Macromolecules 1990, *23*, 163-167

Elastic and Dynamic Properties of a Poly(propylene glycol)–Lithium Perchlorate Electrolyte: A Brillouin Scattering Study

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Received September 27, 1988; Revised Manuscript Received May 31, 1989

ABSTRACT: Acoustic properties and short time ($\sim 10^{-11}$ s) structural relaxation behavior in a poly(propylene glycol)–lithium perchlorate (PPG–$LiClO_4$) complex of concentration O:M = 9:1 (O:M is the backbone oxygen to lithium ratio) have been investigated. Comparisons with results from MSCN–PPG (M = Li, Na, or K) and $NaCF_3SO_3$–PPG complexes show that the elastic properties, which are independent of cation exchange, are dependent on the real part of the relaxing longitudinal modulus through the type of anion. The sound velocity is found to be highest in the SCN^- complex and lowest in the $CF_3SO_3^-$ complex. This result is interpreted in terms of the "structure making" effects of the cation versus the "structure breaking" effects of the anions. The average structural relaxation times are observed to follow a Vogel–Tamman–Fulcher relation in temperature, and the time decay of the process could be well fitted to a Kohlrausch–Williams–Watts relaxation function ($\beta \simeq 0.4$). The average relaxation times for the $LiClO_4$–PPG complex were found to be considerably longer than those of uncomplexed PPG.

Introduction

The usefulness of light scattering as a tool for investigations of structural and dynamical properties of bulk polymers has already been demonstrated.[1] In the present study, a lithium perchlorate–poly(propylene glycol) ($LiClO_4$–PPG) complex is chosen for a detailed Brillouin scattering investigation of high-frequency ($\sim$GHz) acoustic properties and the short time ($\sim 10^{-11}$ s) local dynamics. The technique has recently been used for the first time in studies of polymer–salt complexes.[2,3] The interest in these materials is mainly due to their applicability as solid electrolytes in new types of batteries and other electrochemical devices.[4] $LiClO_4$ is in this context of special interest since it belongs to the group of salts which give the highest conductivities in polymer electrolytes.

In ion conducting polymers, high ionic conductivity is suggested to be related to high internal flexibility of the host polymer matrix.[4] It is therefore of interest to compare the local dynamics of a good conductor like the $LiClO_4$–PPG system with those of other salt–polymer complexes that are characterized by lower conductivities. Moreover, it has previously been found, in a Brillouin scattering study of other salt–polymer complexes, namely, MSNC–PPG (where M = Li, Na, or K), that the local elastic properties remained unchanged as the cation was exchanged at a constant salt concentration (O:M = 12:1).[2] It is therefore of interest to see if anion exchange, which is observed to affect the conductivity, will affect the elastic behavior. Thus, with the elastic properties and the local dynamics in mind, new data of $LiClO_4$–PPG will be presented in this study and compared with those reported for MSCN[2] and $NaCF_3SO_3$[3] complexes. We also include some new data of relaxation characteristics of the MSCN–PPG complexes obtained from an analysis of previously reported results[2] and needed for the present comparison.

The host polymers in solid electrolytes are generally polyethers that are used in a modified form (of high molecular weight or of cross-linked low molecular weight) to obtain the required mechanical stability. In this study, PPG of the low molecular weight is chosen for investigations since a liquid is more convenient to handle in light scattering. It should be noted that PPG of 2000 molecular weight was used in the preparation of the MSCN–PPG complexes, whereas PPG of 4000 molecular weight was used in the preparation of the $NaCF_3SO_3$–PPG and $LiClO_4$–PPG complexes. It has, however, recently been shown that the mechanical properties of PPG obtained by the Brillouin scattering technique, i.e., sound velocity and absorption, are more or less independent of molecular weight[5] and only are related to the local dynamics. Brillouin scattering is therefore in fact probing the segmental motions of the polymer chains which contribute to structural relaxation and which are believed to be important for the ionic conduction process in polyether complexes. This means that the low molecular weight host polymer PPG of the present study can serve as a model for the high molecular weight PPG commonly used in elastomeric applications.

