Polymer 53 (2012) 5706-5716

Contents lists available at SciVerse ScienceDirect

Polymer



journal homepage: www.elsevier.com/locate/polymer

Novel soluble and optically active polyimides containing axially asymmetric 9,9'-spirobifluorene units: Synthesis, thermal, optical and chiral properties

Zuolin Wu, Baochun Han, Chunhua Zhang, Danyang Zhu, Lianxun Gao, Mengxian Ding, Zhenghua Yang*

Polymer Composites Engineering Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

A R T I C L E I N F O

Article history: Received 10 July 2012 Received in revised form 6 October 2012 Accepted 12 October 2012 Available online 22 October 2012

Keywords: Polyimides Optically active Spirobifluorene

ABSTRACT

A new optically active spirobifluorene-based diamine monomer, (*R*)-2,2'-bis(4-amino-2-trifluoromethylphenoxy)-9,9'-spirobifluorene, was synthesized using (*R*)-2,2'-dihydroxy-9,9'-spirobifluorene as starting material. The absolute stereochemistry of the chiral diamine was determined by single crystal Xray diffraction. A series of novel chiral polyimides were prepared from the diamine with various aromatic dianhydrides via a two-stage process with chemical imidization method. All these optically active polyimides were readily soluble in many organic solvents and could afford flexible, tough and transparent films with an UV–vis absorption cutoff wavelength at 351–375 nm. The glass transition temperatures of these polyimides were recorded between 262 and 281 °C by differential scanning calorimetry, and the 5% weight loss occurred at temperatures above 510 °C. The specific rotations of these chiral polyimides ranged from -48.5° to $+73.0^{\circ}$ depending on the structures of the aromatic dianhydrides. All the optically active polyimides exhibited high chiral stability in solid state or in DMAc solvent at high temperature due to introduction of chiral spirobifluorone group into polymer backbones. The circular dichroism (CD) spectroscopic properties of these chiral polyimides in tetrahydrofuran solutions were also studied.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Chiral phenomena play important roles in nature. Many important naturally occurring polymers, such as proteins, DNA, and polysaccharides are optically active. The design, synthesis and characterization of chiral polymers are of particular interest from the viewpoint of material science. Chiral polymers have been successfully used in chiral chromatographic separation of enantiomers [1–3], chiral liquid crystals [4,5], non-liner optical devices [6], optical switches [7], biodegradable materials [8], etc. A direct and effective way for synthesizing optically active polymers is to introduce chiral elements into the polymer backbone or the side chains.

Aromatic polyimides are well known as high performance polymer materials because of their good chemical resistance, high mechanical strength, and excellent thermal stability [9–11]. The introduction of chiral structure units into polyimide backbone is expected to affect the packing of polymer chains and impose noncentrosymmetric structures and may, therefore, lead to different physical properties. Recently, several optically active polyimides have been synthesized, and their chiroptical properties have been investigated [12–16]. However, most of aromatic polyimides have high melting or glass transition temperatures (T_g) and limited solubility in most organic solvents because of their rigid backbones and strong intermolecular interactions, which may restrict their applications in some fields. Therefore, many studies have been made to enhance their processability and solubility while other advantageous polymer properties are retained either by introducing flexible linkages [17–21], bulky lateral groups [22– 26], noncoplannar structures [27–29] and spiroskeletons [30,31] into the polymer backbones. Recent studies demonstrated that polyimides derived from ether bridged aromatic diamines with trifluoromethyl (CF₃) group were generally soluble high temperature polymer materials with low dielectric constant and high optical transparency [32–36].

It has been reported that the spirobifluorene monomer consists of two identical fluorene moieties, connected through a common tetra coordinate carbon atom. In the spiro segment, the rings of the connected bifluorene entities are orthogonally arranged. The resulting polyimides would be expected to have a polymer backbone periodically twisted by an angle of 90° at each spiro center. This structure would restrict the close packing of the polymer chains, thereby reducing the probability of interchain interactions, resulting in higher polymer solubility [37–41]. Additionally, for the spiroannulated segment, the rigidity of the polymer backbone would be preserved. More importantly, in spiro segment, two rings

^{*} Corresponding author. Tel.: +86 431 85262272; fax: +86 431 85685653. *E-mail address*: zhhyang@ciac.jl.cn (Z. Yang).

^{0032-3861/\$ -} see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.polymer.2012.10.024

connected at a quaternary center through σ -bonds, which make racemization of chiral spiro compounds virtually impossible [42]. Recently, a large number of chiral small molecule derived from optically active 1,1'- or 2,2'- dihydroxyspirobifluorene have been synthesized and used in asymmetric catalysis with excellent enantioselectivities [42–47]. However, up to now, the literature on the structure and properties of optically active polymers with chiral spirobifluorene unit are few [48,49].

In this article, we reported the synthesis of a new optically active diamine monomer, (*R*)-2,2'-bis(4-amino-2-trifluoromethylpheno-xy)-9,9'-spirobifluorene, and its use in the preparation of soluble and chiral polyimides by the reaction of the diamine with aromatic dianhydrides. To the best of our knowledge, this is the first case of producing optically active polyimides containing axially asymmetric 9,9'-spirobifluorene skeleton at the polymer backbones. The solubility, crystallinity, thermal, optical and chiral properties of these polyimides were investigated. Optically inactive polyimides based on (\pm) -2,2'-bis(4-amino-2-trifluoromethylphenoxy)-9,9'-spirobifluorene have also been prepared for comparison.

2. Experimental

2.1. Materials

(*R*,*R*)-(+)-2,3-dimethoxy-*N*,*N*,*N*',*N*'-tetracyclohexylsuccinamide was synthesized in five steps from (R,R)-(+)-tartaric acid [50,51]. Optically active ((R)-(+)) and inactive 2,2'-dihydroxy-9,9'-spirobifluorene were prepared according to the literature [44]. Commercially available 2-fluoro-5-nitrobenzotrifluoride (from Aldrich). potassium carbonate (from Acros), hydrazine monohydrate (from Acros) and 10% palladium on activated charcoal (Pd/C) (from Fluka) were used as received. 4,4'-oxydiphthalic anhydride (ODPA, from Acros) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, from Acros) were recrystallized from acetic anhydride. 2,2'bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA, from TCI) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, from TCI) were sublimated before use. N,N'-dimethylacetamide (DMAc, from FLuka) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Other commercially available materials were used without further purification.

