PAPER

Synthesis and properties of transparent polyimides derived from *trans*-1,4-bis(2,3-dicarboxyphenoxy) cyclohexane dianhydride†

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A series of transparent polyimides was prepared from *trans*-1,4-bis(2,3-dicarboxyphenoxy)cyclohexane dianhydride (*trans*-3,3′-CHDPA) with various aromatic diamines *via* one-step solution polycondensation. The glass transition temperatures (T_gs) of the resulting polyimides were in the range of 206–255 °C. These polyimide films showed high optical transparency with cut-off wavelengths of 370–379 nm, and they exhibited good mechanical properties with tensile strengths of 65–88 MPa, tensile moduli of 1.7–2.4 GPa, and elongations at break of 4.7–7.5%. Compared with polyimides based on *trans*-1,4-bis(3,4-dicarboxyphenoxy)cyclohexane dianhydride (*trans*-4,4′-CHDPA), the polyimides derived from *trans*-3,3′-CHDPA showed higher T_g, better solubility and optical transparency due to the 3- and 4-position isomeric effect.

1. Introduction

Colorless high-temperature polymeric materials are one of the most attractive research interests due to the great requirement in some special optical fields, such as flexible display substrates, nonlinear optical (NLO) waveguide materials and optical half-wave plates.[1,2] Polyimides (PIs) have been deemed to be a potential candidate owing to their excellent thermal and mechanical stabilities, and are widely used in the microelectronics industry.[3–6] However, the widespread applications of polyimides in optical fields are often limited because of the deep coloration which is caused by the strong intra- and intermolecular charge transfer (CT) interactions.[7,8] Therefore, a lot of effort has been made to decrease the coloration based on structural design by modification of dianhydrides and diamines, including the incorporation of trifluoromethyl groups,[9–21] bulky groups,[22–24] unsymmetrical[20,25,26] and alicyclic units[27–38] into the polymer chains. Our group has also reported transparent semi-aromatic polyimides by the incorporation of aliphatic cyclohexane-1,4-diol into two phthalic anhydrides or diamines, which introduced an alicyclic structure without sacrificing the reactivity of the monomers.[39,40]

On the other hand, compared with 4,4′-position polyimides, isomeric polyimides derived from 3,4′-dianhydrides or 3,3′-dianhydrides have become a new research interest for researchers due to their own outstanding characteristics, such as higher glass transition temperature (T_g), better solubility, lower melt viscosity, *etc.*[41] However, most of the studies focused on the isomeric dianhydrides and/or diamines at different substituted positions (such as the 3,3′-substituted position and 3,4′-substituted position), and paid less attention to stereoisomers, for example, the *trans* and *cis* configuration. Toshihiko Matsumoto *et al.* first reported stereoisomeric polyimides derived from *trans*- and *cis*-tetracarboxylic dianhydride bearing a cycloaliphatic structure, and indicated that the *trans*-polyimides had better transparency and solubility but lower T_g than the *cis*-polyimides.[31] In addition, *trans*-polyimides derived from *trans*-1,2,4,5-cyclohexanetetracarboxylic dianhydride showed higher transparency, better solubility but lower T_g than *cis*-polyimides, which was reported by Masatoshi Hasegawa.[37] Stereoisomeric polyimides derived from *cis*- and *trans*-1,2,3,4-cyclohexanetetracarboxylic dianhydrides have also been synthesized and showed that *trans*-polyimides had lower T_g and lower solubility than the corresponding *cis*-polyimides.[38] It was found that the *trans*-polyimides which were bearing a cycloaliphatic structure had good transparency but lower T_gs. Recently, our group reported the *trans* and *cis* configuration isomeric effect of polyimides derived from *trans*- and *cis*-1,4-bis(3,4-dicarboxyphenoxy)cyclohexane (4,4′-CHDPA), as shown in Fig. 1, and found that *trans*-polymers had higher T_g, better transparency, better chemical solvent resistance and better mechanical properties, which was quite different from the above reports about the *trans*- and *cis* isomeric effect on stereoisomeric polyimides.[40] Considering isomeric polyimides

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derived from 3,3′-substituted dianhydrides have higher T_g, better solubility and transparency,[41] a new dianhydride monomer containing a 1,4-cyclohexane moiety at the 3-substituted position of phthalic anhydride, *trans*-1,4-bis(2,3-dicarboxyphenoxy) cyclohexane dianhydride (*trans*-3,3′-CHDPA), was designed and synthesized in order to enhance the T_g and transparency of the resulting polyimides. The solubility, thermal properties, mechanical properties and optical properties of these polyimides were investigated thoroughly.

