

# Synthesis and Characterization of New Optically Active Poly(Amide-Imide-Urethane) Thermoplastic Elastomers, Derived from 4,4'-(Hexafluoroisopropylidene)-*N,N'*-bis(phthaloyl-L-leucine-*p*-aminobenzoic Acid) and PEG-MDI

Shadpour Mallakpour, Sepideh Khoee

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

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**ABSTRACT:** A new class of optically active poly(amide-imide-urethane) was synthesized via two-step reactions. In the first step, 4,4'-methylene-bis(4-phenylisocyanate) (MDI) reacts with several poly(ethylene glycols) (PEGs) such as PEG-400, PEG-600, PEG-2000, PEG-4000, and PEG-6000 to produce the soft segment parts. On the other hand, 4,4'-(hexafluoroisopropylidene)-*N,N'*-bis(phthaloyl-L-leucine-*p*-amidobenzoic acid) (**2**) was prepared from the reaction of 4,4'-(hexafluoroisopropylidene)-*N,N'*-bis(phthaloyl-L-leucine) diacid chloride with *p*-aminobenzoic acid to produce hard segment part. The chain extension of the above soft segment with the amide-imide **2** is the second step to give a homologue

series of poly(amide-imide-urethanes). The resulting polymers with moderate inherent viscosity of 0.29–1.38 dL/g are optically active and thermally stable. All of the above polymers 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-urethanes) are reported. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2288–2294, 2004

**Key words:** polycondensation; polyamides; polyimides; thermal properties

## INTRODUCTION

Recently poly(amide-imides) (PAIs) have received much attention because of their favorable balance between processibility and performance.<sup>1–8</sup> The PAIs have excellent thermal, physical, and mechanical properties. On the other hand, segmented polyurethane elastomers are a class of high-performance materials for coatings, adhesives, elastomers, fibers, and foams. Their versatile properties were attributed to a two-phase microstructure. The hard and soft segments alternatively appear in the polymer backbones, which can be described as an  $(A - B)_n$  multiblock polymer. If PAIs chains are introduced into a polyurethane backbone, they may change the properties of the polyurethane. These efforts have been intended by using either high glass transition

temperature ( $T_g$ ) hard segments and/or low  $T_g$  soft segments.

## EXPERIMENTAL

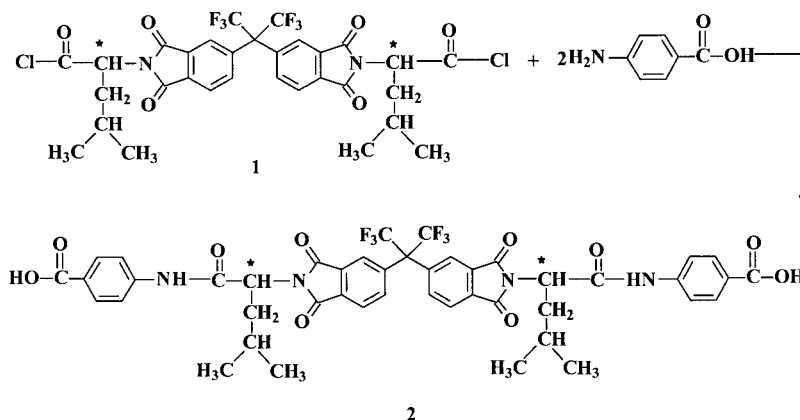
### Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), and Riedel-deHaen AG (Seelze, Germany). 4,4'-Methylene-bis(4-phenylisocyanate) (MDI) (Aldrich Chemical Co.) was distilled under reduced pressure (141°C at 0.01 mmHg). Poly(ethylene glycol) 400, 600, 2000, 4000, and 6000 were degassed under vacuum at 55°C and 600 Pa (4.5 mmHg) for 3 h, to remove any absorbed water, and then stored in a vacuum desiccator. Dimethylsulfoxide (DMSO) was distilled under reduced pressure (69°C at 9.5 mmHg). 4,4'-(Hexafluoroisopropylidene)bis(phthalic anhydride) was kindly obtained from Hoescht-Celanese (Riedel-deHaen AG) as electronic grade material (Germany) and was used as received. 4,4'-(Hexafluoroisopropylidene)bis(phthaloyl-L-leucine) diacid chloride<sup>1</sup> was prepared by the condensation of L-leucine with 4,4'-(hexafluoroisopropylidene)bis(phthalic anhydride), followed by reaction with thionyl chloride, according to the

