

Anomalous Diffusion in an Aqueous System of a Poly(ethylene oxide)–Poly(propylene oxide)–Poly(ethylene oxide) Triblock Copolymer during Gelation Studied by Pulsed Field Gradient NMR

Harald Walderhaug and Bo Nyström*

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway

Received: July 22, 1996; In Final Form: November 7, 1996[®]

The molecular motion of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) block copolymer in water was investigated during the temperature-induced sol–gel transition with the aid of pulsed field gradient NMR. The strong slowing down of the diffusive motion in the gel regime is accompanied by an increased nonexponentiality of the spin echo attenuation function. The value of the stretched exponent, describing the decay of the spin echo attenuation, decreases with increasing temperature, and this trend suggests a broader distribution of diffusion coefficients when approaching the gel state. Ordinary diffusion behavior is observed in the sol phase, whereas anomalous diffusion is detected as the gel evolves, and the mean square displacement $\langle z^2 \rangle$ shows a power law dependence on time ($\langle z^2 \rangle \propto t^\alpha$) with $\alpha < 1$. The value of α decreases as the gelation process proceeds, and α is around 0.5 in the gel zone, but a wave vector dependence of α can be traced at temperatures in the gel regime.

Introduction

Owing to their amphiphilic character, copolymers containing both hydrophilic and hydrophobic blocks such as poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) exhibit many interesting dynamic and rheological properties. The PEO–PPO–PEO triblock copolymers, generally called poloxamers (commercially available from BASF Corp. under the name Pluronics), have recently attracted great attention^{1–14} because of their interesting temperature-induced micellization and gelation phenomena in aqueous solutions. The commercial sample of Pluronic F68 (EO₇₈–PO₃₀–EO₇₈) is an example of a system that at high concentrations (>20 wt %) is transformed from a fluid to a gel on warming from ambient to body temperature. In this thermoreversible gelation process, the block copolymer molecules are associated into micelles and gelation involves a network of interconnected micelles.¹⁰

Dynamic light-scattering¹⁵ and rheological^{15,16} measurements on a concentrated solution (35 wt %) of F68 have recently been carried out at this laboratory. This is a thermoreversible gelling system, which forms a gel at about 37 °C. The results from these studies revealed complex dynamical and rheological features. The decays of the correlation functions and the stress relaxation moduli exhibited interalia stretched exponential and power law behaviors as the gelation zone was approached. These intricate features may portend anomalous behavior of the long-range dynamics probed in the pulsed field gradient nuclear magnetic resonance (PFG NMR) experiments.

In this work we report results from PFG NMR measurements at various temperatures on an aqueous gelling solution (35 wt %) of Pluronic F68. By means of this technique, it is possible to measure the mean square displacements of molecules or, strictly speaking, of their protons, in a given time interval. This method is widely used to investigate self-diffusion processes in polymer systems.^{17–25} Diffusion is a concept associated with random motion of particles in space. For “simple” polymer systems, the classical or Fickian diffusion is usually observed. This diffusion process occurs when the mean squared displacement of the particle during a time interval becomes, for

sufficiently long intervals, a linear function of it. However, for more complex systems, as in the present case, molecular confinement may lead to a breakdown^{21,23–33} of this linearity and the mean square displacement increases less than linearly with the observation time. The present results will reveal anomalous diffusion behavior and other intriguing dynamic features when the gel zone is approached.

Basic Considerations

The PFG NMR technique is well established^{17–21} and has been used to determine self-diffusion coefficients in the range 10^{–14}–10^{–9} m² s^{–1}. The method consists of labeling nuclear spins by their Larmor precession frequencies in a spatially varying magnetic field. In the narrow gradient pulse approximation, the attenuation of the spin echo on applying the field gradient pulse of magnitude g is given by³⁴

$$\psi = \int \rho(r) \int P_s((r|r',t),\Delta) \exp[i\gamma\delta g(r'-r)] dr' dr \quad (1)$$

where γ is the gyromagnetic ratio of the nucleus under consideration (the ¹H nucleus here), Δ is the separation of the gradient pulses (the observation time), and δ is the width of the gradient pulses. The parameter $\rho(r)$ is the static spin density function, and $P_s(r|r',t)$ is the self-correlation function²¹ that gives the conditional probability that a spin initially at r at time 0 will move to r' at time Δ . Since the self-correlation function contains the complete information about the process of molecular propagation, this function is often called the propagator.

