Dynamics of Entangled Solutions of Associating Polymers

Michael Rubinstein*

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

Alexander N. Semenov

Department of Applied Mathematics, University of Leeds, Leeds LS2 9JT, U.K.

ABSTRACT: The process of making and breaking reversible bonds between associating groups (stickers) controls the dynamics of associating polymers. We develop a theory of "sticky reptation" to model the dynamics of entangled solutions of associating polymers with many stickers per chain. At a high degree of association, there are very few unassociated stickers. It is therefore very difficult for a sticker to find a new partner to associate with after breaking the bond with an old one. Typically a sticker returns to its old partner following an unsuccessful search for a new one, prolonging the effective lifetime of reversible bonds. In the sticky reptation model, the search for a new partner is restricted to a part of the tube confining the entangled chain. Another important effect is the increase of the fraction of the interchain associations at the expense of the intrachain ones with increasing polymer concentration. The sticky reptation model predicts a very strong concentration dependence of viscosity in good agreement with experiments.

1. Introduction

Solutions of associating polymers have attracted a lot of attention because they link two major classes of polymeric systems—solutions and networks—and are also very important in a number of industrial processes. The dynamics of associating polymers are still poorly understood despite of more than half a century of theoretical effort.[1−9] The dynamics of unentangled reversible networks formed by polymers with many associating groups per chain are described by a modified Rouse model, called the "sticky Rouse model". Chains move via multiple breaking and reforming of reversible bonds connecting them to each other. These bonds act as effective friction centers (sticky points) of the sticky Rouse model. It is important to realize that only intermolecular associations contribute to viscoelasticity and control dynamics of reversible networks. Therefore, transformation of intramolecular associations into intermolecular ones dominates the concentration dependence of the dynamical properties of associating polymers. At a high degree of association, it is difficult for a sticker to find a new partner to form a bond with. Multiple returns of the sticker to its old partner significantly increase the effective lifetime of the bond. These important effects have been incorporated into a recent theory of unentangled dynamics of associating polymer solutions.[7] In section 2, below, we define the model and review its main thermodynamic properties following ref 6. In section 3 we review the main concepts of the dynamics of unentangled associating polymers[7] that are needed for the generalization of the model to solutions of entangled polymers.

In the present paper, we address the effect of topological entanglements on the dynamics of reversible networks. The theories of dynamics of entangled reversible networks are based on the reptation model.[10−12] The first theory[3] allowed successful reptation steps only in the case of all bonds of a given chain being simultaneously broken. This theory predicts exponential dependence of relaxation time and viscosity on the number of associated groups per chain,[3] which is a much stronger dependence than observed in experiments. A more reasonable assumption was proposed in the sticky reptation model.[4] A chain is able to reptate along the confining tube by breaking only few bonds at a time. The sticky reptation model is effectively a sticky Rouse model in a tube. In section 4 of the present paper, the sticky reptation model is generalized to the case of solutions of entangled associating polymers. We take into account the transformation of intramolecular into intermolecular associations as well as the renormalization of the lifetime of a bond due to the difficulty for a sticker to find a new available partner. In the sticky reptation model, the search for a new partner and separation from an old one takes place along the confining tubes of corresponding chains. In section 5, we summarize the predictions of the model, and in section 6, we compare them with experiments. The model predicts a number of regimes with different concentration dependence of viscosity. This multiplicity of regimes creates an opportunity to design solutions with desired properties by tuning the key parameters (polymer molecular weight, the number of associating groups per chain, strength of associations, polymer concentration, etc.).

2. Solutions of Sticky Polymers[6]

Consider a solution of polymers with degree of polymerization N and monomer size b. Each polymer contains f associating groups (stickers) separated from each other by soluble sections with degree of polymerization l. We assume that there are many associating groups (stickers) per chain ($f \gg 1$) and that there are many monomers between neighboring stickers ($l \gg 1$). The degree of polymerization of each chain is

$$N = fl \qquad (2.1)$$

We limit our consideration in the present paper to the case of pairwise associations of stickers (Figure 1). This means that each sticker can be in one of two states:
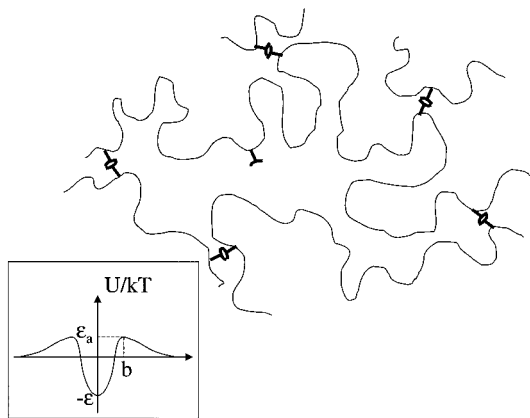
Figure 1. Reversible network with pairwise associating groups. Insert: energy of a pair of stickers as a function of the distance between them (ϵ, binding energy, and ϵ_a, activation barrier).

either "open"—unassociated—or "closed"—associated with another sticker. The fraction of stickers in the associated ("closed") state is denoted by p. The association process is driven by the binding energy ϵkT, where k is the Boltzmann constant and T is the absolute temperature (see insert in Figure 1). A larger binding energy leads to a higher fraction of associated stickers p.

   In addition to the fraction of closed stickers, the dynamics of the reversible networks is controlled by the lifetime of the closed pairs of stickers τ_b. This average time the two stickers spend in the closed state depends both on the binding energy ϵkT and on the additional activation barrier $\epsilon_a kT$

$$\tau_b = \tau_0 \exp(\epsilon + \epsilon_a) \qquad (2.2)$$

where τ_0 is a microscopic time. Note that the activation barrier also slows down the formation of the associated ("closed") state of stickers. A pair of stickers has to spend (on average) time

$$\tau_a = \tau_0 \exp(\epsilon_a) \qquad (2.3)$$

within monomeric distance b of each other before they can associate.

   In the present paper, we limit our consideration to the homogeneous reversible networks and will not study phase separation. We will investigate two types of solvents for the strands between stickers:

   1. The first is good solvents with monomeric excluded volume parameter v on the order of b^3. We do not expect any phase separation of associating polymers in good solvents.

   2. The second is Θ solvents with monomeric three-body interaction parameter $w \sim b^6$. In this case the system is homogeneous at volume fractions ϕ of polymer in solution above the overlap volume fraction ϕ_s of the strands between the stickers

$$\phi > \phi_s \approx \Gamma^{1/2} \quad \Theta \text{ solvent} \qquad (2.4)$$

We will restrict our consideration of associating polymers in Θ solvents to this single-phase concentration regime above the binodal line in the phase diagram.

   Semidilute polymer solutions are characterized by the correlation length[11] ξ. The sections of chains of size ξ with g monomers in each are at the overlap condition with each other at a volume fraction $\phi \approx b^3 g/\xi^3$. The

monomers within each section are interacting mostly with each other, and therefore, the statistics of each section are similar to those of dilute solutions

$$\xi \approx b g^\nu \qquad (2.5)$$

where $\nu = 1/2$ in a Θ solvent and $\nu \approx 0.59$ in a good solvent. The concentration dependence of the correlation length is

$$\xi \approx b \phi^{-\nu/(3\nu-1)} \qquad (2.6a)$$

and the number of monomers in a correlation strand is

$$g \approx \phi^{-1/(3\nu-1)} \qquad (2.6b)$$

The average density of stickers in solution is ϕ/l, and therefore, the a priori probability of finding a sticker next to a given one is ϕ/l for a Θ solvent. In a good solvent, the excluded volume interactions are not screened on length scales smaller than the correlation length ξ. Therefore, there is an additional reduction factor $K(g)$ for bringing two stickers in contact at concentration ϕ. This additional cost is due to excluded volume repulsion of sections containing g monomers[6]

$$K(g) \approx g^{-\nu\Theta_2} \approx g^{3\nu-2-z} \approx \phi^{(2+z-3\nu)/(3\nu-1)} \qquad (2.7)$$

where in a good solvent exponent $\Theta_2 \approx 0.78$ and exponent $z = \nu(3 + \Theta_2) - 2 \approx 0.225$. In a Θ solvent there are no excluded volume interactions, and the reduction factor $K(g) = 1$ (exponent $z = -1/2$ in a Θ solvent). Thus, the a priori probability of two stickers being next to each other is

$$K(g)\phi/l \approx \phi^{(1+z)/(3\nu-1)}/l \qquad (2.8)$$

which is equal to ϕ/l in a Θ solvent and $\phi^{1.59}/l$ in a good solvent. The association parameter x is defined as the product of the probability of finding two stickers next to each other and the statistical weight of pairing. Since there is an energy gain ϵkT for an association between a pair of stickers, there is an additional Boltzmann weight e^ϵ leading to the association parameter

$$x = e^\epsilon K(g)\phi/l \approx e^\epsilon \phi^{(1+z)/(3\nu-1)}/l \qquad (2.9)$$

The Boltzmann weight e^ϵ related to the energy gain of an associated pair of stickers is proportional to an effective attractive volume per sticker, $b^3 e^\epsilon$.

