Temperature dependence of probe diffusion in gels

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We present a dynamic light scattering study of the temperature dependence of the dynamics of probe diffusion in polyacrylamide gels and pregel solutions as a function of crosslink content and scattering angle. Our results show that the spinodal transition in polyacrylamide gels affects the movement of the probe particles. The dynamical behaviour ranges from overdamped vibration of particles controlled by the gel elasticity (relaxational behaviour) at low temperatures to the free diffusion of particles controlled by the sol viscosity at higher temperature. The decay rate of the relaxational mode decreases upon approaching the spinodal temperature, and this decrease is even more pronounced than that of gels without probe particles. Our results suggest that the friction felt by the 50 nm probe particles as they move in the gel appears to diverge at the spinodal temperature, scaling as $\approx (T-T_s)^{-1.5}$. This behaviour is observed over the entire temperature range for probe diffusion in a well gelled sample, whereas in a sample closer to the gel threshold the strong temperature dependence is observed only at low temperatures, the higher temperature behaviour being the same as that in pre-gel solutions. We propose an interpretation of the experimental data in terms of a simple theory of Brownian particles harmonically bound to the gel network.

(Keywords: polyacrylamide gels; probe particles; diffusion; spinodal; dynamic light scattering)

INTRODUCTION

The quantitative characterization of the structure and viscoelastic properties of swollen crosslinked gels is of fundamental importance for many biochemical and medical applications. Gels are extensively used as matrices, for example in gel chromatography, electrophoresis and gel based prosthetic devices. In all of these applications the network structure of the gel and the dynamics of the movement of particles in the network play a crucial role. Therefore, we have studied this problem and developed a novel way to extract information about the static structure of gels or pregel networks and their viscoelastic properties from the dynamical behaviour of probe particles incorporated in gel matrices[1,2].

In a previous paper[1] we reported how a quasi-elastic light scattering study of polystyrene latex microspheres incorporated in polyacrylamide solutions and gels could be used to determine the static structure of the gel network. From the normalized initial amplitude of the time correlation function the fraction of moving particles as a function of crosslink content was estimated and related to the pore-size distribution. It was found that the pore-size distribution of the gel is sharply peaked and strongly dependent on crosslink concentration. A broadening of the distribution of decay rates at and above the gel threshold was also observed[1,3]. In an effort to understand the complex dynamics of particles moving in a gel we have recently reported a detailed analysis of the intensity autocorrelation functions measured over several decades of sampling times[2]. We observed dynamic behaviour ranging from the purely translational diffusive movement of the probes to a relaxational behaviour associated with the local movement of latex particles in the gel. The cross-over from diffusional to relaxational behaviour was found to be a function of the length scale over which the movement is probed, of the mesh size of the network and of the particle diameter. A fast mode due to mechanical coupling of the probe particles and gel matrix itself was also observed.

The present paper is a continuation of this study[2], with the aim of characterizing the local movement of the probe particles in polyacrylamide gels from the point of view of dynamic interaction with the polymer network. Tanaka *et al.*[4,5] have shown that polyacrylamide gels undergo a spinodal transition with very interesting critical behaviour as a function of temperature. At this transition temperature the longitudinal modulus goes to zero and the static light scattering intensity of the gel diverges. In this paper we present evidence that this spinodal transition affects the local movement of latex particles incorporated in gels.

EXPERIMENTAL

The samples used in this study were polyacrylamide gels or solutions into which highly monodispersed polystyrene latex spheres (Polysciences, $d = 50 \pm 5$ nm) were incorporated before polymerization. Details of the polymerization methods are given in Reference 2. The excess scattering intensity of polystyrene latex spheres was adjusted to be about 100 times that of the polymer solutions and gels at room temperature. Measurements of the intensity correlation function, in the temperature range from −10 to 40°C, through scattering angles

