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Slow-Mode Diffusion of Poly(vinylpyrrolidone) in the Semidilute Regime

The overlap concentration, c^* $(=1/[\eta])^1$, is for molecules with $M_w > 10^5$, still a rather low concentration, and solutions with $c^* < c < c^\dagger$ are therefore called semidilute,[1,2] where $c^\dagger = (6^{3/2}/8N_A)(K^{5/2}/K_\Theta{}^4)$ indicates the crossover to concentrated solutions,[3] with K defined by $\langle R^2\rangle = KM^{6/5}$ and K_Θ by $\langle R^2\rangle_\Theta = K_\Theta M$. Our main understanding of semidilute solutions is due to de Gennes,[2] who applied scaling arguments for a description of this regime. A key parameter is the correlation length ξ, which defines a mean distance between two points of entanglement. It becomes shorter with increasing concentration and is given by[2,4]

$$\xi = a(c/c^*)^{-0.75} \qquad \text{for } c > c^* \tag{1}$$

where a is a length parameter that is difficult to calculate quantitatively. For lower concentrations the correlation length is

$$\xi = \langle R^2\rangle^{1/2} \qquad \text{for } c < c^* \tag{2}$$

where $\langle R^2\rangle$ is the mean square end-to-end distance. Beyond c^* a slow decrease to the unperturbed dimensions is predicted with a power law for the mean square radius of gyration

$$\langle S^2\rangle \sim (c/c^*)^{-0.25} \tag{3}$$

for individual chains in a good solvent.[5-7]

In *dilute solutions* only one translational diffusive motion is expected to which the Stokes–Einstein relationship can be applied

$$D = \frac{kT}{6\pi\eta_0}\frac{1}{R_h} \tag{4}$$

which defines a hydrodynamically effective radius of the coil. *Beyond* c^* de Gennes predicts two modes of diffusive motions, i.e., (i) a fast mode, which is given by[2]

$$D_{\text{coop}} \sim kT/6\pi\eta_0\xi \tag{5}$$

and (ii) a slow mode, which should follow[8]

$$D_{\text{self}} \sim N^{-2}(c/c^*)^{-1.75} \tag{6}$$

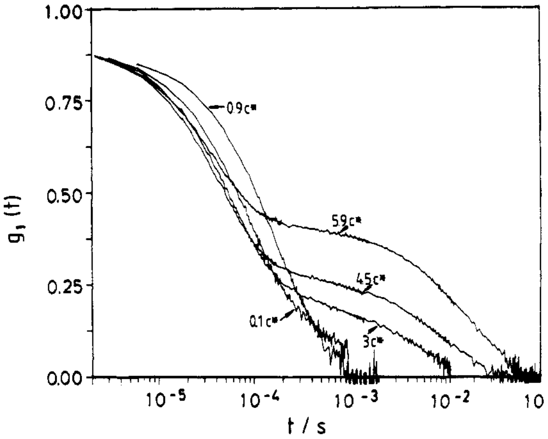

Figure 1. Time correltion function (TCF) $g_1(t)$ for five concentrations of PVP in water at a scattering angle of $\theta = 90°$; M_w 57 × 10^4; $c^* = 0.00731$ g cm^{-3}.

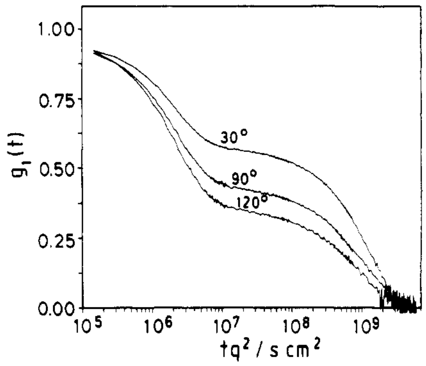

Figure 2. $g_1(t)$ as a function of tq^2 for the same sample as in Figure 1 for three different scattering angles, where $q = (4\pi/\lambda) \sin(\theta/2)$.

Self-diffusion is conceived here as a motion of the chain along its contour length (reptation). Hwang and Cohen[9] introduce two further diffusion coefficients, i.e., D_s, the translational diffusion coefficient of the solvent, and D_{cm}, which they associate with a center-of-mass diffusion (however, see below.)