   The fraction p of closed stickers can be expressed[6] in terms of the association parameter x as the solution of the equation $p/(1-p)^2 = x$

$$p = \frac{2x + 1 - \sqrt{4x+1}}{2x} \qquad (2.10)$$

For large values of association parameter $x \gg 1$ the fraction of closed stickers is very close to unity

$$p \approx 1 - 1/\sqrt{x} \quad \text{for } x \gg 1 \qquad (2.11)$$

and almost all stickers are closed. For small values of association parameter $x \ll 1$ the fraction of closed stickers is very low

$$p \approx x \quad \text{for } x \ll 1 \qquad (2.12)$$

and almost all stickers are open.

At high concentrations the association parameter is large, $x \gg 1$, and the fraction of open stickers p_{open} is low and decreases with increasing concentration

$$p_{open} = 1 - p \approx x^{-1/2} \approx l^{1/2} e^{-\epsilon/2} \phi^{-(1+z)/(6\nu-2)} \quad \text{for} \quad \phi > \phi_s \tag{2.13}$$

The above consideration is valid as long as there are no correlations between stickers (it is the mean field approximation). Correlations between stickers can be ignored as long as a given l-strand (connecting neighboring stickers) overlaps with many other strands. This is the case for high polymer volume fractions

$$\phi > \phi_s \tag{2.14}$$

where the overlap volume fraction of l-strands is

$$\phi_s \approx b^3 l/(bl^\nu)^3 \approx l^{1-3\nu} \tag{2.15}$$

and is a typical volume fraction inside an isolated l-strand. This expression (eq 2.15) for the overlap volume fraction of l-strands reduces to eq 2.4 in a Θ solvent with $\nu = 1/2$.

Pairing of adjacent stickers along the chain has to be taken into account below this overlap volume fraction of l-strands (for $\phi < \phi_s$). Recall that we are considering this regime only for good solvents. It is convenient to define the association parameter x_{intra} for neighboring stickers by analogy with the mean field association parameter x (eq 2.9). It is defined as the product of the probability W_0 of contact between two adjacent stickers and the statistical weight of pairing e^ϵ. The probability that two neighboring stickers, separated by l monomers along the chain, get within volume b^3 of each other can be obtained by substituting volume fraction ϕ_s inside an isolated l-strand (eq 2.15) into eq 2.8

$$W_0 \approx \phi_s^{(1+z)/(3\nu-1)}/l \approx l^{2-z} \tag{2.16}$$

Thus, the local association parameter x_{intra} for neighboring stickers is

$$x_{intra} \approx W_0 e^\epsilon \approx e^\epsilon \phi_s^{(1+z)/(3\nu-1)}/l \approx e^\epsilon l^{2-z} \quad \text{for} \quad \phi < \phi_s \tag{2.17}$$

If the local association parameter is small ($x_{intra} < 1$), the local (intrachain) pairing is not important, i.e., interchain association is still determined by parameter x (eq 2.9). Below we focus on the opposite case ($x_{intra} \gg 1$) with high binding energy ϵ

$$e^\epsilon \gg l^{2+z} \tag{2.18}$$

In this case, the effective interchain association parameter x_{inter} is governed by the competition between the interchain and intrachain pairing

$$x_{inter} \approx x/x_{intra} \approx (\phi/\phi_s)^{(1+z)/(3\nu-1)} \tag{2.19}$$

where eqs 2.9 and 2.17 were used to relate the association parameters x and x_{intra} and the corresponding volume fractions ϕ and ϕ_s. A sticker could be either intermolecularly associated (with probability p_{inter}), intramolecularly associated (with probability p_{intra}), or
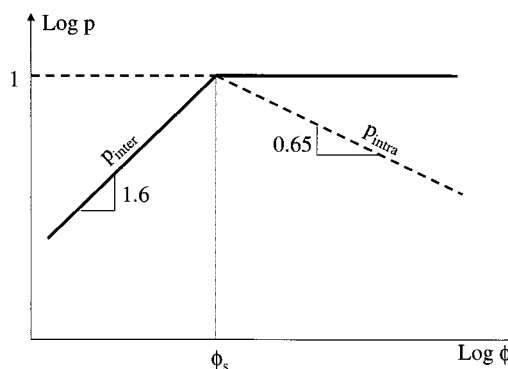

Figure 2. Fraction of interchain associated (p_{inter}) and intrachain associated (p_{intra}) stickers in a good solvent as a function of polymer volume fraction ϕ (logarithmic scales). ϕ_s is the overlap volume fraction for the strands between stickers.

open (with probability p_{open})

$$p_{inter} + p_{intra} + p_{open} = 1 \tag{2.20}$$

The fraction p_{inter} of closed stickers that form interchain bonds is defined by eq 2.10 with association parameter x replaced by the interchain one x_{inter}.[13] For small values of interchain association parameter $x_{inter} < 1$ the fraction of interchain bonds is small (see eq 2.12)

$$p_{inter} \approx x_{inter} \approx (\phi/\phi_s)^{(1+z)/(3\nu-1)} \quad \text{for} \quad \phi < \phi_s \tag{2.21a}$$

For large values of interchain association parameter $x_{inter} > 1$ the fraction of interchain bonds is close to unity (see the solid line in Figure 2 for the volume fraction dependence of p_{inter})

$$p_{inter} \approx 1 \quad \text{for} \quad \phi > \phi_s \tag{2.21b}$$

The fraction p_{intra} of locally paired stickers (involved in intrachain bonds) is close to unity at concentrations below the overlap of strands between stickers (since we have assumed large intrachain association parameter $x_{intra} \gg 1$)

$$p_{intra} \approx 1 \quad \text{for} \quad \phi < \phi_s \tag{2.22a}$$

Above the overlap of strands between stickers, these strands deswell with their size decreasing as $R_l \approx bl^\nu(\phi_s/\phi)^{(\nu-1/2)/(3\nu-1)}$. The fraction p_{intra} of locally paired stickers is determined by the competition between $n \approx R_l^3\phi/(lb^3)$ stickers overlapping with a given strand and a few stickers adjacent along the chain (see the dashed line in Figure 2)

$$p_{intra} \approx 1/n \approx (\phi_s/\phi)^{1/(6\nu-2)} \quad \text{for} \quad \phi > \phi_s \tag{2.22b}$$

At lower concentrations the fraction of open stickers p_{open} is determined by the competition between open stickers and intrachain bonds

$$p_{open} \approx x_{intra}^{-1/2} \approx e^{-\epsilon/2} l^{1+z/2} \quad \text{for} \quad \phi < \phi_s \tag{2.23a}$$

The volume fraction of open stickers is $\phi_{open} = p_{open}\phi/l$ and at lower concentrations it is equal to

$$\phi_{open} = p_{open}\phi/l \approx \phi l^{z/2} e^{-\epsilon/2} \quad \text{for} \quad \phi < \phi_s \tag{2.24a}$$

At higher concentrations the fraction p_{open} of open stickers is defined in eq 2.13

$$p_{\text{open}} \approx x^{-1/2} \approx e^{-\epsilon/2} l^{1/2} \phi^{-(1+z)/(6\nu-2)} \quad \text{for } \phi > \phi_s \quad (2.23b)$$

The volume fraction of open stickers at higher concentrations is

$$\phi_{\text{open}} = p_{\text{open}} \phi/l \approx l^{-1/2} e^{-\epsilon/2} \phi^{1-(1+z)/(6\nu-2)} \quad \text{for } \phi > \phi_s \quad (2.24b)$$

This volume fraction of open stickers increases as $\phi_{\text{open}} \sim \phi^{0.5}$ in Θ solvents and as $\phi_{\text{open}} \sim \phi^{0.28}$ in good solvents.

