constants related to the temperature dependence of the interaction parameter χ between the two polymers

$$\chi = A + B/RT \qquad (8)$$

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Registry No. PS (homopolymer), 9003-53-6; PVME (homopolymer), 9003-09-2.

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Correlation between Ionic Conductivity and the Dynamic Mechanical Property of Polymer Complexes Formed by a Segmented Polyether Poly(urethane urea) and Lithium Perchlorate

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ABSTRACT: Ionic conductivity and the dynamic mechanical property were investigated in the polymer complexes formed by a segmented polyether poly(urethane urea) (PEUU), based on poly(propylene oxide) (PPO), and lithium perchlorate ($LiClO_4$). The PEUU formed a two-phase structure, consisting of the PPO and poly(urethane urea) phases, and $LiClO_4$ was selectively dissolved in the PPO phase. The frequency–temperature superposition for the storage elastic modulus was carried out in the temperature range for the backbone relaxation of the PPO segment, using the glass transition temperature (T_g) as a reference temperature. The ratios of the ionic conductivity at various temperatures (T) to that at T_g plotted againt $T - T_g$ were compared with the shift factors for the mechanical relaxation. The direct relationship between the ionic mobility and the local segmental motion of the PPO segment and the Arrhenius activation process for carrier generation were deduced from this comparison. A higher activation energy for the carrier generation was implied in the polymer complex containing $LiClO_4$ at a higher concentration.

Introduction

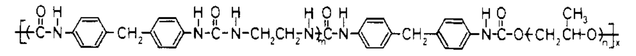
The studies on the ion-conducting behavior in certain kinds of ion-containing polymers are of considerable interest because these ion-containing polymers show relatively high ionic conductivity and are expected to be applicable to solid electrolytes in electrochemical devices.[1–10] Polyethers, such as poly(ethylene oxide)[1–5] and poly(propylene oxide) (PPO),[2,4–7] and polyesters, such as poly(β-propiolactone)[8] and poly(ethylene succinate),[9,10] have been selected as host polymers to alkali metal salts, and their ionic conductivity has been investigated. Glass transition temperatures (T_g) of these polymers lie below room temperature, and the conductivity data have been collected in their rubbery states. Therefore, it has been pointed out by several authors that transport of carrier ions correlates with the local segmental motion of these host polymers and obeys the free volume model[4,5,7] proposed by Cohen and Turnbull[11] or the configurational entropy model[12] proposed by Adam and Gibbs.[13] However, since conductivity is influenced not only by the carrier transport process but also by the carrier generation process, it is very difficult to analyze the conductivity data quantitatively, and only a few studies including the investigation of both carrier transport and generation processes have been carried out.[4,5,7]

We succeeded in a direct measurement of ionic mobility by the isothermal transient ionic current method,[7,14] which enabled the resolution of the conductivity into the ionic mobility and the number of carrier ions. The temperature dependence of the ionic mobility obeyed the free volume mechanism, whereas that of the number of carrier ions obeyed the Arrhenius activation mechanism. The quantitative equation that explains the temperature dependence of ionic conductivity in the rubbery state was, thus, derived from these results.[7] From the standpoint of the equation one can suppose the direct relationship between the ionic conductivity and the local segmental motion of the host polymers when the number of carrier ions is temperature-independent, in other words, when the incorporated salts dissociate completely.

Killis and Cheradame et al.[4,5,15] investigated the relationship between the dynamic mechanical property and ionic conductivity of the polyether networks containing sodium tetraphenylborate and showed that the ratios of the ionic conductivity at various temperatures to that at T_g directly correlated with the shift factors of the viscoelastic relaxation times. Furthermore, they showed[16] that the log–log plots of conductivity vs. salt concentration at constant reduced temperatures ($T - T_g$) were linear with slopes close to unity in the salt-containing poly(ethylene oxide) networks. They interpreted these results by assuming the complete dissociation of the incorporated salt.