2.2. Measurement

¹H NMR and ¹³C NMR spectra were recorded on a Brucker AMX 600 spectrometer with chloroform-d (CDCl₃) or dimethylsulfoxide d_6 (DMSO- d_6) as the solvents, and tetramethylsilane (TMS) as the internal reference. IR spectra were taken with a Nicolet 360 FTIR spectrometer. Elemental analysis was run on an Elementar Vario EL instrument. Ultraviolet-visible (UV-vis) spectra were recorded on a Beckman DU-600 UV-vis spectrophotometer. Melting points were measured by WBR-IB melting point digital apparatus. MALDI-FTICR MS spectra were taken on a Bruker Apex II FTICR mass spectrometer. Chromatographic separation of the racemates was accomplished on a JASCO HPLC system equipped with a UV (254 nm) detector using a DAICEL –AD-H column. The X-ray structure measurement was performed on a Rigaku Satum 724 CCD single crystal X-ray diffractmeter. Detector equipped with graphite monochromatic Mo K α radiation ($\lambda = 0.7107$ Å). Structure analysis was performed utilizing the SHELXTL/PC program. 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 (CD) spectra were carried out at 25 °C on a JASCO J-700 apparatus fitted with a cell of an optical path length of 1 mm. Inherent viscosities were measured at a concentration of 0.5 g/dL in DMAc

with an Ubbelodhe viscometer at 30 °C. Molecular weights were obtained via gel permeation chromatography (GPC) on the basis of polystyrene calibration using Waters 2410 as an apparatus and N,Ndimethylformamide (DMF) as the eluent. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 system at a heating rate of 20 °C min⁻¹ under nitrogen flow. Glass transition temperature (T_g) was read as the midpoint temperature of the heat capacity jump and was taken from the second heating scan after a quick cooling down from 360 °C to room temperature. Thermogravimetric analysis (TGA) was performed under nitrogen and air atmosphere on a Perkin-Elmer TGA-6 thermobalance at a heating rate of 10 °C min⁻¹. Dynamic mechanical thermal analysis (DMA) was performed on thin film specimens (length: 30 mm, width: 6.5 mm, and thickness: $30-60 \,\mu\text{m}$) by using a TA instrument DMA RSA II at a heating of 5 °C min⁻¹, with a load frequency of 1 Hz in air. The peak on the tan δ as a function of temperature curves was regarded as the T_{g} of the films. The tensile properties were performed on an Instron 3365 Tensile Apparatus with a load cell of 5 kg at a drawing speed of 5 mm min⁻¹ on strips approximately 50– $80 \ \mu m$ thick and 0.5 cm wide with a 4 cm gauge length. An average of at least five individual determinations was used. Water uptakes were determined by weighing the changes of polyimide films before and after immersion in deionized water at 25 °C for 3 days. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature with a Siemens Kristalloflex D5000 X-ray diffractionmeter (Cu Ka, 40 kV, 30 mA), and samples were scanned from 2° to 60° at 2° min⁻¹.

2.3. Monomer synthesis

2.3.1. Optical resolution of (\pm) -2,2'-dihydroxy-9,9'-spirobifluorene

(±)-2,2'-dihydroxy-9,9'-spirobifluorene (DHSBF, 2.0 g, 5.74 mmol) and (*R*,*R*)-(+)-2,3-dimethoxy-*N*,*N*,*N*'-tetracyclohexylsuccinamide ((*R*,*R*)-(+)-DMTCHS, 2.90 g, 5.74 mmol) were dissolved in ethanol (25 mL). The mixture was stirred at room temperature for 12 h. The precipitated white solid was collected by filtration. The crude product was recrystallized from ethanol three times to give a complex [(1:1 clathrate of (*R*)-DHSBF and (*R*,*R*)-(+)-DMTCHS)] as colorless prisms (2.08 g, 85%). Mp: 237–239 °C (literature [44] 236–238 °C). The complex was dissolved in 50 mL of benzene and washed with 1 N NaOH. The aqueous layer was acidified by concentrated HCl and extracted with ether. The ether phase was dried with Na₂SO₄ and concentrated to give (*R*)-**4** (0.83 g, 83%) in 99% ee. $[\alpha]_D^{20} = +27.2^{\circ}$ (*c* = 0.50 g/dL, methanol), literature [44] +27.1°.

The mother liquid of the resolution was concentrated under reduced pressure and the residue was purified by column chromatography over silica gel (*n*-hexane/ethyl acetate 2:1) to yield (*S*)-**4** (0.92 g, 92%) in 93% ee. $[\alpha]_D^{20} = -25.3^{\circ}(c = 0.50 \text{ g/dL}, \text{ methanol}).$

The ee values of the resolution products were determined by HPLC analysis on DAICEL-AD-H column. Hexane/*i*-PrOH = 8:2, flow rate = 1 mL min⁻¹ $t_{\rm R}$ = 7.0 min, $t_{\rm S}$ = 17.0 min.

2.3.2. (R)-2,2'-bis(4-nitro-2-trifluoromethylphenoxy)-9,9'spirobifluorene

(*R*)-2,2'-dihydroxy-9,9'-spirobifluorene (3.48 g, 10.0 mmol) and 2-fluoro-5-nitrobenzotrifluoride (4.39 g, 21.0 mmol) were dissolved in 35 mL of *N*,*N*'-dimethylacetamide (DMAc) in an 100-mL round-bottomed flask with stirring. Then, potassium carbonate (2.76 g, 20.0 mmol) was added, and the mixture was heated to 60 °C for 6 h. After cooled to room temperature, the solution was poured into 120 mL of water. The precipitate was collected by filtration and dried under vacuum. The crude product was recrystallized from DMF/methanol to give pale-yellow crystal (6.61 g, 91.1%). mp: 120–122 °C [α]_D^{2D} = -26.9° (*c* = 0.50 g/dL, DMAc). FT-IR (kBr, cm⁻¹): 1530, 1351 (-NO₂), 1259 (Ar–O–Ar), 1143 (–CF₃). ¹H NMR (600 MHz,

CDCl₃, δ , ppm): 8.53 (d, J = 2.4 Hz, 2H, H_j), 8.21 (dd, J = 9.6, 2.4 Hz, 2H, H_i), 7.89 (d, J = 8.4 Hz, 2H, H_e), 7.83 (d, J = 7.8 Hz, 2H, H_d), 7.42 (dd, J = 7.8, 7.2 Hz, 2H, H_c), 7.19 (dd, J = 7.8, 7.2 Hz, 2H, H_b), 7.11 (dd, J = 8.4, 2.4 Hz, 2H, H_f), 6.83 (d, J = 9.6 Hz, 2H, H_h), 6.79 (d, J = 7.8 Hz, 2H, H_a), 6.57 (d, J = 2.4 Hz, 2H, H_g). ¹³C NMR (600 MHz, CDCl₃, δ , ppm): 160.94 (C¹⁴), 153.72 (C¹¹), 150.88 (C¹³), 148.09 (C²), 141.70 (C¹⁷), 140.45 (C⁷), 139.97 (C⁸), 128.75 (C¹⁸), 128.45 (C⁵), 128.39 (C⁴), 124.04 (C³), 123.81 (C¹⁶), 122.11 (q, ¹J_{C-F} = 271.5 Hz, C²⁰), 121.86 (C⁹), 120.60 (C¹⁰), 120.49 (q, ²J_{C-F} = 32.3 Hz, C¹⁵), 120.32 (C⁶), 116.75 (C¹⁹), 116.70 (C¹²), 66.00 (C¹). MALDI-FTICR MS (*m*/*z*): [M]⁺ calcd for C₃₉H₂₀F₆N₂O₆, 726.12; found, 726.12. Elemental analysis: Calcd for C₃₉ H₂₀F₆N₂O₆: C, 64.47%; H, 2.77%; N, 3.86%. Found: C, 64.56%; H, 2.85%, N, 3.81%.

Optically inactive 2,2'-bis(4-nitro-2-trifluoromethylphenoxy)-9,9'-spirobifluorene was synthesized by the same procedure. The yield was 93%. The melting point was 267–269 °C with pronounced effervescence at 115 °C and resolidification around 160–170 °C.

