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Synthesis and properties of polyimides derived from *cis*- and *trans*-1,2,3,4-cyclohexanetetracarboxylic dianhydrides

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Abstract

Cis-1,2,3,4-cyclohexanetetracarboxylic dianhydride (*cis*-1,2,3,4-CHDA) was synthesized. It was found that under such conditions as heating or boiling in acetic anhydride, *cis*-1,2,3,4-CHDA could be converted to its *trans*-isomer. The process of thermal isomerization was monitored by ^{1}H NMR spectra and the mechanism of conversion was proposed. Their absolute structures of *cis*- and *trans*-1,2,3,4-CHDAs were elucidated by single crystal X-ray diffraction. The polycondensations of *cis*- and *trans*-1,2,3,4-CHDAs with aromatic diamines such as 4,4′-oxydianiline (ODA), 4,4′-methylenedianiline (MDA), 4,4′-diamino-3,3′-dimethyldiphenylmethane (DMMDA), 4,4′-bis(4-aminophenoxy)benzene (TPEQ), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) were studied. It is easy to obtain higher molecular weight polyimides from *trans*-1,2,3,4-CHDA using conventional one-step or two-step methods. However, higher molecular weight polyimides derived from *cis*-1,2,3,4-CHDA could not be prepared by the usual methods (solid content ca. 10%) owing to the trend of forming cyclic oligomers. Increasing the concentration of monomers could give higher molecular weight *cis*-polymers. All of the *cis*-polyimides were soluble at room temperature in aprotic polar solvents and phenolic solvents and some of them even soluble in chloroform and tetrahydrofuran, while the corresponding *trans*-polymers showed poor solubility as compared to *cis*-polymers. All of the polyimides showed good thermal stability with the 5% weight loss temperatures in air over 415 °C. Furthermore, polyimides derived from *cis*-1,2,3,4-CHDA have higher glass transition temperatures (T_gs) than corresponding *trans*-polyimides. The flexible polyimide films possessed a tensile modulus range of 2.1–3.6 GPa, a tensile strength range of 42–116 MPa, an elongation at break of 4–18%. These polyimides exhibited cutoffs at wavelengths around 270 nm and were entirely colorless. All the polyimides showed amorphous pattern according to Wide angle X-ray diffraction measurements. The differences of polymerization and properties were explained by the structural changes resulted from isomerism.

Keywords: Cis- and *trans*-1,2,3,4-CHDAs; Isomerization; Aliphatic polyimides

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1. Introduction

Recently, polyimides derived from isomeric aromatic dianhydrides are becoming a new area for polymer researchers due to their higher glass transition temperatures (*T*gs), better solubility, lower melt viscosity, wider processibility window, and comparable thermal and mechanical properties as compared with the usual polyimides [1–16]. Our group is more interested in the structure-property relationships of polyimides based on isomeric dianhydrides to pursue the high performances polymer materials. We have achieved the synthesis of a series of polyimides based on various isomeric aromatic dianhydrides [9–16].

Aliphatic polyimides prepared from aliphatic dianhydrides and aromatic diamines, which were called as 'semiaromatic polyimides' by Japanese researchers, are always soluble, colorless and with low dielectric constants, high T_gs and a moderate thermal stability [17–20]. Thus, aliphatic polyimides have attracted much attention in recent years because of their potential applications including use as liquid crystal orientation layers, nonlinear optical buffer layers, or low dielectric materials [21–23]. It is known that aliphatic dianhydrides always have *cis*- and *trans*-configurations that will impart different properties of polyimides. In comparison, polyimides based on isomeric aliphatic

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dianhydrides have attracted less attention. Matsumoto et al. [24] reported the properties of isomeric polyimides from two alicyclic dianhydrides. Except that *cis*-polymers have higher T_gs than corresponding *trans*-isomers there were no markedly difference for other properties such as solubility, thermal stability, mechanical property, optical property, and electronic property. Shiotani et al. [25] investigated two series of alicyclic polyimides composed of *cis*- and *trans*-dicyclohexyl-3,3′,4,4′-tetracarboxylic dianhydrides and found that *cis*-polymers could be readily prepared both in a one-step method and a two-step method, however, the two-step method is preferably applied in the preparation of *trans*-polymers. Furthermore, the *cis*-polymers had higher T_gs, better solubility, and lower strength and modulus than *trans*-polymers.

As far as we know, few reports on polyimides from *cis*-1,2,3,4-CHDA (**1**) and *trans*-1,2,3,4-CHDA (**2**) have appeared in the literature except for the investigations from Volozhin and coworkers in 1970s and 1980s [26–31]. However, the molecular structures of **1** and **2** and the structure-property relationships of polyimides from the isomeric 1,2,3,4-CHDAs have not been revealed. In this paper, we will report the synthesis and molecular structures of **1** and **2**. The polycondensations of *cis*-1,2,3,4-CHDA and *trans*-1,2,3,4-CHDA with aromatic diamines and the properties of two series of isomeric polyimides will also be investigated.

2. Experimental

2.1. Materials

Isoquinoline was purchased from Aldrich Chemical Co. and used as received. All of the other reagents were from the Shanghai Chemical Reagent Co. and were of analytical grade. *N,N*-Dimethylacetamide (DMAc) was purified by distillation over phosphorus pentoxide and stored over 4-Å molecular sieves. Acetic anhydride and triethylamine (TEA) were used after distillation in the presence of magnesium and calcium hydride, respectively. 4,4′-Oxydianiline (ODA) were purified by sublimation. 4,4′-Methylenedianiline (MDA) and 4,4′-diamino-3,3′-dimethyldiphenylmethane (DMMDA) were recrystallized from ethanol prior to use. 4,4′-Bis(4-aminophenoxy)benzene (TPEQ) was prepared from hydroquinone and *p*-chloronitrobenzene in the presence of K_2CO_3 in DMAc then reduced by Pd/C-H_2 and finally recrystallized from ethanol before use. 2,2-Bis[4-(4-aminophenoxy)phenyl]propane (BAPP) was prepared from biphenol-A and *p*-chloronitrobenzene in the presence of K_2CO_3 in DMAc then reduced by Pd/C-H_2 and finally recrystallized from ethanol before use.

2.2. Measurements

Melting points were determined on a RY-1 melting point apparatus and were uncorrected. FTIR spectra were obtained with a Bio-Rad Digilab Division FTS-80 spectrometer. Elemental analyses were performed on an Elemental Analyses MOD-1106 (Italyd). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity spectrometer at 400 and 100 MHz, respectively, with tetramethylsilane (TMS) as an internal standard. Mass spectra were obtained on a Finnigon LCQ mass spectrometer with electrospray voltage at 5.0 kV and capillary temperature at 200 °C. Inherent viscosities were determined at 30 °C with an Ostward viscometer and the concentration was 0.5 g/dl in DMAc or *m*-cresol. UV–vis spectra were recorded on a Cary 1E Varian spectrophotometer. The concentration of samples was 50 μg/ml. Dynamic mechanical thermal analysis (DMTA) was performed on a dynamic mechanical thermal analyzer (Rheometric Scientific Inc, USA) in a tension mode at a heating rate of 5 °C/min and a frequency of 1 Hz from room temperature. Thermogravimetric analyses (TGA) were carried out at a heating rate of 10 °C/min in air with a Perkin–Elmer TGA-2 thermogravimetric analyzer. The tensile measurements were carried out on an Instron Model 1122 at room temperature. Wide angle X-ray diffraction (WAXD) measurements were undertaken on a Philos X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA) with scanning rate of 2 deg/min.