In an earlier article,[17] we investigated the morphology and ionic conductivity of polymer complexes formed by segmented polyether poly(urethane urea) (PEUU), based on PPO, and lithium perchlorate ($LiClO_4$). PEUU formed

Scheme I
Structure of Segmented Polyether Poly(urethane urea) Based on Poly(propylene oxide)



P E U U

a two-phase structure consisting of the continuous PPO phase and the isolated poly(urethane urea) phase. $LiClO_4$ was selectively dissolved in the polyether phase. The conductivity vs. $LiClO_4$ concentration curves could not be interpreted without taking both terms of the ionic mobility and the number of carrier ions into consideration.

The purpose of this study is to investigate the correlation between ionic conductivity and the dynamic mechanical property of the polymer complexes formed by PEUU and $LiClO_4$. The ratios of the ionic conductivity at various temperatures to that at T_g were compared with the shift factors of the mechanical relaxation times of the PPO segment. The direct relationship between the ionic mobility and the segmental motion and the Arrhenius activation process for carrier generation were deduced from this comparison.

Experimental Section

PEUU with the chemical structure shown in Scheme I was synthesized from 4,4′-methylenebis(phenylene isocyanate) (MDI), ethylenediamine (ED), and PPO (number-average MW = 2800). The ratio of MDI/ED/PPO was kept at 4/3/1, which resulted in the hard-segment content of 29 wt %. The solution viscosity of the resulting PEUU in *N,N*-dimethylformamide at 0.1 g/10 cm^3 was 0.69 dL/g at 30 °C. Precise conditions for the synthesis were described elsewhere.[17] Films for various measurements were prepared by casting a *N,N*-dimethylacetamide solution of PEUU onto glass substrates, followed by evaporating the solvent completely. An immersing method was used for dissolution of $LiClO_4$ in the films. A preweighed PEUU film was immersed in an acetone solution of $LiClO_4$ and was dried under reduced pressure completely. In order to ensure a uniform dissolution of $LiClO_4$ through the film thickness, the immersion was continued till the weight change of the dried film before and after the immersion reached a constant level. The concentrations of $LiClO_4$ in the PEUU films were determined from weight changes of the films before and after the immersion. Since it was clarified that $LiClO_4$ was selectively dissolved in the PPO phase,[17] the concentration was expressed by the molar ratio of $LiClO_4$ to the repeating unit of PPO ($[LiClO_4]/[PO\ unit]$).

Dynamic mechanical measurements were made with a Toyo Rheovibron DDV-II at 3.5, 11, 35, and 110 Hz at a heating rate of 2 °C/min. Ionic conductivity was measured by the complex impedance method. A cell made of a disklike film sandwiched between platinum electrodes was used for the impedance measurements. The bulk resistance of the sample was estimated from the corresponding component of an equivalent circuit required to account for the impedance spectrum, as shown in an earlier article.[17]

Results and Discussion

Dynamic Mechanical Property. Figures 1 and 2 show the storage elastic modulus (E') and the dissipation factor (tan δ) plotted against temperature at various frequencies for the $PEUU\cdot LiClO_4$ complexes with the $LiClO_4$ concentration $[LiClO_4]/[PO\ unit]$ = 0.062 and 0.040, respectively. The tan δ peaks around −100 °C might correspond to the local mode motion of the PO unit. The main relaxations in E' and the main peaks in tan δ correspond to the backbone motion of the PPO segment. Thus, the tan δ peak temperatures correlate with T_g of the PPO segment. The T_g increased with increasing $LiClO_4$ concentration[17] and was somewhat higher in the $PEUU\cdot LiClO_4$ complex with $[LiClO_4]/[PO\ unit]$ = 0.062 in the present system. The salt concentration effect on the increase in T_g is attributed to a strong interaction between Li^+ ions and polarizable ether oxygens. The effect of the interaction on the viscoelastic properties of some polyether–salt systems has already been reported.[5,18,19] Because of the cross-linking and hard-filler effects of the poly(urethane urea) domains, the E' above the relaxations showed rubbery plateau levels. In the temperature ranges around these main relaxations, the other relaxation processes were not observed. Open circles in Figures 3 and 4 show the frequency dependence of the E' values at various temperatures in the backbone relaxation regions for the $PEUU\cdot LiClO_4$ complexes of $[LiClO_4]/[PO\ unit]$ = 0.062 and 0.040, respectively. We tried to carry out frequency–temperature superposition for the E' values by using the tan δ peak temperatures at 11 Hz as reference temperatures. Closed circles in Figures 3 and 4 show the master curves of this superposition. The superposition seemed to be successful in these two kinds of $PEUU\cdot LiClO_4$ complexes. The distribution of the relaxation times was wider in the $PEUU\cdot LiClO_4$ complex with $[LiClO_4]/[PO\ unit]$ = 0.040. The increase in T_g of the PPO segment with increasing $LiClO_4$ concentration is considered to be caused by the composition change in the random copolymer consisting

