

New Optically Active Poly(ester-imide)s Derived from *N,N'*-(4,4'-Carbonyldipthaloyl)-Bis-L-Phenylalanine Diacid Chloride

SHADPOUR E. MALLAKPOUR, ABDOL-REZA HAJIPOUR, MOHAMMAD-REZA ZAMANLOU

Organic Polymer Chemistry Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan, 84156, I.R. Iran

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ABSTRACT: New optically active poly(ester-imide)s containing benzophenone tetracarboxylic and L-phenylalanine moieties were synthesized from *N,N'*-(4,4'-carbonyldipthaloyl)-Bis-L-phenylalanine diacid chloride (**1**) with several aromatic diols such as phenolphthalein (**2a**), hydroquinone (**2b**), 2,4-dihydroxyacetophenone (**2c**), 1,8-dihydroxyanthraquinone (**2d**), bisphenol-A (**2e**), 1,5-dihydroxynaphthalene (**2f**), 1,4-dihydroxyanthraquinone (**2g**) and 4,4'-dihydroxybiphenyl (**2h**) by low-temperature solution polycondensation in $\text{CHCl}_3/\text{Et}_3\text{N}$ solution. The polymerization reactions were started at 0°C and proceeded at room temperature, producing a series of optically active poly(ester-imide)s with inherent viscosities of about $0.12\text{--}0.31\text{ dL g}^{-1}$. All of the above polymers are optically active and have been fully characterized by IR spectroscopy, elemental analyses, and specific rotation. Thermal properties of the poly(ester-imide)s have been investigated using thermal gravimetric analysis. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 315–320, 2002

Key words: polycondensation; thermogravimetric analysis (TGA); thermal properties; poly(ester-imide)s; optically; active polymers

INTRODUCTION

Polyimides and their copolymers are one of the high-performance polymeric materials, and are characterized by high thermal and thermooxidative stability, good mechanical properties, and outstanding solvent resistance.^{1,2} However, most aromatic polyimides are intractable materials so that they usually possess a high glass transition and melting temperature, which results in difficulties in processing. Some methods are used to decrease the melting point of polyimides such as

introduction of a substituted group,³ addition of a flexible swivel-linking group in the main chain^{4,5} and introduction of a flexible spacer.^{6,7} The effects of introducing of a flexible spacer have been reported in the synthesis of polyesters,⁸ poly(ester-imide)s⁹ and poly(ester-amide)s.^{6,7}

The synthesis and application of optically active polymers are topics that have been paid more attention recently, because polymers with chiral structures are biologically very important. Most of the natural polymers are optically active and have special chemical activities such as catalytic properties that exist in genes, proteins, and enzymes. Recently, we have synthesized optically active polymers by different methods.^{10–22}

In previous articles^{23,24} we synthesized a series of novel optically active poly(ester-imide)s **PEIs**. The resulting polymers are optically active and

Correspondence to: S. E. Mallakpour (mallak@cc.iut.ac.ir).

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Table I Synthesis and Some Physical Properties of PEIs 3a–3h

Diol	Polymer	Yield (%)	Polymer η_{inh} (dL/g) ^a	$[\alpha]_D^{25b}$	Color ^c
3a	3a	71.0	0.12	−0.60	Gr
3b	3b	81.4	0.16	−5.60	Gr
3c	3c	84.8	0.15	−3.60	Gr
3d	3d	86.0	0.14	+0.00	Y-G
3e	3e	57.0	0.22	−8.40	Gr
3f	3f	89.2	0.30	+0.00	P-Y
3g	3g	84.0	0.31	−10.00	Gr
3h	3h	75.3	0.31	−2.20	Gr

^a Measured at a concentration of 0.5 g/dL in DMF at 25°C.

^b Measured at a concentration of 0.5 g/dL in DMF at 25°C.

^c Gr = gray, P-Y = pale-yellow, Y-G = yellowish green.

have inherent viscosities in a range of 0.35–1.12 dLg^{−1}.

In this article we wish to report the synthesis and characterization of new optically active **PEIs** from *N,N'*-(4,4'-carbonyldipthaloyl)-bis-L-phenylalanine diacid chloride with aromatic diols by low temperature polycondensation.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Switzerland), Aldrich Chemical Co. (Milwaukee, WI), and Riedel-deHaen AG (Germany). *N,N'*-(4,4'-carbonyldipthaloyl)-bis-L-phenylalanine diacid chloride (**1**) was synthesized according to our previous work.²⁵ 1,8-Dihydroxyanthraquinone (**2d**) and 4,4'-dihydroxybiphenyl (**2h**) were purified by recrystallization from ethanol. Bisphenol A (**2e**) and 1,4-dihydroxyanthraquinone (**2g**) were purified by recrystallization from acetic acid. 1,5-Dihydroxynaphthalene (**2f**) was purified by recrystallization from acetonitrile. The other diols were used as obtained without further purification.