2.   Experimental

2.1.   Materials

Cyclohexane-1,4-diol (*cis* + *trans*, 98%, Jingtan Qingcheng Environmental Technologies Co., Ltd.), 3-nitrophthalonitrile (98%, Leadership Chemical Technologies Co., Ltd.) and sodium hydride (60%, Sinopharm Chemical Reagent Co., Ltd.) were used as received. 2,2′-Bis(trifluoromethyl)biphenyl-4,4′-diamine (TFDB, 98%, Changzhou Sunlight Pharmaceutical Co., Ltd.) and 4,4′-diaminodiphenyl ether (ODA, 98%, Aladdin) were purified by vacuum sublimation prior to use. Bis(4-amino-2-trifluoromethylphenyl) ether (TFODA)[42] and bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl] sulfone (6F-BAPS)[43] were synthesized in our laboratory according to the literature. Bis[4-(3-aminodiphenoxy)phenyl] sulfone (*m*-BAPS, 98%), 4,4′-(1,3-phenylenedioxy)dianiline (TPER, 98%) and 4,4′-(9H-fluorene-9,9-diyl)dianiline (DFA, 98%) were purchased from Changzhou Sunlight Pharmaceutical Co., Ltd. and recrystallized from ethanol before use. N,N-Dimethylformamide (DMF) and N,N-dimethylacetamide (DMAc) were distilled from calcium hydride and stored over 4 Å molecular sieves. 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 of the powder samples were recorded with a Thermo Nicolet 6700 FT-IR spectrometer. All of the FT-IR spectra of the polyimide film samples were collected in the attenuated total reflection (ATR) mode with a 4 cm⁻¹ resolution for 128 scans each by using a Cary 640 spectrometer (Agilent, Australia). Nuclear magnetic resonance (NMR) spectra were performed on a Bruker 400 AVANCE III spectrometer operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR using dimethyl sulfoxide-d_6 (DMSO-d_6) as

the 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⁻¹ in *m*-cresol or DMAc. The weight-average molecular weights (M_w) and number-average molecular weights (M_n) were obtained *via* gel permeation chromatography (GPC) on the basis of polystyrene calibration on a PL-GPC 220 instrument with CHCl₃ as an eluent at a flow rate of 1.0 mL min⁻¹. Differential scanning calorimetry (DSC) measurements of the polyimides were performed on a Mettler Toledo-DSC I at a heating rate of 20 °C min⁻¹ 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 point (m.p.) of the synthesized monomers was measured by micro melting point apparatus. Thermo gravimetric 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⁻¹ from 50 °C to 800 °C under nitrogen or air atmosphere (flow rate of 50 mL min⁻¹). The mechanical properties of the polyimide films such as tensile modulus, tensile strength, and elongation at break were measured and averaged on at least six film specimens by an Instron model 5567 tensile tester at room temperature. 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⁻¹ from 5 to 50°.

2.3.   Monomer synthesis

2.3.1.   1,4-Bis(2,3-dicyanophenoxy)cyclohexane. To a flask containing sodium hydride (4.2 g, 60% in oil, 105 mmol) and anhydrous DMF (50 mL) was added a solution of cyclohexane-1,4-diol (5.8 g, 50 mmol) in 50 mL anhydrous DMF dropwise under nitrogen atmosphere with stirring at room temperature. The mixture was stirred for another 3 h, and a solution of 3-nitrophthalonitrile (18.2 g, 105 mmol) in 50 mL anhydrous DMF was added dropwise. After stirring at room temperature for 5 h, the mixture was trickled into water to afford a precipitate. The precipitate was collected by filtration, washed by water, and dried under vacuum at 95 °C to afford the crude product. The crude product and 150 mL MeCN were added to a flask, and heated under reflux for 4.5 h, the product was collected by filtration, and dried at 95 °C to afford 15.0 g (*trans*/*cis* = 1.8/1), yield: 81%, m.p. = 287 °C. FT-IR (KBr, cm⁻¹): 2228 cm⁻¹ (C≡N stretching). ^{1}H NMR δ_H (400 MHz, DMSO-d_6): 7.89–7.82 (2H, m, H_b), 7.77 (2H, t, H_a), 7.66 (2H, d, H_c), 4.96 (1.3H, s, H_d), 4.85 (0.7H, s, H_{d′}), 2.08–2.01 (2H, m, H_e), 1.95–1.88 (4H, m, H_{e′, f′}) and 1.81–1.72 (2H, m, H_f).

2.3.2.   1,4-Bis(2,3-dicarboxyphenoxy)cyclohexane. In a 1 L flask, a suspension of bis(ether dinitrile) (55.6 g, 150 mmol) in a mixture of ethanol–water (400 mL/400 mL) containing 136.2 g (2.4 mol) of dissolved KOH was boiled under reflux for about 72 h until the evolution of ammonia had ceased. The resulting clear solution was cooled to room temperature and filtered to remove any possible insoluble impurities. Then the filtrate was
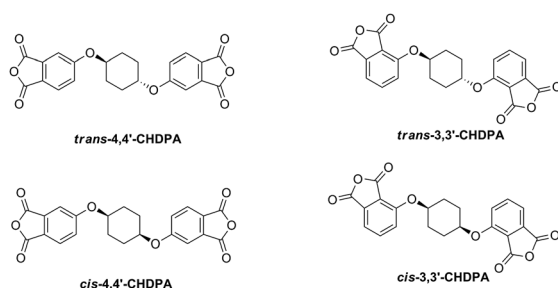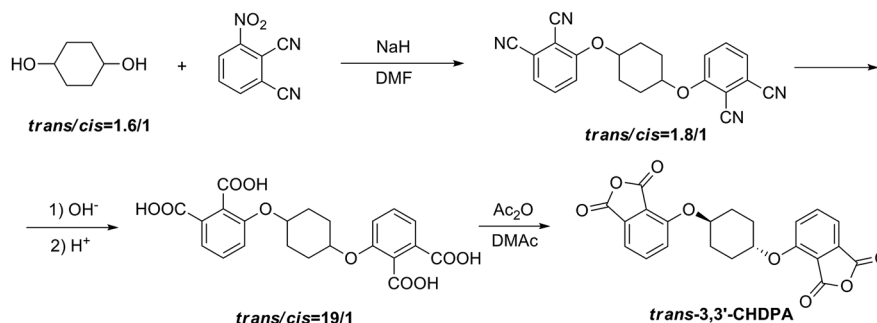

Fig. 1   Chemical structures of 4,4′-CHDPA and 3,3′-CHDPA.

