

Preparation and Properties of New Copoly(amide-imide-ether-urethane)s based on Bis(*p*-amido benzoic acid)-*N*-trimellitylimido-*L*-leucine by Two Different Polymerization Methods

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Summary

Two series of new optically active poly(amide-imide-ether-urethane)s (PAIEU)s based on polytetrahydrofuran (PTHF), of $M_n=1000$ as soft segment were synthesized. These copolymers were prepared via direct polycondensation reaction of an aromatic diacid based on *L*-leucine with preformed imide ring, 4,4'-methylene-bis-(4-phenylisocyanate) (MDI) and PTHF-1000. The effects of different reaction conditions and method of preparation (one-step vs. two-step method) on the physical properties of these new PAIEUs have been investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide angle X-ray scattering (WAXS), FTIR spectroscopy, and dynamic mechanical thermal analysis (DMTA). The effect of the introduction of bis(*p*-amido benzoic acid)-*N*-trimellitylimido-*L*-leucine (BPABTL) (**1**) into PU back-bone on their properties was also studied.

Introduction

The widely known importance of thermoplastic polyurethane elastomers (TPUs) in many industrial fields has resulted in an increase in the research on this subject [1-9] dealing with different topics from structure to applications [10-14]. It has been found that the properties of the final TPUs can be controlled and adjusted to any specific application by optimizing the pre-polymerization and chain extension steps [15,16]. The effect of polymerization method (one or two stage) on the morphology and properties of segmented polyurethanes (PU)s has been also a topic of research interest [17,18].

Regardless of the methods of preparation, PUs are always characterized by a heterogeneous structure in which, the continuous soft phase contains different populations of crystalline hard domains [16]. This microstructure is responsible for most of the extraordinary properties of PUs utilized in many applications [19]. It is well known from the literature that, apart from the phase separation behavior, the structure of PUs is dependent on the synthetic method which has been employed. It

has been shown that the standard two-step polymerization yields a statistical distribution of the hard segment length, which arises from the reaction product of diisocyanate and chain-extender [16]. More ordered structures of the hard segment (HS), characterized by a monodisperse distribution of chain lengths, can be obtained only by adopting specific synthetic techniques [20-23]. Thus, it is expected that, if different methods of synthesis are used, polymers with different structures and properties can be obtained [16].

Although PUs are becoming increasingly important as engineering materials, but their poor heat-resistance limits their applications. One method to improve the thermal stability of PUs is chemical modification of their structures [24,26]. The introduction of highly thermally stable groups such as polyimide, oligoimide, polyamide or poly(amide-imide) units into PUs via a one-shot or a sequential method may alter their properties [26-29].

In addition, amino acid-based chiral polymers can induce crystallinity with the ability to form higher ordered structures that exhibit enhanced solubility characteristics. These properties result in polymers that are ideal candidate for drug delivery systems, biomimetic systems, biodegradable macromolecules, biomaterials and as chiral purification media [30-32].

In connection with our interest in preparing thermally stable chiral polymers based on amino acids [33-40], this work deals with a detailed study on the synthesis and characterization of a series of modified segmented PAIEUs by two different polymerization methods (one-step vs. two-step).

Experimental

Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co. MDI (**2**), a high purity Aldrich product, was used without further purification. PTHF-1000 (Merck Chemical Co.) was dried under vacuum at 80°C for 8 h. Pyridine (Py), triethylamine (TEA) and *N*-methyl pyrrolidone (NMP) (Merck Chemical Co.) were distilled under reduced pressure over BaO. BPABTL (**1**) was prepared according to the reported procedure [41]. The yield of the diacid (**1**) 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 $^1\text{H-NMR}$ (500 MHz) spectra were recorded on a Bruker (Germany) Avance 500 instrument in $\text{DMSO-}d_6$. Multiplicities of proton resonance were designated as broad (br), singlet (s), doublet (d), and multiplet (m). FTIR spectra were recorded on a Jasco FTIR spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber (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-Fenske Routine Viscometer (Germany). Specific rotations were measured by a Jasco Polarimeter to spy the incorporation of diacid (**1**) into the polymer backbone. TGA data for polymers were taken on a Perkin Elmer Thermal Analyzer under N_2 atmosphere. DSC data were recorded on a DSC-PL-1200

