

Thermally Stable and Optically Active Poly(amide-imide)s Derived from 4,4'-(Hexafluoroisopropylidene)-*N,N'*-bis-(phthaloyl-L-methionine) Diacid Chloride and Various Aromatic Diamines: Synthesis and Characterization

Shadpour Mallakpour (✉), Elaheh Kowsari

Organic Polymer Chemistry Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, I.R. Iran. 1-Previous Name: Shadpour E. Mallakpour
E-mail: MALLAK@CC.IUT.AC.IR

Received: 20 June 2005 / Revised version: 5 March 2006 / Accepted: 12 March 2006
Published online: 24 March 2006 – © Springer-Verlag 2006

Summary

Thermally stable and optically active poly(amide-imide)s (PAIs) have been synthesized and their properties such as optical activity, solubility, thermal stability were studied. Polymers were synthesized by solution polymerization of 4,4'-(hexafluoroisopropylidene)-*N,N'*-bis-(phthaloyl-L-methionine) diacid chloride and various aromatic diamines by three different methods. The compounds obtained were characterized by elemental C, H and N analysis, solubility, FTIR, ¹H NMR and ¹⁹F NMR spectroscopy. Thermogravimetric curves were also recorded. All data agree with the proposed structures.

Introduction

There is a growing demand for high strength, and thermally stable polymeric materials such as aromatic polyamides and polyimides [1]. Polyimide oligomers offer considerable promise such as planarizing coatings in the electronic industry. An acetylene-terminated polyimide resin has been investigated for this purpose [2]. However, most commercially available polymers lack structural integrity and thermal stability. The incorporation of the 4,4'-hexafluoroisopropylidenediphthalimide group (6-FDA) into polymer precursors is known [3,4] to provide marked improvements in flexibility and roughness of their polymers a lowering of the glass transition temperature (T_g). Furthermore, these 6-FDA groups prohibit extensive conjugation of the aromatic moieties, thereby providing good electric insulation and resistance to photochemical devices. Aromatic polyimides are certainly one of the most successful classes of high-performance polymers widely used in the microelectronics [5]. However, most polyimides encounter processing difficulty due to their rigidity and poor solubility in organic solvents. The incorporation of flexible bridging groups and introduction of bulky substituents [5-7] into the polymer

structure are some of the approaches used to make polyimides more tractable and soluble. Copolymerization is another synthetic approach used to obtain processable and soluble polyimides. Poly(amide-imide)s (**PAI**)s are one out of many successful classes of copolyimides, which combine the advantages of high-temperature stability and processability. Recently, there has been increasing attention on synthesis of fluorine-containing polyimides [8-12], polyamide [12,13] and **PAI** [5,12,14,15] particularly those with hexafluoroisopropylidene (6F) group. The incorporation of 6F groups into the polymer backbone improves the solubility, thermal stability, glass transition temperature, oxidation resistance, optical transparency, and environmental stability while decreasing dielectric constant, crystallinity, water absorption and color. We have synthesized optically active polymers by different methods [16,19] In these polymers, we also used amino acids as chiral inducing agents. These materials are naturally occurring compounds therefore synthetic polymers based on amino acids are expected to be biodegradable and biocompatible. Optically active polymers are used, as chiral stationary phases for a high chiral recognition ability in high-performance liquid chromatography (HPLC) to resolve a wide range of racemates or chiral media for asymmetric synthesis [20,21].

This report concerns the preparation of optically active fluorinated **PAI**s with side chains prepared from diacid chloride and various aromatic diamines via solution polycondensation as well as microwave-assisted polycondensation techniques.

Experimental

Materials

4,4'-Diaminodiphenylmethane (**5b**) and 4,4'-diaminobiphenyl (**5f**) were purified by recrystallization from water. 4,4'-Diaminodiphenylether (**5c**), 1,4-phenylenediamine (**5d**), 1,3-phenylenediamine (**5e**), were purified by sublimation. *N,N*-Dimethylacetamide (**DMAC**) was dried over BaO, then distilled in vacuum. The other chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI) and Riedel-deHaen AG (Seelze, Germany), and were used without further purification.