Scheme 1 Synthesis of *trans*-3,3′-CHDPA.

acidified by hydrochloric acid to pH = 1. The precipitated product was filtered off, washed with water until it was neutral, and dried at 110 °C to afford 54.3 g of bis(ether diacid) (*trans/cis* = 19/1), yield: 81%, m.p. = 333 °C (decomposed *in situ*). The crude product was used directly for the cyclodehydration reaction without further purification. FT-IR (KBr, cm^{-1}): 1692, 1593 cm^{-1} (C=O stretching), 1291, 1259, 1068, 1019 cm^{-1} (C–O stretching). ^{1}H NMR δ_H (400 MHz; DMSO-d_6): 12.93 (4H, s, H$_g$), 7.48–7.37 (6H, m, H$_a$, H$_b$, H$_c$), 4.65 (1.9H, s, H$_d$), 4.50 (0.1H, s, H$_{d'}$), 2.02–1.92 (4H, m, H$_e$), 1.92–1.67 (0.3H, m, H$_{e'}$, H$_{f'}$) and 1.67–1.57 (4H, m, H$_f$). ^{13}C NMR δ_C (100 MHz, DMSO-d_6, ppm): 168.1, 167.0, 153.8, 130.1, 129.5, 128.1, 121.7, 118.8, 73.5, 25.9.
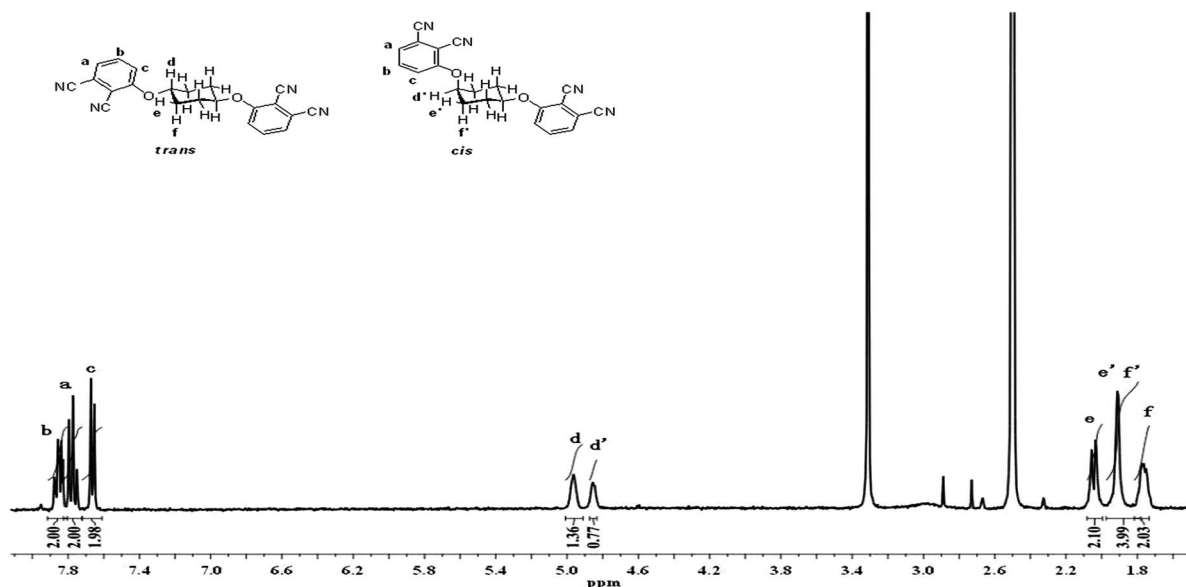
2.3.3. *trans*-1,4-Bis(2,3-dicarboxyphenoxy)cyclohexane dianhydride (*trans*-3,3′-CHDPA). In a 1 L flask, a mixture of 30.0 g (67.5 mmol) of bis(ether diacid) was dissolved in 300 mL DMAc, the resulting solution was filtered to remove any insoluble impurities, then 300 mL acetic anhydride was added and it was heated at a reflux temperature for 1 h. The precipitate was collected by filtration, washed with acetic anhydride, and dried under vacuum at 135 °C to afford 19.4 g of *trans*-3,3′-CHDPA, yield: 71%, m.p. = 342 °C (decomposed *in situ*). FT-IR (KBr,

cm^{-1}): 1835 cm^{-1} (asym C=O stretching), 1763 cm^{-1} (sym C=O stretching), 1287, 1262, 1052, 1009 cm^{-1} (C–O stretching).

2.3.4. Polymerization. Polyimides **PI-1** to **PI-7**, were synthesized from dianhydride *trans*-3,3′-CHDPA with the different diamine monomers TFDB, TFODA, 6F-BAPS, *m*-BAPS, DFA, ODA, and TPER *via* one-step solution polycondensation, respectively.

