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# 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 were 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 ($T_g$s) of 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 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 the *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 the excellent thermal and mechanical stabilities, which were widely used in 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, many efforts have been made to decrease coloration based on structural design by modification of dianhydrides and diamines, including incorporation of trifluoromethyl group,[9-21] bulky group,[22-24] unsymmetrical[20, 25-26] and alicyclic units[27-38] into the polymer chains. Our group also reported transparent semi-aromatic polyimides by incorporation of aliphatic cyclohexane-1,4-diol into two phthalic anhydrides or diamines, which introduced alicyclic structure without sacrificing the reactivity of 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 3,3'-substituted position, 3,4'-substituted position), and paid less attention on stereoisomers, for example, *trans* and *cis* configuration. Toshihiko Matsumoto et al. first reported stereoisomeric polyimides derived from *trans*- and *cis*-tetracarboxylicdianhydride bearing a cycloaliphatic structure, and indicated that *trans*-polyimides had better transparency and solubility but lower $T_g$ than *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 also have been synthesized and showed that *trans*-polyimides had lower $T_g$ and lower solubility than corresponding *cis*-polyimides.[38] It was found that the *trans*-polyimides which bearing a cycloaliphatic structure had good

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transparency but lower $T_g$s. 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 mechanical properties, which was quite different from above reports about *trans*- and *cis* isomeric effect on stereoisomeric polyimides.[40] Considering isomeric polyimides derived from 3,3'-substituted dianhydrides have higher $T_g$, better solubility and transparency,[41] a new dianhydride monomer containing 1,4-cyclohexane moiety at 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 resulting polyimides. The solubility, thermal properties, mechanical properties and optical properties of these polyimides were well investigated.

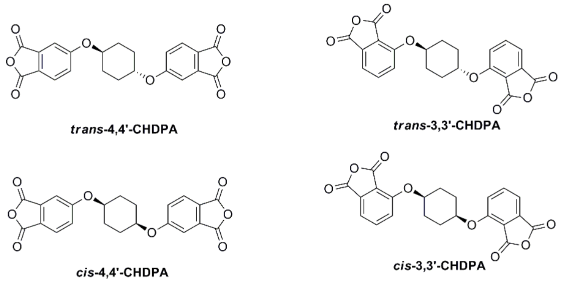


**Fig. 1** Chemical structure of the 4,4'-CHDPA and 3,3'-CHDPA.

## 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.), 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%), 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 4Å 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 powder samples were recorded with a Thermo Nicolet 6700 FT-IR spectrometer. All FT-IR spectra of 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 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 *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 $CHCl_3$ as an eluent at a flow rate of 1.0 mL/min. 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 point (m.p.) of 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 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 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 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$^{o}$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 $^{o}$C to afford 15.0 g (*trans/cis* = 1.8/1), yield: 81%, m.p. = 287 $^{o}$C. FT-IR (KBr, cm$^{-1}$): 2228 cm$^{-1}$ (C≡N stretching). $^1$H NMR $\delta_H$ (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$_{e'}$, H$_{f'}$) 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, 150mmol) 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 filtrate was 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 $^{o}$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 $\delta_H$ (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 $\delta_C$ (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 (67.5mmol) of bis(ether diacid) dissolved in 300 mL DMAc, the resulting solution was filtered to remove any insoluble impurities, then added 300 mL acetic anhydride and 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 $^{o}$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 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: The 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 50 mL flask was stirred in nitrogen at 195°C for 8 h. The reaction mixture was diluted with *m*-cresol and slowly poured into a vigorously stirred ethanol. The precipitate was collected by filtration, washed with hot ethanol and dried.

