

Novel Optically Active Poly(amide-imide)s with Tetrahydropyrimidinone and Tetrahydro-2-Thioxopyrimidine Moieties by Microwave-Assisted Polycondensation

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ABSTRACT: Rapid and highly efficient synthesis of novel poly(amide-imide)s (PAIs) were achieved under microwave irradiation by using a domestic microwave oven from the polycondensation reactions of 4,4'-carbonyl-bis(phthaloyl-L-alanine) diacid chloride [*N,N'*-(4,4'-carbonyldiphthaloyl)] bisalanine diacid chloride (**1**) with six different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds (**2a–2f**) in the presence of a small amount of a nonpolar organic medium that acts as a primary microwave absorber. Suitable organic media was *o*-cresol. The polycondensation proceeded rapidly and was almost completed within 10 min, giving a series of PAIs with inherent viscosities of about 0.25–0.45 dL/g. The resulting PAIs were obtained in high yield and are optically active and thermally stable. All of the above compounds were fully characterized by means of Fourier transform infrared spectroscopy, elemental analyses, inherent viscosity (η_{inh}), solubility test, and specific rotation. Thermal properties of the PAIs were investigated using thermogravimetric analysis. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2416–2421, 2001

Key words: microwave-assisted rapid polycondensation; optically active polymers; poly(amide-imide)s; microwave oven; inherent viscosity

INTRODUCTION

Recently, microwave irradiation has received growing application in organic synthesis for optimization and acceleration of chemical reactions.^{1–6} In some cases, microwave heating is superior to thermal heating and was shown to in-

crease reaction rates, yields of target products, and selectivity, and reduce tarring.⁷ Microwave energy is being investigated as a method to process resins, such as epoxides,^{8–10} polyesters,^{11,12} polyurethanes,^{13,14} and more recently, polyimides^{15–18} because of advantages of shorter processing time, improved energy utilization, and the potential for lower processing temperature and improved product uniformity. The microwave energy is absorbed by the molecules through the polarization or dipole reorientation of functional groups, which is consequently converted to ther-

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mal energy. As a result, heat is generated within each molecule, thereby creating conditions for a homogeneous heating pattern in the material. In the conventional heating process, the heat is transferred from the outside to the inside of the material, resulting in very long processing times to achieve high product uniformity.

Monocyclic six-member ring nitrogen heterocycles such as tetrahydropyr-imidinone and tetrahydro-2-thioxopyrimidine compounds are an extremely important class of compounds that occur in a wide variety of natural products such as purine, caffeine, nucleic acids (DNA, RNA), uric acid, and synthetic products.^{19,20}

However, monomers bearing carbonyl groups attract considerable attention because of the possibility to use them in the preparation of polyimides with enhanced solubility, thermal stability, and improved processibility. Furthermore, the use of monomers containing preformed imide rings is one method of circumventing partial crosslinking, because it avoids high-temperature curing cycles and handles unstable intermediates such as polyamic acids.^{21,22} The synthesis and application of optically active polymers are the newly considered topics that have been given more attention recently. 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. Some other applications could be listed as: 1. constructing chiral media for asymmetric synthesis; 2. chiral stationary phases for resolution of enantiomers in chromatographic techniques; and 3. chiral liquid crystals in ferroelectric and nonlinear optical devices.^{23–26} These applications have caused more consideration to improvement of different synthetic procedures of optically active polymers. Recently, we have synthesized optically active polymers by different methods.^{27–29}

In a previous article,³⁰ we synthesized a series of optically active PAIs containing one group of hexafluoropropylidene as well as two groups of chiral L-leucine by using microwave irradiation. In this article, we report the synthesis and properties of novel optically active poly(amide-imide)s (PAIs) prepared by the polycondensation reactions of 4,4'-carbonyl-bis(phthaloyl-L-alanine) diacid chloride (**1**) with six different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds (**2a–2f**) using a domestic microwave oven.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Switzerland), Aldrich Chemical Co. (Milwaukee, WI), and Riedel-deHaen AG (Germany).

