Dynamics of Wormlike Micelles: The "Bond-Interchange" Reaction Scheme

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We study theoretically the dynamics of systems of elongated wormlike micelles which undergo "bond-interchange" reactions. Bond-interchange reactions may occur when two micelles come into contact at some point along their arc lengths. A transient structure resembling a four-armed star polymer is formed briefly, decaying to give two new micelles with each section of the first micelle fusing to one or other section of the second. First we consider the relaxation of the molecular weight distribution (MWD) of a system of wormlike micelles after an arbitrary (material conserving) perturbation to the MWD. We show that bond-interchange reactions do *not* provide a pathway for the relaxation of the MWD to equilibrium. Second we consider the dynamics of entangled systems of wormlike micelles. We calculate the scaling of the terminal time, viscosity, and monomer diffusion constant with the volume fraction of surfactant in the regime where micellar reactions are rapid on the time scale of reptation. These results may help in identifying systems in which bond-interchange reactions occur. Finally we discuss the validity of the "tube" model in these systems. We consider when a description based on the tube model is appropriate, given that bond-interchange reactions allow chains to pass through one another.

1. Introduction

"Living polymers" are polymers, or other chainlike objects, which can exchange material by reversible reactions. Living polymers are thought to exist in aqueous systems such as CTAB/KBr and CTAC/NaSal[1–4] which, under appropriate conditions, are known to assemble reversibly into flexible wormlike micelles.[5] These are, in favorable cases, extremely long (many thousand angstroms) and flexible and undergo reactions on a relatively rapid time scale. Simple mean field theories can be used to predict that the micelles have exponential polydispersity.[6,7] Throughout this paper we use L to denote the mean micelle length.

In the simplest case the micellar reactions consist of a forward (scission) reaction, where the micelle spontaneously breaks at a random point along its length, and the reverse (recombination) reaction, where one micelle combines end-to-end with another. The dynamics of entangled polymers, which can undergo these "reversible scission" reactions, has received recent theoretical attention.[8–15]

However end-to-end reactions are not the only reactions possible, and in several other systems, such as CTAC/NaSal + NaCl, there is good evidence[14–17] to suggest that the dominant reactions are different. Two of the most obvious possible reactions, in addition to reversible scission, are "bond-interchange" and "end-interchange", which we describe below.

(i) Bond-Interchange Reactions. These reactions occur when two chains come into contact and react at some point along their arc lengths, chosen at random. A transient structure resembling a four-armed star polymer is formed briefly, decaying to given two new chains with each section of the first chain fusing to one or other section of the second chain, chosen at random. This reaction is characterized by a rate constant k_b, and the overall rate is proportional to the square of the arc length density. We define the time scale on which bond-interchange reactions occur to be $\tau_{break} = (\phi L k_b)^{-1}$, where ϕ is the volume fraction of micellar material and k_b the rate constant.

(ii) End-Interchange Reactions. These reactions occur when the end of one chain "bites into" a second chain at a random position along its length. A transient structure resembling a three-armed star polymer is formed briefly, which decays to give two new chains, the end of the first chain having fused to a section of the second chain, chosen at random, the other section breaking off. This process is characterized by a rate constant k_e and the overall rate is proportional both to the arc length density and the density of chain ends. We define the time scale on which end-interchange reactions occur as $\tau_{break} = (C_e L k_e)^{-1} = (\phi k_e)^{-1}$, where C_e is the density of chains, L is the mean chain length, and k_e the rate constant. Thus the volume fraction of micellar material is, in suitable units, $\phi = C_e L$.

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(15) Granek, R.; Cates, M. E. *J. Chem. Phys.* 1992, 96, 4758.
(16) Candau, S. J. Private communication.
(17) Kern, F.; Zana, R.; Candau, S. J. *Langmuir* 1991, 7, 1344.

For completeness we also define reversible scission reactions:

(iii) Reversible Scission. This reaction scheme consists of a forward, unimolecular scission reaction and a reverse, bimolecular recombination reaction. The scission reaction is characterized by a rate constant k_s per unit time per unit arc length and is assumed to be independent of chain length. We define τ_{break} as the expected time for one break to occur on an average chain (which, by detailed balance, is comparable to the expected time for a recombination reaction to occur) $\tau_{break} = (\bar{L} k_s)^{-1}$.

