Synthesis and Characterization of Novel Organosoluble, Thermal Stable and Optically Active Polyesters Derived from 5-(2-Phthalimidiylpropanoylamino)isophthalic Acid

Shadpour MALLAKPOUR[†] and Zahra RAFIEE

Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, IRAN

(Received May 30, 2007; Accepted August 11, 2007; Published October 2, 2007)

ABSTRACT: A new aromatic diacid monomer containing pendent L-alaninephthalimide group was synthesized in three steps in high yield and purity. Several new, highly soluble and optically active aromatic polyesters containing phthalimide and flexible chiral groups were prepared with moderate molecular weights by direct polycondensation with tosyl chloride (TsCl), pyridine (Py) and *N,N*-dimethylformamide (DMF) as condensing agent. The aim of this work was to obtain novel optically active polyesters that were more soluble in common organic solvents while maintaining the high thermal stability. All polymers derived from such a diacid and aromatic diols were highly organosoluble in the solvents like *N*-methyl-2-pyrrolidinone, *N,N*-dimethylacetamide, DMF, Py and dimethyl sulfoxide. These new optically active polyesters with inherent viscosities ranging from 0.21 to 0.81 dL/g were obtained with high yields. Thermogravimetric analysis (TGA) data showed that these polyesters are thermal stable, with 10% weight loss being recorded above 370 °C. Some of the above polymers were characterized by ¹H-NMR, FT-IR, elemental analyses and specific rotation techniques. [doi:10.1295/polymj.PJ2007061]

KEY WORDS Polyester / Optically Active Polymers / TsCl/Py/DMF Condensing Agent / Thermal Properties / Solubility / Direct Polycondensation /

Polyesters (**PE**)s are significant class of high performance and engineering macromolecules, which find utilize in a number of various applications.^{1–3} They are typically prepared by the solution or interfacial polymerization reaction between dicarboxylic acid chlorides and diols,^{4,5} and an acid or phenyl ester exchange reaction of the acetate or ester of the acids under severe conditions (high temperature and reduced pressure). Thermally stable **PE**s derived from isophthalic and terephthalic acids with bisphenol-A have been commercialized.⁶ However, **PE**s are generally difficult to process because of their limited solubility in many organic solvents and their high melting temperature or high glass-transition temperature due to their rigid structures. Hence, expansion of **PE**s for use at high temperature with better solubility is an important ambition.

One of the approaches to improve solubility of the macromolecules without excessive loss of their high thermal stability is the introduction of flexible and bulky groups into the polymer backbone.^{7–10} The amalgamation of bulky pendent groups can also supply beneficial effect for solubility because this approach generates a separation of chains and lowering the chain packing with a gain of free volumes.

Numerous condensing agents appropriate for the direct polycondensation reaction have been developed.^{11,12} On the other hand, 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 preparation of aromatic **PE**s by the direct polycondensation of hydroxybenzoic acids and also aromatic dicarboxylic acids with bisphenols.^{13,14}

The synthesis and properties of novel chiral polymers is of special attention from the point of view of material science, since a high degree of amino acid functionality and chirality can lead to polymers with enhanced solubility and the ability to form regulated higher order structures.^{15–17} Chirality is a major disquiet in the modern pharmaceutical industry. This curiosity can be ascribed largely to a heightened consciousness that enantiomers of a racemic drug may have diverse pharmacological activities, as well as different pharmacokinetic and pharmacodynamic outcomes. The severance of chiral compounds has been of great attention because the majority of bioorganic molecules are chiral. Recent progresses in asymmetric reactions and catalysis as well as in chiral separations have gave a rapid enhance in the number of commercially available optically active compounds and reagents.^{18,19} This circumstance will influence new methodologies for the synthesis of optically active polymers (OAPs) in the coming century. So far, chiral macromolecules have found flourishing applications in chiral chromatographic separations and shown po-

[†]To whom correspondence should be addressed (Tel: +98-311-391-3267, Fax: +98-311-391-2350, E-mail: mallak@cc.iut.ac.ir).

tential uses in chiral catalytic systems, liquid crystals, optical switches, biomedical devices, etc. A direct and efficient approach for synthesizing chiral polymers is to introduce chiral elements into the macromolecule backbone or the side chains.²⁰ We now have a diversity of utensil for the synthesis of novel chiral monomers and polymers. Recently, we have synthesized a variety of OAPs by different methods, such as modification of polybutadiene with an optically active substituted urazole group, Diels-Alder-Ene reactions, and the reaction of an optically active monomer with a number of diamines *via* solution polymerization.^{21–23} In the last case, we use amino acids as a chiral agent in the backbone of the macromolecules. Because the amino acids are naturally occurring compounds, synthetic polymers based on amino acids are anticipated to be nontoxic, biocompatible, and biodegradable. On the other hand, synthetic polymers containing amino acid residues in the main chain or in the side chain can be employed for biomedical applications.