The synthesis of polyimide (**PI-2**) is described below as an example to illustrate the general synthetic route for the preparation: a mixture of *trans*-3,3′-CHDPA (1.6663 g, 4.0 mmol), diamine TFODA (1.3451 g, 4.0 mmol), *m*-cresol (15.0 mL) and 3 drops of isoquinoline in a 50 mL flask was stirred in nitrogen atmosphere at 195 °C for 8 h. The reaction mixture was diluted with *m*-cresol and slowly poured into ethanol which was being vigorously stirred. The precipitate was collected by filtration, washed with hot ethanol and then dried.

2.3.5. Film casting. The polyimide film of **PI-2** was prepared *via* the casting of a 10 wt% homogenous solution of the polyimide powder in *m*-cresol onto a clean glass plate, which was placed in an oven at 80 °C overnight to evaporate most of the solvent and subjected to scheduled heating at 120, 150 and

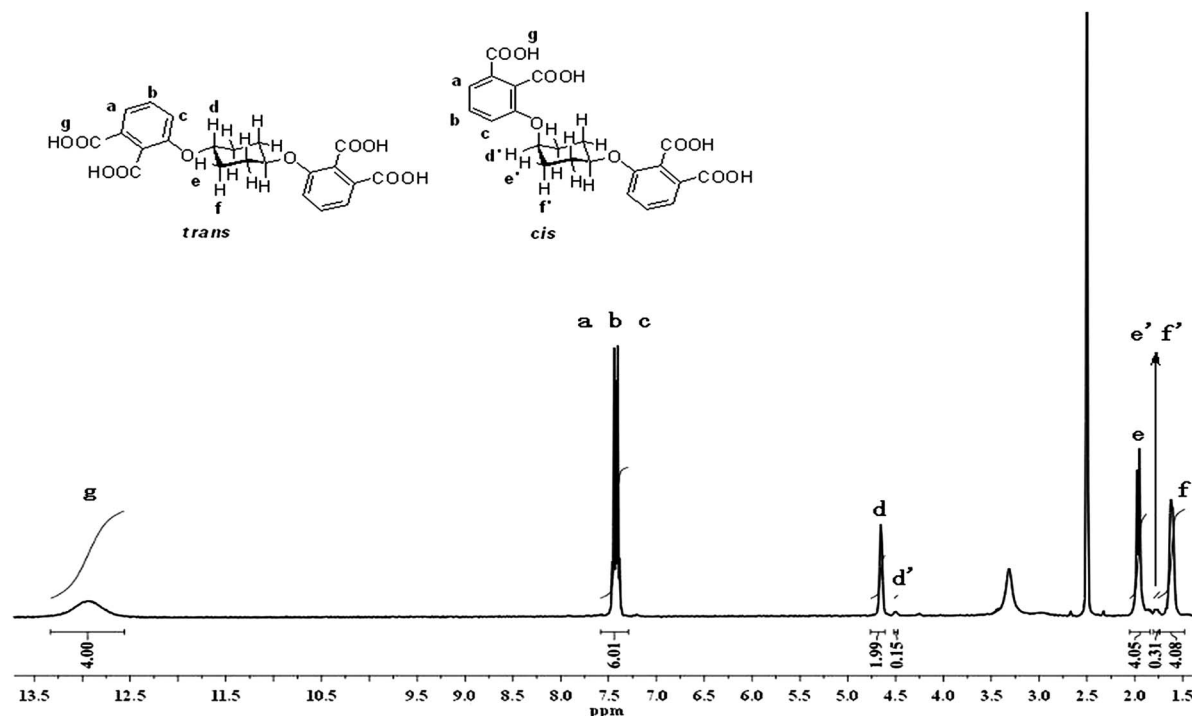**Fig. 2** ^{1}H NMR spectrum of 1,4-bis(2,3-dicyanophenoxy)cyclohexane in DMSO-d_6.

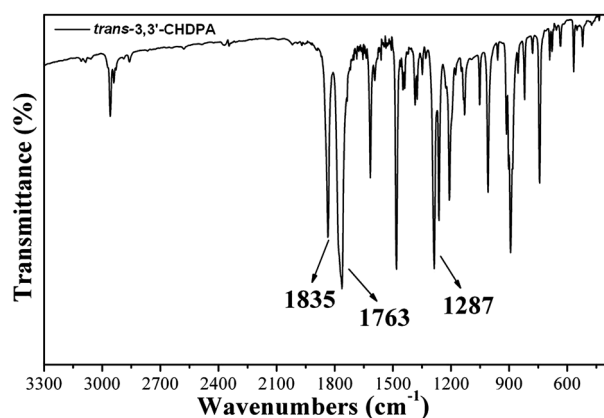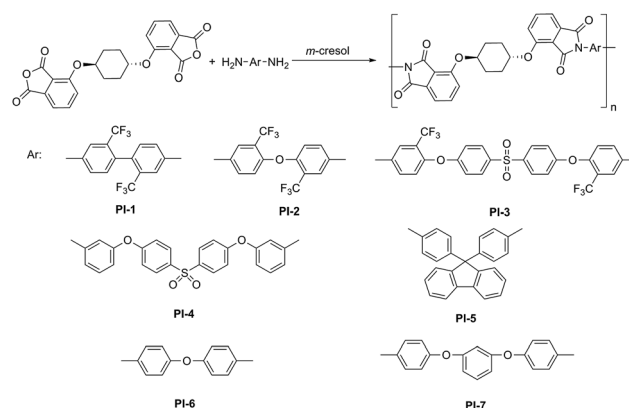**Fig. 3** ^{1}H NMR spectrum of 1,4-bis(2,3-dicarboxyphenoxy)cyclohexane in DMSO-d_6.