Intrachain bonds do not contribute to the formation of the network, and only interchain bonds with fraction p_{inter} are important for gelation. The mean field prediction for gelation threshold is

$$p_{\text{inter}} = p_g = 1/(f-1) \quad (2.25)$$

This equation is valid for a large number of stickers per chain $f \gg 1$, i.e., when $p_g \approx 1/f \ll 1$.[14] The volume fraction ϕ_g at the gelation transition in Θ solvents (see eq 2.21a with $\nu = 1/2$, $z = -1/2$) is

$$\phi_g \approx 1/(f l^{1/2}) \quad \Theta \text{ solvent} \quad (2.26)$$

Note that $\phi_g \ll \phi_s$ since $f \gg 1$ and $\phi_s \approx l^{-1/2}$ in Θ solvents. Hence a strong reversible network structure exists in Θ solvents in the concentration regime specified by the homogeneity condition (eq 2.4).

In good solvents the gelation concentration can be estimated from eqs 2.21a and 2.25

$$\phi_g \approx l^{1-3\nu} f^{(1-3\nu)/(1+z)} \approx l^{-0.77} f^{-0.63} \quad \text{good solvent} \quad (2.27)$$

with the strong association condition (eq 2.18) assumed.

3. Sticky Rouse Model[7]

The sticky Rouse model describes the dynamics of unentangled solutions of associative polymers well above the gelation point. Each closed sticker, involved in the interchain association, acts as an effective friction center with the friction coefficient proportional to the bond lifetime τ_b. There are $f p_{\text{inter}}$ such interchain associated stickers, where f is the total number of stickers per chain and p_{inter} is the fraction of them involved in the interchain associations. Recall that we have assumed strong associations (eq 2.18) $e^{\epsilon} > l^{2+z}$ and the fraction p_{inter} of interchain associated stickers in this case is defined by eq 2.21

$$p_{\text{inter}} \approx (\phi/\phi_s)^{(1+z)/(3\nu-1)} \approx l^{1+z} \phi^{(1+z)/(3\nu-1)} \quad \text{for } \phi < \phi_s \quad (3.1a)$$

$$p_{\text{inter}} \approx 1 \quad \text{for } \phi > \phi_s \quad (3.1b)$$

The increase of p_{inter} with concentration for $\phi < \phi_s$ due to the conversion of the intrachain associated bonds into the interchain associated ones is $p_{\text{inter}} \sim \phi^{1.6}$ in a good solvent (see the solid line in Figure 2). Recall that in a Θ solvent we consider only concentrations above the overlap of strands between neighboring stickers (condition 2.4). Above the overlap concentration ϕ_s of the strands between neighboring stickers (eq 2.15) most of the neighbors of a typical sticker belong to different chains and most of the stickers are involved in the interchain association.

The relaxation time of the unentangled solution of associating polymers well above the gel point is the sticky Rouse time of chains τ_{Rouse}. This sticky Rouse time is equal to the lifetime of a bond τ_b times the square of the number of interchain bonds per polymer

$$\tau_{\text{Rouse}} \approx \tau_b (f p_{\text{inter}})^2 \approx \tau_b f^2 l^{2+2z} \phi^{(2+2z)/(3\nu-1)} \quad \text{for } \phi < \phi_s \quad (3.2a)$$

$$\tau_{\text{Rouse}} \approx \tau_b (f p_{\text{inter}})^2 \approx \tau_b f^2 \quad \text{for } \phi > \phi_s \quad (3.2b)$$

The modulus at the Rouse time τ_{Rouse} is kT per chain (kT times the number density of chains)

$$G_1 \approx kT\phi/(b^3 N) \quad (3.3)$$

The viscosity of the unentangled solution of associating polymers is proportional to the product of the modulus G_1 and the sticky Rouse time τ_{Rouse}

$$\eta \approx G_1 \tau_{\text{Rouse}} \approx (kT\tau_b/b^3) N f^2 l^{2z} \phi^{1+(2+2z)/(3\nu-1)} \quad \text{for } \phi < \phi_s \quad (3.4a)$$

$$\eta \approx G_1 \tau_{\text{Rouse}} \approx (kT\tau_b/b^3) N f^2 \phi \quad \text{for } \phi > \phi_s \quad (3.4b)$$

The nontrivial concentration dependence of viscosity is for $\phi < \phi_s$ with $\eta \sim \phi^{4.2}$ in a good solvent. This behavior is due to the exchange of intra- into intermolecular associations.

3.1. Renormalization of Bond Lifetime. The above results assume that when the bond breaks and the sticker separates from its partner it can always find an open sticker different from its previous partner. In ref 6, it was shown that since most stickers are closed, being involved in either interchain or intrachain associations, the concentration ϕ_{open} of open stickers is very low (see eq 2.24). Therefore, the most likely scenario is that the sticker, having unsuccessfully searched for a new partner, associates again with its old one, prolonging the effective lifetime of the same bond. The renormalized lifetime of the bond consists of many bond-breaking events followed by the formation of a bond between the same two stickers until at least one of them finds a new partner. It is therefore reciprocally proportional to the probability of finding a new open sticker in the volume V_{strand} explored by a sticker during its open state

$$\tau_b^* \approx \tau_b b^3/(\phi_{\text{open}} V_{\text{strand}}) \quad (3.5)$$

For an unentangled strand between neighboring closed stickers containing $L < N_e$ monomers, the volume sampled by an open sticker is on the order of the cube of the size of this strand.

$$V_{\text{strand}} \approx (R_{\text{strand}})^3 \quad (3.6)$$

The size of the strand containing L monomers in a semidilute solution is

$$R_{\text{strand}} \approx b g^\nu (L/g)^{1/2} \approx bL^{1/2} \phi^{-(\nu-1/2)/(3\nu-1)} \quad (3.7)$$

The number of monomers between interchain associated

stickers is

$$L = l/p_{inter} \approx l(\phi_s/\phi)^{(1+z)/(3\nu-1)} \quad \text{for } \phi < \phi_s \quad (3.8a)$$

$$L = l/p_{inter} \approx l \quad \text{for } \phi > \phi_s \quad (3.8b)$$

Combining eqs 3.5–3.8 one obtains the renormalized lifetime of a bond

$$\tau_b^* \approx \tau_b e^{\epsilon/2} l^z \phi^{(2+3z)/[2(3\nu-1)]} \quad \text{for } \phi < \phi_s \quad (3.9a)$$

$$\tau_b^* \approx \tau_b e^{\epsilon/2} l^{-1} \phi^{z/[2(3\nu-1)]} \quad \text{for } \phi > \phi_s \quad (3.9b)$$

Note that renormalized bond time in regime $\phi > \phi_s$ increases with concentration as $\tau_b^* \sim \phi^{0.15}$ in good solvents, while it decreases with concentration as $\tau_b^* \sim \phi^{-0.5}$ in Θ solvents. The reason for this difference in behavior is that the volume fraction of open stickers ϕ_{open} in Θ solvents increases more strongly with concentration than in good solvents (eq 2.24). The volume of the strand V_{strand} does not change with concentration in Θ solvents, while it decreases in good solvents. Therefore, the probability of finding an open sticker within the volume of the strand increases with concentration in Θ solvents but decreases in good solvents.