Techniques

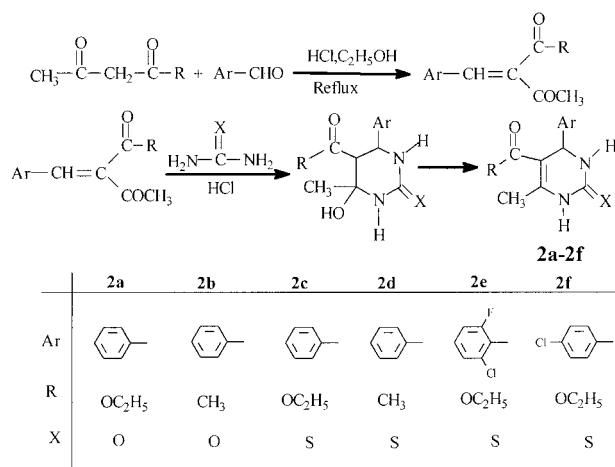
Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu (Japan) 435 IR spectrophotometer. Spectra of solids were performed by using KBr pellets. Vibrational transition frequencies are reported in wave number (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon Fensk Routine Viscometer (Germany). Specific Rotations were measured by a Perkin (Germany) Elmer-241 Polarimeter. Thermogravimetric analysis (TGA) data for polymers were taken on a Mettler (England) TA4000 System under N_2 atmosphere at a rate of $10^\circ\text{C}/\text{min}$. Elemental analyses were performed by the Research Institute of Petroleum Industry, 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.

Monomer Synthesis

4,4'-Carbonyl-bis(phthaloyl-L-alanine) (**4**) and 4,4'-carbonyl-bis(phthaloyl-L-alanine) diacid chloride (**1**) were prepared according to our previous work.³¹ Tetrahydropyr-imidinone and tetrahydro-2-thioxopyrimidine compounds (**2a–2f**) were synthesized according to the Biginelli method³² in Scheme 1.

Polymer Synthesis

An equimolar mixture of diacid chloride (**1**) (0.2 g, 3.99×10^{-4}) and diamide (**2a**) (0.104 g, 3.99×10^{-4}) were placed in a reaction vessel and the mixture was ground until fine powder was formed. Then, 0.45 mL of *o*-cresol was added to the mixture and mixed until a homogeneous solution was formed. The reaction mixture was irradiated in a microwave oven at full power for 10 min. The reaction mixture was poured into 25 mL of methanol. The resulting polymer was filtered off, and was dried, to yield 0.25 g (91%) of brown



Scheme 1

solid. All of the other PAIs **3a–3f** were synthesized by the above method.

Polymer 3a

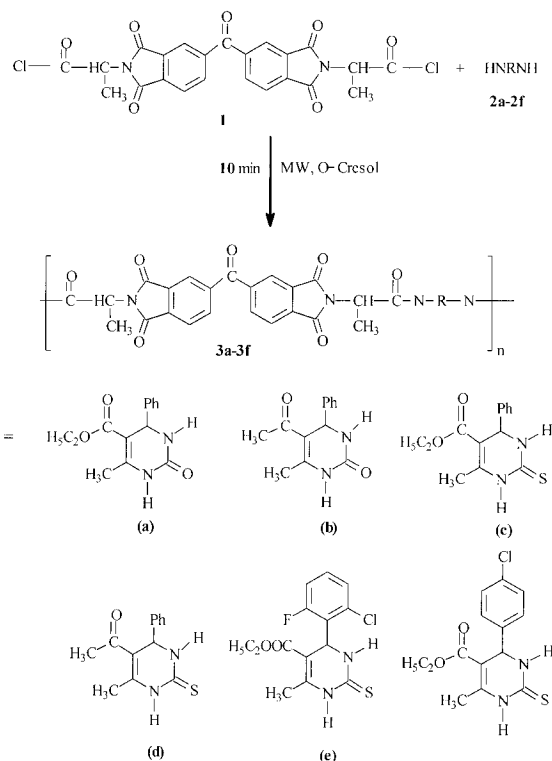
FTIR (KBr): 3100 (w, C=C–H), 2900 (w, C–H), 1780 (s, sh, C=O), 1763 (s, sh, C=O), 1722 (s, br, C=O), 1710 (s, sh, C=O), 1690 (s, sh, C=O), overlapped with C=C), 1491 (w), 1456 (w), 1384 (s), 1296 (m), 1230 (m, sh), 1222 (s), 1170 (m), 1115 (m, sh), 1093 (m), 750 (w), 727 (m) cm⁻¹. Anal: Calcd for C₃₇H₂₈N₄O₁₀: C, 64.56%; H, 4.06%; N, 8.13%. Found: C, 65.30%; H, 4.30%; N, 6.60%.

