

New Optically Active Poly(amide–imide–urethane) Thermoplastic Elastomers Derived from Poly(ethylene glycol diols), 4,4'-Methylene-bis(4-phenylisocyanate), and a Diacid Based on an Amino Acid by a Two-Step Method Under Microwave Irradiation

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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 under microwave irradiation. In these reactions, 4,4'-methylene-bis(4-phenylisocyanate) was reacted with bis(*p*-amido benzoic acid)-*N*-trimellitylimido-*L*-leucine and poly(ethylene glycol diols) (PEGs), such as PEG-400, PEG-600, PEG-1000, and PEG-2000, to furnish a series of new PAIUs. The effects of different reaction conditions, such as the method of preparation (polyol or acid chain extension), the prepolymerization step (NCO-terminated oligoamide or NCO-terminated polyether polyol), the irradiation time and power, the reaction solvent, the soft-segment

length, and the presence or absence of reaction catalysts (e.g., triethylamine, pyridine, and dibutyltin dilaurate), on the properties of the copolymers, including the solubility, viscosity, and thermal behavior, were investigated. The resulting multiblock copolymers had inherent viscosities of 0.15–0.53 dL/g. These multiblock copolymers were optically active, thermally stable, and soluble in amide-type solvents. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1781–1792, 2005

Key words: copolymerization; optically active poly(amide–imide–urethane); thermoplastic elastomers; diisocyanate route

INTRODUCTION

Microwave ovens are a feature of many households, but in the industrial world, microwave energy has been applied to several areas, including bulk food processing, the drying and curing of paper and wood products, the vulcanization of rubber, and the drying of thermoplastics before extrusion. In these areas, microwave processing offers the ability to absorb energy quickly and with control to cook, dehydrate, or cure. Also, microwave energy has the potential for more sophisticated processing and fabrication of polymers, including reactive molding, low shear extrusion, and composite processing.¹ In addition, in the field of polymer synthesis, microwave energy has been used for the radical polymerization of vinyl monomers,^{2,3} for the curing of polymers such as epoxy resins^{4–7} and

polyurethanes (PUs),^{7,8} and for the imidization of poly(amic acid)s.^{9–11}

The industrial use of radiation as an alternative to thermal heating for polymerization has generated interest recently because of the faster time and improved efficiency, minimal thermal lag effects, good thermal control through the use of pulsing techniques, and minimized thermal gradients, which result in more homogeneous curing, smaller amounts of thermal stress, trapped volatiles, and material degradation, and less floor space for equipment.^{1,12,13}

In polymer processing, because the mechanism of microwave heating is independent of the thermal conductivity, microwave heating avoids the heat-transfer-rate problem encountered in conventional thermal heating. In addition, the microwave heating process can be switched at high rates in response to a control signal. Several articles have recently appeared in the literature on the microwave processing and diagnosis of epoxy/amine resins as well as nylon 6,6.^{14–16}

Poly(amide–imide)s (PAIs) are well known for their high temperature stability, excellent mechanical strength, and good chemical resistance, which qualify them as high-performance polymeric materials.¹⁷ Moreover, segmented PUs are a class of high-performance materials for coatings, adhesives, elastomers,

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TABLE I
Effect of the Catalyst on the Polymerization of MDI, Diacid, and PEG-400 at 100% Power (Two-Step Method I)

Polymer ^a	Solvent	Nonsolvent	Catalyst	Yield (%) ^b	η_{inh}^{-1} (dL/g) ^c	$[\alpha]_D^{25}$	$[\alpha]_{Hg}^{c,d}$
P1-400	NMP	Water	None	70	0.39	-0.58	— ^e , —, -0.36, 1.66, 2.04
P2-400	NMP	Water	TEA	85	0.51	-0.61	—, —, -0.46, 1.96, 2.14
P3-400	NMP	Water	Py	50	0.43	-0.48	—, —, -0.26, 1.76, 2.24
P4-400	NMP	Water	DBTDL	89	0.33	-0.59	—, —, -0.33, 1.69, 2.34

^a PAIU based on PEG-400 polyether polyol, first entry and so on.

^b The product was powder-like.

^c Measured at a concentration of 0.5 g/dL in 2% w/w LiCl/DMF as the solvent.

^d Measured with 365-, 435-, 546-, and 577-nm filters and no filter, respectively.

^e Not measurable.

fibers, and foams, but their poor thermal stability and chemical resistance limit their applications. For example, the acceptable mechanical properties disappear above 80–90°C, and thermal degradation takes place at temperatures around 200°C. Some of the block copolymers composed of polyethers and polyamides have already been commercialized as thermoplastic elastomers.^{18,19} It is thought that the copolymerization of PUs with PAI segments can modify the thermal and chemical properties, thus, various attempts to incorporate PAI units into PUs have been made.^{20,21}

In connection with our interest in preparing thermally stable and optically active polymers,^{22–31} this article deals with a detailed study of the synthesis and characterization of a series of novel optically active PUs and explores the possibility of modifying polyether-based PUs by the introduction of imide and amide functions into the PU backbone through the reaction of a new amino acid based diacid, bis(*p*-amido

benzoic acid)-*N*-trimellitylimido-*L*-leucine (BPABTL), with 4,4'-methylene-bis(4-phenylisocyanate) (MDI). For the first time, we set out to investigate using microwave energy for the synthesis and thermal modification of segmented, polyether-based, thermoplastic, optically active PUs. The effects of different reaction conditions, such as the irradiation power, irradiation time, catalysts, solvent, and prepolymerization methods, on the properties of the copolymers, including the viscosity, solubility, and thermal behavior, were also studied.

EXPERIMENTAL

Materials and equipment

All chemicals were purchased from Aldrich (Milwaukee, WI), Riedel-de Haën AG (Seelze, Germany), and Merck (Darmstadt, Germany). MDI (Aldrich) was

TABLE II
Effect of the Catalyst on the Polymerization of MDI, Diacid, and PEG-400 at 100% Power (Two-Step Method II)

Polymer ^a	Solvent	Nonsolvent	Catalyst	Yield (%) ^b	η_{inh} (dL/g)	$[\alpha]_D^{25}$	$[\alpha]_{Hg}^c$
P5-400	NMP	Water	None	76	0.41 ^d	-0.60 ^d	—, ^e —, -0.46, 1.76, 2.14 ^d
P6-400	NMP	Water	TEA	73	0.43 ^d	-0.51 ^d	—, —, -0.56, +1.06, +2.24 ^d
P7-400	NMP	Water	Py	71	0.32 ^f	-0.58 ^f	—, —, -0.36, 1.26, 2.34 ^f
P8-400	NMP	Water	DBTDL	72	0.27 ^f	-0.71 ^f	—, —, -0.34, 1.79, 2.54 ^f

^a PAIU based on PEG-400 polyether polyol, entry 5 and so on.

