6910 *Macromolecules* **2000,** *33,* 6910−6912

Direct ^{7}Li NMR Spectral Evidence for Different Li$^+$ Local Environments in a Polyether Poly(urethane urea) Electrolyte

Hsing-Lung Wang,[†] **Hsien-Ming Kao,**[*,‡] **and Ten-Chin Wen**[*,†]

Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan, and Department of Chemistry, National Central University, Chung-Li, Taiwan 32054

Received May 31, 2000
Revised Manuscript Received July 21, 2000

Solid polymer electrolytes (SPEs) have received considerable attention in the past decade because of their possible room-temperature conductivity up to 10^{-4} S/cm and wide applications in secondary battery systems, fuel cells, and other electrochromic displays. Early work by Armand[1] and others[2] has prompted numerous investigations into the dissolution of alkali-metal salts in polyether polymers. A number of comprehensive reviews have been published on the subject.[3−6] Much work has been devoted to understand how the motion of ions occurs through the polymer host and how the nature of the components of an SPE affects the motion and environment of the charge-carrying species. However, the detailed understanding of the role for ion−polymer/ion−ion interactions, the nature of the charge carrier, and the ionic association process in the ionic conductivity is still relatively limited.

Polyether poly(urethane urea) (PEUU) is composed of a polyether soft segment and a diisocyanate-based hard segment, being characterized by a two-phase morphology.[7,8] The phase separation is due to the fact that the hard and soft phases are immiscible and leads to the formation of a hard-segment domain, a soft-segment matrix, and an ill-defined interphase. van Heumen and Stevens[8] reported that the phase-segregated morphology of the PEUU has been altered as a result of the interaction of lithium cations within the polar hard domains and by the promotion of phase intermixing by the coupling of the hard and soft phases. However, they did not report the environment of lithium ion doped in PEUU. The lithium cation environments need to be characterized as accurately as possible, particularly in the microseparated phases of PEUU electrolytes, since it is the source that supplies the high ionic conductivity. Therefore, the Li$^+$ local environment is the investigated topic. The repeat unit structure of a PEUU with PEG/H$_{12}$MDI/EDA is shown as Scheme 1 for Li$^+$ environment assignment. The hard segment content of the PEUU reported in this study is 47.5 wt %, estimated from the starting materials.

^{7}Li wide-line NMR and relaxation time measurements have been widely used to study the motions of Li ions and their interactions with polymer hosts since the strong receptivity of ^{7}Li makes it a very attractive nucleus to study. Unfortunately, the sensitivity is much reduced because of the small chemical shift range (ca. 6 ppm) and the low quadrupole moment of ^{7}Li. A good resolution of the ^{7}Li NMR spectrum to resolve Li$^+$ different environments has not been easily obtained. Therefore, ^{7}Li relaxation time measurements were commonly employed to differentiate different Li$^+$ species for probing lithium mobility.[9−11] In this study, ^{7}Li magic angle spinning (MAS) NMR spectra with high-power proton decoupling are presented first, providing high spectral resolution to demonstrate the presence of at least two distinct Li$^+$ sites in PEUU-based electrolytes.

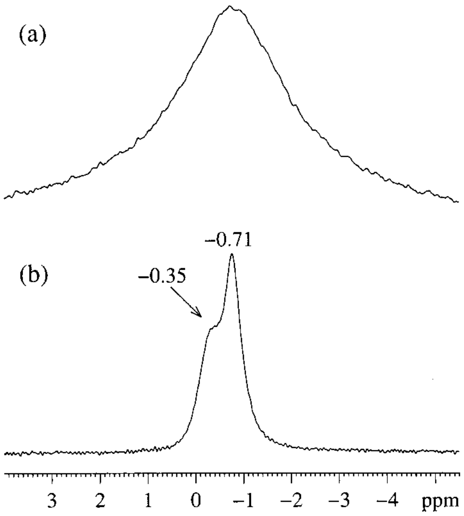


Figure 1. ^{7}Li MAS NMR spectra of PEUU samples doped with 0.5 mmol/g LiClO$_4$, (a) without and (b) with high-power proton decoupling, obtained at room temperature at a spinning speed of 3 kHz.