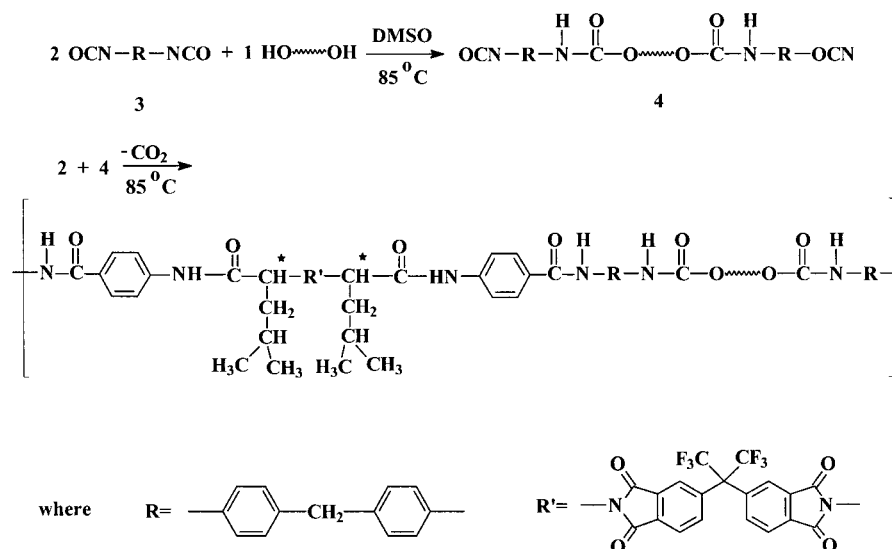
Correspondence to: S. Mallakpour (mallak@cc.iut.ac.ir).

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Step 1 (chain extension):



Step 2 (end-capping):



Scheme 1

previously reported procedure.<sup>7</sup> The yield of the diacid chloride **1** was 96.1%, m.p. = 118°C, and  $[\alpha]_D^{25}$  [0.052 g in 10 mL *N,N*-dimethylformamide (DMF)].

### Characterization

IR spectra were recorded on Shimadzu 435 IR spectrophotometer (Japan) and a Bruker-IFS 48 (Germany)

TABLE I  
Some Physical Properties of PAIUs

PEG	Polymer			
	Code	Yield (%)	$\eta_{inh}$ (dL/g) <sup>a</sup>	$[\alpha]_D^{25a}$
400	PAIU-400	86.19	0.93	+20.5
600	PAIU-600	89.08	1.38	+30.6
2000	PAIU-2000	78.37	0.58	+15.5
4000	PAIU-4000	69.51	0.45	+12.1
6000	PAIU-6000	63.10	0.29	+9.3

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMF at 25°C.

Fourier transform infrared (FTIR) spectrometer. Spectra of solids were carried out by using KBr pellets. Vibrational transition frequencies are reported in wave number ( $\text{cm}^{-1}$ ). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure by using a Cannon-Fensk routine viscometer (Germany). Specific rotations were measured by a Perkin-Elmer 241 Polarimeter (Germany). Thermal gravimetric analysis (TGA) data for polymers were taken on a Stanton-650 TGA (UK) under air atmosphere at a rate of 10°C/min and the first run of differential scanning calorimetry (DSC) data were recorded on a DSC-PL-1200 instrument (UK) under air and  $\text{N}_2$  atmosphere at a rate of 10°C/min by the Iran Polymer Institute (IPI). Elemental analyses were performed by Mallek Ashtar University of Technology (Tehran, Iran).

