

Synthesis and Characterization of New Optically Active Polyesters by Step-Growth Polymerization of Novel Aromatic (2*S*)-4-[(4-Methyl-2-phthalimidyl-pentanoylamino)benzoylamino]isophthalic Acid with Aromatic Diols

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ABSTRACT: A new diacid monomer **9** was synthesized in five steps. Starting from the reaction of L-leucine with phthalic anhydride in acetic acid provided (2*S*)-4-methyl-2-phthalimidylpentanoic acid (**3**) in good yield. The compound **3** was converted to (2*S*)-4-methyl-2-phthalimidylpentanoyl chloride (**4**) by reaction with thionyl chloride. The resulting acid chloride **4** was reacted with *p*-aminobenzoic acid (**5**) in dry tetrahydrofuran and (2*S*)-4-(4-methyl-2-phthalimidylpentanoyl-amino)benzoic acid (**6**) was obtained. Then, it was converted to (2*S*)-4-(4-methyl-2-phthalimidylpentanoylamino)benzoyl chloride (**7**) by treatment with thionyl chloride. The reaction of acid chloride **7** with 5-aminoisophthalic acid in dry *N,N*-dimethylacetamide (DMAc) gave (2*S*)-4-[(4-methyl-2-phthalimidylpentanoylamino)benzoylamino]isophthalic acid (**9**) in high yield. The step-growth polymerization of this diacid with several aromatic diols, such as bisphenol-A (**10a**), phenolphthalein (**10b**), 1,5-naphthalenediol (**10c**), hydroquinone (**10d**), bisphenyl-2,2'-diol (**10e**), 4,4'-dihydroxydi-

phenyl sulfone (**10f**), 4,4'-dihydroxydiphenyl sulfide (**10g**), and 1,8-dihydroxyanthraquinone (**10h**), was carried out in a system of tosyl chloride, pyridine, and *N,N*-dimethylformamide (DMF) to give a series of new optically active polyesters (PE)s with good yield and moderate inherent viscosity ranging from 0.29 to 0.43 dL/g. All of the aforementioned polymers were fully characterized by FTIR and specific rotation. Some structural characterization was performed by ¹H NMR and elemental analysis. These polymers are readily soluble in amide-type solvents such as DMF, DMAc, dimethyl sulfoxide, and protic solvents such as sulfuric acid. Thermal gravimetry analysis showed that the 10% weight loss temperature in a nitrogen atmosphere was more than 360°C, which indicates that the resulting PEs have a good thermal stability as well as excellent solubility. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2942–2949, 2008

Key words: polyester; step-growth polymerization; optically active polymers

INTRODUCTION

The separation of chiral materials has been of great attention because the majority of bioorganic compounds are chiral. Living organisms, for instance, are composed of chiral biomolecules such as proteins, sugars, nucleic acids, and amino acids. In nature these biomolecules exist in only one of the two possible enantiomeric forms, for example sugars in the D-form and amino acids in the L-form. Chirality is a main concern in the current pharmaceutical industry, because each enantiomer of the chiral

drugs shows great differences in pharmacodynamic, pharmacological, and toxicological behavior.^{1,2} Separation of enantiomers can be carried out simultaneously via high-performance liquid chromatography.³ Thus, the synthesis and application of chiral macromolecules are active research areas. Lately, we have synthesized optically active polymers by different methods.^{4–7}

Polyesters (PE)s are one of the most multipurpose polymers. They restrain extensively different materials with large uses, which are made by a variety of manufacturing methods. They have in common the ester group —CO—O— in their backbone, which is a polar group and brings about inter and intramolecular chain interactions that may reflect in some properties.^{8–10} They display good thermal stability, solvent resistance, and good mechanical properties and are consequently, applied widely in the automobile, aviation, and electronic industries. However, most PEs encounter processing difficulties due to

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their high glass transition or melting temperatures coupled with insolubility in most organic solvents.^{11–14}

The direct step-growth polymerization involves the use of free carboxylic acid and diols under gentle conditions using activating reagents. Numerous condensing agents appropriate for the direct step-growth polymerization such as diphenyl chlorophosphate and arylsulfonyl chlorides have been developed in the past decades. It was established that Vilsmeier adduct derived from arylsulfonyl chlorides and *N,N*-dimethylformamide (DMF) in pyridine (Py) was effectively used as a proper condensing agent for the synthesis of aromatic PEs by the direct step-growth polymerization of aromatic dicarboxylic acids and bisphenols.¹⁵

In this article we wish to report the synthesis and characterization of new optically active PEs from aromatic diols and (2*S*)-4-[(4-methyl-2-phthalimidylpentanoylamino)benzoylamino]isophthalic acid as a monomer containing preformed imide group under Vilsmeier adduct derived from arylsulfonyl chlorides and DMF in Py.

EXPERIMENTAL

Materials and equipments

All chemicals were purchased from Fluka chemical (Buchs, Switzerland), Aldrich chemical (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany), and Merck chemical (Darmstadt, Germany) *p*-Aminobenzoic acid and 5-aminoisophthalic acid were recrystallized from H₂O and H₂O/DMF (4/1) mixture, respectively. DMAc was dried over BaO and then distilled under reduced pressure. Tetrahydrofuran (THF) was dried over sodium and then distilled under simple distillation. Bisphenol-A was purified by recrystallization from acetic acid-water. The other diols were used as obtained without further purification.