In continuation of our study to develop new OAPs *via* direct polycondensation,^{21–26} in this investigation, we describe the successful synthesis and characterization of new optically active **PEs** containing chiral L-alanine and thermal stable phthalimide moieties using tosyl chloride (TsCl)/DMF/Py as condensing agent. Furthermore, the resulting polymers due to the presence of phthalimide moieties exhibit a number of applications in biology²⁷ and owing to the presence of amino acid moiety are expected to be biodegradable and biocompatible.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co.). 5-Aminoisophthalic acid was recrystallized from a mixture of DMF/water (v/v ratio 3:1). Bisphenol A (**6a**) was purified by recrystallization from acetic acid-water. The other diols were used as obtained without further purification. *N,N*-dimethylacetamide (DMAc) and DMF were dried over BaO and then were distilled under reduced pressure.

Measurements

Proton nuclear magnetic resonance (¹H NMR, 500 MHz) and ¹³C NMR (125 MHz) spectra were recorded on a Bruker (Germany) Avance 500 instrument. FT-IR spectra were recorded on (Jasco-680, Japan) spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wave numbers (cm^{−1}).

Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon Fensk routine viscometer. Specific Rotations were measured by a Jasco Polarimeter (Japan), with a concentration of 0.5 g/dL in DMF solution under sodium lamp with a wavelength of 589 nm, mercury lamp without a filter and mercury lamp with a filter (wavelength of 365 nm), respectively. Thermal gravimetric analysis (TGA) data for polymers were taken on TGA-PerkinElmer (Pyris 1) in nitrogen atmosphere at a rate heating of 10 °C/min. Elemental analyses were performed by the Iran Polymer and Petrochemical Research Institute (IPPI), Tehran, Iran. DSC data were recorded on a DSC-PL-1200 instrument under N₂ atmosphere also by IPPI. 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

N-Phthalimidiylpropanoic acid (**3**). Into a 100 mL round-bottomed flask 3.00 g (1.66 × 10^{−2} mol) of phthalic anhydride (**1**), 1.47 g (1.66 × 10^{−2} mol) of L-alanine (**2**), 20 mL of acetic acid and stirring bar were placed. The mixture was refluxed for 12 h. The solvent was removed under reduced pressure and to the residue mixture of 100 mL/5 mL cold water/concentrated HCl was added. A white precipitate was formed, filtered off, washed several times with water and dried, to give 3.47 g (96%) of imide acid **3**. Recrystallization from methanol/water gave white crystals, mp 142–143 °C; Lit: mp 145–147 °C,²⁸ [α]_D²⁵ = −48.8 (0.05 g in 10 mL DMF); FT-IR (KBr): 3257 (s, br), 2998 (m), 2950 (m), 2919 (m), 1757 (s), 1692 (s), 1609 (m), 1465 (m), 1445 (m), 1402 (s), 1344 (s), 1288 (m), 1210 (s), 1197 (s), 1170 (s), 1147 (s), 1072 (s), 1022 (s), 1008 (m), 967 (m), 915 (m), 883 (s), 818 (m), 799 (m), 757 (s), 741 (s), 724 (s), 625 (s), 571 (m), 550 (m), 530 (s) cm^{−1}.

N-Phthalimidiylpropanoyl chloride (**4**). Into a 50 mL, a round-bottom flask, 1.00 g (4.56 × 10^{−3}) of imide acid **3**, 10 mL (an excess amount) of thionyl chloride, and stirring bar were placed. The stirrer was started and the mixture was refluxed for 6 h. The thionyl chloride was removed *via* distillation, 20 mL of *n*-hexane was added, the mixture was stirred for 1 h, *n*-hexane was distilled off, and the solid was collected and dried in vacuum to give 1.02 g (94%) of a white solid, mp 62–63 °C, [α]_D²⁵ = −50.3 (0.05 g in 10 mL DMF); FT-IR (KBr): 2950 (m), 1790 (s), 1720 (s), 1630 (m), 1460 (m), 1380 (s), 1260 (m), 1230 (m), 1190 (m), 1160 (m), 1080 (m), 1050 (m), 992 (m), 940 (m), 870 (m), 830 (m), 790 (m), 765 (m), 720 (s), 640 (w), 600 (w) cm^{−1}. ¹H-NMR (500