^{7}Li MAS NMR spectra were recorded with a Bruker AVANCE-400 NMR spectrometer, equipped with a 7 mm double-resonance probe, operating at 400.13 MHz for ^{1}H and 155.5 MHz for ^{7}Li. Typical NMR experimental conditions were as follows: $\pi/2$ duration, 3 μs; recycle delay, 2 s; ^{1}H decoupling power, 65 kHz; spinning speed, 3 kHz. Chemical shifts were externally referenced to solid LiCl at 0.0 ppm.

Parts a and b of Figure 1 show the ^{7}Li MAS NMR room-temperature spectra of a PEUU sample doped with 0.5 mmol/g LiClO$_4$, acquired without and with high-power proton decoupling, respectively.[12] The line widths decrease significantly as the proton decoupling was applied, and two distinct ^{7}Li sites can be resolved. This implies that there is a significant ^{7}Li−^{1}H dipolar interaction of lithium cations and polymer backbones. Previous results have also indicated that the ^{7}Li T_1 relaxation process in similar polymer hosts most probably involves an interaction of the lithium cation with the protons on the polymer backbone.[13,14] To our knowledge, there has been no literature to report the highly resolved ^{7}Li MAS NMR spectra showing two ^{7}Li local environments, as seen in Figure 1b.

By lowering the temperature, two distinct resonances become well resolved as shown in Figure 2. For instance, two signals at −0.33 ppm (site I) and −0.97 ppm (site II) with integrated intensities of approximately 0.55:0.45 are observed at 220 K. Spinning sidebands are also observed at low temperatures, indicating that ^{7}Li quadrupolar interaction is increased due to the decrease in lithium mobility with decreasing the

---

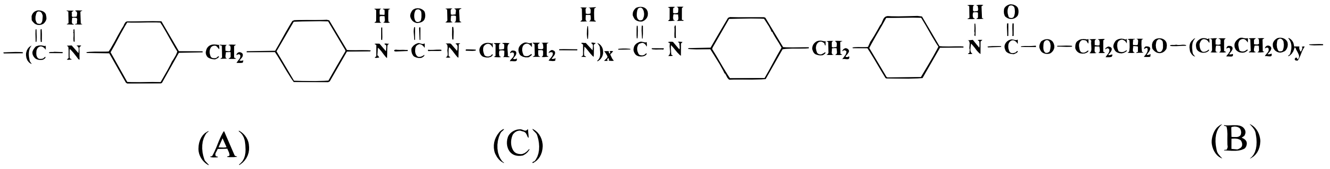
[†] National Cheng Kung University.

[‡] National Central University.

[*] Corresponding author: Phone +886-3-427-5054; Fax +886-3-422-7664; E-mail hmkao@cc.ncu.edu.tw.

10.1021/ma000963i CCC: $19.00

Scheme 1. Structure of the Repeat Unit of PEUU Used in This Study; (A) Denotes the Hard Segment, (B) Denotes the Soft Segment, and (C) Is the Chain Extender



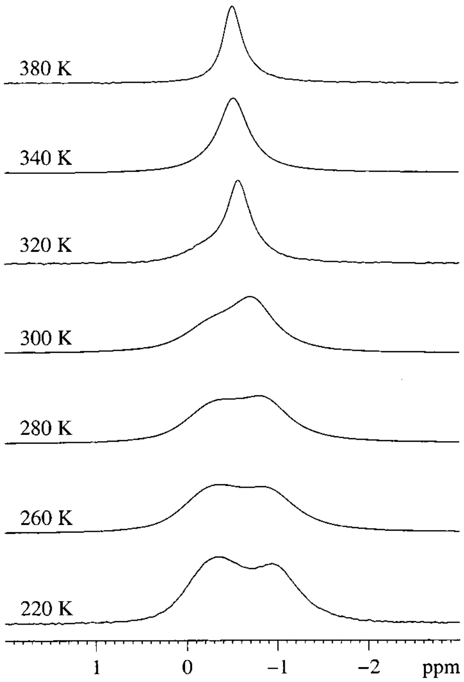


Figure 2. Variable-temperature ^{7}Li proton-decoupled MAS NMR spectra of a PEUU doped with 0.5 mmol/g $LiClO_4$.

