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ORIGINAL PAPER

New photosensitive and optically active organo-soluble poly(amide–imide)s from N,N′-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids and 1,5-bis(4-aminophenyl)penta-1,4-dien-3-one: synthesis and characterization

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Abstract A new series of N,N′-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids **3a–g** were synthesized by the condensation reaction of bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1** with two equimolars of various amino acids such as L-alanine **2a**, L-valine **2b**, L-leucine **2c**, L-isoleucine **2d**, L-phenyl alanine **2e**, L-2-aminobutyric acid **2f** and L-histidine **2g** in an acetic acid solution. Also 1,5-bis(4-aminophenyl)penta-1,4-dien-3-one **7** was synthesized by using a two-step reaction. At first 1,5-bis(4-nitrophenyl)penta-1,4-dien-3-one **6** was prepared from the reaction of two equimolars 4-nitrobenzaldehyde **5** and one equimolar acetone **4** in ethanol and $NaHCO_3$ and dinitro compound **6** was reduced by using Na_2S. Then seven new photosensitive and optically active organo-soluble poly(amide–imide)s (PAIs) **8a–g** with good inherent viscosities were synthesized from the direct polycondensation reaction of new N,N′-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids **3a–g** with 1,5-bis(4-aminophenyl)penta-1,4-dien-3-one **7** by two different methods such as direct polycondensation in a medium consisting of N-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride ($CaCl_2$)/pyridine (py) and direct polycondensation in a tosyl chloride (TsCl)/pyridine (py)/N,N-dimethylformamide (DMF) system. The polymerization reactions produced a series of photosensitive and optically active organo-soluble PAIs with high yield and good inherent viscosity. The resulted polymers were fully characterized by means of FTIR and ^{1}H-NMR spectroscopy, elemental analyses, inherent viscosity, specific rotation, solubility tests, UV-vis spectroscopy, differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), and derivative of thermaogravimetric (DTG). These macromolecules exhibited maximum UV-vis absorption at around 370 and 265 nm in a DMF solution.

Keywords Photosensitive · Optically active · Organo-soluble · Poly(amide–imide)

Introduction

The development of heat resistant high performance polymers in the past decades has been quite dramatic and has drawn the attention of many polymer scientists all over the world. Aromatic polyimides have earned a reputation as high-performance materials because of their excellent thermal stability, chemical resistance, and outstanding mechanical properties [1]. However, poor handling and intractable characteristics have been major problems because of their high melting points and insolubility. To extend the utility of such high-performance materials, it has been a long-desired goal to synthesize polyamide–imides that can offer a compromise between excellent thermal stability and processability [2–8].

Polymers containing photosensitive moieties such as cinnamate, chalcone, coumarine, dibenzalacetone and their derivatives both in main chain or side chain [9–12] have attracted great interest because of their potential use in various applications, the foremost of these including devices for optical data storage [13], photoresists [14], and photolithographic assemblies [15]. Moreover, the

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design and synthesis of polymers highly sensitive to light processing continue to be the most attractive targets because various material properties can be improved by the incorporation of appropriate chemical structures into a polymer backbone.

The synthesis and application of chiral polymers is of particular interest from the viewpoint of material science and newly considered topics. Chiral polymers have found successful uses in chromatographic separation of enantiomers, chiral liquid crystals, non-linear optical devices, optical switches and biomedical devices, etc. [16–25]. A direct and effective way for synthesizing chiral polymers is to introduce chiral elements into the polymer backbone or side chains. The combination of poly(amide–imide)s with chiral elements is of synthetic interest and may also lead to chiral recognition membranes. Recently, we have synthesized optically active polymers by different methods [26–28].

In this article, a series of new photosensitive and optically active organo-soluble PAIs **8a–g** containing dibenzalacetone moiety were synthesized by the direct polycondensation reactions of seven chiral N,N′-(bicyclo [2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids **3a–g** with 1,5-bis(4-aminophenyl)penta-1,4-dien-3-one **7** by two different methods such as direct polycondensation in a medium consisting of N-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride ($CaCl_2$)/pyridine (py) and direct polycondensation in a tosyl chloride (TsCl)/pyridine (py)/N,N-dimethylformamide (DMF) system.

Experimental

Materials

Bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1** (from Aldrich), L-alanine **2a**, L-valine **2b**, L-leucine **2c**, L-isoleucine **2d**, L-phenyl alanine **2e** and L-2-aminobutyric acid **2f**, L-histidine **2g**, 4-nitrobenzaldehyde **5**, acetone **4** and tosyl chloride (TsCl; from Merck) were used without previous purification. Solvent: N-methyl-2-pyrrolidone (NMP; from Fluka), pyridine (from Acros), triphenyl phosphite (TPP; from Merck) and N,N-dimethylformamide (DMF; from Merck) were used as received. Commercially available calcium chloride ($CaCl_2$; from Merck) was dried under vacuum at 150°C for 6 hrs.

Techniques

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 300 MHz instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solid were performed by using KBr pellets. Vibration transition frequencies were reported in wave number (cm^{-1}). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure by using a Technico Regd Trad Mark Viscometer. UV-vis absorptions were recorded at 25°C in the 190–790 nm spectral regions with a Perkin-Elmer Lambda 15 spectrophotometer on DMF solution by using cell lengths of 1 cm. Specific Rotations were measured by an A-Kruss polarimeter. Thermal Gravimetric Analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under N_2 atmosphere at rate of 10°C/min and differential scanning calorimeter (DSC) was conducted with a DSC Metller 110 (Switzerland) at a heating and heating rate of 10°Cmin^{-1} in a nitrogen atmosphere. Elemental analyses were performed were performed by Vario EL equipment by Arak University.

Monomer synthesis

Synthesis of N,N′-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids **3a–g**

1 g (4.03 mmol) of bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1**, 8.06 mmol of L-amino acids **2a–g**, 50 mL of acetic acid and a stirring bar were placed into a 250-mL round-bottomed flask. The mixture was stirred at room temperature for overnight and refluxed for 4 hrs. The solvent was removed under reduced pressure, and the residue was dissolved in 100 mL of cold water, then the solution was decanted and 5 mL of concentrated HCl was added. A white precipitate was formed, filtered off, and dried to give compounds N,N′-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids **3a–g**.

Synthesis of 1,5-bis(4-nitrophenyl)penta-1,4-dien-3-one **6**

0.324 g (5.6 mmol) of acetone **4**, 1.691 g (11.2 mmol) of 4-nitrobenzaldehyde **5**, 15 mL of ethanol, and a stirring bar were placed into a 50-mL round-bottom flask. Then this mixture was heated in 50°C for 1 h and 5 mL of $NaHCO_3$ (1%) was added slowly at this temperature and refluxed for 3 hrs. Then the reaction mixture was cooled to ambient temperature and 50 mL cooled water was added. A yellow crude product formed and was collected by filtration, washed thoroughly with water, and dried to afford 1.52 g (84%). Mp: 262-264°C. FTIR (KBr): 3109 (w), 1670 (m), 1649 (m), 1629 (s), 1604 (s), 1531 (s), 1411 (m), 1344 (s), 1190 (s), 1111 (s), 987 (s), 852 (s), 756 (m), 702 (s), 543 (m) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6, TMS): δ; 8.29–8.31 (d, 4H, J=8.4 Hz), 8.05–8.08 (d, 4H, J=8.4 Hz), 7.89–7.95 (d, 2H, J=16.1 Hz), 7.52–7.58 (d, 2H, J=16.1 Hz) ppm. Elemental analysis: calculated for $C_{17}H_{12}N_2O_5$: C, 62.96; H, 3.73; N, 8.64; found: C, 62.88; H, 3.71; N, 8.23.

