ELSEVIER

European Polymer Journal 36 (2000) 2455–2462

EUROPEAN POLYMER JOURNAL

Direct polycondensation of *N*-trimellitylimido-L-leucine with aromatic diamines

Shadpour E. Mallakpour *, Abdol-Reza Hajipour, Rezvan Roohipour-fard

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

Received 20 May 1999; received in revised form 27 August 1999; accepted 7 January 2000

Abstract

N-trimellitylimido-L-leucine **(3)** was prepared from the reaction of trimellitic anhydride **(1)** with L-leucine **(2)** in toluene solution at refluxing temperature in the presence of triethylamine as a catalyst. The direct polycondensation reaction of the monomer imide–diacid **(3)** with 4,4′-diaminodiphenylsulfone **(4a)**, 4,4′-diaminodiphenylether **(4b)**, 1,4-phenylenediamine **(4c)**, 1,3-phenylenediamine **(4d)**, 4,4′-diaminodiphenylmethane **(4e)** and benzidine (4,4′-diaminobiphenyl) **(4f)** was carried out in a medium consisting of triphenyl phosphite, *N*-methyl-2-pyrolidone, pyridine, and calcium chloride. The resulting poly(amide–imide)s having inherent viscosities 0.24–0.50 dl g^{-1} were obtained in high yield and are optically active and thermally stable. All of the above compounds were fully characterized by IR spectroscopy, elemental analyses and specific rotation. Some structural characterization and physical properties of this new optically active poly(amide–imide)s are reported. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: *N*-trimellitylimido-L-leucine; Poly(amide–imide)s; Direct polycondensation; Optically active polymers; Inherent viscosities; Thermally stable polymers

1. Introduction

Thermally stable polymers have received much interest over the past decade, due to increasing demands for high-performance polymers as a replacement for ceramics or metals in the microelectronic, aerospace and automotive industries. Polyimides and their copolymers are certainly one of the most useful classes of high-performance polymers, which have found many applications in those industries [1,2]. However, most aromatic polyamides are intractable materials that do not melt before thermally decomposing, therefore, would be difficult for processing. Aromatic poly(amide–imide)s (PAIs), however, are very useful high-performance materials that exhibit better processing characteristics when compared with polyimides of analogous structures [3]. A notable example is Torlon® (Amoco Co.), a commercial PAI obtained from trimellitic anhydride chloride and 4,4′-diaminodiphenylmethane [4].

The synthesis and application of optically active polymers are the newly considered topics, which 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. Some other applications could be listed as follows: (1) constructing chiral media for asymmetric synthesis, (2) chiral stationary phases for resolution of enantiomers in chromatographic techniques, (3) chiral liquid crystals in ferroelectrics and nonlinear optical devices [5–8]. These applications have caused more considerations to improve different synthetic procedures of optically active polymers. Optically active homopolymers as well as copolymers have been prepared and reported in the literature [9–19]. Recently, we have synthesized optically active polymers by different methods [20–22].

---

* Corresponding author. Fax: +98-31-8912350.
E-mail address: mallak@cc.iut.ac.ir (S.E. Mallakpour).

PII: S0014-3057(00)00018-5

The triphenyl phosphite activated polycondensation (phosphorylation reaction) technique for the synthesis of polyamides has been reported by Yamazaki et al. [23]. Recently, this technique has been used for the preparation of high molecular weight polyamides as well as PAIs and are reported in the literature [24–26]. In a previous article [27], we synthesized a series of novel optically active PAIs containing one group of hexafluoropropylidene as well as two groups of chiral L-leucines. The resulting polymers are optically active and have inherent viscosities in the range of 0.09–0.29 dl g^{-1}.

In this article, we wish to report the synthesis and characterization of new optically active PAIs from aromatic diamines and *N*-trimellitylimido-L-leucine **(3)**, a monomer containing preformed imide groups, by the direct polycondensation method.

2. Experimental

2.1. Materials

All chemicals were purchased from Fluka Chemical Co., Aldrich Chemical Co. and Riedel-deHaen AG. Trimellitic anhydride **(1)** was synthesized by the dehydration of 1,2,4-benzene tricarboxylic acid with acetic anhydride in boiling acetic acid. 4,4′-diaminodiphenylsulfone **(4a)** was purified by recrystallization from water/ethanol. 4,4′-diaminodiphenylether **(4b)**, 1,4-phenylenediamine **(4c)**, 1,3-phenylenediamine **(4d)**, and benzidine (4,4′-diaminobiphenyl) **(4f)** were purified by sublimation. 4,4′-diaminodiphenylmethane **(4e)** was purified by recrystallization from water.

