Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Photosensitive and Optically Active Poly(amide-imide)s Based on N,N-(pyromellitoyl)-bis-L-amino acid and Dibenzalacetone Moiety in the Main Chain: Synthesis and Characterization

Khalil Faghihi[a]; Mohsen Hajibeygi[a]; Meisam Shabanian[a]
[a] Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, Arak University, Arak, Iran

To cite this Article Faghihi, Khalil , Hajibeygi, Mohsen and Shabanian, Meisam(2010) 'Photosensitive and Optically Active Poly(amide-imide)s Based on N,N- (pyromellitoyl)-bis-L-amino acid and Dibenzalacetone Moiety in the Main Chain: Synthesis and Characterization', Journal of Macromolecular Science, Part A, 47: 2, 144 — 153

To link to this Article: DOI: 10.1080/10601320903458622

URL: http://dx.doi.org/10.1080/10601320903458622

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2010) **47**, 144–153

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320903458622

Photosensitive and Optically Active Poly(amide-imide)s Based on N,N- (pyromellitoyl)-bis-L-amino acid and Dibenzalacetone Moiety in the Main Chain: Synthesis and Characterization

KHALIL FAGHIHI*, MOHSEN HAJIBEYGI and MEISAM SHABANIAN

Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, Arak University, Arak 38156, Iran

Received June 2009, Accepted July 2009

Six new photosensitive and optically active poly(amide-imide)s (PAIs) with good inherent viscosities based on N,N′-(pyromellitoyl)-bis-L-amino acid and dibenzalacetone moiety in the main chain were synthesized from the direct polycondensation reaction of N,N-(pyromellitoyl)-bis-L-amino acids **3a–f** with 2,5-bis(4-aminobenzylidene)cyclopentanone **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. Also, 2,5-bis(4-aminobenzylidene)cyclopentanone **7** was synthesized by using a two-step reaction.

The polymerization reactions produced a series of photosensitive and optically active 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 and UV-Vis spectroscopy. Also thermal properties of the PAIs **8a-f** were investigated using thermal gravimetric analysis(TGA) and derivative of thermogravimetric (DTG) analysis.

Keywords: Poly(amide-imide), photosensitive, optically active polymer, dibenzalacetone; amino acid.

1 Introduction

Aromatic polyimides are well recognized as a class of high performance materials due to their remarkable thermal and oxidative stabilities and excellent electrical and mechanical properties for long time periods of operation (1). Unfortunately, strong interaction between polyimide chains and their rigid structure make them intractable. Poor thermoplastic fluidity and solubility are the major problems for wide application of polyimides. Thus, to overcome these processing problems various approaches have been carried out by incorporating flexible units such as —NHCO—, —O—, and —SO_2—, and some of which are commercialized (2–4). Among them, polyamide-imide (PAI) is the most successful material, which combines the advantages of high-temperature stability and processability (5–12).

Photosensitive polymers are widely used as polymeric photo resists in the field of micro-electronics. Currently, interest in them is widespread because they possess a combination of good properties in dielectric constant, and thermal stability and sensitivity. Polymer responds to ultraviolet or visible light by exhibiting a change in its physical properties or its chemical constitution. Examples of the changes in photosensitive polymers are a change in molecular shape (photo-responsive polymer), a change in its constitution (photo-reactive polymer), and a reversible change in color (photochromic polymer). Photosensitivity in photosensitive polymers means that the polymers are sensitive to the irradiated light leading to some change in properties or structure (13–15). The UV sensitive functional groups in the polymers can be cinnamate, chalcone, coumarine, dibenzalacetone and their derivatives both in main chain or side chain (16–19).

The synthesis and application of optically active polymers are the newly considerable topics which have been paid more attention recently (20–21). Most of the natural polymers are optically active and have special chemical activities, such as catalytic properties that exist in genes, proteins and enzymes. Some other applications are: (1) constructing chiral media for asymmetric synthesis, (2) chiral stationary phases for resolution of racemic mixtures by chromatographic techniques, (3) chiral liquid crystals in

---

*Address correspondence to: Khalil Faghihi, Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, Arak University, Arak 38156, Iran. Tel.: 0098-9188630427; Fax: 0098-861-2774031; E-mail: k-faghihi@araku.ac.ir

ferroelectrics and nonlinear optical devices (22–26). These applications have caused more considerations to improve different synthetic procedures of optically active polymers. Recently, we have synthesized optically active polymers by different methods (27–28, 10).

In this article, a series of new photosensitive and optically active PAIs **8a–f** containing dibenzalacetone moiety were synthesized by the direct polycondensation reactions of six chiral N,N′-(pyromellitoyl)-bis-L-amino acid **3a–f** with 2,5-bis(4-aminobenzylidene)cyclopentanone **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.

2 Experimental

2.1 Materials

Pyromellitic dianhydride (1,2,4,5-benzenetetracarboxylicacid-1,2,4,5-dianhydride) **1**, L-alanine **2a**, L-valine **2b**, L-leucine **2c**, L-isoleucine **2d**, L-phenyl alanine **2e** and L-2-aminobutyric acid **2f**, 4-nitrobenzaldehyde **5**, cyclopentanone **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 h.

2.2 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. Elemental analyses were performed by Vario EL equipment in Arak University.

