(26) Farnoux, B.; Boue, F.; Cotton, J. P.; Daoud, M.; Jannink, G.; Nierlich, M.; de Gennes, P.-G. *J. Phys.* **1978**, *39*, 77.
(27) Landry, C. J. T. Ph.D. Thesis, University of Wisconsin, 1985.
(28) Orofino, T. A. *J. Chem. Phys.* **1966**, *45*, 4310.
(29) Bohdanecky, M.; Berek, D. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 275.
(30) Mays, J. W.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1985**, *18*, 2231.
(31) Brueggeman, B. G.; Minnick, M. G.; Schrag, J. L. *Macromolecules* **1978**, *11*, 119.
(32) Lodge, T. P.; Schrag, J. L. *Macromolecules* **1984**, *17*, 352.
(33) Stokich, T. M., Jr.; Landry, C. J. T.; Schrag, J. L., presented at the Society of Rheology Meeting, Blacksburg, VA, 1985.
(34) Osaki, K. *Adv. Polym. Sci.* **1973**, *12*, 1.
(35) Lodge, T. P.; Hermann, K. C.; Landry, M. R., unpublished results.

Dynamics of Semidilute Solutions Using Photon Correlation Spectroscopy: The Influence of Solvent Quality

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ABSTRACT: Photon correlation spectroscopy data are presented for a high molecular weight (3×10^6) polystyrene fraction in the ethanol/ethyl acetate (isorefractive) mixed-solvent system at semidilute concentrations. Solvent quality decreases with increasing ethanol, and Θ-conditions are approached at 10% ethanol. Two characteristic components may be resolved from the time correlation function using multiexponential analysis over the whole range of solvent quality: (a) a fast (gel) mode, with a concentration exponent decreasing progressively to zero under Θ-conditions; (b) a slow (hydrodynamic) mode with a concentration dependence becoming strongly negative at Θ-conditions. These results harmonize with previous measurements in the Θ-system PS/cyclopentane at 21 °C. While the contributions of several modes in semidilute solutions have been described previously, the progressive change in the exponent $D \sim C^{\gamma}$ as a function of solvent quality has not earlier been documented.

Previous communications[1-3] reported the use of a bimodal model to interpret the diffusive behavior of high molecular weight polystyrenes in semidilute solution, both in a thermodynamically good solvent (THF) and a Θ-solvent (cyclopentane, 21 °C), as well as in the marginal solvent ethyl acetate.[4] Measurements were made with photon correlation spectroscopy (PCS) in the range of q vector corresponding to $qR_g > 1$ but restricted to the q range in which (Γ_q/q^2) was strictly q independent at each concentration. (Here Γ_q is the measured relaxation rate at finite values of q, the scattering vector, and R_g is the radius of gyration of an isolated coil.) For further details, the relevant papers, ref 1–4, should be consulted.

Use of the cumulants method[5] to interpret the time correlation function showed that the normalized second cumulant, $\mu_2/\bar{\Gamma}^2$, was large in the various systems and changed systematically with concentration. Some typical data are shown in Figure 1 for the fraction with $\bar{M}_w = 8 \times 10^6$. This observation suggests the possible presence of several relaxational modes, a feature that was examined in some detail by Chu and Nose for the polystyrene/*trans*-decalin system.[6] When such semidilute solutions are diluted to the dilute regime and reexamined at low angles, they are characterized by essentially single-exponential correlation functions, which effectively refutes polydispersity as a source of the large second cumulant. In order to explore possible sources of this behavior, multiexponential analysis of the time correlation function was used. Using the usual statistical parameters for judging "goodness of fit",[1] this approach gave two molar-mass-independent components in each of the three solvents but with different relative weighting. (This fit was selected as the simplest consistent with the data,[1] but we cannot exclude more complicated alternatives.) These data are summarized in Figure 2 as log–log plots of the dynamic correlation length, ξ_D, vs. concentration. The correlation length is a convenient way of unifying the presentation of data in different media where the focus is on the relative concentration dependences. ξ_D is defined for each mode as

$$\xi_D = kT/6\pi\eta_0 D \qquad (1)$$

where k is Boltzmann's constant, T the absolute temperature, η_0 the solvent viscosity, and $D = (\Gamma_{\text{fast}}/q^2)$ or $(\Gamma_{\text{slow}}/q^2)$. The relaxation rate for each component was estimated by using eq 2, and the respective D values were obtained as the slopes of linear plots of Γ_{fast} and Γ_{slow} vs. q^2. Figure 3 depicts the data obtained in the q range corresponding to $qR_g < 1$.