MHz, CDCl_3): δ 1.82–1.84 (d, 3H, $J = 7.2$ Hz), 5.19–5.23 (q, 1H, $J = 7.2$ Hz), 7.83–7.85 (m, 2H, Ar-H), 7.94–7.97 (m, 2H, Ar-H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 15.88, 56.39, 124.33, 132.05, 135.05, 167.12, 172.47 ppm.

5-(2-Phthalimidiylpropanoylamino)isophthalic acid (5). Into a 25 mL round-bottomed flask fitted with a magnetic stirrer was placed a solution of 0.76 g (4.21×10^{-3} mol) of 5-aminoisophthalic acid in 3 mL of DMAc. The reaction mixture was cooled in an ice water bath. To this solution 1.00 g (4.21×10^{-3} mol) of acid chloride **4** in 2 mL of DMAc was added dropwise. The mixture was stirred in ice bath for 3 h, then 0.58 mL (4.21×10^{-3} mol) of triethylamine was added. The resulting mixture was stirred vigorously for 2 h in ice bath and then for an overnight at room temperature. Finally it was refluxed for 30 min., then the mixture was poured into 100 mL/5 mL of cold water/concentrated HCl. The precipitate was collected by filtration and washed thoroughly with water and dried at 70°C for 7 h, to yield 1.33 g (83%) of diacid **5**. Recrystallization from ethanol/water gave white crystals, mp $285\text{--}286^\circ\text{C}$, $[\alpha]_{\text{D}}^{25} = -32.5$ (0.050 g in 10 mL DMF); FT-IR (KBr): 3330 (m), 2963 (m, br), 1775 (m), 1700 (s, br), 1605 (s), 1540 (s), 1445 (s), 1392 (s), 1260 (m), 1208 (s), 1170 (m), 1150 (m), 1080 (m), 1016 (m), 940 (m), 908 (m), 880 (m), 850 (m), 760 (m), 720 (m), 650 (m) cm^{-1} . ^1H -NMR (500 MHz, $\text{DMSO}-d_6$): δ 1.58–1.59 (d, 3H, $J = 7.3$ Hz), 4.97–5.00 (q, 1H, $J = 7.1$ Hz), 7.87–7.89 (m, 2H, Ar-H), 7.92–7.94 (m, 2H, Ar-H), 8.17 (s, 1H, Ar-H), 8.43 (s, 2H, Ar-H), 10.21 (s, 1H, N-H), 13.27 (s, 2H, COOH) ppm; ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$): δ 15.86, 49.44, 124.05, 125.21, 125.72, 132.50, 132.70, 135.39, 140.22, 167.27, 168.22, 168.97 ppm. Elemental analysis: Calcd. for $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_7$: C, 59.69%; H, 3.69%; N, 7.33%. Found: C, 59.07%; H, 3.24%; N, 7.01%.

Polymer synthesis

All of the polymers were synthesized using two different methods: For synthesis of **PE7a**.

Method I: A Py (0.15 mL, 1.9×10^{-3} mol) solution of TsCl (0.257 g, 1.3×10^{-3} mol) after 30 min. stirring at room temperature, was treated with DMF (0.10 mL, 1.3×10^{-3} mol) for 30 min. and was added dropwise to a solution of diacid **5** (0.100 g, 2.6×10^{-4} mol) in Py (0.15 mL). The mixture was maintained at room temperature for 30 min. and then to this mixture, a solution of bisphenol A (**6a**) (0.060 g, 2.6×10^{-4} mol) in Py (0.15 mL) was added dropwise at room temperature and the whole solution was stirred at room temperature for 30 min. and at 120°C for 5 h. As the reaction ensue, the solution became viscous. Then the viscous liquid was precipitated in 30 mL of

methanol to yield 0.137 g (86%) of the **PE7aI**.

