Lithium Ionic Conductivity in Poly(ether urethanes) Derived from Poly(ethylene glycol) and Lysine Ethyl Ester

K. V. RAMANUJACHARY,* X. TONG, Y. LU, J. KOHN, M. GREENBLATT

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

ABSTRACT: Poly(ether urethanes) obtained by the copolymerization of poly(ethylene glycol)(PEG) and lysine ethyl ester (LysOEt) are elastomeric materials that can be processed readily to form flexible, soft films. In view of these desirable physicomechanical properties, the potential use of these new materials as solid polymer electrolytes was explored. Solid polymer electrolytes were prepared with copolymers containing PEG blocks of different lengths and with different concentrations of lithium triflate ($LiCF_3SO_3$). Correlations between the length of the PEG block, the concentration of lithium triflate in the formulation, and the observed Li^+ ion conductivity were investigated. Solid electrolyte formulations were characterized by differential scanning calorimetry for glass transition temperatures (T_g), melting points (T_m), and crystallinity. Ionic conductivity measurements were carried out on thin films of the polymer electrolytes that had been cast on a microelectrode assembly using conventional ac-impedance spectroscopy. These polymer electrolytes showed inherently high ionic conductivity at room temperature. The optimum concentration of lithium triflate was about 25–30% (w/w), resulting at room temperature in an ionic conductivity of about 10^{-5} S cm^{-1}. For poly(PEG_{2000}–LysOEt) containing 30% of $LiCF_3SO_3$, the activation energy was ~ 1.1 eV. Our results indicate that block copolymers of PEG and lysine ethyl ester are promising candidates for the development of polymeric, solvent-free electrolytes. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1449–1456, 1997

Key words: ionic conductivity; polymer electrolyte; poly(ethylene glycol)–lysine ethyl ester copolymers; lithium triflate; poly(ethylene glycol)

INTRODUCTION

The area of ionically conducting polymer electrolytes has been receiving much attention since the discovery of electrolytes based on poly(ethylene oxides)(PEO) by Wright and co-workers two decades ago.[1] Research since then has concentrated on designing novel polymer systems with high ionic conductivity and good mechanical properties for technological applications.[2–4] Development of polymer-based solid electrolytes is considered crucial in designing new-generation high-energy density batteries, sensors, electrochemical display devices, and "smart" windows because of their obvious advantages over conventional inorganic electrolytes.[5] For example, polymer electrolytes can be cast into thin films of desired shape (a prerequisite for making lightweight batteries) and maintain good electrical contact with the electrodes during charge–discharge cycles because they deform easily under stress. In addition to the differences in their mechanical properties, polymer electrolytes also differ considerably from inorganic electrolytes in their mode of ionic transport.[6] Although there is no general consensus on
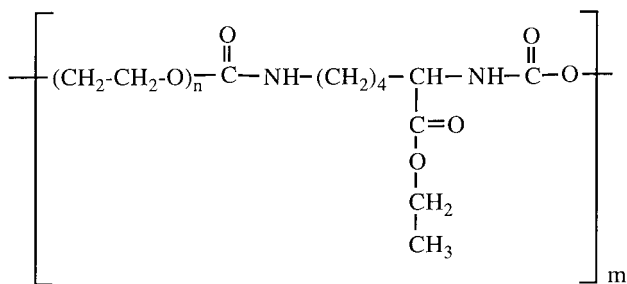
Figure 1 Chemical structure of poly(PEG–LysOEt). This block copolymer consists of PEG blocks linked together by lysine ethyl ester via urethane bonds. The copolymer has a regular, strictly alternating sequence of PEG and lysine ethyl ester units. Using PEG preparations with weight-average molecular weights of 2000 and 4000, the length of the PEG block in the copolymer could be varied.

the exact mechanism of ionic transport in polymer-based electrolytes, it is established that significant ionic motion exists only in the amorphous regions of the polymer while the crystalline regions are nonconducting.[7] Thus, in designing novel polymer electrolytes, emphasis is placed on minimizing the degree of crystallinity of the polymers while maintaining adequate mechanical properties for device applications. Among several polymer electrolyte systems that were investigated, polyether-based electrolytes have shown promising features such as good adherence to the electrodes and the ability to solvate many inorganic salts to form a homogeneous solution, even at very high salt concentrations.[8] Ease of film fabrication is another potential advantage. However, pure PEO is a semicrystalline polymer, possessing both an amorphous and a crystalline phase at room temperature. Hence, acceptable levels of ionic conductivity in many PEO-based systems can only be obtained at elevated temperatures.[9]