Comparison of the data showed the following:

1. The data for the fast component at $qR_g > 1$ fall on the same curve as those for the fast component at $qR_g < 1$. Thus, a single q^2-dependent and molar-mass-independent relaxation is probed over the q range where $q\xi < 1$ (i.e., the hydrodynamic regime) and the solution behaves as a transient gel formed by chain entanglements as anticipated from the theory of de Gennes.[7]

2. The values of (Γ_q/q^2) for the slower molar-mass-independent mode at $qR_g > 1$ (also q independent) were found to lie on an extension of the curve for the data obtained in dilute solution at low angles (single exponentials and corresponding to translational diffusion of the isolated coil). At $qR_g < 1$, however, using a correspondingly greater probing length, the slower mode is molar mass dependent (Figure 3) in the poorer solvents ethyl acetate and cyclopentane. (In the good solvent only the gel mode is detected at $qR_g < 1$.)

3. The exponent characterizing the concentration dependence of the dynamic length ($\xi_D \sim C^{-\gamma}$) was found to range for the fast component from 0.57 in THF to about zero in the Θ-system. With the slower mode, γ decreases from 0.44 (THF) to a negative value (−0.45) in the Θ-solvent. The corresponding exponents in ethyl acetate[4] were intermediate between those in THF and cyclopentane, 0.33

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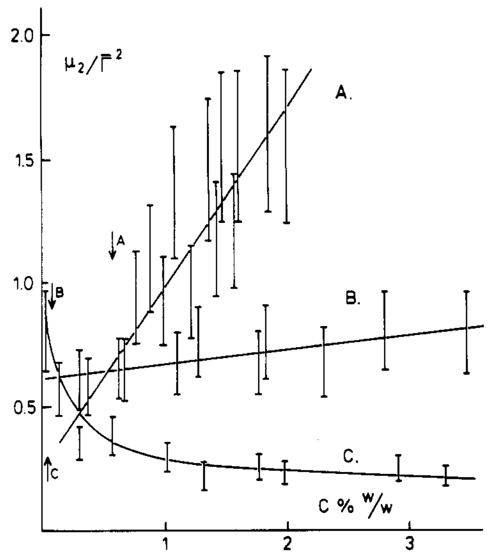

Figure 1. The normalized second cumulant, $\mu_2/\bar{\Gamma}^2$, vs. concentration for semidilute solutions of polystyrene ($\bar{M}_w = 8 \times 10^6$) in (A) cyclopentane, (21 °C, Θ-conditions); (B) ethyl acetate, 25 °C; (C) tetrahydrofuran, 25 °C. The vertical arrows denote the value of C^* ($=3M/4\pi R_g{}^3 N_A$). The error bars are given as ±20% as suggested by Koppel.[5] All measurements are for an angle of 40°, corresponding to $qR_g = 1.02$ (cyclopentane), 1.92 (ethyl acetate), and 2.3 (THF).

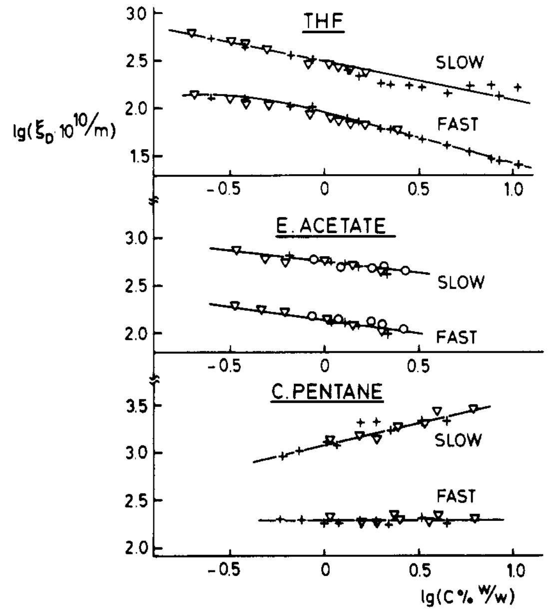

Figure 2. PCS data at $qR_g > 1$. log–log plots of the dynamic correlation length against concentration for fast and slow modes evaluated with eq 2 for data in the solvents shown. Polystyrenes: 3×10^6 (○), 8×10^6 (+), 15×10^6 (▽).

