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Thermoreversible Gelation in Solutions of Associating Polymers. 2. Linear Dynamics

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ABSTRACT: Viscoelastic properties of reversible networks formed in solutions of associating polymers are considered theoretically in the Rouse−Zimm (unentangled) regime. It is shown that the dynamics is governed primarily by the network strand size and by the effective lifetime of reversible junctions. Both frequency and concentration dependencies of viscosity and dynamical moduli are considered. A novel model taking into account the possibility of multiple dissociation and recombination of the same pair of stickers is developed. It is shown that this effect gives rise to an increase of the apparent activation energy which is predicted to be substantially larger than the priming activation energy for dissociation of two stickers.

1. Introduction

Associating polymers contain a small fraction of strongly interacting groups (stickers) which can form stable aggregates (n stickers per aggregate). These aggregates play a role of effective junction points. Interchain junctions could lead to the formation of a physical network (gel) in a semidilute regime. Equilibrium properties of the system near the physical gel point were analyzed in the first article[1] (to be referred to as I) of the series for the case of the pairwise association of stickers ($n = 2$). A general conclusion is that gelation always implies a tendency to a phase separation in the system, which however might be suppressed if the excluded volume repulsion is strong enough, more precisely, if the typical energy of these interactions per one network strand is larger than k_BT.

In the present paper we consider linear dynamics of solutions of associating polymers (in particular, stress relaxation and shear viscosity) both near the gelation point and in the reversible network regime. For simplicity, we limit our consideration in the present paper to unentangled solutions.[2] We consider the same model of an associating polymer as in I: Each polymer chain contains a large number, f, of stickers which are equidistantly spaced along the chain. The stickers are separated by the soluble fragments with degree of polymerization l ($l \gg 1$). The total number of monomers per each chain is thus $N = lf$. Each sticker might be in two states: "closed" when it is associated with another sticker, and "open" otherwise. Association is allowed only in pairs. The fraction p of associated ("closed") stickers is mainly governed by the binding energy (the effective energy of attraction of two stickers), ϵk_BT. The larger the binding energy, the larger the fraction of closed stickers p, thus implying stronger tendency to both gelation and phase separation. Another important parameter which governs dynamic (but not static) properties of the system is the typical lifetime of a closed pair of stickers, τ_b. In the general case dissociation of a pair might be restricted by an additional potential barrier $\epsilon_a k_BT$ (on the top of binding energy, ϵk_BT), so that

$$\tau_b = \tau_0 \exp(\epsilon + \epsilon_a) \tag{1.1}$$

where τ_0 is a microscopic time. Note that $\epsilon_a k_BT$ is also the activation energy for association of two stickers: in order to associate, two stickers must spend a considerable time $\tau_a \simeq \tau_0 \exp(\epsilon_a)$ in the close vicinity of each other (within a distance on the order of the monomer size a).

The dynamic properties of the system crucially depend on both energies ϵk_BT and $\epsilon_a k_BT$. In the next section we briefly review the relevant static properties of the system. Linear dynamics of the system are considered in sections 3, 4, and 5. We start with a *mean-field* dynamical consideration of mechanical stress relaxation and viscosity both in the vicinity of the reversible gelation point and well above this point (section 3). Next we consider the dynamical effects which are due to *correlations* between dissociation and formation of physical bonds between the stickers. We find that a cluster or a network strand breaks and recombines again many times at the same pair of stickers before a final break occurs if the binding energy, ϵk_BT, is high enough. This effect, which makes the dynamics more complicated and more intersting, is considered in section 4 for concentrations slightly above the gelation point. Both classical gelation and percolation regins are considered. In the fifth section we discuss the "correlation" dynamics for concentrations well above the gel point.

2. Statics

As was shown in the first paper in this series[1] (I), we do not anticipate that gelation is accompanied by a phase separation in a solution of associating polymers if the solvent quality is good enough so that the strands

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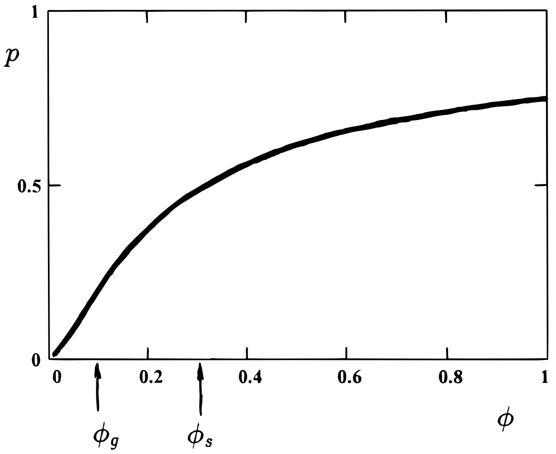

Figure 1. The degree of conversion, p, vs monomer volume fraction ϕ. Note that $p \sim 1$ for $\phi > \phi_s$ where $\phi_s \sim l^{1-3\nu}$ in the case of high enough bond energy ($e^{\epsilon} > l^{2+z}$); ϕ_s is thus the concentration at which soluble fragments start to overlap.

between stickers begin to swell: $v/a^3 \gtrsim 1/l^{1/2}$. Here v is the excluded volume parameter, and a is the monomer size. Below we will assume either good-solvent conditions with $v/a^3 \sim 1$, or a Θ-solvent system. In the latter case it is assumed that ϵ is small enough so that the system does not phase separate near the gelation point (the precise condition was derived in ref. I: $e^{\epsilon} < (w^{1/2}/v_b)l^{-3/2}\ f^{-1/2}$, where w is the three-body interaction parameter for monomers in a Θ-solvent, and v_b is the effective bond volume, i.e., the typical volume available for one sticker associated with a fixed partner due to thermal fluctuations).

The effective degree of conversion depends on both the binding energy ϵ and the monomer volume fraction, ϕ, according to the law derived in ref 1 which is valid for both Θ and good-solvent systems

$$\frac{p}{(1-p)^2} \simeq (l^{-1}\ \phi^{(1+z)/(3\nu-1)}) \min\left(\frac{v_b}{a^3}e^{\epsilon},\ l^{2+z}\right) \tag{2.1}$$

where $\nu \simeq 0.59$ is the Flory exponent for the good-solvent case ($\nu = {}^1/_2$ for a Θ-solvent), $v_b e^{\epsilon}$ is the statistical weight of a bond between two associated stickers. The schematic dependence of the conversion degree on concentration is shown in Figure 1. We can assume that $v_b \sim a^3$ without any lack of generality. Here $z = \nu(3 + \theta_2) - 2$ is the exponent[3] defined in ref 1 which governs the typical number of non-local contacts in a strand containing g monomers: the number of contacts scales as g^{-z} where $z \simeq 0.225$ for the good solvent case and $z = -0.5$ for the Θ-solvent case. The first factor in the rhs of eq 2.1 is proportional to the a priori probability that a given sticker occurs in a vicinity of another sticker: $l^{-1}\ \phi^{(1+z)/(3\nu-1)} \sim \phi/l\ K(g)$, where ϕ/l is the concentration of stickers, and $K(g) \sim g^{3\nu-2-z}$ accounts for the lower contact probability due to excluded volume interactions, where $g \sim \phi^{-1/(3\nu-1)}$ is the number of monomers per concentration blob[4]. Note that this additional factor disappears for the Θ-solvent case, $K(g) = 1$.

The second factor in eq 2.1 is the effective statistical weight of a closed pair of stickers, which is given either by the Boltzmann factor $v_b e^{\epsilon}$, or by the relative probability of pairing with a nearby sticker compared to the probability of pairing with a local neighbor along the same chain (see ref 1 for more details).

As concentration increases the system transforms from a simple solution at low p ($p \ll p_g$) to a reversible gel at high p ($p > p_g$), where p_g corresponds to the gelation transition. For simplicity we begin our discussion with the case of the classical gelation statistics, which are valid since $f \gg 1$.[5] In this case p_g is given by the well-known Flory equation[6]

$$p_g = \frac{1}{f-1} \tag{2.2}$$

The gelation concentration ϕ_g defined by the condition $p(\phi_g) = p_g$ always corresponds to the semidilute regime where the coils strongly overlap. In particular, using eq 2.1 for $e^{\epsilon} > l^{2+z}$, we get

$$\phi_g \sim l^{1-3\nu}\ f^{(1-3\nu)/(1+z)} \tag{2.3}$$

3. The Mean-Field Dynamics

In this section we consider the dynamics of a good-solvent system. The results are also applicable to a Θ-solvent case; in this case, one should put the relevant exponents ($\nu = {}^1/_2$, $z = -{}^1/_2$) in all equations.

3.1. Relaxation Times of Clusters of Associated Chains. Let us first consider the situation below the gel point, $p < p_g$.