We recently developed a new family of materials in which individual blocks of poly(ethylene glycol) (PEG) are copolymerized with L-lysine ethyl ester via urethane linkages to yield strictly alternating *block*-poly(ether urethanes) of high molecular weight.[10,11] These polymers, referred to as poly(PEG–LysOEt) (Fig. 1), form soft, flexible films that retain good mechanical properties and that can form polymer–salt complexes containing high concentrations of lithium salts. Since the copolymers have a well-defined chemical structure in which the length of the PEG block can be controlled readily, these materials facilitate the eluci-

dation of correlations between the molecular structure of the copolymer and its ionic conductivity. In view of the need for polymeric electrolytes that form soft and flexible films, we investigated the possible application of these materials as ionic conductors.

In this article, we report our initial results on the ionic conductivity of adducts of poly(PEG–LysOEt) and lithium triflate. Using copolymers containing PEG blocks of different length and by using formulations containing different concentrations of lithium triflate, compositions with relatively high ionic conductivity were identified and tentative correlations between the molecular structure of the copolymer and its ionic conductivity were established.

EXPERIMENTAL

Materials

The following chemicals were obtained from sources indicated in parentheses: PEG_{2000}, PEG_{4000}, 20% phosgene solution in toluene, and L-lysine ethyl ester dihydrochloride (Fluka), N-hydroxysuccinimide (Schweizerhall), dimethylaminopyridine, and lithium triflate (Aldrich). PEGs were dried azeotropically before use; all other materials were used as received. The solvents for synthesis and gel permeation chromatography (GPC) were HPLC grade.

Synthesis and Characterization of Copolymers

Urethane-linked block copolymers of PEG and lysine ethyl ester, poly(PEG–LysOEt), were prepared and characterized as described in previous publications.[10,11] PEG blocks of molecular weights 2000 and 4000 were used. The resulting copolymers are referred to as poly(PEG_{2000}–LysOEt) and poly(PEG_{4000}–LysOEt), respectively. The chemical structure of the copolymers was confirmed by ^{1}H- and ^{13}C-NMR, recorded on a Varian XL-200 spectrometer, and by FTIR, obtained on a Mattson Cygnus 100 spectrophotometer (see Nathan et al.[10] for spectral data). Polymer molecular weights were determined by aqueous gel permeation chromatography (GPC) relative to PEG standards, using 0.1M acetate buffer (pH 5.4) as the mobile phase at a flow rate of 1.0 mL/min. Two TSK gel columns (TSK G-2000 and TSK G-4000) were used in series. The weight-average molecular weights (M_w) of poly(PEG_{2000}–LysOEt),

Table I   Thermal Transitions of Neat PEG and Poly(PEG–Lys–OEt) Copolymers

Polymer	Glass Transition (°C)	Melting Temperature (°C)	Crystallinity (%)
PEG$_{2000}$[a]	−65	55	83
Poly(PEG$_{2000}$–LysOEt)	−51	38	38
PEG$_{4000}$[a]	−62	59	84
Poly(PEG$_{4000}$–LysOEt)	−58	42	41

[a] From Bailey and Koleske,[12] see pp. 107–108 and 136–138.

and poly(PEG$_{4000}$–LysOEt) were 61,000 and 74,000 g/mol, respectively.

Methods

The salt–polymer adducts were prepared by dissolving a mixture of predetermined amounts of lithium triflate and poly(PEG–LysOEt) in tetrahydrofuran under anhydrous conditions for 24 h. Electrolytes for conductivity measurements were prepared by casting the salt–polymer solution onto Model SAW-302 interdigitated microelectrodes (Microsensor Corp.); the solvent was evaporated to dryness in a dessicator under a dynamic vacuum over anhydrous P$_2$O$_5$ at room temperature for 6 days. The electrode assembly was then quickly transferred to the vacuum oven used in the conductivity measurements and dried under dynamic vacuum (P$_{H_2O}$ = 1 × 10^{-7} atm) over anhydrous P$_2$O$_5$ at room temperature for an additional period of 48 h. Samples for glass transition and melting point determinations were also dried under identical conditions.

