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Dynamics of Pregel Solutions and Gels in a Θ-Solvent near a Spinodal

Čestmír Koňák and Libuše Mrkvièková

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

Rama Bansil*

Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215

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ABSTRACT: We examine the influence of the diverging concentration fluctuations near a spinodal on the dynamics of branched polymer solutions in the vicinity of a sol−gel transition. Dynamic light scattering (DLS) measurements on pregel solutions and gels of methyl methacrylate (MMA) cross-linked with varying amounts of ethylene dimethacrylate (EDMA) in a Θ-solvent (4-heptanone) reveal a fast exponentially decaying cooperative mode and a slow, long-time tail arising from the dynamics of the partially penetrating clusters. Just as in the case of a sol−gel transition in a good solvent, the slow part is a stretched exponential below the gel point and a power law at the gel point. The cooperative diffusion constant $D_c \sim (T - T_s)^{\nu'}$ and the decay rate characterizing the dynamics of the interpenetrating clusters in the pregel solutions $\Gamma_s \sim (T - T_s)^{\nu''}$ as the temperature approaches the spinodal temperature, T_s. While the vanishing of D_c is expected due to the divergence of the concentration correlation length near a spinodal, the vanishing of the stretched exponential relaxation rate with the exponent $\nu'' = 1.20 \pm 0.05$ is a new observation. The exponent ν' varies from 0.5 to 0.85 as the degree of cross-linking approaches the gel point. This implies that the effective viscosity diverges more strongly near T_s than observed in regular fluids. For the sample at the gel point, the decay rate of the power law tail also slows down in the vicinity of the spinodal. We suggest that the unusual temperature dependences arise from a coupling of the cluster diffusion dynamics to the dynamics of the concentration fluctuations in the polymer matrix.

Introduction

Phase transitions in chemically cross-linked, swollen gels have been extensively studied because in many situations there is a discontinuous volume phase transition causing a macroscopic change in the degree of swelling of the gel.[1,2] Another class of phase transitions in gels is the sol−gel transition, where the viscoelastic properties change from that of a viscous liquid to an elastic material.[3−5] These two transitions are fundamentally different types of transitions, the first being the usual thermodynamic phase transition in a binary network plus solvent system, while the second is a connectivity or percolation transition. Several studies of the dynamics and the critical phenomena associated with each of these transitions occurring separately have been reported in the literature.[6−12] The question of what happens when both these transitions occur simultaneously has received much less attention.

There are two ways of combining the sol−gel and binary phase separation transitions so that one may study how they influence each other. One possibility is to consider a system which forms a thermoreversible physical gel in a poor solvent, so that phase separation and sol−gel transition occur simultaneously in the same temperature region at the same time. The physics here is clearly dominated by the kinetics of the two processes.[13,14] Another, totally different approach is to consider chemically cross-linked gels and pregel solutions with varying degrees of cross-linking, f_c, prepared in a Θ solvent. Since the pregel solution or gel samples are in equilibrium, such a system provides a means to investigate the influence of the sol−gel transition on the static and dynamic aspects of the critical behavior associated with the usual binary phase separation phenomena.

In a recent paper,[15] we have reported the results of static light scattering (SLS) measurements from samples on either side of the gel point as the temperature approaches the spinodal. The measurements were made in semidilute pregel solutions and gels of poly(methyl methacrylate) (PMMA) prepared by radical copolymerization of methyl methacrylate and ethylene dimethacrylate in the presence of a Θ-solvent (4-heptanone). This system has considerable advantage over the water-soluble polyacrylamide[6,7] and *N*-isopropylacrylamide[8,9] gels since solvent−polymer interactions are reduced to the excluded volume effect only. Thus we avoid the complications of the long-range electrostatic and H-bond interactions as well as hydrophobic effects which occur in the hydrogels. As expected, we observed the divergence of the correlation length, ξ, and the extrapolated zero-angle scattered intensity, $I_{c,0}$, as the temperature approached the spinodal. Since all the samples had the same total polymer concentration, the divergence is related to approaching a spinodal and not a critical point.

In this paper, we address the question of the dynamics of these pregel solutions and gels near a spinodal using the technique of dynamic light scattering (DLS). Since the sol−gel transition is characterized by unusual dynamics, it is possible that the dynamics of the branched polymer solutions in the vicinity of the sol−gel transition may be significantly different from both linear polymer solutions and well-cross-linked gels. Although there are no studies of the dynamics of concentration fluctuations in gels in Θ-solvents, Adam et al.[16] and Martin et al.[17,18] have shown that in good solvents the dynamics of the pregel clusters gives rise to stretched exponential correlation functions in DLS,

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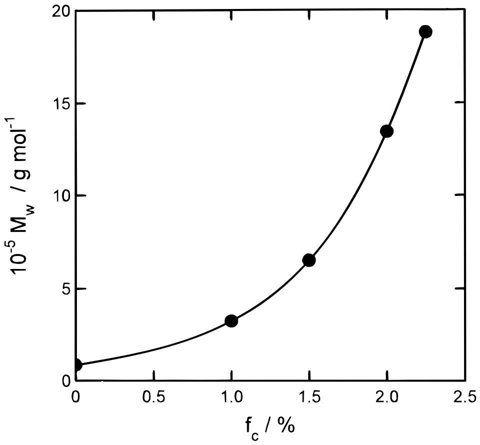

Figure 1. Weight-average molecular weight, M_w, versus the degree of cross-linking, f_c.