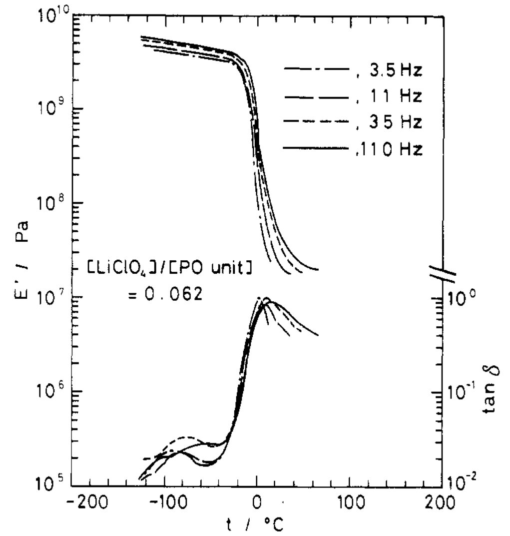


Figure 1. Storage elastic modulus and dissipation factor plotted against temperature at various frequencies for the $PEUU\cdot LiClO_4$ complex with $[LiClO_4]/[PO\ unit]$ = 0.062.

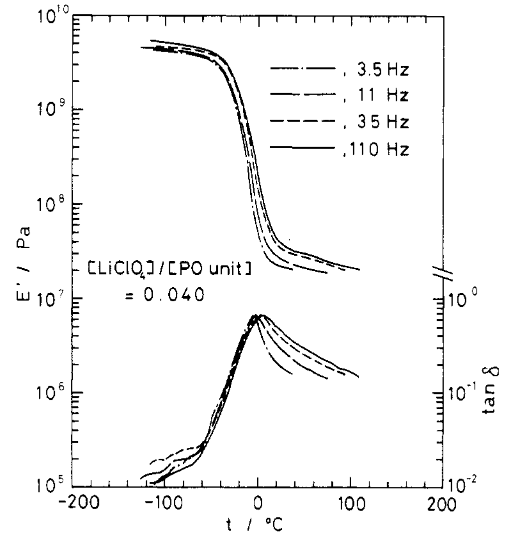


Figure 2. Storage elastic modulus and dissipation factor plotted against temperature at various frequencies for the $PEUU\cdot LiClO_4$ complex with $[LiClO_4]/[PO\ unit]$ = 0.040.

Table I
WLF Parameters of Mechanical Relaxation and Ionic Conductivity

		mechanical relaxation		ionic conductivity		
$[LiClO_4]/[PO\ unit]$	T_g/°C[a]	C_1	C_2/°C	C_1'	C_2'/°C	$\sigma(T_g)$/S cm^{-1}
0.062	7.5	4.59	45.7	10.6	91.9	7.60×10^{-12}
0.040	−0.5	4.31	43.0	8.54	104	1.15×10^{-10}

[a] Peak temperatures of tan δ at 11 Hz.