Method II: A Py (0.15 mL, 1.9×10^{-3} mol) solution of TsCl (0.257 g, 1.3×10^{-3} mol) after 30 min. stirring at room temperature, was treated with DMF (0.10 mL, 1.3×10^{-3} mol) for 30 min. and the solution was added dropwise to a solution of diacid **5** (0.100 g, 2.6×10^{-4} mol) in Py (0.15 mL). The mixture was maintained at room temperature for 30 min. and at 120°C for 1 h. Then to this mixture, a solution of diol **6a** (0.060 g, 2.6×10^{-4} mol) in Py (0.15 mL) was added dropwise at room temperature and the whole solution was stirred at room temperature 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 30 mL methanol to yield 0.131 g (82%) of the **PE7aII**.

FT-IR (KBr): 3362 (m), 3102 (w), 2968 (m), 1780 (m), 1717 (s), 1604 (m), 1547 (m), 1504 (m), 1452 (m), 1426 (s), 1385 (s), 1337 (s), 1200 (s), 1170 (s), 1097 (m), 1078 (m), 1016 (m), 943 (w), 915 (w), 878 (w), 853 (w), 818 (w), 748 (m), 720 (m) cm^{-1} , ^1H -NMR (500 MHz, $\text{DMSO}-d_6$): δ 1.61 (s, br, 9H, CH_3), 4.97 (s, br, 1H, CH), 7.20–7.30 (m, br, 8H, Ar-H), 7.86–7.90 (m, br, 4H, Ar-H), 8.43 (s, 1H, Ar-H), 8.68 (s, 1H, Ar-H), 10.43 (s, 1H, N-H) ppm. Elemental analysis: calcd for $\text{C}_{34}\text{H}_{26}\text{N}_2\text{O}_7$: C, 71.07%; H, 4.56%; N, 4.87%. Found: C, 69.58%; H, 4.44%; N, 4.75%.

The other **PEs**, **7b–7j** were prepared with similar procedures.

PE7b

FT-IR (KBr): 3412 (m), 3095 (w), 1779 (w), 1741 (s), 1715 (s), 1607 (m), 1547 (m), 1487 (s), 1451 (w), 1425 (w), 1386 (s), 1336 (m), 1265 (w), 1194 (s), 1163 (s), 1080 (m), 1013 (m), 945 (w), 914 (w), 879 (w), 848 (w), 810 (w), 746 (w), 721 (m) cm^{-1} , ^1H -NMR (500 MHz, $\text{DMSO}-d_6$): δ 1.63 (d, 3H, CH_3), 4.97 (s, br, 1H, CH), 7.22–7.34 (m, br, 8H, Ar-H), 7.83–7.86 (m, br, 4H, Ar-H), 8.32 (s, 1H, Ar-H), 8.59 (s, 1H, Ar-H), 10.38 (s, 1H, N-H) ppm.

PE7c

FT-IR (KBr): 3413 (m), 3092 (w), 2965 (w), 1778 (w, sh), 1744 (m), 1715 (s), 1637 (m), 1603 (m), 1552 (m), 1507 (m), 1452 (m), 1386 (m), 1337 (m), 1197 (s), 1162 (m), 1099 (m), 960 (w), 881 (w), 784 (w), 745 (w), 721 (w) cm^{-1} .

PE7d

FT-IR (KBr): 3411 (m), 3067 (w), 2966 (w), 1779 (m), 1745 (s), 1716 (s), 1607 (m), 1548 (m), 1467 (m), 1423 (s), 1385 (s), 1337 (s), 1200 (w), 1160 (w), 1095 (w), 880 (w), 795 (w), 746 (w), 720 (m) cm^{-1} .

PE7e

FT-IR (KBr): 3413 (w), 3077 (w), 2941 (w), 1779 (w), 1742 (s), 1714 (s), 1603 (m), 1553 (m), 1499 (s), 1453 (w), 1425 (w), 1386 (s), 1339 (s), 1211 (s), 1170

(s), 1097 (m), 1034 (w), 1013 (w), 947 (w), 915 (w), 879 (w), 817 (w), 796 (w), 747 (w), 721 (m) cm^{-1} .

PE7f

FT-IR (KBr): 3413 (m), 3075 (w), 2965 (w), 1777 (m), 1746 (s), 1715 (s), 1637 (m), 1612 (m), 1547 (m), 1505 (m), 1466 (m), 1386 (m), 1337 (m), 1288 (m), 1197 (s), 1168 (s), 1102 (m), 1084 (m), 1017 (w), 972 (w), 930 (w), 878 (w), 797 (w), 746 (m), 721 (m) cm^{-1} . Elemental analysis: calcd for $\text{C}_{39}\text{H}_{24}\text{N}_2\text{O}_9$: C, 70.48%; H, 3.64%; N, 4.21%. Found: C, 69.36%; H, 3.56%; N, 4.55%.

