

# A Simple and Efficient Way to Synthesize Optically Active Polyamides by Solution Polycondensation of Di-*O*-Methyl-*L*-Tartaryl Chloride with Diamines

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**ABSTRACT:** A series of optically active polyamides containing di-*O*-methyl-*L*-tartaryl moieties in the main chain were synthesized by polycondensation of di-*O*-methyl-*L*-tartaryl chloride **5** with diamines and characterized by gel permeation chromatography, UV-vis, circular dichroism (CD), IR, and NMR spectroscopies. The polycondensation reaction could be carried out under mild conditions and the reaction time was short (2–3 h). The key monomer **5** prepared from *L*-tartaric acid via esterification, etherification, hydrolysis, and chlorination was easily purified by vacuum sublimation. These polyamides with number average molecular weights ranging from 14,000 to 35,000, displayed large opti-

cal activity in dimethyl sulfoxide solution, and their specific optical rotations oscillated between 87.2° and 210.7° depending on the structures of the diamines. The glass transition temperatures of these polyamides were in the range of 106–191°C, and the 10% mass loss occurred at temperature above 300°C. The polyamides derived from aromatic diamines exhibited higher  $T_g$  and thermal stability than those derived from aliphatic diamines. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3558–3567, 2010

**Key words:** di-*O*-methyl-*L*-tartaryl chloride; vacuum sublimation; optically active; synthesis; polyamides

## INTRODUCTION

Polyamides are widely recognized for their excellent thermal, mechanical, and chemical properties.<sup>1</sup> Some optically active polyamides can be used as chiral membrane separation materials or chiral stationary phases for high performance liquid chromatography because of the chiral recognition ability.<sup>2–6</sup> In recent years, the use of carbohydrate derivatives to prepare polyamides has received much attention, and the interest arises not only from the naturally occurring character of the feedstock but also from the potential that such polymers are used for biodegradable and biocompatible materials in the biomedical field.<sup>7–12</sup>

*L*-Tartaric acid ((2*R*, 3*R*)-(+)-2,3-dihydroxybutanedioic acid) is a naturally occurring aldaric acid and is suitable for the preparation of optically active polyamides. Tartaric acid-based polyamides were explored in the 1960–1980 by Minoura et al.<sup>13</sup> and Ogata et al.<sup>14,15</sup> Recently, a lot of work about a wide variety of stereoregular polytartaramides has been

carried out by Muñoz-Guerra and coworkers.<sup>11,16</sup> The atactic or even crosslinked polyamides were easily obtained via conventional direct polycondensation of monomers derived from tartaric acid and diamines at high temperatures. Muñoz-Guerra and coworkers used *L*-tartaric acid as the starting material via esterification, etherification, hydrolysis, and chlorination to produce di-*O*-methyl-*L*-tartaryl chloride **5**. The monomer **5** is not easily purified by common method such as recrystallization because it hydrolyzes during the treating process. Muñoz-Guerra directly converted **5** without separation into bis(pentachlorophenyl)-di-*O*-methyl-*L*-tartarate as activated diester, and then used the activated diester and *N,N'*-bis(trimethylsilyl)alkanediamines prepared from aliphatic diamines via trimethylsilylation to produce the polyamides.<sup>16,17</sup> This method involves multistep reaction pathways including diamines activation and a long time (3–4 days) of polycondensation. Another method used by Ogata et al. was the polycondensation reaction of dimethyl tartarate and aliphatic diamines in the presence of various polymer matrices.<sup>14,15</sup> It is tedious to remove the matrices from the products. Furthermore, the methods used by Muñoz-Guerra and Ogata are not suitable for preparing optically active polytartaramides derived from aromatic diamines owing to the fact that the reactivity of activated diester used by them

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is very low under mild conditions. There are few reports on chiral polytartaramides containing aromatic diamines in the main chain up to date.

In this article, we described a simple and efficient synthesis method for optically active polyamides by solution polycondensation of di-*O*-methyl-*L*-tartaryl chloride **5** with aromatic diamines **6a–e** and aliphatic diamine **6f**. The key monomer **5** is easily purified by vacuum sublimation with high yields (95%). Because of the high reactivity of monomer **5**, activation of diamine is not required and the polycondensation reaction time is shortened to 2–3 h. Inserting aromatic groups into the polytartaramides can enhance the mechanical and thermal properties of the polymers. Comparison is made in this work among the isometric polyamides (polyamides having the same number of main chain atoms in the repeating unit, such as **7c** and **7d**) to evaluate the effect of different structures on the properties of polytartaramides.

## EXPERIMENTAL

### Materials and characterization

The diamines, 4,4'-oxydianiline (**6a**), and *p*-phenylenediamine (**6c**) were purified by vacuum sublimation, and 3,4'-oxydianiline (**6b**), *m*-phenylenediamine (**6d**), and 1,6-hexanediamine (**6f**) were vacuum distilled before use. 2,2'-Bis (trifluoromethyl)-4,4'-diaminobiphenyl (**6e**) was prepared as described in the literature.<sup>18</sup> Solvents were dried and purified, when necessary, by appropriate standard procedures. All the other reagents were used as received from commercial sources unless otherwise specified. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker ARX 300 or ARX 400 spectrometer at ambient temperature with chloroform-*d* (CDCl<sub>3</sub>) or dimethyl sulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>) as the solvents, and tetramethylsilane (TMS) as an internal standard. IR spectra were taken with a Nicolet 360 FTIR spectrometer. Elementary analyses were run on an Elementar Vario EL instrument. Inherent viscosities were measured in *m*-cresol with an Ubbelodhe viscometer at 30°C. Specific optical rotations were measured on a JASCO P-1020 digital polarimeter at 20°C with a sodium lamp as the light source. Circular dichroism measurements were performed in dimethyl sulfoxide (DMSO) solution at 25°C on a JASCO J-700 apparatus fitted with a cell of an optical path length of 1 mm. UV-vis spectra were recorded on a Beckman DU-600 UV-vis spectrophotometer. Differential scanning calorimetry (DSC) was performed on a DuPont TA 2000 instrument at a heating rate of 10°C min<sup>-1</sup> under nitrogen flow. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere on a PerkinElmer TGA-6 thermobalance at a heating rate of 10°C min<sup>-1</sup>. Wide-angle X-ray diffraction pat-

terns were obtained at room temperature with a Rigaku XRD-RU 200 diffractionmeter (Cu K $\alpha$ , 40 mA, 30 kV), and samples were scanned from 0.2° to 60° at 4° min<sup>-1</sup>. The molecular weight and polydispersity of polyamides **7a–e** were determined by gel permeation chromatography (Waters 410 system), against poly (methyl methacrylate) (PMMA) standard using *N,N*-dimethyl formamide (DMF) as the eluent, and polymer **7f** (trifluoroacetylated samples) were measured in chloroform against polystyrene standard.