^b The product was powder-like.

^c Measured with 365-, 435-, 546-, and 577-nm filters and no filter, respectively.

^d Measured at a concentration of 0.5 g/dL in 2% w/w LiCl/DMF as the solvent.

^e Not measurable.

^f Measured at a concentration of 0.5 g/dL in 4% w/w LiCl/DMF as the solvent.

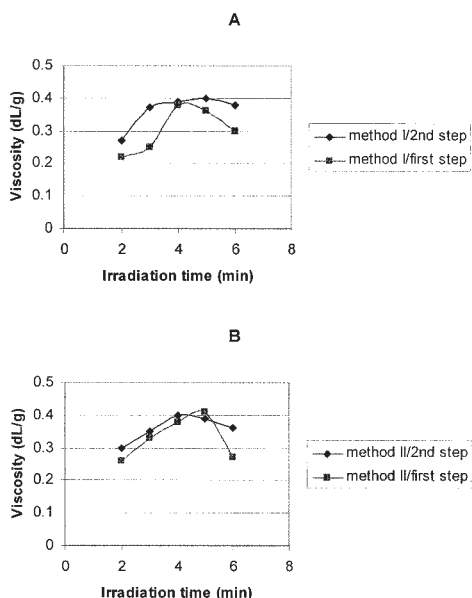


Figure 1 Optimization of the irradiation time for each step in (A) method I and (B) method II for the polymerization of PAIUs based on PEG-400.

used as received. Poly(ethylene glycol diol) (PEG)-400, PEG-600, PEG-1000, and PEG-2000 (Merck) were dried *in vacuo* at 80°C for 10 h. *N,N'*-Dimethylacetamide (DMAc; Merck), dimethyl sulfoxide (DMSO; Merck), *N,N'*-dimethylformamide (DMF; Riedel-de Haën), *N*-methylpyrrolidone (NMP; Merck), pyridine (Py), and triethylamine (TEA; Merck) were distilled under reduced pressure over BaO (Riedel-de Haën). Trimellitic anhydride (TMA; Merck) was recrystallized in acetic anhydride and dried *in vacuo* at 60°C for 6 h. BPABTL was prepared according to the reported procedure by the reaction of *N*-trimellitylimido-*L*-leucine diacid chloride with *p*-amino benzoic acid (Riedel-de Haën)²⁵ and recrystallized from hot meth-

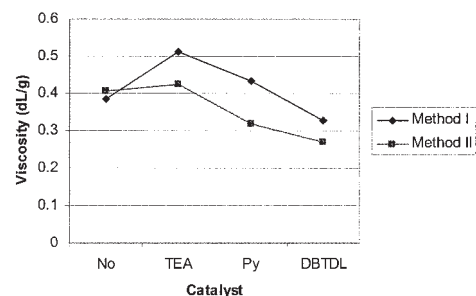


Figure 2 Comparison of the viscosities of PAIUs based on PEG-400 with methods I and II as a function of the catalysts.

anol. The yield of the diacid was 98%, the melting point was greater than 275°C (decomposed), and $[\alpha]_D^{25}$ was 17.6 (0.0520 g in 10 mL of DMF). *N*-Trimellitylimido-*L*-leucine diacid chloride was prepared by the reaction of *N*-trimellitylimido-*L*-leucine with SOCl_2 (Riedel-de Haën) and was recrystallized in *n*-hexane (Merck). The microwave apparatus used for the polycondensation was a Samsung (Seoul, South Korea) microwave oven (2450 MHz and 900 W), and all the polymerization reactions were carried out in a hood with strong ventilation.

¹H-NMR (400 MHz) spectra were recorded on a Varian Inova 400 (Palo Alto, CA) in $\text{DMSO}-d_6$. The multiplicities of the proton resonance were designated as singlet (s), doublet (d), triplet (t), and multiplet (m). Fourier transform infrared (FTIR) spectra were recorded on a Jasco FTIR spectrophotometer (Tokyo, Japan). Spectra of the solids were taken with KBr pellets. The vibrational transition frequencies were reported as wave numbers (cm^{-1}). The band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). The inherent viscosity (η_{inh}) values were measured by a standard procedure with a Cannon-Fenske routine viscometer (Cannon,

TABLE III
Effect of the Catalyst on the Polymerization of MDI, Diacid, and PEG-600 at 100% Power (Two-Step Method I)

Polymer ^a	Solvent	Nonsolvent	Catalyst	Yield ^a (%) ^b	η_{inh} (dL/g) ^c	$[\alpha]_D^{25}$ ^c	$[\alpha]_{\text{Hg}}$ ^{c,d}
P9-600	NMP	Water	None	50	0.27	-0.71	—, ^e —, -0.36, 1.06, 2.16
P10-600	NMP	Water	TEA	76	0.45	-0.61	—, —, -0.66, 1.72, 2.41
P11-600	NMP	Water	Py	76 ^f	0.44	-0.68	—, —, -0.40, 1.46, 2.54
P12-600	NMP	Water	DBTDL	73	0.44	-0.81	—, —, -0.44, 1.89, 2.64

^a PAIU based on PEG-600 polyether polyol, entry 9 and so on.

^b The product was powder-like.

^c Measured at a concentration of 0.5 g/dL in 2% w/w LiCl/DMF as a solvent.

^d Measured with 365-, 435-, 546-, and 577-nm filters and no filter, respectively.

^e Not measurable.

^f The product was a thin brittle film.

TABLE IV
Effect of the Catalyst on the Polymerization of MDI, Diacid, and PEG-600 at 100% of Power (Two-Step Method II)

Polymer ^a	Solvent	Nonsolvent	Catalyst	Yield (%) ^b	η_{inh} (dL/g)	$[\alpha]_D^{25}$	$[\alpha]_{Hg}^c$
P13-600	NMP	Water	None	50	0.46 ^d	-0.55 ^d	- ^e , —, -0.66, +1.96, +2.56 ^d
P14-600	NMP	Water	TEA	59	0.53 ^d	-0.74 ^d	—, —, -0.46, 1.52, +2.81 ^d
P15-600	NMP	Water	Py ^c	61	0.42 ^f	-0.81 ^f	—, —, -0.48, 1.61, 2.86 ^f
P16-600	NMP	Water	DBTDL ^d	54	0.39 ^d	-0.90 ^d	—, —, -0.52, 1.70, 2.74 ^d

^a PAIU based on PEG-600 polyether polyol, entry 13 and so on.

^b The product was powder-like.

^c Measured with 365-, 435-, 546-, and 577-nm filters and no filter, respectively.

^d Measured at a concentration of 0.5 g/dL in 2% w/w LiCl/DMF as the solvent.