temperature. On raising the temperature, on the other hand, two resonances begin to shift and eventually coalesce into a single resonance at the intermediate frequency. It is also noticed that a skewing of intensities of the peaks is observed in the variable temperature spectra, in contrast to the classical peak merging in a two-site exchange process, suggesting these two sites not only undergo a two-site exchange process, probably but also involve a temperature-dependent site preference.[15] Since two resonances are observed at low temperatures, the frequency of the jumps between the two sites must be greater than the separation of the two resonances, i.e., >100 Hz, for site I and site II to coalesce due to the increasing mobility of Li^+. The line shapes that are observed for the two-site exchange can be readily simulated, allowing correlation times for specific jump processes to be extracted. Thus, the correlation time, τ_c, for the jump process is 9.5×10^{-3} s at 220 K. At the temperature above 340 K, cation exchange is fast in comparison to the NMR time scale, resulting in a single resonance with a chemical shift that is a weighted average of the individual components. Since the exchange rate is in the fast-exchange regime at 380 K, a τ_c of 2.7×10^{-3} s can be readily obtained from the line width and the chemical shift difference between two sites.

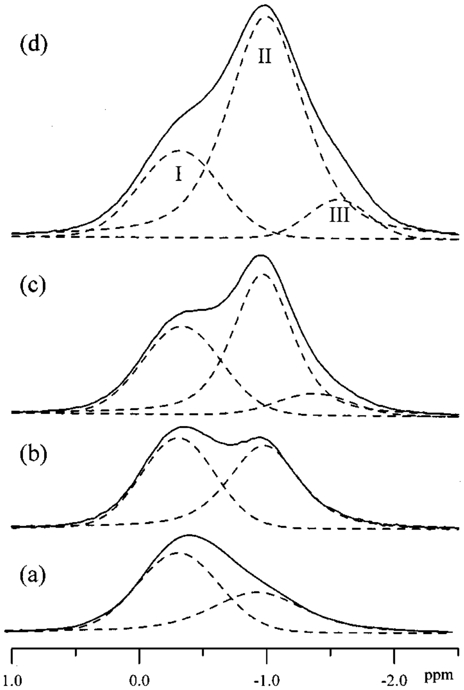


Figure 3. Deconvolution of ^{7}Li proton-decoupled MAS NMR spectra at 220 K for PEUU samples doped with (a) 0.1, (b) 0.5, (c) 1.0, and (d) 1.5 mmol/g $LiClO_4$.

Figure 3 shows the ^{7}Li NMR spectra as a function of salt concentration, recorded at 220 K. At the doping level of 0.1 mmol/g $LiClO_4$ (Figure 3a), the intensity of site I is significantly larger than that of site II, indicating that the Li^+ cation is preferentially coordinated to site I. The intensity of site II increases with increasing salt concentration, where the intensity of site I is normalized, as shown in Figure 3c and d, and a shoulder (site III) becomes visible at lower frequency. Since site III is only observed at high salt concentration and shows a concentration dependence of its chemical shift, site III is assigned to the ion pairs or aggregates.

Conductivity measurements have been performed, and the results show that all samples studied exhibit significant conductivity at 5 °C, except 0.1 mmol/g $LiClO_4$/PEUU sample with undetectable conductivity unless the temperature is above 65 °C. On the basis of the conductivity mainly resulting from the lithium in the soft segment for PEUU-based electrolytes, we conclude that site II is attributable to the Li^+ cations coordinated to ether oxygen atoms in the soft segment, while site I is associated with urethane groups in the hard segment. Furthermore, the deconvolution of low-temperature spectra shows a Gaussian line for site I and a mixture of Lorentzian/Gaussian (1/1) line for site II, suggesting that site II has more motional freedom in comparison to site I, which is also consistent with the above assignment. More recently, poly(dimethylsiloxane-*co*-methylphenylsiloxane)-*graft*-poly(ethylene glycol) doped with $LiClO_4$ has been synthesized and exhibits the same ^{7}Li chemical shift as that of site II.[16] This gives an additional support for the above assignment, since the lithium cation in the latter electrolyte can only be coordinated by PEG units.