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ranging from 15 to 138°, were made using a standard laser light multi-angle spectrometer with 15 mW He–Ne laser ($\lambda = 633$ nm) and a 64 channel, real-time multi-bit Langley Ford 1096 correlator. In view of the previously published results concerning non-single exponentiality of the correlation functions (CF), we measured the intensity correlation function, $G^2(t)$, extended over three orders of delay time by multiplexing the available real-time channels to generate a total of 1024 channels, linearly spaced in time. Eight delay channels used to measure the baseline, B, further increase the dynamic range of measurement by a factor of two. These CFs were analysed by a double exponential force fit to the baseline-subtracted electric-field-normalized CFs

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

in the form

$$g^{(1)}(t) = A_f \exp(-\Gamma_f\, t) + A_s \exp(-\Gamma_s\, t)$$

where Γ_f, Γ_s, A_f and A_s are the apparent decay rates and amplitudes of the fast and slow modes, respectively, with the condition $A_f + A_s = 1$. Force fits were made with the various possible baselines as discussed in Reference 2 and the results were only slightly dependent on the choice of baseline. As discussed in Reference 2, although there is some partial heterodyning in the well gelled samples its effects can at most change decay rates by a factor of 2. Our aim here is to understand changes in decay rates by several orders of magnitude and, therefore, the data are analysed in the homodyne approximation.

RESULTS AND DISCUSSION

The results of the double exponential analysis for selected samples are summarized in *Figure 1*, which shows the apparent decay rates Γ_f and Γ_s corresponding to the fast and slow modes, respectively, as a function of temperature, T, for CFs measured at a fixed scattering vector $K = 1.87 \times 10^5\,\mathrm{cm}^{-1}$, corresponding to the scattering angle $\theta = 90°$. The values of the decay rates Γ_f and Γ_s obtained by a double exponential forced fit to the linearly spaced multiplex CFs are slightly larger than those obtained from the logarithmically spaced multiple-sample-time CFs[2]. This may be a consequence of different densities of measured points, especially at longer delay times, and a shortening of the dynamic range of CFs from 4.5 orders for multiple-sample-time CFs to 3 orders for multiplex CFs. A comparison of the different methods[2] has shown that the main features of the particle dynamics are not substantially influenced, although the actual values of decay rates are slightly affected. For comparison, *Figure 1* also shows the decay rate from a gel sample with $f_{\mathrm{Bis}} = 3.0\%$ without latex probes.

Three different types of temperature dependence can be distinguished in *Figure 1*:

(1) only weak temperature dependence in both Γ_f and Γ_s can be observed in polyacrylamide solutions (i.e. the samples with $f_{\mathrm{Bis}} \leqslant 1.5\%$) and for the samples with $f_{\mathrm{Bis}} = 1.6\%$, which is just above the gel threshold;

(2) a very pronounced temperature dependence of Γ_f and Γ_s was found in the well gelled samples ($f_{\mathrm{Bis}} \geqslant 3.0\%$), which, particularly for Γ_s, is even stronger than that of the collective diffusion mode from an $f_{\mathrm{Bis}} = 3.0\%$ gel without any latex probes; and

(3) a transition from strong temperature dependence at low temperature to a weaker one above room temperature was observed for samples with intermediate crosslink content ($f_{\mathrm{Bis}} = 2.0\%$ and 2.5%).