instrument under N₂ atmosphere by the Research Institute of Polymer and Petrochemical of Iran (IPPI). Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity taken from the heating DSC traces. A sample was first scanned from room temperature to 200°C and maintained for 30 Sec followed by quenching to -100°C at a cooling rate of 10°C/min, and then a second heating scan was used to measure sample's glass transition temperatures of soft (T_{gs}) or hard segment (T_{gh}). A heating rate of 10°C/min was applied to all samples. WAXS analysis was performed at ambient conditions on a Zimence D-5000 using Ni filtered Cu K α radiation by IPPI. The supplied voltage and current were set to 40 kV and 25 mA, respectively. Samples were run at a scan rate of 2 θ = 5°/min between 2 θ = 5 and 70°. Dynamic mechanical testing was carried out on a UK Polymer Lab dynamic mechanical thermal analyzer, Model MK-II, over a temperature range from -80 to 270°C at heating rate of 10°C/min and a frequency of 1 Hz. The dimensions of samples were 15 × 7 × 1 mm³ which were made by solution casting technique. The value of tan δ and the storage modulus, E', verses temperature were recorded for each sample.

Polymer synthesis

Synthesis of PAIEUs copolymers

A typical preparation of PAIEUs by pre-polymerization method is as follow: Into a dried 25 mL round bottom flask **(1)** (0.596 g, 1.09 × 10⁻³ mol) and **(2)** (0.549 g, 2.19 × 10⁻³ mol) were dissolved in 2 mL of NMP and TEA (0.25 mL, 1.80 × 10⁻³ mol) was added. The mixture was stirred for 2 h at room temperature (RT), and then the temperature was gradually increased up to 120°C. Then it was cooled to RT, and PTHF-1000 (1.097 g, 1.09 × 10⁻³ mol) in 2 mL of NMP was added. The reaction mixture was stirred at RT for 2 h then heated up to 100°C gradually. The viscous solution was poured into 10 mL of water, to isolate the polymer. For more purification fractional precipitation method was used by re-dissolving and re-precipitation of polymer in NMP and methanol-water, respectively. The precipitated polymer was collected by filtration, and was dried at 80°C for 10 h under vacuum to give 1.44 g (67%) of polymer **PT-2**.

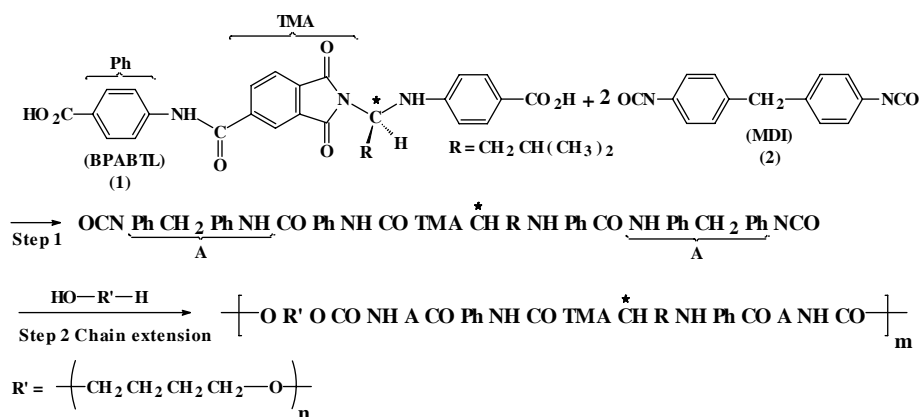
For one-step procedure, the polymerization reaction was performed by adding all of the above mentioned components in one step and the reaction mixture was gradually heated from RT up to 120°C.

Results and discussion

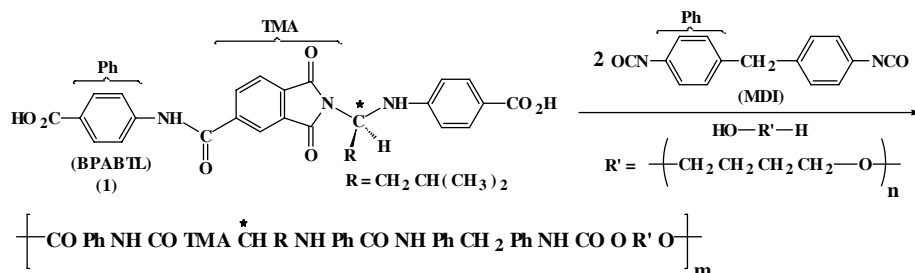
Polymer synthesis

The PAIEU multiblock copolymers based on PTHF-1000 were prepared according to schemes 1 and 2 by two-step or one-shot method. The reactions were performed in NMP in the presence of different catalysts or without catalyst, respectively and NCO to OH ratio was kept 1:1. When the diisocyanate segment is equal to the stoichiometric one, the number of chemical crosslinks is almost negligible and the elastomeric behavior is entirely due to the physical crosslinks [42]. The reaction between diacid and diisocyanate as well as NCO and polyol was followed by FTIR

spectroscopy. After the completion of the reaction upon disappearance of NCO absorption band at 2270 cm^{-1} the reaction mixture was precipitated. These methods furnished PAIEUs whose polyamide-imide blocks are connected with urethane linkages (Polymers 1-6, Tables 1-2).