Structural relaxation in the sample occurs as a result of density fluctuations, both propagating and nonpropagating. Since the density fluctuations are coupled to the dielectric fluctuations, the density fluctuations from the propagation of longitudinal sound waves contribute to the spectrum of scattered light. A more complete discussion can be found elsewhere.[1] Essentially, the Brillouin spectrum contains four components: a pair of Brillouin peaks shifted in frequency from the incident frequency of the laser used, an unshifted Rayleigh peak (whose width is related to thermal transport properties of the sample), and a second unshifted dynamic peak generally referred to as the Mountain peak. An example of a Brillouin spectrum is shown in Figure 1. From the frequency shift (f_B) and full width (Γ_B) of the Brillouin peaks,

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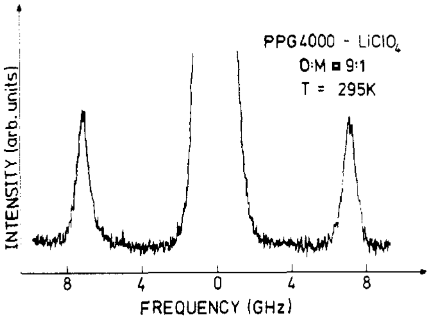

Figure 1. Spectra of PPG–LiClO$_4$ of concentration O:M = 9:1 at T = 295 K.

one can obtain information about the hypersonic velocity (v) and attenuation coefficient (α) of the sound waves involved in the scattering process through the relations

$$v = f_B\lambda_0/(2n \sin(\theta/2)) \qquad (1)$$

and

$$\alpha = \pi\Gamma_B/v \qquad (2)$$

Equation 2 holds for $\alpha/q \ll 1$ or $\Gamma_B/f_B \ll 1$ which is the case for our experiment. Here $q = (4\pi n/\lambda_0)\sin(\theta/2)$, λ_0 is the wavelength of the incident light, n the refractive index of the scattering medium, θ the scattering angle, and Γ_B the full-width at half-maximum (fwhm) of the Brillouin line. Γ_B broadens as the temperature decreases, reaches a maximum, and then decreases. Relaxation times of the order of $1/f_B$ dominate this process; the maximum and decreases in Γ_B result as the strength of the processes with relaxation times of the order $1/f_B$ decreases. With a decrease in temperature, the intensity of the Brillouin peaks decreases and the intensity in the Mountain peak increases. Thus, the Mountain peak arises as a direct result of dispersion in the sample.

When a viscoelastic medium is subject to strain, the induced stress is relieved by structural relaxation processes which have characteristic relaxation times τ. In the case of longitudinal disturbances, the response of the medium is characterized by a frequency-dependent complex longitudinal modulus, M^*, and a broad distribution of relaxation times, $\rho_M(\tau)$, which shifts to longer times as the temperature is decreased

$$M^*(\omega) = \gamma K_0 + M_r \int_0^\infty \frac{\rho_M(\tau) i\omega\tau}{1 + i\omega\tau}\,d\tau \qquad (3)$$

where ω is the frequency shift ($= 2\pi f_B$), M_r is the total strength of all the processes that relax the modulus, K_0 is the zero-frequency modulus of compression, and $\gamma = C_P/C_V$, the ratio of specific heats. The strength of the distribution function has a low value for short relaxation times, increasing with increasing relaxation times until it reaches a maximum value and then decreasing with longer relaxation times. At high temperatures, Γ_B depends on the average relaxation time $\langle\tau\rangle$ ($= \int_0^\infty \rho_M(\tau)\,d\tau$). The line width is $\Gamma_B \approx (q^2/2\rho)(M_r\langle\tau\rangle)$ where $M_r\langle\tau\rangle = n_v + 4/3n_s$. This is the viscous limit. n_v and n_s are the bulk and shear viscosities, respectively, and ρ is the density. $\langle\tau\rangle$ can be approximated from the hypersonic loss maxima, i.e., the maximum width of the Brillouin peak, using the peak condition

$$\omega_m\langle\tau\rangle \approx O(1) \qquad (4)$$

where ω_m is the angular frequency shift of the Brillouin line at maximum damping.