### Synthesis of the monomer

#### Synthesis of diethyl *L*-tartrate

In a 500-mL two-neck round-bottom flask, *L*-tartaric acid (30 g, 0.200 mol), concentrated sulfuric acid (0.3 mL), and carbon tetrachloride (40 mL) were added into 120 mL ethanol, and the mixture was heated to reflux. The water formed during the reaction was removed by azeotropic distillation. After the azeotrope was completely removed, the mixture was cooled to room temperature, sodium hydrogen carbonate was added to neutralize the acid, and the salty solid generated was separated by filtration. The filtrate was concentrated and distilled under reduced pressure to give **2** as a colorless liquid. Yield: 37.51 g (91%), bp: 116–118°C/1 mmHg,  $[\alpha]_D^{20}$ : +27.0° (*c* = 0.60 g/dL, H<sub>2</sub>O). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.34 (t, *J* = 7.2 Hz, 6H), 3.15 (s, 2H), 4.33 (q, *J* = 7.2 Hz, 4H), 4.54 (s, 2H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  13.60, 61.70, 71.91, 171.18. IR (KBr, cm<sup>-1</sup>): 3476 (O–H), 1746 (C=O). Anal. calcd. for C<sub>8</sub>H<sub>14</sub>O<sub>6</sub>: C, 46.60; H, 6.84. Found: C, 46.51; H, 6.79.

#### Synthesis of diethyl di-*O*-methyl-*L*-tartrate

A solution of diethyl *L*-tartrate (30 g, 0.145 mol) in dry ether (80 mL) was added dropwise to a suspension of sodium hydride (97%, 7.20 g, 0.291 mol) in dry ether (220 mL) at room temperature, and then stirred for 1 h. Methyl iodide (82.60 g, 0.582 mol) was added dropwise to the reaction mixture at room temperature. The mixture was refluxed for 2 h. The salty solid generated was removed by filtration. The clear filtrate was concentrated to give a residue, which was distilled under reduced pressure to give **3**. Yield: 28.07 g (82%), bp: 90–92°C/1 mmHg,  $[\alpha]_D^{20}$ : +82.0° (*c* = 0.50 g/dL, C<sub>2</sub>H<sub>5</sub>OH) (Ref. 19, +77.0°). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.33 (t, *J* = 7.2 Hz, 6H), 3.46 (s, 6H), 4.24 (s, 2H), 4.30 (q, *J* = 7.2 Hz, 4H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  13.76, 59.08, 60.71, 80.69, 168.59. IR (KBr, cm<sup>-1</sup>): 1759 (C=O). Anal. calcd. for C<sub>10</sub>H<sub>18</sub>O<sub>6</sub>: C, 51.27; H, 7.75. Found: C, 51.20; H, 7.80.

#### Synthesis of di-*O*-methyl-*L*-tartaric acid

3% NaOH (367 g, 0.275 mol) was added dropwise to a magnetic stirred solution of **3** (30 g, 0.128 mol) at

0–5°C for about 1 h, which continued to react at room temperature for 2 h. Concentrated HCl (36%, 29.37 g, 0.290 mol) was added dropwise to the mixture. After being stirred for 1 h, the solvent was evaporated under reduced pressure and the residue was dispersed in 300-mL boiling ethyl acetate-ethanol (6 : 1). The insoluble sodium chloride was removed by hot filtration. The filtrate was concentrated to produce the crude compound, which was recrystallized from ethyl acetate and methanol to give **4** as white prisms. Yield: 18.40 g (81%), mp: 156–157°C (Ref. 20, 155–157°C),  $[\alpha]_D^{20}$ : +85.2° ( $c = 0.15$  g/dL, C<sub>2</sub>H<sub>5</sub>OH) (Ref. 20, +84.0°). <sup>1</sup>H-NMR [300 MHz, dimethyl sulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>): δ 3.29 (s, 6H), 4.12 (s, 2H), 12.85 (s, 2H). <sup>13</sup>C-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 58.65, 80.50, 170.43. IR (KBr, cm<sup>-1</sup>): 3500–2500 (O–H), 1730 (C=O). Anal. calcd. for C<sub>6</sub>H<sub>10</sub>O<sub>6</sub>: C, 40.45; H, 5.66. Found: C, 40.48; H, 5.60.

#### Synthesis of di-*O*-methyl-*L*-tartaryl chloride

A mixture of di-*O*-methyl-*L*-tartaric acid (30 g, 0.168 mol), phosphorus pentachloride (70.01 g, 0.336 mol), and anhydrous benzene (300 mL) was stirred at room temperature for 30 min, and then heated to reflux for 1 h. After evaporation of solvent under reduced pressure and then direct sublimation, pure compound **5** was obtained as colorless prisms. Yield: 34.40 g (95%), mp: 90–92°C,  $[\alpha]_D^{20}$ : +76.1° ( $c = 0.30$  g/dL, DMSO). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 3.57 (s, 6H), 4.73 (s, 2H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>): δ 60.34, 87.21, 169.14. IR (KBr, cm<sup>-1</sup>): 1795 (C=O). Anal. calcd. for C<sub>6</sub>H<sub>8</sub>O<sub>4</sub>Cl<sub>2</sub>: C, 33.51; H, 3.75. Found: C, 33.55; H, 3.80.

#### Synthesis of polymers

A typical polymerization procedure was as follows. Aliphatic diamine (**6f**, 1 mmol) and pyridine (2.5 mmol) in 5-mL anhydrous chloroform were added dropwise under vigorous stirring to a solution of di-*O*-methyl-*L*-tartaryl chloride (1 mmol) in 3-mL anhydrous chloroform at 0°C, and the mixture was allowed to reach room temperature and continue to react for 2 h. The viscous solution was added slowly into ethanol (50 mL) and the precipitated solid was collected by filtration, washed thoroughly with ethanol and ether, and dried under vacuum at 80°C to produce the corresponding polyamide **7f**. The preparation of **7a–e** was about the same except using *N,N*-dimethylacetamide (DMAc) instead of chloroform and without pyridine (according to Ref. 21, with the DMAc as the solvent at polycondensation of diacyl chloride and diamine, it is not necessary to add bases to neutralize acids).

#### 7a

Yield: 93%. <sup>13</sup>C-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 59.38, 82.52, 118.51, 121.85, 133.78, 152.91, 167.66. IR (KBr, cm<sup>-1</sup>): 3381 (N–H), 1684 (C=O), 1601, 1499 (aromatic C=C), 832 (aromatic C–H).

