



Studying Polymer Solutions using Light Scattering Spectroscopy



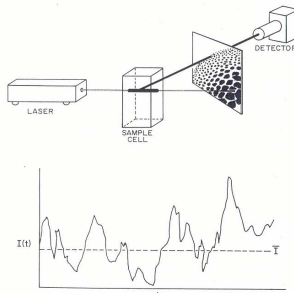
Kiril A. Streletzky, Cleveland State University,
George D. J. Phillies, Worcester Polytechnic Institute

Abstract

Light scattering spectroscopy provides a non-destructive analytic technique for probing structure and dynamics of polymer solutions. Light scattering spectroscopy in our laboratory combines measurement of average scattering intensity (static light scattering-SLS) with monitoring of average temporal evolution of intensity fluctuations (dynamic light scattering-DLS) in samples at thermal equilibrium. While SLS yields polymers molecular weight and radius of gyration, DLS yields information on translational and rotational dynamics of polymers in solution. We also apply optical probe diffusion to measure the transport of dilute mesoscopic probes in polymer solution. If tracer particles are dominant scatterers in solution, their diffusion provides important information for inferring polymer physical properties. By combining DLS, SLS, optical probe diffusion, and low-shear solution viscosity measurement, we studied neutral, high molecular weight, semi-flexible, water-soluble polymer hydroxypropylcellulose (HPC). Important insights into multimodal dynamics of dilute/concentrated solutions of this multi-application polymer are found.

Light Scattering Spectroscopy

We measure intensity $I(t)$ of light scattered in a particular direction by a polymer solution in thermal equilibrium. $I(t)$ is analyzed in two ways: 1) Static Light Scattering looks at an average intensity I , 2) Dynamic Light Scattering studies fluctuations of $I(t)$. Spectrum $S(q,t)$ is analyzed using field correlation function $g^{(1)}(q,t)$, which is determined by positions/motions of scattering molecules



$$S(q, \tau) = \int_0^\tau I(t)I(t+\tau)dt = A(g^{(1)}(q, \tau))^2 + B$$
$$g^{(1)}(q, t) = \sum_{i=1}^N A_i \exp(-\theta_i t^{\beta_i})$$

Measured spectra are multimodal:

At $c < 6g/l$, two stretched exps. are needed
At $c > 6g/l$, a third stretched exp. is required

A need to isolate each mode:

Method of Spectral Time Moments

For any spectrum with Γ -decay rates and $A(\Gamma)$ -normalized amplitude:

$$g^{(1)}(t) = \int_0^\infty d\Gamma A(\Gamma) \exp(-\Gamma t)$$
$$M_n = \int_0^\infty t^n g^{(1)}(t) dt = \int_0^\infty A(\Gamma) \frac{\gamma(1+n)}{\Gamma^{1+n}} d\Gamma$$
$$M_n / n! \equiv \langle \Gamma^{-n-1} \rangle, M_0 = \langle \Gamma^{-1} \rangle = (q^2 D)^{-1}$$

M_n -spectral time moment; M_0 -mean time of relaxation; D -nominal mean diffusion coeff.
Finding M_0 : replace $g^{(1)}(t)$ with fit to a sum of stretched exponentials; integrate analytically.
Each M_0 (or D) comes from each (θ_i, β_i) :

$$M_{0i} = \int_0^\infty dt \exp(-\theta_i t^{\beta_i}) = \gamma(1+1/\beta_i) / \theta_i^{1/\beta_i}$$

Fig.1: Schematic of experiment. Intensity fluctuation measured is also shown (from ref[1]). **Fig.2 (below):** Renormalized spectra of HPC: water at concentrations of (a) 1, (b) 4.5, (c) 7, and (d) 12g/L.

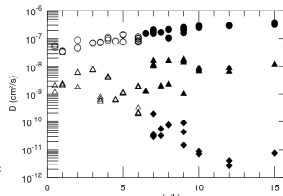
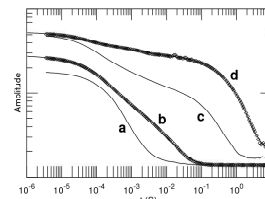


Fig.3: Effective diffusion coefficient $D = \langle \Gamma \rangle^{-1} / q^2$ for fast (circles), intermediate (triangles), and slow (diamonds) spectral modes of HPC.

Phenomenological Transition in Solution Viscosity

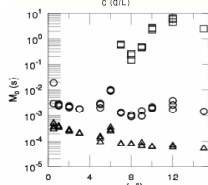
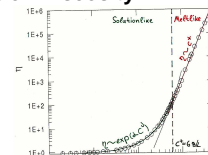
Low-shear viscosity measurements of HPC solutions revealed that the functional dependence of η on concentration has a transition at $c^* \approx 6g/l$, with disparate small- and large- c -dependences[2]:

For $c < c^*$, $\eta(c) \sim \exp(-ac^*)$ - "Solutionlike" behaviour
For $c > c^*$, $\eta(c) \sim c^x$, with $x=4$ - "Meltlike" behaviour

Viscometric crossover at c^* is echoed by:

- 1) appearance of the "ultraslow" mode in HPC: water at $c > c^*$ (Fig. 5)
- 2) optical probe diffusion data (Fig.8,[4]);

Fig.4 (top): $\eta(c)$ has a transition at c^* [2]. **Fig.5 (bottom):** $M_0(c)$ for fast (triangles), slow (circles), ultraslow (squares) modes of HPC: water. Ultraslow mode appears only above c^* .