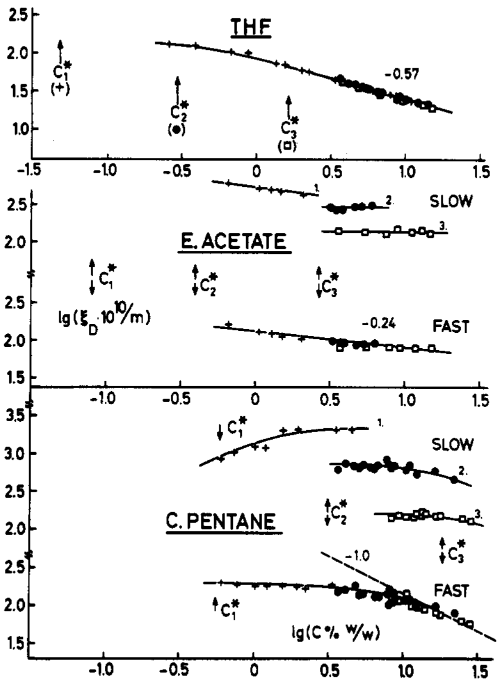

Figure 3. PCS data at $qR_g < 1$. Fast and slow modes evaluated with eq 2 in the solvents shown. Polystyrenes: 9.3×10^4 (□), 9.3×10^5 (●), 8×10^6 (+). The broken line has a negative slope of unity for comparison purposes.

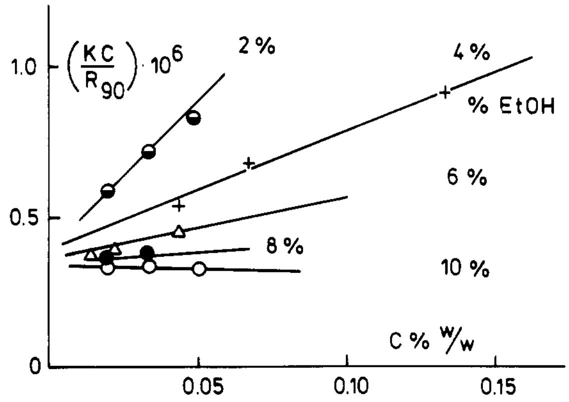

Figure 4. Static light scattering data at a measuring angle of 90° for PS ($\bar{M}_w = 3 \times 10^6$) in dilute solution as a function of solvent composition (percent (v/v) ethanol in ethyl acetate).

for the fast mode and 0.22 for the slow. (The average values of the exponent derived when using a cumulants analysis are in general larger[4] owing to the change in weighting of the participating modes with change in concentration. Thus, for example, the value in THF is 0.67 as previously reported.[19]) The exponents found differ substantially in some cases from the values predicted by theory. Thus $\gamma = 0.75$ is given by scaling theory[7] for the gel mode in a good solvent and a positive slope of unity for a slow cooperative mode at high q in a Θ-solvent.[8,9] The exponent for the gel mode in the Θ-solvent is, however zero in agreement with the predictions of Brochard and de Gennes.[8,9] The value of the exponent is not trivial, of course, since this parameter is one of the main indices used to assess the measure of agreement between theory and experiment. Widely differing values of the exponent have been reported (see, for example, ref 10) and it would appear that a contributory reason could in many cases be the participation of more than one relaxation in the time correlation function, with a varying weighting depending on the particular concentration interval examined.

In an attempt to more precisely establish the change in the exponent with solvent and to investigate the nature of possible contributory modes, an alternative system has been examined here. It was earlier shown[11] that the addition of small relative amounts of ethanol to ethyl acetate (with which it is isorefractive) yields a progressive decrease in solvent quality such that Θ-conditions are realized at about 10% ethanol at 25 °C. Johnsen[11] examined the dilute solution properties of polystyrene ($\bar{M}_w = 1.6 \times 10^5$) in this mixed-solvent system using a variety of techniques, including classical diffusion, PCS, static light scattering, osmotic pressure, and sedimentation equilibrium. The second virial coefficient was found to approach zero in the vicinity of 10% ethanol.

