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# Network Formation in Polyacrylamide Gels

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ABSTRACT: Dynamic light scattering was used to measure the shear modulus of several series of polyacrylamide gels. A power law relating monomer concentration to the critical cross-link density necessary for network formation has been determined and is found to agree closely with that predicted by computations based on dynamic percolation models of gelation. The dependence of shear modulus on cross-link density and initiator concentration was studied, and scaling theories have been employed to ascertain how, at the gel point, the number of equivalent primary chains in a network varies with the monomer and initiator concentrations.

The gelation of acrylamide is an example of vinyl–divinyl radical polymerizations which can result in macroscopic polymer networks. Network formation is quite complicated and depends on the concentration of vinyl and divinyl monomers and on factors which affect gelation kinetics such as solvent viscosity and the rate constants for free radical production and polymer addition.[1,2] Several aspects of such polymerization processes are not yet fully elucidated, particularly phenomena occurring in the neighborhood of the gel point.[3–5]

Polyacrylamide gels have been used as models in many physical investigations. In particular, they have been studied by dynamic light scattering methods since such techniques were first developed for this purpose.[6,7] Recently, Bansil and co-workers[8,9] have used laser Raman spectroscopy to investigate the phase diagram for gelation in such materials. As shown qualitatively in Figure 1, if the initial monomer concentration is too low, continuous networks do not form whatever might be the concentrations of acrylamide, $C_A$, and bis(acrylamide) tetrafunctional cross-linker, $C_B$, in the reaction mixture. Gelation occurs only if the monomer concentration is increased above a critical value $C^*$, where the latter depends on the "cross-linking ratio" $\chi = C_B/(C_A + C_B)$. One of the results of the present study is a quantitative expression for the relationship between $C^*$ and $\chi$. To good approximation we are able to verify a scaling law, previously determined by Monte Carlo calculations,[10,11] which predicts such a relationship between cross-linking ratio and the network concentration at the gel point. Additionally, by modifying a theoretical scheme due to Pearson and Graessley[12] we are able to infer certain properties of the "equivalent primary chains" which constitute a polymer lattice when gelation occurs.

Our principal experimental technique is a dynamic light scattering procedure which can be used to determine the low-frequency storage shear modulus, $G$, of relatively soft gels.[13,14] The technique involves inducing weak mechanical excitations in a gel sample and analyzing the resulting normal mode vibrations. The latter are detected by examining temporal variations in the diffraction pattern of light scattered from a laser beam which is used as a probe. In contrast with various classical rheological methods, this new light scattering technique is essentially nonperturbative. Measurements are quite rapid, and samples can be removed from and inserted into the apparatus without being disturbed, thereby facilitating experimental protocols which until recently were difficult to implement.[15]

Most of the studies reported here have involved measuring the shear moduli of several series of gels in which monomer concentration $C_A$ was constant and the cross-link ratio $\chi$ was varied. (A different value of $C_A$ was chosen for each series.) The effects of varying the initiator concentration also are discussed.

## Methods and Materials

**(a) Dynamic Light Scattering Measurements of Shear Modulus.** The experimental apparatus has been previously described.[14] Gels were polymerized in cylindrical cuvettes to which torsion arms have been attached. On the bottom of each cuvette a plastic baseplate has been epoxied, so that the cuvette can be securely clamped to a pedestal which is rigidly attached to the optical rail upon which components for translating and focusing the incident laser beam are mounted. Weak mechanical excitations were induced in the samples by gently tapping the torsion arms.

The gels stick to the cuvette walls, so the displacement vector at any position within a sample resonates at frequencies given by solutions of macroscopic elasticity equations as[14]

$$\omega_{l,n} = k_{l,n} C_{\mathrm{tr}} \tag{1}$$

where $C_{\mathrm{tr}}$ is the transverse sound speed, related to the shear storage modulus $G'$ and density $\rho$ of the gel as

$$C_{\mathrm{tr}} = (G'/\rho)^{1/2} \tag{2}$$

$k_{l,n}$ is a factor which depends on the geometry of the container, viz.

$$k_{l,n} = \left[\left(\frac{\nu_l}{R}\right)^2 + \left(\frac{n\pi}{h}\right)^2\right]^{1/2} \tag{3}$$

where $\nu_l$ is the $l$th zero of the first-order Bessel function of the first kind and, for gels having a free upper surface, $n$ is half-integer. $R$ and $h$ are, respectively, the radius and height of the sample. Light is scattered by optical heterogeneities in the gel. Since the latter are "frozen" into the gel, the resulting complicated diffraction pattern oscillates with the same periodicities as does the displacement vector. Scattered light which passes through a small pinhole is detected with a phototube and analyzed with a real-time spectrum analyzer (Nicolet Model 444A). The resonance occurring at lowest frequency is associated with the $\{l = 1, n = {}^1/_2\}$ mode (cf. eq 3). Such procedure yields values for $G'$ which agree closely with equilibrium values obtained from mechanical measurements.[13,14] For representative experimental conditions, $G'$ was determined to be essentially independent of frequency by measuring identical samples in several cuvettes of differing dimensions.

