

# Synthesis and Characterization of New Optically Active Segmented Poly(amide imide urethane)s Based on Different Diacids via an Isocyanate Route

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**ABSTRACT:** A new class of optically active poly(amide imide urethane)s (PAIUs) was synthesized via a two-step diisocyanate route. In the first step, 4,4'-methylenebis(phenyl isocyanate) (MDI) was reacted with different diacids to produce an isocyanate-terminated oligo(amide imide). The chain extension of the previous hard segment with poly(ethylene glycol) diols with a molecular weight of 400 was the second step for furnishing a series of new PAIUs. *N*-Trimellitylimido-*L*-leucine was used as a diacid monomer for polycondensation reactions. Polymerization reactions were performed without any catalysts or with pyridine or dibutyltin dilaurate as a catalyst. The optimized reaction conditions were used for the reaction of *N*-trimellitylimido-*L*-isoleucine, *N*-trimellitylimido-*L*-methionine, *N*-trimellitylimido-

*s*-valine, and *N*-trimellitylimido-*L*-phenylalanine as diacid monomers with MDI. The resulting multiblock copolymers had inherent viscosities of 0.25–0.78 dL/g. These multiblock copolymers were optically active, thermally stable, and soluble in amide-type solvents. All these polymers were fully characterized with Fourier transform infrared spectroscopy, <sup>1</sup>H-NMR and ultraviolet–visible spectroscopy, specific rotation measurements, and thermal analyses. Some structural characteristics and physical properties of these new optically active PAIUs were examined. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2975–2982, 2008

**Key words:** biocompatibility; biodegradable; FT-IR; polycondensation; thermogravimetric analysis (TGA)

## INTRODUCTION

Segmented polyurethanes (SPUs) are multiphase copolymers that show a two-phase microstructure, which is due to the chemical incompatibility between the soft and hard segments. The hard, rigid segment separates out into a glassy or semicrystalline domain, and the polyol soft segments form amorphous or rubbery surrounding substances in which the hard segments are dispersed.<sup>1–3</sup> SPUs with the best mechanical properties are normally synthesized from aromatic diisocyanates, mostly 4,4'-methylenebis(phenyl isocyanate) (MDI), polyether or polyester diols, and short-chain aliphatic diols (chain extenders).<sup>4</sup> SPUs are employed in various applications in many industries. Polymers have been made with a large variety of functional groups as a way of modifying their morphology and properties for dif-

ferent applications.<sup>5</sup> Therefore, the preparation, characterization, and exploration of their structure–property relations have constituted a very dynamic field for both industrial and academic researchers for many years.<sup>6</sup> These macromolecules allow the generation of promising new materials, and this is mainly due to the way in which they are prepared and the wide range of components that can be used to form different polyurethanes (PUs).<sup>7</sup>

Unfortunately, conventional PUs usually display deprived resistance to heat, which restricts their applications.<sup>8</sup> The satisfactory mechanical properties (strength, moduli, etc.) vanish around 80–90°C, and thermal degradation occurs above 200°C. Thus, more attention has been paid to the modification of these macromolecules by the introduction of heterocyclic groups into the backbone of PUs.<sup>9–12</sup> Polyimides (PIs) with aromatic heterocyclic structures are heat-resistant and have good chemical and electrical properties. Because of their outstanding thermal stability and mechanical properties,<sup>8</sup> their applicability can be maintained even after revelation at 500°C and higher for several minutes or at 300°C for a couple of months. Although PIs have several better properties, their applications are limited because they have high glass-transition temperature ( $T_g$ ) and melting temperature values. In other terms, the processing of

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PIs is hard and is subject to many tribulations. An effective method for improving the solubility and processibility of PIs is the introduction of several flexible groups into the macromolecule backbone and the preparation of some copolymers such as poly(ether imide), poly(urea imide), poly(amide imide), poly(urethane imide), and silicon-containing poly(urethane imide).<sup>13–15</sup>

Moreover, polymers and copolymers with a number of polar groups (usually oxygen, nitrogen, and sulfur) have been studied, and macromolecular electrolytes based on host polymer matrices integrating oxyethylene chains (i.e., CH<sub>2</sub>—CH<sub>2</sub>—O repeating units) have been found to yield the maximum ionic conductivities. From the aforementioned knowledge essential for designing a novel polymer with a structure resembling poly(ethylene glycol) (PEG), it is expected that PEG-based PUs will also act as hosts for polymer electrolytes. SPUs, like the PEG/diisocyanate system, are a class of macromolecules whose structures and properties can be comparatively diverse, ranging from tough plastics to soft elastomers through the variation of the soft segment, hard segment, or chain extender or through the alteration of their molar ratios.<sup>16</sup>

In addition, the synthesis of macromolecules containing amino acids is a subject of much interest.<sup>17</sup> Because amino acids are naturally occurring compounds, synthetic poly( $\alpha$ -amino acids)s and their copolymers would likely be biodegradable, biocompatible, and nontoxic.<sup>18</sup> Moreover, amino acid based chiral copolymers can incorporate crystallinity with the ability to form higher ordered structures that exhibit improved solubility.<sup>19,20</sup> Synthetic macromolecules containing amino acids are potentially biodegradable because of the incorporation of amino acids, which can be targeted for cleavage by enzymes such as proteases.<sup>21</sup> Lately, more attention has been paid to the synthesis and application of new optically active polymers with chiral structures, which are biologically very significant.<sup>22</sup> For example, interest in macromolecular conjugation with biologically active components has increased amazingly. According to the location and the form of action, macromolecular conjugates possess either tuned degradable or nondegradable bonds. To obtain such bonds, nearly every strategy involves the incorporation of amino acids, peptides, or small chains as spacer molecules through multiple steps to impart protection and deprotection.<sup>23</sup>

