

Synthesis and Properties of Thermoplastic Polyimides with Ether and Ketone Moieties

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ABSTRACT: A series of polyimides containing ether and ketone moieties were synthesized from 1,3-bis(4-fluorobenzoyl) benzene and several commercially available dianhydrides via a conventional two-step polymerization. The inherent viscosities of Polyamide acids ranged from 0.46 to 0.73 dL/g. Thermal properties, mechanical properties, and thermalplasticity of the obtained polyimide films were investigated by focusing on the chemical structures of their repeat units. These films were amorphous, flexible, and transparent. All films displayed low T_g s (184–225 °C) but also excellent thermal stability, the 5% weight loss temperature was up to 542 °C under nitrogen. The films showed outstanding mechanical properties with the modulus up to 3.0 GPa and the elongation at break in the range of

8–160%. The uniaxial stretching of PI-a at high temperature was studied owing to its excellent flexibility. The PI-a had an elongation at break up to 1600% at 245 °C and the uniaxially stretched film exhibited a much higher modulus (3.9 GPa) and strength (240 MPa) than undrawn film. The results indicated that PI-a can potentially be used to prepare materials such as fiber, ultra-thin film or ultra-high modulus film. All the obtained films also demonstrated excellent thermoplasticity (drop of E' at $T_g > 10^3$) which made the polyimides more suitable for melt processing. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 2878–2884, 2010

KEYWORDS: polyimides; synthesis; thermoplastics; thin films

INTRODUCTION Aromatic polyimides (PI) have been widely utilized in industrial applications such as automobile and aircraft parts, electronic packages, films, adhesives, and matrix materials for composite materials due to their outstanding comprehensive properties.^{1,2} However, the technological and industrial applications of rigid polyimides are limited by processing difficulties due to their insoluble and infusible properties.³ The difficult processing behavior is resulted from the rigid rod-like structures and strong interaction between molecular chains. Therefore considerable efforts have been devoted to the development of melt-processable or soluble polyimides.^{4–14}

Comparing with the traditional solution casting method, melt processing is more desirable from economical and environmental standpoints.^{15,16} Recently there has been widespread use of thermoplastic PI films as structural adhesives or laminations for composite plies. The prime requirement for these specific applications is an enhanced melt flow behavior of PI films at relatively low processing temperatures and pressures to achieve proper wetting of adherence or that of fibers.¹⁷ The melt processability and low processing temperatures of polyimides can be improved by two ways. One way is to decrease the cohesion of the molecular chains caused by the strong polarity and high polarizability of the hetero-

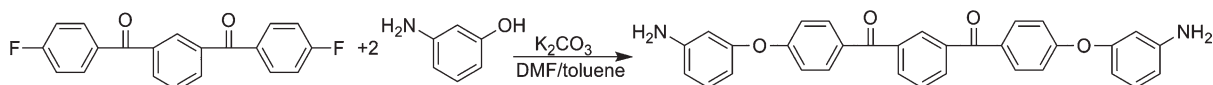
cycles in the amide groups. The other way is to increase the bending of the molecular chains.

Tamai et al.⁹ investigated the relationships between T_g , melt-flowability and PIs structure in detail. They conclude that the T_g values and the melt-flow start temperature of the PIs decreased with the increase of flexible chain length, benzene rings and the *meta*-linkage contents in ether diamines. polyimides¹⁵ derived from *meta*-amino-substituted diamines exhibited melt-flowability when the diamines had more than two benzene rings. While the polyimides prepared from *para*-amino-substituted diamines have no melt-flowability until the number of benzene rings is five or higher.

The presence of ether and carbonyl linkages and higher number of benzene rings causes a decrease in cohesion of polymer chains. Meta linkages increase the bending of chains. Scientists at the NASA Langley Research Center incorporated ether and ketone connecting groups into polyimides to obtain processable and impact resistance polyimides potentially useful as structural resins (e.g., adhesives and composite matrices) on aerospace vehicles.^{18,19} The LARC-CPI was one of the semicrystalline thermoplastic polyimide developed at the NASA Langley Research Center.¹⁸ This polymer was produced from BTDA and 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene and possessed excellent thermal properties.

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SCHEME 1 Synthesis of the diamine 1,3-bis(3-aminophenoxy-4'-benzoyl) benzene.