This renormalization of bond lifetime is important if $\tau_b^* > \tau_b$, which is the case for $\phi > \phi_{ren}$ where the crossover concentration ϕ_{ren} is defined by the condition $\tau_b^* = \tau_b$

$$\phi_{ren} \approx (e^{-\epsilon} l^{-2z})^{(3\nu-1)/(2+3z)} \quad (3.10)$$

Note that $\phi_{ren} < \phi_s$ in the regime of strong association (eq 2.18).

We have assumed that when the bond between two stickers breaks, both stickers typically explore the whole volume accessible to them (the strand volume V_{strand}) before they reassociate again. This condition can be reformulated in the following way: we require that the number $\mathcal{N}$ of attempted contacts of an open sticker with its previous partner during the strand relaxation time is much smaller than $\exp(\epsilon_a)$. This condition is satisfied if $\phi > \phi_{ren}$ and

$$\exp(\epsilon_a) > l^{1/2} \quad (3.11)$$

provided that inequality 2.18 is satisfied.

The relaxation time and viscosity of unentangled associating solutions can be obtained from eqs 3.2 and 3.4 by replacing the bond lifetime τ_b by the renormalized bond lifetime τ_b^*. The relaxation time in this case is

$$\tau_{Rouse} \approx \tau_b N^2 e^{\epsilon/2} l^{3z} \phi^{(6+7z)/[2(3\nu-1)]} \quad \text{for } \phi < \phi_s \quad (3.12a)$$

$$\tau_{Rouse} \approx \tau_b N^2 e^{\epsilon/2} l^{-3} \phi^{z/[2(3\nu-1)]} \quad \text{for } \phi > \phi_s \quad (3.12b)$$

and the zero-shear-rate viscosity is

$$\eta \approx (kT\tau_b/b^3) Ne^{\epsilon/2} l^{3z} \phi^{1+(6+7z)/[2(3\nu-1)]} \quad \text{for } \phi < \phi_s \quad (3.13a)$$

$$\eta \approx (kT\tau_b/b^3) Ne^{\epsilon/2} l^{-3} \phi^{1+z/[2(3\nu-1)]} \quad \text{for } \phi > \phi_s \quad (3.13b)$$

The prediction of the concentration dependence of viscosity in the sticky Rouse model with renormalized
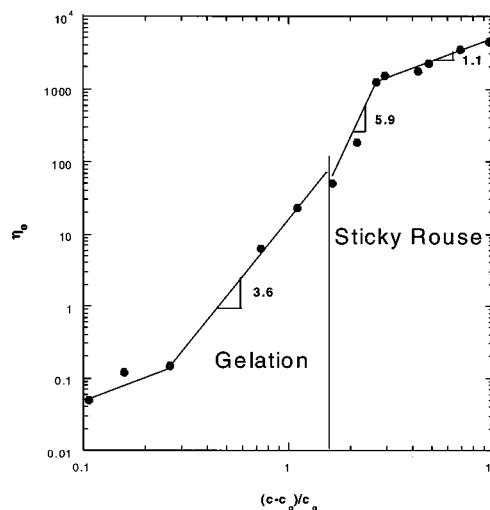

Figure 3. Viscosity η_0 (Pa·S) of poly(ethylene oxide)-*b*-poly-(propylene oxide)-*b*-poly(ethylene oxide)-*g*-poly(acrylic acid) as a function of relative concentration above the gel point ($c - c_g$)/c_g. The concentration behavior in the gelation regime (for ($c - c_g$)/c_g < 1) is consistent with eq 3.14. At higher concentrations the data is consistent with two sticky Rouse regimes (eq 3.13).

bond lifetime is $\eta \sim \phi^{5.9}$ for $\phi < \phi_s$ in a good solvent. For $\phi > \phi_s$, it is $\eta \sim \phi^{1.15}$ in a good solvent and $\eta \sim \phi^{0.5}$ in a Θ solvent.

Recall that closer to the gel point the viscosity was predicted (see ref 7) to increase as

$$\eta \sim [(\phi - \phi_g)/\phi_g]^{3.55} \quad (3.14)$$

Further away from the gel point (for $\phi - \phi_g > \phi_g$) the dynamics of unentangled solutions of associating polymers follows sticky Rouse model with viscosity described by eq 3.13. These predictions of gelation and the two sticky Rouse regimes are compared with experimental data[15] on poly(acrylic acid) modified by pluronic in Figure 3. The predictions of the model are in very good agreement with experiments.

4. Sticky Reptation

4.1. Tube Model. In the present paper, we limit our consideration to entangled reversible networks well above the gelation transition at concentrations $\phi \gg \phi_g$. Solutions of associating polymers near the gelation transition (with $\phi \approx \phi_g$) as well as unentangled associating solutions above the transition were described in ref 7 and reviewed in section 3 above.

Entangled polymer solutions can be characterized by the number of monomers between entanglements[11,12] that depends on polymer volume fraction $N_e(\phi)$. The tube diameter is

$$a \approx \xi(N_e(\phi)/g)^{1/2} \quad (4.1)$$

where ξ is the static correlation length (see eq 2.6a). The plateau modulus due exclusively to entanglements is

$$G_0 \approx kT\phi/(b^3 N_e(\phi)) \quad (4.2)$$

In a good solvent, the number of monomers between entanglements $N_e(\phi)$ is proportional to the number of

monomers in a correlation volume, $g \approx \phi^{-(3\nu-1)}$ (see eq 2.6b)

$$N_e(\phi) \approx gN_{e0} \approx N_{e0}\phi^{-1/(3\nu-1)} \quad \text{good solvent} \qquad (4.3)$$

where N_{e0} is the number of monomers between entanglements in a melt. The tube diameter in a good solvent is

$$a \approx bN_{e0}^{1/2}\phi^{-\nu/(3\nu-1)} \quad \text{good solvent} \qquad (4.4)$$

and the plateau modulus is

$$G_0 \approx \frac{kT}{b^3 N_{e0}}\phi^{3\nu/(3\nu-1)} \quad \text{good solvent} \qquad (4.5)$$

In Θ solvents the correlation length is still given by eq 2.6a, $\xi \approx b/\phi$, but it is controlled by the three-body interactions. The entanglements are still controlled by the two-body interactions, and therefore, the entanglement length (tube diameter) is[16,17]

$$a \approx bN_{e0}^{1/2}\phi^{-2/3} \quad \Theta \text{ solvent} \qquad (4.6)$$

and the number of monomers between entanglements is

$$N_e \approx N_{e0}/\phi^{4/3} \quad \Theta \text{ solvent} \qquad (4.7)$$

The plateau modulus in Θ solvents is[16]

$$G_0 \approx \frac{kT}{a^2\xi} = \frac{kT}{b^3 N_{e0}}\phi^{7/3} \quad \Theta \text{ solvent} \qquad (4.8)$$

4.2. Sticky Reptation: General Equations. The sticky Rouse model reviewed in section 3 can be generalized to solutions of entangled associating polymers. In order for chains to be entangled and reptate along their tubes, there should be many entanglements per chain $N > N_e$, and the solution should be above the entanglement concentration

$$\phi_e \approx (N_{e0}/N)^{3\nu-1} \quad \text{good solvent} \qquad (4.9)$$

In many cases, sticky reptation of associating polymers can be considered as a sticky Rouse motion along the contour of the tube.[4] The reptation time τ_{rep} is the Rouse time $\tau_{Rouse} \approx \tau_b^*(fp_{inter})^2$ times the number of entanglements per chain N/N_e

$$\tau_{rep} \approx \tau_{Rouse}N/N_e \approx \tau_b^*(fp_{inter})^2 N/N_e \qquad (4.10)$$

The zero-shear viscosity is $\eta \approx G_0\tau_{rep}$, i.e.

$$\eta \approx \frac{kT}{b^3}\frac{\phi N}{N_e^2}(fp_{inter})^2\tau_b^* \qquad (4.11)$$

where $N_e = N_e(\phi)$. The above results are independent of whether the strands between neighboring interchain associations are entangled or not (whether $L = l/p_{inter} > N_e$ or $L < N_e$).

