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ORIGINAL PAPER

Synthesis, characterization, and properties of co-poly(ether–urethane–urea)s containing lariat cryptand 22: Li^+ harvesting polymers

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Abstract In this work, some segmented poly(ether–urethane–urea)s (PEUUs) containing aza crown ether (cryptand) were prepared and characterized. These polymers were synthesized via the reaction of kryptofix 22 with 2 mol excess of 4,4′-methylene-bis-(4-phenylisocyanate) (MDI), and different molecular weights of polyethylene glycols (PEGs). Morphology, thermal, and complexation properties of these polymers were studied by Fourier-transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), atomic absorption spectroscopy (AAS), and solid state NMR (S-NMR). The data confirmed complexation ability of these polymers for Li^+ ion absorption and

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revealed the effect of Li^+ ion complexation on the morphology and thermal behavior of the PEUUs.

Keywords Poly(ether–urethane–urea)s · Cryptands · Polyethylene glycol · Ion absorption selectivity

Introduction

Macrocycles such as crown ethers, calixarenes, and cryptands are an important class of ion carriers that were successfully used as extractants for metal ions separation in solvent extraction and as ion carriers in transport through liquid membranes [1]. It is well known that cyclic ethers and related macrocycles can coordinate with metal ions in hydrophobic solvents making separation from their related anions and making their salts soluble in these solvents. These compounds present great possibilities to be useful as metal ions catalysts, ion-exchange membranes, molecular imprinting compounds, surfactants, chirality inductive reagents, etc. [2]. Studies demonstrate that the characteristics of lariat side arm, steric hindrance of the side arm, the composition of solvent system, the nature of the complementary counter anions, and the nature of the externally added cations influence the selectivity of lariat crown ethers toward different metal ions. They show that selectivity behavior of aza-crown or other hetero-macrocyclic compounds for different chemicals depends not only on their cavity size but also on their substituted groups [3]. Polymers containing such chemical structures can potentially show many of the above mentioned applications and therefore different researchers have investigated synthesis, properties, and applications of these polymers, and often for species separation [4–6]. For example the fit between the ionic radius and the ring size of the superabsorbent copolymers having crown ethers or cryptands selects the sorption of the metal ions. These polymeric materials are applied for solving a variety of ecological and industrial waste problems [6].

In addition solid polymer electrolytes have been the subject of many studies involving lithium ion polymer batteries, capacitors, and electrochromic devices [7]. It is known that polyether type PEGs are non-ionic polymers that in non-aqueous media can form complex compounds with alkaline, earth-alkaline, and transition metal ions. The oxygen atoms of the ethylene oxide units appear to be ligands in the respective coordination compounds. It is suggested that pseudo-crown ring of five or six member may be also responsible for ion complexation [8]. Thus, most investigations on polymer electrolytes have used PEG and its derivatives as matrix polymer. Approaches that have been used to increase ion dissociation in PEG-based electrolytes are the use of salts with low lattice energy, the addition of polar plasticizers to the polymer, and the addition of cation complexing agents such as crown ethers or cryptands into the polymer chain [9].

Segmented polyurethanes (SPUs) are polymers that can be tailored for a variety of applications due to their chemistry, block or segment molecular weight, and relative amounts of hard and soft blocks, ability for introducing different functional groups to cover a wide range of applications, etc. It is known that SPUs based polyether segments can also be used for ions transport or ions absorption [10]. The interactions between hard and soft segments make SPUs a microphase separated system, which imparts elastomeric properties to polyurethane (PU). The rubbery soft segments can dissolve metal ions without formation of ionic clusters. On the other hand, the interconnected hard segments act as reinforcing filler and hence contribute to the dimensional stability of the polymer. It is also expected that the molecular interactions between functional groups in the polymer and incorporated ions are different from the interactions in the pristine polymer matrix (polymer before addition of some chemicals, such as additives, plasticizer and metal ions…) [11]. Thus, investigation on the structure property relationship of these polymers is a subject of much interest.

In this paper, we describe the synthesis, characterization, and properties of new poly(ether–urethane–urea)s (PEUUs) obtained from the polycondensation reaction of a diisocyanate, a cryptand, and PEG polyether. The work reported in this article was designed to construct heterocyclic PEUUs containing polyether soft segments, and to study the incorporation of metal ions into polymer chain. The complexation ability of these polymers with different cations was compared. Then the effect of Li^+ ion complexation on the morphology and thermal behavior of the obtained polymers was investigated as well.

Experimental

Materials

MDI (Aldrich, 98%) was used without further purification. PEG-400, -600, -1000, and -2000 were purchased from Merck and were dried under vacuum at 80 °C for 8 h. Pyridine (Py) (Merck, 99%), *N*,*N*-Dimethylformamide (DMF) (Merck, 99%), *N*,*N*-dimethylacetamide (DMAc) (Merck, 99%), dimethyl sulfoxide (DMSO) (Merck, 99%), and 1-methyl-2-pyrrolidone (NMP) (Merck, 99.5%) were distilled under reduced pressure over BaO (Aldrich, 97%). 1,7,10,16-Tetraoxo-4,13-diaza-cyclooctadecane (kryptofix 22) (Merck, 99%) was used as received. All the metal chloride reagents were of analytical grade, purchased from Merck, and used without any purification. Acetonitrile (AC) (Merck, extra pure, 99%) and dibutyltin dilaurate (DBTDL) (Merck, 97%) were used as received.

