

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

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ABSTRACT: A novel dianhydride, *trans*-1,2-bis(3,4-dicarboxyphenoxy)cyclohexane dianhydride (1,2-CHDPA), was prepared through aromatic nucleophilic substitution reaction of 4-nitrophthalonitrile with *trans*-cyclohexane-1,2-diol followed by hydrolysis and dehydration. A series of polyimides (PIs) were synthesized from one-step polycondensation of 1,2-CHDPA with several aromatic diamines, such as 2,2'-bis(trifluoromethyl)biphenyl-4,4'-diamine (TFDB), bis(4-amino-2-trifluoromethylphenyl)ether (TFODA), 4,4'-diaminodiphenyl ether (ODA), 1,4-bis(4-aminophenoxy)benzene (TPEQ), 4,4'-(1,3-phenylenedioxy)dianiline (TPER), 2,2'-bis[4-(3-aminodiphenoxy)phenyl]sulfone (*m*-BAPS), and 2,2'-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]sulfone (6F-BAPS). The glass transition temperatures (T_g s) of the polymers were higher than 198°C, and the 5% weight loss temperatures ($T_{d5\%}$ s) were in the range of 424–445°C in nitrogen and 415–430°C in air, respectively. All the PIs were endowed with high solubility in common organic solvents and could be cast into tough and flexible films, which exhibited good mechanical properties with tensile strengths of 76–105 MPa, elongations at break of 4.7–7.6%, and tensile moduli of 1.9–2.6 GPa. In particular, the PI films showed excellent optical transparency in the visible region with the cut-off wavelengths of 369–375 nm owing to the introduction of *trans*-1,2-cyclohexane moiety into the main chain. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42317.

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INTRODUCTION

Aromatic polyimides (PIs) are widely utilized in aerospace and electronics in the forms of films and moldings for their combined excellent properties, such as thermal stabilities, excellent chemical resistance, mechanical, and electric properties.^{1–5} However, due to their highly conjugated aromatic structures and intra- and intermolecular charge transfer (CT) complex formation, the wholly aromatic PI films have strong absorption on the visible region and show deep coloration, which greatly hinders the application of PIs in the fields with high demands for transparency, such as flexible display substrates, solar cells, lighting, and waveguides.^{6,7} In addition, the high softening temperatures and limited solubility in organic solvents, which are derived from their rigid backbones and strong intermolecular interactions, cause poor processability of PIs in their imidized forms. Therefore, it is a big challenge to improve their transparency and solubility without sacrificing their excellent performance, which has tremendously attracted the attention of researchers.

Typical approaches to improve the transparency and solubility of PIs include the incorporation of trifluoromethyl group,^{8–19} adopting asymmetric backbone as well as bulky substituents,^{20–25} which serve to increase the free volume, and consequently, benefit for both optical transparency and solubility of PIs. Moreover, aliphatic dianhydride monomers are considered as one of the effective ways to enhance the transparency and solubility, which is related to the absence or inhibition of intra- and/or inter-molecular CT interactions.^{26–36} However, it is difficult to obtain high molecular weight polymers because of low reactivity of aliphatic dianhydride monomers. Consequently, introduction of alicyclic structure into aromatic dianhydrides, a feasible way for transparent and organosoluble PIs without sacrificing the reactivity of dianhydrides, have been studied.^{18,37–41} Recently, we have reported the semi-aromatic transparent PIs derived from dianhydrides or diamines containing cyclohexane-1,4-diol moiety, such as *trans*- and *cis*-1,4-bis(3,4-dicarboxyphenoxy)cyclohexane dianhydrides (*trans*- and *cis*-1,4-CHDPA),³⁷ 1,4-bis(4-aminophenoxy)cyclohexane diamines (1,4-HDA),³⁸

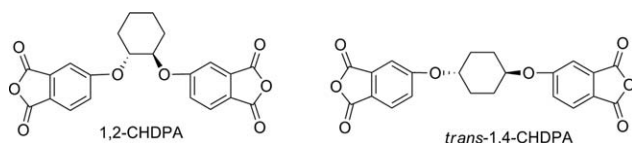


Figure 1. Chemical structure of 1,2-CHDPA and *trans*-1,4-CHDPA.

exhibited good thermal stability and high optical transparency. It was also found that *trans*-polyimides derived from *trans*-1,4-CHDPA had higher T_g , better transparency and mechanical properties, compared with *cis*-polyimides derived from *cis*-1,4-CHDPA.³⁷ The solubility of the *trans*-polyimide should be further enhanced. As we all know, PIs with *ortho*-linked aromatic units exhibited better organosolubility and higher optical transparency in the visible region than the PIs containing *para*-linked aromatic units, due to the formation of bent structure which prevented the extended close chain packing, and consequently, the CT interactions.^{19,42–45}

Therefore, incorporation of bulky *ortho*-alicyclic group, *trans*-cyclohexane-1,2-diol, into aromatic anhydrides would not only weaken electron-acceptability of dianhydride and enhance transparency, but also make the polymer chain more asymmetric and bent, increase the free volume and improve the organosolubility. Herein, a new dianhydride containing *trans*-cyclohexane-1,2-diol moiety, 1,2-CHDPA, was designed and a series of semi-aromatic PIs were prepared by polycondensation of 1,2-CHDPA with various aromatic diamines. The chemical structure of 1,2-CHDPA and *trans*-1,4-CHDPA is shown in Figure 1. The solubility, thermal, mechanical, and optical properties of these PIs as well as the isomeric effect of cyclohexane at 1,2- and 1,4-substituted position were investigated.