2.3.3. (*R*)-2,2'-bis(4-amino-2-trifluoromethylphenoxy)-9,9'-spirobifluorene

Optically active dinitro compound (*R*)-5 (5.09 g, 7.0 mmol) and 10% Pd/C (0.10 g) were suspended in ethanol (80 mL) in a 250-mL flask. The suspension was heated to reflux, and 80% hydrazine monohydrate (3 mL) was added dropwise to the stirred mixture. After a further 6 h reflux, the resulting clear, darkened solution was filtered hot to remove Pd/C, and the filtrate was dried by rotary evaporation. The crude product was purified by recrystallization from 1,2-dichloroethane to afford pale-yellow needle-like crystals (4.01 g, 86%). mp: 262–264 °C $[\alpha]_D^{20}$ = +67.0° (*c* = 0.50 g/dL, DMAc). FT-IR (KBr, cm⁻¹): 3471, 3386 (-NH₂), 1228 (Ar-O-Ar), 1121 (-CF₃). ¹H NMR (600 MHz, DMSO- d_6 , δ , ppm): 7.93 (d, J = 8.4 Hz, 2H, H_e), 7.90 (d, I = 7.2 Hz, 2H, H_d), 7.37 (dd, I = 7.8, 7.2 Hz, 2H, H_c), 7.09 (dd, J = 7.8, 7.2 Hz, 2H, H_b), 6.91 (dd, J = 8.4, 2.4 Hz, 2H, H_f), 6.84 $(s, 2H, H_i), 6.71 (s, 4H, H_h and H_i), 6.59 (d, J = 7.2 Hz, 2H, H_a), 6.05 (d, J = 7.2 Hz, 2Hz, 2H, H_a), 6.05 (d, J = 7.2 Hz, 2Hz, 2Hz, 2Hz, 2Hz, 2Hz,$ J = 2.4 Hz, 2H, H_g), 5.42 (s, 4H, H_k). ¹³C NMR (600 MHz, DMSO- $d_{6_1} \delta$, ppm): 158.49 (\mathring{C}^{11}), 150.01 (\mathring{C}^{13}), 147.81 (\mathring{C}^{2}), 145.75 (\mathring{C}^{14}), 142.12 (C¹⁷), 140.64 (C⁷), 135.80 (C⁸), 128.02 (C⁵), 127.28 (C⁴), 123.30 (C³), (C^{12}) , 110.73 (C^{18}) . MALDI-FTICR MS (m/z): $[M]^+$ for $C_{39}H_{24}F_6N_2O_2$, 666.17; found, 666.17. Elemental analysis: Calcd for C₃₉H₂₄F₆N₂O₂: C, 70.27%; H, 3.63%; N, 4.20%. Found: C, 70.35%; H, 3.60%; N, 4.16%.

Crystal data: pale-yellow crystal grown during slow crystallization in ethanol/ethyl acetate (3:1 v/v), $0.34 \times 0.21 \times 0.12$ mm³, tetragonal $P4_32_12$ with a = 16.198(2) Å, b = 16.198(2) Å, c = 12.285(4) Å, $\alpha = 90^{\circ}$, $\beta = 90^{\circ}$ and $\gamma = 90^{\circ}$, where $D_c = 1.374$ Mg/m³ for Z = 4 and V = 3223.2 Å³. For crystallographic data for the structure, see the Supporting Information (Table S1).

Optically inactive diamine compound **6** was synthesized by the same procedure, except that it was purified by recrystallization from benzene. The yield was 89%, mp: 274-276 °C.

2.4. Synthesis of polyimides

A typical polymerization procedure was as follows. To a solution of 0.9954 g (1.49 mmol) of diamine (R)-**6** in 10 mL DMAc in a 50-mL flask, 0.6634 g (1.49 mmol) of 6FDA was added in one portion. The solid content of the solution is approximately 10%. The mixture was stirred at room temperature for 10 h under nitrogen atmosphere to yield a viscous poly (amic acid) solution. Chemical imidization was carried out by adding a mixture of acetic anhydride (0.60 mL) and triethylamine (0.30 mL) into the poly (amic acid) solution. This mixture was stirred at room temperature for 6 h and then heated at 80 °C for 2 h. After cooling, the viscous solution was collected by filtration,

washed thoroughly with ethanol, and dried under vacuum at 100 °C to produce the corresponding polyimide (R)-**7a**. The polymer was further purified by reprecipitation from DMAc into ethanol twice.

(*R*)-**7a**. FT-IR (KBr, cm⁻¹): 1788 (asymmetric C=O stretch), 1734 (symmetric C=O stretch), 1377 (C–N stretch), 1258 (Ar–O–Ar), 1142 (CF₃), 1053, 744 (imide ring deformation). ¹H NMR (600 MHz, CDCl₃, δ , ppm): 7.97 (d, J = 7.8 Hz, 2H), 7.89 (s, 2H), 7.84 (d, J = 8.4 Hz, 4H), 7.80 (d, J = 7.8 Hz, 2H), 7.66 (s, 2H), 7.42 (d, J = 9.0 Hz, 2H), 7.37 (dd, J = 7.2, 7.2 Hz, 2H), 7.13 (dd, J = 7.2, 7.2 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 6.77 (d, J = 7.2 Hz, 2H), 6.60 (s, 2H). ¹³C NMR (600 MHz, CDCl₃, δ , ppm): 165.77, 165.60, 155.73, 155.00, 150.73, 148.25, 140.77, 139.29, 138.91, 136.03, 132.47, 132.19, 131.23, 128.19, 127.92, 125.62, 125.44, 125.18, 124.25, 124.02, 122.68, 122.36, 121.49, 121.10, 120.06, 118.13, 116.48, 65.95, 65.24.

(*R*)-**7b**. FT-IR (KBr, cm⁻¹): 1783 (asymmetric C=O stretch), 1726 (symmetric C=O stretch), 1376 (C–N stretch), 1260 (Ar–O–Ar), 1138 (CF₃), 1053, 743 (imide ring deformation). ¹H NMR (600 MHz, CDCl₃, δ , ppm): 7.92 (d, J = 7.8 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 7.8 Hz, 2H), 7.66 (s, 2H), 7.46 (s, 2H), 7.44 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H), 7.37 (dd, J = 7.2, 7.2 Hz, 2H). 6.77 (d, J = 7.8 Hz, 2H), 6.60 (s, 2H). ¹³C NMR (600 MHz, CDCl₃, δ , ppm): 165.90, 165.80, 161.16, 155.60, 155.02, 150.75, 148.26, 140.78, 138.90, 134.45, 131.27, 128.19, 127.93, 127.15, 126.37, 125.61, 125.45, 124.88, 124.04, 122.74, 121.50, 120.97, 120.13, 120.06, 117.99, 116.49, 114.04, 65.94.

(*R*)-**7c**. FT-IR (KBr, cm⁻¹): 1784 (asymmetric C=O stretch), 1730 (symmetric C=O stretch), 1376 (C–N stretch), 1259 (Ar–O–Ar), 1139 (CF₃), 1053, 746 (imide ring deformation). ¹H NMR (600 MHz, CDCl₃, δ , ppm): 8.14 (d, J = 7.2 Hz, 2H), 8.10 (s, 2H), 8.00 (d, J = 7.2 Hz, 2H), 7.85 (d, J = 7.8 Hz, 2H), 7.80 (d, J = 6.6 Hz, 2H), 7.67 (s, 2H), 7.47 (d, J = 9.0 Hz, 2H), 7.38 (dd, J = 7.2, 7.2 Hz, 2H), 7.14 (dd, J = 6.6, 7.2 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 6.78 (d, J = 7.2 Hz, 2H) 6.61(s, 2H). ¹³C NMR (600 MHz, CDCl₃, δ , ppm): 192.54, 165.73, 155.98, 154.75, 150.81, 148.20, 141.81, 140.74, 139.08, 135.91, 134.80, 131.99, 131.31, 128.23, 127.99, 125.67, 125.05, 124.67, 124.32, 124.07, 122.70, 121.58, 120.84, 120.41, 120.09, 117.65, 116.64, 65.93.

