Dynamic Light Scattering Study of the Sol–Gel Transition

Liqi Fang and Wyn Brown*

Institute of Physical Chemistry, University of Uppsala, Box 532, 751 21 Uppsala, Sweden

Cestmir Konak

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 16206 Prague 6, Czechoslovakia

Received May 20, 1991; Revised Manuscript Received August 29, 1991

ABSTRACT: The sol–gel transition in the poly(methyl methacrylate)/butyl acetate system has been studied using quasielastic light scattering spectroscopy. Critical dynamical behavior is observed near the sol–gel transition that is characterized by the presence of a power-law spectrum of relaxation times. The results have been interpreted in terms of a simple cluster diffusion model. The experimental results favor the percolation model.

Introduction

The sol–gel transition has attracted a great deal of attention in the past decade.[1,2] The dynamical properties of interacting polymer clusters having a mass distribution of the percolation type have recently been described.[3,4] It was shown by quasielastic light scattering (QELS) measurements on solutions of polydisperse polyurethane clusters at concentrations at which the smaller clusters partly penetrate the larger clusters that the profile of the homodyne autocorrelation function, $g^2(t)$, changes with increasing concentration from a stretched exponential function to a power law.[3] The sol–gel transition was experimentally studied by Martin and Wilcoxon[4] (silica gels) and Lang and Burchard[5] (polysaccharides). In the former case, the long-time tail of the correlation functions measured prior to the gel point can be described by a stretched exponential, $g^2(t) \approx \exp[-(t/\tau_s)^b]$, with $b = 0.65 \pm 0.05$. The power-law time decay (5 decades) of the intensity autocorrelation function, $g^2(t) \approx t^{-\phi}$, $\phi = 0.27 \pm 0.03$, and a critical slowing down of the average relaxation time have been observed as the gel point is approached. In the latter case, the corresponding exponent $\phi = 0.34 \pm 0.015$ was found for a thermoreversible gelling system.[5] A simple cluster diffusion model of the dynamics has been proposed that relies on the concept of a size-dependent viscosity, the hyperscaling form of the size distribution, and the screening of the scattered intensity. The following power laws were predicted for the homodyne correlation function $g^2(t)$:[4]

$$g^2(t) \approx t^{-2\beta/(\nu+k)} \qquad t \ll \tau_s \tag{1}$$

$$\langle \tau \rangle \approx \epsilon^{-(\nu+k-2\beta)} \tag{2}$$

$$g^2(t) \approx \exp[-2(t/\tau_s)^{D/(D+1)}] \qquad t \gg \tau_s \tag{3}$$

$$\tau_s \approx \epsilon^{-\nu-k} \tag{4}$$

where k is the exponent of the bulk viscosity, $\eta \sim \epsilon^{-k}$; ϵ is the distance from the gel point, $\epsilon \approx p_c - p/p_c$, where p_c is the cross-linking probability at the gel point; ν is an exponent of the typical cluster radius (R_z) and β is the exponent of the gel fraction; D is the fractal dimension of the sol clusters; $\langle \tau \rangle$ is the arithmetic average relaxation time; and τ_s is the slowest characteristic time in the system. From the cluster diffusion interpretation, Martin and Wilcoxon deduced values of $\beta = 0.35$ and $k = 1.5$ for silica gels consistent with the diffusion of experimentally rare lattice animals.

Recently we published a study concerning the sol–gel transition in the poly(methyl methacrylate) (PMMA)/butyl acetate system prepared by radical copolymerization of methyl methacrylate and ethylene dimethacrylate (EDMA).[6] It was found that the sol dynamic contribution, particularly in the vicinity of the gel point, is very extensive and covers several orders of magnitude in delay time. Because the system under study differs substantially from those described in refs 3 and 4 (in particular, the present cross-linking content is very low), we have decided to study the critical dynamics of this sol–gel transition in more detail. Surprisingly, we find very similar dynamic behavior as in the case of silica gels.[4] The experimental data are discussed using the cluster diffusion model.