The presently reported measurements are for dynamic and static light scattering on semidilute and dilute solutions, respectively, of a narrow distribution ($\bar{M}_w/\bar{M}_n = 1.06$) polystyrene fraction (PS $\bar{M}_w = 3 \times 10^6$) obtained from Toya Soda Ltd., Tokyo, Japan. The change in the second virial coefficient with solvent composition is shown in Figure 4 by using static light scattering at a measurement angle of 90°. Measurements of angular dissymmetry were not made to characterize the change in coil dimensions with solvent quality, but the results serve as a semiquantitative measure of the change in solvent quality with ethanol addition and confirm the behavior established in detail in the earlier investigation.[11]

PCS measurements were made on semidilute solutions by using the apparatus and experimental conditions previously described[1-4] A measurement angle of 60° was in general employed after it had first been established that the modes, isolated as described below, were both q^2 dependent at all concentrations employed. Thus plots of (Γ_q/q^2) vs. q were strictly horizontal at each concentration over the angular range 30°–110° with no interference detectable from internal motions. The sampling time, τ, was chosen in each run to reflect in a single experiment the main relaxations present as ascertained by a preliminary scanning with a progressive change in τ. Attempts to splice together consecutive runs with different τ values were not found to be completely satisfactory due to uncertainty in the overlap region. A more complete description should, of course, be achieved with a correlator having multiple sampling time options. The data were initially treated with a cumulants fit[5]—any run exhibiting a significant deviation of delayed channels from the calculated base line or unusual intensity was rejected. Multiexponential analysis was subsequently made as previously described,[1-4] employing a nonnegatively constrained, nonlinear least-squares algorithm[12] according to a function of the form

$$g^{(2)}(\tau) - 1 = \beta[A_s \exp(-\Gamma_s \tau) + A_g \exp(-\Gamma_g \tau)]^2 \qquad (2)$$

This expression expresses the second-order time correlation function in terms of (in this sample) two relaxation rates, Γ_s and Γ_g, and A_s and A_g denote the corresponding relative intensities for the slow (subscript s) and fast (subscript g) modes, respectively. No base line term was required. "Goodness of fit" was estimated with the lowest minimum of the reduced sum of squares of residuals to the fit, χ^2, and also the Q parameter.[26] However, the prime justification for using the method of discrete multiexponentials is the expectation from current semidilute solution theory[7] that a small number of modes will be required to describe the dynamical behavior. Thus close to C^* (but possibly at much higher concentrations in poorer solvents) it seems reasonable to expect the coexistence of a fast gel mode and slow translational motions of the chain itself, presuming limited interpenetration of the coils. That this is a strong possibility is supported by a number of experimental studies (see, for example, ref 6 and 13–17). The present concentration range in ethyl acetate extends between 5 and 20 C^*, using the frequently employed definition $C^* = 3M/4\pi R_g{}^3 N_A$, where M is molar mass and N_A Avogadro's number. This definition differs from that used by de Gennes[7] but is considered to produce a more realistic value of the overlap point; see ref 27.

With both simulated experiments and the analysis of mixtures of narrow distribution polystyrene fractions, it was established[1-3] that the present approach gives a more precise definition of the components if closely spaced in relaxation rate than, for example, the intrinsically more general program CONTIN introduced by Provencher.[18] However, it is necessary to assume the number of parameters in successive fitting steps. A recent comparison of methods for use with PCS experiments is that in ref 20.

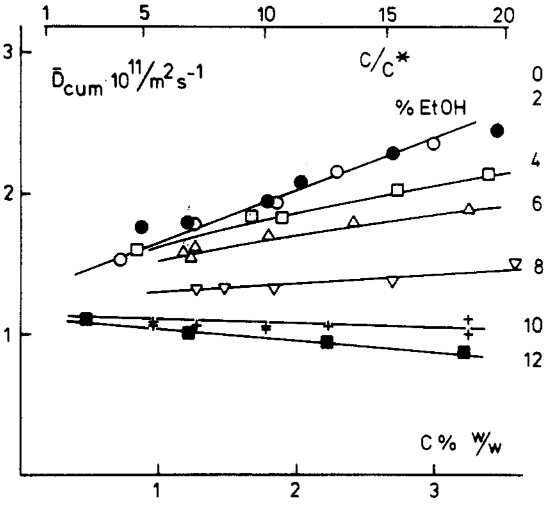

Figure 5. Dynamic light scattering data evaluated with the cumulants method;[5] data for PS ($\bar{M}_w = 3 \times 10^6$) at different values of the solvent composition. Measurements at an angle of 60°.