MALDI-TOF mass spectra were recorded on a Bruker, BIFLEX mass spectrometer equipped with delayed extraction. A 337 nm nitrogen laser producing 3 ns pulses was used and the instrument was operated in the positive reflection mode with an accelerating potential of 20 kV and an extraction delay of 50 ns. Samples were prepared by mixing 10 μl tetrahydrofuran (THF) of the oligomer sample (2 g l^{-1}) with 50 μl of a solution of 15 g l^{-1} 1,8,9-anthracemetriol (dithranol) in THF.

Single crystal X-ray diffraction data were collected at 293(2) K on a Rigaku R-AXIS RAPID diffractometer ($\lambda = 0.71073$ Å). The structures were solved with the SHELXS program [32] and were refined by full-matrix least-squares on F^2 with the SHELXL program [33].

2.3. Synthesis of cis- and trans-1,2,3,4-CHDAs

2.3.1. Synthesis of cis-1,2,3,4-CHDA

Cis-1,2,3,4-cyclohexanetetracarboxylic acids was synthesized by following a method described in the literature [34]. *Cis*-1,2,3,4-CHDA was obtained by treating *cis*-1,2,3,4-cyclohexanetetracarboxylic acids in refluxing acetic anhydride for 0.5 h. Yield, 84%; mp 214–216 °C (lit. [35] 222 °C). ^{1}H NMR (400 MHz, acetone-d$_6$) 1.80 (2H, H-5,6), 2.28 (2H, H-5,6), 3.84 (2H, H-1,4), 4.16 (2H, H-2,3). ^{13}C NMR (100 MHz, acetone-d$_6$) 21.01 (C-5,6), 38.78 (C-1,4), 39.26 (C-2,3), 172.27 (CO), 173.41 (CO). IR (KBr) 1853,1785, 1470, 1450, 1345, 1224, 1073, 941, 915, 790 cm^{-1}. Anal. calcd for $C_{10}H_8O_6$ (224.16): C 53.58%, H 3.59%; found: C, 53.38%; H, 3.45%.

A single crystal of *cis*-1,2,3,4-CHDA was obtained from acetic anhydride solution by slow evaporation of solvent at room temperature for several days. Crystal data: $0.52 \times 0.44 \times 0.32$ mm, $C_{10}H_8O_6$, colorless, $fw = 224.16$, monoclinic, $P2(1)\backslash n$, $a = 7.270(2)$ Å, $b = 10.296(2)$ Å, $c = 12.868(3)$ Å, $\alpha = 90.00°$, $\beta = 97.45(3)°$, $\gamma = 90.00°$, $V = 955.1(3)$ Å^3, $Z = 3$, $T = 293(2)$ K, $R_1(I > 2\sigma(I)) = 0.0394$, ωR_2 (all data) $= 0.0942$, GOF $= 0.784$.

2.3.2. Synthesis of trans-1,2,3,4-CHDA

Trans-1,2,3,4-CHDA was obtained by treating *cis*-1,2,3,4-CHDA in refluxing acetic anhydride for 12 h. Yield, 80%; mp 194–196 °C (lit. [35] 204 °C). ^{1}H NMR (400 MHz, acetone-d$_6$) 2.00 (2H, H-5,6), 2.10 (2H, H-5,6), 3.70 (2H, H-1,4), 4.28 (2H, H-2,3). ^{13}C NMR (100 MHz, acetone-d$_6$) 22.27 (C-5,6), 38.27 (C-1,4), 38.85 (C-2,3), 173.14 (CO), 173.25 (CO). IR (KBr) 1853, 1785, 1470, 1450, 1345, 1224, 1073, 941, 915, 790 cm^{-1}. Anal. calcd for $C_{10}H_8O_6$ (224.16): C 53.58%; H 3.59%; found: C 53.44%; H 3.70%.

A single crystal of *trans*-1,2,3,4-CHDA was obtained from acetic anhydride solution by slow evaporation of solvent at room temperature for several days. Crystal data: $0.52 \times 0.50 \times 0.48$ mm, $C_{10}H_8O_6$, colorless, $fw = 224.16$, monoclinic, $C2\backslash c, a = 13.342(2)$ Å, $b = 6.6980(10)$ Å, $c = 10.214(2)$ Å, $\alpha = 90.00°$, $\beta = 103.10(2)°$, $\gamma = 90.00°$, $V = 889.0(3)$ Å^3, $Z = 4$, $T = 293(2)$ K, $R_1(I > 2\sigma(I)) = 0.0323$, ωR_2 (all data) $= 0.0836$, GOF $= 0.989$.

2.4. Synthesis of model compounds derived from cis- and trans-1,2,3,4-CHDAs

2.4.1. Two-step method

Cis- or *trans*-1,2,3,4-CHDA and a stoichiometric amount of aniline (AN) were stirred in DMAc at room temperature for 3 h; subsequently, the solution was chemically cyclodehydrated using acetic anhydride and triethylamine and was stirred at room temperature for 24 h. The mixture was then diluted by the addition of large amount of water. The crude products obtained by filtration were recrystallized twice from toluene/DMAc (toluene/DMAc = 2:1) for model compound *cis*-1,2,3,4-CHDA/AN, and from toluene/DMAc (toluene/DMAc = 4:1) for model compound *trans*-1,2,3,4-CHDA/AN.

Cis-1,2,3,4-CHDA/AN: mp > 300 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) 1.81 (2H, d), 1.86 (2H, d), 3.26 (2H, s), 3.81 (2H, d), 7.18–7.54 (10H, m); IR (KBr) 1778, 1705, 1594, 1497, 1456, 1390, 766, 701 cm^{-1}. UV–vis (DMAc, λ_{max}): 265 nm. Anal. calcd for $C_{22}H_{18}O_4N_2$ (374.40): C 70.58%, H 4.85%, N 7.48%; found: C 70.94%, H 4.64%, N 7.66%.

Trans-1,2,3,4-CHDA/AN: mp > 300 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$) 1.69 (2H, d), 1.87 (2H, d), 3.26 (2H, s), 3.80 (2H, d), 7.34–7.45 (10H, m). IR (KBr) 1771, 1704, 1594, 1496, 1455, 1389, 766, 701 cm^{-1}. UV–vis (DMAc, λ_{max}): 265 nm. Anal. calcd for $C_{22}H_{18}O_4N_2$ 374.40: C 70.58%, H 4.85%, N 7.48%; found C 70.75%, H 4.68%, N 7.39%.

