Step-Growth Polymerization of 5-[(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)-3-methylbutanoyl-amino]isophthalic Acid with Aromatic Diols

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ABSTRACT: *cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid anhydride (**1**) was converted to imide acid (**2**) by reaction with S-valine. Compound **2** was converted to the acid chloride (**3**) by reaction with thionyl chloride and then treated with 5-aminoisophthalic acid in dry *N,N*-dimethylacetamide to obtain 5-[(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)-3-methylbutanoylamino]isophthalic acid (**4**). Direct step-growth polymerization of this novel chiral diacid monomer **4** with a series of different diols in a system of tosyl chloride, pyridine, and *N,N*-dimethylformamide was carried out. The optically active polyesters (PEs) were obtained with good yield and moderate inherent viscosity ranging from 0.23 to 0.48 dL/g. The resulting polymers were characterized with FTIR, ^{1}H-NMR, and elemental analysis techniques. The prepared PEs showed good thermal stability up to 320°C as measured by thermogravimetric analysis. Specific rotation experiments demonstrated the induction of optical activity due to successful insertion of S-valine in the structure of pendant groups. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3239–3246, 2010

Key words: biodegradable polymers; high-performance polymers; chiral polyesters; polycondensation reaction

INTRODUCTION

The troubles of environmental pollution and waste management from the bioresistant synthetic plastics have become increasingly serious in near several decades. In the mean time, the development of biodegradable polymers offer another way to solve the problems. Biodegradable polymers had been developed and applied in many fields likewise packaging, agriculture, sanitary, and other biomedical applications nowadays. Synthetic biodegradable polymers are also widely utilized in the fabrication of scaffolds for bone tissue engineering and they are useful materials for controlled drug delivery.[1,2] Biodegradable polymers offer a viable alternative to commodity plastics in a number of bulk applications where recycling is impractical or uneconomical. Among these biodegradable materials, the family of aromatic polyesters (PE)s show to be the most attractive and hopeful because of their susceptibility to biological attacks.[3–5] PEs constitute a qualified family of degradable polymeric materials for bioapplications, with the additional advantage that several monomeric precursors can be derived from natural resources. One of the ways of modifying the properties of biodegradable PEs is to incorporate different kinds of amino acids into the polymer backbones. Several studies already indicated that materials based on amino acids exhibit an excellent *in vitro* or *in vivo* biocompatibility. The polymers based on amino acids have attained a unique position in the biomedical field because of their biocompatibility properties.[6]

Polymerization of chiral, nonracemic monomer is one of the most frequently used strategies to prepare optically active polymers. With this approach, the stereo-center in monomer molecule plays an important role in induction of chiral properties.[7,8] Several methods have been reported for the preparation of chiral polymers including incorporation of amino acids into the polymer backbone or side chains.[9] Amino acids have been often employed as chiral sources in the synthesis of chiral polymers because of their accessibility and biological relevance and it can lead to new biomaterials with a wide range of properties that can be easily modulated by varying the components in the building block of the macromolecular backbone during synthesis.[10–14] Chiral polymers, including those bearing main or side chain amino acid units have found successful uses

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in the pharmaceutical industry for enantio-selective separation of drugs, high-performance liquid chromatography as chiral stationary phase, chiral liquid crystals, and biomedical devices, etc.[15,16]

High performance is a general term that can be used to describe many polymers. The high-performance terminology refers to unusual stability upon exposure to some type of harsh environment and to properties that surpass those of conventional polymers.[17] Many aromatic polymers, such as polyimides, polyamides, and PEs have been synthesized during the last five decades. These polymers offer good mechanical, physical, thermal properties, and high chemical resistance, because of the high aromatic content; all of the polymers display excellent thermal stability. PEs synthesized from polyesterification reaction, ring-opening polymerization of cyclic monomers, and polycondensation have been investigated widely because of their superior mechanical properties. However, wholly aromatic PEs exhibit low solubility in organic solvents and high melting temperatures which make them difficult to be processed. Many researchers have focused on modifying PEs for improving solubility by introducing long chain branches as pendant groups into the polymer backbone. Branching influences on PEs properties for new high-performance applications. If the pendant groups, which result in an ordered polymer matrix, are carefully chosen, it is possible to promote the solubility without affecting thermal and mechanical properties to any great extent.[18–20] The incorporation of bulky side groups also decreases the molecular mobility, so that the overall observable effect is an increase of the glass transition temperature and an improvement of solubility at the same time.[18–20]

Anthracene and its derivatives have been extensively considered in many fields, e.g., material chemistry, high fluorescence, thermochromic or photochromic fields, and incorporated into polymers, films, and crystals. In biological systems, anthracene-based compounds are also useful for probing DNA cleavage.[21,22] Generally speaking, the central B-ring of anthracene is considerably more reactive than the other two rings. Moreover, σ-complex at the C9-position of anthracene could be stabilized by the two benzene rings, which might prevent rearomatization.[23]

Throughout this study, we successfully synthesized a series of novel PEs containing anthracene moieties and S-valine amino acid groups in the side chain via direct polyesterification using Vilsmeier adduct. In addition, the introduction of these pendant bulky groups should disrupt interchain interactions and reduce packing efficiency and crystallinity. Therefore, this methodology should enhance the solubility of the resulting polymers without effecting on thermal properties. Because of the existence of amino acids in the polymer pendant group, these polymers are expected to be biodegradable and optically active.