Although the size of the container occasionally was varied, the results presented in this paper were obtained with 8.0-mm-i.d. cuvettes. The half-width at half-height of the resonances is given as[14]

$$\Delta_{1/2} \simeq \frac{3^{1/2}}{2} k_{l,n}{}^2 \eta/\rho \tag{4}$$

where the "internal viscosity" $\eta$ is related to the shear loss modulus $G''(\omega)$ as

$$\eta = \omega^{-1} G''(\omega) \tag{5}$$

This limit corresponds to a linear viscoelastic medium, for example as typified by the Mooney–Rouse model, for which $\eta$ and $G'$ are constants independent of frequency. Thus, $G'$ and $G''$ are mea-

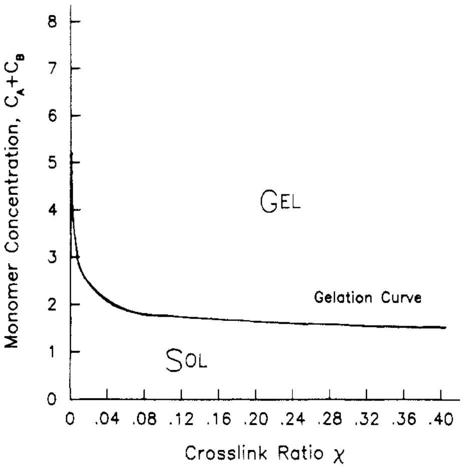

**Figure 1.** Schematic phase diagram of polyacrylamide networks, showing the relationship between acrylamide (vinyl monomer) and bis(acrylamide) (divinyl cross-linker units) necessary for gel formation (after Bansil and Gupta, ref 8). The abscissa is the "cross-link ratio" $\chi = C_B/(C_A + C_B)$, where $C_A$ is the acrylamide concentration and $C_B$ is the bis(acrylamide) concentration.

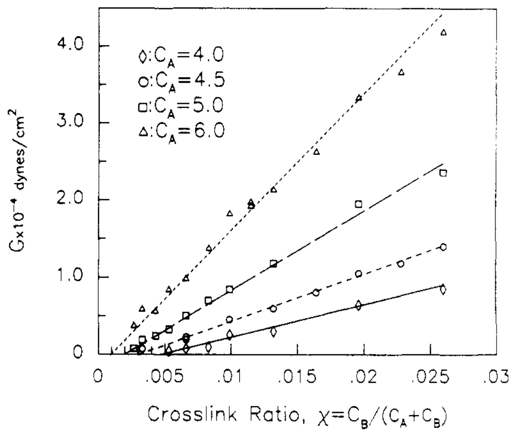

**Figure 2.** Shear modulus as a function of cross-link ratio for differing concentrations of acrylamide monomer $C_A$ (given in % w/v).

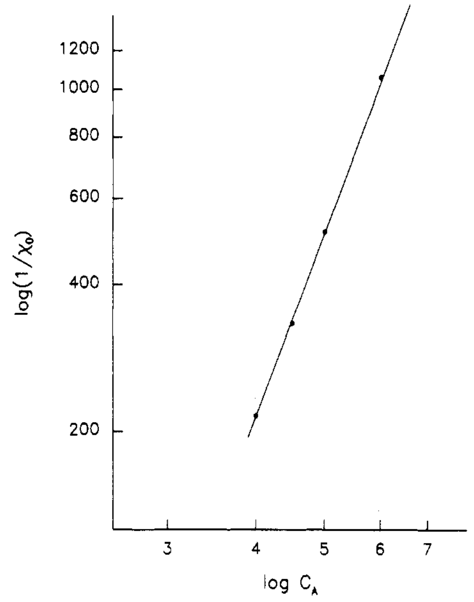

**Figure 3.** Log $(1/\chi_0)$ vs. log $(C_A)$ for the data shown in Figure 2.

sured at resonant frequencies which are determined by the size and shape of the container as well as the viscoelastic properties of the sample. The peaks can be spread out along the frequency axis by using smaller cuvettes, which according to eq 1 and 3 tends to increase spatial resolution roughly in proportion to the inverse of the size of the container, i.e., $\omega \sim k$. However, from eq 4 we see that peak broadening occurs in proportion to the square of this quantity, i.e., $\Delta_{1/2} \sim k^2$, so that, especially for low $Q$ (high tan $\delta$) materials, it may be difficult to determine the locations of the maxima of the peaks if smaller cuvettes are used.

In the remainder of this paper the low-frequency shear modulus will be designated as $G$, rather than $G'$.