2.2. Techniques

Proton nuclear magnetic resonance (^{1}H-NMR, 90 MHz) spectra was recorded on a Varian EM-390 instrument. Tetramethylsilane (TMS) was used as an internal reference. IR spectra were recorded on a Shimadzu 435 IR spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wave numbers (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. Specific rotations were measured by a Perkin Elmer-241 polarimeter. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TGA-50 in air atmosphere at a rate of 10°C/min. Elemental analyses were performed by the Research Institute of Petroleum Industry, Tehran, Iran.

3. Monomer synthesis

3.1. N-trimellitylimido-L-leucine (3)

Into a 250 ml round-bottomed flask 3.00 g (1.50×10^{-2} mol) of trimellitic anhydride **(1)**, 2.03 g (1.50×10^{-2} mol) of L-leucine **(2)**, 140 ml of toluene, 1.96 ml (1.40×10^{-2} mol) of triethylamine and a stirring bar were placed. The stirrer was started and the mixture was refluxed under a Dean–Stark system for 48 h. The solvent was removed under reduced pressure and to the residue 100 ml cold water was added. The solution was then decanted, and 5 ml of concentrated HCl was added. A white precipitate was formed, filtered off and dried, to give 4.38 g (93.0%) of diacid **(3)**. Recrystallization from methanol/water gave white crystals, mp 222–224°C {[28] mp 232–234°C}, $[\alpha]_D^{25} = -31.8°$ (0.050 g in 10 ml DMF).

Elemental analysis: calculated for $C_{15}H_{15}NO_6$, C(59.01%), H(4.96%), N(4.59); found, C(58.90%), H(5.00%), N(4.80%).

4. Polymerization: synthesis of polymer (5a)

The PAIs were prepared by direct polycondensation using the following general procedure: Taking polymer **5a** as an example, into a 10 ml round-bottomed flask fitted with a water cooled condenser and a magnetic stirrer, was placed 0.10 g (3.27×10^{-4} mol) of diacid **(3)**, 0.1 g of calcium chloride, 0.327 ml (1.24×10^{-3} mol) of triphenyl phosphite, 0.29 ml of pyridine, 0.08 g (3.27×10^{-4} mol) of diamine **(4a)** and 0.8 ml of NMP. The stirrer was operated and the mixture was heated under nitrogen atmosphere in an oil bath at 60°C for 1 h, then at 90°C for 0.5 h and finally at 130°C for 8 h. The viscous reaction mixture was poured into 50 ml of methanol. The precipitated polymer was collected by filtration, and was dried at 80°C for 15 h under vacuum to leave 0.022 g (98.0%) of solid **(5a)** mp > 300°C; IR (KBr): 3350 (m, br), 2950 (m), 1770 (w, sh), 1690 (s, br), 1590 (s), 1520 (s), 1490 (m), 1370 (s), 1300 (s), 1250 (s), 1150 (s), 1100 (s), 940 (w, br), 830 (m), 710 (m, br), 690 (m, br) cm^{-1}.

Elemental analysis: calculated for $C_{27}H_{23}N_3O_6S$, C(62.65%), H(4.48%), N(8.12); found, C(59.20%), H(4.80%), N(7.20%).

The other PAIs **(5b–5f)** were prepared in a procedure similar to that mentioned above.

4.1. Polymer (5b)

IR (KBr): 3300 (m, br), 2950 (m), 1770 (m), 1710 (s, br), 1650 (s, br), 1610 (w), 1510 (s, br), 1370 (s, br), 1310 (s, br), 1250 (s), 1080 (s, sh), 930 (w), 830 (m), 750 (w), 720 (m, br) cm^{-1}.

4.2. Polymer (5c)

IR (KBr): 3350 (m, br), 2950 (m), 1770 (m), 1710 (s, br), 1650 (s, br), 1610 (s), 1530 (s, br), 1480 (s, br), 1410 (m, br), 1370 (s), 1300 (w), 1250 (m), 1190 (w, br), 1160 (w), 1080 (m, br), 930 (w), 860 (m, br), 770 (m, br), 720 (m, br), 690 (w) cm^{-1}.

