

Rapid Synthesis of New Block Copolyurethanes Derived from L-leucine-PEG in Ionic Liquids Under Microwave Irradiation

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Received 9 August 2010; accepted 22 March 2011

DOI 10.1002/app.34691

Published online 9 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: This study concerns the synthesis of novel multi block polyurethane (PU) copolymers containing eco-friendly segments, taking the advantage of ionic liquids (IL)s under microwave irradiation. For this, L-leucine anhydride cyclodipeptide (LAC) was prepared and then a new class of poly(ether-urethane-urea)s (PEUUs) was synthesized with two types of ILs, including room temperature imidazolium (RTIL)s and molten ammonium type ILs. ILs were used as reaction media and PUs were prepared via two-step polymerization method. Polymerization reaction was also conducted under conventional heating method in *N*-methyl pyrrolidone (NMP) as reaction solvent. In the first step, 4,4'-methylene-bis(4-phenylisocyanate) (MDI) was reacted with LAC to produce isocyanate-terminated poly(imide-urea) oligomers as hard segment. Chain exten-

sion of the resulting prepolymer with polyethyleneglycol (PEG) of molecular weights of 400 (PEG-400) was the second step to furnish a series of new PEUUs. These multi-block copolymers are optically active, thermally stable and soluble in amide-type solvents. PEUUs prepared in ILs under microwave irradiation showed more phase separation and crystallinity than PEUU prepared under conventional method. Some structural characterization and physical properties of these PEUUs, prepared under different methods, are reported and compared. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1015–1023, 2012

Key words: amino acid anhydride cyclopeptide; ionic liquids; poly(ether-urethane-urea)s; copolymerization; microwave

INTRODUCTION

Amino acid anhydride cyclopeptide are the smallest cyclic peptides known, which are commonly biosynthesized from amino acids by different organisms, and are considered to be secondary functional metabolites or side products of terminal peptide cleavage. Cyclic dipeptides are extensively obtained by extraction from natural sources, and may also be easily synthesized.¹ Amino acid anhydride cyclopeptide attracted attention due to their biological properties such as alteration of cardiovascular and blood-clotting functions.^{2–4} They also have activities as antitumor, antiviral, antifungal, antibacterial, and affinities for calcium channels and oxytocin receptors.^{5–12} Some of the chemical properties of amino acid anhy-

dride cyclopeptide are very interesting for medicinal chemistry, such as resistance to proteolysis, mimicking of peptidic pharmacophoric groups, substituent group stereochemistry, conformational rigidity, and donor-acceptor groups for hydrogen bonding which favors interactions with biological targets.^{13,14}

A large number of degradable polymers have been used in biomedical applications, or as environmental friendly polymers. In addition in response to public concern about the effects of plastics in the environment and damaging effects of plastic wastes on animals and birds, it has become a widely accepted opinion that degradable polymers have a well-grounded job in solving waste problem.^{15,16} Degradable polymers are generally achieved by incorporating labile moieties susceptible to degradation into the polymer chain.^{16,17} Some important classes of degradable polymers are poly(α -hydroxy acid)s, poly(α -amino acid)s and their different block copolymers. Amino acid anhydrides as important precursors prepared from amino acids may be good candidates for preparation of degradable polymers.¹⁸ In addition, copolymers of PEG and peptide sequences were also designed in which PEG has properties appropriate for incorporation in polymers, that are highly water-soluble, nonimmunogenic, degradable, and relatively nontoxic.¹⁹

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Contract grant sponsor: Iran National Science Foundation (INSF) of I.R. Iran; contract grant number: 86121108.

Contract grant sponsor: Research Affairs Division of University of Isfahan (UI).

Segmented polyurethanes (SPU)s consist of hard and soft segments that their variable structure and properties make them suitable for many kinds of applications. Various chemical and/or physical factors may modify their properties such as hydrolysis, thermal properties, thermo oxidation, and etc. To cover a wide range of properties, polymers with different functional groups have been prepared that their morphology and properties are greatly influenced by the compatibility of these functional groups, starting compounds, the ratio of hard and soft block components, average block lengths, the thermal history of materials, and method of polymer preparation.^{20,21}

Ionic liquids (ILs) are molten salts that have attracted much attention in recent years, because they have good solubility for a wide range of organic, inorganic, and organo-metallic materials. ILs benefit from novel properties such as high thermal stability, almost zero vapor pressure, nonflammability as well as easy recycle. They have alterable hydrophobic or hydrophilic behavior via regulating the nature of their cations and anions. Thus ILs have served as good media for variety of organic syntheses. Compared with common organic solvents that have an unfavorable impact on environment, ILs can be considered some times as environmentally friendly green solvents.²²

This study concerns synthesis of novel multi block PU copolymers containing eco-friendly, degradable segments via a green method, taking the advantage of ILs under microwave irradiation, and compared with its conventional synthetic method. Here we report the synthesis and characterization of PEUUs containing LAC, PEG-400 soft segment via different methods and compare their thermal and physical properties.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka, Aldrich (Ald), Riedel-deHaen AG and Merck. 4,4'-methylene-bis(4-phenylisocyanate) (MDI) (Ald) was used without further purification. PEG-400 was dried under vacuum at 80°C for 6 h. *N*-methyl pyrrolidone (NMP) were distilled under reduced pressure over BaO. Ethylene glycol (EG) was distilled under reduced pressure over CaO. ILs including tetrabutylammonium bromide (TBAB) (Merck), tetrapropylammonium bromide (TPAB) (Merck), benzyl tributyl ammonium chloride (BztBAC) (Merck), hexadecyltrimethylammonium bromide (HexDectMAB) (Merck), *n*-dodecylpyridinium chloride (DodecPyCl) (Merck), were dried between 80 and 100°C under reduced pressure for 2 h. 1-butyl-3-methylimidazo-

