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Synthesis and Properties of Novel Optically Active Poly(amide imide urethane) Thermoplastic Elastomers by the Reaction of a *L*-Leucine Based Diacid Chain Extender and PEG-terminated MDI

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ABSTRACT

A new class of optically active poly(amide imide urethane) (PAIU) thermoplastic elastomers was synthesized via the reaction of NCO-terminated polyether polyols with an imide containing optically active amino acid-based dicarboxylic acid chain extender via two-step diisocyanate route. In the first step 4,4'-methylene-bis-(4-phenylisocyanate) (MDI) (6) was reacted with polyethyleneglycol-diols (PEG)s such as PEG-400, PEG-600, PEG-1000, and PEG-2000 to produce the NCO-terminated polyether soft segment. The chain extension of the above soft segment with bis(*p*-amido benzoic acid)-*N*-trimellitylimido-*L*-leucine (BPABTL) (5) was the second step to furnish a series of new optically active PAIUs. The PAIUs were characterized by conventional methods, and their physical properties such as solution viscosity, solubility, and thermal behaviour were studied. The copolymerization reactions were performed in the presence of triethylamine (TEA), pyridine (Py), dibutyltin dilurate (DBTDL), and no catalyst, respectively. The resulting multiblock copolymers had inherent viscosities in the range of 0.12-0.55 dL/g. These copolymers are optically active, thermally stable and soluble in amide-type solvents. Some structural characterization and physical properties of these new optically active PAIU thermoplastic elastomers are reported.

Key Words:
poly(amide imide urethane);
thermoplastic elastomer;
optically active;
diacid chain extender;
NCO-terminated;
diisocyanate route.

INTRODUCTION

Polyurethanes (PUs) are versatile polymers and can be easily formed by a simple polyaddition reaction of a polyol, isocyanate and a chain extender. The tailor made properties from super soft flexible foams to tough elastomers and long-wearing coatings have resulted many final applications [1-4]. Unfortunately, conventional PUs are known to exhibit poor thermal stability which limits their applications. For example, their acceptable mechanical properties, disappear above 80-90°C

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and thermal degradation takes place at temperatures above 200°C. Attempts to improve the thermal stability of PUs have been made for long time. One accepted approach for the improvement of thermal stability of PUs is the chemical modification of their structures by blending or copolymerization with thermally stable polymers.

Recently, more attention has been paid to modifications, by using heterocyclic groups [5-8]. Polyimides are an important class of heterocyclic polymers with remarkable heat resistance and superior mechanical, electrical, and durable properties [9,10]. Various attempts have been made to incorporate polyimide units into PUs. Some of them were consisted of the reaction of isocyanate terminated PUs prepolymer with acid anhydrides [11-13], a modified method including the reaction of isocyanate terminated PUs prepolymer with aromatic diamines and dianhyrides to produce PUs with imide groups in the backbone [14], and the reaction of isocyanate terminated PUs with diols or diacids containing imide groups [15,16].

The intermolecular Diels-Alder reaction of bisdienes, e.g., bis(furans) with bis(maleimides) or 4-methyl-1,3-phenylene bis(2-furanyl-carbamate) with various bis maleimides [17-19], and preparation of PUs using diisocyanates containing built-in imide structure [20], are also well documented. On the other hand ether linkages inserted in amide-imide chains, provide significantly lower energy of internal rotation.

In general, such structural modifications lead to lower glass transition temperature (T_g) and crystalline melting temperature (T_m), as well as, significant improvement in solubility and other process; that are characteristics of these polymers [21]. It is well established that poly(ether urethane) elstomers are phase-segregated copolymers consisting of a hard phase rich in urethane groups, as well as an interface abundant in all the involved functionalities.

Recently, the synthesis of poly(oxyethylene)-polyamide multi-block copolymers from α,ω-diamine-terminated polyamides by direct polycondensation using triphenyl phosphite (TPP) and Py as condensing agent, are also reported [22,23]. It is known that polyamides can be prepared simply from combination of aromatic diisocyanates and dicarboxylic acids without use of any condensing agents, which are generally expensive and difficult to recycle [24]. The diisocyanate route has been applied to the synthesis of poly(oxyethylene)-polyamide multi-block copolymers starting from PEG-diacids, dicarboxylic acids, and aromatic diisocyanates [25].

The synthesis and application of optically active polymers have been attracted more attention. So, we synthesized optically active polymers by different methods such as: reaction of an optically active monomer with several diamines or diols via solution polymerization [25-32]. In these polycondensation reactions, we used amino acids as chiral inducing agents. These naturally occurring compounds, and such synthetic polymers based on amino acids, are expected to be biodegradable and biocompatible.

In connection with our interest in preparing optically active polymers, a series of PAIUs were synthesized by two-step reaction of NCO-terminated PEG with a new optically active imide containing diacid chain extender 5. The effects of different reaction conditions such as: temperature, time, catalysts type, and polyol chain length on the properties of copolymers were investigated.