Synthesis of 1,5-bis(4-aminophenyl)penta-1,4-dien-3-one 7

To solution 0.8 g (10.2 mmol) of Na_2S and 0.35 g (4.16 mmol) of $NaHCO_3$ in 5 mL water, 10 mL methanol was added. The mixture stirred for 30 min in room temperature. The precipitate was filtered, then the filtrate was added to mixture 0.25 g (0.770 mmol) of 1,5-bis(4-nitrophenyl)penta-1,4-dien-3-one 6, and 15 mL methanol, and stirred for 3 hrs under reflux conditions. The mixture was concentrated using rotary evaporator, and the residue poured into water, a red crude product formed and was collected by filtration, washed thoroughly with water, and dried to afford 0.186 g (91%). MP: 295–297°C. FTIR (KBr): 3331 (m), 3211 (m), 3030 (w), 2926 (w), 1624 (m, sh), 1591 (s), 1514 (s), 1438 (m), 1307 (m), 1282 (m), 1172 (s), 1107 (m), 985 (w), 829 (m), 511 (m) cm^{-1}. ^1H-NMR (300 MHz, DMSO-d_6, TMS): δ; 7.51–7.57 (d, 2H, J=16 Hz), 7.43–7.45 (d, 4H, J=7.3 Hz), 6.90–6.95 (d, 2H, J=16 Hz), 6.57–6.60 (d, 2H, J=7.3 Hz), 5.84 (s, br, 4H) ppm. ^{13}C-NMR (300 MHz, DMSO-d_6): δ; 187.96, 151.95, 143.09, 130.84, 122.57, 120.76, 114.11 ppm. Elemental analysis: calculated for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60; found: C, 77.18; H, 6.06; N, 10.60.

Polymer synthesis

Poly(amide–imide)s **8a–g** were synthesized by two different methods that as an example the preparation of PAI **8a** explains in the following.

Method A: *Direct polycondensation in a medium consisting of N-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride ($CaCl_2$)/pyridine (Py)*

0.107 g (0.275 mmol) of N,N′-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-alanine **3a**, 0.072 g (0.275 mmol) of 1,5-bis(4-aminophenyl)penta-1,4-dien-3-one **7**, 0.1 g (0.9 mmol) of calcium chloride, 0.84 mL, (3.00 mmol) of triphenyl phosphite, 0.1 mL of pyridine and 1.5 mL N-methyl-2-pyrrolidone (NMP) were placed into a 25-mL round-bottomed flask, which was fitted with a stirring bar. The reaction mixture was heated under reflux at 120°C for 7 hrs. Then, the reaction mixture was poured into 50 mL of methanol and the precipitated polymer was collected by filtration and washed thoroughly with hot methanol and dried at 60°C for 12 hrs under vacuum to leave 0.158 g (93%) pale yellow solid polymer **8a**.

Method B: *Direct Polycondensation in a Tosyl Chloride (TsCl)/Pyridine (Py)/ N,N-Dimethylformamide (DMF) System*

A solution of 0.1 mL pyridine, 0.0.078 g (0.411 mmol) of TsCl after 30 min stirring at room temperature was treated with 0.1 mL, (1.36 mmol) of DMF for additional 30 min. The reaction mixture was added dropwise to a solution 0.053 g (0.137 mmol) of diacid **3a** in 0.1 mL of pyridine. The mixture was maintained at room temperature for 30 min, and then to this mixture, a solution 0.036 g (0.137 mmol) of 1,5-bis(4-aminophenyl)penta-1,4-dien-3-one **7** in 0.4 mL of Pyridine was added dropwise and the whole solution was stirred at room temperature for 30 min and at 100°C for 2 hrs. As the reaction proceeded, the solution became viscous, then was precipitated in 20 mL of methanol and filtered off, dried under vacuum to leave 0.066 g (79%) brown solid polymer **8a**.

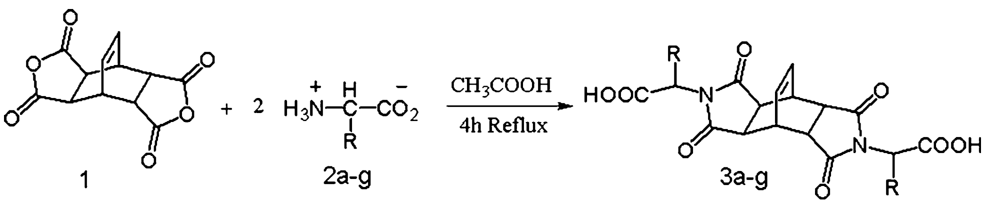
Results and discussion

Synthesis of monomers

The asymmetric diacids **3a–g** were synthesized by the condensation reaction of bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1** with two equimolars of L-alanine **2a**, L-valine **2b**, L-leucine **2c**, L-isoleucine **2d**, L-phenyl alanine **2e**, L-2-aminobutyric acid **2f** and L-histidine **2g** in an acetic acid solution (Scheme 1) [28]. The yields and some physical properties of these compounds are shown in Table 1.

The chemical structure and purity of the optically active diacids **3a–g** were proved by using elemental analysis,

Scheme 1 Preparation of diacids 3a–g



	2a	2b	2c	2d	2e	2f	2g
R	Alanine	Valine	Leucine	Isoleucine	Phenyl alanine	2-Aminobutyric acid	Histidine
	CH_3	$CH(CH_3)_2$	$CH_2CH(CH_3)_2$	$CH_3CHC_2H_5$	CH_2Ph	CH_2CH_3	CH_2-Imidazole

Table 1 Synthesis of chiral diacid derivatives **3a–g**

Entry	Amino acid compound	R	Mp(°C)	Yield(%)	$[\alpha]_{\mathrm{D}}^{25^{a}}$
3a	L-Alanine	CH_3	249–250	92	+155.7
3b	L-Valine	$(CH_3)_2CH$	318–320	93	+138.4
3c	L-Leucine	$(CH_3)_2CHCH_2$	289–290	94	+146.8
3d	L-Isoleucine	$(C_2H_5)(CH_3)CH$	293–295	92	+156.2
3e	L-Phenyl alanine	$PhCH_2$	247–248	91	+160.2
3f	L-2-Aminobutyric acid	CH_3CH_2	251–253	93	+130.2
3g	L-histidine	CH_2-imidazole	310–312	85	+128.4

[a] Measured at a concentration of 0.5 g/dL in DMF at 25°C

FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques and these data shown in Table 2.

The FTIR spectra of all N,N′-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids **3a–g** showed absorption around 2500 and 3400 cm^{-1}, which was assigned to the COOH groups. Peaks appearing at around 1700–1770 cm^{-1} (acid C=O and symmetric imide stretching), 1390 and 700 cm^{-1} (imide characteristic ring vibration) confirmed the presence of imide ring and carboxylic groups in these compounds.