(*R*)-**7d**. FT-IR (KBr, cm⁻¹): 1779 (asymmetric C=O stretch), 1726 (symmetric C=O stretch), 1374 (C–N stretch), 1250 (Ar–O–Ar stretch), 1135 (CF₃), 1052, 736 (imide ring deformation). ¹H NMR (600 MHz, CDCl₃, δ , ppm): 7.88 (d, J = 7.8 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 7.2 Hz, 2H), 7.77 (s, 2H), 7.76 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.37 (dd, J = 6.6, 7.2 Hz, 2H), 7.13 (dd, J = 6.6, 6.6 Hz, 2H), 7.07 (d, J = 7.8 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 7.2 Hz, 2H), 6.61 (s, 2H). ¹³C NMR (600 MHz, CDCl₃, δ , ppm): 166.24, 166.16, 155.89, 154.71, 150.81, 148.20, 144.81, 140.78, 139.06, 133.17, 132.72, 131.43, 128.22, 127.96, 125.78, 125.15, 124.59, 124.07, 122.73, 122.09, 121.59, 120.69, 120.45, 120.09, 117.55, 117.49, 116.64, 65.93.

3. Results and discussion

3.1. Monomer synthesis

The synthetic route to new optically diamine monomer (*R*)-**6** is outlined in Scheme 1. The precursor, 9,9'-spirobifluorene (**1**) was prepared according to literature procedures [44]. On acylation and oxidation, followed by alkaline hydrolysis, **1** gave (\pm) -2,2'-dihydroxy-9,9'-spirobifluorene (**4**). Tartaric acid derivative [(*R*,*R*)-(+)-2,3-dimethoxy-*N*,*N*,*N*'-tetracyclohexylsuccinamide ((*R*,*R*)-(+)-DMTCHS, chiral host)] could selectively recognize (*R*)-**4** (chiral guest) in the solution of ethanol and formed crystalline complex. The absolute stereochemistry of the complex was confirmed by X-ray crystal analysis. In the crystal, the complex was constructed of one (R)-**4** and one (R,R)-(+)-DMTCHS through a hydrogen band between the hydroxyl group of the diol and the carbonyl group of the amide [44]. The inclusion complex was decomposed in aqueous sodium hydroxide and subsequently acidified with hydrochloric acid to give (R)-4 in 99% ee. The aromatic nucleophilic substitution reaction of (R)-4 with 2-fluoro-5-nitrobenzotrifluoride in DMAc/ K_2CO_3 medium vielded (R)-5 in high vields, which on catalytic reduction over hydrazine hydrate and Pd/C afforded the target diamine monomer (R)-6. The structures of the dinitro (R)-5 and diamine (R)-6 were confirmed by elemental analysis, IR, NMR and mass spectroscopy. Figure S1 shows the IR spectra of the dinitro intermediate and the diamine. The nitro groups of compound (R)-5 gave two characteristic bands at 1530 and 1351 cm^{-1} (NO₂ asymmetric and symmetric stretching, respectively). After reduction, the characteristic absorptions of the nitro group disappeared, and the amino group showed the typical N-H stretching bands in the region of 3300-3500 cm⁻¹. The ¹H NMR and ¹³C NMR spectra of diamine monomer (*R*)-**6** in DMSO- d_6 are illustrated in Fig. 1. Assignments of each proton and carbon are assisted by twodimensional NMR spectra shown in Fig. 2 and Figure S2, and these spectra agree well with the proposed molecular structure of (*R*)-**6**. The ¹H NMR spectrum of diamine (*R*)-**6** confirmed that the nitro groups have been completely converted into amino groups by the high field shift of the aromatic protons and by the signal at 5.42 ppm corresponding to the primary aromatic amine protons. In the ¹³C NMR spectrum of diamine (R)-**6**, C¹⁵ and C²⁰ exhibited clear quartet absorptions at 121.00-121.60 and 120.63-126.05 ppm, respectively, due to ${}^{2}J_{C-F}$ and ${}^{1}J_{C-F}$ coupling of the carbons with fluorines. The resonance associated with the central spiro carbon (C^1) appeared in 65.33 ppm. The other spectra of compounds (R)-**5** and (R)-6 were displayed in Figures S3–S6. All the spectroscopic data obtained were in good agreement with the expected structures. The molecular structure of (R)-**6** was also confirmed by X-ray crystal analysis. Single crystal of (*R*)-6 was obtained from ethanol/ ethyl acetate solution by slow evaporation of solvent. Fig. 3 displays the Oak Ridge thermal ellipsoid plot (ORTEP) of (R)-6 accomplished by X-ray diffraction at 295 K. The spiro molecule consists of two



(±)- and (R)-6

Scheme 1. Synthesis of diamine monomer (\pm) - and (R)-6.



Fig. 1. ¹H NMR and ¹³C NMR spectra of (R)-**6** in DMSO- d_6 .

identical 4-amino-2-trifluoromethylphenoxyfluorene moieties connected through a common tetra coordinate carbon atom (the spiro center). In the spiro segment, the arrangement of the connected bifluorene entities is nearly orthogonal (dihedral angle = 88.1°). The structure agrees with the proposed one.

The optical purity of the monomers, (*R*)-**4** and (*R*)-**6**, was determined by HPLC analysis on DAICEL-AD-H column (Figure S8 and Fig. 4). The ee value of (*R*)-**6** is 99%, which showed that there was almost no rotational loss during two-step reactions. The specific rotation and melting points of (*R*)-**5** and (*R*)-**6** are shown in the experimental section. Different melting points $[(\pm)-5, 267-269 \degree C; (R)-5, 120-122 \degree C; (\pm)-6, 274-276 \degree C; (R)-6, 262-264 \degree C]$ between the racemic and chiral compounds were noticed, and this was attributed to the different crystal structures. Optically active diamine (*R*)-**6** could be easily crystallized from chloroform, while the corresponding racemate was almost insoluble in chloroform on heating at boiling temperature.

3.2. Preparation of polymides

Optically active polyimides (R)-**7a**–**d** were prepared by the traditional two-step method, that is, the synthesis of polyamic acid through the reaction of (R)-**6** with aromatic dianhydride in DMAc at room temperature, followed by chemical imidization with acetic

anhydride and triethylamine (Scheme 2). For comparison, a series of corresponding polyimides based on racemic diamine 6 were also prepared and characterized. The results of the polymerization are summarized in Table 1. These optically active polyimides had inherent viscosities ranging from 0.38 to 0.72 dL/g in DMAc. Their number-average (M_n) and weigh-average (M_w) molecular weights were $1.8-4.0 \times 10^4$ and $3.9-9.3 \times 10^4$, respectively, and the polydispersity index (PDI = M_w/M_n) was in the range of 2.12–2.33, as measured by gel permeation chromatography (GPC) using polystyrene standards. The viscosities and molecular weights of optically active polyimides were somewhat lower than the corresponding racemic polyimides prepared from diamine 6. The possible reason was that the relatively regular structures of chiral polyimides (R)-7a-d, which originating from optically active spirodiamine, would inactivate the end-groups of the propagating polymers by the steric hindrance, while the random complymerization of racemic 6 with dianhydrides could overcome this problem [52].

