Quasielastic Light-Scattering Study of the Movement of Particles in Gels

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Quasielastic light scattering of polystyrene latex spheres incorporated in polyacrylamide solutions whose crosslink content was varied through the gelation threshold was performed over a range of k values. From the initial amplitude of the correlation functions we obtain the fraction of moving particles, which decreases monotonically with $1/k$ and crosslink content. The measured pore-size distribution of the gel is sharply peaked. The results suggest that the gel has a large interconnected space as well as many small pores.

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Introduction.—The structure of the percolation cluster at the vicinity of the gelation threshold has attracted a great deal of theoretical attention related to its self-similarity property.[1] In a two-dimensional system, above the threshold the infinite cluster of a gel divides the space into many small disconnected compartments. However, for a three-dimensional system, the internetwork spaces appear "connected" to a very small particle such as a solvent molecule while they are not "connected" for large macromolecules. Thus, we may be able to obtain information about the structure of the three-dimensional network by studying the movement of particles of various sizes incorporated in the gel network. Photon correlation spectroscopy (PCS) of probe spheres in polymer solutions and gels has been used to study probe diffusion.[2-4] In this Letter we present a novel way to extract information about the static structure of gel or pregel networks from PCS data of spherical probe diffusion.

Theory.—The experiment involves mixing a small amount of monodispersed probe microspheres with a very strong light-scattering ability into the monomer mixture prior to polymerization. In this Letter, we concentrate on the most apparent effect of the network on the movement of the probes, namely, their trapping. When the scattered-light intensity from the probe particles is much greater than that scattered by the polymer, and the probe particles do not aggregate, the electric field of the scattered light can be written as the sum of the scattering from individual probes. As polymerization proceeds, some fraction of the probes will be trapped in the network. The electric field of the light scattered by a trapped particle can be factored into a time-independent part, $\exp(-i\mathbf{k}\cdot\mathbf{r}_{0,j})$ and a time-dependent part $\exp[-i\mathbf{k}\cdot\Delta\mathbf{r}_j(t)]$. Here $\mathbf{r}_{0,j}$ is the center of the compartment in which the jth particle is trapped, $\Delta\mathbf{r}_j(t)$ is the time-dependent position of the jth particle inside the compartment, $\mathbf{k}$ is the scattering vector whose magnitude is $|\mathbf{k}| = 4\pi n \sin(\theta/2)/\lambda$, where n is the refractive index of the solution, λ the wavelength of the laser light, and θ the scattering angle. The fluctuation of the phase of the complex number $\exp[-i\mathbf{k}\cdot\Delta\mathbf{r}_j(t)]$ causes the change in the interference pattern of the electric field from different particles and results in the fluctuation of the total scattered light intensity. Since the maximum value of $\mathbf{k}\cdot\Delta\mathbf{r}_j(t)$ is limited by the size L of the compartment, there may not be any significant fluctuation by a particle trapped in a compartment for which $Lk \ll 1$.

To analyze the autocorrelation light-intensity fluctuations, we made the following simplifying assumptions: (1) A particle trapped inside a compartment which satisfies the relation $Lk \ll 1$ does not create any fluctuation of the scattered-light electric field; hence, the corresponding correlation function may not have a significant time dependence and will be nearly constant. (2) A particle trapped inside a compartment for which $Lk \gg 1$ creates a significant amount of scattered-light–intensity fluctuation, and the correlation function of the scattered-light electric field will be the same as if the particle was undergoing unrestricted Brownian motion.[5] These two assumptions [(1) and (2)], valid for the limit of $L \ll 1/k$ and $L \gg 1/k$, respectively, correspond to replacing the smooth function which connects these two limits by a step function. This is valid if any movement of the walls is in a different time scale than the movement of the particles. The effect of flexible walls will be considered in a future paper. (3) The scattering from the polymer solution or gel is negligible compared with that from the probe particle.