The relaxation time can also be obtained from an analysis of the relaxing part of the longitudinal modulus.[3] For $\alpha/q \ll 1$ the reduced form of the real and imaginary parts of $M^*(\omega)$ may be written as

$$N'(\omega) = \frac{M'(\omega) - M_0}{M_r} = \frac{M'(\omega) - M_0}{M_\infty - M_0} = \frac{v^2(\omega) - v_0^2}{v_\infty^2 - v_0^2} \qquad (5)$$

$$N''(\omega) = \frac{M''(\omega)}{M_r} = \frac{M''(\omega)}{M_\infty - M_0} = \frac{2\alpha(\omega)v^3(\omega)}{\omega[v_\infty^2 - v_0^2]} \qquad (6)$$

In eq 5 and 6 the subscripts ∞ and 0 refer respectively to the infinite and zero frequency values of the modulus and the velocity. The former can be extrapolated from the low-temperature side of the dispersion just above the liquid-glass transition while the latter is determined from the high-temperature side. The adiabatic sound velocity depends on the real part of $M^*(\omega)$.

$$v(q) = [M'(\omega)/\rho]^{1/2} \qquad (7)$$

The experimentally determined $N'(\omega)$ and $N''(\omega)$ in eq 5 and 6 can be compared with the analytical expression obtained from

$$N'(\omega\tau) = \omega\tau \int_0^\infty \sin(\omega\tau)\,\phi(t/\tau)\,d(t/\tau) \qquad (8)$$

$$N''(\omega\tau) = \omega\tau \int_0^\infty \cos(\omega\tau)\,\phi(*/\tau)\,d(t/\tau) \qquad (9)$$

where

$$\phi(t/\tau) = \int_0^\infty d\tau\,\rho_M(\tau)\exp(-t/\tau)$$

is the relaxation function. Equations 8 and 9 integrate to give the real and imaginary parts of eq 3. In uncomplexed PPG, it is found that a single relaxation time, i.e., exponential decay, cannot describe the process.[6] It is found that the empirical Kohlrausch–Williams–Watts (KWW) relation can be fitted to the data such that the relaxation function is

$$\phi(t/\tau) = \exp(-(t/\tau)^\beta) \qquad 0 < \beta < 1 \qquad (10)$$

The KWW function has been found to describe relaxation phenomena in many other systems.[7] The average relaxation time for a KWW function is

$$\langle\tau\rangle = \frac{\tau}{\beta}\Gamma\left(\frac{1}{\beta}\right) \qquad (11)$$

and $\langle\omega\rangle \neq 1/\langle\tau\rangle$. If eq 10 is inserted in eq 8 and 9, integrals are obtained whose values are tabulated in Dishon, Weiss, and Bendler[8] for values of β and $\omega\tau$.

Experimental Section

Brillouin Scattering. In the Brillouin scattering setup, the 647.1 nm line of a single mode Kr positive ion laser was used as a light source. This "red" line was used since, at the higher temperatures, fluorescence was sometimes a problem, especially if the samples was on the verge of degradation. The light, vertically polarized to the scattering plane, was incident on the sample situated in a thermostat, and right-angle scattering geometry was employed. The scattered light was frequency resolved by a triple-passed peizoelectrically scanned Fabry-Perot interferometer, and photon counting techniques were used for detection of the signal. The spectral-free range of the interferometer was ~21.7 GHz. Each recorded spectrum was the result of about 20 000 repeated scans of ~1.5 spectral-free ranges. During scanning, the finesse of the interferometer was optimized by a Burleigh DAS 10 stabilization system. The overall finesse of the system was kept at about 35 for all recorded spectra. The temperature was controlled within ±1 K, and the temperature stability was better than ±0.1 K during a measurement.

Material. The MSCN–PPG complexes have been described previously.[2] The preparation of the NaCF$_3$SO$_4$–PPG complex has also been described previously[3] and is identical with the

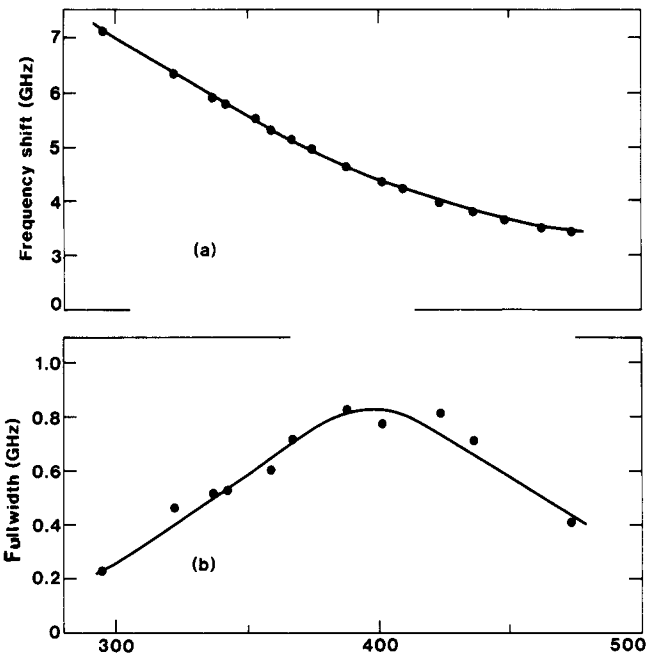

Figure 2. Brillouin frequency shifts (a) and full width (b) versus temperature for PPG–$LiClO_4$ of concentration O:M = 9:1.