Proton nuclear magnetic resonance (¹H NMR, 500 MHz) spectra were recorded in DMSO-*d*₆ solution using a Bruker (Germany) Avance 500 instrument and also Carbon nuclear magnetic resonance (¹³C NMR, 125 MHz) spectrum was recorded on a Bruker (Germany) advance 500 instrument at Sharif University of Technology Tehran, Iran. FTIR spectra were recorded on a spectrophotometer (Jasco-680, Japan). The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wavenumbers (cm⁻¹). Band intensities are assigned as weak (w), medium (m), strong (s), and broad (br). Inherent viscosities were measured by using a Cannon-Fenske Routine Viscometer (Germany) at the concentration of 0.5 g/dL at 25°C. Specific rotations were measured by a Jasco Polarimeter

(Japan). Thermal gravimetric analysis (TGA) data for polymers were taken on a Perkin-Elmer instrument in a nitrogen atmosphere at a rate of 10°C/min, and differential scanning calorimetry (DSC) data were recorded on a rate of 20°C. Elemental analyses were performed by the Iran Polymer and Petrochemical Research Institute, Tehran, Iran. Glass transition temperatures (*T*_g) were read at the middle of the transition in the heat capacity taken from the heating DSC traces.

Monomer synthesis

(2*S*)-4-Methyl-2-phthalimidylpentanoic acid (3)

Into a 25 mL, round-bottomed flask, 2.00 g (1.35 × 10⁻² mol) of phthalic anhydride (1), 1.77 g (1.35 × 10⁻² mol) of L-leucine (2), 15 mL of acetic acid, and a stirred bar were placed. The solution was refluxed for 12 h. The solvent was removed under reduced pressure and to this residue; the solution was poured into a mixture of 100 mL of water and 10 mL of hydrochloric acid. The solution was then stirred for 3 h. A white precipitate was formed, and then filtered off and dried to 3.01 g of compound 3. Yield 80%, m.p. 118–120°C.^{16,17}

(2*S*)-4-Methyl-2-phthalimidylpentanoyl chloride (4)

Into a 25 mL, round-bottomed flask 1.00 g (3.83 × 10⁻³ mol) of compound 3, 2 mL of thionyl chloride, 4 mL of dichloromethane, and a stirring bar were placed. The stirring was started and the mixture was refluxed for 4 h. The solvent was removed via distillation and 20 mL of *n*-hexane was added, and was stirred for 30 min. *n*-hexane was distilled off, and the product was collected and direct in vacuum to give 1.02 g (95%) of a viscous liquid.¹⁸

(2*S*)-4-(4-Methyl-2-phthalimidylpentanoylamino)benzoic acid (6)

Into a 25 mL round-bottomed flask fitted with a magnetic stirrer was placed a solution of 0.49 g (3.51 × 10⁻³ mol) *p*-aminobenzoic acid (5) and 5 mL of dry THF. The mixture of 1.00 g (3.54 × 10⁻³ mol) of acid chloride 4 in 5 mL of dry THF was added to this solution and stirred for 12 h at 0°C. The solution was poured into a mixture of 50 mL of water and 5 mL of hydrochloric acid. The white precipitate was collected by filtration and washed thoroughly with water and dried at 70°C for 10 h, to give 1.36 g (85%) of compound 6. m.p. 206–208°C, [α]_D²⁵ = -27.34 (0.05 g in 10 mL of DMF).

FTIR (KBr): 2400–3600 (acidic OH, br), 3316 (s, br), 2960 (s), 2871 (m), 1718 (s), 1684 (s), 1617 (m), 1598 (s), 1527 (s), 1469 (m), 1409 (s), 1384 (s), 1292 (s), 1252 (s), 1154 (m), 1120 (w), cm⁻¹.

^1H NMR (500 MHz, DMSO- d_6): δ 0.88–0.90 (d, CH_3 , $J = 6.59$ Hz), 0.92–0.93 (d, CH_3 , $J = 6.49$ Hz), 1.42–1.49 (m, CH), 1.96–2.00 (m, CH), 2.20–2.26 (m, CH), 4.94–4.97 (dd, CH, $J_1 = 11.38$ Hz, $J_2 = 4.43$ Hz), 7.67–7.69 (d, 2CH, Ar, $J = 8.69$ Hz), 7.88–7.94 (m, 6CH, Ar), 10.21 (s, NH), 12.73 (s, COOH) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ 21.76 (CH_3 , aliphatic), 24.04 (CH_3 , aliphatic), 25.65 (CH, aliphatic), 37.76 (CH_2 , aliphatic), 53.07 (CH, aliphatic) 120.21 (CH, aromatic), 124.17 (CH, aromatic), 126.45 (CH, aromatic), 131.08 (CH, aromatic), 132.34 (CH, aromatic), 135.56 (CH, aromatic), 143.51 (CH, aromatic), 167.73 (CO, imidic), 168.63 (CO, amidic), 168.79 (CO, acidic) ppm.

(2S)-4-(4-Methyl-2-phthalimidylpentanoylamino) benzoyl chloride (**7**)

Into a 25 mL, round-bottomed flask 1.00 g (3.5×10^{-3} mol) of compound **6**, 2 mL of thionyl chloride, 5 mL of dichloromethane, and a stirring bar were placed. The stirring was started and the mixture was refluxed for 4 h. The solvent was removed via distillation and 20 mL of *n*-hexane was added, and was stirred for 30 min. *n*-hexane was distilled off, and the solid was collected and dried to give 0.94 g (94%) of a white solid.