Polymer 3b

FTIR (KBr): 3100 (w, C=C–H), 2900 (w, C–H), 1776 (s, sh, C=O), 1760 (s, sh, C=O), 1720 (s, br, C=O), 1690 (s, sh, C=O), 1620 (m, C=C), 1610 (m), 1491 (m), 1456 (m), 1384 (s), 1296 (m), 1230 (s, sh), 1222 (s), 1170 (s), 1160 (m), 1109 (m), 750 (m), 727 (m) cm⁻¹. Anal: Calcd for C₃₆H₂₆N₄O₉: C, 65.68%; H, 3.95%; N, 8.51%. Found: C, 67.80%; H, 4.50%; N, 6.30%.

Polymer 3c

FTIR (KBr): 3100 (w, C=C–H), 2900 (w, C–H), 1771 (s, sh, C=O), 1763 (s, sh, C=O), 1720 (s, br, C=O), 1672 (s, sh, C=O, overlapped with C=C), 1491 (m), 1456 (w), 1384 (s), 1296 (m), 1248 (m, sh), 1222 (s), 1170 (s), 1109 (m), 750 (m), 727 (m) cm⁻¹. Anal: Calcd for C₃₇H₂₈N₄O₉S: C, 63.09%; H, 3.98%; N, 7.95%. Found: C, 64.40%; H, 4.10%; N, 6.40%.



Scheme 2

Polymer 3d

FTIR (KBr): 3100 (w, C=C–H), 2900 (w, C–H), 1772 (s, sh, C=O), 1763 (s, sh, C=O), 1720 (s, br, C=O), 1674 (s, sh, C=O), 1610 (m, sh, C=C), 1599 (m), 1491 (m), 1456 (m), 1384 (s), 1296 (m), 1248 (m, sh), 1221 (s), 1172 (s), 1109 (m), 752 (m), 727 (m), 704 (w) cm⁻¹. Anal: Calcd for C₃₆H₂₆N₄O₈S: C, 64.12%; H, 3.86%; N, 8.30%. Found: C, 65.40%; H, 4.40%; N, 6.20%.

Table I Synthesis and Some Physical Properties of PAIs **3a–3f**

Diamine	Polymers ^a			
	Polymer Code	Yield (%)	η_{inh} (dL/g) ^b	$[\alpha]_D^{25b}$
2a	3a	91	0.25	-18.00
2b	3b	90	0.35	-25.00
2c	3c	95	0.41	-10.00
2d	3d	95	0.32	-15.00
2e	3e	92	0.45	-20.00
2f	3f	90	0.40	-18.00

^a All polymerization reactions were performed in *o*-cresol under 10-min irradiation time.

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

Table II Solubility of PAIs 3a–3f

Solvents	3a	3b	3c	3d	3e	3f
DMAc	+	+	+	+	+	+
DMF	+	+	+	+	+	+
THF	–	–	–	–	–	–
DMSO	+	+	+	+	+	+
MeOH	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
CHCl ₃	–	–	–	–	–	–
CH ₂ Cl ₂	–	–	–	–	–	–
H ₂ O	–	–	–	–	–	–

+, Soluble at room temperature; –, insoluble.

Polymer 3e

FTIR (KBr): 3100 (w, C=C–H), 2900(w, C–H), 1776 (s, sh, C=O), 1760 (s, sh, C=O), 1720 (s, br, C=O), 1674 (s, sh, C=O, overlapped with C=C), 1491 (m), 1456 (m), 1384 (s), 1296 (m), 1248 (m, sh), 1221 (w), 1184 (m), 1109 (m), 752 (w), 727 (m) cm⁻¹. Anal: Calcd for C₃₇H₂₆N₄O₉SClF: C, 58.72%; H, 3.44%; N, 7.40%. Found: C, 59.90%; H, 3.70%; N, 8.50%.

Polymer 3f

FTIR (KBr): 3100 (w, C=C–H), 2900 (w, C–H), 1772 (s, sh, C=O), 1763 (s, sh, C=O), 1732 (s, C=O), 1712 (s, C=O), 1680 (s, sh, C=O, overlapped with C=C), 1491 (s), 1462 (m), 1383 (s), 1340 (m), 1296 (s), 1230 (s, sh), 1222 (s), 1185 (s, sh), 1172 (s), 1109 (s), 1100 (s, sh), 752 (s), 727 (s) cm⁻¹. Anal: Calcd for C₃₇H₂₇N₄O₉SCl: C, 60.15%; H, 3.65%; N, 7.58%. Found: C, 61.50%; H, 4.20%; N, 5.30%.