For nuclear spins undergoing a Brownian random walk characterized by a self-diffusion coefficient D , the propagator has a simple Gaussian form, and in the narrow pulse width approximation ($\delta \ll \Delta$) eq 1 reduces to

$$\Psi = \exp(-(1/2)\gamma^2 g^2 \delta^2 \langle z^2 \rangle) \quad (2)$$

where $\langle z^2 \rangle$ is the mean square nuclear displacement along the field gradient direction and may be written as

$$\langle z^2 \rangle = 2D\Delta \quad (3)$$

[®] Abstract published in *Advance ACS Abstracts*, February 1, 1997.

It has been argued²⁸ that eq 2, which originally was derived for ordinary diffusion,^{20,35} is also valid in the case of anomalous diffusion.

In principle, pulsed field gradient NMR is a scattering experiment^{21,24} that measures the intermediate incoherent scattering function of the protons of the polymer molecules, and in the diffusion limit the echo attenuation function may be expressed as

$$\psi = \exp(-q^2 D \Delta) \quad (4)$$

with a "generalized" scattering vector

$$q = \gamma \delta g \quad (5)$$

We may note that the maximum value of the scattering vector is on the order of 10^7 m^{-1} in pulsed field gradient experiments, yielding a lower limit of about 100 nm for the space scale probed in this type of measurement. In neutron-scattering experiments the values of q are much larger, and for diffusion measurements by this technique the maximum displacements are on the order of only a few nanometers. Since the q values in PFG NMR are rather low, the experiments are usually carried out in the long-wavelength limit $qL \ll 1$, where L is the characteristic length. In semidilute solutions and gelling polymer systems L is the correlation length, and in dilute solutions this length can be identified with the hydrodynamic radius. To probe internal modes (segmental motion), one has to work with $qL > 1$, and this condition is usually difficult to attain in PFG NMR.

In homogeneous media, the "normal" diffusion behavior as characterized by eq 3 is usually observed and the central limit theorem is justified; i.e., the subsequent molecular displacements are not correlated. However, in disordered systems correlated motion may be observed, and this type of memory effect may give rise to anomalous diffusion³⁶ or fractal diffusion.^{37–40} This unusual phenomenon may be described by a relationship of the type

$$\langle z^2(t) \rangle \propto t^\alpha \quad (6)$$

with $\alpha < 1$, which represents a generalization of the Einstein equation (eq 3). In the framework of fractal diffusion $\alpha \equiv 2/d_w$, where $d_w > 2$ is a random walk fractal dimension. The slowing down of the diffusion motion is caused by the delay of a diffusing unit because of a hierarchically intricate structure. In thermoreversible gelling polymer systems, as in the present case, we expect that the formation of regions of enhanced and reduced chain densities and reduced chain mobility due to physical cross-links may give rise to anomalous diffusion. The fractal concept is an interesting approach for the description of diffusion under structural confinement. Experimental observations on polymer solutions,⁴¹ polymer melts,^{32,42–48} swollen networks,⁴⁹ swollen spherical microgels in solution,⁵⁰ and porous media^{33,51} have indicated the effect of molecular confinement.

In light of the fractal concept for random walk on fractal structures, a modified form of eq 2 has been advanced,^{21,26,28}

$$\Psi = \exp(-\gamma^2 \delta^2 g^2 D \Delta^{2/d_w}) \quad (7)$$

where $d_w > 2$ is the so-called fractal dimension⁵² of the random walk. Depending on the type of fractal structure, there are a number of theoretical models for the prediction of the value of d_w .

A successful model for the description of gelation processes is the percolation theory^{53–58} in combination with the fractal concept. A gelling polymer system may be viewed as a percolating network that exhibits self-similarity and can be

described by a random fractal. A percolating network can be characterized by the correlation length ξ , which can be interpreted as a length scale up to which the cluster can be regarded as fractal. Above the percolation threshold (an infinite cluster is present as well as finite clusters), the structure of the network may be considered as homogeneous for length scales larger than ξ and as fractal on length scales $L < \xi$. In other words, ξ represents the characteristic size of the voids in the percolating system above the percolation threshold and the characteristic size of a finite cluster below the threshold (at this stage only finite clusters exist).

In a percolating system, the system looks homogeneous on scales $L \gg \xi$ and normal diffusion holds, while for a length scale less than ξ , diffusion is anomalous. The reason for this anomalous diffusion is the structure of the environment that alters the possible diffusion pathway by introducing extra tortuosity on a certain length scale. An illustration of this effect is diffusion in random percolating systems, known also as the "ant-in-the-labyrinth" after de Gennes.⁵⁹ By use of theoretical^{52,57,60,61} and simulation^{62–65} methods for percolating systems, values of the anomalous exponent d_w in the range 3.5–4.0 have been reported. Furthermore, experimental estimates⁵¹ of the anomalous diffusion exponent at the gelation threshold yielded a value of $d_w = 4.2$. These results suggest that the power law exponent α (see eq 6) should be close to 0.5.