FTIR (KBr): 2956 (m), 2927 (m), 1773 (s), 1714 (s), 1594 (s), 1494 (w), 1380 (s), 1204 (s), 1110 (w) 1029 (w), 715 (m) cm^{-1} .

(2S)-4-[(4-Methyl-2-phthalimidylpentanoylamino) benzoylamino]isophthalic acid (**9**)

Into a 25 mL round-bottomed flask fitted with a magnetic stirrer was placed a solution of 0.46 g (3.48×10^{-3} mol) 5-aminoisophthalic acid (**8**) and 5 mL of dry DMAc. A solution of acid chloride **7** in 5 mL of dry DMAc was added dropwise to this mixture and was stirred for 12 h at 0°C . The whole solution was poured into a mixture of 50 mL of water and 5 mL of hydrochloric acid. The white precipitate was collected by filtration and washed thoroughly with water and dried at 70°C for 10 h to give 1.2 g (83%) of compound **9**. m.p. $194\text{--}196^\circ\text{C}$. $[\alpha]_D^{25} = -42.38$ (0.05 g in 10 mL of DMF).

FTIR (KBr): 2400–3600 (acidic OH, br), 3315 (s, br), 3110 (m), 2958 (m), 1778 (w), 1715 (s), 1598 (s), 1536 (s), 1286 (m), 1177 (s) 1124 (w), 717 (s) cm^{-1} .

^1H NMR (500 MHz, DMSO- d_6): δ 0.90–0.91 (d, CH_3 , $J = 6.56$ Hz), 0.94–0.95 (d, CH_3 , $J = 6.45$ Hz), 1.46–1.47 (m, CH), 1.97–2.00 (m, CH), 2.23–2.26 (m, CH), 4.96–4.99 (dd, CH, $J_1 = 11.36$ Hz, $J_2 = 4.44$ Hz), 7.71–7.73 (d, 2CH, Ar, $J = 8.74$ Hz), 7.90–8.01 (m, 6CH, Ar), 8.21 (s, CH, Ar), 8.67 (d, 2CH, Ar, $J = 6.22$ Hz), 10.22 (s, NH), 10.48 (s, NH) 13.22 (s, 2COOH) ppm.

^{13}C NMR (125 MHz, DMSO- d_6): δ 21.76 (CH_3 , aliphatic), 24.07 (CH_3 , aliphatic), 25.68 (CH, aliphatic), 37.77 (CH_2 , aliphatic), 53.10 (CH, aliphatic), 120.18 (CH, aromatic), 124.19 (CH, aromatic), 125.55 (CH, aromatic), 129.49 (CH, aromatic), 129.86 (CH, aromatic), 132.35 (CH, aromatic), 132.48 (CH, aromatic), 135.59 (CH, aromatic), 140.82 (CH, aromatic), 142.76 (CH, aromatic), 165.95 (CO, imidic), 167.80 (CO, amidic), 168.41 (CO, acidic), 168.78 (CO, amidic) ppm.

Elemental analysis: ($\text{C}_{29}\text{H}_{25}\text{N}_3\text{O}_8$): Calcd. C, 64.08, H, 4.64, N, 7.73; Found: C, 63.94; H, 4.80; N, 7.48.

Polymer synthesis

The PEs were prepared by the following procedure: For synthesis of **PE11a**, a Py (0.20 mL) solution of tosyl chloride (TsCl) 0.22 g (1.15×10^{-3} mol), after 30 min stirring at room temperature (RT), was treated with DMF 0.07 g (9.57×10^{-4} mol) for 30 min and the resulting solution was added dropwise to a solution of diacid **9**, 0.100 g (1.84×10^{-4} mol) in Py (0.20 mL). The mixture was maintained at RT for 30 min and then a solution of bisphenol-A (**10a**) 0.042 g (1.84×10^{-4} mol) in Py (0.20 mL) was added dropwise and the whole solution was stirred at RT for 30 min and at 120°C for 2.5 h. As the reaction proceeded, the solution became viscous. Then the viscous liquid was precipitated in 15 mL of methanol to give 0.14 g (99%) of **PE11a**.

The other (PE)s (**11b–11h**) were prepared by a similar procedure.

PE11a: white solid; FTIR (KBr): 3348 (m, br), 2961 (m), 2895 (m), 1776 (w), 1715 (s), 1598 (m), 1467 (w), 1384 (m), 1170 (s), 1122 (w), 1069 (m), 720 (m) cm^{-1} .

PE11b: white solid; FTIR (KBr): 3340 (m, br), 2958 (m), 2871 (w), 1743 (w), 1714 (s), 1599 (s), 1507 (s), 1384 (s), 1197 (s), 1167 (w), 1085 (m), 720 (m) cm^{-1} .

PE11c: brown solid; FTIR (KBr): 3412 (m, br), 2958 (m), 2871 (m), 1774 (w), 1714 (s), 1599 (m), 1531 (m), 1384 (s), 1198 (s), 1161 (m), 720 (m) cm^{-1} .

PE11d: off white solid; FTIR (KBr): 3413 (s, br), 2958 (w), 2883 (w), 1775 (w), 1714 (s), 1599 (m), 1500 (m), 1384 (m), 1211 (s), 1171 (s), 720 (w) cm^{-1} .

PE11e: white solid; FTIR (KBr): 3413 (s, br), 3070 (w), 2958 (w), 1775 (w), 1714 (s), 1599 (m), 1384 (m), 1171 (s), 720 (w) cm^{-1} .