RESULTS AND DISCUSSION

Polymer Synthesis

PAIs **3a–3f** were synthesized by microwave assisted polycondensation reactions of an equimolar mixture of monomer (**1**) with six different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds (**2a–2f**) in *o*-cresol as organic solvent by using a domestic microwave oven, as shown in Scheme 2.

The *o*-cresol was used as polar organic medium that acts as a primary microwave absorber and as a solvent for both of the starting monomers and the resulting polymers which allows inducing of effective homogeneous heating of the reaction

mixture and thereby subsequent polycondensation reaction leading to the polymer formation. The optimum period of reaction time (irradiation time) was found to be 10 min. Below this time produces polymers with lower inherent viscosities, and above this time the materials will degrade.

Polymer Characterization

Synthesis and some physical properties of PAIs (**3a–3f**) are summarized in Table I. These polymers have inherent viscosities in a range of 0.25–0.45 dL/g. PAIs derived from monomer (**1**) may range in color from cream or off-white to brown. All of the resulting polymers show optical rotation and are optically active.

The structures of these polymers were confirmed as PAIs by means of FTIR spectroscopy and elemental analyses. The FTIR spectra of all polymers showed five overlapped carbonyl groups (amide, imide, ketone, and ester C=O,) of absorptions between 1780 and 1672 cm⁻¹. All of them exhibited strong absorbance between 1370–1380 cm⁻¹ and 710–720 cm⁻¹, which shows the presence of the imide heterocycle in these polymers.

The elemental analysis values of the resulting polymers are not in good agreement with the calculated values. This could be due to some impurities and end groups in the resulting polymers.

The solubility of PAIs are listed in Table II. Most of the polymers are soluble in organic solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and dimethylsulphoxide (DMSO) at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water.

Table III Thermal Properties of Some Aromatic PAIs 3b-3c

Polymer	Decomposition Temperature (°C) T ₅ ^a	Char Yield (%) ^b
3b	316	13.24
3c	267	10.29
3d	250	11.76

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

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

Thermal Properties

The thermal decomposition temperature of three PAIs, **3b**, **3c**, and **3d**, were evaluated by means of TGA and derivative thermal analysis, respectively. Table III shows a summary of the thermal properties of some of the PAIs.

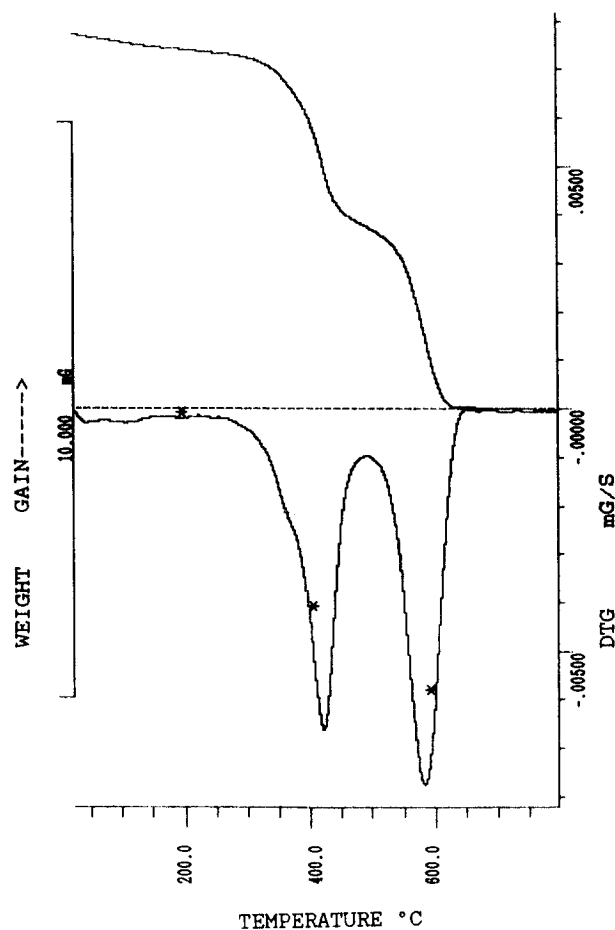


Figure 1 TGA and derivative thermogravimetric DTG curves of PAIs **3b** under nitrogen atmosphere.