Its T_g was 222 °C and melting temperature was 350 °C. However, this thermoplastic polyimide has high melt-processing temperature.

To prepare the thermoplastic polyimides with low melt process temperatures remaining excellent thermal stability, a more flexible isomer diamine 1,3-bis(3-aminophenoxy-4'-benzoyl) benzene was successfully synthesized. And a series of polyimides were synthesized with this diamine and different kinds of aromatic dianhydrides. The obtained polyimides had lower T_g s and exhibited excellent thermoplasticity.

EXPERIMENTAL

Materials

3-Aminophenol (3-AP), potassium carbonate (K_2CO_3) and 1,3-Bis(4-fluorobenzoyl) benzene were commercially available and used as received. *N,N*-Dimethylformamide (DMF), *N,N*-Dimethylacetamide (DMAc) and toluene were vacuum-distilled after drying over calcium hydride. 3,3',4,4'-Biphenyl-tetracarboxylic acid dianhydride (*s*-BPDA, m.p.306 °C) was obtained from Chriskev Company, Benzophenonetetracarboxylic dianhydride (BTDA, m.p.221 °C), 4,4'-oxydiphthalic anhydride (ODPA, m.p.228 °C), pyromellitic dianhydride (PMDA, m.p.285 °C), 2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl] propane dianhydride (BPADA, m.p.190 °C) were purchased from Beijing Jiaohua company. These dianhydrides were dried in a vacuum oven at 150 °C for 4 h.

Characterization

Fourier-transform infrared spectra were obtained on a Bruker Vector22 spectrometer. 1H NMR spectra were measured on a Bruker 500 spectrometer with tetramethylsilane (TMS) as internal standard and $DMSO-d_6$ as a solvent. Mass spectra were performed on an AXIMA-CFR laser desorption ionization flying time spectrometer (COMPACT). Glass transition temperatures (T_g) and melting points were determined on a Mettler Toledo DSC 821^e thermal analyzer under nitrogen atmosphere at a heating rate of 10 °C/min. Elemental analyses were performed with Perkin-Elmer 2400 CHN analyzer. Inherent viscosities (η_{inh}) were obtained at a 0.5 g/dL concentration of polyamide acid solutions with an Ubbelohde viscometer at 25 °C. Thermo gravimetric analysis (TGA) was performed on a Perkin-Elmer (Pyris 1) thermogravimetric analyzer with Pyris data collection and analysis software for Windows. Measurements were carried out on 3–5 mg film samples heated under nitrogen or air atmosphere at a heating rate of 5 °C/min. Dynamic mechanical analysis (DMA) was performed on thin film specimen (ca. $3 \times 0.65 \times 0.005$ cm³) on a TA instrument DMA RSAII at a heating rate of 5 °C/min and at a load frequency of 1 Hz under nitrogen atmosphere. The peak on the $\tan \delta$ as a function of temperature curves was regarded as the T_g of the films. Ultraviolet-Visible (UV-Vis) spectra of the films were recorded on a UV-

Vis 2501 spectrometer. Mechanical properties of the films were measured with a SHIMADZU AG-I tensile apparatus at a crossed speed of 8 mm/min on the strips of approximate 40–60 μ m thickness and 0.3 cm width with a 4 cm gauge length. The equilibrium water uptake was determined by the weight difference of vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 24 h. The crystallization of the films was characterized with a Rigaku Wide-angle X-ray diffractometer (D/max rA, using Cu K α radiation at wavelength $\lambda = 1.541E$). The 2θ scan data were collected at 0.05° intervals over ranges of 10–60° and scan speed was 0.5° (2θ)/min. SAXS was performed using the same instrument over the ranges of 0.5–6° and scan speed was 0.2° (2θ)/min. All the properties of polymers were measured with films.