PE11f: white solid; FTIR (KBr): 3412 (m, br), 3100 (m), 2958 (m), 1774 (w), 1714 (s), 1598 (m), 1529 (m), 1384 (m), 1192 (s), 1151 (s), 719 (w) cm^{-1} .

PE11g: off white; FTIR (KBr): 3361 (m, br), 3095 (m), 2957 (m), 1775 (w), 1714 (s), 1599 (m), 1530 (m), 1384 (m), 1191 (s), 1162 (m), 720 (m) cm^{-1} .

PE11h: yellow; FTIR (KBr): 3414 (s, br), 2958 (m), 1708 (m), 1624 (s), 1600 (m), 1534 (m), 1384 (m), 1208 (s), 1160 (m), 723 (w) cm^{-1} .

PE11a: white solid; ^1H NMR (500 MHz, DMSO-d_6): δ 0.89–0.92 (distorted dd, 6H, CH_3), 1.45 (m, 1H, CH), 1.70 (s, 6H, CH_3), 1.99 (m, 1H, CH), 2.25 (m, 1H, CH), 4.96 (s, 1H, CH), 7.25–8.94 (m, 19H, Ar-H), 10.23 (s, NH), 10.66 (s, br, NH).

PE11g: off white; ^1H NMR (500 MHz, DMSO-d_6): δ 0.89–0.90 (d, 3H, CH_3 , $J = 4.49$ Hz), 0.93–0.94 (d, 3H, CH_3 , $J = 4.46$ Hz), 1.46 (m, 1H, CH), 2.00 (m, 1H, CH), 2.23–2.28 (m, 1H, CH), 4.96–4.98 (distorted d, 1H, CH), 7.41–8.96 (m, 19H, Ar-H), 10.24 (s, NH), 10.64 (s, NH).

RESULTS AND DISCUSSION

Monomer synthesis

The bulky new monomer **9** with chiral architecture was synthesized in five steps. First, the imide-acid **3** was prepared by the condensation reaction of equimolar amount of compounds **1** and **2** in acetic acid. The adduct **3** was converted to acid chloride derivative **4** by reaction with thionyl chloride in dichloromethane. The reaction of compound **4** with *p*-aminobenzoic acid was performed in dry THF at 0°C and imide acid **6** was obtained in high yield. Compound **6** was converted to acid chloride derivative **7** by reaction with thionyl chloride in dichloromethane.

The chemical structure and purity of these compounds were confirmed with thin layer chromatography (TLC), FTIR, ^1H NMR, and ^{13}C NMR spectroscopy techniques. The FTIR spectrum of compound **6** revealed a broad and strong peak at 2600–3600 cm^{-1} , which was assigned to the COOH groups, and two absorption bands at 1718 and 1775 cm^{-1} , which were characteristic peaks for imide rings. The disappearance of the strong acidic hydroxyl peak in the FTIR spectrum of compound **7** confirmed a complete conversion of **6** to **7**. However, because of the electron-withdrawing character of the Cl group, the two carbonyl peaks of acid chloride, as compared with its starting imide acid, were shifted to higher frequency.

The ^1H NMR spectrum (500 MHz) of compound **6** is depicted in Figure 1, which shows the characteristic absorption of two diastrotopic CH_3 (doublet) at 0.88 and 0.92 ppm, CH (multiplet) at 1.46 ppm, CH_2 (multiplet) at 1.98 and 2.21 ppm, CH chiral center (doublet of doublet) at 4.96 ppm, N–H amidic

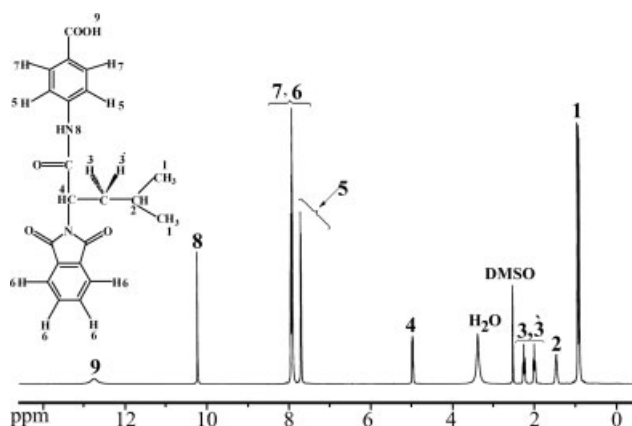


Figure 1 ^1H NMR (500 MHz) spectrum of imide acid **6** in DMSO-d_6 at RT.

group and acidic O–H at 10.21 and 12.73 ppm, respectively.