Scheme 1. Preparation of PAIEU multiblock copolymers by two-step method.



Scheme 2. Preparation of PAIEU multiblock copolymers by one-step method.

The effect of polymerization conditions and catalysts on the viscosity and yield of the PAIEUs

The polymerization reactions were carried out under optimized conditions obtained for solvent type, the ratio of solvent to solid, reaction time and temperature for the direct reaction of diacid and diisocyanate according to our previous work [33-34].

The preparation of PAIEUs based PTHF-1000 was carried out in the presence of some catalysts such as, TEA, Py and dibutyltin dilurate (DBTDL) by two-step method. It can be seen that the results were relatively comparable with that of Py and no catalyst conditions considering viscosity and yield (Table 1). The polymerization reactions were repeated by one shot method in the absence of any catalyst. It is observed that polymer chain growth is lower than that of two-step method (Table 2). In the case of **PT6** the one-step polymerization was performed in a longer period of time and temperature to compensate longer reaction period of two-step method. As it is inferred from Table 2 there was no significant change in the viscosity. It means that

establishing hard segment as oligo amide-imide in the first step, and then chain extension by a polyol in the second step can lead to higher viscosities. It can be explained according to difference in the reactivity of alcoholic and carboxylic groups towards NCO group.

Table 1. Some physical properties of PAIEUs based PTHF-1000 & reaction conditions: Study of the effect of catalysts, two-step method, 1:2:1 was the ratio of Diacid:MDI:Polyol, NMP was used as a solvent.

Polymer	Catalyst	Reaction condition (step 1)	Reaction condition (step 2)	Yield (%)	η_{inh} (dL/g) ^e	$[\alpha]_D^{25}$ ^e	$[\alpha]_{Hg}^{25}$ ^{e,f}
PT1 ^a	NO	A	B	81	0.65	-1.18	-7.47
PT2	TEA ^b	A	B	67	0.55	-0.89	-14.62
PT3	Py ^c	A	B	82	0.67	-0.90	-2.31
PT4	DBTDL ^d	A	B	98	0.57	-1.06	+1.39

^aPoly(amide-imide-ether-urethane) based PTHF-1000, the first PAIEU and etc. ^bTriethylamine. ^cPyridine. ^dDibutyltin dilurate. ^eMeasured at a concentration of 0.5 g/dL in 2% W/W LiCl/DMF as solvent. ^fWide rang was used (no filter was used for the Hg lamp), A: 2 h RT; 2h 50-60°C; 2h 60-80°C; 5h 80°C; 3h 80-120°C; 2h 120°C, B: 2h RT; 2h 50-60°C; 2h 60-80°C; 5h 80°C; 2h 80-100°C, 1h 100°C.

Table 2. Some physical properties of PAIEUs based PTHF-1000 & reaction conditions: One-step method, 1:2:1 was the ratio of Diacid:MDI:Polyol, NMP was used as a solvent.

Polymer	Catalyst	Reaction condition	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_D^{25}$ ^a	$[\alpha]_{Hg}^{25}$ ^{a,b}
PT5	NO	A	88	0.50	+3.12	-3.81
PT6	NO	B	91	0.55	+3.19	-2.99

^aMeasured at a concentration of 0.5 g/dL in 2% W/W LiCl/DMF as solvent. ^bWide rang was used (no filter was used for the Hg lamp), A: 2 h RT; 2h 50-60°C; 2h 60-80°C; 5h 80°C; 3h 80-120°C; 2h 120°C B: 4h RT; 4h 50-60°C; 4h 60-80°C; 8h 80°C; 3h 80-120°C, 2h 120°C.

Thermal properties

Thermal properties of PAIEUs were evaluated with TGA and DSC techniques (Table 3).

