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The role of polymer melt viscoelastic network behavior in lithium ion transport for PEO melt/$LiClO_4$ SPEs: the ‘‘wet gel’’ model

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Abstract

Earlier light scattering studies revealed that melts of the electrolyte polymer poly(ethylene oxide) (PEO) were not homogeneous but were instead structured and behaved as elastic PEO networks. We report the results of subsequent viscometry measurements that provide a more complete picture of PEO melt structure and dynamic behavior. We find that PEO melts behave as ‘‘wet gels,’’ i.e., they behave as elastic PEO networks immersed in a PEO fluid that retards network motions. In addition, a preliminary light scattering examination of the role that PEO melt network dynamic behavior might play in lithium ion transport found that although the light scattering relaxation function mode structure of PEO melt/$LiClO_4$ solutions changed significantly when the salt concentration was increased from 0 to 20 wt.% — the latter concentration being that for which maximum conductivity in the PEO/$LiClO_4$ system has been reported — the network structure and behavior of the melt was retained. Finally, we report the results of exploratory investigations of several aspects of PEO melt behavior that provide promising directions for future studies of this interesting and important system. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: PEO melt/$LiClO_4$ system; Viscoelastic network; Wet gel; Lithium ion transport; PCS; Relaxation function

1. Introduction

Recently, a new class of solid-state ionic materials with great potential for a variety of important applications has been developed. These materials are polymer electrolytes: conducting materials oftentimes referred to as ‘‘solid’’ polymer electrolytes or ‘‘SPEs’’ though they may consist of a solid or liquid polymer medium. Selected salts have been dissolved into this medium so that salt cations (for the most part) are coordinated or complexed with groups along the polymer chain backbone and transported via polymer motions through the polymer medium. The many uses for polymer electrolytes include portable electronic devices, ambient temperature fuel cells, electrodes/sensors, electrochromic devices, supercapacitors, solid-state reference electrode systems, thermoelectric generators, and media in high vacuum electrochemistry and electrochemical switching. Of particular interest to the work proposed here is the use of SPEs in secondary (rechargeable) lithium/polymer batteries.

2. Background and rationale

The poly(ethylene oxide) (PEO)/lithium salt system is widely used as a prototype SPE in the intensive development of state-of-the-art solid-state batteries. For example, a PEO-containing copolymer/lithium salt prototype SPE was recently selected for incorporation into the lithium-polymer battery development program undertaken by the Canadian firm, Hydro-Quebec [1]. Between its melt and glass transition temperatures, the PEO/lithium salt system, and evidently the Hydro-Quebec PEO copolymer/lithium salt system, exists as a metastable, biphasic system consisting both of fluid, amorphous regions along with regions of salt-enriched crystallized polymer. Since it is known that lithium ion transport in such biphasic systems occurs exclusively in the fluid, amorphous regions of the system [2], the Hydro-Quebec system will be heated to maintain its temperature between 60°C and 80°C. In this way, sufficient fluid pathways will exist in the SPE to provide the required lithium ion transport and conductivity. It is worth noting in this regard that pure, high molecular weight PEO melts around 60°C. Hydro-Quebec refers to their system as a ‘‘warm,’’ ‘‘dry’’ (no plasticizers) lithium polymer battery. This system differs distinctly from the

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recently developed Bellcore [3,4] SPE battery that utilizes an SPE ''gel'' of polymer plus liquid additives to enhance ion transport and conductivity. Hydro-Quebec believes that their warm, dry SPE batteries will be safer and have longer lifetimes than batteries utilizing gel SPEs, in part because without plasticizers, electrode deterioration and chemical instability will be reduced.

In the work reported here, we have combined viscometry and light scattering to study the behavior, under a variety of conditions, of plasticizer-free PEO melts with and without selected lithium salts. The focus on PEO *melt* behavior follows directly from the knowledge that it is in this phase that lithium ion transport takes place. The goal of this work is to better understand the relationship between lithium ion transport and PEO melt structure and dynamic behavior. The details of an earlier light scattering investigation of PEO melt dynamic behavior that serves as a principal reference for this article may be found in Ref. [5].