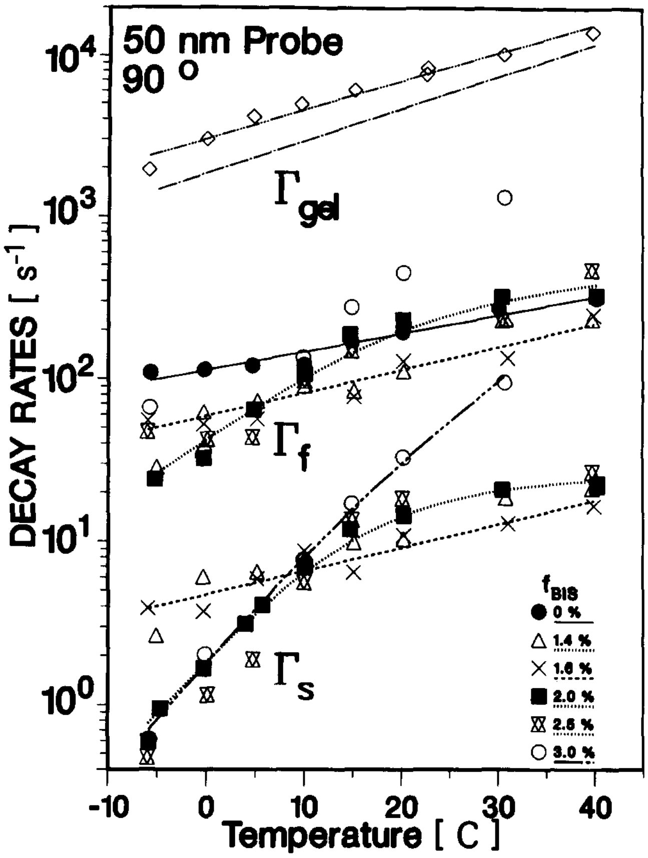

Figure 1 Temperature dependence of apparent decay rates, fast mode (Γ_f) and slow mode (Γ_s) for various values of f_{Bis}. Data for the decay rates measured from a gel without probes, Γ_{gel}; ——, decay rates of the gel mode as published by Tanaka *et al.*[4,5] for a polyacrylamide gel of similar composition

Figure 2 shows the K^2 dependence of the decay rates Γ_f and Γ_s for the sample with $f_{\mathrm{Bis}} = 2.0\%$ at 6 and 40°C. Both modes are almost diffusional (i.e. $\Gamma_f \sim K^{1.5}$, $\Gamma_s \sim K^2$) at 40°C. The cross-over between almost free diffusion and relaxational dynamics can be observed for Γ_s near $K^2 \approx 2.10 \times 10^{-5}\,\mathrm{nm}^{-2}$ at 6°C. This cross-over shifts to higher K^2 with increasing temperature and was found at $K^2 \approx 1.02 \times 10^{-4}\,\mathrm{nm}^{-2}$ in the room temperature measurements[2]. In fact, the cross-over is beyond the measuring range of K^2, i.e. $> 6.16 \times 10^{-4}\,\mathrm{nm}^{-2}$, at 40°C. The fast decay mode Γ_f at 6°C is also independent of K^2 for large K^2. Similar behaviour was observed for all well gelled samples[2].

To explain these observations we suggest an interpretation based on the structure and viscoelastic properties of polyacrylamide gels[2]. Three principal contributions to the dynamically scattered light, differing in temperature and K^2 dependence or both, could be basically distinguished in these samples. Two of them correspond to the movement of the probe particles in different dynamic regimes and the third corresponds to collective thermal excitations of the gel itself.

(1) *Almost free diffusion.* When particles are moving in the large interconnected space outside the gel mesh they are diffusing essentially freely and interact only weakly with the gel network. Thus the Stokes–Einstein relationship is valid in this case and the temperature