PE7g

FT-IR (KBr): 3435 (m), 3089 (w), 2928 (w), 1779 (m), 1716 (s), 1598 (s), 1527 (s, sh), 1473 (w), 1437 (w), 1407 (m), 1383 (m), 1318 (m), 1261 (s, sh), 1195 (s), 1173 (s), 1102 (w, sh), 1068 (m), 1009 (m), 854 (w), 760 (m), 726 (m), 691 (m) cm^{-1} .

PE7h

FT-IR (KBr): 3412 (m), 3085 (w), 2975 (w), 1778 (m), 1747 (s), 1715 (s), 1606 (s), 1552 (m), 1493 (w), 1451 (m), 1425 (w), 1386 (s), 1337 (m), 1250 (m), 1199 (s), 1153 (m), 1125 (m), 1091 (m), 1019 (w), 985 (w), 906 (w), 879 (w), 745 (w), 722 (m) cm^{-1} .

PE7i

FT-IR (KBr): 3413 (s), 3076 (w), 2965 (w), 1749 (m), 1714 (s), 1673 (s), 1637 (m), 1616 (m), 1589 (m), 1552 (m), 1488 (w), 1452 (m), 1386 (s), 1338 (m), 1263 (m), 1185 (s), 1168 (s), 1092 (m), 1033 (w), 1009 (w), 951 (w), 876 (w), 798 (w), 721 (m) cm^{-1} .

PE7j

FT-IR (KBr): 3413 (s), 2980 (w), 1779 (w), 1744 (m), 1715 (s), 1602 (m), 1559 (m), 1507 (m), 1452 (m), 1385 (s), 1338 (m), 1197 (s), 1162 (s), 1099 (m), 961 (w), 784 (w), 745 (w), 721 (w) cm^{-1} .

RESULTS AND DISCUSSIONS

Monomer synthesis

As shown in Scheme 1, the novel monomer 5-(2-phthalimidiylpropanoylamino)-isophthalic acid (**5**) was synthesized by a three-step route. In the first step the reaction of L-alanine with phthalic anhydride in acetic acid afforded the *N*-phthalimidiylpropanoic acid (**3**). The acid chloride **4** was obtained in high yield by treatment of corresponding carboxylic acid with excess thionyl chloride, which was subsequently reacted with 5-aminoisophthalic acid in the presence of triethylamine in a typical low-temperature condensation reaction. The reaction was performed in dry DMAc due to partial solubility of 5-aminoisophthalic acid.

The chemical structure and purity of the optically active acid chloride **4** and diacid **5** were proven with FT-IR, ^1H -NMR and ^{13}C -NMR spectroscopic techniques. The ^1H -NMR spectrum (500 MHz) of com-

Scheme 1. Synthesis of monomer **5**.

Figure 1. ^1H -NMR (500 MHz) spectrum of monomer **5**.

pound **5** is shown in Figure 1. The ^1H NMR of this diacid shows the characteristic absorption of C-H chiral center (quartet), N-H amide group and acidic O-H at 4.98, 10.21 and 13.27 ppm, respectively. Figure 2 shows ^{13}C -NMR spectrum (125 MHz) of monomer **5**. The results of elemental analysis of diacid **5** are in good agreement with the calculated values.

Polymer synthesis

PEs **7a–7j** were synthesized by the direct polycondensation of diacid **5** and various aromatic diols **6a–6j** utilizing $\text{TsCl}/\text{Py}/\text{DMF}$ as condensing agent (Scheme 2).

The polymerization of diacid **5** with aromatic diols **6a–6j** was performed under two different methods. In method **I**, the polycondensation was carried out in the

Figure 2. ^{13}C -NMR (125 MHz) spectrum of monomer **5**.

Scheme 2. Polycondensation reaction of monomer **5** with different aromatic diols.