We should note that there are also other theoretical models, based on a different conceptual background, that predict a value of 0.5 of the power law exponent. The dynamics of short and long polymer chains in melts and/or in concentrated solutions may be described in the framework of the following models. For short chains, the dynamics in the Rouse limit⁶⁶ (hydrodynamic interactions are ignored) is governed by the Rouse time τ_R (the time for a chain to diffuse over a distance on the order of its radius). For times much larger than τ_R , we expect ordinary diffusion to occur. At times $t < \tau_R$, only a portion of the length of the chain will have diffused and the mean square displacement of a polymer chain is predicted to become proportional to $t^{0.5}$. For long chains, the dynamics of entangled polymer molecules is frequently described in terms of the tube/reptation model.^{67,68} The reptation of sufficiently long chains is characterized by a one-dimensional Rouse-like⁶⁸ curvilinear diffusive motion in an entangled tube formed by the topological constraints of surrounding chains. This model is characterized by the so-called reptation or disengagement time τ_d , since it is the time needed for the primitive chain to disengage from the tube it was confined to at $t = 0$, and the time τ_e , which denotes the onset of the effect of tube constraints. The latter time is the time taken to diffuse the interentanglement distance that is on the order of the mesh size of the network. For times $t > \tau_d$ the dynamics is governed by the reptation process and ordinary diffusion behavior is observed for the center-of-mass motion. For $t < \tau_e$ the chain behaves as a Rouse chain in free space and anomalous diffusion with a value of $\alpha = 0.5$ is predicted. The same value of the power law exponent is expected in the time interval $\tau_R < t < \tau_d$, where curvilinear diffusion in the tube is probed.

Experimental Section

Materials. A commercial poloxamer 188 sample (Pluronic F68) obtained from Fluka was used in this study without further purification. According to the manufacturer, this polymer contains approximately 80% by weight oxyethylene units and the nominal molecular weight is $\sim 8350 \text{ g mol}^{-1}$. A solution of 35 wt % was prepared by weighing the components. At this concentration the solution is transformed into a gel at elevated

temperature. Although the dynamic¹⁵ and rheological^{15,16} features of this system are intriguing, the phase diagram of the aqueous Pluronic F68 system is rather simple,⁶⁹ with a single isotropic phase at concentrations below 50 wt % and in the temperature range studied in this work.

NMR Experiments. All NMR experiments were carried out in 5 mm NMR tubes with the aid of the PFG NMR technique¹⁹ on a Bruker DMX-200 spectrometer with the stimulated echo pulse sequence^{20,70} and with employment of the longitudinal eddy current delay sequence (the preemphasis adjustment). The attenuation of the spin echo amplitude after Fourier transformation was sampled as a function of the magnitude, g , of the applied gradient pulse ($0.5 \leq g \leq 8$ T/m).

At these magnetic field gradient strengths, we could not observe any problems associated with a mismatch of the two field gradient pulses or to possible mechanical instabilities that may arise when using large field gradient pulses.^{23,47,71–73} To ensure that the probed signal attenuation with increasing values of g is directly due to diffusion^{23,49} (and not to a mismatch of the two field gradient pulses), we have applied the same PFG NMR pulse program to a chemically cross-linked poly(vinyl alcohol) gel, whose diffusivity (less than 10^{-15} m² s⁻¹) is much smaller than accessible by the present experimental setup. In this case we observed that the signal attenuation was absent, suggesting that the effect of mismatch is not a problem in this study.

The gradient delivery system is completely electronically controlled. The field gradients for the experimental setup with the actual probe head interfaced have been calibrated by the manufacturer. A check has been performed using a sample of dry glycerol at 25 °C. At various observation times Δ , and with the other experimental parameters in the interval used in this study, these experiments gave a diffusion coefficient that agreed with the literature value⁷⁴ of 1.7×10^{-12} m² s⁻¹. The pulse duration δ was kept constant during an experiment and was typically 4 ms. We always have worked in the narrow pulse width approximation, i.e., with $\delta \ll \Delta$. The time window available to the PFG NMR method is determined by the available gradient amplitude and by spin relaxation. For the present system it is limited to $0.1 \text{ s} \leq \Delta \leq 3 \text{ s}$. The measurements were performed between 25 and 40 °C. The gel point of this system is located at 37 °C.¹⁵ By use of a variable temperature control unit, the temperature constancy was better than ± 0.5 °C. The temperature settings were calibrated by using an ethylene glycol sample, giving easily measurable shift differences between the two proton NMR signals that depend strongly on temperature.