Synthesis of 1,3-Bis(3-aminophenoxy-4'-benzoyl) Benzene (BABB)

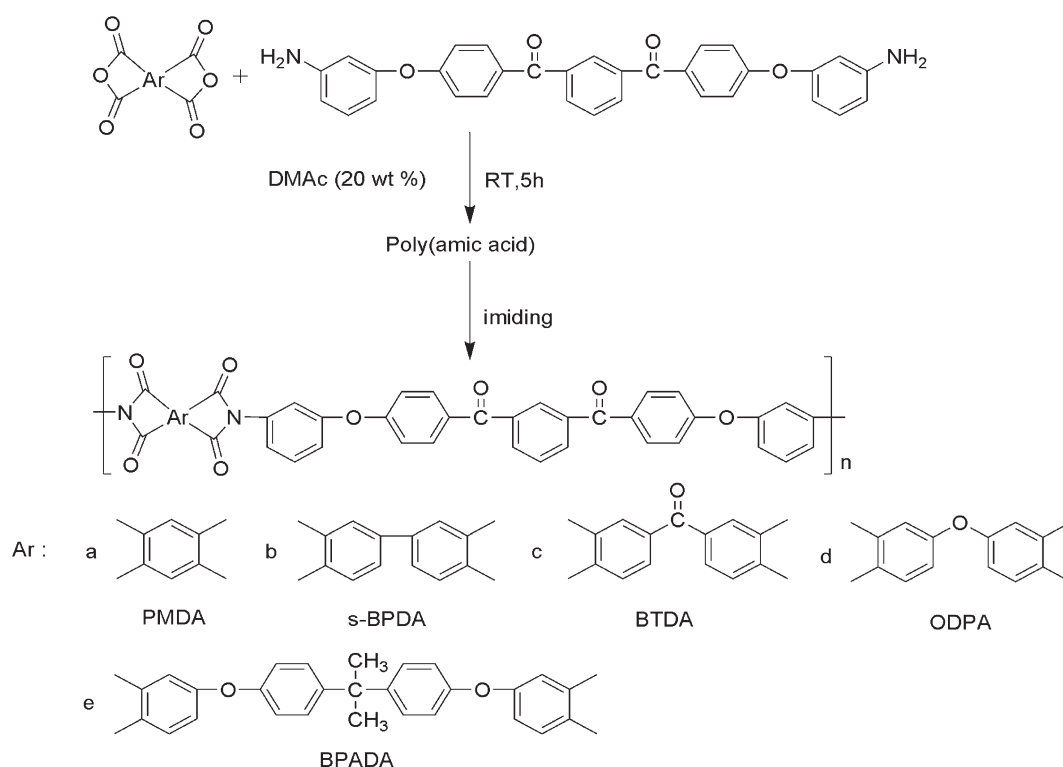
3-Aminophenol (24.01 g, 0.22 mol) was dissolved in a solution of *N,N*-dimethylformamide (226 mL) and toluene (45 mL) in a 500 mL three-neck flask equipped with a magnetic stir, thermometer, N_2 gas inlet, Dean-Stark trap and condenser. Powdered anhydrous potassium carbonate (34.55 g, 0.25 mol) was added and water was removed by azeotropic distillation with toluene. 1,3-Bis(4-fluorobenzoyl) benzene (32.23 g, 0.10 mol) was then added and the reaction mixture stirred at 130–150 °C for 8–15 h under a nitrogen atmosphere. The mixture was allowed to cool and precipitated in water as a solid which was isolated by filtration and dried in a vacuum oven at 40 °C. Recrystallization from methanol afforded a light yellow crystalloid 1,3-Bis(3-aminophenoxy-4'-benzoyl) benzene (BABB) (32.23 g, 64.4%). The Scheme 1 is the synthetic route for the preparation of BABB.

Yield: 64.4%. m.p. (DSC): 148 °C. IR (KBr, powder, cm^{-1}): 3467 and 3379 ($N-H$), 1641 ($C=O$).

1H NMR (500MHz, $DMSO-d_6$, ppm): 5.3 (s, 4H), 6.2 (d, 2H), 6.3 (s, 2H), 6.4 (d, 2H), 7.1 (m, 6H), 7.7 (t, 1H), 7.8 (d, 4H), 7.9 (s, 1H), 8.0 (d, 2H). Anal. Calcd. for $C_{32}H_{24}N_2O_4$: C, 76.78; H, 4.83; N, 5.60. Found: C, 76.77; H, 4.88; N, 5.62.

