Network viscoelastic behavior in poly(ethylene oxide) melts: Effects of temperature and dissolved LiClO_4 on network structure and dynamic behavior

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The "wet gel" model used earlier to describe the results of dynamic light scattering studies of neat poly(ethylene oxide) (PEO) melts has now been successfully applied to PEO-melt/LiClO₄ solutions. The results of static light scattering and viscometry measurements along with measurements from dynamic light scattering revealed that with or without salt, the melt/gel was an overdamped system whose network diffusive relaxations were controlled by the damping liquid component of the gel. Important features of the melt/gel were significantly affected by the addition of LiClO₄. Examples of important changes included increases in the network mesh size even as "petrification" of the network by the salt rendered it less elastic. Nevertheless, for 1 K PEO melts the *essential nature* of the melt/gel remained uneffected. © 2002 American Institute of Physics. [DOI: 10.1063/1.1481059]

I. INTRODUCTION AND BACKGROUND

The use of polymer-based "solid" electrolytes, or "SPEs," is growing rapidly in a wide range of electrical and electronic devices.¹ Polymer electrolytes exhibit a number of advantages over conventional liquid electrolytes. For example, the viscoelasticity of polymers combines both solidlike and liquidlike properties making them particularly suited to battery applications. Already, lithium/polymer electrolytes are in use in high energy density rechargeable batteries, and it is hoped that batteries of this type will eventually serve for off-peak power storage and as light weight power supplies in electric and hybrid electric/internal combustion engine vehicles.

Among the variety of polymers and polymer/solvent formulations examined in the search for optimum electrolyte performance, salt-in-PEO systems are of particular interest. A problem in electrolytes free of additional solvents or plasticizers is the low conductivity they exhibit at ambient temperatures. This has led to the "warm, dry" polymer battery concept in which some battery energy can be used to keep the battery electrolyte temperature above the polymer melting point to ensure adequate electrolyte conductivity.²

To better understand SPE conductivity, attention is focused in this work on the molten state of the polymer electrolyte, i.e., on neat poly(ethylene oxide) (PEO) melts and PEO-melt/LiClO₄ solutions since it is in the molten state that ion transport and conductivity occur.³ To mount a successful attack on relevant SPE problems, such as the problem of low conductivity at ambient temperatures, a better understanding of the relationship between ion transport and polymer structure and dynamic behavior in SPEs is of paramount importance. Therefore, the techniques of static light scattering, dynamic light scattering [photon correlation spectroscopy (PCS)] and viscometry were used to study neat PEO samples and PEO/LiClO_4 samples at temperatures distinctly above their melt values.

Good conductivity in the warm, dry PEO/lithium battery is due principally to the transport of lithium ions. $LiClO_4$ is a particularly attractive choice for use in these polymer electrolyte solutions because it is, relatively speaking, a batteryelectrode "friendly" salt. Here, certain aspects of the structure and dynamic behavior of molten PEO/LiClO₄ solutions at various temperatures and for various salt concentrations are reported.

In two earlier light scattering studies of neat PEO melts,^{4,5} it was demonstrated that molten PEO is not the relatively bland, uniform and featureless medium it had generally been thought to be. Analysis of light scattered from PEO-melt density fluctuations revealed long-ranged structure which could be characterized as a physical network formed by the polymer in the melt. These PEO results were not unique; similar results were obtained in earlier light scattering studies of long-ranged density fluctuations in melt samples of the homopolymers poly (methyl-*p*-tolyl-siloxane) (Ref. 6) and poly(*n*-laurylmethacrylate).⁷

The results of the present and two earlier studies^{4,5} were interpreted in terms of the behavior of a random elastic network immersed in a viscous damping liquid. An example of such a "wet gel" system is the extensively investigated polyacrylamide hydrogel (see, for example, Tanaka *et al.*⁸). This system, as treated in the Tanaka *et al.* reference, serves as the principal basis for the interpretation and understanding of the results of the present study.

The existence of a thermally excited network in molten PEO samples was consistent with analyses of the light scattered from them; scattered light PCS autocorrelation function (ACFs) relaxations were single-exponential in form and originated from light scattered from long-ranged density fluctuations associated with displacements of the gel network. As for polyacrylamide hydrogels, very rapid melt re-

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laxations due to PEO thermal diffusion were not apparent in these ACFs; ACF characteristic times associated with thermal diffusion were estimated to be at least five orders of magnitude faster than those of the gel network. These dynamic light scattering results were supplemented with static light scattering and viscometry measurements for both neat PEO melts and PEO-melt/salt solutions. Interpretation of these results was greatly aided by important insights into the structure and dynamics of molten PEO from the wet gel perspective obtained from the earlier work of Tanaka *et al.*, from Nossal⁹ and from the recent, comprehensive review article of Bastide and Candau.¹⁰

Earlier, the results of PCS measurements used to study solutions of PEO in methanol and neat PEO melts, along with results from preliminary viscometry measurements, were described.^{4,5,11} While results for both highly entangled melts and unentangled melts were discussed ("entanglement" as defined by rheological measurements), the focus was on the unentangled PEO melt system. Although certain comparisons are made here between unentangled and entangled melt systems and a comprehensive study of the highly entangled 50 K PEO melt system initiated, the focus of the present study has remained on the unentangled PEO melt. In particular, the effects of temperature and $LiClO_4$ concentration on PEO melt structure and dynamic behavior were investigated and the utility of the wet gel model in interpreting and understanding PEO melt and PEO-melt/LiClO₄ solution behavior explored further.

II. EXPERIMENT

A low molecular weight PEO sample ($M_W = 1060$) with a narrow molecular weight distribution $(M_W/M_N = 1.03)$ custom synthesized by Polymer Standards Service (Mainz, Germany) was employed for most of the measurements reported here. Additional measurements were made using a custom synthesized high molecular weight sample (M_w) = 50 000, M_W/M_N = 1.05) from Polymer Source, Inc. (Doval, Canada). PEO chain ends for both samples were "capped" with methyl groups to avoid complicating behavior associated with chain hydroxyl end-groups. Based on rheological measurements, the 1 K PEO sample is unentangled in the melt (the critical value for the melt entanglement molecular weight is about 3500), while the environment in the 50 K melt is highly entangled.¹² Before final sample preparation and measurement, additional PEO purification was carried out as described earlier.⁴ Final sample preparation was carried out in a stainless steel glove box (Labconco, Kansas City, MO) filled with purified and dried nitrogen so that the moisture level in the box was maintained below 10 ppm V. Anhydrous lithium perchlorate (Fluka AG, Buchs, Switzerland) was further dried in a dessicator under vacuum before being placed into the glove box. Molten $PEO/LiClO_4$ solutions were made up in two ways. Either the melt/salt solution was made straightaway from a single preparatory methanol solution (anhydrous methanol, J. T. Baker, Phillipsburg, NJ) having the desired salt-to-polymer ratio followed by removal of the methanol using heat and vacuum, or a series of melt/salt solutions was made. This series began with a salt-free PEO/methanol solution followed by the serial addition of successive, measured amounts of salt in methanol. At each stage, another PEO/methanol/salt solution having a higher salt concentration was produced and methanol removed from each such solution using heat and vacuum produced another PEO-melt/salt solution having the desired salt concentration. Light scattering measurements from PEO-melt/LiClO₄ solutions having increasing salt concentrations were interleaved between successive salt additions. For light scattering measurements, PEO/methanol/salt solutions were filtered through 0.2 micron pore-size Teflon membrane filters (Millipore, Bedford, MA) into dust-free 5 mm square spectrofluorometer cuvettes (Starna, Atascadero, CA) or into dust-free 5 mm NMR tubes (Wilmad Glass, Buena, NJ). During methanol evaporation from light scattering cells, solution temperature and vacuum were increased continuously from ambient values to 68 °C and 23 in. of mercury. The progress of methanol evaporation was followed by checking the absolute weight of the sample in the glove box and was considered complete after the sample weight remained unchanged for at least 2 days. After methanol removal, sample cells were sealed under dry nitrogen and taken out of the glove box for measurement.