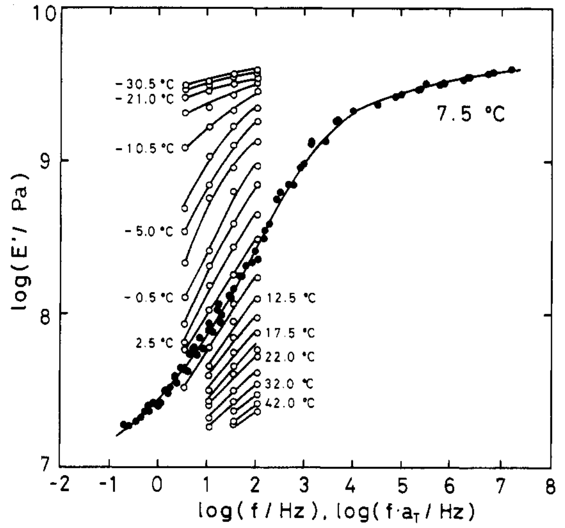


Figure 3. Frequency dependence of the elastic modulus at various temperatures and their master curve for the PEUU·LiClO$_4$ complex with [LiClO$_4$]/[PO unit] = 0.062.

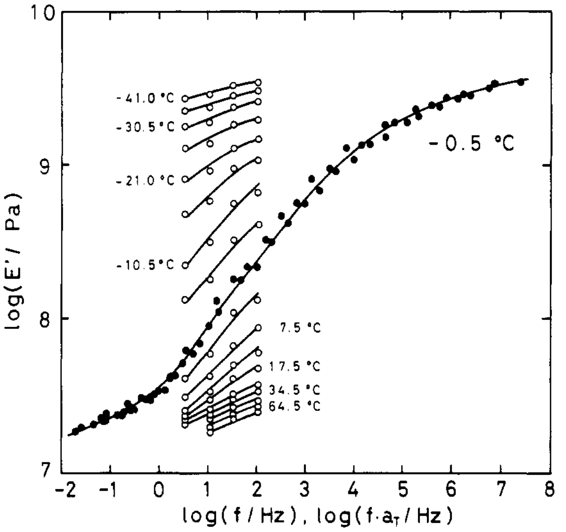


Figure 4. Frequency dependence of the elastic modulus at various temperatures and their master curve for the PEUU·LiClO$_4$ complex with [LiClO$_4$]/[PO unit] = 0.040.

of the free PO units and the complexed PO units with LiClO$_4$.[17] The complexed PO unit has a higher T_g than that of the free PO unit. The copolymer composition also influences the distribution of the relaxation times as a superposition of two relaxation spectra. This may be a reason for the difference in the distribution of the relaxation times. Similar interpretation for breadth of the damping curves has been proposed by Moacanin et al. for the PPO–LiClO$_4$ system.[18]

Comparison between Shift Factor and Ionic Conductivity. Figure 5 shows the temperature dependence of the shift factor (a_T) for the mechanical relaxation and the ionic conductivity. Both dependences did not show Arrhenius behavior but show WLF-type behavior. The temperature dependences of the shift factor and the ionic conductivity were, thus, expressed experimentally by the following equations:[20]

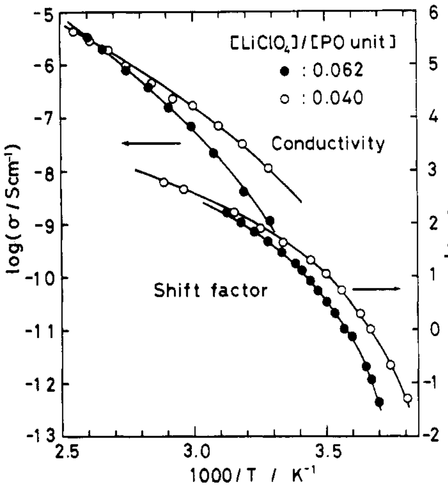


Figure 5. Temperature dependences of ionic conductivity and shift factor.