On small length scales ($r < \xi_H$) the monomer motion is hydrodynamically coupled with that of the solvent (Zimm dynamics), while on larger scales the coupling is screened out, and the chain dynamics becomes Rouse-like.[4] The hydrodynamic screening length ξ_H in good-solvent conditions is of the order of the correlation length (the blob size) ξ: $\xi_H \simeq \xi \simeq a\phi^{-\nu/(3\nu-1)}$.[4,7] Therefore the number of monomers per hydrodynamic blob is roughly equal to that per concentration blob (see section 2), $g \simeq \phi^{-1/(3\nu-1)}$. The blob relaxation time is its Zimm time

$$\tau_\xi \simeq \tau_0 g^{3\nu} \simeq \tau_0 \phi^{-3\nu/(3\nu-1)}$$

where $\tau_0 \sim \eta_0 a^3/(k_B T)$ is the microscopic time, and η_0 is the solvent viscosity. On distance scales larger than the correlation length ξ, the polymers can be considered as nearly Gaussian chains of blobs, the motion of these chains being governed by Rouse dynamics. Thus, for example, the relaxation time of a free chain (with no closed stickers) is

$$\tau_1 \simeq \tau_\xi (N/g)^2 \simeq \tau_0 N^2\ \phi^{(2-3\nu)/(3\nu-1)}$$

and its size is

$$R_1 \simeq \xi (N/g)^{1/2} \simeq aN^{1/2}\ \phi^{-(\nu-1/2)/(3\nu-1)}$$

As the degree of conversion increases, the chains assemble into clusters. The statistics of these clusters on scales larger than R_1 are described by the classical gelation theory which, in particular, implies that the fractal dimension of the clusters is $D = 4$ (as the clusters are Gaussian randomly branched molecules with screened excluded volume interactions[4]. The typical size of a cluster consisting of M chains (primary N-mers) is thus

$$R_M \simeq R_1 M^{1/D} \simeq aN^{1/2}\ M^{1/D}\ \phi^{-(2\nu-1)/2(3\nu-1)} \tag{3.1}$$

where $D = 4$. The friction constant, ζ_M, of an M-cluster is proportional to the total number of blobs, $M(N/g)$, since different blobs nearly do not interact hydrodynamically: $\zeta_M \simeq \zeta_\xi M(N/g)$, where $\zeta_\xi \simeq \eta_0\xi$ is the friction constant per blob. Therefore the self-diffusion constant of a cluster is $D_M = k_B T/\zeta_M \simeq (a^2/\tau_0 N\,M)\,\phi^{-(1-\nu)/(3\nu-1)}$. The relaxation time $\tau_{\text{relax}}(M)$ of the cluster is on the order of the time it diffuses a distance comparable with its own size R_M:

$$\tau_{\text{relax}}(M) \simeq \frac{R_M^2}{D_M} \simeq \tau_1 M^{1+2/D} \simeq \tau_0 N^2\, M^{1+2/D}\, \phi^{(2-3\nu)/(3\nu-1)} \tag{3.2}$$

The classical gelation theory predicts that the characteristic cutoff cluster mass (the number of primary chains in the largest typical cluster), M_{term}, is inversely proportional to the square of the relative distance to the gel point, $\Delta = p/p_g - 1 \sim \phi/\phi_g - 1$:

$$M_{\text{term}} \simeq |\Delta|^{-2} \tag{3.3}$$

Therefore the characteristic relaxation time of a permanent cluster containing M_{term} primary linear chains is

$$\tau_{\text{relax}}(M_{\text{term}}) \simeq \tau_1 {M_{\text{term}}}^{3/2} \simeq \tau_1 |\Delta|^{-3} \tag{3.4}$$

In this estimate of the relaxation time we have assumed that the associations of chains into clusters are permanent and ignored the fact that bonds between chains can break. Thus the above analysis is valid as long as the lifetime $\tau_{\text{life}}(M)$ of a cluster is longer than its relaxation time, $\tau_{\text{relax}}(M)$.

We have to define more precisely what is meant by the lifetime of a cluster. Within the classical gelation theory any cluster of M chains is a tree (i.e. it does not contain any loops). Therefore the cluster contains exactly $M - 1$ closed pairs of stickers. The average time before one of these $M - 1$ bonds breaks is $\tau_b/(M - 1)$ where τ_b is the lifetime of a bond. By detailed balance this is also an average time before another cluster (or a free chain) attaches itself to a chosen M-cluster.[8] Thus after a time of order τ_b/M an M-cluster is not likely to be exactly the same. However for a large cluster most of these frequent changes are very minor (like a leaf falling from a tree or another leaf appearing on it). In the case of, e.g. dissociation, the cluster during the time τ_b/M would typically break into two pieces, one containing $M - m$ units, and the other of m units with $m \sim 1$ (Figure 2a). Thus on this short time scale the cluster, although changing a little, can be considered as almost the same: the stress supported by the small m-part relaxes much faster anyway via conformational relaxation (even if the structure of the cluster were permanent).

We therefore define the lifetime of a cluster as the time during which it breaks into two parts of comparable sizes (this situation corresponds to $m \sim M/2$), i.e. the backbone of the cluster should be broken during this time (Figure 2b). The backbone of a tree (also known as the set of red bonds[9−12]) is a random walk of M_b linear chains with the size $(M_b^{1/2}\,R_1)$ of order R_M. Therefore the backbone of an M-cluster contains $M_b \simeq M^{1/2}$ chains.[13] Thus the lifetime of a cluster, i.e. the lifetime of its backbone, is

$$\tau_{\text{life}}(M) \simeq \tau_b/M_b \simeq \tau_b/M^{1/2}$$

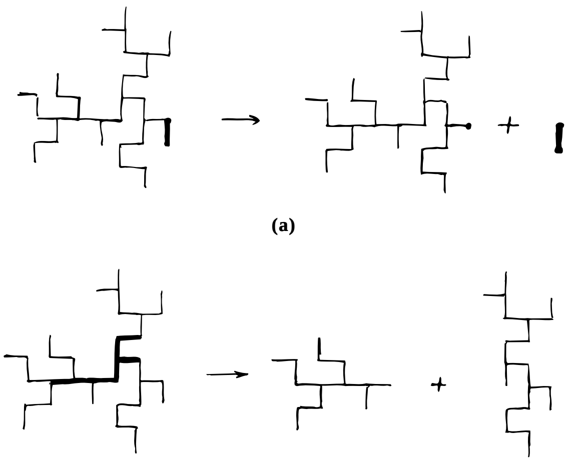

Figure 2. Dissociation of a cluster: (a) a typical event, where one unit (N-mer chain) is dissociated; (b) an essential dissociation into two comparable parts. The backbone of the original cluster is shown by a bold line.

The lifetime of a characteristic cluster is thus proportional to the relative distance to the gel point (see eq 3.3):

$$\tau_{\text{life}}(M_{\text{term}}) \simeq \tau_b/{M_{\text{term}}}^{1/2} \simeq \tau_b|\Delta| \tag{3.5}$$

This result that $\tau_{\text{life}} \propto |\Delta|$ is not surprising and can be explained in the following way. Consider a set of clusters at a degree of conversion $p = p_g(1 - |\Delta|)$. The number of units in a typical terminal cluster is $M_0 = M_{\text{term}} \simeq 1/\Delta^2$ (see eq 3.3). After a time t a fraction t/τ_b of already existing bonds would break, so that counting the survived bonds only we get the *effective* degree of conversion $p(t) = p(1 - t/\tau_b) \simeq p_g(1 - \Delta(t))$, where $\Delta(t) = |\Delta| + t/\tau_b$, and we take into account that $\Delta \ll 1$ and $t/\tau_b \ll 1$. The terminal cluster size $M(t)$ corresponding to this effective degree of conversion, $\Delta(t)$, is actually the size of the largest part of an original cluster that was not broken during the time t; $M(t) \simeq 1/\Delta(t)^2 = 1/(|\Delta| + t/\tau_b)^2$. Obviously most of the original terminal clusters must be broken into two or more smaller pieces by the time corresponding to $M(t)/M_0 \sim 1/2$. Therefore $t = \tau_{\text{life}} \sim \tau_b|\Delta|$.

The two important time scales of the problem—the lifetime $\tau_{\text{life}}(M_{\text{term}})$ and the relaxation time $\tau_{\text{relax}}(M_{\text{term}})$—as functions of Δ are sketched in Figure 3.[14]

It can be observed that for $|\Delta| > \tilde{\Delta}$ the lifetime of the characteristic cluster is larger than its relaxation time. Here $\tilde{\Delta}$ is defined by the condition

$$\tau_{\text{life}} = \tau_{\text{relax}} = \tilde{\tau} \tag{3.6}$$

so that

$$\tilde{\Delta} \sim \left(\frac{\tau_1}{\tau_b}\right)^{1/4} \sim \left(\frac{\tau_0 N^2}{\tau_b}\right)^{1/4} \phi^{(2-3\nu)/4(3\nu-1)} \tag{3.7}$$

and

$$\tilde{\tau} \sim \tau_b\tilde{\Delta} \sim (\tau_0\tau_b^3 N^2)^{1/4}\, \phi^{(2-3\nu)/4(3\nu-1)} \tag{3.8}$$

Thus at low degree of conversion (low concentration), $p < p_g\,(1 - \tilde{\Delta})$, the clusters have time to relax before they break: $\tau_{\text{relax}}(M) < \tau_{\text{life}}(M)$ for $M \lesssim M_{\text{term}} \sim 1/\Delta^2$, so that

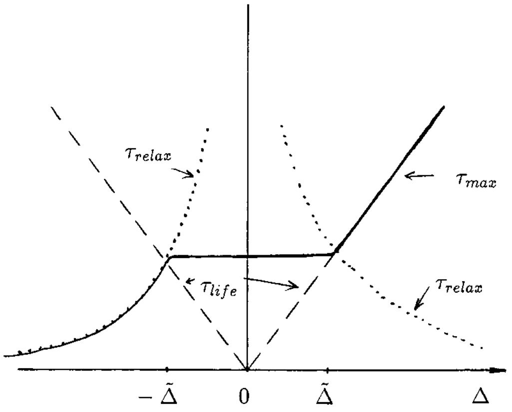

Figure 3. The two important time scales of the problem—the lifetime $\tau_{\text{life}}(M_{\text{term}})$, dashed line, and the relaxation time τ_{relax}-(M_{term}), dotted line, plotted as a function of Δ. The solid line represents the actual terminal relaxation time, $\tau_{\max}$, for the system with reversible junctions.

the rheological properties of the solution are similar to those for gelation with permanent cross-links.

In the region $|\Delta| < \tilde{\Delta}$ the equilibrium terminal clusters are so large that their relaxation time is longer than their lifetime. Hence during conformational relaxation each of these clusters is broken into a set of smaller subclusters of the size of order $\tilde{M}$, which is defined by the condition $\tau_{\text{life}}(\tilde{M}) \sim \tau_{\text{relax}}(\tilde{M})$ $(\equiv\tilde{\tau})$. Thus we get the *dynamical* terminal cluster size

$$M_{\max} \sim \tilde{M} \sim (1/\tilde{\Delta})^2 \qquad (3.9)$$

and the corresponding terminal relaxation time $\tau_{\text{life}} \sim \tau_{\text{relax}} \sim \tilde{\tau}$ in this region.