Table 1. Characteristics of Swollen PMMA Gels

c (v/v)	f_c (v/v)	$M_x \times 10^{-3}$	χ
0.10	0.03	121	0.5
0.10	0.04	103	0.5
0.10	0.05	91	0.5

whereas in gels, close to the sol–gel transition, the time dependence becomes a power law. This lack of a characteristic time scale implies that the incipient gel has a fractal behavior in time, just as the infinite cluster at the gel point is also a fractal in space.

We show that the autocorrelation functions of the gels in a Θ-solvent also follow the same time dependence as in good solvents. However, the behavior in the vicinity of the spinodal shows some novel features arising from the coupling of the concentration fluctuations, which diverge near a spinodal, with the unusual diffusional dynamics of the branched polymers in the vicinity of the sol–gel transition.

Experimental Section

Sample Preparation. The samples used in these experiments were PMMA solutions and gels obtained by copolymerizing methyl methacrylate (MMA) with small amounts of ethylene dimethacrylate (EDMA) as the cross-linking agent in the presence of the Θ-solvent, 4-heptanone (Θ-temperature = 40.4 °C).[19] A set of samples with total monomer concentration $c = 10\%$ (v/v) was prepared with various degrees of cross-linking, f_c = [EDMA]/[MMA], varying between 0 (linear polymer) and 4% (gel). The reaction was initiated with azobis(isobutyronitrile) (10 mg/mL of MMA) and allowed to proceed at 50 °C for 7 days in cylindrical light scattering cells. By the end of this period, the gelation reaction was complete with a conversion better than 95%. All monomer solutions were first filtered using 0.22 μm filters (Millipore). The weight-average molecular weight, M_w, of the pregel clusters was measured by static light scattering experiments in the very dilute concentration limit. The values of M_w, which characterizes the average degree of connectivity of the clusters, increase with increasing f_c and tend to diverge at the gel threshold (cf. Figure 1). The gel threshold cross-link ratio, $f_{c,g}$, was defined as the lowest value of f_c at which the sample formed a weak gel, $f_{c,g} \approx 2.5\%$.

To characterize the gel network at $f_c > f_{c,g}$, swelling experiments were conducted at the Θ-temperature (40.4 °C) on these gels. Swelling equilibrium measurements were interpreted in terms of the Flory-Rehner equation to determine the molecular weights between cross-links, M_x.[3] The Flory interaction parameter $\chi = 0.5$, corresponding to Θ-conditions, was used for calculations. The resulting values of M_x are given in Table 1. The values of M_x are larger than the values expected on the basis of stoichiometry because not all of the EDMA polymerize as cross-links in a dilute solution.[20]

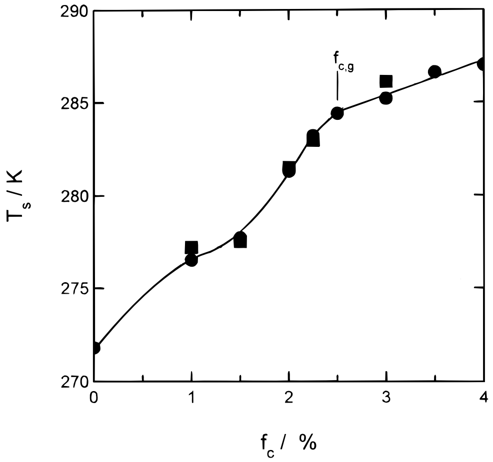

Figure 2. Dependence of the spinodal temperature of pregel solutions and gels with varying degree of cross-linking, f_c. Solid circles and squares denote the spinodal temperatures evaluated from SLS and DLS data, respectively. The spinodal temperature was obtained from the extrapolation of the zero-angle scattered intensity in SLS measurements[15] and from the vanishing of the collective diffusion constant in the DLS measurements, as described later in the text. The position of the gel point is indicated.

The gels used for light scattering experiments were conditioned at 50 °C (the preparation temperature) and examined under isochoric conditions (the gels were not in contact with solvent bath, and all light scattering measurements were realized as fast as possible). Therefore, we can consider the gel volume as constant during each measurement. The spinodal temperatures were measured by extrapolating the inverse of the zero-angle static light scattering intensity to zero.[15]

Dynamic Light Scattering (DLS). Polarized DLS measurements were made at different scattering angles using a light scattering apparatus equipped with a 50 mW He–Ne (632.8 nm) and an ALV 5000 multibit, multi-τ autocorrelator covering approximately 10 decades in delay time, τ. To avoid effects of nonergodicity of gel samples on the dynamic light scattering results, the samples were rotated and the intensity autocorrelation functions, $G^2(t)$ obtained by averaging at least ten measurements at different sample positions were used for analysis. The normalized intensity autocorrelation functions

$$g^2(t) = [G^2(t) - B]/[G^2(0) - B] \qquad (1)$$

are used for demonstration of DLS results and for analysis; B is the baseline. The electric field autocorrelation functions, $g^1(t) = (g^2(t))^{0.5}$, were fitted to the sum of an exponential and a stretched exponential function with exponent b_s:

$$g^1(t) = A_c \exp(-[t/\tau_c]) + A_s \exp(-[t/\tau_s]^{b_s}) \qquad (2)$$

where τ_i (i = s or c) are the characteristic decay times, and A_i the relative scattering amplitudes. The exponent b_s is related to the width of the corresponding distributions of the relaxation times τ; the smaller the value of b_s, the broader is the distribution.