#### 7b

Yield: 94%. <sup>13</sup>C-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 59.36, 82.49, 109.38, 113.11, 114.52, 119.42, 121.83, 129.80, 134.23, 139.77, 151.96, 157.52, 167.64. IR (KBr, cm<sup>-1</sup>): 3379 (N–H), 1684 (C=O), 1598, 1505 (aromatic C=C), 838, 780, 689 (aromatic C–H).

#### 7c

Yield: 94%. <sup>13</sup>C-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 59.43, 82.50, 120.37, 134.17, 167.66. IR (KBr, cm<sup>-1</sup>): 3290 (N–H), 1671 (C=O), 1604 (aromatic C=C), 1517 (N–H), 832 (aromatic C–H).

#### 7d

Yield: 93%. <sup>13</sup>C-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 59.35, 82.47, 112.41, 116.00, 128.60, 138.43, 167.82.

#### 7e

Yield: 91%. <sup>13</sup>C-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 59.60, 82.60, 117.13, 122.40, 125.12, 127.85, 131.58, 132.41, 138.53, 168.65. IR (KBr, cm<sup>-1</sup>): 3390 (N–H), 1699 (C=O), 1619, 1490 (aromatic C=C), 1517 (N–H), 895, 836 (aromatic C–H).

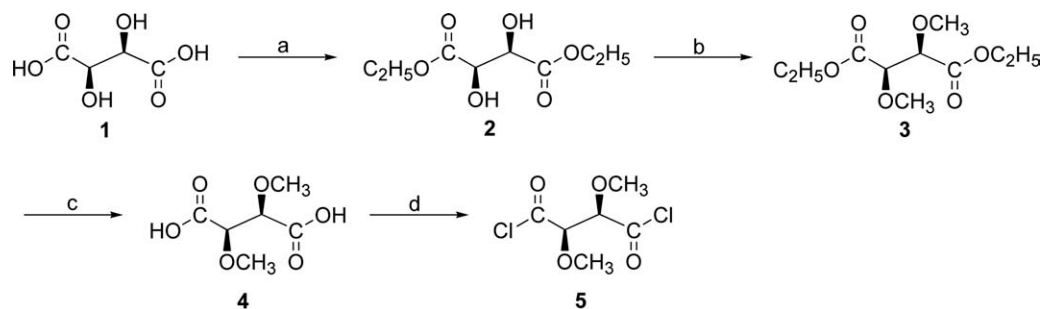
#### 7f

Yield: 92%. <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>): δ 26.38, 29.49, 38.99, 60.56, 82.25, 169.33. IR (KBr, cm<sup>-1</sup>): 3299 (N–H), 1657 (C=O), 1538 (N–H).

## RESULTS AND DISCUSSION

### Synthesis of the monomers

The key monomer, optically active di-*O*-methyl-*L*-tartaryl chloride, was synthesized from the naturally occurring *L*-tartaric acid in four steps as shown in Scheme 1. First, diethyl *L*-tartrate **2** was obtained by using ethanol as the esterification reagent and utilizing tetrachloromethane to remove the by-product water as an azeotrope, so that shortened the reaction time and decreased the quantity of ethanol used. According to the Ref. 19, using sodium hydride and methyl iodide as methylation reagent yielded **3**, subsequently, on hydrolysis in aqueous sodium hydroxide, produced the desired product **4**. It is noteworthy that hydrolysis reaction must be performed at



Reagents: (a)  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{CCl}_4$ ,  $\text{H}_2\text{SO}_4$ ; (b)  $\text{NaH}$ ,  $\text{Et}_2\text{O}$ ,  $\text{CH}_3\text{I}$ ; (c)  $\text{NaOH(aq)}$ ,  $\text{HCl}$ ; (d)  $\text{PCl}_5$ ,  $\text{C}_6\text{H}_6$

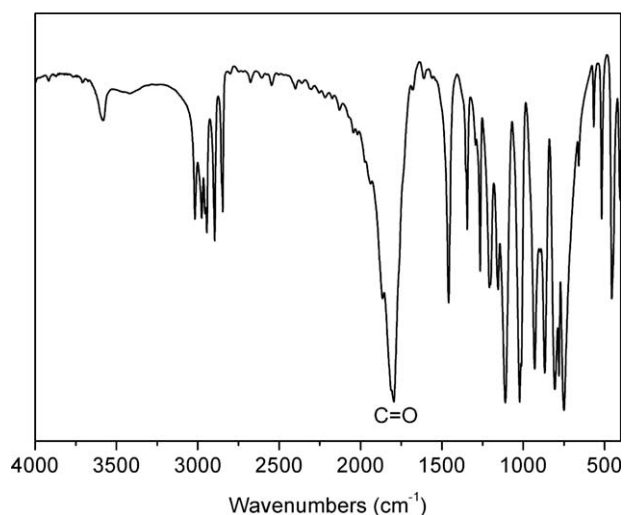
**Scheme 1** Synthesis of the monomer.

low temperature (not over  $30^\circ\text{C}$ ) to avoid racemizing of the diacid. The di-*O*-methyl-*L*-tartaric acid was treated with phosphorus pentachloride in benzene to give the crude product **5**. The analytically pure di-*O*-methyl-*L*-tartaryl chloride was obtained by vacuum sublimation, and di-*O*-methyl-*L*-tartaric acid anhydride, another possible product produced under this reaction conditions was excluded. The structures of compounds **2**–**5** were verified by FTIR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and elementary analyses. The IR spectra of the compound **4** showed characteristic carboxylic group absorption at near  $3500$ – $2500$  ( $\text{O-H}$  stretching) and  $1730\text{ cm}^{-1}$  ( $\text{C=O}$  stretching). For compound **5** (Fig. 1), the hydroxyl group stretching vibration disappeared, and the absorption bands associated with the carbonyl group appeared at  $1795\text{ cm}^{-1}$  ( $\text{C=O}$  stretching). Figure 2 shows the  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of compound **5**. The positions of the chemical shifts for protons were readily assigned and the areas of integration for the protons were consistent with the assignments.  $^{13}\text{C-NMR}$  data provided complementary information. In the  $^1\text{H-NMR}$  spectra of compound **5**, the peak for the carboxylic proton observed for compound **4** has disappeared. The resonances associated with the methyl and methine protons were observed at  $3.57$  and  $4.73$  ppm, respectively. In the  $^{13}\text{C-NMR}$  spectra of compound **5**, the resonance peaks of the methyl and methine carbons appeared at  $60.34$  and  $87.21$  ppm, respectively. The resonances associated with the carbonyl carbons appeared in relatively downfield region ( $169.14$  ppm). All the IR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectra data were consistent with the structure of compound **5**.