In summary, we have demonstrated that the variable-temperature ^{7}Li MAS NMR with high-power proton decoupling provides an extremely effective and unique method for probing different local environments of lithium cations in PEUU-based electrolytes, which would allow the properties of each of the different lithium cation to be observed directly.

Acknowledgment. Dr. J. Schaefer is thanked for many helpful discussions. The financial support of this work by the National Science Council of Taiwan under NSC88-2622-E006-008, NSC89-2214-E006-012 (T.C.W.), and NSC892113-M-008-012 (H.M.K.) is gratefully acknowledged. The authors highly appreciated Ms. Ru-Rong Wu for her profound contribution in NMR experiments.

References and Notes

(1) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. In *Fast Ion Transport in Solids*; Vashista, P., Mundy, J. N., Shenoy, G. K., Eds.; Elsevier: New York, 1979.

(2) Fenton, D. E.; Parker, D. E.; Wright, P. V. *Polymer* **1973**, *14*, 589.

(3) *Proceedings of the Fifth International Symposium on Polymer Electrolytes*; Thomas, J. O., Ed.; *Electrochim. Acta* **1998**, *43*, 1387.

(4) Gray, F. M. *Solid Polymer Electrolytes*; VCH Publishers Inc.: New York, 1991.

(5) MacCallum, J. R., Vincent, C. A., Eds.; *Polymer Electrolyte Reviews*; Elsevier Applied Science: London, 1989; Vol. 2.

(6) Gibson, P. E.; Vallance, M. A.; Cooper, S. L. *Developments in Block Copolymers*; Applied Science Series; Elsevier: London, 1982.

(7) Van Bogart, J. V.; Gibson, P. E.; Cooper, S. L. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 65.

(8) van Heumen, J. D.; Stevens, J. R. *Macromolecules* **1995**, *28*, 4268.

(9) Chung, S. H.; Jeffrey, K. R.; Stevens, J. R. *J. Chem. Phys.* **1991**, *94*, 1803.

(10) Ng, S. T. C.; Forsyth, M.; MacFarlane, D. R.; Garcia, M.; Smith, M. E.; Strange, J. H. *Polymer* **1998**, *25*, 6261.

(11) Forsyth, M.; Garcia, M.; MacFarlane, D. R.; Meakin, P.; Smith, M. E.; Ng, S. *Solid State Ionics* **1996**, *85*, 209.

(12) The PEUU prepolymer was prepared by the reaction of poly(ethylene glycol) (PEG; Showa) with methylene bis(*p*-cyclohexyl isocyanate) (H_{12}MDI; Aldrich) by using di-*n*-butyltin(IV) dilaurate (DBTDL, catalyst) as a catalyst. After 6 h of reaction, dimethylformamide (DMF; Tedia) was added and then the chain extender, ethylenediamine (EDA; Merck), to convert the prepolymer into polymer. The PEUU solution was mixed well with 10 mass % solution of lithium perchlorate ($LiClO_4$, Aldrich) dissolved in DMF to form various ratios.

(13) (a) Forsyth, M.; MacFarlane, D. R.; Meakin, P.; Smith, M. E.; Bastow, T. J. *Electrochim. Acta* **1995**, *40*, 2343. (b) Ali, F.; Forsyth, M.; Garcia, M.; Smith, M. E.; Strange, J. H. *Solid State Nucl. Magn. Reson.* **1995**, *5*, 217.

(14) Forsyth, M.; Meakin, P.; MacFarlane, D. R.; Bulmer, G.; Reid, M. *J. Mater. Chem.* **1994**, *4*, 1149.

(15) Abragam, A. *The Principle of Nuclear Magnetism*; Oxford University Press: Oxford, 1961.

(16) Kuo, P.-L., private communication.

MA000963I