**(b) Sample Preparation.** Gels were prepared by polymerizing acrylamide and *N,N'*-methylenebis(acrylamide), with ammonium persulfate as an initiator and *N,N,N',N'*-tetramethylethylenediamine (TEMED) as a catalyst (BioRad Laboratories). A series of gels containing fixed monomer concentration but differing amounts of cross-linker (bis) were prepared by first making a stock solution of acrylamide (e.g., 5% w/v acrylamide in $H_2O$) to which 0.0025% w/v of 0.109-$\mu$m-diameter polystyrene latex spheres (Dow) usually was added in order to enhance scattering. (Control experiments yielded identical values of shear modulus, whether or not the gels contained such beads.) A second stock solution was prepared by adding a portion of the acrylamide solution to a premeasured amount of bis(acrylamide). A series of solutions of varying cross-linker concentration then was prepared by mixing appropriate amounts of the two stock solutions. Unless otherwise specified, a $6.25 \times 10^{-3}$ fractional volume of 20% ammonium persulfate solution was added to each sample (e.g., 12.5 $\mu$L of 0.2 g/mL persulfate per 2 mL of solution), followed by addition of $6.25 \times 10^{-4}$ volume of TEMED. Immediately after the addition of TEMED to a sample, the solution was mixed and poured into a cuvette where it was left to gel at room temperature (ca. 23 °C). (To ensure that the top surfaces of the gels would be flat, each sample was covered with water-saturated butanol, which later was removed.) The 8.0-mm-i.d. cuvettes were filled with 2.0 mL of sample. A minimum of 24 h elapsed before measurements were performed.

## Results and Discussion

**(a) Shear Modulus as a Function of Cross-Link Ratio.** Results of elasticity measurements on several series of gels, of differing monomer concentration, are shown in Figure 2. We note that, at any given value of cross-link ratio $\chi$, the higher the acrylamide concentration, the more rigid will be the gel that ultimately forms. Also, as the monomer concentration $C_A$ increases, the extrapolated value $\chi_0(C_A)$ of the cross-link ratio (the value at which the shear modulus seems to vanish) tends to decrease in accordance with the behavior shown in Figure 1. The linear dependence of shear modulus on cross-link density is in agreement with many theories of polymer gelation, including that of Pearson and Graessley[12] as discussed below.

When $\chi_0(C_A)$ is plotted as a function of $C_A$ on logarithmic coordinates, we find from the slope of the ensuing curve that, to a good approximation, $\chi_0(C_A) \sim C_A^{-4.0}$ (see Figure 3). This observation substantiates inferences drawn from recent calculations based on a kinetic percolation model of free-radical initiated gelation.[10,11] In the latter studies, Monte Carlo simulations were perfomed over a three-dimensional cubic lattice whose sites are randomly populated with bifunctional or tetrafunctional monomers, or with unreactive solvent molecules. Polymerization is accomplished by placing "free radicals" on a number of reactive sites and moving them in successive steps to nearest-neighbor sites containing unreacted functionalities. The migration of radicals to such sites results in recruitment of new material into growing clusters. If two radicals simultaneously move to the same site they annihilate and the clusters on which they were moving fuse to form a larger cluster. (Radicals also can be depleted by "trapping", i.e., by moving to sites with no nearest-neighbor unreacted functionalities.) The model yields[10] phase diagrams similar to that shown in Figure 1. Gelation occurs when the relative concentrations of bifunctional and tet-

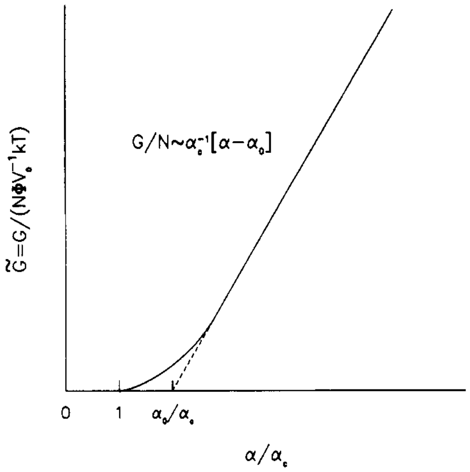

**Figure 4.** "Scaled" modulus, as a function of reduced cross-link density (after Pearson and Graessley, ref 12).

rafunctional sites are sufficiently high that an "infinite" cluster forms. For fixed initiator concentration and solvent site density, the fraction of reacted sites when the infinite cluster first forms, $v_c$, has been found[11] to be related to the cross-link density as $v_c \sim \chi^{-0.28}$.

The Monte Carlo results were obtained by fixing $\chi$ and noting the amount of material that had reacted when an infinite cluster first forms. Our experiments differ in that the amount of material in the polymer clusters is fixed and the critical value $\chi_0$ necessary for gelation to occur subsequently is inferred; otherwise, the two protocols are similar. Thus, the calculated relation $v_c \sim \chi^{-0.28}$ can be compared with the gelation curve data shown in Figure 3, viz., $C_A \sim [\chi_0(C_A)]^{-0.25}$. [We note that $C_A \approx C_A + C_B$ for the low values of $\chi$ chosen in our experiments and assume that when gelation occurs the ratio of tetrafuctional to bifunctional monomers incorporated into clusters is identical with that of the initial polymer solution. Consequently, the values of $C_A$ used to determine the ordinate of Figure 3 can be identified as being proportional to $v_c$.] The exponential dependences obtained in both investigations are remarkably close. Additionally, in another report, Bansil et al.[10] present a computed diagram of the gelation curve and, from those data (Figure 5 of ref 10), we find the power law dependence $v_c \sim \chi^{-\gamma}$ ($\gamma \approx 0.25$) for values of $\chi > 0.55$. Although higher values of $\gamma$ are discerned as $\chi \rightarrow 0$, the lattice model used for the computations did not account for diffusion of monomers within the solvent, thereby leading to accentuated steepness of the gelation curve at low cross-link density.