Factors such as the precise chemical components, salinity, and temperature will determine which of the three reaction mechanisms detailed above are present. On a microscopic scale we expect the attempt frequency for bond interchange to be very much greater than the attempt frequency for end interchange which in turn will be very much greater than the attempt frequency for recombination. However each of the three reaction schemes will also have a different activation energy with the bond- and end-interchange reactions typically having a much higher activation energy than simple scission.

Note that bond-interchange reactions allow one chain to cross through another via the four-armed intermediate state. This implies that chain entanglements are not always effective in constraining the lateral motion of the polymer. In section 6, we suggest that a large regime exists where bond-interchange reactions can be detected, e.g. in the scaling results of section 4 or in the shape of the stress relaxation function,[13,14] without a total breakdown of the tube model.

In the present work we assume all reactions are uncorrelated in time. This assumption should be valid for flexible chains at moderately high concentrations.[5] We also assume that the local reaction rate constants, k_s, k_e, and k_b, do not depend on chain length or surfactant (micelle) concentration. This assumption is appropriate in the entangled regime when reaction rates are determined by the local motion of subsections of chain and not the diffusion of polymers over distances which are large compared to their gyration radii.

Recent experimental[4,18] and theoretical[12,19] work has focused on describing the effects of a temperature jump (T-jump) on systems of wormlike micelles. These previous theoretical studies have concentrated on systems of wormlike micelles which are able to undergo reversible scission or end-interchange reactions *only*. For the case of reversible scission reactions it was shown that, after a small T-jump, the molecular weight distribution (MWD) relaxes to equilibrium on a time scale $\tau_{TJ} = \tau_{break}/2$. This result has been verified in recent experimental work on the system CTAB/KBr.[4] It was also shown that end-interchange reactions do not contribute to the relaxation of the MWD. In section 2 we will show that bond-interchange reactions are similar to end interchange in that they do not provide a pathway for the relaxation of the MWD. This is an important result since it confirms that τ_{TJ} gives a direct measurement of the rate of reversible scission reactions, unaffected by the presence of either end- or bond-interchange reactions.

In section 4 we derive scaling results which predict how the viscosity η, terminal stress relaxation time τ, and monomer diffusion constant D_{mon} vary with the volume fraction of micellar material ϕ. We consider the limit in which micellar reactions are rapid on the time scale of reptation. This is when $\tau_{break} \ll \tau_{rep}$, with τ_{rep} the reptation

(18) Rehage, H. Private communication.
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time for an average micelle (the time required for the micelle to completely disengage from its original tube, assuming it undergoes no reactions in this time). We also consider the regime where the micellar reactions are sufficiently frequent that the dominant motion of a chain end is breathing (contour length fluctuations due to constrained Rouse motion). Our results for reversible scission[9,10] and end-interchange in the reptative regime[17] are not new but are included here for comparison with the new results for bond interchange.

2. Effect of a Material Conserving Perturbation to the MWD

In this section we will show that bond-interchange reactions do not contribute to the relaxation of the MWD following a material conserving perturbation. A material conserving perturbation is one in which the total surfactant volume fraction ϕ remains constant, an example of which is a T-jump.

As has already been mentioned the MWD of micellar systems is predicted to have exponential polydispersity. We write the number density of micelles of length L as $C(L)$

$$C(L) = A \exp(-L/\bar{L}) \qquad (1)$$

The constant prefactor A can be determined by calculating the volume fraction of micelle arc length.[5] We choose units so that this is equal to the surfactant volume fraction ϕ, which requires $A = \phi/\bar{L}^2$.

We now proceed to write an equation describing the rate of change of $C(L)$, written $\dot{C}(L)$. We will show that $\dot{C}(L) = 0$ for any $C(L)$ of the form of (1).

