the specimen exhibits viscoelastic solid-like behavior [9]. From Fig. 7, we can see that PI2, PI3, and PI4 have a tan $\delta > 1$ which manifested that these polymers have viscoelastic liquid-like behavior therefore they are relatively easy to be melt processed. However, PI5 has already showed a tan $\delta < 1$ in most of testing time, which means that the sample is not suitable for melt processing. It was apparent that the molecular weight has a significant effect on processability of copolyimides. On the basis of the above, it was found that the melt processability seems to have a critical molecular weight around the M_w corresponding to $\eta_{inh} = 0.5$ dL g^{-1}, suggesting that more balanced properties can be optimized by the precise M_w control in the present copolyimide system. In other words, well-controlled molecular weight have to be retained to yield a polymer with tan $\delta > 1$, subsequently improving its melt processability under reasonable temperatures. Actually, this critical molecular weight in connection with melt viscosity is accordance with the one related to the fracture behavior presented above, above which the copolyimides undergo a ductile rather than a brittle fracture behavior. From the melt viscosity point of view, it would be manifested that the entanglement of polymer is enhanced significantly above this critical molecular weight.

The other vital factor for melt processing of PIs is the thermo-oxidative stability of polymer. However, the TGA technique by itself is inadequate for reflecting the thermal stability of polymers, since degradation reactions such as crosslinking or chain extension could occur with a small accompanying weight loss. Actually, melt thermo-oxidative stability can be characterized through the rheological analysis by evaluating the change of melt viscosity, which is critically dependant on the molecular weight of the system, with time at a given temperature.

Owing to the PI3 has a moderate melt viscosity and adequate mechanical strength, the melt stability of PI3 at three temperatures was measured. Figure 8 shows the melt viscosity change during 60 min at 320, 340, and 360 °C, respectively. As expected, the melt viscosity dropped when polymer was measured at higher temperature. However, the melt viscosity increased at a more rapid rate during the same period of time. As for the processability, from Fig. 9, the tan δ declined with the testing carrying out. At 320 and 340 °C, the values of tan δ remain higher than one during the testing process (60 min) even though showing some reduction. However, at 360 °C, the value of tan δ has been less than 1 after 40 min, which means that the polymer has become viscoelastic solid-like state. From these results, it was found that the molecular weight change due to the chain extension/crosslinking reaction under melting condition was more prominent in the case of temperature higher than 360 °C. Even though, the thermal stabilities (thermo-oxidative stability and melt viscosity stability mentioned above) of the PIs were estimated to be suitable for injection and extrusion molding at a reasonable temperature.

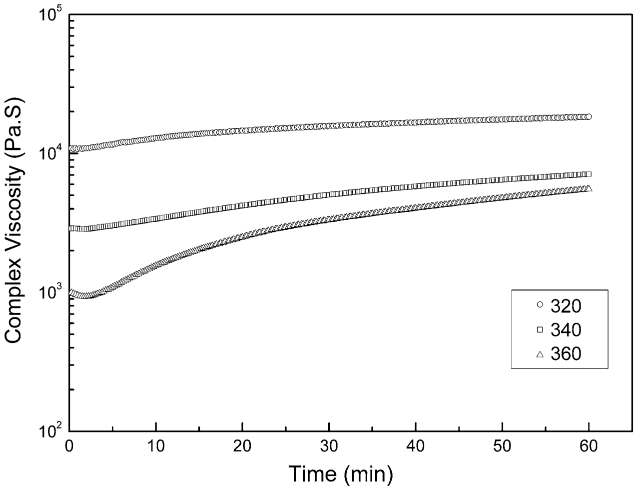


Fig. 8 The complex viscosity of PI3 variation with time at 320, 340, and 360 °C

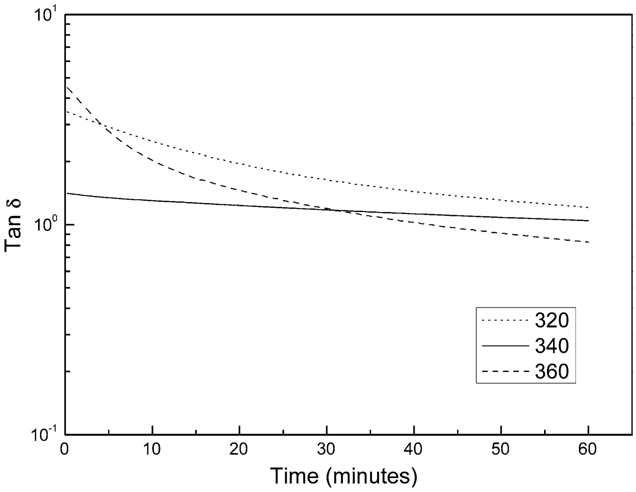


Fig. 9 Tan δ variation of PI3 with time at 320, 340, and 360 °C

Conclusion

In this study, we have synthesized a series of molecular weight controlled copolyimides from mixed TDPAs and 4,4′-ODA with PA as an endcapper. The inherent viscosity and molecular weight were controlled by stoichiometry from 0.1 to 6%. The copolyimides with relative lower molecular weight are easily soluble in polar aprotic solvents and $CHCl_3$. However, the solubility weakens to some extent with the increase of molecular weights in DMF. The copolyimides have T_g values ranging from 248 to 270 °C which increase with the molecular weight but level off after the $\eta_{inh} > 0.5$ dL g^{-1} gradually. According to the TGA analysis, most of the copolyimides have a $T_{5\%}$ above 520 °C in nitrogen and 530 °C in air. The copolyimides possess nice mechanical properties when $M_w > 20{,}000$ g mol^{-1}. Subsequently, the copolyimides exhibit ductile rather than brittle fracture behavior when $M_w > 34{,}000$ g mol^{-1}. The melt processability of copolyimides with moderate molecular weight was characterized by rheological measurements. The copolyimides with the $\eta_{inh} < 0.5$ dL g^{-1} show melt processability and excellent melt stability below 360 °C. The experimental results show that a copolyimide combined with nice processability, mechanical properties, and thermal stability is obtained by means of adjustment and control of molecular weight. As a consequence of the above, the molecular weight controlled copolyimides based on mixed TDPAs are promising to be applied as melt-processable PIs.

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