EXPERIMENTAL

Materials

Trans-cyclohexane-1,2-diol (98%, Aladdin Industrial Corporation Co.), 4-nitrophthalonitrile (98%, Leadership Chemical Technologies Co.), and sodium hydride (60%, Sinopharm Chemical Reagent Co.), were used as received. 2,2'-Bis(trifluoromethyl)biphenyl-4,4'-diamine (TFDB, 98%), 2,2'-bis[4-(3-aminodiphenoxy)phenyl]sulfone (*m*-BAPS, 98%), 1,4-bis(4-aminophenoxy)benzene (TPEQ, 98%), and 4,4'-(1,3-phenylene-dioxy)dianiline (TPER, 98%) were purchased from Changzhou Sunlight Pharmaceutical Co. 4,4'-Diaminodiphenyl ether (ODA, 98%) was purchased from Aladdin. The diamine TFDB and ODA were purified by vacuum sublimation prior to use. The diamines, *m*-BAPS, TPEQ, and TPER, were recrystallized from ethanol before use. Bis(4-amino-2-trifluoromethylphenyl)ether (TFODA) and 2,2'-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]sulfone (6F-BAPS) were synthesized in our laboratory according to the literature.^{12,46} Dimethylformamide (DMF) was purified by distillation under reduced pressure over 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.

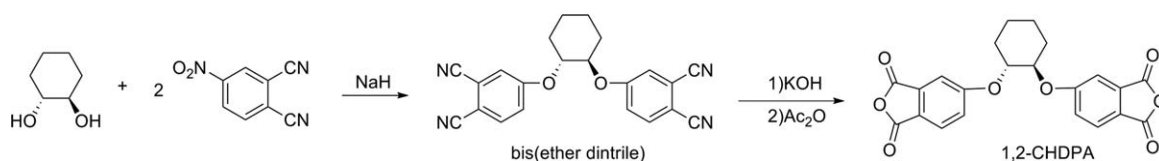
Measurements

The Fourier transform infrared (FT-IR) spectra of powder samples were recorded with a Thermo Nicolet 6700 FT-IR spec-

trometer. The IR spectra of PI films (about 20 μm) were recorded in the attenuated total reflection (ATR) mode with a 4 cm^{-1} resolution for 128 scans each by 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 ^1H 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 $30 \pm 0.1^\circ\text{C}$ with an Ubbelohde viscometer and the concentration was 0.5 g/dL in dimethylacetamide (DMAc). The molecular weight measurement was performed via gel permeation chromatography (TOSOH HLC-8320) equipped with a differential refractometer. *N,N*-Dimethylformamide and 10 mM LiBr were used as the eluent at a flow rate of 0.6 mL/min. M_w and M_n were calibrated with standard polystyrene samples. Differential scanning calorimetry (DSC) measurements of the PIs were performed on a Mettler Toledo-DSC I at a heating rate of $20^\circ\text{C}/\text{min}$ 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 measured by the DSC instrument at a heating rate of $10^\circ\text{C}/\text{min}$ and the melting points were determined from the temperature at the maximum point of the corresponding enthalpy peaks. Thermo gravimetric analyses (TGA) of the PIs were performed on a Mettler Toledo-TGA/DSC I instrument to evaluate the thermal stability of the PIs at a heating rate of $10^\circ\text{C}/\text{min}$ from 50°C to 800°C under nitrogen or air atmosphere (flow rate of 50 mL/min). The mechanical properties of the PI 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 PI films was performed on a Bruker D8 Advance with Cu K α radiation (40 kV, 40 mA) at a scanning rate of $5^\circ/\text{min}$ from 5 to 50° .

Monomer Synthesis

Synthesis of *Trans*-1,2-bis(3,4-dicyanophenoxy)cyclohexane. To a flask containing sodium hydride (9.2 g, 60% in oil, 0.23 mol) and anhydrous DMF (100 mL) was added a solution of *trans*-cyclohexane-1,2-diol (11.6 g, 0.10 mol) in anhydrous DMF (100 mL) dropwise under nitrogen atmosphere with stirring at room temperature. The mixture was stirred for 2 h and a solution of 4-nitrophthalonitrile (36.4 g, 0.21 mol) in anhydrous DMF (100 mL) was added dropwise. After stirring at room temperature for 3 h, the mixture was trickled into dilute hydrochloric acid to afford a precipitate. The precipitate was collected by filtration, washed by water, and dried under vacuum at 85°C to afford crude product. The purified bis(ether dinitrile) was obtained by crystallization from MeCN, yield: 76%, m.p. = 196°C . FT-IR (KBr, cm^{-1}): 2230 cm^{-1} (C \equiv N stretching). ^1H NMR (400 MHz, DMSO- d_6 , δ , ppm): 7.98 (d, J = 8.8 Hz, 2H), 7.81 (d, J = 2.8 Hz, 2H), 7.39 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 2H), 4.82 (s, 2H), 2.22–2.07 (m, 2H), 1.78–1.64



Scheme 1. Synthesis of 1,2-CHDPA.

(m, 2H), 1.56–1.39 (m, 4H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, δ , ppm): 161.6, 136.2, 121.6, 121.0, 116.8, 116.6, 116.1, 106.5, 79.8, 29.7, 23.2.