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 **5** in Py. After a 30 min. a solution of diol in Py was added and the whole solution was maintained at room temperature and elevated temperature for a period of time. Polycondensation

Table I. The optimum conditions for the preparation of **PEs** (methods **I** and **II**)

Optimum Condition		
Method	I	II
TsCl/Diacid (mol/mol)	5.0	5.0
Py/Diacid (mol/mol)	29.5	29.5
DMF (mmol)	0.64	0.64
Aging Time (min)	30	30
Addition Time of Diol	30 min	1.5 h
Reaction Time (h)	5.0	2.5

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 reaction temperature. All of these parameters has effect on the polymer chain growth. The main differences between the method **I** and **II** is the addition of diol to the activated diacid. In method **I** diol was added to the activated diacid after 30 min. of activation at room temperature, while in method **II** the diol was added after 30 min. at room temperature followed by 1 h at 120 °C to effect a clear solution. The optimum conditions for the preparation of **PEs** are summerized in Table I. We obtained comparable yields and better viscosities of **PEs 7a–7j** from method **II**. This finding indicates that when diacid is activated for longer time and higher temperature longer chain growth will occur. The reaction yields and some physical data of these **PEs** are listed in Tables II and III.

The inherent viscosities of the resulting polymers under optimized condition were in the range of 0.21–0.81 dL/g and the yields were 70–97%. All of the **PEs** are optically active. It is interesting to mention that the structure of diols show great effect on the inherent viscosities of the resulting **PEs**. The highest inherent viscosity was obtained with bisphenol A which could be due to the electron releasing effect of isopropyl group which make the diol more reactive. For other diols lower inherent viscosities were obtained which could be due to both electron-withdrawing as well as steric (also rigidity) effects. Diols 6b, 6c, 6h and 6i may exert electron-withdrawing effect, while diols 6d, 6e, 6f, 6g and 6j may have steric and rigidity effects.

Polymer characterization

The introduction of amino acid moiety into synthetic polymers is of attention because these combinations generate new nonbiological polymers with biomimetic structures and properties and consequently have many potential uses, including controlled drug release systems, optical resolution, biologically active and degradable materials.^{15–17}

In this investigation, the novel **PEs** were prepared from an optically active monomer **5** using L-alanine

Table II. Synthesis and some physical properties of **PE7a–PE7j** prepared by method I

diol	Polymer					
	Polymer	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_{Na,589}^{25,b}$	$[\alpha]_{Hg}^{25,b,c}$	$[\alpha]_{Hg,365}^{25,b,d}$
6a	PE7aI	86	0.58	−18.9	+47.6	+43.6
6b	PE7bI	71	0.45	−31.5	+28.0	+21.7
6c	PE7cI	75	0.42	−34.2	+36.4	+53.28
6d	PE7dI	97	0.29	−18.1	+35.2	+23.0
6e	PE7eI	93	0.36	−44.2	+33.8	+73.2
6f	PE7fI	82	0.41	−15.4	+19.4	+51.1
6g	PE7gI	70	0.38	−22.1	+29.3	+21.7
6h	PE7hI	78	0.33	−26.1	+46.6	+89.2
6i	PE7iI	83	0.26	−23.0	+46.1	+34.2
6j	PE7jI	82	0.31	−13.9	+41.6	+90.0

^aMeasured at a concentration of 0.5 g/dL in DMF at 25 °C.^bMeasured at a concentration of 0.5 g/dL in DMF at 25 °C.^cWere measured without filter. ^dWere measured by the use of filter of 365 nm.**Table III.** Synthesis and some physical properties of **PE7a–PE7j** prepared by method II

diol	Polymer					
	Polymer	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_{Na,589}^{25,b}$	$[\alpha]_{Hg}^{25,b,c}$	$[\alpha]_{Hg,365}^{25,b,d}$
6a	PE7aII	82	0.81	−19.2	+38.7	+58.9
6b	PE7bII	92	0.48	−29.8	+28.4	+52.1
6c	PE7cII	91	0.51	−38.2	+56.2	62.1
6d	PE7dII	78	0.21	−17.7	+38.1	+54.1
6e	PE7eII	87	0.45	−25.0	+38.4	+76.0
6f	PE7fII	81	0.48	−14.7	+22.1	+48.5
6g	PE7gII	86	0.26	−20.2	+31.4	+32.9
6h	PE7hII	85	0.38	−24.1	+42.4	+91.2
6i	PE7iII	87	0.22	−25.1	+48.6	+41.9
6j	PE7jII	82	0.33	−18.9	+58.2	+101.2

^aMeasured at a concentration of 0.5 g/dL in DMF at 25 °C.^bMeasured at a concentration of 0.5 g/dL in DMF at 25 °C.^cWere measured without filter. ^dWere measured by the use of filter of 365 nm.