The synthesis and applications of chiral polymers are of particular interest from the perspective of materials science. The use of chiral polymers is flourishing in the chromatographic separation of enantiomers, chiral liquid crystals, nonlinear optical devices, optical switches, biomedical devices, chiral media for asymmetric synthesis, polymeric chiral catalysts, and so

on.<sup>24–28</sup> A direct and effective method for synthesizing chiral macromolecules is to incorporate a chiral structure into the polymer backbone or side chains. The amalgamation of PAIs with a chiral group is of synthetic interest and may also lead to chiral recognition membranes.<sup>29</sup> Pu and coworkers<sup>30,31</sup> developed a new way of preparing optically active macromolecules with main-chain chirality by incorporating chiral units into rigid polymer backbones. For instance, polymeric chiral catalysts were prepared by the connection of a suitable monomeric chiral catalyst to sterically irregular polymer backbones.

We synthesized different optically active polymers such as PAIs and poly(ester imide)s through the reaction of optically active monomers with several diamines, diols, and diisocyanates via polycondensation.<sup>32–39</sup> In connection with our interest in preparing optically active thermally modified polymers, here we describe the synthesis and characterization of segmented poly(amide imide urethane)s (PAIUs) with main-chain chirality through the polycondensation reactions of *N*-trimellitylimido-*L*-leucine (TMILL or **3a**), *N*-trimellitylimido-*L*-isoleucine (TMILL or **3b**), *N*-trimellitylimido-*L*-methionine (TMILM or **3c**), *N*-trimellitylimido-*s*-valine (TMISV or **3d**), and *N*-trimellitylimido-*L*-phenylalanine (TMILP or **3e**) with MDI and subsequent chain extension with poly(ethylene glycol) with a molecular weight of 400 (PEG-400). In our previous work, we studied the synthesis and properties of SPUs based on MDI and different polyether polyols and investigated the effect of the incorporation of an aromatic diacid with a preformed imide ring and amide linkage based on *L*-leucine.<sup>17,37–39</sup> In this work, the effects of the incorporation of different diacid monomers based on different amino acids with aromatic-aliphatic carboxylic acid functionality are studied. In these macromolecules, amide linkages are constructed during the polycondensation reactions of diacids with MDI.

## EXPERIMENTAL

### Materials

PEG-400 (Riedel-de Haën AG, Seelze, Germany) was dried *in vacuo* at 80°C for 6 h. Pyridine (Py; Merck, Darmstadt, Germany) and 1-methyl-2-pyrrolidone (NMP; Merck) were dried over BaO and distilled under reduced pressure. MDI (Aldrich, Milwaukee, WI) was used as received. Trimellitic anhydride (TMA or **1**) was recrystallized in an acetic acid/acetic anhydride mixture (3/1) and dried *in vacuo* at 60°C for 6 h.

### Instruments and measurements

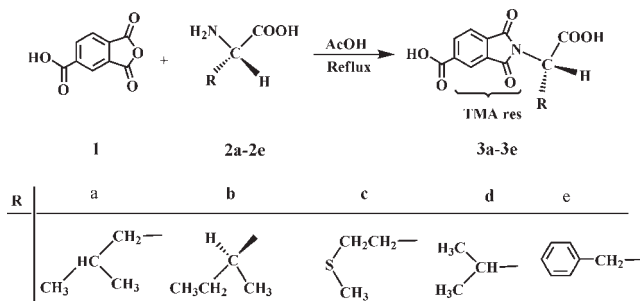
<sup>1</sup>H-NMR (300 MHz) spectra were recorded in a dimethyl sulfoxide (DMSO)-*d*<sub>6</sub> solution with a Bruker (Ettlingen, Germany) Avance 300 instrument. Multi-

plicities of proton resonance were designated as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), or multiplet (m). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Impact 400D IR spectrophotometer (Thunderdome, Germany). Spectra of solids were taken with KBr pellets. Vibrational transition frequencies are reported as wave numbers ( $\text{cm}^{-1}$ ). Band intensities were designated as weak (w), medium (m), shoulder (sh), strong (s), or broad (br). Inherent viscosities were measured by a standard procedure with a Cannon-Fenske routine viscometer (Cannon, Mainz, Germany). Specific rotations were measured with a Jasco (Toyonaka, Osaka, Japan) polarimeter to determine the incorporation of the chiral structure into the polymer backbone. Thermogravimetric analysis (TGA) data for polymers were taken on a PerkinElmer (Karlsruhe, Germany) thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ , and the first-run differential scanning calorimetry (DSC) data were recorded on a DSC-PL-1200 instrument (London, UK) under a nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$  by the Research Institute of Polymers and Petrochemicals of Iran.