Elemental analysis: calculated for $C_{21}H_{19}N_3O_4$, C(66.83%), H(5.07%), N(11.13%); found, C(63.00%), H(5.30%), N(9.80%).

4.3. Polymer (5d)

IR (KBr): 3350 (m, br), 2950 (m), 1770 (m), 1710 (s, br), 1650 (s, br), 1600 (m, sh), 1490 (s, br), 1400 (w), 1370 (s), 1300 (w), 1220 (s), 1160 (w), 1080 (m, br), 840 (m, br), 730 (w), 710 (w) cm^{-1}.

Elemental analysis: calculated for $C_{21}H_{19}N_3O_4$, C(66.83%), H(5.07%), N(11.13%); found, C(63.20%), H(5.20%), N(8.00%).

4.4. Polymer (5e)

IR (KBr): 3310 (m, br), 2950 (m), 1770 (m), 1710 (s, br), 1650 (s, br), 1595 (s, sh), 1510 (s), 1405 (m), 1370 (s, br), 1310 (s, br), 1250 (s), 1080 (m, br), 1010 (w), 980 (w), 850 (m, br), 810 (m, br), 750 (w), 710 (w) cm^{-1}.

Elemental analysis: calculated for $C_{28}H_{25}N_3O_6$, C(71.92%), H(5.39%), N(8.99%); found, C(67.20%), H(5.40%), N(8.20%).

4.5. Polymer (5f)

IR (KBr): 3350 (m, br), 2950 (m), 1770 (m), 1710 (s, br), 1650 (s, br), 1590 (s), 1500 (s, br), 1370 (s, br), 1310 (s, br), 1250 (s), 1180 (w), 1080 (m, br), 1000 (w), 850 (w), 810 (m), 760 (w), 720 (m, br) cm^{-1}.

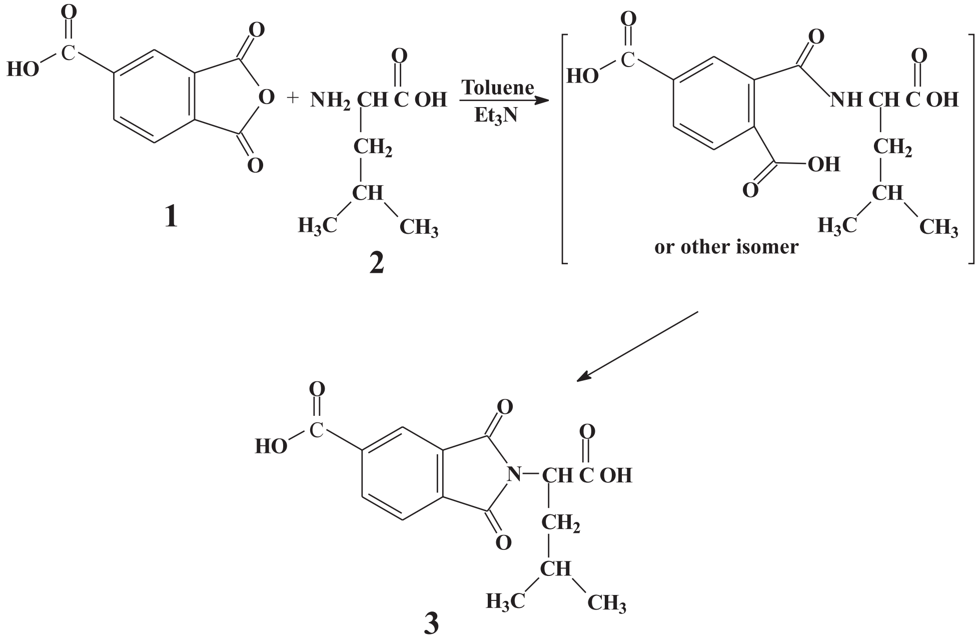
Elemental analysis: calculated for $C_{27}H_{23}N_3O_6$, C(71.51%), H(5.11%), N(9.27%); found, C(66.20%), H(5.30%), N(8.20%).