### 2.3.5. Film Casting

The polyimide film of **PI-2** was prepared via the casting of 10wt% homogenous solution of 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 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 $\delta_H$ (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), 1360cm$^{-1}$ (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-

nitrophthalonitrile in the presence of sodium hydride (NaH) in anhydrous *N,N*-dimethyformamide (DMF) (Scheme 1). The mole ratio of *trans*/*cis* isomers in the $^{1}$H NMR spectrum of bis(ether dinitrile) was 1.8/1 by calculating the integral ratio of corresponding peak areas ($H_d$) to ($H_{d'}$) (Fig. 2). The 1,4-bis(2,3-dicarboxyphenoxy)cyclohexane was formed by hydrolysis of the corresponding bis(etherdinitrile), and the mole ratio of *trans*/*cis* isomers was changed to 19/1 according to the integral ratio of 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 maybe owing to the more thermodynamic stable *trans* configuration. The bis(ether anhydride) monomer, *trans*-3,3'-CHDPA was afforded by dehydration of the resulting tetraacid using acetic anhydride. In the IR spectrum of the bis(ether anhydride), the strong absorption bands around 1835 cm$^{-1}$ ($\nu_{asym}$C=O) and 1763cm$^{-1}$ ($\nu_{sym}$C=O) were assigned to the phthalic anhydride (Fig. 4). The observed bands in the region of 1000-1300 cm$^{-1}$ were due to the 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 the $^{1}$H NMR spectrum of *trans*-3,3'-CHDPA could not performed due to the poor solubility in deuterated solvents such as $CDCl_3$, DMSO-$d_6$, DMF-$d_7$.

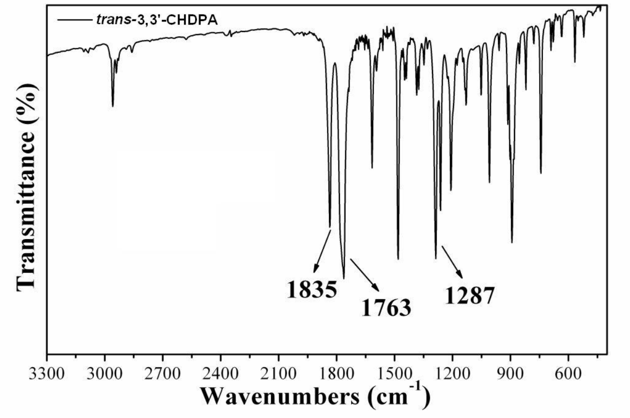
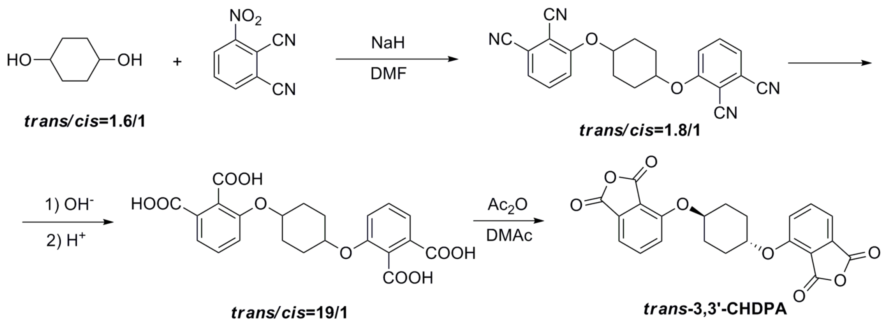