Optical Probe Diffusion Method



In probe diffusion experiment, ternary system containing solvent, polymer, and dilute probes is studied. If probes are dominating scatterers, their dynamics are used to infer the dynamics of the polymer solution.

We studied diffusion of probes with size $14 < d < 455nm$ in water solutions of 1 MDa HPC.

We found a variety of novel phenomena:

- 1) Probe spectra are strongly non-exponential and can be decomposed into sharp and broad spectral modes. Small probes at $c > c^*$ reveal third "ultraslow" mode (Fig.6);
- 2) Probe and polymer relaxations in the same solution sample different aspects of polymer dynamics (compare Figs.5&6);
- 3) Polymer solutions have a characteristic c -independent dynamic length, comparable to polymer's hydrodynamic radius $R_h = 50-70nm$ (Figs.7a-b, [3]);
- 4) Diffusion coefficient of tracer particles in polymer solutions is NOT generally determined by solution macroscopic viscosity (Fig.8,[4]);
- 5) Mode Structure analysis of optical probe diffusion data confirms the reality of Solutionlike-Meltlike transition (Fig.8)

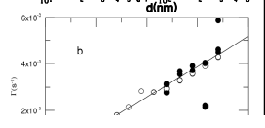
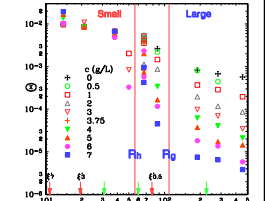
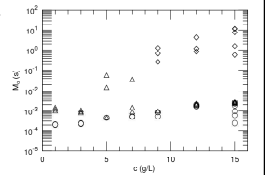


Fig.6 (top): $M_0(c)$ for sharp, broad, and ultraslow modes of 35nm probes in HPC: water.

Fig.7a (middle): Probe size dependences of sharp relaxation pseudorate θ_s at various c . Arrows indicate mesh size based reptation model[3].

Fig.7b (middle): Mean relaxation rates $\langle \Gamma \rangle = M_0^{-1}$ for sharp (open points) and broad (filled) modes of 20nm probes in 4g/l HPC.

Fig.8 (bottom): Correlation between decay pseudorate of broad mode θ_b and solution viscosity against concentration for large probes [4].

Transition from a liquid toward a generalized Kivelson glass?

At $c > c^*$, polymer spectra reveal ultraslow mode, with properties of generalized Kivelson model for incipient glass formation in polymer solution [5]:

- 1) Mode appears discontinuously at well defined c^* - sign of plausible concomitant of clusters
- 2) Only small probes gain ultraslow mode, with M_0 similar to polymer's ultraslow mode - probes smaller than clusters are entrained within cluster
- 3) $1/c$ shows no discontinuity at c^* - as expected for long-lived dynamic structures, but not for local equilibrium regions of elevated polymer c (Fig.9a)
- 4) Mean relaxation rates for sharp & broad probe modes depend on temperature as T/η - solvent motion controls dynamics (Fig.9b, [5]).

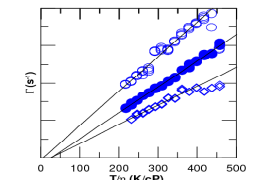
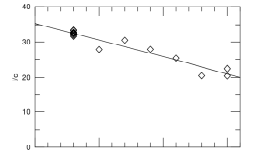


Fig.9a: Static scattering intensity $1/c$ of HPC: water against c . Linear fit shows that scattering per molecule declines uniformly. **Fig.9b:** Temperature dependence of mean relaxation rates $\langle \Gamma \rangle$ for 35nm probes at several c . η is the solvent viscosity [5].

Conclusions

A systematic analysis of the mode structure of diffusive relaxations for probes in HPC: water and for probe-free polymer solutions is presented. Viscometric and light scattering effects found in HPC solutions at elevated concentrations (above c^*) reflect the incipient formation of generalized Kivelson glass.

References:

- [1] G.D.J. Phillies, *Analytic Chemistry* **62**, 1049 (1990)
- [2] G.D.J. Phillies, C. Quinlan, *Macromolecules* **28**, 160 (1995)
- [3] K.A. Streletzky, G.D.J. Phillies, *J.Polym.Sci.,B: Polym.Phys.* **36**,3087 (1998)
- [4] K.A. Streletzky, G.D.J. Phillies, *Macromolecules* **32**, 145 (1999)
- [5] S.A. Kivelson *et al.*, *J. Chem. Phys.* **101**, 2391 (1994); G.D.J. Phillies, R.O'Connell, P. Whitford, K.A. Streletzky, *J. Chem. Phys.* **119**, 9903 (2003)
- [6] G.D.J. Phillies and K.A. Streletzky "Dynamics of Semirigid Rod Polymers from Experimental Studies", book chapter in "Soft Condensed Matter: New Research", ed. F.Columbus, Nova Science: NY, in press.