Instruments and measurements

Inherent viscosities were measured by a standard procedure using a Cannon–Fenske Routine Viscometer. Thermal gravimetric analysis (TGA) data for polymers were taken on a Perkin Elmer Thermal Analyzer under N_2 atmosphere. Differential scanning calorimetry (DSC) data were recorded on a DSC-PL-1200 instrument under N_2 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 150 °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_gs) or hard segment (T_gh). A heating rate of 10 °C/min was applied to all samples. Atomic absorption study was performed using a Perkin-Elmer 2380 Atomic absorption spectrophotometer at emission mode. ^{7}Li-NMR spectroscopy was performed using a 500 MHz Varian infinity plus-50 Solid State NMR Spectrometer at room temperature (RT), spin rate 10 kHz, magnet 11.7 T. Samples were ground to powder before measuring their spectra. ^{1}H-NMR (500 MHz) spectra were recorded on a Bruker Avance 500 instrument in DMSO-d_6. Multiplicities of proton resonance were designated as broad (br), singlet (s), doublet (d), and multiplet (m). FT-IR spectra were recorded on a Jasco FT-IR spectrophotometer. Spectra of solids were recorded 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).

The amount of the absorbed metal ions by polymer was calculated for each cation by using Eqs. 1–3.

$$\begin{aligned}&\text{Mole percentage of the absorbed cation by } \mathbf{P\text{-}3}\ (\%\ \text{absorbed } M)\\&\quad = [C_0 - C/C_0] \times 100\end{aligned} \tag{1}$$

$$\begin{aligned}&\text{The weight of the absorbed metal ions by } \mathbf{P\text{-}3}\ (\text{absorbed } W)\\&\quad = [C_0 - C/C_0]V \times W\end{aligned} \tag{2}$$

$$\begin{aligned}&\text{The amount of the absorbed metal ions by unit mass of the } \mathbf{P\text{-}3}\, U\\&\quad = (C_0 - C)/w\end{aligned} \tag{3}$$

where C_0 (mmol/mL) is the concentration of metal ions in initial solutions, C (mmol/mL) is the concentration of metal ions in aqueous solution after the immersion of polymer for a certain time, V (mL) is the volume of the solution, W (g/mol) is atomic weight of the metal cation, w (g) is the weight of polymer sample, C and C_0 were taken from calibration curve of I, “emission intensities measured by AAS”, vs. C_s, “concentrations of metal ions in standard solutions”, U (mol cation/1 g polymer) is the amount of the metal ion absorbed by unit mass of the polymer.

The difference in the char yield (%) at 700 °C from TGA curve of **P-3** before (**P-3-0**) and after (**P-3-Li**) exposure to Li$^+$ solution can also be related to inorganic contents in **P-3-Li**. According to the Eq. 4 weight percentage of absorbed Li$^+$ ion by **P-3-Li** can be calculated.

$$\begin{aligned}&\{[(b\% - a\%) \div 100] \times w\} \div M_{\mathrm{LiCl}} = n_{\mathrm{LiCl}}\\&\quad \times [(n_{\mathrm{LiCl}} \times M_{\mathrm{Li}}) \div w] \times 100 = q\end{aligned} \tag{4}$$

In which $a\%$ and $b\%$ are char yield (%) at 700 °C from TGA curve of **P-3** before and after exposure to Li$^+$ solution, respectively. w is weight of **P-3-Li** sample used for TGA experiment (0.0005 g). M_{LiCl} is molecular weight of LiCl (42.39 g/mol). n_{LiCl} is number of moles for LiCl. M_{Li} is atomic weight of Li. q is weight percentage of Li metal ion in polymer sample **P-3-Li**.

Synthesis of PEUUs

A typical preparation of PEUUs by pre-polymerization method was as follows: Into a dried two-necked 25 mL round bottomed flask with an addition inlet and a reflux condenser equipped with mechanical stirrer and N_2 inlet–outlet, MDI (**2**) (0.3069 g, 1.2267×10^{-3} mol) was added to molten kryptofix 22 (**1**) (0.1608 g, 6.12×10^{-4} mol) at 115 °C then, 1 mL of NMP was added after 3 min. After stirring for 10 min the temperature was gradually decreased and maintained at 80 °C for 3 h. During this period appropriate amounts of NMP were added. Then it was cooled to 30–40 °C, and a solution of PEG-400 (**3**) (0.2451 g, 6.12×10^{-4} mol) in 1 mL of NMP was added. The reaction mixture was stirred at 40 °C for 0.5 h and Py (0.015 mL, 1.89×10^{-4} mol) was added. Then it was heated up to 80–120 °C over a period of 8 h. The total solid content of the reaction mixture was kept at 45% w/w. According to FT-IR monitoring of NCO group, the reaction progressed to completion. Then the viscous solution of reaction mixture was poured into 10 mL of water. After vigorous grinding and stirring in water, the precipitated polymer was isolated by filtration. Further purification, was applied by re-dissolving and re-precipitation of polymer in DMF and water, respectively. The precipitated polymer was collected by filtration, dried at 80 °C for 10 h under vacuum to give 0.606 g (85%) of polymer **P-3**. The FT-IR and ^{1}H-NMR spectra were consistent with the assigned structure. FT-IR peaks (cm^{-1}) for **P-3**: 3450 (s), 3420 (s, br), 3354 (s) NH v, 3301 (s) NH v, 3208 (m) C–H aromatic, 3116 (w) C–H aromatic, 2958 (m), 2918 (m), 2853 (m) C–H aliphatic, 1771 (w) C=O urethane (non-hydrogen bonded), 1719 (s) C=O urethane (hydrogen-bonded), 1686 (s) C=O urea, 1639 (s) C=O urea, 1614 (s), 1598 (s) C–N v + NH, 1539 (s) C=C, 1500 (s), 1461 (m), 1407 (s), 1383 (s), 1314 (s) C–N v + NH, 1244 (s) C–N v + NH, 1178 (m), 1146 (w), 1102 (m) C–O–C ether, 1070 (m) O=C–O–C, 941 (w), 857 (w), 828 (w), 805 (w), 771 (w) O=C–O, 700 (w), 653 (m), 610 (w), 554 (w), 544 (w).