Perhaps the most significant result of the earlier light scattering work was the discovery that the PEO melt — even when devoid of crystallized regions — was not the bland, uniform and featureless medium envisioned by most researchers. On the contrary, visual observation and photon correlation spectroscopy (PCS) measurements revealed that for both the 1- and 50-K samples employed in the study, the crystallite-free PEO melt was a structured random network formed by extensive inter- and intrapolymer connections [5].

While earlier visual observations of the strong scattering of laser light by PEO melts — with bright, diffuse and grainy scattering volumes (the scattering volume is defined by the intersection of the laser beam and the polymer melt) — had already revealed the existence of large amplitude melt density fluctuations with characteristic sizes necessarily of the order of the wavelength of visible light, monitoring the scattered light intensity as a function of scattering angle confirmed that regions of crystallized polymer were not responsible for the large scattered light intensity observed. In conjunction with these results, the form of PCS scattered light intensity autocorrelation functions (ACFs) obtained for these melts revealed the network nature of these systems (see Ref. [5]).

In Fig. 1 (taken from Ref. [5], with permission), the similarity in structure and dynamic behavior of the 1- and 50-K PEO melts is illustrated in a side-by-side comparison of typical single-mode PCS ACFs. This result is especially interesting since according to rheological measurements, the 1- and 50-K samples are structurally and dynamically quite different: the 1-K sample is ''unentangled'' while the 50-K sample is highly entangled [6–8]. The apparent contradiction between the light scattering and rheology results can be reconciled by recognizing that while rheological measurements are necessarily perturbative, light scattering measurements are noninvasive. The delicate network formed in the 1-K PEO melt was evidently destroyed during rheological measurements, but remained intact in light scattering measurements. Thus PCS can be used to study PEO melt structural features and corresponding dynamic behavior associated with the melt network, including especially delicate networks formed from smaller PEO chains. As a result, the implications of the network structure and the melt dynamic behavior have for SPE ion transport may now be addressed. Results, such as the PEO

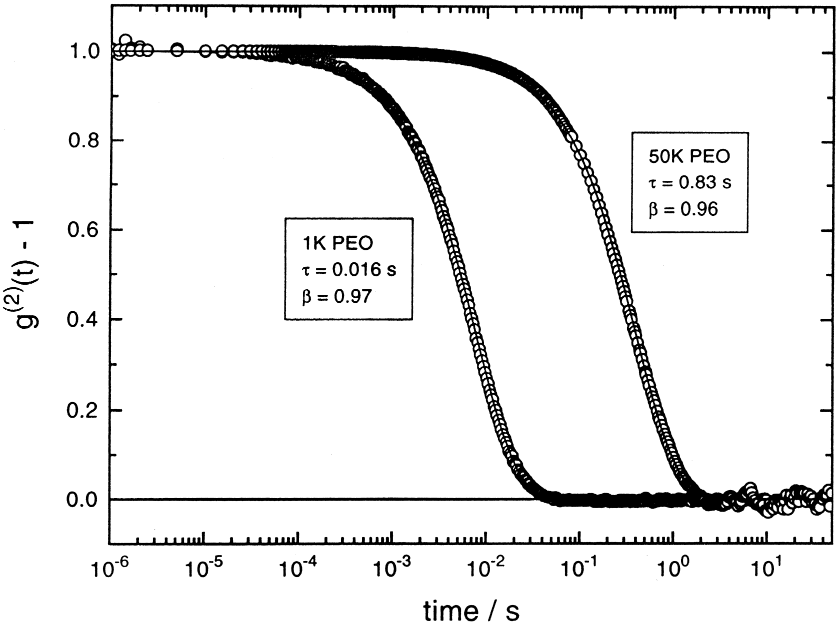

Fig. 1. Normalized monomodal scattered light intensity ACFs for 1- and 50-K PEO melts made at 70°C and a scattering angle of 90°. Relaxation function characteristic times, τ, and dispersity factors, β, were extracted from KWW fits to the data.

melt/network revelation, are also providing interesting new possibilities for theoretical investigations of these melts.