Synthesis of the Polymers

All the polymers were prepared via the two-step solution polymerization and thermal imidization process as shown in Scheme 2. The samples PI-a ~ PI-e were named according to the sequence of dianhydrides. First of all, BABB and distilled DMAc were charged into a dried conical flask equipped with a magnetic stirrer. After the diamine was dissolved, stoichiometric amounts of dianhydride were added gradually, with the solid content controlled to 20 wt %. The mixture was stirred at room temperature for 5h to form a viscous solution of poly (amic acid) (PAA) precursor solution. Films were cast from the PAA solution onto clean and dry glass plates. The solvent was removed by drying in an oven with a



SCHEME 2 Polymerization of thermoplastic polyimides derived from BABB.

programmed procedure (50 °C/2 h, 80 °C/2 h, 100 °C/4 h, 120 °C/2 h, 150 °C/1 h, and 180 °C/1 h). The PI films were obtained by thermal imidization in a vacuum oven at 200 °C/1 h, 250 °C/1 h, 300 °C/1 h, and then cooled from 300 °C to room temperature with a speed of 3 °C/min in the vacuum oven without special heat treatment.

RESULTS AND DISCUSSION

Monomer Synthesis and Polymerization

BABB was successfully synthesized in high yield via a nucleophilic substitution reaction of 3-aminophenol and 1,3-bis(4-fluorobenzoyl) benzene. The synthetic procedure for BABB is

shown in Scheme 1. A series of polyimide films (PI a–e) with ether and ketone moieties were prepared from BABB and several commercial dianhydrides by thermal imidization, as shown in Scheme 2. The inherent viscosity of PAA solutions are listed in Table 1 and are in the range of 0.46–0.73 dL/g, which indicated all prepared polyimides have reasonable molecular weights. The elemental analysis data of PIs were listed in Table 1, showing that the obtained values were reasonable matching with the calculated ones. All obtained films exhibited excellent chemical resistance, they were insoluble in organic solvents for example, NMP, *m*-cresol, DMAc, chloroform etc. The wide-angle X-ray diffraction studies were carried out and showed that PI a–e were essentially amorphous, which

TABLE 1 Elemental Analysis of the PI Films and the Inherent Viscosity of PAAs

Samples	Constitutional Repeating Unit		C%	N%	H%	η_{inh} (g/dL) ^a
PI-a	C ₄₂ H ₂₂ O ₈ N ₂	Calcd.	73.90	4.10	3.25	0.73
		Found	73.86	3.93	3.30	
PI-b	C ₄₈ H ₂₆ O ₈ N ₂	Calcd.	75.98	3.69	3.45	0.62
		Found	76.03	3.54	3.51	
PI-c	C ₄₉ H ₂₆ O ₉ N ₂	Calcd.	74.81	3.56	3.33	0.46
		Found	75.23	3.53	3.44	
PI-d	C ₄₈ H ₂₆ N ₂ O ₉	Calcd.	74.41	3.62	3.38	0.56
		Found	74.46	3.50	3.45	
PI-e	C ₆₃ H ₄₀ O ₁₀ N ₂	Calcd.	76.82	2.84	4.09	0.65
		Found	76.92	2.72	4.11	

^a Inherent viscosity determined with a concentration of 0.5 g/dL in DMAc at 25 °C ± 0.1 °C.

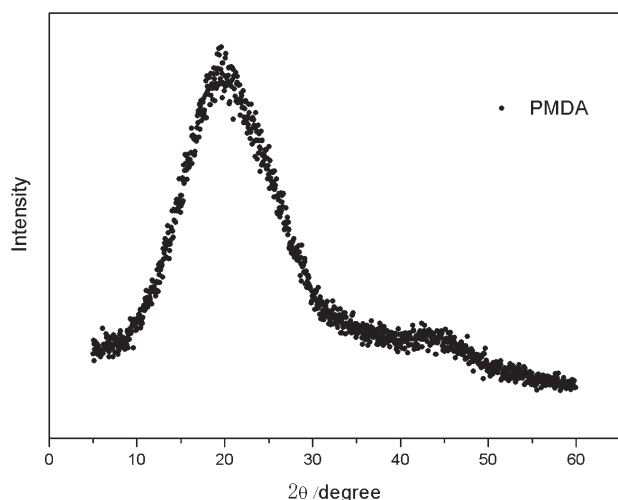


FIGURE 1 Wide-angle X-ray diffraction pattern of PI-a film.

can be attributed to the introduction of multiether linkages and *meta*-substituted aromatic rings along the polymer backbone. A representative wide-angle X-ray diffraction of the polymer PI-a is shown in Figure 1.