EXPERIMENTAL

Material

Commercial products were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany), and Merck Chemical Co. *N*,*N*-dimethylacetamide (DMAc) and *N*,*N*-dimethylformamide (DMF) were dried over BaO and $CaCl_2$, respectively, and then were distilled under reduced pressure. Maleic anhydride and bisphenol A were purified by recrystallization from dichloromethane (CH_2Cl_2) and acetic acid/water, respectively. The other materials were used as obtained without further purification.

Apparatus

Proton nuclear magnetic resonance (^{1}H-NMR, 500 MHz) spectra were recorded in DMSO-d_6 solution using a Bruker (Germany) Avance 500 instrument and also carbon nuclear magnetic resonance (^{13}C-NMR, 125 MHz) spectrum was recorded on a Bruker (Germany) advance 500 instrument. Proton resonances are designated as singlet (s), doublet (d), doublet of doublet (dd), and multiplet (m). FTIR spectra were recorded on Jasco-680 (Japan) spectrophotometer. The spectra of solids were obtained using KBr pellets. Vibration bands were reported as wavenumber (cm^{-1}). The band intensities were classified as weak (w), medium (m), strong (s), and broad (br). Inherent viscosities of polymer solution (0.5% w/v) in DMF were determined at 25°C by a standard procedure using a Cannon Fenske Routine viscometer (Cannon, Mainz, Germany). The specific rotations were measured by a Jasco polarimeter (Japan). Thermogravimetric analysis (TGA) data for polymers were taken on V5.1A DuPont 2000 at a heating rate of 10°C/min under N_2 atmosphere. Differential scanning calorimetric (DSC) data were recorded on a NETZSCH DSC 200 F3 instrument under nitrogen atmosphere by the Research Institute of Polymer and Petrochemical of Iran. Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity taken from the heating DSC traces. Elemental analyses were performed by Tarbit Moalem University, Tehran, Iran.

Monomer synthesis

Preparation of cis-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid anhydride (1)

This compound was synthesized according to the reported procedure.[23]

Preparation of (2S)-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)-3-methylbutanoic acid (2)

Into a 50-mL round-bottomed flask 1.00 g (3.60×10^{-3} mol) of *cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid anhydride (**1**), 0.47 g (4.32×10^{-3} mol) S-valine, 20 mL of acetic acid, and a stirring bar were placed. The solution was refluxed for 12 h. The solvent was removed under reduced pressure and to this residue 150 mL of a cold mixture of water and 5 mL concentrated hydrochloric acid were added. The solution was then stirred for 2 h. A white precipitate was formed, filtered off and dried, to give 1.17 g (86%) of imide acid **2**. Recrystallization from ethanol–water mixture gave white crystals, m.p. 230–232°C, $[\alpha]_D^{25} = -41.18$ (0.050 g in 10 mL DMF).

FTIR (KBr, cm^{-1}): 2500–3500 (br), 3011 (m), 2980 (m), 2965 (m), 1742 (s), 1708 (s), 1697 (s), 1387 (m), 1240 (s), 1176 (s), 1031 (m), 766 (s), 590 (w) cm^{-1}.

^{1}H-NMR (500 MHz, DMSO-d_6): $\delta = 0.01$ (d, $J = 6.90$ Hz, 3H, CH_3), 0.49 (d, $J = 6.80$ Hz, 3H, CH_3), 1.98–2.05 (m, 1H, CH), 3.30 (dd, $J_1 = 8.86$, $J_2 = 3.40$, 1H, CH), 3.42 (dd, $J_1 = 8.86$, $J_2 = 3.34$, 1H, CH), 3.97 (d, $J = 6.80$ Hz, 1H, CH), 4.78 (d, $J = 3.36$ Hz, 1H, CH), 4.80 (d, $J = 3.36$ Hz, 1H, CH), 7.08–7.09 (m, 2H, Ar-H), 7.13–7.14 (m, 2H, Ar-H), 7.25–7.28 (m, 2H, Ar-H), 7.44–7.46 (m, 2H, Ar-H), 12.72 (s, 1H, acidic) ppm.

^{13}C-NMR (125 MHz, DMSO-d_6): $\delta = 18.77$, (CH_3), 21.06 (CH_3), 28.22 (CH), 45.15 (CH), 45.25 (CH), 46.60 (CH), 47.17 (CH), 58.12 (CH), 125.08 (CH, Ar), 125.12 (CH, Ar), 125.77 (CH, Ar), 125.79 (CH, Ar), 127.09 (2CH, Ar), 127.62 (CH, Ar), 127.66 (CH, Ar), 140.40 (CH, Ar), 140.48 (CH, Ar), 143.12 (CH, Ar), 143.15 (CH, Ar), 169.84 (acidic), 176.99 (imidic), 177.19 (imidic) ppm.

Elemental analysis calculated for $C_{23}H_{21}NO_4$: C, 73.58%; H, 5.64%; N, 3.73%. Found: C, 73.63%; H, 5.58%; N, 3.80%.