TABLE II  
Elemental Analysis of PAIUs

Polymer	Formula		Elemental analysis(%)		
			C	H	N
PAIU-400	$(C_{90.4}H_{94.7}F_6N_8O_{19.7})_n$ (1722.5) <sub>n</sub>	Calcd	63.00	5.50	6.50
		Found	58.00	6.80	6.20
PAIU-600	$(C_{99.5}H_{112.9}F_6N_8O_{24.2})_n$ (1922.1) <sub>n</sub>	Calcd	62.16	5.88	5.83
		Found	58.9	6.30	6.08
PAIU-2000	$(C_{163.1}H_{240.2}F_6N_8O_{56.1})_n$ (3324.7) <sub>n</sub>	Calcd	58.95	7.23	3.37
		Found	58.40	6.38	5.81
PAIU-4000	$(C_{254.0}H_{422.0}F_6N_8O_{101.5})_n$ (5326.1) <sub>n</sub>	Calcd	57.29	7.93	2.11
		Found	59.30	6.37	6.20
PAIU-6000	$(C_{344.9}H_{603.8}F_6N_8O_{147.0})_n$ (7329.1) <sub>n</sub>	Calcd	56.54	8.24	1.53
		Found	58.84	6.59	5.83

### Preparation of amide-imide chain extender

4,4'-(Hexafluoroisopropylidene)-*N,N'*-bis(phthaloyl-L-leucine-*p*-amidobenzoic acid)<sup>2</sup> was prepared by the condensation of *p*-aminobenzoic acid with diacid chloride<sup>1</sup> in DMF according to the previously reported procedure.<sup>8</sup> The yield of the diacid **2** was 85.8%,  $T_{dec}$ . 239°C,  $[\alpha]_D^{25}$  (0.05 g in 10 mL DMF).

### Synthesis of poly(amide-imide-urethane) block copolymer

A typical preparation of aromatic PAIUs was as follows: To a dried 10-mL, two-necked round-bottom flask equipped with a stirrer, condenser with a  $CaCl_2$  drying tube, thermometer, and nitrogen inlet was added 0.0599 g ( $9.98 \times 10^{-5}$  mol) of PEG-600 in 0.2 mL DMSO. To this stirred solution was added 0.050 g ( $2.00 \times 10^{-4}$  mol) of MDI and a slow stream of nitrogen was flushed during the addition. The reaction was stirred and heated at 85°C for 2.5 h. Added was 0.0907 g ( $9.98 \times 10^{-5}$  mol) of amide-imide chain extender (described above) in 1 mL DMSO to the rapidly stirred solution and a slow stream of nitrogen was flushed during the reaction. After 1 h of stirring, the viscous solution was poured into the water to isolate the poly-

mer. The precipitated polymer was collected by filtration and was dried at 80°C for 15 h *in vacuo*; this left 0.163 g (89.1%) of polymer PAIU-600.

The other copolymers were prepared in a similar manner.

#### PAIU-400

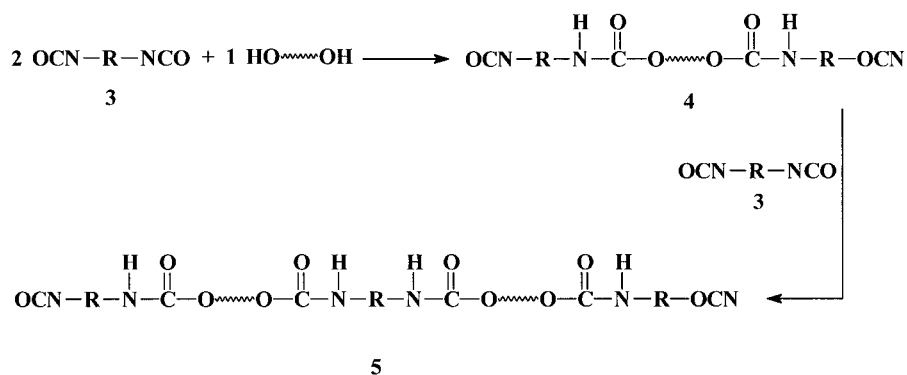
IR (KBr): 3319 (s, br), 2916 (s, br), 1778 (m), 1717 (s, br), 1599 (m), 1539 (s), 1510 (s), 1437 (m), 1414 (m), 1308 (m), 1217 (m, br), 1107 (m, br), 953 (w), 854 (w), 768 (w), 723 (m), 511(w)  $cm^{-1}$ .