Synthesis of *Trans*-1,2-bis(3,4-dicarboxyphenoxy)cyclohexane Dianhydride (1,2-CHDPA). To a 500 mL three-neck flask equipped with a magnetic stirrer and a condenser was charged with suspension of bis(ether dinitrile) (11.1 g, 30 mmol). Ethanol/water mixture (100 mL/100 mL) of dissolved KOH (27.0 g, 481 mmol) was added into the flask. The mixture was boiled under reflux for about 48 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, and the filtrate was acidified by diluted hydrochloric acid to pH=1. The precipitate was recovered by filtration, washed with water until it was neutral, and dried at 100°C. The crude product (12.4 g, 16.2 mmol) was dissolved in 200 mL of acetic anhydride in a flask, and then heated at a reflux temperature for 0.5 h. The resulting clear solution was filtered to remove any insoluble impurities. The filtrate was left undisturbed at ambient temperature for 12 h. The purified dianhydride monomer was collected by filtration and dried under vacuum at 135°C. Yield: 51%, m.p.=202°C. FT-IR (KBr, cm^{-1}): 1846 cm^{-1} (asym C=O stretching), 1772 cm^{-1} (sym C=O stretching), 1291, 1264, 1077, 1033 cm^{-1} (C–O stretching). ^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ , ppm): 7.89 (d, J =8 Hz, 2H), 7.69 (d, J =2 Hz, 2H), 7.34 (dd, J_1 =8 Hz, J_2 =2 Hz, 2H), 4.96 (s, 2H), 2.23–2.08 (m, 2H), 1.80–1.64 (m, 2H), 1.62–1.44 (m, 4H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, δ , ppm): 164.8, 163.5, 163.1, 134.5, 127.7, 124.4, 123.1, 111.0, 80.1, 30.0, 23.2.

Polymer Synthesis and Film Preparation

PIs were synthesized from dianhydride 1,2-CHDPA and several diamines (TFDB, TFODA, ODA, TPEQ, TPER, *m*-BAPS, and 6F-BAPS) via one-step polycondensation reactions in *m*-cresol as shown in Scheme 2. The resulting PIs were referred to as PI-1 to PI-7 successively.

The synthesis of film of PI-2 is used as an example to illustrate the typical synthetic procedure: dianhydride 1,2-CHDPA (1.6343 g, 4.0 mmol), diamine TFODA (1.3429 g, 4.0 mmol), and *m*-cresol (12 mL) were added in a 50-mL two-necked round-bottom flask fitted with a nitrogen gas inlet tube and a dean-stark trap topped by a condenser. After 1,2-CHDPA and TFODA were completely dissolved, three drops of isoquinoline were added successively. The mixture was stirred at 195°C for 8 h. After cooling to 80°C, the mixture was diluted with *m*-cresol and slowly poured into 300 mL ethanol with vigorous stirring. The white precipitates were collected by filtration, washed thoroughly with boiling ethanol and dried at 100°C for 8 h. Film was prepared by casting its DMAc solution (10 wt %)

onto glass plates and dried at 80°C overnight to evaporate most of the solvent, and then scheduled cured at 120, 160, and 200°C for 60 min at each temperature.

PI-1: FT-IR (film): 1779 cm^{-1} (asym C=O stretching), 1722 cm^{-1} (sym C=O stretching), 1358 cm^{-1} (C–N stretching).

PI-2: FT-IR (film): 1778 cm^{-1} (asym C=O stretching), 1721 cm^{-1} (sym C=O stretching), 1376 cm^{-1} (C–N stretching).

PI-3: FT-IR (film): 1775 cm^{-1} (asym C=O stretching), 1716 cm^{-1} (sym C=O stretching), 1379 cm^{-1} (C–N stretching).

PI-4: FT-IR (film): 1776 cm^{-1} (asym C=O stretching), 1713 cm^{-1} (sym C=O stretching), 1374 cm^{-1} (C–N stretching).

PI-5: FT-IR (film): 1776 cm^{-1} (asym C=O stretching), 1713 cm^{-1} (sym C=O stretching), 1373 cm^{-1} (C–N stretching).

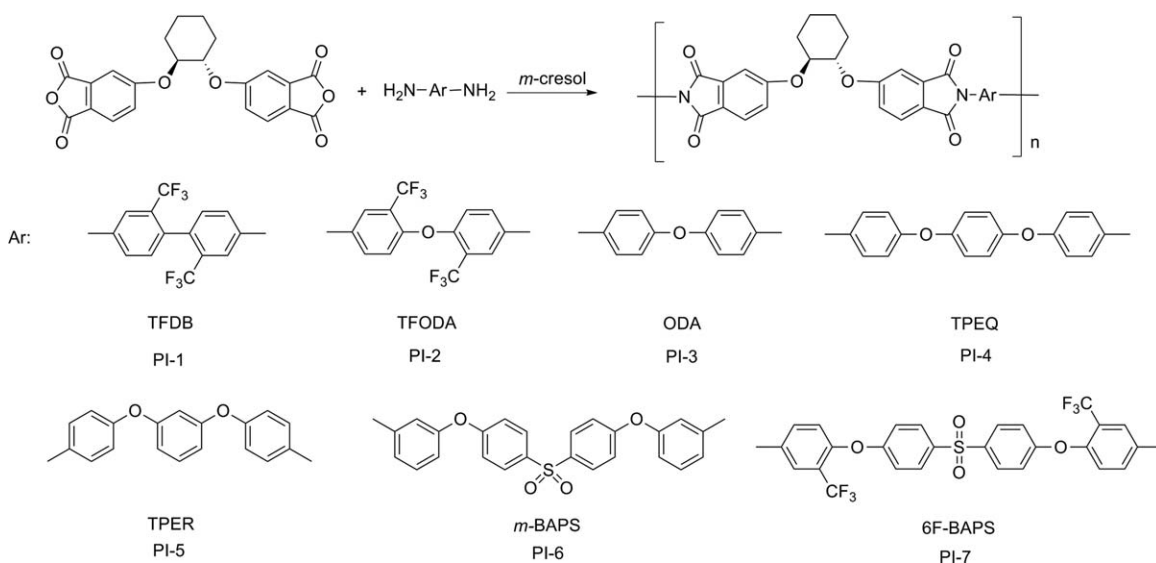
PI-6: FT-IR (film): 1779 cm^{-1} (asym C=O stretching), 1722 cm^{-1} (sym C=O stretching), 1373 cm^{-1} (C–N stretching).