As an example, the ^{1}H-NMR spectrum of diacid **3f** showed in Fig. 1. The protons H(a) relevant to O-H carboxylic groups appeared at 12.95 ppm. Peak in 4.33–4.38 ppm as a doublet of doublet which were assigned to the H(c) protons, which is a chiral center, peaks between 0.66–0.71 ppm were assigned to aliphatic CH_3(g), peak in 1.79–1.93 ppm were assigned to H(f). Protons relevant to olefin bicyclo ring appeared at 6.01–6.10 ppm, H(b). Peaks between 3.20–3.43 ppm were assigned to H(e) (4H) and H

Table 2 ^{1}H-NMR, ^{13}C-NMR, FTIR spectra and elemental analyses data of diacid derivatives **3a–g**

Diimide-diacid	Spectral data
3a	^{1}H-NMR (DMSO-d_6, δ ppm): 12.87–12.93 (s, br, 2H), 5.95–5.98 (t, 2H), 4.50–4.57 (q, 1H, J=7 Hz), 3.37 (s, 2H), 3.16–3.25 (m, 4H), 1.23–1.25 (d, 6H). ^{13}C-NMR (DMSO-d_6, δ ppm): 176.82, 170.61, 130.64, 47.55, 42.47, 33.89, 14.49. FTIR (KBr, cm^{-1}): 2561–3100 (m, sh, br), 1770 (w), 1705 (s, br), 1628 (w), 1467 (w), 1396 (m), 1309 (m), 1207 (m), 1126 (w), 976 (w), 675 (w), 611 (w). Elemental analysis: calcd for $C_{18}H_{18}N_2O_8$: C, 55.39; H, 4.65; N, 7.18; found: C, 54.45; H, 4.56; N, 7.11.
3b	^{1}H-NMR (DMSO-d_6, δ ppm): 12.88 (s, br, 2H), 5.99–6.09 (m, 2H), 4.12–4.15 (d, 2H, J=9 Hz), 3.45 (D_2O exchange, s, 2H), 3.18–3.25 (D_2O exchange, t, 4H), 2.32–2.39 (m, 2H), 0.92–0.94 (d, 6H, J=6 Hz), 0.66–0.68 (d, 6H, J=6 Hz). ^{13}C-NMR (DMSO-d_6, δ ppm): 177.23, 169.55, 131.51, 57.70, 42.61, 33.84, 27.96, 21.28, 19.60. FTIR (KBr, cm^{-1}): 2500–3400 (m, br), 1709–1770 (s, br), 1390 (s), 1199 (s, sh), 1068 (m), 775 (w), 700 (m), 603 (w). Elemental analysis: calcd for $C_{22}H_{26}N_2O_8$: C, 59.19; H, 5.87; N, 6.27; found: C, 58.98; H, 5.87; N, 6.25.
3c	^{1}H-NMR (DMSO-d_6, δ ppm): 12.70 (s, br, 2H), 5.93–6.01 (m, 2H), 4.44–4.49 (dd, 2H, J=6, 3 Hz), 3.40 (s, 2H), 3.21–3.30 (m, 4H), 1.85 (m, 2H), 1.65 (m, 2H), 1.25 (m, br, 2H), 0.75–0.81 (q, 12H). ^{13}C-NMR (DMSO-d_6, δ ppm): 177.09, 170.46, 130.97, 50.73, 42.44, 36.62, 33.80, 24.60, 23.47, 21.14. FTIR (KBr, cm^{-1}): 2500–3200 (m, br), 1770 (w), 1710 (s, br), 1628 (w), 1460 (m), 1380 (m), 1309 (m), 1207 (w), 1126 (w), 976 (w), 670 (w), 600 (w). Elemental analysis: calcd for $C_{24}H_{30}N_2O_8$: C, 60.75; H, 6.37; N, 5.90; found: C, 60.25; H, 6.22; N, 5.88.
3d	^{1}H-NMR (DMSO-d_6, δ ppm): 12.8 (s, br, 2H), 5.97–6.03 (m, 2H), 4.18–4.21 (d, 2H, J=9 Hz), 3.22–3.30 (m, 6H), 2.14–2.15 (d, 2H, J=3 Hz), 1.30–1.37 (m, 2H), 0.89–0.91 (d, 6H, J=6 Hz), 0.71–0.74 (t, 6H). ^{13}C-NMR (DMSO-d_6, δ ppm): 177.59, 169.66, 131.27, 57.03, 42.40, 33.67, 25.24, 16.90, 10.87. FTIR (KBr, cm^{-1}): 2500–3400 (m, br), 1772 (w), 1744 (s, sh), 1709 (s, sh), 1390 (s), 1232 (w), 1225 (m), 806 (w), 717 (w), 599 (w), 314 (m). Elemental analysis: calcd for $C_{24}H_{30}N_2O_8$: C, 60.75; H, 6.37; N, 5.90; found: C, 60.45; H, 6.21; N, 5.91.
3e	^{1}H NMR (DMSO-d_6, δ ppm): 13.15 (s, br, 2H), 7.21–7.23 (q, 6H), 7.02–7.03 (t, 4H), 4.85–4.91 (dd, br, 2H, J=6, 6 Hz), 3.25–3.31 (dd, 2H, J=12, 3 Hz), 3.10–3.12 (d, 2H, J=6 Hz), 3.01–3.05 (d, 4H, J=12 Hz), 2.92–2.94 (d, 2H, J=6 Hz). ^{13}C NMR (DMSO-d_6, δ ppm): 176.69, 169.94, 132.02, 129.32, 128.53, 126.98, 53.07, 42.24, 42.11, 33.45, 33.24. FTIR (KBr, cm^{-1}): 2600–3500 (m, br), 1776 (w), 1703 (s, br), 1498 (w), 1398 (w), 1394 (s), 1234 (m, br), 1174 (s), 933 (w), 698 (m). Elemental analysis: calcd for $C_{30}H_{26}N_2O_8$: C, 66.41; H, 4.83; N, 5.16; found: C, 66.41; H, 4.82; N, 5.10.
3f	^{1}H NMR (DMSO-d_6, δ ppm): 12.95 (s, br, 2H), 6.01–6.10 (m, 2H), 4.33–4.38 (dd, 2H, J=6, 3 Hz), 3.43 (D_2O-exchang, s, br, 2H), 3.20–3.27 (D_2O-exchang, q, 4H), 1.91–1.93 (m, 2H), 1.79–1.81 (m, 2H), 0.66–0.71 (t, 6H). ^{13}C NMR (DMSO-d_6, δ ppm): 177.14, 170.19, 131.06, 56.50, 42.41, 33.79, 21.23, 11.06. FTIR (KBr, cm^{-1}): 2650–3400 (m, br), 1776 (s, br), 1498 (w), 1390 (s), 1224 (m, br), 1170 (s), 933 (w), 698 (m). Elemental analysis: calcd for $C_{20}H_{22}N_2O_8$: C, 57.41; H, 5.30; N, 6.70; found: C, 57.34; H, 5.29; N, 6.70.
3g	^{1}H-NMR (DMSO-d_6, δ ppm): 14.48 (s, br, 4H), 9.11 (s, 2H), 7.30 (s, 2H), 5.38–5.80 (s, 2H), 4.98–5.01 (t, 2H), 3.03–3.32 (m, 10H). ^{13}C-NMR (DMSO-d_6, δ ppm): 176.53, 168.91, 134.22, 130.21, 128.84, 117.86, 51.49, 42.44, 33.31, 23.56. FTIR (KBr, cm^{-1}): 2500–3400 (s, br), 1770 (w), 1707 (s, br), 1626 (m), 1521 (w), 1383 (s), 1228 (s), 1163 (s), 1074 (m), 927 (w), 827 (s), 710 (m), 624 (m). Elemental analysis: calcd for $C_{24}H_{22}N_6O_8$: C, 55.17; H, 4.24; N, 16.09; found: C, 55.03; H, 4.23; N, 16.00.