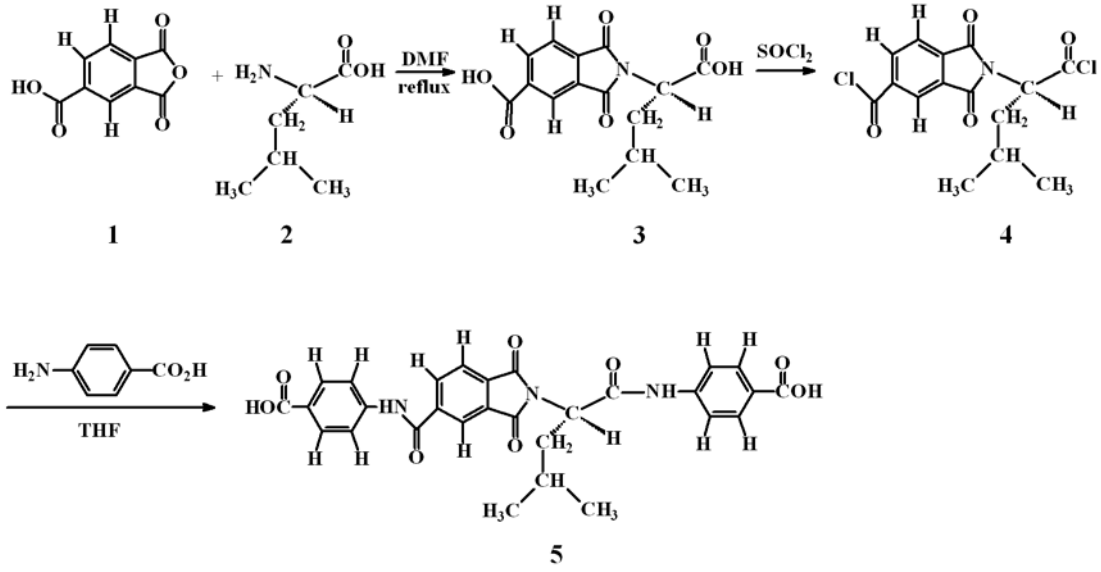
EXPERIMENTAL

Materials

Chemicals used were; 4,4′-methylene-bis-(4-phenylisocyanate) 6 (Aldrich) without further purification. Polyethylene glycol 400, 600, 1000, and 2000 (Merck), dried under vacuum at 80°C for 6 h. Dimethylsulfoxide (DMSO) (Merck), N,N-dimethylformamide (DMF) (Riedel-deHaen AG), Py (Merck) and TEA (Merck) distilled under reduced pressure over BaO. bis-(*p*-amido benzoic acid)-*N*-trimellitylimido-*L*-leucine 5 prepared according to the reported procedure [33] (Scheme 1). The yield of diacid 5 was 98.0%, m.p.> 275°C (dec.), and $[\alpha]_D^{25}$: +17.6 [0.0520 g in 10 mL of DMF].

Instruments and Measurements

Proton nuclear magnetic resonance ^{1}H NMR (500 MHz) spectra were recorded on a Bruker Avance 500 (Germany). Multipilicities of proton resonance were designated as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), and multiplet (m). FTIR spectra were recorded on a Nicolet Impact 400_D IR spectrophotome-



Scheme I

ter. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wave number (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br).

Inherent viscosities were measured by a standard procedure using a Cannon-Fensk Routine Viscometer (Germany). Specific rotations were measured by a Perkin Elmer-241 Polarimeter (Germany). Thermal gravimetric analysis (TGA) data of polymers were taken on a TGA Perkin Elmer 4 Thermal Analyzer, under air atmosphere. The first run of Differential Scanning Calorimetry (DSC) data were recorded on a Perkin Elmer DSC 7- TAC 7 DX Thermal Analyzer, under air atmosphere by the Research Institute of Petroleum Industry (Tehran, Iran). Elemental analyses were performed by Central Laboratory of Malek-Ashtar University of Technology (Tehran, Iran).

Polymer Synthesis

Synthesis of PAIU Block Copolymers

A typical preparation of PAIUs was as follow: In to a dried 25-mL, round bottom flask, a solution of 6 (0.0411 g, 1.64 10^{-4} mol) in 0.20 mL of dry DMF was added to a solution of PEG-400 (0.0328 g, 8.20 10^{-5} mol) and DBTDL (0.0176 g, 2.79 10^{-5} mol) in 0.15 mL of DMF. The mixture was stirred at 0°C for 3 h, at room temperature for 4 h, at 60°C for 4 h, between 70-80°C for 2 h, at 90°C for 4 h and finally at 100°C for 0.5 h.

A solution of 5 (0.0438 g, 8.19 10^{-5} mol) in 0.35 mL of DMF was added to the above viscous solution at room temperature. The solution was stirred at room temperature for 4 h, and then it was heated at 60°C for 4 h, between 70-80°C for 2 h, at 90°C for 4 h and at 100°C for 0.5 h. To the above viscous solution 10 mL of water was added, then under vigorous stirring and trituration a yellow rubber like polymer was precipitated. This polymer was collected by filtration and was dried at 80°C for 10 h under vacum to give 0.1072 g (97.0 %) of polymer PAIU-400-$_4$.

FTIR (KBr, cm^{-1}): 3341 (m), 3299 (m), 3230 (w), 3140 (w), 3042 (w), 2955 (m, sh), 2900 (m), 2865 (m, sh), 1790 (w), 1720 (s), 1600 (s), 1530 (s), 1410 (s), 1390 (m), 1330 (m), 1230 (m), 1180 (w), 1105 (s), 1066 (s), 950 (w), 930 (w), 850 (m), 780 (m), 740 (w), 705 (w), 650 (w), 500 (m).

For $C_{74.34}H_{81.68}N_7O_{17.67}$ (1356.03 g/mol) Elemental analyses calculated: C, 65.85; H, 6.07; N, 7.23. found: C, 65.76%; H, 6.16%; N, 7.36%.

The above polymerization was repeated in the presence of TEA, Py, and no catalyst condition, respectively. The optimized condition was repeated with PEG-600, PEG-1000, and PEG-2000, respectively. For these PEGs, step (1) was started at room temperature.