^e Not measurable.

^f Measured at a concentration of 0.5 g/dL in 3% w/w LiCl/DMF as the solvent.

Mianz, Germany). Specific rotations were measured with a Jasco polarimeter. Thermogravimetric analysis (TGA) data for the polymers were taken on a Stanton 650 TGA instrument (Surrey, UK) under an atmosphere of N₂, and the first run of the differential scanning calorimetry (DSC) data was recorded on a DSC-PL-1200 instrument under an atmosphere of N₂ by the Research Institute of Polymers and Petrochemicals of Iran.

Synthesis of the poly(amide-imide-urethane) (PAIU) block copolymers

Method I (polyol-terminated isocyanate)

The PAIUs were prepared with the following general procedure (with P2-400 as an example). To a porcelain dish, PEG-400 (0.0411 g, 1.03×10^{-4} mol), MDI (0.0514 g, 2.05×10^{-4} mol), TEA (0.03 mL, 2.16×10^{-4} mol), and 0.23 mL of NMP were added. The mixture

was completely ground for 2 min at room temperature. The reaction mixture was irradiated in a microwave oven for a total of 4 min of irradiation (2-min + 2-min intervals of irradiation and grinding) at 100% power. Then, a solution of BPABTL (0.0558 g, 1.03×10^{-4} mol) and TEA (0.03 mL, 2.16×10^{-4} mol) in 0.23 mL of NMP was added immediately, and the mixture was ground for 2 min. Then, it was irradiated in the microwave oven at 100% power for a total of 5 min of irradiation (3-min + 2-min intervals of irradiation and grinding). The resulting product was isolated by the addition of 10 mL of distilled water and trituration. It was then filtered and dried at 80°C for 8 h *in vacuo*; this yielded 0.1181 g (85%) of pale brown P2-400. The previous polymerization was repeated, but the reaction mixture was irradiated with dibutyltin dilaurate (DBTDL) or Py as a catalyst and without a catalyst.

TABLE V
Effect of the Catalyst on the Polymerization of MDI, Diacid, and PEG-1000 at 100% Power (Two-Step Method I)

Polymer ^a	Solvent	Nonsolvent	Catalyst	Yield (%) ^b	η_{inh} (dL/g) ^c	$[\alpha]_D^{25c}$	$[\alpha]_{Hg}^{c,d}$
P17-1000	NMP	Water	None	40	0.15	-0.45	- ^e , —, -0.56, 1.21, 2.46
P18-1000	NMP	Water	TEA	82	0.34	-0.76	—, —, -0.76, 1.44, 2.85
P19-1000	NMP	Water	Py	39	0.44	-0.71	—, —, -0.41, 1.68, 2.83
P20-1000	NMP	Water	DBTDL	92	0.30	-0.80	—, —, -0.55, 1.76, 2.82

^a PAIU based on PEG-1000 polyether polyol, entry 17 and so on.

^b The product was powder-like.

^c Measured at a concentration of 0.5 g/dL in 2% w/w LiCl/DUF as the solvent.

^d Measured with 365-, 435-, 546-, and 571-nm filters and no filter, respectively.

^e Not measurable.

TABLE VI
Effect of the Catalyst on the Polymerization of MDI, Diacid, and PEG-1000 at 100% Power (Two-Step Method II)

Polymer ^a	Solvent	Nonsolvent	Catalyst	Yield (%) ^b	η_{inh} (dL/g) ^c	$[\alpha]_D^{25c}$	$[\alpha]_{Hg}^{c,d}$
P21-1000	NMP	Water	None	40	0.16	-0.36	— ^e , —, -0.26, 1.45, 2.66
P22-1000	NMP	Water	TEA	61	0.26	-0.39	—, —, -0.54, 1.56, 2.6
P23-1000	NMP	Water	Py	48	0.31	-0.73	—, —, -0.46, 1.69, 2.87
P24-1000	NMP	Water	DBTDL	37	0.26	-0.78	—, —, -0.57, 1.74, 2.79

^a PAIU based on PEG-1000 polyether polyol, entry 21 and so on.

^b The product was powder-like

^c Measured at a concentration of 0.5 g/dL in 4% w/w LiCl/DMF as the solvent.

^d Measured with 365-, 435-, 546-, and 577-nm filters and no filter, respectively.

^e Not measurable.

Method II (oligo amide terminated isocyanate)

The PAIUs were prepared with the following general procedure (with P6-400 as an example). To a porcelain dish, BPABTL (0.0595 g, 1.09×10^{-4} mol), MDI (0.0548 g, 2.19×10^{-4} mol), TEA (0.03 mL, 2.16×10^{-4} mol), and 0.25 mL of NMP were added. The mixture was completely ground for 2 min at room temperature. The reaction mixture was irradiated for a total of 5 min of irradiation (3-min + 2-min intervals) at 100% power. Then, a solution of PEG-400 (0.0438 g, 1.09×10^{-4} mol) and TEA (0.03 mL, 2.16×10^{-4} mol) in 0.20 mL of NMP was added immediately, and the mixture was ground for 2 min. Then, it was irradiated at 100% power for a total of 4 min of irradiation (2-min + 2-min intervals of irradiation and grinding). The resulting product was isolated by the addition of 10 mL of distilled water and trituration. It was then filtered and dried at 80°C for 8 h *in vacuo*; this yielded 0.1095 g (73%) of P6-400. The previous polymerization was repeated, but the reaction mixture was irradiated in the presence of DBTDL or Py as a catalyst and without a catalyst.

The aforementioned polymerization methods (I and II) were repeated with PEG-400 but under different reaction conditions, as shown in Tables I and II and Figures 1 and 2. The optimized reaction conditions were repeated for the synthesis of other copolymers with PEG soft segments of different molecular weights (Tables III–VIII).

RESULTS AND DISCUSSION

The PEG polyether polyol based PAIU multiblock copolymers were prepared according to Schemes 1 and 2 by a two-step method (prepolymerization method). In method I (Scheme 1), an NCO-terminated polyether polyol (3) was prepared by the reaction of a solution of polyether polyol (1) as the soft segment with a 2-mol excess of MDI (2) in NMP in the presence of different catalysts or without a catalyst. Then, a diacid chain extender containing an imide ring (4) was reacted with the aforementioned PEG prepolymer, and this resulted in PAIU multiblock copolymers (5), whose PAI blocks were connected with urethane linkages (Tables

TABLE VII
Effect of the Catalyst on the Polymerization of MDI, Diacid, and PEG-2000 at 100% Power (Two-Step Method I)

Polymer ^a	Solvent	Nonsolvent	Catalyst	Yield (%) ^b	η_{inh} (dL/g) ^c	$[\alpha]_D^{25c}$	$[\alpha]_{Hg}^{c,d}$
P25-2000	NMP	Water	None	—	—	—	—
P26-2000	NMP	Water	TEA	26	0.49	-0.39	— ^e , —, -0.43, 1.54, 2.61
P27-2000	NMP	Water	Py	57	0.47	-0.73	—, —, -0.62, 1.70, 2.90
P28-2000	NMP	Water	DBTDL	63	0.34	-0.78	—, —, -0.46, 1.78, 2.83

^a PAIU based on PEG-2000 polyether polyol, entry 25 and so on.