Under these assumptions, the scattered-light electric field can be separated into two parts: time-dependent terms from the freely diffusing particles and time-independent terms from the trapped particles. Labeling the trapped particles from 1 to N' ($N \gg N' \gg 1$), we can write the time-averaged scattered-light intensity and the autocorrelation function of the scattered-light–intensity fluctuations as

$$\langle I(t)\rangle_t = I_0\left[\sum_{j,j'}^{N'} \exp(-i\mathbf{k}\cdot(\mathbf{r}_{0,j}-\mathbf{r}_{0,j'})\right] + I_0(N-N') = I_{\text{trapped}} + I_{\text{mov}}, \tag{1}$$

and

$$c(\tau)=(I_{\text{trapped}}+I_{\text{mov}})^2+A(k)[(I_{\text{mov}})^2\exp(-2D'k^2\tau)+2I_{\text{mov}}I_{\text{trapped}}\exp(-D'k^2\tau)], \qquad (2)$$

where D' is the diffusion coefficient of the freely moving sphere in the gel which may be different from the diffusion coefficient in water, and $A(k)$ represents the efficiency of detection of scattered-light-intensity fluctuations. By combining with the relative amplitude of decaying part of the correlation function $[c(0)-c(\infty)]/c(\infty)$, we can calculate the scattered-light intensity of the moving particle, I_{mov}, as

$$I_{\text{mov}}=\langle I(t)\rangle_t(1-\{1-[c(0)-c(\infty)]/[A(k)c(\infty)]\}^{1/2}). \qquad (3)$$

The ratio $I_{\text{mov}}/\langle I(t)\rangle$, i.e., the dynamic scattering intensity, is directly related to the fraction of the moving particles, f_{mov}. Since f_{mov} goes to 1 for particles suspended in pure water or very dilute polymer solution, the parameter $A(k)$ can be determined by measuring $I_{\text{mov}}/\langle I(t)\rangle$ for particles in water or dilute polymer solution. We note that the unnormalized base line of the correlation function, $c(\infty)$, is sensitive only to the total scattered intensity, and thus can provide no information about the movement of the particles. However, the normalized base line, $c(\infty)/c(0)=\langle I(t)\rangle^2/\langle I^2(t)\rangle$, is dependent on the fraction of moving particles. Moreover, the ratio $\langle I^2(t)\rangle/\langle I(t)\rangle^2$ will be independent of the k-dependent static structure factor even though the average intensity has a k dependence due to the particle structure factor. This assumes that there is no significant change in the size of the trapped particles compared with those of the free particles. Thus, any k dependence of $f_{\text{mov}}(k)$ represents only the effect of the network on the probe particles and not the k-dependent static structure factor. It is possible to relate f_{mov} to the volume fraction of the gel due to compartments with the characteristic size larger than $1/k$. If we denote by $V(r)$ the average volume fraction of the gel made up by compartments of characteristic size r, i.e., the mesh-size distribution, then

$$f_{\text{mov}}\left(\frac{1}{k}\right)\propto\int_{1/k}^{r_{\max}}V(r)dr\propto I_{\text{mov}}/\langle I(t)\rangle_t, \qquad (4)$$

where $r_{\max}$ is the largest mesh size in the gel. Thus, by changing the scattering angle θ, hence varying $\mathbf{k}$, and converting Eq. (4) into a differential form, we can obtain $V(r)$, the pore-size distribution function. Because of the range of k values accessible in light scattering, this technique is ideally suited for studying mesh-size distribution in weak gels or in gels at the gelation threshold.

Experiment.—The samples used in this experiment are polyacrylamide (PA) gels or solutions made by copolymerizing acrylamide (AA), and bisacrylamide (Bis), using ammonium persulfate as initiator (40 mg/100 ml), and tetramethylethylenediamine (TEMED) (160 μl)/100 ml as catalyst. A series of samples with a total monomer concentration [AA]+[Bis]=2.5 wt.%, but differing in the crosslink content, $f_{\text{Bis}}=[\text{Bis}]/([\text{Bis}]+[\text{AA}])$, varying from 0% (linear polymer) to 5% (strong gel) at increments of 0.25%, were prepared with use of standard methods.[6] Prior to the initiation of the polymerization process, a small amount ($\simeq 65$ μl) of highly monodispersed polystyrene latex spheres, PSL (Polysciences), either 500 ± 5 or 1000 ± 10 Å in diameter, suspended in water, was added to each pregel mixture. Because of the strong scattering from the PSL, their scattering intensity was measured to be 100 times larger than that of the pure polymer solution at any stage of the polymerization process. This assures us that the correlation function measured here is directly related to the movement of the probes and has no significant contribution due the movement of the polymer chains, as required in the formalism developed above.