The electric field autocorrelation functions, $g^1(t)$, for samples at the gel point were fitted to the sum of an exponential and a power law function with exponent Φ[18]

$$g^1(t) = a_c \exp(-[t/\tau_c]) + (1 - a_c)/(1 + [t/\tau_s])^{\Phi/2} \qquad (3)$$

where $a_c = A_c/(A_c + A_s)$ is the normalized scattering amplitude of the fast mode.

Results and Discussion

As shown in Figure 2, the spinodal temperature, T_s, increases sharply with increasing f_c up to the gel point

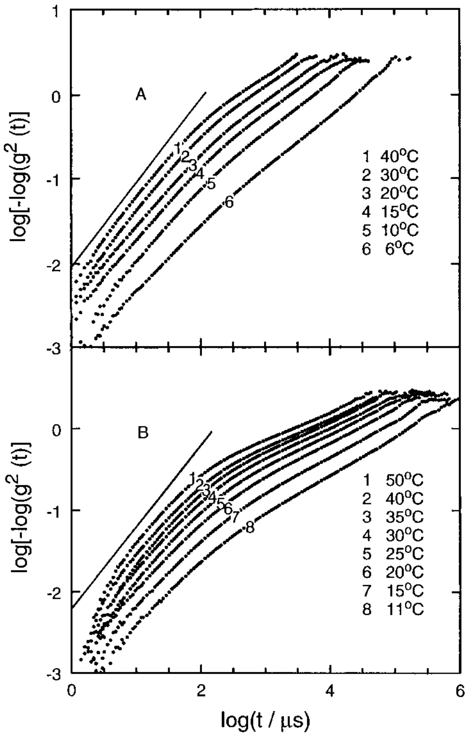

Figure 3. Double logarithm of the autocorrelation functions against logarithm of delay time at the cross-linking content of (A) $f_c = 1\%$ and (B) $f_c = 2\%$ (solutions). Measurements were made at various temperatures as indicated. The line of slope 1 (solid line) corresponds to a normalized single-exponential autocorrelation function.

($f_{c,g} \approx 2.5\%$). This is most likely related to the increase of average M_w and polydispersity of branched molecules on approaching the gel threshold. Since there are no theoretical studies of the effect of branching on the critical behavior, we cannot give any quantitative description of this effect. The small increase of T_s above the gel point can be interpreted in terms of the effect of cross-linking on the Flory interaction parameter.[3,9]

In contrast to semidilute solutions of flexible linear polymers where the dynamics is dominated with a single cooperative diffusion mode, the dynamics in solutions of branched polymers and swollen gels in more complex.[16-18] This is demonstrated in Figure 3A,B, where the double logarithm of the normalized autocorrelation functions $g^2(t)$ measured at several temperatures above T_s are plotted against the logarithm of the delay time t for samples with $f_c = 1$ and 2%. The autocorrelation functions show a fast single-exponential decay initially (slope ≈ 1 in the plot) followed by a long-time tail. This long-time tail is more apparent for the sample with $f_c = 2\%$ in the vicinity of the gel point (see Figure 3B) and can be described by a stretched exponential with $b_s \approx 0.45 \pm 0.02$, independent of temperature. The values of b_s decreased with increasing f_c, ranging from 0.61 ± 0.02 at $f_c = 1.5\%$ to 0.36 ± 0.01 at $f_c = 2.25\%$. The observed exponents are smaller than $b_s = 0.66 \pm 0.05$ reported for silica gels[17,18] and larger than $b_s = 0.26 \pm 0.02$ for branched PMMA polymers in butyl acetate (a good solvent).[21]

The initial fast single-exponential decay (τ_c) may be assumed to correspond to the cooperative motions of the polymer matrix since it has the same value as the cooperative mode in solutions of linear PMMA polymers ($f_c = 0\%$). The long-time tail is due to the dynamics of the partly penetrating polydisperse clusters as has been discussed by Adam et al.[16] and Martin and Wilcoxon.[17,18]

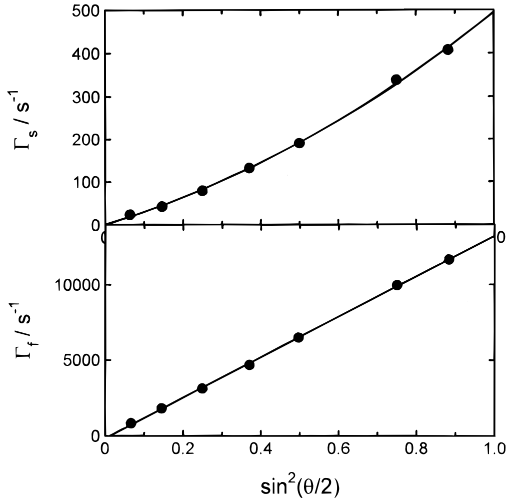

Figure 4. Angular dependence of fast (Γ_f) and slow (Γ_s) decay rates for the sample with $f_c = 2\%$ at $T = 30$ °C.

