Amino Acids (2009) 36:511–518
DOI 10.1007/s00726-008-0113-y

ORIGINAL ARTICLE

Synthesis and characterization of new optically active poly(azo-ester-imide)s via interfacial polycondensation

Abdol R. Hajipour · Saeed Zahmatkesh · Parniyan Roosta · Arnold E. Ruoho

Received: 18 April 2008 / Accepted: 26 May 2008 / Published online: 19 June 2008

Abstract *N,N′*-Pyromelliticdiimido-di-L-amino acids (**1a–1d**) were prepared from the reaction of pyromellitic dianhydride with the corresponding L-amino acids in a solution of glacial acetic acid/pyridine (3:2) at refluxing temperature. 4,4′-sulfonyl bis(4,1-phenylene) bis(diazene-2,1-diyl) diphenol, 4,4′-oxy bis(4,1-phenylene) bis(diazene-2,1-diyl) diphenol and 4,4′-methylene bis(4,1-phenylene) bis(diazene-2,1-diyl) diphenol, were prepared from 4,4′-diamino diphenyl sulfone, 4,4′-diamino diphenyl ether, 4,4′-diamino diphenyl methane, sodium nitrite and phenol following the general procedure of diazo coupling. Interfacial polycondensation method was used to prepare the corresponding poly(azo-ester-imid)s (**PAEI$_{1-12}$**) in biphasic solution of water/dichloromethane. The resulting polymers (**PAEIs**) have been obtained in high yields having good inherent viscosities (0.32–0.57 dl g^{-1}), optical activities and thermal stabilities.

A. R. Hajipour (✉) · S. Zahmatkesh · P. Roosta
Pharmaceutical Research Laboratory,
College of Chemistry,
Isfahan University of Technology,
Isfahan 84156, IR Iran
e-mail: haji@cc.iut.ac.ir

A. R. Hajipour · A. E. Ruoho
Department of Pharmacology,
University of Wisconsin, Medical School,
1300 University Avenue, Madison,
WI 53706-1532, USA

S. Zahmatkesh
Department of Science,
Estahban Payamenoor University,
Estahban 74515/161, Fars, Iran

Keywords Poly(azo-ester-imide) · Interfacial polycondensation · Optically active · Thermally stable · Azo compound · Diazo coupling

Introduction

Chiral polymers including those bearing main- or side-chain amino acid units are used widely in the pharmaceutical industry for enantio-selective separation of drugs. This is achieved mainly via the use of chiral polymers as the stationary phase in chromatography or electrophoresis. Apart from chiral separation, biocompatible amino acid containing polymers are used in drug delivery systems (Feng et al. 2007; Bluhm et al. 2005; Billiot and Warner 2000).

Bifunctional colorants can be used as monomers in synthesis of functional polymers, so designing and synthesis of these compounds is important (Xin et al. 2001). Recently azo polymers have become important due to their potential uses in various optical applications. Photochemical *trans-cis* isomerization induced by UV or visible light is one of the most important properties of them (Kumar and Neckers 1989; Zollinger 1961; Wu et al. 2001). Azo compounds are highly colored and have been used as dyes and pigments for a long time. They have also been used in many practical applications such as coloring fibers, photoelectronic applications, and analytical chemistry (Koh and Greaves 2001; Hallas and Choi 1999; Gup et al. 2007).

Aromatic poly(imide-ester)s are one of the most important classes of high-performance polymers and attract attention for outstanding properties and potential liquid crystalline nature (Kurita et al. 1991). Poly imides are a class of high-temperature polymers which have gained considerable importance in many engineering applications

due to their excellent electrical, thermo-oxidative, and mechanical properties at elevated temperatures. However, applications for polyimides are often limited due to their intractability and insolubility as well as high melting temperatures, which cause a variety of processing problems (Ghassemi and Hay 1993; Wilson 1990; Takekoshi 1990; Sroog 1990; Kaplan and Hirsch 1974). Interfacial polymerization has been used to prepare various condensation polymers, particularly polyamides, polyesters, polyurethanes, and polyureas (Provatas et al. 2000; Chen et al. 1995; Kim et al. 1995; Wang and Nakamura 1995; Morgan 1965; Noll 1968). Interfacial polymerization allows the synthesis of condensation polymers at low temperature with limited side reactions. This method can directly generate finished products such as films, fibers, membranes, etc. and has seen widespread acceptance in many fields, ranging from microencapsulation of pharmaceutical products (Finch 1993) to conducting polymer films (Lando and Rickert 1987).

Materials and methods

All chemicals and solvents were purchased from Fluka, Aldrich or Merck chemical Co. and were used without further purification.

IR spectra were recorded on a FT/IR-680 plus spectrophotometer using KBr pellets. Band intensities are assigned as week (w), medium (m), and strong (s). Band shapes assigned as shoulder (sh), sharp (s), and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon Fenske routine viscometer at 25°C using DMF as solvent. ^{1}H NMR spectra were recorded on 300 MHz instrument, using DMSO-d_6 as solvent and tetramethylsilane as shift reference (tube diameter 5 mm). Specific rotations were measured by a JASCO P-1030 Polarimeter. Thermal gravimetric analysis (TGA) was obtained by a Mettler TGA-50 under air atmosphere at a rate of 5°C/min. Differential scanning calorimetry (DSC) was obtained by a Mettler DSC-30 under nitrogen atmosphere. Elemental analyses were performed with a Perkin Elmer CHNS elemental analyzer. Melting points were measured in open capillaries with a Gallenkamp instrument.

Monomer synthesis

*Synthesis of diacids (**1a–1d**): general procedure*

Into a 25 ml round-bottomed flask equipped with a condenser and an electric stirrer, 1.0 mmol (0.218 g) of pyromellitic dianhydride (**1**), 2 mmol of the corresponding L-amino acid, 10 ml of acetic acid/pyridine (3:2) and a stirring bar were placed. The mixture was stirred at room temperature for 2 h and then refluxed for 8 h. The solvent was removed under reduced pressure, and 5 ml of cold concentrated HCl was added. The formed precipitate was filtered off, washed with hot water and vacuum dried.