We have implicitly assumed in our discussion of experimental results that $\chi_0(C_A)$ is proportional to the true critical cross-link density for gelation $\chi_c$. Pearson and Graessley[12] have shown this generally to be correct, at least to the extent of validity of "classical" analysis[16] of network elasticity whence it is assumed that the number of intramolecular cycles is negligibly small in molecules of finite size. For the specific case of a network formed of $N$ chains, each of $r$ subunits in length and cross-linked by tetrafunctional junctions, Pearson and Graessley's results indicate that the shear modulus can be expressed as a function of $\alpha/\alpha_c$. Here, $\alpha$ is the fraction of all monomers which participate directly in a cross-link, and $\alpha_c$ is the critical fraction below which gelation cannot occur. For large values of $\alpha$, the shear modulus can be shown[12] to be proportional to $(\alpha - \alpha_0)/\alpha_c$, where $\alpha_0$ is a constant (see Figure 4). For cross-linking by tetrafunctional junctions, $\alpha_c$ and $\alpha_0$ are expressed as $\alpha_c = 1/(r-1)$ and $\alpha_0 = 2/r$, implying $\alpha_c \approx \alpha_0/2$; in Appendix A we generalize these results and show that, when the chains are of varying length, $\alpha_0$ and $\alpha_c$ are given as

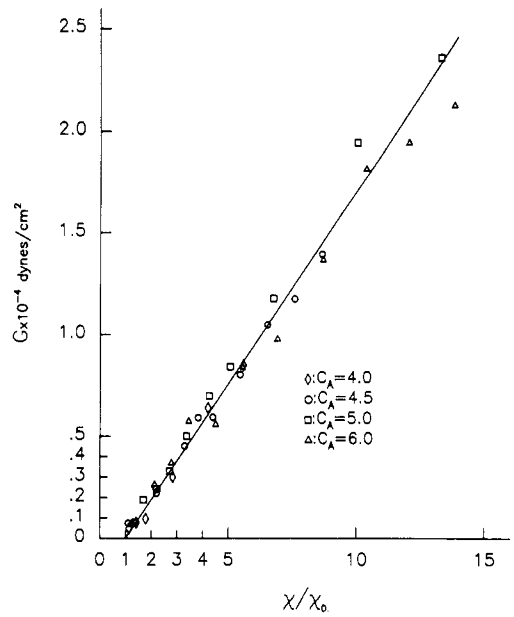

**Figure 5.** Data of Figure 2, plotted as a function of the reduced cross-link ratio $\chi/\chi_0$.

$$\alpha_c \approx \frac{1}{\langle r-1\rangle} \qquad \alpha_0 \approx 2\langle 1/r\rangle \qquad \alpha_c \approx \frac{1}{2}\frac{1}{\langle r\rangle\langle 1/r\rangle}\alpha_0 \tag{6}$$

where the brackets $\langle\ \rangle$ indicate average valuues. Thus, if we assume that the ratio of tetrafunctional to bifunctional units that are incorporated into the network is equal to the ratio of bis(acrylamide) to acrylamide units in the original reaction mixture, if follows that $\chi_c \sim \chi_0$.

The calculations of Pearson and Grasessley provide the result $G \sim (\alpha - \alpha_c)^3$ for values of $\alpha$ very close to $\alpha_c$. From other work it is known that this corresponds to the so-called "classical", or "mean field", description of gelation.[17] Calculations based on percolation theory suggest that certain features which are ignored in a mean field calculation may, in fact, be quite important in determining the details of cluster formation in gel networks.[17] For the most part, however, the arguments put forth in this paper depend only on the assumption that the shear modulus can be scaled as a function of $\alpha/\alpha_c$, whatever might be the actual values and parametric dependences of $\alpha_c$.

**(b) Inferences from Scaling Arguments.** When rigidity due to chain entanglements can be ignored, the shear modulus can be expressed asymptotically as[12,18]

$$\tilde{G} \approx \frac{1}{2}[(\alpha - \alpha_0)/\alpha_c] \qquad \alpha \gg \alpha_c \tag{7}$$

where the "reduced" shear modulus $\tilde{G}$ is related to the low-frequency shear modulus $G$ according to

$$\tilde{G} = G/(N\Phi kT/V_0) \tag{8}$$

In eq 8, $N$ is the number of equivalent primary chains, $\Phi$ is a factor which is of the order of unity and depends on the network connectivity,[19] $k$ is Boltzmann's constant, $T$ is the absolute temperature, and $V_0$ is the volume of the network in the unstrained state. For fixed $V_0$ and $\Phi$, and if $\alpha_0$ is proportional to $\alpha_c$, one thus infers that $G/N$ should scale as $\alpha/\alpha_0$, i.e.