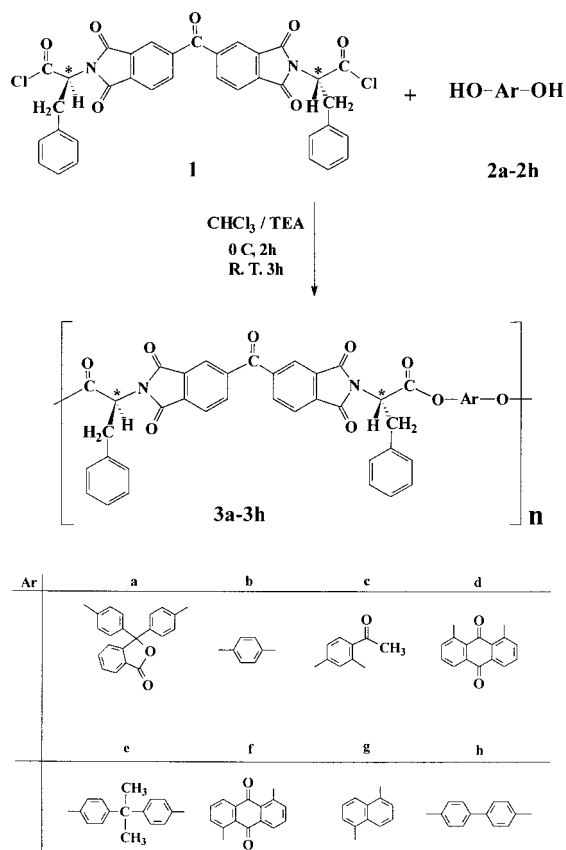
Techniques

Infrared spectra (**IR**) were recorded on a Shimadzu (Japan) 435 IR spectrophotometer. Spectra of polymers were obtained using neat films on NaCl pellets. Vibrational transition frequencies are reported in wave number (cm^{−1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured using a standard pro-

cedure using a Cannon Fenske Routine Viscometer (Germany). Specific rotations were measured using a Perkin-Elmer-241 (Germany) Polarimeter. Thermal Gravimetric Analysis (TGA) data for polymers were taken on a Mettler (England) TGA-50 in N₂ atmosphere at a rate of 10°C/min. Elemental analyses were performed by Tarbiat Modarres University, Tehran, I.R. Iran. As the source of microwave irradiation, we used a Samsung (South Korea) domestic microwave oven (2450 MHz, 900 W) for carrying out polycondensation reactions.

Polymer Synthesis

The **PEIs** were prepared by low-temperature solution polycondensation. Taking polymer (**3h**) as an example, into a 25-mL round-bottomed flask fitted with a magnetic stirrer was placed 0.0854 g (4.59 × 10^{−4} mol) of diol (**2h**), 0.1022 g (1.01 × 10^{−3} mol) of triethylamine, and 1 mL of dry CHCl₃. The solution was cooled in an ice bath then a solution of 0.300 g (4.59 × 10^{−4} mol) of diacid chloride (**1**) in 1 mL of dry chloroform was added dropwise over a period of 10 min. The reaction mixture was stirred for 2 h at 0°C and then 3 h at room temperature. The resulting clear solution was poured into 25 mL of methanol and the precipitated polymer was collected by filtration, and was dried at 80°C for 8 h under vacuum to leave 0.265 g (75.3%) of white solid (**3h**); IR (Neat film on NaCl pellet): 3450 (w), 3050 (m), 3000 (m), 2900 (m), 2850 (w), 1780 (s), 1770 (s), 1720 (s), 1670 (s), 1620 (m), 1600 (m), 1490 (m), 1450 (m), 1430 (m), 1380 (s), 1340 (m, sh), 1290 (m), 1270(m), 1250 (s), 1230 (s), 1190 (s), 1160 (s), 1100 (m), 1030 (w), 1000 (m), 970 (w), 950 (w), 910 (w),



860 (m), 800 (m), 750 (m), 720 (m), 700 (m), 660 (w), cm^{-1} .

The other PEIs **3a-3g** were prepared in a procedure similar to that above.