Instruments

Proton nuclear magnetic resonance ^1H NMR (500 MHz) spectra were recorded on a Bruker Avance 500 instrument (Bruker, Rheinstetten, Germany). The Proton resonances were designated as singlet (s), doublet (d), and multiplet (m). Fourier transform infrared (FTIR) spectra were recorded on a Jasco 680 spectrophotometer (Jasco, Japan). Spectra of solids were obtained with KBr pellets. Vibration bands were reported as wavenumber (cm^{-1}). The band intensities were classified as weak (w), medium (m), strong (s) and broad (br). The inherent viscosities were measured by a standard procedure using a Cannon-Fenske routine viscometer (Cannon, Mainz, Germany). The specific rotations were measured by a Jasco Polarimeter (Japan). Thermal Gravimetric Analysis (TGA) data for polymers were taken on a Stanton-650 TGA under N_2 atmosphere by the Iran Polymer and Petrochemical Institute (IPPI). Elemental analysis was performed at Malek-Ashtar University of Technology and Research Institute of Petroleum Industry (Tehran, Islamic Republic of Iran).

Synthesis of monomer

N,N'-(4,4'-hexafluoroisopropylidenediphthaloyl)-bis-*L*-methionine (**3**).

1.00 g (2.2 mmol) of 4,4'-hexafluoroisopropylidene-2,2-bis-(phthalic acid anhydride) (**1**), 0.82 g (5.5 mmol) of *L*-methionine (**2**), 30 mL of acetic acid and a stirring bar were placed into a 50 mL round-bottomed flask. The mixture was stirred at room temperature for 3 h and then was refluxed for 8 h. The solvent was removed under reduced pressure and 5 mL of cold concentrated HCl was added to the residue. A white precipitate formed and was washed with cold water, and dried under reduced pressure to give 1.47 g (93.2% of compound **3**). mp: 136-138°C, $[\alpha]_D^{25} = -82.2$ deg dm⁻¹ g⁻¹ cm³ (0.050 g in 10 mL DMF); FTIR (KBr): 2919 (m, br), 1778 (m), 1717 (s), 1624 (m), 1436 (w), 1384 (s), 1257 (s), 1211 (m), 1143 (m), 1093 (m), 964 (m), 850 (m), 630 (w) cm⁻¹. ¹H NMR (DMSO-d₆, 500 MHz, ppm): δ = 2.00 (s, 6H, CH₃-S), 2.40 (m, 4H, CH₂), 2.5 (m, 4H, CH₂-S), 4.96-4.98 (m, 2H, CH-N), 7.54-7.60 (s, 2H Ar-H), 7.89-7.90 (d, 2H, J = 8.0 Hz, Ar-H), 8.07-8.09 (d, 2H, J = 10.0 Hz, Ar-H), 13.25 (s, br, 2H, COOH).

C₂₉H₂₄F₆N₂O₈S₂ (706.55): Calcd C, 49.29; H, 3.42; N, 3.96. Found: C, 49.21; H, 3.43; N, 4.11.

Synthesis of 4,4'-(hexafluoroisopropylidene)-*N,N'*-bis-(phthaloyl-*L*-methionine) diacid chloride (**4**).

1.00 g (1.41 mmol) of compound **3** and 2.0 mL of thionyl chloride were placed into a 25 mL round-bottomed flask. The mixture was stirred at room temperature for 0.5 h until the suspension mixture was converted to a clear solution. Unreacted thionyl chloride was removed under reduced pressure and the solid product was washed with fresh dry ether three times, to leave 1.00 g (95.0%) of pale yellow solid. mp: 110-112°C, $[\alpha]_D^{25} : -111.3$ deg dm⁻¹ g⁻¹ cm³ 0.050 g in 10 mL of DMF); FTIR (NaCl): 2919 (w), 2360 (w), 1781 (s), 1725 (s), 1624 (w), 1488 (w), 1436 (m), 1379 (s), 1297(m), 1107 (m), 1020 (w), 965 (m), 914 (w), 884 (w), 799 (w) cm⁻¹. ¹H NMR (DMSO-d₆, 500 MHz, ppm): δ = 2.0 (s, 6H, CH₃-S), 2.40 (m, 4H, CH₂), 2.5 (m, 4H, CH₂-S), 5.0 (m, 2H, CH-N), 7.77 (s, 2H, Ar-H), 7.90 (d, 2H, Ar-H), 8.07-8.09 (d, 2H, J = 10.0 Hz, Ar-H).