Aqueous cation uptake

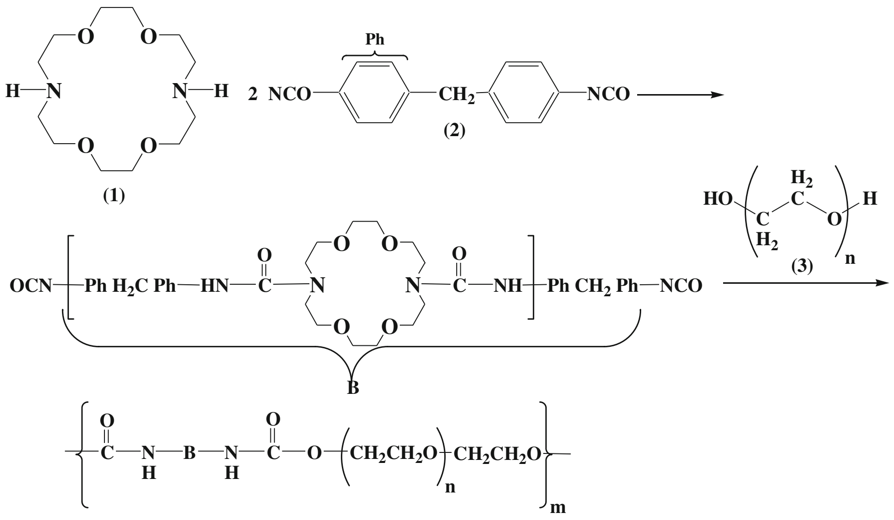
0.5 g of polymer powder was exposed to 20 mL of an aqueous based 1 M solution of metal chlorides. The polymer samples were exposed for 2–24 h and then filtered off, washed with deionized water and dried in a vacuum for 24 h at 70 °C. The concentration of residual metals in aqueous solutions after immersion and filtration of polymer was measured using an atomic absorption spectrophotometer to compare cation uptake ability of polymers for different metals. The metal salts used in this study were: LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$.

Results and discussion

Polymer synthesis

PEUUs based on PEG were prepared according to Scheme 1 by two-step pre-polymerization method. These polymers were prepared via the reaction of MDI (**2**) with kryptofix 22 (**1**) and different molecular weight of PEGs (**3**).

To select a suitable solvent for the preparation of PEUUs, solution polymerization reactions of **1** with MDI and PEG-400 were performed in different solvents including DMF, DMAc, DMSO, AC, and NMP in the absence of any catalysts. The best



Scheme 1 Preparation of PEUUs by the reaction of kryptofix 22 (**1**), MDI (**2**), and different molecular weights of PEG (**3**)

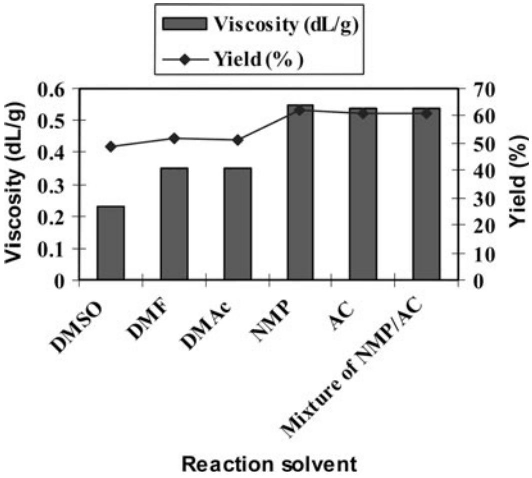


Fig. 1 Comparison of the effect of reaction solvents on the polymer chain growth and yield of the resulting PEUUs

viscosities and yields were obtained in NMP as a solvent (Fig. 1). In solvents such as DMF, DMAc, and DMSO the reaction mixture was not very well soluble. These solvents also showed limited solubility for MDI and **1**. At the beginning of the reaction AC showed good solubility for **1**, but showed a limited solubility for **2.** Thus, two component solvents were tested. For this, **1** was dissolved in AC, and a solution of **2** in NMP was added but growing oligomer chains precipitated after short time. On the other hand, in this case the ratio of solvent to solid has to be higher than in the case of NMP as a reaction solvent. By using NMP as a reaction solvent, a suspension of **1** was heated in the presence of a solution of **2** in NMP. Then a clear viscous

Table 1 The effect of reaction catalyst and PEG molecular weight on the preparation of PEUUs based MDI-kryptofix 22

Polymer	PEG	Catalyst	Yield (%)	η_{inh}[d] (dL/g)
P-1	PEG-400[a]	No	72	0.55
P-2	PEG-400[a]	DBTDL[b]	75	0.60
P-3	PEG-400[a]	Py[c]	85	0.68
P-4	PEG-600[a]	Py[c]	72	0.57
P-5	PEG-1000[a]	Py[c]	62	0.47
P-6	PEG-2000[a]	Py[c]	60	0.32

Mole ratio of kryptofix 22:MDI:PEG was 1:2:1

[a] PEG molecular weight

[b] Dibutyltin dilaurate

[c] Pyridine

[d] Inherent viscosity, measured at a concentration of 0.5 g/dL in DMF as solvent at RT

solution was formed after short time. It was resulted in improved yield and viscosity. However, it was shown that performing polymerization reaction under melt condition at the beginning of the reaction, then adding NMP after a short time, afforded higher viscosity ("Synthesis of PEUUs" section 2–3).