4.3. Good Solvent. 4.3.1. Unrenormalized Bond Lifetime. Let us first consider the case of unrenormalized bond lifetime $\tau_b^* \approx \tau_b$, i.e., the concentration range $\phi_e < \phi < \phi_{ren}$.

The reptation time in this case is defined by eq 4.10 where the fraction of interchain associated stickers p_{inter} is given by eq 2.21 (or eq 3.1).

$$\tau_{rep} \approx \tau_b f^2(N/N_{e0})f^{2+2z}\phi^{(3+2z)/(3\nu-1)} \quad \text{for } \phi_e < \phi < \phi_{ren} \qquad (4.12)$$

The viscosity in a good solvent is

$$\eta \approx G_0\tau_{rep} \approx (kT\tau_b/b^3)f^2(N/N_{e0}^2)f^{2+2z}\phi^{(3+3\nu+2z)/(3\nu-1)} \quad \text{for } \phi_e < \phi < \phi_{ren} \quad (4.13)$$

The concentration dependence of the viscosity in a good solvent is

$$\eta \sim \phi^{6.78} \quad \text{for } \phi_e < \phi < \phi_{ren} \qquad (4.14)$$

Note that $\phi_{ren} < \phi_s$ (see eqs 3.10 and 2.18).

4.3.2. Renormalized Bond Lifetime: Unentangled Strands. The effective (renormalized) bond lifetime crucially depends on the dynamics of strands between neighboring interchain associations. If the strands are not entangled (i.e., if $L < N_e$, where $L = l/p_{inter}$ and $N_e = N_e(\phi)$), then their dynamics are described by the sticky Rouse model. The renormalized bond lifetime τ_b^* is given in eq 3.9.

The entanglement concentration ϕ_e is typically higher than gelation concentration ϕ_g because

$$\phi_e/\phi_g \approx (N_{e0}/f^{1/(1+z)})^{3\nu-1} > 1 \qquad (4.15)$$

as long as $f < N_{e0}^{1+1/z}$. This condition is not very restrictive because typical $N_{e0} \sim 50$ and the exponent $1+1/z \approx 5.44$. The condition (4.15) therefore amounts to $f < 10^9$ and is assumed to be satisfied. The number of monomers between interchain associations $L \approx N(\phi_g/\phi)^{(1+z)/(3\nu-1)}$ decreases with concentration faster than the number of monomers between entanglements $N_e(\phi) \approx N(\phi_e/\phi)^{1/(3\nu-1)}$. Therefore, the condition $L < N_e$ is satisfied in the range of concentrations between gelation and strand overlap (eqs 2.27 and 2.15) $\phi_g < \phi < \phi_s$ provided that $f \ll N_{e0}^{1+1/z}$.

Yet the strands between interchain bonds might become entangled above the strand overlap concentration ϕ_s. In this case the strand entanglement concentration is defined by the condition $L = N_e(\phi_{le})$ (note that $L \approx l$ since $\phi > \phi_s$)

$$\phi_{le} \approx (N_{e0}/l)^{3\nu-1} \qquad (4.16)$$

In the concentration range $\phi_s < \phi < \phi_{le}$, the strands of l monomers between interchain bonds are unentangled.

Substituting p_{inter} and τ_b^* from eqs 3.1 and 3.9 into eq 4.10 one obtains the reptation time for entangled solutions of associating polymers with unentangled strands between interchain bonds ($\phi < \phi_{le}$)

$$\tau_{rep} \approx \tau_b e^{\epsilon/2}f^2(N/N_{e0})f^{2+3z}\phi^{(4+3.5z)/2(3\nu-1)} \quad \text{for } \phi_{ren} < \phi < \phi_s \quad (4.17a)$$

$$\tau_{rep} \approx \tau_b e^{\epsilon/2}f^2(N/N_{e0})l^{-1}\phi^{(1+z/2)/(3\nu-1)} \quad \text{for } \phi_s < \phi < \phi_{le} \quad (4.17b)$$

The viscosity of these solutions is

$$\eta \approx (kT\tau_b/b^3)e^{\epsilon/2}f^2(N/N_{e0}^2)l^{2+3z}\phi^{(4+3\nu+3.5z)/(3\nu-1)}$$
$$\text{for } \phi_{ren} < \phi < \phi_s \quad (4.18a)$$

$$\eta \approx (kT\tau_b/b^3)e^{\epsilon/2}(f^3/N_{e0}^2)\phi^{(1+3\nu+z/2)/(3\nu-1)}$$
$$\text{for } \phi_s < \phi < \phi_{le} \quad (4.18b)$$

The concentration dependence of the viscosity in a good solvent is

$$\eta \sim \phi^{8.52} \quad \text{for } \phi_{ren} < \phi < \phi_s \quad (4.19a)$$

$$\eta \sim \phi^{3.75} \quad \text{for } \phi_s < \phi < \phi_{le} \quad (4.19b)$$

Various concentrations regimes are summarized in Figure 4.

These results are valid if the number N of attempted contacts during the strand relaxation time is smaller than $\exp(\epsilon_a)$ which is true if $\exp(\epsilon_a) > l^{1/2}$ (see eq 3.11). Note that

$$N \approx (b^3/V_{strand})K(g)(\tau_{strand}/\tau_0) \quad (4.20)$$

where

$$\tau_{strand} \approx \tau_0\,\xi^3\,(L/g)^2 \approx \tau_0\,g^{3\nu-2}\,L^2 \quad (4.21)$$

is the strand Rouse relaxation time and

$$V_{strand} \approx \xi^3\,(L/g)^{3/2} \quad (4.22)$$

is the strand volume. Therefore

$$N \approx l^{1/2}p_{inter}^{-1/2}\,g^{3\nu-z-5/2} \quad (4.23)$$

always increases with concentration, so that max $N \approx l^{1/2}$ is attained at $\phi = 1$.

4.3.3. Renormalized Bond Lifetime: Entangled Strands. Consider the most interesting case of associating solutions with entangled strands between neighboring interchain bonds ($L > N_e$), i.e., the regime $\phi > \phi_{le}$.

The renormalized lifetime of a bond τ_b^* (eq 3.5) can be written in a more general way

$$\tau_b^* \approx \kappa\tau_b/\phi_{open} \quad (4.24)$$

where κ is the a priori (geometrical) probability of contact between an open sticker and its previous partner. In the case of an unentangled strand between neighboring closed stickers $L < N_e$, this probability is approximately equal to the ratio of the "contact volume" b^3 and the whole strand volume V_{strand} accessible to both stickers $\kappa \approx b^3/V_{strand}$; i.e., eq 3.5 is recovered.

In the case of entangled strands between neighboring closed stickers $L > N_e$, the situation is more complicated. We have to take into account that the regions accessible to both stickers are (1) different, though partially overlapping and (2) nonspherical.

In fact each sticker is confined to a tube with diameter $a \approx \xi\,(N_e/g)^{1/2}$ (eq 4.1). Each strand is confined to its own tube and the stickers are fluctuating along the confining tubes of their respective strands (see Figure 5). A typical fluctuation of each sticker along its respective confining tube is on the order of the strand size
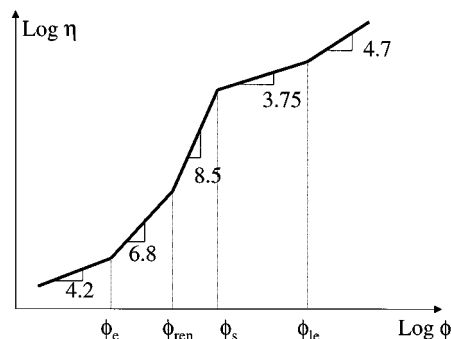
$$R_{strand} \approx \xi\,(L/g)^{1/2} \quad (4.25)$$

Figure 4. Concentration dependence of viscosity of entangled reversible networks in a good solvent (logarithmic scales).
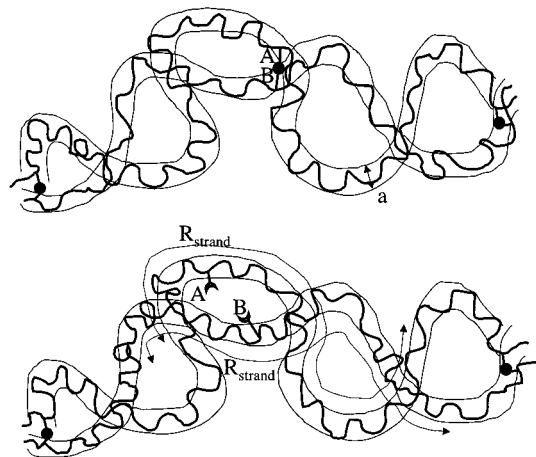

Figure 5. Entangled strands between associated groups. (a) Stickers A and B are in an associated state. (b) The bond between stickers A and B is broken. Each sticker fluctuates by distance R_{strand} along the contour of its tube. Stickers can reassociate if they meet in the common volumes of both tubes.