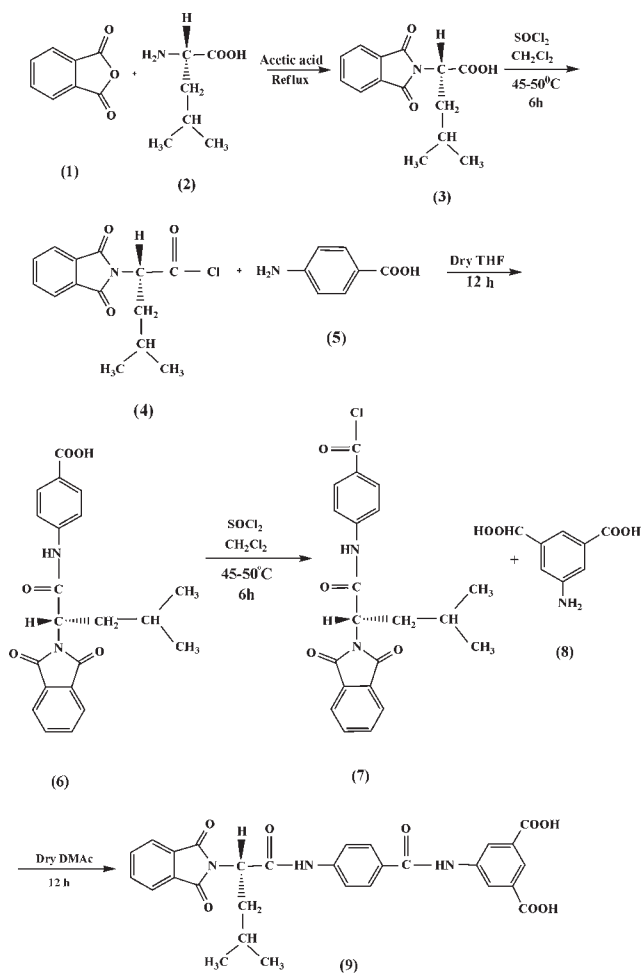
The ^{13}C NMR spectrum (125 MHz) of compound **6** shows carbons for diastrotopic methyl at 21.76 and 24.05 ppm, methyne at 25.63 ppm, methylene bonded to chiral center and chiral center at 37.76 and 53.05 ppm, respectively. In addition the presence of six different aromatic carbons and three carbons for carbonyl groups in this spectrum confirms the structure of compound **6**.

The reaction of compound **7** with 5-aminoisophthalic acid was performed in dry DMAc at 0°C . The resulting novel optically active aromatic diacid **9** with pendent phthalimidyl group was obtained in high yield (Scheme 1), and its chemical structure and purity were confirmed by TLC, elemental analysis, FTIR, ^1H NMR, and ^{13}C NMR spectroscopy techniques.

The FTIR spectrum of compound **9** revealed a broad and strong peak at 2600–3600 cm^{-1} , which was assigned to the COOH groups, and two absorption bands at 1715 and 1778 cm^{-1} , which were characteristic peaks for imide rings.

The ^1H NMR spectrum (500 MHz) of compound **9** is illustrated in Figure 2, which shows the characteristic absorption of two diastrotopic CH_3 (doublet) at 0.90 and 0.94 ppm, CH (multiplet) at 1.47 ppm, CH_2 (multiplet) at 2.00 and 2.25 ppm, CH chiral center (doublet of doublet) at 4.98 ppm, N–H amidic group at 10.22, 10.48 and for acidic group at 13.22 ppm.

The ^{13}C NMR spectrum (125 MHz) of compound **9** shows carbons for diastrotopic methyl at 21.76 and 24.05 ppm, methyne at 25.67 ppm, methylene bonded to chiral center and chiral center carbon at 37.76 and 53.01 ppm, respectively. In addition the presence of 10 different aromatic carbons and three carbons for carbonyl groups in this spectrum also confirms the structure of compound **9** (Fig. 3).



Scheme 1 Synthesis of monomer 9.

The elemental analysis results are in good agreement with the structure of compound 9.

Polymer synthesis

In this work, the Vilsmeier adduct was used for the polycondensation of aromatic diacid and aromatic diols in the following way (Schemes 2 and 3): TsCl

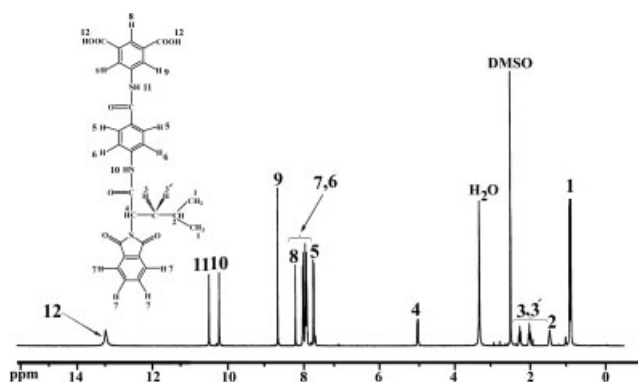


Figure 2 ^1H NMR (500 MHz) spectrum of monomer 9 in DMSO-d_6 at RT.