PI-7: FT-IR (film): 1776 cm^{-1} (asym C=O stretching), 1718 cm^{-1} (sym C=O stretching), 1369 cm^{-1} (C–N stretching).

RESULTS AND DISCUSSION

Monomer Synthesis

The synthetic route for 1,2-CHDPA is outlined in Scheme 1. The bis(ether dinitrile) was successfully prepared through the aromatic nucleophilic substitution reaction of *trans*-cyclohexane-1,2-diol with 4-nitrophthalonitrile in the presence of sodium hydride in anhydrous DMF. The pure bis(ether dinitrile) melting at 196°C was obtained by crystallization from the acetonitrile. The bis(ether anhydride) monomer 1,2-CHDPA was afforded by alkaline hydrolysis of the corresponding bis(ether dinitrile) and subsequent dehydration of the resulting tetraacid. The structure of bis(ether dinitrile) and 1,2-CHDPA monomer were confirmed by FT-IR spectra and ^1H NMR spectra. Bis(ether dinitrile) exhibited characteristic nitrile group absorption around 2230 cm^{-1} [Figure 2(a)]. The strong absorption bands 1846 cm^{-1} (ν_{asym} C=O) and 1772 cm^{-1} (ν_{sym} C=O) were assigned to the phthalic anhydride in 1,2-CHDPA. The observed band in the region of 1000–1300 cm^{-1} was due to the C–O stretching [Figure 2(b)]. The ^1H NMR spectra of the bis(ether dinitrile) and 1,2-CHDPA are shown in Figures 3 and 4, respectively. The aromatic protons (H_a – H_c) in the ^1H NMR spectra of the bis(ether dinitrile), resonated in the region of 7.99–7.37 ppm (Figure 3), and the methine hydrogens (H_d) of cyclohexane revealed signals around 4.82 ppm. It should be noted that the signals assigned to the one methylene hydrogen



Scheme 2. Synthesis of polyimides.

(H_c) of cyclohexane moiety in bis(ether dinitrile) appeared in two separate regions (2.20–2.10 and 1.77–1.65 ppm) and the other methylene hydrogen (H_f) appeared in 1.56–1.38 ppm, respectively. The signals of aromatic protons of 1,2-CHDPA appeared in the region of 7.90–7.32 ppm; and the protons of cyclohexane shifted to a lower field around 4.96 ppm and between 2.23 ppm and 1.44 ppm (Figure 4).

Polymer Synthesis and Characterization

Polymer Synthesis. PIs were synthesized from 1,2-CHDPA and various diamines via a conventional one-step procedure (Scheme 2). The inherent viscosities of the PIs were in range from 0.37 dL/g to 0.67 dL/g, as shown in Table I, which were sufficiently high to form flexible and tough PI films. The molecular weights of these PIs determined by GPC in DMF relative to polystyrene standards were in the range of 50,500–145,300 for *M_w* and 12,800–32,900 for *M_n* with *M_w*/*M_n* values of 2.97–4.42. The chemical structures of PIs were confirmed with IR and ¹H NMR spectra. A typical IR spectrum of PI-1 is shown in Figure 5. The bands at 1779 cm⁻¹ (C=O asymmetrical

stretching), 1722 cm⁻¹ (C=O symmetrical stretching), and 1358 cm⁻¹ (C–N stretching) are the characteristic absorption bands of the PI, together with some strong absorption bands in the region of 1100–1300 cm⁻¹ due to the C–O and C–F stretch vibrations. A typical ¹H NMR spectrum of PI-1 is shown in Figure 6. All the signals have been assigned to the protons of the repeating unit. The signals in the region of 2.4–1.3 ppm assigned to the methylene hydrogens (H_c and H_f) of cyclohexane moiety in the PIs were consistent with the corresponding monomer 1,2-CHDPA, respectively. It also demonstrates that no configurational transformation occurred in the imidization procedure, indicating the stability of *trans* configuration.