Note that these fluctuations are larger than the tube diameter $R_{strand} > a$ since $L > N_e$. Therefore, the volume accessible to each sticker is on the order of

$$V_{tube} \approx a^2 R_{strand} \quad (4.26)$$

The stickers are fluctuating along different tubes (see Figure 5), and the common volume accessible to both stickers is the intersection of the two tube fragments explored by the stickers. The tubes are Gaussian on scales larger than a and the number of contacts between overlapping Gaussian tubes is roughly equal to $n^{1/2}$, where $n \approx R_{strand}/a$ is the number of primitive steps per tube. Thus, the two old partners can meet again in any of $n^{1/2} \approx (R_{strand}/a)^{1/2}$ common primitive segments of volume a^3 each. The probability for one sticker to be inside a particular primitive volume during its fluctuations along the tube is a^3/V_{tube}. The probability for both old partners to be in a particular primitive volume is $(a^3/V_{tube})^2$. The probability that both stickers are in one of $n^{1/2} \approx (R_{strand}/a)^{1/2}$ common primitive volumes is $(a^3/V_{tube})^2(R_{strand}/a)^{1/2}$. The a priori probability of contact between two stickers, given that they are both in a particular common primitive volume, is b^3/a^3. Hence the a priori probability of contact between an open sticker and its old partner, while both are fluctuating along their respective confining tubes is

$$\kappa \approx (a^3/V_{tube})^2(R_{strand}/a)^{1/2}(b^3/a^3) \approx b^3/(aR_{strand})^{3/2}$$
$$(4.27)$$

In a good solvent this a priori probability is

$$\kappa \approx (l\,N_{e0})^{-3/4}\phi^{(3\nu-3/4)/(3\nu-1)} \qquad (4.28)$$

where we have used $L \approx l$ in the concentration range $\phi_s < \phi_{le} < \phi$. Substituting this a priori probability (eq 4.28) into the expression for renormalized lifetime of a bond (eq 4.24) and using eq 2.24b for ϕ_{open}, we obtain

$$\tau_b{}^* \approx \tau_b e^{\epsilon/2}\Gamma^{1/4}(N_{e0})^{-3/4}\phi^{(3+2z)/[4(3\nu-1)]} \qquad (4.29)$$

We need to check the condition

$$\exp(\epsilon_a) \gg \mathcal{N} \qquad (4.30)$$

The number of attempted contacts is modified from eq 4.20

$$\mathcal{N} \approx \kappa K(g)\tau_{strand}/\tau_0 \qquad (4.31)$$

where τ_{strand} is the relaxation time of a strand confined in a tube; i.e., τ_{strand} is its Rouse relaxation time defined in eq 4.21. Hence we get the following condition (rewriting condition 4.30 for $\phi = 1$)

$$\exp(\epsilon_a) \gg l^{5/4}(N_{e0})^{-3/4} \qquad (4.32)$$

Combining it with inequality 3.11, we get the general condition of applicability of the above theory (note that this condition is actually necessary for $\phi = 1$; at lower concentrations a weaker condition is necessary):

$$\exp(\epsilon_a) > \max(l^{1/2}, l^{5/4}(N_{e0})^{-3/4}) \qquad (4.33)$$

The reptation time (eq 4.10) is equal to

$$\tau_{rep} \approx \tau_b l^{3/4}(N_{e0})^{-7/4}f^3 e^{\epsilon/2}\phi^{(7/4+z/2)/(3\nu-1)} \quad \text{for } \phi_{le} < \phi < 1 \qquad (4.34)$$

The viscosity is equal to

$$\eta \approx (kT\tau_b/b^3)l^{3/4}(N_{e0})^{-11/4}f^3 e^{\epsilon/2}\phi^{(7/4+3\nu+z/2)/(3\nu-1)}$$
$$\text{for } \phi_{le} < \phi < 1 \quad (4.35)$$

The concentration dependence of the viscosity for associating polymers in good solvents with entangled strands between reversible bonds is

$$\eta \sim \phi^{4.72} \quad \text{for } \phi_{le} < \phi < 1 \qquad (4.36)$$

4.4. Θ Solvents. The sticky reptation of associating polymers in Θ solvents can be analyzed in exactly the same way as for good solvents. The results can be obtained using the expression for the number of monomers between entanglements for Θ solvents (eq 4.7) instead of the one for good solvents (eq 4.3) and setting the values of the exponents in Θ solvents $\nu = {}^1/_2$ and $z = -{}^1/_2$. We still assume strong association condition (eq 2.18) which reduces to $e^\epsilon \gg l^{3/2}$. This condition ensures that $\phi_{ren} < \phi_s$ (note that from eq 3.10 it follows that $\phi_{ren} \approx le^{-\epsilon}$); i.e., the renormalization of the bond lifetime is always important in the region of interest (eq 2.4). The condition of quasi-equilibrium (inequality 4.33) stays unchanged.

The renormalized bond lifetime (eqs 3.9b and 4.24) for associating solutions in Θ solvents with unentangled strands between stickers

$$\tau_b{}^* \approx \tau_b e^{\epsilon/2}\Gamma^{-1}\phi^{-1/2} \quad \phi_s < \phi < \phi_{le} \qquad (4.37a)$$

and for entangled strands between stickers it is

$$\tau_b{}^* \approx \tau_b e^{\epsilon/2}\Gamma^{-1}\phi^{1/2}(l/N_{e0})^{3/4} \quad \phi_{le} < \phi < 1 \qquad (4.37b)$$

The entanglement volume fraction of strands between stickers is

$$\phi_{le} \approx (N_{e0}/l)^{3/4} \qquad (4.38)$$

The reptation time (eq 4.10) is

$$\tau_{rep} \approx (\tau_b/N_{e0})\,e^{\epsilon/2}\,f^3\phi^{5/6} \quad \max(\phi_e,\phi_s) < \phi < \phi_{le} \quad (4.39a)$$

for unentangled strands between stickers and

$$\tau_{rep} \approx (\tau_b/N_{e0})e^{\epsilon/2}f^3(l/N_{e0})^{3/4}\phi^{11/6} \quad \phi_{le} < \phi < 1 \quad (4.39b)$$

for entangled strands between stickers. The polymer entanglement volume fraction is

$$\phi_e \approx (N_{e0}/N)^{3/4} \qquad (4.40)$$

It is clear that the second regime is only possible if $\phi_{le} < 1$. If the strands between stickers are shorter than entanglement strands in a melt ($l < N_{e0}$) then $\phi_{le} > 1$ and only the first regime (eqs 4.37a and 4.39a) is realized. A similar simple rule should be also applied to all regimes considered above for good solvents.

The viscosity in Θ solvents is equal to $\eta \approx G_0\tau_{rep}$, where G_0 is given by eq 4.8. In the case of unentangled strands between stickers viscosity is

$$\eta \approx kT\tau_b/(b^3 N_{e0}{}^2)\,e^{\epsilon/2}\,f^3\,\phi^{19/6} \quad \max(\phi_e,\phi_s) < \phi < \phi_{le} \qquad (4.41a)$$

while in the case of entangled strands between stickers it is

$$\eta \approx kT\tau_b/(b^3 N_{e0}{}^2)\,e^{\epsilon/2}\,f^3\,(l/N_{e0})^{3/4}\,\phi^{25/6} \quad \phi_{le} < \phi < 1 \qquad (4.41b)$$

The concentration dependence of viscosity in these two regimes is $\eta \sim \phi^{3.17}$ and $\eta \sim \phi^{4.17}$.