Results and Discussion

In “simple” systems of a polymer with a narrow molecular weight distribution, the attenuation of the spin echo amplitude is expected to decay as a single exponential in accordance with eq 2. However, in the case of polydisperse or strongly associating systems, as in the present work, the formation of clusters of various sizes should give rise to a distribution of diffusivities. A number of studies^{30,75–79} on complex systems have shown that the spin echo attenuation data can be well described by a stretched exponential of the following form

$$\Psi = \exp[-(hD_{\text{fe}})^{\beta}] \quad (8)$$

where $h \equiv q^2\Delta$, β ($0 < \beta \leq 1$) is a measure of the width of the distribution of self-diffusion coefficients, and D_{fe} is some effective self-diffusion coefficient. A mean self-diffusion

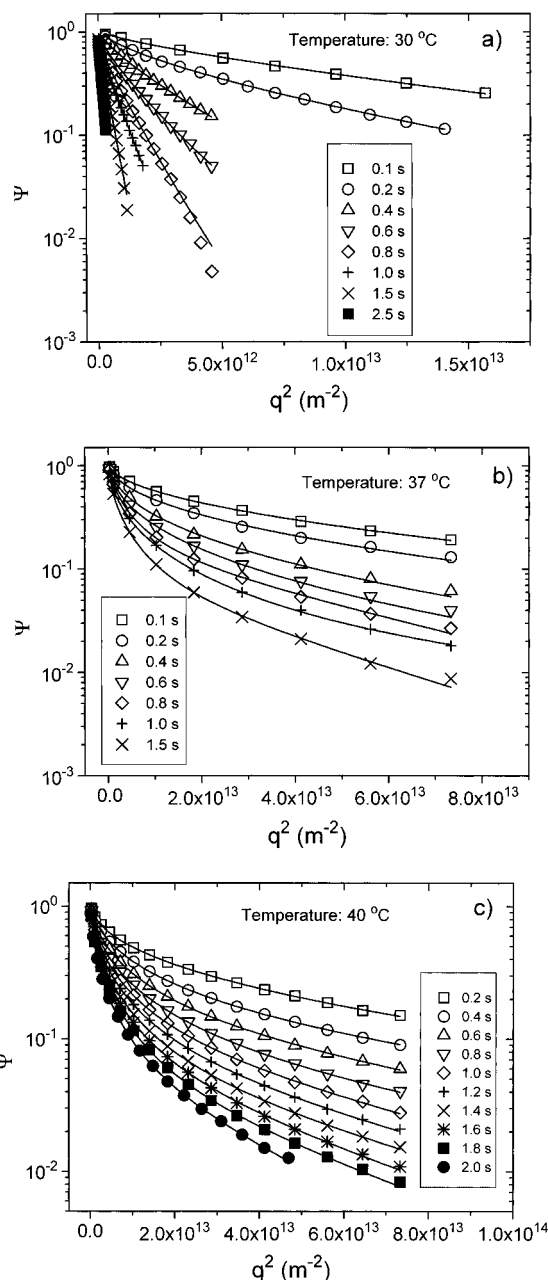


Figure 1. Decays of the stimulated echo amplitude of Pluronic F68 (35 wt %) at the times and temperatures indicated. The abscissa axes refer to the squared wavenumber ($q = \gamma\delta g$). The solid curves represent fits of eq 8 to the experimental data.

coefficient can be calculated from the relation³⁰ $1/D_{\text{f}} = (1/\beta)\Gamma - (1/\beta)(1/D_{\text{fe}})$, where Γ denotes the gamma function.