Preparation of (2S)-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)-3-meth-ylbutanoyl chloride (3)

Into a 50-mL round-bottomed flask, 1.00 g (2.66×10^{-3} mol) of compound **2**, 1.8 mL (2.48×10^{-3} mol) of thionyl chloride ($SOCl_2$), 20 mL of CH_2Cl_2, 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 10 mL of *n*-hexane was added and was stirred for 30 min. *n*-Hexane was distilled off, and the solid was collected and dried in vacuum to give 0.95 g (95%) of a white solid, m.p. 154–156°C, $[\alpha]_D^{25} = -25.18$ (0.050 g in 10 mL DMF).

FTIR (KBr, cm^{-1}): 3070 (w), 3022 (w), 2968 (w), 2894 (w), 1803 (s), 1710 (s), 1464 (m), 1380 (s), 1194 (s), 924 (w), 788 (w), 762 (s), 524 (w) cm^{-1}.

Preparation of 5-[(9,10-dihydro-9,10-ethanoanthracene-11–12-dicarboximido)-3-methylbutanoylamino] isophthalic acid (4)

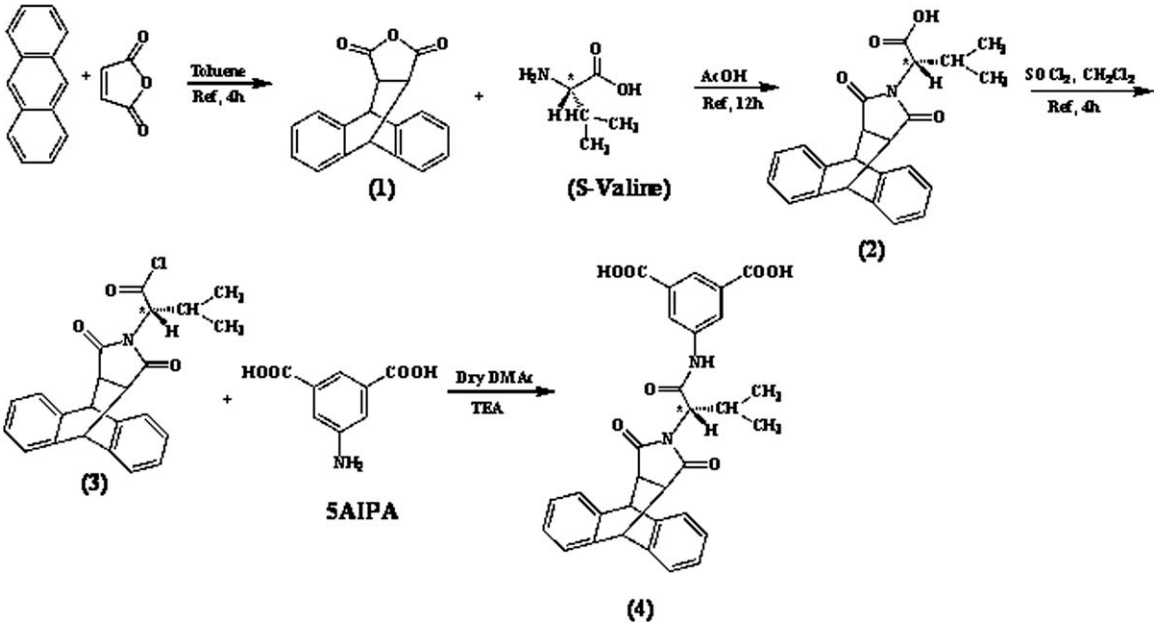
Into a 25-mL round-bottomed flask fitted with a magnetic stirrer, 0.48 g (2.65×10^{-3} mol) 5-aminoisophthalic acid (5AIPA) was dissolved in 5 mL of dry DMAc. The resulting mixture was cooled in an ice bath for 0.5 h. Then a solution of 1.00 g of acid chloride **3** in 5 mL of dry DMAc was added dropwise to this solution and stirred for 3 h at 0°C. 0.33 mL of triethylamine (TEA) was added to this mixture after 1 h and stirred at room temperature overnight, then was heated at 80°C for 6 h. The solution was poured into a mixture of 150 mL of water and 5 mL of concentrated hydrochloric acid. The product was obtained by filtration and washed with water and dried at 100°C for 10 h, to give 1.12 g (88%) diacid. Recrystallization from acetic acid–water mixture gave white crystals, m.p >300°C (decompose), $[\alpha]_D^{25} = -37.92$ (0.050 g in 10 mL DMF). FTIR (KBr, cm^{-1}): 2500–3500 (br), 3471 (m), 3070 (m), 2964 (m), 1778 (w), 1714 (s), 1600 (w), 1400 (s), 1234 (s), 1191 (s), 841 (w), 763 (s), 670 (m), 623 (w), 550 (m) cm^{-1}.