C₂₉H₂₂F₆Cl₂N₂O₆S₂ (743.45): Calcd. C, 46.85; H, 2.98; N, 3.76. Found: C, 47.00; H, 2.99; N, 3.91.

Polymerization

All of the polymers were synthesized with three different methods:

Method I: Low temperature solution polycondensation

Taking polymer **6aI** as an example, the general procedure consisted of adding 0.20 g (0.26 mmol) of diacid chloride **4** to a cooled (-5.0 °C) stirred solution of 0.064 g (0.26 mmol) of diamine **5a** in 0.25 mL of 1-methyl-2-pyrrolidone (NMP). After the reagents dissolved completely, trimethylsilyl chloride (TMSCl) (0.05 mL) was added and reaction was allowed to proceed for 2 h under a blanket of nitrogen. Then the temperature was raised to room temperature. The reaction mixture was stirred for 5 h. The viscous solution was poured into 40 mL of methanol and the precipitated solid was filtered off and dried at 80 °C for 10 h under vacuum to leave 0.187 g (76.0%) of solid polymer **6aI**. ¹H NMR (DMSO-d₆, 500 MHz): δ = 2.0 (s, 6H, CH₃-S), 2.20 (m,

4H, CH₂), 2.4 (m, 4H, CH₂-S), 5.0 (m, 2H, CH-N), 7.77 (s, 2H, Ar-H), 7.90 (d, 2H, Ar-H), 8.07-8.09 (d, 2H, Ar-H), 10.0 (s, 2H, N-H) .

Method II: High temperature solution polycondensation

Taking polymer **6aII** as an example, into a 5 mL round-bottomed flask were placed 0.20 g (0.26 mmol) of diacid chloride **4**, 0.064 g (0.26 mmol) of diamine **5a**, DMAc (0.25 mL) and TMSCl (0.05 mL) were added. The mixture was refluxed for 1 min. The viscous solution was poured into 40 mL of methanol and the precipitated solid was filtered off and dried at 80°C for 10 h under vacuum to leave 0.160 g (65.3%) of polymer **6aII**.

The other PAIs (**6bII-6fII**) were prepared with similar procedures.

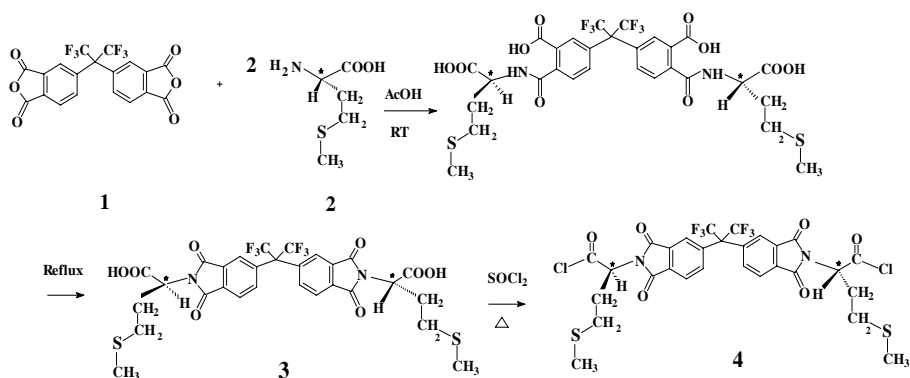
Method III: polymerization under microwave irradiation

The PAIs were prepared by the following general procedure (using polymer **6aIII** as an example). Into a porcelain dish were placed 0.20 g (0.26 mmol) of diacid chloride **4** and 0.064 g (0.26 mmol) of diamine **5a**. After the reagents were completely ground, o-cresol (0.25 mL) was added as a solvent. The mixture was ground for 5 min. The reaction mixture was irradiated in the microwave oven for 4 min with 100%. The resulting product was isolated by adding methanol and triturating, following by filtration and was dried at 80°C for 10 h under vacuum to leave 0.229 g (93.2%) of solid **6aIII**.