Thermal Properties. DSC and TGA were used to evaluate the thermal properties of the polymers. The thermal behavior data of polymers is presented in Table I. DSC experiments rapidly cooled from 350°C to room temperature produced predominantly amorphous samples. The *T_g*s of all the synthesized PIs could be easily read in the subsequent DSC heating trace in the range of 198–240°C, depending on the structure of the diamine

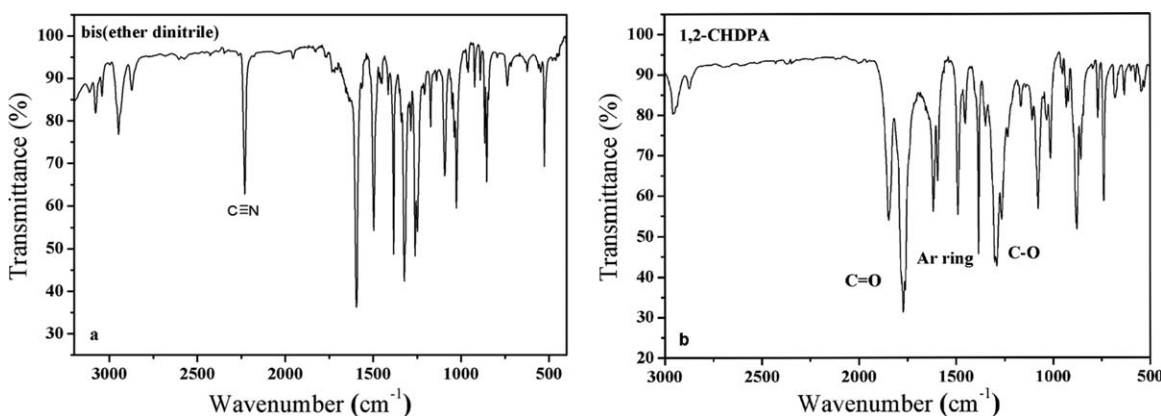


Figure 2. FT-IR spectra of (a) bis(ether dinitrile) and (b) 1,2-CHDPA.

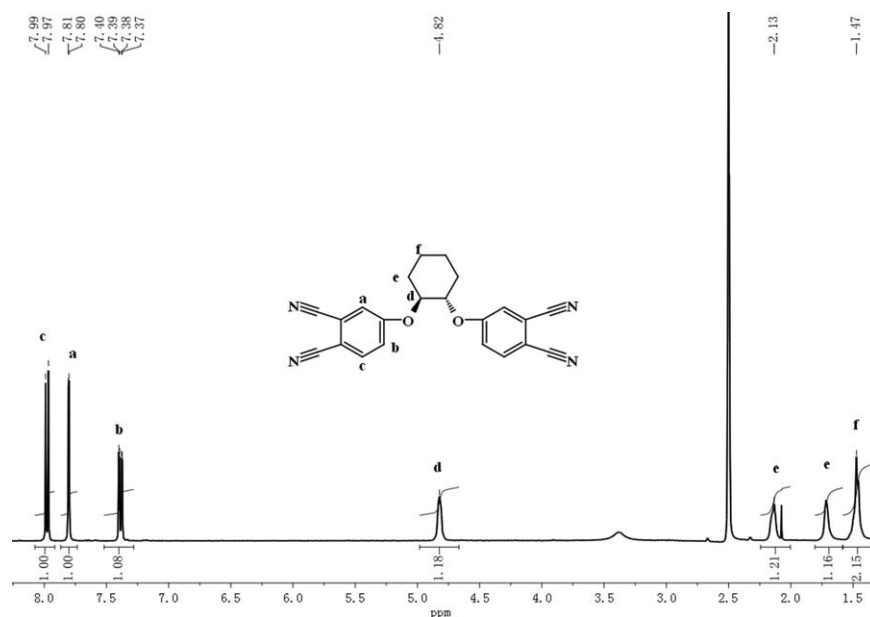


Figure 3. ^1H -NMR spectrum of bis(ether dinitrile) in $\text{DMSO}-d_6$.

component. The PI-1 with TFDB as diamine showed the highest T_g of 240°C for its rigid structure which impedes the chain mobility, while the T_g of PI-2 was lower as a result of flexible ether linkages. In contrast, the lowest T_g of 198°C was observed for PI-5 derived from TPER which can be attribute to the presence of two flexible ether linkages between the phthalimide units and the twisty structure at the 1,3-position of benzene moiety,^{35,42} which decreased the packing and interactions of the macromolecular chain, hence tended to increase the chain mobility. PI-4 exhibited an increased T_g by 15°C as compared

to its analogous PI-5 without the 1,3-position of benzene moiety.⁴² It was found that the PIs derived from 1,2-CHDPA exhibited lower T_g than the corresponding PIs based on *trans*-1,4-CHDPA, which was correspond with the regularity of polymer chain.

The thermal stability of the PIs was studied by TGA at a heating rate of $10^\circ\text{C}/\text{min}$. The temperatures of 5% weight loss ($T_{d5\%}$) and 10% weight loss ($T_{d10\%}$) in nitrogen and air are also listed in Table I. Typical TGA thermograms of polymers are shown in Figure 7. The decomposition temperatures at a 5% weight loss