Figure 1 shows plots of the spin echo attenuation versus q^2 at different observation times and temperatures. The solid curves represent least-squares fits of eq 8 to the experimental data. At 30 °C (in the pregel zone), the attenuation curves are only moderately nonexponential ($\beta \approx 0.9$), while the feature of curvature increases as the gel evolves (at 37 °C (the gel point) $\beta \approx 0.4$ and at 40 °C (the postgel zone) $\beta \approx 0.4$). At lower temperatures (see Figure 1a), the feature of nonexponentiality of the NMR spin echo attenuation seems to increase slightly (the value of β decreases) as the observation time Δ decreases. This may indicate that at short Δ the exchange times of the polymer molecules between the micelles or clusters approach the experimental observation time. With increasing temperatures (parts b and c of Figures 1), the value of β decreases gradually, but no time dependence of β is found at these higher temperatures. The feature of increasing nonexponentiality in

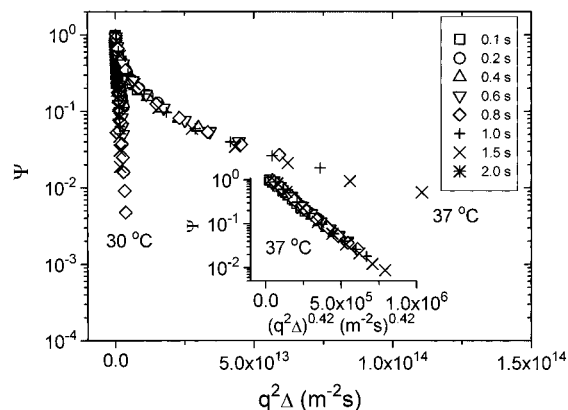


Figure 2. Spin echo attenuation of Pluronic F68 (35 wt %) as a function of $q^2\Delta$ for the temperatures and observation times indicated. The inset plot demonstrates the stretched exponential character of the spin echo decay.

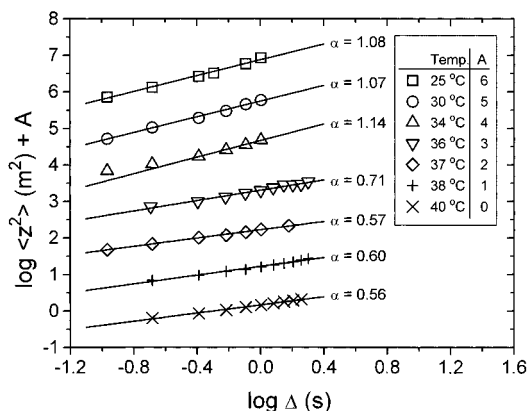


Figure 3. Mean square displacements as a function of observation time for Pluronic F68 (35 wt %) during gelation. The values of the power law exponent are indicated. The data sets for the different temperatures have been shifted vertically by a factor A of the value listed in the inset to avoid overlap.

the echo attenuation when the gel zone is approached is consistent with the results reported^{3,6} for other gelling Pluronic systems. In the course of the temperature-induced gelation, the gradual association process will probably give rise to a broader distribution of cluster sizes; i.e., the polydispersity effect increases. As a consequence of this, the width of the distribution of diffusivities increases and the value of β decreases. Furthermore, the motion of the polymer segments will be slowed down in the course of gelation because of the interconnection of the micelles in the network formation process. It is likely that this slowing down leads to correlated molecular motions²⁰ and thereby gives rise to anomalous diffusion behavior.

In Figure 2 a plot of the spin echo attenuation against the reduced variable $q^2\Delta$ is displayed. In this type of plot, the data points, representing different observation times, condense fairly well and again the temperature-induced polydispersity effect gives rise to the enhanced curvature in the $\log \Psi$ versus $q^2\Delta$ relation at elevated temperature. The inset plot, where Ψ is plotted versus the scaling variable $(q^2\Delta)^\beta$ ($\beta = 0.42$), yields a practically straight line representation of the data, demonstrating the stretched exponential character of the spin echo attenuation.

Figure 3 shows the dependence of the mean square displacements (calculated with the aid of eq 2) on the observation time for the Pluronic sample (35 wt %) at various temperatures during the gelation process. The data have been evaluated at a fixed low value ($\sim 1.6 \times 10^6 \text{ m}^{-1}$) of q . The general trend is that the power law exponent α (see eq 6) decreases during the gelation process, which is probably a result of enhanced molecular

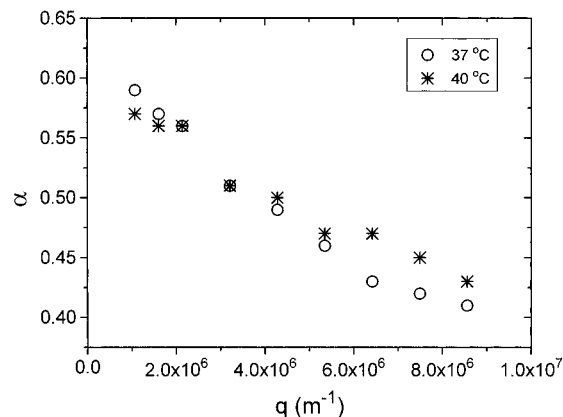


Figure 4. q dependence of the power law exponent α (see eq 6) for Pluronic F68 (35 wt %) at temperatures in the gel regime.