Thermal Properties of PI Films

The thermal properties of the films were examined by means of DSC, TGA and DMA. The results are listed in Table 2. The typical DSC curves are shown in Figure 2. The incorporation of multiple ether linkages and *meta*-substituted aromatic rings along the polymer backbone results in the low glass transition temperatures (184–225 °C) and no melting points of all obtained films. The T_g of PI-c (210 °C) is lower than that of LARC-CPI with the isomer structure (222 °C), which indicated that the amino at meta position, compared with para position, had a greater effect on T_g . The T_g values correlated well with the stiffness of dianhydrides (PMDA > BPDA > BTDA > ODPDA > BPADA). PI-e had the lowest T_g and it was suggested that the bulky methyl groups in the BPADA units could increase free volume and lower the interaction between polymer chains. The stick-like structure of PMDA and BPDA increased the interaction between polymer

TABLE 2 Thermal Properties of PI Films

Samples	T_g (°C) ^a		T_d 5% (°C) ^b		T_d 10% (°C) ^b		R_{800} (%) ^c
	DSC	DMA	N ₂	Air	N ₂	Air	
PI-a	225	228	524	518	541	549	59
PI-b	216	216	542	535	560	567	63
PI-c	211	214	525	511	544	554	64
PI-d	198	200	496	486	520	524	59
PI-e	184	185	497	487	513	531	58

^a Glass transition temperature (T_g) measured by DSC and DMA at a heating rate of 10 °C/min and 5 °C/min, respectively.

^b Temperatures at 5% and 10% weight loss were recorded by TGA at a heating rate of 5 °C/min under nitrogen or air atmosphere.

^c Residual weight retention at 800 °C under nitrogen.

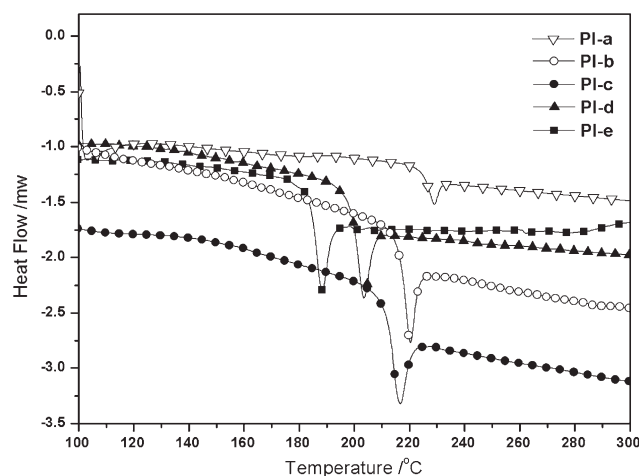


FIGURE 2 DSC diagrams of PI films under nitrogen atmosphere.

chains, therefore leading to the higher glass transition temperatures. All T_g signals are similar to the T_m peaks and had large enthalpies that were not caused by the molecular relaxation, so it was suggested that the polymers can form partial regular structure easily in high temperature. The proposed mechanism can be supported by the SAXS dispersion of polymers. The Small Angle X-ray Scattering dispersions of PI a–e are shown in Figure 3. The existence of clear dispersion peaks demonstrated regular arrangements of the polymer chains along the axis. All the obtained films had obvious partial regular structure, the average length of the ordered regions in these polymers can be calculated according to Bragg's equation ($d = \lambda/2 \sin \theta$). Where, θ is the X-ray diffraction angle and $\lambda = 1.54\text{Å}$. The calculated d values are listed in Table 3 where the average length is between 83 and 93 Å.

