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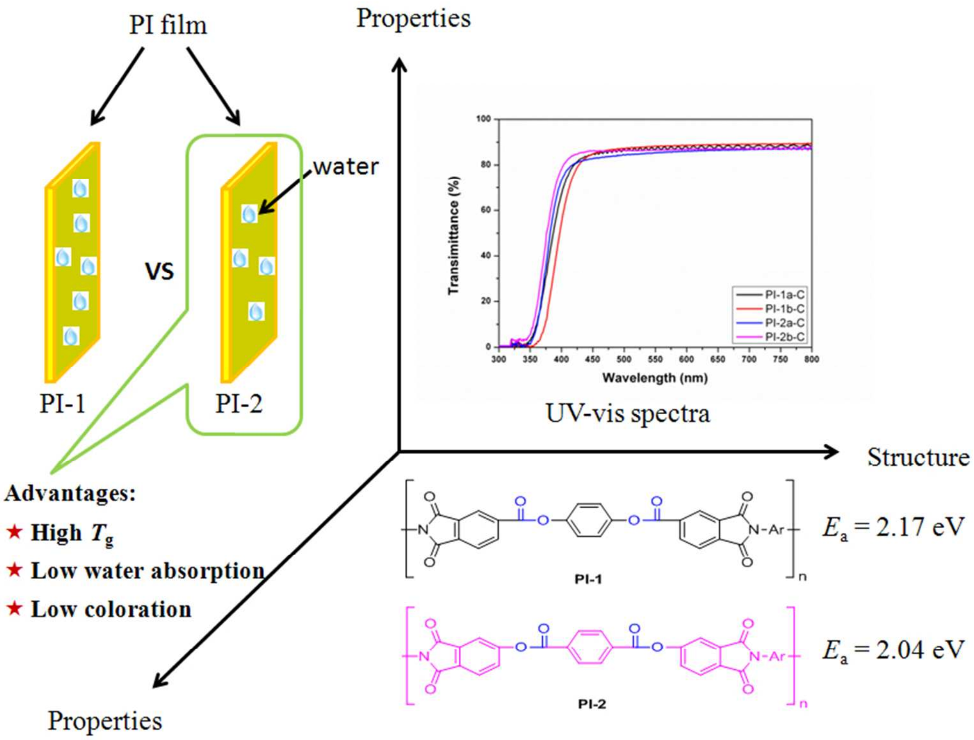
PI film
Properties
water
VS
PI-1
PI-2
Advantages:
★ High T_g
★ Low water absorption
★ Low coloration
Properties
Transimittance (%)
Wavelength (nm)
PI-1a-C
PI-1b-C
PI-2a-C
PI-2b-C
UV-vis spectra
Structure
N-Ar
PI-1
E_a = 2.17 eV
PI-2
E_a = 2.04 eV

Journal Name

ARTICLE

Synthesis and characterization of transparent polyimides derived from ester-containing dianhydrides with different electron affinities

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Two series of poly(ester imide)s derived from bis(trimellitic acid anhydride) phenyl ester (TAHQ) and bis[(3,4-dicarboxylic anhydride) phenyl] terephthalate (PAHP), as well as poly(ether imide)s based on hydroquinone diphthalic anhydride (HQDPA), were synthesized with aromatic diamines via solution polycondensation. These polyimide films were transparent with an ultraviolet–visible absorption cut-off wavelength below 375 nm, and with the tensile strengths of 42.0-83.8 MPa, tensile moduli of 2.5-4.7 GPa and elongations at break of 2.1-5.4%. Compared with the poly(ether imide)s, the poly(ester imide)s showed higher glass transition temperature (T_g), lower water absorption (W_A) and lower temperature of 5% weight loss ($T_{d5\%}$). Moreover, the poly(ester imide)s derived from PAHP with low electron affinity of 2.04 eV by theoretical calculation achieved better transparency, lower W_A and slightly lower T_g than the corresponding TAHQ-based poly(ester imide)s.

1. Introduction

Aromatic polyimides (PIs) have been widely utilized in a variety of electric and microelectronic applications for their reliable and excellent properties, i.e., considerably high glass transition temperatures (T_g), high resistance to chemicals, good dielectric and mechanical properties.[1-5] However, the widespread applications of polyimides in optical fields are often limited because of deep coloration which is caused by the strong intra- and intermolecular charge transfer (CT) interactions.[6,7] So far, much effort has been devoted to development of transparent polyimide films based on structural design. The most effective approach for inhibiting CT interactions is to use non-aromatic (cycloaliphatic) monomers either in diamines or tetracarboxylic dianhydrides.[8-15] Unfortunately, this approach somewhat sacrifices high-temperature stability. For fully aromatic polyimides, the best way is incorporation of trifluoromethyl group in the monomers, such as 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 2,2'-bis(trifluoromethyl)biphenyl-4,4'-diamine (TFDB), which are commercial available but expensive.[16] Another strategy for obtaining transparent polyimides is to use dianhydrides with low electron-acceptability and diamines with low electron-donatability as monomers for weakening both intra- and intermolecular CT interactions.[7] For example, the polyimide films derived from bis(ether anhydride)s with electron-donating atom “O” in phthalic anhydride, which decreased the electron affinity (E_a) of dianhydride, showed good transparency.[17-25] However, poly(ether imide)s (PEIs) based on bis(ether anhydride)s decrease the T_g due to the introduction of flexible ether linkage.