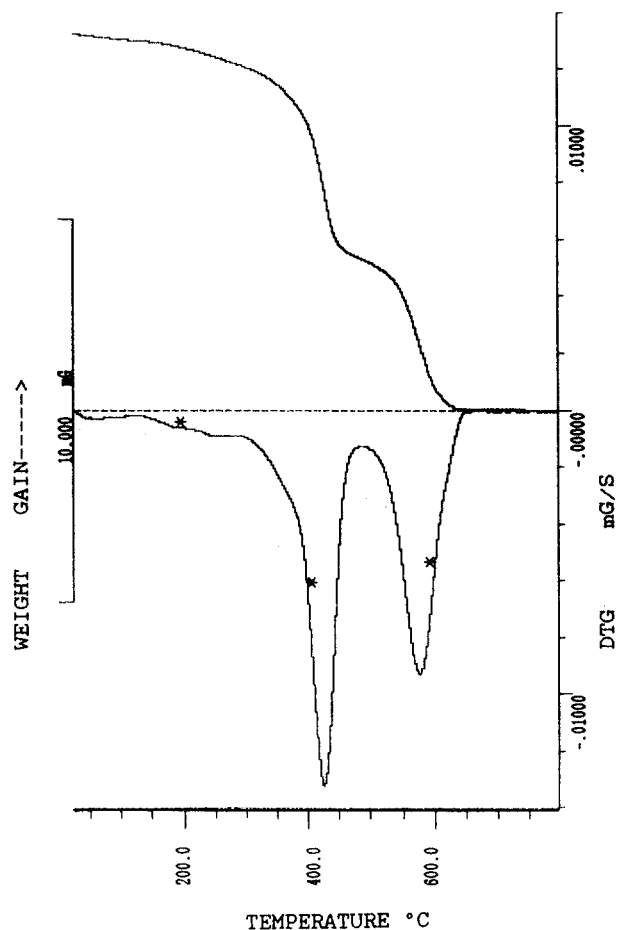


Figure 2 TGA and derivative thermogravimetric DTG curves of PAIs **3c** under nitrogen atmosphere.

The PAIs **3b**, **3c**, and **3d** exhibited good resistance to thermal decomposition up to 230–255°C in nitrogen and began to decompose gradually above that temperature. The temperature of 5% weight loss for all of the polymers ranged from 250 to 316°C and the residual weight for these polymers at 600°C ranged from 11.76 to 13.24% in nitrogen.

CONCLUSIONS

The present work has shown that 4,4'-carbonyl-bis(phtaloyl-L-alanine) diacid chloride (**1**) is an interesting monomer which contains both benzophenoneimide groups as well as chiral L-alanine groups. Thus, a series of new optically active PAIs having inherent viscosities of 0.255–0.45 dL/g were synthesized by microwave-assisted polycondensation reaction of the optically active monomer (**1**) with six different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine com-

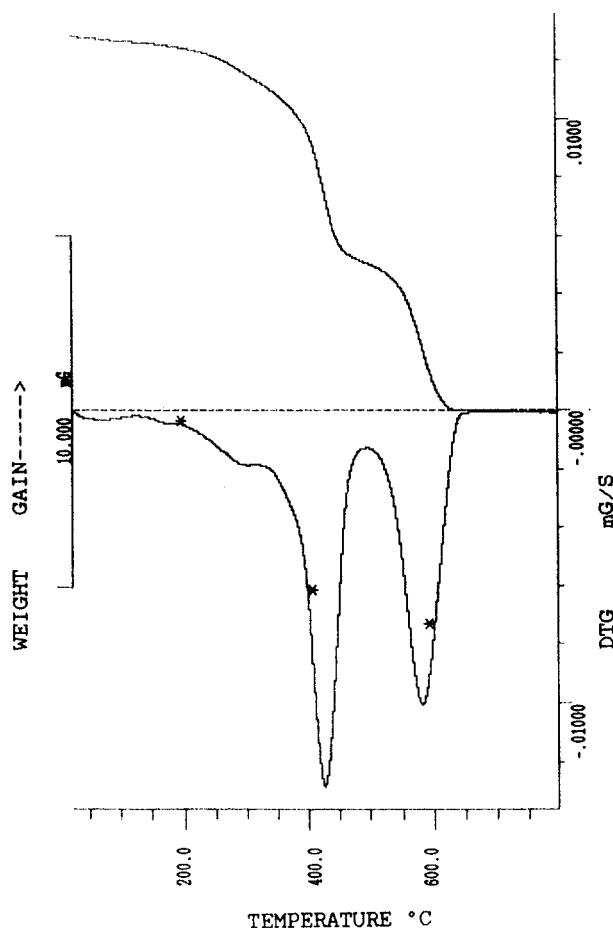


Figure 3 TGA and derivative thermogravimetric DTG curves of PAIs **3d** under nitrogen atmosphere.

pounds (**2a–2f**). These aromatic PAIs are optically active and are soluble in various organic solvents and have good thermal stability. The resulting novel polymers have potential to be used in a proper column chromatography technique for the separation of enantiomeric mixtures. PAIs **3e** and **3f** also could have flame-retardant properties. Furthermore, the above results demonstrate that microwave heating is an efficient method (shorter reaction time and high efficiency of energy) for the polycondensation reactions. We are currently using this method for the synthesis of novel polymers and modification of polymers.