We have carried out dynamic light scattering (LS) measurements on poly(vinylpyrrolidone) (PVP) in aqueous and ethanolic solutions. These are both good solvents, and we have indeed found a fast and a slow mode of motion at $c > c^*$, but only one mode in the dilute regime. This behavior is shown in Figure 1 for five typical concentrations of a polymer with $M_w = 57 \times 10^4$ (LS), $M_n = 27.4 \times 10^4$ (OS), and $A_2 = 4.60 \times 10^{-4}$ cm^3 mol g^{-2} (LS) in water. For the two concentrations c_1 and $c_2 < c^*$ we obtain a time correlation function (TCF) that decays approximately as a single exponential. For the concentrations c_3 to $c_5 > c^*$ a slower decay of the TCF becomes apparent in addition to the fast one and becomes more and more prominent with increasing concentration. Both modes are essentially diffusive since the characteristic relaxation times occur, for measurements at different angles, at the same value of q^2t. The amplitudes, however, depend on the scattering angle and have been extrapolated to zero angle (see Figure 2). Similar TCF have been found recently by Nose and Tanaka[10] for PMMA in 2-butanone. The diffusivities of the modes can be evaluated quantitatively by the program CONTIN provided by Provencher[11] and are plotted in Figure 3 against c/c^* for the PVP samples shown in Figures 1 and 2. We find in both solvents for the fast and the slow modes an exponent of +0.60 and −1.50, respectively. Both exponents are lower in value than +0.75 and −1.75 predicted by de Gennes for an entangled system. Experimental data

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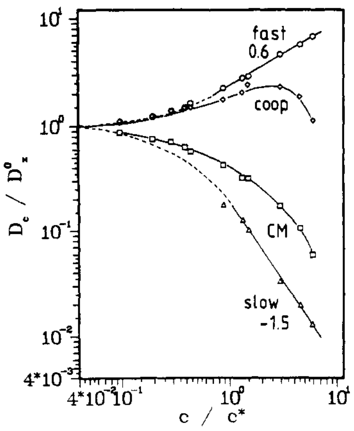

Figure 3. Concentration dependence of D_{fast}, D_{slow}, D_{coop}, and D_{cm} (for definitions and details, see text). The numbers indicate the exponents.

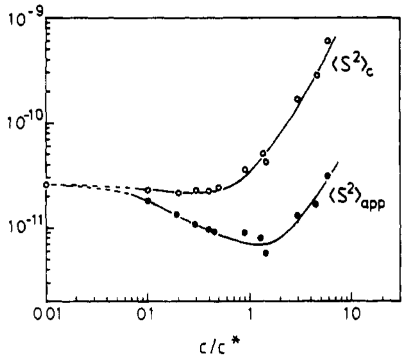

Figure 4. Concentration dependence of the apparent and corrected mean square radius of gyration for the same sample as in Figure 1. (See also eq 8.)

obtained for other polymer good solvent systems range from 0.66–0.77 for the exponent and are discussed by Candau et al.[12]

Additional information on the system could be obtained from the static LS data which were recorded simultaneously with the dynamic LS data.[13] From Debye's well-known equation

$$\frac{Kc}{R(q)} = \frac{1 + \frac{1}{3}\langle S^2\rangle q}{M_w} + 2A_2c + ... = (1/M_w + 2A_2c + ...)(1 + \tfrac{1}{3}\langle S^2\rangle_{\text{app}}q^2) \quad (7)$$

one obtains

$$\langle S^2\rangle_z = \langle S^2\rangle_{\text{app}}(M_w/M_{\text{app}}) \quad (8)$$

$$1/M_{\text{app}} = 1/M_w + 2A_2c + 3A_3c^2 + ... \quad (9)$$

where $\langle S^2\rangle_{\text{app}}$ is the apparent mean square radius of gyration obtained from the slope/intercept of the angular dependence at a certain concentration c in the Zimm plot, and $\langle S^2\rangle_z$ is the true mean square radius of the molecules or particles at the corresponding concentration. Equation 7 is only an approximation for fairly dilute solutions, since the interparticle factor $Q(q)$ defined in the papers of Albrecht[14a] and of Flory and Bueche[14b] has been neglected. Figure 4 shows $\langle S^2\rangle_z$ and $\langle S^2\rangle_{\text{app}}$ for the PVP sample. As expected, $\langle S^2\rangle_z$ remains essentially constant up to c^* but increases drastically for concentrations higher than c^*. Dautzenberg[15] has observed similar behavior for $\langle S^2\rangle_{\text{app}}$ with PS chains of $M_w = 7.1 \times 10^6$ in benzene. In Figure 5 this static correlation length (which is not ξ of eq 1) is plotted against the slow-mode diffusion coefficient. The line drawn represents the relationship