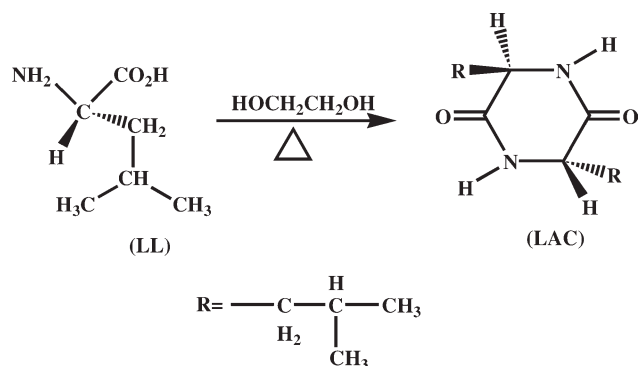
lium hexafluorophosphate (bmimPF₆) (Merck), 1-Butyl-3-methylimidazolium bromide (bmimBr) (Merck), 1-butyl-3-methylimidazolium chloride (bmimCl) (Merck), 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄) (Merck), 1-butyl-3-methyl imidazolium trifluorosulphate (bmim tFS) (Merck), were used as received.

Characterization techniques

Proton nuclear magnetic resonance ¹H NMR (400 MHz) spectra were recorded on a Bruker, Avance 400 instrument in dimethyl sulfoxide (DMSO-*d*₆) at room temperature (RT). Multiplicities of proton resonance were designated as singlet (s), doublet (d), doublet of doublet (dd), multiplet (m), and broad (br). FT-IR spectra were recorded on a Jasco FT-IR spectrophotometer. IR spectra of solids were carried out using KBr pellets. FTIR assignments are reported in wave number (cm⁻¹). Band intensities and designations are assigned as weak (w), medium (m), shoulder (sh), strong (s) broad (br), stretching (st.), and bending (bend). Inherent viscosities were measured by a standard procedure using a Cannon-Fensk Routine Viscometer. Specific rotations were measured by a Jasco Polarimeter to confirm the incorporation of LAC into polymer backbone. Thermal Gravimetric Analysis (TGA) data for polymers were taken on a Mettler-Toledo TG-50 Thermal Analyzer under N₂ atmosphere at heating rate of 20°C/min. Differential Scanning Calorimetry (DSC) data for polymers were recorded on a DSC-30/S instrument under N₂ atmosphere. Glass transition temperatures (*T*_g) were read at the middle of the transition in the heat capacity taken from heating DSC traces. A sample was first scanned from room temperature to 140°C and maintained for 1 min 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 *T*_g of soft (*T*_{g,s}) or hard segment (*T*_{g,h}). A heating rate of 10°C/min was applied to all samples. Wide angle X-ray diffraction measurements (WAXS) were carried out with a Bruker, D8ADVANCE XRD Diffractometer using a graphite monochromatized Cu Ka radiation (40 kV; 40 mA). The apparatus used for the polycondensation was a Samsung Microwave oven (M9G-4500, 900 W). All of the polymerization reactions were performed in a hood with strong ventilation.

Synthesis of L-leucine anhydride, LAC

LAC was prepared according to the reported procedure with little modification²⁴ (Scheme 1). Thus, into a dried 25-mL round bottom flask connected with a reflux condenser, drying tube and N₂ balloon, L-leucine (LL) (1 g, 7.62 × 10⁻³ mol) was heated in dried EG (10 mL) at 180°C for 10 h then cooled



Scheme 1 Synthesis of L-leucine anhydride cyclopeptide (LAC) from cyclization reaction of L-leucine (LL).

ethanol was added at room temperature. Precipitate was filtered and recrystallized from hot ethanol-water (5/1) and dried under vacuum at 80°C for 6 h to give LAC in 54% yield. M.p. > 280°C (dec.). $[\alpha]_D^{25}$: -0.34 [0.02 g in 5 mL of DMF at room temperature].