preparation of the $LiClO_4$–PPG complex, except that the O:M ratio is approximately 8:1. The O and M represent respectively the number of monomers and metal atoms. The salt concentration of the investigated sample, a solution of $LiClO_4$ (Ventron division, Alfa products, anhydrous, 99.5%) and poly(propylene glycol) of molecular weight 4000, was around an O:M ratio of 9:1. The salt and PPG were mixed at an elevated temperature (~335 K) under argon atmosphere after which the sample was freeze-dried and sealed at a vacuum of better than 10^{-4} Torr. The sample was contained in a cylindrical Pyrex tube of 7-mm diameter with an optical window fused to the bottom. The complex was transparent, clear, and of high optical quality. Further details of the experimental setup and the sample preparation are given in ref 3.

Results

Brillouin spectra of the PPG–$LiClO_4$ system were recorded in the temperature range 295–474 K. Figure 1 illustrates a spectrum obtained for the PPG-4000–$LiClO_4$ complex at 295 K. The upper temperature limit was set by degradation of the material, which manifested itself in irreproducible measurements and by a color change of the material. The observed frequency shifts and half-widths of the longitudinal Brillouin components are respectively shown versus temperature in parts a and b of Figure 2. The transverse modes, normally present in the spectrum of viscous liquids, are often too weak in intensity to be observable in polymers[9] and as can be seen in Figure 1 were not detected in the present salt–polymer complex. A strong dispersion in the frequency shifts of the longitudinal modes was found, from a value of ~7.1 GHz at room temperature to ~3.4 GHz at the upper temperature limit; see Figure 2a. In the dispersion range, the width of the Brillouin line is affected. Figure 2b reveals a broadening of the Brillouin half-width from a value of ~0.2 GHz at room temperature to a maximum value of ~0.9 GHz at ~400 K. Thereafter, a narrowing of the components follows as the temperature is further raised.

From the Brillouin frequency shift, the hypersonic longitudinal velocity v was obtained by using eq 1 and results are shown in Figure 3. Values of the refractive index used were those obtained by Wixwat et al.[10] Data from uncomplexed PPG[6] are also shown in the same figure for comparison together with the results from other polymer electrolytes, namely, PPG–MSCN solutions[2] of concentration O:M = 12.1 (M = Li, Na, or K) and a PPG–$NaCF_3SO_3$ solution[3] of concentration O:M = 8:1. It has been reported that, in the case of PPG–MSCN complexes, the effect of cation exchange is negligible on properties such as hypersonic velocity, sound attenuation, and structural relaxation times for a constant salt concentration of O:M ~ 12:1.[2] If we assume that this is also the case for complexes of the MCF_3SO_3 and $MClO_4$, we can investigate the effect of anion exchange by comparing results from the present $LiClO_4$ complex with those previously obtained for MSCN complexes as well as those of PPG–$NaCF_3SO_3$. The absorption coefficient α, calculated from the observed fwhm of the Brillouin components by using eq 2, is plotted in Figure 4 versus temperature for the PPG–$LiClO_4$ complex and compared with reported data for uncomplexed PPG.[6] It can be seen that salt complexation shifts the absorption peak to higher temperatures. In Figure 5 the hypersonic velocity is plotted against temperature referenced to $T_{\alpha_{max}}$, the temperature at which the maximum in the hypersonic loss occurs for each case studied. Values of $T_{\alpha_{max}}$ are listed on Figure 5. It is found that the velocities are ordered SCN^-, ClO_4^-, and $CF_3SO_3^-$ with the SCN^- systems characterized by the largest velocity values. This is further emphasized when the various salt concentrations are considered since it has been shown that increasing the salt concentration raises the sound velocity value monotonically.[3]

The velocity and absorption data of the PPG–$LiClO_4$ complex were used to calculate the normalized imagi-