^b The product was a thin, brittle film.

^c Measured at a concentration of 0.5 g/dL in 2% w/w LiCl/DMF as the solvent.

^d Measured with 365-, 435-, 546-, and 577-nm filters and no filter, respectively.

^e Not measurable.

TABLE VIII
Effect of the Catalyst on the Polymerization of MDI, Diacid, and PEG-2000 at 100% Power (Two-Step Method II)

Polymer ^a	Solvent	Nonsolvent	Catalyst	Yield (%) ^b	η_{inh} (dL/g) ^c	$[\alpha]_D^{25c}$	$[\alpha]_{Hg}^{c,d}$
P29-2000	NMP	Water	None	—	—	—	—
P30-2000	NMP	Water	TEA	21	0.27	-0.40	- ^e , —, -0.54, 1.62, 2.60
P31-2000	NMP	Water	Py	23	0.29	-0.63	—, —, -0.64, 1.68, 2.86
P32-2000	NMP	Water	DBTDL	20	0.32	-0.74	—, —, -0.56, 1.80, 2.86

^a PAIU based on PEG-2000 polyether polyol, entry 29 and so on.

^b The product was a thin brittle film.

^c Measured at a concentration of 0.5 g/dL in 4% w/w LiCl/DMF as the solvent.

^d Measured with 365-nm, 435-, 546-nm, and 577-nm filters and no filter, respectively.

^e Not measurable.

I, III, V, and VII). In method II (Scheme 2), an NCO-terminated oligo amide as a hard segment was prepared by the reaction of a solution of a diacid (4) with a 2-mol excess of MDI (2) in NMP in the presence of TEA, Py, and DBTDL or without a catalyst; this afforded an oligo amide prepolymer (3'). Then, a PEG (1) chain extender as a soft segment was reacted with the aforementioned prepolymer, and this resulted in PAIU multiblock copolymers (5'; Tables II, IV, VI, and VIII).

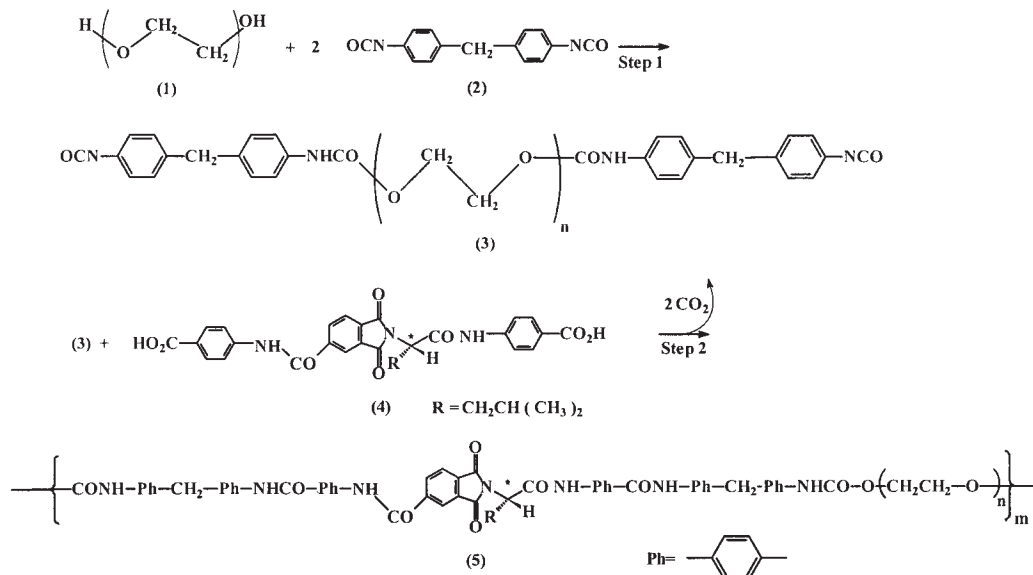
Some physical properties of the synthesized P-400 copolymers are shown in Tables I and II. Three series of block copolymers—P-600 (Tables III and IV), P-1000 (Tables V and VI), and P-2000 (Tables VII and VIII)—were prepared to investigate the effect of the PEG block length and method of preparation (the formation of the hard segment in the first step and polyol

chain extension or the formation of the soft segment in the first step and diacid chain extension) on the physical properties of PAIU copolymers and reliability of microwave irradiation for the synthesis of PAIUs.

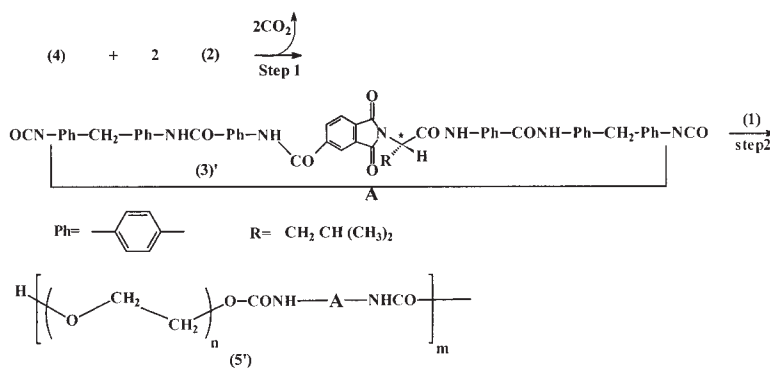
Polymer synthesis

Effect of the polymerization conditions on the viscosity and yield of the PAIUs

In a previous work,³² we carried out the polymerizations with PEG-400 under different reaction conditions, such as the reaction solvent, the irradiation power and time, the amount of the solvent, and the reaction catalysts, to optimize them by the one-step method. In each case, other undefined parameters were set according to our other previous work on the preparation of nonseg-



Scheme 1 Copolymerization reaction of a 2-mol excess of MDI with PEG polyol and chain extension of an NCO-terminated polyol by a diacid monomer (two-step method I).



Scheme 2 Copolymerization reaction of a 2-mol excess of MDI with diacid BPABTL and chain extension of an NCO-terminated oligoamide by PEG polyether polyol (two-step method II).

mented PAIs via a diisocyanate route.³³ In that article, the reaction was performed in NMP, DMAc, DMSO, DMF, and *o*-cresol. Then, NMP with a solvent/solid ratio of about 2 : 2.5 (v/w) and 4–5 min of irradiation at 100% power were recognized as preferable conditions, providing the best viscosities and yields.