Fig. 4 FT-IR spectrum of *trans*-3,3′-CHDPA.

Scheme 2 Synthesis of the polyimides.

200 °C for 60 min at each temperature. FT-IR (film): 1777 cm^{-1} (asym C=O stretching), 1720 cm^{-1} (sym C=O stretching), 1379 cm^{-1} (C–N stretching). ^{1}H NMR δ_H (400 MHz, DMSO-d_6): 8.02 (2H, s, H$_g$), 7.88–7.78 (4H, m, H$_b$, H$_h$), 7.66 (2H, d, H$_a$), 7.52 (2H, d, H$_c$), 7.39 (2H, d, H$_i$), 4.99 (2H, s, H$_d$), 2.20–2.07 (4H, m, H$_e$) and 1.83–1.73 (4H, m, H$_f$).

PI-1. FT-IR (film): 1779 cm^{-1} (asym C=O stretching), 1721 cm^{-1} (sym C=O stretching), 1370 cm^{-1} (C–N stretching).

PI-3. FT-IR (film): 1777 cm^{-1} (asym C=O stretching), 1720 cm^{-1} (sym C=O stretching), 1380 cm^{-1} (C–N stretching).

PI-4. FT-IR (film): 1775 cm^{-1} (asym C=O stretching), 1714 cm^{-1} (sym C=O stretching), 1376 cm^{-1} (C–N stretching).

PI-5. FT-IR (film): 1779 cm^{-1} (asym C=O stretching), 1722 cm^{-1} (sym C=O stretching), 1360 cm^{-1} (C–N stretching).

PI-6. FT-IR (film): 1775 cm^{-1} (asym C=O stretching), 1712 cm^{-1} (sym C=O stretching), 1379 cm^{-1} (C–N stretching).

PI-7. FT-IR (film): 1775 cm^{-1} (asym C=O stretching), 1713 cm^{-1} (sym C=O stretching), 1378 cm^{-1} (C–N stretching).

3. Results and discussion

3.1. Monomer synthesis

Bis(ether dinitrile) was prepared through the nucleophilic substitution reaction of cyclohexane-1,4-diol with 3-nitro-phthalonitrile in the presence of sodium hydride (NaH) in anhydrous *N,N*-dimethylformamide (DMF) (Scheme 1). The mole ratio of the *trans/cis* isomers in the ^{1}H NMR spectrum of bis(ether dinitrile) was 1.8/1 and was calculated using the

Table 1 Thermal properties of the polyimides

PI	$\eta_{inh}{}^{a}$ (dL g^{-1})	M_w (g mol^{-1})	M_n (g mol^{-1})	M_w/M_n	$T_g{}^{b}$ (°C)	$T_{d5\%}{}^{c}$ (°C)		$T_{d10\%}{}^{c}$ (°C)	
						In N$_2$	In air	In N$_2$	In air
PI-1	1.23^d	—	—	—	255	368	362	375	372
PI-2	0.96	158 900	62 400	2.55	245	365	368	374	374
PI-3	0.68	135 000	54 400	2.48	232	370	370	390	396
PI-4	0.34	75 800	41 200	1.84	208	368	376	389	415
PI-5	0.42	100 300	48 200	2.08	225	369	375	384	393
PI-6	0.47	—	—	—	240	367	372	379	381
PI-7	0.47	—	—	—	206	374	376	387	388

^{a} The inherent viscosities of polyimides were measured at a concentration of 0.5 g dL^{-1} in m-cresol at 30 °C. ^{b} Baseline shift in the second heating DSC traces, with a heating rate of 20 °C min^{-1}. ^{c} Temperatures at which 5% weight loss and 10% weight loss were recorded by TGA at a heating rate of 10 °C min^{-1}. ^{d} The inherent viscosity was measured in DMAc due to the poor solubility of **PI-1** in m-cresol.