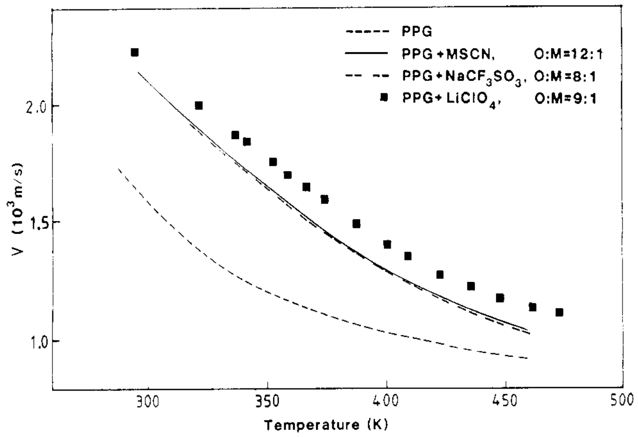

Figure 3. Hypersonic velocity results for the PPG–salt complexes PPG–$LiClO_4$ (■, present results), PPG–MSCN (solid line, ref 2), and PPG–$NaCF_3SO_3$ (interrupted dashed line, ref 3). Data of uncomplexed PPG (dashed line) are from ref 6.

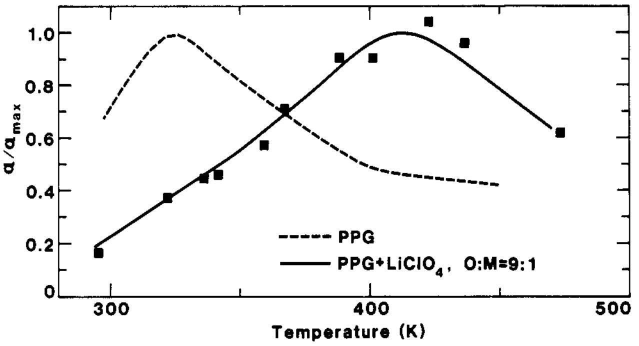

Figure 4. Temperature dependence of sound absorption coefficient in a PPG–$LiClO_4$ complex of concentration O:M = 9:1 (■). Results for uncomplexed PPG (dashed line) are from ref 6.

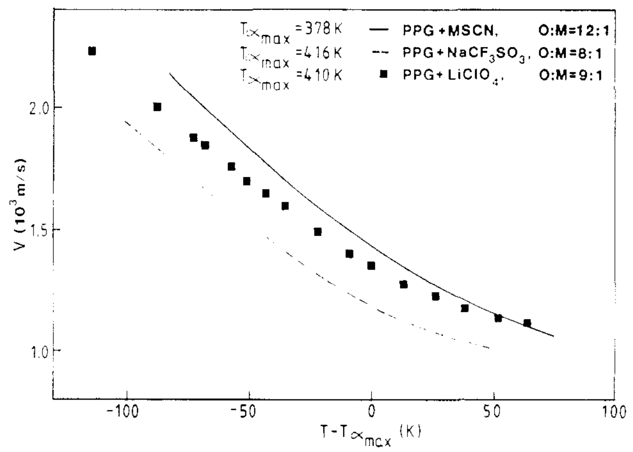

Figure 5. Hypersonic velocity results versus $T - T_{\alpha_{\max}}$ for the PPG–salt complexes PPG–LiClO$_4$ (■, present results), PPG–MSCN (solid line, ref 2), and PPG–NaCF$_3$SO$_3$ (interrupted dashed line, ref 3).

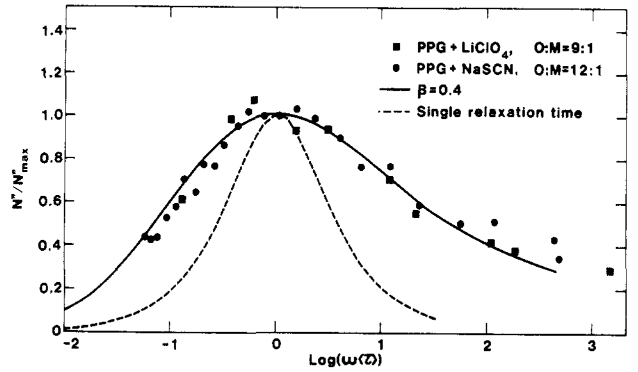

Figure 6. Reduced imaginary part of the elastic modulus versus log $(\omega\langle\tau\rangle)$ for a PPG–LiClO$_4$ complex (■) and for a PPG–MSCN complex (●). Solid line corresponds to a Kohlrausch–Williams–Watts relaxation function with $\beta = 0.4$. Dashed line represents single relaxation time behavior.