*Diacid (**1a**):* White; Yield (%) = 92; m.p. (°C) > 250; $[\alpha]_D^{25}$ = +3.54 (0.050 g in 10 ml DMF); IR (KBr): 3500–2800 (br, s), 2950 (s, s), 1780 (sh, w), 1720 (s, s), 1590 (s, m), 1390 (s, s), 1380 (sh, w), 1290 (s, w), 1210 (s, w), 1160 (s, w), 920 (s, w), 810 (s, w), 720 (s, m), 640 (s, w) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 0.9 (t, 12H), 1.52 (m, 2H), 1.9 (td, 2H), 2.2 (td, 2H), 4.88 (dd, 2H), 13.4 (s, 2H) ppm; Elemental analysis: calculated for $C_{22}H_{24}N_2O_8$: C (59.45%), H (5.44%), N (6.30%); found C (59.10%), H (5.80%), N (6.71%).

*Diacid (**1b**):* White; Yield (%) = 96; m.p. (°C) > 250; $[\alpha]_D^{25}$ = +5.18 (0.050 g in 10 ml DMF); IR (KBr): 3600–2500 (br, s), 2900 (s, m), 1780 (sh, s), 1720 (sh, s), 1700 (s, s), 1590 (sh, w), 1460 (s, s), 1390 (s, s), 1380 (sh, s), 1260 (s, s), 1160 (s, m), 1140 (sh, w), 1080 (s, s), 1010 (s, s), 910 (s, s), 850 (s, s), 800 (sh, w), 720 (s, s), 600 (s, m) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.6 (d, 6H), 4.9 (q, 2H), 8.3 (s, 2H), 13.4 (s, 2H) ppm; Elemental analysis: Calculated for $C_{16}H_{12}N_2O_8$: C (53.34%), H (3.36%), N (7.77%); found C (52.90%), H (3.40%), N (7.30%).

*Diacid (**1c**):* White; Yield (%) = 89; m.p. (°C) > 250; $[\alpha]_D^{25}$ = +20.86 (0.050 g in 10 ml DMF); IR (KBr): 3400–2700 (br, s), 2900 (s, s), 1750 (sh, m), 1700 (s, s), 1580 (sh, w), 1450 (sh, w), 1390 (s, s), 1350 (sh, m), 1250 (sh, w), 1190 (s, m), 1120 (sh, w), 1060 (sh, w), 890 (s, w), 720 (s, m) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 0.95 (t, 6H), 1.09 (d, 6H), 1.2 (m, 4H), 2.4 (m, 2H), 4.65 (d, 2H), 8.4 (s, 2H), 13.2 (s, 2H) ppm; Elemental analysis: Calculated for $C_{22}H_{24}N_2O_8$: C (59.45%), H (5.44%), N (6.30%); found C (59.20%), H (5.70%), N (5.90%).

*Diacid (**1d**):* White; Yield (%) = 90; m.p. (°C) > 250; $[\alpha]_D^{25}$ = + 1.56 (0.050 g in 10 ml DMF); IR (KBr): 3600–2800 (br, s), 2900 (sh, w), 1760 (sh, w), 1720 (s, s), 1560 (s, m), 1490 (s, w), 1370 (s, s), 1350 (sh, m), 1220 (sh, w), 1180 (sh, w), 1090 (s, m), 900 (sh, w), 800 (s, w), 720 (s, m), 690 (s, w) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 3.32 (dd, 2H), 3.52 (dd, 2H), 5.2 (dd, 2H), 7.2 (m, 10H), 8.23 (s, 2H) ppm; Elemental analysis: Calculated for $C_{28}H_{20}N_2O_8$: C (65.62%), H (3.93%), N (5.46%); found C (65.30%), H (4.10%), N (5.30%).

Synthesis of diacyl chlorides: general procedure (Banihashemi and Pourabbas 2000)

Finely powdered diacid (0.5 g) was placed into a 50 ml round-bottomed flask and redistilled thionyl chloride (30 ml) was added. The mixture was refluxed for 3 h with stirring. The unreacted thionyl chloride was distilled off by an ordinary distillation and the remaining was driven out

by rotary evaporation. Solids were treated with *n*-hexane, and collected after filtration. The diacyl chloride was dried in a vacuum oven at 40°C.

*Diacid chloride (**1′a**):* White; Yield (%) = 70; m.p. (°C) = 168 (d); $[\alpha]_D^{25} = +3.18$ (0.050 g in 10 ml DMF); IR (KBr): 3482 (s, w), 3224 (br, w), 3108 (s, w), 2958 (s, s), 2933 (sh, w), 2872 (s, m), 1811 (s, s), 1776 (s, m), 1720 (s, s), 1468 (s, m), 1383 (s, s), 1366 (s, s), 1272 (s, w), 1231 (s, w), 1172 (s, m), 1155 (s, m), 1077 (s, s), 1047 (sh, w), 992 (s, s), 939 (s, m), 921 (sh, m), 876 (s, m), 840 (s, s), 819 (sh, m), 765 s, s), 719 (s, m), 663 (s, w), 603 (s, s), 563 (s, m), 481 (s, m), 417 (s, m) cm^{-1}.

*Diacid chloride (**1′b**):* White; Yield (%) = 78; m.p. (°C) = 173 (d); $[\alpha]_D^{25} = +5.50$ (0.050 g in 10 ml DMF); IR (KBr): 3489 (br, m), 2940 (s, m), 1778 (sh, s), 1731 (s, s), 1456 (s, s), 1381 (s, s), 1364 (s, s), 1275 (s, w), 1181 (s, m), 1156 (s, m), 1126 (s, m), 1082 (s, m), 1065 (s, m), 1015 (s, m), 942 (s, s), 901 (s, m), 842 (s, s), 736 (s, s), 712 (s, m), 663 (s, w), 624 (s, m), 601 (s, s), 562 (s, m), 443 (s, w), 405 (s, m) cm^{-1}.