For viscosity measurements, PEO melt samples were produced using procedures similar to those used to produce light scattering samples and PEO/methanol/LiClO₄ solutions were loaded directly into the viscometer cell in the glove box. To check the course of methanol evaporation in the viscometer sample cell, the sample viscosity was monitored at regular intervals. When the viscosity had not changed for at least 2 days, melt viscosity measurements were made in the glove box using a Viscolab-3000 viscometer (Cambridge Applied Systems, Boston) thermostatted to control set temperatures to within 0.02 °C.

A melting point apparatus (Laboratory Devices, Inc./ Barnstead Thermolyne, Dubuque, Iowa) and/or direct, *in situ* observations, were used to determine sample melt temperatures.

For the most part, light scattering measurements were made employing a VV scattering geometry.¹³ Occasionally, a VH geometry was used to determine if behavior associated with transverse PEO network relaxations was apparent, to check for the presence of regular structure in the melt, and to verify the absence of multiple scattering in PEO melt samples. As was found in an earlier study,⁴ no evidence of multiple scattering or scattered light depolarization in the time window of interest was observed (Fig. 1). Samples were illuminated by the 514.5 nm emission of an argon-ion laser (Coherent, Palo Alto, CA) or the 647.1 nm emission of a krypton-ion laser (Coherent). In PCS measurements, scattered light was detected using an automated goniometer incorporating post-sample detection optics and electronics (Brookhaven Instruments, Holtsville, NY) with a BI-9000 multidecadic digital correlator (Brookhaven Instruments) then used to form scattered light intensity autocorrelation functions. Static light scattering (SLS) measurements were made using a model BI-2030 digital correlator (Brookhaven Instruments) and square cuvettes (Starna, Atascadero, CA) as sample cells. The angle-dependent signal in SLS measurements was corrected taking into account the cell geometry,



FIG. 1. A comparison between VV and VH scattered light intensity profiles $[I(q) \text{ vs } q^2]$ for the 16 wt. % 1 K PEO-melt/LiClO₄ solution at 60 °C. The incident laser vacuum wavelength was 647.1 nm and scattering angles ranged from 13° to 53°.

the angle dependence of the scattering volume, and the refractive indices of sample, toluene index matching liquid, and cell walls. In all measurements, the sample cell assembly was thermostatted maintaining sample temperatures within 0.1 °C of set values. PEO refractive index measurements at 514.5 nm and 647.1 nm were made over the appropriate range of temperatures for neat melt samples and PEO melt/ salt solutions with the appropriate range of salt concentrations using a model 60LR research refractometer (Bellingham and Stanley, Tunbridge Wells, UK).

III. RESULTS AND DISCUSSION

A. The wet gel model

As discussed in earlier work,^{4,5} strong scattering, singleexponential scattered light autocorrelation functions in the VV scattering geometry, and the absence of scattering in the VH scattering geometry for neat 1 K PEO melts could be explained if PEO melts behaved as "wet gels." The PEOmelt wet gel consists of a random physical network, having a range of mesh sizes, immersed in an amorphous damping liquid. The single-exponential character of scattered light ACFs demonstrated that the average mesh size was small compared to the wavelength of the probing laser light employed in light scattering measurements.⁸ The network formed in neat melts via association of PEO with itself creating "tie points" (the "physical bonds") from place-toplace, presumably due to hydrogen bonding and short-ranged attractive interactions between permanent dipoles along PEO chains. The network is physical since network tie points do not involve covalent bonds. Collagen hydrogels, such as "Jello" (gelatine) gels, are physical networks of the fibrous protein collagen in water. The polyacrylamide hydrogel mentioned in Sec. I is an example of a permanent, chemical wet gel.

In PEO melts, the gel network was continually displaced from its equilibrium conformation by spontaneous thermal fluctuations. These displacements then relaxed diffusively as the network moved through the damping liquid on its return to an equilibrium conformation.

As mentioned above, PEO melts are not the only systems exhibiting the type of cooperative, long-ranged behavior of the kind studied here. Similar behavior was reported in earlier PCS studies of the melts of at least two other linear, flexible homopolymers^{6,7} though the wet gel model was not used to interpret the results of these studies.

PEO-melt density fluctuations of wave vector **q** are responsible for the scattered light detected at a scattering angle θ in light scattering measurements. The particular fluctuation detected depends on several parameters with the magnitude of **q** given by $q=4\pi n \sin(\theta/2)/\lambda_0$. Here, *n* is the melt refractive index, θ is the scattering angle, and λ_0 is the vacuum wavelength of the incident laser light.¹³ In the Tanaka *et al.* treatment, reduced electric-field autocorrelation functions (ACFs) for PCS measurements from 1 K PEO melt wet gels were determined to be of the form (Fig. 2),

$$g^{(1)}(q,t) \sim e^{-\Gamma t} = e^{-(G/f)q^2t}$$
(1)

with Γ the exponential decay constant associated with the gel network relaxation, f the frictional force per unit volume on the network as it moves with unit velocity relative to the damping liquid, t the ACF time-shift variable, and G the network elastic modulus. Note that the roles of the gel elastic network and of the gel damping liquid are clearly separated in Eq. (1) with the former expressed in terms of the network modulus G in the numerator and the latter expressed in terms of the damping liquid friction coefficient f in the denominator.

