A Light Scattering Investigation of a Sol/melt–gel Transition: the Poly(ethylene oxide) (PEO)/methanol/LiClO₄ System

Shufu Peng, James C. Selser, Radoslav Bogoslovov, Greg Piet

Introduction
Photon correlation spectroscopy (PCS) has been widely used for investigating polymer dynamics in solutions as well as in the melt because PCS is a noninvasive technique that can access a broad time window, via 10⁻¹⁰ s. In “standard”, theoretical treatments describing the behavior of semidilute polymer solutions, polymer chains are assumed to be infinitely long, perfectly flexible strands having negligible points develop due to the inability of chains to pass through one another. In fact, in the present study, hydrogen bonding and dipole-dipole interactions play significant roles in the development and behavior of poly(ethylene oxide) (PEO) networks in semidilute solutions as well as in melts. In general, PCS measurements have revealed two relaxation modes in polymer chains.

Samples
Polymer: Poly(ethylene oxide) (PEO)
Chain were synthesized with methyl group end caps.
Molecular Weight: \( M_w = 50600\) Daltons, \( M_w/M_n = 1.05\)
Overlap concentration: \( C^* = M_w/(N_A/3π\xi^2) = 12\) wt%
Rheological Entanglement Molar Mass: \( 3500\) Dalton
Solvent: methanol (CH₃OH)
Salt: Lithium Perchlorate (LiClO₄)

Polymer Concentration Dependence

Sol/melt-gel Transitions

A smooth one-mode → two-modes → one-mode evolution in scattering light autocorrelation function (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.

Data Analysis

The intensity-intensity time autocorrelation function:

- Siegert relation

- Normalized field-field autocorrelation function:

- Double Kohlrausch-Williams-Watts Function:

- Diffusive behavior:

- Stokes-Einstein expression:

- Arhenius plot: Activation Energy \( E_D \)

- Ornstein-Zernike function:

The concentration dependence of \( A_0/(A_0^*A_i^*) \)

Concentration dependence of the relative contribution of “fast” and “slow” ACF modes, expressed by the mode amplitude ratio \( A_0/(A_0^*A_i^*) \), driven from double KWW fits, illustrates this sol/melt-gel transition very clearly. The sigmoid shape of the transition highlights the shift from coil individual behavior in dilute solution to coil collective network behavior in the semidilute solution.

Sample Preparation

Dry-box filled with dried/purified \( N_2 \) and kept at moisture level <10 ppm V

Dry-box

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While with increasing network consolidation as polymer concentration increased and \( \xi \) increased, i.e. with increasing consolidation of the polymer network, the distance over which the effects of dynamic perturbations of the network were communicated increased significantly.

The structure and dynamics of 50K PEO methanol solutions and PEO melts, with and without LiClO4, were studied using static light scattering (SLS) and photon correlation spectroscopy (PCS). Scattering light intensity autocorrelation functions revealed that with increasing PEO concentration, fast PEO concentration fluctuation relaxations gradually disappeared even as slow mode relaxations emerged. The fast relaxation was diffusive, exhibiting \( q^2 \) dependence. Associated dynamic screening lengths, \( \xi \), scaled the \(-0.73\) power of polymer concentration in semidilute solution regime. Significantly, the slow mode relaxation was also diffusive, both in solution and in PEO melts, behavior interpreted in both cases as due to the long-ranged relaxation of a transient PEO network. ACF data illustrates the transition form individual coil behavior in solution to coil collective or network behavior and the homogeneity of semidilute solutions. Moreover, for a given polymer concentration, the degree of PEO chain entanglement varied depending on the salt concentration.

Conclusions

The structure and dynamics of 50K PEO methanol solutions and PEO melts, with and without \( \lambda_{KDP} \) were studied using static light scattering (SLS) and photon correlation spectroscopy (PCS). Scattering light intensity autocorrelation functions revealed that with increasing PEO concentration, fast PEO concentration fluctuation relaxations gradually disappeared even as slow mode relaxations emerged. The fast relaxation was diffusive, exhibiting \( q^2 \) dependence. Associated dynamic screening lengths, \( \xi \), scaled the \(-0.73\) power of polymer concentration in semidilute solution regime. Significantly, the slow mode relaxation was also diffusive, both in solution and in PEO melts, behavior interpreted in both cases as due to the long-ranged relaxation of a transient PEO network. ACF data illustrates the transition form individual coil behavior in solution to coil collective or network behavior and the homogeneity of semidilute solutions. Moreover, for a given polymer concentration, the degree of PEO chain entanglement varied depending on the salt concentration.

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