The obtained films also exhibited excellent thermal stability, as shown in Figure 4. The TGA curves suggest that PI a–e were imidized completely at 300 °C for 1 h. TGA results also show the films had a 5% weight loss temperature in the

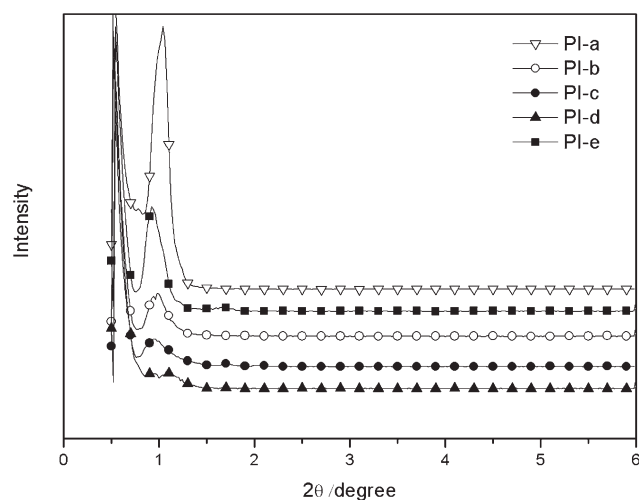


FIGURE 3 SAXS dispersion of PI films.

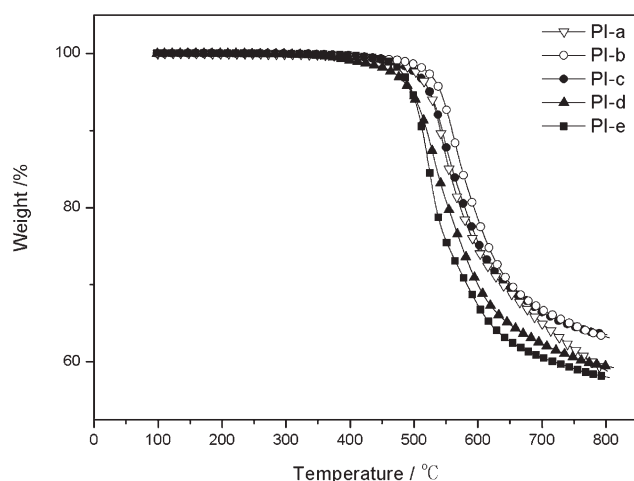
TABLE 3 Optical Data of PI Films

Samples	Color	UV (%)	λ_0 (nm)	d (Å)	Water Absorption (%)
PI-a	Yellow	87.2	396	84.9	0.89
PI-b	Yellow	87.5	388	90.1	0.46
PI-c	Brown	84.5	391	93.9	0.62
PI-d	Yellowish	87.9	364.5	93.9	0.55
PI-e	Yellowish	88.0	378	93.9	0.27

range of 496–542 °C in N₂, 486–535 °C in air and the char yield at 800 °C was up to 64%. The high thermal stability could be attributed to the phenylation of the backbone and symmetric structures. The results indicate that the introduction of flexible structure could lower T_g but without sacrificing thermal and thermooxidative stabilities of the polyimides.

In the DMA profiles of obtained films (Figure 5), T_g s were observed in the range of 185–225 °C (regarding the peak temperature in the $\tan \delta$ curves as the T_g), which corresponded to the T_g values measured by DSC technique. The T_g depended on the structure of the dianhydride component and the stiffness of the polymer backbones. The presence of flexible structure (i.e., ether bond and methyl groups) in the dianhydrides ODPDA and BPADA resulted in lower T_g s of films d and e. The rigid structure of PMDA, s-BPDA, BTDA led to the strong interaction between polyimide chains, so the films a, b and c had higher T_g s. These films exhibited high $\tan \delta$ (ca. 2.0 ~ 3.0) in a wide range of temperatures, indicating these obtained polymers maybe useful as materials for shock absorption and sound insulation.

PI a–e had high storage modulus (2.1–3.3GPa) below 250 °C as shown in Figure 5, and the value order corresponded to the tensile modulus: PI-a < PI-e, PI-d < PI-b, PI-c. The films also retained high modulus at very high temperatures. Between 250 and 400 °C, PI-c had the highest modulus owing to the strong interaction between molecular chains.

**FIGURE 4** TGA traces of PI films under nitrogen atmosphere.

This also explains why PI-c had the deepest color and the lowest transparency. PI-a had the smallest modulus, this abnormal phenomenon resulted from the conformation of the molecule chains. A detailed explanation will be provided in the mechanical properties section. The storage modulus of all films declined rapidly at T_g (drop of E' at $T_g > 10^3$), suggesting that the obtained films had excellent thermoplasticity and may be suitable for melt processing.