^{1}H-NMR (500 MHz, DMSO-d_6): $\delta = 0.05$ (d, $J = 6.65$ Hz, 3H, CH_3), 0.56 (d, $J = 6.65$ Hz, 3H, CH_3), 2.31–2.36 (m, 1H, CH), 3.30 (dd, $J_1 = 8.80$, $J_2 = 3.30$, 1H, CH), 3.34 (dd, $J_1 = 8.80$, $J_2 = 3.30$, 1H, CH), 4.09 (d, $J = 7.55$ Hz, 1H, CH), 4.78 (d, $J = 3$ Hz, 1H, CH), 4.84 (d, $J = 3$ Hz, 1H, CH), 7.05–7.06 (m, 2H, Ar-H), 7.14–7.15 (m, 2H, Ar-H), 7.27–7.28 (m, 2H, Ar-H), 7.43–7.48 (m, 2H, Ar-H), 8.15 (m, 1H, Ar-H), 8.34 (m, 2H, Ar-H), 10.04 (s, 1H, amidic), 13.26 (s, 2H, acidic) ppm.

^{13}C-NMR (125 MHz, DMSO-d_6): $\delta = 18.76$, (CH_3), 20.65 (CH_3), 27.54 (CH), 45.20 (CH), 45.27 (CH), 46.86 (CH), 47.48 (CH), 60.93 (CH), 125.02 (2CH, Ar), 125.15 (2CH, Ar), 125.65 (CH, Ar), 125.74 (CH, Ar), 125.81 (CH, Ar), 127.09 (2CH, Ar), 127.57 (2CH, Ar), 132.44 (2CH, Ar), 140.05 (CH, Ar), 140.40 (CH, Ar), 140.55 (CH, Ar), 143.02 (CH, Ar), 143.19 (CH, Ar), 167.14 (amidic), 167.28 (2CH acidic), 177.12 (imidic), 177.70 (imidic) ppm.

Polymer synthesis

A typical polymerization procedure was used as follows. For synthesis of polymer **6a**, a pyridine (Py) (0.15 mL) solution of tosyl chloride (TsCl) (0.180 g; 9.44×10^{-4} mol), after 30 min stirring at room temperature, was treated with DMF (0.10 mL; 1.29×10^{-3} mol) for 30 min and the resulting solution was added dropwise to a solution of diacid **4** (0.100 g;



Scheme 1 Synthesis of monomer **4**.

1.9×10^{-4} mol) in Py (0.10 mL). The mixture was maintained at room temperature for 30 min and then to this mixture, a solution of bisphenol A (**5a**) (0.043 g; 1.9×10^{-4} mol) in Py (0.20 mL) was added dropwise and the whole solution was stirred at room temperature for 20 min and at 120°C for 4.5 h. As the reaction proceeded, the solution became viscous. The resulting viscous polymer solution was poured into 30 mL of methanol to precipitate 0.130 g polymer **6a** (86% yield). **PE6b–PE6f** were prepared by a similar procedure.

PE6a: ^{1}H-NMR (500 MHz, DMSO-d_6): 0.04 (s, 3H, CH_3), 0.54 (s, 3H, CH_3), 1.68 (s, 6H, $2CH_3$), 2.33 (s, 1H, CH), 3.29 (s, 1H, CH), 3.32 (s, 1H, CH), 4.11 (s, 1H, chiral center), 4.76 (s, 1H, CH), 4.82 (s, 1H, CH), 7.04 (s, 2H, Ar-H), 7.11 (s, 2H, Ar-H), 7.22–7.25 (m, 6H, Ar-H), 7.32 (s, 4H, Ar-H), 7.41–7.45 (m, 2H, Ar-H), 8.42–8.43 (m, 1H, Ar-H), 8.62–8.64 (m, 2H, Ar-H), 10.28 (s, 1H, amidic).

PE6e: ^{1}H-NMR (500 MHz, DMSO-d_6): 0.06 (d, J = 6.10 Hz, 3H, CH_3), 0.57 (d, J = 6.10 Hz, 3H, CH_3), 2.34–2.38 (m, 1H, CH), 3.32 (d, J = 3.50 Hz, 1H, CH), 3.37 (s, 1H, CH), 4.14 (d, J = 6.50 Hz, 1H, chiral center), 4.78 (s, 1H, CH), 4.84 (s, 1H, CH), 7.06 (s, 2H, Ar-H), 7.14 (s, 2H, Ar-H), 7.27 (s, 2H, Ar-H), 7.45–7.52 (m, 6H, Ar-H), 8.44–8.49 (m, 1H, Ar-H), 8.64–8.68 (m, 2H, Ar-H), 10.32 (s, 1H, amidic).

RESULTS AND DISCUSSION

Monomer synthesis

Scheme 1 outlines the synthetic route applied for the synthesis of the novel compound **4**. The imide acid **2** containing optically active moiety was synthesized via imidization of one equivalent of **1** with one equivalent of optically active S-valine in acetic acid. The chemical structure and purity of this compound was confirmed with thin layer chromatography, FTIR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy techniques. The FTIR spectrum showed a broad peak at 2500–3500 cm^{-1}, which was assigned to the COOH group, and two absorption bands at 1708 and 1742 cm^{-1}, which were characteristic peaks for imide rings.