Results and discussion

Monomer Synthesis

The diacid **3** was synthesized by the condensation of dianhydride **1** with two mols of L-methionine (**2**). The intermediate amic acid was not isolated and ring closure for the formation of the imide ring was performed under reflux conditions (scheme 1). diacid **3** was converted to diacid chloride derivative **4** by reaction with thionyl chloride. The chemical structure and purity of the compounds **3** and **4** were detected using elemental analysis, FTIR and ¹H NMR and ¹⁹F NMR spectroscopic techniques. The ¹⁹F NMR spectrum showed a single peak at -63.32 ppm and confirms the presence of F atoms and only one type of it in the new monomer **3**. Figure 1 demonstrates ¹H NMR spectrum of diacid **3**.



Scheme 1. Synthesis of monomer **4**.

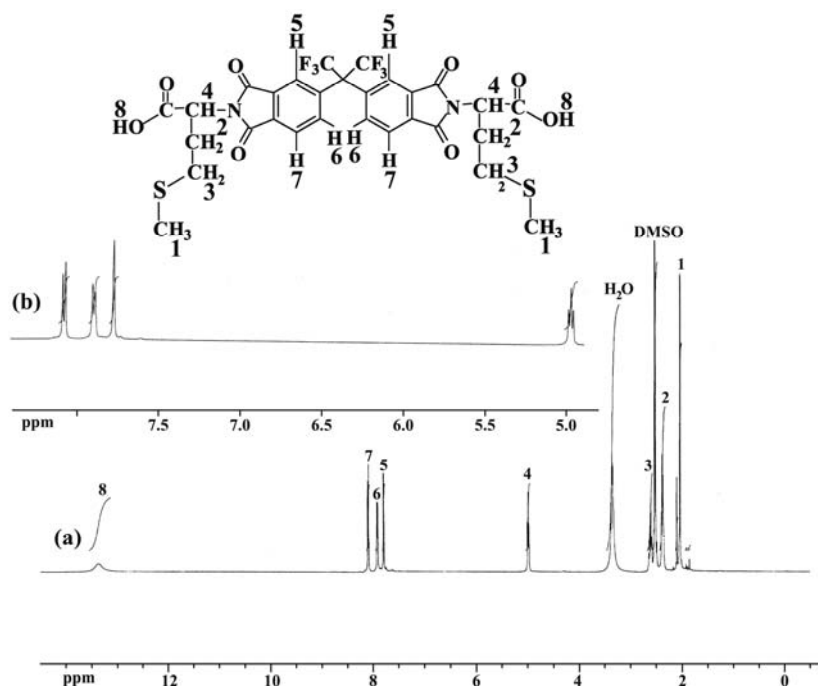
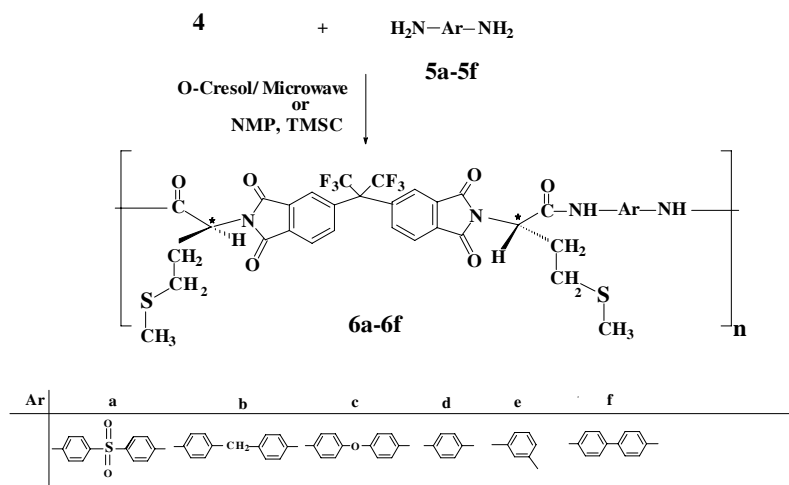


Figure 1. (a) ^1H NMR Spectrum of diacid **3** in $\text{DMSO-}d_6$ at rt. (b) Expanded region for the aromatic protons ($\delta = 5.0\text{-}8.0$ ppm).