On the other hand, the poly(ester imide)s (PEsIs) derived from trimellitic acid anhydride achieved higher T_g and low water absorption (W_A) etc, which was widely used in electronic devices such as integrated circuits.[26-31] The introduction of polar ester linkage in the polymer chain, increased the intermolecular interaction, which was beneficial to improve T_g and lower water absorption, but also increased the electron affinity of dianhydride due to the electron-withdrawing C=O group directly substituted at phthalic anhydride, which enhanced the electron-acceptability of dianhydride leading to increase the coloration of resulting polyimides at the same time.

Therefore, PEsIs derived from hydroxyl phthalic anhydride would be a best strategy to obtain combined excellent properties. The existence of ester group would remain the excellent properties of poly(ester imide)s, such as high T_g and low W_A, while using electron-donating atom “O” linked with phthalic anhydride would decrease the electron affinity of dianhydride to improve the transparency of films (Fig. 1). To the best of our knowledge, there is no report on the isomeric effect of such linkage on the polyimides.[32] Herein, two series of PEsIs were prepared from two dianhydrides with different electron affinities, bis(trimellitic acid anhydride) phenyl ester (TAHQ) and bis[(3,4-dicarboxylic anhydride) phenyl] terephthalate (PAHP), with various aromatic diamines via solution polycondensation. The thermal stability, solubility, water absorption, coefficient of thermal expansion (CTE), mechanical and optical properties of these polyimides as well as the different properties caused by the different ester linkages were well investigated. The polyimides derived from hydroquinone diphthalic

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anhydride (HQDPA) were also prepared and investigated for comparison.

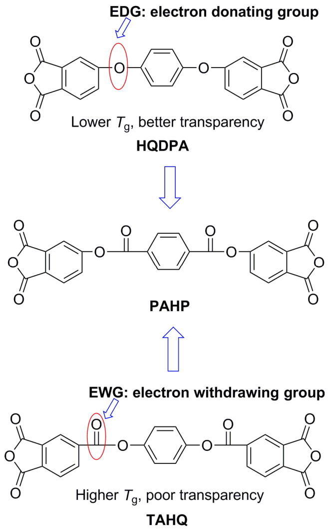


Fig. 1 Chemical structure of HQDPA, PAHP and TAHQ.

2.Experimental

2.1. Materials

4-Nitrophthalonitrile (98%, Leadership Chemical Technologies Co., Ltd.), terephthaloyl chloride (Sinopharm Chemical Reagent Co., Ltd.) and hydroquinone diphthalic anhydride (HQDPA) (Hipolyking Chemical Reagent Co., Ltd.) were used as received. Bis[4-(3-aminodiphenoxy)phenyl] sulfone (*m*-BAPS, 98%, Changzhou Sunlight Pharmaceutical Co., Ltd.) was recrystallized from ethanol before use. Bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl] sulfone (6F-BAPS),[33] and bis(trimellitic acid anhydride) phenyl ester (TAHQ)[29] were synthesized in our laboratory according to the literature. *N*,*N*-Dimethylacetamide (DMAc) was distilled from calcium hydride and stored over 4 Å molecular sieves. Anhydrous tetrahydrofuran (THF) was distilled from sodium. All other reagents for the study were commercially obtained and used as received without further purification.

2.2. Instrumentation

Fourier transform infrared (FT-IR) spectra were recorded with a Thermo Nicolet 6700 FT-IR spectrometer. Nuclear magnetic resonance (NMR) spectra were performed on a Bruker 400 AVANCE III spectrometer operating at 400 MHz for ^{1}H NMR using dimethyl sulfoxide-d_6 (DMSO-d_6) as solvent. The inherent viscosities of the polymers were measured at 30 ± 0.1 °C with an Ubbelohde viscometer and the concentration was 0.5 g/dL in DMAc. Differential scanning calorimetry (DSC) measurements of the polyimides were performed on a Mettler Toledo-DSC I at a heating rate of 20 °C/min under nitrogen atmosphere, and the temperature at the middle of the thermal transition from the second heating scan was assigned as the glass transition temperature (T_g). The melting points (m.p.) of synthesized monomers were also measured by the DSC instrument at a heating rate of 10 °C/min and the melting points were determined from the temperature at the maximum point of the corresponding enthalpy peaks. Thermogravimetric analyses (TGA) of the polyimides were performed on a Mettler Toledo-TGA/DSC I instrument to evaluate the thermal stability of the polyimides at a heating rate of 10 °C/min from 50 °C to 800 °C under nitrogen or air atmosphere (flow rate of 50 mL/min). The mechanical properties of the polyimide films such as tensile modulus, tensile strength, and elongation at break were measured and averaged on at least five film specimens by an Instron model 5567 tensile tester at a crosshead speed of 5 mm/min at room temperature. The specimen gauge lengths were 50 mm and the specimen widths were 10 mm. Ultraviolet-visible (UV-vis) spectra of the polymer films were recorded on a Lambda 950 UV/Vis/NIR spectrophotometer. The wide-angle X-ray diffraction (WAXD) measurement of the polyimide films was undertaken on a Bruker D8 Advance with Cu Kα radiation (40 kV, 40 mA) at a scanning rate of 5°/min from 5 to 50°. The equilibrium water absorption (W_A) was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 24 hr. The water absorption was calculated from the following equation:

$$\text{Water absorption (\%)} = [(W_{wet} - W_{dry}) / W_{dry}] * 100\%$$

Where W_{dry} is the initial weight of the dry film and W_{wet} is the weight of the film after immersion in deionized water. The water absorption of the PIs is the mean data of three parallel samples. Thermo mechanical analysis (TMA) was performed by a METTLER TMA/SDTA841 at a heating rate of 10 °C/min. The coefficient of thermal expansion (CTE) was recorded at the temperature range of 100-200 °C.