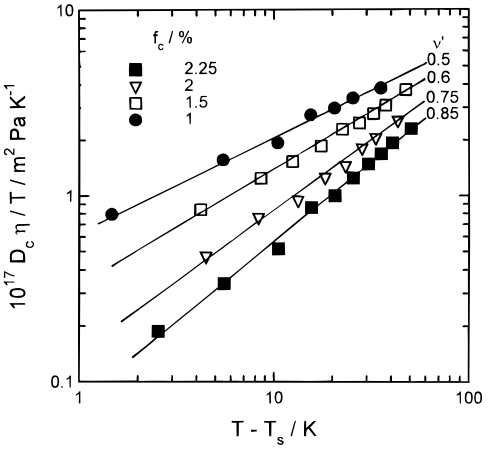

Figure 5. log–log plot of $(D_c\eta/T)^{1/\nu'}$ vs. $(T - T_s)$ for the pregel samples with $f_c = 1$, 1.5, 2, and 2.25%. Values of ν' are indicated on the right side of the plot.

The decay rates of the fast, Γ_f ($=1/\tau_c$), and slow, Γ_s ($=1/\tau_s$), modes obtained by fitting the experimental correlation functions to the sum of the single exponential and stretched exponential functions are plotted as a function of $\sin^2(\theta/2)$ in Figure 4. The fast mode exhibits a linear dependence on q^2, which allows us to define the cooperative diffusion coefficient, $D_c = \Gamma_f/q^2$. We found that D_c vanishes at the spinodal temperature. The vanishing of the diffusion coefficient, D_c, as T approaches T_s can also be used to estimate T_s. Results for several samples differing in f_c are shown in Figure 2. The spinodal temperatures, T_s, obtained independently from the analysis of SLS and DLS data agree with each other within an error of about ±0.5°C.

As shown in Figure 5, the temperature dependence of D_c is described by a power law relationship $D_c\eta/T \approx (T - T_s)^{\nu'}$. Since $D_c\eta/T$ is proportional to the inverse of the correlation length ξ, one expects ν' to be the same as ν, the critical exponent characterizing the divergence of the static correlation length. However, we found that the values of ν' increase with increasing f_c, changing from 0.5 to 0.85. In contrast, the static light scattering experiments[15] gave ν values which agreed with either the meanfield (0.5) or Ising (0.62) exponents. For the samples far away from the gel point with $f_c = 1$ and 1.5%, the values of $\nu' = 0.5$ and 0.62 were in agreement with the values of ν. The change from the mean field value of 0.5 to the Ising value of 0.62 simple reflects the fact that the sample with the higher cross-link content, $f_c = 1.5\%$, was closer to the critical concentration than the lower cross-link content sample, $f_c = 1\%$.

Larger exponents $\nu' = 0.8$ and 0.9 were found for samples with $f_c = 2$ and 2.25%, respectively, in the vicinity of the gel point ($f_{c,g} \approx 2.5\%$). This additional temperature dependence of $D_c\eta/T$, apart from the temperature dependence of the correlation length in these samples, implies that the effective viscosity, η_{eff}, in the Stokes−Einstein relationship has a critical temperature dependence for samples in the vicinity of the gel threshold. Thus, the exponent $x_\eta\nu$ of the temperature dependence of η_{eff}/η should be about 0.2 and 0.3 samples with $f_c = 2$ and 2.25%, respectively. A diverging zero-shear viscosity in the vicinity of the critical point is predicted by the mode coupling and dynamical renormalization group (RG) theories including the nonlinear coupling of the velocity and concentration fluctuations.[22−24] Mode coupling calculations in three dimensions and ϵ expansion RG estimates give $x_\eta\nu \cong 0.04$ ($x_\eta = 0.065$),[25] much smaller than observed in this study. The RG result is supported by experimental results in polymer solutions ($x_\eta\nu = 0.041$,[26] 0.029 ± 0.001[27]) and binary liquid mixtures ($x_\eta = 0.0635 \pm 0.004$[28]). On the other hand, a higher value of the exponent $x_\eta\nu = 0.34$ comparable with our findings was observed in a ternary ethanol−water−chloroform system.[29] A strong temperature dependence of η_{eff}/η in the vicinity of the critical temperature was also observed by Tanaka et al.[7] in weak polyacrylamide gels. A divergence of the relative viscosity η_{eff}/η could arise from a strong, nonlinear coupling of the velocity and concentration fluctuations for branched polymers and gels under conditions when both the sol−gel and thermodynamic phase transitions occur simultaneously.

As mentioned earlier, the temperature dependence of the fast D_c mode in samples with low degree of cross-linking can be explained in terms of the divergence of the concentration correlation length with the mean field or Ising model without any additional divergence of solvent viscosity. However, in these samples ($f_c \leq 1.5\%$), the hydrodynamic correlation length, ξ_h, calculated from the D_c values using the Stokes−Einstein relation is about a factor of 2 larger than the static correlation length ξ obtained from SLS experiments.[15] This result is in agreement with recent results on concentrated polystyrene solutions[30,31] where the same factor of 2 was observed.

