Melt processable homo- and copolyimides with high thermo-oxidative stability as derived from mixed thioetherdiphthalic anhydride isomers

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Abstract. A series of homo- and copolyimides based on mixed thioetherdiphthalic anhydride isomers (mixed-TDPA) were synthesized with several kinds of aromatic diamines. The properties of these polyimides were characterized by glass transition temperature (T_g), thermal decomposition temperature, and melt processability. A series of copolyimides were prepared to achieve high T_g concurrently with melt processability by means of selecting appropriate diamines and their composition in the copolyimides. As a result, we obtained rheological information for a series of polyimide resins as a function of temperature, time and shear rate. It is found that the processability (e.g., melt viscosity of polyimides) and ultimate product properties (e.g., T_g of polyimides) can be systematically varied by changing the variety and composition of the aromatic diamines. It has been demonstrated that the incorporation of meta- or flexible diamines improve the melt processability of polyimides significantly. Meanwhile, T_g of copolyimides from dual-diamines can be predicted and regulated. Accordingly, copolyimides from 1,3-phenylenediamine (*m*-PDA) and 3,4'-oxydianiline (3,4'-ODA) were obtained with higher T_g and lower melt viscosity. Such correlations of chemical structures and rheological behavior provide the necessary database for tailor-making new polyimide systems with desirable processability and physical properties.

Keywords: thermal properties, melt processable, isomeric polyimide, rheology

1. Introduction

Aromatic polyimides (PIs), due to their excellent thermal stability, superior mechanical strength and good chemical resistance properties, found their application in many industrial fields [1]. The outstanding properties of PIs are based on the combination of their stiff chain structures and ordered structure formation caused by strong interchain interactions. However, these advantages, meanwhile, give rise to poor solubility and processability of PIs. General methods to improve the processability are to incorporate flexible linkage into the polymer backbones [2–4]. This approach, nevertheless, inevitably leads to a decrease of glass transition temperature (T_g) in many cases. For instance, commercial thermoplastic polyimide Ultem possesses excellent melt processability but its long-term service temperature is limited to lower than 170°C. Moreover, the thermoxidative stability of Ultem is also relatively poor because of the presence of thermally unstable isopropylidene groups in the polymer backbones [5].

Thermoplastic PIs are commonly applied in various industries because of the ease of processing, handling, and storage. Most application requires thermoplastic PIs to exhibit enhanced melt flow behavior at relatively low processing temperatures. However, the high melt viscosity of these materials

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requires high pressure to be used in processing to fabricate structural composites and adhesive joints. Therefore, improvements are required to reduce the melt viscosities without compromising other properties.

It was reasoned that introduction of the monomers containing asymmetric or noncoplanar structure to replace the linear symmetrical dianhydride in polymer chain could weaken the interchain interaction thus enhancing the solubility and melt flowability [6]. As of result of that, it has been further demonstrated that replacement of the symmetrical dianhydride in PIs with asymmetric ones decreases the melt viscosity but increases the T_g relative to the corresponding symmetrical PIs [4, 7–9]. Thioetherdiphthalic anhydride (TDPA) is an aromatic bridged dianhydride which has three isomers as shown in Figure 1. The flexible thioether moiety offers the polymer with flexibility and easy melt processability. As a consequence, thioether links have been introduced to many polymers. And polythioetherimides have been synthesized by many researchers for different purposes [10–12]. In previous research, PIs based on 2,3,3',4'-thioetherdiphthalic anhydride (3,4'-TDPA) exhibited a higher T_g than that of symmetric 3,3',4,4'-thioetherdiphthalic anhydride (4,4'-TDPA) and also presented a remarkable drop in the complex viscosity above T_g [13]. This is attributed to the remarkable decrease in the intermolecular interactions of the geometrically irregular 3,4'-TDPA-based PI. According to the research on a similar dianhydride ODPA, TDPA-based polyimides show similar thermal stability and mechanical properties as ODPA-based polyimides, meanwhile, more excellent melt flowability. Moreover, the synthesis of TDPA is more convenient than that of ODPA [4].

Copolymerization by incorporating monomers with flexible moieties, which disrupts the regularity of molecular chain and prevents the interaction of polymer chains, is a simple but effective way for structure modification to balance the processability and the desired properties [14, 15]. For example, 3,4'-oxydianiline (3,4'-ODA) has been proved to be a diamine with polyimide derivatives having better melt flowability than polymers from its isomer 4,4'-oxydianiline(4,4'-ODA) [16]. Other isomeric diamines, such as 1,3-bis(4-aminophenoxy) benzene (TPER) and 1,3-phenylenediamine (*m*-PDA), can also offer polyimides relatively lower melt viscosity than the corresponding *para*-isomers [5, 17]. As a consequence, the processability of copolyimides is enhanced dramatically. The T_g of these copolyimides generally range between that of homopolyimides from the two dianhydrides or diamines [5, 16, 18]. This principle makes it possible to predict the T_g of copolyimides by appropriately selecting the structure and ratios of dianhydride and diamine component while obtaining improved melt flowability of PIs.