The chemical structures of the polyimides were characterized by the elemental analysis, IR and NMR spectra. The elemental analysis values of the polyimides were in good agreement with their respective structures. The FT-IR spectra (Fig. 5) of the polyimides exhibited characteristic imide absorptions at around 1783 and 1730 cm⁻¹ (typical of imide carbonyl asymmetric and symmetric





stretches), 1376 (C–N stretch), and 1053 and 743 (imide ring deformation), together with strong absorption bands in the region of 1100–1300 cm⁻¹ due to the C–O and C–F stretching. The typical ¹H NMR spectrum of optically active polyimide (*R*)-**7a** is shown in Fig. S9. All the protons resonated in the region of 6.60–7.98 ppm. The protons H_m close to the imide appeared at the farthest



Fig. 3. ORTEP diagram of diamine (*R*)-6.



Fig. 4. (a) HPLC resolution of (\pm) -**6** and (b) the determination of optical purity of (*R*)-**6** on DAICEL-AD-H column. Eluent: Hexane: *i*-PrOH = 7:3; flow rate: 1 mL min⁻¹ at room temperature.



Scheme 2. Synthesis of polyimides (\pm) - and (R)-**7a**-**d**.

downfield region of the spectrum because of the resonance. The protons H_g shifted to higher field because of the electron-donating property of aromatic ether. The other NMR spectra of these chiral polyimides (*R*)-**7a**-**d** are shown in Supporting Information (Figures S10–S16). All the spectroscopic data obtained were in good agreement with the desired polymer structures.

3.3. Polymer solubility and crystallinity

Table 1

The solubility of these polyimides was tested in various organic solvents, and the results are listed in Table 2. All these polyimides exhibited good solubility in dipolar amide-type solvents, such as NMP, DMAc and DMF at room temperature or upon heating. They were also soluble in pyridine and phenol solvent *m*-cresol, as well

as chlorinated solvents like chloroform and dichloromethane. The good solubility of these polyimides might be attributed to the presence of kinked spirobifluorene units, with bulky tri-fluoromethyl pendent groups and flexible aryl ether linkages along the polymer backbone. This kind of macromolecular architecture would restrict the close packing of the polymer chains and lessen the probability of interchain interactions, so that it improved the solubility of resultant polymers. Optically active polyimides (*R*)-**7c** and (*R*)-**7d** exhibited slightly better solubility than corresponding racemic polymers in tetrahydrafuran and 1,4-dioxane solvents.

The crystallinity of the polyimides was characterized by wide angle X-ray diffraction (WAXD) and the results are shown in Figures S17 and S18. All these polymides showed amorphous patters. The amorphous nature of these polyimides was attributed



Fig. 5. FT-IR spectra of polyimides (R)-7a-d.

Inherent vi	scosity,	molecular weig	ht and elemental analysis of polyimides.
Polymer	$\eta_{\mathrm{inh}}{}^{\mathrm{a}}$	GPC data	Elemental analysis (%)
	(dL/g)		

	(dL/g)	$\frac{M_w^{\ b}}{(\times 10^4)}$	$M_{\rm w}/M_{\rm n}$	Formula (formula weight)		С	Η	N		
(±)-7a	0.51	5.3	2.21	(C ₅₈ H ₂₆ F ₁₂ N ₂ O ₆) _n	Calcd.	64.81	2.44	2.61		
				(1074.82)	Fould	64.76	2.53	2.68		
(R)- 7a	0.47	4.8	2.14	$(C_{58}H_{26}F_{12}N_2O_6)_n$	Calcd.	64.81	2.44	2.61		
				(1074.82)	Fould	64.56	2.51	2.49		
(±)- 7b	0.75	8.9	2.34	$(C_{55}H_{26}F_6N_2O_7)_n$	Calcd.	70.22	2.79	2.98		
				(940.79)	Fould	70.12	2.97	2.88		
(R)- 7b	0.73	8.5	2.28	$(C_{55}H_{26}F_6N_2O_7)_n$	Calcd.	70.22	2.79	2.98		
				(940.79)	Fould	69.97	2.92	2.95		
(±)- 7c	0.78	9.9	2.15	$(C_{56}H_{26}F_6N_2O_7)_n$	Calcd.	70.59	2.75	2.94		
				(952.81)	Fould	70.68	2.79	2.83		
(R)- 7c	0.76	9.3	2.33	$(C_{56}H_{26}F_6N_2O_7)_n$	Calcd.	70.59	2.75	2.94		
				(952.81)	Fould	70.65	2.81	2.76		
(±)-7d	0.39	4.1	2.16	$(C_{55}H_{26}F_6N_2O_6)_n$	Calcd.	71.43	2.83	3.03		
				(924.80)	Fould	71.26	2.88	2.95		
(R)-7d	0.38	3.9	2.12	$(C_{55}H_{26}F_6N_2O_6)_n$	Calcd.	71.43	2.83	3.03		
				(924.80)	Fould	71.10	2.89	2.92		

^a Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

 $^{\rm b}$ Molecular weight was determined by GPC in DMF based on polystyrene standards.

Table 2Solubility of the polyimides.^a

Solvent ^b	Polyimide							
	(R)- 7a	(±)-7a	(R)- 7b	(±)- 7b	(R)- 7c	(±)- 7c	(R)- 7d	(±)-7d
NMP	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
DMAc	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
DMF	+ +	+ +	+ +	+ +	+ +	+ +	+	+
DMSO	+ +	+ +	+	+	+	+	+ -	+ -
m-Cresol	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Chloroform	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Dichloromethane	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Pyridine	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+
1,4-Dioxane	+ +	+ +	+ +	+ +	+ +	+	+ +	+
THF	+ +	+ +	+ +	+ +	+ +	+	+ +	+
Acetone	+ +	+ +	+ -	+ -	+ -	+ -		

The symbol + +: soluble at room temperature; +: soluble on heating at 100 °C or boiling temperature; + -: partially soluble or slightly swollen on heating; - -: insoluble even on heating.

^a Solubility was tested with a 5 mg sample in 1 mL of stirred solvent.

^b NMP: *N*-methyl-2-pyrolidone; DMF: *N*,*N*'-dimethylformamide; DMAc: *N*,*N*'-dimethylacetamide; DMSO: dimethylsulfoxide; THF: tetrahydrofuran.

not only to the bulkiness of the CF₃ substituent but also to the spiroskeletons structure coming from the diamine monomer.

3.4. Thermal properties

The thermal properties of these polyimides were evaluated by DSC, DMA and TGA, and the results are summarized in Table 3. The incorporation of rigid spirobifluorene units in the polymer backbone resulted in polyimides with high glass transition temperature (T_g). DSC curves for the polyimides (R)-**7a**-**d** and (\pm)-**7b** are displayed in Fig. 6. The T_{gs} of the optically active polyimides (*R*)-**7a**d were in the range of 260-281 °C depending on the chemical structure of the aromatic dianhydride component. As expected, polymer (R)-7d showed the highest T_g of 281 °C, which can be attributed to the rigid biphenyl group in the polymer chain. On the contrary, polyimide (*R*)-**7b** showed the lowest $T_{\rm g}$ of 260 °C due to the relative flexible ether linkage. Figures S19 and S20 show the DMA curves of polyimides (*R*)-7a–d and (\pm) -7a–c, respectively. Regarding the peak temperature in the tan curves as the $T_{\rm g}$, the $T_{\rm g}$ values obtained by DMA were comparable to that measured by DSC method. The optically active polyimides (R)-7 and optically inactive polyimides 7 exhibited almost identical T_{gs} , though the melting point of diamine (R)-4 differed from that of (\pm) -4. This result seemed to imply that there was no stereocomplex formed as for other optically active polymers [53].