The decay rate of the slow mode, Γ_s, was evaluated only for the sample with $f_c \geq 1.5\%$, where the stretched exponential long-time tail was well developed and could safely be analyzed. The q dependence of Γ_s was found to be different from the usual q^2 dependence and may be expressed as $\Gamma_s \sim q^{\alpha_s}$, where $\alpha_s \approx 2.6$ for the particular case shown in Figure 4. This is in agreement with results of a number of studies on associating polymer systems[32] and gelling systems, both physical[33−35] and chemical gels,[16−18] where the q dependence of the slow mode is significantly stronger than that of the fast mode. Such a behavior of the slow mode can be at least qualitatively explained by the coupling model of Ngai and co-workers[36] dealing with the problem of how the relaxation of a specific cluster is “slowed down” due to the coupling to complex surroundings. The coupling model predicts that $\alpha_s = \alpha_c/(1 - n)$, where the coupling parameter n ($0 < n < 1$) is a measure of the coupling strength of the dynamic mode to its surrounding and α_c is the exponent for the corresponding fast mode. The quantity $(1 - n)$ should be proportional to the exponent b_s. This very interesting problem is beyond the main scope of this paper, and, therefore, a separate study of the coupling interactions is in progress. Because of the stronger q dependence of Γ_s, a slow, cluster diffusion coefficient cannot be defined. Instead, the quantity Γ_s/q^2 measured at the scattering angle of 90° will be discussed further.

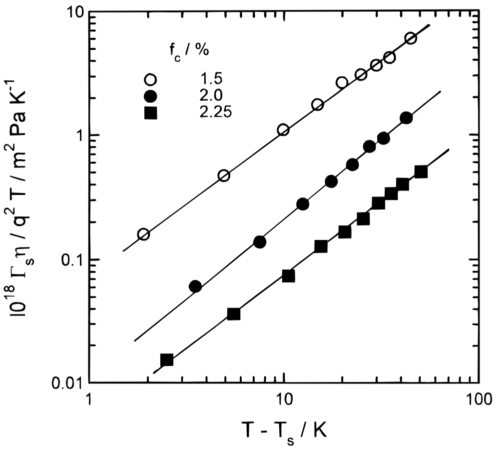

Figure 6. log−log plot of the slow decay rate of the stretched exponential contribution to the correlation function, $\Gamma_s(\theta{=}90°)\ \eta/q^2T$, vs $(T - T_s)$ for the pregel samples with $f_c = 1.5$, 2, and 2.25%; the mean value of $\nu'' \approx 1.20 \pm 0.05$.

The temperature variations of Γ_s/q^2 may again be described by the power law dependence ($\Gamma_s\eta/q^2T \approx (T - T_s)^{\nu''}$) (see Figure 6). Contrary to the behavior of the collective mode, ν'' seems to be independent of f_c (f_c = 1−2.25%) within the experimental accuracy; $\nu'' \approx 1.20 \pm 0.05$. The decrease of Γ_s on approaching T_s cannot be explained by the temperature dependence of the viscosity alone and may be due to a coupling of cluster diffusion to the dynamics of the critical concentration fluctuations in the polymer matrix. Although the cluster size is fixed, the interpenetration of the clusters will be affected by fluctuations in the correlation length. Thus, on length scales comparable to the correlation length, the diffusional dynamics of the interpenetrating clusters will be coupled to the dynamics of the concentration fluctuations. To the best of our knowledge, this problem has not been studied either theoretically or experimentally, until now.

The temperature dependence of the normalized scattering amplitude a_c ($=A_c/(A_c + A_s)$) is shown in Figure 7. The amplitude of the fast mode $a_c \propto (T - T_s)$, vanishing in the vicinity of T_s. This observation is surprising since critical behavior is expected for the fast D_c mode. Probably, the coupling of the fast to the slow mode is reflected not only in the temperature dependence of Γ_s/q^2 shown in Figure 6 but also in the more general transmission of critical behavior from the fast to the slow mode.

The profile of the long-time tail of the normalized autocorrelation function, $g^2(t)$, changes with increasing cross-link content from a stretched exponential function to a power law function with an exponent $\Phi \approx -0.35$ at the gel point $f_c = 2.5\%$ as demonstrated in Figure 8A,B. The observed exponent is close to the value $\Phi = -0.34 \pm 0.03$ reported by Martin and Wilcoxon for silica gels[17] and $\Phi = -0.27 \pm 0.03$ for PMMA gels swollen in butyl acetate[21] (a good solvent for PMMA). The crossover from stretched exponential to power law form upon crossing the sol−gel transition has been described by Martin and Wilcoxon.[18] According to their model, $\Phi =$

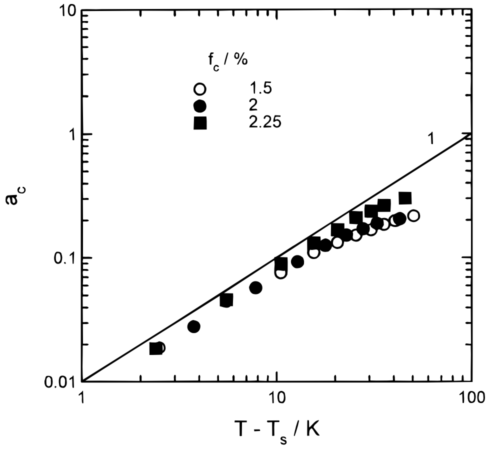

Figure 7. Logarithm of the normalized scattering amplitude, a_c, vs. logarithm of $(T - T_s)$ for the pregel samples with f_c as indicated. The solid line has a slope of 1.