Based on the thermal and rheological behavior of 3,4'-TDPA based polyimides, we have successfully prepared copolyimides from mixture of three TDPA isomers (mixed-TDPA) [19]. These kinds of isomeric copolyimides show excellent melt processability similar to the homopolyimide from 3,4'-TDPA. Even though PIs from mixed-TDPA didn't show obviously better melt flowability than that from 3,4'-TDPA, the mixed isomeric dianhydrides can be synthesized by a more convenient routine than that of 3,4'-TDPA [20], which is favorable to prepare a novel melt processable PI with relatively low cost. Meanwhile, it has also been proved that regulating the number-average molecular weight at an appropriate level by stoichiometric imbalance has a significant effect on the melt flowability and the T_g of the copolyimides.

We wish to lower the viscosity of PIs by the replacement of the rigid repeat unit, namely 4,4'-ODA, in the backbone with more flexible ones in order to obtain a high performance melt processable PI. It is expected that the combination of flexible bonds, unsymmetrical moieties in the same macromolecule would yield new PIs offering a compromise between processability, on one side, and the physical and thermal characteristics, on the other. More-
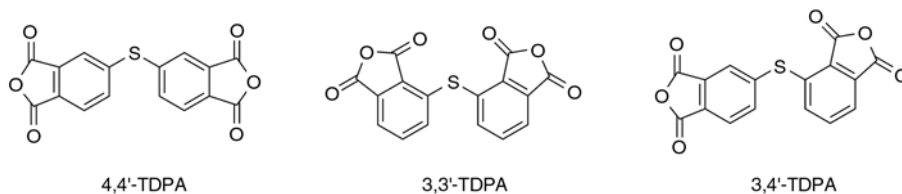
Figure 1. The structures of thioetherdiphthalic anhydride isomers

over, to tailor a PI to satisfy specific requirements between processability and high T_g, a careful examination and selection of variety and composition of diamines is of great importance. Therefore, the first part of this work is to establish the basic structure-property relationships in homopolyimides derived from mixed-TDPA and a variety of aromatic diamines. On the basis of T_gs, thermal stability, and rheological properties, some promising combination of diamines were selected to synthesized melt-processable copolyimides afterwards. And the characterization was focused on processability of these copolyimides systems.

2. Experimental
2.1. Monomer and other chemicals

3- and 4-chlorophthalic anhydrides were obtained from Harbin Shidai Science and Technology Co., Ltd., China and used as received. Anhydrous sodium sulfide was purchased from Inner Mongolia Lichuan Chemistry Co., Ltd., China and used as received. Phthalic anhydride (PA) was purified by sublimation before use. 4,4'-ODA, mp 189~190°C, was purchased from Sinopharm Chemical Reagent Co., Ltd., China and used as received. 3,4'-ODA, mp 74~75°C, was purchased from Changzhou Sunlight Medical Raw Material Co., Ltd., China and recrystallized from a 9/1 ratio of toluene/ethanol before use. 1,4-Phenylenediamine (PDA), mp 138~140°C, was purchased from Sinopharm Chemical Reagent Co., Ltd., and recrystallized from ethyl acetate. *m*-PDA, mp 63~65°C, was purchased from Aladdin and recrystallized from a 9/1 ratio of toluene/cyclohexane before use. 1,4-bis(4-aminophenoxy)benzene (TPEQ), mp 173°C, and TPER, mp 116°C, were purchased from Changzhou Sunlight Medical Raw Material Co., Ltd., and used as received. All of the other reagents were from the Sinopharm Chemical Reagent Co., Ltd. and were of analytical grade.

2.2. Characterization

The inherent viscosities (η_{inh}) were determined at 30°C with an Ubbelohde viscometer and the concentration was 0.5 g·dL^{-1} in *m*-cresol. ^{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 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 nitrogen or an air atmosphere. 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 properties of PIs were performed on a rotational Physica MCR 301 rheometer in an air flow. The parallel plate diameter was 25 mm and the gap was set to about 1.0 mm in all the runs. Sample discs of 25 mm diameter and 1 mm thickness were prepared by press-molding of the powder-like PI at 80°C under high pressure. The complex viscosity (η^*) of PIs was measured by scanning the temperature from 280 to 420°C at a ramp rate of 3°C/min with a frequency of 1 Hz and a strain of 1%. Data acquisitions began 30 min after sample mounting. Meanwhile, dynamic time sweep test was performed at 340°C to evaluate the melt stability of PIs. The η^*, storage elastic modulus (G') and the loss elastic modulus (G'') data were isothermally collected at 340°C with a frequency of 1 Hz and a strain of 1%. Steady shear viscosity of PIs was obtained subjected to small amplitude oscillatory shear at 1% strain over a frequency range from 0.01 to 100 s^{-1}.

2.3. Monomer synthesis

3,3'-TDPA and 4,4'-TDPA and the isomer mixtures, mixed-TDPA were synthesized as reported in the literature [21]. 3,4'-TDPA was synthesized by a method revealed by a Chinese patent [20].

The composition of isomers in mixed-TDPA was calculated according to integrals of ^{1}H NMR spectra of the mixture and three isomers. The detailed information was as presented in reference [19]. As a result, the content of each isomer in the mixture was determined as follows: 21% (3,3'-TDPA), 18% (4,4'-TDPA), and 61% (3,4'-TDPA).