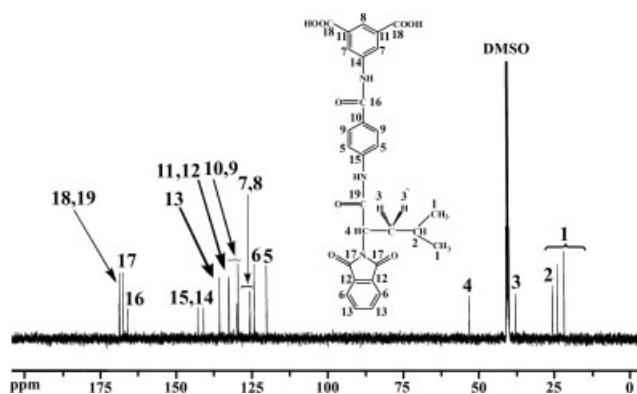
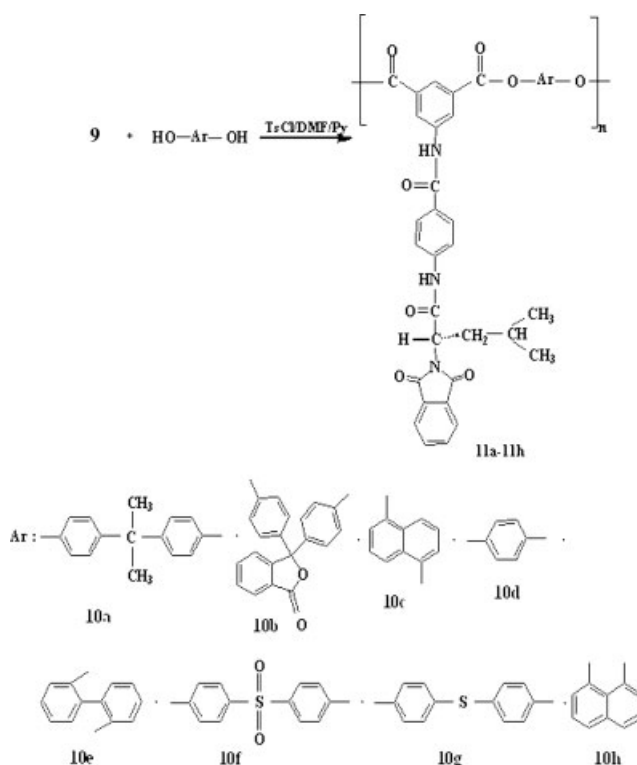
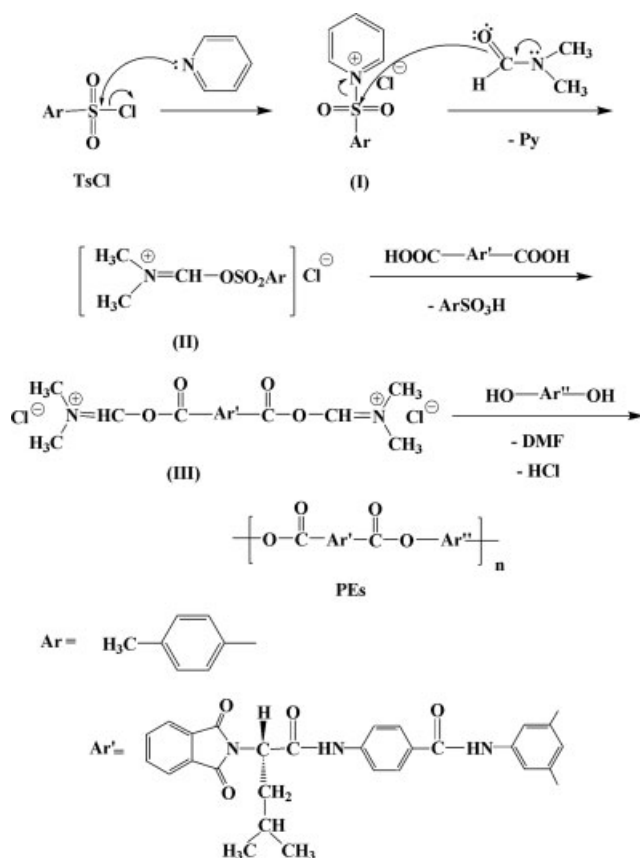


Figure 3 ^{13}C NMR (125 MHz) spectrum of monomer 9 in DMSO-d_6 at RT.

was dissolved in Py to yield sulfonium salt (I) and after a certain period of time (aging time) the solution was treated with DMF for 30 min to form Vilsmeier adduct (II) as proposed by Higashi and coworkers.^{19,20} The reaction mixture was added to a solution of diacid in Py to form activated acid (III). After 30 min a solution of diol in Py was added and the whole solution was maintained at RT and then at an elevated temperature for a period of time. In our previous work, the polycondensation with this condensing agent was carried out by varying the aging time of the initial reaction of TsCl and Py, the molar ratio of DMF to diacid, the reaction time, and the reaction temperature.²¹ All of these parameters



Scheme 2 Synthesis of PEs.



Ar'' = different aromatic group as identified in scheme 2

Scheme 3 Mechanistic representation of polycondensation reaction of monomer **9** with aromatic diols using TsCl/DMF as a condensing agent.

had a vital effect on the polymer chain growth. For direct polycondensation of monomer **9** the reported optimized conditions²¹ were selected and polymerization was carried out under these conditions.

The synthesis and some physical properties of these novel optically active PEs are listed in Table I. The inherent viscosities of the resulting polymers under optimized conditions were in the range of 0.29–0.43 dL/g and the yields were 54–99%. The

TABLE II
Elemental Analysis of PE11a and PE11b

Polymer	Formula	Elemental analysis (%)			
		C	H	N	
PE11a	(C ₄₄ H ₃₇ N ₃ O ₈) _n (735) _n	Calcd.	71.84	5.04	5.72
		Found	69.77	5.07	5.61
PE11b	(C ₄₉ H ₃₅ N ₃ O ₁₀) _n (825) _n	Calcd.	71.27	4.24	5.21
		Found	68.72	4.42	5.08

incorporation of a chiral unit into the polymer backbone was confirmed by measuring the specific rotations of polymers with different source lamps (Table I). The specific rotation of polymers based on different diols showed random changes. These observations are the result of different polymer structures and inherent viscosities. This is a normal behavior for all optically active compounds. Since optical rotation is highly dependent on the chemical structures of the resulting polymeric materials, any small changes in the chemical structures of any chiral molecules has substantial random effect on the optical rotations and is not predictable. As shown in Table I all of the polymers show optical rotation and are therefore optically active.