2.4.2. One-step method

A mixture of *cis*- or *trans*-1,2,3,4-CHDA, the stoichiometric amount of aniline (AN), and a few drops of isoquinoline were stirred in *m*-cresol under N_2 atmosphere at room temperature for 2 h; subsequently, the solution was gradually increased to 200 °C for 18 h. The mixture was then diluted by the addition of large amount of methanol to give the crude products.

2.5. Synthesis of polyimides derived from cis- and trans-CHDAs

All polymerization reactions were carried out in dry nitrogen atmosphere with a mechanical stirrer. An equimolar amount of dianhydride and diamine monomers were used in all cases. The representative polymerization procedures for polymer **1a** (*cis*-1,2,3,4-CHDA/ODA) are as follows:

2.5.1. Two-step method

4,4′-Oxydianiline (ODA) (1.0530 g, 5.25 mmol) and DMAc (5 ml) were charged in a 50 ml three-necked, round-bottomed flask equipped with a mechanical stirrer and dry nitrogen gas inlet. After the dissolving of ODA, *cis*-1,2,3,4-CHDA (1.1793 g, 5.25 mmol) was delivered as a solid into the flask over 0.5 h. With the viscosity increasing, DMAc (15 ml) was gradually added to the polyamic acid (PAA) solution. After stirring at room temperature for 20 h, PAA was formed in the viscous solution. An aliquot of PAA solution was taken out and cast on a glass plate and dried at 80 °C for 18 h, followed by heating at 150 °C (1 h), 200 °C (1 h), 250 °C (1 h) and 300 °C (1 h) to afford film of polyimide **1a**. The film was used for DMTA and tensile measurements. Then acetic anhydride (6 ml) and triethylamine (3 ml) were added to the reminder PAA solution, as the reaction progressed for 24 h to have a brown viscous solution. The solution was poured slowly into 300 ml of methanol with stirring. The precipitate was collected by filtration and extracted with methanol in a Soxhlet extractor for 6 h and dried in vacuo, to afford powder of polyimide **1a**.

2.5.2. One-step method

A mixture of *cis*-1,2,3,4-CHDA (1.2250 g, 5.46 mmol), 4,4′-oxydianiline (ODA) (1.0938 g, 5.46 mmol) and a few drops of isoquinoline in *m*-cresol (5 ml) was stirred at 60 °C for 2 h under nitrogen. With the viscosity increasing, *m*-cresol (18 ml) was gradually added to the solution, which was then gradually increased to 200 °C for 18 h. The viscous solution was poured slowly into methanol (600 ml) with stirring. The polymer powder was collected by filtration and extracted with methanol in a Soxhlet extractor for 24 h and dried in vacuum. Dissolving polyimide powder in DMAc gave the polymer solution, which was cast on a glass plate and dried at 80 °C for 18 h, followed by heating at 300 °C (1 h) to afford polyimide film. The film was used for DMTA and tensile measurements.

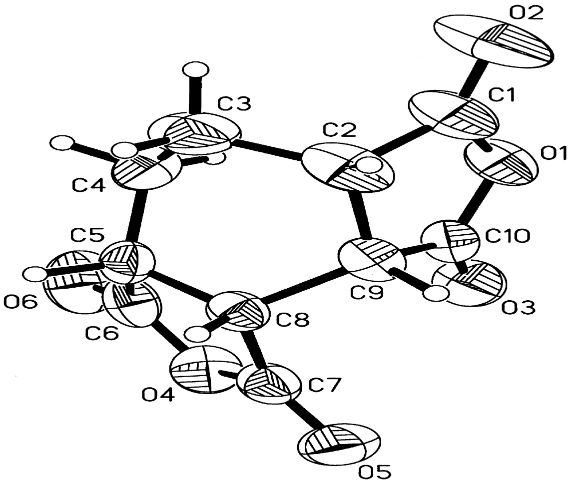


Fig. 1. The molecular structure of *cis*-1,2,3,4-CHDA.

2.5.3. Polymer characterizations

Polyimide **1a**. Yield, 90%. ^{1}H NMR (400 MHz, DMSO-d_6) 1.57 (1H, s), 1.69 (1H, s), 1.84 (1H, s), 1.99 (1H, s), 3.24 (1H, s), 3.37 (1H, s), 3.70 (1H, s), 3.80 (1H, s), 7.18–7.39 (8H, m). IR (KBr): 1780 (imide C=O asym. stretching), 1712 (imide C=O sym. stretching), 1386 (C–N stretching), 712 cm^{-1}(C=O bending). UV–vis (DMAc, λ_{max}): 263 nm. $(C_{22}H_{16}O_5N_2)_n$ $(388.38)_n$: calcd C 68.04, H 4.15, N 7.21; found C 68.84, H 4.22, N 7.02.

Polyimide **2a**. Yield, 89%. ^{1}H NMR (400 MHz, DMSO-d_6) 1.70 (2H, s), 1.87 (2H, s), 3.26 (2H, s), 3.81 (2H, d), 7.21–7.42 (8H, m). IR (KBr): 1780 (imide C=O asym. stretching), 1710 (imide C=O sym. stretching), 1383 (C–N stretching), 711 cm^{-1}(C=O bending). UV–vis (DMAc, λ_{max}): 263 nm. $(C_{22}H_{16}O_5N_2)_n$ $(388.38)_n$: calcd C 68.04, H 4.15, N 7.21; found C 68.55, H 4.36, N 7.08.

Polyimide **1b**. Yield, 86%. IR (KBr): 1780 (imide C=O asym. stretching), 1712 (imide C=O sym. stretching), 1382 (C–N stretching), 710 cm^{-1}(C=O bending). UV–vis (DMAc, λ_{max}): 263 nm. $(C_{23}H_{18}O_4N_2)_n$ $(386.41)_n$: calcd C 71.49, H 4.70, N 7.25; found C 70.94, H 4.82, N 7.33.

Polyimide **2b**. Yield, 91%. IR (KBr): 1780 (imide C=O asym. stretching), 1713 (imide C=O sym. stretching), 1374 (C–N stretching), 708 cm^{-1}(C=O bending). UV–vis (DMAc, λ_{max}): 263 nm. $(C_{23}H_{18}O_4N_2)_n$ $(386.41)_n$: calcd C 71.49, H 4.70, N 7.25; found C 71.23, H 4.88, N 7.46.

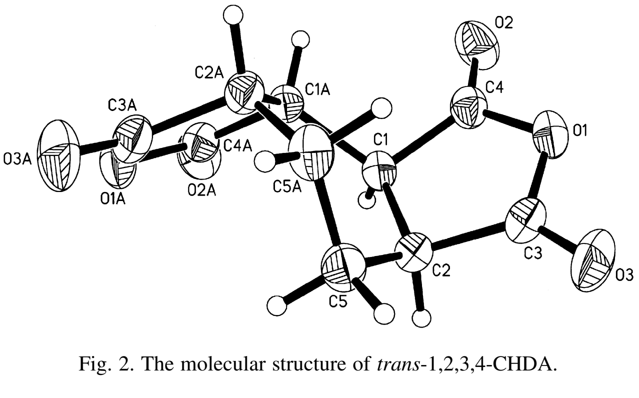


Fig. 2. The molecular structure of *trans*-1,2,3,4-CHDA.

