Preparation and properties of a novel quaternary copolymerized thermoplastic polyimide

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Abstract. A series of quaternary copolymerized thermoplastic polyimides (PI) films with good thermal resistance has been synthesized via two-step method from bicomponent isomeric dianhydrides, 2,3',3,4'-biphenyltetracarboxylic dianhydride (α -BPDA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA), and bicomponent flexible diamines, 4,4'-oxydianiline (ODA) and 1,3-bis(4'-aminophenoxy)benzene (TPE-R). By adjusting the molar ratio of dianhydrides to diamines, its effects on the thermal stability, thermoplasticity and solubility of PI films were investigated in detail. The results showed that these quaternary copolymerized PI films were in possession of both thermoplasticity and excellent thermal stability. It is derived from the synergetic effect of isomeric dianhydrides and flexible diamines. It has also been found that there is one critical molar ratio between dianhydrides and diamines, that is, α -BPDA:s-BPDA:ODA:TPE-R = 50:50:50:50, at which the overall performance is optimal.

Keywords: tailor-made polymer, quaternary copolymerized, polyimide, thermoplastic, thermal resistance

1. Introduction

Aromatic polyimides (PI) have been widely applied in aerospace, military, microelectronics, medical, etc. for their outstanding comprehensive properties such as thermal stability, good mechanical properties, low thermal expansion coefficient and excellent dielectric properties [1–8]. However, for traditional wholly aromatic polyimides, their highly symmetrical rigid chains and existence of strong inter- and intramolecular interactions result in poor solubility and non-melting properties of the polymer [3, 9]. Although conventional PIs have many excellent properties, their own non-processability limits their use. In practical applications, it is inevitable to choose PI films with adhesive characteristics to achieve the desired performance. For example, flexible copper clad laminates (FCCLs) for advanced microelectronic components [10, 11], it has to cooperate with epoxy,

acrylic, silica gel or fluoropolymer to achieve adhesion between the PI film and the metal substrate [12–14]. This would inevitably increase the thickness of the components and reduce the heat resistance in extreme conditions. Therefore, polyimides with excellent processability (or thermoplasticity) and thermal stability represent consistently a research goal for these fields.

It is well accepted that the introduction of flexible units such as ether, alkyl or carbonyl linkages into PI molecular chains will contribute to improve the flexibility of PI [15–17]. DuPont has obtained a commercial thermoplastic PI film, Kapton®-KJ, by introducing a large number of flexible ether linkages, but its glass transition temperature (T_g) is only 220 °C [16]. The films derived from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and flexible diamines, such as 2,2-bis[4-(4-aminophenoxy)

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phenyl]propane (BAPP), 4,4'-Oxydianiline (ODA), have been reported to have good thermoplasticity [18]. It has also been found that BTDA/TPE-R is a new type of high temperature semi-crystalline PI [15]. In addition, by introducing functional groups, twisted and non-planar structures on the main chain or the side chain, it is desired to increase the free volume of PI and reduce the regularity of molecular chain [19]. A series of thermoplastic PI films with high T_g from 2,3,3',4'-oxydiphthalic anhydride (α -ODPA) and bicomponent diamines, 4,4'-oxydianiline (ODA) and para-phenylenediamine (PDA) were developed by Hong *et al.* [20]. The introduction of PDA has greatly improved the thermal stability of thermoplastic PI films, but it has also increased the difficulty of processing to some extent. When only one diamine of PDA is used, even if it is polymerized with the dianhydrides having non-coplanar structure, such as 3,3',4,4'-oxydiphthalic anhydride (s-ODPA)/PDA and 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (s-BTDA)/PDA, those PI films derived from PDA usually exhibit non-thermoplasticity because of the tight stacking between molecular chains [21]. Besides, these α -BPDA-derived PIs generally exhibit excellent combined properties due to the high irregularity of α -BPDA, such as higher glass transition temperature (T_g), better thermoplasticity and so on [22]. Based on α -BPDA, UBE has developed a heat-sealable PI film, Upilex® VT [23]. Zhang *et al.* [24] have successfully synthesized novel copolyimides from diamine monomers p-phenylenediamine (p-PDA) and 4,4'-diaminodiphenylmethane (MDA) with different proportions and 2,3,3',4'-biphenyltetracarboxylic dianhydride (α -BPDA). Yokota *et al.* [25] have also developed α -BPDA-based phenylethynyl-terminated, addition-type α -BPDA imide oligomers (TriA-PI) with high T_g and excellent processability. The crosslinked PIs had high temperature resistance and greater than 20% ϵ_b after curing at 370 °C for 1 h. On the basis of 'TriA-PI' resin, decyldiamine 9,9-bis(4-aminophenyl)fluorene (BAFL) was introduced, the imide oligomers had good processability. The T_g values of the cured resins were higher than 340 °C [26]. In addition, a novel phenylethynyl-terminated addition-formed imide oligomer derived from PMDA and p-ODA was found to have good solubility and processability [27, 28]. However, their curing temperature is relatively high (>350 °C), which requires higher equipment performance and higher processing cost. The thermal

stability and thermoplasticity of PI films are two opposite properties. PI films with good thermoplasticity can be obtained at the expense of their thermal resistance [29]. Therefore, in practical applications, we can only seek a reasonable balance between the various ideal performances.