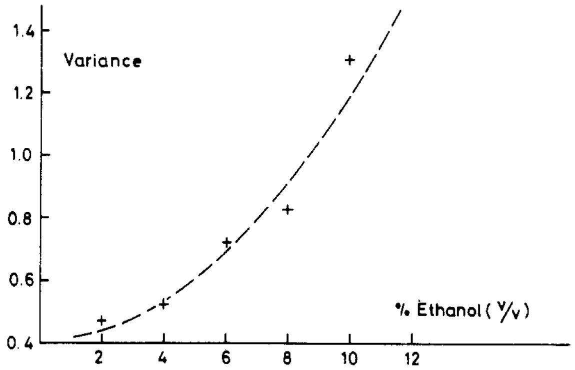

Figure 6. Relative variance as a function of solvent composition in the ethanol/ethyl acetate system. The data refer to dynamic light scattering measurements on PS ($\bar{M}_w = 3 \times 10^6$) at angle 60° and a cumulants fit used.

Figure 5 shows the cumulants fit[5] data. The slope of the curves decreases progressively with increasing ethanol content ($\gamma = 0.43$ at 0% ethanol and −0.16 at 12%). The use of weight percent concentration introduces a slight (about 1%) discrepancy in the values of the exponent in $D \sim C^\gamma$, but is not considered to be significant over the limited range of ethanol content and the small difference in densities of the solvents. Figure 6 shows the corresponding increase in the relative variance with solvent composition. Such large values of the variance in semidilute solutions of narrow distribution fractions can best be understood in terms of complementary modes of relaxation, as earlier pointed out by Chu and Nose[6] in investigations on the PS/*trans*-decalin system. However, the cumulants[5] method permits no deeper understanding of the sources of this behavior. Multiexponential analysis in the present system led to a bimodal fit as the simplest choice on the basis of the usual statistical parameters.[1] It is thus possible to rationalize and indicate a potential source of the systematic changes in the variance. Division into the two components should not be taken to mean that these are "monodisperse" in relaxation rate but rather to show that the semidilute solution structure is more complex than would be implied by a mean-value fit using the cumulants method or a single-exponential approximation.

Figure 7 illustrates data obtained with eq 2 in the form of D vs. C diagrams for the two modes. The upper part of the figure illustrates the decreasing concentration dependence for the fast gel mode with increasing ethanol concentration. The corresponding exponent in $D \sim C^\gamma$

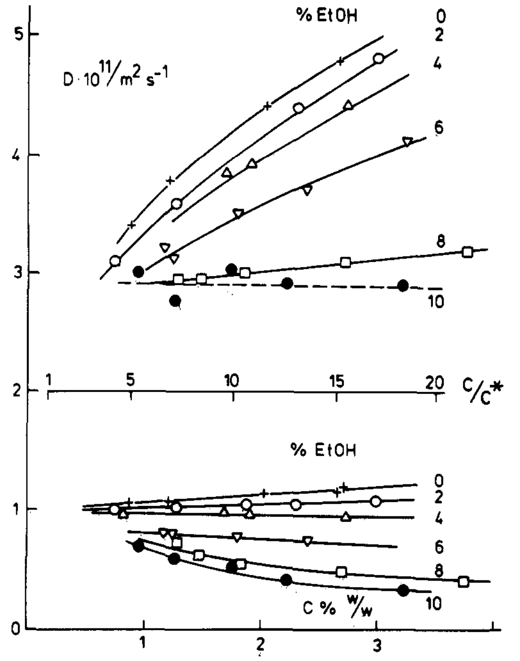

Figure 7. Dynamic light scattering data evaluated with eq 2: upper part, fast (gel) mode as a function of solvent composition in a D vs. C plot for PS $\bar{M}_w = 3 \times 10^6$; lower part, slower mode derived with eq 2.