2.3 Monomer Synthesis

2.3.1. *N,N-(pyromellitoyl)-bis-L-amino acid 3a–f*

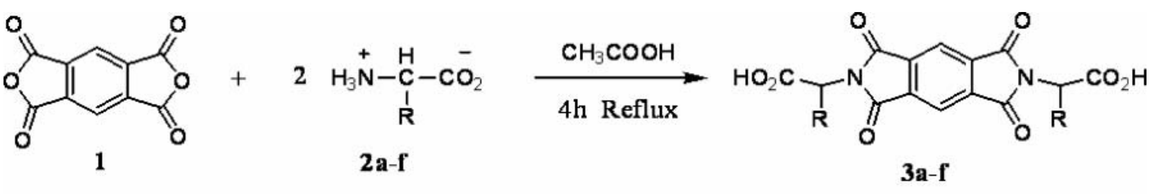
4.36 g (20.00 mmol) of pyromellitic dianhydride (1,2,4,5-benzenetetracarboxylic acid 1,2,4,5-dianhydride) **1**, 40.00 mmol of L-amino acids **2a–f**, 80 mL of acetic acid and a stirring bar were placed into a 250-mL round-bottomed flask. The mixture was stirred at room temperature overnight and refluxed for 4 h. 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-(pyromellitoyl)-bis-L-amino acid **3a–f** (9–11, 26).

2.3.2. *2,5-Bis(4-nitrobenzylidene)cyclopentanone 6*

0.475 g (5.6 mmol) of cyclopentanone **4**, 1.691 g (11.2 mmol) of 4-nitrobenzaldehyde **5**, 12 mL of a mixture of ethanol and water (2:1), and a stirring bar were placed into a 100-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 h. The reaction mixture was then cooled to ambient temperature and 50 mL cooled water was added. A light brown crude product formed and was collected by filtration, washed thoroughly with water, and dried to afford 1.62 g (82%). Mp: 265–267°C. FTIR (KBr): 3088 (w), 2908 (w), 1685 (s), 1604 (s), 1518 (s), 1415 (m), 1344 (s), 1253 (s), 1184 (s), 1113 (s), 983 (m), 856 (s), 756 (m), 677 (m), 507 (m), 416 (m) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6, TMS): δ; 8.30–8.32 (d, 2H, $J = 6$ Hz), 7.96–7.98 (d, 2H, $J = 6$ Hz), 7.57 (s, 2H), 3.19 (s, 4H) ppm. Elemental analysis: calculated for $C_{19}H_{14}N_2O_5$: C, 65.14; H, 4.03; N, 8.00; Found: C, 65.09; H, 4.01; N, 8.00.

2.3.3. *2,5-Bis(4-aminobenzylidene)cyclopentanone 7*

To the 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 at room temperature. The precipitate was filtered, then the filtrate was added to a mixture 0.25 g (0.714 mmol) of 2,5-bis(4-nitrobenzylidene)cyclopentanone **6**, and 15 mL methanol, and stirred for 3 h 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 0.191 g (yield 92%). MP: 285–287°C. FTIR (KBr): 3319 (m), 3217 (m), 3030 (w), 2926 (w), 1656 (m), 1585 (s), 1512 (s), 1438 (m), 1311 (m), 1282 (m), 11170 (s), 985 (w), 831 (m), 705 (w), 534 (m), 484 (m) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6, TMS): δ; 7.36–7.37 (d, 4H, $J = 7.5$ Hz), 7.23 (s, 2H), 6.62–6.65 (d, 4H, $J = 7.5$ Hz), 5.83 (s, 4H), 2.95 (s, 4H) ppm. ^{13}C-NMR (300 MHz, DMSO-d_6): δ; 194.76, 150.96, 133.23, 133.11, 132.74, 123.59, 114.27, 26.54 ppm. Elemental analysis: calculated for $C_{19}H_{18}N_2O$:



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

Sch. 1. Synthesis of diacids **3a–f**.

C, 78.59; H, 6.25; N, 9.65; Found: C, 78.44; H, 6.21; N, 9.36.

2.4 Polymer Synthesis

Poly(amide-imide)s **8a–f** were synthesized by two different methods. As an example, the preparation of PAI **8a** is explained in the following. PAI **8a** was prepared from the reaction of N,N-(pyromellitoyl)-bis-L-alanine **3a** with 2,5-bis(4-aminobenzylidene)cyclopentanone **7** by two different methods.

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

0.099 g (0.275 mmol) of N,N-(pyromellitoyl)-bis-L-alanine **3a**, 0.079 g (0.275 mmol) of 2,5-bis(4-aminobenzylidene)cyclopentanone **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 on an oil bath at 110°C for 7 h. 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 h under vacuum to leave 0.152 g (90%) yellow solid polymer **8a**.

2.4.2. *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 an additional 30 min. The reaction mixture was added dropwise to a solution 0.049 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 0.04 g (0.137 mmol) of 2,5-bis(4-aminobenzylidene)cyclopentanone **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 h. As the reaction proceeded, the solution became viscous, then was precipitated in 20 mL of methanol and filtered off, dried under vacuum to leave 0.065 g (78%) brown solid polymer **8a** (8).

3 Results and Discussion

3.1 Monomer Synthesis

The asymmetric diacids **3a–f** were synthesized by the condensation reaction of pyromellitic dianhydride (1,2,4,5-

Table 1. Synthesis of chiral diacid derivatives **3a–f**

Entry	*Amino acid compound*	*R*	*Mp(°C)*	*Yield (%)*	$[\alpha]_D^{25}$[a]
3a	L-Alanine	CH_3	303–305	78	−6.5
3b	L-Valine	$(CH_3)_2CH$	276–278	85	−3.0
3c	L-Leucine	$(CH_3)_2CHCH_2$	318–320	87	+0.2
3d	L-Isoleucine	$(C_2H_5)(CH_3)CH$	279–282	88	−8.0
3e	L-Phenyl alanine	$PhCH_2$	305–307	90	+0.2
3f	L-2-Aminobutyric acid	CH_3CH_2	295–297	85	+12.1