2.4. Polyimides synthesis

All PIs were prepared through one-pot method in *m*-cresol as shown in Figure 2. The inherent viscosity of PIs was regulated in the range of 0.4 to
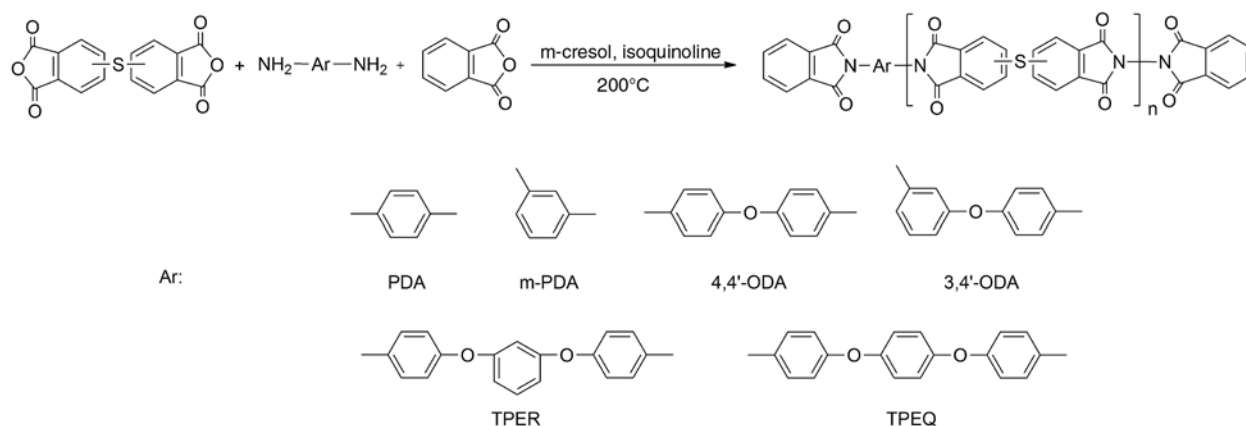
Figure 2. Synthesis of polyimides derived from mixed-TDPA via one-step polymerization

0.5 dL·g⁻¹ by the stoichiometric imbalances between dianhydrides and diamines. PA as an end-capper was added for improving thermal stability of PIs. A typical procedure is described as follows as an example.

To a 100 ml completely dried three-neck flask were added 2.0024 g (10.0 mmol) of 4,4'-ODA, 45 ml *m*-cresol under nitrogen flow with stirring. After 4,4'-ODA was completely dissolved, 3.1975 g (9.8 mmol) of mixed-TDPA, 0.0592 g (0.4 mmol, designated as 2%) of PA, and several drops of iso-quinoline were added. The mixture was stirred at room temperature for a few minutes and then heated at 100°C for 1 h and 200°C for 8 h. After cooling to room temperature, the viscous solution was diluted with additional 50 ml *m*-cresol and then poured into 500 ml of ethanol with stirring. The precipitate was filtered off, washed with boiling ethanol twice and dried in vacuo at 100°C for 10 h.

The copolyimides based on mixed-TDPA and two different diamines were prepared by similar process as above. Mixed-TDPA was added in the *m*-cresol solution of two diamines until the diamines were completely dissolved.

3. Results and discussion
3.1. Mixed-TDPA-based melt-processable homopolyimides
3.1.1. Basic properties of homopolyimides
In order to appreciate the basic relationships between structure and properties of mixed-TDPA-based PIs, especially the melt processability, we synthesized a series of controlled molecular weight PIs from mixed-TDPA and a variety of diamines via one-step polymerization. Table 1 shows the basic prop-

Table 1. Properties of controlled molecular weight homopolyimides based on mixed-TDPA

Diamines	η_{inh} [dL·g⁻¹]	T_g [°C]	$T_{5\%}$ [°C]		R_w[a]
			N₂	Air	
4,4'-ODA	0.42	265	529	534	60%
3,4'-ODA	0.45	246	527	538	60%
PDA	0.45	320	537	550	61%
m-PDA	0.41	289	524	530	62%
TPEQ	0.48	234	525	538	55%
TPER	0.47	217	529	518	58%

[a]Residual weight at 700°C in N₂

erties of mixed-TDPA-based homopolyimides, each of which are designated by the abbreviation of diamines. The inherent viscosities of these PIs, which were controlled by the stoichiometric imbalances between dianhydrides and diamines, ranged from 0.4 to 0.5 dL·g⁻¹, indicating the polymer had similarly moderate molecular weights for comparing effectively while ensuring these PIs hold enough mechanical properties. According to our previous investigation, the value of η_{inh} = 0.36 corresponds to the critical molecular weight for obtaining a flexible film from PIs based on mixed-TDPA and ODA, below which the films become brittle. Meanwhile, all of the PIs in this range of molecular weight exhibit some extent of melt-flow behavior at elevated temperatures. PA was used as an endcapper for the high-temperature stability of the melt viscosity.