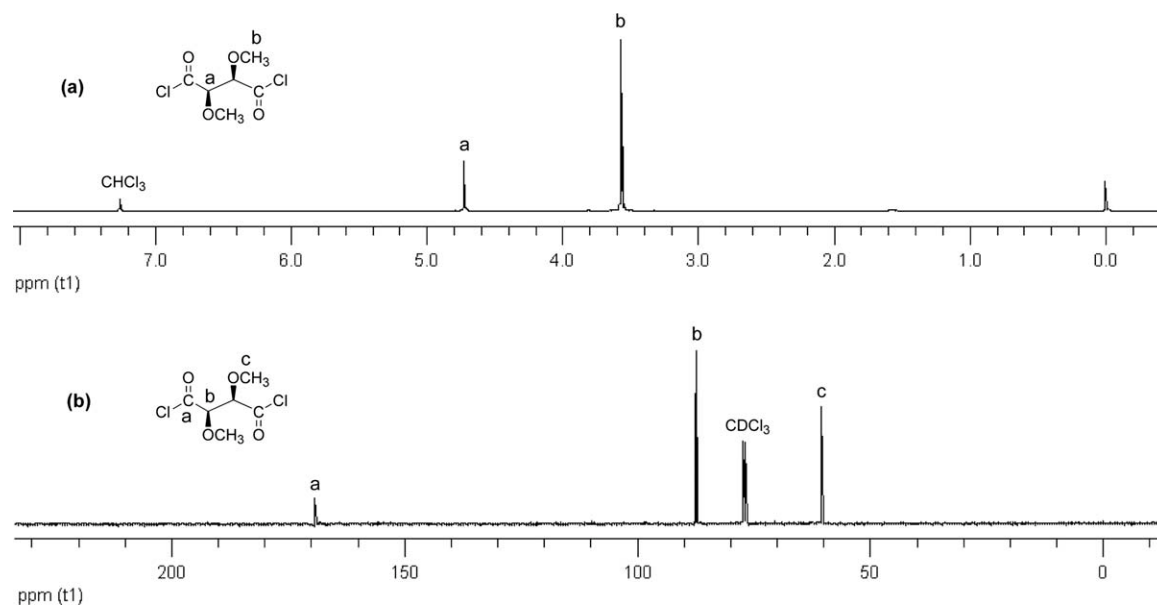
### Preparation of the polyamides

There were two methods of polycondensation of dicarboxylic acid chloride with diamine: solution polycondensation and interfacial polycondensation. Owing to the rapid hydrolysis of the aliphatic dicarboxylic acid dichloride and premature precipitation of the polymers, high-viscosity polyamides were

rarely obtained using the interfacial polycondensation method,<sup>9</sup> and therefore, the solution polycondensation method was used to prepare polyamides in this work (Scheme 2). The structures of the obtained polyamides were verified by FTIR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectroscopies. In the FTIR spectra, these polymers showed characteristic amide group absorptions at  $3390$ – $3290$  ( $\text{N-H}$  stretching),  $1699$ – $1657$  ( $\text{C=O}$  stretching) and  $1538$ – $1517\text{ cm}^{-1}$  ( $\text{N-H}$  deformation), which supported the formation of polyamides. Absorption peaks near  $1600$  and  $1500\text{ cm}^{-1}$  indicated the presence of benzene ring in the structure of polyamides **7a**–**e**. The main distinction of IR spectra between **7c** and **7d** was that deformation vibration for  $\text{C-H}$  in benzene ring appeared at  $832\text{ cm}^{-1}$  in **7c**, whereas at  $783$  and  $689\text{ cm}^{-1}$  in **7d**, which could be attributed to the different site of substituted group at the aromatic ring. The IR spectra of **7a** and **7b** exhibited similar differences. In the  $^1\text{H-NMR}$  spectra (Fig. 3), the chemical shifts and the intensities were consistent with the structures expected for these polyamides, the amido group protons of **7a**–**e** derived from aromatic diamines



**Figure 1** FTIR spectrum of di-*O*-methyl-*L*-tartaryl chloride.



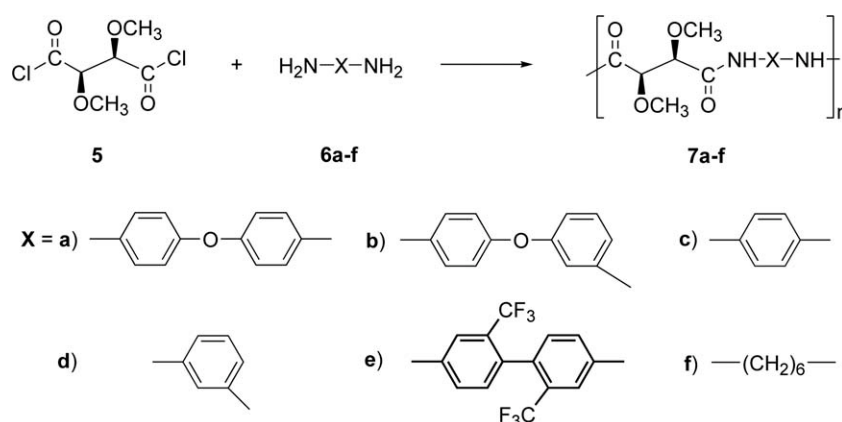
**Figure 2** NMR spectra of di-*O*-methyl-L-tartaryl chloride in  $\text{CDCl}_3$ : (a)  $^1\text{H}$ -NMR (300 MHz) and (b)  $^{13}\text{C}$ -NMR (400 MHz).

were observed between 9.79 and 10.37 ppm as broad singlet, whereas the corresponding protons of **7f** appeared at 6.75 ppm because of different chemical environment of amido in the polymers. The presence of the multiply peaks around 6.68–8.33 in polyamides **7a–e** suggested the incorporation of the benzene ring unit in the backbone. The resonances peaks at 4.22–4.27 ppm attributed to the methine protons in the tartaric moiety were clearly visible. We have also noticed that methoxyl peak in **7d** could not be discriminated because it overlapped with the peak of water protons in DMSO solvent. In  $^{13}\text{C}$ -NMR spectra, resonances associated with the carbonyl carbon of the amide group appeared in the relatively downfield region (167.64–169.33), the chemical shift of the aromatic carbons in **7a–e** located at 109.38–157.52, the resonances peaks at 59.35–60.56 and 82.25–82.60 were also clear visible, which were attributed to the methoxyl and methine carbons in the polymers. The molec-