Polymer 3a

3450 (w), 3050 (m), 3000 (m), 2900 (m), 1780 (s), 1720 (s), 1670 (m), 1620 (w), 1600 (w), 1500 (m), 1450 (m), 1430 (m), 1380 (s), 1290 (m), 1250 (s), 1220 (s), 1200 (s), 1170 (s), 1100 (s), 1020 (w), 970 (m), 930 (w), 850 (m), 750 (m), 720 (m), 700 (m), cm^{-1} .

Polymer 3b

3450 (w), 3050 (w), 3000 (w), 2900 (w), 1780 (s), 1720 (s), 1670 (m), 1620 (w), 1600 (w), 1450 (w), 1420 (w), 1380 (s), 1290 (m), 1250 (m), 1230 (m), 1160 (s), 1100 (m), 1010 (w), 990 (w), 970 (w), 920 (w), 860 (m), 750 (m), 720 (m), 700 (m), cm^{-1} .

Polymer 3c

3450 (w), 3060 (w, sh), 3050 (m), 3000 (m), 2900 (m), 1780 (s), 1720 (s), 1670 (s), 1640 (m), 1600

(m), 1490 (m), 1450 (m), 1420 (m), 1380 (s), 1290 (m), 1270 (m), 1250 (s), 1230 (s), 1150 (s), 1120 (s), 1100 (s), 1050 (w), 1000 (m), 980 (m), 930 (m), 870 (m), 750 (s), 720 (m), 700 (m), 650 (w), cm^{-1} .

Polymer 3d

3450 (w), 3000 (w), 2900 (w), 1770 (s), 1720 (s), 1670 (s), 1630 (m), 1590 (m), 1500 (w), 1470 (w), 1450 (m), 1430 (m), 1380 (s), 1340 (w), 1320 (m), 1280 (m), 1250 (m), 1220 (m), 1150 (m), 1100 (m), 1030 (w), 1000 (w), 980 (w), 920 (w), 850 (w), 830 (w), 780 (w, sh), 750 (m), 720 (m), 700 (m) cm^{-1} .

Polymer 3e

3000 (m), 2950 (m), 2900 (m, sh), 2850 (w), 1780 (s), 1720 (s), 1670 (s), 1630 (s), 1590 (s), 1450 (m), 1425 (m), 1380 (s), 1340 (w), 1320 (w), 1280 (m), 1250 (s), 1240 (s), 1200 (s), 1150 (s), 1120 (m), 1090 (m), 980 (m), 910 (m), 850 (m), 830 (m), 750 (m), 720 (m), 650 (w), cm^{-1} .

Polymer 3f

3050 (m), 3000 (m), 2900 (m), 1770 (s), 1720 (s), 1670 (s), 1640 (m), 1620 (m), 1590 (m), 1490 (m), 1450 (m), 1430 (m), 1410 (m, sh), 1380 (s), 1320 (m), 1290 (m), 1260 (m), 1250 (m), 1230 (m), 1210 (m), 1150 (s), 1100 (m), 1030 (w), 1000 (m), 970 (m), 950 (m), 920 (w), 850 (m), 790 (m, sh), 750 (m), 720 (m), 700 (m), cm^{-1} .

Polymer 3g

3450 (w), 3050 (m), 3000 (m), 2900 (m), 1780 (s), 1720 (s), 1670 (s), 1630 (w), 1610 (w), 1590 (m),

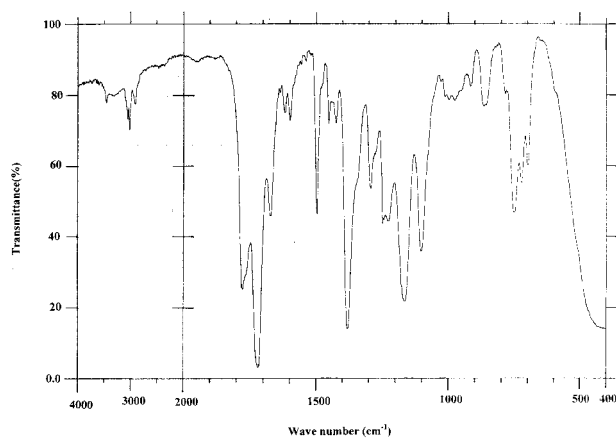


Figure 1 IR (Neat Film on NaCl Pellet) spectrum of PEI **3b**.