Experimental Section

Sample Preparation. The samples used in these experiments are PMMA solutions and gels obtained by copolymerizing methyl methacrylate monomer (MMA) with small amounts of ethylene dimethacrylate as the cross-linking agent in the presence of butyl acetate. A set of samples with total monomer concentration $c = 10\%$ (v/v) was prepared with different degrees of cross-linking: f_c = [EDMA]/[MMA] varying between 0 (the linear polymer) and 3% (gel). The reaction was initiated with azobis(isobutyronitrile) (10 mg/mL of MMA) and allowed to proceed for 7 days at 50 °C in cylindrical light scattering cells. By the end of this period, the gelation reaction was complete with a conversion between than 95%. All monomer solutions were first filtered using 0.22-μm filters (Millipore).

Apparatus. Measurements were made using the dynamic light scattering apparatus in Uppsala previously described.[7] The light source was a 35-mW He/Ne laser. An ALV-Langen, multibit, multi-τ autocorrelator was operated with 23 simultaneous sampling times covering approximately 8 decades in delay time. The samples were thermostated at 25 °C in a refractive index matching liquid (decalin).

Oscillatory shear viscosity measurements were made using a Rheometrics RFS 8500 instrument with a fluid bath temperature control. A cone-plate geometry cell (diameter 50 mm, angle 0.02 rad) was used for the measurements. Storage and loss moduli, G' and G'', were measured as a function of frequency between 10^{-2} and 10^2 rad/s; 5–10 points per decade were measured. Measurements were only performed in the linear range where moduli were independent of strain amplitude. These data will be presented elsewhere. The molecular weight dependence of the bulk viscosity is given in Table III.

Data Treatment. The arithmetic average decay time $\langle \tau \rangle$ was obtained by direct numerical integration of the experimental second-order correlation functions ($g^2(t)$) over 5 decades of delay time. The correlation functions were also fitted to the sum of

0024-9297/91/2224-6839$02.50/0

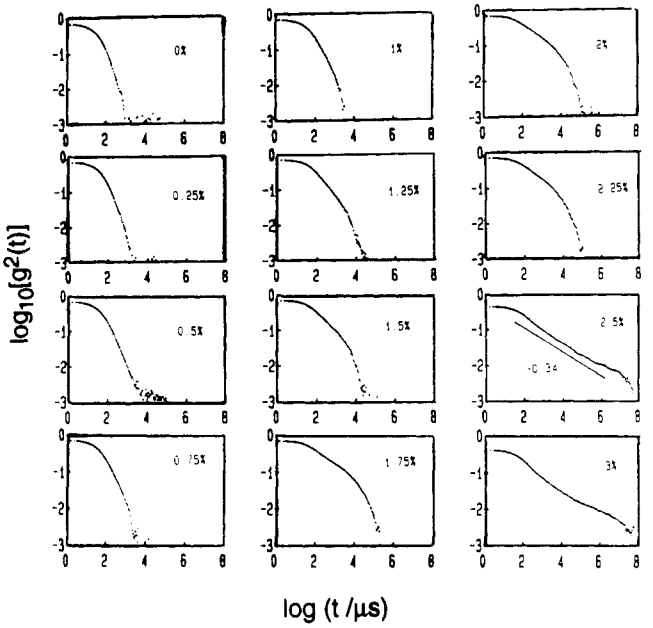

Figure 1. Logarithm of autocorrelation functions against logarithm of time at cross-linking contents from 0 to 3%. Measurements were made at $\theta = 90°$ and 25 °C.

two distributions. One is Gaussian in log τ and represents the fast K^2-dependent peak:

$$w_1(\tau) = \pi^{-1/2}(\tau\sigma)^{-1} \exp[-(\log(\tau/\tau_d)/\sigma)^2] \quad (5)$$

The other is the so-called generalized exponential (GEX) distribution representing the total of all slow components:

$$w_2(\tau) = |s|\tau^{p-1}\tau_0^{-p} \exp[-(\tau/\tau_0)^s]/\Gamma(p/s) \quad (6)$$