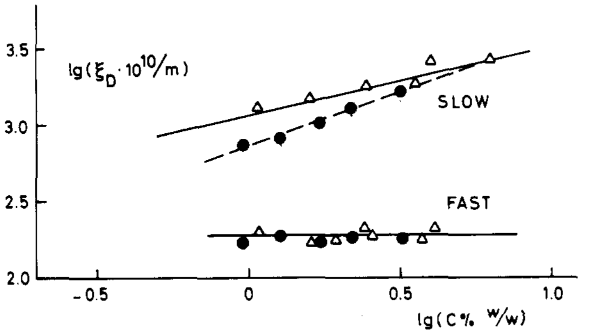

Figure 8. Comparison of the concentration dependence of the dynamic correlation length in 10% (v/v) ethanol in ethyl acetate (●) solutions of PS $\bar{M}_w = 3 \times 10^6$ with data for the same fraction obtained in cyclopentane (21 °C, Θ-conditions)[3] (△).

decreases from 0.33 at 0% to approximately 0 at 10% ethanol. The increasing scatter with increasing ethanol content is due, in part, to the lower relative intensity of the fast mode, which falls from about 0.35 in pure ethyl acetate to about 0.25 at 10% ethanol at a concentration of polystyrene of 3%. The slower mode shown in the lower part of Figure 7 has a decreasing dependence on polymer concentration ($\gamma = 0.22$ at 0% ethanol to $\gamma = -0.6$ at 10% ethanol).

The data in 10% ethanol, corresponding approximately to Θ-conditions, are compared in Figure 8 with previous data from ref 3 from the Θ-system PS/cyclopentane at 21 °C in the form of a log–log plot of the dynamic correlation length vs. concentration. The gel mode data are coincident, as should be the case in the absence of differences in specific solvent effects, in the two systems. A concentration-independent gel mode is thus apparently confirmed for high molar mass fractions at low volume fraction of polymer but with the condition $C > C^*$ satisfied. This agrees with the prediction of Brochard.[9] The slower mode in these Θ-systems decreases in relaxation rate with increasing polymer concentration as for the isolated coil in dilute Θ-solutions, except that we have noted that it is molar mass independent at q vectors corresponding to $qR_g > 1$. Thus it is not possible to probe translational motions of large coils at these q values.

The interpretation to be placed on this slower mode is still unclear due to lack of a comprehensive theory. The presence of a slower mode both in a good solvent[2] and the marginal solvent[4] with high molar mass fractions is recalled. (We note, however, that there is no indication of a "slow mode" in the sense of a very slow relaxation leading to a "floating" base line in the characterization of the present two modes.)

The observation that the data for the slower mode fall onto an extension of the curve for the dilute solution/low-angle data (i.e., translational diffusion for the single coil) suggests that the bimodal behavior may derive from a limited interpenetration of large coils. This would probably be expected to be more pronounced in the poor solvents due to extensive self-knotting, and this agrees with the finding that the relative intensity for the fast mode is greater for better, thermodynamically speaking, solvents.[4] With such a model, one could anticipate a slow relaxation having a characteristic length of the magnitude of the effective coil size in addition to a gel mode. These conclusions find some support from the recent results of Koberstein et al.[21] using static light scattering and neutron scattering in semidilute PS solutions in both good and Θ-solvents.

The presence of a mode having a negative concentration exponent was, however, unexpected and conflicts with the prediction of theory[8,9] ($D_{slow} \sim C^1$) for a slow cooperative mode in semidilute Θ-solutions, which follows from the hypothesis of a smooth decrease in the correlation length as concentration increases. The measurements at $qR_g < 1$ in Figure 3 show that the slower mode is molar mass dependent in cyclopentane on a time scale at which the chains are able to disentangle (i.e., $\Gamma T_R < 1$, where T_R is the disentanglement time defined by de Gennes[7]). With lower molar mass fractions and at concentrations close to C^*, one could understand the slower mode as translational diffusion of the single coil within an imperfect network as previously concluded.[1,6] It is not surprising that translational motions may be probed in semidilute solutions using PCS, particularly in poor solvents in which the coil is contracted and to a great extent self-entangled. Taken together, the above observations (i.e., of the behavior at both $qR_g > 1$ and $qR_g < 1$) tend to confirm the presence of a correlation of the magnitude of the coil dimension throughout the semidilute region, together with a length scale typifying the transient gel segment length.