Therefore the dynamical terminal relaxation time, $\tau_{\max}$, is equal to $\tau_{\text{relax}}(M_{\max})$ where $M_{\max}$ is the number of primary chains in the dynamical terminal cluster defined by eq 3.3 in the region $|\Delta| > \tilde{\Delta}$, $\Delta < 0$ and by eq 3.9 for $|\Delta| \sim \tilde{\Delta}$. Thus $\tau_{\max} \sim \tau_1|\Delta|^{-3} \simeq \tilde{\tau}(\tilde{\Delta}/|\Delta|)^3$ for $|\Delta| > \tilde{\Delta}$, $\Delta < 0$ and $\tau_{\max} \sim \tilde{\tau}$ for $|\Delta| \sim \tilde{\Delta}$ (thick solid line in Figure 3). Note that the precise shape of the dependence of $\tau_{\max}$ vs Δ in the region $|\Delta| \sim \tilde{\Delta}$ cannot be captured by the scaling arguments; the flat dependence shown in Figure 3 in this region is just the simplest assumption.

Above the gel point, $p > p_g$, the largest clusters form a network with typical strand size $M_{\text{strand}} \sim M_{\text{term}} \sim 1/\Delta^2$. In the region $\Delta = p/p_g - 1 > \tilde{\Delta}$, the system can be characterized by the two long-scale relaxation times: the time $\tau_{\text{relax}} = \tau_{\text{relax}}(M_{\text{strand}})$ of conformational relaxation of a typical strand and the lifetime of a typical strand (until it breaks)

$$\tau_{\max} = \tau_{\text{life}}(M_{\text{strand}}) \simeq \tau_b\Delta \simeq \tilde{\tau}\frac{\Delta}{\tilde{\Delta}} \qquad (3.10)$$

The conformational relaxation of a network strand above the gel point is not complete, as the longest mode of the strand end-to-end vector does not relax (unless the strand breaks).

Note that all other modes of the strand have time to relax before the strand breaks since its lifetime τ_{life} is larger than the conformational relaxation time $\tau_{\text{relax}} \sim \tilde{\tau}(\Delta/\tilde{\Delta})^3$. On the time-scales between τ_{relax} and τ_{life} the system behaves as a permanent network. At longer time scales it flows by breaking network strands. We can summarize the dependence of the terminal relaxation time $\tau_{\max}$ on the relative distance to the gel point Δ as follows (see thick solid line in Figure 3):

$$\tau_{\max} \sim \begin{cases} \tilde{\tau}\left(\dfrac{\tilde{\Delta}}{|\Delta|}\right)^3 & \text{for } \Delta < -\tilde{\Delta} < 0 \\ \tilde{\tau} & \text{for } -\tilde{\Delta} < \Delta < \tilde{\Delta} \\ \tilde{\tau}\dfrac{\Delta}{\tilde{\Delta}} & \text{for } \tilde{\Delta} < \Delta < 1 \end{cases} \qquad (3.11)$$

3.2. The Dynamic Moduli. Let us consider the frequency dependence of the elastic modulus of the system in the region $p < p_g$ (in the region $\Delta = p/p_g - 1 < -\tilde{\Delta}$). The system is characterized by the following set of the typical relaxation times: the Zimm time of hydrodynamic blob, τ_ξ, the single-chain relaxation time τ_1, and the dynamical terminal time $\tau_{\max}$. In the frequency region $1/\tau_1 < \omega < 1/\tau_\xi$ the viscoelastic response of the system is due to relaxation modes on length scales between the blob size ξ and the chain size R_1. In this region the cluster structure of the system is irrelevant, and therefore the dynamics is Rouse-like (note that the system is assumed to be unentangled) as for a solution of linear chains with no stickers[15]. For $\omega \sim 1/\tau_\xi$ both storage (G') and loss (G'') moduli are proportional to the concentration of hydrodynamic blobs (ϕ/g): $G' \sim G'' \sim (k_BT/a^3)(\phi/g) \sim (k_BT/a^3)\phi^{(3\nu/3\nu-1)} \equiv G_\xi$, and for $\tau \sim \tau_1$ the moduli are proportional to the chain concentration, $G \sim (k_BT/a^3)(\phi/N) \equiv G_1$. The well-known Rouse dynamics scaling law bridging these two limiting values is[4]

$$G' \sim G'' \sim \frac{k_BT}{a^3}\frac{\phi}{N}(\omega\tau_1)^{1/2}, \quad 1/\tau_1 < \omega < 1/\tau_\xi \qquad (3.12)$$

For $\omega \sim 1/\tau_{\text{relax}} = 1/\tau_{\max}$ the terminal clusters give the dominant contribution to the moduli, which are proportional to the concentration of these clusters $c(M_{\text{term}})$. The classical gelation theory[4,6] predicts that $c(M)$ is proportional to $M^{-3/2}$ if M does not exceed the terminal size, i.e. $c(M) \sim (\phi/a^3N)M^{-3/2}$. Thus $G' \sim G'' \sim (k_BT/a^3)(\phi/N)$ $M_{\max}{}^{-3/2} \equiv G_0$ for $\omega \sim 1/\tau_{\max}$. The corresponding scaling law is[16]

$$G' \sim G'' \sim \frac{k_BT}{a^3}\frac{\phi}{N}\omega\tau_1, \quad 1/\tau_{\max} < \omega < 1/\tau_1 \qquad (3.13)$$

In the region of the lowest frequencies, $\omega < 1/\tau_{\max}$, the dynamic behavior of the system is essentially governed by the longest relaxation time, $\tau_{\max}$: the complex modulus $G = G' + iG''$ is proportional to $i\omega\tau_{\max}/(1+i\omega\tau_{\max})$ (liquidlike viscoelastic behavior). A smooth crossover between the regions $\omega > 1/\tau_{\max}$ and $\omega < 1/\tau_{\max}$ thus implies that

$$G' \sim \frac{\kappa_BT}{a^3}\frac{\phi}{N}\tau_1\tau_{\max}\omega^2, \quad G'' \sim \frac{\kappa_BT}{a^3}\frac{\phi}{N}\tau_1\omega, \quad \omega < 1/\tau_{\max} \qquad (3.14)$$

The log–log frequency behavior of the moduli is sketched in Figure 4a.

Let us now turn to the region above the gel point, $p/p_g - 1 > \tilde{\Delta}$ (see Figure 4b). Here we distinguish two relaxation processes that contribute to the moduli: (1) relaxation within the strands and free clusters on the scales smaller than the typical strand size; (2) the stress relaxation due to breakage of the strands.

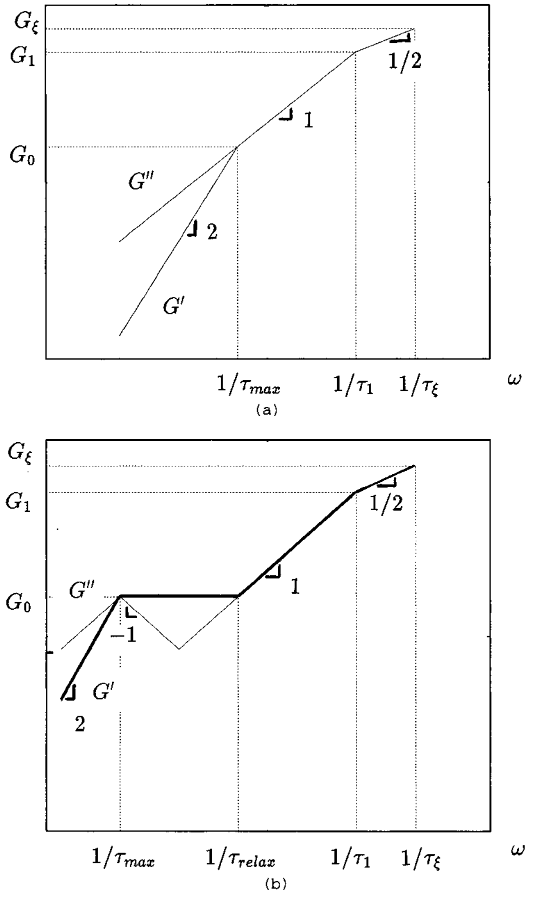

Figure 4. The log-log plots of storage, G', and loss, G'', moduli as a function of frequency ω: (a) $\Delta < \tilde{\Delta}$, $G_\xi \sim k_BT/a^3\ \phi^{3\nu/(3\nu-1)}$, $G_1 \sim (k_BT/a^3)(\phi/N)$, $G_0 \sim (k_BT/a^3)(\phi/N)|\Delta|^3$; (b) $\Delta > \tilde{\Delta}$.

At times shorter than the relaxation time of a network strand, τ_{relax}, the dynamic moduli scale in the same way as below the gel point (see eqs 3.12 and 3.13). Indeed, at short length scales smaller than the network strand the system does not “know” that it is above the gel point. The value of the dynamical moduli at $\omega \sim 1/\tau_{relax}$ are proportional to the concentration of network strands: $G' \sim G'' \sim k_BTc(M_{strand}) \sim (k_BT/a^3)\ (\phi/N)\Delta^3 \equiv G_0$. The longest mode of the network strands corresponding to their end-to-end vector cannot relax unless the strands break. Therefore at time-scales between τ_{relax} and τ_{max} the system behaves as a virtually permanent network, so that the storage modulus is nearly constant in this regime: $G' \simeq G_0$. At times longer than τ_{max} ($\omega < 1/\tau_{max}$) the moduli decrease due to network strand breakage which is characterized by the single relaxation time τ_{max}. Therefore the complex network modulus is

$$G_{net}(\omega) = \frac{i\omega\tau_{max}}{1+i\omega\tau_{max}} G_0 \tag{3.15}$$

The above picture implies that in general the elastic moduli can be represented as a sum of two contributions

$$G = G_{str} + G_{net}$$

where G_{str}, defined by eqs 3.12 and 3.13, accounts for the relaxation of network strands on scales smaller than the strand size, and G_{net}, defined by eq 3.15, accounts for the network elasticity and breakage of the strands. Thus we get the following scaling behavior:

$$G' \sim \frac{k_BT}{a^3}\frac{\phi}{N} \times \begin{cases} (\omega\tau_1)^{1/2}, & 1/\tau_1 < \omega < 1/\tau_\xi \\ \omega\tau_1, & 1/\tau_{relax} < \omega < 1/\tau_1 \\ \Delta^3, & 1/\tau_{max} < \omega < 1/\tau_{relax} \\ \Delta^3(\omega\tau_{max})^2, & \omega < 1/\tau_{max} \end{cases}$$

$$G'' \sim \frac{k_BT}{a^3}\frac{\phi}{N} \begin{cases} (\omega\tau_1)^{1/2}, & 1/\mathrm{t}_1 < \omega < 1/\tau_\xi \\ \omega\tau_1, & 1/\tau_2 < \omega < 1/\tau_1 \\ \Delta^3/(\omega\tau_{max}), & 1/\tau_{max} < \omega < 1/\tau_2 \\ \Delta^3\omega\tau_{max}, & \omega < 1/\tau_{max} \end{cases} \tag{3.16}$$

where $\tau_2 = (\tau_{max}\tau_{relax})^{1/2}$ is a new characteristic time scale equal to the geometric mean between the lifetime of a typical strand, τ_{max}, and its conformational relaxation time.