confinement and reduced chain mobility as the cross-linking process proceeds. At temperatures up to 34 °C (in the pregel regime) the center-of-mass motion occurs according to the laws of ordinary diffusion with a mean square displacement increasing in proportion to the observation time. At higher temperatures, however, a dramatic decrease in the displacements, and hence in the translational mobilities, is observed. Thus, with increasing temperature the deviation from the time dependence of ordinary diffusion becomes increasingly significant and anomalous diffusion is revealed. These results demonstrate that the determined time exponent α of anomalous diffusion decreases significantly as the gel evolves, indicating an enhancement of molecular confinement and reduced chain mobility. The value of α is around 0.5 in the gel zone. However, as will be discussed below, a q dependence of α is revealed in the gel regime, and therefore, the value of 0.5 should not be considered to represent a universal state.

Under the influence of the hierarchical confinement by fractal structures, a value of 0.5 of the power law exponent is consistent with the model for percolating networks (see the section "Basic Considerations"). However, it should be noted that a power law exponent of 0.5 is also compatible with concepts of an origin entirely different from concepts of the percolation model, e.g., the Rouse model for short chains or the tube/reptation model for entangled chains. It is difficult to distinguish between these models, but it may be interesting to discuss these results in light of the findings obtained from rheological measurements^{15,16} on the same system (35 wt %). At long times, the stress relaxation modulus $G(t)$ was found to exhibit a power law behavior of the form $G(t) \approx t^{-n}$, with $n \approx 0.5$ at 37 and 40 °C. This value of n is lower than the percolation prediction $n \approx 0.7$.^{58,80} However, a dynamical scaling analysis of flexible fractals in the Rouse limit⁸¹ gives a viscoelastic exponent of $n = d_f/(2 + d_f)$, where d_f is the mass fractal dimension. For example,⁸² the θ chain with $d_f = 2$ yields a value of $n = 0.5$. When it comes to the tube/reptation model, it is doubtful whether the entanglement tube concept is relevant for the present polymer of such a low molecular weight ($M \approx 8000$).

The q dependence of α in the gel regime is illustrated in Figure 4. The value of α decreases with increasing q , and this trend may be rationalized in the following way. The dimensional scale probed in a PFG NMR experiment is proportional to $1/q$. This means that smaller space scales are monitored at high q , and as a consequence, the effect of displacement restrictions should be more pronounced at high q .

Conclusions

Pulsed field gradient NMR experiments have been carried out on a triblock copolymer (Pluronic F68) dissolved in water

that undergoes a temperature-induced sol-gel transition. The results from this study of molecular motion show the following essential features. The decay of the spin echo attenuation exhibits an increasing feature of nonexponentiality as the gel zone is approached. The profile of the decay can be described by a stretched exponential, and the decreasing value of this parameter when the gel regime is entered suggested a broader distribution of diffusion coefficients. This polydispersity effect can probably be attributed to the formation of intermolecular association structures in the gel regime.

In the sol-phase ordinary diffusion is observed, but as the gelation proceeds, a strong slowing down of the diffusive motion is evident. At this stage, anomalous diffusion is detected and the mean square displacement $\langle z^2 \rangle$ shows a power law dependence on time $\langle z^2 \rangle \propto t^\alpha$, with $\alpha < 1$. The value of α decreases during the gelation process, and values around 0.5 are observed in the gel regime. Furthermore, a wave vector dependence of α is detected in the gel regime.