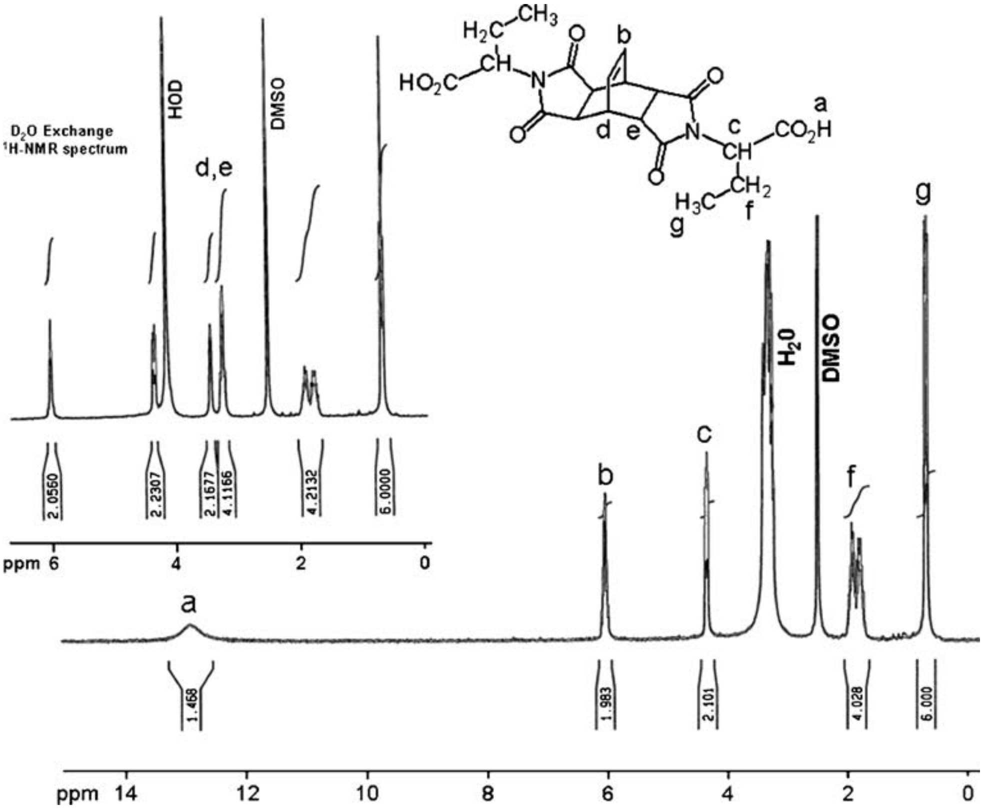


Fig. 1 ^{1}H-NMR spectrum of diacid 3f

(d) (2H), that appeared in D_2O exchange ^{1}H-NMR spectrum. Also the ^{13}C-NMR spectrum of diacid **3f** showed 8 signals, including C(b) and C(a) in carboxylic acids and carbonyl imide rings, and C(c) in carbon atoms olefin in bicyclo (Fig. 2). These peaks in ^{1}H-NMR and ^{13}C-NMR spectra along with elemental analyses data confirmed the proposed structure of compound **3f**.

Also 1,5-bis(4-aminophenyl)penta-1,4-dien-3-one **7** was synthesized by using a two-step reaction. At first 1,5-bis(4-nitrophenyl)penta-1,4-dien-3-one **6** was prepared from the

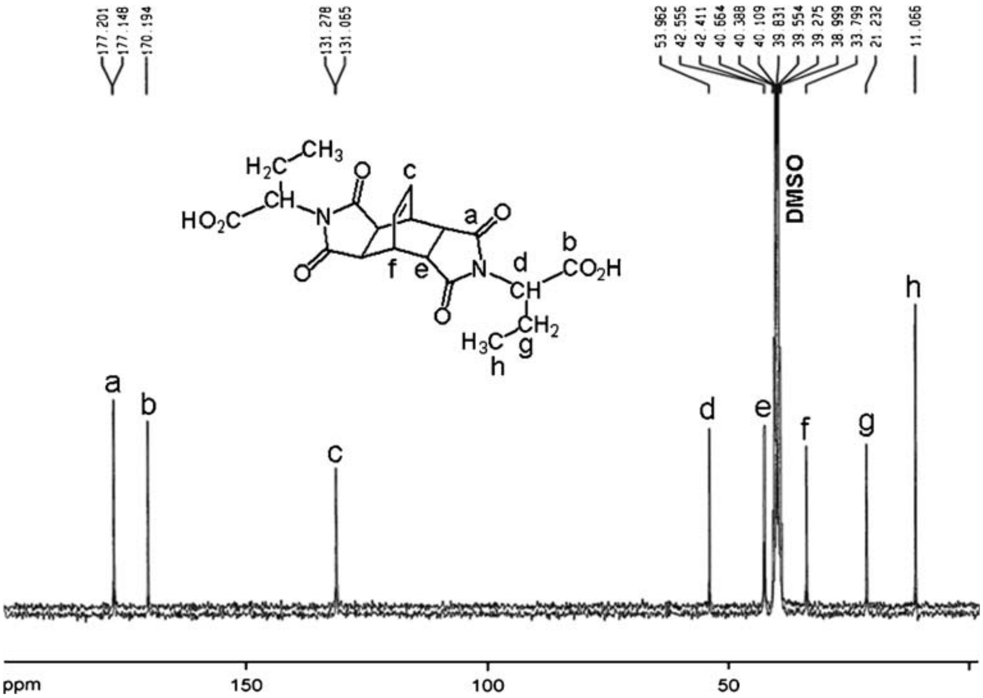


Fig. 2 ^{13}C-NMR spectrum of diacid 3f

reaction of two equimolars 4-nitrobenzaldehyde **5** and one equimolar acetone **4** in ethanol and a solution of $NaHCO_3$ (1%, *w*/*v*) [30]. Then dinitro compound **6** was reduced by using Na_2S (Scheme 2) [31].

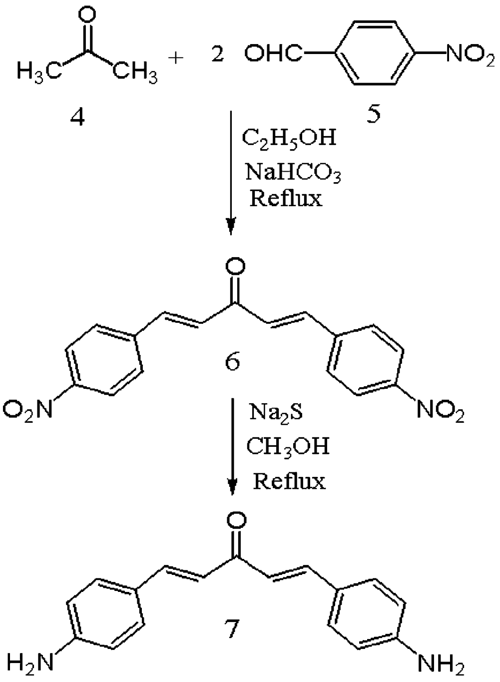
The chemical structure and purity of compound **6** were proved with elemental analysis, ^{1}H-NMR and FTIR spectroscopy and compound **7** were proved with elemental analysis, FTIR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy.

The measured results in elemental analyses of these compounds were closely corresponded to the calculated ones, demonstrating that the expected compounds were obtained. The FTIR spectrum of compound **7** showed two peaks at 3331 and 3211 cm^{-1}, which were assigned to the NH_2 groups.

^{1}H-NMR spectrum of compound **7** showed peaks as a doublet of doublet at 7.43–7.45 ppm and 6.577–6.601 ppm were assigned to the H(b) and H(d) related to aromatic protons and peak as a doublet of doublet at 7.51–7.57 ppm and 6.90–6.95 ppm were assigned to the H(a) and H(c) related to olefin protons. Also a broad singlet peak at 5.84 ppm which was assigned to the H(e) protons of the NH_2 groups in this compound (Fig. 3). Also ^{13}C-NMR spectrum of compound **7** showed seven different carbon atoms (Fig. 4).