Polyimide **1c**. Yield, 93%. IR (KBr): 1782 (imide C=O asym. stretching), 1714 (imide C=O sym. stretching), 1380 (C–N stretching), 714 cm^{-1}(C=O bending). UV–vis (DMAc, λ_{max}): 263 nm. $(C_{25}H_{22}O_4N_2)_n$ $(414.46)_n$: calcd C 72.45, H 5.35, N 6.76; found C 72.87, H 5.51, N 6.26.

Polyimide **2c**. Yield, 95%. IR (KBr): 1781 (imide C=O asym. stretching), 1713 (imide C=O sym. stretching), 1379 (C–N stretching), 712 cm^{-1}(C=O bending). UV–vis (DMAc, λ_{max}): 263 nm. $(C_{25}H_{22}O_4N_2)_n$ $(414.46)_n$: calcd C 72.45, H 5.35, N 6.76; found C 71.94, H 5.92, N 6.18.

Polyimide **1d**. Yield, 94%. IR (KBr): 1781 (imide C=O asym. stretching), 1713 (imide C=O sym. stretching), 1386 (C–N stretching), 711 cm^{-1}(C=O bending). UV–vis (DMAc, λ_{max}): 265 nm. $(C_{28}H_{20}O_6N_2)_n$ $(480.48)_n$: calcd C 69.99, H 4.20, N 5.83; found C 70.14, H 4.16, N 5.79.

Polyimide **2d**. Yield, 92%. IR (KBr): 1780 (imide C=O asym. stretching), 1712 (imide C=O sym. stretching), 1382 (C–N stretching), 710 cm^{-1}(C=O bending). UV–vis (DMAc, λ_{max}): 263 nm. $(C_{28}H_{20}O_6N_2)_n$ $(480.48)_n$: calcd C 69.99, H 4.20, N 5.83; found C 70.26, H 4.11, N 5.68.

Polyimide **1e**. Yield, 90%. IR (KBr): 1782 (imide C=O asym. stretching), 1716 (imide C=O sym. stretching), 1385 (C–N stretching), 709 cm^{-1}(C=O bending). UV–vis (DMAc, λ_{max}): 263 nm. $(C_{37}H_{30}O_6N_2)_n$ $(598.66)_n$: calcd C 74.23, H 5.05, N 4.68; found C 73.86, H 5.51, N 4.77.

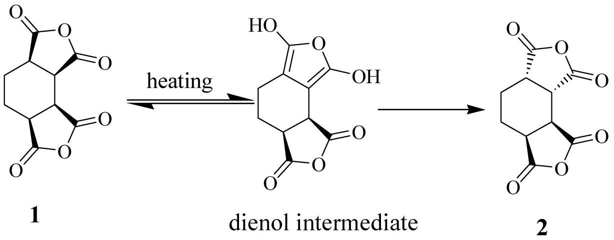
Polyimide **2e**. Yield, 93%. IR (KBr): 1780 (imide C=O asym. stretching), 1714 (imide C=O sym. stretching), 1383 (C–N stretching), 710 cm^{-1}(C=O bending). UV–vis (DMAc, λ_{max}): 263 nm. $(C_{37}H_{30}O_6N_2)_n$ $(598.66)_n$: calcd C 74.23, H 5.05, N 4.68; found C 75.08, H 5.38, N 4.52.

3. Results and discussion

3.1. Synthesis of cis- and trans-1,2,3,4-CHDAs

There are several reports on the synthesis of *cis*-1,2,3,4-cyclohexanetetracarboxylic acid [34,36,37]. The usual method is oxidation of the adduct of malic anhydride and 1,3-cyclohexane with nitric acid or potassium permanganate. The configurational relationship between the four carboxyl groups of *cis*-tetraacids was identified by the known Diel–Alder order [35,36] or ^{1}H NMR of their tetramethyl ester [34]. As far as we know, only one report dealt with the synthesis of *trans*-1,2,3,4-cyclohexanetetracarboxylic acid [35]. In this literature, the authors found the isomerization of **1** to **2** under heating or boiling acetic anhydride. However, they did not give the specific isomerization conditions and process, as well as the molecular structures of *cis*- and *trans*-1,2,3,4-CHDAs.

We synthesized *cis*-1,2,3,4-cyclohexanetetracarboxylic acid according to the literature method [34]. The structure of *cis*-1,2,3,4-CHDA was confirmed by IR, NMR, MS, elemental analyses and single crystal X-ray diffraction.



1 dienol intermediate 2

Fig. 3. The possible mechanism of thermal isomerization of **1** to **2**.

Fig. 1 gives the molecular structure of *cis*-1,2,3,4-CHDA. The two five-numbered anhydride rings adopt *cis*-configuration, locating one side of the plane of cyclohexane ring.

Interestingly, a small amount of pure **2** (yield, 12%) was obtained by sublimation when treatment **1** at 230 °C under argon atmosphere. A single crystal X-ray diffraction study of **2** (Fig. 2), which was formed in acetic anhydride, confirmed its absolute structure was *trans*-1,2,3,4-CHDA. The two five-numbered anhydride rings adopt *trans*-configuration, locating two sides of the plane of cyclohexane ring. Moreover, vacuum sublimation of **1** afforded the isomer mixtures of **1** and **2** (**1**:**2** = 20:80, as determined by ^{1}H NMR).

From the configurational transformation, we propose the mechanism shown in Fig. 3. One of the five-numbered rings has intramolecular hydride-transfer and forms dienol intermediate, leading to inversion of configuration. It is evident that a small amount of acid tend to enolize more rapidly. So, it would be of some interest to determine the effect of adding a small amount of acid on the isomerization. In this regard, we sought a different route to effect the transformation by treatment **1** with acetic anhydride and xylene at the same temperature (140 °C), respectively. It is gratifying that, as shown in Fig. 4, **1** could be completely isomerized to **2** in refluxing acetic anhydride for 4 h.