5. Results and discussion

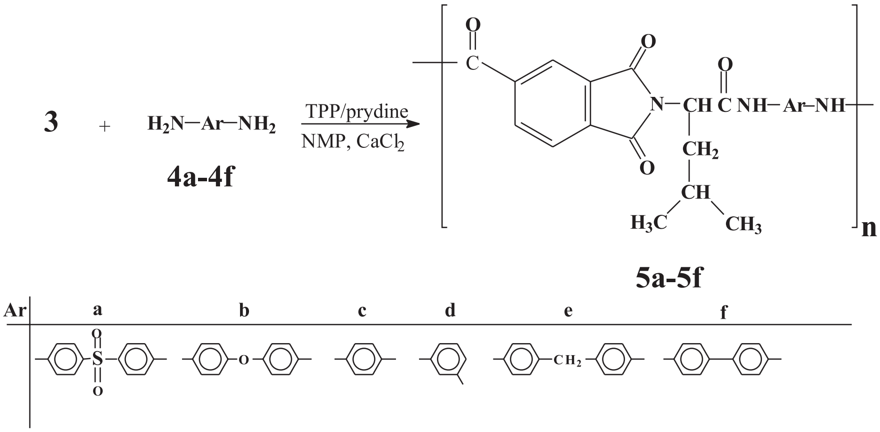
5.1. Monomer synthesis

N-trimellitylimido-L-leucine **(3)** has been reported in the literature [28]; we used a modified procedure for the preparation of diacid **(3)**. Thus, the unsymmetric diacid compound **(3)** was synthesized by the condensation reaction of one equimolar of anhydride **(1)** with one equimolar of L-leucine **(2)** in toluene and in the presence of triethylamine as a base. In order to shift the reaction conversion to a quantitative yield, the resulted water by-product was removed from the reaction media by a Dean–Stark apparatus. Washing the residue in cold water yields a gummy layer that breaks by adding concentrated HCl and gives a white solid (Scheme 1).

The chemical structure and purity of the optically active monomers **(3)** was proved using elemental analysis IR, and ^{1}H-NMR spectroscopic techniques.



Scheme 1.



Scheme 2.

5.2. Polymer synthesis

The PAIs **(5a–5f)** were synthesized by the direct solution polycondensation reactions of an equimolar mixture of monomer **(3)** with six different aromatic diamines **(4a–4f)** using triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 2).

The synthesis and some physical properties of these novel optically active PAIs are given in Table 1. The entire polycondensation readily proceeded in a homogeneous solution. In some cases of the reaction, such as the formation of polymers **(5d)** and **(5f)** an additional amount of NMP must be supplemented to maintain a degree of agitation, because the polymer solutions were too viscous to stir. Tough and stringy precipitates formed when the viscous PAIs solutions were trickled into the stirred methanol. All the polymers were obtained in quantitative yields with moderate inherent viscosities of 0.24–0.50 dl g^{-1} and show optical rotation and therefore, are optically active.

5.3. Polymer characterization

The formation of PAIs was confirmed by the IR spectroscopy analysis. As an example, the IR spectrum of PAI **(5b)** showed the characteristic absorptions of amide and imide groups occurred around 3300, 1770, 1710 and 1650 cm^{-1}, peculiar to N–H stretching and carbonyls stretching of imide and amide, respectively. All of these PAIs exhibited strong absorption at 1370 and 710–720 cm^{-1}, that show the presence of the imide heterocycle in these polymers. The polymer **(5a)** showed characteristic absorptions at 1300 and 1150 cm^{-1} due to the sulfone moiety (SO_2 stretching). PAIs derived from monomer **(3)** may range in color from white to yellow.

The solubility of PAIs was tested quantitatively in various solvents and are given in Table 2. All of the PAIs are soluble in organic solvents such as DMF, DMAc, DMSO, NMP and H_2SO_4 at room temperature, and are insoluble in solvents, such as chloroform, methylene chloride, methanol, ethanol and water.

Table 1
Synthesis and some physical properties of PAIs **(5a–5f)**

Diamine	Polymer				
	PAIs	Yield (%)	η_{inh} (dl g^{-1})[a]	$[\alpha]_D^{25}$[b]	Color[c]
4a	**5a**	98	0.24	−26.8	W
4b	**5b**	95	0.25	–[d]	PY
4c	**5c**	98	0.34	−10.0	PY
4d	**5d**	99	0.39	−10.2	W
4e	**5e**	99	0.41	−7.6	PY
4f	**5f**	98	0.50	−38.0	Y

[a] Measured at a concentration of 0.5 g(dl)$^{-1}$ in DMF at 25°C.