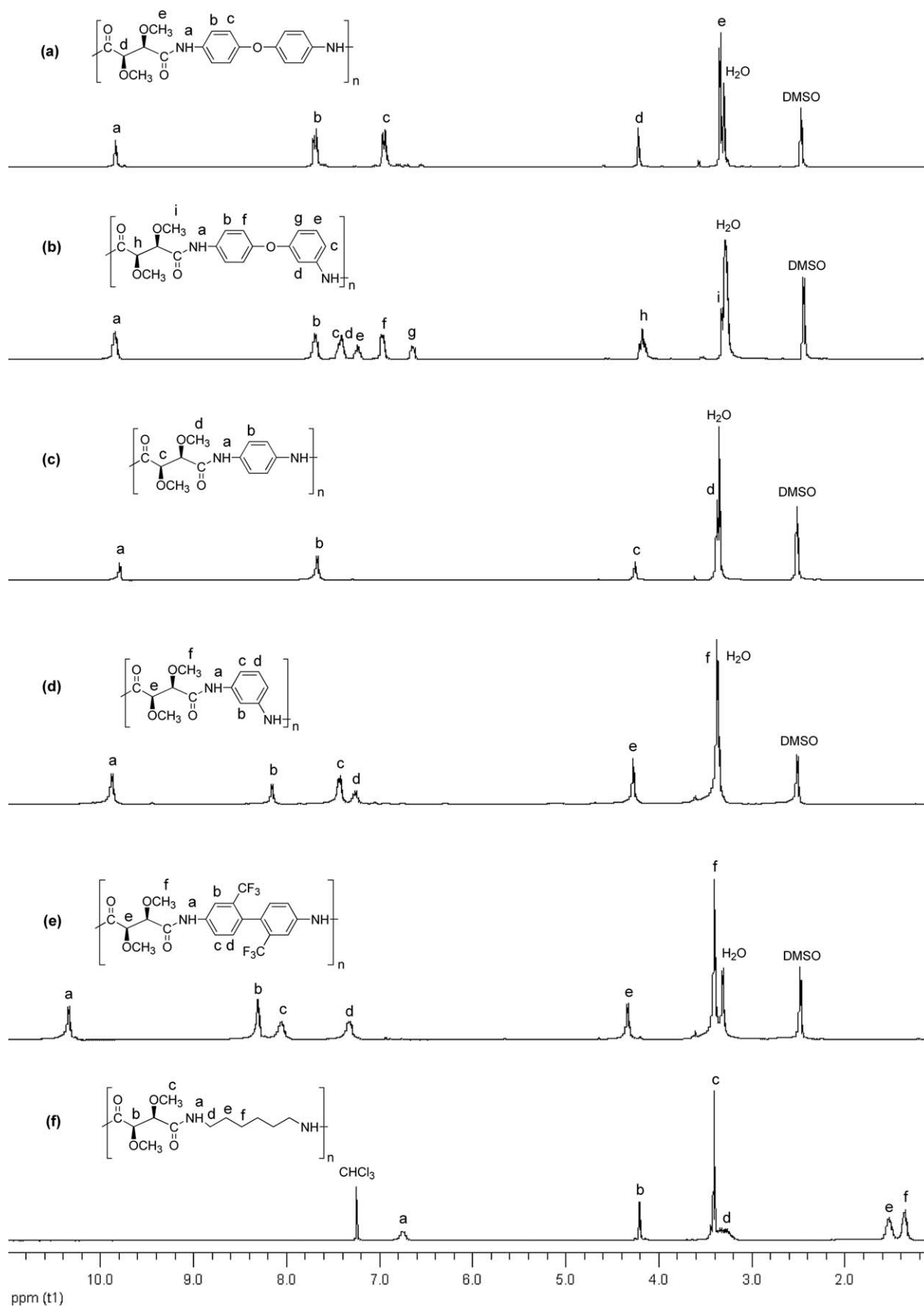
ular weights of polyamides **7a–e** were determined by GPC with DMF as the eluent, calibrated against PMMA standard. According to Ref. 16, **7f** was first trifluoroacetylated, then eluted with chloroform, the calibration being based on PS standard. The results are presented in Table I. Number average molecular weights of the prepared polymers were between  $1.4 \times 10^4$  and  $3.5 \times 10^4$ , with polydispersities ( $M_w/M_n$ ) ranging from 1.44 to 1.71. When compared with Refs. 9 and 16, solution polycondensation of di-*O*-methyl-L-tartaryl chloride with diamines to prepare optically active polyamides does not need activation of the diamines and is characterized with shorter reaction time.

### Solubility

The solubility of these polyamides **7a–f** was tested in a series of solvents of different nature, and the results are summarized in Table II. All these



**Scheme 2** Synthesis of polymers **7a–f**.



**Figure 3**  $^1\text{H-NMR}$  (300 MHz) spectra of polyamides (a) **7a**, (b) **7b**, (c) **7c**, (d) **7d**, (e) **7e** in  $\text{DMSO-}d_6$ , and (f) **7f** in  $\text{CDCl}_3$ .

TABLE I  
Synthesis Results

| Polyamides | $[\eta]$ (dL/g) <sup>a</sup> | $M_n$ <sup>b</sup> | $M_w$ <sup>b</sup> | $M_w/M_n$ | $[\alpha]_D^{20}$ (°) <sup>c</sup> |
|------------|------------------------------|--------------------|--------------------|-----------|------------------------------------|
| 7a         | 0.48                         | 28,000             | 42,000             | 1.50      | 151.2                              |
| 7b         | 0.39                         | 23,000             | 34,000             | 1.48      | 131.3                              |
| 7c         | 0.69                         | 35,000             | 55,000             | 1.57      | 210.7                              |
| 7d         | 0.33                         | 16,000             | 23,000             | 1.44      | 183.1                              |
| 7e         | 0.55                         | 32,000             | 54,000             | 1.69      | 111.4                              |
| 7f         | 0.43                         | 14,000             | 24,000             | 1.71      | 87.2                               |

<sup>a</sup> Polymers 7a–f were first dissolved in *m*-cresol at 60°C, and then cooled to 30°C. After dissolution, the inherent viscosities of polymers 7a–f were measured at 0.5 g/dL in *m*-cresol at 30°C.

<sup>b</sup> 7a–e molecular weights were determined by GPC in DMF based on PMMA standards. 7f was determined by GPC of the trifluoroacetylated samples in CHCl<sub>3</sub>, and calibrated against polystyrene standards.