Polymer Synthesis

The polymerization of diacid chloride **4** with aromatic diamines **5a-5f** was performed under low temperature (method I), reflux condition (method II) and microwave-assisted polycondensation reaction (method III) (Scheme 2). In method I



Scheme 2. Polycondensation reactions of monomer **4** with aromatic diamines.

polycondensation reaction was performed in cold NMP solution ($-5\text{ }^{\circ}\text{C}$) in the presence of small amount of TMSC. In this method the polymerization reactions occurred within 2 h. In method II, polycondensation reactions proceeded rapidly at the reflux temperature of solvent in 1 min. Comparable yields and viscosity of **PAIs 6a-6f** were obtained from methods I and II.

The reaction yields and some physical data of the solution polycondensations are listed in Tables 1 and 2.

Table 1. Some Physical Properties of Poly(amide-imide)s **6aI-6fI** Prepared by Method I.

Diamine	Polymer					
	Polymer code	Yield (%)	η_{inh} (dLg ⁻¹) ^a	$[\alpha]_{589}^{25}$	$[\alpha]_{577}^{25}$	$[\alpha]_{546}^{25}$
5a	6aI	76.0	0.35	-14.2	-15.3	-18.3
5b	6bI	83.2	0.28	-21.5	-35.3	-40.2
5c	6cI	85.3	0.25	-29.2	-35.2	-54.3
5d	6dI	95.3	0.32	-23.2	-36.2	-56.8
5e	6eI	84.3	0.28	-32.3	-55.3	-80.3
5f	6fI	80.2	0.31	-35.3	-52.4	-81.2

^aMeasured at a concentration of 0.5 gdL⁻¹ in DMF at 25 °C.

$[\alpha]_{\lambda}^{t_0}$ = Specific Rotation = deg dm⁻¹ g⁻¹ cm³

Table 2. Some Physical Properties of Poly(amide-imide)s **6aII-6fII** Prepared by Method II.

Diamine	Polymer					
	Polymer code	Yield (%)	η_{inh} (dL/g)	$[\alpha]_{589}^{25}$	$[\alpha]_{577}^{25}$	$[\alpha]_{546}^{25}$
5a	6aII	65.3	0.32	-11.3	-13.5	-20.2
5b	6bII	82.3	0.29	-11.5	-17.2	-36.8
5c	6cII	83.2	0.33	-29.1	-36.5	-44.2
5d	6dII	92.5	0.37	-28.2	-56.3	-64.1
5e	6eII	70.3	0.25	71.3	-36.3	-52.4
5f	6f II	81.2	0.28	-64.1	-32.3	-55.1

^aMeasured at a concentration of 0.5 gdL⁻¹ in DMF at 25 °C.

$[\alpha]_{\lambda}^{t_0}$ = Specific Rotation = deg dm⁻¹ g⁻¹ cm³

To compare conventional solution polycondensation reaction methods with microwave-assisted polycondensation, the reactions were also carried out under microwave conditions in the presence of small amount of *o*-cresol that acts as a primary microwave absorber. The reaction mixture was irradiated for 6 min with 100% of radiation power. At higher radiation times dark products were obtained, and on the other hand under low radiation times or power, reactions gave low yield and viscosity. The reaction yields and some physical data for **PAIs 6aIII-6fIII** are listed in Table 3.

Table 3. Some Physical Properties of Poly(amide-imide)s **6aIII-6fIII** Prepared by Method III.