In Eq. (1), $G = G_l$, the compressional modulus for network longitudinal displacements was probed in PCS measurements using the VV scattering geometry. For PCS measurements using the VH scattering geometry, $G = G_t$, the shear modulus for transverse displacements of the network. Oftentimes, G is written in terms of the bulk modulus K and the shear modulus μ with $G_l = K + \frac{4}{3}\mu$ and $G_t = \mu$. It is important to emphasize again that in the Tanaka *et al.* treat-



FIG. 2. Reduced and scaled light scattering intensity ACFs for 1 K PEO (open circles) and 50 K PEO salt-free melts at 70 °C. The peaks are the corresponding "equal area" characteristic relaxation time distributions, $\tau A(\tau)$, from CONTIN fits to the data. To facilitate comparison, each peak was scaled so its maximum value was 1. The scattering angle for both measurements was 90°.

ment, these moduli refer to the network component of the gel and not to the gel as a whole (network plus damping liquid). This choice amounts to assuming that the gel network relaxation is dominated by network elastic retractile forces rather than by osmotic forces. More recently, light scattering studies of gels have been carried out under conditions in which the retractile tension of the swollen network was balanced by the osmotic swelling force of the network/damping liquid "solution." Consequently, the roles of the osmotic as well as the network elastic contribution to the bulk modulus of the whole gel had to be considered in detail in interpreting the results of these studies.¹⁰ In the Tanaka et al. study, the conclusion that network elastic forces dominated gel dynamic behavior was borne out by the excellent agreement between the prediction that $\Gamma_I = 2 \mu / f$ for PCS measurements of polyacrylamide hydrogels and the direct verification of this prediction using independently determined values of μ and of f measured in the laboratory. Like the hydrogel, the PEO melt network was "soft" (G_l was small, roughly comparable to that of the softer polyacrylamide network treated in Ref. 8). In contrast to the hydrogel, the 1 K PEO melt was a single component system. Because the PEO-melt wet gel is envisioned as a PEO network immersed in a PEO damping liquid, osmotic restoring forces were assumed to be negligible in comparison to network retractile forces. Correspondingly, the osmotic contribution to the bulk modulus K was assumed to be negligible.

In Eq. (1), the exponential decay constants for the longitudinal and transverse relaxation modes are expressed as $\Gamma_{l,t} = D_{l,t}q^2$ with diffusion coefficients, $D_{l,t} = G_{l,t}/f$. Thus it is the $D_{l,t}$ that embody the behavior of the gel, per se, while the corresponding $\Gamma_{l,t}$ via q^2 reflect the geometry of the light scattering measurement as well.

In practice, the scattered light intensity for PEO melt measurements made using the VV scattering geometry was plentiful while that for measurements made using the VH geometry was negligible (see Fig. 1). In VV PCS measurements, the wave vector \mathbf{q} defines a direction in the otherwise

isotropic PEO melt, and it is the longitudinal diffusion, i.e., the diffusion of the network displacement along the axis defined by \mathbf{q} , that is probed. Then,

$$\Gamma_l = D_l q^2 = \frac{G_l}{f} q^2. \tag{2}$$

So, in VV PCS measurements of PEO melts, relaxations associated with the uniaxial, longitudinal compression of the gel network are probed.⁸

For soft networks of the kind studied here, it is revealing to express the network moduli *K* and μ in terms of the network Poisson's ratio σ and Young's modulus *E*,⁸

$$K = \frac{E(1-\sigma)}{3(1+\sigma)(1-2\sigma)},\tag{3}$$

$$\mu = \frac{E}{2(1-\sigma)}.\tag{4}$$

Because PEO melt networks are soft, σ is small compared to 1 (however, σ for the gel as a whole is *not* small compared to 1), and to a good approximation $G_l = E = 2\mu$. Consequently, as far as the network is concerned, for VV measurements the decay rates of PCS ACFs and their corresponding relaxation functions $\phi(t)$ are generally determined by the Young's modulus *E* of the PEO network along with *f* [see discussion and Eq. (6) concerning relaxation functions]. Explicitly,

$$E = \frac{\delta P}{\delta l/l} \tag{5}$$

with δP the pressure change associated with the uniaxial compression of the gel network and $\delta l/l$ its corresponding fractional length change along **q**. For "soft" networks, the modulus $G_l \cong E$ is small while for "stiff" networks G_l is large.



FIG. 3. Temperature dependence of reduced, normalized light scattering intensity ACFs for 10 wt. % 1 K and 50 K PEO-melt/LiClO₄ solutions taken at a scattering angle of 90°. 1 K PEO data (open circles) represent measurements from 40 to 80 °C in 5 °C increments while those for 50 K PEO are for 50 to 80 °C in 5 °C increments. The corresponding Arrhenius activation energies are 35 and 52 kJ/ mol, respectively. The solid curves are KWW function fits to the data which amount to fits to single exponential decay functions since throughout, $\beta \approx 1$.

B. Data reduction and analysis

While single-mode relaxation behavior had already been reported for neat 1 K and 50 K PEO melt samples in Ref. 4, bimodal ACFs consisting of a faster relaxation mode along with a slower relaxation mode were also observed. The slower mode was attributed to gradual rearrangements of the physical network as a whole while the faster mode was shown to be due to diffusive network relaxations. The complete absence of the slow mode in all the ACF measurements made in this study is considered to have resulted from evolutionary improvements in sample preparation. In particular, improvements resulted from a more effective sample purification procedure. Details of this procedure will be made available to the interested reader upon request. In effect, melt networks studied here were trapped in a permanent state, a state having network characteristic rearrangement times so long they were well outside the correlator time-shift window. As a result, the present work deals solely with single-mode, single-exponential diffusive relaxation functions.

Reduced ACFs, labeled as $g^{(2)}-1$, were computed by subtracting measured intensity ACF baselines from these ACFs and then dividing the resulting function by the baseline. Comparisons between these reduced ACFs were facilitated (as was done earlier, see Ref. 4) by scaling initial $g^{(2)}$ -1 values to 1 (Figs. 2 and 3). Relaxation function decay constants Γ were then extracted from electric field autocorrelation function moduli, $g^{(1)}(q,t)$, via the relation $[g^{(1)}]^2 = g^{(2)}-1$ with the relaxation function $\phi(q,t)$ proportional to $g^{(1)}$. For a given q, $g^{(1)}$ —and thus the relaxation function $\phi(t)$ —can be represented in terms of a continuous distribution of exponential relaxations,¹⁴

$$g^{(1)}(t) = \int_0^\infty w(\Gamma) e^{-\Gamma t} d\Gamma = \int_0^\infty A(\tau) e^{-t/\tau} d\tau$$
(6)

with $\tau = 1/\Gamma$, τ a characteristic relaxation time, and $w(\Gamma)$ and $A(\tau)$ the "frequency space" and "time space" relaxation distribution functions, respectively. Again, in the present

work, Γ and τ are characteristic parameters for longitudinal relaxations of the melt network and so, for example, Γ is denoted as Γ_l .

In practice, it has been found that PCS relaxation functions for polymeric liquids are oftentimes well fit by the semiempirical Kohlrausch–Williams–Watts (KWW), or "stretched exponential" relaxation function. For a given q, $\phi(t)$ is of the form,¹⁵

$$\phi(t) \sim \exp[-(\Gamma_l t)^{\beta}]. \tag{7}$$

The dispersion parameter β , $0 < \beta \le 1$, then provides a measure of the width of the distribution of decay rates, Γ_l . A β value of 1 corresponds to single-exponential relaxation behavior, while smaller β values indicate broader distribution functions. In analyzing PCS relaxation functions, $\phi(q,t)$, either the inversion routine CONTIN (Ref. 16) was used to determine the distribution function $w(\Gamma)$ or $A(\tau)$ from $g^{(1)}(t)$ (Fig. 2) and/or KWW fits to $g^{(2)}-1$ were used. Both approaches produced consistent results yielding essentially the same relaxation rates. For KWW analyses, the dispersion parameter β was close to 1 (deviating at most by about 10%) and, correspondingly, narrow relaxation rate (or relaxation time) distributions were obtained using CONTIN. Taken together, the two methods confirmed the singleexponential nature of measured monomodal ACFs at different temperatures and different salt concentrations for both the 1 K and 50 K PEO melts.