*Diacid chloride (**1′c**):* White; Yield (%) = 70.45; m.p. (°C) = 165 (d); $[\alpha]_D^{25} = +14.08$ (0.050 g in 10 ml DMF); IR (KBr): 3481 (br, m), 2969 (s, m), 2936 (sh, w), 2879 (sh, w), 2360 (sh, w), 1795 (s, s), 1775 (sh, m), 1721 (s, s), 1475 (s, m), 1377 (s, s), 1360 (s, s), 1152 (sh, w), 1110 (sh, w), 1086 (s, m), 1046 (s, w), 1001 (s, w), 962 (s, w), 891 (s, m), 854 (s, m), 817 (s, m), 740 (s, s), 637 (s, m), 561 (s, m) cm^{-1}.

*Diacid chloride (**1′d**):* White; Yield (%) = 68; m.p. (°C) = 162 (d); $[\alpha]_D^{25} = +4.56$ (0.050 g in 10 ml DMF); IR (KBr): 3063–2926 (br, m), 1773 (s, s), 1728 (s, s), 1603 (sh, w), 1497 (s, m), 1455 (s, m), 1378 (s, s), 1363 (sh, s), 1330 (sh, w), 1201 (s, w), 1157 (s, w), 1131 (sh, m), 1105 (sh, m), 1078 (s, w), 1027 (s, m), 966 (s, m), 919 (s, m), 888 (s, w), 847 (s, s), 827 (sh, s), 773 (s, m), 735 (s, s), 700 (s, s), 621 (s, m), 606 (s, m), 565 (s, m) cm^{-1}.

*Preparation of monomer **2a**: general procedure*

Into a 50 ml round-bottomed flask, a stirring bar, 1.0 mmol (0.248 g) of 4,4′-diamino diphenyl sulfone, 0.366 ml of HCl (Conc.) and 10 ml of water were added. The solution was then cooled to 0–5°C in an ice bath. A solution of 2.0 mmol (0.138 g) sodium nitrite in 5 ml of water was prepared and then added dropwise to the mixture. Stirring was continued for 10 min at the same temperature. This solution was added portion wise to the coupling component solution prepared by mixing a solution of 2.0 mmol (0.188 g) of phenol, 2.0 mmol (0.080 g) of NaOH and 10 ml of water. During the reaction, the temperature was maintained at 0–5°C. After 1 h, the colorful precipitate was filtered off, washed with cold water, and vacuum dried.

The other monomers (**2b**, **2c**) were synthesized following the same procedure using 1.0 mmol (0.200 g) of 4,4′-diamino diphenyl ether or 1.0 mmol (0.198 g) of 4,4′-diamino diphenyl methane correspondingly.

*Monomer **2a***: Dark red; Yield (%) = 86.9; m.p. (°C) = 227; IR (KBr): 3600–3300 (br, s), 2925 (sh, w), 2361 (sh, w), 1585 (s, s), 1504 (s, m), 1464 (sh, w), 1430 (s, s), 1401 (sh, w), 1325 (s, w), 1301 (s, m), 1255 (sh, m), 1138 (s, s), 1101 (s, s), 1067 (s, w), 1008 (s, m), 923 (s, w), 848 (s, s), 795 (s, m), 738 (s, m), 720 (s, m), 703 (s, w), 642 (sh, w), 610 (s, s), 577 (s, s), 545 (sh, w) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.00 (d, 4H), 7.88 (d, 4H), 8.00 (d, 4H), 8.19 (d, 4H), 10.6 (s, 2H) ppm; Elemental analysis: Calculated for $C_{24}H_{18}N_4O_4S$: C (62.87%), H (3.96%), N (12.22%), S (6.99%); found C (62.60%), H (4.20%), N (11.90%), S (6.70%).

*Monomer **2b***: Dark red; Yield(%) = 69.3; m.p. (°C) = 216; IR (KBr): 3600–3400 (br, m), 2800 (sh, w), 2360 (sh, w), 2239 (s, w), 1581 (s, s), 1489 (s, m), 1435 (sh, m), 1384 (sh, w), 1240 (s, s), 1145 (s, s), 1096 (s, m), 1006 (s, w), 874 (sh, m), 842 (s, s), 781 (sh, w), 727 (sh, w), 649 (sh, m), 619 (sh, w), 551 (s, m), 517 (sh, w), 482 (sh, m) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.00 (d, 4H), 7.27 (d, 4H), 7.81 (d, 4H), 7.92 (d, 4H), 10.70 (s, 2H) ppm; Elemental analysis: Calculated for $C_{24}H_{18}N_4O_3$: C (70.23%), H (4.42%), N (13.65%); found C (70.00%), H (4.60%), N (13.40%).

*Monomer **2c***: Dark brown; Yield(%) = 75.5; m.p. (°C) = 195; IR (KBr): 3600–3100 (br, s), 2922 (sh, m), 1600 (br, w), 1587 (s, s), 1502 (s, s), 1463 (s, m), 1432 (s, s), 1410 (sh, m), 1384 (sh, m)m 1235 (s, s), 1138 (s, s), 1098 (s, m), 1101 (s, m), 924 (sh, w), 870 (sh, m), 837 (s, s), 802 (sh, m), 774 (sh, w), 724 (s, w), 647 (s, w), 621 (s, m), 547 (s, m), 529 (sh, m), 477 (s, m), 417 (sh, w) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 4.12 (s,2H), 6.96 (d, 4H), 7.45 (d, 4H), 7.78 (d, 4H), 7.81 (d, 4H), 10.4 (s, 2H) ppm; Elemental analysis: Calculated for $C_{25}H_{20}N_4O_2$: C (73.51%), H (4.93%), N (13.71%); found C (73.40%), H (5.10%), N (13.90%).