Here we report our complementary findings on the microwave-assisted synthesis of new optically active PAIUs with two-step methods. The microwave-assisted preparation of PAIUs based on PEG-400 were carried out with methods I and II in NMP, in the absence of any catalysts, with different irradiation times. According to Figure 1(A,B), the reaction was carried out at a fixed time of about 4 min in step 1 or 2; then, the viscosities were observed as a function of changes in the other step's irradiation time. According to these data, 4 min of irradiation in step 1 and 5 min in step 2 for method I [Fig. 1(A)] and 5 min in step 1 and 4 min in step 2 for method II [Fig. 1(B)] were preferred.

The aforementioned polymerization were carried out in NMP at the optimized irradiation power and time in the presence of catalysts such as TEA, Py, and DBTDL (Tables I and II). Table I shows that TEA for polymerization by method I is the best catalyst as far as the viscosity and yield are concerned. For method

II, the results of TEA and the no-catalyst condition are comparable (Table II). The results from the two methods for each catalyst show that method I is an upcoming method for achieving higher viscosities for the synthesis of PAIUs based on PEG-400 (Fig. 2).

Effect of changes in the soft-segment length on the viscosity of the copolymers

To investigate the effect of the soft-segment length on the viscosities and some other physical properties of PAIU copolymers, three series of block copolymers based on PEG-600, PEG-1000, and PEG-2000 were synthesized (Tables III–VIII). The optimized conditions obtained for the formation of PAIUs based on PEG-400 were used to study the polymerization behavior of other PEG molecular weights. Furthermore, in our previous work on solution polymerization by a conventional heating method,^{34,35} PEGs of different molecular weights showed different responses to reaction catalysts.

As shown in Tables III and IV, the catalytic condition is essential for the preparation of PAIUs based on PEG-600 with method I, and there are comparable results with catalysts such as TEA, Py, and DBTDL. For method II, although TEA is the preferred catalyst,

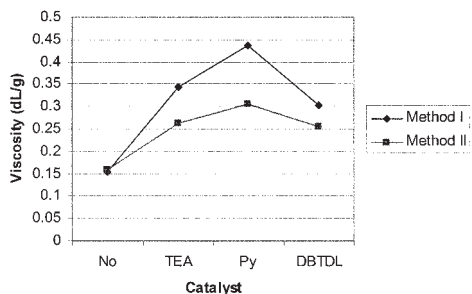


Figure 3 Comparison of the viscosities of PAIUs based on PEG-1000 with methods I and II as a function of the catalysts.

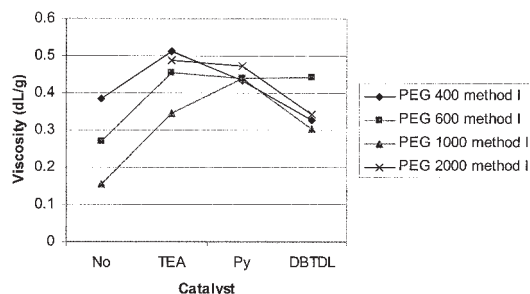


Figure 4 Comparison of the viscosities of PAIUs based on PEGs of different molecular weights with method I as a function of the catalysts and soft-segment length.

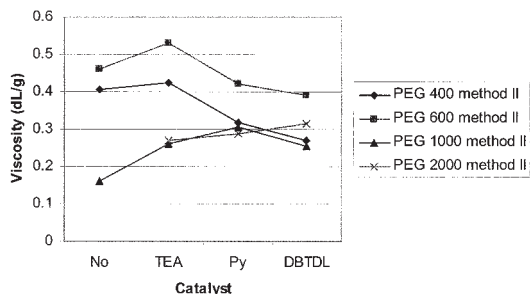


Figure 5 Comparison of the viscosities of PAIUs based on PEGs of different molecular weights with method II as a function of the catalysts and soft-segment length.

in the absence of any catalyst, the results are comparable too.

In the case of other PAIUs based on PEG-1000 and PEG-2000, in the absence of any catalyst, polymer chain growth drastically decreases, and the catalytic condition seems to be essential. This could be due to the low mobility of polyols under fast microwave-promoted reactions. According to Tables V and VI, Py as a catalyst can be suggested for the preparation of PAIUs based on PEG-1000 because of the better yield and viscosity. Method I is recognized to be better (Fig. 3).

For PEG-2000, with method I, TEA, Py, and DBTDL behaved differently with respect to the viscosity and yield of the resulting PAIUs (Table VII). DBTDL showed the best yield, whereas TEA and Py showed better viscosities. With method II, DBTDL showed the highest viscosity but the lowest yield, and Py showed the best yield (Table VIII). Method I seems to be a superior method for the formation of PAIUs based on PEG-2000 in the presence of Py and TEA.

The aforementioned results show that the best catalysts for the copolymerization reactions of PEGs of different molecular weights, with respect to the viscosity, in NMP as a solvent at 100% power with 4–5 min of irradiation time are TEA for PEG-400, TEA, Py, and DBTDL for PEG-600, Py for PEG-1000, and finally TEA or Py for PEG-2000 with method I (Fig. 4). As for the viscosity for method II, the best catalysts for each

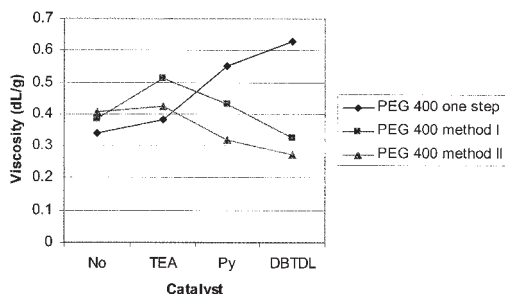


Figure 6 Comparison of the viscosities of PAIUs based on PEG-400 with the one-step method, method I, and method II as a function of the catalysts.

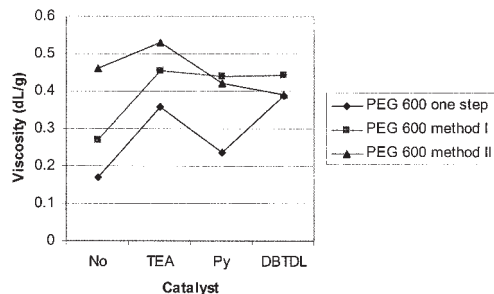


Figure 7 Comparison of the viscosities of PAIUs based on PEG-600 with the one-step method, method I, and method II as a function of the catalysts.

polyol include TEA and no catalyst for PEG-400 and PEG-600, Py for PEG-1000, and DBTDL for PEG-2000 (Fig. 5).