Note that the scaling picture considered above is valid if network strands (or terminal clusters) consist of more than one linear chain, $M_{strand} > 1$, that is if $|\Delta| < 1$.

3.3. Concentration and Frequency Dependence of Viscosity. Using eqs 3.14 and 3.16 we get the zero-shear viscosity $\eta = \lim_{\omega\to 0} G''/\omega$ in the vicinity of the gel point, $\phi \sim \phi_g$ (recall that $\tau_{max} = \tau_b\Delta$)

$$\eta \sim \frac{k_BT}{a^3}\frac{\phi_g}{N}\tau_1 \simeq \eta_0 N\, {\phi_g}^{1/(3\nu-1)} \equiv \eta_g, \quad \Delta < \tilde{\Delta} \tag{3.17}$$

$$\eta \sim G_0\tau_b\Delta \sim \frac{k_BT}{a^3}\frac{\phi_g}{N}\tau_b\Delta^4 \simeq \eta_0\frac{\phi_g}{N}\mathrm{e}^{\epsilon+\epsilon_a}\,\Delta^4, \quad \tilde{\Delta} < \Delta < 1 \tag{3.18}$$

where $\Delta \sim \phi/\phi_g - 1$, and $\eta_0 = (k_BT/a^3)\tau_0$ is the solvent viscosity. Thus η turns out to be almost independent of the distance to the gel point (up to logarithmic corrections) and nearly equal to that of the solution of linear precursor chains in the reigon $\Delta < \tilde{\Delta}$. In the gel region $1 > \Delta > \tilde{\Delta}$ the viscosity increases as Δ^4.

The frequency dependent viscosity can be defined as $\eta(\omega) = G''(\omega)/\omega$. In the region above the gel-point, $\Delta > \tilde{\Delta}$, both frequency and concentration behavior of $G''(\omega)$ are defined by eqs 3.16. Thus the viscosity nearly does not depend on frequency, $\eta(\omega) \simeq \eta(0)$, in the low-frequency region, $\omega < 1/(\tau_b\Delta)$. It is interesting to note that there is another region, $\Delta/(\tau_b\tau_1)^{1/2} < \omega < 1/\tau_1$, where the viscosity is nearly constant (essentially does not depend either on frequency or on concentration) and is equal to the viscosity of the solution of linear precursor chains at $\phi = \phi_g$, $\eta \sim \tau_0 N\phi^{1/(3\nu-1)} = \eta_g$. This plateau value of $\eta(\omega)$ is much lower than the zero-shear-rate value, $\eta(0)$, by a factor of order $(\Delta/\tilde{\Delta})^4 \gg 1$.

3.4. Dynamics Well above the Gelation Point. Further above the gel point the typical number of closed interchain sticker pairs per chain is large, $fp \gg 1$, giving rise to a reversible network regime[17,18] with Rouse-like relaxation behavior: $\tau_{max} \sim \tau_b(fp)^2$. Using eq 2.1 we obtain the following concentration dependence of the relaxation time

$$\tau_{max} \sim \begin{cases} \tau_b f^2 l^{2+2z} \phi^{(2+2z)/(3\nu-1)}, & \phi_g \ll \phi < \phi_s \\ \tau_b f^2, & \phi_s < \phi < 1 \end{cases} \tag{3.19}$$

where $\phi_s \sim l^{1-3\nu}$ if the attraction between stickers is strong enough, $\mathrm{e}^\epsilon > l^{2+z}$ (this condition is assumed below). Note that the dependencies, eqs 3.11 and 3.19, smoothly cross over at $\Delta = \phi/\phi_g - 1 \sim 1$.

The zero-frequency viscosity can be estimated as $\eta \sim \tau_{\max} G_1$, where $G_1 \sim k_B T\,(\phi/a^3)\,(1/N)$ is the characteristic elastic modulus corresponding to the main Rouse mode of polymer coils. Hence

$$\eta \sim \eta_0 N \epsilon^{\epsilon+\epsilon_a} \times \begin{cases} l^{2z}\, \phi^{(2z+2)/(3\nu-1)+1}, & \phi_g \ll \phi < \phi_s \\ l^{-2}\phi, & \phi_s < \phi < 1 \end{cases} \tag{3.20}$$

The concentration dependence of viscosity in this sticky Rouse regime is $\eta \propto \phi^{4.2}$ for $\phi_g < \phi < \phi_s$. The viscosity of the sticky Rouse model (the first line in eq 3.20) smoothly crosses over to eq 3.18 near the gel point at $\phi \sim 2\phi_g$ (i.e. at $\Delta \sim 1$).

4. Dynamics Near the Gel Point: Correlation Effects

Let us assume that ϵ is large enough so that the stickers strongly prefer to be in a closed state, so that the fraction of open stickers is very small. According to the analysis of ref 1 this is true if $e^{\epsilon} \gg l^{2+z}$. In this case the simple picture of the cluster or network strands relaxing via dissociation of pairs of stickers adopted in the previous section needs to be modified. The new important process is that once a cluster is dissociated into, e.g., two parts, it could recombine again by reassociating of the broken pair of stickers.[19] This process is not probable if there are a lot of other open stickers around (e.g., in the volume of the cluster). In this case two open stickers formed due to dissociation would later create different pairs rather than associate again with each other. However the probability of a reassociation is very high if there are almost no other open stickers available. This is the case we are considering in the present section. In this regime a cluster (or a network strand) would break and recombine again at exactly the same pair of stickers many times before it finally breaks (a final break means that the stickers reassociate in a different way).

4.1. Fraction of Open Stickers. In order to proceed quantitatively we need to calculate the concentration of open stickers, $\phi_1 = (\phi/l)p_1$, where ϕ/l is the concentration of all stickers and p_1 is the fraction of open stickers. We classify the stickers in three groups: open (p_1), locally (intrachain) paired (p_2), and inter-chain paired (p); $p_1 + p_2 + p = 1$. Note that the fraction of inter-chain bonds, p, might be also small: $p \sim 1/f$ near the gel-point. This means that the majority of stickers are locally paired, i.e. are paired with their immediate neighbors along the polymer chain, $1 - p_2 \ll 1$. Therefore an open sticker would most probably appear via dissociation of a *local* pair.

A naive way to proceed with the calculation of p_1 is the following. Let us consider a pair of neighboring (along the polymer chain) stickers and compare the statistical weight of their associated state, W_2, with that of the open state, W_1. If the binding energy, ϵ, were zero, then $W_2 \sim W_1 P_{\text{contact}}$, where

$$P_{\text{contact}} \sim \frac{1}{l^{3\nu}} K(l) \tag{4.1}$$

is the a priori probability of a contact between two stickers. Here $l^{3\nu}$ is the relevant volume (in a^3 units) accessible for one sticker around a fixed second sticker, and the factor $K(l) \sim l^{3\nu-2-z}$ takes into account additional effective repulsion between the stickers due to the excluded-volume statistics (see section 2 or ref 1 for more details). With local attraction between the stickers the statistical weight of a contact must be increased by a factor e^{ϵ}:

$$W_2 \sim W_1 P_{\text{contact}} e^{\epsilon}$$

Therefore the probability of an open state is $p_1 = W_1/(W_1 + W_2) \simeq W_1/W_2 \sim l^{2+z}e^{-\epsilon}$. This result is surely correct for a single pair or for a system of independent pairs of stickers. However, the result implies that open stickers always appear as pairs, i.e. a second open sticker can be *always* found near a given open sticker. This is not the case however for the system under consideration: two open stickers which are initially close to each other can easily diffuse along the chain far away, as shown in Figure 5.

Thus at equilibrium open stickers are almost uniformly distributed along the chains with concentration p_1, like a one-dimensional nearly ideal gas.

It is convenient to use the following dynamical arguments in order to estimate p_1. Note that the fraction of open stickers is an equilibrium characteristic. Therefore it must not depend on the activation energy ϵ_a, which we now temporary put equal to zero in order to simplify the argument. The main idea is to balance the dissociation (ν_d) and association (ν_a) rates. The first rate (number of open stickers which is produced per unit time per one sticker) is $\nu_d \sim 1/\tau_b = 1/(\tau_0 e^{\epsilon})$. The association rate is proportional to the probability that two open stickers come close to each other which is equal to p_1^2, and to the frequency of virtual contacts between two neighboring stickers, $1/\tau_{\text{contact}}$: $\nu_a \sim p_1^2/\tau_{\text{contact}}$. Obviously $\tau_0/\tau_{\text{contact}} = P_{\text{contact}}$ since the mean time of a virtual contact is τ_0, and τ_{contact} is the mean time between contacts. Thus using eq 4.1, we get $\nu_a \sim p_1^2 l^{-2-z}/\tau_0$. Using now the condition $\nu_a = \nu_d$ we finally obtain

$$p_1 \sim l^{1+z/2} e^{-\epsilon/2} \tag{4.2}$$

Note that the final estimate for p_1 is exactly the square root of the "naive" one (because the "naive" way was to regard the pairs of stickers as the elementary objects).