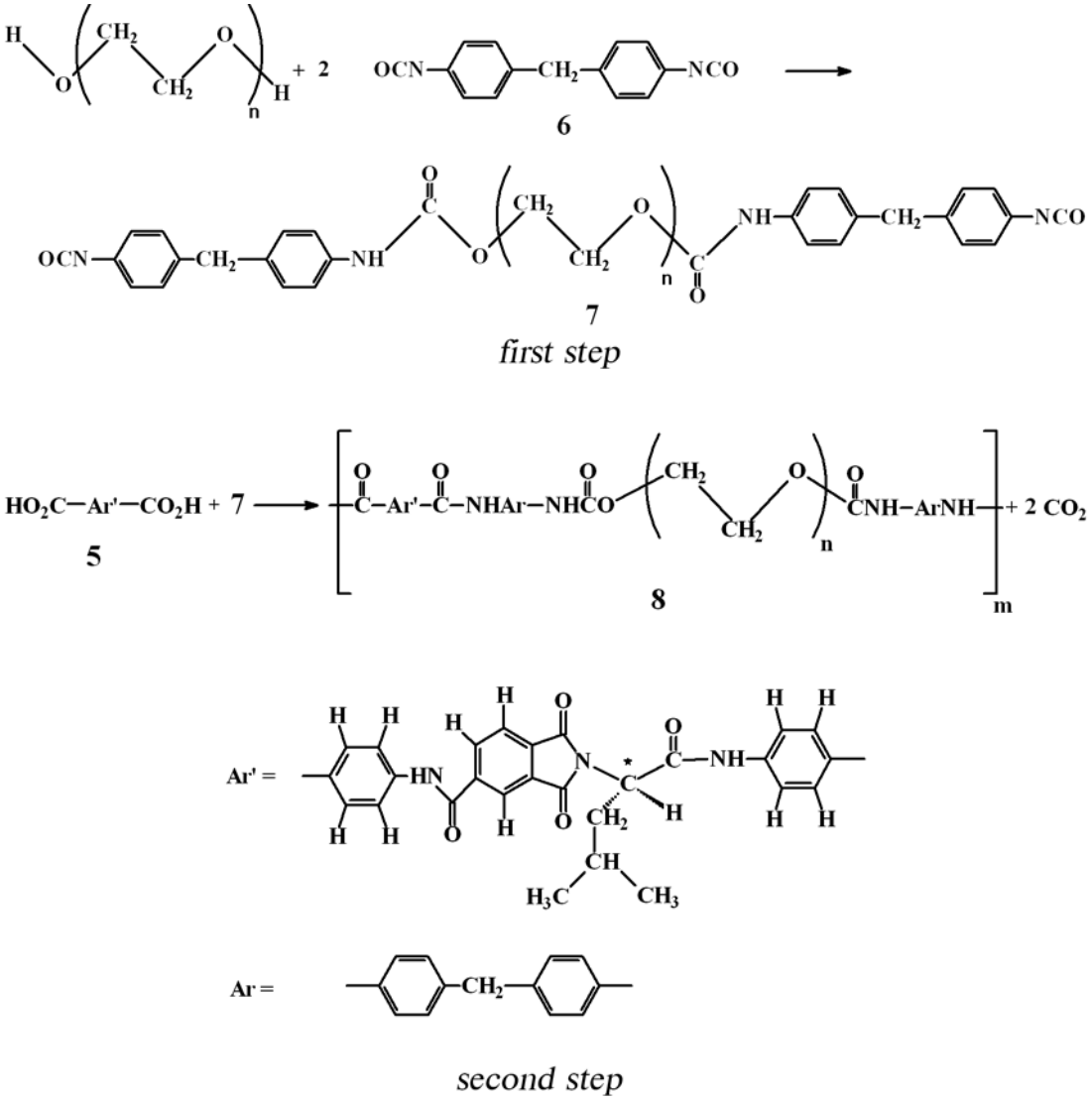
RESULTS AND DISCUSSION

Polymer Synthesis

The PEG-based PAIU multiblock copolymers were synthesized according to Scheme II by the two-step method. In this method, a solution of NCO-terminated PEG 7 was prepared by the reaction of 6 (excess) with PEG in DMF in the presence of TEA, DBTDL, Py, and without catalyst, respectively. Then, diacid chain extender 5 (Scheme 1) along with TEA, Py, and without catalyst was added and the reaction was continued to furnish PAIU multiblock copolymers 1-18 (8), whose polyamide-imide blocks connected with urethane linkages. Some physical properties of the synthesized PAIUs -400 under different reaction conditions are listed in Table 1.

Three series of block copolymers PAIUs-600, PAIUs-1000, and PAIUs-2000 (Table 2) were prepared to investigate the effect of the PEG block length on the physical properties of PAIUs including viscosity, solubility and thermal properties (Figures 2 and 3; Tables 1-3).

According to the Table 1, the effect of DMSO and DMF as solvents on the formation of PAIUs-400-$_1$ and PAIUs-400-$_3$ were compared. In DMSO the resulting copolymer had low yield and viscosity, which could be related to the limited solubility of the reaction mixture during the reaction. The effect of solvent amount was also investigated, and it was found that the ratio of 3/1-5/1 (w/w) of solvent to solid is the best ratio for the copolymerization of PEG-400 (PAIU-400-$_1$ and PAIU-400-$_2$).



Scheme II

Table 1. Some physical properties of PAIUs-400 and reaction conditions.

Polymer	Solvent	Catalyst	Reaction time and Temperature (step 1)	Reaction time and Temperature (step 2)	Yield (%)	Inherent viscosity (dL/g)	$[\alpha]_D^{25}$ a
PAIU-400-$_1$	DMSO	—	A	B	31	0.169[i]	_
PAIU-400-$_2$	DMF (Dilute)	—	A	B	63	0.260[i]	-0.427
PAIU-400-$_3$	DMF (Conc.)	—	A	B	70	0.350[j]	-0.867
PAIU-400-$_4$	DMF	DBTDL[b]	A	B	96	0.315[j]	-0.198
PAIU-400-$_5$	DMF	TEA (2)[c]	A	B	91	0.276[i]	-0.182
PAIU-400-$_6$	DMF	TEA (2)[c]	A	B	78	0.338[i]	-0.576
PAIU-400-$_7$	DMF	Py (2)[d]	A	B	84	0.240[j]	-0.195
PAIU-400-$_8$	DMF	TEA (1)[e]	A	B	74	0.328[j]	-0.543
PAIU-400-$_9$	DMF	Py (1)[f]	A	B	85	0.218[j]	-0.424
PAIU-400-$_{10}$	DMF	DBTDL (1) TEA (2)[g]	A	B	81	0.306[j]	-1.176
PAIU-400-$_{11}$	DMF	DBTDL (1) Py (2)[h]	A	B	90	0.325[j]	-0.204

[a] Measured at a concentration of 0.5 g/dL in solvent (the same as solvent used for viscosity). [b] Dibutyltin dilurate was used from the first step (for both steps was the same). [c] Triethylamine was used in the second step. [d] Pyridine was used in the second step. [e] Triethylamine was used in the first step. [f] Pyridine was used in the first step. [g] Dibutyltin dilurate was used in the first step and triethylamine was used in the second step. [h] Dibutyltin dilurate was used in the first step and pyridine was used in the second step. [i] Measured at a concentration of 0.5 g/dL in DMF. [j] Measured at a concentration of 0.5 g/dL in DMF containing 2% W/W of LiCl. A: 3 h 0°C; 4-5 h at room temperature; 4 h 60°C; 4 h 80-90°C; 0.5 h 100°C. B: 4 h at room temperature; 4 h 60°C; 2 h 70-80°C; 4 h 80-90°C; 0.5 h 100°C.

Table 2. Physical properties of PAIUs-600, 1000, 2000, and reaction conditions.