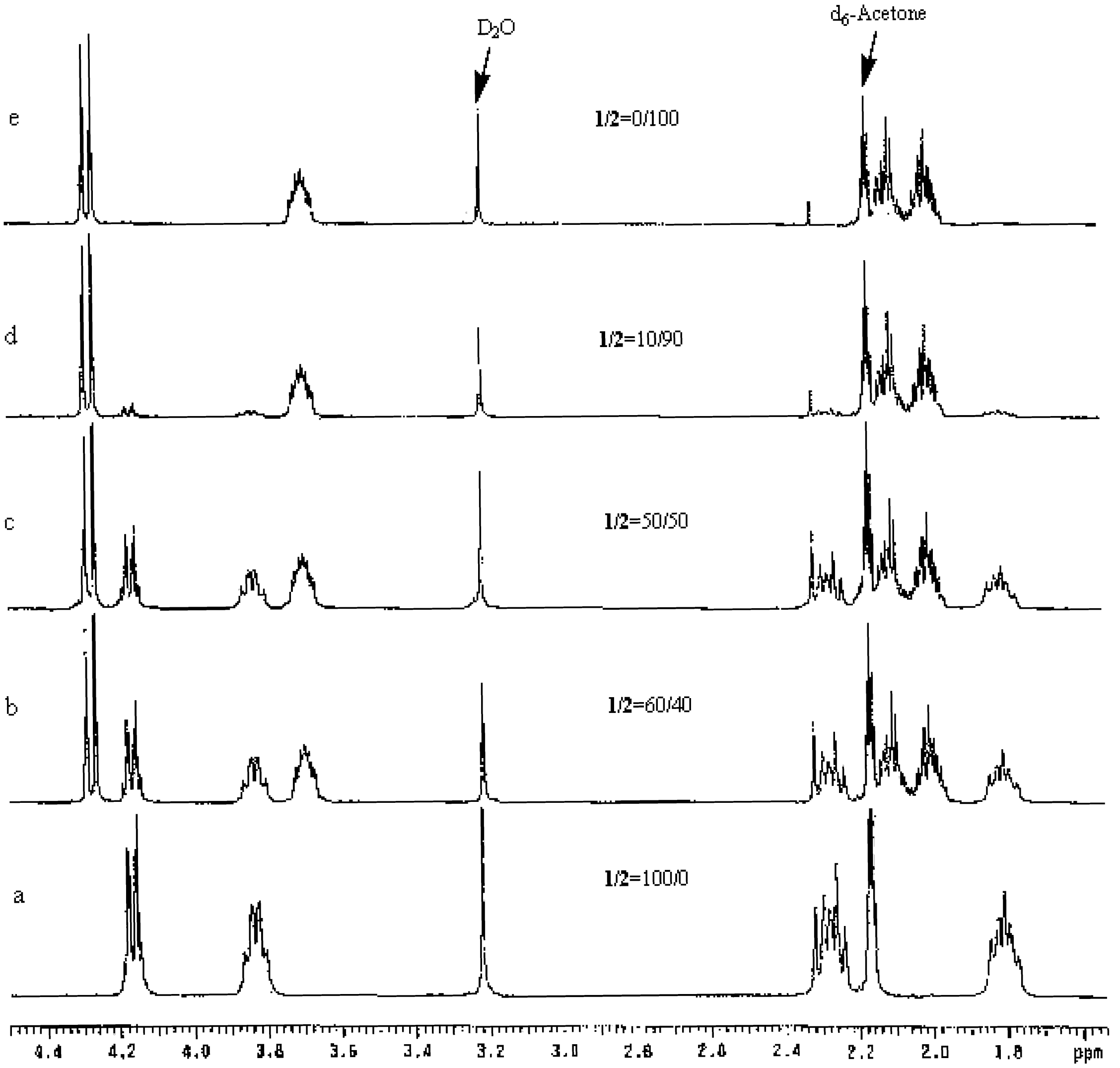
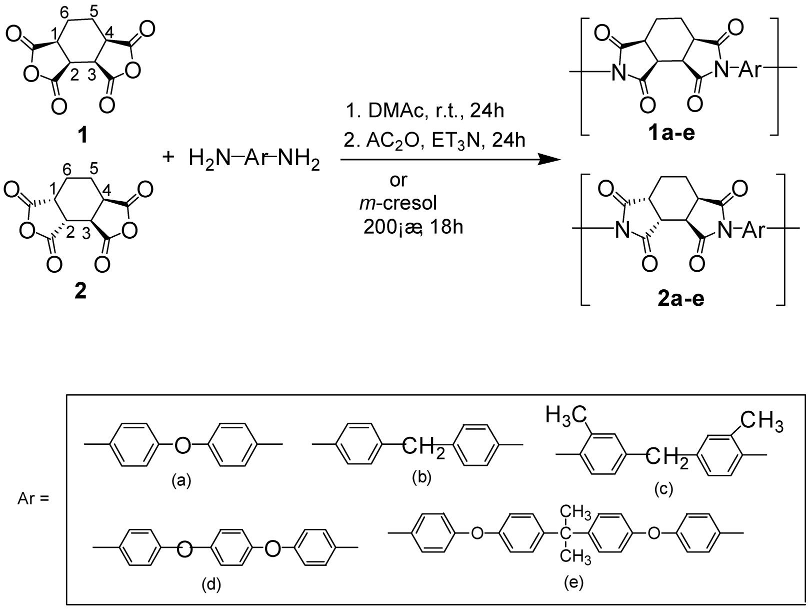


Fig. 4. ^{1}H NMR spectra (in acetone-d$_6$ with TMS) of: (a) compound **1**; (b) treatment **1** with acetic anhydride in refluxing for 2.5 h; (c) treatment **1** with acetic anhydride in refluxing for 3 h; (d) treatment **1** with acetic anhydride in refluxing for 3.5 h; (e) treatment **1** with acetic anhydride in refluxing for 4 h.



Scheme 1. Synthesis of polyimides from *cis*- and *trans*-1,2,3,4-CHDAs.

However, there are no changes with refluxing xylene at the same temperature even for 24 h.

In contrast to **1**, **2** could not have isomerization either by heating or refluxing in acetic anhydride. So we can conclude that **1** is more stable in kinetics, but **2** is more stable in thermodynamics, there is an energy barrier between **1** and **2**. To assess these phenomena, quantum chemical calculations were performed on **1**, **2** and their transition state by the semiempirical AM1 method [38]. As expected, the final heat of formation of **2** (-219.71 kcal/mol) is a litter higher than **1** (-216.16 kcal/mol). Their transition state is -198.93 kcal/mol. The energy difference is very small, which shows the thermal isomerization of **1** to **2** is possible. Isomerization of **2** to **1** is difficult because of the more stability of **2**.

Table 1
Properties of isomeric polyimides

Polymer	η^a (dl/g)	$T_g{}^b$ (°C)	$T_{5\%}{}^c$ (°C)	Modulus (MPa)	Tensile strength (MPa)	Elongation (%)
1a	0.86	350	444	3600	116	18
2a	1.29[d]	334	432	3580	95	7.6
1b	0.39	346	450	2362	42	3.8
2b	1.01[d]	336	437	2811	86	8.5
1c	0.22	342	436	1900	88	7.3
2c	0.76	338	422	2100	91	6.9
1d	0.27	298	415	3120	94	7.7
2d	0.64[d]	250	429	2410	93	10.6
1e	0.38	268	440	2730	78	6.8
2e	0.78[d]	259	435	2176	90	9.6

[a] Inherent viscosity measured with 0.5 g/dl in DMAc at 30 °C.
[b] Obtained from DMTA at a heating rate of 5 °C/min at 1 Hz.
[c] Five percent weight loss in air obtained from TGA at a heating rate of 10 °C/min.
[d] Inherent viscosity measured with 0.5 g/dl in *m*-cresol at 30 °C.