Note also that p_1 is small since $e^{\epsilon} \gg l^{2+z}$ as was assumed before.[20] The concentration of open stickers is

$$\phi_1 = \frac{\phi}{l} p_1 \sim \phi\, l^{z/2} e^{-\epsilon/2} \tag{4.3}$$

4.2. The Renormalized Lifetime of a Red Bond. As we discussed above, although a bond would typically break after a time of order τ_b, it will recombine again many times until at least one other open sticker (potential new partner) moves near its neighborhood. The effective lifetime of the bond, τ_b^*, is therefore much larger than τ_b, if the concentration of open stickers, ϕ_1, is small enough. Here we define τ_b^* as the mean time during which at least one of the initially paired stickers will find a new partner. We are mostly interested in red bonds—pairs of stickers involved in a backbone of a large cluster, although the approach can be easily generalized and applied to any bond (see section 5 below).

In order to estimate τ_b^* let us consider the motion of the red-bond stickers on the time scale $t \gg \tau_b$. Some part of the time, t', the stickers are apart (both are open); otherwise they are associated, the total time of the associated state being $t'' = t - t'$. It is reasonable to assume that the stickers are paired during the lion's share of the time: $t' \ll t''$, if the binding energy ϵ is large enough (this assumption is verified below), so that $t'' \simeq t$. We also assume that reassociation of a sticker with another partner could occur only if both partners are currently open.[21] The probability that a third open sticker comes close to a given one (one of the two initially involved in the red bond) is $P_c \sim \phi_1 K(g)$, where $K(g) \sim \phi^{(z+2-3\nu)/(3\nu-1)}$ is the additional small factor accounting for indirect excluded-volume interactions between the stickers (see section 2). Therefore the total time during which the sticker is in contact with a third one is $t_c \sim t'P_c \sim t'\phi_1 K(g)$. Obviously in order to make a bond with the third sticker with the probability of, e.g., $1/2$, the contact time t_c must be of the order of the association time: $t_c \sim \tau_a = \tau_0 e^{\epsilon_a}$. This condition defines the duration of the open stage:[22]

$$t' \sim \tau_0 e^{\epsilon_a}/(\phi_1 K(g)) \tag{4.4}$$

Now we need to calculate the total time t corresponding to the known t'.

We note that the motion of stickers during the open stage virtually does not depend either on their binding energy ϵ or on the activation energy ϵ_a. In particular the typical volume V explored by the stickers depends on the time t' in the same way as if they were not directly interacting: $V = V(t') \sim R^3(t')$, where $R(t')$ is the typical displacement. The fractal structure of the clusters implies that the displacement time t' should be nearly equal to the relaxation time of a subcluster m of size R.[23] Thus using eqs 3.1 and 3.2 with $R_m = R$ and $\tau_{relax}(m) = t'$, we get

$$V(t') \sim R^3(t') \sim a^3 \left(\frac{N}{\phi}\frac{t'}{\tau_0}\right)^{1/2} \tag{4.5}$$

Here we assume that the time t' is shorter than the relaxation time of the whole terminal cluster (network strand):

$$t' \ll \tau_{relax}(M_{term}) \tag{4.6}$$

This condition will be checked later. We also assume that $t' \gg \tau_1$; using the results obtained below, it is possible to show that this condition is weaker than the condition $\tau_b^* \gg \tau_b$, which is also considered below.

The total time in the associated state t'' is proportional to the product of the number of returns to each other of the initially paired stickers, n_r, and the average time in the associated state per one attempted contact, $\tau_0 e^{\epsilon}$: $t'' \sim n_r \tau_0 e^{\epsilon}$ (note that e^{ϵ_a} attempted contacts roughly correspond to the time $\tau_0 e^{\epsilon+\epsilon_a}$ in the associated state). The number of returns can be estimated assuming no direct interactions between the stickers: $n_r \sim (t'/\tau_0)p_r$, where p_r is the probability that the two stickers come close to each other (within a distance of order a). The probability p_r should be on the order of the *equilibrium* probability of a contact between the stickers provided that they are both trapped in the volume $V(t')$. Thus $p_r \sim (a^3/V(t'))K(g)$. Therefore we get

$$t'' \sim t' e^{\epsilon} \frac{a^3}{V(t')} K(g) \tag{4.7}$$

Now using eqs 4.4, 4.5, and 4.7, we obtain the effective lifetime of a pair, $\tau_b^* = t \simeq t''$:

$$\tau_b^* \sim \left(\frac{\phi K(g)}{\phi_1 N}\right)^{1/2} \tau_0 e^{\epsilon+\epsilon_a/2} \tag{4.8}$$

Using also eq (4.3) we get

$$\tau_b^* \sim \tau_0 \exp(5\epsilon/4 + \epsilon_a/2)\, N^{-1/2} l^{-z/4}\, \phi^{(2-3\nu+z)/(2(3\nu-1))} \tag{4.9}$$

This result is valid only if τ_b^* is much larger than the bare bond lifetime τ_b (see eq 1.1). Otherwise a renormalization of τ_b can be neglected. The condition of validity of eq 4.9, $\tau_b^* \gg \tau_b$, can be rewritten as

$$e^{\epsilon_a} \ll e^{\epsilon/2}\, N^{-1} l^{-z/2}\, \phi^{(2-3\nu+z)/(3\nu-1)} \sim e^{\epsilon/2} l^{3\nu-3-3z/2}\, f^{(3\nu-3-2z)/(1+z)} \tag{4.10}$$

where we take into account that $\phi \sim \phi_g \sim (lf^{1/(1+z)})^{1-3\nu}$ since $e^{\epsilon} \gg l^{2+z}$ (see eq 2.3 and ref 1). Condition 4.10 essentially implies that the activation energy is smaller than half of the binding energy: $\epsilon_a < \epsilon/2$, if we neglect ln N in comparison with ϵ.

Another condition we have actually used is $t' \ll t''$. Using the above eqs 4.4, 4.5, and 4.7 and also assuming that the condition 4.10 is fulfilled, it is possible to check that the condition $t' \ll t''$ is always obeyed if

$$e^{\epsilon} \gg f^2 l^{2+z} \tag{4.11}$$

This condition is assumed below.

In order to get the critical distance to the gel point $\tilde{\Delta}$, corresponding to the onset of the viscosity increase, we need to substitute τ_b^* instead of τ_b is eq 3.7. The result is

$$\tilde{\Delta} \sim l^{(3\nu+1.5z+3)/8} f^{(3+6z+3\nu)/8(1+z)} \exp(-5\epsilon/16 - \epsilon_a/8) \tag{4.12}$$

In the region $\Delta > \tilde{\Delta}$ the terminal relaxation time is the lifetime of a network strand, $\tau_{max} = \tau_{life} \sim \tau^*{}_b\Delta$ (i.e. we use the renormalized bond time τ_b^* instead of the bare time τ_b in eq 3.10). Hence the terminal relaxation time and the zero-shear viscosity in this region are (see eq 3.18)

$$\tau_{max} \sim \tau_b^*\Delta, \quad \eta \sim \frac{k_B T}{a^3}\frac{\phi}{N}\tau_b^*\Delta^4 \tag{4.13}$$

where τ_b^* is defined by eq 4.9 if condition 4.10 is fulfilled; in the opposite case $\tau_b{}^*$ should be formally set to be equal to τ_b.

Therefore for a fixed $\Delta > \tilde{\Delta}$ both τ_{max} and η are proportional to $\exp(5\epsilon/4 + \epsilon_a/2)$ if condition 4.10 is fulfilled, so that the *apparent* activation energy, E_{app}, which can be deduced from rheological measurements near the gel point, is not just $k_B T(\epsilon + \epsilon_a)$, but is a more complicated combination, $E_{app} = k_B T(5\epsilon/4 + \epsilon_a/2)$, which is higher than $k_B T(\epsilon + \epsilon_a)$ since $\epsilon_a < \epsilon/2$.

Finally we should check that the duration of the open stage is shorter than the relaxation time of a network strand, condition 4.6. Taking into account eq 3.4, this condition can be rewritten as $\Delta < \Delta_c$ with

$$\Delta_c \sim l^{(3\nu-1-z/2)/3} f^{(3\nu-1+z)/3(1+z)} \exp(-\epsilon/6 - \epsilon_a/3) \quad (4.14)$$

If $\Delta > \Delta_c$, then t' turns out to be much longer than the strand relaxation time $\tau_{\text{relax}}(M_{\text{strand}}) \sim \tau_1\Delta^{-3}$ (see eq 3.4). In this situation we should consider $V_{\text{strand}} \sim R_{\text{strand}}{}^3$ instead of $V(t')$, eq 4.5, since the stickers can not explore volume larger that V_{strand}. Taking into account that $R_{\text{strand}} = R_M$ is defined by eq 3.1 with $M \sim 1/\Delta^2$, see eq 3.3, and using also eqs 4.4 and 4.7, we get the renormalized lifetime of a sticker pair

$$\tau_b^* \sim \tau_b a^3/(\phi_1 V_{\text{strand}}) \quad (4.15)$$

or

$$\tau_b^* \sim \tau_0 l^{-1-z/2} f^{(1/2(1+z))-3/2} \Delta^{3/2} \exp(3\epsilon/2+\epsilon_a) \quad (4.16)$$

Note that in the region $\Delta > \Delta_c$ the terminal relaxation time $\tau_{\max} \sim \tau_b^*\Delta$ is proportional to $\Delta^{2.5}$, and the zero-shear viscosity is proportional to $\Delta^{5.5}$. The apparent activation energy in this region is $E_{\text{app}} = 3\epsilon/2 + \epsilon_a$:

$$\tau_{\max} \propto \Delta^{2.5} \exp(3\epsilon/2 + \epsilon_a), \quad \eta \propto \Delta^{5.5} \exp(3\epsilon/2 + \epsilon_a) \quad (4.17)$$

If the activation energy ϵ_a is large enough so that the inequality opposite to inequality 4.10 is fulfilled (that basically means that $\epsilon_a > \epsilon/2$), then the consideration of the previous section (with unrenormalized τ_b) is valid in the vicinity of the critical point. In particular $\tilde{\Delta}$ is defined by eq 3.7 in this region. However as the concentration increases (Δ increases), the strand size decreases, and thus the volume that a red bond sticker could explore also decreases. As a result the probability of reassociation of a sticker with its original partner increases, so that renormalization of the bond lifetime becomes important if Δ exceeds some critical value Δ_c. It is physically clear (and also could be directly checked) that eq 4.16 becomes valid in the region $\Delta > \Delta_c$. Therefore Δ_c in this regime is defined by the condition $\tau_b^* \sim \tau_b$, where τ_b^* is defined in eq 4.16. Thus we get

$$\Delta_c \sim l^{(2+z)/3} f^{1-(1/3(1+z))} \exp(-\epsilon/3) \quad (4.18)$$

Note that if the binding energy is high, $\epsilon \gg 1$, then Δ_c is small and independent of the activation energy (the barrier) ϵ_a which could be arbitrary large. That means that even for a very high barrier, $\epsilon_a \gg \epsilon$, the dynamical picture presented in section 3 is valid only in a narrow region around the gel point, $\Delta < \Delta_c$. Outside this narrow region, the renormalized theory, eqs 4.16 and 4.17, should be applied.