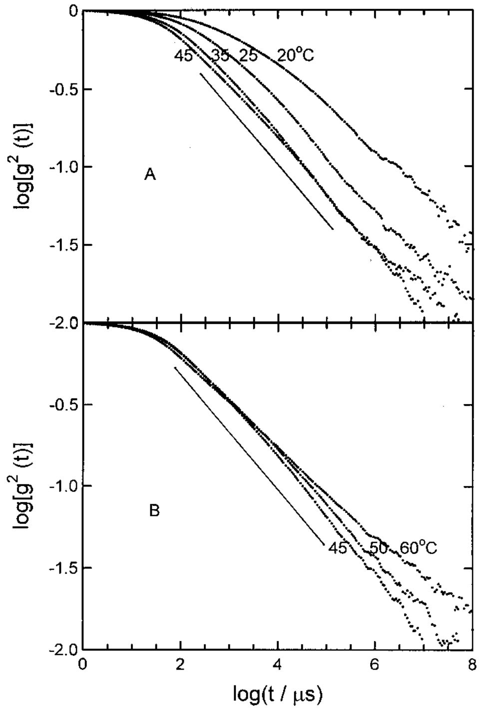

Figure 8. Logarithm of the autocorrelation functions against logarithm of delay time for the sample at the gel point, f_c = 2.5%. Measurements were made at various temperatures as indicated: (A) 45 °C > T > T_s; (B) $T \geq$ 45 °C. The solid line corresponds to a power law in time with an exponent −0.35.

1 − D_p, where D_p is the fractal dimension of the detected photons scattered from the critical gel. For gels in poor solvent, we obtain $D_p \cong 0.65$. Just as a fractal has no internal characteristic length, similarly fractal time lacks an internal characteristic time. This general type of behavior is observed in spin glasses, due to the percolative structure of a random alloy.[18] It has also been observed in microemulsions, where both percolation and critical phenomena occur simultaneously.[37] To separate the initial exponential contribution from the power law tail, the experimental correlation functions were fitted to eq 3. The results of the fit are given in Table 2. Contrary to the behavior of the samples below the gel point where a_c decreased on approaching T_s, a_c increases for the gel point sample (see Table 2). The dynamics of partly penetrating polydisperse clusters (power law function) dominates the autocorrelation functions at temperatures far from T_s (≥45 °C) (cf. Table 2 and Figure 8B) while the cooperative motion contribution (single-exponential function) is significant in the vicinity of T_s (cf. Table 2 and Figure 8A). The slow decay rate, Γ_s, which is associated with the start of the power law tail, seems be approximately linearly dependent on q^2, although these data are less accurate since τ_s is a weaker fitting parameter.

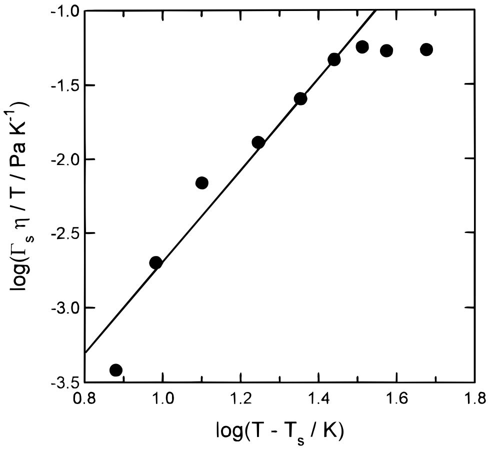

Figure 9. log−log plot of the decay rate of the power law contribution to the autocorrelation function, $\Gamma_s(\theta = 90°)\eta/T$, vs $(T - T_s)$ for the sample at the gel point with f_c = 2.5%. The solid line has a slope of −3.

Table 2. Results of Analysis of Autocorrelation Functions According to Eq 3 for the Critical Gel Sample (f_c = 2.5)

temp (K)	τ_c (μs)	τ_s (μs)	a_c	Φ
333		25.8	0	0.37
323		30.2	0	0.30
318		30.6	0	0.30
313		40.2	0	0.27
308		80.0	0	0.37
303	64.7	170	0.06	0.34
298	101	345	0.09	0.34
295	225	1260	0.12	0.27
293	570	6800	0.17	0.31

The temperature dependence of $\Gamma_s\eta/T$ is shown in Figure 9. It can be seen that the dependence of $\Gamma_s\eta/T$ on $(T - T_s)$ cannot be described by a power law in the entire temperature range. Thus, $\Gamma_s\eta/T$ is independent of temperature for $(T - T_s) \geq 25$ K and decreases approximately with exponent −3 in the vicinity of T_s. A similar slowing down of the tracer diffusion of particles as a result of the decrease of the particle mobility was observed in binary liquid mixtures of phenol−water.[38] The slowing-down effect was observed if the correlation length of concentration fluctuations, ξ, was comparable to or larger than the particle diameter. The observation was qualitatively explained by a coupling of concentration fluctuations to the tracer diffusion. This explanation could be adopted even for the cluster diffusion in our study. The different dynamic behavior of samples below and at the gel point is not well understood, and the problem calls for new theoretical studies.