An important aspect of this study is the effect of the structural changes on the T_g. As presented in Table 1, the T_g of mixed-TDPA-based PIs determined by DSC varies in a broad range from 217~320°C depending on the structures of the diamines. The introduction of flexible linkage diamines significantly decreases the T_g such as TPER and TPEQ contrary to the effect of more

rigid diamines such as PDA and *m*-PDA. As for the influence of isomerism, the results are as expected in terms of the effect of para/meta isomerism on the T_gs. PIs derived from para diamines show higher T_g's, i.e. $T_g = 265°C$ (mixed-TDPA/4,4'-ODA) > 246°C (mixed-TDPA/3,4'-ODA), 320°C (mixed-TDPA/PDA) > 289°C (mixed-TDPA/*m*-PDA), 234°C (mixed-TDPA/TPEQ) > 217°C (mixed-TDPA/TPER). This phenomenon can be attributed to the PIs with meta linkages disturb the intimate chain stacking necessary for intermolecular interaction [5]. As a result, the introduction of meta-linkages causes a significant decrease in T_g. These PI powders displayed no melting peak in the DSC scan, indicating that these polymers are totally amorphous. It is reasonable because the polyimides derived from three isomeric TDPA are amorphous as well [13]. In the case of mixed-TDPA-based PIs, the less ordered nature attributed by copolymerization of isomers suggests a greater degrees of molecular freedom and less intermolecular interaction.

Thermogravimetric analysis was performed to provide an insight into the thermal and thermoxidative stability of the PIs and to measure their decomposition temperatures. The temperatures at which a weight loss of 5% occurred both under N_2 and air were recorded, along with the char yield at 700°C in N_2. From the results in Table 1, mixed-TDPA-based PIs have a high thermal and thermoxidative stability ($T_{5\%} > 520°C$ both in N_2 and air). 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 is ascribed to the different degradation mechanisms in various atmospheres [12, 22].

3.1.2. Melt rheological properties of homopolyimides

In order to obtain melt processable mixed-TDPA-based PIs, we investigate the relationships between melt viscosity and the structure of diamines. Molecular weight is one of the most important variables affecting the viscosity of a polymer melt. Therefore, all of the PIs were prepared at an established range of moderate molecular weight.

Similar to the variation of T_g values with chemical structures, the more rigid structures tend to impart higher melt viscosities to the PIs. Within a series of

PIs based on a several diamines and the same level of molecular weight, melt viscosity generally increases in the order of increasing rigidity of the diamines.

The dynamic melt complex viscosity (η^*) curves are shown in Figure 3 and the η^* in three temperatures and minimum melt viscosity data are tabulated in Table 2. The melt viscosity of all the samples monotonically decreased with increasing temperature except the mixed-TDPA/PDA which has quite a high viscosity during the testing range, the curve of which was not presented in the figure. It is known that the asymmetric structure and meta linkages, such as the moieties in 3,4'-ODA and TPER, significantly decrease the degree of molecular packing and weaken the intermolecular force [17]. As a consequence, the melt flowability is improved by incorporation of these diamines. As presented in the table, the melt viscosity at three temperatures as well as the minimum viscosity of the PIs from TPER and 3,4'-ODA is much lower than that of 4,4'-ODA, which has similar melt viscosity in our previous research [19]. Take the η^* of PI (4,4'-ODA) and PI (3,4'-ODA) as an example, the former has a η^* of 21 100 Pa·s when the processing temperature was 340°C, and the minimum η^*

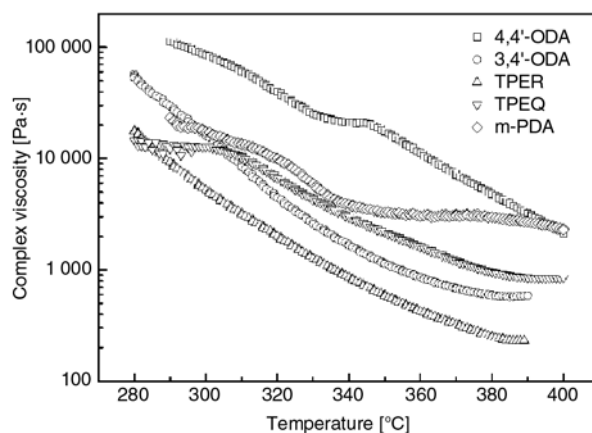**Figure 3.** Melt complex viscosity of homopolyimides based on mixed-TDPA

Table 2. Melt complex viscosity of homopolyimides based on mixed-TDPA

Diamines	Melt complex viscosity [Pa·s] at			Min melt viscosity [Pa·s]
	320°C	**340°C**	**380°C**	
4,4'-ODA	39 900	21 100	4 790	2 110 at 400°C
3,4'-ODA	4 440	1 700	595	577 at 385°C
TPER	2 010	858	250	231 at 387°C
TPEQ	6 650	2 970	962	840 at 396°C
m-PDA	9 970	3 890	2 990	2 290 at 400°C
PDA	–	25 300	43 000	25 000 at 341°C

was approximately 2000 Pa·s at 400°C. As for the PI (3,4'-ODA), the polymer has a η^* of 1700 Pa·s at 340°C and a minimum η^* of 577 Pa·s at 385°C. Replacement of the rigid diamine with the more flexible ones causes a sharp decrease in the η^*. These results suggests that molecular interactions of the TPER and 3,4'-ODA based PIs are weaker than the other PI systems. In addition, the PI (*m*-PDA) shows a lower melt viscosity than 4,4'-ODA. This phenomenon is valuable because the incorporation of *m*-PDA could impart a higher T_g to the polymer than that of 4,4'-ODA.