It is important to recognize that not all melts of linear, flexible polymers form networks. The development of this highly cooperative behavior in melts of linear, flexible polymers requires certain intra- and interpolymer interactions, and not all such polymers do this. For example, melts of high molecular weight polystyrene do not exhibit network behavior [9]. Therefore, it is particularly suggestive and intriguing that PEO, regarded perhaps as the ''canonical'' SPE polymer, forms networks in the melt.

3. Experimental

The PEO samples used in the work reported here are those extensively studied earlier [5]. The preparation of PEO melt samples suitable for investigation — particularly using light scattering — is difficult, and considerable time and effort were expended in developing a procedure to produce such samples. To ''bracket'' the study, two PEO samples with molecular weights distinctly above and distinctly below the melt entanglement molecular weight were custom synthesized ($M_e \approx 1600$: note that the ''critical molecular weight for entanglement,'' M_c, is roughly twice M_e). These samples have molar masses of 1060 Da (the ''1-K'' sample) and 50,600 Da (the ''50-K'' sample) with very narrow molecular weight distributions ($M_W/M_N = 1.02$ and 1.05, respectively). Moreover, PEO chain ends were capped with methyl groups to avoid complications arising from chain end interactions in the melt and great care was taken to produce dehydrated samples. Further details on sample preparation for light scattering measurements are presented in Ref. [5].

The $LiClO_4$ used in this work was a highly purified grade (Fluka, Buchs, Switzerland) first dried in a vacuum oven and then further dried under high vacuum in a desiccator. Following the procedure for the preparation of neat PEO melt samples, PEO/$LiClO_4$ solutions were prepared in a dry box by controlled evaporation of methanol from PEO/$LiClO_4$/methanol solutions.

The light scattering technique employed in these studies was PCS. PCS is a noninvasive, dynamic light scattering technique used extensively in the study of the dynamic behavior of macromolecular systems [10,11]. Measurements were made using the 514.5-nm emission of an argon-ion laser (Coherent, Palo Alto, CA) or the 676.4-nm emission of a krypton-ion laser (Coherent). Scattered light was detected using an automated goniometer incorporating post-sample detection optics and electronics (Brookhaven Instruments, Holtsville, NY) and the resultant output processed with a BI-9000 multidecadic digital correlator (Brookhaven Instruments) to form scattered light relaxation functions. The sample cell assembly was thermostatted maintaining PEO melt sample temperatures during measurement within 0.1°C of set values.

Significantly, the characteristic times and lengths directly probed by PCS are significantly greater than those probed by other spectroscopic techniques such as NMR spectroscopy and Raman spectroscopy and those currently being considered in computer simulations, molecular dynamics calculations and theoretical treatments. In fact, characteristic lengths and times directly probed by PCS — hundreds of nanometers and fractions of seconds to thousands of seconds — may be considered to be on ''engineering'' scales.

To extend our understanding of PEO melts as transient, physical networks, it was necessary to test the wet gel model. To do this, the ''fluidity'' of PEO melt samples had to be assessed. Therefore, the viscosities of 1-K PEO melt samples with and without lithium salt were measured using a viscometer (Viscolab 3000, Cambridge Applied Systems, Boston) thermostatted to control set temperatures to within 0.02°C. This viscometer is quite compact allowing PEO melt viscosities to be measured in the dry box used for melt sample preparation. Unfortunately, the considerably higher viscosities of neat 50-K PEO melts could not be measured over the temperature range of interest so another viscometer, whose viscosity measurement range overlaps the upper end of the Viscolab 3000 range, ca. 20,000 cP, but also capable of measuring viscosities as large as ca. 10^6 cP, will be used to measure 50-K PEO melt sample viscosities.

Melt samples were made directly in the viscometer by controlled evaporation of methanol from volumes of PEO/methanol solution introduced sequentially into the viscometer well. The final such volume introduced was followed by the viscometer piston, and then the viscometer well containing the sample and piston was sealed with a custom fabricated cap so that a vacuum could be drawn on the well to facilitate the evaporation of the methanol. The evaporation occurred in three stages. The first stage employed a vacuum of roughly half an atmosphere at room temperature. In the second stage, both vacuum and temperature were increased to 2/3 of an atmosphere and 55°C, respectively. In the third stage, the temperature was further increased to 65°C (the boiling point of *neat* methanol at one atmosphere is 65°C), and solvent evaporation was considered complete when the viscosity, which increased as the solution methanol concentration decreased, leveled off and remained stable for a period of about 8 h. The whole process was undertaken very gradually typically requiring 1 to 2 weeks to complete.