5. Summary

In the present paper, we have developed a model for the dynamics of solutions of entangled associating polymers in both good and Θ solvents. Entanglements significantly modify rheological properties of polymer solutions, such as molecular weight and concentration dependencies of relaxation times and viscosities. The molecular weight dependence of viscosity changes from linear in unentangled solutions to a much stronger power (theoretically $\eta \sim M^3$) in entangled ones.[11,12] The molecular weight dependence is the same in associating and unassociating solutions. The concentration dependence of viscosity of ordinary (nonassociating) polymers[16] changes from $\eta \sim \phi^{1/(3\nu-1)}$ in unentangled semidilute solutions ($\eta \sim \phi^{1.3}$ for a good solvent and $\eta \sim \phi^2$ in a Θ solvent) to a stronger dependence in entangled solutions ($\eta \sim \phi^{3/(3\nu-1)} \sim \phi^{3.9}$ in good solvents and $\eta \sim \phi^{4.7}$ in Θ solvents). There are three different classes of relaxation modes in ordinary entangled polymer solutions. The dynamics is nondraining Zimm-like on length scales up to correlation length ξ. It is draining Rouse-like on

length scales between correlation length ξ and tube diameter a. On length scales larger than tube diameter a, the dynamics is reptation-like.

The process of breaking and reforming reversible bonds dominates the dynamics of solutions of associating polymers. On time scales shorter than the lifetime of these reversible bonds τ_b, the solution behaves as a network. As bonds break and reform, the network rearranges and begins to flow. Intermolecular associations (sticky points) act as dissipative friction centers dominating the long time dynamics. Thus, the sticky Rouse model describes the dynamics of the unentangled solutions of associating polymers, while the sticky reptation model describes the dynamics of the entangled solutions.

There are two important phenomena that need to be accounted for in the dynamics of associating polymers.

1. Transformation of intramolecular associations into intermolecular ones with increasing concentration. This process leads to strong increase of the number of "sticky" points per chain and therefore to strong concentration dependence of relaxation time and viscosity. The transformation of intra- into intermolecular associations occurs at volume fractions $\phi < \phi_s$ below the overlap of strands between stickers. We consider this regime only in good solvents, because in Θ solvents it corresponds to a phase-separated state.

2. Renormalization of the lifetime of an association (bond) due to the deficit of new partners and multiple returns of a sticker to its old partner. The renormalized lifetime of the closed state of a sticker increases with concentration in a good solvent, but decreases with increasing concentration in a Θ solvent. Renormalization of the lifetime of a bond is important at volume fractions $\phi > \phi_{ren}$ (eq 3.10).

There are three sticky Rouse regimes of unentangled associating polymers in a good solvent with the following expressions for viscosity.

(i) The first is sticky Rouse in a good solvent with unrenormalized bond lifetime (eq 3.4a)

$$\eta \approx (kT\tau_b/b^3)Nl^{0.45}\phi^{4.2} \quad \text{for } \phi < \phi_{ren} \qquad (5.1)$$

Strong concentration dependence of viscosity in this regime is due to the transformation of intramolecular bonds into intermolecular ones.

(ii) The second is sticky Rouse in a good solvent with renormalized bond lifetime in the concentration regime corresponding to the transformation of intramolecular bonds into intermolecular ones. (eq 3.13a)

$$\eta \approx (kT\tau_b/b^3)Ne^{\epsilon/2}l^{0.675}\phi^{5.9} \quad \text{for } \phi_{ren} < \phi < \phi_s \qquad (5.2)$$

iii) sticky Rouse in a good solvent with renormalized bond lifetime and mostly intermolecular bonds (eq 3.13b)

$$\eta \approx (kT\tau_b/b^3)Ne^{\epsilon/2}I^{-3}\phi^{1.1} \quad \text{for } \phi_s < \phi < \phi_e \qquad (5.3)$$

Note that as soon as most bonds become intermolecular, the concentration dependence becomes very weak.

In a Θ solvent, one can have only one unentangled regime with renormalized bond lifetime and mostly intermolecular bonds $\eta \approx (kT\tau_b/b^3)Ne^{\epsilon/2}I^{-3}\phi^{0.5}$ (see eq 3.13b).

The unentangled sticky Rouse regimes are restricted to a relatively narrow concentration range (of about 1 decade) between the gelation transition and entanglement concentration ($2\phi_g < \phi < \phi_e$) (see, for example, Figure 3).

At higher concentrations ($\phi > \phi_e$) polymers are entangled and their dynamics are described by the sticky reptation model. In addition to three regimes in a good solvent similar to the ones described above for the sticky Rouse model (regimes i–iii), there is an additional fourth regime with entangled strands between stickers.

(i) The first is sticky reptation in a good solvent with unrenormalized bond lifetime (eq 4.13)

$$\eta \approx (kT\tau_b/b^3)(N^3/N_{e0}^2)l^{0.45}\phi^{6.8} \quad \text{for } \phi_e < \phi < \phi_{ren} \qquad (5.4)$$

(ii) The second is sticky reptation in a good solvent with renormalized bond lifetime in the concentration regime corresponding to the transformation of intramolecular bonds into intermolecular ones (eq 4.18)

$$\eta \approx (kT\tau_b/b^3)e^{\epsilon/2}(N^3/N_{e0}^2)l^{0.675}\phi^{8.52} \quad \text{for } \phi_{ren} < \phi < \phi_s \qquad (5.5)$$

(iii) The third is sticky reptation in a good solvent with renormalized bond lifetime and mostly intermolecular bonds (eq 4.18b)

$$\eta \approx (kT\tau_b/b^3)e^{\epsilon/2}(N^3/N_{e0}^2)I^{-3}\phi^{3.75} \quad \text{for } \phi_s < \phi < \phi_{le} \qquad (5.6)$$

This is the regime with overlapping, but not entangled, strands between stickers. As in the case of the sticky Rouse model, the concentration dependence of viscosity becomes weaker as soon as most bonds are intermolecular (for $\phi > \phi_s$).

(iv) Finally, there is sticky reptation in a good solvent with renormalized bond lifetime and entangled strands between stickers.

$$\eta \approx (kT\tau_b/b^3)(N^3/N_{e0}^2)(N_{e0}\,I^3)^{-3/4}e^{\epsilon/2}\phi^{4.72}$$
$$\text{for } \phi_{le} < \phi < 1 \quad (5.7)$$

The concentration dependence of the viscosity is stronger in this regime than in regime iii because in regime iv volume V_{tube} accessible to an open sticker in its confining tube (eq 4.26) decreases with increasing concentration. These four regimes, i–iv, are sketched in Figure 4.

In a Θ solvent there are two sticky reptation regimes with renormalized bond lifetime and mostly intermolecular bonds. The first one corresponds to the unentangled strands between stickers (eq 4.41a). The second one is for entangled strands between stickers (eq 4.41b).

The large number of predicted regimes for associating polymers provides an opportunity to tune the properties of their solutions to the desired range of concentration dependence of viscosity by adjusting strength of associations, the number of associating group per chain and other important parameters.

6. Comparison with Experiments

There are many rheological experiments of associating polymer solutions that report significant increase of viscosity and relaxation time compared to nonassociating ones (without stickers). Below we briefly describe

the results of some of these experiments and compare them with predictions of our model.

In section 3, we have already compared viscosity[15] of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly-(ethylene oxide)-*g*-poly(acrylic acid) with predictions of our sticky Rouse model. It was experimentally verified that solutions were unentangled in the concentration range described in ref 15 with frequency dependence of dynamic moduli following Rouse dynamics $G' \sim G'' \sim \omega^{1/2}$ (see Figure 8 of ref 15). The observed concentration dependence of viscosity of unentangled solutions of associating polymers (Figure 3) is in excellent agreement with our predictions (eqs 3.14, 5.2, and 5.3).

