

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

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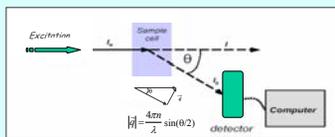


Introduction

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, viz $10^{-7} - 10^3$ 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 thickness. Moreover, chains are chemically inert and networks form as chain contact crossing 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 semidilute polymer solutions. This work reports the results of a PCS study of the sol-gel transition occurring in methanol solutions having increasing concentrations of PEO and is part of an ongoing investigation of the structure and dynamic behavior of PEO-melt/salt solutions. In particular, by scrutinizing the scattering wavevector, concentration and temperature dependences of solution fast and slow relaxation modes, the dynamic behavior of PEO with and without salt in dilute and semi-dilute methanol solutions up to and including the melt limit was studied.

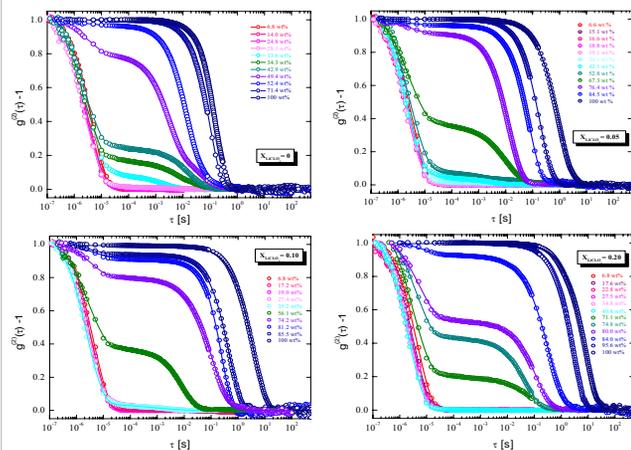
PCS Measurements

Laser: Argon $\lambda = 514.5$ nm
Ref. Index of PEO:
 $n = 1.44 - 1.47$
Scattering angle range
 $30^\circ \leq \theta \leq 130^\circ$
Scattered wavevector range
 $8.4 \times 10^4 \leq q \leq 2.9 \times 10^5 \text{ cm}^{-1}$



Polymer Concentration Dependence

Sol/melt-gel Transitions

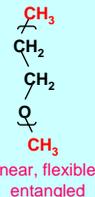


Typical normalized intensity autocorrelation functions ACF of PEO with and without salt measured at the scattering angle $\theta = 90^\circ$ and temperature $T = 65^\circ\text{C}$ in methanol solutions over a wide concentration range

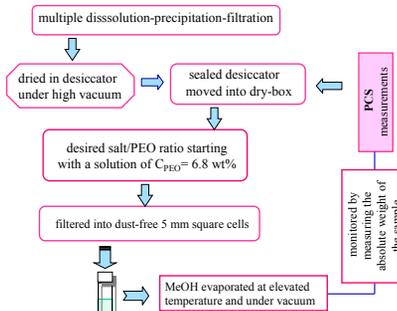
A smooth one-mode \rightarrow two-modes \rightarrow one-mode evolution in scattering light autocorrelation function (ACF) mode structure clearly revealed that with increasing polymer concentration in solution maps out the transition from dilution behavior to melt/gel behavior for the PEO/methanol.

Samples

Polymer: Poly(ethylene oxide) (PEO)
 Chain were synthesized with methyl group end caps.
Molecular Weight: $M_w = 50600$ Dalton, $M_w/M_n = 1.05$
Overlap concentration: $C^* = M_w/(N_A/3\pi R^2) = 12$ wt%
Rheological Entanglement Molar Mass: 3500 Dalton
Solvent: methanol (CH_3OH)
Salt: Lithium Perchlorate (LiClO_4)



Sample Preparation



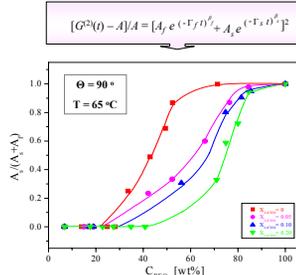
Dry-box filled with dried/purified N_2 and keep at moisture level < 10 ppm V