References and Notes

- (1) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Colloid Polym. Sci.* **1990**, 268, 101.
- (2) Deng, Y.; Ding, J.; Stubbersfield, R. B.; Heatly, F.; Attwood, D.; Price, C.; Booth, C. *Polymer* **1992**, 33, 1963.
- (3) Malmsten, M.; Lindman, B. *Macromolecules* **1992**, 25, 5440.
- (4) Beddells, A. D.; Arafah, R. M.; Yang, Z.; Attwood, D.; Heatly, F.; Padgett, J. C.; Price, C.; Booth, C. *J. Chem. Soc., Faraday Trans.* **1993**, 89, 1235.
- (5) Fleischer, G.; Bloss, P.; Hergeth, W.-D. *Colloid Polym. Sci.* **1993**, 271, 217.
- (6) Fleischer, G. *J. Phys. Chem.* **1993**, 97, 517.
- (7) Schillén, K.; Glatzer, O.; Brown, W. *Prog. Colloid Polym. Sci.* **1993**, 93, 66.
- (8) Nakashima, K.; Anzai, T.; Fujimoto, Y. *Langmuir* **1994**, 10, 658.
- (9) Jørgensen, E. B.; Jensen, J. H.; Hvidt, S. *J. Non-Cryst. Solids* **1994**, 172-174, 972.
- (10) Mortensen, K.; Brown, W.; Jørgensen, E. *Macromolecules* **1994**, 27, 5654.
- (11) Wu, G.; Chu, B.; Schneider, D. K. *J. Phys. Chem.* **1995**, 99, 5094.
- (12) Almgren, M.; Brown, W.; Hvidt, S. *Colloid Polym. Sci.* **1995**, 273, 2.
- (13) Alexandridis, P.; Hatton, T. A. *Colloids Surf., A* **1995**, 96, 1.
- (14) Mortensen, K. *J. Phys.: Condens. Matter* **1996**, 8, A103.
- (15) Nyström, B.; Walderhaug, H.; Hansen, F. K. *Discuss. Faraday Trans.* **1995**, 101, 335.
- (16) Nyström, B.; Walderhaug, H. *J. Phys. Chem.* **1996**, 100, 5433.
- (17) von Meerwall, E. D. *Adv. Polym. Sci.* **1983**, 54, 1.
- (18) Callaghan, P. T. *Aust. J. Phys.* **1984**, 37, 359.
- (19) Stilbs, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1987**, 19, 1.
- (20) Kärger, J.; Pfeifer, H.; Heink, W. *Adv. Magn. Reson.* **1988**, 12, 1.
- (21) Callaghan, P. T. *Principles of Nuclear Magnetic Resonance Microscopy*; Oxford University Press: New York, 1991.
- (22) Nose, T. *Ann. Rep. Nucl. Magn. Reson. Spectrosc.* **1993**, 27, 217.
- (23) Kärger, J.; Fleischer, G. *Trends Anal. Chem.* **1994**, 13, 145.
- (24) Fleischer, G.; Fujara, F. *NMR* **1994**, 30, 159.
- (25) Price, W. S. *Annu. Rep. NMR Spectrosc.* **1996**, 32, 51.
- (26) Jug, G. *Chem. Phys. Lett.* **1986**, 131, 94.
- (27) Kärger, J.; Vojta, G. *Chem. Phys. Lett.* **1987**, 141, 411.
- (28) Kärger, J.; Pfeifer, H.; Vojta, G. *Phys. Rev. A* **1988**, 37, 4514.
- (29) Stepišnik, J. *Physica B* **1993**, 183, 343.
- (30) Nyström, B.; Walderhaug, H.; Hansen, F. K. *J. Phys. Chem.* **1993**, 97, 7743.
- (31) Fleischer, G.; Sillescu, H.; Skirda, V. D. *Polymer* **1994**, 35, 1936.
- (32) Appel, M.; Fleischer, G.; Kärger, J.; Fujara, F.; Chang, I. *Macromolecules* **1994**, 27, 4274.
- (33) Appel, M.; Fleischer, G.; Kärger, J.; Fujara, F.; Siegel, S. *Europhys. Lett.* **1996**, 34, 483.
- (34) Stejskal, E. O. *J. Chem. Phys.* **1965**, 43, 3597.
- (35) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, 42, 288.
- (36) Gefen, Y.; Aharony, A.; Alexander, S. *Phys. Rev. Lett.* **1983**, 50, 77.
- (37) Sahimi, M.; Hughes, B. D.; Scriven, L. E.; Davis, H. T. *J. Chem. Phys.* **1983**, 78, 6849.
- (38) Blinc, R.; Lahajnar, G.; Zidansek, A. *Croat. Chem. Acta* **1992**, 65, 439.
- (39) Sahimi, M. *Transp. Porous Media* **1993**, 13, 3.
- (40) Widom, A.; Chen, H. J. *J. Phys. A: Math. Gen.* **1995**, 28, 1243.
- (41) Callaghan, P. T.; Coy, A. *Phys. Rev. Lett.* **1992**, 68, 3176.