[b] Measured at a concentration of 0.5 g(dl)$^{-1}$ in DMF at 25°C.

[c] W = white, PY = pale yellow, Y = yellow.

[d] Specific rotation was not measured.

Table 2
Solubility of PAIs **(5a–5f)**[a]

Solvents	5a	5b	5c	5d	5e	5f
DMAc	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
H_2SO_4	+	+	+	+	+	+
MeOH	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
$CHCl_3$	–	–	–	–	–	–
CH_2Cl_2	–	–	–	–	–	–
H_2O	–	–	–	–	–	–

[a] Concentration: 5 mg ml^{-1}: +, soluble at room temperature; –, insoluble.

5.4. Thermal properties

The thermal properties of PAIs **(5c**, **5d**, **5f)** were evaluated by means of TGA/DTG in air atmosphere. All of these polymers show similar decomposition behavior (Figs. 1–3). They show three different decomposition maxima. The first two which are slower decomposition occur at lower temperatures and the third one occurs at higher rates and higher temperatures. Thus, PAIs **(5c**, **5d**, **5f)** show first decomposition with an end temperatures at 234.0°C, 223.0°C and 237.7°C with a corresponding weight loss of 8.9%, 12.0% and 13.1%, respectively. The second decomposition occurs with an end temperatures at 432.0°C, 435.7°C and 432.0°C with a corresponding weight loss of 20.2%, 22.0% and 21.2%, respectively.

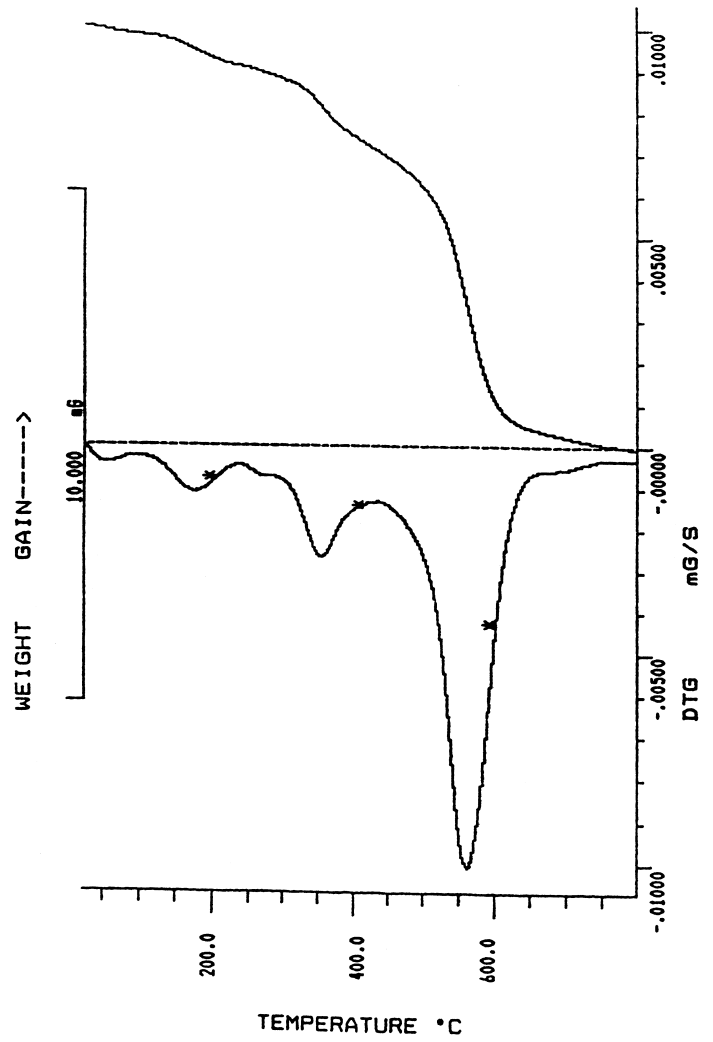


Fig. 1. TGA/DTG thermograms of PAI **(5c)** in air atmosphere.