The dominant dynamic process in gels well beyond the gel point (f_c = 3%) is the cooperative (gel) mode as demonstrated in Figure 10. The broad long-time tail is not the slow cluster mode found for samples below the gel point but is probably due to a diffusion of sol in the gel matrix.[20] The result that the slow mode disappears when the gel is formed was already observed on several chemically gelled systems.[39−41] In the gels, D_c follows the power law temperature dependences with the

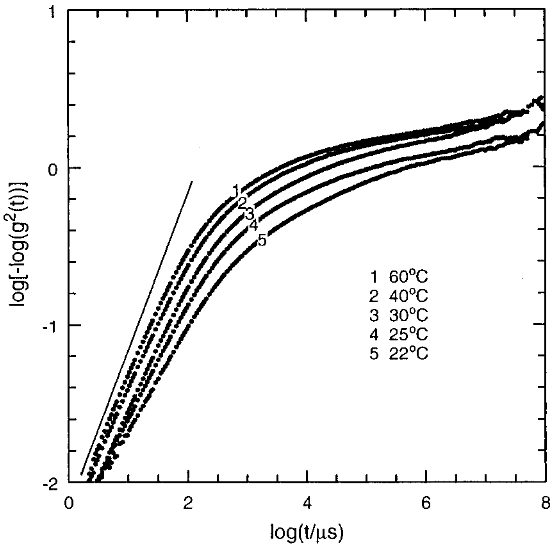

Figure 10. Double logarithm of the autocorrelation functions against logarithm of delay time for a well-gelled sample, $f_c = 3\%$. Measurements were made at various temperatures as indicated. The line of slope 1 (solid line) corresponds to a single-exponential autocorrelation function.

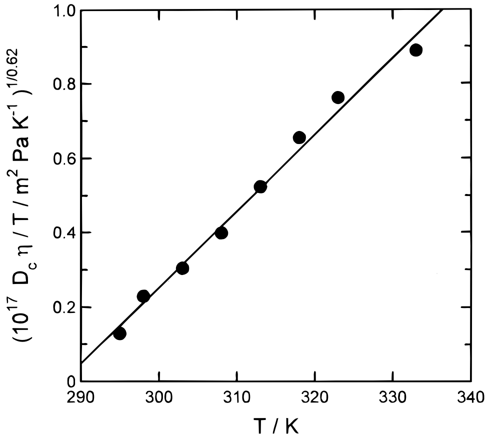

Figure 11. Temperature dependence of the cooperative diffusion constant $(D_c\eta/T)^{1/\nu}$ ($\nu = 0.62$) for the gel sample with $f_c = 3\%$.

exponent $\nu \approx 0.6$ (see Figure 11), as has been reported for other gels near the spinodal or critical point.[6−9]

Conclusion

We have observed a coupling between the dynamics at the sol−gel transition with the dynamics of the critical fluctuations near a spinodal point. The intensity autocorrelation functions for solutions of pregel branched polymers consist of two contributions where the fast mode is attributed to the cooperative motions of the polymer matrix and the stretched exponentially decaying, slow mode is due to the dynamics of the partly penetrating polydisperse clusters. At the gel point, the autocorrelation function develops a power law tail at long times. In this regard, the dynamics in the poor solvent case is similar to that seen previously in sol−gel transition in a good solvent.[16−18] The slow decay rates characterizing both the stretched exponential part in the pregel samples and the power law part in the sample at the gel point as well as the collective diffusion constant D_c vanish upon approaching the spinodal temperature. Each of these quantities follows a power law scaling relationship with a different exponent. Contrary to the static light scattering results, the exponent ν', which characterizes the vanishing of D_c, was significantly larger than either the mean field or the Ising values for the samples in the vicinity of the gel point. This implies that the effective viscosity diverges with an exponent of 0.2−0.3 as the spinodal temperature is approached. Such a strong divergence can be explained by assuming a nonlinear coupling of the velocity and concentration fluctuations for pregel branched polymers and gels under conditions when both the sol−gel and thermodynamic phase transitions occur close to each other. The critical slowing down of the slow mode in the pregel samples implies a strong coupling of the cluster diffusion to the concentration fluctuations. Similarly, for the sample at the gel point, the decay rate associated with the power law tail slows down due to coupling with the concentration fluctuations. The temperature dependence of the amplitudes and the relaxation rates of the slow cluster dynamics for samples near and at a sol−gel transition in the vicinity of the spinodal is not well understood, and the problem calls for new theoretical studies.