**Fig. 4** FT-IR spectrum of *trans*-3,3'-CHDPA.



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

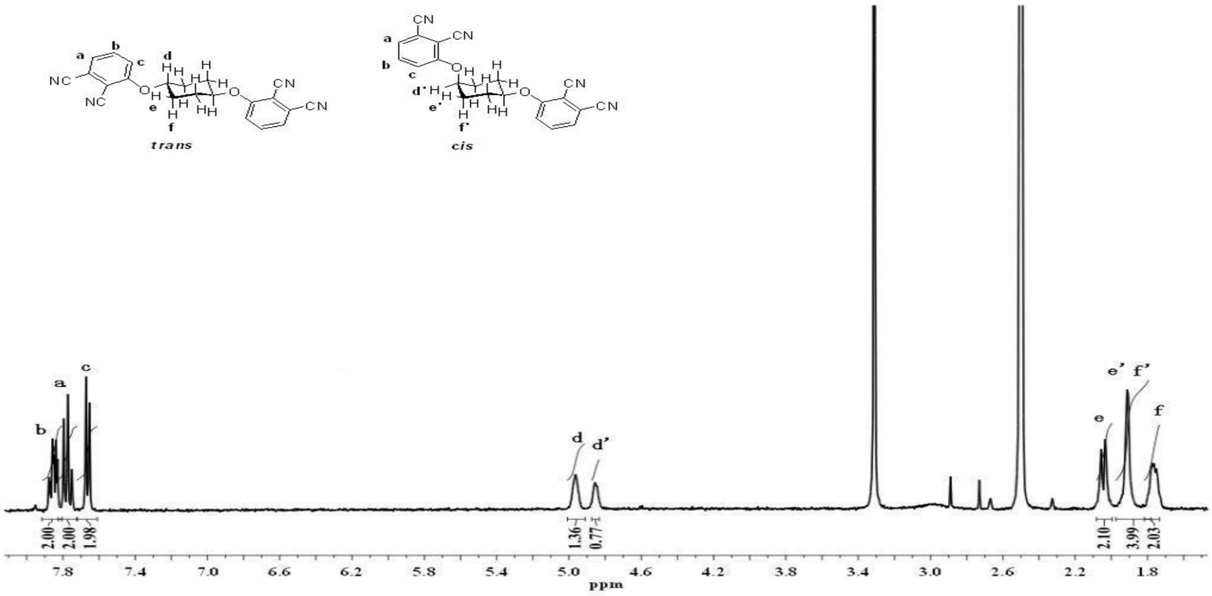


**Fig. 2** $^{1}$H NMR spectrum of 1,4-bis(2,3-dicyanophenoxy)cyclohexane in DMSO-$d_6$.

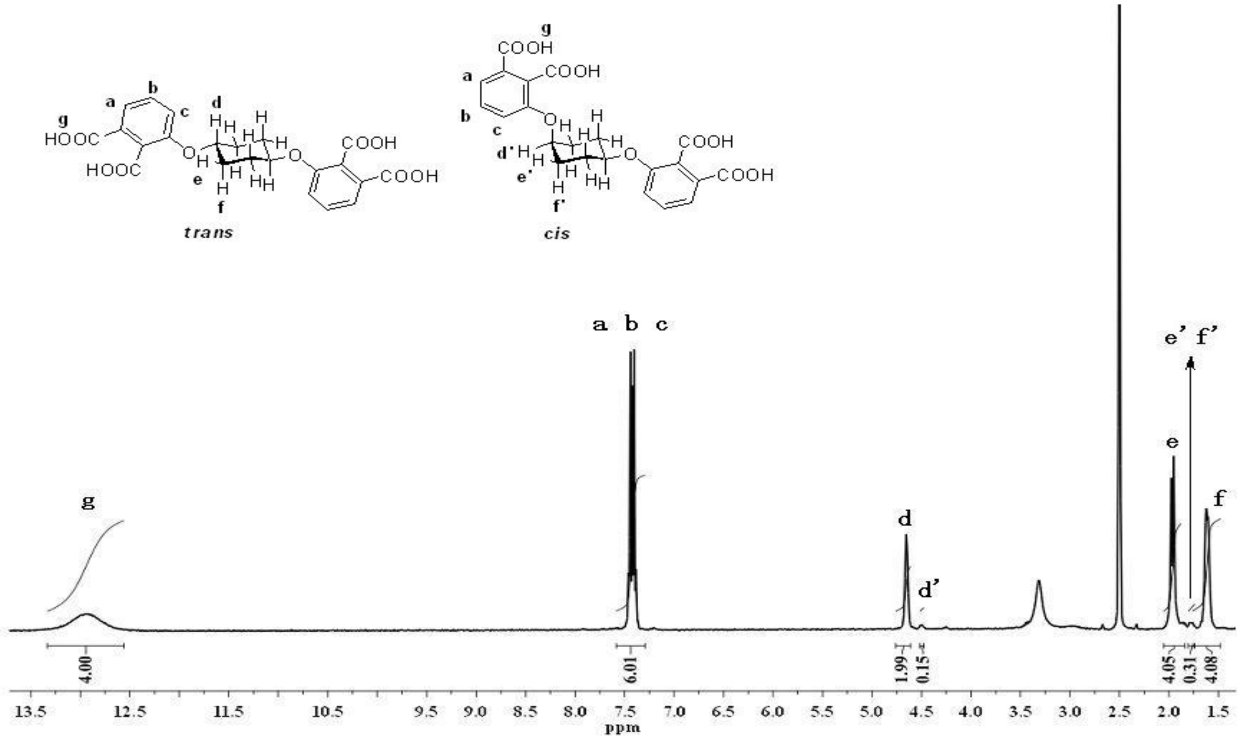
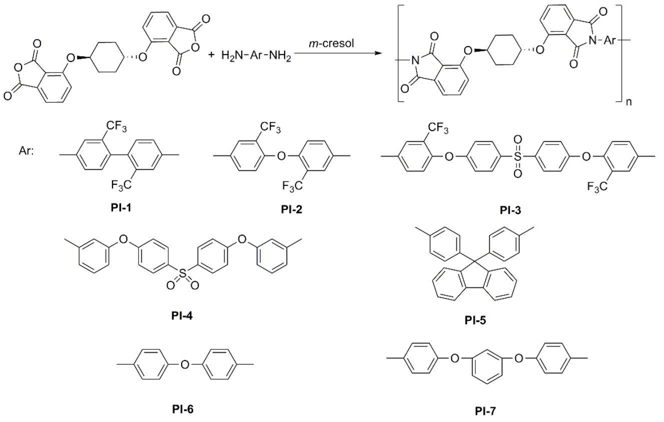