Polymer	Solvent	Catalyst	Reaction time and Temperature (step 1)	Reaction time and Temperature (step 2)	Yield (%)	Inherent viscosity (dL/g)	$[\alpha]_D^{25}$ a
PAIU-600-$_{12}$	DMF	TEA (2)[b]	A	B	75	0.328[c]	-0.311
PAIU-600-$_{13}$	DMF	—	A	B	85	0.531[c]	-0.800
PAIU-1000-$_{14}$	DMF	—	A	B	45	0.551[c]	-0.558
PAIU-1000-$_{15}$	DMF	TEA (2)[b]	A	B	54	0.171[c]	-0.135
PAIU-2000-$_{16}$	DMF	TEA (2)[b]	A	B	40	0.136[c]	-0.313
PAIU-2000-$_{17}$	DMF	—	A	B	40	0.129[c]	-0.808
PAIU-2000-$_{18}$	DMF (Conc.)	TEA (2)[b]	A	B	55	0.511[d]	-

[a] Measured at a concentration of 0.5 g/dL in solvent (the same as solvent used for viscosity). [b] Triethylamine was used in the second step. [c] Measured at a concentration of 0.5 g/dL in DMF. [d] Measured at a concentration of 0.5 g/dL in DMF containing 2% W/W of LiCl. A: 4-5 h at room temperature; 4 h 60°C; 4 h 80-90°C; 0.5 h 100°C. B: 4 h at room temperature; 4 h 60°C; 2 h 70-80°C; 4 h 80-90°C; 0.5 h 100°C.

In the case of PAIU-$_3$-PAIU-$_{11}$ the effects of different catalysts in different steps of polymerization on the viscosities of PAIUs were studied. From data pertaining to Table 1 and Figure 1, the results of using DBTDL and TEA 2; and DBTDL 1 and TEA 2 are comparable. It means that there isn t any distinct difference between the synergic effect of using tin and amine catalysts together, or using each of them alone. In addition, any preference between TEA and DBTDL is not observed. On the other hand, there isn t any remarkable effect on the viscosity of the resulting PAIUs either, using catalyst in the first step or in the chain extension step.

In the case of Py 1 or Py 2, their viscosities are lower than those of DBTDL or TEA. But under DBTDL (1) Py (2) condition, the viscosity increases and become comparable with that of DBTDL or TEA. According to the data associate with Figures 1-4 and Table 1, TEA and no catalyst condition has comparable results for the preparation of PAIUs-based PEG-400. Thus they were selected to investigate the effect of PEG soft segment length on the sythesis and viscosity of the PAIUs-based PEG 600, 1000, and 2000, respectively (Table 2).

Referring to Table 2, and Figures 2-4 it can be seen that, in the presence of TEA, viscosity decreases by increasing PEG length. On the other hand, no catalyst condition, by providing higher viscosity and lower cost is a better condition for the preparation of PAIUs.

In the case of PAIU-2000-$_{18}$ the reaction was performed by the addition of a solution of 6 (excess) in DMF to the melted PEG-2000 at 60-70ºC (Table 2). PAIUs-2 (Series 2), which were resulting from two-step reaction of NCO-terminated polyether polyols with a diacid chain extender, comparing with PAIUs-1 (Series 1) [29], have better solubility, lower T_g and T_m, and lower thermal stability and viscosity. Unlike

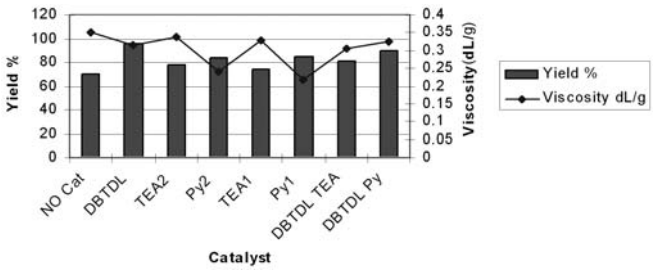


Figure 1. The effect of different catalysts in different steps of the copolymerization reaction of MDI (6) + PEG-400 + BPABTL (5).

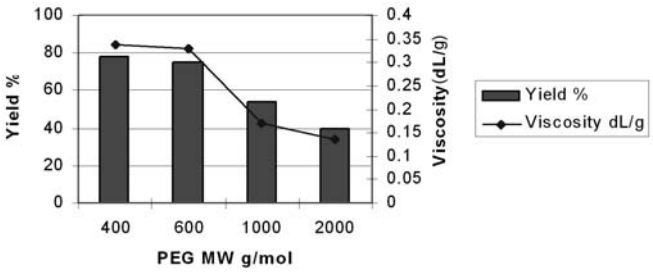


Figure 2. The effect of PEG chain length on the viscosity (dL/g) and yield % of the resulting copolymers in the presence of TEA as a catalyst.

(PAIUs-$_1$), they are also soft and rubbery instead of being rigid and powder-like. These differences can be explained according to formation of more aggregation between amide moieties, closer interactions and longer amide segment lengths that in the case of PAIUs-$_1$, the insersion of nodal crystalline rigid segments between soft amorphous segments (Scheme III). Thus two different methods of copolymerization can provide PAIUs with different properties.

Thermal Property

Thermal properties of PAIUs were evaluated by TGA and DSC under air atmosphere (Table 3). TGA results for all samples, are shown in Figure 5. TGA curves for PAIU-400-$_3$, PAIU-600-$_{13}$, PAIU-1000-$_{14}$ and PAIU-2000-$_{18}$ show smooth sinusoidal manners, as well as, shoulders. This suggests a three step thermal degradation of PAIU-400-$_3$ and PAIU-600-$_{13}$ and a two step thermal degradation of PAIU-1000-$_{14}$ and PAIU-2000-$_{18}$. It can be seen that TGA curves show a decrease in the initial thermal stability of PAIUs by decreasing PEGs length (Figure 6).

According to Figures 5 and 6, the initial degradation occurs in the soft segments. Thus, by increasing

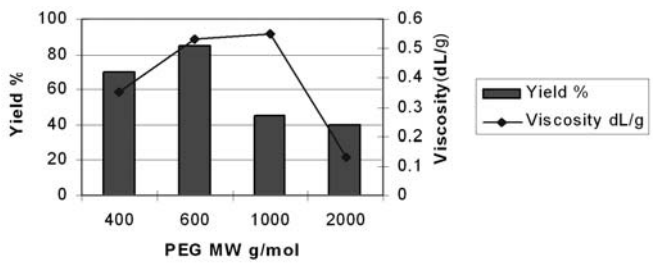


Figure 3. The effect of PEG chain length on the viscosity (dL/g) and yield% of the resulting copolymers in the absence of any catalyst.