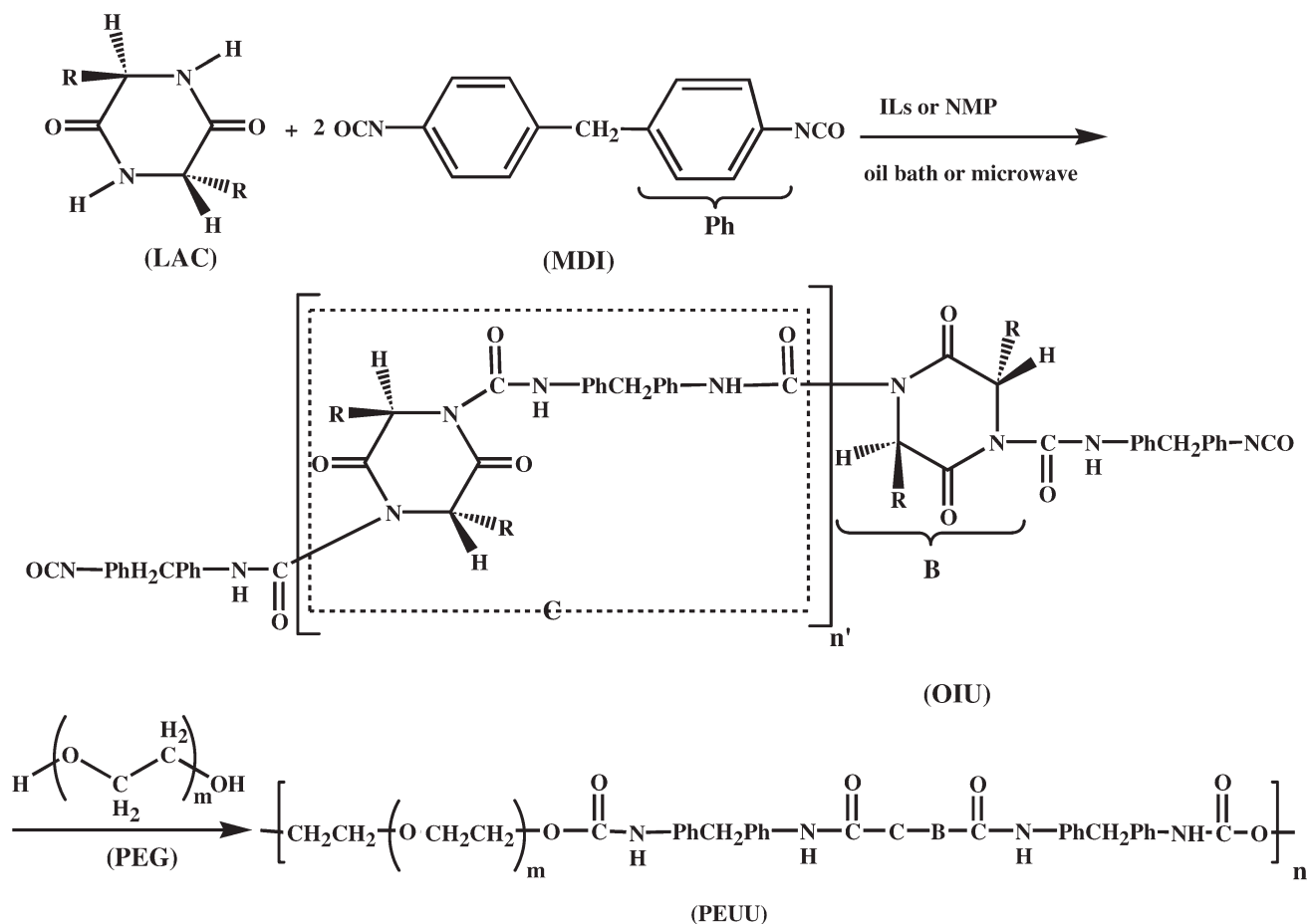
Polymer synthesis

PEUU multiblock copolymers were synthesized via two-step method. In the two-step procedure, a solu-

tion of diisocyanate-terminated oligo(imide-urea) OIU was prepared by the reaction of two mole excess of MDI with LAC in NMP/LiCl (1%, w/w) or ILs, respectively. Then, PEG-diol as soft segment was added and reaction was continued, affording PEG based PEUU multiblock copolymers, whose OIU blocks connected with urethane linkages.

Synthesis of PEUUs block copolymers under conventional method (Method 1)

A typical preparation of PEUUs by prepolymerization method is as follow (Scheme 2): Into a dried 25 mL round bottom flask with an addition inlet, connected with drying tube and N₂ balloon, LAC (0.055 g, 2.43 × 10⁻⁴ mol) was dissolved in 0.15 mL of NMP/LiCl (1%, w/w) (It means NMP which contains 1%, w/w LiCl as solubility assistant for better dissolving of growing polymer) at 110°C. After decreasing temperature a solution of MDI (0.122 g, 4.87 × 10⁻⁴ mol) in 0.15 mL of NMP/LiCl (1%, w/w) was added at 80°C. The solution was heated between 80 and 90°C for 4 h, then 2h at 100°C and finally for 1h at 120°C. During this period appropriate amounts of NMP/LiCl (1%, w/w) were added



Scheme 2 Synthesis of PEUUs by two step polymerization method.

upon building-up of viscosity of reaction mixture. Then the reaction mixture was cooled to 50°C, and a solution of PEG-400 (0.097 g, 2.43×10^{-4} mol) in 0.2 mL of NMP/LiCl (1%, w/w) was added. The reaction mixture was stirred between 50 and 70°C for 1 h then it was heated up to 80–110°C over a period of 6 h and NMP/LiCl (1%, w/w) was also added. The total solid content of reaction mixture was kept at about 50% W/V. Then the viscous solution of reaction mixture was poured into 5 mL of methanol-water. After vigorous grinding and stirring for 0.5 h, precipitated polymer was isolated. For additional purification, fractional precipitation method was applied by redissolving and reprecipitation of polymer in DMF and methanol-water, respectively. The precipitated polymer was collected by filtration, dried at 80°C for 6 h under vacuum to give 0.192 g (72%) of polymer **P-1** with inherent viscosity of 0.8 (dL/g) [measured at a concentration of 0.5 g/dL in DMF as solvent at room temperature]. Specific rotation of polymer was about $[\alpha]_D^{25} = + 0.4$ [measured at a concentration of 0.5 g/dL in DMF as solvent at room temperature]. The FT-IR and ^1H NMR spectra were consistent with the assigned structure.