**Fig. 3** $^1$H NMR spectrum of 1,4-bis(2,3-dicarboxyphenoxy)cyclohexanein DMSO-$d_6$.

### 3.2 Synthesis of Polyimides

The polyimides were synthesized from diahhydride monomer *trans*-3,3'-CHDPA and various aromatic diamines (TFDB, TFODA, 6F-BAPS, *m*-BAPS, DFA, ODA, and TPER) in *m*-cresol via conventional one-step method (Scheme 2). The inherent viscosities of prepared polyimides **PI-2** to **PI-7** were between 0.34-0.96 dL/g in *m*-cresol at 30 °C and the inherent viscosity of **PI-1** was 1.23 dL/g in DMAc due to its poor solubility in *m*-cresol (Table 1). The molecular weights of these PIs determined by GPC in $CHCl_3$ relative to polystyrene standards were in the range of 75800-158900 for $M_w$ and 41200-62400 for $M_n$ with $M_w/M_n$ values of 1.84–2.55 except the polyimides **PI-1**, **PI-6** and **PI-7**. The chemical structure of 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 the signals have been assigned to the protons of the repeating unit, and completed imidization was confirmed by the absence of 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 cyclohexane moiety with a chair form in the polyimides, respectively. Furthermore, the COSY spectrum of **PI-2** (Figure S1) was measured for the further assignments of 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 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$^{-1}$ ($\nu_{asym}$C=O), 1720 cm$^{-1}$ ($\nu_{sym}$C=O), and 1379 cm$^{-1}$ ($\nu_{C\text{-}N}$ 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.