Interfacial polycondensation: general procedure

Into a 100 ml round-bottomed flask, a stirring bar, 1.0 mmol of a corresponding diacyl chloride (**1′a**–**1′d**), and 10 ml of dichloromethane were placed. The mixture was stirred for 5 min. A solution of 1.0 mmol of diazo compound (**2a**–**2c**), 20 ml of NaOH (0.1 N), and catalytic amount of tetraethylammonium bromide (0.1 g) in 10 ml of H_2O was prepared. This solution was added dropwise to the flask, while stirring vigorously in an ice bath. After 1 h, the formed polymer was filtered off, washed with methanol, and vacuum dried.

PAEI_1 IR (KBr): 3600–3100 (br, s), 2959 (sh, m), 2871 (sh, w), 1779 (sh, s), 1725 (s, s), 1593 (s, s), 1495 (s, m),

1468 (sh, m), 1437 (sh, w), 1383 (s, s), 1363 (sh, m), 1301 (s, m), 1195 (sh, m), 1142 (sh, m), 1100 (sh, m), 1010 (s, m), 918 (s, w), 849 (s, m), 797 (s, w), 728 (s, m), 617 (sh, m), 576 (s, m), 561 (sh, w), 415 (sh, w) cm^{-1}. Elemental analysis: Calculated for $C_{46}H_{38}N_6O_{10}S$: C (63.73%), H (4.42%), N (9.69%), S (3.69%); found C (63.50%), H (4.60%), N (9.40%), S (3.50%).

PAEI$_2$ IR (KBr): 3600–3100 (br, s), 1750 (sh, m), 1723 (s, s), 1635 (sh, w), 1590 (sh, m), 1559 (sh, w), 1496 (sh, m), 1457 (sh, m), 1384 (s, s), 1300 (s, m), 1193 (sh, m), 1141 (sh, m), 1101 (s, m), 1076 (sh, w), 849 (s, m), 796 (sh, w), 729 (s, m), 611 (sh, w), 559 (sh, w), 468 (sh, w), 419 (s, w) cm^{-1}. Elemental analysis: Calculated for $C_{40}H_{26}N_6O_{10}S$: C (61.38%), H (3.35%), N (10.74%), S (4.09%); found C (61.40%), H (3.60%), N (10.60%), S (4.00%).

PAEI$_3$ IR (KBr): 3600–3300 (br, s), 2968 (sh, m), 2360 (sh, w), 1800 (sh, w), 1779 (sh, m), 1724 (s, s), 1635 (sh, w), 1495 (s, m), 1457 (s, m), 1384 (s, s), 1359 (sh, m), 1141 (sh, m), 1101 (sh, m), 1000 (sh, w), 728 (s, m), 575 (sh, w), 561 (sh, w), 419 (sh, w) cm^{-1}. Elemental analysis: Calculated for $C_{46}H_{38}N_6O_{10}S$: C (63.73%), H (4.42%), N (9.69%), S (3.69%); found C (63.60%), H (4.50%), N (9.40%), S (3.80%).

PAEI$_4$ IR (KBr): 3600–3300 (br, s), 2360 (sh, m), 2342 (sh, w), 1774 (sh, m), 1725 (s, s), 1578 (s, s), 1495 (s, m), 1418 (sh, m), 1383 (s, s), 1192 (sh, m), 1140 (sh, m), 1104 (s, m), 1010 (sh, w), 829 (sh, w), 727 (s, m), 699 (s, m), 618/ (sh, m), 461 (sh, w) cm^{-1}. Elemental analysis: Calculated for $C_{52}H_{34}N_6O_{10}S$: C (66.80%), H (3.66%), N (8.98%), S (3.43%); found C (66.5%), H (3.80%), N (8.70%), S (3.50%).

PAEI$_5$ IR (KBr): 3600–3400 (br, s), 2924 (sh, m), 1773 (s, m), 1725 (s, s), 1582 (s, s), 1488 (s, s), 1382 (s, m), 1239 (s, s), 1145 (s, s), 841 (sh, m), 726 (s, m), 548 (s, m) cm^{-1}. Elemental analysis: Calculated for $C_{46}H_{38}N_6O_9$: C (67.47%), H (4.67%), N (10.26%); found C (67.40%), H (4.70%), N (10.10%).

PAEI$_6$ IR (KBr): 3600–3300 (br, m), 2850 (sh, w), 1750 (sh, w), 1722 (s, s), 1580 (s, s), 1488 (s, m), 1383 (s, s), 1364 (sh, w), 1238 (s, m), 1192 (sh, w), 1146 (s, m), 1078 (sh, w), 1012 (s, w), 925 (s, w), 843 (s, m), 725 (s, m), 620 (sh, w), 550 (sh, w) cm^{-1}. Elemental analysis: Calculated for $C_{40}H_{26}N_6O_9$: C (65.39%), H (3.56%), N (11.44%); found C (65.30%), H (3.70%), N (11.20%).

PAEI$_7$ IR (KBr): 3600–3400 (br, s), 2965 (sh, m), 2361 (sh, m), 1778 (sh, w), 1725 (s, s), 1583 (s, s), 1488 (s, s), 1381 (s, s), 1357 (s, s), 1239 (s, m), 1192 (s, m), 1146 (s, m), 1009 (s, w), 841 (sh, w), 728 (s, m), 548 (sh, w) cm^{-1}. Elemental analysis: Calculated for $C_{46}H_{38}N_6O_9$: C (67.47%), H (4.67%), N (10.26%); found C (67.20%), H (4.80%), N (10.40%).