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

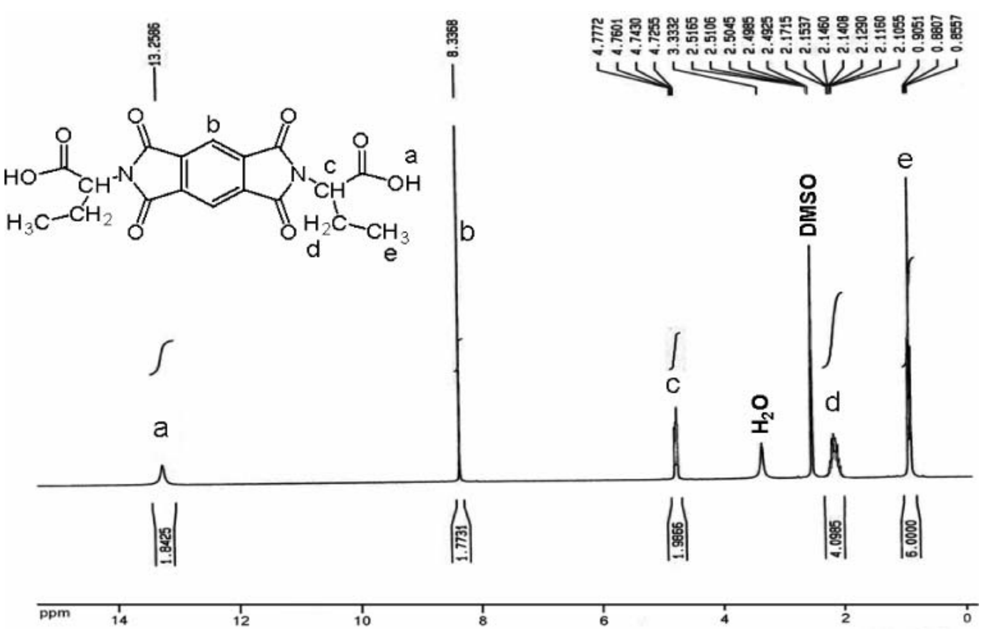
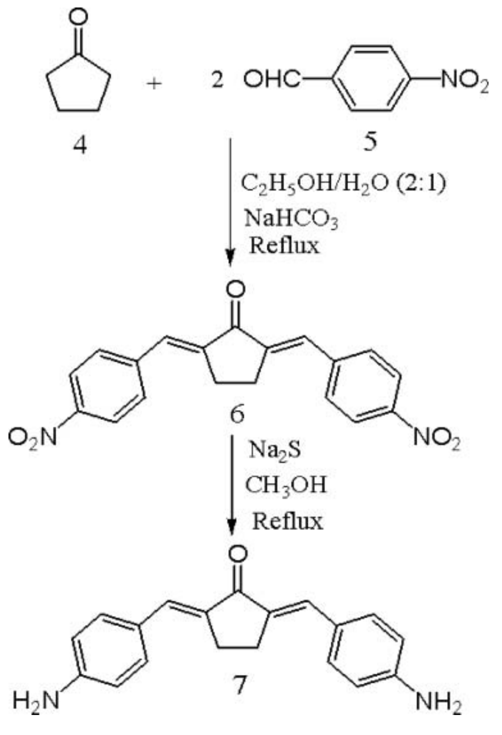


Fig. 1. ^{1}H-NMR spectrum of N,N′-(pyromellitoyl)-bis-L-2-aminobutyric acid **3f**.

benzenetetracarboxylicacid-1,2,4,5-dianhydride) **1** with two equimolars of L-alanine **2a**, L-valine **2b**, L-leucine **2c**, L-isoleucine **2d**, L-phenyl alanine **2e** and L-2-aminobutyric acid **2f** in an acetic acid solution (Scheme 1). In this work, we used six diacids **3a–f** for direct polycondensation. The diacids **3a-e** are synthesized previously (9–11, 2), but diacid **3f** is a new compound that is synthesized by our research group. The yields and some physical properties of these compounds are shown in Table 1.



Sch. 2. Synthesis of diamine **7**.

The chemical structure and purity of the optically active diacids **3a–f** were proved by using elemental analysis, FTIR and ^{1}H-NMR spectroscopic techniques (10).

As an example, the ^{1}H-NMR spectrum of diacid **3f** showed peaks between 0.85 and 0.90 ppm as a triplet, which were assigned for two CH_3(e), and peaks between 2.10 and 2.17 ppm as a multiplet, which was assigned to the CH_2(d), and peaks between 4.72 and 4.77 ppm as a doublet of doublet (J= 3 Hz), which was assigned to the CH(c) protons, which are chiral centers. The peak at 8.35 ppm was assigned to aromatic protons (b). Also a broad peak in 13.25 ppm was assigned to COOH groups (Fig. 1).

2,5-Bis(4-aminobenzylidene)cyclopentanone **7** was synthesized by using a two-step reaction. At first, 2,5-bis(4-nitrobenzylidene)cyclopentanone **6** was prepared from the reaction of two equimolars 4-nitrobenzaldehyde **5** and one equimolar cyclopentanone **4** in ethanol/water (2:1) and $NaHCO_3$. Then dinitro compound **6** was reduced by using Na_2S (Sch. 2).

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 closely corresponded to the calculated ones, demonstrating that the expected compounds were obtained.

The FTIR spectrum of compound **7** showed two peaks at 3319 and 3217 cm^{-1}, which were assigned to the NH_2 groups. Also, ^{1}H-NMR spectrum of compound **7** showed a peak as a doublet of doublet at 7.36–7.38 ppm and 6.62–6.65 (J = 7.5 Hz) were assigned to the H(a) and H(c) related