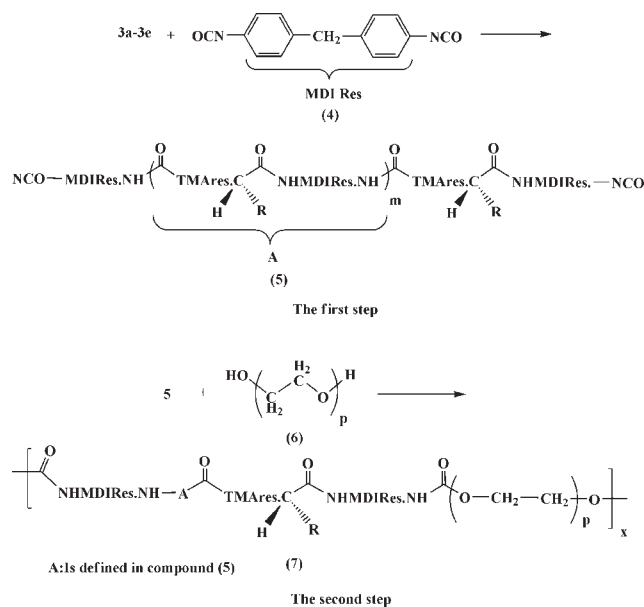
### Synthesis of the monomer TMILM (3c)

For the synthesis of TMILM (3c), into a 25-mL, round-bottom flask equipped with a magnetic stirrer, 1.0 g ( $5.20 \times 10^{-3}$  mol) of TMA (1), 0.776 g ( $5.20 \times 10^{-3}$  mol) of L-methionine, and 25 mL of acetic acid were placed. The solution was stirred for 2 h to yield amic acid, and then the mixture was refluxed for 8 h. The solvent was removed under reduced pressure, and the mixture was poured into 20 mL of a 5% HCl solution. A white precipitate was formed, filtered off, washed with water, and dried to yield 1.52 g (86%) of the diacid (3c). Recrystallization from methanol/water gave white crystals.

mp:  $195\text{--}197^\circ\text{C}$ . FTIR (KBr): 2400–3400 (br), 1779 (m, sh), 1725 (s), 1487 (m), 1418 (m), 1381 (s), 1279 (s), 1203 (m), 1169 (m), 1121 (m), 1103 (s), 953 (m), 898 (w), 804 (s), 756 (w, sh), 731 (s),  $568\text{ cm}^{-1}$  (m).  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-}d_6$ ,  $\delta$ ): 1.99 (s, 3H), 2.25



**Scheme 1** Synthesis of the optically active monomers TMILL, TMIIL, TMILM, TMISV, and TMILP (3a–3e).



**Scheme 2** Copolymerization reactions of MDI with the diacid monomers TMILL, TMIIL, TMILM, TMISV, and TMILL (3a–3e) with a molar ratio of 2 : 1 and chain extension of an NCO-terminated oligo(amide imide) by PEG-400.

(m, 2H), 2.53 (m, 2H), 4.96 (distorted dd, 1H,  $J = 7.2$  Hz), 8.01 (d, 1H,  $J = 7.7$  Hz), 8.25 (s, 1H), 8.38 (d, 1H,  $J = 7.7$  Hz), 13.54 ppm (s, 2H). Mass (electron ionization (EI),  $m/z$ ): 323 ( $[\text{M}^+]$ , 8%), 231 (100%), 176 (60%), 148 (52%), 75 (30%), 61 (55%).  $[\alpha]_D^{25}$ :  $-5.8$  [0.050 g in 10 mL of *N,N*-dimethylformamide (DMF)].

TMILL (3a), TMIIL (3b), TMISV (3d), and TMILP (3e) were prepared according to our previous work.<sup>32,33,35,36</sup>

### Synthesis of the PAIU block copolymers

A typical preparation of PAIUs was as follows. In a 10-mL, round-bottom flask, TMILL (3a; 0.1020 g,  $3.35 \times 10^{-4}$  mol) was heated up to  $190^\circ\text{C}$  in the presence of one drop of NMP; then, MDI (2; 0.0744 g,  $2.97 \times 10^{-4}$  mol) was added, and the clear reaction mixture was stirred at  $190^\circ\text{C}$  for 1 min. The temperature was reduced, and the reaction mixture was stirred for 1 min at  $120^\circ\text{C}$ . After cooling, it was heated gradually from  $60$  to  $90^\circ\text{C}$  for 3 h, at  $100^\circ\text{C}$  for 2 h, and finally at  $120^\circ\text{C}$  for 1 h. During this period, 0.2 mL of NMP was added. Then, the temperature was reduced, and a solution of PEG-400 (0.1340 g,  $3.35 \times 10^{-4}$  mol) in 0.18 mL of NMP was added at room temperature (RT). The solution was stirred for 2 min at RT, and then 0.027 mL ( $6.68 \times 10^{-4}$  mol) of Py and 0.02 mL of NMP were added. The solution was heated at  $80\text{--}90^\circ\text{C}$  for 5 h, at  $100^\circ\text{C}$  for 3 h, and finally at  $120^\circ\text{C}$  for 2 h. The viscous solution was poured into 10 mL of water. The precipitated polymer was collected by filtration and was dried at  $80^\circ\text{C}$  for 10 h *in vacuo* to give 0.281 g (72%) of PAIU1.