With s and p negative, the distribution is of the Pearson type. τ_d and τ_0 are relaxation times which position $w_1(\tau)$ and $w_2(\tau)$ on the log (time) axis; σ characterizes the width of the Gaussian distribution and the parameters s and p determine the shape of the GEX distribution. The relaxation time distributions obtained in this way are very similar to those obtained using inverse Laplace transformation (ILT) but with the slow modes replaced by a single-peaked smooth broad distribution. A more comprehensive discussion has been given in ref 8. The long-time tails of the correlation functions are well described by a stretched exponential function; see also ref 6. The Pearson distribution used to fit the long-time tails of the correlation functions differs only slightly from the Williams–Watts function corresponding to stretched exponential time correlation functions.

The slowest characteristic time τ_s has been evaluated from the stretched exponential long-time tail of correlation functions in Figure 2.

Results and Discussion

The gelation point can be approached by changing the degree of conversion in the polymerization (e.g., by terminating the reaction by quenching), the content of cross-links, or the concentration of initiator at complete conversion. The latter approach is used in the present work. Figure 1 shows autocorrelation functions, plotted logarithmically, for cross-link contents extending from 0 to 3% as indicated. The autocorrelation functions change from close to a single-exponential function at $f_c = 0$ to the function which, after an initial exponential part, is followed by a power-law decay tail with an exponent $\phi = 0.34$ at $f_c = 2.5$. Such a correlation function corresponds to the sample just beyond the gel point (very weak gel). The observed exponent is close to the value $\phi = 0.27 \pm 0.03$ reported by Martin and Wilcoxon for silica gels.[4] $\phi = 0.34$ for polysaccharides was given by Lang and Burchard;[5] this value is smaller than the exponents reported (0.4–0.6) for semidilute solutions of polyurethane clusters.[3] (Lang and Burchard compared their value of 0.34 with Martin's value of 0.27; since the latter value corresponded to the intensity–intensity correlation function, $g^2(t)$, it is implied that the value of 0.34 also applies to the second-order correlation function.) The initial exponential decay (τ_d) may be assumed to correspond to the cooperative motions of the polymer matrix as it has the same relaxation frequency as the gel mode in gelled samples well above the gel point. Furthermore, the concentrations of the solutions ($C \approx 0.1$ g/mL) are well above C^* ($C^* = 0.02$ g/mL for $M_w = 10^5$). The power-law tail is due to the dynamics of the partly penetrating polydisperse clusters as has been discussed above. The long-time tail of the correlation functions for the samples in the pregel state ($f_c = 1.25$–2.25%) can be described by a stretched exponential with a nearly independent value of $b = 0.26 \pm 0.02$, as is demonstrated in Figure 2, where the double logarithm of the correlation functions is plotted versus log t. In order to separate the cooperative diffusion mode from slow dynamic processes contributing to the long-time tail of correlation functions, the GEX program has been applied. The values of τ_d and τ_0 evaluated from this analysis are shown together with the arithmetic average relaxation times $\langle\tau\rangle$ and the slowest characteristic times τ_s in Table I.