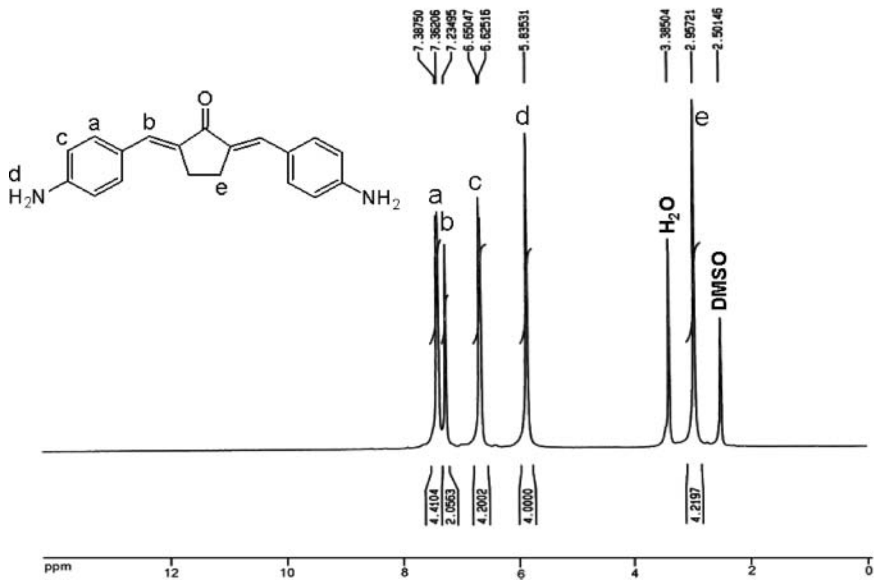


Fig. 2. ^{1}H-NMR Spectrum of 2,5-bis(4-aminobenzylidene)cyclopentanone **7**.

to aromatic protons and a peak as a singlet at 7.23 ppm, which was assigned to the H(b) related to olefin protons. Also, a singlet peak at 5.83 ppm was assigned to the H(d) protons of the NH_2 groups. Peak at 2.95 ppm (as a singlet) was assigned to the H(e) protons of the methylene groups (Fig. 2). ^{13}C-NMR spectrum of compound **7** also showed eight different carbon atoms (Fig. 3).

3.2 Synthesis of Polymer

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–f** containing dibenzalacetone moiety by the direct polycondensation reactions of six chiral N,N′-(pyromellitoyl)-bis-L-amino acids **3a–f** with 2,5-bis(4-aminobenzylidene)cyclopentanone **7**

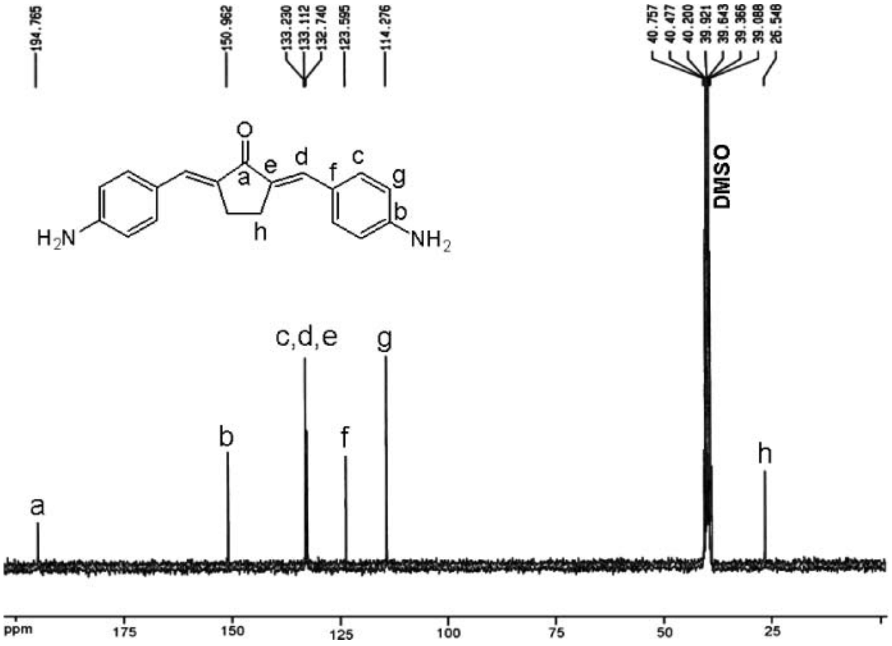


Fig. 3. ^{13}C-NMR Spectrum of 2,5-bis(4-aminobenzylidene)cyclopentanone **7**.

Table 2. Synthesis and some physical properties PAIs **8a–f** by method A

diacid	*Polymer*	*Yield(%)*	$\eta_{inh}(dL/g)^a$	$[\alpha]_D^{25^a}$	*Color*^{b}
3a	**8a**	90	0.74	+85	Y
3b	**8b**	91	0.78	+105	O
3c	**8c**	93	0.69	+94	C
3d	**8d**	90	0.65	+90	C
3e	**8e**	94	0.81	+111	Y
3f	**8f**	92	0.67	+86	O

[a]Measured at a concentration of 0.5g/dL in DMF at 25°C.
[b]C = Cream, O = Orange, Y = Yellow.

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).

In method A, for direct polycondensation, TPP/Py/$CaCl_2$ as activating agent was used according to a typical procedure that was shown in Scheme 3. The syntheses and some physical properties of these new PAIs **8a–f** 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. The resulting polymers due to presence chiral amino acid moieties **2a–f** in the polymer backbone are optically active and Specific Rotations measured at a concentration of 0.5 g/dL in DMF at 25°C. Also, the resulting polymers have a range of color between cream and orange (Table 2).

In method B, for the direct polycondensation of diacids **3a–f** 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 in 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 h (8).

Table 3. Synthesis and some physical properties PAIs **8a–f** by method B

diacid	*Polymer*	*Yield(%)*	$\eta_{inh}(dL/g)^a$	$[\alpha]_D^{25^a}$	*Color*^{b}
3a	**8a**	78	0.41	+88	B
3b	**8b**	81	0.33	+100	DR
3c	**8c**	80	0.36	+93	R
3d	**8d**	75	0.39	+91	R
3e	**8e**	83	0.43	+104	B
3f	**8f**	79	0.42	+79	DR

[a]Measured at a concentration of 0.5g/dL in DMF at 25°C.
[b]B= Brown, DR= Dark Red, R=Red.