The ^{1}H-NMR spectrum (500 MHz) of compound **2** depicted in Figure 1 shows the characteristic resonance of two diastereotopic CH_3 (doublet) at 0.01 and 0.49 ppm, CH group bonded to chiral center (multiplet) at 2.49 ppm, two CH groups (two doublet of doublet) at 3.30 and 3.42 ppm, CH chiral center (doublet) at 3.97 ppm, two CH (two doublets) at 4.78 and 4.80 ppm, and acidic O—H at 12.72 ppm. According to the ^{1}H-NMR spectrum, appearance of two diastereotopic CH_3 groups of S-valine in high field (0.01 and 0.49 ppm) show the anisotropic effect of aromatic ring.

The ^{13}C-NMR spectrum (125 MHz) of compound **2** shows carbons for diastereotopic methyl at 18.76 and 21.06 ppm, methyne bonded to chiral center at 28.21 ppm, and chiral center at 58.11 ppm. In addition, the presence of four another aliphatic carbons, 12 different aromatic carbons, and three carbons for carbonyl groups in this spectrum confirms the structure of compound **2**.

The compound **2** was treated with $SOCl_2$ in CH_2Cl_2 to give corresponding acid chloride **3** in quantitative yield. Disappearance of broad peak

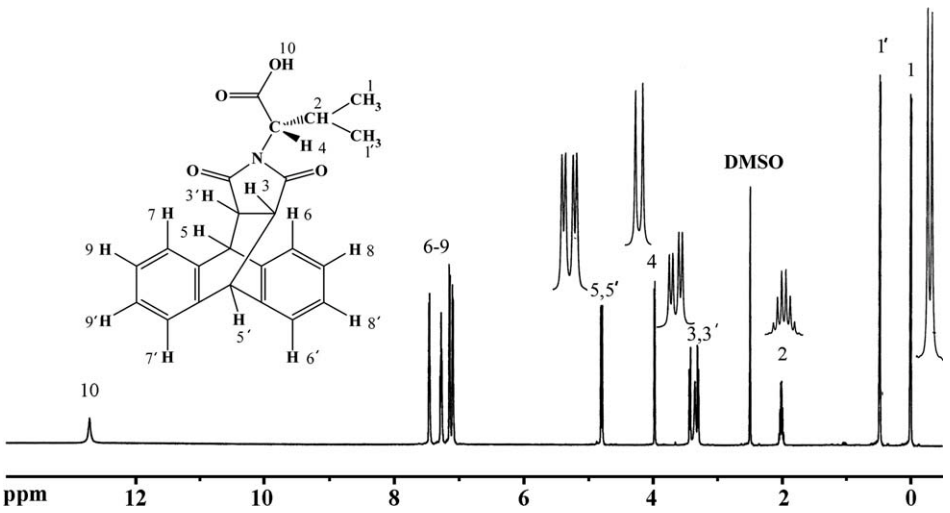


Figure 1 ^{1}H-NMR (500 MHz) spectrum of imide acid **2** in DMSO-d_6 at RT.

around 2500–3500 cm^{-1} in FTIR spectrum confirms the complete conversion of imide acid **2** to acid chloride **3**. However, because of the electron-withdrawing character of the Cl group, the two carbonyl peaks of acid chloride, when compared with its starting imide acid, were shifted to higher frequency. The reaction of 5AIPA with compound **3** in dry DMAc in the presence of TEA gave the novel chiral diacid **4** in high yield (Scheme 1). FTIR and NMR (^{1}H, ^{13}C) spectra confirmed the structure of this compound. The ^{1}H-NMR spectrum of this monomer (Fig. 2) shows the characteristic resonance of the C—H chiral center (doublet), N—H amide group, and acidic O—H at 4.09, 10.04, and 13.26 ppm, respectively. The ^{13}C-NMR spectrum shows eight different carbons for the aliphatic segment, 18 carbons for aromatic parts, imidic, amidic, and acidic carbon groups. The purity of this monomer **4** was also confirmed by thin layer chromatography technique which shows single spot.

Polymer synthesis

The PEs were prepared by polycondensation of diacid (**4**) with commercially available aromatic diols (**5a–5f**) in the TsCl/Py/DMF system as a condensing agent (Scheme 2). The polycondensation was carried out in the following way: TsCl was dissolved in Py and after a certain period (aging time), the solution was treated with DMF for 30 min. The reaction mixture was added to a solution of diacid **4** in Py. After a period of time, a solution of diol in Py was added and the whole solution was maintained at elevated temperature for several hours. In our pervious work,

