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(24) However, Krause et al.[23] found that ΔT_g was generally larger in the microphase of block copolymers than in a corresponding homopolymer.

Ionic Conductivity of Polyether–Polyurethane Networks Containing Alkali Metal Salts. An Analysis of the Concentration Effect

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ABSTRACT: The ionic conductivity of poly(oxyethylene)–polyurethane networks containing either sodium tetraphenylborate or lithium perchlorate was studied as a function of the salt concentration at constant reduced temperature $T - T_g$. Two different types of networks, based on poly(oxyethylene) of molecular weight 400 and 1000, respectively, were investigated. The log–log plots of the conductivity vs. the salt concentration at constant reduced temperature were linear with slopes close to unity. These results are explained by assuming complete dissociation of the salt under most conditions studied.

The increasing interest in ion-containing polymers is directly related to their properties. Polyether–alkali metal salt systems have been thoroughly studied in view of their potential applications as solid electrolytes in electrochemical solid-state primary or secondary generators. Wright first reported high ionic conductivity for mixtures of poly(oxyethylene) and alkali metal salts.[1] Armand et al. have extensively investigated their electrical properties and their behavior as solid electrolytes.[2] Our interest in this field has focused on polyether–polyurethane *networks* containing sodium or lithium salts. In previous papers we demonstrated the important role played by the glass transition temperature on their ionic conductivity[3] as well as on their viscoelastic properties.[4,5] The overall effect of an increase in the salt concentration on the viscoelastic properties of these networks (with $NaBPh_4$) is to increase the glass transition temperature,[4] as expected on the basis of free volume considerations. Indeed, at constant reduced temperature $T - T_g$ there is no noticeable effect of the salt concentration on the viscoelastic properties.[4] Similar considerations, based on a free volume diffusion model for the ions, lead us to a WLF relationship to describe the conductivity behavior with temperature at constant salt concentration.[3,7] We were also able to establish a direct correlation between the viscoelastic properties of these networks and their ionic conductivity, as predicted by theoretical considerations.[7,8] ^7Li spin–spin relaxation times (T_2) were also found to correlate well with the respective ionic conductivities.[6] This is not surprising since all the transport properties of the materials, e.g., viscoelastic, ionic conductivity, and spin–spin relaxation properties, are a consequence of the local segmental mobility, which, in turn, depends on free volume through classical relationships.

In the present paper we examine the variations of the conductivity with the salt concentration, at constant free volume fraction, i.e., at constant reduced temperature, for two types of materials: urethane-cross-linked poly(oxyethylene) (POE), $M = 400$, containing $NaBPh_4$ and urethane-cross-linked poly(oxyethylene), $M = 1000$, containing $LiClO_4$.

Experimental Section

The preparation and conditioning of the membranes have been described in previous papers.[4,6] Conductivities were measured either on an Alcatel Model 2531 impedance meter or on a Solartron 1174 frequency response analyzer controlled by an Apple II computer. The conductivity is obtained from the complex impedance diagram.[9] ^7Li broad-line NMR analysis was carried out on a Bruker WP-100 spectrometer. Loss-tangent measurements and the corresponding peak temperatures ($T_{\delta_{max}}$, Table I) at 11 Hz were made on a Rheovibron DDV II viscoelastometer.[1,4] The glass transition temperatures were measured on a DuPont 990 thermoanalyzer. The main characteristics of the samples are shown in Table I. The $T_{g,DSC}$ (Table I) values reported correspond to the lower temperature of the transition zone.[10] The conductivity values at a given reduced temperature were obtained by interpolation on log σ vs. T diagrams.

Results and Discussion

Since we have shown in previous papers that the ionic conductivity follows a WLF relationship at constant salt concentration,[3,6,7] we assume here that measurements at constant reduced temperature relate to iso-free-volume conditions. This assumption is in agreement with the fact that the C_1 and C_2 constants of the WLF relationships found for different materials similar to those used in this study are almost independent of the salt concentration.[11,12] As shown respectively for POE 400–$NaBPh_4$ and POE 1000–$LiClO_4$ networks in Figures 1 and 2, the log–log plots of the conductivity vs. the salt concentration are reasonably linear. Moreover, the slope of these lines is close to unity. This implies that the conductivity increases linearly with salt concentration at constant free volume, at least in the temperature and concentration ranges studied here. This observation can be rationalized by assuming that the degree of disssociation α of the ionogenic functions is con-