$$G/N \sim [\alpha/\alpha_0 - 1] \sim [\chi/\chi_0 - 1] \tag{9}$$

In Figure 5 we show the data of Figure 2, plotted as a

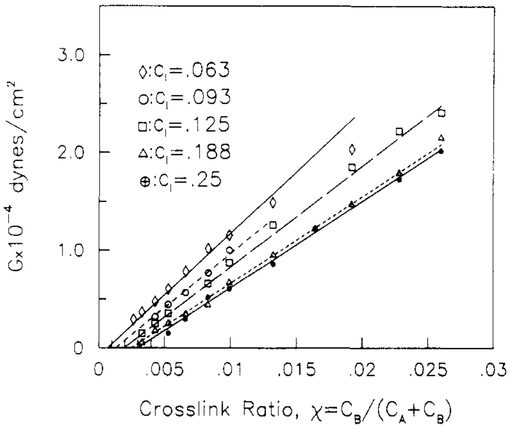

**Figure 6.** Shear modulus as a function of cross-link ratio, for different values of initiator (persulfate) concentration $C_I$. (Monomer concentration $C_A$ = 5.0 mg/mL.)

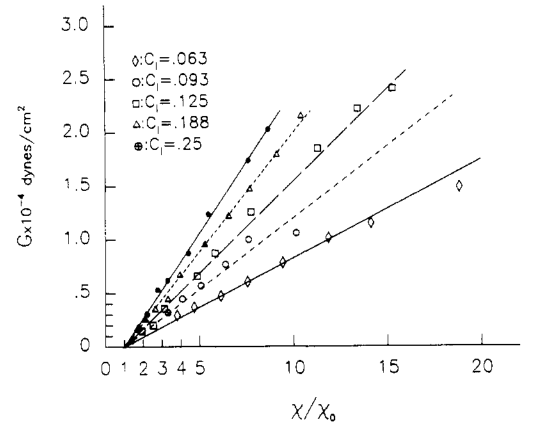

**Figure 7.** Data of Figure 6, plotted as a function of the reduced cross-link ratio $\chi/\chi_0$.

function of $\chi/\chi_0$. To a very good approximation they indeed appear to scale. Because these shear moduli data scale with $\alpha/\alpha_0$ without any adjustment of the ordinates, we infer from eq 9 that the number of chains, $N$, essentially is independent of monomer concentration $C_A$ over the range which we have studied. This result, $N \approx$ constant, is in accordance with simplified theoretical models of free radical polymerization (Appendix B). It should be noted, however, that $N$ changes markedly when the initiator concentration (and, therefore, the free-radical concentration) is varied (see below).

According to eq 6, the extrapolated intercept of the cross-link density on the abscissa is given as $\alpha_0 \sim \langle 1/r \rangle$. Consequently, the relationship deduced from the experimental data shown in Figure 3, namely $\alpha_0 \sim C_A^{-4}$, implies that $\langle r \rangle$, the average mass per equivalent primary chain in the network, is given as

$$\langle r \rangle \approx \langle 1/r \rangle^{-1} \sim \alpha_0^{-1} \sim C_A^{4} \qquad (10)$$

Because the number of chains $N$ does not depend on $C_A$, the mass per chain varies as $C_A + C_B \approx C_A$. Thus, the number of cross-links $n_\chi$ per primary chain at gelation threshold, i.e., the minimum necessary for gelation to occur, varies as $n_\chi = \alpha_c C_A \sim C_A^{-3}$ (assuming, once again, that $\alpha_c \sim \alpha_0$). Consequently, from eq 10 we find that $n_\chi$ varies with the degree of polymerization of the equivalent primary chains as $n_\chi \sim \langle r \rangle^{-3/4}$. Finally, as the linear geometrical extension of a network chain generally can be written as $\langle R \rangle \sim \langle r \rangle^{\nu}$, we find

$$n_\chi \sim \langle R \rangle^{-3/4\nu} \qquad (11)$$

Equation 11 relates the number of cross-links necessary for gelation $n_\chi$ to the mean geometrical length of chain extension $\langle R \rangle$.

If a separate argument now could be invoked to express $n_\chi$ in terms of $\langle R \rangle$, the value of $\nu$ that appears in eq 11 could be deduced. The internal structure of the polymer matrix at the gelation threshold thereby could be inferred. Alternatively, were the internal structure of the gel to be known, it would be possible to deduce $n_\chi$. Here, we merely remark that if $n_\chi \sim 1/\langle R \rangle$, eq 11 would imply $\langle R \rangle \sim \langle r \rangle^{3/4}$. This would be consistent with a growth mechanism where the primary chains are distributed as relatively flat pancake or platelike structures.[20]

**(c) Effects of Varying the Initiator Concentration.** Measurements similar to those described above were undertaken to examine the effects of varying the initiator concentration. Data are presented in Figure 6 which show the shear modulus as a function of cross-linker density, for fixed acrylamide concentration (5.0% w/v) but for differing amounts of persulfate $C_I$. In this instance, when the data are plotted along the abscissa as a function of normalized cross-link concentration $\chi/\chi_0$, the ensuing curves do not superimpose unless the ordinates also are scaled (Figure 7). We thus infer from eq 9 that the number of equivalent primary chains, $N$, changes as the initiator concentration is varied.