Measurements of the scattered-light-intensity correlation function, at a constant temperature of 20.0 ± 0.01 °C, were performed with use of a standard laser light-scattering apparatus with a 15-mW He-Ne laser (6328 Å) and a 64-channel multibit Langley-Ford 1096 correlator. To avoid the effects of inhomogeneity inside the gel, ten different positions along the vertical axis of the samples were studied. The absence of chemical-bond formation between probes and polymer and/or aggregation of the probes was carefully studied by taking out the probes using centrifugation, and their hydrodynamic size was monitored; no significant change over the experimental error of 1% was detected from a mixture of linear polymer ($R_H \simeq 500$ Å) and probe spheres. To further test the possibility of bonding, we measured the probe size, R_H, of three samples of dispersions of 600 Å PSL microspheres, (a) in water, (b) in a 2.5% linear PA solution (molecular weight 65.000), and (c) in a 2.5% solution of AA which was allowed to polymerize. In all cases the particles diameter was the same and remained unchanged over a time period of the order of days, suggesting that even when polymerization occurs in the presence of latex spheres [case (c) above] there is no detectable bonding of the polymer on the probes. The same conclusion was obtained by Allain, Drifford, and Gauthier-Manuel.[2] Furthermore, we have observed that latex suspended in a polyacrylamide gel is more stable with respect to aggregation, than latex in water over prolonged periods of time.

Results and Discussion.—Figure 1(a) shows typical normalized correlation functions, $c(\tau)/c(0)$, observed from 1000-Å diam PSL embedded in pregel solutions and in gels observed at a scattering angle of 90°. The figure also shows the last eight channels measured with a

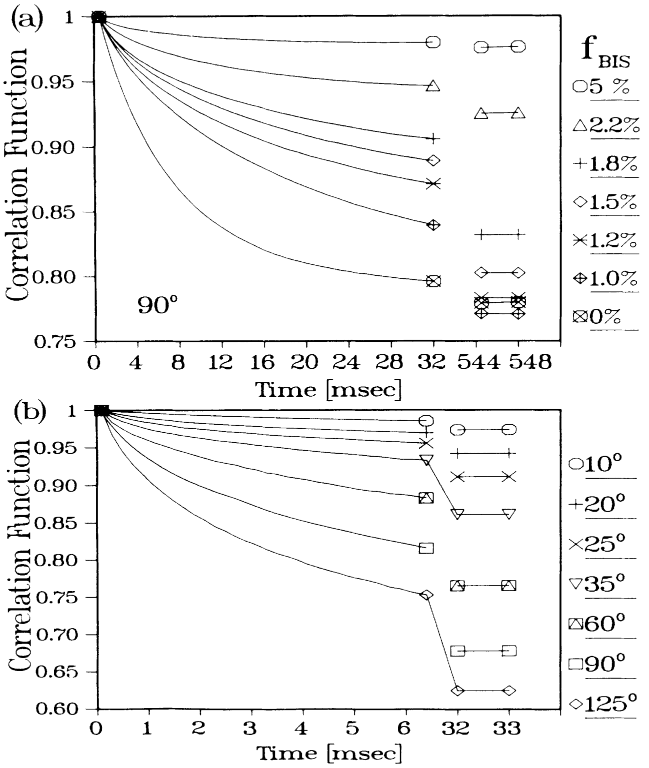

FIG. 1. (a) Normalized correlation functions, $c(\tau)/c(0)$, from 1000-Å polystyrene latex spheres incorporated in polyacrylamide samples with different crosslink content, f_{Bis}. The base line measured at a 256-channel delay is indicated at the right. (b) k dependence of the correlation functions from a polyacrylamide gel sample (total monomer 2.5% and $f_{\mathrm{Bis}} = 1.8\%$), containing 500-Å PSL spheres.