integral ratio of the corresponding peak areas (H$_d$) to (H$_{d'}$) (Fig. 2). 1,4-Bis(2,3-dicarboxyphenoxy)cyclohexane was formed by the hydrolysis of the corresponding bis(ether dinitrile), and the mole ratio of the *trans/cis* isomers was changed to 19/1 according to the integral ratio of the corresponding peak areas (H$_d$) to (H$_{d'}$) of tetraacid in the ^{1}H NMR spectrum (Fig. 3). It should be noted that the *cis* configuration had been converted to the *trans* configuration during the hydrolysis procedure in harsh reaction conditions and this may have been because of the more thermodynamic stable *trans* configuration. The bis(ether anhydride) monomer, *trans*-3,3′-CHDPA was afforded by the dehydration of the resulting tetraacid using acetic anhydride. In the IR spectrum of the bis(ether anhydride), the strong absorption bands around 1835 cm^{-1} (ν_{asym}C=O) and 1763 cm^{-1} (ν_{sym}C=O) were assigned to the phthalic anhydride (Fig. 4). The observed bands in the region of 1000–1300 cm^{-1} were due to C–O stretching. The *trans* configuration of 3,3′-CHDPA was deduced from the ^{1}H NMR spectrum of the corresponding polyimide **PI-2** although recording the ^{1}H NMR
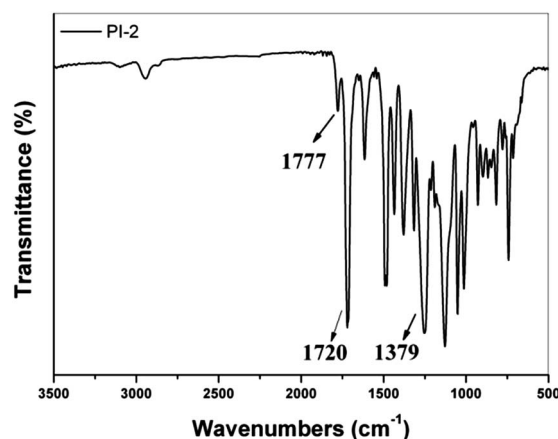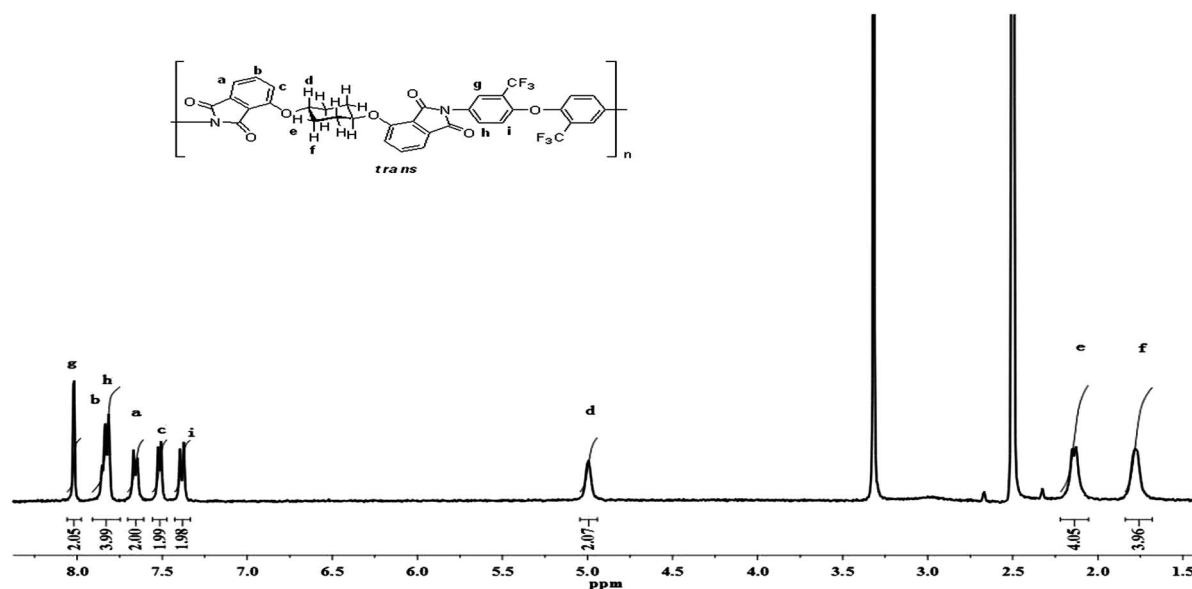

Fig. 6 FT-IR spectrum of **PI-2**.

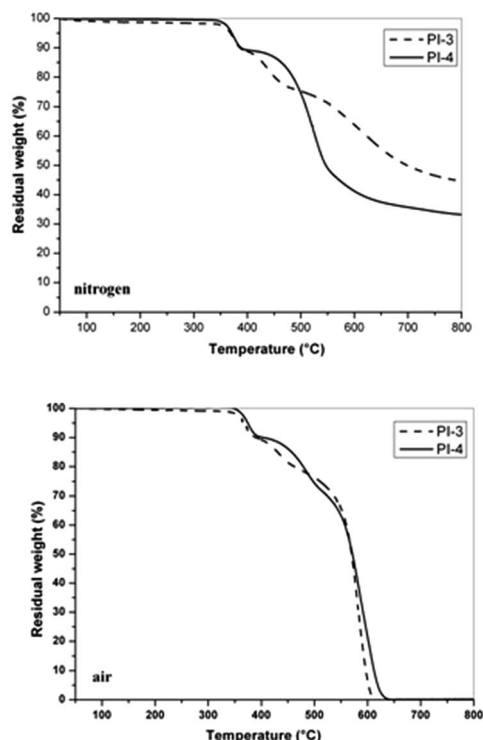**Fig. 5** ^{1}H NMR spectrum of **PI-2** in DMSO-d_6.

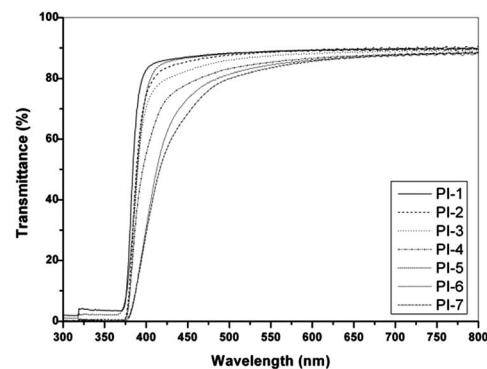Fig. 7 TGA curves of polyimides in nitrogen or air.

Fig. 8 UV-vis spectra of polyimide films.