In this study, polyamic acids having a semi-interpenetrating or interpenetrating network structure were formed by quaternary copolymerization of bicomponent isomeric dianhydrides, 2,3',3,4'-biphenyltetracarboxylic dianhydride (α -BPDA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA), with bicomponent flexible diamines, 4,4'-oxydianiline (ODA) and 1,3-bis(4'-aminophenoxy)benzene (TPE-R), followed by thermal imidization. The synergistic effect of flexible diamines and isomeric dianhydrides endows excellent processability (or thermoplasticity) and thermal stability of the PI films. Further, such properties of the PI films can be manipulated by adjusting the molar ratio between the dianhydrides and the diamines, and therefore, its effects on the overall performances can be surveyed.

2. Experimental

2.1. Materials

2,3,3',4'-biphenyl-tetracarboxylic acid dianhydride (α -BPDA), 3,3',4,4'-biphenyl tetracarboxylic dianhydride (s-BPDA), 4,4'-oxydianiline (ODA) and 1,3-bis(4-aminophenoxy) benzene (TPE-R) were purchased from Shanghai Macklin Biochemical Co., Ltd., China, and their chemical structures are shown in Figure 1. The dianhydrides were dried in vacuo at 160 °C for 5 h and the diamines were dried in vacuo at 60 °C for 5 h prior to use. *N,N*-dimethylformamide (DMF), which was purchased from Sinopharm Chemical Reagent Co., Ltd., China, was distilled prior to use. The other commercially available reagents were used as received.

2.2. Characterization

Inherent viscosity was measured with PAA in DMF at a concentration of 0.5 g/dl at 30 °C. Fourier-transform infrared (FT-IR) spectra were measured with a NEXUS670 (Nicolet, America) infrared microscope. The measuring resolution was 4 cm⁻¹ and iterations were performed for 32 times in the range 400–4000 cm⁻¹. ¹H-NMR spectra were performed on an Avance digital 400 spectrometer (Baker, Germany) operating at 400 MHz in DMSO-*d*₆. Wide angle X-ray diffraction (XRD) was conducted on a X' Pert3

Powder X-ray diffractometer (using Cu/K α radiation at wavelength of 0.154 nm) over the range of 2–60°, operated at 40 kV and 40 mA.

Thermal stability test was performed on a thermogravimetric analyzer (TG209, Netzsch, Germany). PI

films were heated from 30 to 800 °C at a heating rate of 20 °C/min under nitrogen atmosphere. Dynamic mechanical thermal analyses (DMA Q800, TA, America) of PI films were conducted with heating rate of 10 °C/min from 25 to 300 °C and a frequency of 1 Hz

Figure 1. Synthesis of PI films.

in nitrogen. The water contact angle of the film was obtained on a Data Physics-DCA 40 micro contact-angle measuring device (DATA Physics, Germany). Peeling strengths of the PI/Cu composite films were obtained by T-type peeling test on a tensile equipment (Instron 5566, USA).

2.3. Polymer synthesis

As shown in Figure 1, PI was synthesized via two-step method. In the first step, the polyamic acid (PAA) was obtained by reacting with dianhydrides and diamines in a non-proton polar solvent. The second step is to remove the solvent and thermal imidization by a heating program to obtain PI films. The specific monomer contents of the five PI films are listed in Table 1. As an example, the detailed synthesis process of PI-4 was as follows.

In a 500 ml three-neck round-bottomed flask equipped with mechanical stirring, 2.78 g (13.8 mmol) of ODA, 4.06 g (13.8 mmol) of TPE-R and 90 ml of DMF were added. The reaction mixture was stirred under nitrogen atmosphere at 25 °C until clear, so that the diamine can be completely dissolved. And then 4.08 g (13.8 mmol) of α -BPDA, 4.08 g (13.8 mmol) of s-BPDA was added under the condition of ice-water

bath, which achieved a 15 wt% solid content. The reaction mixture was stirred for another 5 h under nitrogen atmosphere to afford the PAA.

The PI film was prepared via the coating method, firstly the prepared PAA was coated onto a clean glass plate by an automatic film applicator, then thermal imidization of PAA was performed by using the following heating program: 80, 100, 150, 200, 250, 300 °C/1 h. The other PI films were prepared according to the same procedure as described above.