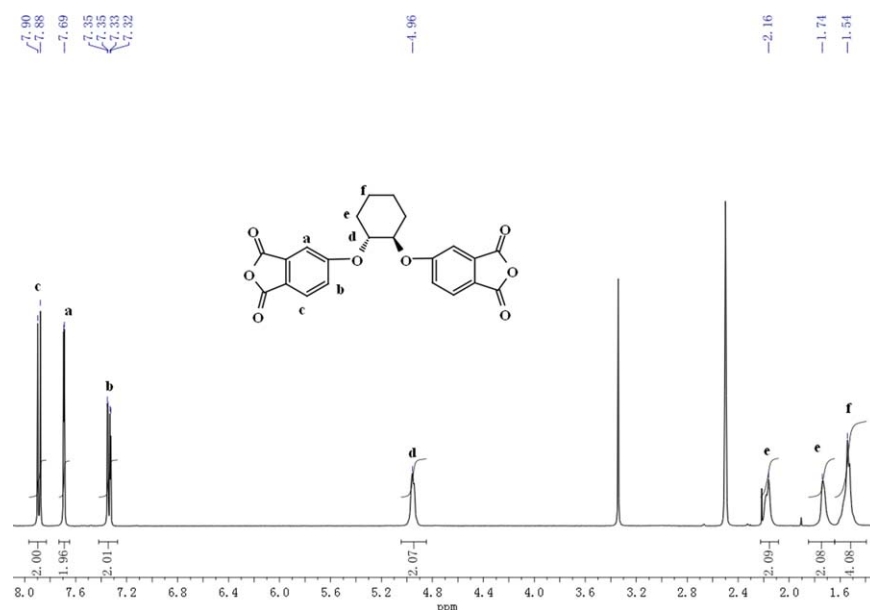


Figure 4. ^1H -NMR spectrum of 1,2-CHDPA in $\text{DMSO}-d_6$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. The Molecular Weight Data and Thermal Properties of the Polyimides

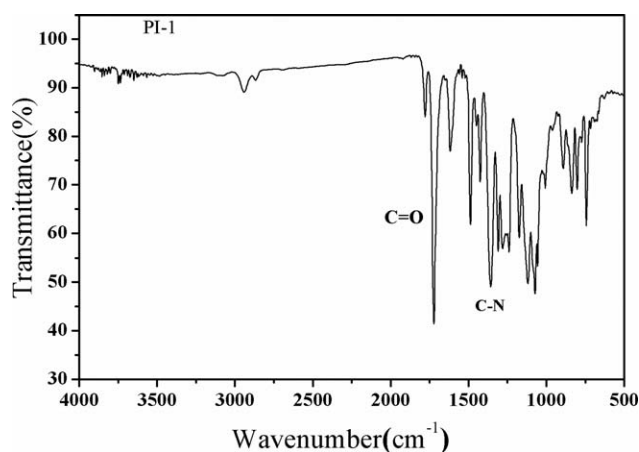
PI	η_{inh}^a (dL/g)	M_w (g/mol)	M_n (g/mol)	M_w/M_n	T_g^b (°C)	$T_{d5\%}^c$ (°C)		$T_{d10\%}^c$ (°C)		Char yield ^d (%)
						N ₂	air	N ₂	air	
PI-1	0.37	50,500	13,400	3.78	240	425	421	439	430	40
PI-2	0.47	52,600	12,800	4.11	225	424	415	438	433	43
PI-3	0.46	56,900	15,800	3.61	223	439	419	451	441	41
PI-4	0.49	80,300	21,300	3.76	213	442	422	458	443	36
PI-5	0.51	66,500	19,100	3.48	198	445	422	460	444	37
PI-6	0.40	80,900	27,300	2.97	205	433	419	451	440	37
PI-7	0.67	145,300	32,900	4.42	221	431	430	443	444	45

^a The inherent viscosities of polyimides 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 and 10% weight loss were recorded by TGA at a heating rate of 10°C/min in nitrogen and air.

^d Residual weight (%) when heated to 800°C in nitrogen.

**Figure 5.** FT-IR spectrum of PI-1.

are recorded in the range of 424–445°C in nitrogen, and 415–430°C in air, which is about 100°C lower than that of fully aromatic PIs. The $T_{d5\%}$ and $T_{d10\%}$ values in nitrogen atmosphere are higher than that in air atmosphere due to the oxidation and degradation were accelerated by oxygen in air atmosphere. It is quite reasonable that the semi-aromatic PIs began to decompose at lower temperature, because the cyclohexane moiety might decompose first at elevated temperatures.^{19,42} It was observed that the temperatures for $T_{d5\%}$ of these PIs based on 1,2-CHDPA in nitrogen and air atmospheres revealed 30°C higher than that of PIs based on *trans*-1,4-CHDPA. It was probably because the presence of *ortho*-links of cyclohexane moiety in polymers would reduce inter-chain interaction and increase the mobility of polymer, thus polymers could absorb more energy.⁴⁷

Solubility. The solubility of the PIs was tested in various organic solvents, and the results are summarized in Table II. PIs

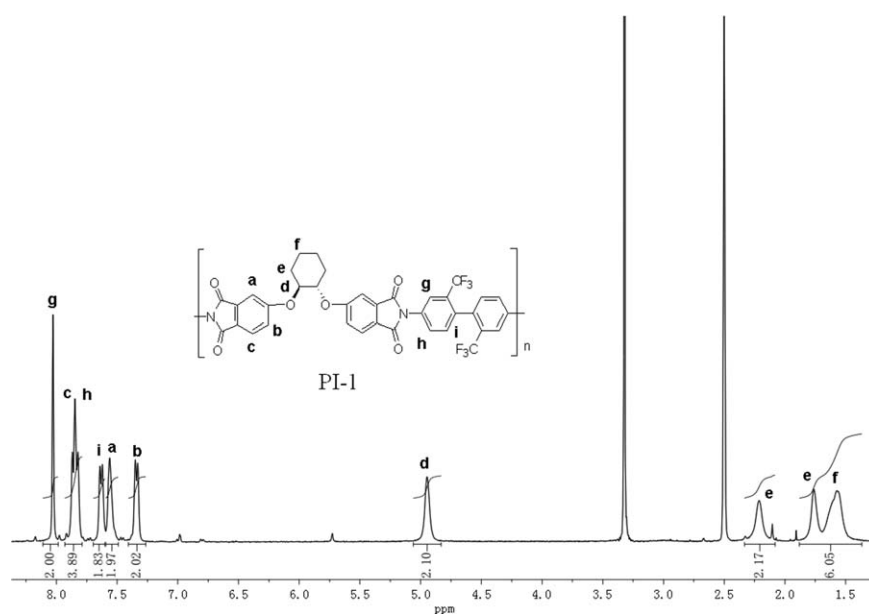
**Figure 6.** ¹H-NMR spectrum of PI-1 in DMSO-*d*₆.