3.2. Synthesis of model compounds and polyimides derived from cis- and trans-1,2,3,4-CHDAs

Model compounds derived from *cis*- and *trans*-1,2,3,4-CHDA were prepared by the usual two-step or one-step methods and characterized by DSC, IR, ^{1}H NMR, UV–vis and elemental analysis. It was found that model compound *cis*-1,2,3,4-CHDA/AN could not convert to its isomer *trans*-1,2,3,4-CHDA/AN under high temperature conditions. This can be suggested that the intramolecular hydride-transfer of model compounds to form dienol intermediate was more difficult, which further confirmed the mechanism of thermal isomerization of **1** to **2**.

As shown in Scheme 1, all the polyimides were synthesized in two-step or one-step method by the polycondensation reactions of **1** and **2** with five aromatic diamines ODA, MDA, DMMDA, TPEQ, and BAPP. Polyimides derived from *trans*-1,2,3,4-CHDA could be readily prepared by the conventional two-step or one-step method. However, the polymerizations of **1** with aromatic diamines did not proceed as expected using the usual methods (solid content ca. 10%). The polyimide films based on *cis*-1,2,3,4-CHDA are always brittle because of the lower molecular weight ($\eta_{\mathrm{inh}} = 0.10$–$0.18$ dl/g). As shown in Fig. 5, MALDI-TOF-MS indicated that polymer *cis*-1,2,3,4-CHDA/ODA prepared by the usual methods consist principally of cyclic oligomers range from $n = 1$ to $n = 4$. It is believed that the *cis*-configuration of **1** would be favorable to form cyclic polyimides.

In view of the monomer concentration have an effect on molecular weight of PAA, increasing the monomer concentration can suppress the formation of cyclics and favors high molecular weight of products [39]. So all the polymerizations of **1** was conducted in higher solid content

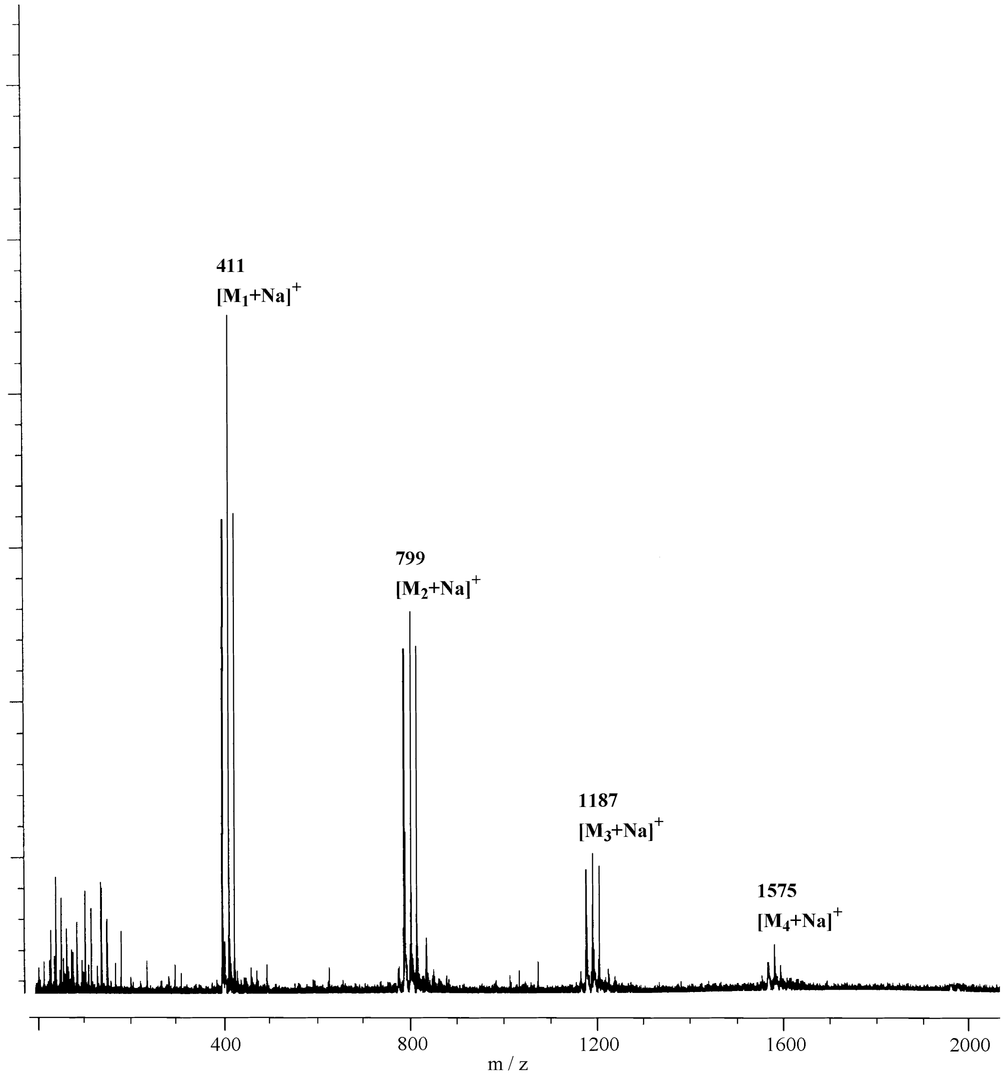


Fig. 5. MALDI-TOF-MS spectrum of *cis*-1,2,3,4-CHDA/ODA prepared by the usual methods using 1,8,9-anthracemetriol as matrix.

(ca. 30%) to form PAA in the beginning, subsequently diluted to 10% with the viscosity increasing, followed by thermal or chemical imidization. The properties of isomeric PIs are listed in Table 1. Inherent viscosities of the polymers were in the range of 0.27 and 1.29 dl/g in DMAc or *m*-cresol at 30 °C.

The formation of polyimides was confirmed by means of elemental analysis and IR and NMR spectroscopy. The complete imidization of the polymers was confirmed by IR spectra. All the polymers showed the characteristic absorption bands of the imide ring near 1780 (asym C=O stretching), 1720 (sym C=O stretching), 1380 (C–N stretching), and 725 (imide ring deformation) cm^{-1}. There was no existence of the characteristic absorption bands of the amide groups near 3363 (N–H stretching) and 1674 (C=O stretching) cm^{-1}, indicating that the polymers had been fully imidized. Fig. 6 shows a typical set of ^{1}H NMR spectra of isomeric polyimides **1a** and **2a** in DMSO-d_6, indicating a little difference of the chemical shifts for two isomeric polymers. In addition to IR and NMR spectra, the elemental analysis values of the polymers generally agreed well with the calculated values for the proposed structures.