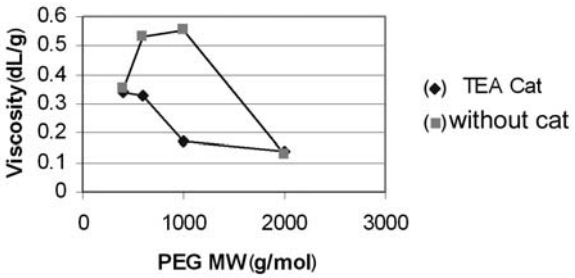
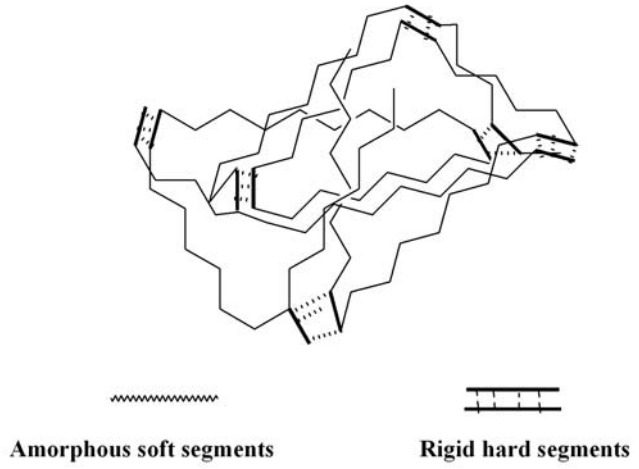


Figure 4. Comparison between the effect of PEG chain length on the viscosity (dL/g) of the resulting copolymers in the presence of TEA as a catalyst and without catalyst conditions.

PEG molecular weight, as well as, distance between nodal rigid amide segments (i.e., more degree of freedom and ease of internal rotation), the capability of damping energy at the beginning of degradation will be increased. If the stability parameters of the PAIUs are taken as a function of temperatures at which 5% and 10% weight loss occurred, the same conclusion can be achieved (Table 3; Figure 6).

Relaying on the data obtaining from char yield (Figure 6), with shorter PEG length, higher char yield is obtained. This could be explained in terms of more participation of hard segment in PAIUs.

Glass transition temperature (T_g) of PAIUs are extracted from DSC diagrams (Table 3). A typical diagram for PAIU-400-$_3$ has been shown in Figure 7. DSC curve of PAIU-400-$_3$ shows no transition associated with softening, or melting. Although a soft segment glass transition temperature (T_gs) and hard segment glass transition temperature (T_gh) were observed around 15°C and 100°C, respectively. It is inferred from



Scheme III

Table 3. Thermal properties of some PAIUs.

Code	DSC	TGA data		
	T_gh/T_gs °C[e]	T_5 °C[a]	T_{10} °C[b]	Char Yield (%)[c]
PAIU-400-$_3$	100/15	275	290	21
PAIU-600-$_{13}$	102	290	305	21
PAIU-1000-$_{14}$	100	312	327	27
PAIU-2000-$_{18}$	226	320	327	(10)[d]

[(a)] Temperature at which 5% weight loss was recorded by TGA at heating rate of 30°C/min in air; [(b)] Temperature at which 10% weight loss was recorded by TGA at heating rate of 30°C/min in air; [(c)] Percentage of weight residue at 600°C in air; [(d)] Percentage of weight residue at 500°C in air; [(e)] T_gh: Glass transition temperature of hard segment. T_gs: Glass transition temperature of soft segment.

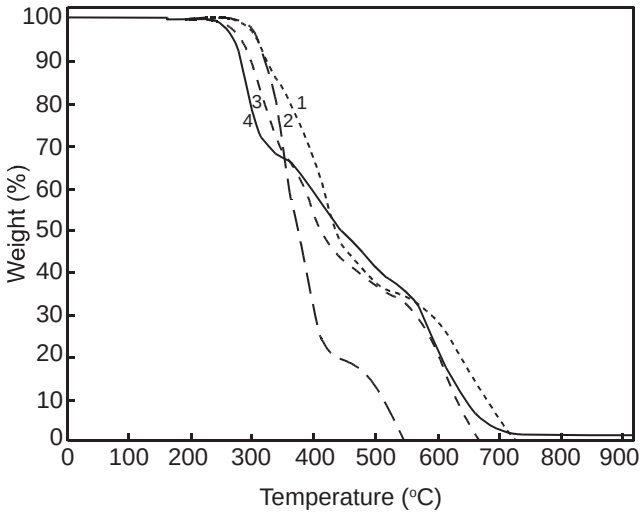


Figure 5. TGA thermograms of PAIUs: (1) = PAIU-1000-$_{14}$, (2) = PAIU-2000-$_{18}$, (3) = PAIU-600-$_{13}$, (4) = PAIU-400-$_3$ under air atmosphere at heating rate of 30°C/min.

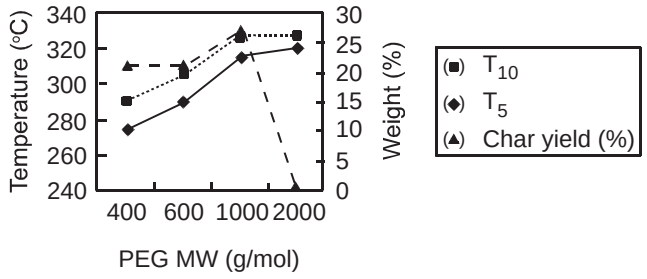


Figure 6. TGA data T_5, T_{10}°C and weight residue % at 600°C of PAIUs versus PEG molecular weight.