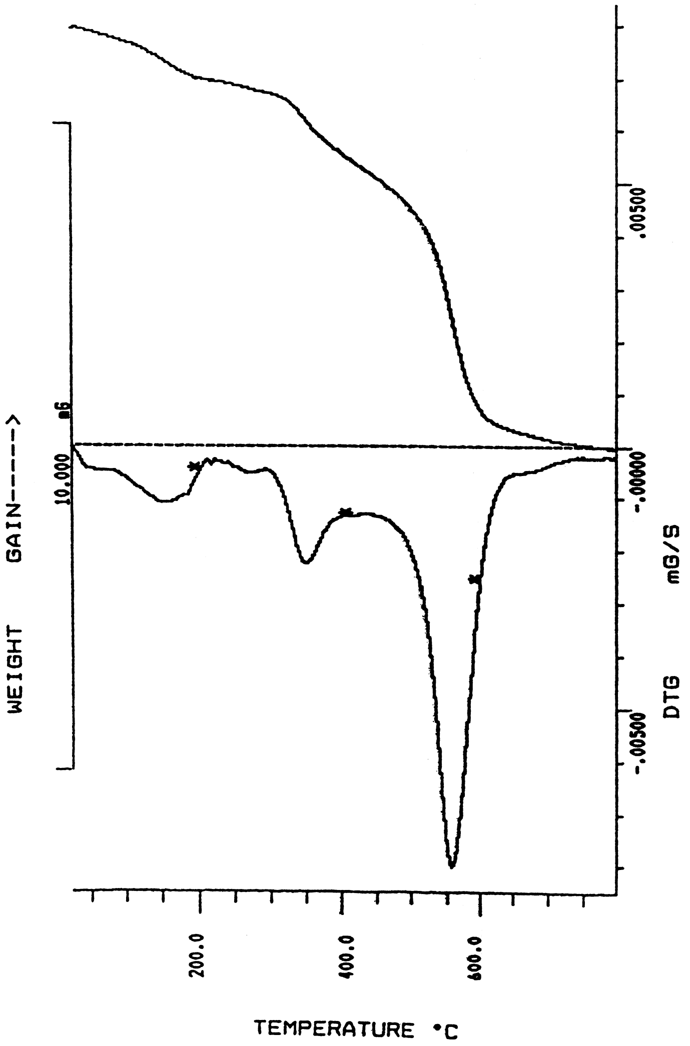


Fig. 2. TGA/DTG thermograms of PAI **(5d)** in air atmosphere.

The third decomposition occurs with an end temperature at 754.7°C, 784.0°C and 743.7°C with a corresponding weight loss of 69.5%, 66.8% and 65.3%, respectively. An examination of the data reveals that all of the above polymers are thermally stable up to around 200°C.

6. Summary and conclusions

A series of optically active PAIs having inherent viscosities of 0.24–0.50 dl g^{-1} was synthesized for the first time by direct polycondensation of the optically active *N*-trimellitylimido-L-leucine **(3)** as a diacid having a preformed imide ring as an "enlarged" monomer containing one chiral L-leucine group with some aromatic diamines. These aromatic PAIs show optical rotation and are readily soluble in various organic solvents and have a moderate thermal stability.

Acknowledgements

We wish to express our gratitude to the Research Affairs Division Isfahan University of Technology (IUT), Isfahan, for partial financial support through Grant no. 1CHA 781. We thank the Amine Pharmaceutical center, Isfahan, Iran for recording optical rotations.