#### PAIU-600

IR (KBr): 3342 (m, br), 2872 (m, br), 1780 (m), 1720 (s, br), 1599 (m), 1535 (s), 1510 (s), 1439 (m), 1308 (m), 1240 (m, br), 1105 (m, br), 951 (w), 854 (w), 750 (w), 723 (m), 509(w)  $cm^{-1}$ .

#### PAIU-2000

IR (KBr): 3350 (m, br), 2870 (m, br), 1780 (m), 1720 (s, br), 1600 (m), 1537 (s), 1510 (s), 1305 (m), 1245 (m, br), 1105 (m, br), 951 (w), 850 (w), 750 (w), 725 (m),  $cm^{-1}$ .



Scheme 2

TABLE III  
Solubility of PAIUs

Solvents	PAIU-400	PAIU-600	PAIU-2000	PAIU-4000	PAIU-6000
DMAc	+	+	+	+	+
DMF	+	+	+	+	+
NMP	+	+	+	+	+
DMSO	±	±	±	±	±
MeOH	-	-	-	-	-
EtOH	-	-	-	-	-
CHCl <sub>3</sub>	-	-	-	-	-
CH <sub>2</sub> Cl <sub>2</sub>	-	-	-	-	-
H <sub>2</sub> O	-	-	-	-	-

+, Soluble at room temperature; -, insoluble; ±, partially soluble.

### PAIU-4000

IR (KBr): 3330 (m, br), 2870 (m, br), 1780 (m, sh), 1720 (s, br), 1600 (m), 1537 (s), 1512 (s), 1410 (w), 1380 (m), 1308 (w), 1248 (m, br), 1100 (m, br), 955 (w), 856 (w), 718 (m) cm<sup>-1</sup>.

### PAIU-6000

IR (KBr): 3325 (m, br), 2918 (m, br), 1780 (m, sh), 1720 (s, br), 1601 (m), 1539 (s), 1512 (s), 1439 (w), 1381 (m), 1308 (w), 1248 (m, br), 1103 (m, br), 951 (w), 856 (w), 723 (m) cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

These block copolyurethanes are synthesized in a two-step procedure.<sup>9</sup> The equation for the first step indicates the formation of an amide-imide chain extender **2**. The formation of an isocyanate end-capped monomeric soft segment **4**, which is then chain extended with the above amide-imide, is the second step to give the (AB)<sub>n</sub> multiple block copolymer structure and la-

beled as poly(amide-imide-urethanes) or (PAIU)s (Scheme 1).

Some physical properties of the synthesized PAIU copolymers are shown in Table I. Inherent viscosity increased markedly by changing the PEG molecular weight from 400 to 600 and then decreased when PEG molecular weight varied from 600 to 6000. The reason would be related to the lower conversion of polymerization reaction in the case of PEG-400, which is because of a glassy and bulk layer formation after 15 min that was insoluble even by increasing the solvent amount. This was not observed for PEG-600 and the polymer chain was able to build up to higher molecular weight. For PEG-2000, -4000, and -6000, we were obliged to use more solvent to have a homogeneous solution in the end-capping step. This dilution caused a decrease in inherent viscosity by increasing the PEGs' molecular weight.