Consider two general chains, one of length $L_A = L_1 + L_2$ and the other of length $L_B = L_3 + L_4$. They undergo a bond interchange reaction at a point which is L_1 from a certain end of the A chain and a distance L_3 from a certain end of the B chain. By including the appropriate rate constant k_b, recalling that the rate is proportional to the product of chain densities, and restricting the values of $\{L_1, L_2, L_3, L_4\}$ to those for which a chain of length L will be created (or destroyed), we can write the following equation for $\dot{C}(L)$:

$$\dot{C}(L) = k_b \int_{L_1=0}^{L} \int_{L_2=0}^{\infty} \int_{L_3=0}^{L} \int_{L_4=0}^{\infty} \delta(L_1 + L_3 - L) C(L_1 + L_2) \times$$
$$C(L_3 + L_4) \, dL_1 \, dL_2 \, dL_4 - k_b \int_{L_1=0}^{L} \int_{L_2=0}^{L} \int_{L_3=0}^{\infty} \int_{L_4=0}^{\infty} \delta \times$$
$$(L_1 + L_2 - L) C(L_1 + L_2) C(L_3 + L_4) \, dL_1 \, dL_2 \, dL_3 \, dL_4 \qquad (2)$$

The first of the integrals in (2) describes the rate of creation of chains of length L and the other integral describes the rate of destruction of chains of this length. It now only remains to note that for any C of the form of (1) we have $C(x + y) \propto C(x)C(y)$ and so $\dot{C}(L) = 0$ by inspection. This result demonstrates that bond-interchange reactions *alone* can have no effect on any exponential length distribution. The equilibrium MWD (prior to a perturbation) is just such a distribution. For the case of a T-jump, which has the effect of shifting the equilibrium value of $\bar{L}(T)$, it has already been shown that the size distribution remains exponential at all subsequent times, even in the presence of reversible scission and/or end-interchange reactions.[12] For this reason the relaxation of the MWD after a T-jump, in systems where a mixture of all three reaction schemes is present, is unaffected by the presence of bond-interchange reactions.

This result can be argued in the following alternative

way.[20] Bond-interchange reactions (in common with end-interchange) preserve the total number of micelles in the system; two micelles are present both before and after any single reaction. A T-jump has the effect of changing the preferred number of chains in the system, via a change in L. However bond-interchange reactions have no way of changing the total chain number and therefore cannot provide a pathway to equilibrium.

3. Stress Relaxation in the Presence of Micelle Reactions

In this section we consider how τ, the stress relaxation time for the system, varies with τ_{break}, τ_{rep}, and the dimensionless parameter $\alpha \equiv l_e/\bar{L}$, where l_e is the mean curvilinear length between entanglement points. We treat separately the cases when each of the three reaction schemes (bond interchange, reversible scission, and end interchange) are present.

In section 4 we will use these results to make predictions for the scaling of the stress relaxation time τ, the viscosity η, and the monomer diffusion constant D_{mon} with surfactant volume fraction for each of the three reaction schemes. With this aim in mind we look first at the process of stress relaxation in entangled systems of micelles.

3.1. Stress Relaxation: The Reptative Regime. We consider here the regime where the dominant motion on the lifetime of a chain end τ_{end} is reptation. We are mainly interested in the limit of rapid micellar reactions, $\tau_{break} \ll \tau_{rep}$.[21] This is the limit in which chain reactions occur many times before the average chain would have reptated out of its original tube.

In the entangled (semidilute) regime, each polymer (micelle) is constrained by a "tube", consisting of the entanglements of the polymer with its neighbors.[22] We consider first the imposition of a small step strain on the system, which is initially at equilibrium. The effect of this small strain is to constrain the polymer to a non-equilibrium conformation. The stress associated with this is relaxed by curvilinear diffusion (reptation) of the chain out of its initial tube and into a new tube, which is at equilibrium. We can include the effects of the micelle reactions by using the stress relaxation model of refs 9 and 10, which can be modified to include bond- and end-interchange reactions and can be cast as a one-dimensional process in the following way.

The curvilinear diffusion constant of a chain of length L in its tube $D_c(L)$ varies as L^{-1}. Since stress is associated with the deformation of tube segments, it is easier to imagine the chain stationary and the tube diffusing relative to it. In this case, a given tube segment relaxes when it reaches the end of the chain. We consider the motion of a hypothetical "particle" (representing a tube segment) of diffusivity $D_c(L)$ on a line of length L (representing the chain) with absorbing boundary conditions at the chain ends. We may include the effects of the chain reactions by allowing the absorbing ends of the line segment to make random jumps with appropriate transition probabilities. By considering an average chain, one obtains the expected time for the relaxation of an average tube segment,[9] which is the terminal stress relaxation time τ.