The glass transition temperatures (T_g) and melting points (T_m) were determined by differential scanning calorimetry (DSC) using a Model 910 scanning calorimeter from TA Instruments (Wilmington, DE) at a heating rate of 10°C/min.

The microelectrodes used in the conductivity measurement consist of 50 pairs of equally spaced interdigitated gold electrodes printed onto a quartz substrate. The geometric factor (i.e., the area-to-length ratio) for this configuration is 0.317 cm, which is calculated using the expression [(2n − 1)·L·H]/d, where n = number of electrode paris (50), L = length of the electrode (4800 microns), H = thickness of the electrode (0.1 microns), and d = interelectrode spacing (15 microns). Impedance measurements were carried out using a 1280 Solartron frequency-response analyzer coupled internally to an electrochemical interface under computer control. The real and imaginary components of the impedance were measured at various frequencies in the interval of 1–20 kHz. The bulk conductivities of the films were estimated from the Cole–Cole plots of the real and imaginary impedances with the aid of ZPLOT/ZVIEW software (Solartron Instruments). The conductivities were corrected for the geometric factor before processing the data for further analysis. The impedance measurements were also carried out on the "naked" electrode to ensure high resistivity of the open circuit. A few measurements were also performed at ambient temperature as a function of drying time in the vacuum oven to examine the effect of residual moisture content on the conductivity behavior of the films.

RESULTS AND DISCUSSION

To understand the effect of the copolymer network on the thermal properties of the individual PEG blocks, the melting temperature (T_m), glass transition temperature (T_g), and the degree of crystallinity were determined by DSC for PEG$_{2000}$ and PEG$_{4000}$ and the corresponding linear poly(PEG–LysOEt) copolymers (Table I).

It is evident that both the degree of crystallinity and the melting points increased slightly with increasing length of the PEG block (Table I). This was expected since the crystallinity in PEG increases with increasing molecular weight. However, for each PEG block length, the crystallinity of the PEG block in the copolymer was significantly lower than the crystallinity of the corresponding free PEG chain. Likewise, the melting temperatures of the copolymers were significantly lower than those of the individual PEG chains.

Table II Thermal Transitions of Polymer Electrolytes as Function of the Salt Concentration

	Li Concentration (%)				
	0	10	20	30	40
Part A: Data for poly(PEG$_{2000}$–Lys–OEt)					
Glass transition (°C)	−51	−48	−42	−38	−32
Melting temperature (°C)	38	35	27	n/a	n/a
Crystallinity (%)	38	30	1	n/a	n/a
Part B: Data for poly(PEG$_{4000}$–Lys–OEt)					
Glass transition (°C)	−58	−49	−47	−42	−37
Melting temperature (°C)	42	40	35	29	n/a
Crystallinity (%)	41	30	23	4	n/a

n/a: no reproducible melting transition observed.

In previous studies of oxomethylene–PEG copolymers, the glass transition temperatures (−65°C) of the copolymers were similar to that of the pure PEG.[13,14] In contrast, in poly(PEG–LysOEt), the glass transition temperature of the copolymers was higher than that of pure PEG. This suggests relatively stronger interchain coupling in poly(PEG–LysOEt) than in PEG. The stronger chain interactions in poly(PEG–LysOEt) are presumably mitigated by hydrogen bonds involving the amidic hydrogens and Lewis base sites such as the oxygens or the nitrogens of the polymer backbone. This additional interaction between the chains can also account for the significantly improved mechanical strength of poly(PEG–LysOEt) films compared to films prepared from pure PEO of similar molecular weight.