Table 4 Optical properties of the polyimide films

PI	d (μm)	$\lambda_0{}^a$ (nm)	$T_{400}{}^b$ (%)	$T_{450}{}^b$ (%)	$T_{500}{}^b$ (%)
PI-1	16	372	83	87	88
PI-2	18	375	74	85	88
PI-3	24	376	70	83	86
PI-4	22	375	55	78	83
PI-5	20	370	75	87	88
PI-6	19	379	31	73	81
PI-7	23	377	29	68	80

[a] λ_0: UV cut-off wavelength. [b] T_{400}, T_{450}, T_{500}: transmittance at 400, 450, 500 nm, respectively.

Table 2 Solubility of the polyimides[a]

PI	Solvents[b]						
	m-cresol	DMAc	DMF	NMP	DMSO	CHCl$_3$	THF
PI-1	+	++	+−	++	+−	+−	+−
PI-2	++	++	++	++	++	++	++
PI-3	++	++	++	++	++	++	++
PI-4	++	++	++	++	++	++	+−
PI-5	++	++	++	++	++	++	++
PI-6	++	+−	+−	++	+−	++	+−
PI-7	++	+−	+−	++	+−	+−	+−

[a] The qualitative solubility was tested with 10 mg samples in 1 mL of solvent. ++: Soluble at room temperature; +: soluble on heating; +−: partially soluble on heating. [b] DMAc: N,N-dimethylacetamide; DMF: N,N-dimethylformamide; NMP: N-methyl-2-pyrrolidone; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

Table 3 Mechanical properties of the polyimide films

PI	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
PI-1	85.8	2.3	5.4
PI-2	65.1	1.7	5.5
PI-3	79.3	2.2	5.5
PI-4	75.5	2.2	4.7
PI-5	88.3	2.4	7.0
PI-6	74.9	2.1	5.6
PI-7	74.0	1.8	7.5

spectrum of *trans*-3,3′-CHDPA was not possible due to poor solubility in deuterated solvents such as CDCl$_3$, DMSO-d_6, DMF-d_7.

3.2. Synthesis of polyimides

The polyimides were synthesized from the dianhydride monomer *trans*-3,3′-CHDPA and various aromatic diamines (TFDB, TFODA, 6F-BAPS, m-BAPS, DFA, ODA, and TPER) in m-cresol *via* a conventional one-step method (Scheme 2). The inherent viscosities of the prepared polyimides **PI-2** to **PI-7** were between 0.34–0.96 dL g^{-1} in m-cresol at 30 °C and the inherent viscosity of **PI-1** was 1.23 dL g^{-1} in DMAc due to its poor solubility in m-cresol (Table 1). The molecular weights of these PIs were determined by GPC in CHCl$_3$ relative to polystyrene standards and they were in the range of 75 800–158 900 for M_w and 41 200–62 400 for M_n with M_w/M_n values of 1.84–2.55 except for the polyimides **PI-1**, **PI-6** and **PI-7**. The chemical structure of the polyimides was confirmed by ^{1}H NMR and FT-IR spectroscopy. The representative ^{1}H NMR spectrum of **PI-2** is shown in Fig. 5. All of the signals have been assigned to the protons of the repeating unit, and completed imidization was confirmed by the absence of the corresponding amide signals and carboxylic acid functions. The signals in the region of 4.99, 2.20–2.00 and 1.90–1.73 ppm were assigned to the methine proton (H$_d$), equatorial methylene protons (H$_e$) and axial methylene protons (H$_f$) of the cyclohexane moiety with a chair form in the polyimides, respectively. Furthermore, the COSY spectrum of **PI-2**

(Fig. S1†) was measured for further assignment of the aromatic protons. It should be noted that the configuration of polyimide **PI-2** was confirmed to be *trans* due to the absence of signals corresponding to *cis* configuration in the ^{1}H NMR spectrum, which also proved that the configuration of 3,3′-CHDPA was *trans*. The typical IR spectrum of **PI-2** is shown in Fig. 6. The strong absorption bands around 1777 cm^{-1} (ν_{asym}C=O), 1720 cm^{-1} (ν_{sym}C=O), and 1379 cm^{-1} (ν_{C-N} imide) were assigned to the phthalimide unit. The observed bands in the region of 1000–1300 cm^{-1} were due to C–O and C–F stretching vibrations.

3.3. Thermal properties

The thermal behavior data of the polyimides are listed in Table 1. The T_gs of the polyimides were in the range of 206–255 °C. Generally, T_g is correlated with the stiffness and conformation of the polymer chain. The highest T_g value was for **PI-1** and it was attributed to the rigidity of the TFDB moiety while there were lower T_g values for **PI-4** and **PI-7** and this may have been due to the presence of two flexible ether linkages and the *meta* substituent of the *m*-BAPS and TPER moieties. In addition, **PI-2** containing a trifluoromethyl group in the side chain had a higher T_g than the corresponding polyimide **PI-6** without the trifluoromethyl group. The T_g of **PI-5** was higher than **PI-3** and **PI-4** due to the bulky tetraphenylene moiety in the diamine which would restrain the rotation of the polymer chain. The T_gs of **PI-2** and **PI-4**, based on *trans*-3,3′-CHDPA, were higher than the corresponding polyimides derived from *trans*-1,4-bis(3,4-dicarboxyphenoxy)cyclohexane (*trans*-4,4′-CHDPA), except for **PI-1** with TFDB as the diamine.[40] Such behavior may have been observed because of the steric effect of the suppressed rotation of the ether bond between the 3-substituted phthalimide and the 1,4-cyclohexane.[41]