If the micelles were unbreakable, we would be able to ignore the effects of the reactions and each chain would simply have to diffuse, on average, a curvilinear distance

L to disengage completely from its tube. This process would occur after a time of order τ_{rep}. The mean-squared curvilinear displacement s^2 traveled by the chain[23] in a time $\tau_R \lesssim t \lesssim \tau_{rep}$ is proportional to t. This inequality restricts us to time scales longer than τ_R, which is the time scale on which breathing motion becomes important (see section 3.2 below). Hence s^2 is given by

$$s(t)^2 \simeq L^2(t/\tau_{rep}) \qquad (3)$$

We consider first the process of stress relaxation in the presence of bond-interchange reactions, for which the stress relaxation time τ scales according to $\tau \sim \tau_{break}^{1/3} \tau_{rep}^{2/3}$ in the limit $\tau_{break} \ll \tau_{rep}$. To see this we assume that the stress relaxation time for a typical tube segment, initially not close to the end of the chain, is the time it takes for a chain end to appear within a distance λ of the tube segment, where λ is the distance that the tube segment can be expected to diffuse before the newly formed chain end is lost through another chain reaction. We note that a newly formed chain end (which is a distance λ from the tube segment) is lost when another bond-interchange reaction takes place on the piece of chain of length λ (substituting, on average, a piece of length $\bar{L}$). This happens after a time $\tau_{end} = (\bar{L}/\lambda)\tau_{break}$. Thus $\lambda = s(\tau_{end})$ is determined from (3)

$$\lambda \simeq \bar{L}\zeta^{1/3} \qquad (4)$$

where we have introduced the definition $\zeta \equiv \tau_{break}/\tau_{rep}$. The stress relaxation time τ is then merely the waiting time for a chain end to appear within a distance λ of our typical tube segment. We must wait, not only for a bond interchange reaction to occur within a length of order λ but also for one such reaction to substitute a short piece of chain with length less than λ. Only a proportion $\lambda/\bar{L}$ of all bond-interchange reactions satisfy this last condition. Thus the waiting time for stress relaxation is $(\bar{L}/\lambda)^2\tau_{break}$, where the time for a bond-interchange reaction to occur on a length λ is $(\bar{L}/\lambda)\tau_{break}$ and the extra factor $\bar{L}/\lambda$ comes from the proportion of these reactions which are "successful" in substituting a short piece of chain of length less than λ. Using (4) we find

$$\tau \simeq (\bar{L}/\lambda)^2\tau_{break} \simeq \zeta^{1/3}\tau_{rep} \qquad (5)$$

These results apply whenever $\tau_R \lesssim \tau_{end} \lesssim \tau_{rep}$. In this case the dominant motion on the time scale τ_{end} is reptation and the "reptation-reaction" model described above is appropriate. Using (4), our definition of $\tau_{end} = (\bar{L}/\lambda)\tau_{break}$ and the fact[23] that $\tau_R \simeq \alpha\tau_{rep}$ we may rewrite this inequality as $\alpha^{3/2} \lesssim \zeta \lesssim 1$, where we recall our definition of $\alpha \equiv l_e/\bar{L}$.

We now give, for comparison, the corresponding results for τ in the presence of reversible scission or end-interchange reactions,[9] in the same limit $\tau_{break} \ll \tau_{rep}$. Our model for stress relaxation is the same: We must wait for an end to appear within a distance λ of a typical tube segment, where λ is the distance that the chain can be expected to diffuse in the time $\tau_{end} = \tau_{break}$ before the newly formed end is lost in another reaction.[24] In this case λ is given by

$$\lambda \simeq \bar{L}\zeta^{1/2} \qquad (6)$$

Now τ is merely the waiting time for a break to appear within a distance λ. This is larger than τ_{break} (which is the

(20) Pfeuty, P. Private communication.

(21) In the regime $\tau_{break} \sim \tau_{rep}$ a numerical technique becomes necessary, see refs 13 and 14, whereas for $\tau_{break} \gg \tau_{rep}$ the chains are essentially unbreakable and the chain motion is simple reptation.