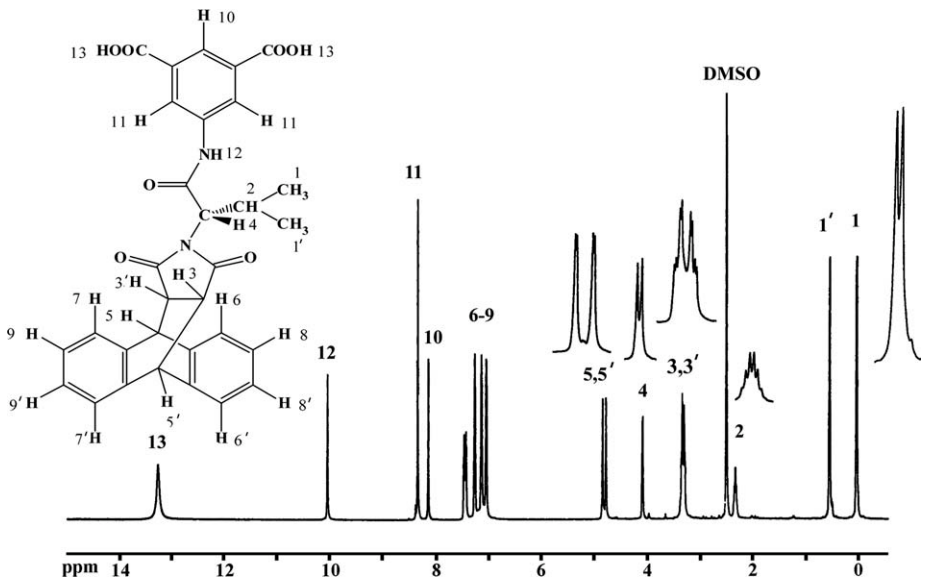
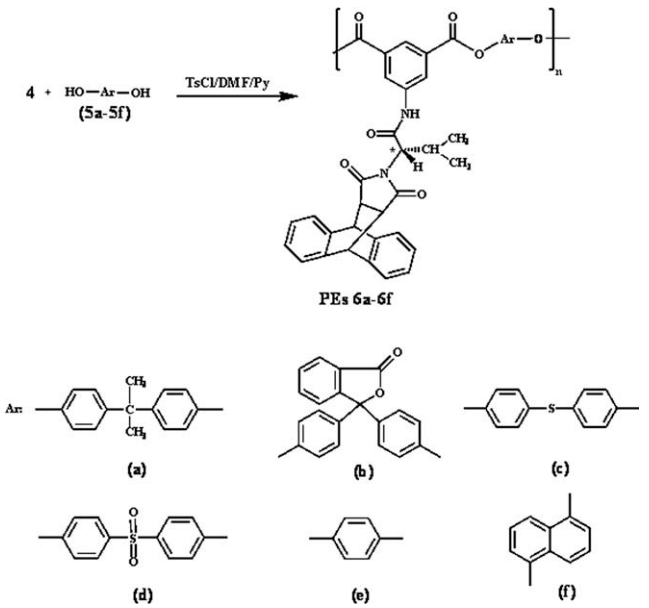


Figure 2 ^{1}H-NMR (500 MHz) spectrum of monomer **4** in DMSO-d_6 at RT.



Scheme 2 Polyesterification of diacid **4** with aromatic diols.

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[24]; therefore, the optimized conditions were used for this work. The synthesis and some physical properties of these novel optically active PEs are listed in Table I. Elemental analysis values of the resulting polymers are also in good agreement with calculated values of carbon, hydrogen, and nitrogen in the polymers (Table II).

FTIR analysis

To obtain a more complete and reliable chemical characterization, the structure of synthesized PEs were also studied by FTIR technique. The FTIR spectra of all polymers showed absorptions band at 3400 cm^{-1} due to the N—H stretching. Moreover, absorption bands at 3070 cm^{-1} and 2960 cm^{-1} corresponded to the stretching vibration of aromatic CH and aliphatic CH, respectively. The absorption peaks due to the asymmetric C=O imide and symmetric C=O imide appear at 1747 and 1708 cm^{-1}, whereas the absorption bands corresponding to the imide heterocycle appear at 1383 and 747 cm^{-1}.

^{1}H-NMR study

The ^{1}H-NMR spectrum of **PE6a** (Fig. 3) shows the N—H proton of amide group at 10.28 ppm as a singlet peak, which indicates the presence of amide group in the polymer's side chain. The resonance of aromatic protons appeared in the range of 7.05–8.65 ppm. The proton of the chiral center appeared as doublet at 4.11 ppm. The peak of C—H isopropyl group of S-valine appeared at 2.33 ppm as a multiple peak. The resonance of the two diastereotopic CH_3 protons groups of S-valine appeared around 0.04 and 0.54 ppm.

TABLE I
Synthesis and Some Physical Properties of PE6a–PE6f Prepared Using TsCl/DMF/Py System

	Polymer				
Diol	Polymer	Yield (%)	η_{inh} (dL g^{-1})[a]	$[\alpha]_D^{25}$[a]	Color[b]
5a	**PE6a**	86	0.48	−29.12	OW
5b	**PE6b**	91	0.35	−25.54	OW
5c	**PE6c**	88	0.23	−30.92	OW
5d	**PE6d**	84	0.26	−22.26	OW
5e	**PE6e**	93	0.25	−26.24	OW
5f	**PE6f**	85	0.27	−7.60	LB

[a] Measured at a concentration of 0.5 g dL^{-1} in DMF at 25°C.
[b] OW, off white; LB, light brown.