Data relating to the thermal transitions of poly-(PEG–LysOEt) containing different amounts of lithium triflate are presented in Table II. It is evident that the glass transition temperatures of the polymer–salt complexes increased linearly with the concentration of lithium triflate (see Fig. 2). This suggests a stronger interaction between
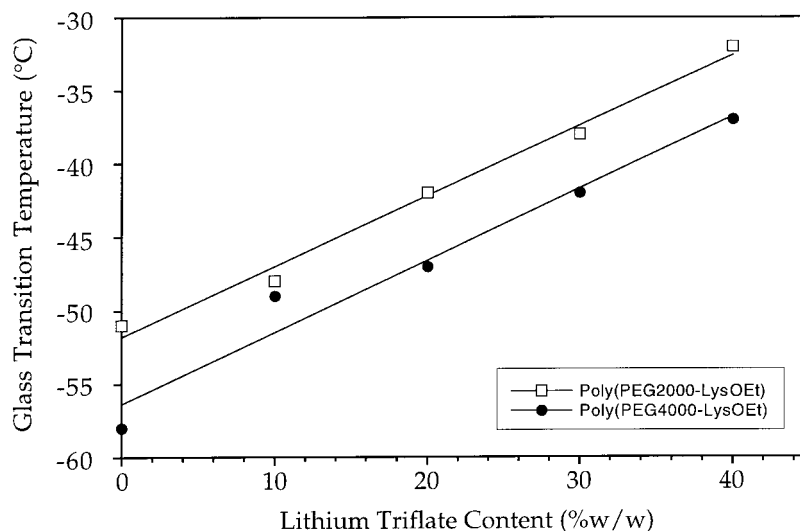

Figure 2 A linear correlation was observed between the glass transition temperature (T_g) of the polymer–salt complexes and the concentration of lithium triflate. Open squares correspond to poly(PEG$_{2000}$–LysOEt), and filled circles, to poly(PEG$_{4000}$–LysOEt).
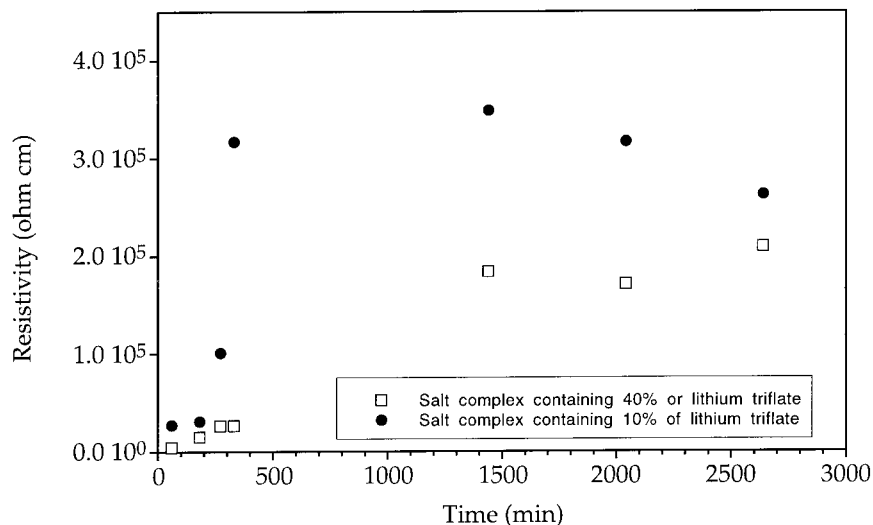
Figure 3 Resistivity as a function of the drying time under dynamic vacuum (10^{-3} Torr) at room temperature for poly(PEG_{2000}–LysOEt) containing (filled circles) 10% (w/w) of $LiCF_3SO_3$ and (open squares) 40% (w/w) of $LiCF_3SO_3$.

the Li ions and the polymer backbone, resulting in higher rigidity of the network. On the other hand, the melting temperatures decrease significantly with increasing concentration of the lithium triflate. With increasing content of lithium triflate, the corresponding melting transitions became smaller and increasingly difficult to observe. For poly(PEG_{2000}–Lys–OEt), reliable data could only be obtained for lithium triflate concentrations up to 20% (w/w), while for poly(PEG_{4000}–Lys–OEt), reliable measurements were possible up to 30% (w/w). These observations suggest that the interactions between the lithium ions and the polyether backbone tend to disturb the crystalline regions.