The ratio of solvent (NMP) to solid, reaction time and reaction temperature were changed and the molar ratio of (kryptofix:MDI:PEG-400) was kept (1:2:1). It was shown that the best result was obtained by adding MDI to molten kryptofix 22 then adding NMP as solvent after short time and gradual heating from 40 to 120 °C.

The effect of catalyst on the preparation of PEUUs, concerning viscosity and yield of the resulting polymers, was studied in the presence of Py, DBTDL, and in the absence of any catalyst, respectively. It was shown that in the presence of Py the reaction mixture was soluble during whole reaction period, affording higher viscosity than other catalysts.

These studies showed that the best results were obtained in the presence of Py as catalyst, NMP as reaction solvent and PEG-400 as polyether soft segment (Table 1, **P-3**). In addition, polymer **P-3** showed better film forming ability than other samples. Thus, further studies were performed on **P-3**. In the case of **P-4**, **P-5**, and **P-6** the ratio of NMP to solid had to be higher than in the case of **P-3**, to prevent gel formation during the reaction. This might be the reason for the decrease in viscosities and yields of these polymers comparing with **P-3**.

Polymer characterization

The resulting polymers were characterized by FT-IR and ^{1}H-NMR spectroscopies. The ^{1}H-NMR spectrum of **P-3** showed peaks that confirms its chemical structure (Fig. 2). It showed peak for CH_2s (1), which appeared as broad singlet at 2.5 ppm. Peaks in the region of 3.3–3.8 ppm are related to CH_2s (2–5). The aromatic protons appeared in the region of 7.1–7.3 (dd) ppm that are related to CHs (6) and (7) of MDI ring moiety. The peaks in the region of 8.3–8.5 ppm are assigned for N–H of urea and urethane groups.

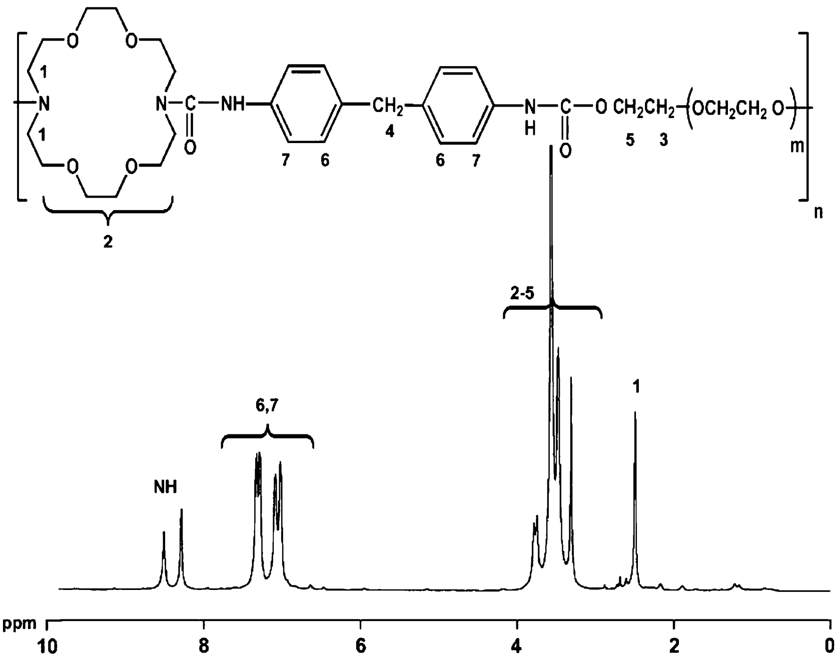


Fig. 2 ^{1}H-NMR (500 MHz) spectra of **P-3** in DMSO-d_6 at RT

The FT-IR spectra of the PEUUs showed characteristic absorption bands representative of the PEUUs. For example, the FT-IR spectrum of **P-3** showed the characteristic absorptions of urea and urethane groups around 3450, 3420, 3354, 1771, 1719, 1686, 1598, and 1539 cm^{-1}, which were associated with N–H, C=O, and C–N vibrations of urea and urethane groups, respectively. Absorptions bands around 1050–1200 cm^{-1} are assigned for C–O of ether groups.

Study of aqueous cation uptake

The method involved in exposing polymer powder to an aqueous based 0.5 or 1 M solution of metal chlorides. The concentration of residual metals in aqueous solutions was measured using an atomic absorption spectrophotometer. From the resulting emission intensities the cation loading were then compared. It was shown that Li$^+$ was preferentially taken up (Fig. 3). Competitive cationic uptake was also studied in ionic mixture of the above mentioned salts. The polymer sample, **P-3**, was exposed to mixture comprising 0.5 M of each of the metal ions. The selectivity observed in the previous separate cation uptake experiments was applicable in the competitive cationic absorption results. In addition polymer powder was exposed to an aqueous based 1 M solution of metal chlorides for 2, 12, and 24 h and mole percentages of the absorbed metals by the 0.5 g of **P-3** were compared (Table 2). It can be seen that by increasing the immersion time mole percentage of absorbed metals has increased specially in the case of Li$^+$ and Mg$^+$ ions which have similar radii. However, the increasing trend for Li$^+$ ion is more remarkable than for other