4. Results and discussion

In PCS measurements, it is the scattered light intensity ACF that is measured. In the figures illustrating these functions presented here, ACFs are labeled as $g^{(2)} - 1$ and have been normalized to facilitate comparison between different measurements. PEO melt relaxation functions, $\phi(q,t)$, were extracted from the $g^{(2)}-1$ functions and then analyzed (see Ref. [5] for details). In $\phi(q,t)$, t is a time-shift variable and q is the magnitude of the scattering wave-vector. q is readily determined experimentally and depends mostly on the scattering angle in a light scattering measurement. The $\phi(q,t)$ obtained from a PCS measurement is proportional to the dynamic structure factor (or scattering function), $S(q,t)$, which is what is calculated in theoretical treatments of light scattering and used to help interpret PCS results. Generally, the relaxation behavior of the medium is considered to be due to a continuous distribution, $f(\Gamma)$, of exponential relaxations. For a given q, the relaxation function is expressed as

$$\phi(t)=\int_0^{\infty} f(\Gamma)\mathrm{e}^{-\Gamma t}\mathrm{d}\Gamma \tag{1}$$

with Γ as the ‘‘characteristic frequency’’ or ‘‘decay constant’’ for a given relaxation. The goal is then to extract the distribution function $f(\Gamma)$ from $\phi(t)$. This may be accomplished via a numerical inversion of the $\phi(t)$, or for polymer liquids, the approach can be more direct since oftentimes (the normalized version of) $\phi(t)$ has already been determined to be of the Kohlrausch, Williams and Watts (KWW) form [12,13],

$$\phi(t)=\exp\left[-(t/\tau)^{\beta}\right], \tag{2}$$

and the data are fit to Eq. (2) to determine β and an average value of τ. β is a measure of the width of the relaxation distribution function, $0\angle\beta\leq 1$, and τ is a relaxation function characteristic decay time corresponding to Γ, $\tau=1/\Gamma$. Fits to the data using Eq. (2) or inverting the data using Eq. (1) should lead to consistent results. In fact, we routinely use this consistency criterion to check our data.

In our measurements, KWW fits to monomodal relaxation functions yielded $\beta\cong 1$, demonstrating single-exponential behavior so that a single value of Γ (or of τ) represented the observed relaxation. When the decay of $\phi(t)$ is slower than exponential due to a distribution of relaxations in the sample — behavior we did not observe — β is less than 1. However, β values distinctly less than 1 have been observed in PCS studies of poly(propylene oxide) melts [14].

An interpretation of the light scattering results that describes the observed behavior is the following: at least for PEO molar masses of about 1000 Da and above, the PEO melt is a transient, physical network. In Fig. 2 (taken from Ref. [15], with permission) a computer-generated ‘‘snapshot’’ of a section of such a network is shown. The PEO network is transient and physical since bonds are temporary and are not covalent. Collagen hydrogels such as ‘‘Jello’’ are examples of transient, physical networks. An example of a permanent chemical gel is the extensively studied polyacrylamide hydrogel described in Ref. [16]. Note also that both are wet gels with water as the damping medium in which these networks are immersed. PEO melt network ‘‘cells’’ have a range of sizes, but the average cell size is ‘‘large,’’ i.e., of the order of the wavelength of light that is considerably larger, for example, than the gyration radius of 1- or 50-K PEO in an ideal environment. These large-scale inhomogeneities (the cells) and their fluctuations scatter light strongly and give rise to a diffuse and grainy appearance of the scattering volume. The network forms because PEO can associate with itself creating ephemeral ‘‘tie points’’ (the ‘‘physical’’ bonds) from place-to-place in the polymer, presumably as a result of short-ranged attractive interactions between permanent dipoles along the PEO chains. The single-exponential behavior and diffusive character of the observed monomodal relaxation functions arise because the PEO network behaves as a ‘‘wet gel,’’ that is it behaves as an elastic network immersed in a viscous medium [16,17]. In our samples, the wet gel consists of a PEO network in a viscous PEO fluid. Note that the cells illustrated in Fig. 2 are empty (the diffusive network dynamics is ‘‘built in’’ in the computer simulation — see Ref. [15] for details) whereas in a wet gel, these cells are filled by the viscous medium. The network is displaced from its equilibrium conformation by spontaneous thermal fluctuations. In turn, the network is continually relaxing — diffusively — moving through the viscous medium back to the equilibrium conformation. So it is the network displacement that is diffusing. It should be noted that highly cooperative behavior similar to the wet gel behavior described here for PEO has been reported in earlier PCS studies of the melts of at least two other linear, flexible polymers (Refs. [18,19]).