(22) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithica, NY, 1979.

(23) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon, Oxford, 1986.

(24) A chain end can be lost either by a simple recombination reaction or by an end-interchange reaction which adds a piece of chain to the chain end. In either case the time scale on which the chain end is lost is τ_{break}.

waiting time for an end to appear *anywhere* on the chain[25])-by the factor $\bar{L}/\lambda$. Using (6) we have[9]

$$\tau \simeq (\bar{L}/\lambda)\tau_{\text{break}} \simeq \zeta^{1/2}\tau_{\text{rep}} \qquad (7)$$

These results apply whenever $\tau_R \lesssim \tau_{\text{end}} \lesssim \tau_{\text{rep}}$, as before. Using (6) we write this as $\alpha \lesssim \zeta \lesssim 1$. Note that this inequality does not coincide with the one for the case of bond-interchange reactions, introduced earlier in this section. This is due to the different scaling of τ_{end} in the two cases.

We may compare the two results for the stress relaxation time (7) when reversible scission or end-interchange reactions are present and (5) when bond-interchange reactions are present, with the results of an earlier numerical study.[14] The power laws are both in good agreement with the results of this earlier study. We note also that the stress relaxation time is longer for the case of bond-interchange reactions by a factor $\zeta^{-1/6} \gg 1$. Thus bond-interchange reactions are much less efficient at relaxing stress, as found in the earlier study.[14]

3.2. Stress Relaxation: The Breathing Regime. The constrained Rouse-like motion of a chain in its tube is known as "breathing" motion.[23,26,27] This motion leads to fluctuations in the total tube length of order $\Delta L \simeq (l_e \bar{L})^{1/2} = \bar{L}\alpha^{1/2}$ on a time scale $\tau_R \simeq \alpha\tau_{\text{rep}}$. The mean-squared curvilinear distance, s^2, traveled by the chain end (or any other segment) in a time $\tau_e \lesssim t \lesssim \tau_R$ (where $\tau_e \simeq \alpha^3\tau_{\text{rep}}$ is the time scale on which Rouse motion becomes important[23]) is proportional to $t^{1/2}$. Hence

$$s(t)^2 \simeq \bar{L}^2\alpha(t/\tau_R)^{1/2} \qquad (8)$$

We wish to calculate the stress relaxation time τ, in the regime where the dominant motion of a chain end is breathing. We retain the model used in section 3.1 above although now the chain end need not reptate to the position of the chosen tube segment, but may get there much faster by way of breathing fluctuations.

We first consider the case of bond-interchange reactions. In this case the curvilinear distance $\lambda = s(\tau_{\text{end}})$, within which a chain end must appear in order to relax a given tube segment, is determined from (8), where $\tau_{\text{end}} = (\bar{L}/\lambda)\tau_{\text{break}}$ is chosen to be the lifetime of a piece of chain of length λ in the presence of bond-interchange reactions. Rearranging we obtain the following expression for λ

$$\lambda \simeq \bar{L}(\alpha\zeta)^{1/5} \qquad (9)$$

where we recall the definition $\zeta \equiv \tau_{\text{break}}/\tau_{\text{rep}}$. In analogy with (5) the stress relaxation time is identified with the waiting time for a chain end to appear within a distance λ of a given tube segment.

$$\tau \simeq (\bar{L}/\lambda)^2\tau_{\text{break}} \simeq \alpha^{-2/5}\zeta^{3/5}\tau_{\text{rep}} \qquad (10)$$

These results apply whenever $\tau_e \lesssim \tau_{\text{end}} \lesssim \tau_R$. This inequality can be rewritten as $\alpha^4 \lesssim \zeta \lesssim \alpha^{3/2}$ using our definition of τ_{end} and (9).

For comparison we again consider the case when reversible scission or end-interchange reactions are present. In this case the length $\lambda = s(\tau_{\text{end}})$ is determined from (8), as before, but in this case $\tau_{\text{end}} = \tau_{\text{break}}$ is the lifetime of a chain end.