nary ($N''/N''_{\max}$) part of the reduced elastic modulus (Figure 6). This may be done by first calculating the ratio $M''/M' - M_0$ (independent of v_∞) from experimental data. This value is compared for values of $\omega\tau$ at $T_{\alpha_{\max}}$ with the N''/N' ratios of values for the integrals[8] in eq 8 and 9 with eq 10 inserted. A value of $\beta = 0.4$ can thus be obtained and used to construct Figure 6. In doing this a temperature dependence

$$\langle\tau\rangle = \langle\tau_0\rangle \exp\left(\frac{B}{T - T_0}\right) \tag{12}$$

is assumed. Here $\langle\tau_0\rangle$, i.e., the relaxation time at temperatures in the $(1/T) \to 0$ limit, was assumed to be the same as that of uncomplexed PPG,[6] i.e., 3.46×10^{-14} s. The ideal glass transition temperature T_0 was taken to be respectively 218 and 232 K for the thiocyanate and perchlorate complexes, i.e., 30 K below the glass transition temperatures (T_g)[11,12] in correspondence with observations in uncomplexed PPG.[6,12] Using the peak condition for $\omega\langle\tau\rangle$ at the observed N'' maximum, average relaxation time values of $\sim 6 \times 10^{-11}$ s for PPG(2000)–MSCN and $\sim 9 \times 10^{-11}$ s for PPG(4000)–LiClO$_4$ were obtained for $T = 378$ K and $T = 410$ K, respectively. With use of the latter data and eq 12, the B parameters could be estimated to be $\sim$1200 K for the SCN$^-$ complex and $\sim$1400 K for the ClO$_4^-$ system. For the denser system PPG(4000)–NaCF$_3$SO$_3$, $\langle\tau\rangle \sim 1 \times 10^{-10}$ s and $B \sim 1430$ ($T = 416$ K).

Discussion

PPG is a nonionic polyelectrolyte. PPG-4000 has an "OH" number (mg of KOH/g) of 37 and therefore is mainly aprotic since in our preparation it was thoroughly dried and sealed under vacuum. Thus, like polyethers in general, PPG is a macromolecular array of Lewis bases of low polarity: strong donors through the ether oxygens but poor acceptors since sources of hydrogen bonding are lacking for anion solvation. Thus when salts like NaSCN, LiClO$_4$, and NaCF$_3$SO$_3$ are complexed with PPG, the alkali-metal cations coordinate with the ether oxygen atoms because of the their polarity, their suitable distances of separation, and the flexibility of the PPG chain; the anions fill up the voids.

The solvation of the cation results in a compression of the solvent near the cation, Li$^+$ having the greatest effect, then Na$^+$, and then K$^+$. While the cations are trying to compress the solvent, the anions are trying to open it up. Measurements of refractive index ($\sim\epsilon^{1/2}$ where ϵ is the permittivity) show that the CF$_3$SO$_3^-$ anion is the most effective in opening up the structure, so effective that for PPG–MCF$_3$SO$_3$ complexes (M = Li, Na) the refractive index decreases with increasing concentration; SCN$^-$ is the least effective and the refractive index for PPG–LiClO$_4$ and PPG–MSCN complexes increases with concentration.[10]

As the concentration of salt in PPG-4000 increases, T_g goes up.[12] Since we have shown that the temperature ($T_{\alpha_{\max}}$) at which the peak in the attenuation is a maximum correlates with T_g,[3] we can remove this effect by plotting the hypersonic velocity versus $T - T_{\alpha_{\max}}$ (Figure 5). We are then left with evidence of the "structure making", "structure breaking" effects of the cations and ions: PPG–NaCF$_3$SO$_3$, the lowest velocities, PPG–LiClO$_4$ and PPG–NaSCN, the highest velocities. This separation is even more pronounced when one considers that PPG–NaSCN has the lowest O:M ratio (12:1) and PPG–NaCF$_3$SO$_3$ the highest O:M ratio (8:1). The velocity increases monotonically with concentration since generally the salt (anions) is filling in the holes in the initial PPG structure and the increase in M' far exceeds the increase in ρ (eq 7).[3]

We, therefore, conclude that the hypersonic velocity is sensitive to the solvation properties of the anions studied here; the attenuation insensitive.