We try to elaborate the intrinsic disparity of melt flowability between PIs from different diamines by means of investigating the melt shear viscosity dependence on shear rate of PIs (4,4'-ODA and 3,4'-ODA) at several temperatures to demonstrate the effect of diamines. And the melt flow activation energy of polymer was calculated to compare between each other. The shear viscosity data as a function of shear rate for PIs from 4,4'-ODA and 3,4'-ODA at 330, 340, 350, 360, and 370°C are presented in Figure 4. Burks and St. Clair [10] had introduced sulfur in polyetherimides for the purpose of obtaining melt processable polyimides. According to the variation of apparent viscosity with shear rate, polythioetherimides in our system have shown better melt flowability than PIs based on 4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride. PIs from mixed-TDPA and 4,4'-ODA, 3,4'-ODA show shear viscosity less than 10^3 Pa·s when shear rate are close to 10^2 s^{-1}.

Simple mathematical models formulated for representing steady-flow viscosity data in terms of shear rate, the Carreau-Yasuda model has the following form (Equation (1)) [23]:

$$\frac{\eta(\gamma) - \eta_\infty}{\eta_0 - \eta_\infty} = \left[1 + (\lambda\gamma)^a\right]^{\frac{n-1}{a}} \qquad (1)$$

where η_0 is called the zero-shear viscosity, η_∞ is the infinite-shear-rate viscosity. λ is a characteristic viscous relaxation time that defines the location of the transition from Newtonian to shear-thinning behavior. a is a dimensionless parameter (sometimes called 'the Yasuda constant' since it was a parameter added to the Carreau equation by Yasuda) which describes the transition zone between the Newtonian plateau and the shear-thinning region and is inversely related to the breadth of this zone. The exponent $(n-1)$ defines the slope of the $\eta(\gamma)$ versus γ curve within the power law region. For our purposes, η_∞ is negligible (zero). Then the Carreau-Yasuda model was employed and the η_0 was calculated by the software of rheometer automatically. The continuous curves drawn in this figure are the Carreau-Yasuda equation fits of the experimental data. For each temperature, one can observe that the low shear rate viscosity plateau broadly spans to 10^{-2} s, which allows the determination of the zero-shear-rate viscosity η_0 with satisfactory accuracy.

The values of η_0 are listed in Table 3. The η_0 of PI (3,4'-ODA) are lower than that of PI (4,4'-ODA) at

Table 3. The zero-shear-rate viscosity of PI (4,4'-ODA) and PI (3,4'-ODA)

T [°C]	η_0 [Pa·s]	
	4,4'-ODA	3,4'-ODA
330	44 813	20 343
340	20 985	10 083
350	15 106	6 900
360	8 013	6 328
370	4 565	4 148
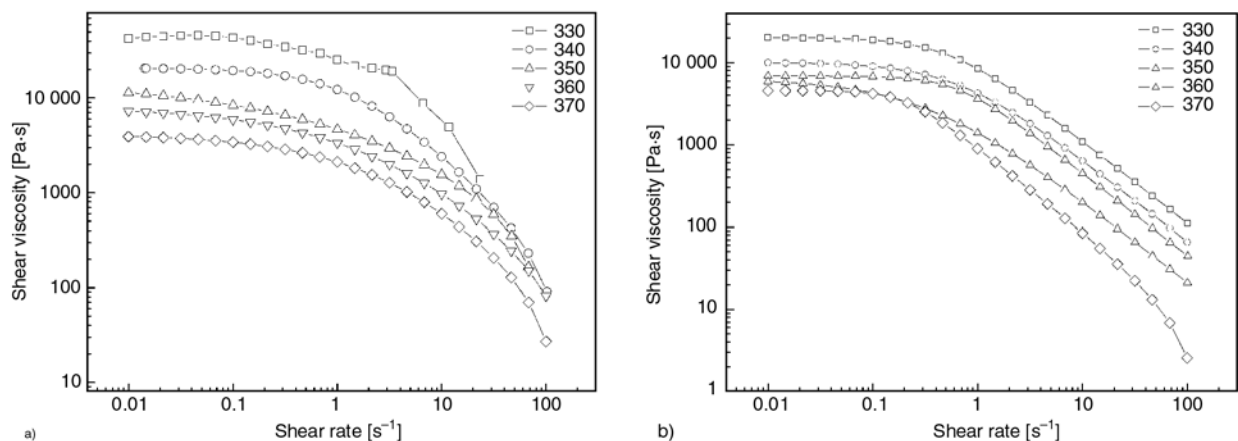
Figure 4. Shear viscosity as a function of shear rate at different temperatures (a): PI(4,4'-ODA), (b): PI(3,4'-ODA)

each temperature, indicating that the former exhibits higher melt flowability. The temperature dependence of the melt shear viscosity of polymer melts is one of the most important parameters in polymer flow, which can be expressed by the Arrhenius expression (Equation (2)) form [24]:

$$\eta_0 = A \exp \frac{E_a}{RT} \qquad (2)$$

where R is the gas constant, A is a constant, and E_a is flow activation energy. E_a varies widely from polymer to polymer, and depends on chain composition. In our system, PIs possess different chain flexibility values related to the diamine structure. This disparity in flexibility and melt flowability are reflected in the different values of E_a.