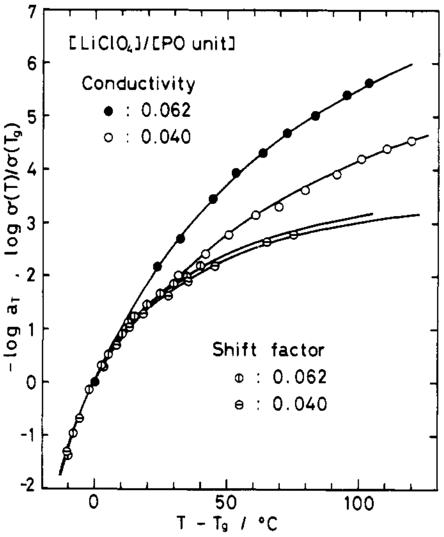


Figure 6. Correlation between $-\log a_T$ or $\log[\sigma(T)/\sigma(T_g)]$ and $T - T_g$.

$$\log a_T = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \tag{1}$$

$$\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1'(T - T_g)}{C_2' + (T - T_g)} \tag{2}$$

The tan δ peak temperatures at 11 Hz were used as T_g's in eq 1 and 2. The WLF parameters for the ionic conductivity were calculated so as to linearize the correlation between $1/[\log(\sigma(T)/\sigma(T_g))]$ and $1/[T - T_g]$, since the $\sigma(T_g)$ values could not be measured by the complex impedance method. Table I shows the WLF parameters obtained. Figure 6 shows the $-\log a_T$ and $\log[\sigma(T)/\sigma(T_g)]$ values plotted against $T - T_g$. Solid lines in the figure are calculated curves from eq 1 and 2 by using the WLF pa-

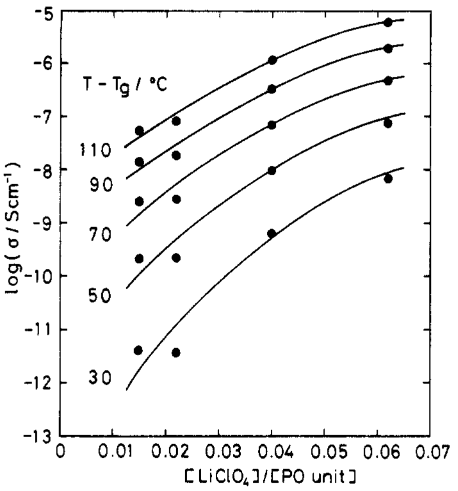


Figure 7. Ionic conductivity of PEUU·LiClO$_4$ complexes plotted against LiClO$_4$ concentration at various reduced temperatures ($T - T_g$).

rameters shown in Table I. Fitting of the curves to the experimentally obtained values was fairly good. The change in $\log[\sigma(T)/\sigma(T_g)]$ with $T - T_g$ increased with increasing the LiClO$_4$ concentration, whereas the change in $-\log a_T$ was not so large. When the comparison is made between $-\log a_T$ and $\log[\sigma(T)/\sigma(T_g)]$ at the same LiClO$_4$ concentration, the changes in the latter with $T - T_g$ were larger than those in the former.

The temperature dependence of the ionic conductivity was assumed to be expressed by the following equation:[7]

$$\sigma = \frac{e^2 N_0 D_0}{kT} \exp\left[-\left(\frac{U/2\epsilon}{kT} + \frac{\gamma V_i^*}{V_f}\right)\right] \qquad (3)$$