2.3. Monomer synthesis

2.3.1 4-Hydroxyphthalonitrile

To a flask containing 4-nitrophthalonitrile (103.9 g, 600 mmol) and DMSO (800 mL) was added K_2CO_3 (91.6 g 660 mmol) and $NaNO_2$ (46.0 g, 660 mmol) under nitrogen atmosphere with stirring at room temperature. The mixture was stirred for 3 h at 160 °C, then the resulting solution was poured into the water after cooled to room temperature and acidified by hydrochloric acid to pH = 3. The precipitate was filtered off, washed with water, and dried at 110 °C under vacuum to afford 73.3 g of 4-hydroxyphthalonitrile, yield: 85%, m.p. = 219 ^oC. FT-IR (KBr, cm^{-1}): 3269 cm^{-1} (O-H stretching), 2243 cm^{-1} (C≡N stretching). ^{1}H NMR δ_H (400 MHz, DMSO-d_6, δ, ppm): 11.46 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.39 (s, 1H) and 7.21 (d, *J* = 8.0 Hz, 1H).

2.3.2 4-Hydroxyphthalic acid

In a 1 L flask, a suspension of 4-hydroxyphthalonitrile (69.2 g, 480 mmol) in a 800 mL water containing of dissolved KOH (230.0 g, 4.11 mol) was boiled under reflux for about 90 h. The resulting clear solution was cooled to room temperature and filtered to remove any possible insoluble impurities. Then filtrate was acidified by hydrochloric acid to pH = 1, extracted with ethyl acetate three times, washed with brine and dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude product 82.9 g was afforded and dried at room temperature under vacuum, yield: 95%, m.p. = 196 ^oC. The crude product was used directly for the cyclodehydration reaction without further purification. FT-IR (KBr, cm^{-1}): 3483, 3103 cm^{-1} (O-H stretching), 1686, 1598 cm^{-1} (C=O stretching). ^{1}H NMR δ_H (400 MHz, DMSO-d_6, δ, ppm): 12.78 (s, 2H), 10.37 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H) and 6.84-6.82 (m, 2H).

2.3.3 4-Hydroxyphthalic anhydride

The 4-hydroxyphthalic anhydride (10.8 g) was afforded by sublimation of 4-hydroxyphthalic acid (12.3 g, 67.5 mmol) directly, yield: 95%, m.p. = 172 ^{o}C. FT-IR (KBr, cm^{-1}): 3293 cm^{-1} (O-H stretching), 1846, 1762 cm^{-1} (C=O stretching). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 11.40 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H) and 7.34-7.25 (m, 2H).

2.3.4 Bis[(3,4-dicarboxylic anhydride) phenyl] terephthalate (PAHP)

To a solution of 24.6180 g (150 mmol) of 4-hydroxyphthalic anhydride in 400 mL of anhydrous THF was added terephthaloyl chloride (15.2265 g, 75 mmol) in portions under stirring. Pyridine (35.0 mL) was then added as catalyst and acid absorbent. The reactive mixture was stirred for 24 h at room temperature and the solid separated during reaction was filtered and washed with water, methanol and trichloromethane. A white solid product (28.20 g) was obtained and dried at 150 °C under vacuum, yield: 82%, m.p. = 277 ^{o}C. FT-IR (KBr, cm^{-1}): 1846 cm^{-1} (asym C=O stretching), 1783 cm^{-1} (sym C=O stretching), 1737 cm^{-1} (C=O stretching), 1258, 1060, 1018 cm^{-1} (C-O stretching). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.40 (s, 4H), 8.23 (d, *J* = 8.4 Hz, 2H), 8.21 (s, 2H) and 8.01 (d, *J* = 8.4 Hz, 2H).

2.3.5 Polymer synthesis and film preparation

Utilizing TAHQ, PAHP and HQDPA as dianhydride monomers, six kinds of polyimides were synthesized by polycondensation with diamine monomer *m*-BAPS and 6F-BAPS via two-step procedure with different methods (thermal imidization (**H**) and chemical imidization (**C**)), respectively. The resulting PIs were referred to as **PI-1a** to **PI-3b** successively.

The synthesis of the film of polyimide (**PI-2a**) is used below as an example to illustrate the general synthetic route for the preparation: dianhydride PAHP (1.8334 g, 4.0 mmol) was added in one portion to a solution of diamine *m*-BAPS (1.7300 g, 4.0 mmol) in DMAc (14.2536 g) in a 50 mL flask. The mixture was stirred in nitrogen at room temperature for 24 h to yield a viscous poly(amic acid) (PAA) solution with 20 wt% solid concentration. Then the resulting viscous poly(amic acid) solution was diluted to 15 wt% with additional DMAc.

For the thermal imidization procedure, the PAA solution was taken out and cast onto a glass plate. The glass plate was placed in an oven at 80 °C for 2 h to remove most of the solvent. The semidried PAA film was further dried and imidized by heating at 150 and 260 °C for 60 min at each temperature. The resulting films PI-2a-H were obtained by immersion the glass plate in water followed by dry in an oven at 100 °C.