As expected, the ionic conductivity of poly-(PEG–LysOEt) films was sensitive to atmospheric moisture. To illustrate this, we plotted in Figure 3 the resistivity of poly(PEG_{2000}–LysOEt) complexed with 10 and 40% lithium triflate as a function of the drying time in a vacuum chamber at room temperature. It is evident that, in both samples, the resistance increased significantly as water was removed from the sample. However, as indicated in Figure 3, drying can be a time-consuming process, especially for formulations containing a higher concentration of triflate: The polymer–salt complex containing 10% lithium triflate reached a maximum resistivity in about 3 h, while the corresponding time for the polymer–salt complex containing 40% salt was about 20 h. These results can be explained based on the well-

known affinity of the PEG units and the lithium ions to moisture. Furthermore, samples with higher lithium content are expected to be hydrated to a larger extent, accounting for the longer time required for drying. Accordingly, all conductivity measurements reported here were obtained using samples that had been dried in a vacuum chamber for a period of 48 h.

The ionic conductivity at room temperature (23°C) of poly(PEG_{2000}–LysOEt) electrolytes as a function of the lithium ion concentration is presented in Figure 4. The ionic conductivity rose with increasing lithium concentration up to about 25–30% (w/w) and seemed to be reaching a plateau at about 30% (w/w) salt content. The data
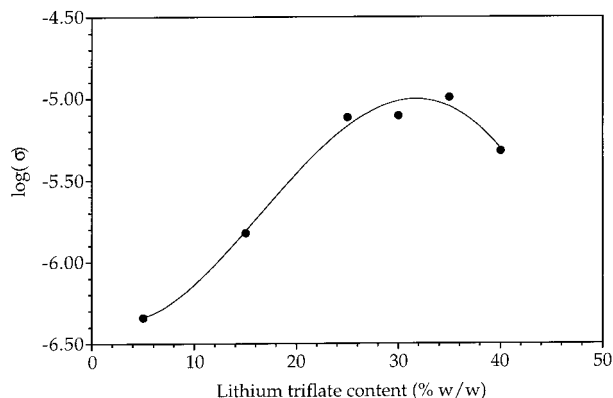

Figure 4 Effect of the concentration of lithium triflate on the ionic conductivity (expressed as log σ) of poly(PEG_{2000}–LysOEt) at room temperature (23°C).
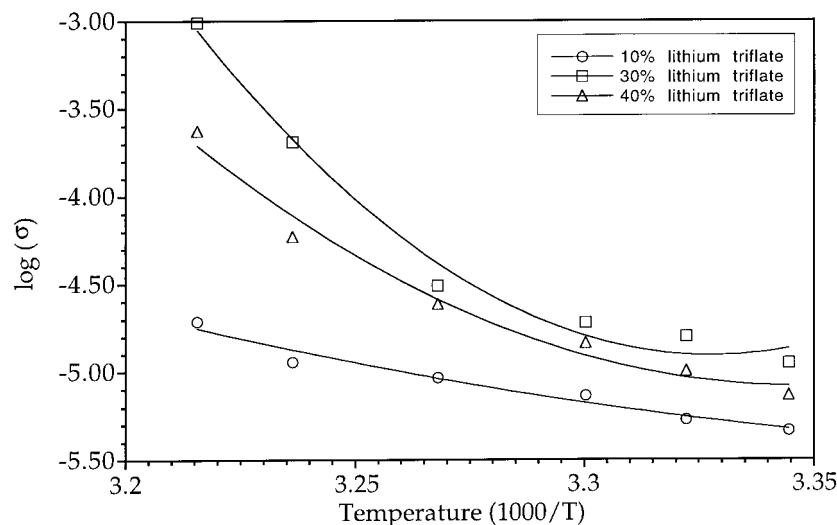
Figure 5 Temperature variation of the ionic conductivity (expressed as log σ) of (circles) poly(PEG$_{2000}$–LysOEt) containing 10% (w/w) of LiCF$_3$SO$_3$; (squares) 30% (w/w) of LiCF$_3$SO$_3$; (triangles) 40% (w/w) of LiCF$_3$SO$_3$.

point obtained at a salt content of 40% seemed to indicate that the ionic conductivity may decrease at higher salt contents. Thus, it appears that there is an optimum salt concentration. At concentrations below the optimum value, the increase in the ionic conductivity with increasing salt concentration can be related to the increase in the number of mobile charge carriers. The possible decrease in the ionic conductivity at a salt concentration of greater than 40% can be attributed to either an incomplete dissociation of the salt or the formation of ion triplets.[15] Ionic conductivities close to 10^{-5} S cm^{-1}, attractive for electrochemical device applications, were observed at room temperature (23°C) for poly(PEG$_{2000}$–LysOEt) containing 25–30% of LiCF$_3$SO$_3$.