Elemental analysis values of the resulting polymers are listed in Table II. It was observed that the obtained

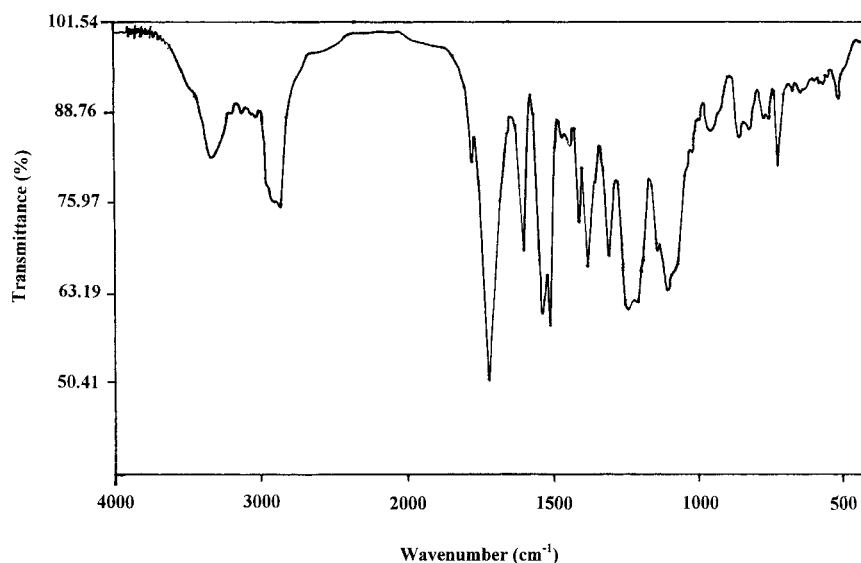


Figure 1 FTIR spectrum of PAIU-600.

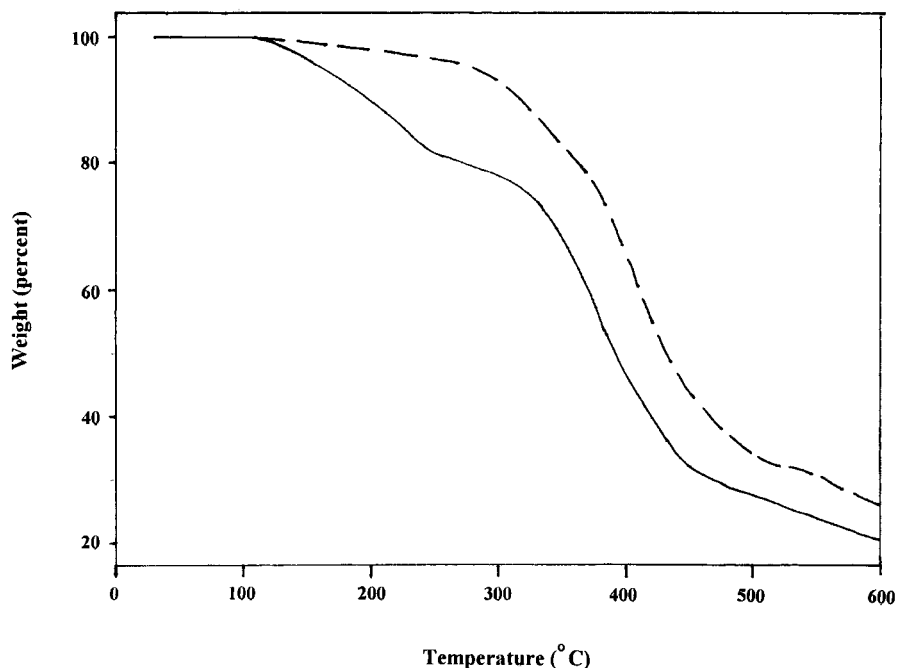


Figure 2 TGA thermograms of PAIU-400 (—) and PAIU-600 (---) with a heating rate of  $10^{\circ}\text{C min}^{-1}$  in air atmosphere.