Polymer synthesis

The direct polycondensation of a dicarboxylic acid and diamine is one of the well-known methods for PAI synthesis. In this article, we synthesized PAIs **8a–g** containing dibenzalacetone moiety by the direct polycondensation reactions of seven chiral N,N′-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids **3a–g** with 1,5-bis (4-aminophenyl)penta-1,4-dien-3-one **7** by two different methods such as direct polycondensation in a medium consisting of N-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride ($CaCl_2$)/pyridine (py) (method A, Scheme 3) and direct polycondensation in a tosyl chloride (TsCl)/pyridine (py)/N,N-dimethylformamide (DMF) system (method B, Scheme 3).



Scheme 2 Synthesis of diamine 7

In method A for direct polycondensation used TPP/Py/$CaCl_2$ as activating agent according to a typical procedure that was shown in Scheme 3. A triphenyl phosphite (TPP)-activated polycondensation (phosphorylation reaction) technique for the synthesis of polyamides was reported by Yamazaki et al [32].

The syntheses and some physical properties of these new PAIs **8a–g** are given in Table 3. The entire polycondensation reaction readily proceeds in a homogeneous solution, tough and stringy precipitates formed when the viscous PAIs solution was obtained in good yields. Also the resulting polymers have a range of color between pale yellow and yellow (Table 3).

In method B for the direct polycondensation of diacids **3a–g** and aromatic diamine **7**, a Vilsmeier adduct was prepared by dissolving TsCl in a mixed solvent of Py and DMF. The polycondensation was carried out as the following way: TsCl was dissolved in Py and after a certain period of time (aging time), the solution was treated with DMF for 30 min. The reaction mixture was added to a solution of diacid in Py. After 30 min, a solution of diamine in Py was added and the whole solution was maintained at room temperature, and then elevated temperature for 2 hrs [16].

Less than this time, the polymers obtained will have lower inherent viscosities, and more than this time, the materials will be degraded. The syntheses and some physical properties of these new PAIs **8a–g** are given in Table 4. The entire polycondensation reaction readily proceeds in a homogeneous solution, tough and stringy precipitates formed when the viscous PAIs solution was obtained in moderate yields. Also the resulting polymers have a range of color between red and brown (Table 4). Although PAIs **8a–g** obtained in a shorter period by method B, but these polymers obtained with higher inherent viscosities and good yields by method A.

One of the main methods for synthesis of optically active polymers is incorporation of chiral segments in the monomer structure. In this work we used of chiral amino acid moieties for synthesis of chiral diacids **3a–g**. Also resulting polymers due to presence chiral amino acid moieties **2a–g** in the polymer backbone are optically active and Specific Rotations measured at a concentration of 0.5 g/dL in DMF at 25°C (Tables 3 and 4).

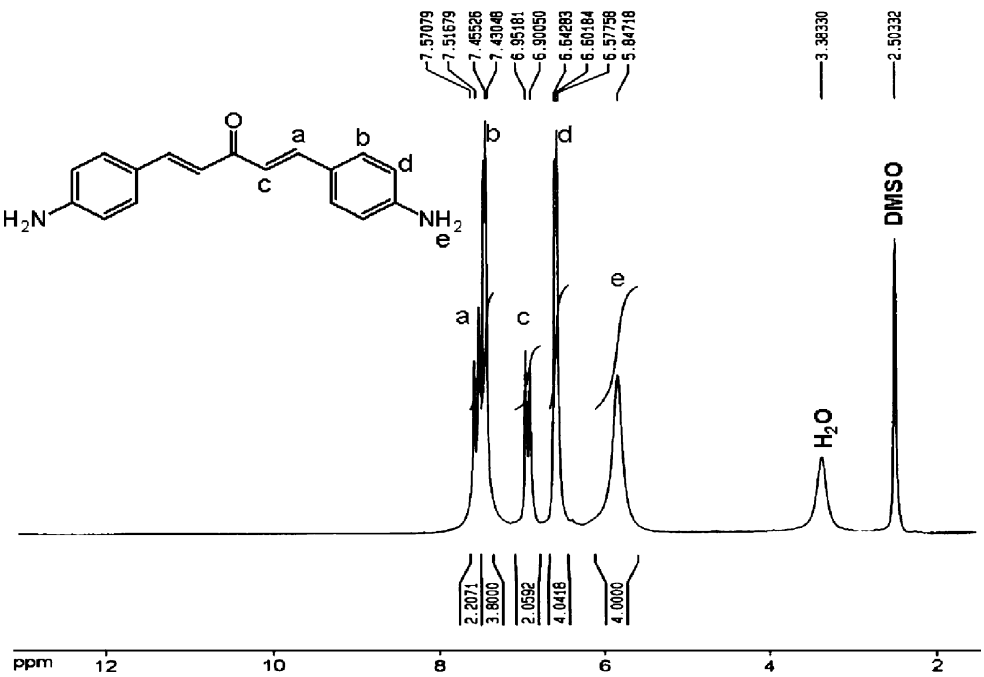


Fig. 3 ^{1}H-NMR spectrum of diamine 7

Polymer properties

The elemental analyses of the resulting PAIs **8a–g** were in good agreement with the calculated values for the proposed structure (Table 5).

Solubility of the PAIs

One of the main objectives of this study was producing modified poly(amide–imide)s with improved solubility. The incorporation of monomers with dibenzalacetone moiety