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Table I
Main Characteristics of the Two Sets of Membranes Studied

polyether[a]	salt	molar ratio of salt/ether units	concn, mol kg^{-1}	$T_{g,DSC}$, °C	$T_{\delta_{max}}$ (11 Hz), °C
POE 400	$NaBPh_4$	0	0	0	25
		0.26	0.036	−4	18
		0.52	0.071	−7	23
		1.03	0.139	3	26
		1.71	0.223	6	31
		3.44	0.415	14	41
		5.01	0.582	20	45
POE 1000	$LiClO_4$	0	0	−42	−26
		0.27	0.049	−46	
		0.53	0.096	−44	−27
		1.03	0.185	−41	−19
		1.70	0.299	−38	−18
		3.48	0.594	−28	−11
		4.95	0.823	−31	−9
		9.97	1.521	−21	2
		20.67	2.688	−3	21

[a] The cross-linking agent was *p,p′,p″*-triphenylmethane triisocyanate added in stoichiometric amounts so that [NCO]/[OH] = 1.

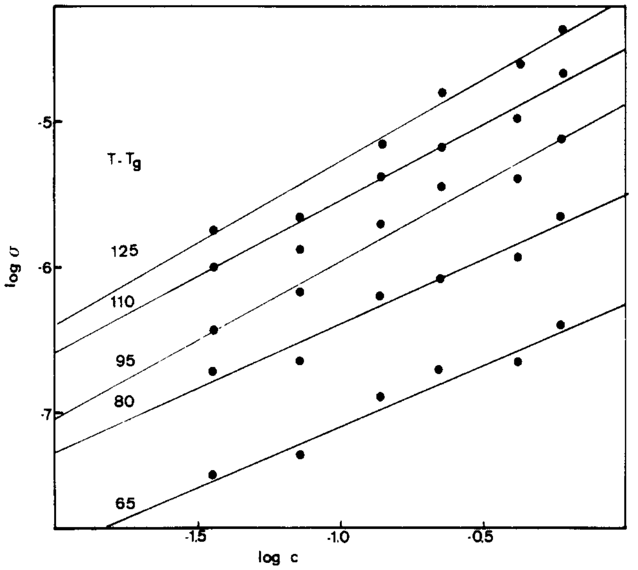

Figure 1. log–log plots of the ionic conductivity vs. the salt concentration at constant $T - T_g$ for POE 400–$NaBPh_4$ networks ($\sigma/\Omega^{-1}\ cm^{-1}$).

stant throughout the range of conditions of this work. The general law expressing the ionic conductivity is given by

$$\sigma = unZF \qquad (1)$$

F being the faraday, Z the valence of the charge carriers, $n = \alpha C_0$ their concentration, and u their mobility. In the case of scarcely dissociated ionogenic functions giving rise to two ions, the number of carriers will approximately be proportional to the square root of the initial salt concentration C_0 and consequently, at constant mobility, i.e., $T - T_g$ constant in our context, the ionic conductivity should increase linearly with the square root of the added salt concentration. If, on the other hand, complete, or nearly complete, dissociation is attained, the conductivity should obviously be proportional to the salt concentration. The latter situation is reflected in the behavior of our membranes. For the system POE 400–$NaBPh_4$ the salt seems to be totally dissociated up to the highest concentration of 0.6 mol kg^{-1} (Figure 1). With POE 1000–$LiClO_4$ networks we went to higher concentrations and can conclude from Figure 2 that the degree of $LiClO_4$ dissociation is close to unity up to about 1 mol kg^{-1}. Using eq 1 we calculate at $T - T_g$ = 75 °C an ionic mobility of about 2×10^{-12} m^2 V^{-1} s^{-1} for Na^+ (Figure 1) and of 10^{-11} m^2 V^{-1} s^{-1} for Li^+ (Figure 2). These values fall in the range of expected mobilities in bulk polymers.[13] The dependence of the dielectric constant of the system on the salt concentration has been neglected in this discussion, although it usually plays an important role[14] in the sense that an increase in the dielectric constant should enhance the dissociation of the salt. However, in the present context the salts seem to be completely dissociated, even at high concentration, and thus the variations of the dielectric constant cannot affect the conductivity.