Table II Elemental Analysis of PEIs 3a–3h

Polymer	Formula		Elemental Analysis (%)		
			C	H	N
3a	$(C_{55}H_{34}N_2O_{11})_n$ (898.880) _n	Calcd	73.49	3.81	3.12
		Found	70.07	3.97	4.06
3b	$(C_{41}H_{26}N_2O_9)_n$ (690.664) _n	Calcd	71.29	3.79	4.06
		Found	69.22	3.91	4.36
3c	$(C_{43}H_{28}N_2O_{10})_n$ (732.701) _n	Calcd	70.48	3.85	3.82
		Found	68.92	4.07	3.75
3d	$(C_{49}H_{28}N_2O_{11})_n$ (820.766) _n	Calcd	71.71	3.44	3.41
		Found	70.36	3.69	3.34
3e	$(C_{48}H_{36}N_2O_9)_n$ (784.821) _n	Calcd	71.28	4.49	3.46
		Found	70.43	4.36	3.78
3f	$(C_{49}H_{28}N_2O_{11})_n$ (820.766) _n	Calcd	71.71	3.44	3.41
		Found	70.29	3.62	3.36
3g	$(C_{45}H_{28}N_2O_9)_n$ (740.724) _n	Calcd	72.97	3.81	3.78
		Found	71.22	3.94	3.75
3h	$(C_{47}H_{30}N_2O_9)_n$ (766.762) _n	Calcd	73.62	3.94	3.65
		Found	72.04	4.20	3.75

1500 (m), 1490 (m), 1470 (w), 1450 (m), 1430 (m), 1380 (s), 1340 (m, sh), 1300 (m), 1280 (m), 1250 (s), 1230 (s), 1170 (s), 1150 (s), 1110 (s), 990 (m), 960 (m), 940 (m), 920 (m), 860 (m), 780 (m), 750 (m), 720 (m), 690 (m), cm^{-1} .

RESULTS AND DISCUSSION

Polymer Synthesis

Diacid chloride (**1**) was synthesized according to our previous work.²⁵ Several methods have been reported for polyesterification in the literature such as bulk polycondensation, solution polycondensation, and interfacial polymerization using phase transfer catalyses. On the other hand, nowadays microwave irradiation is also applied to the

organic and macromolecular synthesis.^{26,27} In this research project we first were interested in preparing PEIs by microwave irradiation, but we were not successful in this case. Even after 12 min of irradiation time, the reaction of diacid chloride (**1**) (0.1 g) with diols (**2a**) (0.0487 g), (**2c**) (0.0233 g), and (**2d**) (0.0368 g) in the presence of *o*-cresol as heat absorbent and solvent did not give any precipitate after pouring the reaction mixture into methanol. Another method for polycondensation that we used was interfacial polymerization using benzyltriethyl ammonium chloride (BTEAC) as a phase transfer catalyst (PTC). This method gave products with some diols in which some of them had good yields with low inherent viscosity. But this method failed for the other diols, in which the reaction mixture turned

Table III Solubility of PEIs 3a–3h^a

Solvents	3a	3b	3c	3d	3e	3f	3g	3h
DMAc	+	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+	+
H ₂ SO ₄	+	+	+	+	+	+	+	+
MeOH	–	–	–	–	–	–	–	–
EtOH	–	–	–	–	–	–	–	–
CHCl ₃	+	+	+	+	+	+	+	+
H ₂ O	–	–	–	–	–	–	–	–

^a Concentration: 5 mg mL⁻¹; +; Soluble at room temperature, –; Insoluble.

to a dark solution and no precipitate was obtained after pouring the reaction mixture into methanol. The direct polycondensation of diacid chloride (**1**) with diol (**5**) by a tosyl chloride–DMF²⁸ system was the third method for polyesterification. The product of the reaction has no precipitated material in methanol. Finally, the low temperature solution polycondensation (LSP) was selected for the formation of polymeric materials. The synthesis and some physical properties of **PEIs 3a–3h** obtained by this method are summarized in Table I. Scheme 1 shows the reaction of diacid chloride (**1**) with several aromatic diols.

PEIs derived from monomer (**1**) may range in color from gray to yellow. The resulting polymers show optical rotation, and therefore, are optically active.