Mechanical Properties of PI Films

The mechanical properties of the polyimide films are summarized in Table 4. The films exhibited tensile strength of 109–133 MPa, elongations at break of 7.9–156.2% and initial modulus of 2.7–3.0 GPa, which indicated the PIs containing ether and ketone moieties have excellent toughness. The mechanical properties of PIs depend strongly on their supramolecular structure and morphology, which is influenced by their composition and processing conditions. The dianhydride PMDA has a planar structure, which makes the polymer chains stack regularly. The film PI-a had the lowest modulus and an excellent elongation at break. It presumed that the molecular chains of PI-a can glide easily when it was drafted at room temperature. With the increased flexibility of the dianhydrides, the films had higher modulus and

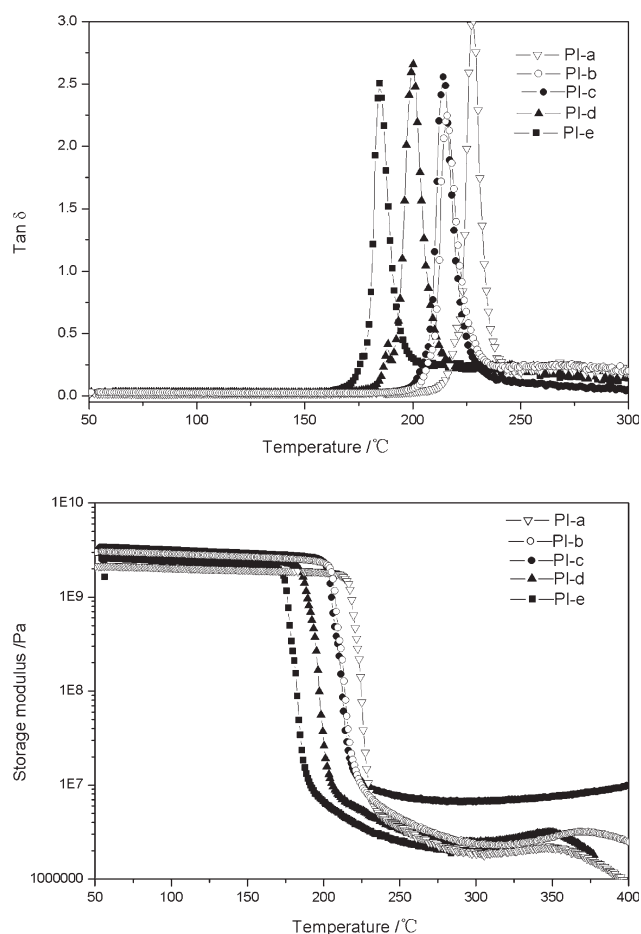
**FIGURE 5** Storage modulus (E') and $\tan \delta$ spectra as a function of temperature for PI films.

TABLE 4 Mechanical Properties of PI Films

Samples	Tensile Strength (MPa) ^a	Tensile Modulus (GPa) ^a	Elongation at Break (%) ^a
PI-a	109.3	2.7	156.2
PI-b	123.1	3.0	36.4
PI-c	130.3	3.0	11.9
PI-d	123.2	2.9	8.5
PI-e	113.1	2.9	7.9
PI-a-1	4.0	3.3×10^{-3}	1607.2
PI-a-2	239.3	3.9	13.4

PI-a-1 Measured at 245 °C in air at a drawing rate of 8 mm/min.

PI-a-2 The drawn film measured at room temperature with a drawing rate of 8 mm/min.

^a Measured at room temperature in air at a drawing rate of 8 mm/min.

lower elongation at break. It was attributed to the enhanced interaction between polymer chains arising from the tortility and physical crosslink of the molecular chains. Due to the presence of weak ether bonds and methyl groups in dianhydrides ODPA and BPADA, the film PI-d and PI-e had lower modulus and elongation than PI-b, PI-c.