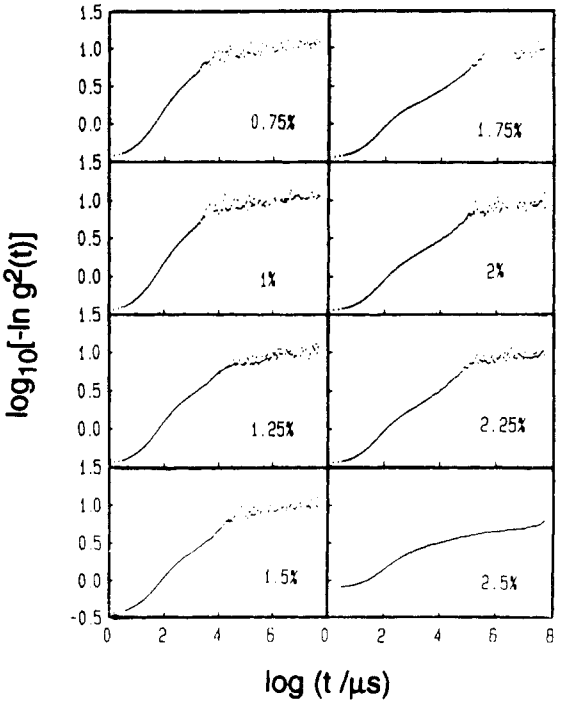

Figure 2. Double logarithm of the autocorrelation function against logarithm of time at cross-linking contents from 0 to 2.5%. Measurements at $\theta = 90°$ and 25 °C.

Since the theories of gelation predict a divergence of $\langle\tau\rangle$ and τ_s at the gel point according to a power law,[4] both quantities are plotted logarithmically in Figure 3 as a function of the reduced parameter $\Delta f_c/f_{cg}$, where $\Delta f_c = f_c - f_{cg}$ and f_{cg} is the content of cross-links in the sample at the gel point. The value of f_{cg} was selected to be close to the midpoint between f_c (=2.5%) at which the first weak gel was observed and f_c (=2.25%) at which the last solution was observed. It can be seen in Figure 3a that $\langle\tau\rangle$ shows a power divergence with the exponent $\Psi = 2.5 \pm 0.1$ and the slowest decay time τ_s scales with the exponent $\Psi = 2.50 \pm 0.10$ (cf. Table III). Contrary to the silica gels,[4] the values of both exponents are practically the same. It suggests that a contribution of the initial exponential part

Table I
Decay Times (μs) of the Correlation Functions Obtained from Numerical Integration, GEX Fit, and the Tail of the Correlation Functions

f_c, %	τ_d	$\langle\tau\rangle$	τ_0	τ_s
0	60	65.3	49	67
0.25	62	82.7	71	86
0.5	61	93	63	105
0.75	60	176.7	111	194
1.0	70	275.3	369	369
1.25	71	563.4	487	675
1.5	76	650.9	592	903
1.75	79	2903	2270	3024
2.0	86	3807	2354	4316

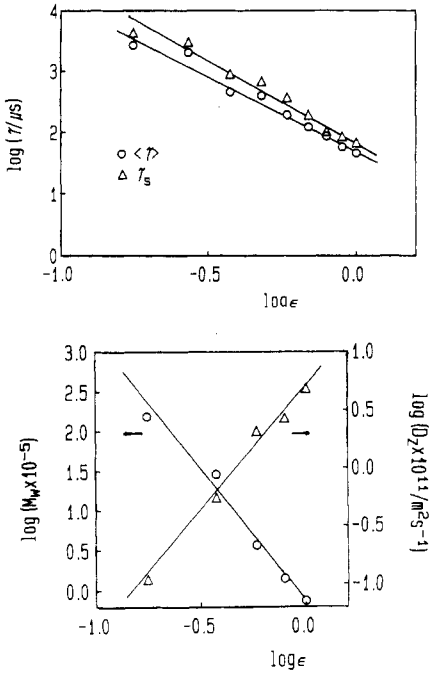

Figure 3. (a, top) log–log plots for average relaxation time $\langle\tau\rangle$ from integration and the slow relaxation time τ_s versus the reduced parameter ϵ. (b, bottom) log–log plots for the weight-average molecular weight and z-average diffusion coefficient versus the reduced parameter ϵ.

of the correlation function to the arithmetic average relaxation time $\langle\tau\rangle$ is smaller in the PMMA/butyl acetate system than in the case of silica gels. Moreover, the τ_s values have a large uncertainty and, therefore, will not be further used in discussion.