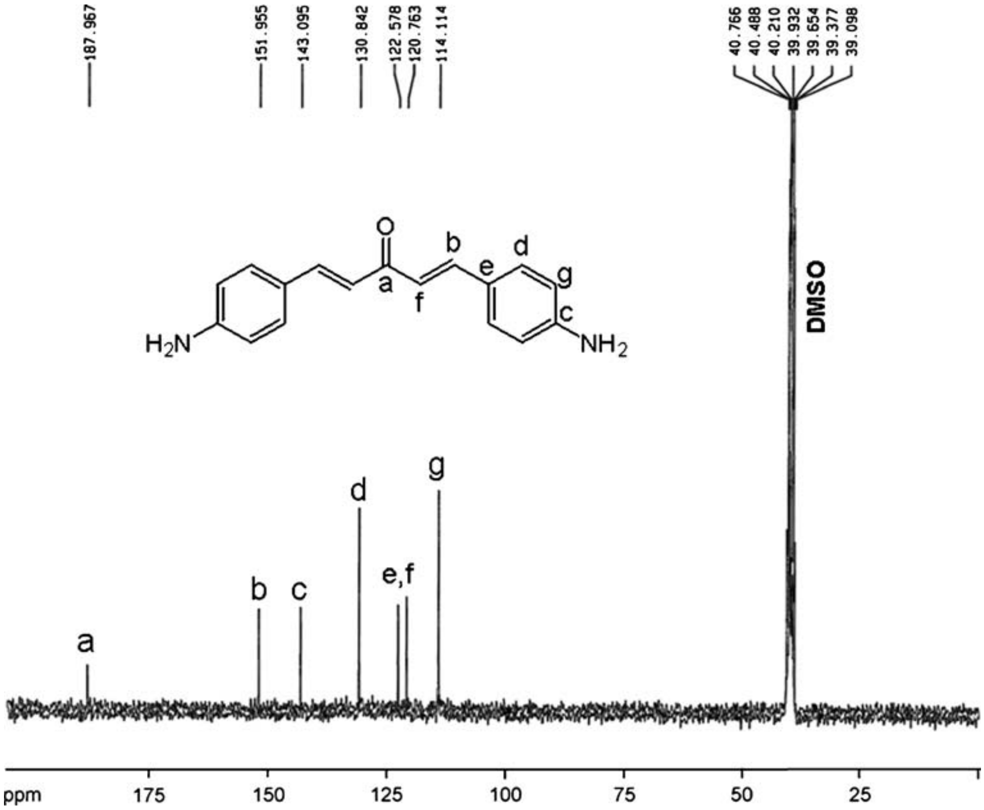


Fig. 4 ^{13}C-NMR spectrum of diamine 7

Scheme 3 Synthesis of PAIs 8a–g by two different methods

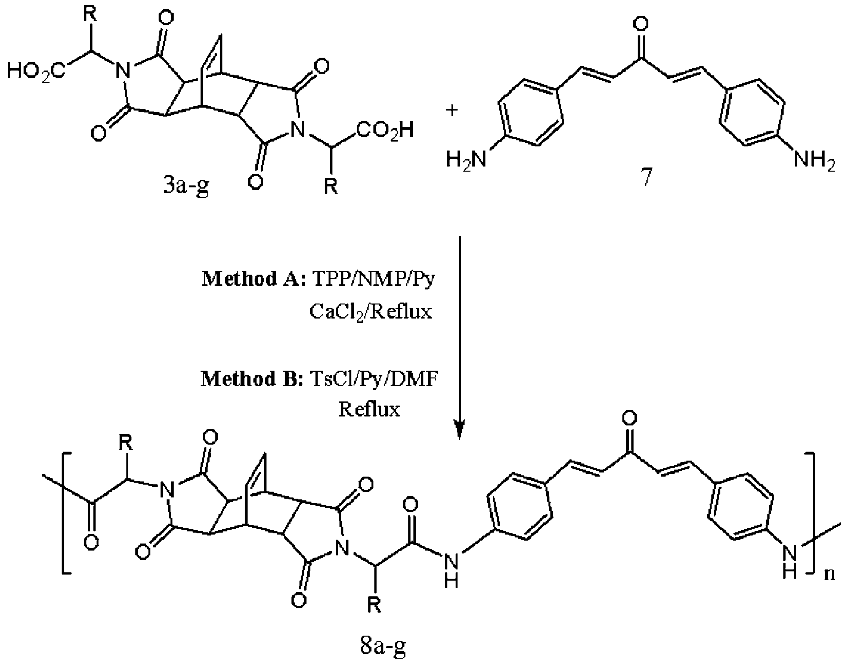


Table 3 Synthesis and some physical properties PAIs **8a–g** by method A

Diacid	Polymer	Yield(%)	η_{inh}(dL/g)[a]	$[\alpha]_{D}^{25}$[a]	Color[b]
3a	**8a**	93	0.80	+130	PY
3b	**8b**	94	0.65	+144	Y
3c	**8c**	96	0.68	+123	PY
3d	**8d**	90	0.69	+111	Y
3e	**8e**	93	0.77	+129	PY
3f	**8f**	95	0.63	+156	PY
3g	**8g**	94	0.71	+147	PY

[a] Measured at a concentration of 0.5 g/dL in DMF at 25°C

[b] *P* pale yellow, *Y* yellow

Table 4 Synthesis and some physical properties PAIs **8a–g** by method B

Diacid	Polymer	Yield(%)	η_{inh}(dL/g)[a]	$[\alpha]_{D}^{25}$[a]	Color[b]
3a	**8a**	79	0.40	+135	B
3b	**8b**	77	0.34	+140	R
3c	**8c**	81	0.35	+133	DR
3d	**8d**	78	0.31	+123	R
3e	**8e**	83	0.41	+114	B
3f	**8f**	80	0.36	+148	DR
3g	**8g**	76	0.37	+156	R

[a] Measured at a concentration of 0.5 g/dL in DMF at 25°C

[b] *B* brown, *DR* dark red, *R* red

prevents an efficient molecular packing and restricts the formation of interchain hydrogen bonds, which are responsible of the PAIs intractability. Also these polymers are expected to have higher solubility. The solubility of PAIs **8a–g** was investigated as 0.01 g of polymeric sample in 2 mL of solvent. Remarkably, all of these PAIs were easily soluble at room temperature in aprotic polar solvents such as N-methyl-2-pyrrolidinone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), soluble on heating at 70°C and partially soluble on heating at 70°C in tetrahydrofuran (THF), pyridine (Py) and cyclohexanone,

Table 5 Elemental analysis of PAIs **8a–g**

Polymer	Formula		C%	H%	N%
8a	$C_{35}H_{30}N_4O_7$	Calcd	67.95	4.89	9.06
	$(618.21)_n$	Found	67.05	4.83	9.00
8b	$C_{39}H_{38}N_4O_7$	Calcd	69.42	5.68	8.30
	$(674.74)_n$	Found	68.33	5.61	8.28
8c	$C_{41}H_{42}N_4O_7$	Calcd	70.07	6.02	7.97
	$(702.79)_n$	Found	69.11	5.98	7.94
8d	$C_{41}H_{42}N_4O_7$	Calcd	70.07	6.02	7.97
	$(702.79)_n$	Found	69.04	6.02	7.93
8e	$C_{47}H_{38}N_4O_7$	Calcd	73.23	4.97	7.27
	$(770.27)_n$	Found	72.12	4.93	7.26
8f	$C_{37}H_{34}N_4O_7$	Calcd	68.72	5.30	8.66
	$(646.69)_n$	Found	67.88	5.29	8.65
8g	$C_{41}H_{34}N_8O_7$	Calcd	65.59	4.56	14.93
	$(750.76)_n$	Found	64.88	4.49	14.91

Table 6 Solubility of PAIs **8a–g**

Solvent	8a	8b	8c	8d	8e	8f	8g
H_2SO_4	+ +	+ +	+ +	+ +	+ +	+ +	+ +
DMAc	+ +	+ +	+ +	+ +	+ +	+ +	+ +
DMSO	+ +	+ +	+ +	+ +	+ +	+ +	+ +
DMF	+ +	+ +	+ +	+ +	+ +	+ +	+ +
NMP	+ +	+ +	+ +	+ +	+ +	+ +	+ +
THF	+	+	+	+	+	+	+
Pyridine	+	+	+ +	+ +	+	+ +	+ +
Cyclohexanone	+ −	+ −	+	+	+ −	+ −	+ −
$CHCl_3$	−	−	−	−	−	−	−
Acetone	−	−	−	−	−	−	−
EtOH	−	−	−	−	−	−	−
MeOH	−	−	−	−	−	−	−
H_2O	−	−	−	−	−	−	−

Solubility: + +: soluble at room temperature; +: soluble on heating at 70°C; + −: partially soluble on heating at 70°C; −: insoluble on heating