The following concentration dependence of the terminal relaxation time and the viscosity is predicted near the gel point (see eqs 3.10, 4.13, 3.18, and 4.17):

$$\tau_{\max} \propto \begin{cases} \Delta, & \Delta < \Delta < \Delta_c \\ \Delta^{5/2}, & \Delta_c < \Delta < 1 \end{cases} \quad (4.19)$$

$$\eta \propto \begin{cases} \Delta^4, & \tilde{\Delta} < \Delta < \Delta_c \\ \Delta^{11/2}, & \Delta_c < \Delta < 1 \end{cases} \quad (4.20)$$

where the crossover parameters $\tilde{\Delta}$ and Δ_c are defined by eq 4.12 or 3.7 and eq 4.14 or 4.18 depending on the regime (i.e. whether the inequality 4.10 or the opposite inequality is fulfilled). These equations can be rewritten in more compact form:

$$\tilde{\Delta} = \min\Big[l^{(6\nu+3z+6)/16} f^{(3\nu+6z+3)/8(1+z)} \exp\left(-\frac{5}{16}\epsilon - \frac{1}{8}\epsilon_a\right), \\ l^{(3/4)\nu} f^{(3\nu+2z)/4(1+z)} \exp\left(-\frac{1}{4}\epsilon - \frac{1}{4}\epsilon_a\right)\Big] \quad (4.21)$$

$$\Delta_c = \max\Big[l^{(3\nu-1-z/2)/3} f^{(3\nu-1+z)/3(1+z)} \exp\left(-\frac{1}{6}\epsilon - \frac{1}{3}\epsilon_a\right), \\ l^{(2+z)/3} f^{1-(1/3(1+z))} \exp\left(-\frac{1}{3}\epsilon\right)\Big] \quad (4.22)$$

4.3. The Percolation Regime. There is another limitation to the above treatment, which might be more important than the condition $\Delta > \Delta_c$: the results are based on the classical gelation theory. The classical gelation picture is valid if the network strands strongly overlap

$$c(M)R_M{}^3 \gg 1$$

where $c(M) \sim (\phi/Na^3)M^{-3/2}$ is the concentration of strands (see comments before eq 3.13), and $R_M{}^3 \sim R_1{}^3M^{3/4}$ is the strand volume (see eq 3.1). Taking into account that $M = M_{\text{strand}} \sim 1/\Delta^2$ and that $\phi \simeq \phi_g$, the last condition can be rewritten as $\Delta \gg \Delta_{\text{perc}}$, where

$$\Delta_{\text{perc}} \sim f^{-(1/3)z/(1+z)} \simeq f^{-0.06} \quad (4.23)$$

In the region $\Delta < \Delta_{\text{perc}}$ percolation statistics should be applied. In this region the elastic modulus of the percolation network is

$$G_0 \propto R_{\text{strand}}{}^{-3} \propto \Delta^{3\nu'}$$

where $R_{\text{strand}} \propto \Delta^{-\nu'}$ is the typical strand size, and $\nu' \simeq 0.85$ is the percolation critical exponent. The renormalized lifetime of a red bond in the regime $\Delta > \Delta_c$ (where Δ_c is calculated below) can be estimated using the general eq 4.15, where we have to take into account that now $V_{\text{strand}} = R_{\text{strand}}{}^3 \propto \Delta^{-3\nu'}$. Thus we get

$$\tau_b^* \sim \tau_0 \exp(3\epsilon/2 + \epsilon_a)\Delta^{3\nu'} l^{-1-z/2} f^{1/(2(1+z))-3/2} \quad (4.24)$$

for $\Delta_c < \Delta < \Delta_{\text{perc}}$.

The regime $\Delta < \Delta_c$ can be considered as well in exactly[24] the same way as with classical gelation statistics (see the previous section). The only difference is that we should use the percolation result, $D \simeq 2.5$, for the fractal dimension of strands (instead of $D = 4$ for classical trees), and also use the percolation relation

$$M_{\text{term}} = M_{\text{strand}} \sim \Delta^{-\nu' D} \simeq \Delta^{-2.1}$$

instead of eq 3.3. Thus we get

$$\tau_b^* \sim \max[\tau_b, \tau_0 e^{\epsilon(1+(1/2)(D-1)/(D+2))+\epsilon_a(D-1)/(D+2)} \times \\ \phi^{3/(D+2)(z+4-6\nu)/(3\nu-1)+(3/2)(2\nu-1)/(3\nu-1)-(D-1)/(D+2)} \times \\ l^{-(z/2)(D-1/D+2)} N^{-(3/2)(D-2)/(D+2)}] \quad (4.25)$$

if $\Delta < \Delta_c$. Substituting numerical values we can rewrite eq 4.25 as $\tau^* \sim \tau_0 \max[e^{\epsilon+\epsilon_a}, e^{1.17\epsilon+0.33\epsilon_a} l^{-0.674} f^{-0.55}]$. The crossover concentration parameter, Δ_c, is determined by the condition that both eqs 4.25 and 4.24 are simultaneously applicable. Thus we get

$$\Delta_c \sim \max[e^{-0.17\epsilon} l^{0.44} f^{0.43}, e^{-0.13\epsilon-0.26\epsilon_a} l^{0.17} f^{0.21}] \quad (4.26)$$

The lifetime of a typical strand is $\tau_{\text{life}} \sim \tau_b^*/M_b$, where M_b is the typical number of red bonds per strand. Using the general argument presented after eq 3.5, it is possible to show that $M_b \sim 1/\Delta$; this relation holds both in classical gelation and in percolation theory. Thus $\tau_{\max} \simeq \tau_{\text{life}} \sim \tau_b^*\Delta$ (compare with eq 3.10), and we arrive at the following behavior for the terminal relaxation time of the reversible gel, $\tau_{\max}$, and the zero-shear viscosity, $\eta \sim G_0\tau_{\max}$:[25]

$$\tau_{\max} \propto \begin{cases} \Delta, & \Delta < \Delta < \Delta_c \\ \Delta^{1+3\nu'} \simeq \Delta^{3.55}, & \Delta_c < \Delta < \Delta_{\text{perc}} \end{cases} \quad (4.27)$$

$$\eta \propto \begin{cases} \Delta^{1+3\nu'} \simeq \Delta^{3.55}, & \tilde{\Delta} < \Delta < \Delta_c \\ \Delta^{1+6\nu'} \simeq \Delta^{6.1}, & \Delta_c < \Delta < \Delta_{\text{perc}} \end{cases} \quad (4.28)$$

The crossover concentration $\tilde{\Delta}$ is determined by the condition $\tau_{\text{life}} = \tau_{\text{relax}}$ (see eq 3.6), where $\tau_{\text{life}} \sim \tau_b^*\Delta$ and τ_{relax} is defined in eq 3.2 with the percolation exponent $D \simeq 2.5$:

$$\tilde{\Delta} \sim \min[e^{-0.21(\epsilon+\epsilon_a)} l^{0.37} f^{0.38}, e^{-0.24\epsilon-0.07\epsilon_a} l^{0.507} f^{0.49}] \quad (4.29)$$

In the region $0 < \Delta < \tilde{\Delta}$ both $\tau_{\max}$ and η are nearly independent of Δ.

Eqs 4.26, 4.27, 4.28, and 4.29 should be used in the percolation regime instead of eqs 4.19, 4.20, 4.22, and 4.21.

5. Dynamical Correlation Effects Far above the Gel Point

It is straightforward to generalize the treatment presented in the previous section in order to consider the dynamics in the regime of a more concentrated reversible gel, $\phi \gg \phi_g$. All general ideas are the same as introduced in the previous section. In order to find the basic dynamic quantities, the relaxation time $\tau_{\max}$, and the viscosity η, we first have to calculate the concentration of open stickers, ϕ_1.

Equation 4.3 defining the concentration ϕ_1 is valid not only in the vicinity of the gel point but also for higher concentrations provided that most stickers are *locally* paired. This is true if the mean concentration of immediate neighbors of a given sticker, $\phi_{\text{local}} \sim 1/l^{3\nu}$, is higher than the concentration of stickers belonging to other chains, ϕ/l; i.e., $\phi < \phi_s \sim l^{1-3\nu}$. At $\phi > \phi_s$ the spacers between the chains strongly overlap (the concentration blob size, g, is smaller than l), so that most stickers form interchain (rather than intrachain) bonds. In this situation the unrenormalized classical gelation theory should be directly applicable. The fraction of closed stickers, p^* (including both intra- and interchain pairs, $p^* = p + p_2$) is then given by equation

$$\frac{p^*}{(1-p^*)^2} = \frac{\phi}{l} e^{\epsilon} K(g) \simeq \frac{1}{l} e^{\epsilon} \phi^{(1+z)/(3\nu-1)} \quad (5.1)$$

which was derived in ref 1 (compare with eq 2.1).

Therefore the fraction of open stickers, $p_2 = 1 - p^*$, in the region $\phi > \phi_s$ is

$$p_1 \sim l^{1/2} e^{-\epsilon/2} \phi^{-(1+z)/(2(3\nu-1))} \quad (5.2)$$

Note a smooth crossover between eqs 4.2 and 5.2 in the region $\phi \sim \phi_s$.