Table 4. Elemental analysis of PAIs **8a–f**

Polymer	*Formula*		*C%*	*H%*	*N%*
8a	$C_{36}H_{27}N_3O_7$	Calcd	70.47	4.44	6.85
	$(613.62)_n$	Found	69.13	4.32	6.73
8b	$C_{40}H_{35}N_3O_7$	Calcd	71.74	5.27	6.27
	$(669.72)_n$	Found	70.28	5.13	6.21
8c	$C_{42}H_{39}N_3O_7$	Calcd	72.29	5.63	6.02
	$(697.77)_n$	Found	70.89	5.58	6.00
8d	$C_{42}H_{39}N_3O_7$	Calcd	72.29	5.63	6.02
	$(697.77)_n$	Found	71.14	5.61	6.01
8e	$C_{48}H_{35}N_3O_7$	Calcd	75.28	4.61	5.49
	$(765.81)_n$	Found	74.11	4.56	5.45
8f	$C_{38}H_{31}N_3O_7$	Calcd	71.13	4.87	6.55
	$(641.67)_n$	Found	70.03	4.79	6.51

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–f** 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 moderate yields. Also the resulting polymers have a range of color between red and brown (Table 4). Although PAIs **8a–f** obtained in a shorter period by method B, but these polymers obtained with higher inherent viscosities and good yields by method A.

3.3 Polymer Characterization

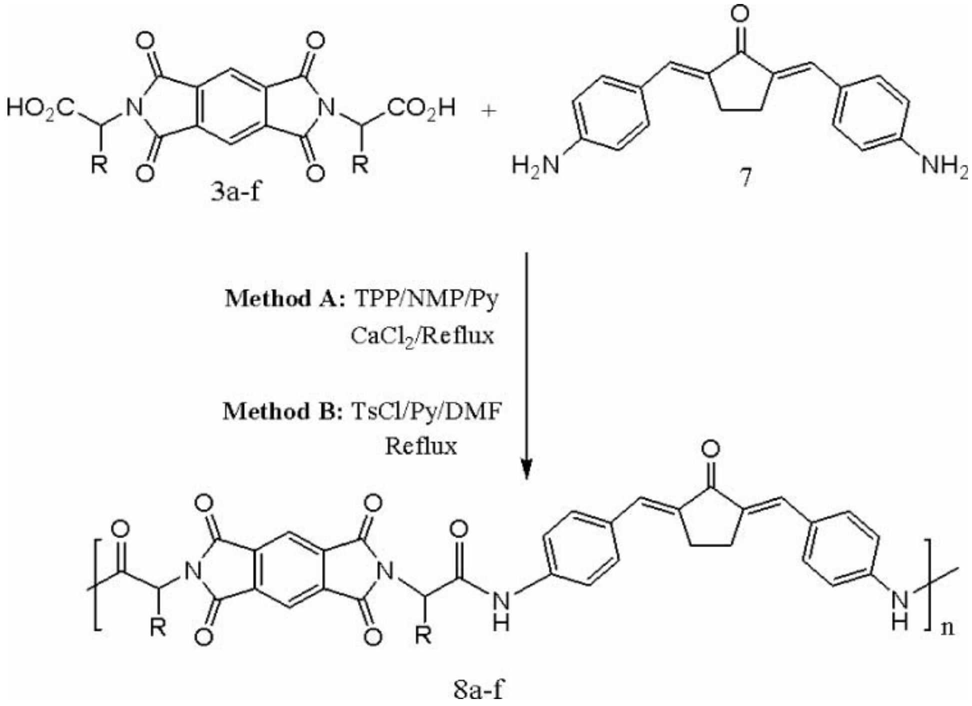
The elemental analyses of the resulting PAIs **8a–f** were in good agreement with the calculated values for the proposed structure (Table 4).

The solubility of PAIs **8a–f** was investigated as 0.01 g of polymeric sample in 2 mL of solvent. All of the polymers are soluble in DMSO, DMF, NMP and H_2SO_4 and are

Table 5. Solubility of PAIs **8a–f**

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

+, Soluble at room temperature.
−, Insoluble at room temperature.



Sch. 3. Synthesis of PAIs **8a–f** by two different methods.