Structural characterization of polymers

The structures of these polymers were confirmed as PEs with elemental analysis and FTIR and ¹H NMR spectroscopy techniques. Elemental analysis data of the resulting polymers are listed in Table II. FTIR spectra of all polymers indicate the characteristic absorption peaks for the imide ring at 1714 and 1775 cm⁻¹ because of the symmetrical and asymmetrical carbonyl stretching vibrations. Bands of the amide N–H groups appeared around 3340–3414 cm⁻¹ (hydrogen band) and 1500–1600 cm⁻¹ (amide II band). Figure 4 portrays a typical FTIR spectrum of PE11a. The ¹H NMR spectra of PE11a and PE11g are

TABLE I
Synthesis and Some Physical Properties of PE11a–PE11h Prepared Using TsCl/DMF/Py

Polymer	Diol	Yield (%)	η (dL/g) ¹	[α] _D ^{25, a}	[α] _{HG} ^{25, a}	Color ^b
PE11a	10a	99	0.43	–18.22	–9.10	W
PE11b	10b	95	0.35	–14.08	–16.64	W
PE11c	10c	79	0.29	–8.74	–45.38	B
PE11d	10d	84	0.37	–15.04	–33.76	OW
PE11e	10e	72	0.30	–8.44	–14.48	W
PE11f	10f	54	0.34	–12.74	–15.58	W
PE11g	10g	93	0.43	–13.72	–20.38	OW
PE11h	10h	58	0.38	–10.74	–46.92	Y

^a Measured at a concentration of 0.5 g/dL in DMF at 25°C.

^b W = white, OW = off white, Y = yellow, B = brown.

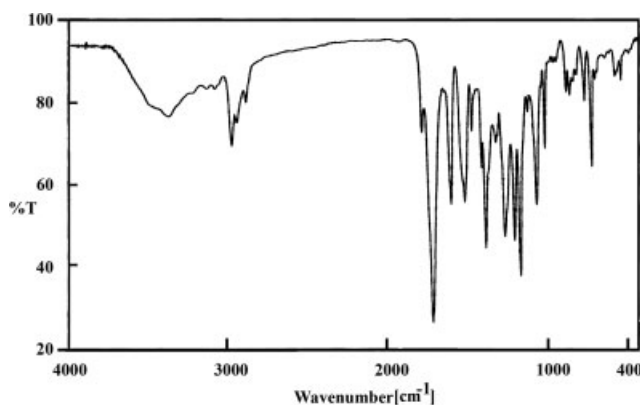


Figure 4 FTIR spectrum of PE11a.

given in Figures 5 and 6. The pattern of the spectra is similar to those of monomer **9** and the corresponding diols.

Thermal properties of PEs

The thermal stability of some PEs was investigated by TGA measurements. Typical TGA curves of representative polymers are illustrated in Figure 7 and Table III. The temperatures of 5 and 10% weight loss with the char yield at 600°C for PE11a and PE11d were calculated from their thermograms. The DSC analyses for PE11a and PE11d show T_g around 150 and 149°C, respectively, (Table III).

Solubility of PEs

Solubility of PE11a–PE11h at RT has been investigated in various solvents. All polymers were soluble in organic polar solvents such as DMAc, DMF, and NMP. These polymers were insoluble in solvents such as chloroform, cyclohexane, and water. Higher solubility of PEs can be interpreted by the effects of

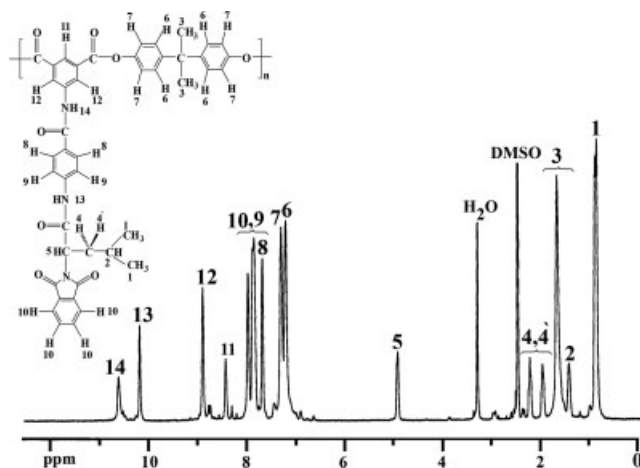


Figure 5 ^1H NMR (500 MHz) spectrum of PE11a in DMSO- d_6 at RT.

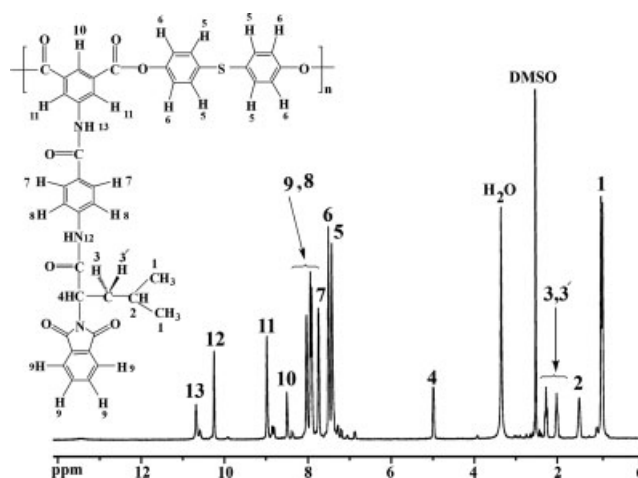


Figure 6 ^1H NMR (500 MHz) spectrum of PE11g in DMSO- d_6 at RT.

flexible amide and imide groups in polymers side chain.