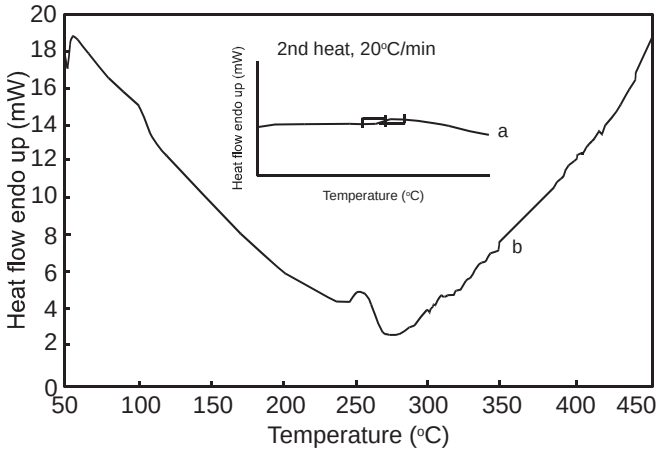


Figure 7. DSC curve of PAIU-400-$_3$ under air atmosphere at heating rate of 20°C/min. Low temperature run (a). High temperature run (b).

T_gh and T_gs that, some phase mixing has occurred. It is showed an endotherm around 250°C, which is due to its melting, as well as, thermal degradation. According to TGA thermogram, it shows an exotherm around 265°C that is in agreement with T_5. Also onset of an endotherm which is observed around 300°C, is in agreement with T_{10} in TGA thermogram.

Structural Characterization

The resulting PAIUs were characterized by FTIR, ^{1}H NMR spectroscopy and elemental analyses. The data are shown in tables 4 and 5. The ^{1}H NMR spectrum of PAIU-2000-$_{17}$ showes peaks that confirm its chemical structure (Table 4, Figures 8-12). It showes peaks for CH_3 (1), (1′) which are appeared as doublets according to their coupling with H (2) with J=6.34 and 6.26 Hz, respectively, in the region of 0.91-0.95 ppm. Peak at 1.48 ppm is due to H (2) and peaks in the region of 1.99-2.03 ppm and 2.20-2.23 ppm are related to the diastereotopic hydrogens of CH_2 (3,3') which are appeared as mutiplets. Peaks in the regions of 3.41 and 3.63 ppm are pertained to CH_2s 4 and 5, respectively. Peak at 4.98-5.01 ppm is assigned to CH of 6. The aromatic protons peaks are appeared in the region of 7.09-8.49 ppm. Peaks in the region of 8.10-8.49 ppm are related to trimellitylimido ring moiety. The peaks in the region of 10.24-10.86 ppm are assigned to NH of

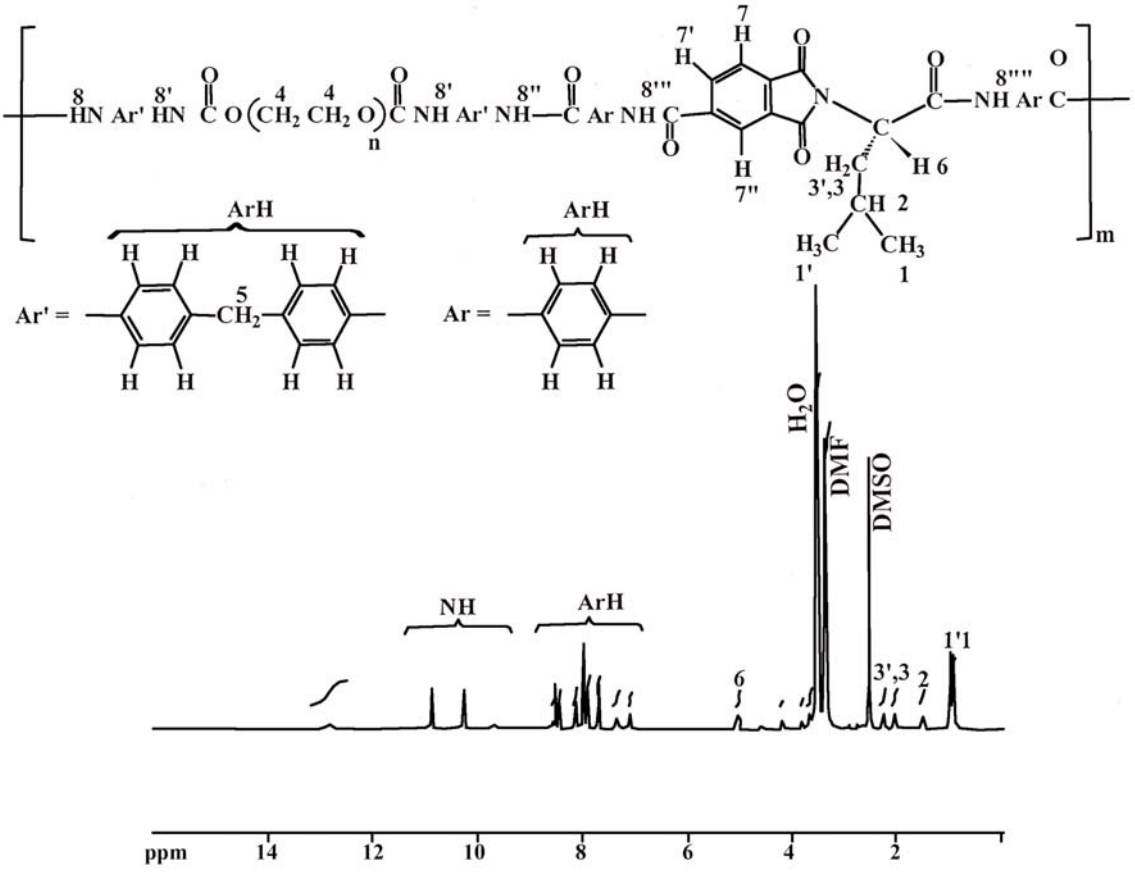


Figure 8. ^{1}H NMR (500 MHz) spectrum of PAIU-2000-$_{17}$ in DMSO-d_6 at RT.

Table 4. ^{1}H NMR and FTIR characterization of some PAIUs.