Synthesis of PEUUs block copolymers in molten ammonium salt ILs under microwave irradiation (Method 2)

Polymerization reaction was performed in the presence of different ammonium type ILs. A typical preparation of PEUUs by two-step polymerization method is as follow (Scheme 2): As an example Tetra-butylammonium bromide (TBAB) was selected for the preparation of **P-2**. Mixture of LAC 0.023 g (9.99×10^{-5} mol), MDI 0.05 g (1.99×10^{-4} mol) and TBAB 0.56 g (1.736×10^{-3} mol) were placed in a porcelain dish and the mixture was ground completely for 2 min. The reaction mixture was irradiated in a microwave oven for a period of 8.5 min ($t_m + t1$) at 100% of power level, including 3.5 min irradiation for melting IL (t_m) and 2 + 2+1 min intervals of irradiation. Finally an orange and viscous solution was obtained. Then PEG-400 0.04g (9.99×10^{-5} mol) was added to the above viscous mixture and the mixture was pulverized completely for 1 min and was irradiated in a microwave oven for a period of 2.5 min ($t2$) at 100% of power level. The resulting polymer was isolated by addition of 5 mL of distilled water. The white-cream solid was filtered off, dried under vacuum at 50°C to give 0.09379 g (83%) of **P-2**, whose inherent viscosity was 0.66 (dL/g) [measured at a concentration of 0.5 g/dL in DMF as solvent at room temperature]. Specific rotation of polymer was about; $[\alpha]_D^{25} = + 0.6$ [measured at a concentration of 0.5 g/dL in DMF as solvent at

room temperature]. The FT-IR spectra were consistent with the assigned structure.

Synthesis of PEUUs block copolymers in imidazolium type RTILs under microwave irradiation (Method 3)

Different 1-butyl-3-methylimidazolium salts were used in this work. General procedure for preparation of **P-4** in 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆⁻) as an example is as follow (Scheme 2): Mixture of LAC 0.023 g (9.99×10^{-5} mol) and MDI 0.05 g (1.99×10^{-4} mol) were placed in a porcelain dish and was ground completely for 2 min then 0.17 mL of (bmimPF₆⁻) (8.255×10^{-4} mol) was added to the first mixture and was pulverized completely. The pasty-crummy reaction mixture was irradiated in a microwave oven for a period of 4 min and 20 s (2 min + 2-min intervals of irradiation) ($t1$) at 70% of power level until a viscous solution was obtained. Then PEG-400 0.04g (9.99×10^{-5} mol) was added to the above viscous mixture and the mixture was pulverized completely for 1 min and was irradiated in a microwave oven for a period of 2.5 min ($t2$) at 70% of power level. The resulting polymer was isolated by addition of 5 mL of distilled water. The white-cream solid was filtered off, dried under vacuum at 50°C to give 0.1028 g (91%) of **P-4**, whose inherent viscosity was 0.6 (dL/g) [measured at a concentration of 0.5 g/dL in DMF as solvent at room temperature]. Specific rotation of polymer was about; $[\alpha]_D^{25} = + 0.7$ [measured at a concentration of 0.5 g/dL in DMF as solvent at room temperature]. The FT-IR spectra were consistent with the assigned structure.

RESULT AND DISCUSSION

LAC as an amino acid based monomer was prepared via heating LL in dried EG and recrystallization from hot ethanol (Scheme 1). Chemical structure and purity of the resulting compounds were confirmed by FTIR, melting point measurement and thin layer chromatography (TLC). Table I shows characterization data of resulting product. Then LAC, a preformed amide containing heterocyclic monomer, was reacted with MDI diisocyanate to obtain NCO terminated hard segment containing urea linkages.

PEUU multiblock copolymers were synthesized according to Scheme 2 via two-step method. Polymerization reactions were performed via different methods (Method 1 to 3). Method 1 refers to a conventional synthesis procedure whereas Methods 2 and 3 use different ILs under microwave radiation. Polymerization reaction conditions including reaction time, solvent to monomers ratio were also