where e is the elementary electric charge, N_0 and D_0 are constants, k is the Boltzmann constant, U is the lattice energy of the salt (LiClO$_4$), ϵ is the dielectric constant of the polymer complex, γ is a numerical factor, V_i^* is the minimum hole size allowing the ionic migration, and V_f is the free volume. This equation was derived experimentally from the temperature dependences of the ionic conductivity and ionic mobility.[7] A similar form to this equation has already been proposed by Miyamoto and Shibayama[21] in order to interpret the temperature dependence of the conductivity of some kinds of commerical insulating polymers both above and below their T_g's. Furthermore, Cheradame has applied this type of equation to the conductivity data of the polyether networks containing sodium tetraphenylborate.[5] In eq 3, the first and second terms in the exponential are concerned with the Arrhenius process for the carrier generation and the free volume process for the carrier migration, respectively. If the temperature dependence of the ionic conductivity is assumed to be dominated only by the second term in the exponential of eq 3, that is, to obey completely the free volume theory, eq 2 can be derived mathematically from eq 3. On this assumption, we have to consider that the number of carrier ions is temperature-independent. In this case the incorporated LiClO$_4$ may completely dissociate. A constant reduced temperature $T - T_g$ is generally known to be the iso-free-volume state in the free volume theory. Thus, the ionic mobility should be nearly constant at a given $T - T_g$, and the ionic conductivity should increase with an increase in the number of carrier ions (dissociated ions). However, if the conductivity values of the PEUU·LiClO$_4$ complexes[17] are plotted against the LiClO$_4$ concentration at various reduced temperatures, the increase in the conductivity was larger than that expected by the complete dissociation of LiClO$_4$, as shown in Figure 7. A similar observation has also been reported for the PPO-based networks containing sodium tetraphenylborate.[4] We considered that this was due to the change in the number of carrier ions with temperature and was due to the fact that the first term in the exponential of eq 3 could not be negligible. Thus, the good fitting of the conductivity data to eq 2 does not necessarily mean that the first term is negligible.

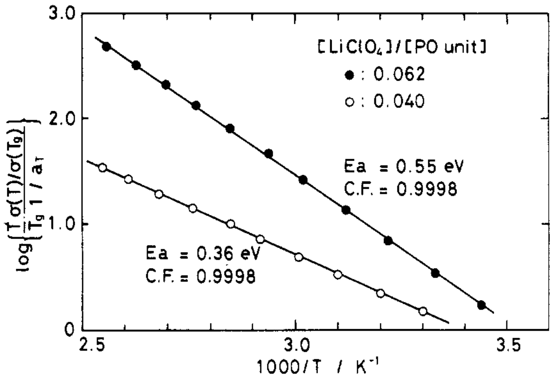


Figure 8. Arrhenius plots of the left term of eq 6.

From this point of view, the difference in the changes in $-\log a_T$ and $\log[\sigma(T)/\sigma(T_g)]$ with $T - T_g$ (Figure 6) may be caused by the carrier generation process, because the ionic transport process seems to closely correlate with the backbone motion of the PPO segment. With on this idea, we analyzed the conductivity and mechanical data. The temperature dependence of the mechanical relaxation time (τ) can be expressed by the following equation, if one applies the free volume mechanism to the backbone motion:

$$\tau^{-1} = \tau_0^{-1} \exp\left(-\frac{\gamma V_s^*}{V_f}\right) \qquad (4)$$

where V_s^* is the minimum hole size allowing the motion of the elementary unit involved in the mechanical relaxation process. The ratio of $\sigma(T)/\sigma(T_g)$ to $1/a_T$ [= $\tau(T)^{-1}/\tau(T_g)^{-1}$] is derived from eq 3 and 4 as follows:

$$\frac{\sigma(T)/\sigma(T_g)}{1/a_T} = \frac{T_g}{T} \exp\left[\frac{U/2\epsilon}{kT_g} + \frac{\gamma(V_i^* - V_s^*)}{V_{fg}}\right] \exp\left[-\frac{U/2\epsilon}{kT} - \frac{\gamma(V_i^* - V_s^*)}{V_f}\right] \qquad (5)$$

where V_{fg} is the free volume at T_g. If we assume that the temperature dependence of V_i^* and V_s^* is negligible, the first exponential term is considered constant. Thus, eq 6 is derived from eq 5, where A is a constant. Figure 8

$$\frac{T}{T_g} \frac{\sigma(T)/\sigma(T_g)}{1/a_T} = A \exp\left[-\frac{U/2\epsilon}{kT} - \frac{\gamma(V_i^* - V_s^*)}{V_f}\right] \qquad (6)$$