Diamine	Polymer					
	Polymer code	Yield (%)	η_{inh} (dL/g)	$[\alpha]_{589}^{25}$	$[\alpha]_{577}^{25}$	$[\alpha]_{546}^{25}$
5a	6aIII	93.2	0.45	-12.3	-18.2	-32.1
5b	6bIII	88.3	0.35	-32.5	-56.3	-61.3
5c	6cIII	83.2	0.28	-56.2	-72.5	-84.6
5d	6dIII	92.3	0.36	-76.2	-85.2	-93.1
5e	6eIII	86.3	0.32	-35.2	-56.2	-60.4
5f	6fIII	85.1	0.33	-56.3	-32.3	-58.2

^aMeasured at a concentration of 0.5 g dL⁻¹ in DMF at 25 °C.

$[\alpha]_{\lambda}^{T_0}$ = Specific Rotation = deg dm⁻¹ g⁻¹ cm³

Polymer Characterization

The structures of these polymers were confirmed as **PAIs** by means of elemental analysis, FTIR and ¹H NMR and ¹⁹F NMR spectroscopy. Elemental analysis data of the resulting polymers are listed in Table 4.

Table 4. Elemental Analysis of Poly(amide-imide)s **6aI-6fI**.

Polymer	Formula		Elemental Analysis (%)			Moisture Content (%) ^a
			C	H	N	
6aI	(C ₄₁ H ₃₂ N ₄ O ₈ S ₃ F ₆) _n (918.8) _n	Calcd	53.59	3.51	6.09	0.23
		Found	53.61	3.50	6.26	
		Corr ^b	53.73	3.49	6.27	
6bI	(C ₄₂ H ₃₄ N ₄ O ₆ S ₂ F ₆) _n (869.8) _n	Calcd	58.06	3.94	6.44	0.31
		Found	58.11	3.98	6.63	
		Corr ^b	58.29	3.96	6.65	
6cI	(C ₄₁ H ₃₂ N ₄ O ₇ S ₂ F ₆) _n (870.7) _n	Calcd	56.55	3.70	6.43	0.42
		Found	56.61	3.71	6.56	
		Corr ^b	56.84	3.69	6.58	
6dI	(C ₃₅ H ₂₈ N ₄ O ₆ S ₂ F ₆) _n (778.6) _n	Calcd	53.98	3.62	7.19	0.25
		Found	53.91	3.65	7.31	
		Corr ^b	54.00	3.64	7.31	
6eI	(C ₃₅ H ₂₈ N ₄ O ₆ S ₂ F ₆) _n (778.68) _n	Calcd	53.98	3.62	7.19	0.20
		Found	53.90	3.63	7.30	
		Corr ^b	54.00	3.62	7.30	
6fI	(C ₄₁ H ₃₂ N ₄ O ₆ S ₂ F ₆) _n (854.78) _n	Calcd	57.61	3.77	6.55	0.15
		Found	57.69	3.79	6.69	
		Corr ^b	57.77	3.78	6.70	

^a Moisture Content (%) = $\frac{(W - W_0)}{W_0} \times 100$, W = weight of polymer sample after standing at room temperature and W₀ = weight of polymer sample after dried in vacuum at 100 °C for 10 h.

^b Corrected value for C and N = Found value $\times \frac{(100 + \text{moisture content})}{100}$, and Corrected value for H = Found value $\times \frac{(100 - \text{moisture content})}{100}$.

FTIR spectra of all polymers show the characteristic absorption peaks for the imide ring at 1780 and 1718 cm^{-1} due to the symmetrical and asymmetrical carbonyl stretching vibrations. Bands of amide N-H groups appeared *ca.* 3345 cm^{-1} (hydrogen bonds) and 1455-1511 cm^{-1} (amide II bonds). All of them exhibited strong absorptions at 1381 cm^{-1} and 750 cm^{-1} that show the presence of the imide heterocycle ring in these polymers. The pattern of ^1H NMR spectra is similar to those of monomer diacid chloride and corresponding diamine. The ^{19}F NMR spectrum of **PAI-6aI** shows only one peak at -63.25 ppm which also confirms the presence of F atom and only one type of it in the resulting polymer backbone.