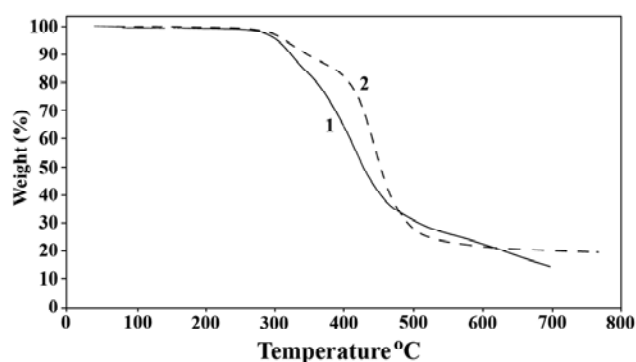
TGA studies for **PT1** and **PT6** are presented in figure 1. TGA curve associated with **PT1** prepared by two-step method shows relatively greater thermal stability than **PT6** (Figure 1). It may be explained that the so-called regular two-step synthesis seems to favor the MDI+BPABTL+MDI sequences as the largest constitutive part of the hard phase and led to better interaction and stability between them. It is well known that the regularity of the HS affects the morphology, interchain interactions and the calorimetric behavior of SPUs.

Typical DSC diagrams for **PT1** and **PT6** have been shown in figure 2. Three endotherms are almost observed. The low temperature endotherms located below 50°C, that can be ascribed to short range reorganization within the HS microdomains distributed in the soft phase and melting the crystalline region of soft segment.

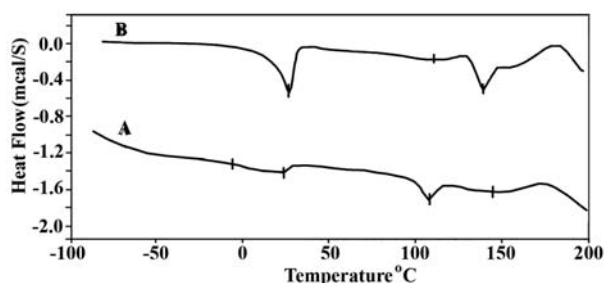
Table 3. Thermal properties of PAIEUs based PTHF-1000^a.

Polymer	¹ T _{gs} (°C)	² T ₂ (°C)	³ T _{gh} (°C)	⁴ T _c (°C)	⁵ T _{10%} (°C)	⁶ char yield%
PT1	⁷ -19	26.8 _{sh}	107 _{br}	140 _{sh}	357	20
PT6	-10 _{br}	25 _{br}	-	108.5	323	12

³Center of the region was considered for transitions observed by DSC. ¹Glass transition temperature of SS, ²Melting temperature of crystalline domain of SS and /or crystalline microdomin of HS distributed in SS, ³Glass transition temperature of HS, ⁴Melting temperature of crystalline domain of HS, br = broad, sh = sharp. ⁵Temperature at which 10% weight loss was recorded by TGA at heating rate of 20°C/min in N₂ atmosphere, ⁶Percentage of weight residue at 700°C in N₂ atmosphere by TGA. ⁷ By DMTA.

**Figure 1.** TGA thermogram of PAIEUs prepared by one-step (1) and two-step (2) methods.

The endotherm observed at temperatures ranging between 75-125°C is associated with the disruption of long-range structures in HS and/or Tgh, finally the endotherm observed above 125°C can be assigned to the melting of crystalline regions of hard domains (Table 3). DSC trace of **PT6** shows a broad base line change between -30 to 12°C (T_{gs}), a broad endotherm peak at 25°C (T₂), a peak at 108°C (T_c) and a broad endotherm between 125-165°C (T_{c2}). Copolymer of **PT1** exhibit more or less similar endothermic effects that are summarized in Table 3. The distinct and sharp peak of **PT1** at 140°C (T_c) compared to **PT6** suggests more crystalline structure for HS, relatively regular distribution of HS length and more cohesiveness of HS. This phenomenon was confirmed by FTIR and WAXS observations. Also it could be concluded from the endotherm of **PT1** at 26.8°C (T₂), crystalline region of soft segment is more than that of **PT6**. We deem that T₂, T_c and T_{c2} are melting

**Figure 2.** DSC curve of PAIEUs prepared by one-step (A) and two-step (B) methods.

temperatures of microcrystalline regions in soft segment (SS), and different crystalline domains in HS essentially built up from MDI+BPABTL+MDI segments.