Figure 9 presents data derived from gradient diffusion measurements. Here an average length has been derived from $\bar{D}_{CGD}$ by using eq 1, where $\bar{D}_{CGD}$ is the coefficient obtained from macroscopic concentration-gradient relaxation. This quantity represents some average of the relaxational modes contributing to the decay of the gradient and thus is not to be identified with D_{slow} from PCS measurements. Due to its composite nature,[1,6,15] $\bar{D}_{CGD}$ is observed[3,25] to first decrease, pass through a minimum, and finally increase as the concentration passes through C^*. Such a feature undermines the use of $\bar{D}_{CGD}$ values for characterizing a slow cooperative mode in Θ-systems.[10,22,24] In the same spirit, it is unsuitable to use the composite coefficient derived by a cumulants evaluation for estimating concentration exponents in semidilute solutions. This leads to the apparently anomalous behavior described, for example, in ref 10. With both high and low molar mass fractions, the correlation function is highly nonexponential in poor solvents throughout the semidilute regime.

The data for cyclopentane in Figure 3 shows that the nature of the concentration dependence of the slow mode

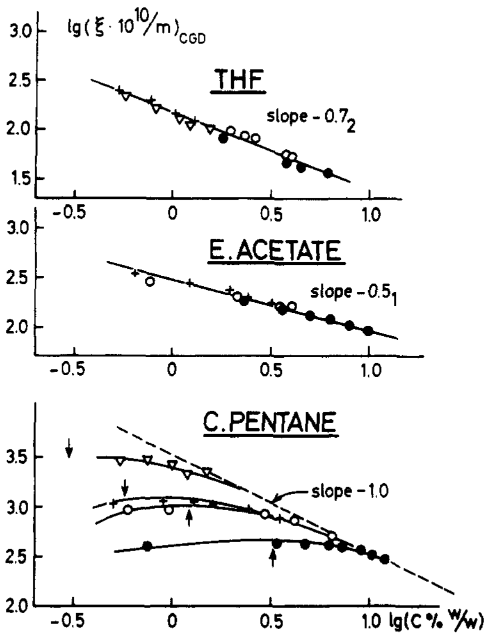

Figure 9. log–log plots of an apparent correlation length derived from gradient diffusion coefficients, $\bar{D}_{\mathrm{CGD}}$, by means of eq 1, vs. concentration in different solvents as shown. Polystyrenes: 9.3 × 10^5 (●), 3 × 10^6 (○), 8 × 10^6 (+), 15 × 10^6 (▽). The broken line has a negative slope of unity for comparison. The vertical arrows indicate C^* ($=3M/4\pi R_g{}^3N_A$).

is very dependent both on the molar mass of the sample and on the concentration interval studied. This may well underlie the apparently discordant results of various investigating groups.[1,3,16,22,24] This feature could possibly reflect a nonhomogeneous nature of the slow component isolated here. Recent results of Štěpánek et al.[23] on the PS/cyclohexane Θ-system demonstrate that the dynamics become much more complex as the concentration is increased. Štěpánek et al.[23] report at least four resolvable components using a Simplex analysis[30] of the time correlation function at a concentration of 8.8% of a PS fraction with $\bar{M}_w = 3.84 \times 10^6$. The measurements were made at 34 °C. The correlation functions, measured in consecutive runs over a range of sampling times, were spliced together in a computer prior to analysis; the span of the relaxation times was nearly 4 decades. Such observations cast doubt on the validity of a bimodal interpretation of semidilute Θ-solution structure as postulated by Brochard[9] and suggest a considerably more complex distribution of relaxational modes. We are currently approaching the problem[28] by an alternative route, which is yielding results relevant to this discussion. With decreasing temperature, the solvent quality of ethyl acetate for polystyrene decreases and the Θ-point is reached at −44 °C.[29] PCS measurements as a function of temperature have been made from ambient down to temperatures in the vicinity of the Θ-temperature as a function of concentration. The correlation functions for a wide range of sampling times have been assembled as described above and analyzed by a number of analytical methods. The results show a striking consistency in that a distribution of slow relaxational components is found which becomes more complex with lower temperatures and also increasingly weighted to the long relaxation times at the lowest temperatures. This shows that the slower mode described in the present paper is probably a mixture of unresolved components; its composition changes as the relative weighting shifts as a function of both concentration and solvent quality (in this case, altered by temperature change). It is thus clear why the slower mode is found to decrease with increasing concentration.