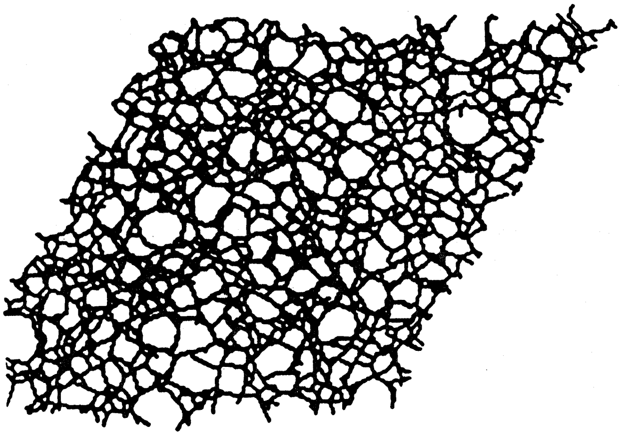

Fig. 2. Computer-generated representation of a polymer gel section.

Viscosity measurements of the 1-K melt made recently in our laboratory have allowed us to extend the transient, physical network view of the PEO melt based on light scattering results to the view that the melt can be considered to be a wet gel. In a wet gel, motions of the polymer network as it is displaced from and relaxes back to its equilibrium conformation are retarded by the viscous damping of the medium in which it is immersed. Accordingly, the characteristic decay constant, Γ, associated with the exponential decay of the relaxation function varies inversely as the damping medium viscosity, η [16]. So, for example, as Γ increases and η decreases with increasing temperature for the gel, the product $\eta\Gamma$ should remain fixed. For the 1-K PEO melt, the increase of Γ with temperature is illustrated in Fig. 7 of Ref. [5]. The measured decrease in η with increasing temperature for the 1-K PEO melt is illustrated here in Fig. 3. The results presented in Fig. 4 then demonstrate that $\eta\Gamma$ indeed remains fixed, at least over the temperature range examined (50–80°C), supporting the contention that the 1-K PEO melt behaves as a wet gel.

On occasion, bimodal, rather than monomodal, relaxation functions for PEO melts were observed (see Ref. [5]). Bimodal relaxation functions are discussed now because they were observed in our preliminary study of the effect of $LiClO_4$ on a 50-K PEO melt. In the neat 50-K PEO melt, the faster decay mode in the bimodal relaxation function was determined to be exponential and diffusive in character. This mode was due to the creation and dissipation of displacements of the PEO melt network from the equilibrium conformation. The second mode, slower than the diffusive mode, was also an exponential decay, but was not diffusive and attributed instead to more gradual rearrangements of the PEO network as a whole. Thus, in bimodal relaxation functions there is a diffusive characteristic time and a characteristic time corresponding to the overall rearrangement of the network as time goes by. To explain the observation of isolated diffusive relaxation modes, as for the monomodal relaxation functions discussed above (isolated network rearrangement modes were never observed), it was assumed that network rearrangements proceeded so slowly that their contribution to the relaxation function occurred outside the observation window of the PCS instrumentation.