Table 7 FTIR charcterization of PAIs **8a–g**

Polymer	Spectra data
8a	**FTIR Peaks (cm^{-1}):** 3369 (w), 2945 (w), 1772 (w), 1707 (s), 1595 (m), 1518 (m), 1386 (m), 1319 (m), 1178 (m), 1105 (w), 979 (w), 835 (w), 730 (w).
8b	**FTIR Peaks (cm^{-1}):** 3348 (m, br), 2966 (m), 1774 (w), 1705 (s, br), 1595 (s), 1516 (s), 1379 (s), 1315 (s), 1178 (m), 1097 (w), 983 (m), 835 (m), 730 (w), 704 (w).
8c	**FTIR Peaks (cm^{-1}):** 3345 (w), 2965 (w), 1776 (w), 1718 (s, br), 1590 (m), 1518 (m), 1383 (m), 1319 (m), 1177 (m), 1105 (w), 979 (w), 835 (w), 729 (w).
8d	**FTIR Peaks (cm^{-1}):** 3352 (w, br), 2968 (m), 1772 (w), 1709 (s), 1595 (m), 1516 (m), 1379 (m), 1348 (m), 1315 (m), 1180 (s), 983 (w), 837 (w), 705 (w).
8e	**FTIR Peaks (cm^{-1}):** 3344 (w), 2968 (m), 1774 (w), 1709 (s), 1595 (m), 1516 (m), 1380 (m), 1350 (m), 1311 (m), 1182 (s), 983 (w), 837 (w), 728 (w).
8f	**FTIR Peaks (cm^{-1}):** 3347 (w), 2981 (m), 1772 (w), 1712 (s), 1588 (m), 1515 (m), 1381 (m), 1353 (m), 1311 (m), 1181 (s), 983 (w), 837 (w), 729 (w).
8g	**FTIR Peaks (cm^{-1}):** 3343 (w), 2988 (m), 1776 (w), 1709 (s, br), 1590 (m), 1510 (m), 1382 (m), 1351 (m), 1312 (m), 1182 (s), 983 (w), 837 (w), 729 (w).

and insoluble in solvents such as acetone, chloroform, ethanol and methanol (Table 6).

The structure of these polymers was confirmed as PAIs by means of FTIR spectroscopy and elemental analyses. The representative FTIR spectrum of PAI **8d** was shown in Fig. 5. The polymer exhibited characteristic absorption bands at 1772 cm^{-1} for the imide ring (asymmetric C=O stretching vibration), 1709 cm^{-1} (symmetric C=O stretching and amide stretching vibration) in the main chain, 1379 cm^{-1} (C-N stretching vibration). The absorption bands of amide groups appeared at 3352 cm^{-1} (N-H stretching). FTIR characterizations of all PAIs are given in Table 7.

The ^{1}H-NMR spectra of PAIs **8b** and **8f** showed peaks that confirm their chemical structure that display in Figs. 6 and 7. Figure 6 displays ^{1}H-NMR spectrum of PAI **8b** that the aromatic protons and four olefin protons related

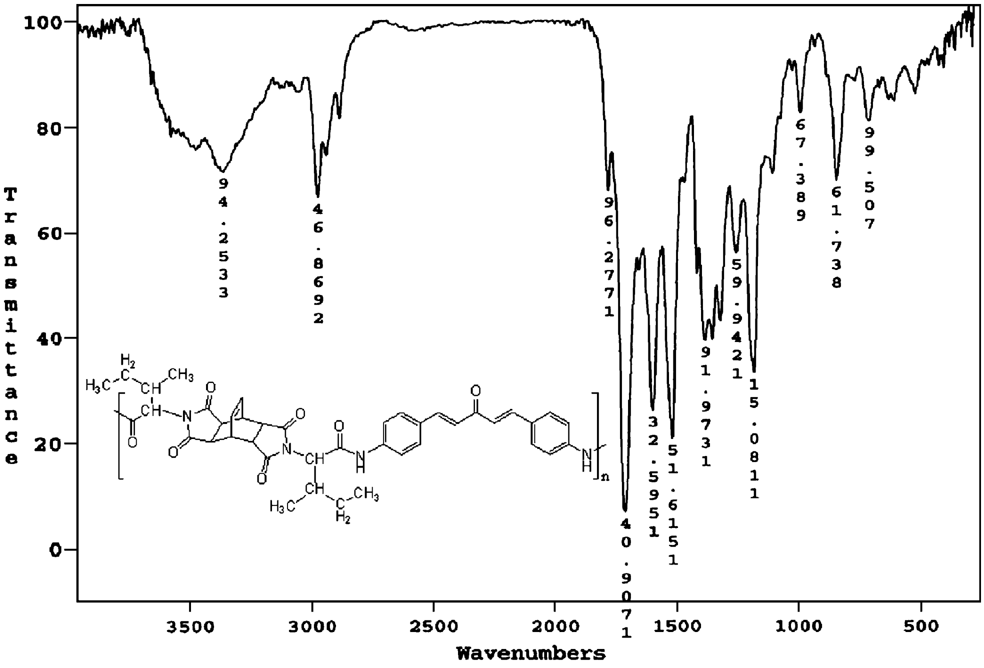
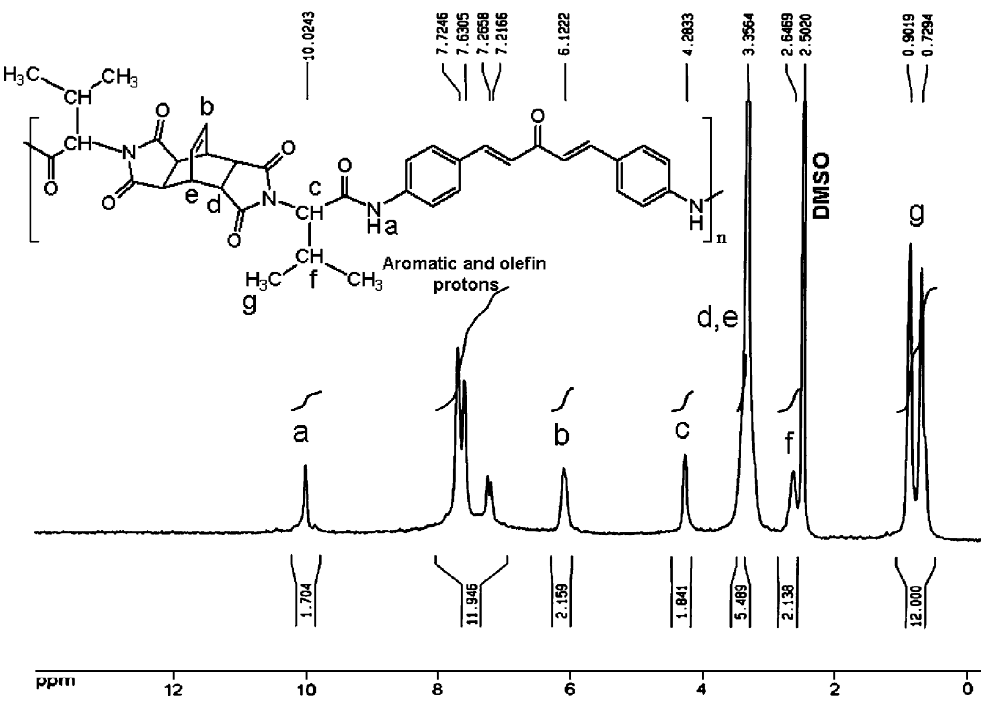