Concluding, we note that semidilute solutions are much more complicated than has been appreciated both in the theoretical approaches and the treatment of data obtained from PCS measurements. The problem is accentuated as the solvent quality decreases. The cumulants evaluation of PCS data in the semidilute regime (or use of classical gradient measurements) will lead to a misleading description of the dynamical behavior. While the bimodal model may be adequate to describe good-solvent systems,[2] it is clearly inadequate for poor-solvent systems. It is, however, a first step to an improved description of the relaxation behavior. We are currently using a new multi-τ correlator (ALV-Langen Co., FRG) enabling 23 different τ ranges to be covered and accumulated simultaneously, encompassing, for example, the lag-time range 1 μs to 1 min, to obtain an improved characterization of Θ-semidilute solutions of very high molar mass fractions.

Registry No. PS, 9003-53-6.

References and Notes

(1) Brown, W.; Johnsen, R. M. *Macromolecules* **1985**, *18*, 379.
(2) Brown, W. *Macromolecules* **1985**, *18*, 1713.
(3) Brown, W. *Macromolecules* **1986**, *19*, 387.
(4) Brown, W. *Macromolecules* **1986**, *19*, 1083.
(5) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(6) (a) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 590, 599. (b) Chu, B.; Nose, T. *Ibid.* **1980**, *13*, 122.
(7) (a) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 587, 594. (b) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University, Press: London, 1979.
(8) Brochard, F.; de Gennes, P.-G. *Macromolecules* **1977**, *10*, 1157.
(9) Brochard, F. *J. Phys.* (*Les Ulis, Fr.*) **1983**, *44*, 39.
(10) Schaefer, D. W.; Han, C. C. In *Dynamic Light Scattering*; Pecora, R., Ed.; Plenum: New York, 1985.
(11) (a) Johnsen, R. M. *Chem. Scripta* **1971**, *1*, 81. (b) Johnsen, R. M. *Ibid.* **1972**, *2*, 31.
(12) Marquardt, D. W. *SIAM J. Appl. Math.* **1963**, *11*, 431.
(13) Nishio, I.; Wada, A. *Polym. J.* (*Tokyo*) **1980**, *12*, 145.
(14) Amis, E.; Han, C. C. *Polymer* **1982**, *23*, 1403.
(15) Kubota, K.; Abbey, K. M.,; Chu, B. *Macromolecules* **1983**, *16*, 137.
(16) Amis, E.; Han, C. C.; Matsushita, Y. *Polymer* **1984**, *25*, 650.
(17) Hwang, D.-h.; Cohen, C. *Macromolecules* **1984**, *17*, 1679.
(18) (a) Provencher, S. W.; Hendrix, J.; De Maeyer, L.; Paulussen, N. *J. Chem. Phys.* **1979**, *69*, 4273. (b) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.
(19) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229.
(20) Stock, R. S.; Ray, W. H. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1393.
(21) Koberstein, J. T.; Picot, C.; Benoit, H. *Polymer* **1985**, *26*, 673.
(22) Adam, M.; Delsanti, M. *Macromolecules* **1985**, *18*, 1760.
(23) Štěpánek, P.; Zimmermann, K.; Koňák, C. *Polym. Bull.* (*Berlin*), submitted.
(24) Hecht, A.-M.; Bohidar, H. B.; Geissler, E. *J. Phys. Lett.* **1984**, *45L*, 121.
(25) Roots, J.; Nyström, B. *Macromolecules* **1980**, *13*, 1595.
(26) *Q* is the ratio of the autocorrelation of residuals with a displacement of 1 and their autocorrelation with a displacement of 0, i.e., their variance.
(27) Wells, J. D. *J. Chem. Soc., Faraday Trans 1* **1984**, *80*, 1233.
(28) Štěpánek, P.; Koňák, C.; Brown, W., in preparation.
(29) Saeki, S.; Konno, S.; Kuwahara, N.; Nakata, M.; Kaneko, M. *Macromolecules* **1974**, *7*, 521.
(30) Zimmermann, K.; Delaye, M.; Licinio, P. *J. Chem. Phys.* **1985**, *82*, 2228.