PAEI$_8$ IR (KBr): 3600–3400 (br, m), 1834 (s, m), 1777 (sh, w), 1725 (s, s), 1584 (s, m), 1479 (s, m), 1455 (sh, w), 1389 (s, s), 1363 (sh, w), 1240 (s, m), 1147 (s, w), 1106 (s, m), 993 (sh, w), 843 (sh, w), 727 (s, m), 700 (s, m) cm^{-1}. Elemental analysis: Calculated for $C_{52}H_{34}N_6O_9$: C (70.42%), H (3.86%), N (9.47%); found C (70.20%), H (3.70%), N (9.30%).

PAEI$_9$ IR (KBr): 3600–3300 (br, s), 2960 (sh, m), 2931 (sh, w), 2872 (sh, w), 2362 (sh, w), 1777 (sh, m), 1725 (s, s), 1578 (s, s), 1491 (sh, w), 1414 (sh, w), 1382 (s, s), 1364 (sh, w), 1195 (sh, m), 1152 (sh, m), 1011 (s, m), 923 (s, m), 865 (s, w), 826 (s, w), 727 (s, m), 648 (s, w), 620 (s, w), 563 (sh, w) cm^{-1}. Elemental analysis: Calculated for $C_{47}H_{40}N_6O_8$: C (69.10%), H (4.93%), N (10.28%); found C (68.80%), H (5.10%), N (10.00%).

PAEI$_{10}$ IR (KBr): 3600–3300 (br, s), 2850 (sh, w), 1760 (sh, w), 1721 (s, s), 1578 (s, s), 1491 (s, m), 1417 (sh, m), 1383 (s, s), 1364 (sh, w), 1194 (s, m), 1152 (s, m), 1077 (s, m), 1012 (s, m), 925 (s, w), 846 (s, w), 728 (s, m), 648 (sh, w), 620 (sh, w), 562 (sh, w) cm^{-1}. Elemental analysis: Calculated for $C_{41}H_{28}N_6O_8$: C (67.21%), H (3.85%), N (11.47%); found C (67.40%), H (4.10%), N (11.30%).

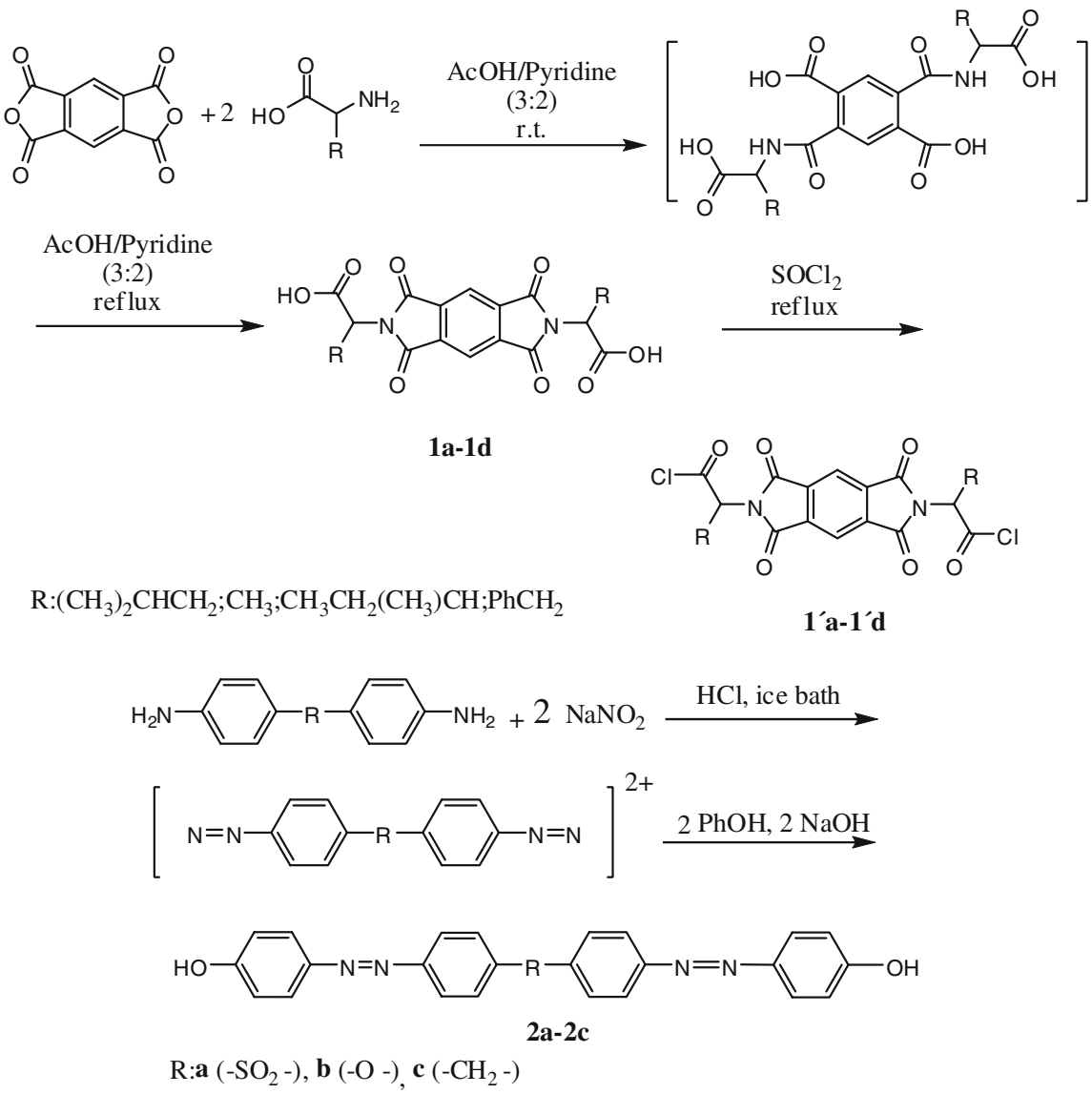
PAEI$_{11}$ IR (KBr): 3600–3400 (br, m), 2965 (sh, m), 1778 (sh, m), 1725 (s, s), 1591 (s, m), 1492 (s, m), 1458 (s, m), 1381 (s, s), 1357 (s, s), 1195 (sh, m), 1152 (s, w), 1011 (s, w), 833 (sh, w), 727 (s, m), 549 (sh, w) cm^{-1}. Elemental analysis: Calculated for $C_{47}H_{40}N_6O_8$: C (69.10%), H (4.93%), N (10.28%); found C (68.90%), H (5.00%), N (10.00%).