Fig. 5 FTIR spectrum of PAI 8d

Fig. 6 ^{1}H-NMR spectrum of PAI 8b

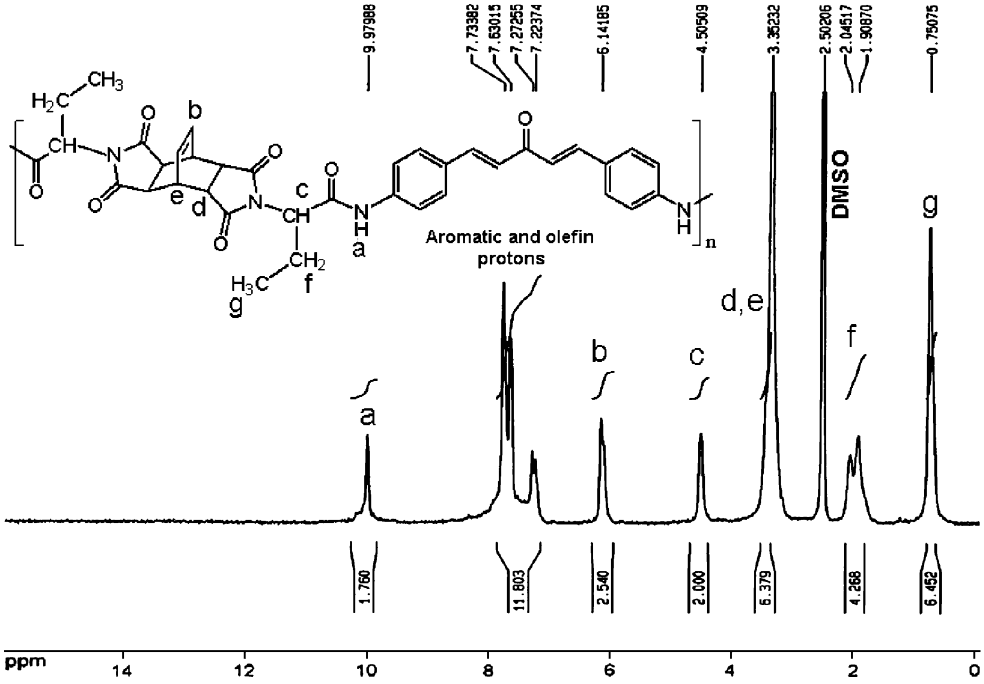


diamine **7** appeared in the region of 7.21–7.72 ppm and the peak in the region of 10.02 ppm is assigned for N-H amide groups in the polymer backbone. Also Fig. 7 displays ^{1}H-NMR spectrum of PAI **8f** that the aromatic protons and four olefin protons related diamine **7** appeared in the region of 7.22–7.73 ppm and the peak in the region of 9.97 ppm is assigned for N-H amide groups in the polymer backbone.

UV-vis absorption characteristics

The photosensitive property of the new poly(amide–imide)s **8a–g** in the DMF solution was studied by a UV-vis spectrophotometer. Due to presence of dibenzalacetone moiety in the polymer backbone, these PAIs have photosensitive properties [11, 33]. All polymer solutions exhibit

Fig. 7 ^{1}H-NMR spectrum of PAI 8f



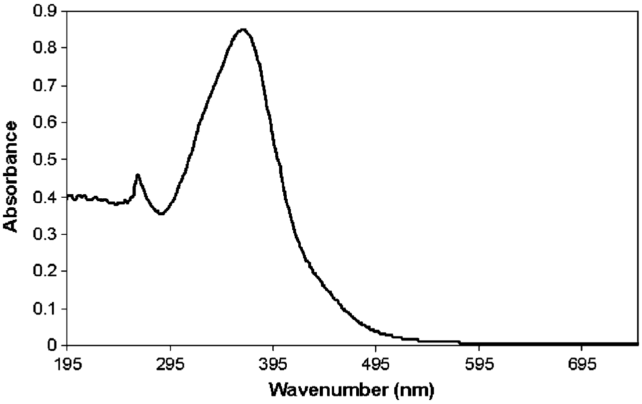


Fig. 8 UV-vis absorption spectrum of PAI 8f in DMF solution

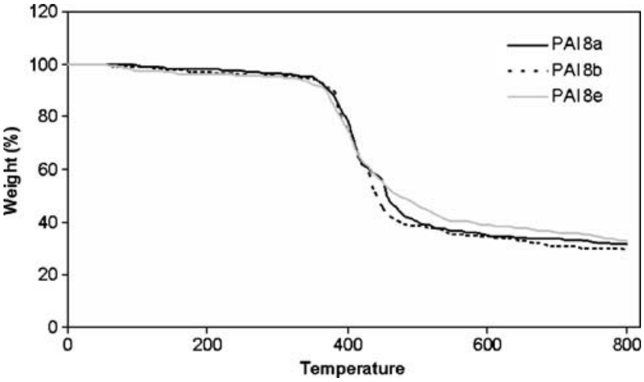


Fig. 9 TGA curves of PAIs 8a, 8b and 8e

two same positions of absorption maximum in UV-vis spectra around 370 nm and 265 nm.

The absorption maximum at around 265 nm corresponds to $\pi \rightarrow \pi^*$ transition of the olefinic double bond present in the dibenzalacetone moiety and carbon double bonds in aromatic rings in the polymer backbone. Also the absorption maximum at around 370 nm corresponds to $n \rightarrow \pi^*$ transition of the nonbonding electrons present in nitrogen and oxygen atoms in the polymer backbone. The UV-vis absorption spectrum of PAI **8f** in N,N-dimethyl formamide is shown in Fig. 8. The spectrum of PAI **8f** exhibited two typical peaks at 265.71 nm ($\pi \rightarrow \pi^*$) and 369.81 nm ($n \rightarrow \pi^*$).

Thermal properties

TGA and derivative of thermaogravimetric (DTG) analysis at a rate of 10°Cmin^{-1} in a nitrogen atmosphere were utilized to examine the thermal properties of these PAIs, and the obtained results are summarized in Table 8. Figure 9 show TGA results of PAIs **8a**, **8b** and **8e**, respectively.

Table 8 Thermal behavior of PAIs **8a**, **8b** and **8e**

Polymer	T_g[a]	T_5(°C)[b]	T_{10}(°C)[b]	Char yield [c]	LOI[d]
8a	161	350	370	31.45	30
8b	157	340	380	29.73	29
8e	173	310	370	32.98	30

[a] glass transition temperature was recorded at a heating rate of 10° Cmin^{-1} in a nitrogen atmosphere

[b] Temperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of 10°C/min under N_2

[c] Weight percentage of material left after TGA analysis at a maximum temperature of 800°C under N_2

[d] Limiting Oxygen Index

The thermal stability of the polymers was studied on the basis of 5 and 10% weight losses (T_5 and T_{10}, respectively) of the polymers and the residue at 800°C (char yield). The results revealed that the PAIs were thermally stable up to 310°C. TGA data showed that the resulting polymers were good thermally stable. Also the DSC analyses for PAIa showed T_g around 157–173°C (Table 8).

The char yield can be applied as a decisive factor for estimated the limiting oxygen index (LOI) of polymers according to the equation of Van Krevelen and Hoftyzer [29]:

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

Where CR is the char yield.

PAIs **8a**, **8b** and **8e** had LOI values around 30, which were calculated from their char yield. On the basis of the LOI values, such macromolecules can be classified as self-extinguishing polymers.

Conclusions

A series of new photosensitive and optically active organo-soluble PAIs **8a–g** containing dibenzalacetone moiety were synthesized by the direct polycondensation reactions of seven chiral N,N′-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids **3a–g** with 1,5-bis(4-aminophenyl)penta-1,4-dien-3-one **7** by two different methods. The photosensitive property of the new poly(amide–imide)s **8a–g** in the DMF solution was studied by a UV-vis spectrophotometer. Due to presence of dibenzalacetone moiety in polymer backbone, these PAIs are photosensitive. Because the resulting polymers contained optically pure L-amino acid moieties, they showed optical rotations and were optically active. Because of presence of dibenzalacetone moiety in polymer chain, these polymers are expected to have higher solubility. Potential applications of amino acid based polymers include drug delivery agents, chiral stationary phases for the resolution of enantiomers in chromatographic techniques, and biomaterials.

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