- (42) Peterlin, A. *Makromol. Chem.* **1983**, 184, 2377.
- (43) Zupanic, I.; Lahajnar, G.; Blinc, R.; Reneker, D. H.; Vanderhart, D. L. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, 23, 387.
- (44) Fleischer, G.; Fujara, F. *Macromolecules* **1992**, 25, 4210.
- (45) Weber, H. W.; Kimmich, R. *Macromolecules* **1993**, 26, 2597.
- (46) Appel, M.; Fleischer, G. *Macromolecules* **1993**, 26, 5520.
- (47) Heink, W.; Kärger, J.; Seiffert, G.; Fleischer, G.; Rauchfuss, J. J. *Magn. Reson. A* **1995**, 114, 101.
- (48) Fischer, E.; Kimmich, R.; Fatkullin, N. *J. Chem. Phys.* **1996**, 104, 9174.
- (49) Skirda, V. D.; Doroginikij, M. M.; Sundukov, V. I.; Maklakov, A. I.; Fleischer, G.; Häusler, K. G.; Straube, E. *Makromol. Chem., Rapid Commun.* **1988**, 9, 603.
- (50) Fleischer, G.; Sillescu, H.; Skirda, V. D. *Polymer* **1994**, 35, 1936.
- (51) Suzuki, Y.; Nishio, I. *Phys. Rev. B* **1992**, 45, 4614.
- (52) Gefen, Y.; Aharony, A.; Alexander, S. *Phys. Rev. Lett.* **1982**, 50, 77.
- (53) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
- (54) Stauffer, D.; Coniglio, A.; Adam, M. *Adv. Polym. Sci.* **1983**, 44, 103.
- (55) Stauffer, D.; Aharony, A. *Introduction to Percolation Theory*, 2nd ed.; Taylor & Francis: London, 1992.
- (56) Sahimi, M. *Mod. Phys. Lett. B* **1992**, 6, 507.
- (57) Nakayama, T.; Yakubo, K.; Orbach, R. L. *Rev. Mod. Phys.* **1994**, 66, 381.
- (58) Adam, M.; Lairez, D. In *Physical Properties of Polymeric Gels*; Cohen Addad, J. P., Ed.; John Wiley & Sons: Chichester, 1996.
- (59) De Gennes, P.-G. *Recherche* **1976**, 7, 919.
- (60) Havlin, S.; Ben-Avraham, D. *Adv. Phys.* **1987**, 36, 695.
- (61) Bouchaud, J.-P.; Georges, A. *Phys. Rep.* **1990**, 195, 128.
- (62) Harder, H.; Havlin, S.; Bunde, A. *Phys. Rev. B* **1987**, 36, 3874.
- (63) Movshovitz, D.; Havlin, S. *J. Phys. A* **1988**, 21, 2761.
- (64) Roman, H. E. *J. Stat. Phys.* **1990**, 58, 375.
- (65) Netz, P. A.; Dorfmueller, T. *J. Chem. Phys.* **1995**, 103, 9074.
- (66) Daoud, M. In *Fractals in Science*; Bunde, A., Havlin, S., Eds.; Springer-Verlag: Berlin/Heidelberg, 1994.
- (67) De Gennes, P.-G. *J. Chem. Phys.* **1971**, 55, 1972.
- (68) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.
- (69) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Macromolecules* **1994**, 27, 4145.
- (70) Burstein, D. *Concepts Magn. Reson.* **1996**, 8, 269.
- (71) Callaghan, P. T. *J. Magn. Reson.* **1990**, 88, 493.
- (72) Kimmich, R.; Unrath, W.; Schnur, G.; Rommel, E. *J. Magn. Reson.* **1991**, 91, 136.
- (73) Kimmich, R.; Fischer, E. *J. Magn. Reson. A* **1994**, 106, 229.
- (74) Hrovat, M. I.; Wade, C. G. *J. Magn. Reson.* **1981**, 44, 62.
- (75) Walderhaug, H.; Hansen, F. K.; Abrahamsen, S.; Persson, K.; Stilbs, P. *J. Phys. Chem.* **1993**, 97, 8336.
- (76) Abrahamsen-Alami, S.; Stilbs, P. *J. Phys. Chem.* **1994**, 98, 6359.
- (77) Söderman, O.; Stilbs, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1994**, 26, 445.
- (78) Rao, B.; Uemura, Y.; Dyke, L.; McDonald, P. M. *Macromolecules* **1995**, 28, 531.
- (79) Uemura, Y.; McDonald, P. M. *Macromolecules* **1996**, 29, 63.
- (80) Martin, J. E.; Adolf, D. *Annu. Rev. Phys. Chem.* **1991**, 42, 311.
- (81) Martin, J. E.; Adolf, D.; Wilcoxon, J. P. *Phys. Rev. Lett.* **1988**, 61, 2620.
- (82) Adolf, D.; Martin, J. E. *Macromolecules* **1991**, 24, 6721.