Thermal properties

DSC and TGA were used to investigate the thermal properties of the PEs. TGA was performed in a nitrogen atmosphere at a heating rate of 10°C/min. Thermal stability of the polymers were studied based on 5 and 10% weight loss (T_5, T_{10}) of the polymers and residue at 800°C (char yield). The DSC analyses for **PE6a** and **PE6b** show T_g around 173–226°C. Some of the thermal behavior data of these polymers are reported in Table III. These polymers exhibited good resistance to thermal decomposition up to 320°C in nitrogen and began to decompose gradually above that temperature. Figure 4 shows the TGA thermograms of **PE6a** and **PE6b**. For **PE6a**, the TGA thermogram reveals a 5% weight loss at 325°C and the residual weight percent at 800°C is 25%. For **PE6b**, the TGA thermogram shows a 5% weight loss at 335°C and the residual weight percent at 800°C is 35%. According to Table III, it is clear that the **PE6b** (based on phenolphthalein) has better thermal stability than **PE6a** (based on bisphenol A). It could be pertained to aromatic, rigid structure of diol for **PE6b** compared with aliphatic, flexible structure of diol for **PE6a**. Char yield can be applied as

TABLE II
Elemental Analysis of Typical PE6a and PE6e

			Elemental analysis (%)		
Compound	Formula		C	H	N
PE6a	$(C_{46}H_{38}N_2O_7)_n$	Calcd.	75.60	5.24	3.83
		Found.	74.86	5.17	3.80
PE6e	$(C_{37}H_{28}N_2O_7)_n$	Calcd.	72.54	4.61	4.57
		Found.	72.68	4.55	4.47

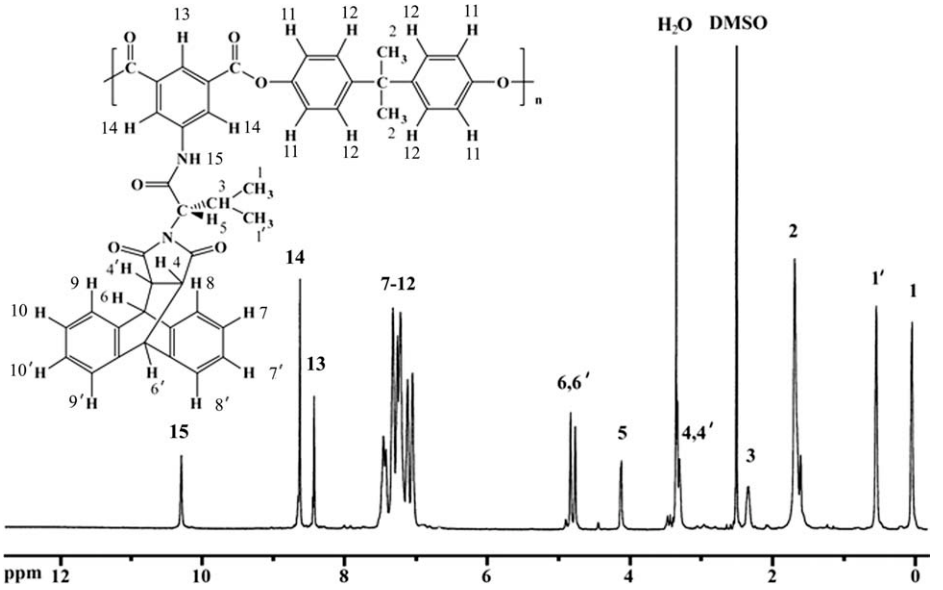


Figure 3 ^{1}H-NMR (500 MHz) spectrum of **PE6a** in DMSO-d_6 at RT.

decisive factor for estimated limiting oxygen index (LOI) of the polymers based on Van Krevelen and Hoftyzer equation.[25]

$$\mathrm{LOI} = 17.5 + 0.4\ \mathrm{CR}$$

where CR = char yield.

The **PE6a** and **PE6b** have LOI values around 30 which were calculated from their char yield at 800°C. On the basis of LOI values, all macromolecules can be classified as self-extinguishing polymers (Table III).

Solubility of PEs

The solubility of PEs was tested at a concentration of 5 mg/mL in different solvents. Because of flexible group and amide and imide groups in a polymer's pendent group, these polymers are expected to have a higher solubility. Polymers are soluble in organic polar solvents such as DMAc, DMF, *N*-methyl-2-pyrrolidone (NMP), and in sulfuric acid at R.T. and are insoluble in solvents such as chloroform, methylene chloride, acetone, cyclohexane, tetrahyrofuran, methanol, ethanol, and water.

TABLE III
Thermal Properties of PE6a and PE6b

Polymer	Decomposition temperature (°C)		Char yield (%)[c]	T_g[d] (°C)	LOI[e]
	T_5[a]	T_{10}[b]			
PE6a	325	340	25	194	28
PE6b	335	345	35	226	32

[a] Temperature at which 5% weight loss was recorded by TGA at heating rate of 10°C min^{-1} in a N_2 atmosphere.
[b] Temperature at which 10% weight loss was recorded by TGA at heating rate of 10°C min^{-1} in a N_2 atmosphere.
[c] Weight percent of the material left undecomposed after TGA at maximum temperature 800°C in a N_2 atmosphere.
[d] Glass transition temperature was recorded at a heating rate of 20°C/min^{-1} in a nitrogen atmosphere.
[e] Limiting oxygen index (LOI) evaluating at char yield at 800°C.