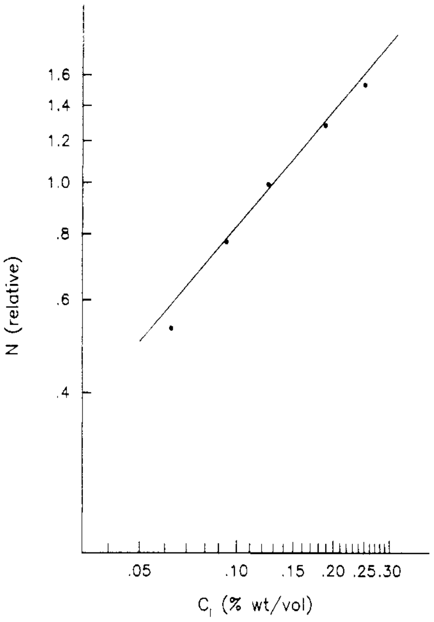

**Figure 8.** Relative number of primary chains, plotted as a function of initiator concentration on log–log coordinates (calculated from the data shown in Figure 7). The line drawn through the data points implies $N \sim C_I^{\epsilon}$, where $\epsilon \approx 0.72$.

In Figure 8 we show, on logarithmic coordinates, the values of $N$ relative to the number of chains in our standard sample ($C_I = 0.125 \times 10^{-3}$ g/mL); that is, we plot the relative slopes of the lines shown in Figure 7. The relationship between $N$ and $C_I$ which can be inferred from this plot is $N \sim [C_I]^{\epsilon}$, where $\epsilon \approx {}^3/_4$. This value differs significantly from the value $\epsilon = {}^1/_2$, which is predicted from a simplified model of radical polymerization (see Appendix B).

**(d) Further Remarks.** Although polyacrylamide gels are formed by free radical polymerization, the theoretical analysis developed by Pearson and Graessley[12] is based on a model of condensation polymerization. However, our samples have been examined only after network formation has been completely effected, and we thus find experimental results to be consistent with theoretical inferences.

The detailed history of the gelation process affects network features such as the number of pendant chains, the degree of chain entanglement, and the extent of cyclization. At the low cross-link concentrations which are used to establish gel points, the number of pendant chains is substantial. For example, by using eq 8 we find for a standard 5% acrylamide gel ($C_B = C_A/37.5$; $C_I = 1.25 \times 10^{-3}$ g/mL) that only ca. 6% of the bis(acrylamide) units which are present in the reaction mixture actually are incorporated into the gel as active cross-links. Similar observations previously have been reported by Janas et al.[21]

One of the most interesting observations reported in this study is the power law dependence between the amount of monomer incorporated into the network at the gelation threshold, $C_A$, and the cross-link ratio, $\chi$. Our results show $C_A \sim \chi^{-0.25}$, in accordance with computations based on a percolation model of kinetic gelation.[10,11,22] This dependency differs significantly from that predicted by a mean field model.[11] A recent dynamic light scattering study of pregelation clusters formed by the radical copolymerization of styrene-*m*-divinylbenzene[23] similarly indicates that percolation models are appropriate for studying various aspects of polymer gelation.

**Acknowledgment.** The author thanks Professor R. Bansil for her encouragement and several stimulating discussions.

### Appendix A. Derivation of Eq 6[24]

When the primary chains which constitute the network are of differing lengths, a generalization of Pearson and Graessley's results[12] must be used. Motivated by the classic work of Scanlan[25] and Case,[26] Pearson and Graessley have shown that the number of elastically active strands $\nu$ and elastically active junctions $\mu$ can be calculated once one knows the number of network junctions, $c_{ij}$, which unite $j$ monomer units and have $i$ paths to the gel. This quantity is given as

$$c_{ij} = n_j t_{ij} \tag{A1}$$

where $n_j$ is the number of network junctions containing $j$ cross-linked units (i.e., junctions of functionality $2j$), and $t_{ij}$ is the probability that $i$ paths lead from such junctions to the gel. A simple generalization of Pearson and Graessley's expression for $n_j$, which was derived for chains of uniform length, is

$$n_j = \alpha \langle r \rangle N w_j / j \tag{A2}$$

where $w_j$ is the fraction of cross-linked units located in junctions which contain $j$ units, and $\alpha$, $\langle r \rangle$, and $N$ are defined in the text, above. $t_{ij}$ is given as[12]

$$t_{ij} = \sum_{0 \le k \le i/2} \frac{j! {p_0}^{j-i+k} {p_1}^{i-2k} {p_2}^{k}}{(j-i+k)!(i-2k)!k!} \tag{A3}$$

where $p_l$ is the probability that a randomly selected non-cross-linked unit of a polymer strand is connected to the gel by $l$ paths. $\nu$ and $\mu$ are calculated, respectively, as

$$\nu = \frac{1}{2} \sum_{j=2}^{\infty} \sum_{i=3}^{2j} i C_{ij} \qquad \mu = \sum_{j=2}^{\infty} \sum_{i=3}^{2j} C_{ij} \tag{A4}$$