All the polymers showed FTIR absorption peaks at 3410, 2956, 1776, 1720, 1665, 1532, 1409, 1235, and

TABLE I  
Reaction Conditions and Physical Properties of PAIUs<sup>a</sup>

Polymer	Catalyst	Reaction condition		Yield (%)	Viscosity (dL/g) <sup>b</sup>	[ $\alpha$ ] <sub>D</sub> <sup>25c</sup>	[ $\alpha$ ] <sub>Hg</sub> <sup>25d</sup>
		Step 1	Step 2				
PAIU1	Py	A	B	72	0.56	+1.58	+0.78
PAIU2	No catalyst	A	B	90	0.57	-6.12	—
PAIU3	DBTDL	A	B	75	0.76	-1.08	-0.24
PAIU4	DBTDL	A	B	88	0.25	-1.52	+8.10
PAIU5	DBTDL	A	B	80	0.58	-0.72	—
PAIU6	DBTDL	A	B	60	0.49	-4.94	-5.84
PAIU7	DBTDL	A	B	80	0.32	+2.26	+2.84
PAIU3(1)	DBTDL	A	B	74	0.75	-1.20	-0.22
PAIU3(2)	DBTDL	A	B	73	0.77	-1.30	-0.20
PAIU3(3)	DBTDL	A	B	71	0.76	-1.22	-0.31
PAIU3(4)	DBTDL	A <sub>1</sub>	B	75	0.78	-1.19	-0.20
PAIU3(5)	DBTDL	A <sub>2</sub>	B	70	0.71	-1.27	-0.27
PAIU3(6)	DBTDL	A <sub>3</sub>	B	73	0.76	-1.20	+0.25
PAIU3(7)	DBTDL	A <sub>4</sub>	B	72	0.69	+1.19	+0.20
PAIU3(8)	DBTDL	A	B <sub>1</sub>	71	0.62	-1.10	-0.23
PAIU3(9)	DBTDL	A	B <sub>2</sub>	68	0.60	+0.08	+0.04
PAIU3(10)	DBTDL	A	B <sub>3</sub>	75	0.61	+1.02	+0.02
PAIU3(11)	DBTDL	A	B <sub>4</sub>	70	0.42	+0.97	+0.20

PAIU1–PAIU3 = PAIU based on TMILL (**3a**) as a diacid; PAIU3(1)–PAIU3(11) = PAIU based on TMILL (**3a**) as a diacid; PAIU4 = PAIU based on TMILL (**3b**) as a diacid; PAIU5 = PAIU based on TMILM (**3c**) as a diacid; PAIU6 = PAIU based on TMISV (**3d**) as a diacid; PAIU7 = PAIU based on TMILP (**3e**) as a diacid; A = 3 h at 60–90°C, 2 h at 100°C, and 1 h at 120°C; B = 5 h at 80–90°C, 3 h at 100°C, and 2 h at 120°C; A<sub>1</sub> = 3 h at 80–90°C, 3 h at 100°C, and 1 h at 120°C; A<sub>2</sub> = 3 h at 80–90°C, 2 h at 100°C, and 2 h at 120°C; A<sub>3</sub> = 4 h at 80–90°C, 2 h at 100°C, and 2 h at 120°C; A<sub>4</sub> = 4 h at 80–90°C, 2 h at 100°C, 1 h at 120°C, and 1 h at 130°C; B<sub>1</sub> = 6 h at 80–90°C, 3 h at 100°C, and 2 h at 120°C; B<sub>2</sub> = 5 h at 80–90°C, 4 h at 100°C, and 2 h at 120°C; B<sub>3</sub> = 5 h at 80–90°C, 3 h at 100°C, and 3 h at 120°C; B<sub>4</sub> = 5 h at 80–90°C, 3 h at 100°C, and 3 h at 120°C.

<sup>a</sup> All these polymerization reactions were performed in NMP as a solvent and were precipitated in water.

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

<sup>c</sup> Measured under the same condition for the viscosity with a sodium lamp.

<sup>d</sup> A wide range was used (no filter was used for the mercury lamp). It was measured with a mercury lamp.

725 cm<sup>-1</sup> related to the urethane, amide N–H, aliphatic C–H, urethane, and amide carbonyl groups and imide I, II, III, and IV vibrations.

FTIR peaks (cm<sup>-1</sup>, KBr) for PAIU1: 3331 (m, br, NH v), 3121 (m, NH v), 2956 (m), 2921 (m), 2870 (m), 1775 (m, C=O urethane, amide I; non-hydrogen-bonded), 1718 (s, C=O urethane, amide I; hydrogen-bonded), 1671 (s, C=O, amide I), 1598 (s), 1535 (s, C–N v + NH, amide II), 1509 (s), 1410 (m), 1382 (s), 1316 (s, C–N v + NH, amide IV), 1232 (m, C–N v + NH, amide V), 1085 (m, C–O–C, ether), 944 (w), 917 (w), 814 (w), 772 (w), 727 (w, O=C–O), 610 (w), 511 (w).

The aforementioned polymerization method was also carried out with dibutyltin dilaurate (DBTDL) as a catalyst and without a catalyst (PAIU1–PAIU3). Then, the best catalytic condition for the inherent viscosity was used for the reactions of different diacids with MDI to prepare PAIU4–PAIU7.