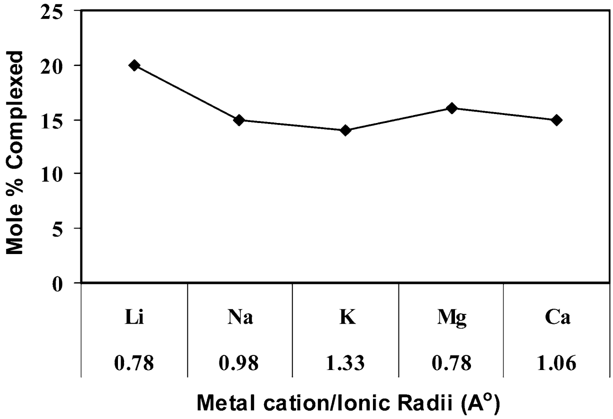


Fig. 3 Influence of cationic radius in metal cation uptake by **P-3** after exposing 0.5 g polymer to 1 M solution of metal cations for 2 h

Table 2 Study of comparative aqueous cation uptake of PEUUs

Metal	% Sorbed[a] *M*/Immersion time (h)	Sorbed[b] *W* (mg)/ Immersion time (h)	U^c (mol/g) × 100/ Immersion time (h)	% Sorbed[a] *M*/Immersion time (h)	% Sorbed[a] *M*/Immersion time (h)
Li	20/2	27.8/2	40/2	70/12	90/24
Na	15/2	68.9/2	30/2	49/12	53/24
K	14/2	109.4/2	28/2	42/12	45/24
Mg	16/2	77.79	32/2	55/12	58/24
Ca	15/2	120.24/2	30/2	48/12	51/24

Exposing 0.5 g of polymer powder (**P-3**) to an aqueous based 1 M solution of metal chlorides for certain period of time at RT

[a] Mole percentage of the absorbed metal by the 0.5 g of **P-3** after the treatment for certain period of time at RT

[b] The weight (mg) of the absorbed metal ion by 0.5 g of **P-3** after the treatment for certain period of time at RT

[c] *U* (mol cation/1 g polymer) is the amount of the absorbed metal ions by unit mass of the **P-3** after the treatment for certain period of time at RT (mole ratio of (**1**):(**2**):(**3**) was 1:2:1)

cations. From this, it may be inferred that the polymer has taken up Li^+ ion preferentially (Fig. 4).

The amount of the absorbed metal ions was calculated for each cation by using Eqs. 1–3. The results are given in Table 2.

These studies have indicated the potential of crown containing PEUUs in cation exclusion. Increasing cation absorption in the case of Li^+ and Mg^{2+} (Fig. 3) shows, to some extent, the size selectivity of the polymer with respect to cation uptake and can also be indicative of the crown role in selective cation absorption process. However, it seems that PEG residues play an important role in assisting the binding process, thus in the case of Li^+ absorption, the polymer displayed the above mentioned selectivity and it showed more tendency to absorb Li^+ (Fig. 3; Table 2).

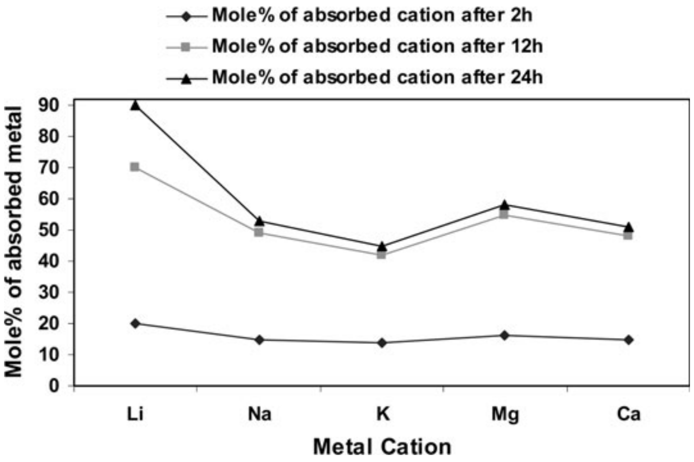


Fig. 4 Metal cation uptake by **P-3** as a function of immersion time after exposing 0.5 g polymer to 1 M solution of metal cations

Table 3 Study of comparative aqueous Li^+ ion uptake of PEUUs

C (mmol/mL)[a]	% Sorbed[b,c] *M*/Immersion time (h)	Mole ratio of (**1**):(**2**):(**3**)[d]	% Sorbed[e] *M*/Immersion time (h)
0.5	30/12	1:2:1	70/12
1	70/12	1:3:2	88/12
2	90/12	2:3:1	80/12

Exposing 0.5 g of polymer powder to an aqueous based solution of LiCl at different concentration of metal salt or different mole ratio of (**1**):(**2**):(**3**) for certain period of time at RT

[a] Concentration of the Li^+ ion aqueous solution

[b] Mole percentage of the absorbed metal by the 0.5 g of **P-3** after exposure to solutions of LiCl at different concentrations for certain period of time at RT (column 1)

[c] Mole ratio of kryptofix 22:MDI:PEG used for the synthesis of PEUUs was 1:2:1

[d] Mole ratio of kryptofix 22:MDI:PEG used for the synthesis of PEUUs

[e] Mole percentage of the absorbed metal by the 0.5 g of polymer after the treatment for certain period of time at RT obtained by exposing polymer powder with different mole ratio of (**1**):(**2**):(**3**) (column 3) to an 1 M aqueous solution of LiCl

It has been shown that PEG polyelectrolytes have good ability for the ionic dissociation. In polyurethanes containing PEG as soft phase, the polyether soft domain can be used as a Li^+ transport environment [12].