<sup>c</sup> Specific optical rotations of polymers were measured at 20°C in DMSO,  $c = 0.10$  g/dL.

polyamides exhibited good solubility in trifluoroacetic acid and were also soluble in phenolic solvent *m*-cresol on heating at 60°C. The polyamides derived from aromatic diamines, except for 7c, were soluble in polar aprotic solvents such as DMF, DMAc, and NMP. The poor solubility of 7c in these solvents is possibly due to the rigid nature of the benzene moiety and the symmetric substitution in benzene ring, which enhance the close packing of the polymer chain. These polyamides were insoluble in common organic solvents such as diethyl ether and ethanol, and also insoluble in water, although there were hydrophilic methoxyl groups in the polymer chains. When compared with 7a–d, polymer 7e was partially soluble in chloroform and tetrahydrofuran due

to the introduction of trifluoromethyl group into the benzene ring, which hinders the interaction between neighboring molecules.<sup>18</sup>

### Optical activity

Because of the asymmetry of the tartaric unit, all these polyamides exhibited large optical activity. The specific optical rotations were measured in DMSO solvent and the data are listed in Table I. The values of all these polyamides were higher than that of monomer 5 building up into the polymers. As expected, the optical activity of polyamides 7c (+210.7°) and 7d (+183.1°) were much larger than that of polymer 7f (+87.2°), which can be explained clearly in terms of the differences in rigidity of their backbones. Hexamethylene group is more flexible than the benzene ring, so that 7f can change more easily the molecular conformation in solution. It should be noticed that specific optical rotation displayed by 7c is significantly higher than that of the positional isomer polymer 7d. Such a difference may

TABLE II  
Solubility of Polyamides 7a–f

| Solvent <sup>b</sup> | Solubility <sup>a</sup> |    |    |    |    |    |
|----------------------|-------------------------|----|----|----|----|----|
|                      | 7a                      | 7b | 7c | 7d | 7e | 7f |
| Water                | --                      | -- | -- | -- | -- | -- |
| Diethyl ether        | --                      | -- | -- | -- | -- | -- |
| Ethanol              | --                      | -- | -- | -- | -- | -- |
| Chloroform           | --                      | -- | -- | -- | -+ | ++ |
| Pyridine             | --                      | -- | -- | -- | -- | -- |
| Tetrahydrofuran      | --                      | -- | -- | -- | -+ | -- |
| Formic acid          | --                      | -- | -- | -- | -- | ++ |
| DMF                  | ++                      | ++ | -+ | ++ | ++ | -- |
| DMAc                 | ++                      | ++ | -+ | ++ | ++ | -- |
| NMP                  | ++                      | ++ | -+ | ++ | ++ | -- |
| DMSO <sup>c</sup>    | ++                      | ++ | -+ | ++ | ++ | -+ |
| <i>m</i> -cresol     | +-                      | +- | +- | +- | ++ | +- |
| TFA                  | ++                      | ++ | ++ | ++ | ++ | ++ |

<sup>a</sup> Solubility: measured at a polymer concentration of 0.50 g/dL. (--) insoluble; (-+) partially soluble or slightly swollen; (+-) soluble on heating at 60°C; (++) soluble at room temperature.

<sup>b</sup> DMF: *N,N*-dimethylformamide; DMAc: *N,N*-dimethylacetamide; NMP: *N*-methyl-2-pyrrolidone; DMSO: dimethyl sulfoxide; TFA: trifluoroacetic acid.

<sup>c</sup> Polymers 7c and 7d were soluble in DMSO at 20°C,  $c = 0.10$  g/dL.

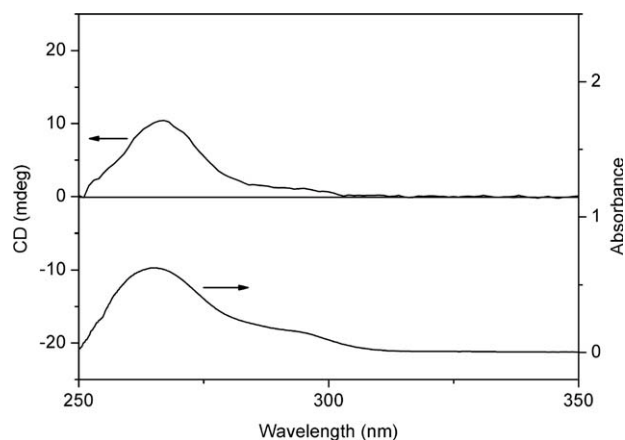


Figure 4 UV-vis absorption and CD spectra of polymer 7e in DMSO at 25°C. Concentration:  $3 \times 10^{-5}$  (repeating unit) mol/L.

TABLE III  
Thermal Properties of Polyamides 7a–f

| Polymer | DSC <sup>a</sup> |            | TGA <sup>b</sup> |              |                |              |                |              |                |
|---------|------------------|------------|------------------|--------------|----------------|--------------|----------------|--------------|----------------|
|         | $T_m$ (°C)       | $T_g$ (°C) | $T_{10\%}$ (°C)  | $T_d^1$ (°C) | $\Delta W$ (%) | $T_d^2$ (°C) | $\Delta W$ (%) | $T_d^3$ (°C) | $\Delta W$ (%) |
| 7a      | –                | 179        | 329              | 346          | 70             | 443          | 53             | 639          | 32             |
| 7b      | –                | 157        | 324              | 343          | 75             | 423          | 56             | 612          | 38             |
| 7c      | –                | 185        | 352              | 396          | 65             | 606          | 13             |              |                |
| 7d      | –                | 166        | 323              | 334          | 83             | 601          | 30             |              |                |
| 7e      | –                | 191        | 344              | 364          | 64             | 594          | 28             |              |                |
| 7f      | 223              | 106        | 303              | 311          | 84             | 469          | 43             | 660          | 11             |

<sup>a</sup> DSC data;  $T_g$ : glass transition temperature recorded on heating from quenched sample at a rate of 10°C min<sup>-1</sup>.

<sup>b</sup> TGA data;  $T_{10\%}$ : temperature at which 10% of the initial mass was lost.  $T_d^1$ ,  $T_d^2$ ,  $T_d^3$ : the temperature at the maximum degradation rate on step I, II, and III, respectively.  $\Delta W$ : the remaining weight of the initial mass at the corresponding  $T_d$ .

suggest different conformations between the two polyamides. 7a and 7b also displayed the similar differences. Figure 4 shows the UV–vis absorption and circular dichroism (CD) spectra of polymer 7e in dilute DMSO solution. The CD spectrum exhibited a positive Cotton effect at 250–290 nm, which was mainly attributed to the  $\pi \rightarrow \pi^*$  transition of the phenyl group in polyamide 7e. Polymers 7a–d gave similar CD behavior as polymer 7e. All these results indicated that the aromatic rings of the polymers 7a–e were located in a chirally perturbed environment in DMSO solution.