CHN values have some differences than the calculated ones. However, computer studies<sup>10</sup> on the diisocyanate-diol reaction suggest that the copolyurethane materials are not simple  $(AB)_n$  block copolymers and could contain significant amounts of dimeric soft- and hard-repeat segments, depending upon the relative reactivities of the polydiol and the diisocyanate. The

presence of these dimeric segments will affect the overall morphology of these materials. The presence of end-capped dimeric soft segments 5 and free diisocyanate 3 (which in the second step will lead to dimeric hard segments), in addition to the end-capped monomeric soft segment 4, would give rise to more complex copolymer chain structure when this reaction

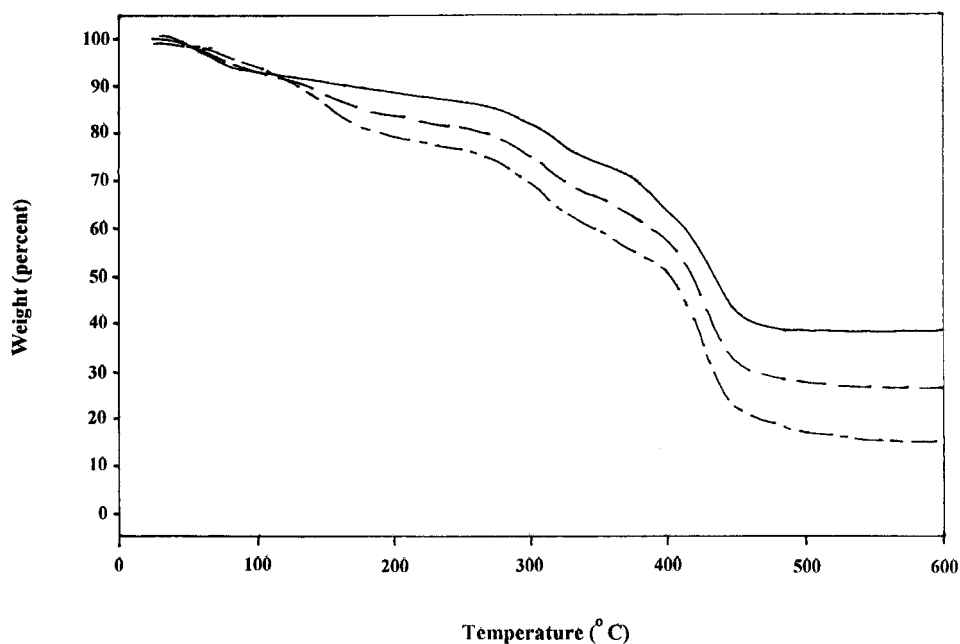


Figure 3 TGA thermograms of PAIU-2000 (—), PAIU-4000 (---), and PAIU-6000 (- · -) with a heating rate of  $10^{\circ}\text{C min}^{-1}$  in air atmosphere.

TABLE IV  
Thermal Properties of Some Aromatic PAIUs

PEG			TGA				
Code	$T_g^a$	$T_g^b$	Code	$T_g$	$T_5^c$	$T_{10}^d$	Char yield(%) <sup>e</sup>
PEG-400	-63.0	-90.5	PAIU-400	28.4	164.0	200.0	20.4
PEG-600	-60.6	-88.8	PAIU-600	65.67	288.1	320.9	26.2
PEG-2000	-58.1	-86.5	PAIU-2000	31.5	68.5	164.4	36.1
PEG-4000	-56.7	-84.7	PAIU-4000	34.3	74.0	149.3	25.9
PEG-6000	-55.9	-83.8	PAIU-6000	36.6	95.5	140.3	15.4

<sup>a</sup> Extracted from DSC thermograms.

<sup>b</sup> Extracted from Bueche eq. [14].

<sup>c</sup> Temperature at which 5% weight loss was recorded by TGA at heating rate of 10°C/min in air.

<sup>d</sup> Temperature at which 10% weight loss was recorded by TGA at heating rate of 10°C/min in air.

