

An Investigation of Dynamic and Viscoelastic Properties of Entangled Poly(ethylene oxide)/Lithium Perchlorate System



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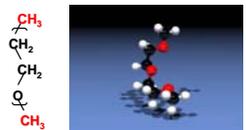
INTRODUCTION

Since the discovery of ionic conductivity in polymer-salt complexes, great efforts have been made to develop solid polymer electrolytes (SPEs) for use in rechargeable lithium batteries due to potential for higher energy densities and improved safety. Poly(ethylene oxide) (PEO) is one of the extensively studied polymer hosts for SPEs. Hence, studies of PEO/LiClO₄ melts were undertaken to provide insight into the mechanisms of ion transport in SPEs. In the present work, the long time dynamics of entangled PEO melts is well described by the scaling theory supported by PCS and SLS measurements. In the scaling treatment, polymer chains are assumed to be infinitely long, perfectly flexible strands having negligible thickness. Moreover, chains are chemically inert and temporary networks form as chains cross each other but cannot pass through one another thus producing contact-point junctions. However, and very significantly, the network contact-point junctions are accompanied by PEO network tie-points, i.e. by temporary physical associations resulting from intra- and inter-polymer dipole-dipole interactions. In addition, rheometry measurements have shown that PEO-melt/salt systems behave as viscoelastic systems, i.e. as elastic gel networks at sufficiently short times and as viscous fluids at longer times.

EXPERIMENTAL

Samples

Polymer: Poly(ethylene oxide) (PEO), linear, flexible chain.
 Chain were synthesized with methyl group end caps.
 Molecular Weight: $M_w = 50600$ Dalton, $M_w/M_n = 1.05$
 Rheological Entanglement Molar Mass: 3500 Dalton
 Salt: Lithium Perchlorate (LiClO₄)



Data Analysis

- The intensity-intensity time autocorrelation function: Siegert relation

$$G^{(2)}(t) = A[1 + a|g^{(1)}(t)|^2]$$

- Normalized field-field autocorrelation function:

$$|g^{(1)}(t)| = \int_0^t w(t) e^{i\omega t} d\omega$$

- Double Kohlrausch-Williams-Watts (KWW) function:

$$[G^{(2)}(t) - A]A = [A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}]^2$$

- Diffusive behavior:

$$F = D \cdot q^2$$

- Stokes-Einstein expression:

$$D = k_B T / (6\pi\eta_s a)$$

- Activation energy E_D for diffusive relaxation:

$$F \sim \exp(-E_D/RT)$$

- Activation energy E_η for viscous flow:

$$\eta \sim \exp(-E_\eta/RT)$$

- Ornstein-Zernike function:

$$I = \frac{I(0)}{1 + \xi_s^2 q^2}$$

RESULTS

Sol/melt-gel Transitions

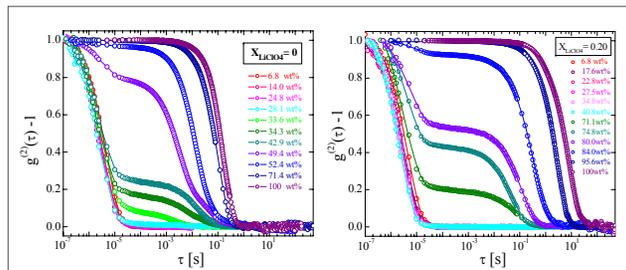


Figure 1. Typical normalized intensity autocorrelation functions ACF of PEO with and without salt measured at the scattering angle $\theta = 90^\circ$ and temperature $T = 65^\circ\text{C}$ in methanol solutions. A smooth one-mode \rightarrow two-modes \rightarrow one-mode evolution in ACF mode structure clearly revealed that with increasing polymer concentration in solution maps out the transition from dilution behavior to melt/gel behavior for the PEO/methanol.

PCS Results for PEO Melts

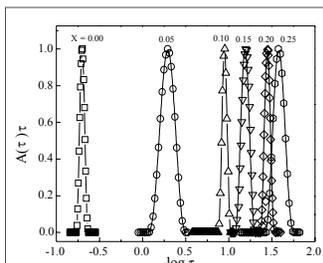


Figure 2. CONTIN analyses results illustrating the single mode in the ACF for neat melt and salt-plus melts. Here $T = 65^\circ\text{C}$ and $\theta = 90^\circ$. All melts exhibited monomodal, single-exponential relaxation behaviors.

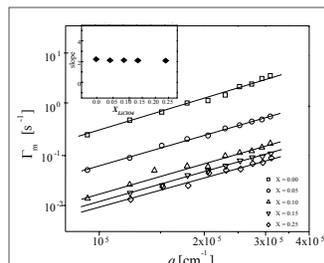


Figure 3. Relaxation rates Γ_m versus the scattering vector q in a log-log plot. The inset shows the slope is equal to 2 for all melts. Note that Γ_m depends linearly on q^2 , indicating diffusive characteristics behavior of PEO melt/gel network.