For the chemical imidization procedure, the PAA solution was added the mixture solution of acetic anhydride (2 mL) and pyridine (1 mL). After stirring for 24 h, the solution was diluted with DMAc and slowly poured into a vigorously stirred ethanol. The precipitate was collected by filtration, washed thoroughly with hot ethanol and dried. The polyimide film PI-2a-C was prepared via the casting of 10 wt% homogenous solution of above polyimide powder in DMAc onto a clean glass plate, which was then placed in an oven at 80 °C overnight to evaporate most of the solvent and subjected to scheduled heating at 150 and 200 °C for 60 min at each temperature.

PI-1a-C: FT-IR (film): 1782 cm^{-1} (asym C=O stretching), 1722 cm^{-1} (sym C=O stretching), 1371 cm^{-1} (C-N stretching).

PI-1b-C: FT-IR (film): 1784 cm^{-1} (asym C=O stretching), 1725 cm^{-1} (sym C=O stretching), 1378 cm^{-1} (C-N stretching).

PI-2a-C: FT-IR (film): 1780 cm^{-1} (asym C=O stretching), 1722 cm^{-1} (sym C=O stretching), 1370 cm^{-1} (C-N stretching).

PI-2b-C: FT-IR (film): 1783 cm^{-1} (asym C=O stretching), 1724 cm^{-1} (sym C=O stretching), 1371 cm^{-1} (C-N stretching).

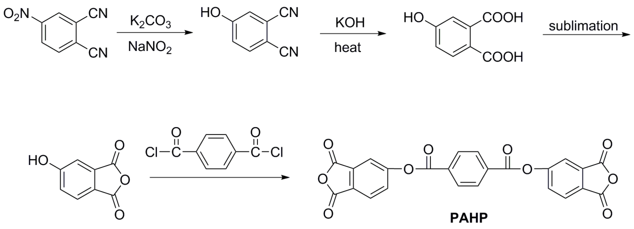
PI-3a-C: FT-IR (film): 1778 cm^{-1} (asym C=O stretching), 1725 cm^{-1} (sym C=O stretching), 1378 cm^{-1} (C-N stretching).

PI-3b-C: FT-IR (film): 1779 cm^{-1} (asym C=O stretching), 1722 cm^{-1} (sym C=O stretching), 1373 cm^{-1} (C-N stretching).

3.Results and discussion

3.1. Monomer synthesis

As shown in Scheme 1, 4-hydroxyphthalic anhydride was obtained by substitution reaction with 4-nitrophthalonitrile, alkaline hydrolysis in the presence of KOH, and then sublimation under the vacuum. The bis(ester anhydride), bis[(3,4-dicarboxylic anhydride) phenyl]terephthalate (PAHP), was afforded through esterification reaction of terephthaloyl chloride with 4-hydroxyphthalic anhydride. Fig. 2 shows the IR spectrum of the bis(ester anhydride) PAHP. The strong absorption bands around 1846 cm^{-1} (v_{asym} C=O) and 1783 cm^{-1} (v_{sym} C=O) were assigned to the phthalic anhydride, while the strong absorption bands around 1737 cm^{-1} was assigned to the ester group in PAHP. The observed bands in the region of 1000-1300 cm^{-1} were due to the C-O stretching. The ^{1}H NMR spectrum of PAHP is shown in Fig. 3, in which all the signals were assigned. The aromatic protons in terephthalate (H$_a$) and phthalic anhydride (H$_b$-H$_d$) resonated in the region of 8.40 and 8.23-8.01 ppm, respectively.



Scheme 1. Synthesis of dianhydride PAHP.

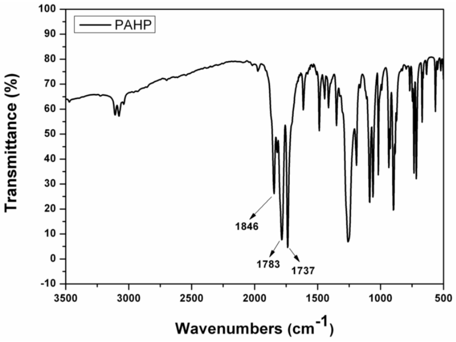


Fig. 2 FT-IR spectrum of PAHP.

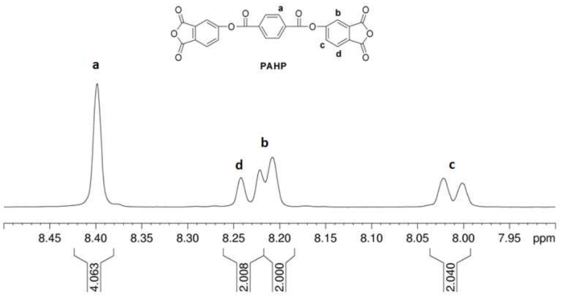


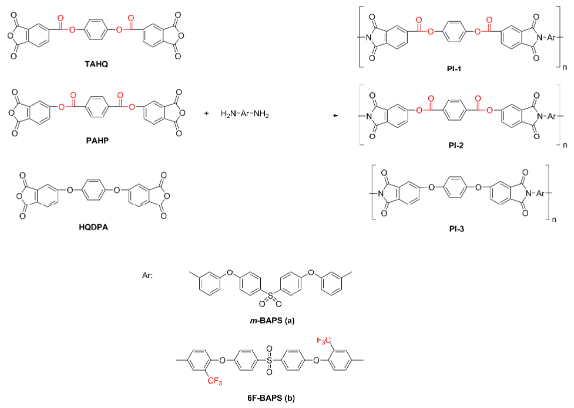
Fig. 3 ^{1}H NMR spectrum of PAHP in DMSO-d_6.