**Scheme 2.** Synthesis of polyimides

**Table 1** Thermal properties of the polyimides.

| PI | $\eta_{inh}{}^{a}$(dL/g) | $M_w$ (g/mol) | $M_n$ (g/mol) | $M_w/M_n$ | $T_g{}^{b}$ (°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 | 158900 | 62400 | 2.55 | 245 | 365 | 368 | 374 | 374 |
| **PI-3** | 0.68 | 135000 | 54400 | 2.48 | 232 | 370 | 370 | 390 | 396 |
| **PI-4** | 0.34 | 75800 | 41200 | 1.84 | 208 | 368 | 376 | 389 | 415 |
| **PI-5** | 0.42 | 100300 | 48200 | 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 in *m*-cresol 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 and 10% weight loss were recorded by TGA at a heating rate of 10 °C /min.

[d] The inherent viscosities were measured in DMAc due to the poor solubility of **PI-1** in *m*-cresol.

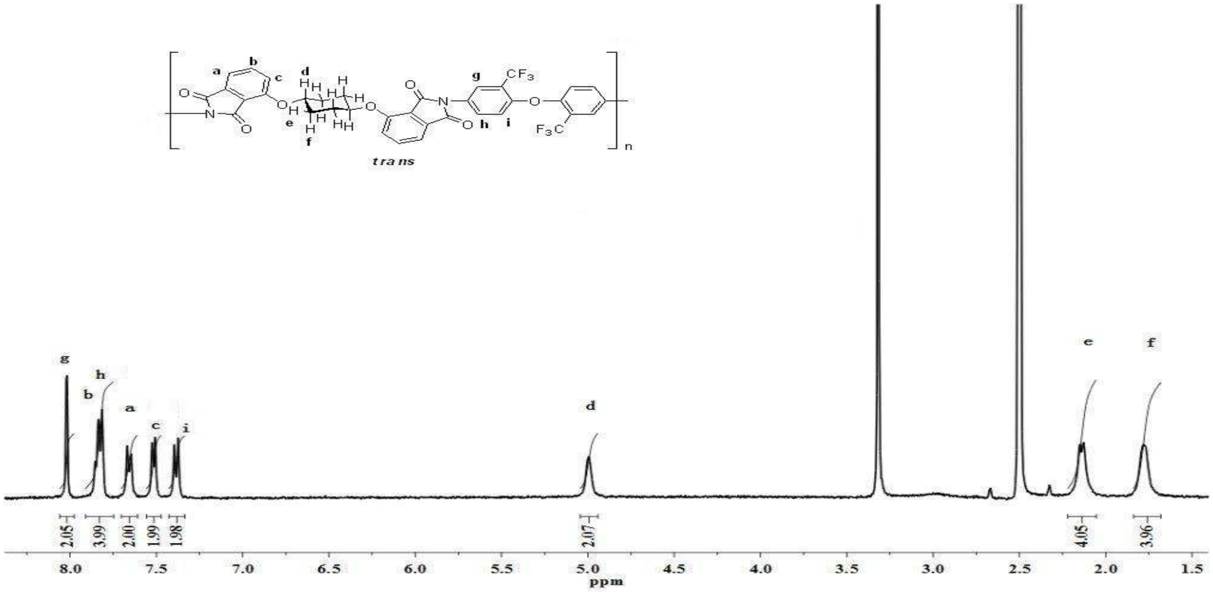


**Fig. 5** $^{1}$H NMR spectrum of **PI-2** in DMSO-$d_6$.

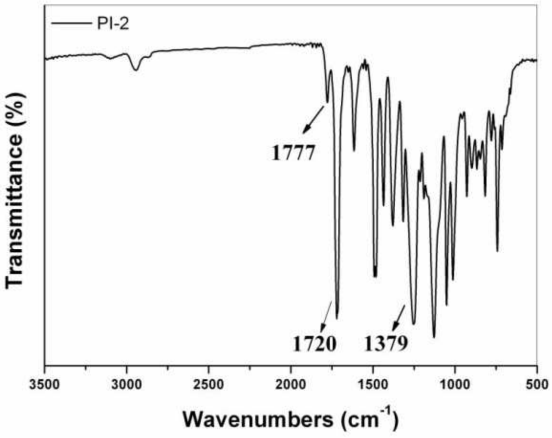


**Fig. 6** FT-IR spectrum of **PI-2**.

### 3.3. Thermal properties

The thermal behavior data of polyimides are listed in Table 1. The $T_g$s of polyimides were in the range of 206-255°C. Generally, $T_g$ is correlated with the stiffness and conformation of polymer chain. The highest $T_g$ value of **PI-1** is attributed to the rigidity of TFDB moiety while the lower $T_g$ values of **PI-4** and **PI-7** is may be due to the presence of two flexible ether linkages and *meta* substituent of *m*-BAPS and TPER moiety. In addition, **PI-2** containing a trifluoromethyl group in the side chain had higher $T_g$ than the corresponding polyimides **PI-6** without trifluoromethyl group. The $T_g$ of **PI-5** is higher than **PI-3** and **PI-4** due to the bulky tetraphenylene moiety in diamine which would restrain the rotation of the polymer chain. The $T_g$s of **PI-2** and **PI-4,** based on *trans*-3,3'-CHDPA are higher than the corresponding polyimides derived from *trans*-1,4-bis(3,4-dicarboxyphenoxy)cyclohexane (*trans*-4,4'-CHDPA), except **PI-1** with TFDB as diamine.