Ionic Conductivity and NMR Self-Diffusion in Poly(macromonomer)s of Vinylbenzyl Poly(ethylene oxide)s

Yasuhisa Tsukahara,* Kazuhiko Hashimoto, Kyoji Kaeriyama, Arei Niwa,† Mary Anne Mehta,† Tatsuo Fujinami,†
and Kikuko Hayamizu††
Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Kyoto 606-8585
† *Department of Materials Science, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu 432-8561*
†† *National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565*

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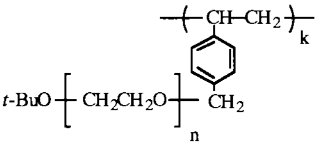
Ionic conductivity and NMR self-diffusion in the complex of poly(macromonomer)s of VB–PEO doped with the lithium salt $Li(CF_3SO_2)_2N$ were investigated. Ionic conductivity was enhanced by the multibranched structure of the poly(macromonomer). The NMR spin–lattice relaxation times showed that the hopping motion of the Li ions were correlated with PEO chain motion. NMR self-diffusion data showed evidence of the multisite diffusion of anions in the complex at near room temperature.

Complexes of polyethylene oxide (PEO) with salts such as $LiCF_3SO_3$ have been extensively studied as solid polymer electrolytes for solid-state rechargeable batteries. Ionic conductivity in the polymer/salt system depends on polymer structural characteristics such as molecular weight, branching structure, and network formation.[1] On the other hand, chain polymerization of vinyl-terminated macromonomers easily produces multibranched polymers of extremely high branch density.[2,3] Such poly(macromonomer)s show very unique properties associated with the multibranched architecture. In this paper, we measured the ionic conductivity and NMR self-diffusion of lithium, and anion in the poly(macromonomer) of vinylbenzyl-terminated PEO (VB–PEO) doped with lithium salt $Li(CF_3SO_2)_2N$ to investigate the effect of the multibranched architecture on the ionic conductivity, the diffusion of ions and the segmental motion of the base polymers.

The poly(macromonomer)s, PMs, used in this study have the chemical structure shown below and were prepared by free radical polymerization of vinylbenzyl-terminated poly(ethylene oxide) (VB–PEO) macromonomers.

Poly(VB-PEO) :



The number-average molecular weights, M_n, of the VB–PEOs were 3100 (n = 66) and 5100 (n = 112), which were prepared by the living anionic polymerization of ethylene oxide (EO) with potassium *t*-butoxide, followed by termination with vinylbenzyl chloride.[4,5] The weight-average molecular weight, M_w, and the number of branches, k, determined by a GPC (Tosoh HLC 802A) equipped with a low angle light scattering detector (LS-8)[3] were 217×10^3 and 41 for poly(VB–PEO5100), and 649×10^3 and 209 for poly(VB–PEO3100), respectively.

All manipulations of the electrolytes were carried out on a dry nitrogen/vacuum line or in an argon-filled glove box. The polymer samples were dried at 40 °C under vacuum for 1 day before being transferred to the glove box. All solvents and the lithium salt $Li(CF_3SO_2)_2N$ were dried rigorously before use. Polymer electrolytes based on the PMs with an EO:Li^+ ratio of 16:1 were prepared by hot pressing as reported previously.[6] Ionic conductivity was determined by ac impedance measurement in the frequency range 1 MHz–10 mHz using a Solarton 1260 frequency response analyzer and 1287 electrochemical interface. The thermal characteristics of the host polymers and the polymer electrolytes were determined by DSC measurements (heat-cool-reheat cycles at 10 °C/min). Thermal transitions were recorded for the second heating cycle.

The ^1H, ^7Li, and ^{19}F NMR measurements were made using a JEOL GSH-200 spectrometer with a 4.7 T wide bore magnet for the temperature range between 303 and 353 K. The self-diffusion coefficients of the anion were measured by the simple Hahn spin-echo based sequence incorporating a gradient pulse in each τ period. The attenuation E for ordinary isotropic diffusion is given by eq (1):

$$E = \exp[-\gamma^2 g^2 \delta^2 D(\Delta - \delta/3)] \qquad (1)$$

where D is the diffusion coefficient, γ is the gyromagnetic ratio, g is the amplitude of the gradient pulses of duration δ, and Δ is the separation between the gradient pulses. Δ defines the time-scale over which the diffusion is measured.

Host PMs exhibited melting endotherms which were ascribed to the melting of crystalline PEO regions. Incorporation of salt into the polymer gave predominantly amorphous electrolytes. The reduced crystallinity was ascribed to the plasticizing nature of $Li(CF_3SO_2)_2N$, which has been reported previously.[7] A significant melting endotherm was however observed for poly(VB–PEO5100) due to the increased length of the EO component in the electrolyte, whereas the endotherm observed for poly(VB–PEO3100) was very small.

The Arrhenius plots of the ionic conductivity, σ, of the electrolytes are shown in Figure 1. The data for linear PEO were obtained under the same conditions and are included for comaprison. Both of the multibranched polymer electrolytes exhibited relatively high ionic conductivity at room temperature. The DSC data are in agreement with the conductivity data. The poly(VB–PEO5100) based electrolyte exhibits a small discontinuity in the Arrhenius plots characteristic of semicrystalline systems. In order to confirm the mechanism of ion conduction, the ionic conductivity data were fitted to the VTF eq (2):

$$\sigma = AT^{-1/2} \exp[-B/(T-T_0)] \qquad (2)$$

where A is a constant related to the number of charge carriers in the electrolyte, B is a constant related to the activation energy for ion transport, and T_0 is a constant usually found to be about

50 K below the glass transition temperature. All of the data in the $\ln(\sigma T^{1/2})$ versus $1/(T - T_0)$ plots were well described by a straight line and can be said to obey the VTF equation. Thus, as expected, the conductivity mechanism in the polymer electrolytes can be ascribed to ion motion promoted by the segmental motion of the oligoethylene oxide branch chains.