### Thermal properties

The thermal behavior of these polyamides has been comparatively studied by DSC and TGA, and the results are listed in Table III. The typical DSC curves of the polyamides are displayed in Figure 5. Except for 7f, all these polyamides didn't show well-defined melting peak in DSC traces indicating an amorphous

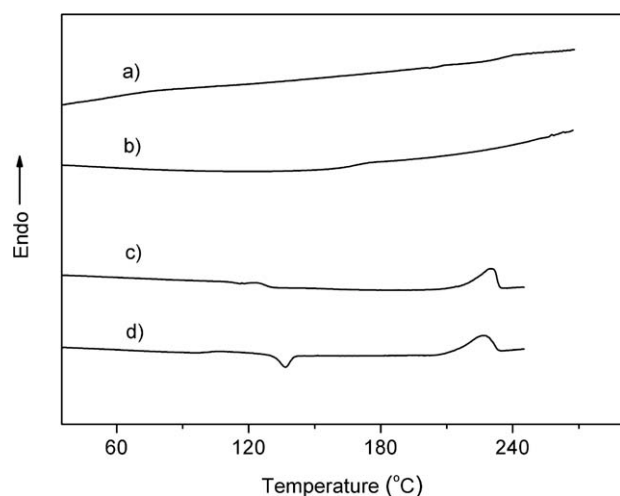


Figure 5 DSC traces of polyamides 7d and 7f (heating rate: 10°C/min): (a) 7d, sample directly from synthesis, (b) 7d, second heating after rapid cooling, (c) 7f, sample directly from synthesis, and (d) 7f, second heating after rapid cooling.

character of these samples, which was also confirmed by wide-angle X-ray diffraction patterns. The possible reason is that these polymers 7a–e do not easily crystallized when they are precipitated from DMAc with ethanol. The WAXD trace for polyamide 7e is shown in Figure 6, and it is consistent with that reported by Muñoz-Guerra.<sup>17</sup> The  $T_g$  of the polymers 7a–f were in the range of 106–191°C depending on the structure of the diamines moiety. As expected, polyamides 7c and 7d with benzene ring in the polymers backbone had higher  $T_g$  values, whereas polymer 7f with a flexible linkage exhibited a lower  $T_g$ . Because of the symmetry of the *p*-phenylene moiety in the polymer backbone, the  $T_g$  of 7c was higher than that of the positional isomer 7d, and polymers 7a and 7b showed similar differences.

The thermal stability of polyamides 7a–f was evaluated by TGA. The temperatures of 7c and 7d at 10% mass loss in nitrogen atmosphere were 352 and 323°C, respectively, which were higher than that of polymer 7f (303°C). The TGA data indicated that the polymers derived from aromatic diamines had higher thermal stability than those derived from aliphatic diamines. Decomposition of polyamides 7a,

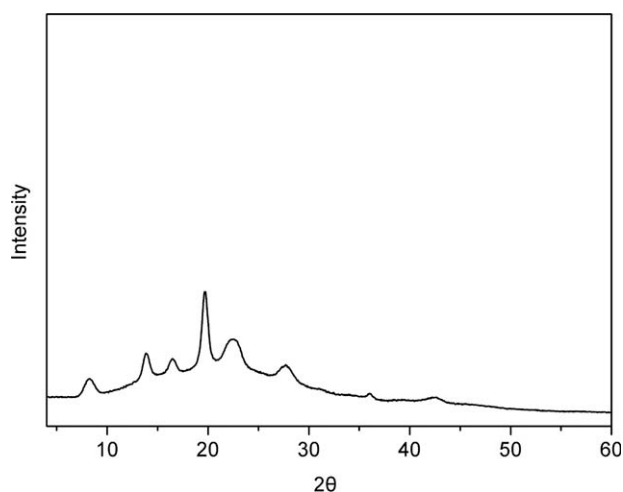
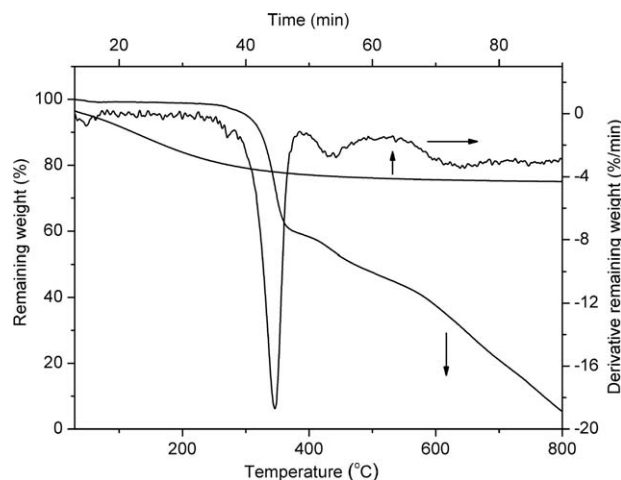


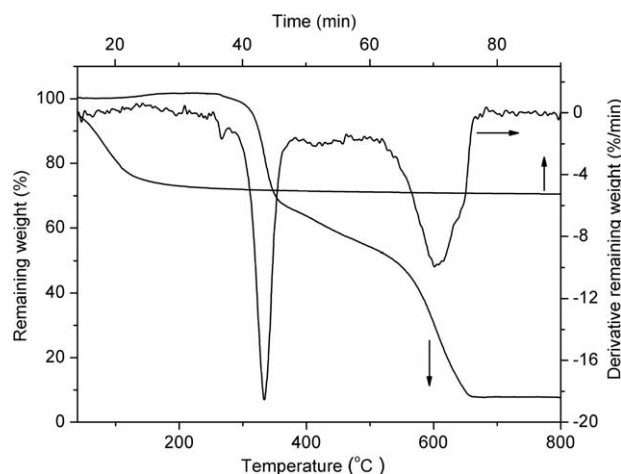
Figure 6 WAXD pattern of polyamide 7f.



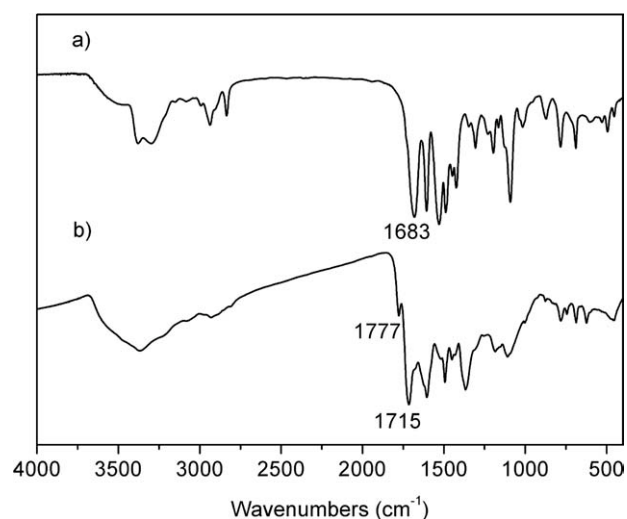


**Figure 7** TGA traces of **7a**. The isothermal trace was recorded at 290°C.

**7b**, and **7f** was found to occur in three stages, whereas that of **7c–e** consisted of two steps. In the first stage, the temperature at the maximum degradation rate ranged from 311 to 396°C, with the corresponding remaining mass of initial sample between 65% and 84%. The second and the third stages appeared at above 420°C. Decomposition at higher temperatures (above 420°C) is known to happen by extensive scission of main chain C–C bonds to produce volatile compounds and carbonaceous residues and ashes.<sup>22</sup> The regular trend observed in the first decomposition step is interesting and deserving of specific attention. Representative TGA curves for polyamides **7a** and **7d** are shown in Figures 7 and 8, respectively. Polymer **7d** was found to lose 30% mass on isothermal heating at 310°C for 1.5 h. Because the degraded sample of polymer **7d** was not soluble in solvent, the valuable data of <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopies were not obtained. The IR spectra of the residue and the original polymer **7d**