Values of E_a are calculated by using η_0 data at temperatures from 330 to 370°C. Thus, the E_a values decrease from 178 to 118 kJ/mol, for the PI (4,4'-ODA) and PI (3,4'-ODA), respectively. And there is no doubt that this decrease is induced by the incorporation of asymmetrical moiety into polymer. Increasing flexibility by introduction of flexible bonds and unsymmetrical groups in PIs creates a lower energy barrier for the movement of the molecular chains in polymer melts. As a consequence, this modification leads to a reduction of E_a demonstrating that a more flowable structure is obtained.

3.2. Mixed-TDPA-based melt-processable copolyimides

3.2.1. T_g of copolyimides

It has been known that copolymerization is a simple and effective way for structure modification to balance desired properties, such as melt processability, thermal stability and mechanical properties [14]. Therefore, a series of copolyimides based on mixed-TDPA were prepared on the basis of the structure-property relationships for the homopoly-

imides with the purpose of obtaining PIs with both nice melt-processability and a relative higher T_gs. Table 4 summarizes the properties of copolyimides based on mixed-TDPA and several compositions of diamines. The DSC scans of the copolyimides exhibited only one T_g, indicating that the various repeating units were randomly distributed along the polymer chain, thus a random copolymer structure had been formed. The T_gs of these copolyimides were found to be in the range 229~255°C. The Fox equation is usually used to estimate T_g depending on composition for miscible blends and random copolymers in a bulk state [25]. In this study, the Fox equation was used to estimate composition dependence of the T_gs of copolyimides. The constructed Equation (3) is as follows:

$$\frac{1}{T_g^*} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (3)$$

where w_1 and w_2 ($w_1 + w_2 = 1$) are the weight fractions of diamine components, T_{g1} and T_{g2} represent the T_g of each homopolyimides. Thus T_g^* is the predicted glass transition temperature depending on the composition of the diamines and the results are listed in the table as well. Most of the T_g^* values predicted by the Fox equation generally are very close to the actual T_gs of the copolyimides. It is worth noting that the T_g of PI (*m*-PDA/TPER) is obviously higher than the predicted value T_g^*. This could be explained by the asymmetric structures of both these diamines significantly offered polymer a more twisted structure resulting that the movement of segment need more space and energy. However, the Fox equation could still be applied to estimate a T_g value of copolyimides in our system.

3.2.2. Melt rheological properties of copolyimides

The dynamic melt complex viscosity curves of copolyimides are shown in Figure 5 and the com-

Table 4. Properties of copolyimides based on mixed-TDPA

Diamines X/Y [mol ratio]	η_{inh} [dL·g⁻¹]	T_g [°C]	T_g^* [°C]	$T_{5\%}$ [°C]		R_w^a
				N₂	AIR	
3,4'/4,4'-ODA(1/1)	0.48	255	255	532	539	59%
TPER/TPEQ(1/1)	0.47	229	226	521	525	56%
TPER/3,4'-ODA(1/1)	0.46	231	228	528	535	59%
m-PDA/TPER(1/1)	0.42	242	233	517	527	56%
m-PDA/3,4'-ODA(3/7)	0.44	255	253	520	529	59%
PDA/3,4'-ODA(15/85)	0.44	249	251	518	529	56%

aResidual weight at 700°C in N₂

Table 5. Complex melt viscosity of copolyimides based on mixed-TDPA

Diamines	Complex melt viscosity [Pa·s] at			Min melt viscosity [Pa·s]
	320°C	**340°C**	**380°C**	
TPER/TPEQ(1/1)	4 020	2220	1270	1260 at 385°C
TPER/3,4'-ODA(1/1)	5 440	2620	980	909 at 389°C
4,4'/3,4'-ODA(1/1)	10 900	8100	2580	1560 at 403°C
m-PDA/TPER(1/1)	7 090	4100	999	745 at 395°C
m-PDA/3,4'-ODA(3/7)	15 200	5190	800	410 at 403°C
PDA/3,4'-ODA(15/85)	13 200	7420	1 800	1190 at 400°C
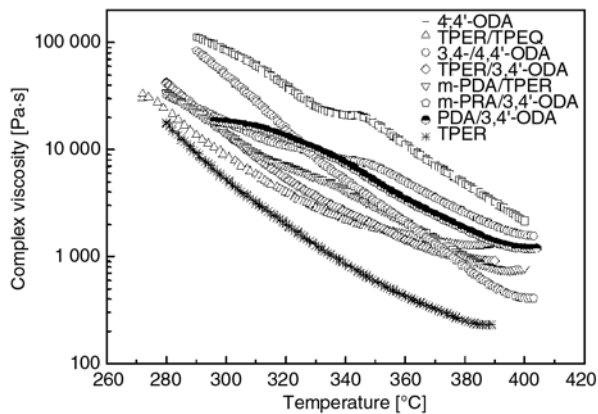
Figure 5. Melt complex viscosity of copolyimides based on mixed-TDPA