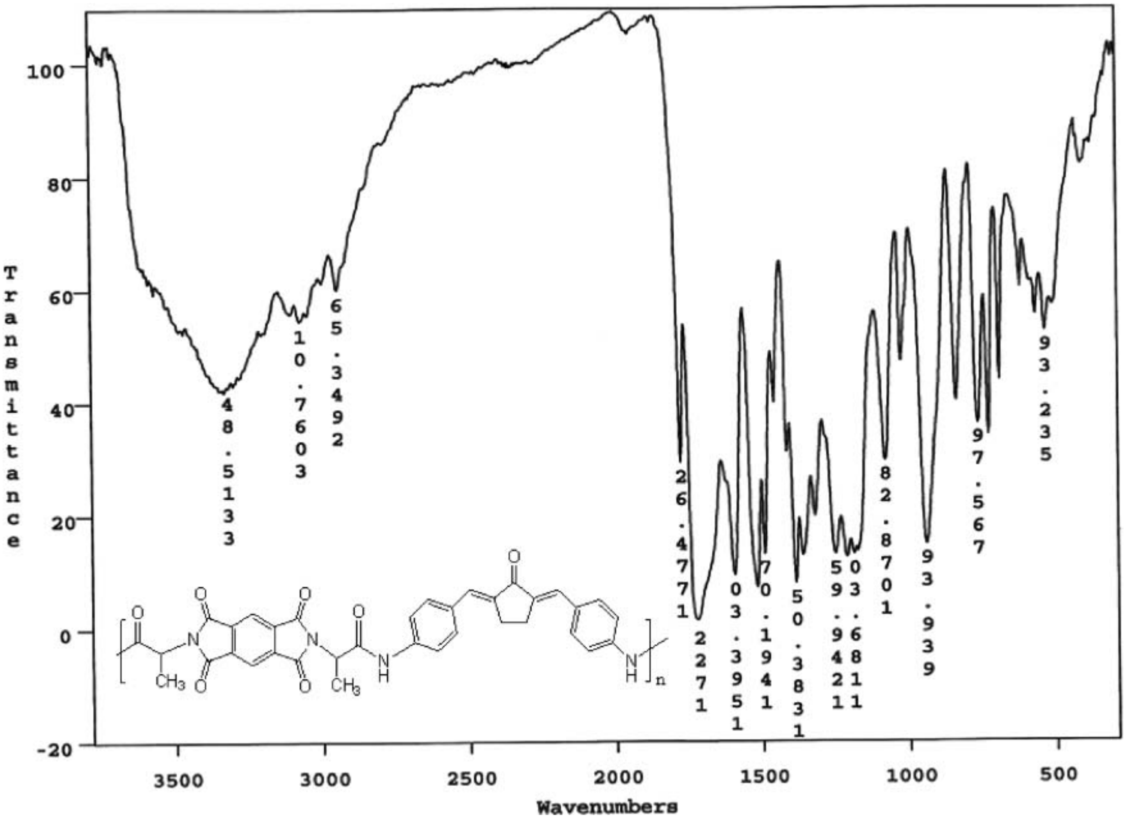


Fig. 4. FTIR Spectrum of PAI **8a**.

Table 6. FTIR Characterization of PAIs **8a–f**

Polymer	*Spectra data*
8a	**FTIR Peaks (cm^{-1})**: 3315 (m, br), 2943 (m, sh), 1774 (m), 1722 (s, br), 1593 (s), 1491 (s), 1383 (s), 1249 (s), 1186 (s), 1078 (m), 939 (s), 765 (m), 532 (m).
8b	**FTIR Peaks (cm^{-1})**: 3319 (m, br), 2966 (m, sh), 1776 (m), 1722 (s, br), 1593 (s), 1516 (s), 1383 (s), 1350 (s), 1211 (s), 1080 (s), 937 (s), 835 (w), 763 (m), 690 (m), 509 (w).
8c	**FTIR Peaks (cm^{-1})**: 3342 (m, br), 2966 (m), 1776 (m), 1722 (s, br), 1593 (s), 1516 (s), 1380 (s), 1350 (s), 1251 (s), 1170 (s), 1078 (m), 985 (m), 835 (m), 729 (m), 532 (m).
8d	**FTIR Peaks (cm^{-1})**: 3346 (m, br), 2941 (m), 1774 (m), 1724 (s, br), 1589 (s), 1516 (s), 1383 (s), 1249 (s), 1170 (s), 1078 (m), 985 (w), 939 (w), 839 (m), 729 (m), 613 (w), 532 (m).
8e	**FTIR Peaks (cm^{-1})**: 3367 (m, br), 3030 (m, br), 2922 (w), 1776 (m), 1724 (s, br), 1589 (s), 1514 (s), 1383 (s), 1356 (s), 1249 (s), 1172 (s), 1107 (m), 985 (w), 829 (m), 727 (m), 532 (w).
8f	**FTIR Peaks (cm^{-1})**: 3327 (m, br), 2970 (m), 1774 (m), 1722 (s, br), 1589 (s), 1514 (s), 1383 (s), 1354 (s), 1249 (s), 1072 (m), 983 (m), 835 (m), 727 (m), 532 (m).

insoluble in solvents such as chloroform, acetone, methanol and ethanol (Table 5).

The structure of these polymers was confirmed as PAIs by means of FTIR spectroscopy and elemental analyses.

The representative FTIR spectrum of PAI **8a** was shown in Fig. 4. The polymer exhibited characteristic absorption bands at 1722 and 1774 cm^{-1} for the imide ring (symmetric and asymmetric C=O stretching vibration), below 1722 cm^{-1} (peak in region of 1722 cm^{-1} is shoulder and broad) for the amide group (C=O stretching vibration) in the main chain, 1383 cm^{-1} (C-N stretching vibration). The absorption bands of amide groups appeared at 3315 cm^{-1} (N-H stretching). FTIR characterizations of all PAIs are given in Table 6.

The ^{1}H-NMR spectra of PAIs **8a** and **8b** showed peaks that confirm their chemical structure that display in Figures 5 and 6. Figure 5 displays ^{1}H-NMR spectrum of PAI **8a** that the aromatic protons and two olefin protons related diamine **7** appeared in the region of 7.36–8.33 ppm and the peak in the region of 10.20 ppm is assigned for N-H amide groups in the polymer backbone. Also, Fig. 6 displays ^{1}H-NMR spectrum of PAI **8b** that the aromatic protons and two olefin protons related diamine **7** appeared in the region of 7.29–8.34 ppm and the peak in the region of 10.31 ppm is assigned for N-H amide groups in the polymer backbone.

3.4 UV–Vis Absorption Characteristics

The photosensitive property of the new poly(amide-imide)s **8a–f** in the DMF solution was studied by a UV spectrophotometer. All polymer solutions exhibit the two same positions of absorption maximum in UV-Vis spectra at 325–335 nm and 260–270 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