As shown by Figures 6–9, the viscosities of the resulting PAIUs change under microwave energy with respect to the method of polymerization (one-step method³² and two-step methods I and II), reaction catalyst, and soft-segment length. As shown in Figure 6, for PAIUs based on PEG-400, the maximum of all curves occurs at the point of the one-step method in the presence of DBTDL as a catalyst. For PEG-600, the maximum is method II in the presence of TEA (Fig. 7). For PEG-1000, the maximum occurs at the point of the one-step method and method I in the presence of

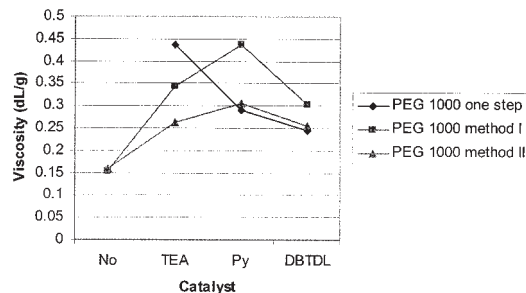


Figure 8 Comparison of the viscosities of PAIUs based on PEG-1000 with the one-step method, method I, and method II as a function of the catalysts.

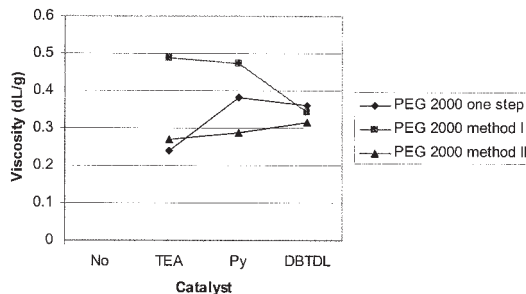


Figure 9 Comparison of the viscosities of PAIUs based on PEG-2000 with the one-step method, method I, and method II as a function of the catalysts.

TABLE IX
Thermal Properties of the PAIUs

Code	DSC (°C)		TGA		
	T_{gs}^a	T_{gh}^a	T_5	T_{10} (°C)	Char yield (%) ^b
P2-400	60	154	313	336	38
P10-600	—	—	304	334	27
P6-400	80	165	314	341	35
P14-600	—	—	300	325	38
P19-1000	107	171	—	—	—
P23-1000	113	180	285	321	27
P32-2000	—	—	308	325	36

^a The center of the peak was recorded by DSC at heating rate of 20°C/min in N₂.

^b Percentage of weight residue at 600°C in a N₂ atmosphere.

TEA and Py, respectively (Fig. 8). For PEG-2000, the maximum occurs at the point of method I in the presence of TEA or Py (Fig. 9). To the best of our knowledge, in addition to the viscosity, the microphase separation and, therefore, some physical and thermal properties of

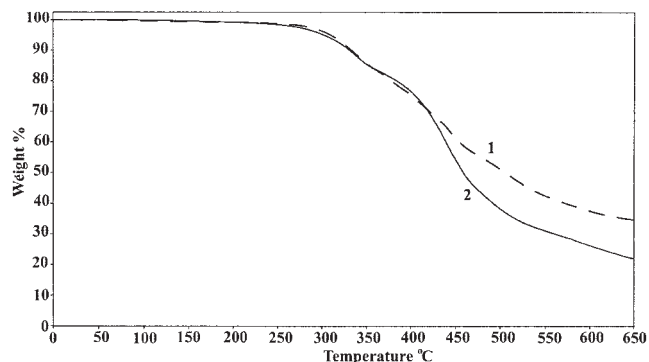


Figure 10 TGA thermograms of (1) P2-400 and (2) P10-600 prepared by method I under an atmosphere of N₂ at a heating rate of 20°C/min.

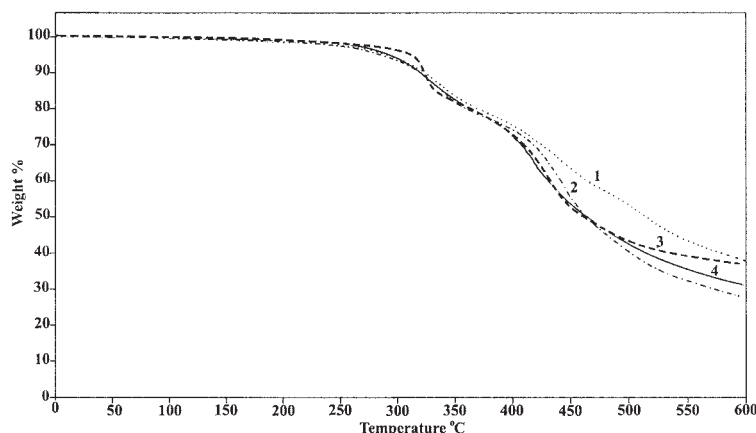


Figure 11 TGA thermograms of (1) P14-600, (2) P23-1000, (3) P32-2000, and (4) P6-400 prepared by method II under an atmosphere of N₂ at a heating rate of 20°C/min.

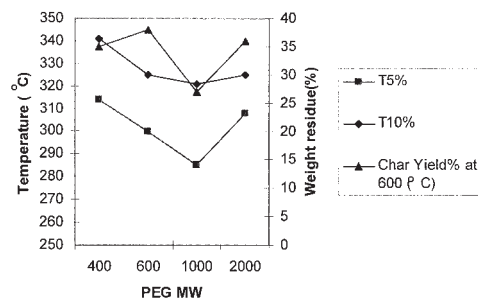


Figure 12 Comparison of the thermal stability of PAIUs based on PEG soft segments of different molecular weights (MWs) and prepared by method II with reference to TGA data.

the obtained PAIUs depend on the different methods of polymerization and the reaction parameters.

Thermal properties

The thermal properties of the PAIUs were evaluated with TGA and DSC (Table IX).

The thermal stability of P2-400 and P10-600 (Fig. 10), the PAIUs resulting from method I, and P6-400, P14-600, P23-1000, and P32-2000 (Fig. 11), the PAIUs obtained by method II, were studied with the TGA technique.