Static light scattering was used to further characterize the long-ranged order and structure evident in neat 1 K PEO melts from visual observation and from PCS measurements. Using a range of small q values, i.e., small scattering angles (the smallest angle employed was 13°) along with the 647.1 nm emission of a krypton-ion laser, long-ranged fluctuations in these melts were probed. The static density–density correlation function $\rho(r)$ for long-ranged fluctuations is given by¹⁷



FIG. 4. Reciprocal Orstein–Zernicke plots { $[I(q)]^{-1}$ vs q^2 } for the neat 1 K PEO melt (solid circles) and for a 16 wt. % 1 K PEO-melt/LiClO₄ solution at temperatures ranging from 45 to 80 °C. The incident laser vacuum wavelength was 647.1 nm.

$$\rho(r) \sim \frac{e^{-r/\xi_S}}{r},\tag{8}$$

with *r* a separation distance between pairs of points in the fluctuation and the "correlation length," ξ_s , a measure of the size of the fluctuation. By this measure, the melt is considered to be "uniform" for distances greater than ξ_s . The corresponding expression for the scattered light intensity I(q) is given by the Ornstein–Zernicke equation,¹⁷

$$I(q) = \frac{I_0}{1 + q^2 \xi_s^2},\tag{9}$$

with $I_0 = I(q)$ for $q \to 0$. Melt correlation lengths ξ_s were extracted from fits of the reciprocal function $[I(q)]^{-1}$ to the reciprocal of Eq. (9) (Figs. 1 and 4).

C. Neat PEO melts

The neat 1 K PEO melt is the reference system for the present work. Having investigated the structure and dynamic behavior of the neat melt, the effects of LiClO_4 on PEO melts were interpreted in part by comparing these results with those of the neat melt system. In addition, preliminary results for the 50 K PEO melt, with and without salt, are also presented for comparison with 1 K PEO results and to introduce the study of highly entangled PEO melts. Neat 1 K and 50 K PEO melt temperatures were determined to be about 40 °C and 60 °C, respectively.

As for earlier measurements, the q^2 dependence of Γ_l (Fig. 5, Fig. 8 in Ref. 4) confirmed the diffusive character of

neat 1 K PEO melt relaxations. Similarly, the diffusive character of ACF relaxations for neat 50 K PEO melts had been demonstrated earlier (Fig. 9 in Ref. 4).

As for the 1 K PEO neat melt, VH scattering from 50 K PEO neat melt samples was negligible demonstrating that as for 1 K PEO melts, regular structure and multiple scattering were also absent in 50 K melts.



FIG. 5. Wave vector dependence of Γ for the neat 1 K PEO melt and four 1 K PEO melt/LiClO₄ solutions measured at 60 °C and scattering angles from 20 to 120°. The incident vacuum wavelength was 514.5 nm. Γ values were extracted from KWW function fits to the data. A rescaled Γ axis is used in the inset to better depict the behavior of the three slowest relaxations. Γ uncertainties were estimated to be about 20% and 10% for q^2 values below and above about 2×10^{10} cm⁻², respectively.

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FIG. 6. The salt concentration dependence of activation energies (filled circles and open triangles) E_D and E_η , respectively, from light scattering and viscosity measurements of 1 K PEO-melt/LiClO₄ solutions. Also shown are relaxation rates, Γ , extracted from KWW fits to light scattering data (open circles). Γ values from different samples and multiple measurements of the same sample are shown to illustrate the difference in the variability of measurements made with and without salt. The inset presents Γ on a logarithmic scale to illustrate the exponential decrease in Γ with increasing X and to emphasize the reduction of scatter in Γ upon the addition of salt.

A side-by-side comparison of scattered light intensity ACFs for neat 1 K PEO and neat 50 K PEO melt samples at 70 °C and a scattering angle of 90° is shown in Fig. 2. Also illustrated are the corresponding τ distribution functions. For comparison, these are presented using the "equal area" representation,¹⁴ $\tau A(\tau)$, with peak maximum values scaled to 1. Despite the difference in their states of entanglement, apparent in the significant slowing down of the relaxation in the 50 K melt compared to that for the 1 K melt, both samples exhibited monomodal, single-exponential relaxation behavior. The factor of about 50 difference in Γ_l between the neat 1 K and 50 K PEO melt samples (Fig. 2) cannot account for the reported four-orders-of-magnitude increase in the 50 K melt viscosity over that of the 1 K melt.¹⁸ This considerable increase in the melt viscosity with increasing molecular weight reflects the transition in the PEO melt from the unentangled to the entangled state. Considering Eq. (2), this disparity in changes in the relaxation rate and in the viscosity for the two molecular weights suggests that in the highly entangled environment of the 50 K PEO melt, the network elastic modulus G_1 increased by a factor of about 200. However, suggesting that G_1 increased in this way assumes that as for 1 K PEO melts, the wet gel model can also be used to describe 50 K PEO melts. Verification of this assumption awaits the results of further 50 K PEO melt studies.

While for a given temperature η values were stable and reproducible, Γ_l varied considerably (Fig. 6, open circles). Note in Fig. 6 that the results from different samples and multiple same-sample measurements for $\theta = 90^\circ$ and $T = 60^\circ$ C are not averaged. In this way, the rather large change in data variation between samples with and without salt is highlighted. In contrast with neat melt results, the addition of salt resulted in relaxation rates Γ_l that were stable and reproducible. This stability and reproducibility was observed both between different samples and for observations of the same sample made at different times (a discussion of the effects of LiClO₄ in this regard and of the determination of reliable neat-melt Γ_l results is presented below).



FIG. 7. Arrhenius plots of PCS ACF relaxation rates, Γ , for six 1 K PEO-melt/LiClO₄ solution with temperatures ranging from 40 to 80 °C. Measurements were made at a scattering angle of 90° with Γ values extracted from KWW fits to light scattering ACFs. Corresponding activation energies E_D are presented in Fig. 6.

The especially tenuous nature of neat 1 K PEO melt transient networks was demonstrated earlier by the disappearance of network behavior altogether upon the addition of a very small amount of methanol to a 1 K PEO melt.⁴ It is also well known that small amounts of water can dramatically effect the properties of PEO melts.¹ In the present work, same-sample measurements were repeated after a period of typically 1–2 weeks with Γ_l values both increasing and decreasing. It was concluded that despite great care in sample preparation, variations in residual amounts of moisture and solvent resulted in large variations in neat melt Γ_l values both for measurements of the same sample at different times as well as for measurements of different samples (Fig. 6).