3. Results and discussion

3.1. Structural analysis

As shown in Figure 1, a series of PI films (PI-1–PI-5) with different molar ratios of dianhydrides and diamines were synthesized via a two-step method. The inherent viscosities of the polyamic acid were listed in Table 2 (0.84–1.82 dl/g), which indicates the high molecular weight of the polymers. The chemical structures of the PI films were characterized with the FT-IR and $^1\text{H-NMR}$ spectra. The FT-IR spectra of the five PI films are shown in Figure 2. After imidization, absorption peaks appeared at around 1779 and 1717 cm^{-1} , which were respectively the asymmetric and symmetric stretching vibration peaks of C=O. Absorption bands at 1377 and 73 cm^{-1} were assigned to the amide C–N stretching and deforming vibrations. Furthermore, the stretching vibration peak around 1250 cm^{-1} for C–O–C appears in the spectra. As shown in Figure 3, the structure of molecular chain was found to be in good agreement with signal of $^1\text{H-NMR}$ spectrum. All results indicate that PI has been successfully prepared.

Table 1. The contents of dianhydrides and diamines in the synthesized PI films.

Samples	α -BPDA	s-BPDA	ODA	TPE-R
PI-1	0	100	100	0
PI-2	0	100	50	50
PI-3	20	80	50	50
PI-4	50	50	50	50
PI-5	50	50	70	30

Figure 2. FT-IR spectra for PI films.

Table 2. Inherent viscosities of PAA and solubility properties of PI films.

Samples	$[\eta]_{\text{inh}}$	DMF	DMAc	NMP	DMSO	Acetone	THF
PI-1	1.82	N	N	N	N	N	N
PI-2	0.84	Y–	Y–	Y–	Y–	N	N
PI-3	1.32	Y–	Y–	Y–	Y–	N	N
PI-4	0.88	Y	Y	Y	Y	N	N
PI-5	0.87	Y–	Y–	Y	Y–	N	N

$[\eta]_{\text{inh}}$: inherent viscosity measured with PAA in DMF at a concentration of 0.5 g/dl at 30 °C;

Y: completely soluble at room temperature, 24 h;

Y–: partially soluble;

N: insoluble;

DMF: *N,N*-dimethylformamide;

DMAc: *N,N*-dimethylacetamide;

NMP: *N*-methyl-2-pyrrolidinone;

DMSO: dimethyl sulfoxide;

THF: tetrahydrofuran.

Figure 3. Typical ^1H -NMR spectrum for the PI-3.

3.2. Solubility

There are a large number of rigid benzene rings and five-membered imide rings connected to the benzene ring in the molecular structure of the polyimide. These structures provide a guarantee for the formation of large π bonds in the polyimide segment and the existence of the large π bond increases interaction between molecular chains, creating conditions for the close packing of the polymer segments, which ultimately leads to the poor solubility of the polyimide. However, the introduction of non-coplanar structures through molecular design increases the distortion of the polyimide segments, which can destroy the large π bond structure of the polyimide segment and reduce the close packing between the molecular segments, thereby improving the solubility of polyimide.

The solubility of the prepared PI films was investigated by dissolving 10 mg of the sample in 1 ml of solvent, and the results were summarized in Table 2. It was found that all PI films were insoluble in acetone and tetrahydrofuran (THF). In polar aprotic solvents, except for PI-1, the PI-2–PI-5 have good solubility. In particular, PI-4, which exhibits the best solubility, is completely soluble in DMF, DMAc, NMP and DMSO. In addition, we have found that those PI films that are partially soluble at room temperature are completely soluble under heating. The good solubility is attributed to the synergistic effect of α -BPDA distorted, non-planar structures and flexible ether linkages, which decreases inter-molecular interactions. As shown in Figure 4 (PI-3, PI-4, and PI-5 as representatives), it was found by XRD spectra

Figure 4. Typical wide-angle XRD patterns of PI films (PI-3, PI-4 and PI-5).

that all of the PI films exhibited broad diffraction peaks, indicating amorphous aggregate structures. Benefitting the loose chain stacking density, PI films have good solubility in polar aprotic solvents.

3.3. Thermal properties

The thermal properties of the PI films were evaluated by using TGA, DMA, and the specific data are listed in Table 3. As can be seen from Figure 5, all the PI films show no obvious thermal weight loss before 500 °C. The temperature at 5% weight loss ($T_{5\%}$) is above 535 °C, and the temperature at 10% weight loss ($T_{10\%}$) is around 570 °C. In addition, the maximum decomposition rate ($T_{\max}$) of the five PI films is above 590 °C, and the residue weight ratios at 800 °C approximate 60%.

For polymers, T_g to evaluate its heat resistance is another important factor. As shown in Figure 6a, the DMA-tan δ curves of the PI films are shifted to the

Figure 5. TGA curves of PI films.