TABLE I
Characterizations Data of LAC and PEUUs

Product	Characterizations data
LAC	FT-IR Peaks (cm^{-1}) (KBr pellet): 3317 (m) NH st., 3199 (s, br) NH st., 3091 (s) NH st., 3056 (s) NH st., 2956 (s) CH st., 2923 (s) CH st., 2871 (s) CH st., 1681 (m) C=O (amide I) (non-H-bonded) st., 1630 (s) C=O (amide I) (H bonded) st., 1530 (m) C–N st + NH bend (amide II), 1512 (w) C–N st. + NH bend (amide II), 1455 (s) C–N st., 1407 (m), 1386 (m), 1368 (m), 1347 (m), 1324 (s), 1261 (w) C–N st. + NH bend, 1234 (w), 1172 (w), 1142 (m), 1122 (m), 1093 (m), 899 (m), 822 (m, br), 805 (m, br) NH bend., 766 (m), 487 (m). $^1\text{H NMR peaks}$, DMSO- d_6 at room temperature, δ ppm: 8.01 (br, 2H, NH), 4.53 (m, 2H, CH ring), 1.81 (m, 2H, CH side chain), 1.77 (m, 4H, CH_2 side chain), 1.03 (m, 12H, CH_3 side chain). CHN analysis: Calculated: C% = 63.7, N% = 12.4, H% = 9.7. Found: C% = 63.61, N% = 11.74, H% = 9.53.
P-1	FT-IR Peaks (cm^{-1}) (KBr pellet): 3350 (m, br) NH st., 3200 (m, br) NH st., 3100 (m) NH st., 3060 (m) CH aromatic st., 2960 (m) CH st., 2926 (m) CH st., 2872 (m) CH st., 1772 (w, sh) C=O urethane st., 1705 (m, sh) C=O urethane-amide st., 1672 (s) C=O urea st., 1599 (m) C=C st., 1540 (m) C–N st. + NH bend, 1510 (s) C=C st., 1460 (m) C=C st., 1412 (m) C–N st., 1400 (m) CH bend, 1385 (m), 1370 (w), 1347 (w), 1313 (m), 1236 (m) C–N st. + NH bend, 1203 (m), 1201 (w), 1180 (w), 1144 (w), 1117 (m) C–O–C ether st, 1042 (m) O=C–O–C st., 1018 (w), 917 (w), 850 (w), 808 (w) NH bend, 764 (w) O=C–O, 663 (w), 509 (w), 482 (w). $^1\text{H NMR spectrum}$, DMSO- d_6 at room temperature, δ ppm: 0.90–0.96 (distorted d, $J = 17$ Hz, 6 H, CH_3 (1, 1')), 1.5 (m, 2 H, diastereotopic hydrogens of CH_2 (2,2')), 1.8–1.9 (m, 1 H, CH (3)), 3.3–3.5 (br t, CH_2s (4) of PEG), 3.7–3.9 (br t, CH_2s (5) of PEG), 3.7–4.1 (m, 2+2 H, CH_2 (6) of MDI moiety and CH_2 (7) of urethane linkages), 4.35–4.57 (m, CH (8)), 7.2–7.5 (d, aromatic protons), 8.1–8.6 (br, NH of urea and urethane groups).
P-2	FT-IR Peaks (cm^{-1}) (KBr pellet): 3316 (s, N–H), 2871 (m, C–H, CH_2), 1707 (s, C=O), 1644 (s, C=O), 1600 (s, C=C), 1540 (s, C–N, + N–H (bending)), 1500 (s, C=C), 1413 (m), 1232 (s, C–O), 1107 (s, C–O), 950 (w, C=C, opp), 816 (w, C=C, opp). $^1\text{H NMR spectrum}$, DMSO- d_6 at room temperature, δ ppm: 0.90–0.95 (distorted d, $J = 17$ Hz, 6 H, CH_3 (1, 1')), 1.5 (m, 2 H, diastereotopic hydrogens of CH_2 (2,2')), 1.8–1.9 (m, 1 H, CH (3)), 3.2–3.4 (br t, CH_2s (4) of PEG), 3.6–3.8 (br t, CH_2s (5) of PEG), 3.8–4.2 (m, 2+2 H, CH_2 (6) of MDI moiety and CH_2 (7) of urethane linkages), 4.4–4.6 (m, CH (8)), 7.1–7.4 (d, aromatic protons), 8.1–8.6 (br, NH of urea and urethane groups).
P-3	FT-IR Peaks (cm^{-1}) (KBr pellet): 3317 (s, N–H), 2874 (m, C–H, CH_2), 1707 (s, C=O), 1646 (s, C=O), 1602 (s, C=C), 1541 (s, C–N, + N–H (bending)), 1502 (s, C=C), 1414 (m), 1230 (s, C–O), 1107 (s, C–O), 950 (w, C=C, opp), 817 (w, C=C, opp).

optimized for each method considering resulting yields, viscosities, and product appearance (Table II).

Table I shows characterization data of resulting products. The FT-IR and $^1\text{H NMR}$ spectra were consistent with the assigned structures. The FTIR spectra of polymers showed peaks, which confirm their chemical structures. As an example, the FTIR spectrum of P-2 showed the characteristics absorptions of urethane, imide, and urea groups around 3316,

1707, 1644, and 1540 cm^{-1} , peculiar to NH, C=O and C–N stretching (and bending) of urethane, imide, and urea groups, respectively, (Fig. 1).

The $^1\text{H NMR}$ spectrum of PEUUs showed peaks that confirm their chemical structures. As an example, $^1\text{H NMR}$ spectrum of P-2 is shown in Figure 4. It showed peaks in the region of 0.91–0.96 ppm which are related to CH_3 (1, 1'). Diastereotopic hydrogens of CH_2 (2,2'), and CH (3) are appeared in

TABLE II
Preparation of PEUUs via Different Methods Under Optimized Reaction Conditions for Each Method

Polymer ^a	Reaction solvent	Heating method	Yield (%) / η_{inh} (dL/g) ^e	t_1 min ^f	t_2 min ^g	Soluble in
P-1 ^b	NMP/LiCl1% ^c	Conventional	72/0.8	7 h	7 h	DMF/LiCl 1% ^h
P-2	TBAB	MW, 100% ^d	83/0.66	4.5 ⁱ	2	DMF
P-3	bmimBF ₄	MW, 70% ^d	70/0.67	3.5	5.5	DMF
P-4	bmimPF ₆	MW, 70% ^d	91/0.6	4.5	5.5	DMF
P-5	bmimCl	MW, 70% ^d	77/0.67	9	5.5	DMF
P-6	bmimTFS	MW, 70% ^d	70/0.4	9	5.5	DMF

^a Prepared via two step polymerization method.

^b **Step one:** Reaction mixture was heated between 80 and 90°C for 4 h, for 2 h at 100°C and for 1 h at 120°C. **Step two:** Reaction mixture was heated between 50 and 70°C for 1 h then between 80 and 110°C over a period of 6 h.

^c N-methyl pyrrolidone containing 1%, w/w LiCl.

^d Microwave-Irradiation power level.

^e Inherent viscosities of polymers were measured at a concentration of 0.5 g/dL in solvent mentioned in column VII.

^f Irradiation time for step 1.

^g Irradiation time for step 2.

^h N,N-dimethyl formamide containing 1%, w/w LiCl.

ⁱ Was calculated after $t_m = 3.5$ min, Irradiation time needed for melting TBAB.