## RESULTS AND DISCUSSION

### Monomer synthesis

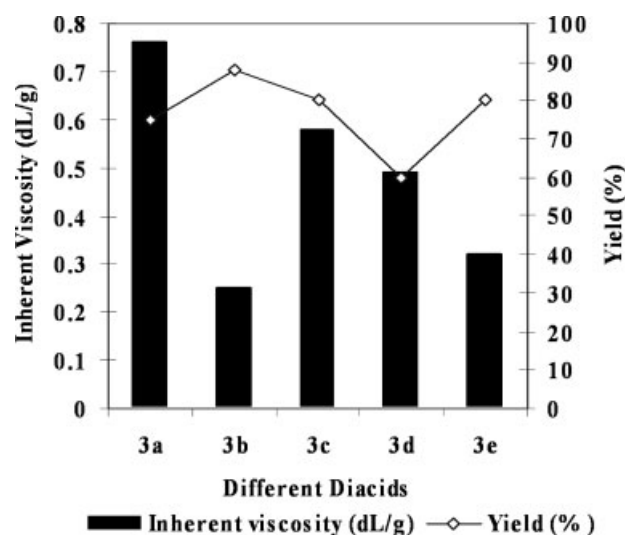
The unsymmetrical aliphatic–aromatic dicarboxylic acids **3a–3e** were prepared by the condensation reac-

tion of equimolar amounts of TMA (**1**) and amino acids **2a–2e** in refluxing acetic acid (Scheme 1). This method afforded chiral dicarboxylic acids with a preformed imide ring to incorporate chiral and thermally stable units into the polymer backbones. The aliphatic–aromatic diacids TMILL (**3a**), TMILL (**3b**), TMILM (**3c**), TMISV (**3d**), and TMILP (**3e**) were prepared according to our previous work.<sup>32–36</sup>

### Polymer synthesis

The PEG-based PAIU multiblock copolymers were synthesized according to Scheme 2 by a two-step method. In the two-step procedure, a solution of a diisocyanate-terminated oligo(amide imide) (**5**) was prepared through the reaction of MDI and TMILL in a molar ratio of 2/1 in NMP in the presence of Py or DBTDL or without any catalyst. Then, PEG-400 (**6**) was added to the solution of **5**, and this afforded PEG-based PAIU multiblock copolymers PAIU1–PAIU3 (**7**), whose poly(amide imide) blocks were connected with urethane linkages (Table I). The viscosities of PAIUs based on TMILL in the presence of Py and in the absence of any catalysts were comparable, and the highest viscosity was obtained in the



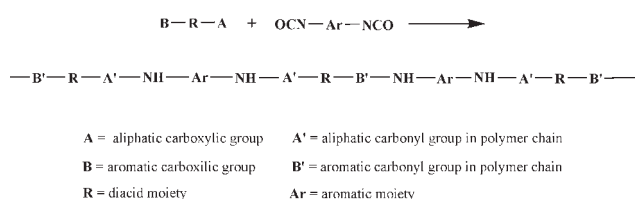


**Figure 1** Effects of different types of diacids on the yields and inherent viscosities of PAIUs.

presence of DBTDL. The optimized catalytic reaction conditions obtained for the copolymerization reaction of TMILL were used for the reactions of diacids **3b–3e** (Scheme 2). The effects of the polymerization reaction time and temperature were also studied. Thus, in one method, MDI was added to the molten diacid (**3a**), and then the temperature was decreased up to 60°C and again gradually increased. In another method, a solution of MDI in NMP was added to a solution of the diacid (**3a**) in NMP at RT, and then the temperature was gradually increased. The viscosities and yields of polymers resulting from the former method were higher than those of the polymers from the latter method.

To investigate the effects of changes in the hard-segment composition with changing diacid monomers, the polymerization reactions were carried out through the reaction of MDI with TMILL (**3b**), TMILM (**3c**), TMISV (**3d**), or TMILP (**3e**) in NMP as a solvent and in the presence of DBTDL as a catalyst. Among diacids **3a–3e**, TMILL (**3a**) and TMILM (**3c**) afforded polymers with the highest viscosities (Table I and Fig. 1).

The incorporation of a chiral unit into the polymer backbone was confirmed by the measurement of the



**Scheme 3** Presentation of random head-to-tail or tail-to-head polymerization.

**TABLE II**  
Thermal Properties of PAIU3, PAIU5, PAIU6, and PAIU7

Polymer	$T_5$ (°C) <sup>a</sup>	$T_{10}$ (°C) <sup>b</sup>	Char yield (%) <sup>c</sup>	$T_g$	$T_c$
PAIU3	267	273	41	180	264
PAIU5	288	295	26	192	284
PAIU6	287	295	30	— <sup>d</sup>	— <sup>d</sup>
PAIU7	272	275	37	182	270

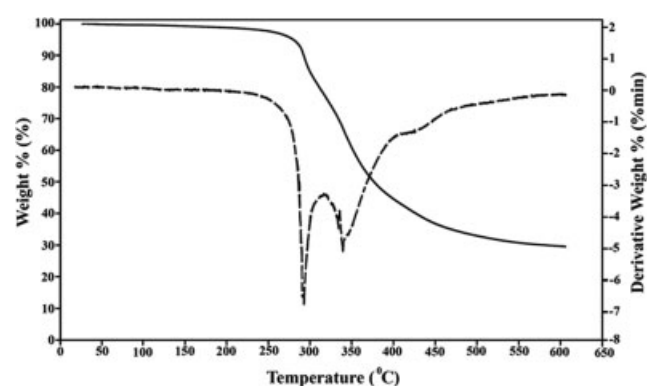
<sup>a</sup> Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10°C/min under a nitrogen atmosphere.

<sup>b</sup> Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min under a nitrogen atmosphere.