Following the derivation of Pearson and Graessley,[12] one thus finds that, for the special case of tetrafunctional cross-linking, $\nu$ and $\mu$ are given as[12]

$$\nu = \frac{1}{2} \alpha \langle r \rangle N (3 p_1 p_2 + 2 {p_2}^2) \qquad \mu = \frac{1}{2} \alpha \langle r \rangle N (2 p_1 p_2 + {p_2}^2) \tag{A5}$$

with

$$p_2 = 1 + s/\upsilon - 2 \sum_r \frac{P_r}{r} ((1 - \upsilon^r)/(1 - \upsilon))$$

$$p_0 = \sum_r P_r \upsilon^{r-1} \qquad p_1 = 1 - p_0 - p_2 \tag{A6}$$

where $s$ is the fraction of all units which do not belong to the gel (and therefore constitute the "sol"). $P_r$ is the probability that a structural unit is located in a chain of length $r$, and $\upsilon$ is the probability that a randomly selected unit is not cross-linked to the the gel. We note that $s_r = \upsilon^r$ is the probability that a randomly selected chain of $r$ units length is part of the sol fraction, and $s \equiv \sum_r P_r s_r = \sum_r P_r \upsilon^r$ is the probability that any randomly selected chain belongs to the sol. Thus, $p_0 = s/\upsilon$, and $p_2 = 1 + p_0 - 2\sum_r P_r r^{-1}((1 - s_r)/(1 - \upsilon))$.

Let us now consider the case $\alpha/\alpha_c \gg 1$, for which the sol fraction $s$ is expected to be negligible. If the cross-link density is high, it is reasonable to assume that the average degree of polymerization $\langle r \rangle$ of the chains is large and that the chain length distribution is peaked about a value $r \gg 1$. Consequently, because $\upsilon \ll 1$ under these conditions, $s_r \equiv \upsilon^r \approx 0$ for almost all values of $r$ for which $P_r > 0$, and we also may assume that $s/\upsilon = \sum_r P_r \upsilon^{r-1} \approx 0$. Thus, from eq A6 one observes

$$p_0 \approx 0 \qquad p_2 \approx 1 - \frac{2}{1 - \upsilon} \sum_r P_r / r \qquad (\alpha/\alpha_c \gg 1) \tag{A7}$$

However, because for $\alpha \gg \alpha_c$ the quantity $\upsilon$ can be expressed in terms of $\alpha$ as[12] $\upsilon \approx (1 - \alpha) + \alpha \sum_j w_j s^{j-1}$, it follows that $1/(1 - \upsilon) \approx 1/\alpha$ (where we again note that $s \approx 0$). Thus, $p_2 \approx 1 - 2\alpha^{-1}\langle 1/r \rangle$ and $p_1 \approx 2\alpha^{-1}\langle 1/r \rangle$, so from eq A5 it is seen that $\nu$ and $\mu$ are given as

$$\nu = \alpha \langle r \rangle N [1 - \alpha^{-1}\langle 1/r \rangle - 2\alpha^{-2}\langle 1/r \rangle^2]$$

$$\mu = \alpha \langle r \rangle N \left[ \frac{1}{2} - 2\alpha^{-2}\langle 1/r \rangle^2 \right] \tag{A8}$$

Thus, since[12] the contribution to the shear modulus due to cross-links $G$ varies as $G \sim (\nu - \mu)$, we find

$$G \sim \left[ \frac{1}{2} - \alpha^{-1}\langle 1/r \rangle \right] \qquad (\alpha/\alpha_c \gg 1) \tag{A9}$$

which extrapolates to zero at the value $\alpha \rightarrow \alpha_0 = 2\langle 1/r \rangle$ as given above in eq 6.

How is $\alpha_0$ related to the critical cross-link density for gelation, $\alpha_c$? To calculate $\alpha_c$ we remark that the gel fraction $g$ is given as

$$g = 1 - s = 1 - \sum_r P_r \upsilon^r \tag{A10}$$

and that $g(\alpha_c) = 0$ defines $\alpha_c$. A general expression which relates $\upsilon$ to the probability $\varphi$ that a randomly selected non-cross-linked unit belongs to the sol is[12]

$$\upsilon = (1 - \alpha) + \alpha \sum_j w_j \varphi^{j-1} \tag{A11}$$

From eq A10 and A11 one thus has

$$\partial g/\partial\alpha = -\sum_r r P_r \upsilon^{r-1} \partial\upsilon/\partial\alpha$$

$$= -\sum_r r P_r \upsilon^{r-1} \left\{ -1 + \sum_j w_j \varphi^{j-1} + \alpha \sum_j w_j (j-1) \varphi^{j-2} \left( \frac{\partial\varphi}{\partial g} \right) \frac{\partial g}{\partial\alpha} \right\} \tag{A12}$$