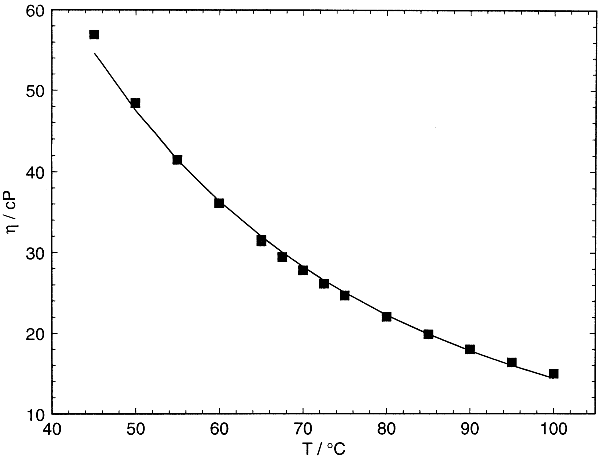

Fig. 3. Viscosity (η) dependence on temperature for a neat 1-K PEO melt sample.

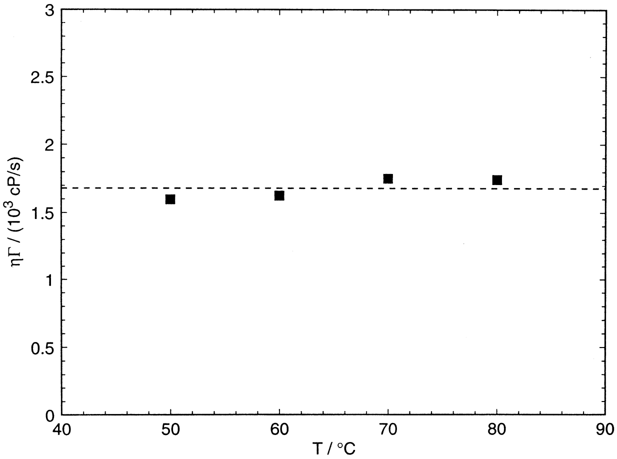

Fig. 4. Plot showing the temperature independence of $\eta\Gamma$ for a neat 1-K PEO melt.

$LiClO_4$ was chosen for the preliminary salt study because the PEO/$LiClO_4$ SPE system has been extensively studied and documented. Conductivity data for a variety of salt concentrations and temperatures are available (Chap. 4 in Ref. [20]) and these results could be correlated to PCS and viscosity measurement results in our lab. Moreover, from two PEO/$LiClO_4$ phase diagrams (Refs. [20,21]: data supplementary to Ref. [20] are presented in Ref. [21]), it was apparent that we could make meaningful and relevant measurements over a range of salt concentrations that included the concentration for which the maximum in conductivity had been measured. PEO/$LiClO_4$ melt temperature measurements made in our lab were consistent with the phase diagram data for the salt concentration range of interest. Also, melt temperatures over this concentration range are readily accessible in our lab, and at these temperatures it is easy to control sample temperatures accurately. Finally, $LiClO_4$ was selected because it is known to be particularly ‘‘friendly’’ to lithium foil electrodes that are commonly used in prototype lithium/polymer batteries.

With the results for neat PEO melts as a reference, PCS was then used to study the 50-K PEO melt at a temperature of 65°C with a salt mass fraction, X, of 0.20 (the mass of salt ratioed to the mass of [salt + polymer]). This salt concentration was chosen as the first to be investigated because it corresponds to the measured maximum in conductivity for the PEO/$LiClO_4$ system (Chap. 4 in Ref. [21]). At this concentration, the effect of the salt on the 50-K PEO melt dynamic behavior was dramatic (Fig. 5). A powerful and reliable inversion routine, CONTIN [22–24], was used to analyze PCS relaxation functions. This program extracted $f(\Gamma)$ and its corresponding temporal counterpart, $A(\tau)$. By using $\tau A(\tau)$ on the ordinate in Fig. 5, it