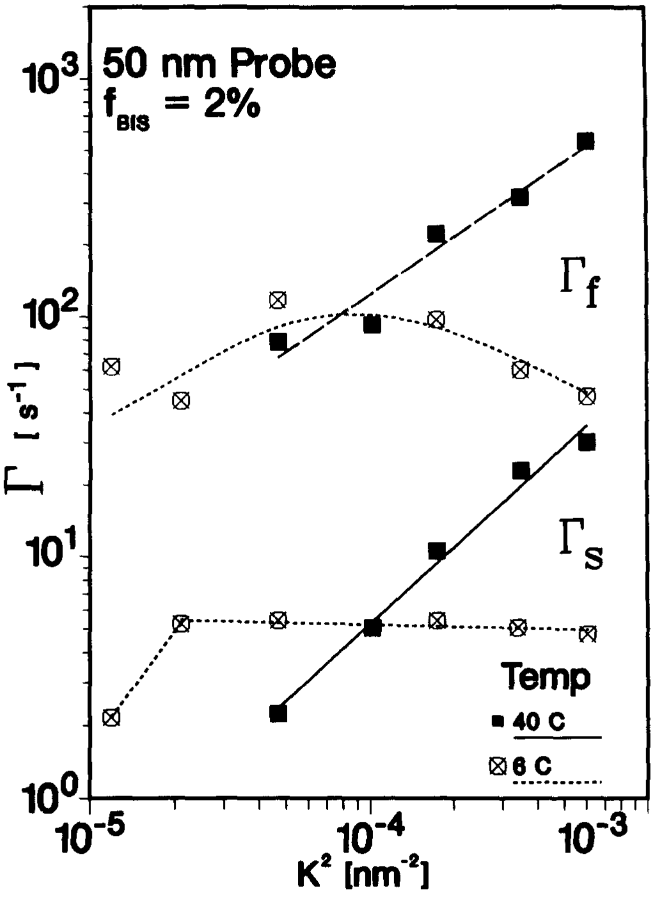

Figure 2 K^2 dependence of decay rates for sample with $f_{\mathrm{Bis}}=2\%$ taken at 6 and 40°C. ······, ——, Lines guide the eye; ——, line of slope 1 corresponding to $D_s \sim K^2$

dependence of decay time rates is controlled mostly by temperature changes of the ratio T/f, where f is the friction felt by the particle as it moves in the gel or pregel solutions. Corresponding decay rates should be *K^2-dependent* and the dynamic light scattering intensity is practically independent of K^2.

(2) *Relaxational dynamics from particles in cages.* If particles are moving in the fine mesh of the gel, whose size is of the order of few particle diameters, the interaction with the gel network is significant and the movement of particles is localized in such fine gel mesh. This type of behaviour can be modelled by considering the Brownian movement of harmonically bound particles in a cage[6,7]. In this case the dynamics are characteristic of a relaxational behaviour with decay rates *independent* of K^2, as long as $\xi_{\mathrm{mesh}} < 1/K$ (see, for example, References 8 and 9). The temperature dependence of the decay rate should be controlled mostly by temperature changes of E/f, where E is the longitudinal elastic modulus of the gel network. Since E goes to zero as one approaches the phase transition temperature, in this case the movement of particles should slow down significantly with decreasing temperature and thus indirectly reflect the effect of the phase transition of the gel. The decay rate also depends on the cage size (ξ_{mesh}), becoming larger as the cage size decreases, and hence this decay rate increases as f_{Bis} increases.

The intensity, I, of the light dynamically scattered by particles displaying relaxational behaviour is proportional to $1-\exp(-2K^2\xi^2_{\mathrm{mesh}})$ and decreases significantly as $K\xi_{\mathrm{mesh}}$ decreases[8,9]. Since ξ_{mesh} decreases with increasing temperature[4], the contribution of the relaxational modes would clearly be large at lower temperatures and of course at higher K.

(3) *Collective thermal excitations of gel and coupling of gel and probe particle motions.* The fast concentration fluctuations of gel due to collective thermal excitations of the polymer network[10] contribute only slightly to the total dynamic light scattering under the conditions of our experiment but can affect the measured decay rates by coupling with probe particle motion.

The coupling of motions of different kinds of polymers in ternary homopolymer semidilute solutions has recently been proposed using the random phase approximation technique[11] and experimentally verified by dynamic light scattering experiments[12–15]. The correlation function of scattered intensity was found to be a sum of two exponential functions, where the two components are termed the cooperative and interdiffusion modes, respectively. The latter mode becomes equal to the self-diffusion mode at sufficiently low concentrations of one of the polymers (probe polymer) in the matrix of the other. These results are similar to those of the earlier studies of Phillies[16,17] and Pusey *et al.*[18] on dilute solutions of interacting latex particles of two different sizes, although different arguments were used.

In analogy with the above mentioned theoretical and experimental results, we suggest[2] that a dynamical (mechanical) coupling between the motion of the probe particles and the gel matrix could result in two modes: a fast mode (Γ_f) corresponding to the coupling of gel and probe motions; and a slow mode reflecting mostly the particle dynamics.