DMTA study

The dynamic mechanical thermal behaviors of prepared PAIEUs were studied by DMTA measurements. The performance of PU elastomers at elevated temperature is dependent upon the structure of the rigid segments and their ability to remain coherent at a higher temperature. As it can be seen from figure 3 the storage moduli of **PT1** is higher than that of **PT6** over a wide range of temperature and the temperature to which the plateau extends is also increased. It can be explained upon more crystallinity and interchain H-bonding of HS of **PT1**. Generally, increased material strength not only can be in terms of improved phase separation, but also is rather as an effect of the hard domain cohesiveness produced by Vander Waals or H-bonding. As it can be seen in the case of **PT1**, the α -type Tg increased; while the β -type Tg decreased in comparison with **PT6**. This can be due to the relatively more phase separation of **PT1** comparing with **PT6**. The $\tan \delta$ vs. temperature curves (Figure 4) display loss peaks associated with glass transition and damping capacity of the soft

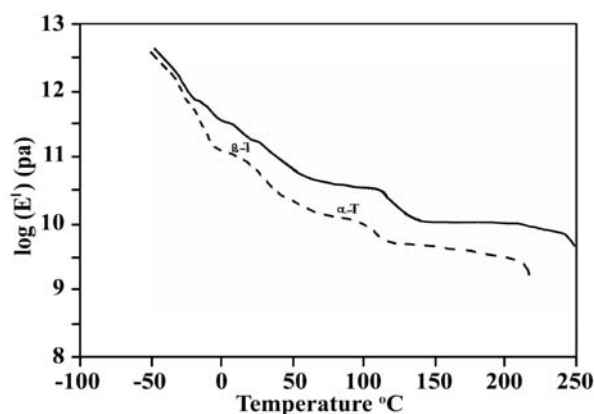


Figure 3. Dynamic storage modulus (E') for PT1 (—) and PT6 (---).

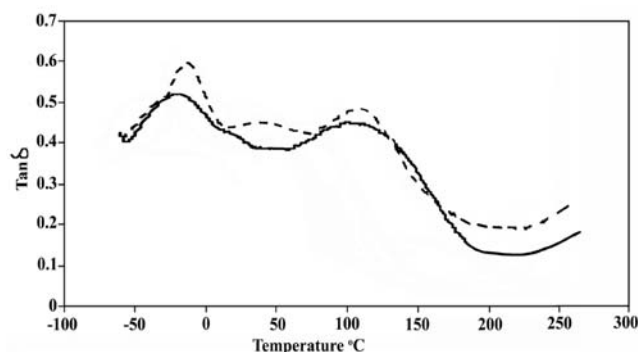


Figure 4. DMTA $\tan \delta$ curves for PT1 (—) and PT6 (---).

domains at -19 and -14°C for **PT1** and **PT6**, respectively. An additional small shoulder can be seen at approximately 30°C for **PT1** that may be due to the melting of micro-crystalline domain of SS. The sharpness and height of the damping peaks of **PT6**, suggests less crystallinity of this polymer comparing with **PT1** that has been confirmed by WAXS study.

FTIR study for phase miscibility

Infrared spectroscopy is a useful tool for morphological probe of PUs, and it is common to study the hydrogen bonding in segmented polyurethanes [43,44]. For PUs, the carbonyl absorption region is of interest, since it gives information on inter-urethane H-bonding. More ordered structure of HS and interchain H-bonding interaction of PAIEUs prepared by two-step method relative to one-step method can be confirmed by FTIR study of characteristic bands of carbonyl of urethane and amide groups. For example FTIR spectrum of **PT1** shows absorption bands at 1774 cm^{-1} due to free C=O (non H-bonded), 1721 and 1679 cm^{-1} due to urethane and amide C=O (H-bonded), respectively (figure 5, A). For **PT6** peak of free C=O is relatively more intense, and peaks of urethane and amide C=O (H-bonded) shifted to higher wave number, e.g. 1723 and 1680 cm^{-1} (figure 5, B).

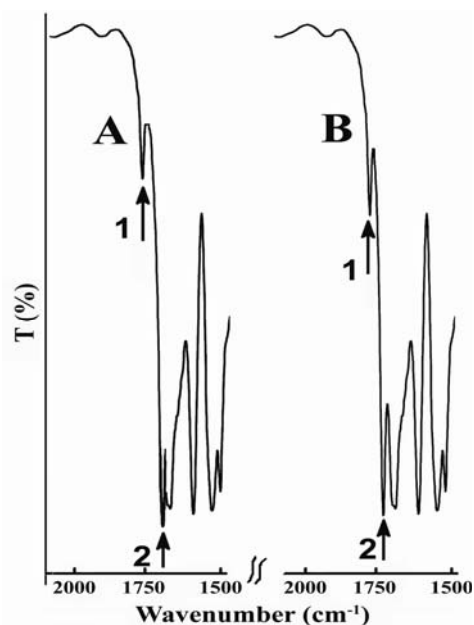


Figure 5. FT-IR peaks of carbonyl groups for PAIEUs prepared by two-step (A) and one-step (B) methods. C=O free (1), C=O H-bonded (2).