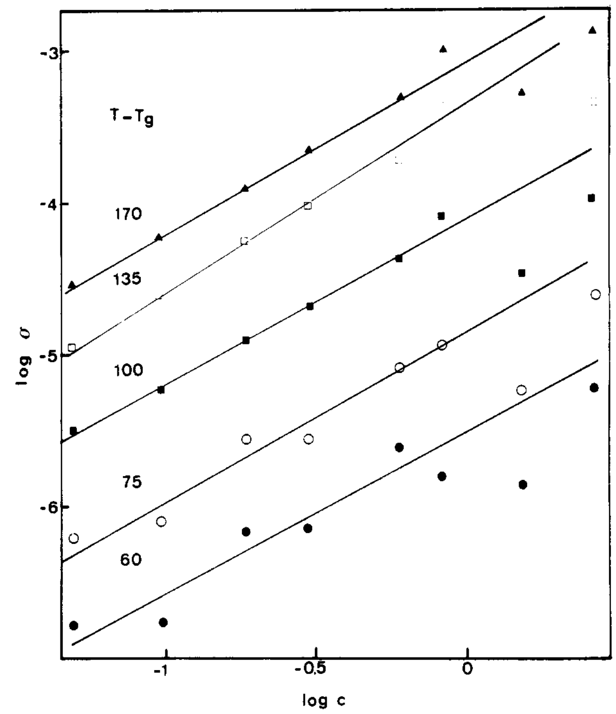

Figure 2. log–log plots of the ionic conductivity vs. the salt concentration at constant $T - T_g$ for POE 1000–$LiClO_4$ networks ($\sigma/\Omega^{-1}\ cm^{-1}$).

A similar type of analysis was carried out previously,[8] but the interpretation was different. In that paper the conductivity at the glass transition temperature was determined by graphical extrapolation and used to establish the plot log σ vs. salt concentration at constant reduced temperature $T - T_g$. The basic underlying assumption in the interpretation that followed[8] was that the number of

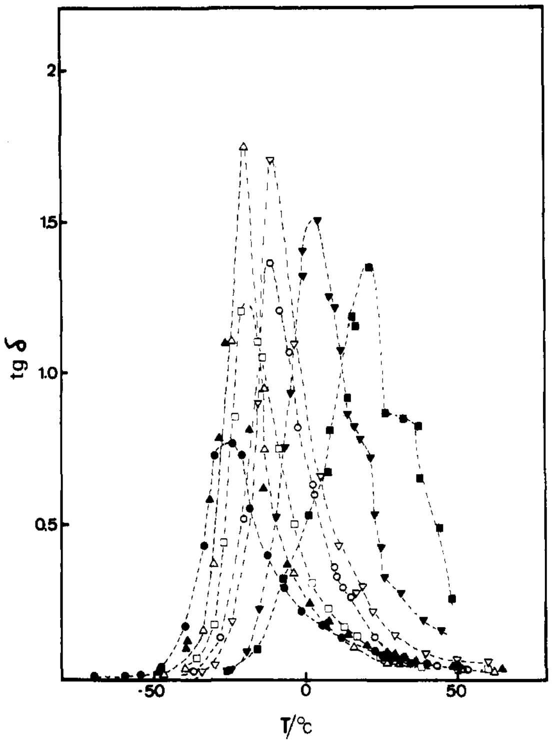

Figure 3. Variation of the loss tangent at 11 Hz as a function of temperature for POE 1000-LiClO$_4$ networks containing different salt concentrations. % Li/-O-: (■) 20.67; (▼) 9.97; (▽) 4.95; (○) 3.48; (□) 1.70; (△) 1.03; (▲) 0.53; (●) 0 (see Table I).

charge carriers did not vary in the temperature range T_g to T, which is in fact not verified. We show here instead that this is true only in the range T_g +60 °C to T_g +170 °C. Consequently, the conclusion given in ref 8 that the minimum free volume hole size for cation jumps varies with the salt concentration cannot be considered as firmly established.