PAEI$_{12}$ IR (KBr): 3600–3400 (br, w), 2360 (sh, w), 1834 (s, m), 1777 (sh, m), 1725 (s, s), 1590 (sh, m), 1496 (s, m), 1455 (s, m), 1382 (s, s), 1362 (sh, m), 1193 (sh, w)1106 (s, m), 992 (sh, w), 916 (sh, w), 828 (s, w), 727 (s, m), 699 (s, m), 620 (s, w), 563 (s, w) cm^{-1}. Elemental analysis: Calculated for $C_{53}H_{36}N_6O_8$: C (71.94%), H (4.10%), N (9.49%); found C (71.60%), H (4.20%), N (9.30%).

Results and discussion

Monomer synthesis

We synthesized the diimide-diacids [*N,N′*-pyromellitic-diimido-di-L-aminoacids (**1a–1d**)] by the condensation reaction of pyromellitic dianhydride with L-aminoacids (**a–d**) (1:2 molar ratio) in a solution of refluxing acetic acid/pyridine (3:2), and then treating the residue with cold concentrated HCl to get the corresponding diacid



Scheme 1 Preparation of monomers

(Scheme 1). The mixture of reaction was allowed to stir for 2 h, in this part amic acid formation occurs. Refluxing for 8 h causes the dehydration and cyclic imide formation. Refluxing a diacid with an excess amount of thionyl chloride allows the diacyl chloride formation. After removing the thionyl chloride by distillation under reduced pressure, the residue was washed with *n*-hexane to remove the remaining thionyl chloride. Compounds (**2a**–**2c**) were synthesized by the reaction of a diamine such as 4,4′-diamino diphenyl sulfone, 4,4′-diamino diphenyl ether or 4,4′-diamino diphenyl methane (1.0 mmol), sodium nitrite (2.0 mmol) and HCl in water. The mixture was stirred for 10 min. A solution of phenol (2.0 mmol), and NaOH (0.1 M, 20 ml) in 10 ml of water was prepared and added dropwise to the first solution and then the mixture was stirred for 1 h (Scheme 1). The chemical structure and the purity of optically active monomers (**1a**–**1d**, **2a**–**2c**) were proved by FT-IR and ^{1}H NMR spectroscopy, and elemental analysis. Figure 1 represents the ^{1}H NMR spectra of diacid (**1b**) and monomer (**2a**).

Polymer synthesis

The **PAEIs (1–12)** were synthesized by the interfacial polycondensation reaction between an equimolar mixture of one of the diacyl chlorides and one of the diphenols (**2a**–**2c**) using tetraethylammonium bromide as a phase transfer catalyst in a biphasic solution (water/CH_2Cl_2) (Scheme 2). Interfacial polymerization behaves more like the chain polymerization since the monomer diffusion to the interface layer is much faster than to the second phase. This method allows the reaction to proceed much faster and at

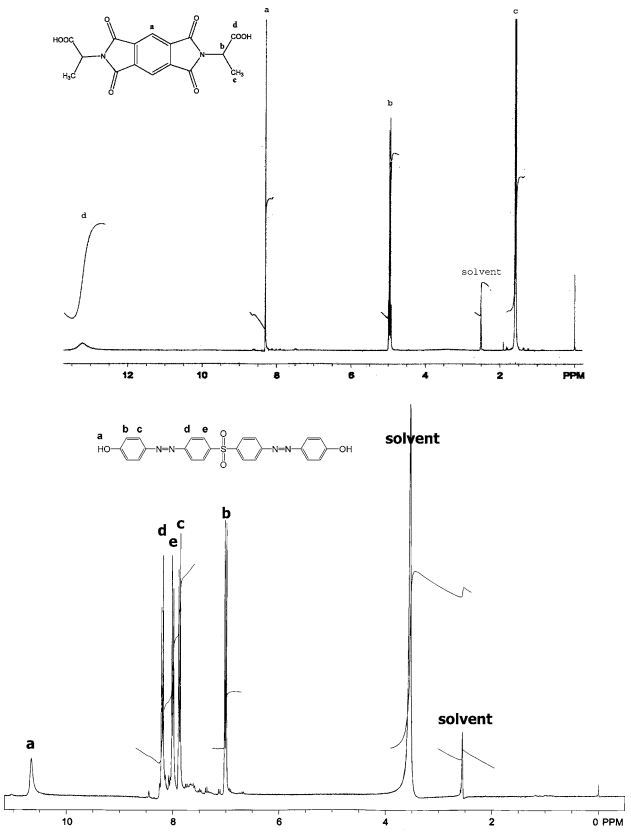


Fig. 1 ^{1}H NMR spectra of diacid **1b** and compound **2a**

lower temperature, so it is a very good method to prepare chiral polymers. The synthesis and some physical properties of these novel optically active **PAEIs** are given in Table 1.

All the polymers were obtained in good yields with good inherent viscosities (0.32–0.57 dl g^{-1}), and show optical rotation and therefore are optically active.