shows the Arrhenius plots of the left term of eq 6. Since the temperature dependences of $\log[\sigma(T)/\sigma(T_g)]$ and $\log a_T$ were expressed by eq 1 and 2 and the parameters shown in Table I, the left term of eq 6 was numerically calculated by using these equations and parameters. As can be seen from Figure 8, the dependences were expressed by linear lines with correlation factors (CF) close to unity. If the second term in the exponential of eq 6 is appreciable, the Arrhenius plots of Figure 8 may not result in linear lines. Thus, this result implies that the following equation holds in the PEUU·LiClO$_4$ complexes:

$$V_i^* \simeq V_s^* \qquad (7)$$

The carrier migration closely correlates with the segmental motion of the PPO backbone. Substituting eq 7 to eq 6, one obtains

$$\frac{T}{T_g}\,\frac{\sigma(T)/\sigma(T_g)}{1/a_T} = A'\exp\left(-\frac{U/2\epsilon}{kT}\right) \qquad (8)$$

where A' is a constant. The activation energies (E_a) for the dependences of Figure 8 were calculated from the slopes of the linear lines, as shown in the figure. The E_a values were compared with the calculated $U/2\epsilon$ values. In the strict sense, the term U should be the effective dissociation energy of the ion pair (U') in the ionic atmosphere. However, the assumption that $U \simeq U'$ greatly simplifies the analysis. The U of $LiClO_4$ calculated from Kapunstinskii's equation[22] was 7.43 eV. The ϵ values, which could be estimated from the complex impedance measurements, were 7–12. Thus, we could calculate that the $U/2\epsilon$ values were roughly 0.3–0.5 eV. The calculated $U/2\epsilon$ values approximately corresponded to the experimentally obtained E_a values. This might imply that the E_a values shown in Figure 7 are the activation energy for carrier generation. $LiClO_4$ incorporated in PEUU does not completely dissociate, and the carrier generation in the PEUU·$LiClO_4$ complexes obeys the Arrhenius activation process. However, the calculated $U/2\epsilon$ values did not clearly increase with $LiClO_4$ concentration. Thus, it is still not clear that the activation energy for carrier generation is expressed simply by the term $U/2\epsilon$. A higher activation energy for the PEUU·$LiClO_4$ complex with $[LiClO_4]/[\text{PO unit}] = 0.062$ may be caused by a stronger ion–ion interaction energy for the carrier generation.

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Sedimentation Behavior of Block and Random Copolymers in the Semidilute Regime

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ABSTRACT: Sedimentation velocity measurements have been carried out on 1,2-dibromoethane semidilute solutions of styrene–isoprene diblock and random copolymers of various molecular weights in the range $2 \times 10^5 < M_w < 1 \times 10^6$, all having a styrene content of about 50% by weight. The concentration dependence of the sedimentation coefficient s has been examined for both the copolymers and the corresponding homopolymers over the concentration range $0.015 < c < 0.07$ g/cm^3, for which the data were molecular weight independent. The results show that s decreases as $c^{-0.79\pm0.01}$ for both the copolymers and the homopolymers. Though 1,2-dibromoethane is a solvent with moderate affinity for homo-PS and homo-PI, the present behavior is very similar to that observed previously for flexible homopolymers in good solvent conditions. The sedimentation data were analyzed in terms of the permeability coefficient defined by Mijnlieff and Jaspers and the screening effect described by Brochard and de Gennes. The results show that the permeability data for the block polymers are superimposable on the data for homo-PS and homo-PI, the latter being fortuitously identical. They also show that permeability of random copolymers is less than that of block polymers because of the larger number of repulsive heterocontacts inherent in their random structure.

Introduction

The sedimentation behavior of flexible polymer chains in the semidilute regime, that is, above the critical concentration c^* at which chains begin to overlap, has received much attention in recent years.[1-8] At $c > c^*$ the sedimentation process is no longer governed by the hydrodynamic properties of the individual chains as evidenced by the independence of the sedimentation coefficient, s, on molecular weight. The flexible chains form a transient network, and it is the permeability of this network to solvent that governs the sedimentation velocity at a given concentration. Mijnlieff and Jaspers[1] were the first to