The TGA curves for all the samples show a smooth, stepwise manner, suggesting a two-step thermal degradation. For P2 and P14, the changes associated with step 2 are very smooth. The temperatures at which 5 and 10% weight losses were recorded by TGA at a heating rate of 20°C/min in an atmosphere of N₂ (T_5 and T_{10} , respectively) for all entries of method II (Fig. 12) decrease with the PEG molecular weight, and this shows a decrease in the stability of PAIUs (Fig. 11). At the same molecular weight of final PAIUs based on different PEGs, the participation of the PEG length with respect to the amide-imide hard segment and, therefore, the oxygen content of the polymer chain

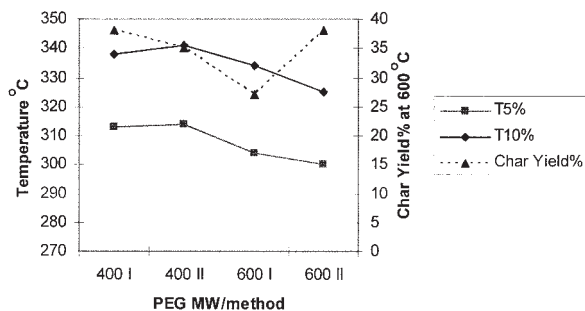


Figure 13 Comparison of the thermal stability of PAIUs based on PEG soft segments of different molecular weights (MWs) and prepared by methods I and II with reference to TGA data.

will be increased with increasing PEG length. This suggests faster initial oxidative thermal degradation.

On the basis of data obtained from char yields (Table IX and Fig. 12), the results at 600°C for P6-400, P14-600, and P32-2000 are to some extent comparable, but it has decreased a little in the case of P23-1000. The values of T_5 , T_{10} , and the char yield of PAIUs obtained with the two methods (I and II) for each polyol are almost the same (Fig. 13). For example, the T_5 values of P2-400 (400I) and P6-400 (400II) are about 313 and 314°C, respectively. The same can be seen for T_{10} and the char yield of P2-400 and P6-400 (the T_{10} values are 338 and 341°C and the char yields are 38 and 35%, respectively). The data associated with the thermal study of the one-step and two-step methods of polymerization (Fig. 14) show that T_5 and T_{10} of the one-step method are higher than those of the two-step method, especially for PEGs of higher molecular weights. The same is true about the char yields of the methods, with the exception of P14-600. This could be explained by more phase mixing (Table X, ΔT_g by DSC) of PAIUs with the one-step method because hard segments act in the same way as nodal thermally stable points. Also, T_5 of the one-step method in-

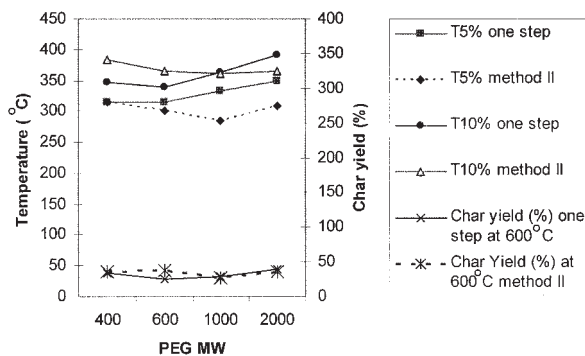


Figure 14 Comparison of the thermal stability of PAIUs based on PEG soft segments of different molecular weights (MWs) and prepared by method II and the one-step method with reference to TGA data.

TABLE X
Changes in the Transition Temperatures of the PAIUs as a Function of the Method of Polymerization and the PEG Molecular Weight from DSC

Code (method)	ΔT_g ($T_{gh} - T_{gs}$; °C)	Code (method)	ΔT_g ($T_{gh} - T_{gs}$; °C)
P2-400 (I)	94	P19-1000 (I)	64
P6-400 (II)	85	P23-1000 (II)	67
P-400 (one-step)	107	P-1000 (one-step)	50

creases with increasing PEG molecular weight,³² but in the case of method II, it decreases with the PEG molecular weight, except for P32-2000.

Typical DSC curves for P2-400 and P6-400 and for P19-1000 and P23-1000 are shown in Figures 15 and 16. The experimental glass-transition temperature (T_g) for PEGs varies from -63.0 to -55.9°C. DSC traces of P2-400, P6-400, P19-1000, and P23-1000 show no transition associated with melting, although soft-segment glass-transition temperatures (T_{gs} 's) were observed around 60, 80, 107, and 113°C, respectively. These data show a large shift to higher temperatures in comparison with those of pure PEGs. Also, they showed smooth baseline changes around 154, 165, 171, and 180°C, respectively, which can be assigned to hard-segment glass-transition temperatures (T_{gh} 's). Table IX shows that the transition temperatures shift to higher temperatures from method I to method II at the same

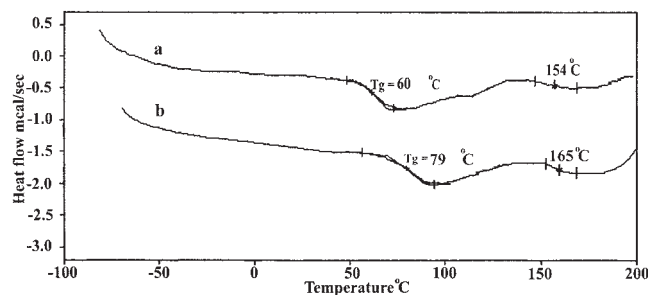


Figure 15 DSC curves of (a) P2-400 and (b) P6-400 under an atmosphere of N_2 at a heating rate of 20°C/min.

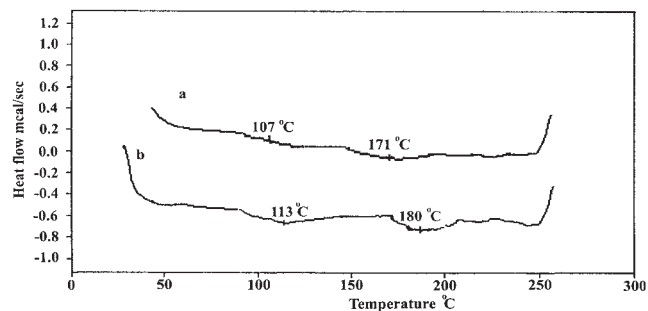


Figure 16 DSC curves of (a) P19-1000 and (b) P23-1000 under an atmosphere of N_2 at a heating rate of 20°C/min.

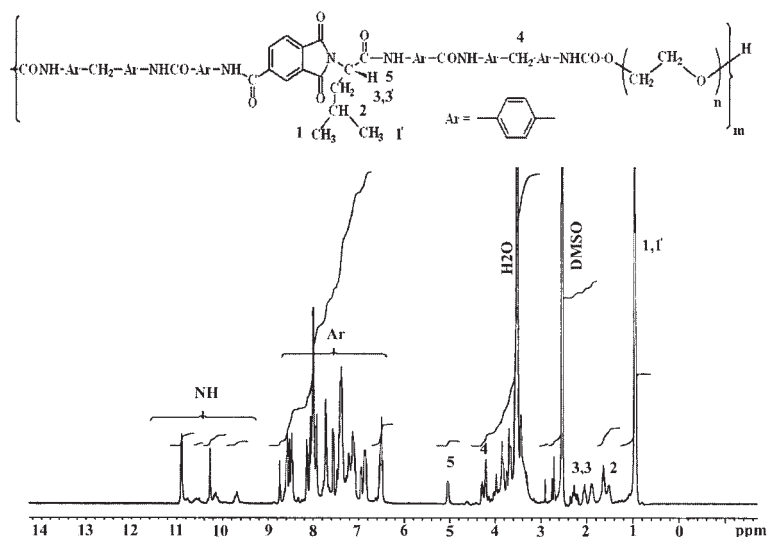


Figure 17 $^1\text{H-NMR}$ (400 MHz) spectrum of P10-600 in $\text{DMSO-}d_6$ at room temperature.