X-ray diffraction study

WAXS analyses for PAIEUs based PTHF-1000 are presented in figure 6 and Table 4. The diffraction patterns for **PT1** and **PT6** show two main crystalline regions A and B

divided into 1, 2, 3, and 4 maxima as main peaks. These peaks present for PAIEUs samples regardless of the degree of phase separation, degree of crystallinity, and method of polymerization. The peaks at $2\theta = 16.4$, 21.2 and 24.1 ($^\circ$) can be matched to literature values for MDI, MDI-O(CH₂)₄-O-, and PTHF crystallinity [45-47]. The other peaks presented in Table 4 can be due to BPABTL and MDI+BPABTL segments. Our recent study [48] shows that the intensity of maxima at 1, 2, 3, and 4 (specially at 3 and 4) grows and sharpen as HS content increases. The effect of polymerization method on the crystallinity of PAIEUs is obvious from figure 6. The percentage of crystallinity obtained for **PT1** at A and B regions is 5% and 66%, respectively. These data for **PT6** are 3.5% and 56%, respectively. This means that two-step method has resulted in polymer with more crystallinity than one prepared by one-step method.

Table 4. WAXS peak position for PAIEU based PTHF-1000.

Polymer	Diffraction Angles, 2θ ($^\circ$)	d -Spacing ($^\circ$ A)
PT1	9.8, 11.1, 16.5 ^a , 18.8, 20.5 ^b , 21.2, 24.1 ^b , 26.9, 28.5	8.8, 7.9, 5.4, 4.8, 4.3, 4.1, 3.5, 3.3, 3.1

^aMatches with literature MDI-OCH₂CH₂CH₂CH₂O- lattice and MDI-MDI plane interaction,

^bMatches with literature PTHF lattice [45-47].

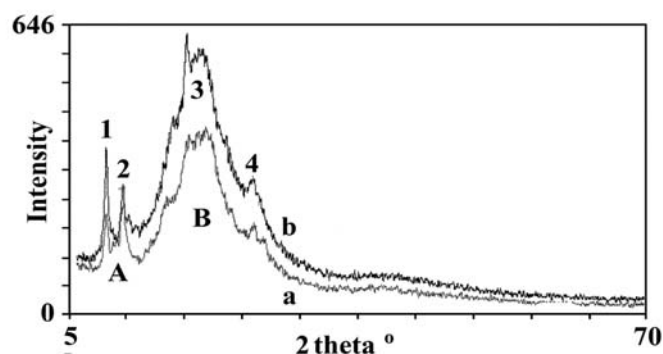


Figure 6. WAXS pattern for PAIEUs prepared by one-step (a) and two-step (b) methods.

Structural characterization

The resulting PAIEUs were characterized by FTIR and ¹H-NMR spectroscopy (Table 5). The ¹H-NMR spectrum of **PT6** showed peaks that confirms its chemical structure (Figure 7). It showed peak for CH₃ (1, 1') which appeared as distorted doublet according to their coupling with H (2) with $J = 17$ Hz, in the region of 0.91-0.95 ppm. Peaks in the region of 1.57-2.26 ppm are related to H (2) and the diastereotopic hydrogens of CH₂ (3,3') which appeared as multiplet. Peaks in the regions of 3.50 and 3.80-4.08 ppm are pertain to CH₂s (4), (4'), (5) and (6), respectively. Peak at 5.01 ppm is assigned for CH (7). The aromatic protons appeared in the region of 7.12-8.64 ppm that peaks in the region of 8.06-8.64 ppm are related to TMA ring moiety. The peaks in the region of 9.6-10.6 ppm are assigned for NH of amide and urethane groups.

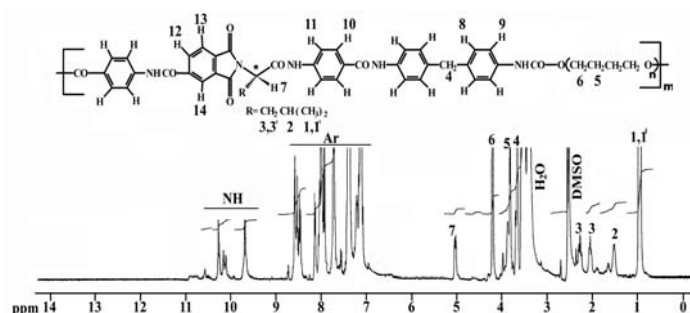


Figure 7. $^1\text{H-NMR}$ (500 MHz) spectrum of PT6 in DMSO-d_6 at RT.