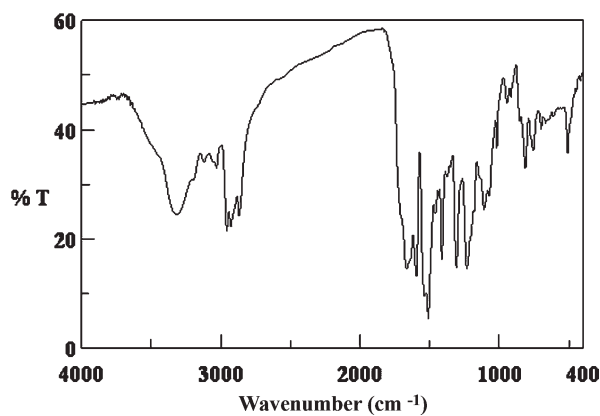


Figure 1 FTIR spectrum of P-2 (KBr pellets).

the regions of 1.42 and 1.8–1.9 ppm, respectively. CH_2s (4) of PEG and CH_2s (5) of PEG are appeared in the regions of 3.3–3.5 and 3.7–3.9 ppm, respectively. Peaks in the region of 3.7–4.1 ppm are related to CH_2 (6) of MDI moiety and CH_2 (7) of urethane linkages. CH (8) of side chain of LAC ring moiety appeared in the region of 4.35–4.57 ppm. The aromatic protons appeared in the region of 7.2–7.5 ppm. Broad peaks in the region of 8.0–8.6 ppm are assigned for NH of urea and urethane groups (Fig. 2).

Different ILs with different anions were used for Methods 2 and 3. Polymerization reactions were performed under different reaction conditions including different ILs as reaction media, different ratio (W/W) of each IL to (LAC+MDI), different irradiation power and irradiation time during Steps 1 and 2. t_1 was considered as irradiation time during Step 1, and t_2 was considered as irradiation time during Step 2.

It was shown that in the case of ammonium salts with melting point ranging 100–270°C optimum power level of 100% can be used for Steps 1 and 2 of polymerization reaction. Using TBAB (mp = 100–103°C), $t_1 = 4$ min and $t_2 = 4$ min, under 100% of irradiation power the optimized ratio of IL to (MDI+LAC) was obtained as 5/1 w/w. Then the effect of various t_1 and t_2 under the same reaction conditions on viscosities and yields of resulting polymers was studied. Finally $t_1 = 4$ –4.5 min and $t_2 = 2$ –3 min were selected as favorite reaction time for other studies under the obtained optimized reaction conditions including 100% of irradiation power, and (ammonium IL)/(MDI+LAC) = 5/1 w/w ratio. Under the aforementioned reaction conditions polymers were formed only in the presence of TBAB (m.p. = 100–103°C), BztBACl (m.p. = 152–159°C) and TBAI (m.p. = 143–146°C). Reactions in the presence