In Figure 2 an important decrease in the slope of d(log σ)/d(log C) is noticed when the salt concentration is above 1 mol kg^{-1} (i.e., >5% Li/-O-). Since POE of molecular weight 1000 contains about 22 monomer units per chain, 5% Li/-O- roughly corresponds to *one cation per network segment*. This calculation suggests that complete dissociation is achieved as long as there are POE chains in the network available for the solvation of one cation and that the accommodation of two cations in one segment of POE is much less favored. Similar results were obtained by other authors in a recent study on chelation of cations by polyether-polyurethanes.[15]

Our data from dynamic mechanical loss tangent and ^{7}Li broad-line NMR experiments indicate that a new phase appears at concentrations higher than about 5% Li/-O-. Figure 3, for instance, shows the loss tangent at 11 Hz measured at different temperatures for POE-LiClO$_4$ networks. The temperatures corresponding to the maximum are reported in Table I. These temperatures vary with the salt concentration in the same way as the glass transition temperatures measured by differential scanning calorimetry, but with a shift of about 20 °C (this shift has been observed in the case of other polymers[10]). The other relevant feature of Figure 3 is the appearance of a second peak for networks containing either 10% or 20% Li/-O-. This new peak is interpreted as showing the formation of a new phase containing polyether segments coordinated to several salt molecules or ions.

^{7}Li broad-line NMR has been used as a means of investigating the salt dissociation in the case of POE 1000-LiClO$_4$ networks. In Figure 4 the variations of the ionic conductivity and of the corresponding ^{7}Li peak area at 60 °C have been represented on a log-log plot against the salt concentration. A transition concentration is observed around [LiClO$_4$] = 1 mol kg^{-1}. Below this concentration the conductivity and the ^{7}Li NMR peak area follow the same dependence on salt concentration, i.e., direct proportionality. Above it the conductivity decreases and then becomes independent of C while the ^{7}Li NMR peak area still increases but with a slope close to 0.5, within experimental error. These observations can be interpreted, at least qualitatively, as follows. The area of the ^{7}Li NMR peak increases when the salt concentration increases. The differences between the rates of increase below and above about 1 mol kg^{-1} are due to changes in the relaxation conditions for the lithium nuclei. The decrease in conductivity above about 1 mol kg^{-1} is due to a drastic decrease in the product un (eq 1). Indeed, due to electrostatic interactions, two neighboring lithium ions solvated by the same POE chain segment cannot move freely along it and will therefore tend to "stiffen" it, thus decreasing the ionic mobility. Also, the number of carriers must decrease above that critical salt concentration due to trapping of the salt in the clusters that begin to form. These observations and interpretations are in line with those drawn by other authors who claimed the appearance of a segregated phase above a critical ion concentration in ion-containing polymers.[16,17]

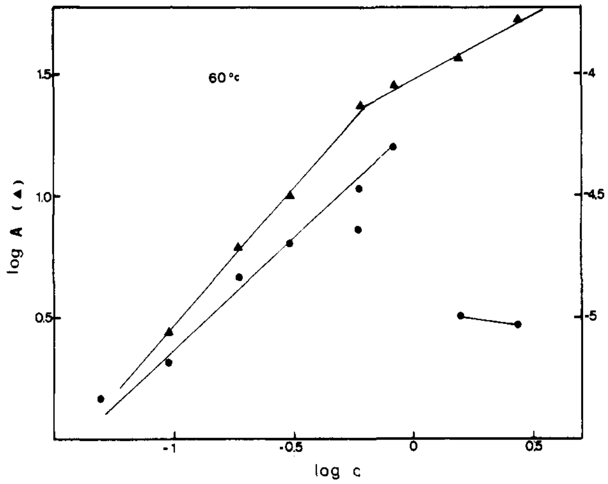

Figure 4. ^{7}Li NMR peak area (A) and ionic conductivity (σ) at 60 °C vs. salt concentration (C) for POE 1000-LiClO$_4$ networks (σ/Ω^{-1} cm^{-1}).

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Registry No. (Polyethylene glycol)·(4,4',4''-triphenylmethane triisocyanate) (copolymer), 75587-26-7; lithium perchlorate, 7791-03-9; sodium tetraphenylborate, 143-66-8.