plex viscosity in three temperatures and minimum melt viscosity data are tabulated in Table 5. From the figure, most of the copolyimides exhibit enhanced melt flowability compared to PI (4,4'-ODA) which has melt viscosity around 2000 Pa·s at 400°C. In our previous research [19], PIs based on mixed-TDPA and 4,4'-ODA have a similar melt viscosity when the inherent viscosity was between the range of 0.4~0.5 dL/g. However, the T_gs of copolyimides decrease to a certain extent owing to the incorporation of flexible structures. Among the mixed-TDPA-based copolyimides, PI (*m*-PDA/TPER) and PI (*m*-PDA/3,4'-ODA) simultaneously

satisfied the demands of good melt flowability and less sacrifice of T_gs. Therefore, it has been demonstrated that processability of PIs as derived from mixed-TDPA can be be regulated in terms of diamine variety and composition. From the variations of T_gs we can also figure out that flexible diamine with a relatively high molecular weight, namely a greater weight fraction in the composition, has a prominent effect on the physical properties of PIs.

3.3. Melt stability of homo- and co-polyimides based on mixed-TDPA

Isothermal viscosity measurements at 340°C were also conducted on most of the PIs to evaluate the melt stability in air. The curves of melt viscosity and data were showed in Figure 6 and Table 6, respectively. The melt viscosity ratio (*MVR*) calculated by Equation (4) was usually employed to describe the melt stability [26]:

$$MVR = \frac{MV30}{MV5} \tag{4}$$

where *MV*5 and *MV*30 are the melt viscosities [Pa·s] measured at 5 and 30 min, respectively, after the solid sample was completely molten. The polymer
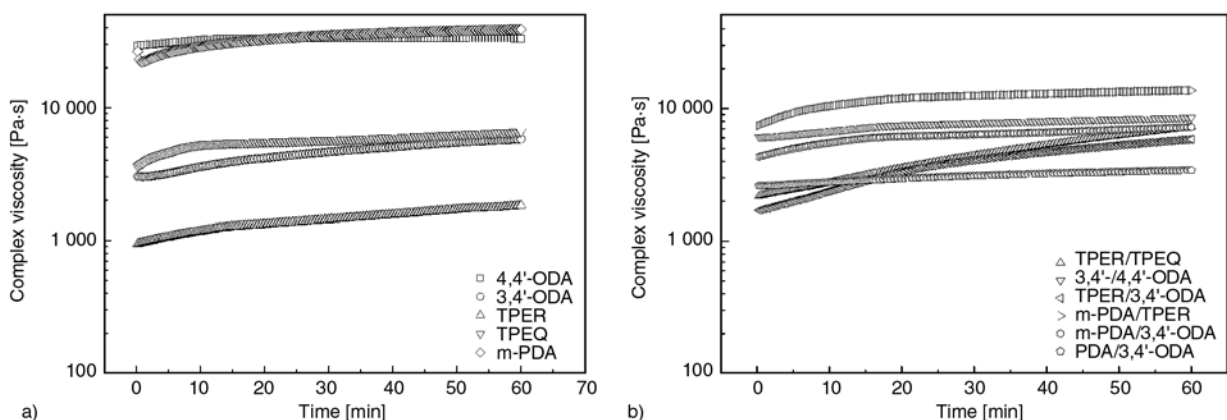
Figure 6. Complex viscosity of homopolyimides (a) and copolyimides (b) in air as a function of time at 340°C

Table 6. Melt stability of homo- and copolyimides based on mixed-TDPA

Diamines	Complex melt viscosity [Pa·s] at			MVR
	5 min	30 min	60 min	
4,4'-ODA	30 800	33 500	33 200	1.1
3,4'-ODA	3 190	4 640	5 800	1.4
TPER	1 060	1 430	1 830	1.3
TPEQ	4 600	5 690	6 600	1.2
m-PDA	26 000	35 100	38 900	1.3
TPER/TPEQ (1/1)	2 450	4 410	7 220	1.8
TPER/3,4'-ODA (1/1)	2 000	4 090	5 850	2.0
4,4'/3,4'-ODA (1/1)	6 370	7 780	8 560	1.2
m-PDA/TPER (1/1)	9 170	12 500	13 700	1.3
m-PDA/3,4'-ODA (3/7)	4 970	6 360	7 240	1.3
PDA/3,4'-ODA (15/85)	2 670	3 100	3 410	1.2