In investigating neat-melt temperature behavior, $\Gamma_l(T)$ results obtained both for time-to-time measurements of the same sample and for measurements from different samples were well described by Arrhenius plots of the data [a more complete discussion of this temperature behavior is presented below in the discussion of the behavior of $D_l(T)$]. Despite variations in neat-melt $\Gamma_l(T)$ values, these plots yielded a family of parallel, straight lines (not shown here), each having the same slope and thus the same value for the activation energy for network diffusion. Selecting a reliable neat-melt $\Gamma_l(T)$ data set, as described below (Fig. 7, open squares), the activation energy, E_D , for the diffusive relaxation of the gel network was determined to be 29 kJ/mol.

The variability observed in Γ_l for neat 1 K PEO melts was not observed in viscosity measurements; repeated samesample and sample-to-sample viscosity data were consistent and reproducible for all samples, with or without salt. Neat melt Γ_l variations and the invariance of the η results may be explained by differences in the techniques of light scattering and of viscometry. Light scattering was noninvasive and sufficiently sensitive to detect and monitor gel network behavior. On the other hand, viscosity measurements, made by pushing a piston through the melt, did not distinguish between the gel network and the gel damping liquid, responding instead to an averaged, "uniform" liquid medium. Moreover, because of the tenuous nature of the network, it was



FIG. 8. Arrhenius plots of viscosities, η , for seven 1 K PEO-melt/LiClO₄ solutions with temperatures ranging from 50 to 90 °C. Corresponding activation energies E_{η} are presented in Fig. 6.

assumed that these viscosity measurements fairly represented the viscosity of the damping liquid component of the 1 K PEO melt. Due to the relative insensitivity of viscosity measurements, the variability observed in Γ_1 was not observed for η . In this regard, recall also that the network detected by light scattering for 1 K PEO melt samples was not apparent in earlier rheological measurements either. In fact, the value of the critical molecular weight for entanglement in the melt was determined to be about 3500 daltons,¹² a value distinctly greater than the 1000 dalton molar mass of the 1 K PEO sample studied here. Nonetheless, viscosity measurements are known to be sensitive to small amounts of moisture present in PEO melts.¹ Evidently, the amounts of residual water and solvent in PEO melts were sufficiently small that although their effects were not detectable in viscometry measurements, they were clearly evident in light scattering measurements.

From the neat melt $\eta(T)$ Arrhenius plots (Fig. 8), η $\sim e^{E_{\eta}/RT}$ and the activation energy for viscous flow of the gel damping liquid, E_{η} , was determined to be 25 kJ/mol. The Arrhenius behavior and the 1 K neat melt results presented here are consistent with the results of earlier 1 K PEO-melt viscosity measurements made over a similar range of temperatures using a cone-and-plate Shirley-Ferranti viscometer.¹⁹ The equivalence for the neat melt of independently determined values for E_{η} and E_D —the activation energies for viscous flow of the gel damping liquid and for diffusive relaxation of the gel network, respectively-reveals the nature of the coupling between the network and the damping liquid. Viewed from the perspective of the wet gel model, the 1 K PEO melt is an overdamped system with the network relaxation governed by the viscosity of the damping liquid. This conclusion is consistent with the singleexponential form of the relaxation function $\phi(t)$ and with the earlier assertion that the modulus of the 1 K PEO-melt network was small, i.e., the assertion that the network was "soft." Moreover, the equivalence of E_n and E_D , implying overdamping in the PEO melt wet gel system, persisted throughout the range of LiClO_4 concentrations examined (see below).

For network diffusion, $D_l = G_l/f$ [Eq. (1)], and quite generally, the network modulus depends directly on the absolute temperature.¹⁷ Since $f \propto \eta$, from Eq. (1) and the direct dependence on absolute temperature of G_l , the temperature dependence of D_l goes as $D_l \sim Te^{-E_\eta/RT}$, a result consistent with the observation that $E_D = E_\eta$. So, although the form of the temperature dependence for D_l was not strictly Arrhenius, network diffusion was nonetheless a thermally activated process, and meaningful determinations of E_D could be obtained using $D_l(T)$ Arrhenius plots, $\ln D_l \sim \ln T - E_D/RT$. Plot slopes, and thus activation energies E_D (equivalent to E_η), were uneffected by the $\ln T$ term, a "shift" term contributing an essentially constant value to $\ln D_l$ over the range of temperatures employed.

By combining the light scattering and viscometry results in the product ηD_l , since $\eta D_l \sim G_l$, the behavior of the gel network modulus G_l could be examined [see Eq. (2)]. This was possible because independently determined PCS and viscometry measurements of the temperature dependences of $D_{l}(T)$ and $\eta(T)$ were very consistent throughout; $E_{D} \cong E_{n}$ both for neat melts and for PEO-melt/LiClO₄ solutions over the range of LiClO₄ concentrations examined. Then E_D $-E_{\eta} \cong 0$ in the exponent of the product ηD_{l} so that the strong exponential temperature dependence in $\eta(T)$ was "canceled" by the equally strong exponential temperature dependence in $D_{l}(T)$. As a result, the temperature dependence of ηD_1 was apparent. Significantly, and somewhat unexpectedly, the temperature dependence of G_l for this complex PEO melt gel network was that expected for an idealized network; it was linear in T and thus consistent with the wet gel model (Fig. 9, first panel). Based on the linear temperature dependence of G_l , ηD_l was expected to increase about 9% over the temperature range examined. From linear fits to the data, ηD_1 actually increased somewhat more slowly for one sample and somewhat more rapidly for the other (first panel Fig. 9, open and filled squares, respectively; for a discussion of the selection of these two neat-melt samples, see Sec. III D). It should also be noted that in an earlier study, $\eta \Gamma_l$ for the neat 1 K PEO melt appeared to be temperature independent (Fig. 4, Ref. 5). However, when plotted alongside the neat melt data from the present study (Fig. 9), the temperature dependence of the earlier results recast as ηD_1 is apparent and is seen to be consistent with that observed here since all three plots have comparable slopes. However, the data from the earlier study are distinctly larger in magnitude than those from the present study. This difference is a reflection of the large variability in *neat* melt Γ values resulting from variations in melt sample residual methanol and water, as discussed above (this variability is clear in Fig. 6, as well).

Static correlation lengths ξ_s and $q \rightarrow 0$ I(q) values, I_0 , for neat 1 K PEO melts were obtained from static light scattering measurements by fitting the reciprocal of I(q), measured for a number of scattering angles, to the reciprocal of the Orstein–Zernicke expression [Eq. (9)]. Strictly speaking, fits to the Orstein–Zernicke expression require $q\xi_s < 1$. Because ξ_s values were large, this criterion was not met across



FIG. 9. Temperature behavior of viscosity and diffusion coefficient products, ηD_l , for 1 K PEO-melt/LiClO₄ solutions at eight salt concentrations with temperatures ranging from 50 to 80 °C. Light scattering measurements were made at a scattering angle of 90° and Γ values were extracted from KWW fits to light scattering ACFs.

the entire range of scattering angles employed. Nonetheless, the fits are convincingly good and higher and lower angle data fall on the same straight lines throughout the range of angles employed (Fig. 4, solid circles).