[40] Such behavior is may be observed due to the steric effect of the suppressed rotation of 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. 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 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 first decomposition of aliphatic cyclohexane moiety at elevated temperature.[13,44] However, the polyimides synthesized from *trans*-3,3'-CHDPA showed lower $T_d$ than PIs derived from *trans*- and *cis*-4,4'-CHDPA due to the 1,4-cyclohexane moiety in polymers which would decrease the mobility of polymer and make polymers absorb less thermal energy.[45]

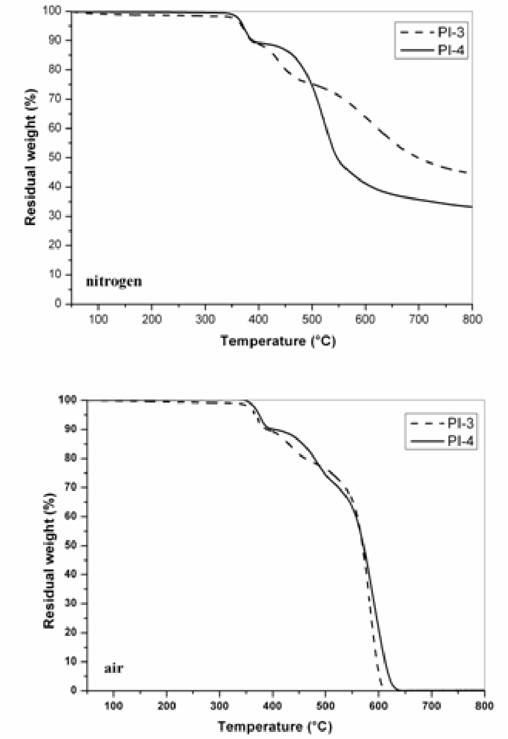


**Fig. 7** TGA curves of polyimides in nitrogen or air.

### 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 $CF_3$ group which inhibited close packing and reduced the inter-chain interaction to enhance 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 the comparatively poor solubility than others PIs due to their regularity of polymer chains and increasing denser chain stacking, thereby being difficult for the attack of solvent. It was also observed that the polyimides derived from *trans*-3,3'-CHDPA showed better solubility than *trans*-4,4'-CHDPA-based polyimides,[40] probably because the *trans*-3,3'-CHDPA moiety in polymer chain disturbed the regularity of molecular chain, which reduced the intermolecular interaction and hindered molecular chain close stacking, and therefore the solvent molecules penetrated easily.[41]