Table II. Solubility of the Polyimides

PI	Solvents ^a						
	<i>m</i> -Cresol	DMAc	DMF	NMP	DMSO	CHCl ₃	THF
PI-1	++	++	++	++	++	++	++
PI-2	++	++	++	++	++	++	++
PI-3	++	++	+	++	+	++	+-
PI-4	++	++	++	++	+	++	+-
PI-5	++	++	++	++	+	++	+-
PI-6	++	++	++	++	++	++	++
PI-7	++	++	++	++	++	++	++

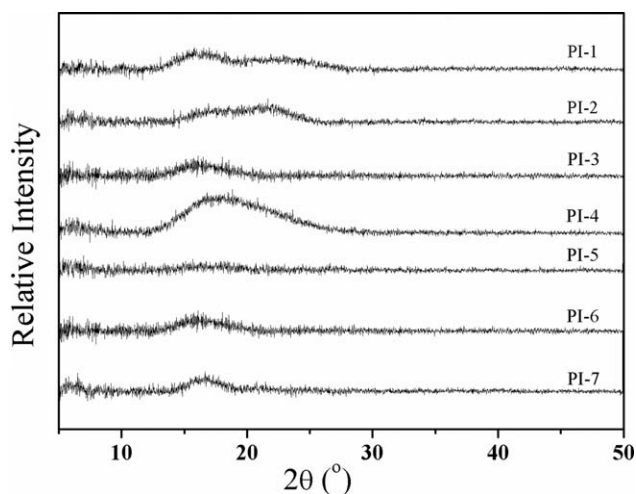
The qualitative solubility was tested with 10 mg samples in 1 mL of solvent. ++: soluble at room temperature; +: soluble on heating; +-: partial soluble on heating.

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

Table III. Mechanical Properties of the Polyimide Films

PI	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
PI-1	77	1.9	4.9
PI-2	97	2.6	6.3
PI-3	105	2.4	7.2
PI-4	85	2.3	7.6
PI-5	85	2.4	5.5
PI-6	76	2.4	4.7
PI-7	89	2.3	7.1

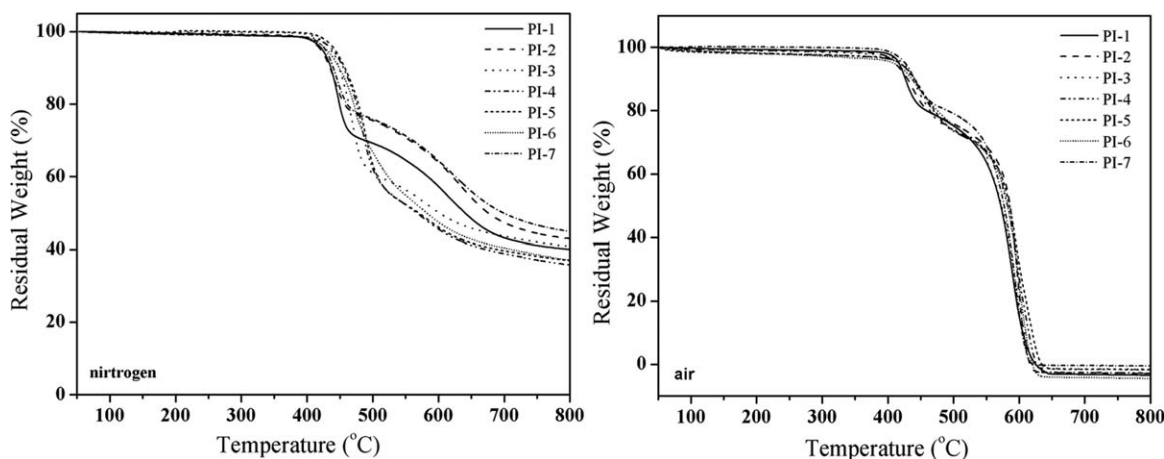
based on 1,2-CHDPA exhibited better solubility in strong dipolar solvents and common organic solvents, compared with the PIs derived from *trans*-1,4-CHDPA, due to the presence of asymmetric structure as well as bent conformation in dianhydride moiety, which disrupted regularity of polymer chains and hindered denser chain packing.^{19,43} PI-1, PI-2, and PI-7 were easily dissolved in both strong dipolar solvents and common organic solvents such as *m*-cresol, DMAc, DMF, NMP, DMSO,

**Figure 8.** Wide-angle X-ray diffraction of polyimide films.

CHCl₃, and THF, and this is possibly attributed to the presence of bulky CF₃ groups, which reduces the interchain interactions.^{7,43,48} Moreover, PI-3, PI-4, and PI-5 were also soluble in *m*-cresol, DMAc, DMF, NMP, CHCl₃, but less soluble in DMSO and THF for the relatively regularity of chain structure.