3.3. Thermal and mechanical properties of isomeric polyimides

DMTA was used to evaluate the thermal properties of the polymers. As shown in Table 1, the T_g values of the *cis*-polyimides **1a**–**1e** were in the range of 268–350 °C, whereas the range of T_g values for the *trans*-polyimides **2a**–**2e** series was 259–334 °C. Interestingly, it was found that all *cis*-polymers had higher T_g values than corresponding *trans*-polymers. Fig. 7 displays the dynamic storage modulus (E') and loss tangent (tanδ) as a function of temperature for isomeric polymer films **1a**, **2a** and **1b**, **2b**. Regarding the peak temperature in the tanδ curves as the glass transition temperature (T_g), the polymer *cis*-1,2,3,4-CHDA/ODA showed an higher T_g at 350 °C than polymer *trans*-1,2,3,4-CHDA/ODA at 334 °C and polymer *cis*-1,2,3,4-CHDA/MDA showed an higher T_g at 346 °C than

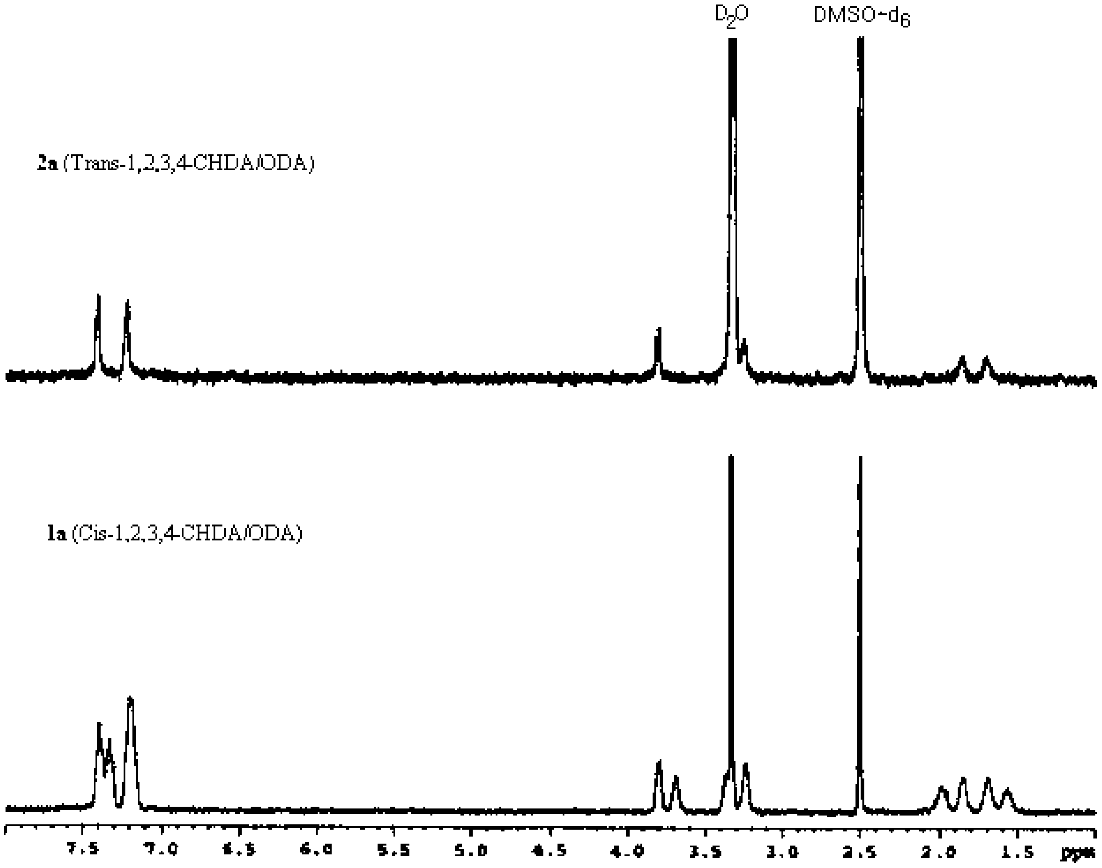


Fig. 6. ^{1}H NMR spectra (in DMSO-d_6 with TMS) of isomeric polymers **1a** and **2a**.

polymer *trans*-1,2,3,4-CHDA/MDA at 336 °C. Slightly higher T_gs for the *cis*-series in comparison with the *trans*-series might be a result of more restricted rotation around the bond [3] due to the two imide groups locating one side of cyclohexane ring for the **1** based on polyimides. This result also agrees well with those obtained from polyimides based on other isomeric aliphatic dianhydrides [24,25].

As shown in Table 1, the thermal stability of the polyimides was evaluated by TGA and the temperatures for 5% weight loss in air atmospheres for these isomeric PIs stayed within 415–450 °C. The TGA data indicated that these isomeric polyimides had good thermal stability. Furthermore, the isomeric polymers had tensile strengths at break of 78–116 MPa, elongations at break of 3.8–18%, and initial moduli of 1.9–3.6 GPa, indicating that they could be cast into flexible and tough films.

3.4. Solubility property of isomeric polyimides

The solubility properties of all polyimides are summarized

Table 2
Solubility of isomeric polyimides

Polymer	TCE[a]	$CHCl_3$	THF	Dioxane	DMF	DMAc	DMSO	NMP	*m*-cresol	Conc.H_2SO_4
1a	±	−	−	−	++	++	++	++	++	++
2a	±	−	−	−	±	±	+	+	+	++
1b	±	−	−	−	++	++	++	++	++	++
2b	±	−	−	−	±	±	+	+	+	++
1c	+	++	+	+	++	++	++	++	++	++
2c	+	±	±	±	±	++	++	++	++	++
1d	+	+	±	±	++	++	++	++	++	++
2d	±	±	−	−	±	±	+	+	+	++
1e	++	++	++	++	++	++	++	++	++	++
2e	++	++	++	++	++	++	++	++	++	++

Key: ++, fully soluble at room temperature; +, fully soluble on heating; ±, partially soluble on heating; −, insoluble on heating.

[a] TCE = 1,1,2,2-tetrachloroethane.