Some of the experimental studies deal with pairwise associating polymers. For example, solutions of poly-butadiene modified by introducing 1% of 1,2,4-triazoli-dine-3,5-dione (urazole) groups was studied by Stadler and de Lucca Freitas in squalene.[18] The viscosity of these pairwise associating polymers increases as sixth power of solution concentration. This is a much stronger dependence than the one observed in unmodified poly-butadiene solutions.

In most experimental systems, associations are due to lyophobic groups (hydrophobic groups in aqueous solutions) and are typically not pairwise. But even in these systems, the experimental results are in good agreement with predictions of our model. For example the viscosity of (hydroxypropyl)guar increases by several orders of magnitude upon modification with 1.2% of mixture $C_{22}-C_{28}$ *n*-alkyl epoxides.[19] In addition one observes a decrease of the power law exponent of viscosity at higher concentrations (Figure 1 of ref 19). Such decrease is not observed in nonassociating polymers. We attribute it to saturation of intermolecular associations at ϕ_s. Similar results were reported for solutions of hydrophobically modified alkali-soluble copolymers[20] (see Figure 9 of ref 20).

Up to 4 orders of magnitude increase of viscosity was observed upon grafting poly(ethylene oxide) side chains onto a 2-acrylomido-2-methylpropanesulfonic acid back-bone.[21] The electrostatic repulsion between polyelectro-lyte backbones was screened by 16.6% K_2CO_3 salt. Very strong concentration dependencies of viscosity (with exponents as high as 8.5) were observed in solutions with 1.2 molar percentages of grafted side chains (see Figure 8 of ref 21). Similar trends were observed for another hydrophobically associating polyelectrolyte con-sisting of methacrylic acid/ethyl acrylate copolymer backbone with pendant C_{18} hydrophobes.[22]

Systematic studies of viscoelastic behavior of water-soluble polyacrylamides hydrophobically modified with low amounts of *N,N*-dihexylacrylamide have been re-ported recently.[23] Concentration dependence of the zero-shear viscosity for samples with similar backbone molecular weights and hydrophobic block length is presented in Figure 6. Samples differ only by the number of hydrophobes per chain. The viscosity data corresponding to the unmodified polymer are denoted by "x" (the lowest set of points in Figure 6). The concentration dependence of viscosity of unmodified samples suggests that solutions at higher concentrations are entangled. Viscosities of solutions with polymers containing $f \approx 18$ stickers per chain are denoted by circles (the highest set of data). Squares correspond to polymers with $f \approx 9$ stickers per chain, and rhombuses—to polymers with $f \approx 4.5$ stickers per chain. Viscosity increases by more than 3 orders of magnitude between
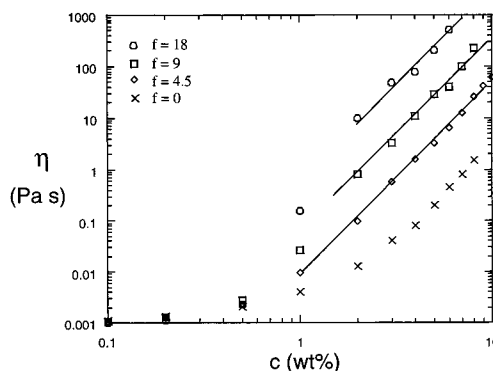

Figure 6. Zero-shear viscosity of *N,N*-dihexylacrylamide with different number *f* of hydrophobes per chain ($M_w \approx 450\,000$). Symbols correspond to $f = 0$ (crosses), $f = 4.5$ (rhombuses), $f = 9$ (squares), and $f = 18$ (circles).
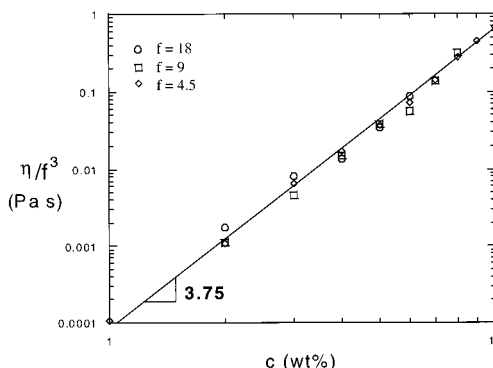

Figure 7. Zero shear viscosity of the associating samples ($f > 0$) of Figure 6 reduced by the cube of the number of hydrophobes per chain. Symbols are the same as in Figure 6.

solutions of unmodified polymers ("*x*") and solutions of associating polymers with $f \approx 18$ stickers per chain (circles). Note change in slope from stronger concentra-tion dependencies at lower concentrations (0.5 wt % < c < 2 wt %) to weaker ones at higher concentrations (2 wt % < c < 10 wt %) for the two upper sets of data (for $f \approx 9$ and $f \approx 18$). This can be explained by the transformation from mostly intramolecular associations at lower concentrations to mostly intermolecular ones at $\phi > \phi_s$. From eq 2.15, one can estimate the overlap concentrations for the strands between stickers to be $\phi_s \approx 1$ wt % for a polymer with $f \approx 4.5$; $\phi_s \approx 1.7$ wt % for a polymer with $f \approx 9$; and $\phi_s \approx 3$ wt % for a polymer with $f \approx 18$. Above the overlap concentration for strands between stickers, the sticky reptation model predicts (see eq 5.6)

$$\eta \sim f^3 \phi^{3.75} \quad \text{for } \phi_s < \phi < \phi_{le} \qquad (5.8)$$

Lines with slopes 3.75 (drawn on a double logarithmic plot in Figure 6) are consistent with the three sets of data for associating solutions. To check the scaling predictions of the sticky reptation model, the ratio η/f^3 is plotted as a function of concentration in Figure 7 for the three associating solutions at concentrations $\phi > \phi_s$. The data for all samples collapse onto a single universal line (see also insert in Figure 5 in ref 23) in excellent agreement with the prediction of the sticky reptation model (eq 5.8). Note that the experimental data[23] are consistent with the cubic dependence of viscosity η on the number *f* of associating groups per chain ($\eta \sim f^3$). The earlier model[14] predicted quadratic dependence of viscosity η on the number of associating groups *f* per

chain ($\eta \sim Nf^2\tau_b$; see eq 4.11) because it did not take into account the renormalization of the bond lifetime (it assumed $\tau_b{}^* \approx \tau_b$). At concentrations above the overlap of strands between stickers (for $\phi > \phi_s$), the renormalized lifetime of the bond is proportional to the number of associating groups per chain $\tau_b{}^* \sim \tau_b/l \sim \tau_b f/N$ (eq 3.9b) and leads to stronger (cubic) dependence of viscosity on f (eq 5.8) in excellent agreement with experiment.[23]

We believe that similar systematic experiments in different regimes for different model associating polymer solutions will provide additional tests of our model.

References and Notes

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(13) In this paper, we tend to keep the mathematics as simple as possible. That is why we use simplified scaling arguments to derive the equations below. In fact, we developed a rigorous mean-field approach to the reversible gel statistics with both interchain and intrachain bonds following ref 6. The problem is exactly solvable if intrachain associations between nearest neighbors only are allowed. We found the following mass action laws: $p_{inter} = xp_{open}{}^2$; $(2 - p_{intra})p_{intra} = x_{intra}p_{open}{}^2$. These equations together with eq 2.20 define three unknown quantities: p_{open}, p_{inter}, and p_{intra}. If intrachain bonds are suppressed ($x_{intra} = 0$), then eq 2.10 is recovered. One can easily verify that all the scaling equations considered below (eqs 2.21−2.23) are in agreement with (and may be derived from) the mass action equations quoted above. Here the local association parameter is defined as $x_{intra} = 4W_{closed}/W_{open}$, where W_{open} is the statistical weight of an open isolated l-strand, and W_{closed} is the strand statistical weight when its two end stickers are associated with each other. This definition is obviously in agreement with eq 2.17.
(14) The mean-field eq 2.25 is NOT valid for strong association (if the binding energy is high, eq 2.18) if $f \sim 1$ (in this case the gelation follows a percolation scenario; see ref 7).
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