Table 3

Polymer	T_g^a (°C)		$T_{5\%}^{b}$ (°C)		$T_{10\%}^{b}(^{\circ}C)$		$R_{w}^{c}(\%)$	$[\alpha]_D^{20d} (^\circ)$
	DSC	DMA	N_2	Air	N ₂	Air		
(R)- 7a	275	279	527	512	546	531	58	+73.0
(±)-7a	276	280	530	517	550	537	60	
(R)- 7b	260	262	556	535	584	562	65	+16.5
(±)-7b	258	262	562	539	586	568	64	
(R)- 7c	269	272	549	528	576	557	63	+12.9
(±)- 7c	270	274	555	533	579	559	62	
(R)- 7d	280	286	569	543	592	565	68	-48.5
(±)- 7d	281	e	567	541	591	562	67	

^a Glass transition temperature (T_g) was measured by DSC and DMA at a heating rate of 20 °C min⁻¹ and 10 °C min⁻¹, respectively.

^b Temperature at 5% and 10% weight loss were recorded by TGA at a heating rate of 10 °C min⁻¹.

^c Residual weight percentage at 800 °C in nitrogen.

^d Specific rotations of polymers were measured at 20 °C in DMAc, c = 0.10 g/dL.

^e The polymer film was too brittle to be measured.



Fig. 6. DSC traces of polyimides (*R*)-**7** \mathbf{a} -**d** and (\pm)-**7** \mathbf{b} .

The thermal stability of these polyimides was evaluated by TGA measurements in both air and nitrogen atmospheres. Fig. 7 shows the typical TGA curves for optically active polymers (R)-**7a** and (R)-**7d**. Almost all the polyimides did not show remarkable weight loss below 500 °C in nitrogen or air atmosphere. The 5% weight loss temperatures of these polyimides in nitrogen and air were in the range of 527–569 and 512–543 °C, respectively. They left more than 58% char yield at 800 °C in nitrogen. Especially, the chiral polyimide (R)-**7d** derived from BPDA had the highest residue yield up to 68%. The TGA data indicated that these polyimides containing spirobifluorene moieties in the backbone had fairly high thermal stability even with the introduction of bulky trifluoromethyl pendent groups.

3.5. Optical and mechanical properties

Except for polyimide (\pm) -7d, all these polyimides could be processed to flexible and tough films conveniently by casting from polymer solutions. The optical properties of these polyimide films are given in Table 4 and the UV-vis spectra of polymer films (R)-7a-d about 20 µm thicknesses are shown in Fig. 8. The cut-off wavelength (λ_0) values of the optically active polyimide films ranged from 351 to 375 nm, and the optical transmittance values at a wavelength of 500 nm were all high than 78%. Because of the highly conjugated aromatic structures and intermolecular charge transfer complex (CTC) formation, most polyimides showed strong absorption in UV and the visible region. However, these polyimides which had bulky spirobiflurene structure and trifluoromethyl groups in the center of diamine broke the conjugation along the polymer backbone and reduced the intermolecular CTC between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties. The polyimides (R)-7a and (R)-7b derived from 6FDA and ODPA showed the lower λ_0 values together with higher optical transparency in comparison to polyimides based on other dianhydrides, which could be explained from the decreased intermolecular interactions [31]. The optically inactive polyimides films 7a-d showed similar UV-vis spectra to the corresponding optically active polymers.

The polyimide films were subjected to tensile tests, and the results are summarized in Table 4. The optically active polyimide films had tensile strengths of 72.0–84.8 MPa, elongations at break of 3.6–4.3% and tensile moduli of 3.11–3.67 GPa, which indicate



Fig. 7. TGA curves of polyimides (*R*)-7a and (*R*)-7d at a heating rate of 10 $^{\circ}$ C min⁻¹.

that they are strong and tough polymeric materials. These chiral polymers have the potentials to be used as the chiral membrane separation materials for the resolution of racemates.

These polyimides showed low water uptakes in the range of 0.20-0.54% (Table 4). Obviously, the low water absorption could mainly be attributed to the polymer hydrophobicity derived from the concentration and distribution of trifluoromethyl groups in the polyimide backbones. Among these optically active polyimides, polymer (*R*)-**7a** exhibited the lowest water absorption (0.23%) due to its highest fluorine content.

3.6. Chiro-optical properties

The specific rotations of these polyimides (*R*)-**7a**–**d** were measured in DMAc at a concentration of 0.10 g/dL at 20 °C and the data are listed in Table 3. The value of the polyimide (*R*)-**7a** ($[\alpha]_D^{20} = +73.0^\circ$) derived from 6FDA was slightly higher than that of diamine (*R*)-**6** ($[\alpha]_D^{20} = +67.0^\circ$) building up into the polymer. Polyimides (*R*)-**7b** and (*R*)-**7c** exhibited specific rotation values of +16.5° and +12.9°, respectively. It is noteworthy that the polyimide (*R*)-**7d** was levorotatory and showed an $[\alpha]_D^{20}$ value of -48.5° . Similar phenomena were reported that the optical rotations for the chiral polymers were opposite to those of the corresponding monomers [54]. The reversal in optical rotations indicates that the optical activity of the polymer (*R*)-**7d** does not only arise from the chiral spirodiamine moiety and suggests that a higher ordered structure, likely a secondary helical structure, has been formed. All

Table	4
-------	---

Water absorption, optical and mechanical properties of the polyimide films.

Polymer	λ _{cut off} (nm)	T ₅₀₀ (%)	Water absorption (%)	Tensile strength (MPa)	Elongation to break (%)	Initial modulus (GPa)
(R)- 7a	351	86	0.23	84.8 ± 2.5^a	3.9 ± 0.3	3.11 ± 0.10
(±)-7a	348	85	0.20	$\textbf{78.7} \pm \textbf{2.3}$	$\textbf{3.5} \pm \textbf{0.2}$	2.97 ± 0.12
(R)- 7b	357	83	0.43	$\textbf{72.0} \pm \textbf{1.9}$	$\textbf{3.7} \pm \textbf{0.2}$	3.67 ± 0.14
(±)- 7b	354	82	0.46	$\textbf{76.2} \pm \textbf{2.6}$	$\textbf{3.3} \pm \textbf{0.1}$	$\textbf{3.30} \pm \textbf{0.09}$
(R)- 7c	372	77	0.54	77.1 ± 2.4	$\textbf{4.3} \pm \textbf{0.3}$	$\textbf{3.63} \pm \textbf{0.13}$
(±)- 7c	370	78	0.52	80.1 ± 2.7	4.1 ± 0.2	3.52 ± 0.15
(R)- 7d	375	79	0.31	$\textbf{73.1} \pm \textbf{1.8}$	$\textbf{3.6} \pm \textbf{0.1}$	$\textbf{3.34} \pm \textbf{0.11}$
(±)- 7d	377	80	0.35	_b	-	-

 $^{\rm a}$ The former value (84.8) was the mean of the five determinations, while the latter (2.5) was the sample standard deviation.