Most of the polymers are soluble in aprotic polar solvents such as DMF, *N,N*-DMAc, dimethyl sulfoxide (DMSO), NMP and even in less polar solvents such as, *o*-cresol, *m*-cresol and acetone. They are insoluble in chloroform, acetonitril, cyclohexane and water.

Thermal Properties

The thermal stability of the polymers, **6aI** and **6bI** was characterized by TGA conducted in nitrogen, at a heating rate of 10°Cmin^{-1} . In these polymers, the thermal stability is very good. The temperature at which the decomposition begins is never under 300 $^\circ\text{C}$. Typical TGA curves of representative polymers are shown in Figure 2.3. The temperatures of 5% and 10% weight loss together with char yield at 600 $^\circ\text{C}$ for **PAIs 6aI** and **6bI** have been calculated from their thermograms. It is clear from the obtained data that the resulting polymers are thermally stable. The thermo analyses data of **PAIs 6aI** and **6bI** are summarized in Table 5.

Table 5. Thermal properties of **PAIs**

Polymer	T_5 ($^\circ\text{C}$) ^b	T_{10} ($^\circ\text{C}$) ^c	Char Yield (%) ^d
6aI	337	357	28
6bI	329	350	26

^a The initial decomposition temperature by TGA at heating rate of $10^\circ\text{C min}^{-1}$ in N_2 .

^b Temperature at which 5% weight loss was recorded by TGA at heating rate of $10^\circ\text{C min}^{-1}$ in N_2 .

^c Temperature at which 10% weight loss was recorded by TGA at heating rate of $10^\circ\text{C min}^{-1}$ in N_2 .

^d Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600 $^\circ\text{C}$ in N_2 .

Conclusion

By applying different solution polycondensation methods, fluorine containing **PAIs** having inherent viscosities in a range of 0.25-0.45 dLg^{-1} (molecular weight ranging 15000-25000 gmol^{-1}) were synthesized. These polymers exhibit a higher thermal stability than non-fluorine bearing polymers with comparable structures. These polymers showed excellent solubility and could be made into film upon casting. The synthetic polymers are expected to have potential as packing materials in chromatography technique. Furthermore the resulting polymers due to the presence of amino acid moieties could have biodegradability and biocompatibility properties, so could be environmentally friendly.

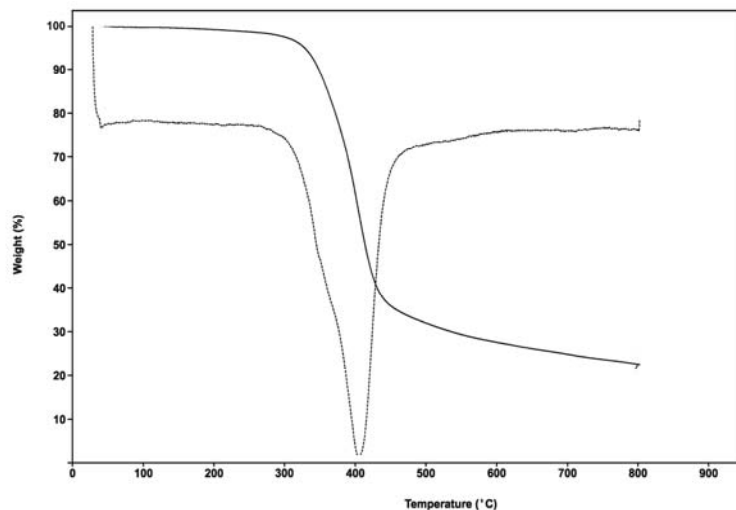


Figure 2. TGA/DTG of **PAI-6a** with a heating rate of 10 °C/min in nitrogen atmosphere.