The FT-IR spectrum of **PT1** showed the characteristic absorption of amide, imide and urethane groups around 3404, 3323, 1774, 1721, 1679, 1602, 1538 cm^{-1} , peculiar to NH, C=O and C-N vibrations of amide (I, II) imide and urethane groups, respectively. Peaks at 1408, 1315, 771, and 756 cm^{-1} show the presence of imide heterocyclic ring in the polymer structure (Table 5).

Table 5. FT-IR and $^1\text{H-NMR}$ assignments of PAIEUs.

PT1	FTIR Peaks (cm^{-1}): 3404 (s, br), 3323 (s, sh), 3270 (s, sh), 3208 (m), 2940 (s), 2856 (s), 2796 (w), 1774 (w), 1721 (s), 1679 (s), 1602 (s), 1539 (s), 1509 (s), 1408 (s), 1383 (s), 1375 (s), 1315 (s), 1256 (m), 1234 (m), 1176 (m), 1112 (s), 1017 (w), 990 (w), 958 (w), 857 (w), 771 (m), 756 (w), 729 (w), 710 (w), 549 (w), 510 (w).	$^1\text{H-NMR}$ Peaks (ppm): 0.91-0.96 (d, CH_3 , $J=17$ Hz), 1.57-1.62 (m, CH), 1.83-2.26 (m, CH_2 , br), 3.47-3.49 (m, CH_2), 3.8-4.08 (m, CH_2), 5.01 (m, CH), 7.12-8.64 (Ar-H), 9.6-10.6 (s, br, NH).
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Solubility Properties

The solubility properties of PAIEUs were studied in different solvents. 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, chloroform and dichloromethane. It is interesting to mention that PAIEUs prepared by one-shot method dissolve faster than those prepared by two-step method probably because of lower crystallinity, better accessibility of their structure and lower interchain interactions.

Conclusions

The following conclusions can be drawn from this study:

Three to four DSC endotherms provided evidence to hypothesize that the regular two-step synthesis seems to favor the MDI+BPABTL+MDI sequence, as the largest constitutive part of the hard phase in the sense that calorimetric transitions were better defined (sharpen), and the morphology was more regular. However, in this case, phase separation will not be complete, and it will be possible that soft domains contain some dissolved hard blocks and vice versa. From TGA and DMTA data it can be concluded

that two-step method resulted in polymers with higher thermal stability. It was shown that BPABTL is an interesting candidate to incorporate amide, imide and amino acid moieties into SPUs and prepare them with more thermal stability, induced more crystallinity as well as good solubility. It was observed that establishing hard segment as oligo amide-imide in the first step, and chain extension by a polyol in the second step can lead to polymers with higher viscosities, crystallinity, thermal stability and more interchain H-bonding interaction. Since the resulting PAIEUs contain amino acid, urethane and polyether linkages they could be biodegradable and biocompatible.