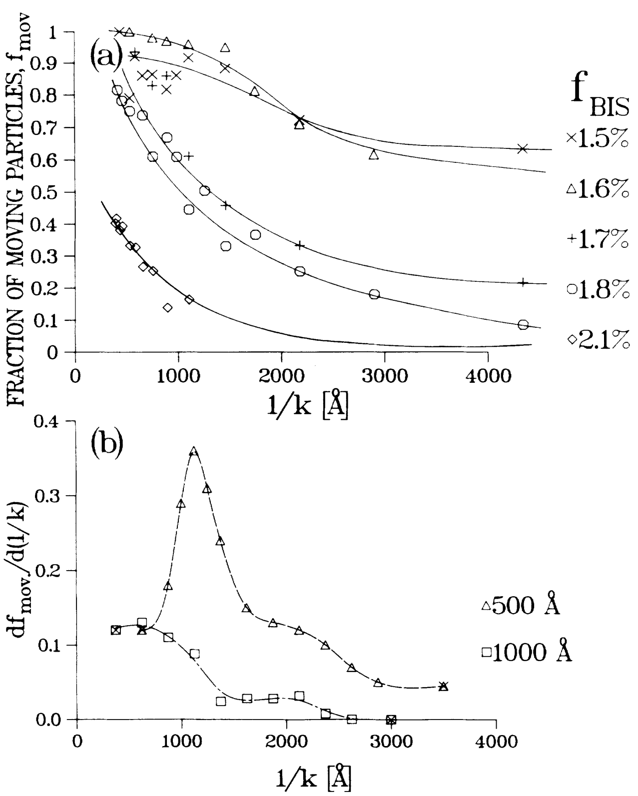

FIG. 2. (a) Fraction of moving particles (500-Å diameter), calculated from Eq. (4), plotted vs $1/k$. The different curves are for samples with f_{Bis} as indicated. (b) Magnitude of the derivative $df/d(1/k)$ calculated for the gel-threshold sample of $f_{\mathrm{Bis}} = 1.8\%$, with different probe sizes: 500 Å (triangles) and 1000 Å (squares).

256-channel delay. The theoretical base line was calculated from the square of the total number of counts divided by the number of sampling times. It was found that an exponential fit of the experimental data with a floating base line gave a base-line value within 1% of the theoretical base line. However, an exponential fit only worked well with samples far from the gelation threshold. This result was also observed by Allain, Drifford, and Gauthier-Manuel.[2] The exact functional form of the correlation function and the dependence of the decay constant on f_{Bis} will be discussed in a future paper. In view of this, the theoretical base line was used in these calculations. The figure shows that for solutions up to 1.5% the normalized base line, i.e., $c(\infty)/c(0)$, does not vary much, but for values of f_{Bis} higher than 1.6% the normalized base line steadily increases showing the lack of mobility, i.e., trapping of the probes.

Figure 1(b) shows a typical scattering-angle dependence of the normalized correlation functions, observed from 500-Å particles embedded in a gel with 1.8% of Bis. For the same sample the normalized base line, which is related to the amount of dynamic scattering [see comments on Eq. (3)], shows a very strong k dependence. The increase in the normalized base line with decreasing k implies that the fraction of the probes capable of diffusing at large length scales is much smaller than the fraction capable of diffusing on short length scales. This is true in a gelled sample as the one shown. For a slightly crosslinked sample, the probes are capable of diffusing freely on a wider range of length scales. In a totally free Brownian motion the probes should be able to diffuse equally at all length scales. This is observed when the probe spheres are embedded in a dilute linear-polymer solution; the base line shows essentially no dependence on k.