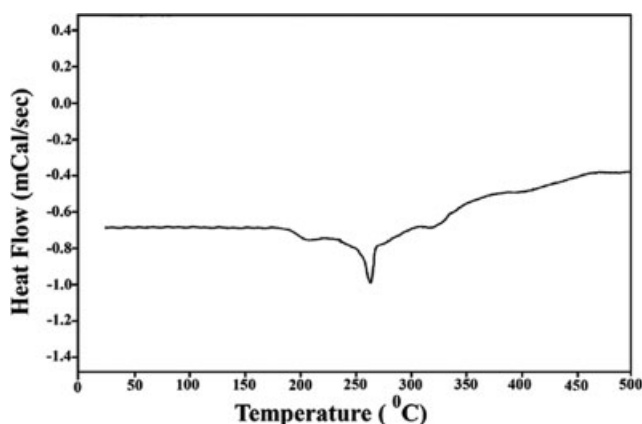
<sup>c</sup> Weight percentage of material left undecomposed after TGA at a temperature of 600°C under a nitrogen atmosphere.

<sup>d</sup> DSC was not determined.

specific rotations. The effects of the monomer, catalyst, reaction time, and temperature on the specific rotations were studied. The specific rotations of polymers based on the same diacid prepared under different catalytic conditions were different (Table I, PAIU1–PAIU3). Polymers based on the same diacid prepared under the same catalytic conditions with different batches showed similar specific rotations [Table I, PAIU3(1)–PAIU3(3)]. The specific rotations of polymers based on different diacids and/or under different catalytic conditions showed random changes (Table I, PAIU3–PAIU7). Polymers prepared by the reaction of the same monomers with different reaction times and temperatures showed different specific rotations [Table I, PAIU3(4)–PAIU3(11)]. This is a normal behavior for all optically active compounds. Because the optical rotation is highly dependent on the chemical structures of the resulting polymeric materials, any small changes in the chemical structures of any chiral molecules have substantial random effects on the optical rotations



**Figure 2** TGA thermogram of PAIU6 under a nitrogen atmosphere at a heating rate of 10°C/min.



**Figure 3** DSC curve of PAIU3 under a nitrogen atmosphere at a heating rate of 10°C/min.

that are not predictable. Therefore, in this investigation, during polymerizations under different conditions, different molecular structures could be formed. It is very important to mention that under different reaction conditions, different inherent viscosities were also obtained, which could have substantial effects on the optical rotations. It is also worth mentioning that the polymerizations of these monomers with MDI, as shown in Scheme 3, can randomly occur either head to tail (the reaction of the aliphatic carboxylic acid group with NCO) or tail to head (the reaction of the aromatic carboxylic acid group with NCO), and this can produce macromolecules with different molecular structures. Therefore, the resulting polymers showed different specific rotations. In our previous work,<sup>37–39</sup> we also observed random changes in specific rotations by

changing different parameters such as the reaction time and temperature and catalyst.

### Thermal properties

The thermal properties of PAIUs were evaluated with TGA and DSC techniques (Table II). TGA results for PAIU6 are shown in Figure 2. The TGA curves of PAIU3, PAIU6, and PAIU7 show a smooth stepwise character, suggesting a two-step thermal degradation. The TGA curve of PAIU5 shows one-step thermal degradation. If the thermal stability parameters of the PAIUs are taken as the temperatures at which 5 and 10% weight losses occurred, it can be concluded that the order of the initial thermal stability of PAIUs based on different diacids is as follows: PAIU5 ≥ PAIU6 > PAIU7 > PAIU3 (Table II). It can be concluded that with an increase in the amino acid side-chain branch, the initial thermal stability decreases. Table II also presents char yields of polymers at 600°C. PAIU3 and PAIU7 had higher char yields than PAIU6 and PAIU5, respectively. Thus, in comparison with typical PUs,<sup>8</sup> these PAIUs possessed higher 10% weight loss temperatures and char residues because of the presence of imide and aromatic groups in the polymer chains.

Thermal behaviors of PAIUs were also studied by the DSC technique. A typical DSC diagram for PAIU7 is shown in Figure 3. The DSC curve of PAIU3 shows a baseline change around 180°C that can be assigned to  $T_g$  and an endotherm around 264°C that can be assigned to melting of the crystalline domain of the hard segment distributed in the soft segment ( $T_c$ ) accompanied by oxidative decom-