PAIU-400-$_5$	FTIR Peaks (cm^{-1}): 3340 (m) NH v, 3297 (m) NH v, 3230 (w), 3140 (w), 3040 (w), 2950 (m, sh), 2900 (m), 2864 (m, sh), 1790 (w) C=O urethane (amide I) (non-H-bonded), 1719 (s) C=O urethane (amide I) (H bonded), 1599 (s), 1532 (s) C-N v + NH (amide II), 1412 (s), 1390 (m), 1330 (m) C-N v + NH (amide IV), 1232 (m) C-N v + NH (amide V), 1180 (w), 1105 (s) C-O-C ether, 1066 (s) O=C-O-C, 950 (w), 930 (w), 850 (m), 780 (m), 740 (w) O=C-O, 700 (w), 650 (w), 500 (m).
PAIU-1000-$_{14}$	FTIR Peaks (cm^{-1}): 3284 (m, br), 3200 (w), 3100 (w), 2950 (m, sh), 2931 (m), 2850 (m), 1770 (m), 1725 (s), 1690 (s), 1599 (s), 1526 (s), 1419 (m), 1370 (m), 1300 (m), 1246 (m), 1200 (w), 1160 (w), 1073 (s), 980 (w), 950 (w), 850 (m), 760 (w), 710 (w), 690 (w), 545 (w), 500 (w).
PAIU-2000-$_{17}$	^{1}H NMR Peaks (500 MHz, DMSO-d_6, δ; ppm): 0.91 (d, CH_3, J = 6.34 Hz), 0.95 (d, CH_3, J = 6.26 Hz), 1.48 (m, br, CH), 1.99-2.03 (m, CH in CH_2), 2.20-2.23 (m, CH in CH_2), 3.41 (m, CH_2, overlapped with DMF peak), 3.63 (s, br, CH), 4.98-5.01 (distorted dd, CH), 7.09-7.99 (m, ArH), 8.10 (distorted d, CH in TMA, J = 7.63 Hz), 8.43 (distorted d, CH in TMA, J = 7.78 Hz), 8.49 (s, br, CH in TMA), 10.24-10.86 (s, NH).

amide and urethane groups.

The FTIR spectrum of PAIUs showed peaks that confirm their chemical structures (Table 4). As an example the FTIR spectrum of PAIU-400-$_5$ (Figure 13) is shown the characteristic absorption of amide, imide, and urethane groups around 3340, 1790, 1719, 1599, and 1532 cm^{-1} peculiar to N-H, C=O and C-N vibrations of amide (I, II), imide, and urethane groups, respectively (Table 4). Peaks at 1412, 1330, 780, and 700 cm^{-1} are showed the presence of imide heterocyclic ring in the polymer.

Table 5. Elemental Analyses Data of Some PAIUs[a].

Formula		C %	H %	N %
PAIU-400-$_7$	Calculated	65.85	6.07	7.23
$C_{74.34}H_{81.68}N_7O_{17.67}$	Found	65.76	6.16	7.36
1356.03 g/mol				
PAIU-600-$_{13}$	Calculated	64.39	6.47	6.30
$C_{83.42}H_{99.84}N_7O_{22.21}$	Found	64.27	6.59	6.50
1555.98 g/mol				

[(a)] The polymer sample was dried in vacuo at 100°C for 10 h.

The elemental analyses results are also in good agreement with calculated percentages of carbon, hydrogen and nitrogen contents in the polymer repeating units (Table 5) that, suggest a regular alternate structure for copolymers.

Solubility Properties of PAIUs

Solubility properties of PAUIs were studied in different solvents (Table 6). The polymers are soluble in amide type solvents such as NMP, DMF, DMAc, and to some extent in DMSO. They are insoluble in solvents such as water, methanol, acetone, cyclohexane, and chloroform.

CONCLUSION

Four different series of optically active thermoplastic

Table 6. Solubility properties of PAIUs.

Solvents	PAIU-600	PAIU-1000	PAIU-2000	PAIU-2000
DMAc	+	+	+	+
DMF	+ +	+ +	+ +	+ +
NMP	+ + +	+ + +	+ + +	+ + +
DMSO	±	±	±	±
MeOH	-	-	-	-
EtOH	-	-	-	-
$CHCl_3$	-	-	-	-
CH_2Cl_2	-	-	-	-
H_2O	-	-	-	-
Acetone	-	-	-	-
Cyclohexane	-	-	-	-

(+): Soluble at boiling temperature, (++); Soluble at boiling water temperature, (+++); Soluble at room temperature , (–); insoluble, (±); partially soluble.

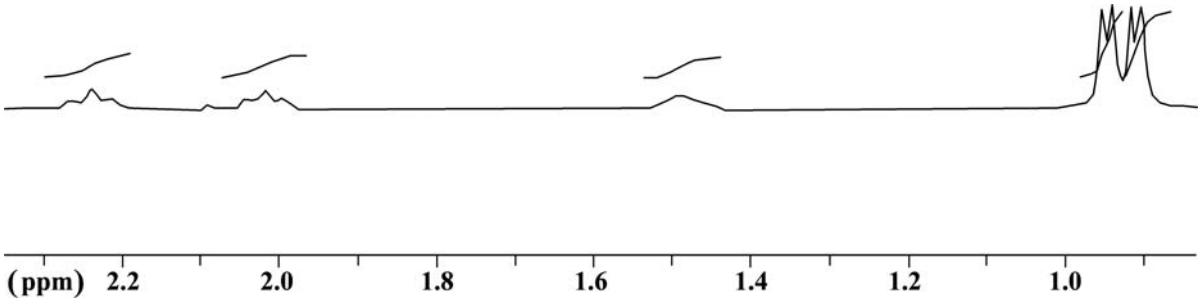


Figure 9. ^{1}H NMR (500 MHz) spectrum of PAIU-2000-$_{17}$ in DMSO-d_6 at roomtem. Expanded region for the aliphatic protons # (H:1-3) (δ = 0.91-2.23 ppm).