3.2. Synthesis of Polyimides

Utilizing bis(trimellitic acid anhydride) phenyl ester (TAHQ), bis[(3,4-dicarboxylic anhydride) phenyl] terephthalate (PAHP) and hydroquinone diphthalic anhydride (HQDPA) as dianhydride monomers, six kinds of polyimides were synthesized by polycondensation with diamine monomer *m*-BAPS and 6F-BAPS via two-step procedure, which is shown in Scheme 2. Whenever aromatic diamines were used, the reaction smoothly proceeded and led to homogeneous after 24 hours. The inherent viscosities of prepared poly(amic acid)s (PAAs) were between 0.57-1.02 dL/g in DMAc at 30 °C (Table 1). The polyimide films derived from TAHQ and HQDPA were successfully afforded by thermal imidization. To our surprise, no flexible polyimide films based on PAHP were obtained by thermal imidization, although the PAAs had higher inherent viscosities with 0.87-1.02 dL/g, which indicated that PAAs were degraded quickly during the thermal imidization conditions. Fortunately, all the polyimides were highly soluble in DMAc at room temperature, so that polymerization were conducted by chemical imidization (**C**) and the resulting polyimides could be cast to form flexible films.

The chemical structures of polyimides were confirmed by ^{1}H NMR and FT-IR spectroscopy. The representative ^{1}H NMR spectra of **PI-1b-C**, **PI-2b-C** and **PI-3b-C** are shown in Fig. 4, Fig. 5, Fig. 6, respectively, in which all the signals have been assigned to the protons of the repeating unit. The aromatic protons (H_a) in the middle benzene of dianhydride moiety in **PI-1b-C**, **PI-2b-C** and **PI-3b-C** were resonated in 7.55, 8.41 and 7.33 ppm, respectively. Furthermore, the COSY spectra of **PI-1b-C**, **PI-2b-C** and **PI-3b-C** (see Figures in SI) were measured for the further assignments of protons. The completed imidization was confirmed by the absence of corresponding amide signals and carboxylic acid functions.

The typical IR spectra of **PI-1b-C**, **PI-2b-C** and **PI-3b-C** are shown in Fig. 7. The strong absorption bands around 1783 cm^{-1} (ν_{asym}C=O), 1724 cm^{-1} (ν_{sym} C=O), and 1373 cm^{-1} ($\nu_{C\text{-}N}$ imide) were assigned to the phthalimide unit, while the absorption bond around 1316 and 1147 cm^{-1} were assigned to the sulfone unit.



Scheme 2. Synthesis of polyimides.

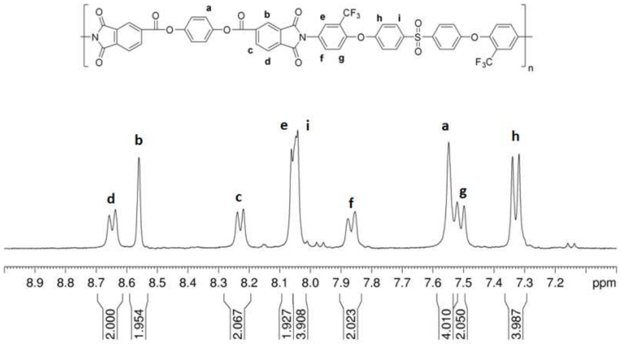


Fig. 4 ^{1}H NMR spectrum of **PI-1b-C** in DMSO-d_6.

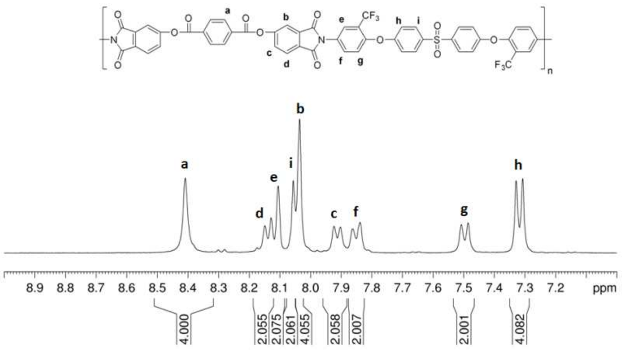


Fig. 5 ^{1}H NMR spectrum of **PI-2b-C** in DMSO-d_6.

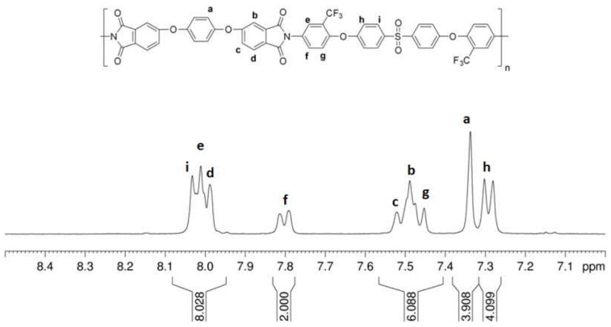


Fig. 6 ^{1}H NMR spectrum of **PI-3b-C** in DMSO-d_6.