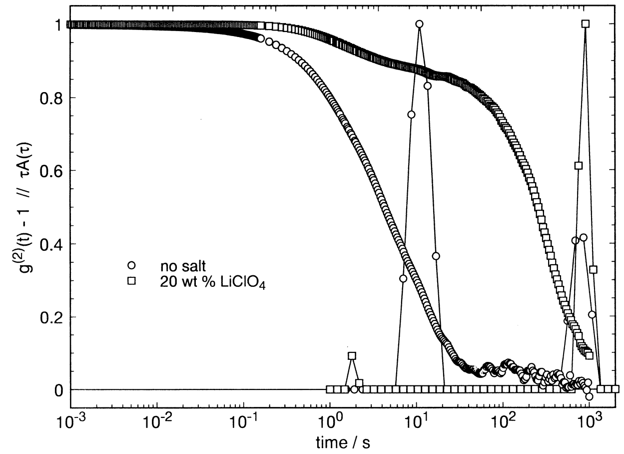

Fig. 5. Plot showing the dramatic effect of $LiClO_4$ on the relaxation function mode structure for a 50-K PEO melt sample. Measurements were made at 65°C and a scattering angle of 90°.

was possible to superimpose the relaxation function mode structure $[\tau A(\tau)]$ on the relaxation function itself. Use of $\tau A(\tau)$ rather than $A(\tau)$ compensates for the log scaling of the time-shift axis providing an ''equal area representation'' of mode peaks, i.e., the amplitudes of the modes may be compared directly to assess their relative contributions to the relaxation function.

The inversion found two well-separated single-exponential relaxation modes and their corresponding relaxation mode characteristic times. It is important to recognize that the analysis program found these two modes ''naturally,'' i.e., the program was not forced to find a relaxation function consisting of two exponential modes. Without salt, the characteristic time for the diffusive mode was about 100 times *smaller* than that for the rearrangement mode. With the salt ($X = 0.20$), the characteristic time for the diffusive mode was about 500 times *greater* than that for the rearrangement mode. Significantly, the network structure of the melt was retained upon the addition of $LiClO_4$. Interestingly, the two modes had switched roles: without salt, the diffusive mode is the faster of the two modes whereas at $X = 0.20$, the rearrangement mode was the faster of the two. Moreover, the separation between the characteristic times of the two modes increased from a factor of about 100 to a factor of about 500.

The reasons for these dramatic changes in PCS relaxation mode structure remain to be determined though the preliminary result suggests that they may be associated with the maximum observed for the conductivity at $X = 0.20$. To find out more about what is going on, a careful study will be made of the dependence of PCS relaxation mode behavior on salt concentration for a number of concentrations in the range $0 \leq X \leq 0.20$ for both the 1- and 50-K PEO samples. It may also be necessary to extend the upper limit of this salt concentration range. The slowing down of the diffusive mode upon addition of salt is certainly due in part to the increase in the viscosity of the medium in which the PEO network moves.

5. Future directions

Having demonstrated its utility in studying bulk polymer electrolyte structure and dynamic behavior, we address the use of PCS as a tool for studying SPE behavior at the electrode/electrolyte interface. For example, ions transported by the PEO network to the interface may then be transferred to the electrode. Thus it will be important to have information about the chain segment density in the transfer region (it is known that this density differs from that in the bulk — see Refs. [17,25,26]). In fact, it is possible to profile the chain segment density at such a boundary using the laser light scattering technique of evanescent wave PCS [25,26]. Moreover, in situ optical, spectroscopic and microscopic techniques using a similar internal reflection technique have been successfully employed in characterizing solid electrolyte interphase structures in rechargeable lithium batteries (see, e.g., Ref. [27]).

Earlier light scattering results demonstrated that PCS is a sensitive tool for studying the effects of solvents on PEO melts [5]. In this regard, water is a solvent of particular interest. ''Solid'' films of PEO are known to be hygroscopic and even small amounts of water can profoundly affect the condition of battery electrodes as well as the behavior of battery SPEs [20,21]. We have discovered that bulk PEO *melts* are also hygroscopic: when exposed to ambient humidity, bulk samples were ''plasticized'' via absorption of water. More quantitatively, the viscosity of a 1-K PEO melt measured at several temperatures was found to be consistently greater for a dehydrated sample measured in a dry box than that measured for a sample