In the region $\phi \gg \phi_g$ the network strands are chain segments of length $L \sim l/p$ (rather than clusters of chains). Here p is the effective fraction of "active" (interchain) bonds, which is defined by eq 2.1, where we take into account condition 4.11 (see ref 1 for more detail):

$$\frac{p}{(1-p)^2} \sim l^{1+z} \phi^{(1+z)/(3\nu-1)} \quad (5.3)$$

Using eq 5.3, we get the network strand between the interchain bonds

$$L = l/p \sim \begin{cases} l\left(\dfrac{\phi_s}{\phi}\right)^{(1+z)/(3\nu-1)}, & \phi_g \ll \phi < \phi_s \sim l^{1-3\nu} \\ l, & \phi > \phi_s \end{cases} \quad (5.4)$$

The strand spatial size is

$$R_{\text{strand}} \sim a(L/g)^{1/2} g^{\nu} \sim aL^{1/2} \phi^{-(\nu-1/2)/(3\nu-1)} \quad (5.5)$$

Substituting $V_{\text{strand}} \sim R_{\text{strand}}{}^3$ and $\phi_1 = (\phi/l)p_1$, where R_{strand} is defined by eqs 5.5 and 5.4 and p_1 by eq 4.2 for $\phi < \phi^*$ and eq 5.2 for $\phi > \phi_s$, in the general equation (eq 4.15), we get the lifetime of an associated interchain pair of stickers:

$$\tau_b^* \sim \tau_0 \exp(1.5\epsilon + \epsilon_a) \times \begin{cases} l^z \phi^{(2+3z)/2(3\nu-1)}, & \phi_g \ll \phi < \phi_s \\ l^{-1} \phi^{z/2(3\nu-1)}, & \phi > \phi_s \end{cases} \quad (5.6)$$

Equation 4.15 (and also eq 5.6) is valid in the whole region $\phi \gg \phi_g$ if $\Delta_c < 1$ as assumed above. In the case $\Delta_c > 1$ we get an additional regime where eq 5.6 is not applicable: $2 < \Delta < \Delta_c$. In this regime a strand might not have enough time to relax before reconnection, i.e. $\tau_{\text{strand}} > t'$. However it is easy to show that the latter condition automatically implies that $\tau_b^* = \tau_b$; i.e., that the renormalization of the effective bond time is not important, if

$$e^{(\epsilon/2)-3\epsilon_a} l^{-z/2} \phi^{(13+3z-21\nu)/(3\nu-1)} < 1 \quad (5.7)$$

This condition (eq 5.7) is assumed below; it is always fulfilled if $\epsilon_a > \epsilon/6$. Therefore τ_b^* is given by eq 5.6 if $\Delta > \Delta_c$ and $\tau_b^* = \tau_b$ in the opposite case provided that $\Delta_c > 1$. The crossover concentration parameter, Δ_c, can be obtained by comparing the rhs of eq 5.6 and τ_b. Using the first line of eq 5.6, we get

$$\Delta_c \sim (e^{-\epsilon} l^{2+3\nu-2z} f^{(2+3z)/(1+z)})^{(3\nu-1)/(2+3z)} \quad (5.8)$$

Equation 5.8 is valid if $1 < \Delta_c < \phi_s/\phi_g$.

Note that in the region $\phi \gg \phi_g$ the strand relaxation time is just equal to τ_b^*. However the longest relaxation time of a polymer chain is larger than τ_b^* since there are a lot of active (interchain paired) stickers per chain. Thus a macromolecule can be considered as a super-chain of active stickers with the effective jump-time τ_b^*. The global motion of a super-chain is Rouse-like. Therefore the chain relaxation time is

$$\tau_{\max} \sim \tau_b^*(N/L)^2$$

where N/L is the number of active stickers per chain.

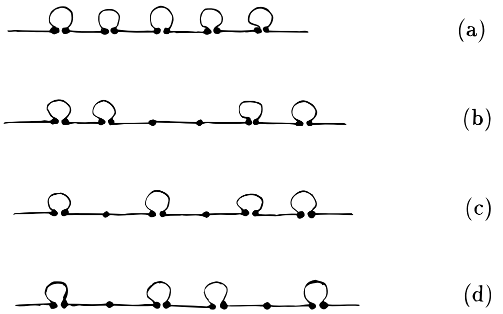

Figure 5. Independent diffusion of open stickers along the polymer chain: (a) a state with all stickers locally paired; (b) a state where a pair of open stickers had appeared; (c) the left open sticker moved one step to the left; (d) a state where the right open sticker moved one step to the right.

Hence we get

$$\tau_{\max} \sim \tau_0 N^2 \exp(1.5\epsilon + \epsilon_a) \times \begin{cases} l^{3z}\phi^{(3+3.5z)/(3\nu-1)}, & \phi_g \ll \phi < \phi_s \\ l^{-3}\,\phi^{z/2(3\nu-1)}, & \phi > \phi_s \end{cases} \tag{5.9}$$

Thus we predict a rather strong concentration dependence of the longest relaxation time, $\tau_{\max} \propto \phi^{4.96}$, in the region $\phi_g < \phi < \phi^*$, and a much weaker dependence, $\tau_{\max} \propto \phi^{0.15}$, in the more concentrated regime, $\phi > \phi_s$. The sharp (4.96) increase of $\tau_{\max}$ in the region $\phi_g < \phi < \phi_s$ is due to the fact that both the effective conversion degree and the effective bond time strongly depend on concentration in this region.

Thus we identify two characteristic time-scales: the lifetime of a typical strand of the reversible network, τ_b^*, and the chain relaxation time $\tau_{\max}$. The plateau modulus corresponding to the first time-scale is actually the elastic modulus of the reversible network, which is proportional to the concentration of strands:

$$G_0 = \frac{k_B T}{a^3}\frac{\phi}{L} \sim \frac{k_B T}{a^3 l} \times \begin{cases} l^{1+z}\,\phi^{(3\nu+z)/(3\nu-1)}, & \phi_g \ll \phi < \phi_s \\ \phi, & \phi > \phi_s \end{cases}$$

The second time-scale is associated with another, lower, modulus, G_1, which is proportional to the concentration of chains:

$$G_1 \sim \frac{k_B T}{a^3}\frac{\phi}{N}$$

The zero-shear viscosity is dominated by the longest time scale:

$$\eta \sim G_1 \tau_{\max} \sim \eta_0 \exp(1.5\epsilon + \epsilon_a) N \times \begin{cases} l^{3z}\,\phi^{1+(3+3.5z)/(3\nu-1)}, & \phi_g \ll \phi < \phi_s \\ l^{-3}\,\phi^{1+(0.5z)/(3\nu-1)}, & \phi > \phi_s \end{cases} \tag{5.10}$$

Thus $\eta \propto \phi^{5.96}$ for $\phi_g < \phi < \phi_s$, and $\eta \propto \phi^{1.15}$ for $\phi > \phi_s$. The schematic log−log plot of the viscosity vs the reduced concentration $\Delta \equiv \phi/\phi_g - 1$ is shown in Figure 6.

Note that both eqs 5.9 and 5.10 can be obtained by simple substitution of the renormalized bond time τ_b^*, eq 5.6, instead of the bare τ_b in eqs 3.19 and 3.20.

6. Discussion

In this paper we considered Rouse−Zimm dynamics of semidilute solutions of associating polymers with many ($f \gg 1$) stickers per chain. The dynamics are governed by two important parameters: the effective energy of a bond between two stickers ϵ (in k_BT units), and the activation energy, ϵ_a, corresponding to the bond formation.

We found that association of stickers does not affect the dynamics well below the reversible gelation point, ϕ_g. In the vicinity of the gel point (below it) the longest conformational relaxation time of the system starts to increase due to formation of large clusters of associated chains. The viscosity however is only weakly concentration dependent in this region. Above the gel point the viscosity starts to increase, being proportional to a power of the distance to the gel point. The mean-field mechanism of breakage of a network strand (which assumes no correlation between dissociation of a pair of stickers and its recombination) implies that this power is equal to 4 (this result is also based on the classical gelation approach; the percolation exponent of 3.55 is valid in the vicinity of the gel point). The frequency-dependent viscosity shows two regions where it is almost independent of frequency. At low frequencies the viscosity is governed by the lifetime of the reversible bonds; at the higher frequency regime the viscosity is much lower and does not depend either on the distance to the gel point or on the association energy.

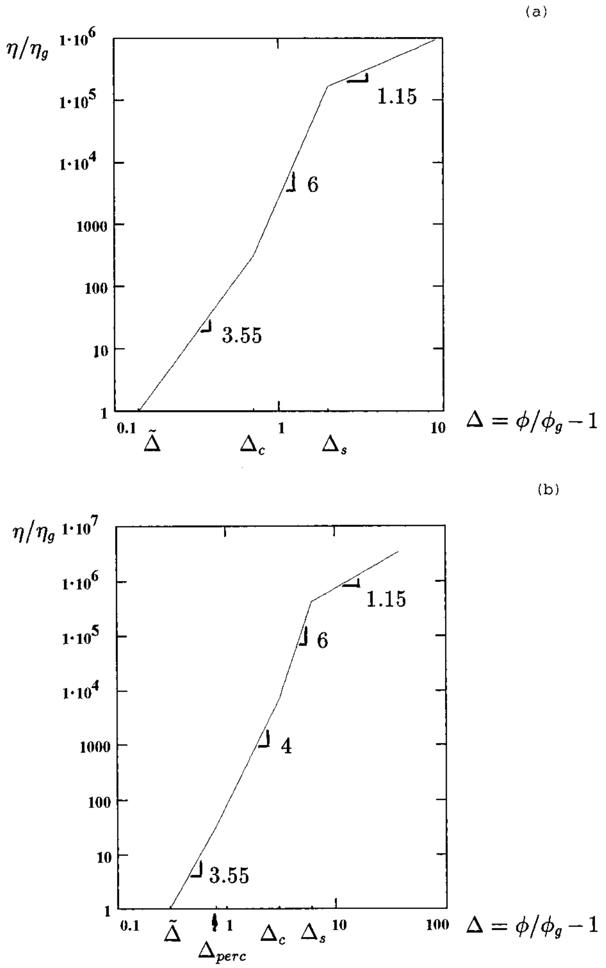

Figure 6. The log-log plot of the reduced zero−shear viscosity η/η_g vs reduced concentration $\Delta = \phi/\phi_g - 1$ above the gel point, where ϕ_g is the gelation concentration, $\phi_g \ll \phi_s \sim l^{1-3\nu}$, and η_g is the viscosity at $\Delta \simeq \tilde{\Delta}$ which is also nearly equal to the viscosity at the gelation point. Key: (a) $l = 5$, $f = 5$; (b) $l = 10$, $f = 20$.