<sup>e</sup> Weight percent of the material left undecomposed after TGA at maximum temperature 600°C in air.

mixture is chain extended in chain extension step (step 2) (Scheme 2). This more complex structure will greatly affect the elemental analysis, microphase separation, and surface morphology of the urethane material.<sup>11</sup>

Table III summarizes the solubilities of PAIUs; most of the polymers are soluble in organic solvent such as *N,N*-dimethyl acetamide (DMAc), DMF, and NMP at room temperature, partially soluble in DMSO, and are insoluble in solvents such as chloroform, dichloromethane, methanol, ethanol, and water.

A typical FTIR spectrum of PAIU-400 is shown in Figure 1. All IR spectra show characteristic absorptions of polyurethanes between 3319 and 3350 cm<sup>-1</sup> and around 1720 cm<sup>-1</sup> because of N—H and C=O bands of urethane group. The characteristic absorption bands for the imide ring appear around 1779 cm<sup>-1</sup> (C=O). Other key features in the IR spectrum include the absorption band around 723 cm<sup>-1</sup>, owing to imide ring deformation. It is apparent that the bonded C=O band in PEG copolymers is dominant. This suggests that the domain–matrix interfaces are quite broad for the PEG-based copolymer and that more phase mixing occurs in these materials.

### Thermal analysis

TGA results for all samples are shown in Figures 2 and 3. Smooth sinusoidal TGA curves were obtained for the PAIU-400 and PAIU-600, suggesting a two-step mechanism for its thermal degradation (Fig. 2). Alternatively, the shoulder present in the TGA curves of PAIU-2000, PAIU-4000, and PAIU-6000 may denote that three stages of degradation occur. By increasing the PEG molecular weight of copolymers, the stability of PAIUs decreased and the weight loss started at a lower temperature (compare Figs. 2 and 3). If the stability parameters of the PAIUs are taken as the temperature at which 5 and 10% weight loss occurred, the same conclusion can be reached (Table IV). According to Figures 2 and 3, it has been indicated that

the initial degradation occurs in the soft segments; this may imply that the hard domains in the PEG-based sample are more perfect.

$T_g$  of PAIUs was extracted from DSC diagrams. A typical diagram for PAIU-400 and PAIU-600 has been shown in Figure 4. The soft- and hard-segments  $T_g$  values of all copolymers are similar.  $T_g$  of infinite molecular weight PEG,  $T_g(\infty)$ , is an important molecular parameter dependent on intra- and intermolecular forces.<sup>12</sup> The  $T_g(\infty)$  values may be obtained generally by at least two methods. The first involves direct experimental measurement of  $T_g$  of a polymer with sufficiently high molecular weight, because it is well known<sup>13</sup> that  $T_g$  is essentially independent of chain length when the degree of polymerization exceeds a few hundred (Table IV). Another approach is based on various extrapolation procedures of  $T_g$  for amorphous copolymers or low molecular weight homologues to obtain the value for a pure high molecular weight polymer. According to the second method and by using the plot of  $T_g$  versus (average molecular weight)<sup>-1</sup> fitted on the Bueche equation,<sup>14</sup> the data for the PEG series were also extracted (Table IV). Unfortunately, these methods often lead to discordant results. For example, the theoretical  $T_g(\infty)$  values for PEGs range from -90.5°C to -83.8°C despite the fact that their experimental values varied from -63.0°C to -55.9°C. The points for samples with  $n \geq 4$  in the PEG series with the general formula HO[CH<sub>2</sub>O]<sub>*n*</sub>(CH<sub>2</sub>)<sub>2</sub>R are reasonably close, whereas those for samples with  $n < 4$  widely diverge.

Table IV also shows char yield at 600°C in air atmosphere. In comparison with TGA results of typical polyurethanes, PAIUs show higher char residue because of the presence of imide group in the polymer chains.