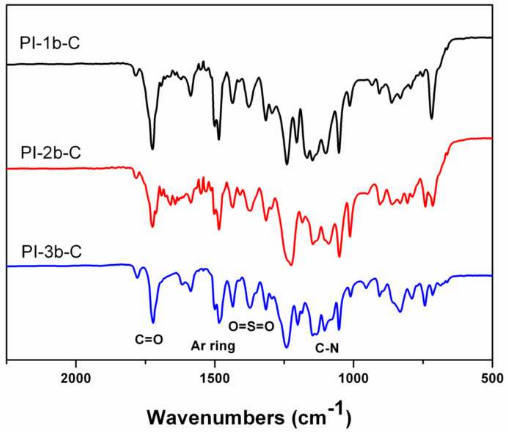


Fig. 7 FT-IR spectra of PI.

3.3. Thermal properties

The thermal behavior data of polyimides are listed in Table 1. The T_gs of polyimides were in the range of 211-250 °C. T_g is correlated with the structure of polymer chain. **PI-1a-C**, **PI-2a-C** and **PI-3a-C** derived from *m*-BAPS displayed a relatively lower T_g than the other PIs derived from 6F-BAPS due to their more flexible backbones with *meta* substitution. **PI-1b-C** showed the highest T_g value of 250°C because of the increase of chain rigidity with *para* substitution and steric effect of the trifluoromethyl group.[32] The T_g values of the TAHQ and PAHP series of polyimides were higher than those of the corresponding counterparts of HQDPA-based PIs. What's more, the PIs derived with PAHP exhibited slightly lower T_g compared with TAHQ-based polyimides, which indicated that intermolecular interactions were weak due to the different ester linkages.

The thermal stability of the polyimides was evaluated by dynamic TGA conducted at a heating rate of 10 °C/min. The temperature of 5% weight loss ($T_{d5\%}$) in nitrogen and air atmospheres were determined from original TGA thermograms, which are listed in the Table 1 and the TGA curves of **PI-1a-C** to **PI-3b-C** are shown in Fig. 8. The $T_{d5\%}$ values of these PIs were recorded in the range of 481-556°C in nitrogen and 451-542°C in air. It was obvious that poly(ester imide)s showed lower $T_{d5\%}$ than the poly(ether imide)s, because the ester groups started to decompose at a lower temperature. However, there was no obvious differences on the $T_{d5\%}$ regardless of different ester linkage due to the similar chemical compound.

The CTE values of poly(ester imide)s and poly(ether imide)s are also summarized in Table 1, which were in the range of 52.7-75.3 ppm/K and 61.0-120.0 ppm/K, respectively.

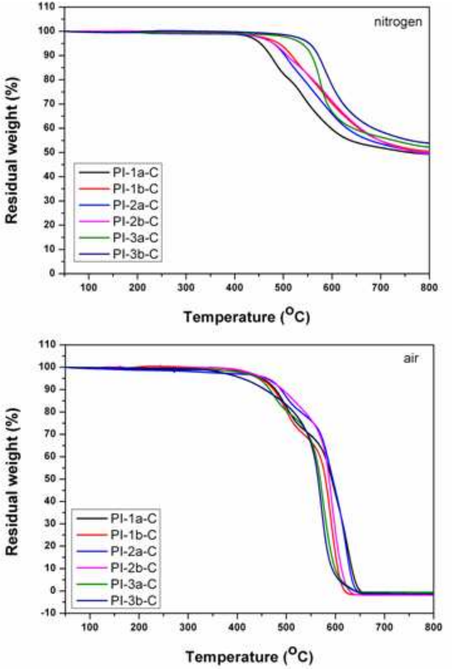


Fig. 8 TGA curves of polyimides in nitrogen and air.

3.4 Water absorption

As summarized in Table 1, all the PI films showed low water absorption in the range of 0.28-0.62%, which were much lower than commercially available Kapton-H film (PMDA/4,4'-ODA) with W_A of 2.9%.[13] The results are probably related to a significant decrease in the content of highly polarizing imide groups in the structures.[14,29] Moreover, the PIs based on 6F-BAPS showed lower water absorption than the PIs based on *m*-BAPS. This phenomenon was probably due to the trifluoromethyl groups, which induced greater water proofing effect.[13] Furthermore, the PAHP-based PIs exbihited lower W_A than the corresponding TAHQ-based PIs. The low water absorption ensured their applications in the microelectronic industry.

Table 1 Thermal properties and water absorption of the polyimides.

PI	η_{inh}[a](dL/g)	T_g[b] (^{o}C)	$T_{d5\%}$[c](^{o}C)		Char yield (%)	CTE[d] (ppm/K)	W_A[e] (%)
			In N_2	In air			
PI-1a-C	0.59	220	481	454	46	73.6	0.58
PI-1b-C	0.72	250	494	451	50	56.9	0.54
PI-2a-C	1.02	217	481	460	50	52.7	0.32
PI-2b-C	0.87	236	484	461	50	75.3	0.28
PI-3a-C	0.75	211	541	535	52	120.0	0.62
PI-3b-C	0.57	222	556	542	54	61.0	0.40

[a] The inherent viscosities of poly (amic acid)s were measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

[b] Baseline shift in the second heating DSC traces, with a heating rate of 20 °C/min.