The temperature dependence of the ionic conductivities of lithiated poly(PEG$_{2000}$–LysOEt) and poly(PEG$_{4000}$–LysOEt) electrolytes are presented in Figures 5 and 6, respectively. It is interesting to note that although the room temperature conductivities of both these polymers are comparable, the conductivity of poly(PEG$_{2000}$–LysOEt) at high temperatures is superior to that containing the longer PEG$_{4000}$ blocks. For example, the conductivity of poly(PEG$_{2000}$–LysOEt) containing 30% of lithium triflate is 10^{-3} S/cm at 38°C. This is an order of magnitude higher than the conductivity (10^{-4} S/cm) observed for poly(PEG$_{4000}$–LysOEt) at the same temperature. Clearly, the length of the PEG block is an important parameter when optimizing the molecu-

lar structure of the copolymer for maximum ionic conductivity.

Furthermore, the data presented in Figure 5 confirmed the trend seen in Figure 4: At all measured temperatures, the polymer–salt complex containing 30% lithium triflate had a higher ionic conductivity than the one containing 40% lithium triflate. The difference in ionic conductivity between polymer–salt complexes containing different salt concentrations increased with increasing temperature and the trend seen in Figure 4 (data obtained at 23°C) is becoming more pronounced at higher temperatures. In the case of poly(PEG$_{2000}$–LysOEt), there is clearly an optimum value for the lithium triflate content of the polymer–salt complex.

Poly(PEG$_{4000}$–LysOEt) showed a different behavior (Fig. 6). For this material, the ionic conductivity seemed to reach a plateau at 30–40% lithium triflate content and no maximum of the ionic conductivity as function of the salt concentration was identified in our studies. However, it is reasonable to assume that a reduction in ionic conductivity may be observed for this polymer at salt concentrations above 50% (w/w). Thus, the optimum salt concentration appears to be dependent on the exact molecular structure of the polymer.

Deviations from ideal Arrehenius-type behavior were observed for both poly(PEG$_{2000}$–LysOEt) and poly(PEG$_{4000}$–LysOEt). The curvature observed in the Arrhenius plots is typical for amor-
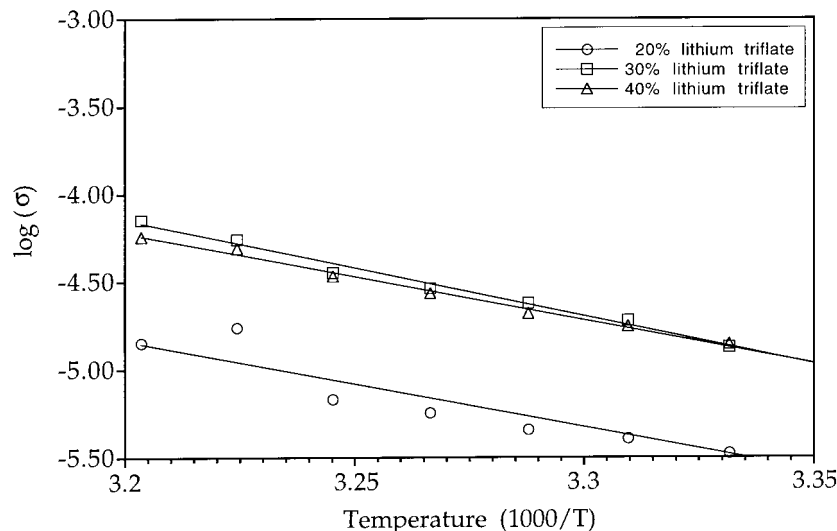
Figure 6 Temperature variation of the ionic conductivity (expressed as log σ) of poly(PEG_{4000}–LysOEt) containing (circles) 20% (w/w) of $LiCF_3SO_3$; (squares) 30% (w/w) of $LiCF_3SO_3$; (triangles) 40% (w/w) of $LiCF_3SO_3$.

phous polymer electrolytes and is often explained in terms of "free-volume" or "configurational entropy" models. The activation energy was calculated to be about 1.1 eV for poly(PEG–LysOEt) containing 25–30% of $LiCF_3SO_3$, independent of the length of the PEG block.