as amino acid which has a carbon chiral center. It is interesting to mention that, the incorporation of L-alanine not only make the resulting **PEs** optically active, but also gave polymers with improved solubility. The resulting polymers show optical rotation, therefore are optically active. The formation of **PEs** was confirmed by FT-IR spectroscopy analysis. As an example, the FT-IR spectrum of **PE7f** (Figure 3) was showed. FT-IR spectra of all polymers show the characteristic absorption peaks for the imide ring, and ester and amide at 1777, 1746, 1715, 1637 cm^{−1} respectively due to the symmetrical and asymmetrical carbonyl stretching vibrations. Band of amide N–H group appeared around 3413 cm^{−1}. All of them exhib-

Figure 3. FT-IR spectrum of **PE7f**. **Figure 4.** ¹H-NMR (500 MHz) spectrum of **PE7a**.

ited strong absorptions around 1384 cm^{−1} and 711–747 cm^{−1} that show the presence of the imide heterocycle ring in these polymers.

The ¹H NMR spectra (500 MHz) of **PE7a** and **PE7b** are shown in Figures 4 and 5. In the ¹H NMR spectra of these two polymers, appearance of the N–H proton of amide groups around 10.43 ppm point to amide group in the polymer's chain. The absorption of aromatic protons appeared at a range of 7.20–8.68 ppm. The proton of the chiral center appeared at 4.97 ppm. The absorption of the CH₃ protons group of L-alanine appeared at 1.61 ppm. In the spectrum of **PE7a** CH₃ protons of bisphenol A appeared at 1.61 ppm which overlapped with CH₃ protons of L-alanine group.

The solubility of **PEs** was tested quantitatively in various solvents are listed in Table IV. All of the **PEs** are soluble in organic solvents such as DMF, DMAC, dimethyl sulfoxide, *N*-methyl-2-pyrrolidone, Py and in H₂SO₄ at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water. The incorporation of the pendent alaninephthalimide in the side chain **PEs** enhanced their solubility in polar solvents.

Figure 5. ^1H -NMR (500 MHz) spectrum of **PE7b**.

Thermal properties

The thermal stability of polymers was studied by TGA/DTG under a nitrogen atmosphere. Figure 6 presents typical TGA thermograms of **PE7aII** and **PE7cII**. The 5 and 10% weight loss (T_5 and T_{10}) of the polymers and residue at 600 °C (char yield) for these polymers are summarized in Table V. The polymers are thermally stable up to above 320 °C as indicated by the weight loss in TGA thermograms. The initial decomposition temperatures of these polymers are 372 and 320 °C, respectively. **PE7aII** showed higher thermal stability than **PE7cII**. This could explain that higher inherent viscosity resulting from **PE7aII** could be responsible for its higher thermal stability. Upon evaluating the chemical structures of the pendent groups, it is seen that the introduction of phthalimide side group along the polymers backbone improved their thermal stability compared with other **PEs** which were reported earlier.^{23–26} The DSC analyses for **PE7aII** and **PE7cII** show T_g around 131 and 157 °C, respectively.

CONCLUSION

A series of new optically active aliphatic-aromatic

Figure 6. TGA of (—) **PE7aII** and (---) **PE7cII** at a heating rate of 10 °C/min under a nitrogen atmosphere.

Table V. Thermal Properties of **PE7aII** and **PE7cII**

Polymer	Decomposition Temperature (°C)		Char Yield (%) ^c	T_g ^d
	T_5 ^a	T_{10} ^b		
PE7aII	372	400	58	131
PE7cII	320	372	33	157

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

^bTemperature at which 10% weight loss was recorded by TGA at a heating rate of 10 °C/min in nitrogen atmosphere.

^cPercentage weight of material left undecomposed after TGA analysis at maximum temperature 600 °C in nitrogen atmosphere. ^dGlass transition temperature was recorded at a heating rate of 20 °C/min in a nitrogen atmosphere.