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REFERENCES

1. Abramovitch, R. *Org Prep Proced Int* 1991, 23, 683.

2. Bose, A. K.; Manhas, M. S. *Tetrahedron Lett* 1995, 36, 213 (also references cited therein).
3. Oussaid, B.; Moeini, L.; Martin, B.; Villemin, D.; Garrigues, B. *Synth Commun* 1995, 25, 1451.
4. Caddick, S. *Tetrahedron* 1995, 51, 10403.
5. Hajipour, A. R.; Mallakpour, S. E.; Afrousheh, A. *Tetrahedron* 1999, 55, 2311.
6. Hajipour, A. R.; Mallakpour, S. E.; Imanzahdeh, G. *J Chem Res* 1999, 228.
7. Michael, D.; Mingos, P.; Baghurst, R. *Chem Soc Rev* 1991, 20, 1.
8. Wei, J.; DeLong, J. D.; DeMeuse, M.; Hawley, M. C. *Polym Eng Sci* 1993, 33, 1132.
9. Thuillier, F. M.; Jullien, H. *Makromol Chem Macromol Symp* 1989, 25, 63.
10. Mijovic, J.; Fishbain, A.; Wijaya, J. *Macromolecules* 1992, 25, 986.
11. Stand, N. *Soc Manuf Eng* 1979, EM79, 369.
12. Hottong, U.; Wei, J.; Dhulipala, R.; Hawley, M. C. *Ceram Trans* 1991, 21, 587.
13. Jullien, H.; Valot, H. *Polymer* 1985, 26, 505.
14. Nonninger, K. *Preparation of Cured, Mechanically Post-Processible Polyurethane Moldings*; 1990, DE3842656.
15. Ward, T. C.; Chen, M. *Polym Mater Sci Eng* 1992, 66, 335.
16. Lewis, D. A. *Mater Res Soc Symp Proc* 1992, 269, 21.
17. Lewis, D. A.; Shaw, T. M. *MRS Bull* 1993, 18, 37.
18. Xiao, Y.; Scola, D. A. *ACS Prepr Polym Mater Sci Eng* 1995, 72, 344.
19. Katritzky, A. R.; Ress, C. W. *Comprehensive Heterocyclic Chemistry*; Pergamon: Oxford, UK, 1984.
20. Bose, A. K.; Banik, B. K.; Manhas, M. S. *Tetrahedron Lett* 1995, 36, 213.
21. De Abajo, J.; Gabarda, J. P.; Fontan, J. *Angew Makromol Chem* 1978, 31, 3081.
22. Imai, Y.; Maldar, N. N.; Kakimoto, M. *J Polym Sci Part A Polym Chem* 1984, 22, 2189.
23. Wulff, G. *Angew Chem Int Ed Engl* 1989, 28, 21.
24. Ciardelli, F. *Ecycl Polym Sci Eng* 1987, 10, 463.
25. Farina, M. *Top Stereochem* 1987, 17, 1.
26. Fontanille, M.; Guyot, A., Eds. *Recent Advances in Synthetic and Mechanistic Aspects of Polymerization*; Kluwer: Dordrecht, The Netherlands, 1987.
27. Mallakpour, S. E.; Hajipour, A. R.; Khoei, S.; Mahdavian, A. R. *J Polym Sci Polym Chem Ed* 1999, 37, 1211.
28. Mallakpour, S. E.; Hajipour, A. R.; Mahdavian, A. R.; Rafiemanzelat, F. *Polym Int* 1999, 48, 109.
29. Mallakpour, S. E.; Hajipour, A. R.; Khoei, S. *Polym Int* 1999, 48, 1133.
30. Mallakpour, S. E.; Hajipour, A. R.; Khoei, S. *J Appl Polym Sci* 2000, 77, 3003.
31. Mallakpour, S. E.; Dabbagh, H. A.; Faghihi, K. H. *Iranian Polym J* 2000, 9, 41.
32. Esfandiary D. M.S. Thesis, University of Arak, Arak, I. R. Iran, 1999.