Polymer Characterization

The structure of these polymers was confirmed as **PEIs** by IR spectroscopy and elemental analysis. IR spectra of all polymers showed bonds between 3050 and 2900 cm^{-1} assigned to aromatic and aliphatic C–H stretching. The characteristic absorptions of imide and ester groups occurred around 1780, 1720, and 1670 cm^{-1} . The bonds around 1250 to 1050 cm^{-1} are assigned to O=C=O stretching ester groups. All of these **PEIs** exhibited absorptions at 1380 and 720–750

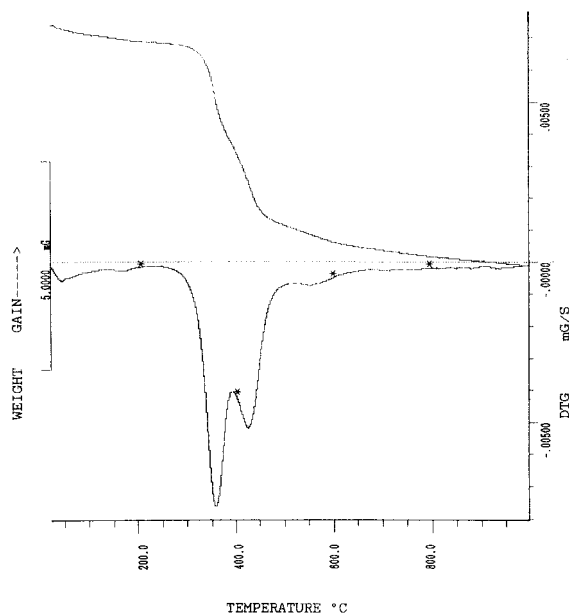


Figure 2 TGA/DTG thermograms of PEI **3f** in N_2 atmosphere.

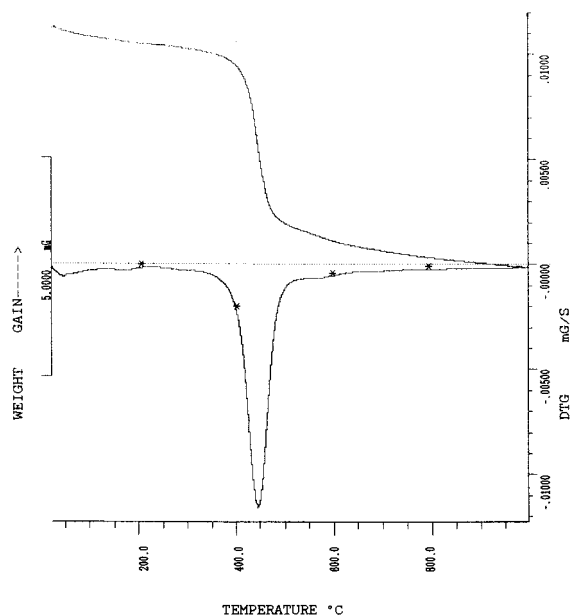


Figure 3 TGA/DTG thermograms of PEI **3h** in N_2 atmosphere.

cm^{-1} , which show the presence of the imide heterocycle group in these polymers. The bond in 3450 cm^{-1} is assigned to overtone bond of carbonyl stretching in 1720 cm^{-1} . Figure 1 shows a typical IR spectrum of **PEI (3b)**. Elemental analysis values of the resulting polymers are listed in Table II. Although we have purified all the resulting **PEIs**, in some cases the resulted elemental analysis do not agree well with the calculated data. These observation may be due to incomplete combustion of polymers in furnace. We have observed from TGA data in **PEIs (3f and 3h)** even at 996°C more than 10% of polymers have remained unchanged.

The solubility of **PEIs** is listed in Table III. All of the **PEIs** are soluble in organic solvents such as dimethylformamide (DMF), dimethylacetamide (DMAc), chloroform, and H_2SO_4 at room temperature, and are insoluble in solvents such as acetone, methanol, ethanol, and water.

Thermal Properties

The thermal properties of **PEIs 3f and 3h** were evaluated by means of TGA/DTG in nitrogen atmosphere (Figs. 2–3). Table IV summarizes the thermal properties of these **PEIs**. The **PEIs** exhibited thermal decomposition between 180 and 240°C in nitrogen, and began to decompose gradually above that temperature. The temperature of

Table IV Thermal Properties of PEIs 3f–3h

Polymer	T_5 (°C)	T_{10} (°C)	Char Yield (%)
3f	243	329	27.8
3h	188	382	21.7

^a Temperature at which 5% weight loss was recorded by TGA at heating rate of 10°C/min in N₂.

^b Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600°C in N₂.

5% weight loss for these polymers ranged from 188 to 243°C, the temperature of 10% weight loss ranged from 329 to 382°C, and the residual weight for these polymers at 600°C ranged from 21.7 to 27.8% in nitrogen.