PEG length. Moreover, the differences between T_{gs} and T_{gh} decrease from method I to method II and from PEG-400 to PEG-1000 (Table X). These behaviors, in addition to the fading of T_{gh} , might be results of the phase mixing of hard and soft microdomains in the copolymers. Also, this suggests that the formation of hard segments in the first step (method II) can increase thermal transition temperatures, especially with increasing PEG molecular weight. These temperature shifts related to method II are probably due to the formation of longer hard-segment blocks that provide stronger van der Waals and hydrogen-bonding interactions between polymer chains. Thus, higher restriction of mobility in hard domains will hinder rotation at the ether sites of polyol soft segments.

Characterization

The resulting PAIUs were characterized with FTIR and $^1\text{H-NMR}$ spectroscopy. The $^1\text{H-NMR}$ spectrum of P10-600 showed peaks that confirmed its chemical structure (Fig. 17). It showed peaks for CH_3 (1 and 1'), which appeared as distorted doublets according to their coupling with H (2) with $J = 6.4$ Hz, in the region of 0.95–0.96 ppm. Peaks in the region of 1.51–1.68 and 1.84–2.28 ppm were related to H (2) and the diastereotopic hydrogens of CH_2 (3 and 3'), which appeared as multiplets, respectively. Peaks in the regions of 4.19 and 5.03 ppm pertained to CH_2 (4) and CH (5), respectively. The aromatic protons appeared in the region of 6.47–8.74 ppm; peaks in the region of 8.05–8.74 ppm were related to TMA ring protons. The peaks in the region of 10.29–10.90 ppm were assigned to NH of amide and urethane groups.

The FTIR spectra of the PAIUs showed characteristic absorption bands representative of the PAIUs. For

example, the FTIR spectrum of P27-2000 (Fig. 18) showed the characteristic absorptions of amide, imide, and urethane groups around 3420, 3301, 1771, 1719, 1686, 1598, and 1539 cm^{-1} , which were associated with NH, C=O, and C—N vibrations of amide (I and II), imide, and urethane groups, respectively. Peaks at 1407, 1314, 771, and 720 cm^{-1} showed the presence of an imide heterocyclic ring in the polymer structure.

FTIR peaks (cm^{-1}) for P27-2000: 3420 (s, br) NH v, 3301 (s) NH v, 3208 (m) C—H aromatic, 3116 (w) C—H aromatic, 2958 (m), 2918 (m), 2853 (m) C—H aliphatic, 1771 (w) C=O urethane (amide I; non-hydrogen-bonded), 1719 (s) C=O urethane (amide I; hydrogen-bonded), 1686 (s) C=O amide (I), 1639 (s), 1598 (s) C—N v + NH (amide II), 1539 (s) C=C, 1500 (s), 1407 (s), 1383 (s), 1314 (s) C—N v + NH (amide IV), 1244 (s) C—N v + NH (amide V), 1178 (m), 1102 (m) C—O—C ether, 1070 (m) O=C—O—C, 941 (w), 857 (w), 828 (w), 805 (w), 771 (w) O=C—O, 720 (w), 653 (m), 610 (w), 544 (w), 500 (w).

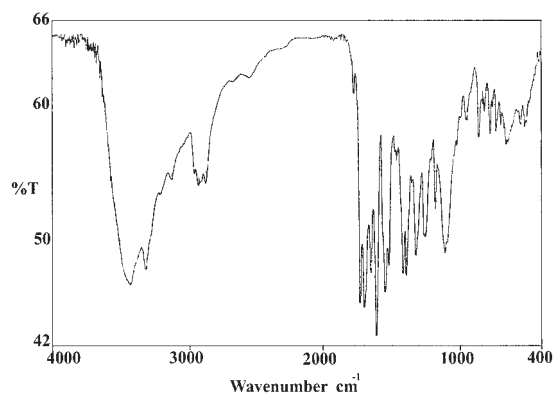


Figure 18 FTIR (KBr) spectrum of polymer P27-2000.

TABLE XI
Solubility Properties of the PAIUs

Solvent	P2-400	P6-400	P14-600	P23-1000	P32-2000
DMAc	+	+	+	+	+
DMAc (LiCl)	++	++	++	++	++
DMF	++	++	++	++	++
DMF (LiCl)	+++	+++	+++	+++	+++
NMP	++	++	++	++	++
NMP (LiCl)	+++	+++	+++	+++	+++
THF	±	±	±	±	±
DMSO	±	±	±	±	±
MeOH	–	–	–	–	–
EtOH	–	–	–	–	–
CHCl ₃	–	–	–	–	–
CH ₂ Cl ₂	–	–	–	–	–
H ₂ O	–	–	–	–	–

+ = soluble at boiling temperature; ++ = soluble at boiling water temperature; +++ = soluble at room temperature; – = insoluble; ± partially soluble.

Solubility properties

The solubility properties of the PAIUs were studied in different solvents (Table XI). The polymers are soluble in amide-type solvents such as NMP, DMF, and DMAc and especially in the aforementioned solvents containing LiCl. They are also slightly soluble in DMSO and tetrahydrofuran (THF). They are insoluble in solvents such as water, methanol, chloroform, and dichloromethane.

CONCLUSIONS

For the first time, four series of new optically active thermoplastic PAIUs with modified thermal stability were successfully synthesized under microwave irradiation. They were prepared by the two-step polymerization reactions of PEG polyether polyols of different molecular weights, MDI, and an amino acid based diacid incorporating both imide and amide functionalities via a diisocyanate route. The synthesis involved the polycondensation of MDI with a diacid or polyol resulting in an NCO-terminated prepolymer followed by a chain-extension step. A systematic study of PAIUs obtained under different reaction conditions has demonstrated a drastic influence of the reaction conditions on the polymer chain growth and microphase separation. The data obtained from this study suggest that microwave irradiation is an interesting alternative for preparing these kinds of PAIUs in competition with conventional heating methods. According to thermal studies based on TGA and DSC techniques, these polymers exhibited good thermal stability and phase mixing. Weight losses of 10% occurred in the range of 320–340°C, and this indicated relatively good heat resistance of these copolymers in

comparison with conventional PUs whose thermal degradation starts around 100–200°C.

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