CONCLUSIONS

We prepared solid electrolytes by complexing poly(PEG–LysOEt) with lithium triflate. The thermal, spectral, and ionic transport properties of the polymer–salt complexes were characterized as a function of the PEG block length and as a function of the concentration of lithium triflate. The melting point as well as the degree of crystallinity of PEG decreased significantly when the PEG blocks were copolymerized with lysine ethyl ester. On the other hand, the glass transition temperature of the copolymers was higher than that of the free PEG blocks. This effect was attributed to interchain hydrogen bonding between the amidic hydrogens and oxygen and/or nitrogen atoms of the copolymer backbone. Upon complexation with lithium triflate, a further decrease in crystallinity and melting temperature was observed, while the glass transition temperatures increased with the salt concentration. The lithium ion conductivity was investigated as a function of tempera-

ture, salt concentration, and length of the PEG blocks.

Poly(PEG–LysOEt) appears to be a promising candidate material for use as a polymeric, solvent-free electrolyte. At room temperature, ionic conductivities of about 10^{-5} S cm were observed which increased to 10^{-3} S cm at slightly higher temperatures (about 38°C).

The PEG portion of the copolymer promotes chain segmental motion and facilitates ion transport through the PEG-rich phase of the copolymer. At the same time, the lysine ethyl ester units disrupt the inherent crystallinity of the PEG blocks and provide interchain hydrogen bonding which improves the mechanical strength of the copolymer. The final result is a material that exhibits reasonable handling properties and significant ionic conductivity at room temperature.

REFERENCES

1. D. E. Fenton, J. M. Parker, and P. V. Wright, *Polymer,* **14,** 589 (1973).

2. M. S. Mendolia and G. C. Farrington, in *Materials Chemistry: An Emerging Discipline,* L. V. Interante, L. A. Caspar, and A. Ellis, Ed., Advances in Chemistry Series, Vol. 245, American Chemical Society, Washington, DC, 1995, p. 107.

3. C. A. Vincent, *Prog. Solid State Chem.,* **17,** 145 (1987).

4. J. M. G. Cowie and S. H. Cree, *Annu. Rev. Phys. Chem.,* **40,** 85 (1989).

5. C. A. Vincent, *Chem. Br.,* **April,** 391 (1989).

6. M. A. Ratner and D. F. Shriver, *Chem. Rev.,* **88,** 109 (1988).

7. C. Berthier, W. Gorecki, M. Minier, M. B. Armand, J. M. Chabagno, and P. Rigaud, *Solid State Ionics,* **11,** 91 (1983).

8. M. Armand, *Solid State Ionics,* **9,10,** 745 (1983).

9. G. C. Farrington and R. G. Linford, in *Polymer Electrolyte Reviews—2,* J. R. MacCallum and C. A. Vincent, Eds., Elsevier, London, 1989, p. 255.

10. A. Nathan, D. Bolikal, N. Vyavahare, S. Zalipsky, and J. Kohn, *Macromolecules,* **25,** 4476 (1992).

11. A. Nathan, S. Zalipsky, S. I. Ertel, S. N. Agathos, M. L. Yarmush, and J. Kohn, *Bioconj. Chem.,* **4,** 54 (1993).

12. F. E. Bailey and J. V. Koleske, *Poly(ethylene oxide),* Academic Press, New York, 1976.

13. F. M. Gray, *Solid State Ionics,* **40/41,** 637 (1990).

14. J. P. Lemmon and M. M. Lerner, *Macromolecules,* **25,** 2907 (1992).

15. J. R. MacCallum, A. S. Tomlin, and C. A. Vincent, *Eur. Polym. J.,* **22**(10), 787 (1986).