Figure 2(a) shows the fraction of moving, 500-Å particles, $f_{\mathrm{mov}}(1/k)$, as a function of the length scale $1/k$, calculated with use of Eqs. (3) and (4). The efficiency constant $A(k)$ was determined by setting $f_{\mathrm{mov}}(1/k) = 1$ for a sample with $f_{\mathrm{Bis}} = 0.25\%$, well below the gel threshold. As seen in the figure, for samples just below the gel threshold ($f_{\mathrm{Bis}} = 1.5\%$ and 1.6%) $f_{\mathrm{mov}}(1/k)$ remains approximately 1 up to 1500 Å, but decreases to approximately 0.6 at large distances. The samples with

$f_{\mathrm{Bis}} = 1.7\%$ and 1.8% are at or past the gelation threshold, and they show a significant decrease of f_{mov} at large length scales. These data imply that a large fraction of probe particles can diffuse more or less freely on distances up to 1000 Å, whereas very few particles can diffuse distances beyond 2000 Å in these gel-threshold samples.

As discussed earlier, Eq. (4) shows that if we calculate the derivative $df/d(1/k)$ we should get $V(r)$, the volume fraction of pores of size $r = 1/k + D$, where D is the probe's diameter, and $1/k$ is the distance over which the diffusion of the center of mass of the particle is probed. Figure 2(b) shows the derivative $df/d(1/k)$ as a function of $1/k$ for the gel-threshold sample with $f_{\mathrm{Bis}} = 1.8\%$ calculated from the data with 500- and 1000-Å particles. It is clear from the 500-Å data that the distribution of pore sizes is peaked. The position of the peak corresponds to the inflexion point of the graph of f_{mov} vs $1/k$ and the width of the pore-size distribution corresponds to the range of $1/k$ over which f_{mov} shows a significant drop. Since the peak in the distribution function occurs at $1/k \sim r_0 - D$, where r_0 denotes the most characteristic pore size, we would expect that the peak position would shift to lower values of $1/k$ as the particle diameter increases. This is supported by our data: The entire $df/d(1/k)$ curve shifts to the left by approximately 500 Å when the particle diameter is increased from 500 to 1000 Å. In fact, the peak would occur around $1/k \simeq 400$ Å with a 1000-Å particle which is outside the range of k of this measurement. Thus for the sample with 500-Å probes, total monomer concentration of 2.5% and $f_{\mathrm{Bis}} = 1.8\%$, the most characteristic pore size is of the order of 1100+500 Å = 1600 Å, and a large fraction of the volume of the gel is made up of pores of size between 1300 and 2100 Å.

Figure 2(a) displays the clear decrease in the fraction of moving particles observed at a given length scale $1/k$, when the amount of the crosslinking is increased. The peak position, r_0, shifts to lower values of $1/k$ with increasing f_{Bis}, and in the case of the post-gel threshold samples of 2.1% Bis the peak has shifted below 500 Å, i.e., pore size less than 1000 Å and cannot be detected by the experiment with 500-Å probes. This result can be easily interpreted as arising from the decrease of the compartment size with increasing crosslinking.

Figure 2(b) also shows that the distribution function does not go to zero even at 4000 Å for 500-Å probes, suggesting that in the gel there exist interconnected spaces which are quite big in size compared with the characteristic compartment size. Thus, it appears that just above the gelation threshold a significant trapping of the particles is observed only at a rather large length scale which is several times larger than the size of the probes. Our results are consistent with a picture of the gel network consisting of rather dense walls and rather empty spaces enclosed by such walls, as well as many small pores. Electron microscopic studies of polyacrylamide gels[7] also support this model of gel structure.

In conclusion, we have demonstrated a new way to characterize the gel network around the gelation threshold. By introducing the concept of particles trapped in the network, we have measured the compartment size using PCS. From these measurements, we have shown that the probes are trapped in a rather large compartment surrounded by dense walls which they are unable to penetrate. As the number of crosslinks increases, the compartment size becomes smaller monotonically. Our preliminary experiment with varying sizes of the probe particles suggests that the compartment size at the vicinity of the threshold is possibly a universal parameter to describe the structure of the gel network.

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