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References and Notes

(1) Shibayama, M.; Tanaka, T. *Adv. Polym. Sci.* **1993**, *109*, 1.
(2) Ilavsky, M. *Adv. Polym. Sci.* **1993**, *109*, 173.
(3) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(4) Stauffer, D.; Coniglio, A.; Adam, A. *Adv. Polym. Sci.* **1982**, *44*, 103.
(5) Family, F.; Landau, D. P., Eds. *Kinetics of Aggregation and Gelation*; North-Holland: Amsterdam, 1984.
(6) Tanaka, T.; Ishiwata, S.; Ishimoto, C. *Phys. Rev. Lett.* **1977**, *38*, 771.
(7) Tanaka, T. *Phys. Rev. A* **1978**, *17*, 17.
(8) Sato, E.; Tanaka, T. *J. Chem. Phys.* **1989**, *90*, 5161.
(9) Shibayama, M.; Tanaka, T.; Han, C. C. *J. Chem. Phys.* **1992**, *97*, 6829.
(10) Adam, M. *Makromol. Chem., Mac. Symp.* **1991**, *45*, 1.
(11) Kajiwara, K.; Burchard, W.; Dusek, K.; Kowalski, M.; Matejka, L.; Nerger, D.; Tuzar, Z. *Makromol. Chem.* **1984**, *185*, 2543.
(12) Grof, K.; Mrkvickova, L.; Konak, C.; Dusek, K. *Polymer* **1993**, *34*, 2816.
(13) Sciortino, F.; Bansil, R.; Stanley, H. E.; Alstrom, P. *Phys. Rev. E* **1993**, *47*, 4615.
(14) Bansil, R.; Lal, J.; Carvalho, B. *Polymer* **1992**, *33*, 2961.
(15) Konak, C.; Bansil, R. *Il Nuovo Cimento* **1994**, *16*, 689.
(16) Adam, M.; Delsanti, M.; Munch, J. P.; Durand, D. *Phys. Rev. Lett.* **1988**, *61*, 706.
(17) Martin, J. E.; Wilcoxon, J. P. *Phys. Rev. Lett.* **1988**, *61*, 373.
(18) Martin, J. E.; Wilcoxon, J. P.; Odinek, J. *Phys. Rev. A* **1991**, *43*, 858.
(19) Brandrup, J.; Immergut, E. H., Eds. *Polymer Handbook*, John Wiley & Sons: New York, 1967.
(20) Pajevic, S.; Bansil R.; Konak, C. *Macromolecules* **1993**, *26*, 305.
(21) Fang, L.; Brown, W.; Konak, C. *Macromolecules* **1991**, *24*, 6839.
(22) Onuki, A.; Kawasaki, K. *Ann. Phys.* **1979**, *121*, 456.
(23) Onuki, A.; Yamazaki, K.; Kawasaki, K. *Ann. Phys.* **1981**, *131*, 217.
(24) Sengers, J. V. *Int. J. Thermophys.* **1985**, *6*, 203.
(25) Douglas, J. F. *Macromolecules* **1992**, *25*, 1468.
(26) Berg, R. F.; Moldover, M. R. *J. Chem. Phys.* **1990**, *93*, 1926.
(27) Izumi, Y.; Sawano, H.; Miyake, Y. *Phys. Rev. A* **1984**, *29*, 826.

(28) Burstyn, H. C.; Sengers, J. V. *Phys. Rev. A* **1982**, *25*, 448.
(29) Chu, B.; Lin, F. L. *J. Chem. Phys.* **1974**, *61*, 5132.
(30) Brown, W.; Nicolai, T. *Colloid Polym. Sci.* **1990**, *268*, 977.
(31) Wang, C. H.; Zhang, X. Q. *Macromolecules* **1995**, *28*, 2288.
(32) Nystrom, B.; Walderhaug, H.; Hansen, F. K. *J. Phys. Chem.* **1993**, *97*, 7743.
(33) Ren, S. Z.; Shi, W. F.; Zhang, W. B.; Sorensen, C. M. *Phys. Rev. A* **1992**, *45*, 2416.
(34) Ren, S. Z.; Sorensen, C. M. *Phys. Rev. Lett.* **1993**, *70*, 1727.
(35) Nystrom, B.; Lindman, B. *Macromolecules* **1995**, *28*, 967.
(36) Ngai, K. L. In *Structure and Dynamics of Strongly Interacting Colloids and Supramolecular Aggregates in Solution*; Chen, S. H., Huang, J. S., Tartaglia, P., Eds.; NATO ASI Series C.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. 369, p 221.
(37) Rouch, J.; Tartaglia, P.; Chen, S. H. *Phys. Rev. Lett.* **1993**, *71*, 1947.
(38) Baltsevich, Ya. A.; Martynets, V. G.; Matizen, E. V. *Sov. Phys.—JETP (Engl. Transl.)* **1967**, *24*, 654.
(39) Horkay, F.; Burchard, W.; Geissler, E.; Hecht, A.-M.; Zrinyi, M. *Makromol. Chem., Macromol. Symp.* **1993**, *76*, 145.
(40) Fang, L.; Brown, W. *Macromolecules* **1990**, *23*, 3284.
(41) Suzuki, Y.; Nozaki, K.; Yamamoko, T.; Itoh, K.; Nishio, I. *J. Chem. Phys.* **1992**, *97*, 3808.

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