CONCLUSIONS

In this study, we have successfully synthesized a novel chiral aromatic dicarboxylic acid **9**, containing a rigid phthalimide and flexible L-leucine pendent group. A series of new optically active aromatic PEs were prepared by the direct polycondensation from compound **9** with various aromatic diols using TsCl/DMF/Py as a condensing agent. Flexible pendent groups of these polymers disturbed the strong interchain forces and inherent macromolecular rigidity. The results presented herein also clearly demonstrate that incorporating the phthalimide group into the polymer side chain as well as combination of the wholly aromatic backbone and aliphatic pendent group in the presence of several functional groups remarkably enhanced the solubility while maintaining good thermal stability of the new polymers. From the chemical point of view, the ester group

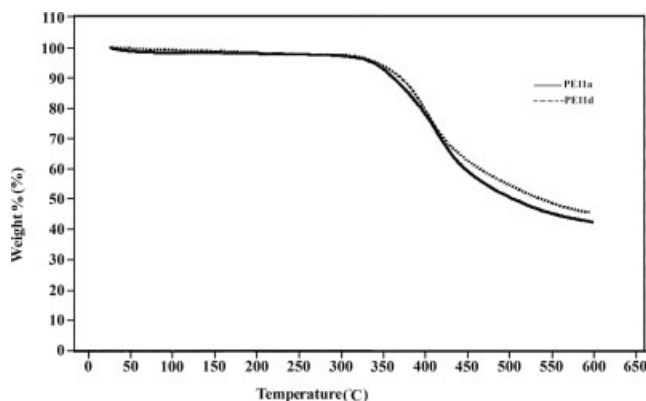


Figure 7 TGA thermograms of PE11a and PE11d under N_2 atmosphere and a heating rate of 10°C/min.

TABLE III
Thermal Properties of PE11a and PE11d

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield (%) ^c	T_g (°C)
PE11a	350	360	42	150
PE11d	350	380	48	149

^a Temperature at which 5% weight loss was recorded by TGA at heating rate of 10°C/min in N₂.

^b Temperature at which 10% weight loss was recorded by TGA at heating rate of 10°C/min in N₂.

^c Weight percentage of material left undecomposed after TGA analysis at a maximum temperature of 600°C in N₂.

imparts to the polymer's main chain increased sensitivity to hydrolysis that can cause chain breaking. In addition because of the existence of amino acids in the polymer pendent group these polymers are expected to be biodegradable and are therefore classified under environmentally friendly polymers.

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References

- Collins, A. N.; Sheldrake, G. N.; Crosby, J. *Chirality in Industry*; Wiley: New York, 1994.
- Mallakpour, S.; Seyedjamali, H. *Amino acids* 2007, 34, 531.
- Subramanian, G. *Chiral Separation Techniques*; Wiley-VCH: New York, 2001.
- Mallakpour, S.; Kowsari, E. *Polym Adv Technol* 2005, 16, 466.
- Mallakpour, S.; Kowsari, E. *J Appl Polym Sci* 2005, 96, 435.
- Mallakpour, S.; Kowsari, E. *J Appl Polym Sci* 2004, 91, 2991.
- Mallakpour, S.; Zamanlou, M. R. *J Appl Polym Sci* 2004, 91, 3281.
- Liaw, D. J.; Fan, C. L.; Lin, C. C.; Wang, K. L. *J Appl Polym Sci* 2004, 92, 2486.
- Liaw, D. J.; Hsu, J. J.; Liaw, B. Y. *J Polym Sci Part A: Polym Chem* 2001, 39, 2951.
- Zhang, S.; Li, Y.; Yin, D.; Wang, X.; Zhao, X.; Shao, Y. *Eur Polym J* 2005, 41, 1097.
- Sharmila, R. J.; Premkumar, S.; Alagar, M. *J Appl Polym Sci* 2007, 103, 167.
- Honkhambe, P. N.; Avadhani, C. V.; Wadgaonkar, P. P.; Salunkhe, M. M. *J Appl Polym Sci* 2007, 106, 3105.
- Nazare, S.; Kandola, B. K.; Horrocks, A. R. *Polym Adv Technol* 2006, 17, 294.
- Yang, S. C.; Kim, Y. P. *J Appl Polym Sci* 2007, 106, 1274.
- Mallakpour, S.; Kowsari, E. *Polym Adv Technol* 2006, 17, 174.
- Mallakpour, S. E.; Hajipour, A. R.; Khoee, S.; Sheikholeslami, B. *Polym Int* 1998, 47, 193.
- Bose, A. K.; Greer, F.; Price, C. C. *J Org Chem* 1958, 23, 1335.
- Mallakpour, S.; Kolahdoozan, M. *J Appl Polym Sci* 2007, 104, 1248.
- Higashi, F.; Tobe, A. *Macromol Chem Phys* 2001, 202, 745.
- Higashi, F.; Takashi, I.; Akyama, N. *J Polym Sci Polym Chem Ed* 1984, 22, 3607.
- Mallakpour, S.; Kolahdoozan, M. *Iranian Polym J* 2006, 15, 307.