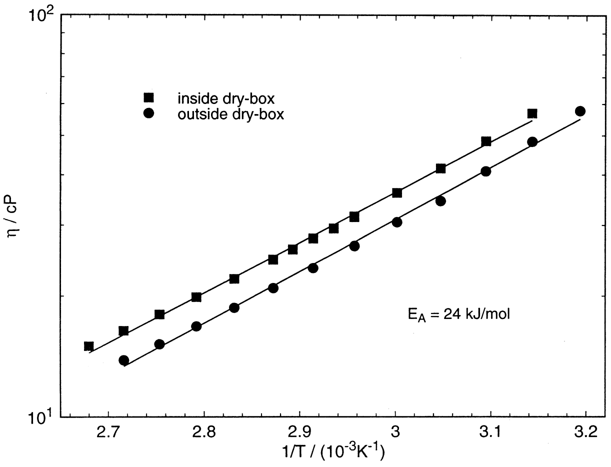

Fig. 6. Arrhenius plots showing the effect of humidity on the viscosity of a neat 1-K PEO melt sample. Note that the activation energy associated with viscous flow in this melt (24 kJ/mol) compares well with that for network diffusive motion (29 kJ/mol).

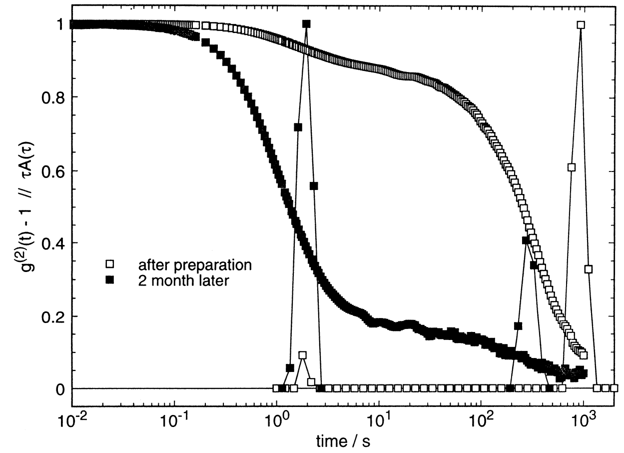

Fig. 7. Plot showing the effect of aging on the relaxation function mode structure for a 50-K PEO melt sample with $X = 0.20$. Measurements were made at 65°C and a scattering angle of 90°.

exposed to ambient humidity outside the box (Fig. 6). Based on these results and those from the earlier light scattering study, viscometry and PCS can be used as sensitive probes to study the effects of humidity on PEO melts. The possibility that water may even prove useful as a plasticizing agent in PEO SPEs has been suggested [28].

It is also important to understand how PEO melts ''age'' with time. As Fig. 7 shows, certain changes in a PEO/$LiClO_4$ melt ($X = 0.20$) over a 2-month period were readily detected in PCS relaxation functions. While the characteristic times of the diffusive and rearrangement modes remained essentially unchanged, the amplitude of the rearrangement mode increased by a factor of about 10 while that of the diffusive mode decreased by a factor of about 0.4. Although the mechanism(s) responsible for these changes are not yet clear and their elucidation awaits the results of further work, it is clear that PCS can be used to monitor and study PEO SPE changes with time.

Finally, in PCS measurements for both the 1- and 50-K PEO melts [5], we observed a small amplitude relaxation distinctly faster than those corresponding to the diffusive and rearrangement modes discussed above. These faster orientational relaxations — or ''structural'' relaxations — are of great interest as they too may play an important role in lithium ion transport in PEO melts. However, limitations in the fast-end detection capability of PCS instrumentation mean that PCS cannot be used to study such fast behavior. By using another noninvasive light scattering technique, namely that of Fabry–Perot interferometry, we will be able to study this behavior in detail.

6. Conclusions

Based on recent viscometry measurements, the picture of the PEO melt as an elastic network, as deduced from earlier light scattering measurements, has been refined to that of the ''wet gel,'' i.e., that of an elastic PEO network immersed in a viscous PEO medium. In addition, a preliminary comparison between light scattering measurement results for a neat PEO melt and a PEO melt containing 20% $LiClO_4$ demonstrates that the network structure in the melt remained after the addition of the salt and suggests that the salt affects the network behavior significantly. Finally, several promising lines of study for certain important features of PEO SPE behavior have been uncovered.

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