^b The polymer film was too brittle to be measured.



Fig. 8. UV-vis spectra of polyimide films (R)-7a-d.

of the resulting polyimides show optical rotation and therefore are optically active. We have also studied the optical stability of (R)-**7a**-**d** in solid state or in DMAc solvent. We found that the optical rotation of (R)-**7a**-**d** remained unchanged after heating at 250 °C in solid state for 48 h or after fluxing in DMAc for 24 h. The high optical stability of polyimides (R)-**7a**-**d** at high temperatures might be attributed to incorporation spirobifluorene units into the polymer structures. In the spiro segment, the two fluorene rings of the spiro compound lie in perpendicular planes. This structure feature not only restricts the rotation of the two rings and gives rises to an axial chirality in spiro compounds having substituents on rings but also increases molecular rigidity [42].

In order to obtain further information on the conformation, CD and UV–vis spectra of the monomers (*R*)-**5**, (*R*)-**6** and the polyimides (*R*)-**7a**–**d** in THF were measured (Figure S21 and Fig. 9) and the CD spectra data are listed in Supporting Information (Table S2). In the UV–vis spectra of polyimide (*R*)-**7a** solution (Fig. 9), an absorption band at around 279 nm was observed due to $\pi \rightarrow \pi^*$ electronic transition of aromatic rings. The UV–vis spectra of polyimide (*R*)-**7a** also showed shoulder peak at around 313 nm due to the $n \rightarrow \pi^*$ transition of non-bonding electrons present in oxygen or nitrogen atoms in the polymer backbone. Other optically active polyimides (*R*)-**7b–d** exhibited similar UV–vis spectra. The CD spectra of



Fig. 9. UV–vis absorption and CD spectra of polyimides (*R*)-7a–d in THF at 25 °C. Concentration: 3×10^{-5} (repeating unit) mol/L.

polyimide (*R*)-7a exhibited a weak negative Cotton effect at 264 nm and two medium positive bands at 239 and 294 nm, respectively. If a comparison is made between the CD spectra of polyimides (*R*)-**7b** and (*R*)-7a, we can see clearly that the intensity and position of the peaks are different. In polyimide (R)-7b, the negative peak at 271 nm showed an increase in intensity while the positive peaks at 245 and 298 nm displayed decrease in their ellipicity. Polyimide (R)-7d (levorotatory) also exhibited a significantly different CD pattern from polymers (*R*)-7a–c (dextrorotatory). (*R*)-7d showed a strong negative peak at 274 nm and only one positive Cotton effect at 316 nm. The intense CD signal of (*R*)-7d indicated that it probably formed well-defined secondary structure such as helix. In the optically active polyimide (*R*)-7d, the neighboring axial chirality of spirodiimide is interlinked by the rigid biphenyl unit, and this results in a persistence of the asymmetric structure of 9,9'-spirobifluorene along the backbone. The addition of flexible ether linkage, carbonyl or hexafluoroisopropyl groups to the dianhydride moieties allows variations of polymer chain conformation and, therefore, breaks the communication between neighboring chiral spirodiimides, and this results in relatively low structures ((*R*)-7a–c).

4. Conclusions

A novel optically active diamine monomer. (R)-2.2'-bis(4amino-2-trifluoromethylphenoxy)-9.9'-spirobifluorene. was successfully synthesized and characterized in the present work, which was employed in polycondensation with various aromatic dianhydrides to prepare a series of chiral polyimides. The resulting polyimides exhibited good solubility in many organic solvents such as chloroform, NMP and m-cresol. For THF and 1,4-dioxane, optically active polyimides (R)-7c and (R)-7d derived from BTDA and BPDA showed slightly better solubility than corresponding racemic polymers. The specific rotations of these chiral polyimides were in the range of -48.5° to $+73.0^{\circ}$. Attributed to the spiro structure, all the chiral polyimides exhibited high optical stability in solid state or in DMAc solvent at high temperatures. In the case of the spiro segment, the two mutually perpendicular fluorene rings were connected at a quaternary center through σ -bonds, which restricted the rotation of the two rings and increased the rigidity of the polymers. These optically active polyimides also displayed high thermal stability and outstanding mechanical property. The synthetic chiral polyimides are expected to have the potential as chiral catalysts for asymmetric synthesis, chiral membrane separation materials and chiral stationary phases in chromatographic technique for the resolution of racemates.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (gs1) (No. 20674082) and Science & Technology Development Project Agreement, Jilin Province (gs2) (20106022). The authors thank Doctor Zhen Bian (Changchun Institute of Applied Chemistry, Chinese Academy of Sciences) for his help with the measurements of CD spectra.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2012.10.024.

References

 (a) Xi XJ, Liu GX, Lu W, Jiang LM, Sun WL, Shen ZQ. Polymer 2009;50(2):404– 9:

(b) Okamoto Y, Ikai T. Chem Soc Rev 2008;37(12):2593-608.

- [2] (a) Ikeuchi Y, Nakagawa M, Yoshikawa M, Yoshida H, Sakurai S. J Polym Sci Part A: Polym Chem 2009;47(10):2530–8;
- (b) Li ZB, Lin J, Pu L. Angew Chem Int Ed 2005;44(11):1690–3.
- [3] (a) Goto H, Zhang HQ, Yashima E. J Am Chem Soc 2003;125(9):2516–23;
 (b) Yamamoto C, Yashima E, Okamoto Y. J Am Chem Soc 2002;124(42): 12583–9.
- [4] (a) Onouchi H, Okoshi K, Kajitani T, Sakurai S, Nagai K, Kumaki J, et al. J Am Chem Soc 2008;130(1):229–36;
- (b) Pérez-Méndez M, Berenguel RM, Garrido L, Martín-Pastor M. Macromolecules 2003;36(21):8049-55.
- [5] (a) Jeong HS, Kim YH, Lee JS, Kim JH, Srinivasarao M, Jung HT. Adv Mater 2012; 24(3):381–4;

(b) Oda M, Nothofer HG, Scherf U, Šunjić V, Richter D, Regenstein W, et al. Macromolecules 2002;35(18):6792–8.