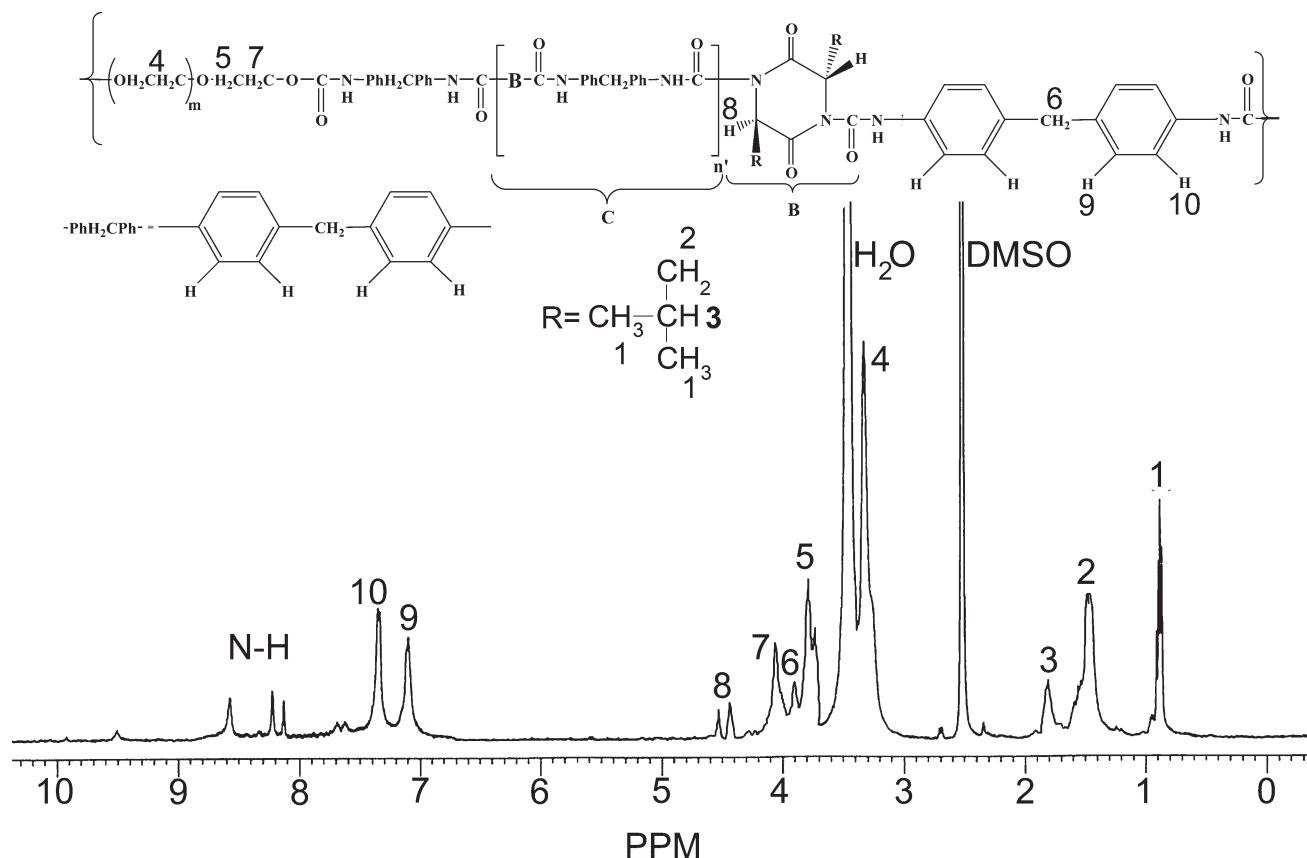


Figure 2 ^1H NMR (400 MHz) spectra of P-2 in DMSO-d_6 at RT.

TABLE III
Thermal Properties Data of PEUUs

Polymer	Reaction solvent	T5% °C ^a	T10% °C ^b	Char yield % ^c	T _g s °C ^d	T _g h/T _m °C ^e	ΔT _g °C ^f
P-2	TBAB	215	260	12	20	210	180
P-3	bmimBF ₄	290	312	10	30	230	180
P-4	bmimPF ₆	285	310	18	55	260	192
P-5	bmimCl	270	295	14	25	252	210
P-1	NMP/LiCl (1%, w/w)	270	285	12	60	175	115

^a Temperature at which 5% weight loss was occurred by TGA in N₂ atmosphere.

^b Temperature at which 10% weight loss was occurred by TGA in N₂ atmosphere.

^c The percentage of weight residue of polymer sample at 600°C in N₂ atmosphere by TGA.

^d Glass transition temperature of soft segment recorded by DSC in N₂ atmosphere.

^e Glass transition temperature of hard segment recorded by DSC in N₂ atmosphere/or melting transition temperature of crystalline domain of hard segment recorded by DSC in N₂ atmosphere.

^f ΔT_g = (T_gh/T_m) - T_gs.

of other ammonium salts with higher m.p because of higher *t_m* (irradiation time need to melt IL), lead to decomposition of reaction mixture.

In the case of Method 3, imidazolium types RTILs bearing different anions including BF₄⁻, CF₃SO₃⁻, Cl⁻, and PF₆⁻ were used as reaction media. The polymerization reaction of LAC, MDI, and PEG-400 was first carried out under the optimized reaction conditions obtained for TBAB (Table II). It was shown that no product was formed and reaction mixture was decomposed. Thus, because of more reactivity of imidazolium types RTILs comparing with molten salt ILs, lower power level and amount of IL would be needed. PEUUs were prepared in different imidazolium types RTILs as reaction media, under irradiation power of 70%, at IL/(MDI+LA) = 3/2 w/w. Optimized *t*₁ and *t*₂ for each RTIL were also obtained separately.

Thermal properties

Thermal properties of PEUUs were evaluated with TGA and DSC techniques (Table III). TGA curves show smooth stepwise manner which their slopes are relatively similar. It can be inferred the rate and manner of thermal degradation of polymers are relatively similar. If stability parameters of PEUUs are taken at the temperature at which 10% weight loss was occurred, it can be concluded that PEUUs prepared in RTILs show higher thermal stability than others prepared in NMP or molten ILs. In comparison with TGA results of typical PUs, these PEUUs show higher T10 and char residue due to the presence of imide, urea, and aromatic groups in the polymer chains. Table III show thermal properties of PEUUs prepared in imidazolium types RTILs. Polymers prepared in (bmimPF₆⁻) and (bmimCl⁻) show higher percent char yields and higher T_gh/T_m (glass transition temperature of hard segment/or melting transition temperature of crystalline domain of hard segment) comparing with polymers prepared in

other RTILs. It can be said that the final weight residue and T_gh are more related to hard segment residue, hard segment incorporation and hard segment cohesiveness in polymer chain, respectively. Thus it can be implied that polymers prepared in (bmimPF₆⁻) and (bmimCl⁻) have higher final thermal stability than other polymer prepared in (bmimBF₄⁻). This may be due to relatively more chain growth of hard segment during Step 1, and better hard segment cohesiveness.

DSC curves for PEUUs are shown in Figure 3. Assignments of T_gs (glass transition temperature of soft segment) and T_m of each sample are presented in Table III. DSC curve of P-1 shows broad transitions associated with T_gs and T_m between 27 and 97°C and 137–210°C. DSC curve of P-2 showed broad-deep transitions associated with T_gs and T_m at about 20°C and 210°C, respectively. By comparing ΔT = T_m - T_gs better information about interaction between soft and hard segments could be indicated. Among polymers prepared in RTILs, it can be seen that ΔT of P-4 and P-5 are greater than ΔT of P-3. These results indicate that there is more interaction between hard segments of P-4 and P-5 than P-3 which may be because of relatively more hard segments' chain growth and phase separation in the former polymers. Comparing these transitions data,

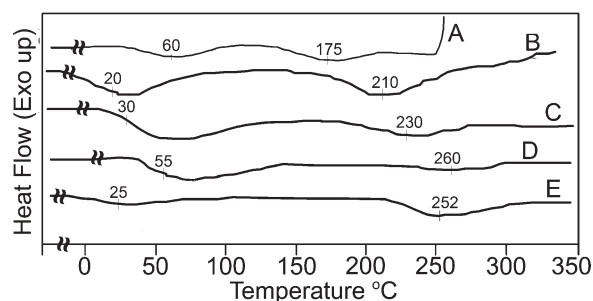


Figure 3 DSC trace of PEUUs (A) P-1, (B) P-2, (C) P-3, (D) P-4, and (E) P-5 at heating rate of 10°C/min under N₂ atmosphere.