Temperature dependence of slow mode

From the above summary it is clear that the temperature dependence of Γ_s is controlled either by the sol friction or by the ratio E/f. *Figure 1* shows that the temperature dependences of Γ_f and Γ_s for the samples with $f_{\mathrm{Bis}}=1.4$ and 1.6% are practically the same and close to that of polyacrylamide solution (the sample with $f_{\mathrm{Bis}}=0\%$), which implies that the free diffusional mode (case (1) above) is the dominant contribution to the total dynamically scattered light intensity. For samples just above the gel threshold ($f_{\mathrm{Bis}}=1.6\%$) the network is so ramified that small particles can move essentially freely in large interconnecting spaces and interactions with the network are negligible.

Tanaka *et al.*[4,5] have shown that the longitudinal modulus E vanishes at the spinodal temperature T_s of the gel, which for polyacrylamide gel of similar composition to that used in this study was reported to be approximately −17°C. They further found that $E \approx (T-T_s)$. Since the relaxational dynamics of the particle is mostly governed by E/f one would expect to see a temperature dependence of the corresponding decay rate similar to the case of the gel mode as the spinodal temperature is approached. For the well gelled samples ($f_{\mathrm{Bis}}=3.0\%$) where the dynamics is largely relaxational, we observe a stronger temperature dependence of Γ_s, compared with both Γ_f and Γ_{gel} (see *Figure 1*).

Figure 3 shows a log–log plot of $\Gamma_s\eta_0/T$ *versus* $(T-T_s)$, where $T_s=255$ K is the spinodal temperature, η_0 is the solvent viscosity and T is the temperature (in K). For the $f_{\mathrm{Bis}}=3.0\%$ sample we find $\Gamma_s(\eta_0/T) \sim (T-T_s)^{2.5}$. Since $\Gamma_s\eta_0/T$ is proportional to E/f and since E scales as

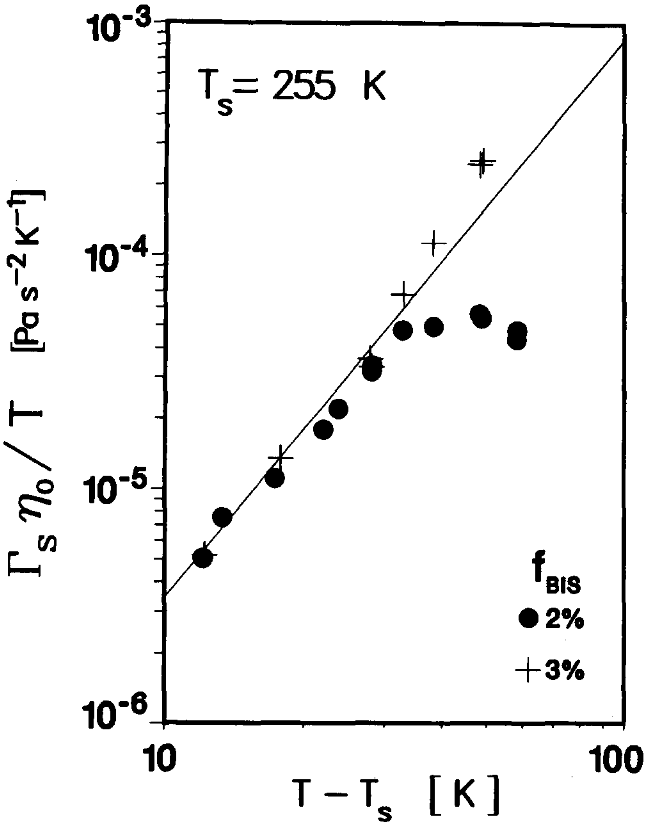

Figure 3 Scaling behaviour of decay rate Γ_s as temperature T decreases to the spinodal temperature $T_s = 255$ K. The decay rate has been normalized by η_0/T to remove the temperature dependences normally occurring in the behaviour of the decay rates. Here η_0 is taken as the viscosity of water (in Pa s^{-1}) and T is in K. The decrease of $\Gamma_s\eta_0/T$ with decreasing $T - T_s$ thus reflects the behaviour of E/f near the spinodal transition of the gel. ——, Scaling behaviour close to T_s, with $\Gamma_s\eta_0/T \sim (T - T_s)^{2.5}$