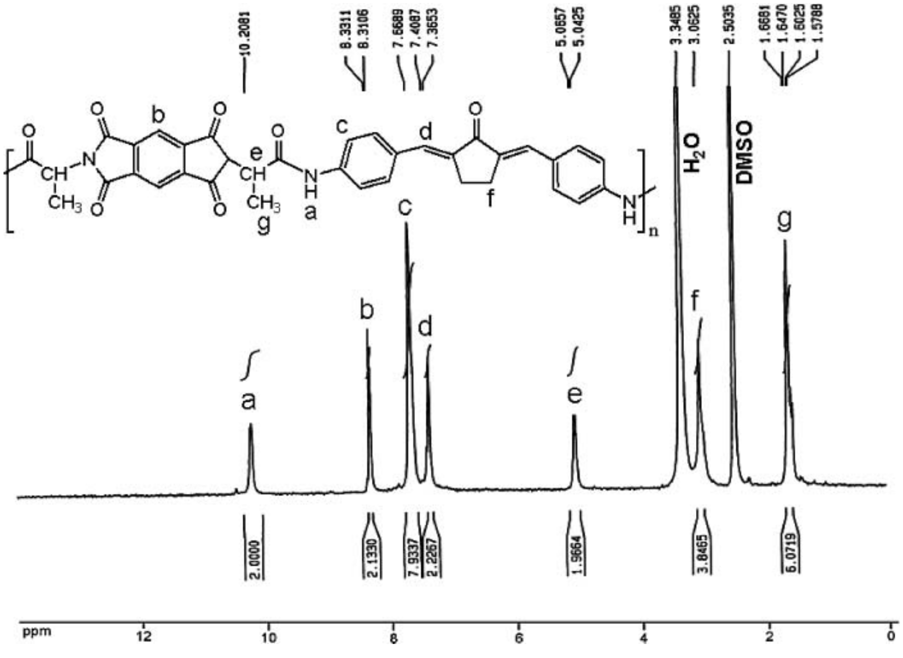


Fig. 5. ^{1}H-NMR Spectrum of PAI **8a**.

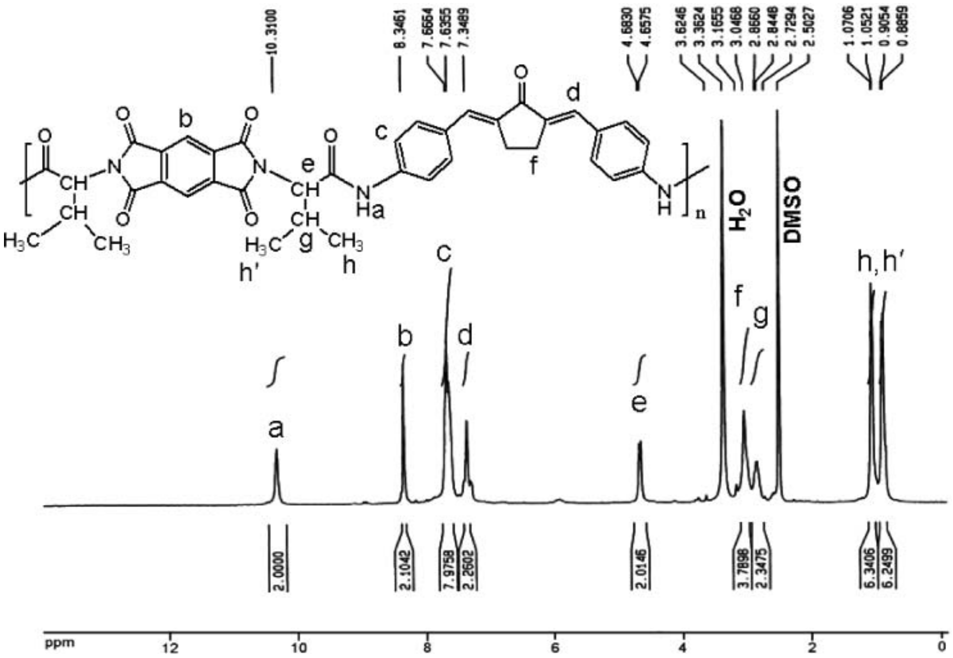


Fig. 6. ^{1}H-NMR Spectrum of PAI **8b**.

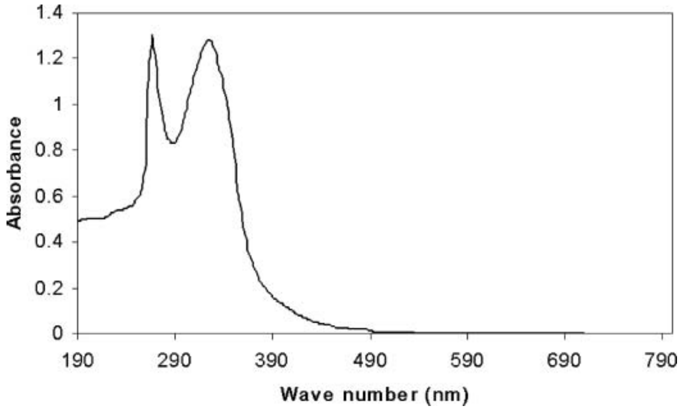


Fig. 7. UV-Vis absorption spectrum of PAI **8f** in DMF solution.

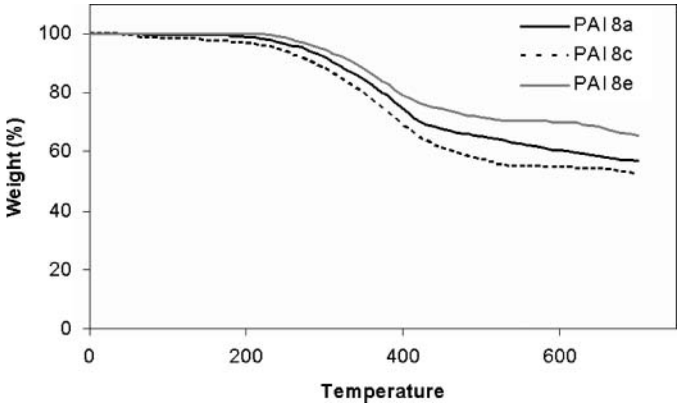


Fig. 8. TGA curves of PAIs **8a**, **8c** and **8e**.

carbon double bonds in aromatic rings in the polymer backbone. Also, the absorption maximum at around 390 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-dimethylformamide is shown in Fig. 7. The spectrum of PAI **8f** exhibited two typical peaks at 268 nm ($\pi \rightarrow \pi^*$) and 329 nm ($n \rightarrow \pi^*$).