In order to characterize the PMMA/butyl acetate system, intensity and quasielastic light scattering experiments were performed in the zero-concentration limit. The values of the mean weight-average molecular weight, M_w, which characterizes the mean degree of connectivity of clusters, and the z-average diffusion coefficient, D_z, evaluated from these measurements diverge at the gel threshold (cf. Figure 3b) with the respective exponents $\gamma = 3.2 \pm 0.1$, $\nu_H = 2.0 \pm 0.1$ (cf. Tables II and III). Assuming that the reduced parameter $|\Delta f_c|/f_{cg} \approx \epsilon \approx |p_c - p|/p_c$, with p_c being the cross-linking probability at the gel point,[1,2] the exponents γ and ν_H may be interpreted as critical exponents and compared with theoretical ones. Since both the hydrodynamic radius from quasielastic light scattering and the radius of gyration from static light scattering are z-averaged quantities and have been shown theoretically to diverge with the same critical exponent,[9] we can to a first approximation use the R_h exponent with the theoretical values of ν. As can be seen in Table II, the experimental exponents are systematically higher than the predictions of both the classical and percolation

Table II
Critical Exponents of the Weight-Average Molecular Mass and the z-Average Diffusion Coefficient[a]

exponent	experimental	classical	percolation
γ	3.2 ± 0.1	1	1.76
ν_H	2.0 ± 0.1	0.5	0.89

[a] $M_w \sim \epsilon^{-\gamma}$; $D_z \sim \epsilon^{\nu_H}$.

Table III
Slopes of log–log Plots[a]

independent variable	dependent variable	exptl slope	exponent
log ϵ	log D_z	2.0 ± 0.1	ν_H
	log $\langle\tau\rangle$	−2.5 ± 0.1	$-\Psi$
	log τ_s	−2.5 ± 0.1	
	log τ_0	−2.4 ± 0.1	
	log M_w	−3.2 ± 0.1	$-\gamma$
	log η	−2.1 ± 0.15	$-k$
log M_w	log D_z	−0.64 ± 0.05	$-\nu_H/\gamma$
	log $\langle\tau\rangle$	0.81 ± 0.06	Ψ/γ
	log η	0.67 ± 0.06	k/γ
log t	log $[g^2(t)]$	−0.34 ± 0.02	$-\phi$
	log $[-\ln g^2(t)]$	0.26 ± 0.02	b

[a] $\phi = 2\beta/(\nu + k)$; $\Psi = \nu + k - 2\beta$.

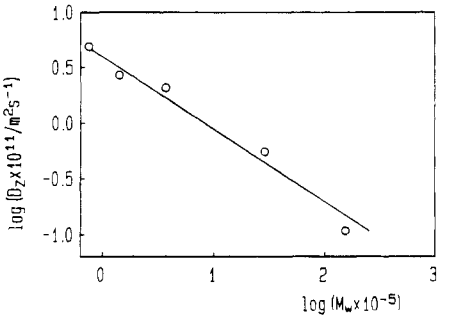

Figure 4. log–log plots for the z-average diffusion coefficient against molecular weight.

theories. It seems that characterization of the cross-linking probability in a free-radical copolymerization is a more complex problem[10] and cannot be reduced in the way described above. At the least, the extent of ring formation of the second double bonds from the EDMA units should be considered.[10]

In order to avoid the ambiguity associated with ϵ, the molecular weight dependences of the hydrodynamic radius, R_h ($\sim 1/D_z$) (see Figure 4), and the bulk viscosity, η, have been evaluated (cf. Table III). The exponents $\nu_H/\gamma = 0.64 \pm 0.05$ (cf. Table III) are close to the prediction for both the classical (0.5) and percolation (0.51) models.[2] Similar values of ν_H/γ were observed previously with samples prepared by radical copolymerization of styrene and biunsaturated comonomers, 0.57 ± 0.05.[11] The value of the exponent $k/\gamma = 0.67 \pm 0.06$ (cf. Table III) is only slightly lower than the prediction for the classical (0.75) and percolation (0.76) theories.[12] The above scaling results are not suitable to provide a test of the theoretical models, however.