**TABLE III**  
**<sup>1</sup>H-NMR and FTIR Characterization of PAIUs**

PAIU1	FTIR peaks (cm <sup>-1</sup> ): 3331 (m, br, NH v), 3121 (m, NH v), 2956 (m), 2921 (m), 2870 (m), 1775 (m, C=O urethane, amide I, non-hydrogen-bonded), 1718 (s, C=O urethane, amide I, hydrogen-bonded), 1671 (s, C=O, amide I), 1598 (s), 1535 (s, C–N v + NH, amide II), 1509 (s), 1410 (m), 1382 (s), 1316 (s, C–N v + NH, amide IV), 1232 (m, C–N v + NH, amide V), 1085 (m, C–O–C, ether), 944 (w), 917 (w), 814 (w), 772 (w), 727 (w, O=C–O), 610 (w), 511 (w).	
PAIU3	<sup>1</sup> H-NMR peaks (ppm): 0.91 (distorted d, CH <sub>3</sub> ), 1.15 (distorted d, CH <sub>3</sub> ), 1.46 (m, br, CH), 1.85–2.02 (m, CH <sub>2</sub> ), 2.11–2.35 (m, CH <sub>2</sub> ), 2.71 (s, CH <sub>2</sub> ), 3.85 (m, CH <sub>2</sub> ), 4.91 (distorted dd, CH), 7.15–7.41 (m, Ar–H), 8.10 (distorted d, CH, TMA), 8.42 (distorted d, CH, TMA), 8.55 (s, br, CH, TMA), 9.91–10.62 (s, NH).	
PAIU4	FTIR peaks (cm <sup>-1</sup> ): 3548 (s, br), 3477 (m), 3412 (m), 2959 (m, sh), 2924 (m), 2854 (m, sh), 1776 (w), 1718 (s), 1662 (m), 1598 (s), 1538 (s), 1411 (m), 1382 (m), 1315 (m), 1233 (m), 1201 (m), 1105 (w), 1018 (w), 916 (w), 856 (w), 728 (w), 613 (w), 511 (w).	
PAIU5	FTIR peaks (cm <sup>-1</sup> ): 3412 (s, br), 2922 (s, sh), 2852 (s), 1776 (m), 1719 (s), 1663 (s), 1598 (s), 1535 (s), 1509 (s), 1410 (s), 1381 (s), 1314 (s), 1232 (s), 1102 (m), 917 (w), 814 (w), 727 (w), 700 (w), 609 (w), 489 (w).	<sup>1</sup> H-NMR peaks (ppm): 1.20 (s, CH <sub>3</sub> ), 1.54 (distorted t, CH <sub>2</sub> ), 2.01–2.62 (distorted dd, CH <sub>2</sub> ), 3.63 (s, CH, overlapped with H <sub>2</sub> O), 3.81–4.15 (m, CH <sub>2</sub> ), 4.91 (m, CH), 7.01–7.35 (distorted dd, Ar–H), 8.02–8.60 (m, CH, TMA), 9.70–10.53 (s, NH).
PAIU6	FTIR peaks (cm <sup>-1</sup> ): 3310 (m, br), 3140 (w), 3050 (w), 2950 (w), 2924 (w), 2890 (w), 1790 (w), 1730 (s), 1719 (s), 1600 (s), 1540 (s), 1506 (s), 1421 (s), 1380 (m), 1310 (s), 1232 (s), 1195 (w), 1170 (w), 1099 (w), 900 (w), 840 (w), 800 (w), 750 (w), 500 (m).	
PAIU7	FTIR peaks (cm <sup>-1</sup> ): 3412 (s, br), 2920 (m, sh), 1776 (m), 1719 (s), 1597 (s), 1536 (s), 1509 (s), 1410 (s), 1383 (s), 1309 (s), 1227 (s), 1101 (s), 946 (w), 813 (w), 765 (w), 727 (w), 608 (w), 519 (w).	

TABLE IV  
UV-vis Characterization of PAIU2 and PAIU7

Sample	$\lambda_{\max}$ (nm) <sup>a</sup>
TMA	224 (0.81), 232 (sh, 0.79), 267 (0.10), 281 (0.10), 289 (0.10) <sup>b</sup>
TMILL	226 (0.82), 319 (0.53), 321 (0.05) <sup>b</sup>
PAIU2	265 (0.85), 316 (sh, 0.21) <sup>c</sup>
TMILP	265 (0.80), 308 (sh, 0.61) <sup>d</sup>
PAIU7	264 (0.98), 342 (sh, 0.1) <sup>c</sup>

<sup>a</sup> The numbers in parentheses are values of  $A$ .

<sup>b</sup> Measured at a concentration of  $1.25 \times 10^{-5}$  g/dL in DMF at 25°C.

<sup>c</sup> Measured at a concentration of  $2.05 \times 10^{-4}$  g/dL in DMF at 25°C.

<sup>d</sup> Measured at a concentration of  $8.50 \times 10^{-3}$  g/dL in DMF at 25°C.

position. The DSC curve of PAIU5 shows an endotherm around 284°C as  $T_c$  or oxidative decomposition. The DSC curve of PAIU7 shows a baseline change around 182°C that can be assigned to  $T_g$  and an endotherm around 270°C associated with  $T_c$ ; it is very important to mention that this endotherm overlaps with the thermal degradation assigned in the TGA thermogram.

### Characterization

The resulting PAIUs were characterized with FTIR spectroscopy and <sup>1</sup>H-NMR and ultraviolet-visible (UV-vis) spectroscopy. The results are shown in Tables III and IV, respectively. The <sup>1</sup>H-NMR spectrum of PAIU5 illustrates peaks that confirm its chemical structure (Fig. 4). It shows a peak for CH<sub>3</sub> (1) that appears as a singlet at 1.20 ppm. Peaks for CH<sub>2</sub> (2) appear as broad distorted triplets at 1.54 ppm according to their coupling with CH<sub>2</sub> (3,3'). The peaks in the region of 2.01–2.62 ppm are related to diastereotopic hydrogens of CH<sub>2</sub> (3,3'), which appear as a distorted doublet of doublet. The peaks in the region of 3.63 ppm are related to CH<sub>2</sub> (4), which overlaps with H<sub>2</sub>O. Peaks in the region of 3.81–4.15 ppm pertain to CH<sub>2</sub> (5 and 6). Peaks at 4.91 ppm are assigned to CH (7). The aromatic protons appear in the region of 7.01–8.60 ppm. Peaks in the region of 8.02–8.60 ppm are related to the TMA ring moiety. The peaks in the region of 9.70–10.53 ppm are assigned to NH of amide and urethane groups.