Mechanical Properties. All polymers were found to possess good film forming ability and the mechanical properties of the PI films are summarized in Table III. The PI films have good mechanical properties with tensile strengths of 76–105 MPa, elongations to break of 4.7–7.6%, and initial moduli of 1.9–2.6 GPa. Among these PI films, PI-3, PI-4, and PI-7 displayed better flexibility with elongations at break over 7%. These results could be easily explained by the difference in flexibility/rigidity of polymer chain.

X-ray Diffraction. The crystallinity of the PI films was analyzed by WAXD. The WAXD patterns of all the films were broad without obvious peak features which indicated their amorphous nature (Figure 8), and the very broad around $2\theta = 15\text{--}19^\circ$ in WAXD patterns indicated that molecular chains are randomly aligned within the film plane and the intermolecular order in PIs is not as high as in the crystalline state.⁴⁹ This result could

**Figure 7.** TGA curves of PI-1~PI-7 in nitrogen and air.

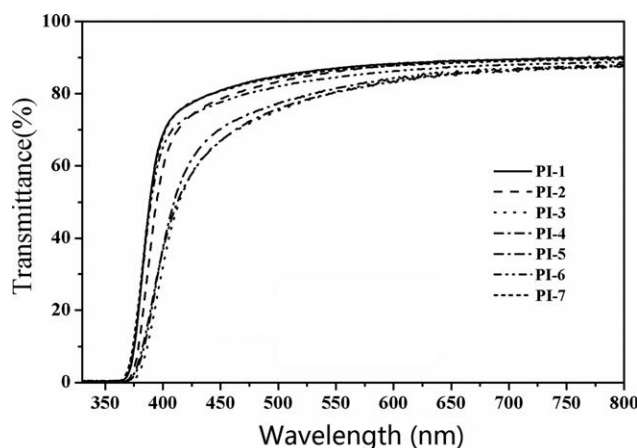


Figure 9. UV-vis spectra of the polyimide films.

be interpreted by the presence of *trans ortho*-linked cyclohexyl units.¹⁹ The high solubility of these PIs is also affected by the amorphous structure.¹⁹ Among the PI films, PI-4 showed a relatively distinct broad peak, which indicated somewhat regularity of intermolecular packing or short-range-order structure present, owing to the relatively symmetric flexible chain structure and no CF₃ substitution in diamine TPEQ.

Optical Properties. The transmission UV-visible spectra were measured for PI films with thickness about 20 μm (Figure 9). The cutoff wavelengths (absorption edge, λ_0) and the transmittance at 400, 450, and 500 nm from the UV-visible spectra are listed in Table IV. All PI films exhibited cut-off wavelengths shorter than 375 nm and were highly transparent due to the introduction of cyclohexyl group.^{18,37–41} The *trans* 1,2-position of cyclohexyl group made the structure of polymer more asymmetric and more bent, which weakened intermolecular CT formation by breaking the conjugation and decreasing electron-acceptability of dianhydride. The PIs based on 1,2-CHDPA displayed high optical transparency, which was similar to PIs based on *trans*-1,4-CHDPA. The transparency of PIs not only depends on the dianhydride, but also on the diamine moieties.⁶ The color intensity of PIs was affected by diamine moieties, and decreased in the following order: TFDB > 6F-BAPS > TFODA > *m*-BAPS > TPER > TPEQ > ODA. PI-1, PI-2, and PI-7 with CF₃ group substituent showed noticeably better transparent than other PI films without CF₃ groups, which was attributed to the steric hindrance and inductive effect of bulky electron-withdrawing CF₃ in diamine.^{10–17} For example, PI-2 displayed a higher transmittance and lower λ_0 as compared to its analogous PI-3 without CF₃ groups. Besides, PI-5 and PI-6 with *meta* substituent are slightly lighter in color than PI-3 and PI-4.⁴²

CONCLUSION

A novel dianhydride containing *trans*-1,2-cyclohexane moiety (1,2-CHDPA) was designed and the PIs derived from 1,2-CHDPA with various diamines were synthesized in *m*-cresol via one-step method. All the PI films showed high optical transparency in the visible region which demonstrated the incorporation of *trans*-1,2-cyclohexane moiety into the polymer chains was a

Table IV. Optical Properties of the Polyimide Films

PI	d (μm)	λ_0 (nm) ^a	T ₄₀₀ (%) ^b	T ₄₅₀ (%) ^b	T ₅₀₀ (%) ^b
PI-1	20	370	69	81	85
PI-2	21	371	59	78	83
PI-3	20	375	32	67	75
PI-4	19	373	37	67	76
PI-5	20	374	37	71	78
PI-6	20	370	65	78	82
PI-7	20	369	68	81	84

^a λ_0 : UV cut-off wavelength.

^b T₄₀₀, T₄₅₀, T₅₀₀: transmittance at 400, 450, and 500 nm, respectively.

useful method for reducing CT complex formation. It was found that PIs derived from 1,2-CHDPA exhibited better organosolubility and higher decomposition temperatures due to the 1,2-position isomeric effect. The WAXD measurement also indicated the amorphous nature of all PI films. The PI-1 exhibited the highest T_g , and best optical transparency which may be a promising film for optical communication applications.

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