In order to shed some more light on this issue that, where complexation will preferentially happen, cation absorption capacity was measured as a function of ion concentration as well as the molar ratio of kryptofix 22, and PEG which were used for the preparation of PEUUs (Table 3). According to the results given in Table 3, for Li^+ cations, the sorption capacities at $C = 0.5$ M were lower than it at the other studied concentrations. Comparing sorption capacity at $C = 0.5$ and 1 M, mole percentage of absorbed metal at $C = 1$ M is about twofolds higher than that at $C = 0.5$ M. The same relation is not applicable for $C = 1$ and $C = 2$ M. It can be said that, when cation concentration is increased, the sorption capacity for Li^+ ions increased initially and finally reached constant value.

Table 3 shows that by increasing the mole ratio of each of PEG or kryptofix 22, the mole percentage of the Li^+ ion sorbed by polymer increased. This may show the contribution of each of these structural components of polymer in ion uptake. However, it seems that there is not any direct relationship between molar ratio of (**1**):(**2**):(**3**) and mole percentage of absorbed Li^+ ion. On the other hand, the sorption capacity for Li^+ ions reached constant value. From the data presented in Table 3 it can be seen that ion uptake capacity was affected by changes in PEG mole ratio more than it by changes in kryptofix 22 mole ratio. Thus, it can be inferred that PEG component strongly assists in the binding process.

Thermal and FT-IR studies were also performed on polymer samples before and after exposure to a solution of LiCl, as well as ^{7}Li-S-NMR study.

FT-IR study

FT-IR was used to study the interaction of the groups in PEUU with Li^+ ions, and its effect on the morphology of the PEUU. For example, Fig. 5 presents the FT-IR

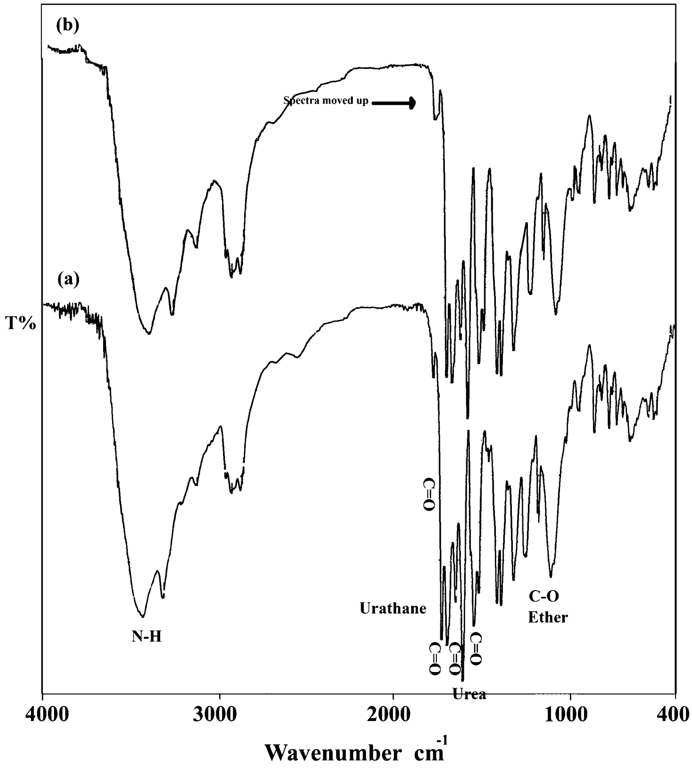
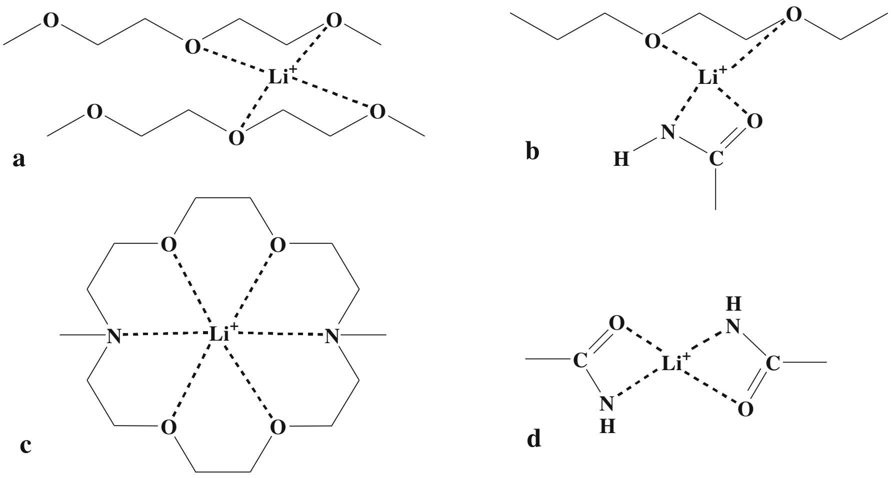


Fig. 5 The FT-IR spectra of the NH, C=O, and C–O stretching regions for PEUU-**P**-**3**, before (*a*) and after (*b*) Li^+ ion loading. The spectra were moved up



Scheme 2 Different possible interactions of Li^+ ions with different functional groups within PEUU: **a** PEG polyether chains, **b** PEG polyether chains and urethane or urea groups, **c** kryptofix ring, **d** NH and C=O groups of urethane or urea linkages

spectra of carbonyl stretching regions for **P-3-0** and **P-3-Li**. Free and hydrogen-bonded urethane carbonyl absorption bands at 1770 and 1720 cm^{-1} shift to low frequency with the presence of Li^+ salt because of the coordination between Li^+ ions and carbonyl groups. Furthermore, the absorption bands of the disordered hydrogen-boned urea carbonyl groups shift to lower frequency in the presence of Li^+ salt. This may be due to coordination of the urea carbonyl groups with Li^+ ions. Also the frequencies of absorption bands of the ether oxygen at 1150–1050 cm^{-1} and NH at 3450–3420 cm^{-1} shift to low frequency with the presence of Li^+ salt in consequence of the coordination between Li^+ ions and the ether oxygen of the kryptofix and PEG chain as well as NH groups (Scheme 2).