$$D_{c,\text{slow}} = K\langle S^2\rangle_z^{-(0.90\pm0.10)} \quad (10)$$

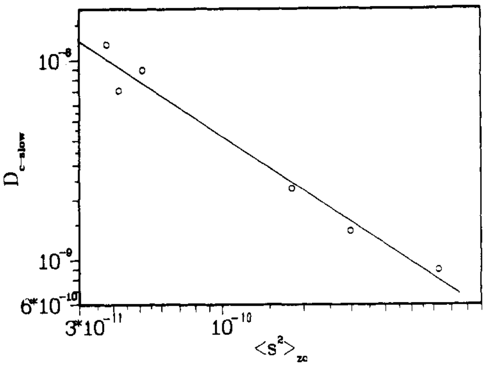

Figure 5. Plot of the slow-mode diffusion coefficient against the corrected mean square radius of gyration. (See eq 10.)

Slow-mode motion has been observed previously by several authors with other systems[10,16-21] but not for polystyrene in cyclopentane.[22] Mostly this mode is associated with self-diffusion, i.e., reptation. Doubts of this interpretation have been formulated by Patterson[18] and Brown.[22,23] Our findings confirm these doubts: The correlation length of reptating chains is supposed to be not larger than the radius of gyration of freely moving individual chains.[2] The observed strong increase in $\langle S^2\rangle^{1/2}$ seems to indicate transient clusters of loosely entangled chains. The formation of such clusters and their lifetime may be favored or inhibited by special enthalpic interactions. The $D_{c,\text{slow}}$ dependence on $1/\langle S^2\rangle$ is, on the other hand, strange and remains to be clarified by further experiments and theory. Our tentative interpretation stands not necessarily in contradiction to the concept of reptation. So far, we have measured the slow mode only in the limited region from c^* to $6c^*$. In this regime the relative amplitude w_{slow} (extrapolated to $q = 0$) increases with concentration approximately as

$$w_{\text{slow}} \sim (c/c^*)^{0.60} \quad (11)$$

The curve in Figure 5 would reach 100% at about $10c^*$. Then clusters fill the total volume and form a gel, which in the picture by de Gennes[2] is the starting condition for the reptation model. Thus beyond $c = 10c^*$ we may expect the observation of the reptation mode (the bulk state corresponds for this macromolecule to $c \simeq 150c^*$). Experiments in this very difficult region are in progress.

We conclude this short contribution with two further remarks: (1) The cooperative or mutual diffusion coefficient D_{coop} is obtained from the first cumulant of the TCF if Γ/q^2 is extrapolated to $q^2 \to 0$. The result is shown by Figure 3 by the curve D_{coop}. (2) According to irreversible thermodynamics the mutual diffusion coefficient contains a thermodynamic and a hydrodynamic friction contribution and is given by[24,25]

$$D_{\text{coop}} = (M_w/N_Af_c)(\partial\pi/\partial c)(1 - c\bar{v}_2) \quad (12)$$

where f_c is the friction coefficient of the particles at concentration c. The osmotic compressibility $\partial\pi/\partial c$ can be obtained from the simultaneously recorded static light scattering, which is given by

$$(Kc/R(q))_{q=0} = (1/RT)(\partial\pi/\partial c) = 1/M_{\text{app}} \quad (13)$$

Hence

$$D_{\text{coop}} = (kT/f_c)(M_w/M_{\text{app}})(1 - c\bar{v}_2) \quad (14)$$

The term $kT/f_c \equiv D_{\text{cm}}$ corresponds to a diffusion coefficient where the subscript "cm" stands for center of mass. f_c corresponds to the frictional coefficient that is measured by sedimentation. But D_{cm} contains still the contributions of the fast and the slow modes and cannot be considered as a self-diffusion coefficient for $c > 0$.

Our notation of the various diffusion coefficients differs from that given by Cohen.[9] He does not distinguish between D_{coop} and D_{self}; also, the slow-mode diffusion is interpreted as the center-of-mass diffusion with the transport in a centrifuge, which has not been determined by him.

A more detailed publication including measurements on other molecular weights is in preparation.

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