The FTIR spectra of PAIUs showed peaks that confirmed their chemical structures. For example, the FTIR spectrum of PAIU4 showed IR absorption peaks at 3410, 2956, 1776, 1720, 1665, 1532, 1409, 1235, and 725 cm<sup>-1</sup> related to the urethane and amide N–H, aliphatic C–H, imide I, II, III, and IV vibrations, urethane and amide carbonyl groups, and imide ring moiety (Fig. 5).

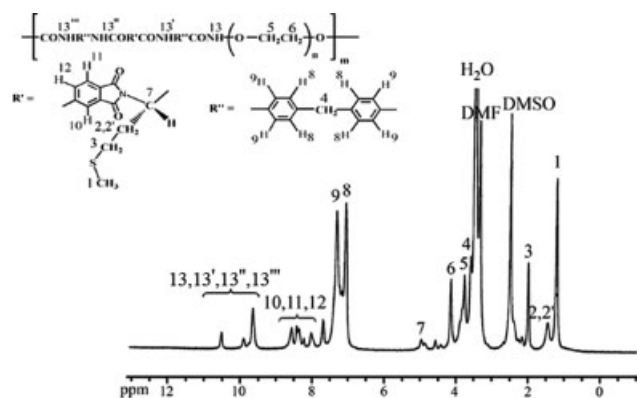


Figure 4 <sup>1</sup>H-NMR (300 MHz) spectrum of PAIU5 in DMSO-*d*<sub>6</sub> at RT.

The UV-vis spectra of the PAIUs, including PAIU2 and PAIU7, were recorded in DMF as a solvent. The positions of the absorbent bands ( $\lambda$ ) and their intensities ( $A$ ) are reported in Table IV. The UV-vis spectra of TMA, TMILL, and TMILP were also recorded to compare the spectra of the polymers with their basic components. The maximum absorption band of TMA appeared at  $\lambda = 224$  nm. Different absorption bands with a lower intensity also appeared at  $\lambda$  values of 267, 281, and 289 nm, respectively. The UV-vis spectrum of diacid TMILL showed similar behavior, but the  $\lambda$  values shifted to higher wavelengths (redshift). The  $\lambda$  values were 266, 319, and 321 nm, respectively. Similarly, in the case of PAIU2 and PAIU7,  $\lambda_{\max}$  appeared at 265 and 364 nm, respectively. The position of the maxima of the absorption bands of TMA, TMILL, TMILP, and their related polymers showed redshifts with a comparative increase in the number of aromatic rings and conjugated systems (Table IV).

### Solubility properties of the PAIUs

The solubility properties of PAIUs were studied in different solvents (Table V). These polymers were

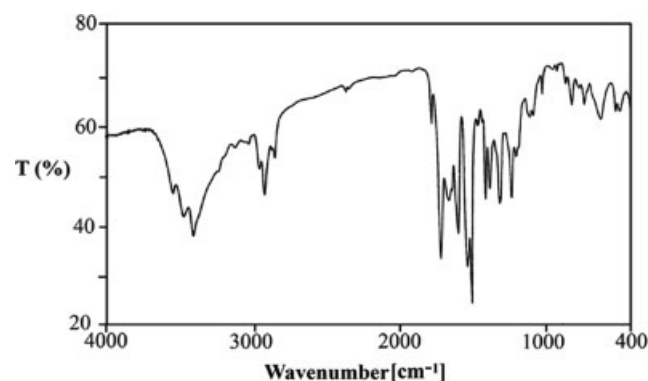


Figure 5 FTIR (KBr) spectrum of PAIU4.

**TABLE V**  
**Solubility of the PAIUs**

Solvent	PAIU3	PAIU4	PAIU5	PAIU6	PAIU7
DMAc	+	+	+	+	+
DMF	++	++	++	++	++
DMF <sup>a</sup>	+++	+++	+++	+++	+++
NMP	+++	+++	+++	+++	+++
DMSO	±	±	±	±	±
MeOH	–	–	–	–	–
EtOH	–	–	–	–	–
CHCl <sub>3</sub>	–	–	–	–	–
CH <sub>2</sub> Cl <sub>2</sub>	–	–	–	–	–
H <sub>2</sub> O	–	–	–	–	–
THF	±	±	±	±	±

+ = soluble at the boiling temperature of related solvents; ++ = soluble at the boiling temperature of water; +++ = soluble at RT; – = insoluble; ± = partially soluble.

<sup>a</sup> DMF with 2% (w/w) LiCl.

soluble in amide-type solvents such as NMP, DMF, and *N,N*-dimethylacetamide (DMAc) and to some extent in DMSO and tetrahydrofuran (THF). They were insoluble in solvents such as water, methanol, chloroform, and dichloromethane.

## CONCLUSIONS

Five different series of new optically active segmented PAIUs based on PEG–MDI and dicarboxylic acids based on amino acids were successfully synthesized. PAIUs based on different diacids showed distinct viscosities, solubilities, and thermal stability properties. This study shows that the best way to synthesize these new optically active PAIUs is DBTDL as a catalyst in NMP as a solvent via method I. TGA data indicate that these types of SPUs are more stable than typical ones. Weight losses of 10% occurred in the range of 273–295°C, and the weight residues at 600°C were 26–41%. On the other hand, these PAIUs based on aliphatic diacids showed lower 5 and 10% weight loss temperatures than polymers synthesized in our previous work that were based on aromatic–aromatic diacids,<sup>17,37–39</sup> however, these PAIUs showed much better solubility properties than previous ones.

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