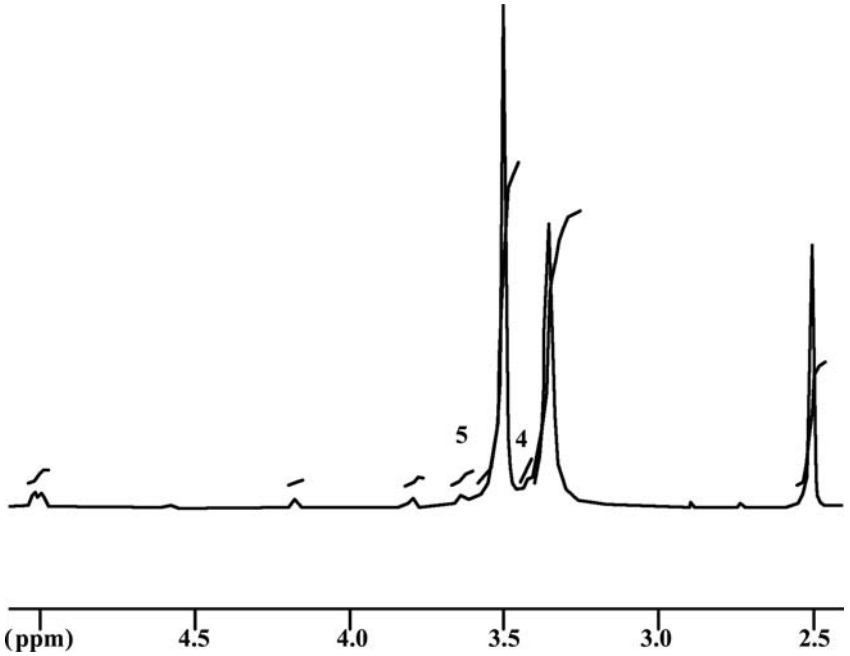


Figure 10. ^{1}H NMR (500 MHz) spectrum of PAIU-2000-$_{17}$ in DMSO-d_6 at roomtem. Expanded region for the aliphatic protons # (H: 4-6) (δ = 2.51-5.01 ppm).

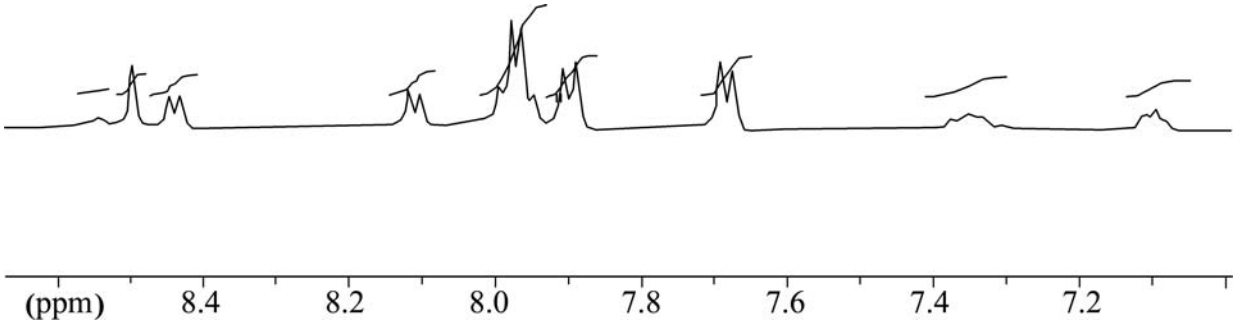


Figure 11. ^{1}H NMR (500 MHz) spectrum of PAIU-2000-$_{17}$ in DMSO-d_6 at roomtem. Expanded region for aromatic protons (δ = 7.09-8.49 ppm).

PAIUs based on PEG-MDI and a new optically active diacid were synthesized successfully. These PAIUs were obtained by the chain extension reaction of NCO-terminated PEGs prepared from the reaction of different PEG with excess of 6. Then chain extension of the above soft segment with a chiral amino acid based-

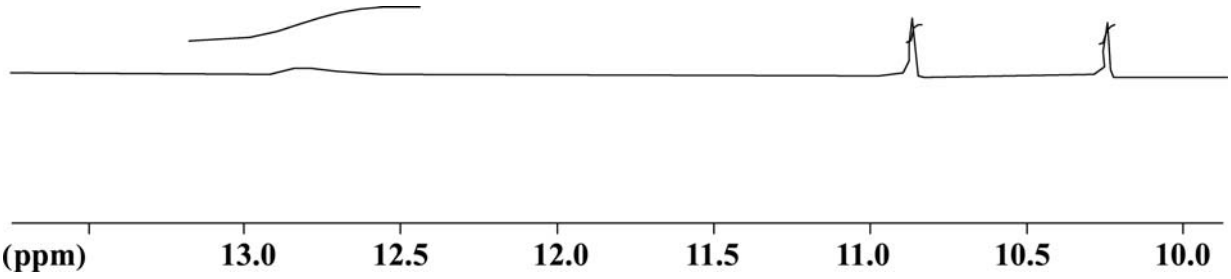


Figure 12. ^{1}H NMR (500 MHz) spectrum of PAIU-2000-$_{17}$ in DMSO-d_6 at roomtem. Expanded region for NH protons (δ = 10.24-10.86 ppm).

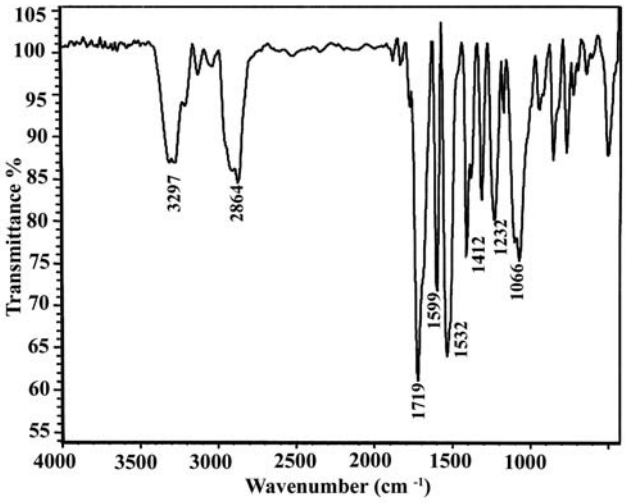


Figure 13. FTIR (KBr) spectrum of polymer PAIU-400-$_5$.

dicarboxylic acid containing a preformed imide ring, furnished these copoly(amide imide urethane)s. The synthetic procedure, referred to as two-step method, is effective for the synthesis of multiblock copolymers having high structural regularity. Systematic synthesis of PAIUs was performed in the presence of different catalysts under different reaction conditions. These studies demonstrate how the reaction conditions, catalysts, and sequence of chain extension steps influence the efficiency of polymer chain growth, physical properties, and hence, porocessability of PAIUs.

According to the data obtained from this study, the best condition for preparation of these types of optically active PAIUs is using DMF as a solvent in the absence of any catalyst. TGA data indicate that these types of thermoplastic elastomers are relatively more stable than typical PUs. In addition, increasing soft segment length caused an increase in phase separation along with increasing initial thermo-oxidative stability.

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