We also show that when the association energy, $\epsilon k_B T$, is high enough, the *effective* lifetime, τ_b^*, of a reversible bond, which governs all the dynamical properties of the system, is much larger than the bare lifetime, τ_b, given by eq 1.1, outside a narrow region around the gel point. Outside this region a strand breaks and recombines again (in exactly the same way) many times before the network topology is finally changed. This is due to the fact that the network topology could alter only if an active sticker (involved in an interchain bonding) would change its partner, which must be an extremely rare event since the concentration of free partners (open stickers) is very low. The strand relaxation time and the zero-shear viscosity are thus appreciably increased due to this effect by a large factor which is proportional to $\exp(\epsilon/2)$. The apparent activation energy, E_{app}, which can be deduced from measurements of the temperature dependence of viscosity or relaxation time in the reversible gel regime, is thus larger than the activation energy $(\epsilon + \epsilon_a)k_B T$ for a dissociation of two stickers: $E_{app} = (1.5\epsilon + \epsilon_a)k_B T$.

The predicted concentration dependence of viscosity above the gel point is schematically shown in Figure 6a. A reduced distance to the gel point, $\Delta = \phi/\phi_g - 1$, is used in this figure instead of concentration ϕ. The following parameters are used to get a rough estimate of the cross-over concentrations: $\epsilon = 10$ (i.e. the bond energy of $10k_B T$), $\epsilon_a = 5$ (an activation barrier of $5k_B T$), $f = 5$ (5 stickers per chain), $l = 5$ (5 monomers between stickers). Then the gelation point is $\phi_g \simeq 0.1$ (see eq (2.3)), and $\phi_s \simeq l^{1-3\nu} \simeq 0.3$ (see eq 3.19 and below). The crossover concentration parameters are $\tilde{\Delta} \simeq 0.14$ (eq 4.29), $\Delta_c \simeq 0.7$ (eq 4.26), $\Delta_{perc} \simeq 0.9$ (eq 4.23), and

$$\Delta_s = \phi_s/\phi_g - 1 \simeq f^{(3\nu-1)/(1+z)} - 1 \simeq 2 \qquad (6.1)$$

The maximum value of Δ, corresponding to $\phi = 1$, is $\Delta_{max} = 1/\phi_g - 1 \simeq 9$. Since both Δ_c and Δ_{perc} turn out to be of order 1, an unambiguous discrimination between the regimes $\Delta_c < \Delta < \Delta_{perc}$, $\Delta_{perc} < \Delta < 1$, and $1 < \Delta < \Delta_s$ is not possible for this particular example. Fortunately the predicted viscosity exponents are nearly the same for all three regimes (6.1, 5.5, and 5.96, correspondingly) and are close to 6. Thus three basic regimes are shown in Figure 6a: $\tilde{\Delta} < \Delta < \Delta_c$, where $\eta \propto \Delta^y$ with $y \simeq 3.55$, $\Delta_c < \Delta < \Delta_s$, where the exponent $y \simeq 6$, and $\Delta_s < \Delta < \Delta_{max}$, where $y \simeq 1.15$.

Another example of the predicted viscosity behavior for longer chains with $f = 20$ stickers and $l = 10$ monomers between stickers, and the same energetic parameters, $\epsilon = 10$ and $\epsilon_a = 5$, is shown in Figure 6b. The gelation concentration is $\phi_g \simeq 0.026$. The main difference from the previous case is that now $\Delta_c > 1$ as can be found using either eq 4.26 or eq 4.22. Hence the additional regime, $1 < \Delta < \Delta_c$, where Δ_c should be calculated using eq 5.8. The following viscosity exponents are predicted: $y \simeq 3.55$ for $\tilde{\Delta} < \Delta < \Delta_{perc}$ (see first line of eq 4.28), $y \simeq 4$ for $\Delta_{perc} < \Delta < \Delta_c$ (see eq 3.18 and the first line of eq 3.20; note that both equations imply nearly the same exponent: $y = 4$ and $y \simeq 4.2$), $y \simeq 6$ for $\Delta_c < \Delta < \Delta_s$ (see the first line of eq 5.10), and $y \simeq 1.15$ for $\Delta > \Delta_s$ (the second line of eq 5.10). The crossover concentration parameters are defined by eqs 4.29, 4.23, 5.8, and 6.1: $\tilde{\Delta} \simeq 0.3$; $\Delta_{perc} \simeq 0.8$; $\Delta_c \simeq 3$; $\Delta_s \simeq 6$.

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Glossary of Symbols

$k_B T$, thermal energy
f, number of stickers per chain
N, number of monomers per chain
$l = N/f$
$\epsilon k_B T$, the sticker binding energy
$\epsilon_a k_B T$, activation energy for sticker association
τ_0, microscopic monomer time
τ_b, priming sticker lifetime
a, monomer size
v, monomer excluded volume
p, degree of conversion
p_g, degree of conversion at the gel point
$\nu \simeq 0.59$, the Flory exponent
$\theta_2 \simeq 0.78$, the des Cloizeaux exponent
ϕ, polymer volume fraction
ϕ_g, the gelation point
g, number of monomers per concentration blob
τ_ξ, the blob relaxation time
η_0, the solvent viscosity
η, viscosity of the solution
τ_1, free chain relaxation time
R_M, cluster size
$\tau_{relax}(M)$, cluster relaxation time
M_{term}, the cutoff cluster mass
Δ, the relative distance to the gel point
$\tau_{life}(M)$, cluster lifetime
M_{max}, dynamical cutoff cluster mass
τ_{max}, terminal relaxation time
G', G'', elastic moduli
$z = \nu(3 + \theta_2) - 2 \simeq 0.225$

References and Notes

(1) Part 1. Semenov, A. N.; Rubinstein, M. *Macromolecules* **1998**, *31*, 1373−1385.
(2) The effects of entanglements will be analyzed in a future publication.
(3) The exponent $\theta_2 \simeq 0.78$ corresponds to the reduction of the number of contacts between two overlapping polymer coils due to excluded volume interactions in a good solvent.[26−28]
(4) De Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell Univ. Press: Ithaca, NY, 1985.
(5) The classical gelation picture fails only in a very close vicinity of the gel point p_g (in the critical region[4,29]). The critical regime is considered in section 4.3.
(6) Flory, P. J. *Principles of Polymer Chemistry*; Cornell Univ. Press: Ithaca, NY, 1971.
(7) Rubinstein, M.; Colby, R. H. *Macromolecules* **1990**, *23*, 2753.
(8) Actually we should consider here slightly different process: two smaller clusters combining into a chosen M-cluster. However the rates of the two processes are of the same order of magnitude.
(9) Stauffer, D. *Introduction to Percolation Theory*; Taylor and Francis: London, 1985.
(10) Hermann, H. *Phys. Rep.* **1986**, *136*, 153.
(11) Coniglio, A. *Phys. Rev. Lett.* **1981**, *46*, 250.
(12) *Gelation and Associating Polymers*. Cates, M. E. *NATO ASI* Ser. **1989**, *211*, 319. Cates, M. E.; McLeish, T. C. B.; Rubinstein, M. *J. Phys. C* **1990**, *2*, 749.
(13) This statement is true for treelike clusters which are formed in the classical gelation regime considered here. In the critical (percolation) regime, i.e., in a close vicinity to the gel point, the cluster structure is more complicated. In particular, clusters might include closed cycles (loops) of connected chains. In this regime the fraction of red bonds is lower than in the classical gelation regime. The percolation regime is considered in section 4.3. We are grateful to the reviewer who commented on this point.
(14) The idea to compare these time scales was first suggested by Cates.[12]
(15) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Claredon Press: Oxford, England, 1986.
(16) The scaling law, eq 3.13, is valid up to logarithmic corrections which are entirely neglected here and below.

(17) Tobolsky, A. V. *Properties and Structure of Polymers*; Wiley: New York, 1960.

(18) Green, M. S.; Tobolsky, A. V. *J. Chem. Phys.* **1946**, *14*, 80.

(19) This possibility was considered for a system of living polymers.[30]

(20) An alternative purely equilibrium method to get p_1 is to note that $p_1 = 1 - p^*$, where p^* is the fraction of all closed stickers defined by eq 5.1. Although this method leads to the same result, eq 4.2, it is less preferable since applicability of eq 5.1 in the regime where p^* is dominated by *local* pairs is not obvious.

(21) Hence three- or four-sticker aggregates are not considered here; i.e., these states are assumed to be unfavorable.

(22) This estimate, eq 4.4, is not always correct. The above derivation is based on an implicit assumption that the time intervals between contacts of the given sticker with a third sticker are all more or less equal to the mean time between contacts. This is not the case in general: the contacts occur as series of many repeated collisions with the same third partner separated by longer time intervals. Equation 4.4 is valid if the typical number of contacts in a series is smaller than e^{ϵ_a}, so that it is not probable that association would happen during one series of contacts. An analysis shows that this is always the case (for any concentration) provided that $e^{\epsilon_a} \gg l^{1/2}$. This condition is assumed below.

(23) One can easily apply this concept to, say dynamics of a Rouse linear chain to get the well-known law $R \propto t^{1/4}$.[15,31]

(24) We assume Rouse dynamics of clusters also in the percolation regime.

(25) Here and below we assume that $\Delta_c < \Delta_{perc}$, which is always true if ϵ is large enough; see eqs 4.23 and 4.26.

(26) Des Cloizeaux, J.; Jannink, G. *Polymers in Solution*; Clarendon Press: Oxford, England, 1990; Section 13.1.6.

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