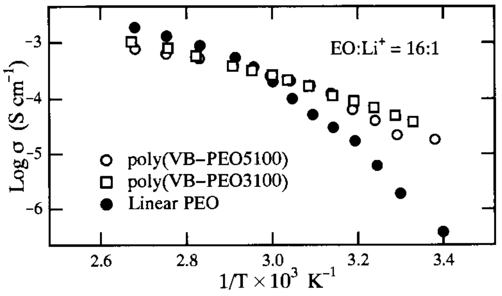


Figure 1. Arrhenius plots of σ for the electrolytes.

The spin–lattice relaxation (T_1) of all the resonances (i.e., ^1H, ^7Li, and ^{19}F) for poly(VB–PEO5100) was well described by single-exponentials, indicating that the fast motions can be described by a single component for each case. The temperature dependencies of the T_1 of the polymer and lithium exhibited minima in the observed temperature range as shown in Figure 2. Similar phenomena have been reported by us for polymer electrolytes composed of PEO and PPO and enabled reorientational correlation times to be obtained for the segmental motion of the $-CH_2CH_2O-$ moiety in the polymer chains and the correlated hopping motions of the Li ions.[8,9] Since the anion relaxation was probed by the ^{19}F NMR relaxation of the CF_3 group, a major part of the relaxation should result from the spin-rotation interaction.

The anion diffusion coefficient of poly(VB–PEO5100) was estimated by the pulse-gradient spin echo (PGSE) method according to eq (1). When the temperatures were higher than 323 K, the attenuation of the echo signals for the anion diffusion was plotted as straight lines according to eq (1) for various Δ. If the anion diffusion was homogeneous, the diffusion coefficients obtained at different Δ should give the same value. However, when Δ became shorter, the self-diffusion coefficient D became larger in this study, which indicates that the anions diffuse quicker in the shorter range. This observation is similar to our previous results for electrolytes composed of the cross-linked poly(ethylene oxide)-based polymers, where the plots gave straight lines with different slopes.[8,9] Moreover, the diffusion plots showed curvature for shorter Δ as shown in Figure 3 for 303 K. When the diffusion plots are straight lines, the apparent self-diffusion coefficients can be assumed to be a single component or the fast exchange of multi components. Since the diffusion plots are concave, multicomponents with slower exchange rates than the NMR time scale can be assumed in these ranges. The anion diffusion coefficients determined are between 2×10^{-12} and 13×10^{-12} m^{2}s^{-1} at temperatures between 313 and 353 K when Δ equals 70 ms. Thus, anions provide the main contribution to the ionic conductivity as described in our previous papers.[8,9] The Arrhenius plot of the diffusion coefficients at D = 70 ms gave an activation energy E_a of 43.0 ± 0.8 kJ/mol.

Measurements of Li$^+$ diffusion were attempted but typical plots similar to Figure 3 were not obtained, probably due to the much slower and non-isotropic diffusion. We found evidence that some lithium ions diffuse with a self-diffusion coefficient of about 1×10^{-12} m^{2}s^{-1} above 343 K. From the T_1 data of lithium ions in a similar temperature range, the rate of the hopping motions is in the order of 10^{-9} s. Although the short distance flipping motions of the Li$^+$ are very fast, the diffusion over longer distances is reduced. This latter effect will reduce the Li$^+$ contribution to ionic conductivity.

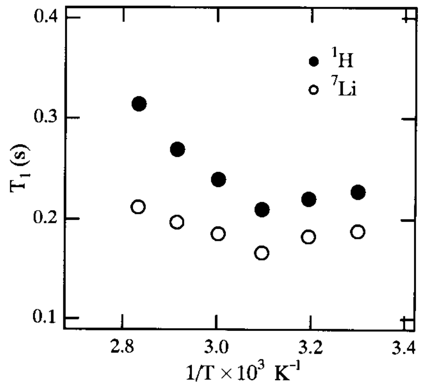


Figure 2. Temperature dependences of T_1 for ^{7}Li and ^{1}H.

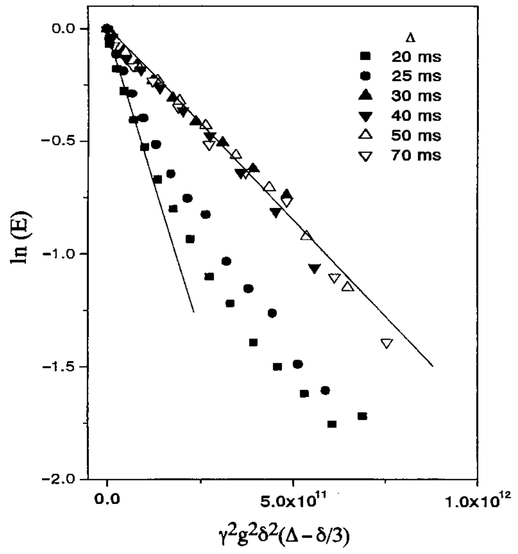


Figure 3. PGSE signal attenuation for anions at 303 K plotted against $\gamma^2 g^2 \delta^2(\Delta - \delta/3)$. The base polymer was poly(VB–PEO5100).

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