Typical results for I(q) are presented in the plot of I(q) vs q^2 in Fig. 1 (see also Sec. III D). It was found that both neat-melt I(0) values $[I(0) \cong 100 \text{ Hz}]$ and ξ_S values $(\xi_S \cong 200 \text{ nm})$ remained constant across the temperature range explored (Fig. 4, solid circles). The temperature independence of I(0) was in accord with the expected dependence with temperature,^{10,17}

$$I(0) \sim T/G_l, \tag{10}$$

since it had already been determined that $\eta D_l \sim T$ and thus $G_l \sim T$.

Large, order-of-visible-light wavelength ξ_s values reveal unusually long-ranged order in neat PEO melts. ξ_s magnitudes are consistent with the visual observation of strong scattering and slow relaxations seen in PCS ACFs (Figs. 2 and 3). Values of ξ_s are of the order of the probe wavelength, $2\pi/q$, and associated characteristic times for network relaxation are correspondingly quite long. Note that these ξ_s values are much larger than the size (the gyration radius, for example) of an individual 1 K PEO chain in the amorphous component of the melt.

While it is tempting to interpret ξ_s as a measure of network mesh size, this is generally not the case.¹⁰ As mentioned above, the single-exponential character of PCS ACFs demonstrates that it was not the case here either. In this regard, it is important to note that the earlier interpretation of ξ_S as a measure of gel "cell" size⁵ was incorrect. ξ_S is a measure of the size of the density fluctuations responsible for the scattered light. In turn, these density fluctuations are associated with displacements of the elastic gel network. As far as static light scattering measurements are concerned, the system is "uniform" for distances greater than ξ_S .

The temperature independence of ξ_s for the neat melt (Fig. 4) reveals a certain network thermal stability presumably originating from its mechanical integrity.

Long characteristic times, $1/\Gamma$, corresponded to slow relaxations of long-ranged network displacement fluctuations and large associated dynamic lengths, ξ_D , were extracted from D_l results using the Stokes–Einstein expression,^{13,17}

$$D_l = \frac{k_B T}{6\pi \eta \xi_D},\tag{11}$$

with k_B the Boltzmann constant. Note that $\xi_D \sim T/\eta D_l$ and the insensitivity of ξ_D to variations in temperature reflects the linear dependence on temperature of the network modulus ($G_l \sim \eta D_l \sim T$, Figs. 9 and 10, first panel). ξ_D is the hydrodynamic screening length in the system; the behavior of the gel network is affected by perturbations in the gel fluid for distances as great as ξ_D and negligibly affected for dis-



FIG. 10. Temperature dependence of dynamic correlation lengths, ξ_D , for eight 1 K PEO-melt/LiClO₄ solutions with temperatures ranging from 50 to 80 °C. Light scattering measurements were made at a scattering angle of 90° and ξ_D [Eqs. (2), (11)] values were extracted from KWW fits to light scattering ACFs.

tances greater than ξ_D . In neat melts, ξ_D and ξ_S are of the same order of magnitude (first panel in Figs. 4 and 10). However, Eq. (11) was derived for idealized networks possessing regular crosslink functionality with crosslinks connected by individual polymer strands having well-defined conformations. Moreover, the 6π factor in the denominator is not to be taken literally; it is there "as a convenient reminder of the similarity (of the expression) with the Stokes Law for viscous motion of a sphere." ¹⁷ So, ξ_D values calculated using Eq. (11) are approximate to the order of a constant multiplier. Nevertheless, the behavior of ξ_D is important and the fact that ξ_D and ξ_S are large and of comparable magnitude is significant in that it shows that long-ranged, highly cooperative behavior in 1 K PEO melts was observed in both static and dynamic light scattering measurements.

D. PEO-melt/LiClO₄ solutions

Adding $LiClO_4$ reduced PEO melt temperatures across the range of salt concentrations examined. This behavior is consistent with the PEO/LiClO₄ phase diagram presented in Ref. 1. However, it must be noted that PEO molecular weights from such studies were presumably significantly greater than the 1000 dalton sample studied here and were thus well above the critical molecular weight for polymer entanglement. As the sample warms up and the melt temperature is approached from below, the premelt exists as a metastable, two-phase system consisting of a population of salt-sequestering spherulitic crystallites immersed in a PEO melt/salt solution. It has been shown that up to the eutectic, addition of salt lowers the melting temperature,¹ a reduction attributed to increasing disruption of otherwise crystalline or semicrystalline regions in the premelt system. As an example of this behavior from the present study, the maximum LiClO₄ concentration of 30 wt.% (X_S =0.30) in the 1 K PEO melt/salt solution reduced the melt temperature 15 °C relative to the neat melt value.

As for neat melts, results for 1 K PEO-melt/LiClO₄ solutions were consistent with the wet gel model. PCS ACFs were monomodal, single-exponential decays and Γ_l was found to depend linearly on q^2 at all salt concentrations, demonstrating again the diffusive nature of the gel network relaxation process in these polymer-plus-salt solutions (Fig. 5).

A comparison between 1 K and 50 K PEO melt behaviors was made, this time at a LiClO₄ concentration of 10 wt. % (Fig. 3). PCS ACFs for the 50 K melt exhibited the monomodal, single-exponential relaxation character characteristic of 1 K melts with and without salt. In addition, in Fig. 11, the shift of $\tau A(\tau)$ peaks (equal area representation) to successively longer characteristic times illustrates the systematic, monotonic slowing down of network relaxations with increasing salt concentration for a given temperature. Note that to facilitate comparison, $\tau A(\tau)$ peaks have been scaled to have a maximum value of 1.

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FIG. 11. Equal-area relaxation time distributions, $\tau A(\tau)$, extracted from CONTIN fits to light scattering ACFs for six 1 K PEO-melt/LiClO₄ solutions. For comparison purposes, peak maximum values were scaled to 1. Salt concentrations increase monotonically as τ increases: $X_s = 0.00, 0.05, 0.10, 0.17, 0.23$, and 0.27. Measurements were made at a scattering angle of 90° and a temperature of 60 °C.

As for the neat melt, there was about a 50-fold slowing down in the ACF relaxation for the 50 K polymer-plus-salt melt compared to that for the 1 K polymer-plus-salt melt. However, the 50 K sample ACF relaxation rates exhibited stronger temperature dependence than did the 1 K sample. Arrhenius analyses of $\Gamma_l(T)$ for the 1 K and 50 K PEO samples yielded activation energies of 35 kJ/mol and 52 kJ/ mol, respectively, reflecting the greater barrier height for the diffusive relaxation of the gel network in the entangled melt as compared to that for the unentangled melt.