Table 1 Synthesis and some physical properties of ***PAEIs***

Diacid chloride	Diazo compound	***PAEI***	Yield (%)	η_{inh} (dl g^{-1})[a]	$[\alpha]_D^{25b}$	Color
1′a	2a	1	77	0.32	−7.94	O
1′b	2a	2	72	0.32	−7.96	O
1′c	2a	3	80	0.38	+1.76	O
1′d	2a	4	85	0.39	−7.86	O
1′a	2b	5	84	0.46	−8.08	LB
1′b	2b	6	78	0.50	−8.00	LB
1′c	2b	7	90	0.49	−7.64	DY
1′d	2b	8	88	0.52	−8.44	LB
1′a	2c	9	91	0.33	−8.12	DY
1′b	2c	10	84	0.43	−8.2	LB
1′c	2c	11	82	0.57	−8.66	LB
1′d	2c	12	85	0.52	−8.24	DY

O orange, *LB* light brown, *DY* dark yellow

[a] Measured at a concentration of 0.5 dl g^{-1} in NMP (5% LiCl) at 25°C

[b] Measured at a concentration of 0.5 dl g^{-1} in NMP (5% LiCl) at 25°C

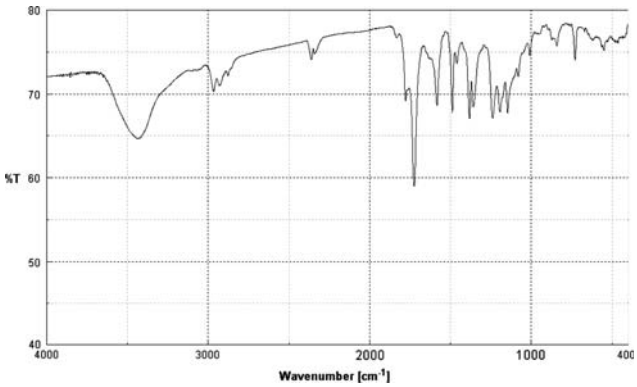


Fig. 2 IR spectrum of ***PAEI$_7$***

Polymer characterization

The formation of **PAEIs** was confirmed by the FT-IR spectroscopy and elemental analysis. As an example, Fig. 2 shows the IR spectrum of **PAEI$_7$** with the characteristic absorptions at 1778 (C=O, asymmetric, imidic), 1725 (C=O, symmetric, imidic), 1583 (N=N, azo), 1509 (C–N, imide), 1381 and 726 (imidic ring). The colors of **PAEIs** range from dark yellow to light brown. The solubility of **PAEIs** was tested qualitatively in various organic solvents and the results are summarized in Table 2. All of the **PAEIs** are soluble or partially soluble in organic solvents

Scheme 2 Interfacial polymerization

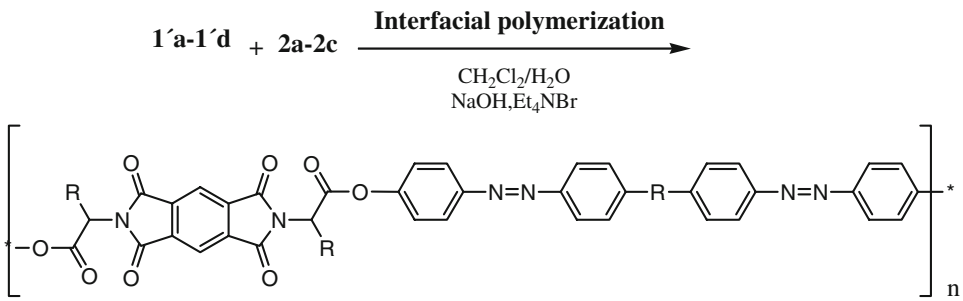


Table 2 Solubility of ***PAEIs(1–12)***

PAEI	NMP (5%LiCl)	THF	Cyclohexane	EtOH	DMSO	DMF	NMP	H_2SO_4	CH_2Cl_2	Acetone
1	+	+	−	−	P	+	P	+	−	−
2	+	P	−	−	P	P	+	+	−	−
3	+	+	−	−	P	P	+	+	P	−
4	+	P	−	−	P	P	P	+	−	−
5	+	P	−	−	P	P	P	+	−	−
6	+	+	−	−	+	+	+	+	P	−
7	+	P	−	−	P	P	−	+	P	−
8	+	P	−	−	+	P	P	+	−	−
9	+	P	−	−	P	P	+	+	P	−
10	+	P	−	−	P	P	P	+	−	−
11	+	P	−	−	P	P	P	+	P	−
12	+	P	−	−	+	+	P	+	P	−

+ soluble, − insoluble, *P* partially soluble

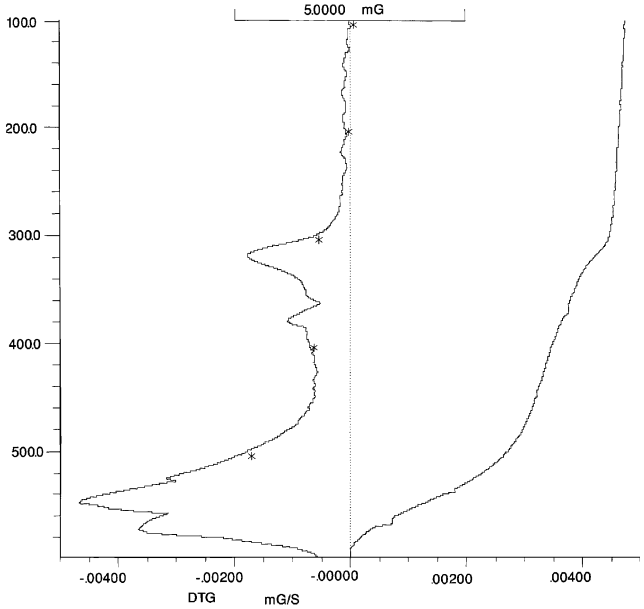


Fig. 3 TGA/DTG thermogram of ***PAEI*$_7$**

such as DMF, DMSO, NMP and H_2SO_4 at room temperature, and are partially soluble or insoluble in solvents such as methylene chloride and acetone.

