Communications to the Editor

Observation of a Pseudo-Transition Phenomenon between Dilute and Semidilute Regimes in a Polymer Solution†

Recent studies by Adam and Delsanti[1] have shown that the time correlation function $(A\beta)^{1/2}|g^{(1)}(t)|$ $(\equiv Z_i^{1/2}$, with subscript i denoting the channel number) of dilute polystyrene coils ($M = 8.4 \times 10^6$ and 24×10^6) in a good solvent (benzene) can be described surpisingly well with the use of the Dubois-Violette and de Gennes (DD) theory[2] whereby

$$|g^{(1)}(K,t)| = (t/\tau)^{2/3}\int_0^\infty du\, \exp[-(t/\tau)^{2/3}u(1 + h(u))] \qquad \text{when } t \neq 0 \quad (1a)$$

$$|g^{(1)}(K,t)| = 1 \qquad \text{when } t = 0 \qquad (1b)$$

with $h(u) = (4/\pi)\int_0^\infty dy\, \cos y^2/y^3(1 - \exp(-y^3u^{-3/2}))$. Equation 1 is valid for isolated polymers of infinite size. At infinite dilution, the corresponding characteristic decay rate τ is given by

$$1/\tau = \alpha(k_BT/\eta_0)K^3 \qquad (2)$$

where η_0 and K are the solvent viscosity and the magnitude of the momentum transfer vector, respectively. $\alpha = 1/2^{3/2}3\pi$ in a Θ solvent and has a slightly higher value in a good solvent. In this communication, we report a comparison of eq 1 with $A\beta|g^{(1)}(\tau)|^2$ of polystyrene ($M_w = 13 \times 10^6$) in carbon tetrachloride (a marginal solvent) from dilute solution to the neighborhood of the overlap concentration C^* $(= M/N_A\rho_s r_g^3$, with ρ_s, M, N_A, and r_g being the density, the molecular weight, the Avogadro number, and the radius of gyration, respectively) and observation of a dynamical slow down representing a new pseudo-transition region which occurs before the overlap concentration C^*.

A brief experimental procedure is described as follows. Carbon tetrachloride was filtered through a Millipore filter of nominal pore diameter of 0.22 μm. All solutions were prepared from the same centrifuged (6000 g for 8 h) stock solution of 0.328 wt% polystyrene in CCl_4 by dilution and flame sealed. We used a 96-channel single-clipped photon correlation spectrometer.[3] The sample chamber was controlled to ±0.01 °C at 18 °C.

Partial homodyning over the entire concentration range of our studies can be shown to be negligibly small because we are able to retrieve the expected molecular weight by extrapolation of absolute zero-angle scattered intensity to infinite dilution and to obtain the corresponding translational diffusion coefficient at small scattering angles with the use of a scaling approach. The details will be reported in the full paper. If the concentrated stock solution indicates no dust upon dilution, we consider that we have succeeded in preparing clean solutions at fairly high concentrations even for a high molecular weight polystyrene sample.

At each concentration C, the measured net signal correlation function $(A\beta)^{1/2}|g_m^{(1)}(t)|$ $(\equiv Y_i^{1/2})$ was fitted by the method of least squares according to eq 1 with the use of a single characteristic frequency $(1/\tau(C))$ and the initial amplitude $(A\beta)^{1/2}$ as the two unknown parameters. Figure 1 shows plots of $1/\tau K^2$ versus concentration at $\theta = 45$ and 135°. According to eq 2, we can compute the $1/\tau K^2$ value at infinite dilution, using known values of η_0, K, and T. As the DD theory is valid for a *single* polymer molecule of *infinite* size, the large Kr_g value of about 8.3 at $\theta = 135°$ signifies that the dynamical behavior expressed in terms of $1/\tau$ represents internal motions of the polymer coil in solution. Consequently, the experimental $1/\tau$ value which has been extrapolated to infinite dilution should agree with the computed $1/\tau$ value based on eq 2. Unfortunately, eq 2 is based on a preaveraging of the Oseen tensor, and the theoretical α value without preaveraging should be higher by about 15%.[4] Thus, the agreement is surprising. At $\theta = 45°$ where $Kr_g \approx 3.4$, the experimental $1/\tau$ value at infinite dilution is somewhat larger than the theoretical value calculated by eq 2 because the observed dynamics contain information involving translational motion of the center of mass of the entire polymer coil. It is important to note that the effect of the transition from asymptotic limit (eq 2) appears at $Kr_g \approx 3.4$, which is appreciably greater than one.

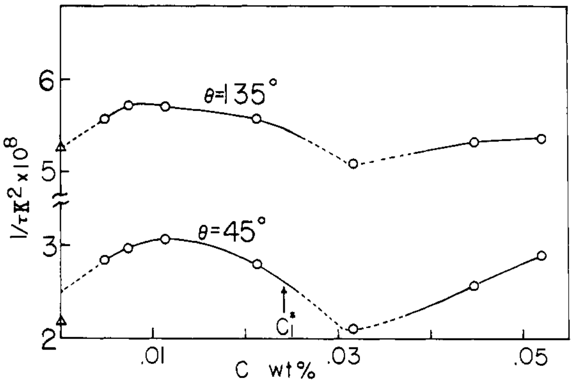

Figure 1. Plots of $1/\tau K^2$ vs. concentration. Hollow triangles represent computed $1/\tau K^2$ values from eq 2 with the use of known values of $T = 291$ K, $\eta_0 = 1.00047$ cP, and $K = 1.4469 \times 10^5$ cm^{-1} and 3.4932×10^5 cm^{-1} at $\theta = 45$ and 135°, respectively.