As pointed out earlier, the addition of $LiClO_4$ to 1 K PEO melts effectively eliminated the Γ_l variability found in neat melts between different samples and for the same sample at different times (Fig. 6). This reduction in Γ_l variability upon the addition of salt can be accounted for in at least two ways. First, recalling that LiClO₄ disassociates essentially completely in both water and methanol, Li⁺ and ClO_4^- ions in the melt, along with other ion complexes, "tied up" residual water and methanol reducing their effect on the melt. Second, along with attractive dipole-dipole interactions and those due to hydrogen bonding (as in the neat melt), additional ion mediated intra- and interchain links between portions of PEO chains stabilized the network¹ reducing its susceptibility to residual water and methanol solvation effects. At the same time, linking increased the viscosity of the damping liquid component of the gel.

Bearing in mind the variability of neat-melt Γ determinations, a method to determine more reliable neat-melt values of Γ is illustrated in Fig. 6; extrapolation of stable $\Gamma(X)$ values to zero-salt concentration (the cross-hatched point) gave reproducible zero-salt results. For example, in Fig. 6, $\Gamma(0) \approx 25$ Hz. This extrapolated value agreed well with the 60 °C Γ result from two of several neat melt samples studied. Because of this good agreement for extrapolated values of Γ and the reasonable temperature behaviors of ηD_l cited above, these two neat-melt samples were assumed to have been least effected by residual moisture and solvent and were therefore selected for further study. They are illustrated in the data in the first panels of Figs. 9 and 10 as the open and solid

squares and in the $60 \,^{\circ}$ C neat-melt result (open squares) in Fig. 7.

As for neat melts, viscosity values were stable: η values for different samples and values for the same sample at different times remained consistent throughout the range of salt concentrations examined.

The temperature behaviors of Γ and of η for different LiClO₄ concentrations are illustrated in the Arrhenius plots presented in Figs. 7 and 8. With increasing T at a given salt concentration X_S , Γ increases monotonically and η decreases monotonically. With increasing X_S at a given temperature T, Γ decreases monotonically (see also Fig. 11) and η increases monotonically. For example, at 60 °C, Γ_l decreased markedly and η increased markedly—about two orders of magnitude each-over the salt concentration range, $0 \le X_S \le 0.27$. Figures 7 and 8 also illustrate increasing slope magnitudes with increasing salt concentration, i.e., E_D and E_n increased monotonically with increasing X_S . This behavior is clearly illustrated in Fig. 6. Moreover, it is seen in Fig. 6 that $E_D \cong E_n$ over the salt concentration range investigated (the viscosity measurement for the highest salt concentration was less reliable than the other measurements because it was made at the limit of the measurement range of the viscometer). This equivalence in activation energies and the single exponential character of relaxation functions demonstrated that with added salt, as for the neat melt, the gel system was overdamped with gel network relaxations controlled by corresponding damping liquid viscosities. The decrease in Γ and the increase in E_D with increasing X result from corresponding increases in η , an increase consistent with the corresponding increase in the numbers of ion mediated intra- and interpolymer links in the damping liquid component of PEO melts. Restated, the increase in the activation energy for the diffusive relaxation of the gel network resulted from the increase in activation energy for the viscous flow of the damping liquid through the network.

As for neat melts, the equivalence of E_D and E_{η} throughout the salt concentration range studied meant that the product ηD_1 could be used to examine the behavior of the gel network modulus G_l in polymer/salt solutions. Because of the exceptional stability and smoothness of the viscosity data (Fig. 8), where necessary, interpolated or extrapolated values of η were used to determine ηD_l to match the salt concentrations used in corresponding Γ measurements (Fig. 9). For the most part, the increasing "jumpiness" evident in the ηD_1 data as one proceeds from panel 2 to panel 8 of Fig. 9 can be attributed to two sources. The first source was the accumulation of uncertainty in the melt sample salt concentration. This uncertainty increased as small, stepwise additions of salt were made to produce the PEO/methanol solutions used in preparing a succession of melt samples for both light scattering and viscometry measurements. The second source of uncertainty was the reduction in the statistical quality of PCS ACFs and the corresponding increase in statistical uncertainty in Γ with increasing salt concentration arising from longer and longer gel network relaxation times. This reduction in the statistical quality of the data could only be partially offset by increasing measurement times since these times eventually became intractably long.

Compared with neat melt results, both the magnitude of ηD_1 and its dependence on temperature were reduced after the addition of salt (see panels 2–8 of Fig. 9), ηD_l dropped from about 130×10^{-17} N to about 95×10^{-17} N indicating that the network had become somewhat "softer" since ηD_1 and thus G_l had become smaller. In turn, the network mesh size became larger with the addition of salt since G_l varies inversely with the mesh size. In contrast to neat melt behavior, there was no apparent temperature dependence in ηD_1 at any salt concentration, although fluctuations in ηD_1 values increased somewhat with increasing salt concentration. In panels 2-8 of Fig. 9, ηD_l values fluctuated about a mean value of 95×10^{-17} N with a rms deviation of 29 $\times 10^{-17}$ N. Initially, the uncertainty in individual measurements of ηD_1 was estimated to be about 20×10^{-17} N, a result in reasonable accord with this rms deviation. Of the two, 29×10^{-17} N was taken to be perhaps the more reasonable (at least the more conservative) estimate of the uncertainty associated with values of ηD_1 , and correspondingly it was concluded that there was also no clear dependence of ηD_1 on salt concentration.

Since the linear temperature dependence of G_l arises from the thermal work k_BT required to stretch and displace the elastic network from equilibrium during a thermal fluctuation, it was concluded that while it had become "softer" $(\eta D_l \sim G_l$ decreased), the network had also become somewhat less elastic. That is, the network had at the same time become somewhat "stiffer" (smaller ηD_l temperature dependence). This apparent contradiction in network behavior can be resolved by considering the way in which melt samples were prepared. Salt-containing PEO melts were produced by evaporating methanol from methanol solutions containing both LiClO₄ and PEO. In an earlier study¹¹ it was shown that PEO coils in methanol solutions containing LiClO₄ were larger than those in salt-free methanol solutions due to repulsive interactions between PEO/salt-ion complexes along PEO chains which had formed in saltcontaining solutions. Corresponding to this increase in PEO coil size in salt-containing methanol solutions, upon the evaporation of methanol, network mesh sizes in solvent-free salt-containing melts were larger than mesh sizes in salt-free melts. This mesh size increase upon the addition of LiClO₄ is consistent with the results of a recent neutron diffraction study of the same system.²² In that study it was determined that "... intermediate-range order is enhanced relative to the pure polymer by the expansion of the network on the addition of the salt."

The single-exponential character of scattered light ACFs from salt-containing melts demonstrated once again that as for neat melts, network mesh sizes remained distinctly smaller than the wavelength of visible light; even though the effect of added salt was to increase the this mesh size. However, in addition to stabilizing salt-containing melts, additional intra- and interpolymer bridging and bonding also served to "petrify" the network so that it was more resistant to thermal stretching. In summary, the presence of salt produced a melt network with a larger average mesh size that was more difficult to stretch. These effects, along with the stabilizing effect of the added salt on Γ , remained consistent

throughout the salt concentration range examined with no more than a concentration of 5 wt. % LiClO_4 needed to produce them.