Acknowledgment. This program is financially supported by the Swedish National Board for Technical Development and the Natural Sciences and Engineering Research Council of Canada. We gratefully acknowledge partial support from Axel and Margaret Ax:son Johnsson's Foundation.

Registry No. PPG, 25322-69-4; LiClO$_4$, 7791-03-9.

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Evaluation of Cross-Linking and Scission Yields in Irradiated Polymers from the Dose Dependence of the Weight- and *z*-Average Molecular Weights

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ABSTRACT: A procedure has been developed for the determination of scission and cross-linking yields, $G(S)$ and $G(X)$, in irradiated polymers by combination of the ordinate intercepts of plots of $([\bar{M}_w(0)/\bar{M}_w(D)] - 1)/D$ and $([\bar{M}_z(0)/\bar{M}_z(D)] - 1)/D$ versus dose (D). The required weight- and z-average molecular weight data for a given sample can be obtained by using the Rayleigh and schlieren optical systems, respectively, to record the solute distribution in a single sedimentation equilibrium experiment. The procedure has been tested by application to simulated data for a range of initial molecular weight distributions and values of $G(S)/G(X)$ and applied to previous sedimentation equilibrium results (Nichol, J. M.; O'Donnell, J. H.; Rahman, N. P.; Winzor, D. J. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2919) for a polystyrene sample with $\bar{M}_w(0)/\bar{M}_n(0) = 1.03$ and $G(S)/G(X) = 1$.

Introduction

Irradiation of polymers produces cross-linking and scission, which have pronounced effects on the physical and mechanical properties of the polymer.[1,2] Determination of the radiation chemical yields of scission ($G(S)$) and cross-linking ($G(X)$) per 16.02 aJ (100 eV) of energy absorbed by the polymer is therefore important in characterizing the effects of irradiation. Traditionally, $G(S)$ and $G(X)$ for systems that predominantly cross-link ($G(S) < 4G(X)$) have been determined by a Charlesby–Pinner analysis[3,4] of soluble fractions after different doses. This method has the disadvantage that high irradiation doses are required to obtain the necessary extrapolation to infinite dose, especially for polymers that do not have the most probable molecular weight distribution ($\bar{M}_w/\bar{M}_n = 2$). Also, since scission and cross-linking yields may be different for linear and extensively cross-linked polymer, values of $G(S)$ and $G(X)$ appropriate to the initial polymer should be obtained from studies of samples subjected to low radiation doses. $G(S)$ and $G(X)$ may also be obtained from changes in the molecular weight distribution or in the two molecular weight averages $\bar{M}_w$ and $\bar{M}_n$.[5] Doses less than half of the gel dose (D_g) have been recommended to avoid significant errors in the measurement of average molecular weights.[5]

Although theoretical relationships have been derived[4,6] for the dose dependences of the average molecular weights $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ of samples with an initial Schulz–Zimm distribution,[7,8] convenient experimental procedures for analyzing such data in terms of $G(S)$ and $G(X)$ are confined to $\bar{M}_n(D)$[1,4] and $\bar{M}_w(D)$.[4,9] Combination of the relationships for both $\bar{M}_w(D)$ and $\bar{M}_n(D)$ is required to determine $G(S)$ and $G(X)$.[9] Osmometry is the conventional procedure for measuring $\bar{M}_n$, and light scattering has been used for evaluating $\bar{M}_w$. Gel permeation chromatography is widely used to determine $\bar{M}_n(D)$ and $\bar{M}_w(D)$ for irradiated polymers, but changes in relative hydrodynamic volume with cross-linking lead to serious errors, especially in weight-average molecular weight.

It is preferable to employ a single experimental technique for determination of the two molecular weight averages for the one sample. Sedimentation equilibrium in the analytical ultracentrifuge is an appropriate technique that has been largely ignored. It is the only thermodynamically rigorous procedure to yield more than one type of average molecular weight. The Chervenka[10] adaptation of the high-speed sedimentation equilibrium technique[11] has recently been recommended[12,13] for simultaneous evaluation of $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ for polydisperse polymers. However, $\bar{M}_n$ can only be determined if a rotor

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