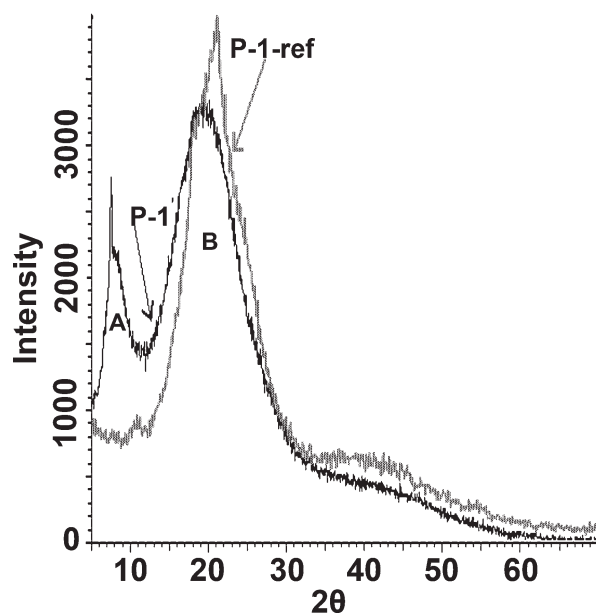


Figure 4 WAXS spectra of P-1 and P-1-ref.

with T_g s (ranging from -60 to -53°C) and melting temperature (T_m) of pure PEGs (PEG-400; 4 – 8°C) great shifts to higher temperatures can be observed. Such results indicate that the presence of LAC in PU backbone resulted in more interaction and compatibility between hard and soft segments.

WAXS studies

WAXS measurements were carried out for PEUUs prepared in different solvents. The percentage of crystallinity was calculated through graphical integration of the diffracted intensity data in the 2θ range 10 – 60° and subtraction of the amorphous scattering band intensity.

Diffraction patterns for PEUUs show two main crystalline regions A and B. Figure 4 presents WAXS diffractograms of P-1 and P-1-ref (The reference sample based on MDI, BD, and PEG-400). WAXS of P-1 shows two crystal reflection patterns at A and B regions with maximum at about $2\theta = 7$ and 20° , respectively, while WAXS of P-1-ref shows a broad diffusion scattering (amorphous halo) with maximum at $2\theta = 7^\circ$ at A region and a crystal reflection pattern at about $2\theta = 20^\circ$ at B region. This result suggests that the crystalline phase which develops at A region in PEUUs containing LAC is associated with crystallization of MDI-LAC hard segment. WAXS diffractograms of P-2 and P-4 show reflection patterns the same as P-1.

The percentage of crystallinity obtained for P-1 at A and B regions are 20 and 39%, respectively, for P-2 at A and B regions are 21%, and 40%, respectively, for P-4 at A, and B regions are 22 and 43%, respectively.

These data show that crystalline phases which developed in A regions of PEUUs associated with crystallization of their hard segments show the following order: $\text{P-4} > \text{P-2} \geq \text{P-1}$. The observed crystallization trend is similar to their total crystallinity order as well, which can explain the observed thermal stability trend. Crystalline phases developed in B regions of PEUUs which can be associated with crystallization of their soft segments and MDI-PEG, show the following order: $\text{P-4} > \text{P-1} > \text{P-2}$. On account of the results related to total crystallinity of PEUUs, it can be said that polymer prepared in RTILs show more crystallinity than polymers prepared in TBAB and NMP. Also PEUUs prepared under microwave irradiations in ILs are more crystalline than PEUUs prepared under conventional method in conventional organic solvent.

Solubility properties of PEUUs

The solubility properties of PEUUs were studied in different solvents. These 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. The concentration at which the solubility tests were conducted was 0.005 g of polymer in 1 mL of each solvent. Film of each polymer sample was prepared via casting from concentrated polymer solution in DMF.

CONCLUSIONS

New segmented PEUUs based on PEG-400 were successfully synthesized by the chain extension reaction of NCO terminated oligo imide-urea consisting of MDI-LAC with PEG as soft segment. Oligo imide-urea prepolymer was prepared from the reaction of a chiral amino acid based monomer having a preformed amide ring with MDI. Polymerization reactions were performed in NMP 1% as a conventional organic solvent under conventional heating method as well as microwave irradiation in ILs. Polymers prepared in different solvents showed different thermal resistance as well as different interchain interaction, phase miscibility and crystallinity. Thermal properties studies indicate that these types of PEUUs are relatively more stable than typical PUs. The resulting PEUUs have cyclopeptide moiety in polymer chain; they are optically active and soluble in amide type solvents. Thus they could be considered as new processable high-performance polymers and are expected to be classified as environmentally friendly polymers. PEUUs prepared under microwave irradiations in ILs are more crystalline than PEUUs prepared under conventional method in conventional organic solvent. Polymers prepared in

RTILs are more thermally stable than others. In addition, it was found that the synthesis of PEUUs in ILs via microwave-assisted method provided a very rapid means of synthesizing a peptide based copolyurethane. This method has been shown a reduced reaction time, and at the same time comparable yields and viscosities of the desired products with conventional methods. It also shows the advantages of using ILs as solvents in green chemistry processes, and ILs' great ability to absorb microwave energy due to their highly polar characteristic. This study shows ability of microwave irradiation and ILs as reaction media as fast and green method for efficient copolyurethanes preparations.

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