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:
 $|g^{(1)}(t)| = \int_0^\infty w(\Gamma) e^{-\Gamma t} d\Gamma$
- Double Kohlrausch-Williams-Watts Function:
 $[G^{(2)}(t) - A]A = [A_f e^{-(\tau_f)^{\beta_f}} + A_s e^{-(\tau_s)^{\beta_s}}]$
- Diffusive behavior:
 $\Gamma = D \cdot q^2$
- Stokes-Einstein expression:
 $D = k_B T / (6\pi\eta_0 \xi_0)$
- Arrhenius plot: Activation Energy E_D
 $\Gamma = \exp(E_D/RT)$
- Ornstein-Zernike function:
 $I = \frac{I(0)}{1 + \xi^2 q^2}$

$A = (I(\infty))^2$ - baseline
 a - experiment constant
 $w(\Gamma)$ - distribution function
 Γ - relaxation rate
 E_D - Activation Energy
 q - wavevector factor
 $A_{f,s}$ - amplitudes of fast and slow modes
 $\beta \approx 1$ - "single exponential" relaxation
 D - diffusion coefficient
 k_B - Boltzmann constant
 η_0 - viscosity of solvent
 ξ_0 - dynamic correlation length
 ξ^2 - long-range correlation length

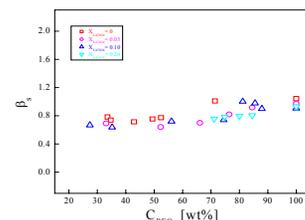
The concentration dependence of $A_s/(A_f + A_s)$

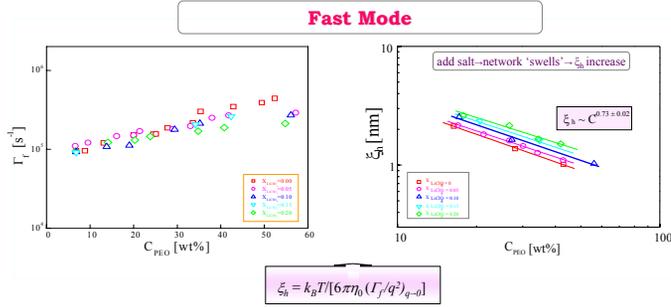


Concentration dependence of the relative contribution of "fast" and "slow" ACF modes, expressed by the mode amplitude ratio $A_s/(A_f + A_s)$ derived from double KWW fits, illustrates this sol/melt-gel transition very clearly. The sigmoid shape of this ratio transition highlights the shift from coil individual behavior in dilute solution to coil collective network behavior in the semidilute solution.

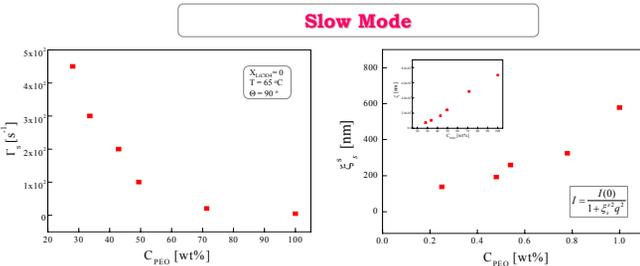
Concentration Dependence of β

In double-KWW fits, β_f and β_s provide a measure of the distribution widths associated with the relaxation rates Γ_f and Γ_s . While a value of $\beta \approx 1$ corresponds to a narrow distribution of relaxations, i.e. to a single-exponential relaxation.

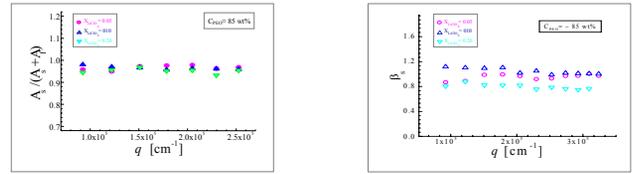




Fast ACF relaxations were attributed to diffusive motions of chain segments between network tie points with a characteristic length associated with these motions comparable to the network mesh size. The consistent increase of the fast relaxation rate Γ_f with increasing polymer concentration resulted from the monotonic decrease in ξ_h . $\xi_h \sim C^{0.73}$, a power law decrease in reasonable agreement both with theoretical predictions and with earlier measurements.