Thermal properties of PEUUs

The effect of Li^+ ion complexation on the morphology and thermal behaviors of the PEUUs was elucidated using DSC technique. Figure 6 shows DSC thermograms of **P-3** before (**P-3-0**) and after (**P-3-Li**) exposure to 0.5 M solution of LiCl for 2 h. DSC curve of **P-3-0** shows broad endothermic peaks at about 15, 150, and 205 °C that can be attributed to T_gs, T_gh, and T_c, respectively. We supposed that T_gs is glass transition temperature of soft segment, T_gh is glass transition temperature of hard segment, and T_c is melting temperature of microcrystalline regions of hard segment. On the other hand, the T_gs for **P-3-Li** increased with Li^+ doping (Fig. 6). It has been shown that the coordination of Li^+ ions with the PEG soft segment restricts the local motion of the polymer segments and also forms physical cross-linking, causing an increase in T_gs [13, 14]. Increasing hard and soft phase miscibility due to interactions between the coordination sites and Li^+ ions, including PEG segments and –NH–CO– of urea and urethane links can be another reason for increasing T_gs (Scheme 2b). The same manner can be observed for T_gh of **P-3-Li** because of the interactions between the NH

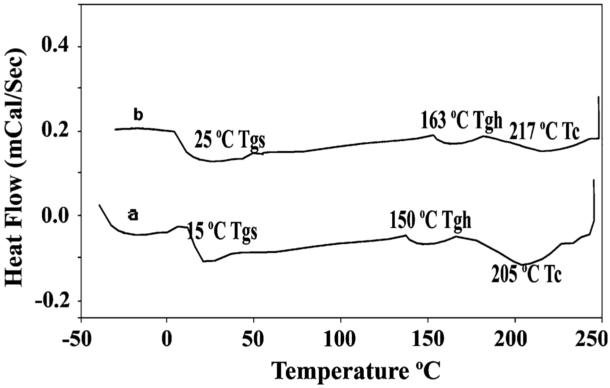


Fig. 6 DSC traces of (*a*) **P-3-0** and (*b*) **P-3-Li** at heating rate of 10 °C/min under N_2 atmosphere. Center of the region was considered for transition observed by DSC

and carbonyl groups of urea, urethane links, and the Li^+ ions, leading to physical cross-linking in hard segment region (Scheme 2d). Meanwhile, the coordination complex in Scheme 2c causes restricted motion of the polymer hard segments and increasing T_gh. Another interesting feature of the DSC curve of **P-3-Li** is that the endothermic peak at T_c decreased (Fig. 6). This phenomenon indicates that the crystalline structure of PEUU may be disrupted to some extent.

Thermal stability of **P-3** before and after exposure to Li^+ ions was compared with TGA technique. Figure 7 shows TGA of **P-3-0** and **P-3-Li** after exposure to 0.5 M solution of LiCl for 2 h. TGA curve associated with **P-3-Li** shows relatively greater thermal stability than **P-3-0**. T5% and T10% for **P-3-0** started at about 280 and 300 °C, respectively. Its weight residue at 700 °C was 9%. The aforementioned results for **P-3-Li** were 320, 350 °C, and 22%, respectively. Thus, it can be said that

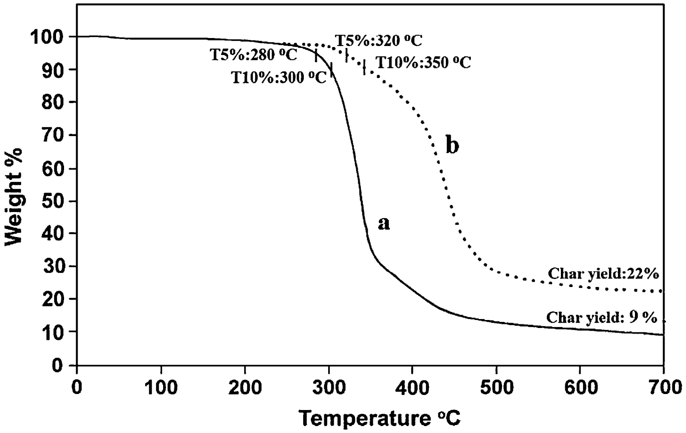


Fig. 7 TGA thermograms of (*a*) **P-3-0** and (*b*) **P-3-Li** (polymer sample after exposure to 0.5 M solution of LiCl for 2 h) at heating rate of 10 °C/min in N_2 atmosphere. T5% and T10%: The temperature at which 5 and 10% weight loss were recorded by TGA, respectively. Char yield%: The percentage of weight residue at 700 °C in N_2 atmosphere by TGA

incorporation of Li^+ ions improved thermal stability of the resulting PEUUs comparatively. Coordination of Li^+ ions may led to better inter-chain interaction, more physical cross-linking and consequently more thermal stability of resulting polymers. According to Eq. 4 weight percentage of Li^+ ion can be calculated from the difference in the char yield (%) at 700 °C from TGA curve of **P-3-Li** and **P-3-0**. The calculated amount of Li^+ ion is about 0.027 g per unit mass of the **P-3-Li**, that is one half of the amount of Li^+ ions absorbed by unit mass of the polymer measured by AAS (27.8×10^{-3} g Li/0.5 g **P-3** = 0.055 g Li^+ per unit mass of the polymer which was exposed to 1 M solution of LiCl for 2 h; Table 2, column 3). The results are in accordance with the data obtained from ASS method and also confirm concentration dependence of metal uptake capacity of polymer concluded from Table 3. In other words, the amount of Li^+ ions sorbed by unit mass of the polymer after exposure to 0.5 and 1 M solution of LiCl for the same periods of time, 2 h, is 0.027 and 0.055 g per unit mass, respectively (Footnotes of Tables 2 and 3; Fig. 7).