CONCLUSIONS

A series of optically active **PEIs** having inherent viscosities of 0.12–0.31 dL/g were synthesized by solution polycondensation of the optically active *N,N'*-(4,4'-carbonyldipthaloyl)-bis-*L*-phenylalanine diacid chloride (**1**) having a preformed imide ring as an “enlarged” monomer containing one chiral *L*-Phenylalanine group with some aromatic diols. These **PEIs** show optical rotation and are readily soluble in various organic solvents and have moderate thermal stability. The resulting poly(ester-imide)s have potential to be used as packing materials in column chromatography.

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REFERENCES

- Mittal, K. L., Ed. *Polyimides: Synthesis, Characterization and Application*; Plenum Press: New York, 1984.
- Abade, M. J. M.; Sillion, B. *Polyimides and Other High-Temperature Polymers*; Elsevier: New York, 1991.
- Krigbaum, W. R.; Hakemi, H.; Kotek, R. *Macromolecules* 1985, 18, 965.
- Zhang, W.; Jin, J. I.; Lenz, R. W. *Makromol Chem* 1988, 189, 2219.
- Percec, V.; Yourd, R. *Makromol Chem* 1990, 191, 49.
- Noel, C.; Friedrich, C.; Bosio, L.; Strazielle, C. *Polymer* 1984, 25, 1281.
- Jedlinski, Z.; Franek, J.; Uryu, K.; Song, J. C.; Kato, T. *Polym J* 1989, 21, 409.
- Liu, S. F.; Lee, Y. D. *J Polym Sci Part B Polym Phys* 1995, 33, 133.
- Hsu, T. F.; Lin, Y. C.; Lee, Y. D. *J Polym Sci Part B Polym Chem* 1998, 36, 1791.
- Mallakpour, S. E.; Hajipour, A. R.; Khoe, S.; Sheikholeslami, B. *Polym Int* 1998, 47, 193.
- Mallakpour, S. E.; Hajipour, A. R.; Mahdavian, A. R.; Khoe, S. *J Polym Sci Polym Chem Ed* 1999, 37, 1211.
- Mallakpour, S. E.; Hajipour, A. R.; Mahdavian, A. R.; Rafiemanzelat, F. *Polym Int* 1999, 48, 109.
- Mallakpour, S. E.; Hajipour, A. R.; Khoe, S. *Polym Int* 1999, 48, 1133.
- Mallakpour, S. E.; Dabbagh, A. H.; Faghihi, Kh. *Iranian Polym J* 2000, 9, 41.
- Mallakpour, S. E.; Hajipour, A. R.; Khoe, S. *J Polym Sci Polym Chem Ed* 2000, 38, 1154.
- Mallakpour, S. E.; Hajipour, A. R.; Mahdavian, A. R.; Khoe, S. *J Appl Polym Sci* 2000, 76, 240.
- Mallakpour, S. E.; Hajipour, A. R.; Roohipour-fard, R. *Eur Polym J* 2000, 36, 2455.
- Mallakpour, S. E.; Hajipour, A. R.; Faghihi, Kh. *Eur Polym J* 2001, 37, 119.
- Mallakpour, S. E.; Hajipour, A. R.; Zamanlou, M. R. *J Polym Sci Polym Chem Ed* 2001, 39, 177.
- Mallakpour, S. E.; Hajipour, A. R.; Habbibi, S. *Polym Int* 2001, 50, 331.
- Mallakpour, S. E.; Hajipour, A. R.; Roohipour-fard, R. *Polym Sci Ser B* 2001, 43, 11.
- Mallakpour, S. E.; Hajipour, A. R.; Habbibi, S. *J Appl Polym Sci* 2001, 80, 1312.
- Mallakpour, S. E.; Hajipour, A. R.; Khoe, S. *J Appl Polym Sci* 2000, 77, 3003.
- Mallakpour, S. E.; Hajipour, A. R.; Faghihi, Kh. *Polym Int* 2000, 49, 1383.
- Mallakpour, S. E.; Hajipour, A. R.; Zamanlou, M. R., accepted for publication.
- Gedye, R.; Smith, F.; Westaway, H. A.; Baldisera, L.; Laberge, L.; Rousell J. *Tetrahedron Lett* 1986, 27, 279.
- Hajipour, A. R.; Mallakpour, S. E.; Imanzadeh, G. *J Chem Res* 1999, 228.
- Higashi, F.; Mashimo, T. *J Polym Sci Polym Chem Ed* 1985, 23, 2999.