[c] Temperatures at which 5% weight loss were recorded by TGA at a heating rate of 10 °C /min.

[d] CTE is recorded from 100 to 200 ^{o}C at a heating rate of 10 °C/min by TMA.

[e] Water absorption of polyimide films were measured by immersing the films of these polyimides in deionized water at 25°C for 24 hr.

Table 3 Mechanical properties of the polyimide films.

PI	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
PI-1a-C	68.0	2.9	3.3
PI-1b-C	83.8	2.8	5.4
PI-2a-C	62.6	2.5	4.3
PI-2b-C	42.0	2.5	2.1
PI-3a-C	79.1	4.7	2.6
PI-3b-C	74.9	4.4	2.6

Table 4 Optical properties of the polyimide films.

PI	Imidization	d (μm)	λ_0 (nm)[a]	T_{400} (%)[b]	T_{450} (%)[b]	T_{500} (%)[b]	α[c] (cm^{-1})
PI-1a-H	H	30	375	27	72	79	188
PI-1a-C	C	20	360	50	82	85	151
PI-1b-H	H	22	370	32	76	84	223
PI-1b-C	C	27	360	55	85	87	97
PI-2a-C	C	26	351	73	83	85	52
PI-2b-C	C	22	343	78	86	86	48
PI-3a-H	H	22	371	65	84	86	84
PI-3a-C	C	23	365	67	84	85	74
PI-3b-H	H	24	366	63	85	87	83
PI-3b-C	C	21	360	71	87	88	70

[a] $\lambda_{0:}$ UV cut-off wavelength.

[b] T_{400},T_{450},T_{500}: transmittance at 400, 450, 500 nm, respectively.

[c] The absorption coefficient of the polymer at 400 nm was calculated by dividing absorbance by the film thickness.

3.5 Solubility

Table 2 Solubility of the polyimides.

PI	Solvents[a]						
	m-cresol	DMAc	DMF	NMP	DMSO	$CHCl_3$	THF
PI-1a-C	++	++	+	++	+	+−	+−
PI-1b-C	++	++	++	++	++	+−	+
PI-2a-C	++	++	+	++	+	+−	+−
PI-2b-C	++	++	++	++	++	+−	++
PI-3a-C	++	++	+−	+	+−	+−	+−
PI-3b-C	++	++	++	++	++	++	++

The qualitative solubility was tested with 10 mg samples in 1 mL of solvent.++: soluble at room temperature; +: soluble □on heating; +−: partial soluble on heating.

[a] DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; NMP: *N*-methylpyrrolidone; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

The solubility of the polyimides was tested qualitatively in various organic solvents, and the results are shown in Table 2. The solubility of **PI-1b-C**, **PI-2b-C** and **PI-3b-C** is better than **PI-1a-C**, **PI-2a-C** and **PI-3a-C** owing to CF_3 group which inhibited close packing and reduced the inter-chain interaction to enhance solubility. In almost all cases, the PEsIs based on the *m*-BAPS exhibited better solubility than the PEIs, while the 6F-BAPS-containing PEsIs showed worse solubility than the corresponding PEIs. Furthermore, the PIs derived from PAHP exhibited slightly better solubility compared with TAHQ-based polyimides.

3.6 Mechanical properties

The mechanical properties of the flexible polyimide films are listed in Table 3. The polyimide films exhibited good mechanical properties with tensile strengths of 42-84 MPa, tensile moduli of 2.5-4.7 GPa, and elongations at break of 2.1-5.4%. Among these polyimide films, the tensile strength and tensile modulus of PI-1b-C was more than 83 MPa and 2.8 GPa, respectively, which were attributed to rigid structure in the polymers backbone. What's more, the TAHQ-based PEsIs showed slightly better mechanical properties than the PAHP-based PEsIs.

3.7 X-ray diffraction

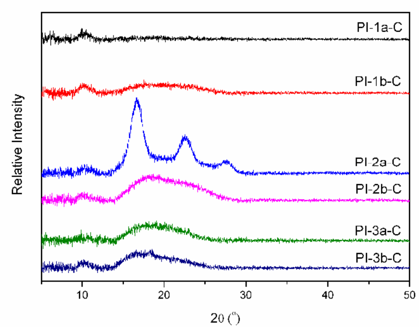


Fig. 9 Wide-angle X-ray diffractograms of the polyimide films.

The crystallinity of the polyimide films was analyzed by wide-angle X-ray diffraction (WAXD). **PI-2a-C** exhibited some diffraction peaks in the 2θ range from 15 and 30°, which suggested that polyimide had relatively some regularity of intermolecular packing or short-range-order structure. The WAXD patterns of the other films were broad without obvious peak features, which indicated that they were all amorphous (Fig. 9).

3.8 Optical properties

The UV-visible absorption spectra of some representative polyimide films are illustrated in Fig. 10, while the transmittance spectra and absorption coefficient curves are showed in Fig. S7 and S8 (see Figures in SI). The cut-off wavelength (absorption edge, λ_0), transmittance at 400, 450, 500 nm and absorption coefficient at 400 nm from these spectra are listed in Table 4.