$T - T_s$, it follows that f, the friction encountered by the large particles moving in well gelled samples, is not the same as that encountered by the solvent molecules and our data imply that this friction f diverges at the spinodal temperature scaling as $f \sim (T - T_s)^{-1.5}$. We note that since the decay rates were normalized by η_0/T the temperature dependence of f represents additional effects arising from the interaction of the particle with the gel network. For the sample with $f_{\mathrm{Bis}} = 2.0\%$ the strong temperature dependence in E/f is seen at low temperatures, but at higher temperatures the behaviour of the decay rate is similar to that observed in solutions. This implies a transition from primarily relaxational behaviour at low temperatures to primarily diffusional behaviour at high temperatures in samples which are not very well gelled and can be explained by a competition of two different dynamic contributions to the total dynamically scattered light: (a) free diffusion of particles in some large interconnected regions and (b) relaxational motion of particles localized in the fine gel mesh. As the temperature increases, the effective 'pore size' becomes smaller[4] and thus the relaxational mode's contribution to the total dynamically scattered light decreases with increasing temperature. Therefore, the free diffusion contribution becomes dominant above room temperature. This observation suggests that there may be some structural heterogeneity in such weakly crosslinked gels. Thus in these gels, besides the fine mesh in a homogeneous polymer network, some large interconnected regions also exist. The heterogeneity of the gel should decrease with increasing crosslink density and, therefore, the free diffusion mode has not been detected in the well gelled sample with $f_{\mathrm{Bis}} = 3.0\%$ even at higher temperatures.

The decrease of mesh sizes with increasing temperature is demonstrated even in K^2 dependences of Γ_s in *Figure 2* (see also Figure 4 in Reference 2) for the sample with $f_{\mathrm{Bis}} = 2.0\%$. The cross-over between almost free diffusion and relaxational dynamics observed for the data Γ_s at 6°C has its origin again in the strong dependence of the amplitude of the contribution of the relaxational mode on $K^2\xi^2_{\mathrm{mesh}}$. Decrease of ξ_{mesh} with increasing temperature induces a shift of this crossover to higher K and at 40°C no relaxation contribution was observed (the crossover is above the range of K values measured).

Temperature dependence of fast mode

The temperature and K^2 dependence of Γ_f reflect the motion of both the gel and the particle and are dominated by which of the two contributes more strongly to the coupled mode. The temperature dependence of Γ_f for gelled samples ($f_{\mathrm{Bis}} \geqslant 2\%$) is intermediate to those of Γ_{gel} and Γ_s. Similar conclusions can be reached for K dependences of Γ_f. Thus Γ_f for the sample with $f_{\mathrm{Bis}} = 2.0\%$ at 40°C scales as $K^{1.5}$, with an exponent which is close to the free diffusion dynamics as a result of coupling of two diffusive modes (Γ_{gel} and Γ_s). In contrast, the high temperature behaviour Γ_f is independent of K^2 at 6°C and reflects the fact that the relaxational particle dynamics is the dominant contribution to the coupled mode.

CONCLUSION

The dynamics of particles moving in gels is strongly influenced by temperature, in sharp contrast to the weak dependence in solutions. The occurrence of a phase transition in the gel indirectly affects the movement of the localized particles. The temperature dependence of the measured correlation function gives strong support to the model that the particle movement in gels can be described by a combination of almost free diffusion in the large interconnected spaces plus a localization of movement in the smaller pores of the gel network. We observe a very strong temperature of the friction encountered by the large particles as they move in the gel network, in contrast to the friction felt by solvent molecules. The fact that dynamic properties of the probe particles reflect the viscoelastic properties of the gel, particularly near the vicinity of T_s, suggests that such techniques can be used for characterization of the gel network.

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