At low concentrations ($C < 0.015$ wt %), $|g_m^{(1)}(K,t)|$ is in excellent agreement with eq 1 as can be shown by Figure 2 representing a plot of the RSQ as a function of concentration where RSQ is defined as $\text{RSQ} = 1 - \sum_i^N(Y_i - Z_i)^2/(\sum_i^N Y_i^2 - (\sum_i^N Y_i)^2/(N + 1))$. The agreement suggests that $|g^{(1)}(K,t)|$ is not a sensitive function to concentration changes in dilute solution and that we can obtain reasonable values of $1/\tau$ even though we do not know the exact theoretical form of $|g^{(1)}(K,t)|$ at finite concentrations.[5] It is interesting to note that at low concentrations the least-squares fitting of $A\beta|g_m^{(1)}(\tau)|^2$ to eq 1 at $\theta = 45°$ is noticeably better than that at $\theta = 135°$, while the reverse is true for the $1/\tau$ value at infinite dilution. We believe that the main reason for the decrease in the RSQ value at $\theta = 135°$ is a reduction in the probing wavelength $(\equiv 2\pi/K)$ whereby relative motions of different regions of the polymer molecules are observed and $1/\tau$ becomes an averaged characteristic frequency.

In defining the overlap concentration C^*, de Gennes was concerned mainly with the order of magnitude of the concentration where polymer coils begin to get entangled. In practice, we know that this arbitrary definition can be

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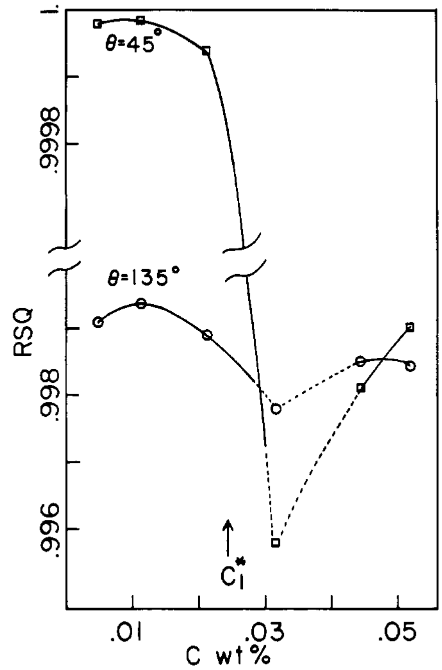

Figure 2. Plots of RSQ vs. concentration.

reformulated,[3] such as C_0^* $(=M/N_A\rho_s(2r_g)^3)$ or C_1^* $(=M/N_A\rho_s(^4/_3\pi r_g^3))$, and the separation between dilute and semidilute regions is not sharp. Figure 1 shows that the characteristic frequency $1/\tau$ goes through a maximum and then a minimum with increasing concentration. Near C_1^*, the polymer chain dynamics goes through a pseudo-transition region where the single characteristic frequency of the polymer chain $(1/\tau)$ slows down without appreciable entanglement formation. Qualitatively, we may consider that the slowdown is produced by interpenetration of some neighboring polymer molecules without creating a substantial amount of intermolecular polymer coil entanglement because the form of $|g^{(1)}(K,t)|$ has remained essentially unchanged. In the pseudo-transition region, the polymer solution is made up neither of individual polymer molecules in a homogeneous sea of solvent nor of entangled polymer coils where the distribution of entanglement points becomes relatively uniform throughout the solution. The transition from the dilute solution to the semidilute solution gives rise to an anomalous concentration dependence[6] which cannot be explained according to the classical Flory–Huggins theory.[7] We believe that the slowdown of $1/\tau$ is related to the hydrodynamic screening effect[5] and represents the *first* dynamical observation of this crossover transition region. In the neighborhood of the pseudo-transition region, equilibration time becomes very long. Detailed experiments in this aspect will be reported in the full paper.

The emergence of the pseudo-gel motion in the semidilute region has been reported.[3] At higher concentrations $(C > C_1^*)$, measurable amounts of entanglement have occurred and two characteristic frequencies appear. However, $|g_m^{(1)}(K,t)|$ can still be fitted according to eq 1 because the apparent characteristic frequency reflects mainly the diffusive chain motion. The apparent $1/\tau$ value increases with increasing concentration due to increasing contributions of the faster pseudo-gel mode which is related to the correlation length ξ $(<r_g)$ between polymer entanglement points.

References and Notes

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CORRECTIONS

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Equation 6 for the characteristic time ρ of the diffusive rotational motions should read

$$\log \rho = \log \tau - 2 \log m$$

Accordingly, the model assuming diffusing motions along the chain backbones leads to a steeper temperature dependence of ρ than expected from eq 4.