Static Light Scattering Results

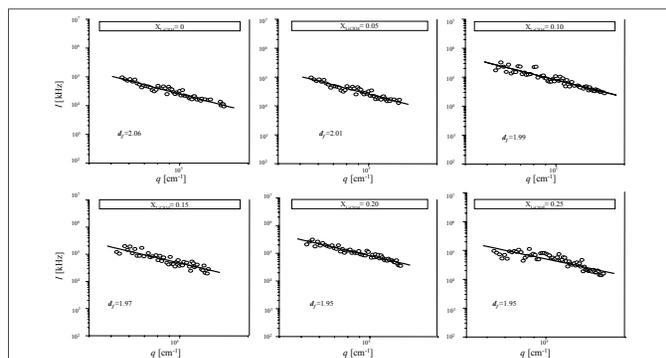


Figure 4. Power-law plots of the scattering wave vector q dependencies of the scattered light intensity $I(q)$, for neat melt and salt-plus melts of PEO-50K. Here temperature $T = 65^\circ\text{C}$.

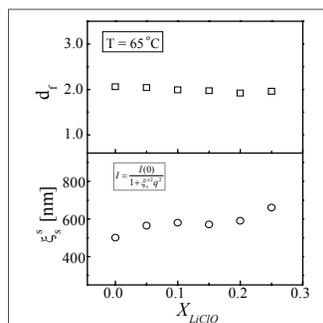


Figure 5. Salt concentration X_{LiClO_4} dependencies of the fit exponent d_f and the correlation length ξ_s^s extracted from static light scattering measurements at $T = 65^\circ\text{C}$.

Static scattering measurements revealed power law behavior in all PEO melts, $I(q) \sim q^{-2.0 \pm 0.1}$ in agreement with the percolation theory, i.e., PEO melt/gel networks remained percolation systems containing numerous polymer pathways spanning the melt sample.

Salt concentration increases swell the gel network while the addition of salt makes the network more difficult to stretch. This result is reasonable that salt bridging and associated network stiffening would presumably increase the extent of long ranged network fluctuations.

Rheometry Measurements

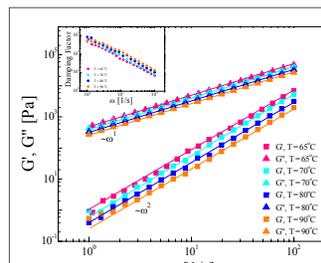


Figure 6. Storage modulus G' and loss modulus G'' of the neat melt as a function of angular frequency ω at different temperatures. The inset shows the damping factor G''/G' as a function of ω .

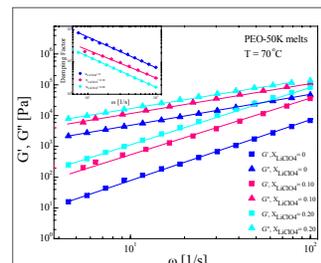


Figure 7. Storage modulus G' and loss modulus G'' of the neat melt and salt-plus melts as a function of angular frequency ω at temperature $T = 70^\circ\text{C}$. The inset shows the damping factor G''/G' as a function of ω .

Rheometry Results

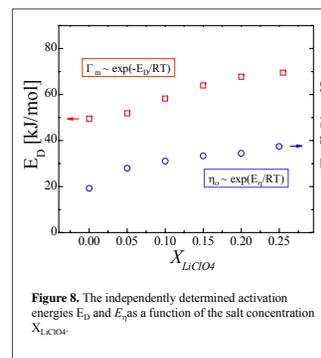


Figure 8. The independently determined activation energies E_D and E_η as a function of the salt concentration X_{LiClO_4} .

Storage modulus G' and loss modulus G'' of the neat melt and salt-plus melts are respectively proportional to ω^2 and ω^1 at the wide frequencies range. G'' are higher than G' and both moduli increase in parallel slowly with more salt added. Such a behavior is characteristic of the liquid-like structure. The damping factor decreases with increasing X_{LiClO_4} , indicating the more "bridging", "tie-up points" in the PEO50K melt/gel network.

The increase in E_D and E_η within increasing X_{LiClO_4} due to increase in the numbers of ion mediated intra- and inter-polymer links in PEO mobile chains. Additional intra- and inter-polymer bridging and bonding also served to "petrify" the network so that it was more resistant to thermal stretching. Non-equivalence of E_D and E_η implying long-ranged fluctuations in the melt are governed by viscous flow and elasticity of melt/gel network.

CONCLUSIONS

LLS measurements are employed to investigate the dynamics of entangled PEO50K with and without salt. The single-exponential ACF relaxation mode was observed and exhibited q^2 dependence in all melts; behavior interpreted as due to the relaxation of a transient PEO network. From rheometry measurements, damping factors are very large (>1) and decrease with more salt added, indicating that the behavior is characteristic of liquid-like structure but the level of entanglement of PEO chains depending on the existence of LiClO₄. Furthermore, static scattering measurements revealed that the structure factor exhibits a universal power law $I(q) \sim q^{-2.0}$ in all melts. Significantly, the melt/gel was shown to be a percolation system—a result linking microscopic and macroscopic behaviors in PEO melt/gels with important implications for solid-polymer-electrolyte battery technology.

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