Comparing the static light scattering results for the 16 wt. % salt PEO-melt/salt solution to that of the neat melt, the static correlation length ξ_S was observed to have increased substantially upon the addition of salt. ξ_s in the neat 1 K PEO melt and in the 16 wt. % 1 K PEO-melt/LiClO₄ solution were determined to be 200 nm and 530 nm, respectively. This increase is readily apparent in the significant increase in reciprocal intensity plot slopes for all eight panels in Fig. 4 and was also apparent in the redistribution of the scattered light. For example, the scattered light intensity at higher scattering angles, $\theta = 90^{\circ}$, e.g., was observed to decrease. The increase in ξ_s was also consistent with ηD_l behavior. Network petrification resulting from salt induced linking and bridging resulted in the creation of melt density fluctuations in PEO-melt/LiClO₄ solutions that were larger than those in the neat melt.

Upon the addition of salt, hydrodynamic screening lengths, ξ_D , increased from about 200 nm to about 280 nm [Fig. 10, Eq. (11)]. This increase reflects an increase in the range of influence of perturbations in the damping liquid. It is consistent with the increase in ξ_S associated with the petrification of the network and with the increase in η , a perturbation in a more viscous damping liquid had a more extended influence on a more rigid network. Considering the pattern of variation in ξ_D seen in Fig. 10, the ξ_D appeared to be constant across the temperature and salt concentration ranges examined (the mean ξ_D value was 280 nm with a rms deviation of 27%).

For 16 wt.% salt solutions, reciprocal intensity intercepts, $1/I_0$, agreed with those for neat melts (Fig. 4)—except for the results at temperatures too close to the melt temperature (T=45-55 °C). Close to the melt temperature, the anomalous increase in the intensity of the scattered light was due to aggregation and/or incipient crystallization in the melt. Interestingly, this behavior was not observed in the neat-melt sample. This difference in behavior between saltfree melts and salt-containing melts demonstrated that for temperatures somewhat above the melt temperature, the salt actually promoted aggregation and/or crystallization in the melt as the melt cooled and the melt temperature was approached from above.

The consistency in I_0 for higher temperature extrapolations both with and without salt [the mean 60–80 °C $1/I_0$ values with and without salt were 0.0087 and 0.0089 (kHz)⁻¹, respectively, with corresponding rms deviations of about 10% and 5%] further validated the static scattering results. As zero scattering angle was approached, the scattered light intensity arose from scattering by the total mass of scattering material and had become insensitive to the distribution of this material in the sample. Moreover, the agreement between salt and no-salt intercepts for the 60–80 °C range demonstrated that scattering by the salt, per se, was insignificant.

As can also be seen in Fig. 4 (the lowest three temperatures excepted), I_0 is temperature independent, behavior consistent with the expectation that $I_0 \sim T/G_l$ (see Ref. 10) when $G_1 \sim T$ (as for the neat melt, Fig. 9, first panel). However, this temperature independence seems to contradict the result I_0 $\sim T$ expected after the addition of salt because, ηD_l , which is proportional to G_1 , rather than varying directly with T as for the neat melt, exhibited little, if any, temperature dependence (Fig. 9). The ηD_1 behavior suggests that with salt, the gel network was no longer ideal. The temperature independence of I_0 is then seen as a further consequence of network nonideality. Correspondingly, the expression $I_0 \sim T/G_1$ was no longer valid. Perhaps some of the thermal energy of the gel system was no longer available to stretch the saltpetrified network. The petrified network was "lossy" as thermal energy was needed not only for network stretching, but for other behavior as well. Consequently, less than k_BT was available for network stretching, and the temperature dependence of G_l was reduced, perhaps to the point of having become negligible.

IV. COMMENTS

In interpreting PEO melt structure and behavior in terms of the wet gel model, PEO was assumed to play two distinct roles. One role was that of a random network and the other was that of an amorphous damping liquid. This division of polymer structure and behavior into different roles in polymer melts had been made earlier-although the wet gel version for this partitioning of roles was not considered-and important issues such as system equilibrium and metastability were appreciated and considered in some detail.²⁰ The position taken here is that in the PEO melt, the two states, or configurations, network and amorphous damping liquid, coexisted in thermodynamic equilibrium. In other words, under the conditions studied, molten PEO was a liquid polymorph (liquid bimorph) consisting of two coexisting states of the same composition but differing structures and densities. The existence of liquid polymorphs is well established (see Ref. 21, and references therein). Moreover, the fact that light scattering probes polymer melt density fluctuations wherein entropic considerations are paramount in determining structure and dynamic behavior supports the contention that the PEO melt system investigated here may have been a liquid bimorph. To investigate this idea further, a project has been initiated to map out PEO melt structure and dynamic behavior as a function of the melt pressure and temperature.

In addition, in a battery polymer electrolyte a net transport of charge-carrier ions from one electrode to the other results when an electrical potential difference is applied across the electrodes. For example, in PEO/LiX electrolytes, lithium ions were the charge carriers.³ The discovery of a network structure spanning PEO-melt/LiClO₄ solutions suggests the possibility that along with helping stabilize the network, lithium ions may move along pathways provided by the network structure itself or may be transported through the damping liquid via intra network channels. For example, based on the results of the neutron diffraction study of the PEO-melt/LiClO₄ system (Ref. 22), it was concluded, "The excess volume introduced (by network expansion resulting from the addition of salt) must play a key role in facilitating the lithium ion conduction."

In this regard, it is worth mentioning that an improved understanding of SPE conductivity might result from considering the electrode-spanning connectivity of the PEO melt network within the framework of percolation theory which has already been used to describe the structure and behavior of certain gel systems.²³ Note that "percolation" as used here refers to long-range, global behavior and not to the well known "dynamic bond percolation theory" used to describe SPE conductivity and which treats fast, local behavior in these SPEs.¹

V. CONCLUSIONS

Viewed from the perspective of the wet gel model, the 1 K PEO melt, with and without LiClO_4 , is an overdamped system with the PEO network relaxation governed by the viscosity of the PEO damping liquid. Increases in melt static and dynamic correlation lengths ξ_s and ξ_D upon the addition of salt were attributed to salt-induced linking and bridging in the gel network while the temperature independence of these lengths, with and without salt, was attributed to the integrity and stability of the network.

By examining ηD_l , the product of the gel damping liquid viscosity and the gel network diffusion coefficient, the behavior of the gel network modulus G_l was investigated. Significantly, for neat melts, G_l was found to depend linearly on *T*, and the scattered light intensity at zero forward angle, I_0 , to be independent of *T*, as for an ideal network.

However, the addition of salt reduced G_l and reduced or eliminated its temperature dependence altogether while I_0 remained independent of temperature, as for the neat melt, illustrating the nonideal behavior of the salt-petrified network. Moreover, the addition of salt resulted in a gel network with a larger average mesh size than that of the neat melt, a network more difficult to stretch whose dynamic behavior was governed by a gel damping liquid of higher viscosity.

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