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References

- Chen W, Frisch KC, Wong S. (1992) *Advance in Urethane Science and Technology*; 11, Chap 3, Frisch KC, Klempner D. Eds; Lancaster: Technomic.
- Huang YJ, Chu CJ, Dong JP (2000) *J. Appl. Polym. Sci.*, 78 (3):543-557.
- Yamaguchi I, Takenaka Y, Osakada K, Yamamoto T (1998) *Polymer Bulletin*, 41: 29-35.
- de Groot JH, Spaans CJ, Dekens FG, Pennings AJ (1998) *Polymer Bulletin*, 41: 299-306.
- Li J (2006) *Polymer Bulletin*, 56: 377-384.
- Spaans CJ, de Groot JH, Dekens FG, Pennings AJ (1998) *Polymer Bulletin*, 41: 131-138.
- Mirceva A, Zigon M (1998) *Polymer Bulletin*, 41: 447-453.
- Jayakumar R, Nanjundan S, Prabakaran M (2006) *React. & Funct. Polym. J.*, 66: 299-314.
- Yilgor I, Yilgor E, Guler IG, Ward TC, Wilkes GL (2006) *Polymer*, in press.
- Gupta T, Adhikari B (2001) *J. Polym. Sci. Patr A: Polym. Chem.*, 39: 2978-2992.
- Kaushiva BD, Dounis DV, Wilkes GL (2000) *J. Appl. Polym. Sci.*, 78 (4): 766-786.
- Major R, Czarnowska E, Sowinska A, Kustos R, Lackner JM, Waldhauser W, Wozniak M, Wierzchon T, Major B (2005) *e-Polymers*, 026.
- Digar M, Wen TC (2000) *Polym. J.*, 32 (11): 921-931.
- Song M, Xia HS, Yao KJ, Hourston DJ (2005) *Eur. Polym. J.*, 41: 259-266.
- Sanchez-Aduar MS, Papon E, Villenave JJ (2000) *J. Appl. Polym. Sci.*, 76(10): 1590-1595.
- Tonellia C, Ajroldib G, Turturroc A, Marigo A (2001) *Polymer*, 42 (13): 5589-5598.
- Abouzahr S, Wilkers GL (1984) *J. Appl. Polym. Sci.*, 29 (9): 2695-2711.
- Kim YS, Lee JS, Ji Q, McGrath JE (2002) *Polymer*, 43 (25): 7161-7170.
- Roussos M, Konstantopoulou A, Kalogeras IM, Kanapitsas A, Pissis P, Savelyev Y, Vassilikou DA (2004) *e-Polymers*, 042.
- Eisenbach CD, Heinemann T, Ribbe A, Stadler S (1992) *Angew. Makromol. Chem.*, 201: 221-241.
- Harrel Jr LL (1969) *Macromolecules*, 2(6): 607-612.
- Eisenbach CD, Hayen H, Nefzger H (1989) *Makromol. Chem. Rapid. Commun.*, 10(9): 463-475.
- Lai YC, Quinn ET, Valint PL (1995) *J. Polym. Sci, Part A: Polym. Chem.*, 33 (11): 1767-1772.
- Min Z, Tsutomu T (1999) *Polymer* 40: 5153-5160.
- Trofimov DM, Kol'tsov NI (2004) *Int. Polym. Sci. & Tech.*, 31 (7): 58-61.
- Wang TL, Huang FJ (1998) *Polym. Int.*, 46 (4): 280-284.
- Yeganeh H, Barikani M, Noei Khodabadi F (2000) *Eur. Polym. J.*, 36: 2207-2211.
- Yeganeh H, Shamekhi MA (2004) *Polymer* 45 (1): 359-364.

29. Takeichi T, Suefuji K, Inoue K (2002) *J. Polym. Sci, Part A: Polym. Chem*, 40: 3497-3503.
30. Birchall AC, Bush SM, North M (2001) *Polymer*, 42 (2): 375-389.
31. Fernandez AM, Abraham GA, Valentin JL, Roman JS (2006) *Polymer*, 47: 785-798.
32. Sanda F, Yukawa Y, Masuda T (2004) *Polymer*, 45 (3): 849-853.
33. Mallakpour S, Rafiemanzelat F (2004) *J. Appl. Polym. Sci*, 93: 1647-1659.
34. Mallakpour S, Rafiemanzelat F (2005) *Eur. Polym. J*, 41: 2945-2955.
35. Mallakpour S, Kowsari E (2005) *Polymer Bulletin*, 53: 169-180.
36. Mallakpour S, Kowsari E (2005) *J. Polym. Sci: Part A: Polym. Chem*, 43: 6545-6553.
37. Mallakpour S, Kowsari E (2005) *Iran. Polym. J*, 14(1): 81-90.
38. Mallakpour SE, Hajipour AR, Zamanlou MR (2003) *J. Polym. Sci: Part A: Polym. Chem*, 41(8): 1077-1090.
39. Mallakpour S, Moghaddam E (2006) *Polymer Bulletin*, 56: 339-347.
40. Mallakpour S, Khoee S (2004) *J. Appl. Polym. Sci*, 91(4): 2288-2294.
41. Mallakpour SE, Hajipour AR, Vahabi R (2002) *J. Appl. Polym. Sci*, 84 (1): 35-43.
42. Kim HD, Huh JH, Kim EY, Park CC (1998) *J. Appl. Polym. Sci*, 69: 1349-1355.
43. van der Schuur M, Noorderover B, Gaymans RJ (2006) *Polymer*, 47: 1091-1100.
44. Mishra AK, Chattopadhyay DK, Sreedhar B, Raju KVS (2006) *Prog. Org. Coat*, 55: 231-243.
45. Vasanthan N, Shin D, Tonelli AE (1995) *J. Polym. Sci: Part B: Polym. Physics*, 33 (9): 1385-1393.
46. Martin DJ, Meijs GF, Renwick GM, McCarthy SJ, Gunatillake PA (1996) *J. Appl. Polym. Sci*, 62 (9): 1377-1386.
47. Quay JR, Sun Z, Black J, Briber RM, Thomas EL (1990) *Polymer*, 31 (6): 1003-1008.
48. Mallakpour S, Rafiemanzelat F Submitted for publication.