Table 3. Thermal properties of PI films.

Samples	T_d [°C]	$T_{5\%}$ [°C]	$T_{10\%}$ [°C]	$T_{\max}$ [°C]	$R_{800^\circ\text{C}}$ [%]	T_g [°C]
PI-1	472.3	546.1	569.3	593.0	62.98	272
PI-2	471.5	546.7	577.8	601.2	64.27	240
PI-3	508.5	561.3	582.5	614.7	59.25	262
PI-4	505.2	559.3	579.3	595.2	61.24	271
PI-5	504.5	535.8	570.7	592.2	48.71	283

T_g : glass-transition temperatures;
 T_d : initial thermal decomposition temperature;
 $T_{5\%}$: 5% weight loss temperature;
 $T_{10\%}$: 10% weight loss temperature;
 $T_{\max}$: maximum decomposition rate;
 $R_{800^\circ\text{C}}$: residual weight ratios at 800 °C.

right, and the T_g value obtained are tabulated in Table 3, respectively, 240–283 °C. Referring to Figure 5 and Table 3, it indicates that, the T_g value of the prepared PI films show an increasing trend with the introduction of α -BPDA and ODA. It is attributed to the asymmetric structure of α -BPDA, which suppress rotation of the molecular chains [30], thereby reinforcing the rigidity of the molecular chains. Furthermore, compared with TPE-R, the relative ratio of ether linkage to benzene ring in ODA is smaller, which reduces the flexibility of molecular chains.

3.4. Thermoplasticity and wettability

The conventional PI films are insoluble and do not melt. It is essential to make the PI films soluble and fusible to have thermoplastic properties. DMA is an effective method for characterizing the thermoplasticity of PI films, because the molecular chain begins to move near the glass transition temperature, and the storage modulus is very sensitive to the mobility of molecular chains. As shown in Figure 6b, the storage modulus (E') of the PI films near the glass transition temperature (T_g) dropped sharply and the dropped amplitudes are above 2000 MPa, indicating that they have good thermoplasticity and thus have the potential for adhesion. Undoubtedly, PI films have a highly free volume, low chain packing density and weak interchain interaction by introducing α -BPDA with distorted asymmetric structure. In addition, the introduction of flexible diamine increases the flexibility of the molecular chains, thereby endowing excellent thermoplasticity to the PI films. In addition, excellent surface wettability promotes contact, interdiffusion and entanglement of molecular chains, which makes the wettability of PI films as another factor in the adhesive Property. Therefore, the surface wettability of these films was characterized

Figure 6. DMA curves of PI films: (a) $\tan \delta$ and (b) storage modulus.

by the contact angle. The water contact angles of these PI films were found to be below 70° . Generally, small contact angle means high surface energy, which is beneficial to adhesion. As representatives, the contact angles are shown in Figure 7 (PI-3–PI-5).

Subsequently, the adhesion of these films to the copper foil was measured by compression molding PI film onto the surface of the copper foil. The peel strengths characterized by the T-type peeling test are listed in Table 4. Benefitting from the high thermoplasticity, the PI films have good adhesion to copper foil, and the peeling strength of PI-4 and PI-5 was both higher than 1 N/mm , which further demonstrates that the PI films have good thermoplasticity.

Figure 7. Typical contact angles (CA) of PI films: (a) PI-3, (b) PI-4, and (c) PI-5.

Table 4. Adhesion properties of PI films.

PI	T_{hp} [°C]	t_{hp} [s]	P_{hp} [MPa]	P_s [N·mm ⁻¹]
PI-3	350	60	15	0.61
PI-4	355	60	15	1.01
PI-5	360	60	15	1.22

T_{hp} : hot pressing temperature;

t_{hp} : hot pressing time;

P_{hp} : hot pressing pressure;

P_s : peeling strength for PI/copper composite films.

4. Conclusions

In order to obtain PI films with good thermoplasticity and excellent thermal properties, we successfully prepared a series of polyimides from 2,3',3,4'-biphenyltetracarboxylic dianhydride (α -BPDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA), 4,4'-oxydianiline (ODA) and 1,3-bis(4'-aminophenoxy)benzene (TPE-R) via two-step method. The T_g of all PI films were $240\text{--}283^\circ\text{C}$. In addition, the quaternary copolymerized PI films derived from α -BPDA exhibited good solubility in polar aprotic solvents. Especially for PI-4, it is completely soluble in polar aprotic solvents at room temperature. And the residual mass is about 60% at 800°C . The obtained quaternary copolymerized PI achieves a good balance between thermoplasticity and thermal stability due to the synergy between the asymmetric α -BPDA and the flexible diamines. Due to their excellent comprehensive properties, these quaternary copolymerized PI films have great application potential in high-tech field.

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