If we adopt the percolation model for the present system, then eq 1 gives $\phi = 0.35$ ($\phi = 2\beta/(\nu + k)$, $\nu = 0.89$, $\beta = 0.39$, $k = 1.33$) in good agreement with the experimental value (0.34). The "classical" value $\phi = 1.6$ ($\nu = 0.5$, $\beta = 1.0$, $k = 0.75$) is more than 4 times higher than the experimental value. Solving eqs 1 and 2, we obtain the expression $\beta/\gamma = \phi\Psi/2\gamma(1 - \phi)$ for the gel-fraction exponent. Using $\phi = 0.34$, $\Psi/\gamma = 0.81$ (cf. Table III) and we get $\beta/\gamma = 0.21$ in good agreement with the percolation prediction of $\beta/\gamma = 0.22$. The classical value of β/γ is 1.0. Using the relationship

$\Psi/\gamma = (\nu + k - 2\beta)/\gamma$ from eq 2, we obtain $\Psi/\gamma = 0.89$ ($\nu_H/\gamma = 0.64$), which is only slightly higher than the experimental value of $\Psi/\gamma = 0.81$. The classical and percolation values of Ψ/γ are 0.8 and 0.82, respectively. The above discussion of experimental results seems to favor the percolation model. It is also worth noting that in the reaction considered here, the presence of solvent favors the occurrence of the percolation mechanism over a large domain of ϵ.

Finally, if the lattice-animal dimension $D = 2$ is used in eq 3, we obtain $b = 0.67$,[4] which is more than 2 times higher than the experimental value, $b = 0.26$. It seems that the cluster diffusion model of the polymeric dynamics[4] can well describe the critical dynamics of the sol–gel transition, but there may be some dispute in a region well below gel threshold.

Conclusion

Critical dynamics near the sol–gel transition have been observed that are characterized by the presence of a power-law spectrum of relaxation times. The experimental data have been interpreted in terms of a simple cluster diffusion model. This model well describes the critical dynamics at the gel threshold. The experimental results favor the percolation method.

Acknowledgment. We are indebted to Dr. Søren Hvidt, University of Roskilde, Denmark, for carrying out oscillatory shear viscosity measurements. We acknowledge financial support from the Bo Rydin Fund, (SCA, Sundsvall, Sweden) and the Swedish Board for Technical Development (STU).

References and Notes

(1) Stauffer, D.; Coniglo, A.; Adam, M. *Adv. Polym. Sci.* **1982**, *44*, 103.
(2) Stauffer, D. *Introduction to Percolation Theory*; Tayer and Frances: London, 1985.
(3) Adam, M.; Delsanti, M.; Munch, J. P.; Durand, D. *Phys. Rev. Lett.* **1988**, *61*, 706.
(4) Martin, J. E.; Wilcoxon, J. P. *Phys. Rev. Lett.* **1988**, *61*, 373.
(5) Lang, P.; Burchard, W. *Macromolecules* **1991**, *24*, 814.
(6) Konak, C.; Jakes, J.; Brown, W.; Fang, L. *Polymer* **1991**, *32*, 1077.
(7) Brown, W.; Zhou, P. *Macromolecules* **1989**, *22*, 4031.
(8) Jakes, J. *Czech. J. Phys. B* **1988**, *38*, 1305.
(9) Martin, J. E.; Ackerson, B. *Phys. Rev. A* **1985**, *31*, 1180.
(10) Schmidt, M.; Burchard, W. *Macromolecules* **1981**, *14*, 370.
(11) Candau, S. J.; Ankrim, M.; Munch, J. P.; Rempp, P.; Hild, G.; Okasha, R. In *Physical Optics of Dynamic Phenomena and Processes in Macromolecular Systems*; Sedlacek, B., Ed.; Walter deGruyter: Berlin, 1985; p 145.
(12) Douglas, A.; Martin, J. E.; Wilcoxon, J. P. *Macromolecules* **1990**, *23*, 527.