### CONCLUSION

This article describes our synthetic studies on the two-step polymerization of the copoly(amide-imide-ure-

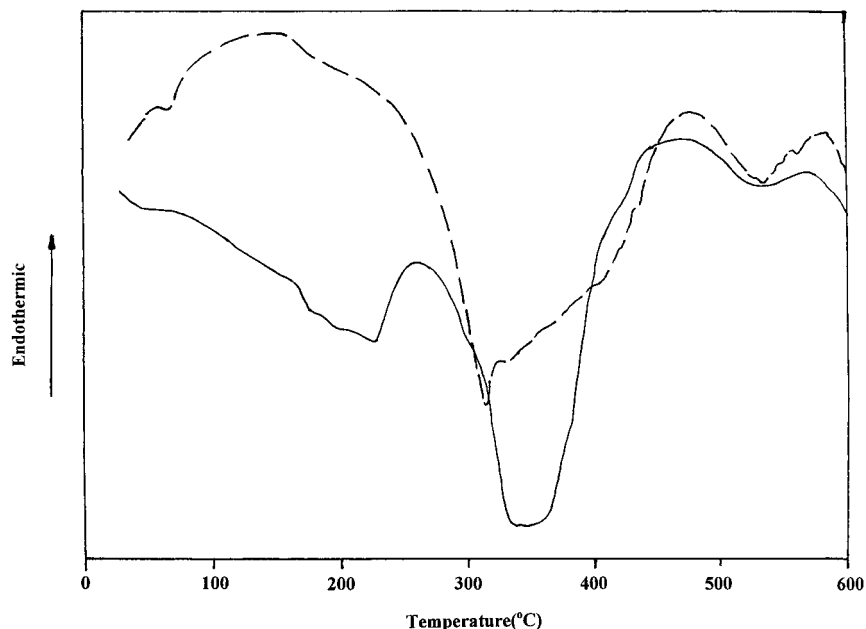


Figure 4 DSC thermograms of PAIU-400 (—) and PAIU-600 (---) with a heating rate of  $10^{\circ}\text{C min}^{-1}$  in air atmosphere.

thane) thermoplastic elastomers based on PEG with different molecular weights and 4,4'-(hexafluoroisopropylidene)-*N,N'*-bis(phthaloyl-L-leucine-*p*-amido-benzoic acid)<sup>2</sup> as chain extender, as well as the IR, TGA, and DSC data were fully investigated. Simultaneous thermal analysis (STA) diagrams indicated that the type of PAIU is generally more stable than typical polyurethanes.

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## References

1. Yi, M. H.; Jin, M. Y.; Choi, K. Y. *Angew Makromol Chem* 1955, 233, 89.
2. Lin, J. H.; Yang, C. P. *J Polym Sci, Part A: Polym Chem* 1996, 34, 747.
3. Avella, N.; Maglio, G.; Palumbo, R. *J Polym Sci, Part A: Polym Chem* 1996, 34, 1219.
4. Patel, H. S.; Mathur, A. B.; Bhardwaj, I. S. *J Macromol Sci, Pure Appl Chem* 1995, A32, 2025.
5. Kricheldorf, H. R.; Gurau, M. *J Macromol Sci, Pure Appl Chem* 1995, A32, 1831.
6. Mallakpour, S. E.; Hajipour, A. R.; Khoee, S. *Polym Int* 1999, 48, 1133.
7. Mallakpour, S. E.; Hajipour, A. R.; Khoee, S. *J Polym Sci, Polym Chem Ed* 2000, 38, 1154.
8. Mallakpour, S. E.; Hajipour, A. R.; Khoee, S. *Eur Polym Mater* 2011 2002, 38.
9. Lyman, D. J. in *Kinetics and Mechanisms of Polymerization: Step-Growth Polymerizations*; Solomon, D. H., Ed.; Dekker: New York, 1972; Chapter 3.
10. Peebles, L. H. *Macromolecules* 1974, 7, 872.
11. Wang, T. L. D.; Lyman, D. J. *J Polym Sci, Polym Chem Ed* 1993, 31, 1983.
12. Privalko, V. P.; Lipatov, Y. S. *Vysokomolek Soedin* 1971, A13, 2733.
13. Boyer, R. F. *Rubber Chem Technol* 1963, 36, 303.
14. Privalko, V. P.; Lobodina, A. P. *Eur Polym Mater* 1974, 10, 1033.