The thermal stability of the polyimides was evaluated by dynamic TGA conducted at a heating rate of 10 °C min^{-1}. The temperature of 5% weight loss ($T_{d5\%}$) in nitrogen and air atmospheres was determined from original TGA thermograms, which are listed in the Table 1 and the typical TGA curves of **PI-3** and **PI-4** are shown in Fig. 7. The $T_{d5\%}$ values of these PIs were recorded in the range of 365–374 °C in nitrogen and 362–376 °C in air. The low decomposition temperature in comparison with fully aromatic polyimides was caused by the first decomposition of the aliphatic cyclohexane moiety at elevated temperature.[13,44] However, the polyimides synthesized from *trans*-3,3′-CHDPA showed a lower T_d than the PIs derived from *trans*- and *cis*-4,4′-CHDPA due to the 1,4-cyclohexane moiety in the polymers which would decrease the mobility of polymer and make the polymers absorb less thermal energy.[45]

3.4. Solubility

The solubility of the polyimides was tested qualitatively in various organic solvents, and the results are shown in Table 2. The solubility of **PI-2** and **PI-3** is better than **PI-6** and **PI-4**, owing to the CF$_3$ group which inhibited close packing and reduced the inter-chain interaction which enhanced the solubility. **PI-5** also showed better solubility in common organic solvents because of the bulky cardo group. In addition, **PI-6** and **PI-7** showed

comparatively poor solubility compared to the other PIs due to the regularity of their polymer chains and the increasing denser chain stacking, thereby making it difficult for the solvent to attack. It was also observed that the polyimides derived from *trans*-3,3′-CHDPA showed better solubility than the *trans*-4,4′-CHDPA based polyimides,[40] probably because the *trans*-3,3′-CHDPA moiety in the polymer chain disturbed the regularity of the molecular chain, which reduced the intermolecular interactions and hindered the close stacking of the molecular chains, and therefore the solvent molecules could penetrate easily.[41]

3.5. 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 65–88 MPa, tensile moduli of 1.7–2.4 GPa, and elongations at break of 4.7–7.5%. Among these polyimide films, the tensile strength and tensile modulus of **PI-1** and **PI-5** were more than 85 MPa and 2.3 GPa, respectively, which were attributed to the rigid structure in the polymers' backbone. Polyimides based on *trans*-4,4′-CHDPA exhibited higher elongation and somewhat higher tensile strength and modulus than the other isomers.[40] For the polyimides based on *trans*-3,3′-CHDPA, the 3,3′-position may tend to cyclize in some instances and they seldom attain molecular weights as high as the others.[41]

3.6. X-ray diffraction

The crystallinity of the polyimide films was analyzed by wide-angle X-ray diffraction (WAXD). The WAXD patterns of all the films were broad without obvious peak features, which indicated that they were all amorphous (Fig. S2†). The amorphous nature of the polyimides could be attributed to the introduction of the alicyclic hexane moiety in the dianhydride resulting in loose chain packing and aggregation.[36]

3.7. Optical properties

The transmission UV-visible spectra were measured for the thin polyimide films. The UV-visible spectra of some representative polyimide films are illustrated in Fig. 8, and the cut-off wavelength (absorption edge, λ_0) and the transmittance at 400, 450, 500 nm from these spectra are listed in Table 4. All of the polyimide films exhibited cut-off wavelengths shorter than 379 nm and were highly transparent. The cyclohexane moiety in the dianhydride weakened both intra- and intermolecular charge transfer interactions by breaking the conjugation and decreasing the electron-acceptability of the dianhydride. Furthermore, compared with PIs derived from *trans*-4,4′-CHDPA, the PIs synthesized from *trans*-3,3′-CHDPA showed better transparency due to the 3,4′-position isomeric effect which was effective in decreasing charge transfer (CT) complex formation between the polymer chains through steric hindrance and increasing free volume.[12] Moreover, the incorporation of the trifluoromethyl group (**PI-1**, **PI-2**, **PI-3**) and bulky group (**PI-5**) in the diamines also enhanced the optical transparency by decreasing CT complex formation between the

polymer chains through steric hindrance and an inductive effect (decreasing the electron-donating property of the diamine moieties).[8] Among all the polyimides, **PI-1** showed the best optical transparency.

4. Conclusion

A series of polyimides derived from *trans*-1,4-bis(2,3-dicarboxyphenoxy)cyclohexane dianhydride (*trans*-3,3′-CHDPA), containing 1,4-cyclohexane at the 3-position of the phthalic anhydride, was synthesized *via* a one-step method and could form transparent, flexible, and tough films with tensile strengths of 65–88 MPa, tensile moduli of 1.7–2.4 GPa and elongations at break of 4.7–7.5%. The polyimide films from *trans*-3,3′-CHDPA showed higher T_gs and lower coloration compared with *trans*-4,4′-CHDPA-based polyimides. This proved the combination of 1,4-cyclohexane and the 3-substituted position on the phthalic anhydride, which could decrease the electron-acceptability of the dianhydride and reduce the intra-/intermolecular interaction, was a successful method for reducing charge transfer complex formation and enhancing the T_g and solubility. **PI-1** exhibited the highest T_g, and best optical transparency and so may be a promising film for further application.

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