Thermal properties

The thermal properties of **PAEI$_7$** were evaluated by means of TGA/DTG (under air atmosphere) and DSC (under nitrogen atmosphere). The temperatures of 5 and 10% weight loss are 295 and 320°C, correspondingly, and the Tg is about 105°C. TGA/DTG thermogram of **PAEI$_7$** is represented in Fig. 3.

Conclusions

A series of optically active **PAEIs** having inherent viscosities in the range of 0.32–0.57 dl g^{-1} were synthesized for the first time by the interfacial polycondensation of optically active *N,N′*-pyromelliticiimido-di-L-amino acid chlorides (**1′a–1′d**) as an acidyl chloride with aromatic diphenols containing azo groups (**2a–2c**). These aromatic **PAEIs** show optical rotation and can be used in chiral separation, via the use of chiral polymers as the stationary phase. They are readily soluble in various organic solvents and have a good thermal stability. These polymers can potentially be used as liquid crystals, dyes and pigments, in photoelectronics, in optical light storage due to the characteristics of the azo functional group. These polymers also have amino acid groups in the main chain, and so may be biocompatible with applications in drug delivery systems and biodegradable materials.

Acknowledgments We gratefully acknowledge the funding support received for this project from Isfahan University of Technology (IUT), IR Iran (ARH) and grant GM 33138(AER) from the national Institute of health, USA. Further financial support from center of Excellency in chemistry research (IUT) is gratefully acknowledged.

References

Banihashemi A, Pourabbas B (2000) New thermally stable polyamides derived from 2,9-diamino benzofuro[2,3-b]benzofuran, a new monomer. Eur Polym J 36:2031–2038

Billiot E, Warner IM (2000) Examination of structural changes of polymeric amino acid-based surfactants on enantioselectivity: effect of amino acid order, steric factors, and number and position of chiral centers. Anal Chem 72:1740–1748

Bluhm L, Huang JM, Li TY (2005) Recent advances in peptide chiral selectors for electrophoresis and liquid chromatography. Anal Bioanal Chem 382:592–598

Chen Y, Fang J, Kao SC (1995) Preparation of polyamides derived from 1,6-diamantane dicarboxylic chloride by solution polycondensation and interfacial polycondensation. J Polym Sci Part A 33:2833–2840

Feng L, Hu J, Liu ZH, Zhao F, Liu G (2007) Preparation and properties of optically active poly(*N*-methacryloyl L-leucine methyl ester). Polymer 48(13):3616–3623

Finch CA (1993) Encapsulation controlled release. Royal Soc Chem 138:1

Ghassemi H, Hay AS (1993) Novel poly(ether imides) utilizing hydrazine as the diamine. Macromolecules 26:5824–5826

Gup R, Giziroglu E, Kirkan B (2007) Synthesis and spectroscopic properties of new azo-dyes and azometal complexes derived from barbituric acid and aminoquinoline. Dyes Pigments 73:40–46

Hallas G, Choi JH (1999) Synthesis and properties of novel aziridinyl azo dyes from 2-aminothiophenes—Part 2: application of some disperse dyes to polyester fibres. Dyes Pigments 40:119–129

Kaplan SL, Hirsch SS (1974) In: New Industrial Polymers, ACS Symposium Series 4. American Chemical Society, Washington DC, p 100

Kim K, Lee S, Ryu K, Lee K (1995) The effect of temperature and solvent on the polymerization of 2-propenylfuran. Polym Bull 35:57–62

Koh J, Greaves AJ (2001) Synthesis of heteroaryl pyridone methine dyes. Dyes Pigments 50:13–19

Kumar GS, Neckers DC (1989) Photochemistry of azobenzene-containing polymers. Chem Rev 89:1915–1925

Kurita K, Mikawa N, Ishii SH, Nishimura SH (1991) Polymers based on p-aminophenol. 7. Newsynthetic approaches to the simplest wholly aromatic poly(imide ester) via the corresponding poly(amic acid) precursor. Macromolecules 24:6853–6855

Lando JB, Rickert SE (1987) Phase-controlled surface reactions. Thin Solid Films 152:327–333

Morgan PW (1965) Condensation polymers: by interfacial and solution methods. John Wiley, New York

Noll W (1968) Chemistry and technology of silicon. Academic Press, New York

Provatas A, Matisons J, Clarke S (2000) Synthesis of poly (methylphenylsiloxane)-*block*-poly(dimethylsiloxane) block copolymers by interfacial polymerization. Macromolecules 33:9156−9159

Sroog CE (1990) In: Wilson D, Stenzenberger HD, Hergenrother PM (eds) Polyimides. Chapman and Hall, New York, p 252

Takekoshi T (1990) Polyimides, advances in polymer science, vol 94. Springer, Berlin, p 1

Wang C, Nakamura S (1995) Synthesis of reactive copolyesters derived from isophthaloyl chloride, bisphenol a, and aliphatic diols with additional reactive groups. J Polym Sci Part A 33:2027−2031

Wilson D (1990) In: Wilson D, Stenzenberger HD, Hergenrother PM (eds) Polyimides. Chapman and Hall, New York, p 187

Wu L, Tuo X, Cheng H, Chen ZH, Wang X (2001) Synthesis, photoresponsive behavior, and self-assembly of poly(acrylic acid)-based azo polyelectrolytes. Macromolecules 34:8005–8013

Xin Z, Sanda F, Endo T (2001) Synthesis and characterization of coloured monomers based on 2-methylresorcinol. Dyes Pigments 49:1−7

Zollinger H (1961) Azo and diazo chemistry. Interscience Publishers Inc., New York