All polyimide films exhibited cut-off wavelengths shorter than 375 nm and were highly transparent. The lower coloration of the polyimide derived from 6F-BAPS with the bulky and electron-withdrawing CF_3 groups in their diamine moieties could be explained by the decreased CTC formation of polymer chains through higher steric hindrance and lower inductive effect. A secondary positive effect of the CF_3 groups on the film transparency was the weakened intermolecular dispersion forces due to low polarizability of the C–F bond.[18]

As expected, the PAHP-based PIs exhibited better optical properties than TAHQ-based PIs due to the lower electron affinity (E_a) value of PAHP, which reduced the CTC effect formation. What's more, the PAHP-based PIs even showed lower cut-off wavelength and higher transmittance at 400 nm than the HQDPA-based polyimides, although HQDPA-based polyimides showed better transparency after 450 nm. (Fig. 11) The absorption coefficients of the polyimides at 400 nm excluding the film thickness factor were also supported these results. On the other hand, the HQDPA based polyimide films revealed slightly better transparent in the visible wavelength spectrum of 400-800 nm than their respective analogue based on the TAHQ and PAHP, among which the **PI-3b-C** showed the best optical transparency, probably due to the ether moiety in the dianhydride weakened both intra- and intermolecular charge transfer interactions by decreasing electron-acceptability of dianhydride.[7] Furthermore, the polyimide films prepared via chemical imidization (**C**) tend to show higher T_{400} values than the corresponding thermally imidized (**H**) films. This was probably due to an end-capping reaction of the thermally less stable terminal amino groups with Ac_2O during chemical imidization.[13]

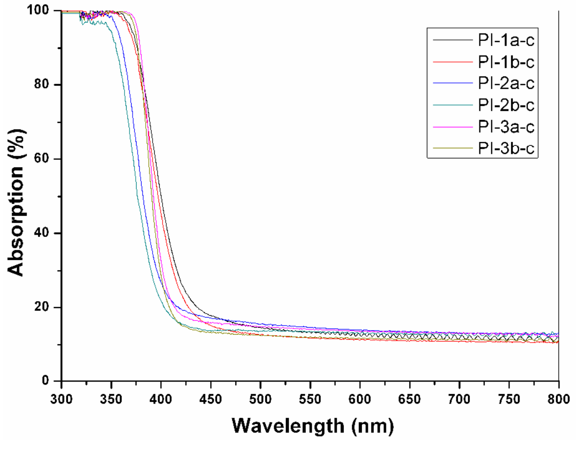


Fig. 10 UV-vis absorption spectra of polyimide films.

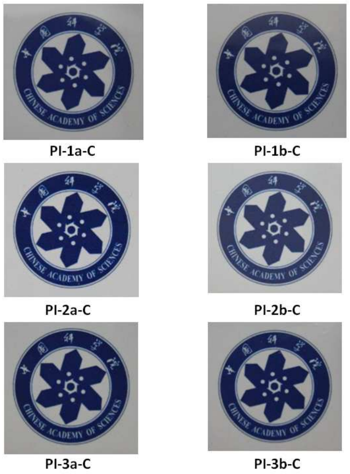

PI-1a-C
PI-1b-C
PI-2a-C
PI-2b-C
PI-3a-C
PI-3b-C

Fig. 11 Photographs of the polyimide films.

To interpret the coloration of polyimide films clearly, the electron affinities (E_a)[34] of TAHQ, PAHP as well as HQDPA, were carried out by a theoretical calculation employing the DFT method in the Gaussian 09 package.[35] The exchange correlation functional B3LYP is carefully mixed with Hartree–Fock exchange calculated with Kohn–Sham orbits and the B88 exchange functional plus the LYP correlation functional.[36] The all-electron basis set 6-31g (d) was used to describe the C, O and H atoms. The calculation results for the values of E_a of the dianhydrides were calculated from equation 1 and the results are tabulated in Table 5. As expected, the E_a values of PAHP is 2.04 eV, which is much lower than that of TAHQ with value of 2.17 eV, indicates that the ester group decrease the electron acceptability of dianhydride, therefore, the corresponding polyimides based on PAHP exhibit a relatively better transparency than that of TAHQ. And the PIs derived from HQDPA show the best transparency due to the lowest E_a value of 1.62 eV.

$E_a = E(\text{optimized neutral geometry}) - E(\text{optimized anion geometry})$ (1)

Table 5 Electronic characteristics of TAHQ, PAHP, and HQDPA

Dianhydride	E_a (a.u.) Calculated from energies difference	E_a (eV)	q_1[a]	q_2[a]
TAHQ	0.0798	2.17	0.814	0.816
PAHP	0.0749	2.04	0.814	0.816
HQDPA	0.0597	1.62	0.813	0.816

[a] Refer to the values of the positive charges on the carbonyl carbon atoms of the dianhydrides.

4.Conclusion

Two series of novel poly(ester imide)s were synthesized from bis(trimellitic acid anhydride) phenyl ester (TAHQ), bis[(3,4-dicarboxylic anhydride) phenyl] terephthalate (PAHP) and hydroquinone diphthalic anhydride (HQDPA) with various aromatic diamines by polycondensation, which could be formed transparent, flexible, and tough films with tensile strengths of 42.0-83.8 MPa, tensile moduli of 2.5-4.7 GPa and elongations at break of 2.1-5.4%. The polyimide films from PAHP showed better transparency, lower W_A and slightly lower T_g compared with TAHQ-based polyimides. The optical properties of these polyimide films are well coincident with the electron affinities (E_a) values by theoretical calculation. This proves that poly(ester imide)s derived from PAHP are a successful method for improving transparency and remaining properties of poly(ester imide)s.

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