^{7}Li-S-NMR study

The ^{7}Li-S-NMR spectrum of **P-3-Li** showed peak that confirms coordination of Li^+ ion to the polymer (Fig. 8). Due to the presence of different coordination sites in the PEUU, various complexes are possible to be formed by the interaction of these coordination sites with the Li^+ ions (Scheme 2). Variable-temperature ^{7}Li MAS NMR was used to acquire evidence on the possible interaction of Li^+ ions with the chelating sits of kryptofix 22, PEG, and urethane–urea groups (FT-IR study; Fig. 5). It is inferred from Fig. 9 that the presence of more than one resonance is caused by the presence of various local environments of Li^+ ions results in peak broadening at lower temperature. Raising the temperature causes these resonance peaks to shift and eventually combine to form a single sharp resonance peak. Since different resonance peaks are not distinctly separated at lower temperatures, it may indicate that most of Li^+ ions may preferentially be coordinated to chelating sites of kryptofix 22 and PEG.

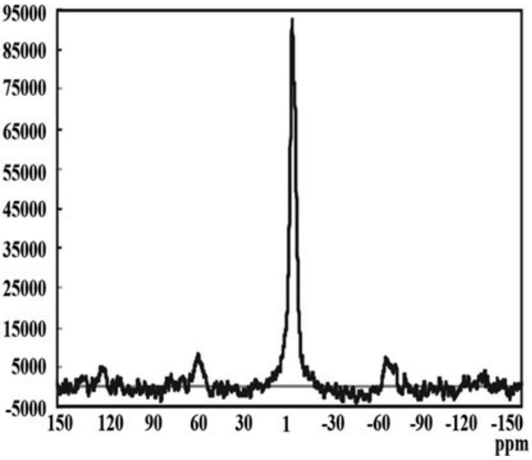


Fig. 8 ^{7}Li-S-NMR (500 MHz) spectrum of **P-3-Li** at RT

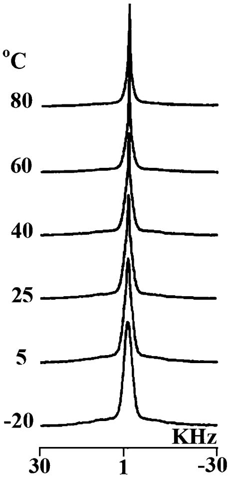


Fig. 9 Variable-temperature ^{7}Li MAS NMR of **P-3-Li**

Data presented in "^{7}Li-S-NMR study" section show why T_g of both soft and hard segment influenced by Li$^+$ ion complexation. Data presented in "Thermal properties of PEUUs" section together with FT-IR study show not only –O– of ether linkages in soft segment but also C=O and NH in hard segment influenced by Li$^+$ ion complexation. Data presented in Table 3 and related discussion at the end of "FT-IR study" section show that Li$^+$ ion uptake can be affected by molar ratio of both PEG and kryptoifix. All of these evidences show the participation of different functional groups in Li$^+$ ion complexation and all support the obtained conclusion in the final section by S-NMR study. In addition, there are some studies in literatures that they concluded the presence of different coordination sites for Li$^+$ complexation by using FTIR and S-NMR data [15, 16]. There are different studies about different Li$^+$ ion complexing compounds which show complexation of Li$^+$ ion in different compounds with –O–, N, and C=O sites [17, 18].

Solubility properties of PEUUs

The resulting polymers are soluble in solvents such as DMF, NMP, DMAc, DMSO, CH_2Cl_2, $CHCl_3$, dioxane, and AC at RT or between 80 and 100 °C. They are insoluble in solvents such as water, methanol, CCl_4, or acetone (the concentration at which the solubility tests were conducted was 0.005 g of polymer in 1 mL of each solvent).

Conclusions

Some new segmented PEUUs containing aza crown ether (cryptand) based on MDI, and different molecular weights of PEGs were prepared and characterized. The complexation ability of these polymers with different cations was also compared. The study of aqueous cation uptake of polymers has indicated the potential of crown containing PEUUs in cation exclusion especially for Li$^+$ ion. It was shown that PEG residues play an important role in assisting the binding process. Thus, in the case of Li^+ absorption, the polymer as a whole displayed more selectivity than other cations. It was shown that the efficiency of Li^+ ion exclusion from its aqueous solution was more than 70%. FT-IR frequencies of the absorption bands of the ether oxygen at 1150–1050 cm^{-1} shift to low frequency with the presence of Li^+ salt in consequence of the coordination between the Li^+ ions and ether oxygens of the kryptofix and PEG chain. Thermal properties study of polymers show that the coordination of Li^+ ions has led to better inter-chain interaction, more physical cross-linking and consequently better thermal stability of resulting polymers. S-NMR study showed Li^+ ions may preferentially be coordinated to chelating sites of kryptofix 22 and PEG.

For suggesting some further probable applications for these PEUUs, it is expected that the resulting PEUUs because of PEG segments show solvating power for various alkaline salts despite of its low dielectric constant. Also it was known that a number of PEG's solid polymer electrolytes derivatives exhibit relatively appealing ion transport properties in the amorphous phase. In addition, it was shown that some kinds of polymers, containing heterocyclic compounds, have been useful in filters and diffusion membranes and have shown selectivity towards different ions, gases, or liquids depending on polymer and heterocyclic structure.

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