As the film PI-a had an unexpected elongation at break, we also studied its mechanical properties at higher temperature (20 °C higher than T_g) using the same tensile tester. The tensile properties of PI-a are listed in Table 4. PI-a-1 represented the results of film samples with dimensions of about 4 cm length and 1 cm width were measured at 245 °C in air. The samples of PI-a-2 were prepared from the PI-a-1, as follows: The sample PI-a-1 (4 cm length \times 1 cm width) was uniaxially stretched to the ratio about 800% and maintain for 10min with the tensile tester at 245 °C in air, then the stretched film was cut into tensile test specimens (4 cm length \times 0.3 cm width). These obtained samples were measured at room temperature and the results are represented as PI-a-2. The drawn film had a modulus of 3.9 GPa, the strength of 240 MPa and the elongation about 13%. The data suggested that drawn film had excellent flexibility and much higher modulus and strength than the undrawn film (2.7 GPa and 109 MPa). The improved mechanical properties can be attributed to the molecular chains of PI-a being extended and compactly packed under the conditions of high temperature stretching. Polyimide made from PMDA was shown to have outstanding ductility which can potentially be used to prepare materials such as PI fiber, ultra-thin film, ultra-high strength, and ultra-high modulus film. Further work is in progress and will be reported in the future.

Optical Properties

The optical properties of the polyimide films were studied using UV-Vis 2501 spectrometer. The absorption spectra are displayed in Figure 6 and the results are summarized in Table 3. All the films exhibited high transparency ($>87\%$) and low λ_0 (364 nm). The color of the polyimide films depended markedly on the chemical structures of the dianhydride components, which can be explained by electron affinity of the dia-

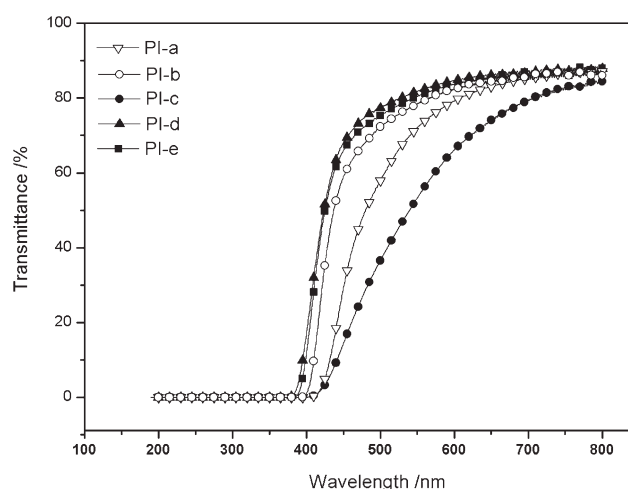
nydrides or the charge transfer complex (CTC) formation between polymer chains.²⁰ The colors of the obtained PI films ranged from brown to yellowish. Film PI-c had the deepest color and lowest transparency, as a result of the C—O group in BTDA which increased the charge transfer complex (CTC) effect of intramolecular. The deep color and low transparency of PI-c can also be explained by the curves of DMA, PI-c exhibited higher modulus at very high temperature, which indicated that the PI-c molecular chains had stronger interaction than other films. The PI-d and PI-e films were colorless and had the smallest λ_0 , which was due to the lower electron affinity as compared to the other dianhydrides and the decreased intermolecular CTC formation caused by the ether linkages and a bulky, weakly polarizable ($-\text{C}(\text{CH}_3)_2-$) group.

Water Absorption of PI Films

The results of water absorption are listed in Table 3. Dry films which had been weighed (m_0) were immersed in water at room temperature for 24 h. The surfaces of the films were wiped to remove the water and weighed again (m). Water absorption was calculated by this formula: $(m-m_0)/m_0$. The results showed that the polyimide films have low water absorption, which is in agreement with the report “Development of Thermoplastic Polyimide” published in Chinese Polymer Bulletin.

CONCLUSIONS

A series of polyimides were synthesized by the two-step method from 1,3-bis(3-aminophenoxy-4'-benzoyl) benzene (BABB) and several commercial dianhydrides. All the obtained films were amorphous with low glass transition temperatures (<225 °C) due to the inherent flexibility of the ether bonds and *meta*-substituted rings of the diamine. The obtained films also exhibited the outstanding mechanical properties and thermooxidative stability. All the films demonstrated excellent thermoplasticity (drop of E' at $T_g > 10^3$) which made the polyimides more suitable for melt

**FIGURE 6** UV-Vis spectra of PI films.

processing than traditional PIs. In addition, the results of film PI-a indicated that PI-a can potentially be used to fabricate materials such as fiber, ultra-thin film or ultra-high modulus film.

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