But, $\upsilon(\alpha = \alpha_c) = 1$ and $\varphi(\alpha = \alpha_c) = 1$ implies from eq A12 that

$$\partial g/\partial\alpha|_{\alpha_c} = \left[ -\alpha_c\langle r\rangle(\textstyle\sum jw_j - 1)\dfrac{\partial\varphi}{\partial g}\Big|_{\alpha_c} \right]\dfrac{\partial g}{\partial\alpha}\Big|_{\alpha_c}$$

i.e., that

$$\alpha_c = \left[ \langle r\rangle(\textstyle\sum jw_j - 1)\left( -\dfrac{\partial\varphi}{\partial g} \right)\Big|_{\alpha_c} \right]^{-1} \qquad \text{(A13)}$$

Finally, we assume that $\varphi \approx s$ near the gel point (i.e., that if a non-cross-linked subunit is randomly selected, the probability that it is found to belong to the sol is approximately equal to the sol fraction of polymer chains). Hence, $\partial\varphi/\partial g|_{\alpha_c} \approx \partial(1-g)/\partial g = -1$, and we obtain the result given in eq 6, viz., $\alpha_c = 1/\langle r\rangle$ (since, for tetrafunctional junctions, $w_j = \delta_{j2}{}^{\mathrm{kr}}$).

## Appendix B. Theory of Free Radical Polymerization in the Presence of an Initiator[1]

The dependence of chain length on such factors as monomer and initiator concentration can be predicted theoretically as follows.[1] When free radicals are produced from persulfate or similar initiator (assumed to be in excess), one has $I \rightarrow 2R\cdot$ with the rate constant $k_d$, where the free radicals $R\cdot$ then attach to monomer units M to form activated chains $M_1\cdot$ as $R\cdot + M \rightarrow M_1\cdot$ with rate constant $k_a$, which then grow as $M_x\cdot + M \rightarrow M_{x+1}\cdot$ with rate constant $k_p$. Assuming that chain termination occurs either by combination ($M_x\cdot + M_y\cdot \rightarrow M_{x+y}$) or by "disproportionation" ($M_x\cdot + M_y\cdot \rightarrow M_x + M_y$), the rate of chain termination can be written as

$$R_t = -(\mathrm{d}[M\cdot]/\mathrm{d}t)_t = 2k_t[M\cdot]^2 \qquad \text{(B1)}$$

where $M\cdot \equiv \sum_x M_x\cdot$. If monomers are in excess during polymerization, the rate of *initiation of activated chains* is

$$R_i = (\mathrm{d}[M\cdot]/\mathrm{d}t)_i = 2fk_dC_I \qquad \text{(B2)}$$

where $f$ is the fraction of primary radicals which initiate chains. Thus, if we assume that [M] changes very slowly, the concentration of activated chains will rapidly assume a "quasi-steady state", where $R_i = R_t$. One finds the concentration of chain radicals in that instance to be

$$[M\cdot] = (fk_dC_I/k_t)^{1/2} \qquad \text{(B3)}$$

so that the steady-state rate of propagation (i.e., polymerization) is given as

$$R_p \approx k_p[M][M\cdot]$$
$$= k_p[M](fk_dC_I/k_t)^{1/2} \qquad \text{(B4)}$$

However, for the experiments which we have performed, [M] changes markedly over the times of observation. Consequently, to a first approximation we replace [M] in eq B4 by $zC_A$, which is an average value of [M] during the course of polymerization. (The factor $z$ would be $^1/_2$ if the monomers were depleted at a constant rate; in fact, [M] probably varies as an exponential function.[5])

Thus, *for fixed initiator concentration* we find from eq B4 that the average rate of propagation, which is the rate at which monomers are incorporated into growing chains, varies as $\langle R_p\rangle \sim C_A$. The total time necessary to deplete the monomer population varies as $\tau \sim \langle R_p\rangle^{-1}zC_A$, which is independent of $C_A$. Since by eq B2 the rate of chain initiation also is independent of $C_A$, it follows that, to a first approximation, the number of chains formed during polymerization should not be affected by changes in monomer concentration. Such behavior indeed is observed in the data shown in Figure 5.

Let us now consider a series of gels having a fixed *monomer* concentration but differing initiator concentration. From eq B4, the time for complete polymerization of the monomers varies approximately as $\tau \sim R_p^{-1} \sim C_I^{-1/2}$ and, from eq B2, we see that the rate $R_i$ at which new chains are formed is proportional to $C_I$. Thus, the total number of chains which are initiated before the monomer population is depleted is predicted to vary as $N \sim R_i\tau \sim C_I^{1/2}$, which differs from the behavior shown in Figure 8. Note, however, that the dependence of $f$ on [M] and $C_I$ has been neglected. Also, we have implicitly ignored the presence of tetrafunctional bis(acrylamide) cross-linking monomers, which might have different kinetic constants than do bifunctional acrylamide monomers.[5] In addition, the dependence of rate constants on physical variables such as microgel cluster size has not here been taken into account. (The formation of microscopic aggregates during gelation is strongly indicated by results of permeability studies.[27])

**Registry No.** (Acrylamide)·(*N,N'*-methylenebis(acrylamide)) (copolymer), 25034-58-6.

## References and Notes

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