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Slow-Mode Diffusion in Semidilute Solutions Examined by Dynamic Light Scattering

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ABSTRACT: A slow relaxation, which is 1–2 orders of magnitude slower than that corresponding to self-diffusion, has been investigated in semidilute polymer solutions by dynamic light scattering. The slow relaxation is considered to reflect the translational diffusion of intermolecularly entangled coils in this concentration regime. Five fractions of narrow-distribution poly(ethylene oxide) ($M = 4 \times 10^4$ to 6.6×10^5) were used in aqueous solution. Measurements were made at $\theta = 90°$ of diffusion coefficients and the amplitudes of the fast and slow components, resolvable using a suitable choice of sampling times with cumulant analysis, as a function of concentration and temperature. The molar mass/concentration regime covers the transition region where the slow relaxation is initially observed up to conditions where it is a dominant feature of the autocorrelation function. The amplitude of the slow mode increased with increasing concentration and the relative amplitude (slow/fast) was found to slowly decrease with increasing temperature. Further measurements were made on semidilute solutions of polystyrene ($M = 1.1 \times 10^5$) in the Θ system cyclopentane (20.4 °C); only a single-exponential relaxation could be detected in the concentration interval investigated ($\leq 17\%$ (w/w)).

Introduction

There has been growing interest in competing "fast" and "slow" modes of relaxation observed in dynamic light scattering measurements, which are a striking feature of the dynamics of semidilute solutions of monodisperse polymers.[1–9] These modes are detected experimentally by the departure of the photocount autocorrelation function from the single-exponential characteristic of dilute solutions; there is, for example, a pronounced increase of the variance of the average decay rate with increasing concentration. Chu and Nose[1] made the first detailed description of the different modes and used a histogram method to analyze the autocorrelation function and establish the existence of two modes in the system polystyrene/*trans*-decalin. In a subsequent contribution[2] they approximated the experimental curves with a squared sum of two exponentials. Mathiez et al.[3] and Nishio and Wada[4] used a similar approach. There has, however, been substantial disagreement between authors regarding the source of the slow relaxation. Chu and Nose[2] concluded that in the semidilute region, the slower mode (here, $\bar{\Gamma}_s$ is the line width of the slow mode and $\bar{\Gamma} = \bar{D}\cdot\mathbf{q}^2$, where $\mathbf{q}$ is the scattering vector: $\mathbf{q} = (4\pi n/\lambda) \sin(\theta/2)$) is related to translation of the entangled polymer, including a finite lifetime of the network (disentanglement) and which at infinite dilution would correspond to translational diffusion of the coil itself. The faster mode ($\bar{\Gamma}_f$) corresponds to local internal motions and pseudogel motions. It was noted that $\bar{\Gamma}_s$ decreases with increasing concentration, while $\bar{\Gamma}_f$ increases. The data thus involve a resolvable composite of fast and slow components but their separation was found to be difficult. The whole picture is complicated by the necessity of defining the dynamical regime (in the $\mathbf{q}\cdot R_G$–C/C^* plane) in which the measurements in question have been made[13]—a feature that is frequently neglected (R_G is the radius of gyration and C^* is the concentration of incipient overlap). A recent review of these concepts as applied to diffusion (and sedimentation) has been given by Nyström and Roots.[10]

Mathiez et al.[3] described measurements on semidilute solutions of poly-A and polystyrene and examined the roles of concentration, molar mass, and solvent quality on observable fast and slow modes and their interrelationship. They attributed the slow mode to transient knots which diminish in number as time elapses after preparation of a solution. Nishio and Wada[4] considered a slow relaxation in polystyrene in 2-butanone to represent diffusion of the "whole polymer" which becomes slower as the concentration and solution viscosity increase.

More recently, workers have[8,9] used a judicious choice of sampling times to obtain a more complete separation of fast and slow relaxations and make an identification of a slow component with the self-diffusion coefficient (D^*). The latter identification was tenuous, however, since it rested primarily on the negative concentration dependence, which had not been expected in a good solvent, but it was not validated by a comparison with experimental D^* values.

Brown et al.[11] subsequently made dynamic light scattering and pulsed field gradient NMR measurements on several narrow-distribution fractions of poly(ethylene oxide) in semidilute aqueous solutions. Comparison of the apparent diffusion coefficients derived from the slow relaxation with self-diffusion coefficients showed that the former are between one and two orders of magnitude slower than self-diffusion but have a qualitatively similar concentration dependence within the semidilute region.

The present paper comprises a more detailed extension of the earlier report.[11] It describes measurements on PEO fractions in aqueous solution, at various concentrations and