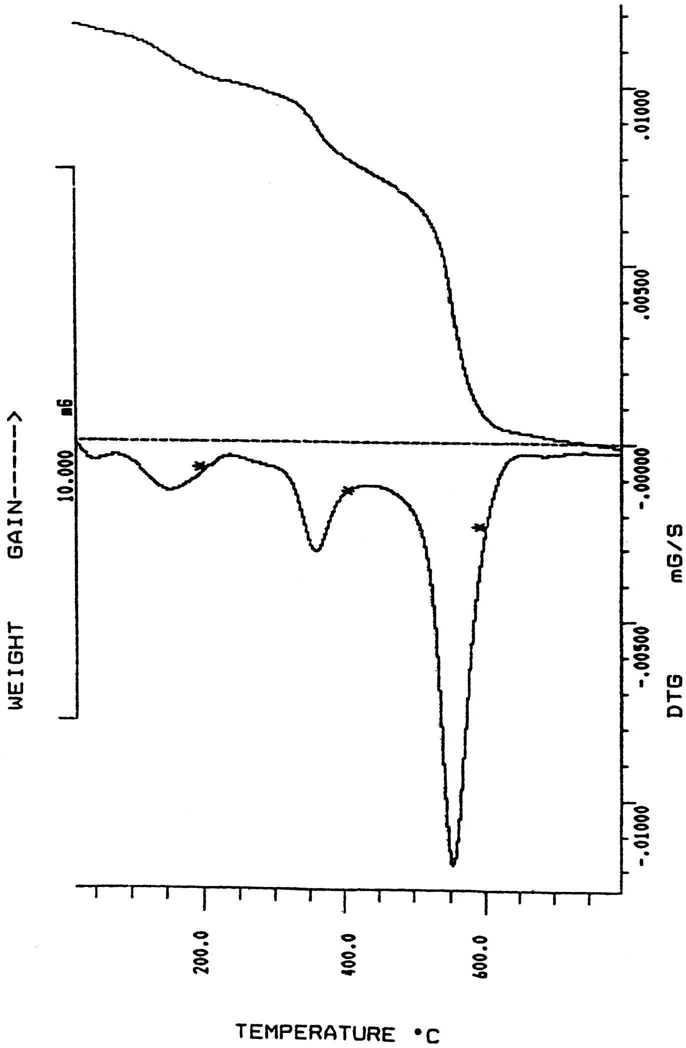


Fig. 3. TGA/DTG thermograms of PAI (**5f**) in air atmosphere.

References

[1] Mittal KL, editor. Polyimides: synthesis, characterization and application. New York: Plenum Press, 1984.

[2] Abade MJM, Sillion B, editors. Polyimides and other high-temperature polymers. New York: Elsevier, 1991.

[3] Yang HH. Aromatic high-strength fibers. New York: Wiley, 1989.

[4] Brillerbeck CJ, Henke SJ. In: Margolis JM, editor. Engineering thermoplastic. New York: Marcel Dekker, 1985.

[5] Wulff G. Angew Chem Int Engl Ed 1989;28:21.

[6] Ciardelli F. Ecycl Polym Sci Engng 1987;10:463.

[7] Farina M. Topics Stereochem 1987;17:1.

[8] Fontanille M, Guyot M, editors. Recent advances in synthetic and mechanistic aspects of polymerization. Dordrecht, Netherlands: Kluwer Academic, 1987.

[9] Marvel CS, Frank RL, Prill E. J Am Chem Soc 1943;65:1647.

[10] Marvel CS, Overberger CG. J Am Chem Soc 1946;68:2106.

[11] Overberger CGG, Palmer L. J Am Chem Soc 1956;78:666.

[12] Berejick N, Schuerch C. J Am Chem Soc 1958;80:1633.

[13] Schmitt GJ, Schuerch C. J Polym Sci 1960;45:313.

[14] Yamaguchi H, Minoura Y. J Polym Sci Part A-1 1970;8:929.

[15] Ciardelli F, Menieagli J. J Polym Sci Polym Symp 1978;62:143.

[16] Ciardelli F, Chiellini E, Carlini C, Nocci R. Prepr Paper Nat Meet Am Chem Soc Polym Div 1976;17:88.

[17] Ciardelli F, Chiellini E, Carlini C, Aglietto M. Pure and Appl Chem 1980;52:857.

[18] Okamoto Y, Suzuk K, Yuki H. J Polym Sci Polym Chem Ed 1980;18:3043.

[19] Majumdar RN, Carlini C, Bertucci C. Makromol Chem 1982;183:2047.

[20] Mallakpour SE, Hajipour AR, Khoee S, Sheikholeslami B. Polym Int 1998;47:193.

[21] Mallakpour SE, Hajipour AR, Mahdavian AR, Khoee S. J Polym Sci Polym Chem Ed 1999;37:1211.

[22] Mallakpour SE, Hajipour AR, Mahdavian AR, Rafiemanzelat F. Polym Int 1999;48:109.

[23] Yamazaki N, Matsumoto M, Higashi F. J Polym Sci Polym Chem 1975;13:1373.

[24] Yang CP, Hsiao SH, Yang CC. J Polym Sci Polym Chem Ed 1997;35:2147.

[25] Liaw DJ, Liaw BY. J Polym Sci Polym Chem Ed 1998;36:1075.

[26] Liaw DJ, Liaw BY. J Polym Sci Polym Chem Ed 1998;36:2301.

[27] Mallakpour SE, Hajipour AR, Khoee S. Polym Int 1999;48:1133.

[28] Staubli A, Ron E, Langer R. J Am Chem Soc 1990;112:4419.