Table 7. Tensile properties of homo- and copolyimides based on mixed-TDPA

Diamines	Tensile properties		
	Strength [MPa]	Modulus [MPa]	Elongation [%]
4,4'-ODA	116	3 200	6.4
3,4'-ODA	120	3 305	5.1
PDA	121	3 521	7.9
m-PDA	111	3 655	8.4
TPEQ	101	2 623	6.8
TPER	116	3 046	6.6
4,4'-ODA/3,4'-ODA(1/1)	113	3 025	6.1
TPEQ/TPER(1/1)	110	2 997	5.8
TPER/3,4'-ODA(1/1)	107	3 012	5.0
m-PDA/TPER(1/1)	108	3 140	4.3
m-PDA/3,4'-ODA(3/7)	121	3 435	7.4
PDA/3,4'-ODA(15/85)	122	3 174	8.6

could be considered as having good melt stability if its *MVR* value was located in the range of 1.0~1.5. In the experiment, the test specimen was loaded when the chamber was preheated, and the measurement was started when the temperature of the specimen and chamber was stabilized at 340°C.

The isothermal viscosity data demonstrate that the viscosity increase after 60 min hold periods is acceptable and most of their *MVR* are below 1.5. This indicates that undesirable crosslinking occurred slightly during the heating process which is favorable for melt-processing.

3.4. Tensile properties of homo- and co-polyimides based on mixed-TDPA

All PIs formed flexible films by dissolving polymer powder in *m*-cresol solution followed by volatizing the solvent in a forced air oven. The tensile properties of the thin films (20~30 μm) were measured at room temperature, and are summarized in Table 7. As shown in the table, the tensile properties of PIs derived from mixed-TDPA indicated strengths at break of 100~120 MPa, tensile moduli ranging from 2600 to 3500 MPa, with an elongation at break of 4~8%. As mentioned above, PIs with molecular weights in this range have nice mechanical properties as thermoplastic engineering materials. It is worthy to note that in the homopolyimides derived from mixed-TDPA, the meta-diamine-based PIs showed a higher tensile modulus than the para-diamine-based PIs. A similar behavior has been observed in PIs from isomeric biphenyltetracarboxylic dianhydrides (BPDA). The a-BPDA/ meta-diamine-based PIs showed a higher storage

modulus measured by DMA as well as a higher tensile modulus. This phenomenon may be explained by a mechanism that a segment containing the meta-linkages can take a more extended conformation form than that containing the para-linkages [7–8]. However, this tendency is hard to distinguish in copolyimides based on mixed-TDPA, which may be attributed to that additional monomers disrupt the conformational consistency resulting in the loss of tensile modulus.

3.5. Solubility

Solubility is a major indicator for the intermolecular interaction, chain flexibility and conformation of PIs. Solubility of all the copolyimides were measured quantitatively by dissolving 0.1 g polymer powder in 2 ml solvents and the results are summarized in Table 8. In general, the more bent and non-coplanar structure of molecular backbone result in weaker intermolecular interaction. Thus the PIs derived from *m*-PDA and 3,4'-ODA are more soluble than their counterparts from PDA and 4,4'-ODA. However, PIs from TPER and TPEQ show similarly nice solubility because of their flexible nature. Copolymerization is an effective method to enhance the solubility of insoluble PIs since the addition of a new component disrupts the symmetry and recurrence regularity of the polymer chain. It is also verified by investigating the solubility of copolyimides from diamines resulting better and less soluble PIs, such as *m*-PDA/3,4'-ODA, *m*-PDA/TPER, and PDA/3,4'-ODA. From the results of table, these copolyimides show improved

Table 8. Solubility of homo- and copolyimides based on mixed-TDPA

Diamines	DMAC	DMF	DMSO	NMP	m-cresol	CH₃Cl
PDA	–	–	–	+ –	+	–
m-PDA	–	–	+ –	+ –	+	–
3,4'-ODA	+ +	+ –	+ +	+ +	+ +	+ +
4,4'-ODA	+ –	+ –	+ –	+ –	+	+ +
TPEQ	+ +	+ +	+ +	+ +	+ +	+ +
TPER	+ +	+ +	+ +	+ +	+ +	+ +
m-PDA/3,4'-ODA	+ +	+ +	+	+ +	+ +	+ –
m-PDA/TPER	+ +	+ –	+	+ +	+ +	–
PDA/3,4'-ODA	+ +	+ +	+ +	+ +	+ +	+ +

+ +: soluble at room temperature; +: soluble on heating; + –: partially soluble on heating; –: insoluble

solubility than the homopolyimides based on m-PDA and PDA, respectively.

4. Conclusions

A series of PIs based on mixed-TDPAs have been synthesized with a variety of aromatic diamines. According to the basic structure-property relationships several promising melt processable copolyimides combined with melt flowability and relatively higher T_g were developed. The copolyimides with controlled molecular weights were characterized by good mechanical properties, lower melt viscosities compared to the PI (mixed-TDPA/4,4'-ODA) while remaining high thermal stability. The decrease of E_a from 178 kJ/mol of PI (4,4'-ODA) to 118 kJ/mol of PI (3,4'-ODA) demonstrated that the incorporation of unsymmetrical structure into the polyimide backbone enhances the melt flowability. From the melt thermal stability point of view, this series of copolyimides are favorable to be applied as thermoplastic engineering materials.

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