3.5 Thermal Properties

TGA and derivative of thermogravimetric (DTG) analysis at a rate of 10°C min^{-1} in a nitrogen atmosphere were utilized to examine the thermal properties of these PAIs, and the obtained results are summarized in Table 7. Figure 8 show TGA results of PAIs **8a**, **8c** and **8e**, respectively. An examination of the data reveals that all PAIs are thermally stable up to 235°C in a nitrogen atmosphere. The temperatures of 5 and 10% wt loss together with

Table 7. Thermal Behavior of PALs **8a**, **8c** and **8e**

Polymer	$T_5(^\circ C)^a$	$T_{10}(^\circ C)^a$	*Char yield*[b]
8a	270–275	310–315	60.40
8c	235–240	285–290	54.82
8e	295–300	340–345	70.34

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

[b] Weight percentage of material left after TGA analysis at a maximum temperature of 600°C under N_2.

char yield at 600°C for PAIs **8a**, **8c** and **8e** are 270°C, 310°C, and 60.40%, 235°C, 285°C, and 54.82% and 295°C, 340°C, and 70.34%, respectively, (Table 7). The high char yields of these PAIs in the high temperature region are important. It shows that these polymers have good thermal stability.

4 Conclusions

A series of new photosensitive and optically active PAIs **8a–f** containing dibenzalacetone moiety were synthesized by the direct polycondensation reactions of six chiral N,N′-(pyromellitoyl)-bis-L-amino acids **3a–f** with 2,5-bis(4aminobenzylidene)cyclopentanone **7** by two different methods. The photosensitive property of the new poly(amide-imide)s **8a–f** in the DMF solution was studied by a UV-Vis spectrophotometer. Due to present dibenzalacetone moiety in the polymer chain, these poly(amide-imide)s have photosensitive property (18). Also, these PAIs are optically active and soluble in various organic solvents and have good thermal stability. These resulting new polymers have the potential to be used in column chromatography technique for the separation of the enantiomeric mixtures and these properties could make these PAIs attractive for practical applications such as processable high-performance engineering plastics. We are currently using this method for the synthesis of novel polymers and modification of polymers.

References

1. Ghosh, M.K. and Mittal, K.L. Polyimide: Fundamental and Applications, Dekker: New York, 1996.
2. Liaw, D.J. and Liaw, B.Y. (2001) *Polymer*, 42, 839–845.
3. Zhang, Q., Li, S., Li, W. and Zhang, S. (2007) *Polymer*, 48, 6246–6253.
4. Zhang, Q., Chen, G. and Zhang, S. (2007) *Polymer*, 48, 2250–2257.
5. Saxena, A., Rao, V.L., Prabhakaran, P.V. and Ninan, K.N. (2003) *Eur. Polym. J.*, 39, 401–405.
6. Yang, C.P., Chen, Y.P. and Woo, E.M. (2004) *Polymer*, 45, 5279–5293.
7. Liaw, D.J. and Chen, W.H. (2006) *Polym. Degrad. Stab.*, 91, 1731–1739.
8. Mallakpour, S. and Kolahdoozan, M. (2007) *J. Appl. Polym. Sci.*, 104, 1248–1254.
9. Hajipour, A.R., Zahmatkesh, S., Banihashemi, A. and Ruoho, A.E. (2007) *Polym. Bull.*, 59, 145–159.
10. Faghihi, Kh. (2008) *J. Appl. Polym. Sci.*, 109, 74–81.
11. Mallakpour, S. and Shahmohammadi, M.H. (2005) *Iran. Polym. J.*, 14(5), 473–483.
12. Faghihi, Kh. and Naghavi, H. (2005) *J. Appl. Polym. Sci.*, 96, 1776–1782.
13. Redy, A.V.R., Subramania, K., Krishnasamy, V. and Ravichandran, J. (1996) *Eur. Polym. J.*, 32, 919–926.
14. Allocock, H.R. and Cameron, C.G. (1994) *Macromolecules*, 27, 3131–3135.
15. Faghihi, Kh. and Mozafari, Z. (2008) *Turk. J. Chem.*, 32, 673–683.
16. Mihara, T., Nakao, Y. and Koide, N. (2005) *Polymer. J.*, 36, 899–908.
17. Lee, S.W. and Ree, M. (2003) *J. Polym. Sci. Part A. Polym. Chem.*, 42(6), 1322–1344.
18. Balakrishnan, P.S. and Murugavel, S.C. (2009) *J. Appl. Polym. Sci.*, 111, 2340–2344.
19. Feng, K., Tsushima, M., Matsumoto, T. and Kurosaki, T. (1998) *J. Polym. Sci. Part A. Polym. Chem.*, 36, 685–693.
20. Mallakpour, S.E., Hajipour, A.R. and Khoee, S. (2000) *J. Polym. Sci. Polym. Chem. Ed.*, 38, 1154–1160.
21. Hu, Q.S., Sun, C. and Monaghan, C.E. (2001) *Tet. Lett.*, 42, 7725–7728.
22. Mallakpour, S. and Zamanlou M.R. (2004) *J. Appl. Polym. Sci.*, 91, 3281–3291.
23. Mallakpour, S. and Kowsari, E. (2003) *J. Polym. Sci. Part A. Polym. Chem.*, 41, 3974–3988.
24. Farina, M. (1987) *Topics. Stereochem.*, 17, 1–111.
25. Fontanille, M. and Guyot, M., Recent advances in synthetic and mechanistic aspects of polymerization. Netherlands: Dordrecht, 1987.
26. Mallakpour, S. and Shahmohammadi, M.H. (2004) *J. Appl. Polym. Sci.*, 92, 951–959.
27. Faghihi, Kh., Zamani, Kh., Mirsamie, A. and Mallakpour, S. (2004) *J. Appl. Polym. Sci.*, 91, 516–524.
28. Faghihi, Kh. (2004) *Macromol. Res.*, 12, 258–262.