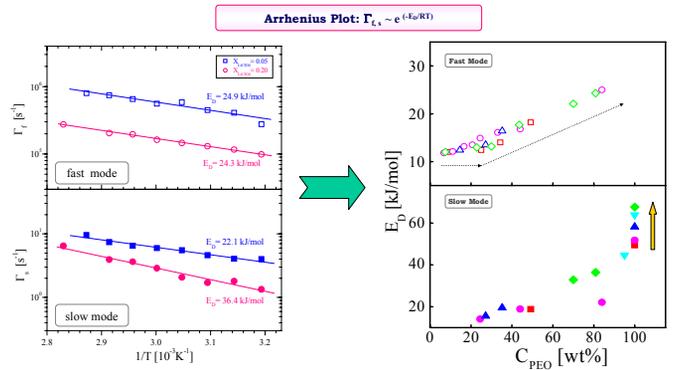


While with increasing network consolidation as polymer concentration increased and ξ_h increased, i.e. with increasing consolidation of the polymer network, the distance over which the effects of dynamic perturbations of the network were communicated increased significantly.



Wavevector q independence of the mode ratio $A_s/(A_s+A_f)$ and of β_s for well-established networks illustrates the homogeneity. Slower dynamic behavior result from the diffusive relaxation of long-ranged network fluctuations

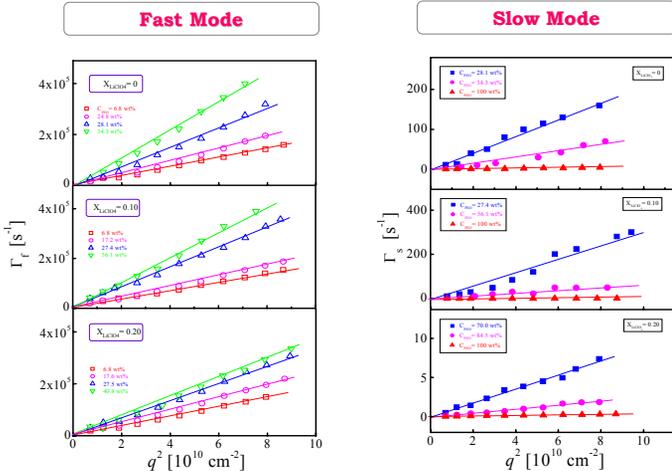
Temperature Dependence



E_D^f unaffected by added salt. E_D^s transitions from being independent of C_{PEO} to increasing linearly with increasing C_{PEO} , reflecting the transition from individual coil behavior in solution to network behavior.

Evidently, while local dynamic behavior was relatively unaffected by polymer/salt complexing and consequent network swelling, the energy barrier increased for the diffusive relaxation of regions of the network correlated over longer distances.

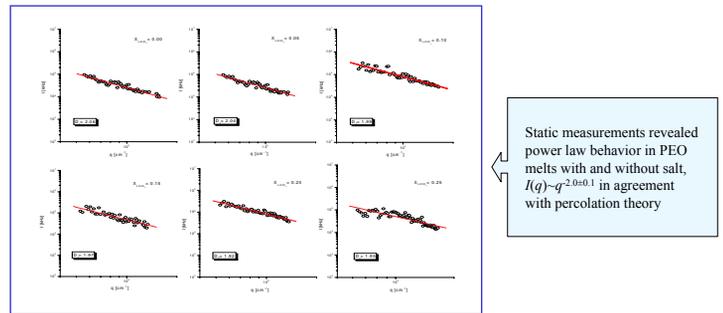
Scattering Wavevector Dependence



Γ_f of the fast relaxation mode is a linear function of q^2 and the extrapolation of Γ_f to $q \rightarrow 0$ passes the origin, indicating that the fast relaxation is related to the cooperative diffusion.

Slow mode in semidilute solutions as well as in the melts are confirmed to be diffusive. This supports the contention that the slow mode becomes the single "surviving" diffusive mode observed in 50K PEO melt.

Static Light Scattering



Conclusions

The structure and dynamics of 50K PEO methanol solutions and PEO melts, with and without $LiClO_4$ 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, ξ_h , scaled as 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 from 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.

Acknowledgements

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References

- de Gennes, P. G. *Scaling Concepts In Polymer Physics*, Cornell University Press: Ithaca, NY, 1979.
- Brown, W.; Nicolai, T. In *Dynamic Light Scattering, the Methods and Application*, Brown, W. Ed.; Clarendon, Oxford, 1993.
- Walter R.; Selsler J. C.; Smith M.; Booslovov R.; Piet G., J. Chem. Phys. 2002, 117, 417.
- Adam, M.; Delsanti, M.; Munch, J. P.; Durand, D. Phys. Rev. Lett. 1988, 61, 706.