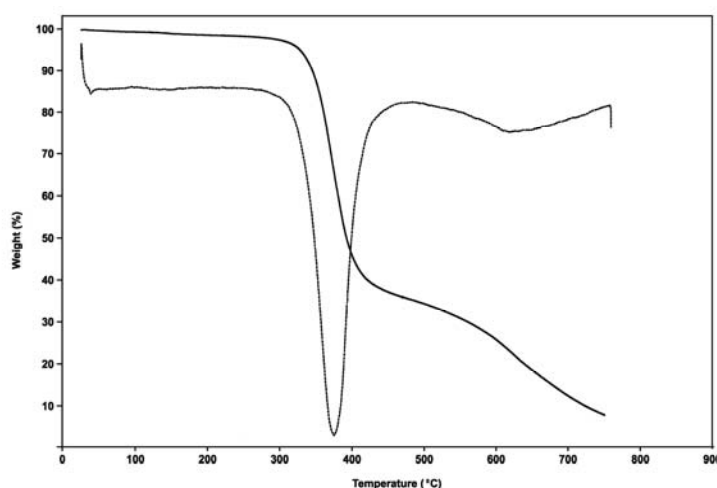


Figure 3. TGA/DTG of **PAI-6b** with a heating rate of 10 °C/min in nitrogen atmosphere.

Acknowledgements: We wish to express our gratitude to the Research Affairs Division Isfahan University of Technology (IUT), Isfahan, for partial financial support. Further financial support from Management and Programming Organization of I.R. Iran and from Center of Excellency in Chemistry Research (IUT) is gratefully acknowledged.

References

1. Shiraishi K, Kanbara, T, Yamamoto T, Groenendaal, LB (2001) *Polymer* 42:7229.
2. Harris FW, Pamidimukkala A, Gupta R, Das S, WuT, Mock GJ (1986) *Macromol Sci Chem A*, 21: 1117.
3. Kumar D, Fohlen GM, Parker JA (1983) *J Polym Sci Polym Chem Ed* 21: 2017.

4. Schmiegel WW (1995) Chemistry of organic fluorine compounds II: a critical review, in: M. Hudlicky, A.E. Pavlath (Eds.), ACS Monography 187, American Chemical Society, Washington, DC, p 1101.
5. Liaw D J, Liaw BY, Tseng JM (1999) J Polym Sci Part A: Polym Chem 37: 2629.
6. Matsuura TN, Yamada Nishi S, Hasuda Y (1993) Macromolecules 26: 419.
7. Namata S, Oochara S, Fujisaki K, Imaizumi J, Kinjo N (1986) J Appl Polym. Sci 31: 101.
8. Misra AC, Tesoro G, Hougham G, Pendharkam SM (1992) Polymer 33: 1078.
9. Park JW, Lee M, Lee MH, Liu JW, Kim S D, Chang JY et al. (1994) Macromolecules 27: 3459.
10. Ghasemi HA, Hay S (1994) Macromolecules 27: 3116.
11. Liaw DJ, Wang KL (1996) J Polym Sci Part A: Polym Chem 34: 1209.
12. Onah EJ (2001) Polymers with low dielectric constants: synthesis and fabrication of their ultrathin films. Doctorate thesis, Dresden University Press.
13. Tagle LH, Diaz FR, Cerda G, Oyarzo M, Penafiel G (1997) Polym. Bull 39: 9.
14. Bruma M, Mercer F, Fitch J, Cassidy PE (1995) J Appl Polym Sci 56: 527.
15. Irvin DJ, Cassidy PE, Meurer DL, Fitch JW, Taylor DA, Clair A St et al. (1996) Polymer 37: 2227.
16. Mallakpour S, Shahmohammadi MH (2004) Polym Int 53: 184.
17. Mallakpour S, Zamanlou MR (2004) J Appl Polym Sci 91: 3281.
18. Mallakpour S, Kowsari E (2004) J Appl Polym Sci 91: 992.
19. Mallakpour S, Kowsari E (2003) J Polym Sci Part A 41: 3974.
20. Akekah A, Sherrington DS (1981) Chem Rev 8: 557.
21. Okamoto YE, Yashima E (1999) Angew Chem Int Ed Engl 37: 1020.
22. Elias HG (1997) An Introduction to Polymer Science VCH Press, Weinheim, Germany.
23. Mallakpour S, Kowsari E (2006) J Appl Polym Sci 99: 1038.