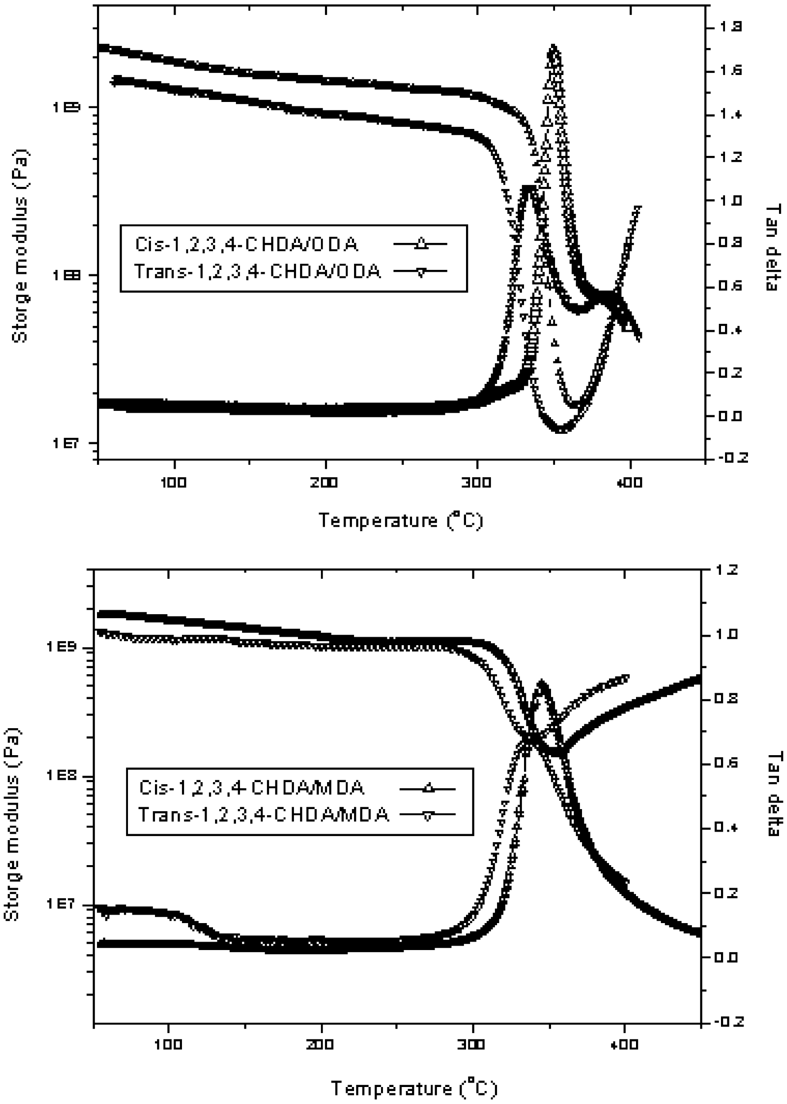


Fig. 7. Dynamic mechanical thermal analysis (DMTA) plots for isomeric polyimides **1a**, **2a** and **1b**, **2b**.

in Table 2. On comparing the solubility behaviors with polyimides **1a**–**1e**, the isomeric polyimides **2a**–**2e** revealed a relatively decreased solubility. For example, all polyimides derived from *cis*-1,2,3,4-CHDA were soluble in aprotic polar solvents such as NMP, DMAc, DMF, and DMSO and in polar solvents like *m*-cresol at room temperature. Polymer **1c** was even soluble in 1,1,2,2-tetrachloroethane (TCE), chloroform, THF, and dioxane on heating. However, polyimides **2a**, **2b**, **2c**, and **2d** were only soluble or partly soluble in aprotic polar solvents on heating. Polymer **2c** was even partly soluble in chloroform, THF, dioxane and DMF on heating. It is known that the excellent solubility associated with these polyimides might be due in part to the presence of the introduction of a cycloaliphatic unit into the polyimide backbone would facilitate less polymer–polymer interaction [18]. The large differences in solubility between the *cis*- and *trans*-series could be attributed to the two imide groups locating one side of cyclohexane ring in the *cis*-polymers. The imide groups create a steric hindrance effect and inhabit interchain interaction and chain packing, thus reducing the chain–chain interactions and increasing solubility.

3.5. Optical property and morphology structure of isomeric polyimides

The UV–vis spectra of all polyimide solutions exhibited cutoffs at wavelengths around 270 nm, indicating that they were entirely colorless. The lack of color is generally associated with the absence or inhibition of intra- and/or intermolecular charge-transfer interactions for aliphatic polyimides [18]. WAXD measurements for polyimide powders showed that all these polyimides are amorphous (Fig. 8). There were no marked differences in optical property and morphology structures for isomeric polyimides.

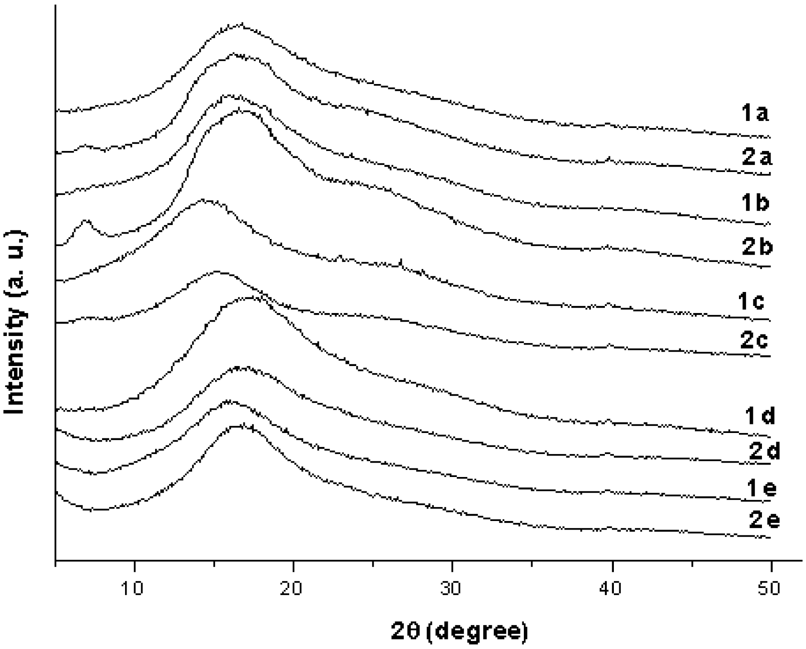


Fig. 8. WAXD curves for isomeric polyimide powders.

4. Conclusions

Cis-1,2,3,4-CHDA synthesized by a reported method could be converted to the *trans*-isomer by heating or refluxing in acetic anhydride. The process of thermal isomerization was monitored by ^{1}H NMR spectra and the mechanism of conversion was proposed. The molecular structures of *cis*- and *trans*-1,2,3,4-CHDAs were detailed by single crystal X-ray diffraction. Higher molecular weight polyimides from *trans*-1,2,3,4-CHDA were easily obtained by conventional one-step or two-step methods. However, higher molecular weight polyimides derived from *cis*-1,2,3,4-CHDA could not be prepared by the usual methods due to the formation of cyclic oligomers. Increasing the concentration of monomers could give higher molecular weight *cis*-polyimides. Polyimides based on *cis*-1,2,3,4-CHDA showed better solubility and higher T_gs than that of *trans*-polyimides. The dramatic isomeric effect in glass transition temperature and solubility may be attributed to the two imide groups locating one side of cyclohexane ring for the *cis*-polyimides, creating more steric hindrance and inhabiting chain rotation and chain packing. There are no marked differences in other properties such as thermal-oxidative stability, mechanical property, optical property, and morphology structures. Nevertheless, strong, flexible and colorless films were obtained from both isomers.

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