PEs having phthalimide, amide and L-alanine moieties were synthesized by two different methods. Direct polycondensation was carried out by reaction of phthalimide containing diacid and aromatic diols using $\text{TsCl}/\text{DMF}/\text{Py}$ as condensing agent. The polycondensation leads to the formation of polymers having inherent viscosity ranging from 0.21–0.81 dL/g. The resulting **PEs** are thermally stable and are readily soluble in common organic solvents. Since these

Table IV. Solubility of **PE7a–PE7j**^a

Solvent	PE7a	PE7b	PE7c	PE7d	PE7e	PE7f	PE7g	PE7h	PE7i	PE7j
DMAc	+	+	+	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+	+	+	+
NMP	+	+	+	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+	+	+	+
Py	+	+	+	+	+	+	+	+	+	+
H_2SO_4	+	+	+	+	+	+	+	+	+	+
MeOH	–	–	–	–	–	–	–	–	–	–
EtOH	–	–	–	–	–	–	–	–	–	–
CHCl_3	–	–	–	–	–	–	–	–	–	–
CH_2Cl_2	–	–	–	–	–	–	–	–	–	–
H_2O	–	–	–	–	–	–	–	–	–	–

^aConcentration: 5 mg mL^{–1}; (+) Soluble at room temperature, (–) Insoluble at room temperature.

PEs are soluble in many organic solvents, they can be used for film forming and coating materials.

Acknowledgment. We wish to express our gratitude to the Research Affairs Division Isfahan University of Technology (IUT), for financial support. Further financial support from Center of Excellency in Sensors and Green Chemistry Research (IUT) is gratefully acknowledged.

REFERENCES

1. J. K. Fink, in "Reactive Polymers Fundamentals and Applications," New York, Plastics Design Library, 2005.
2. H. Han and P. K. Bhowraik, *Prog. Polym. Sci.*, **22**, 1431 (1997).
3. J. Y. Jadhav and S. W. Kantor, in "High Performance Polymers and Composites" J. I. Kroschwitz, Ed., New York, Wiley, 1991.
4. Y. Chen, Y. Yang, J. Su, L. Tan, and Y. Wang, *React. Funct. Polym.*, **67**, 396 (2007).
5. E. Bucio, J. W. Fitch, S. R. Venumbaka, E. Patrick, and P. E. Cassidy, *Polymer*, **46**, 3971 (2005).
6. P. E. Cassidy, in "Thermally stable polymers" New York, Marcel Dekker, 1980.
7. B. Tamami, H. Yeganeh, and G. A. Kohmareh, *Eur. Polym. J.*, **40**, 1651 (2004).
8. T. Vlad-Bubulac, C. Hamciuc, O. Petreus, and M. Bruma, *Polym. Adv. Technol.*, **17**, 647 (2006).
9. H. J. Jeong, M. A. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem.*, **32**, 1057 (1994).
10. D. J. Liaw and P. S. Chen, *J. Polym. Sci., Polym. Chem.*, **34**, 885 (1996).
11. F. Higashi and T. Mashimo, *J. Polym. Sci., Part A: Polym. Chem.*, **24**, 1697 (1986).
12. F. Higashi and T. Mashimo, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 2999 (1985).
13. F. Higashi and A. Tobe, *Macromol. Chem. Phys.*, **202**, 745 (2001).
14. F. Higashi, R. Hayashi, and T. Yamazaki, *J. Appl. Polym. Sci.*, **86**, 2607 (2002).
15. F. Sanda and T. Endo, *Macromol. Chem. Phys.*, **200**, 2651 (1999).
16. R. Katsarava, *Macromol. Symp.*, **199**, 419 (2003).
17. T. W. Baughman and K. B. Wagener, *Adv. Polym. Sci.*, **176**, 1 (2005).
18. Y. Okamoto, *Prog. Polym. Sci.*, **25**, 159 (2000).
19. G. Wulff, *Angew. Chem., Int. Engl. Ed.*, **28**, 21 (1989).
20. E. Abdul Rahim, F. Sanda, and T. Masuda, *J. Polym. Sci., Part A: Polym. Chem.*, **44**, 810 (2006).
21. S. Mallakpour and E. Kowsari, *Polym. Eng. Sci.*, **46**, 558 (2006).
22. S. Mallakpour and M. Kolahdoozan, *e-polymer*, no. 020 (2006).
23. S. Mallakpour and M. H. Shahmohammadi, *Iranian Polym. J.*, **14** (11), 974 (2005).
24. S. Mallakpour and E. Kowsari, *J. Appl. Polym. Sci.*, **101**, 455 (2006).
25. S. Mallakpour and M. Kolahdoozan, *Iranian Polym. J.*, **15**, 307 (2006).
26. S. Mallakpour and E. Kowsari, *Polym. Bull.*, **55**, 51 (2005).
27. J. R. Casimir, G. Guichard, and J. P. Briand, *J. Org. Chem.*, **67**, 3764 (2002).
28. A. K. Bose, F. Greer, and C. C. Price, *J. Org. Chem.*, **23**, 1335 (1958).