- [6] Koeckelberghs G, Sioncke S, Verbiest T, Severen IV, Picard I, Persoons A, et al. Macromolecules 2003;36(26):9736–41.
- [7] Lustig SR, Everlof GJ, Jaycox GD. Macromolecules 2001;34(7):2364-72.
- [8] (a) Wu RZ, Al-Azemi TF, Bisht KS. Biomacromolecules 2008;9(10):2921-8;
 (b) Marín R, Alla A, Muñoz-Guerra S. Macromol Rapid Commun 2006;27(20): 1955-61.
- [9] (a) Li YQ, Chu YY, Fang RC, Ding SJ, Wang YL, Shen YZ, et al. Polymer 2012; 53(1):229–40;
- (b) Sydlik SA, Chen ZH, Swager TM. Macromolecules 2011;44(4):976-80.
- [10] (a) Wilson D, Stenzenberger HD, Hergenrother PM, editors. Polyimides. Glasgow and London: Blackie; 1990;
 - (b) Ghosh MK, Mittal KL, editors. Polyimides: fundamentals and applications. New York: Marcel Dekker; 1996.
- [11] (a) Ko YG, Kwon W, Yen HJ, Chang CW, Kim DM, Kim K, et al. Macromolecules 2012;45(9):3749–58;
 - (b) Park S, Kim K, Kim JC, Kwon W, Kim DM, Ree M. Polymer 2011;52(10): 2170-9;
 - (c) Hahm SG, Lee TJ, Chang T, Jung JC, Zin WC, Ree M. Macromolecules 2006; 39(16):5385-92;
 - (d) Ree M. Macromol Res 2006;14(1):1-33;
 - (e) Lee SW, Lee SJ, Hahm SG, Lee TJ, Lee B, Chae B, et al. Macromolecules 2005; 38(10):4331–8;
 - (f) Ree M, Shin TJ, Lee SW. Korea Polym J 2001;9(1):1–19;
- (g) Ree M, Kim K, Woo SH, Chang H. J Appl Phys 1997;81(2):698-708.
 - [12] Mallakpour S, Rafiee Z. Polymer 2008;49(13):3007-13.
 - [13] Faghihi K, Hajibeygi M, Shabanian M. Polym Int 2010;59(2):218–26.
- [14] Rifter N, Senkovska I, Kaskel S, Weber J. Macromol Rapid Commun 2011; 32(5):438–43.
- [15] Ding MX. Prog Polym Sci 2007;32(6):623-68.
- [16] Song NH, Qi W, Qiu XP, Gao LX, Ding MX. J Polym Sci Part A: Polym Chem 2004;42(17):4318–26.
- [17] Lin CH, Chang SL, Cheng PW. J Polym Sci Part A: Polym Chem 2011;49(6): 1331-40.
- [18] Liu Y, Zhang YH, Guan SW, Li L, Jiang ZH. Polymer 2008;49(25):5439-45.
- [19] Yu XH, Zhao XG, Liu CW, Bai ZW, Wang DM, Dang GD, et al. J Polym Sci Part A: Polym Chem 2010;48(13):2878-84.
- [20] Lin CH, Chang SL, Cheng PW. Polymer 2011;52(5):1249–55.
- [21] Yang CP, Su YY. J Polym Sci Part A: Polym Chem 2006;44(9):3140-52.
- [22] Huang LT, Yen HJ, Liou GS. Macromolecules 2011;44(24):9595–610.
- [23] Kung YC, Lee WF, Hsiao SH, Liou GS. J Polym Sci Part A: Polym Chem 2011; 49(10):2210-21.
- [24] Lin CH, Chang SL, Peng LA, Peng SP, Chuang YH. Polymer 2010;51(17):3899–906.
- [25] Mathews AS, Kim D, Kim Y, Kim I, Ha CS. J Polym Sci Part A: Polym Chem 2008;46(24):8117–30.
- [26] Cheng SH, Hsiao SH, Su TH, Liou GS. Macromolecules 2005;38(2):307-16.
- 27] Wang CY, Li G, Jiang JM. Polymer 2009;50(7):1709-16.
- [28] Liaw DJ, Chang FC, Leung MK, Chou MY, Muellen K. Macromolecules 2005; 38(9):4024-9.
- [29] Wang CY, Li G, Zhao XY, Jiang JM. J Polym Sci Part A: Polym Chem 2009; 47(13):3309–17.
- [30] Zhang QY, Chen G, Zhang SB. Polymer 2007;48(8):2250–6.
- [31] Zhang SJ, Li YF, Ma T, Zhao JJ, Xu XY, Yang FC, et al. Polym Chem 2010;1(4): 485-93.
- [32] Chung CL, Lee WF, Lin CH, Hsiao SH. J Polym Sci Part A: Polym Chem 2009; 47(7):1756-70.
- [33] Chung CL, Hsiao SH. Polymer 2008;49(10):2476-85.
- [34] Qiu ZM, Wang JH, Zhang QY, Zhang SB, Ding MX, Gao LX. Polymer 2006; 47(26):8444–52.
- [35] (a) Liu Y, Xing Y, Zhang YH, Guan SW, Zhang HB, Wang Y, et al. J Polym Sci Part A: Polym Chem 2010;48(15):3281-9;
 (b) Hsiao SH, Wang HM, Chen WJ, Lee TM, Leu CM. J Polym Sci Part A: Polym Chem 2011;49(14):3109-20.
- [36] (a) Hahm SG, Jin KS, Park S, Ree M, Kim HS, Kwon SK, et al. Macromol Res 2009;17(12):976–86;

(b) Hahm SG, Choi S, Hong SH, Lee TJ, Park S, Kim DM, et al. Adv Funct Mater 2008;18(20):3276–82;

(c) Hahm SG, Lee TJ, Ree M. Adv Funct Mater 2007;17(8):1359-70;

(d) Pyo SM, Kim SI, Shin TJ, Park YH, Ree M. J Polym Sci Part A: Polym Chem 1999;37(7):937–57.

[37] Jiang ZQ, Yao HQ, Zhang ZQ, Yang CL, Liu ZY, Tao YT, et al. Org Lett 2009; 11(12):2607-10.

- [38] Rashidnadimi S, Hung TH, Wong KT, Bard AJ. J Am Chem Soc 2008;130(2):634–9.
- [39] Chou CH, Reddy DS, Shu CF. J Polym Sci Part A: Polym Chem 2002;40(21): 3615-21.
- [40] Kim YH, Kim HS, Kwon SK. Macromolecules 2005;38(19):7950-6.
- [41] Weber J, Su Q, Antonietti M, Thomas A. Macromol Rapid Commun 2007; 28(18):1871–6.
- [42] Xie JH, Zhou QL. Acc Chem Res 2008;41(5):581–93.
- [43] Cheng X, Hou GH, Xie JH, Zhou QL. Org Lett 2004;6(14):2381–3.
- [44] Thiemann F, Piehler T, Haase D, Saak W, Lützen A. Eur J Org Chem 2005; 2005(10):1991–2001.
- [45] Cheng X, Zhang Q, Xie JH, Wang LX, Zhou QL. Angew Chem Int Ed 2005;44(7): 1118–21.
- [46] Cheng X, Zhu SF, Qiao XC, Yan PC, Zhou QL. Tetrahedron 2006;62(34):8077-82.

- [47] Cheng X, Xie JH, Li S, Zhou QL. Adv Synth Catal 2006;348(11):1271-6.
- [48] Yan JC, Cheng X, Zhou QL, Pei J. Macromolecules 2007;40(4):832-9.
- [49] Seto R, Maeda T, Konishi G, Takata T. Polym J 2007;39(12):1351–9.
- [50] Toda F, Tanaka K. J Org Chem 1988;53(15):3607–9.
- [51] Wu ZL, Huang YJ, Zhang CH, Zhu DY, Bian Z, Ding MX, et al. J Appl Polym Sci 2010;117(6):3558–67.
- [52] Seto R, Kojima T, Hosokawa K, Koyama Y, Konishi G, Takata T. Polymer 2010; 51(21):4744–9.
- [53] Sinfield KL, Klass JM, Brown GR. Macromolecules 1995;28(24):8006-15.
- [54] (a) Zhi J, Guan Y, Cui JX, Liu AH, Zhu ZG, Wan XH, et al. J Polym Sci Part A: Polym Chem 2009;47(9):2408–21;
 (b) Abe M, Ohmori K, Suzuki K, Yamamoto T. J Polym Sci Part A: Polym Chem 2010;48(8):1844–8.