**Figure 8** TGA traces of **7d**. The isothermal trace was recorded at 310°C.

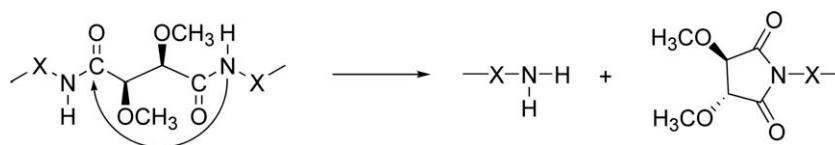


**Figure 9** FTIR of **7d**: (a) Pristine sample and (b) residue after heating at 310°C for 90 min.

are shown in Figure 9. The bands at 1777 and 1715  $\text{cm}^{-1}$  and no peak at 1683  $\text{cm}^{-1}$  (C=O stretching) were observed in the spectrum of the degraded sample, which revealed that the cyclic imide structures were produced in the residue. The absorption above 3000  $\text{cm}^{-1}$  broadened, intensified, and shifted to higher wavenumber values, indicating that amino groups have formed in the thermal decomposition. The similar results were obtained from the analysis of the residue of polyamide **7a** on heating at 290°C for 1.5 h. The imidation reaction probably occurred in the first decomposition step of polyamides **7a–f** is depicted in Scheme 3. A mechanism based on imide formation during the pyrolysis due to the intramolecular nucleophilic attack of the amidic nitrogen to the neighboring carbonyl carbon of the amide group has been reported in the literature.<sup>22,23</sup>

## CONCLUSIONS

In this article, a simple and convenient method for preparing optically active polytartaramides by solution polycondensation of di-*O*-methyl-*L*-tartaryl chloride **5** with diamines was described. The reaction could be carried out under mild conditions and high molecular weight polymers were easily obtained. Because of the high reactivity of the acyl chloride **5**, activation of diamine was not required and the polycondensation reaction time was shortened. Di-*O*-methyl-*L*-tartaryl chloride was easily purified by vacuum sublimation. As expected, all these polyamides exhibited large optical activity in DMSO solution. They were soluble in trifluoroacetic acid. The polyamides derived from aromatic diamines displayed higher  $T_g$  and thermal stability than those derived from aliphatic diamines. Thermal degradation of these polymers was possible to happen through



**Scheme 3** The imidation reactions of polymers **7a–f** in the first decomposition step.

imide cyclization reaction, which was confirmed by IR spectroscopy. Further studies on these polyamides as chiral membrane separation materials and chiral stationary phases for high performance liquid chromatography are in progress.

## References

- Lin, J.; Sherrington, D. C. *Adv Polym Sci* 1994, 111, 179.
- Wulff, G. *Angew Chem Int Ed Engl* 1989, 28, 21.
- Saigo, K.; Shiwaku, T.; Hayashi, K.; Fujioka, K.; Sukegawa, M.; Chen, Y.; Yonezawa, N.; Hasegawa, M. *Macromolecules* 1990, 23, 2830.
- Okamoto, Y.; Nakano, T. *Chem Rev* 1994, 94, 349.
- Goto, H.; Zhang, H. Q.; Yashima, E. *J Am Chem Soc* 2003, 125, 2516.
- Ikeuchi, Y.; Nakagawa, M.; Yoshikawa, M.; Yoshida, H.; Sakurai, S. *J Polym Sci Part A: Polym Chem* 2009, 47, 2530.
- Kiely, D. E.; Chen, L.; Lin, T. H. *J Am Chem Soc* 1994, 116, 571.
- Orgueira, H. A.; Erra-Balsells, R.; Nonami, H.; Varela, O. *Macromolecules* 2001, 34, 687.
- Mancera, M.; Roffé, I.; Al-kass, S. S. J.; Rivas, M.; Galbis, J. A. *Macromolecules* 2003, 36, 1089.
- Kenawy, E.-R.; Abdel-Hay, F. I.; Shahada, L.; El-Shanshoury, A. E.-R. R.; El-Newehy, M. H. *J Appl Polym Sci* 2006, 102, 4780.
- Marín, R.; Martínez de Ilarduya, A.; Romero, P.; Sarasua, J. R.; Meaurio, E.; Zura, E.; Muñoz-Guerra, S. *Macromolecules* 2008, 41, 3734.
- Varela, O.; Orgueira, H. A. *Adv Carbohydr Chem Biochem* 2000, 55, 137.
- Minoura, Y.; Urayama, S.; Noda, Y. *J Polym Sci Part A-1: Polym Chem* 1967, 5, 2441.
- Ogata, N.; Sanui, K.; Nakamura, H.; Kuwahara, M. *J Polym Sci Polym Chem Ed* 1980, 18, 939.
- Ogata, N.; Sanui, K.; Tanaka, H.; Matsuo, H.; Iwaki, F. *J Polym Sci Polym Chem Ed* 1981, 19, 2609.
- Bou, J. J.; Rodríguez-Galán, A.; Muñoz-Guerra, S. *Macromolecules* 1993, 26, 5664.
- Iribarren, I.; Alemán, C.; Bou, J. J.; Muñoz-Guerra, S. *Macromolecules* 1996, 29, 4397.
- Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N. *Macromolecules* 1991, 24, 5001.
- Shishido, K.; Takahashi, K.; Fukumoto, K. *J Org Chem* 1987, 52, 5704.
- Felner, I.; Schenker, K. *Helv Chim Acta* 1970, 53, 754.
- Mansour, E. M. E.; Kandil, S. H.; Hassan, H. H. A. M.; Shaban, M. A. E. *Eur Polym J* 1990, 26, 267.
- Regaño, C.; Martínez de Ilarduya, A.; Iribarren, J. I.; Muñoz-Guerra, S. *J Polym Sci Part A: Polym Chem* 2000, 38, 2687.
- Regaño, C.; Alla, A.; Martínez de Ilarduya, A.; Muñoz-Guerra, S. *Macromolecules* 2004, 37, 2067.