CONCLUSIONS

In this article, for the first time, we have demonstrated the synthesis of chiral dicarboxylic acid **4**, containing S-valine and cis-9,10-dihydro-9,10-ethanoanthracene-11–12-dicarboxyimide moieties. Then for the preparation of novel optically active PEs, reactions of compound **4** with aromatic diols via

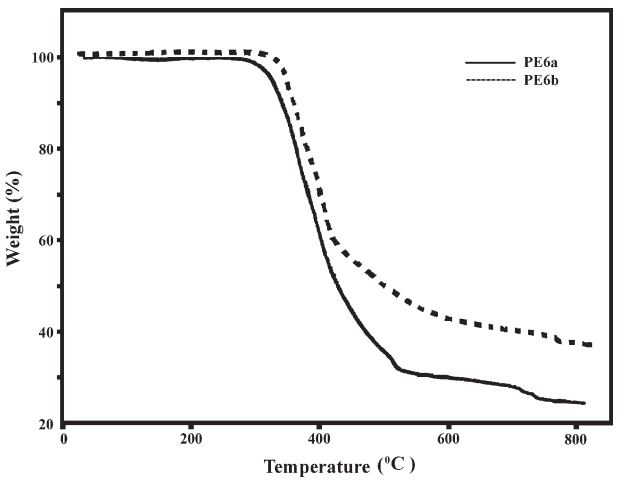


Figure 4 TGA thermograms of **PE6a** and **PE6b** under a nitrogen atmosphere at a heating rate of 10°C/min.

Vilsmeier adduct were investigated. The results presented herein also clearly demonstrate that incorporating the heterocyclic ring into the polymer side chain as well as combination of the wholly aromatic backbone and aliphatic pendant group in the presence of several functional groups remarkably enhanced the solubility while maintaining good thermal stability of the new polymers. The prepared polymers had good thermal stability and excellent solubility in various organic solvents. Since, these optically active polymers have amino acids in the polymer architecture, they are expected to be biodegradable, and therefore are classified under environmentally friendly polymers and also, they have the potential to be used as optically active packing materials in column chromatography for resolution of racemic mixtures.

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References

1. Lutz, J. F.; Andrieu, J.; Zgu1n, S.; Rudolph, C.; Agarwal, S. Macromolecules 2007, 40, 8540.
2. Shi, X.; Hudson, J. L.; Spicer, P. P.; Tour, J. M.; Krishnamoorti, R.; Mikos, A. G. Biomacromolecules 2006, 7, 2237.
3. Shikanov, A.; Domb, A. J. Biomacromolecules 2006, 7, 288.
4. Tsai, C. T.; Chang, W. C.; Chen, C. H.; Lu, H. Y.; Chen, M. Eur Polym J 2008, 44, 2339.
5. Wang, Z.; Hou, X.; Mao, Z.; Ye, R.; Mo, Y.; Finlow, D. E. Iran Polym J 2008, 17, 791.
6. Sanda, F.; Endo, T. Macromol Chem Phys 1999, 200, 2651.
7. Cheuk, K. K. L.; Lam, J. W. Y.; Li, B. S.; Xie, Y.; Tang, B. Z.. Macromolecules 2007, 40, 2633.
8. Zhi, J.; Zhu, Z..; Liu, A.; Cui, J.; Wan, X.; Zhou, Q. Macromolecules 2008, 41, 1594.
9. Mallakpour, S.; Rafiee, Z.. Iran Polym J 2008, 17, 907.
10. Mallakpour, S.; Taghavi, M. React Funct Polym 2009, 69, 206.
11. Mallakpour, S.; Dinari, M. J Appl Polym Sci 2009, 112, 244.
12. Qing, G.; Sun, T.; Chen, Z.; Yang, X.; Wu, X.; He, Y. Chirality 2008, 21, 363.
13. Buruiana, E. C.; Buruiana, T.; Hahui, L. J Photochem Photobiol A Chem 2007, 189, 65.
14. Fu, Z.; Xi, X.; Jiang, L.; Shen, Z.. React Funct Polym 2007, 67, 636.
15. Cancelliere, G.; Dacquarica, I.; Gasparrini, F.; Maggini, M.; Misiti, D.; Villani, C. J Sep Sci 2006, 29, 770.
16. Silva, G. A.; Czeisler, C.; Niece, K. L.; Beniash, E.; Harrington, D. A.; Kessler, J. A.; Stupp, S. Science 2004, 303, 1352.
17. Hergenrother, P. M. High Perform Polym 2003, 15, 3.
18. Wang, D. H.; Cheng, S. Z. D.; Harris, F. W. Polymer 2008, 49, 3020.
19. Mallakpour, S.; Kolahdoozan, M. Eur Polym J 2007, 43, 3344.
20. Tamami, B.; Yeganeh, H.; Kohmareh, G. A. Eur Polym J 2004, 40, 1651.
21. Tan, W. B.; Bhambhani, A.; Duff, M. R.; Rodger, A.; Kumar, C. V. Photochem Photobiol 2006, 82, 20.
22. Carey, F. A.; Sundberg, R. J. Advanced Organic Chemistry Part A, 4th ed.; Kluwer Academic/Pluneum: New York, NY, 2000; Chapter 10.
23. Bachmann, W. E.; Kloetzel, M. C. J Am Chem Soc 1938, 60, 481.
24. Mallakpour, S.; Kolahdoozan, M. Iran Polym J 2006, 15, 307.
25. Van Krevelen, D. W.; Hoftyzer, P. J. Properties of Polymers; Elsevier Scientific Publishing Company: New York, 1976.