**Table 2** Solubility of the polyimides.

| PI | Solvents[a] | | | | | | |
|---|---|---|---|---|---|---|---|
| | *m*-cresol | DMAc | DMF | NMP | DMSO | $CHCl_3$ | THF |
| **PI-1** | + | ++ | +− | ++ | +− | +− | +− |
| **PI-2** | ++ | ++ | ++ | ++ | ++ | ++ | ++ |
| **PI-3** | ++ | ++ | ++ | ++ | ++ | ++ | ++ |
| **PI-4** | ++ | ++ | ++ | ++ | ++ | ++ | +− |
| **PI-5** | ++ | ++ | ++ | ++ | ++ | ++ | ++ |
| **PI-6** | ++ | +− | +− | ++ | +− | ++ | +− |
| **PI-7** | ++ | +− | +− | ++ | +− | +− | +− |

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*-methyl-2-pyrrolidone; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

### 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 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 seldom attain molecular weights as high as the others.[41]

**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 |

### 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 (Figure S2). The amorphous nature of the polyimides could be attributed to the introduction of alicyclic hexane moiety in 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, $\lambda_0$) and the transmittance at 400, 450, 500 nm from these spectra are listed in Table 4. All 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 electron-acceptability of 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 was effective in decreasing the charge transfer (CT) formation between polymer chains through steric hindrance and increase of free volume.[12] Moreover, the incorporation of 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 polymer chain through steric hindrance and inductive effect (decreasing the electron-donating property of diamine moieties).[8] Among the all polyimides, the **PI-1** showed the best optical transparency.

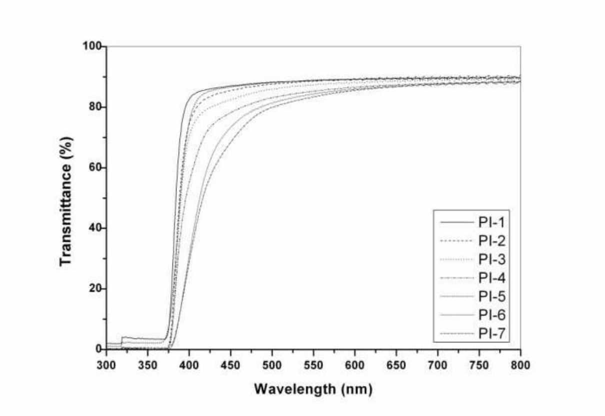


**Fig. 8** UV-vis spectra of polyimide films.

**Table 4** Optical properties of the polyimide films.

| PI | d (μm) | $\lambda_0$ (nm)[a] | $T_{400}$ (%)[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] $\lambda_{0:}$ UV cut-off wavelength.

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

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

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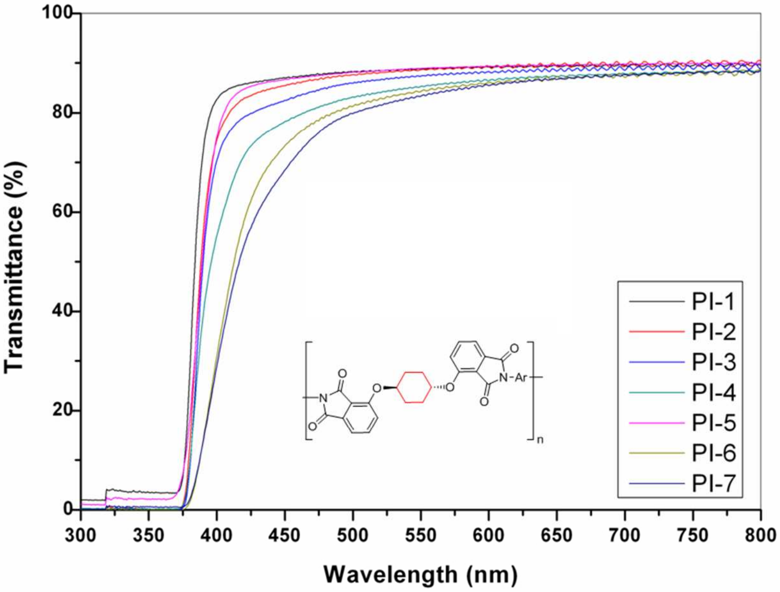

Graphical Abstract
385x268mm (72 x 72 DPI)