(25) A chain end can be formed either by a simple scission reaction or by an end-interchange reaction which "snips" off a portion of the chain, leaving a new chain end. In either case the time scale on which these events occur, somewhere on a portion of length λ, is $\tau_{\text{break}}\bar{L}/\lambda$.

(26) de Gennes, P. G. *J. Chem. Phys.* **1980**, *72*, 4756.

(27) de Gennes, P. G. *J. Chem. Phys.* **1982**, *76*, 3322. Doi, M. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 265; *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 667.

$$\lambda \simeq \bar{L}(\alpha\zeta)^{1/4} \qquad (11)$$

In analogy with (7) τ is merely the waiting time for a chain end to appear within a distance λ of the tube segment.[9]

$$\tau \simeq (\bar{L}/\lambda)\tau_{\text{break}} \simeq \alpha^{-1/4}\zeta^{3/4}\tau_{\text{rep}} \qquad (12)$$

These results apply throughout the breathing regime $\tau_e \lesssim \tau_{\text{end}} \lesssim \tau_R$. Using $\tau_{\text{end}} = \tau_{\text{break}}$ this inequality translates to $\alpha^3 \lesssim \zeta \lesssim \alpha$.

3.3. Stress Relaxation: Summary. To describe stress relaxation for larger values of ζ than those considered above, we note that when $\zeta \gtrsim 1$ the chains are essentially unbreakable and the stress relaxation time is merely the reptation time τ_{rep}.

We can therefore summarize our results, for bond interchange, as follows:

$$\tau \simeq \begin{cases} \tau_{\text{rep}} & \text{for } \zeta \gtrsim 1, \text{ "unbreakable" chains} \\ \zeta^{1/3}\tau_{\text{rep}} & \text{for } \alpha^{3/2} \lesssim \zeta \lesssim 1, \text{ reptative regime} \\ \alpha^{-2/5}\zeta^{3/5}\tau_{\text{rep}} & \text{for } \alpha^4 \lesssim \zeta \lesssim \alpha^{3/2}, \text{ breathing regime} \end{cases} \qquad (13)$$

Finally we note that bond-interchange reactions allow chains to pass through one another. This leads to a process that we call "tube evaporation", which modifies the result given above for the breathing regime. This effect is discussed fully in section 6 below.

For the case when reversible scission or end-interchange reactions are present, we have instead[9]

$$\tau \simeq \begin{cases} \tau_{\text{rep}} & \text{for } \zeta \gtrsim 1, \text{ "unbreakable" chains} \\ \zeta^{1/2}\tau_{\text{rep}} & \text{for } \alpha \lesssim \zeta \lesssim 1, \text{ reptative regime} \\ \alpha^{-1/4}\zeta^{3/4}\tau_{\text{rep}} & \text{for } \alpha^3 \lesssim \zeta \lesssim \alpha, \text{ breathing regime} \end{cases} \qquad (14)$$

4. Scaling of the Stress Relaxation Time τ and Viscosity η with Surfactant Volume Fraction ϕ

In this section we calculate the scaling of τ and η with ϕ for each of the three reaction schemes. We proceed by estimating first the scaling of $\tau_{\text{break}}(\phi)$ and $\tau_{\text{rep}}(\phi)$, we then use the results (13 or 14) in order to determine the scaling of τ with ϕ. We also predict the scaling of η.

Simple mean field theories,[6,7] which ignore excluded volume effects, suggest that $\bar{L} \sim \phi^{1/2}$ (this can be seen directly from the discussion following (1), assuming that the constant A is independent of ϕ). This mean field theory has been extended[10] to a semidilute solution where the chain "monomer" is replaced by a "blob" of size ξ, which is the length over which excluded volume interactions are screened.[10,28,22] This scaling approach has the effect of altering the scaling of $\bar{L}$

$$\bar{L} \sim \phi^{0.6} \qquad (15)$$

We recall that our model for bond-interchange reactions (section 1) implies $\tau_{\text{break}} \propto (\phi\bar{L})^{-1}$. Thus τ_{break} is given by

$$\tau_{\text{break}} \sim \phi^{-1.6} \qquad (16)$$

Simple scaling arguments[22] predict that for semidilute polymer solutions the reptation time scales as

$$\tau_{\text{rep}} \simeq \alpha^{-3}\tau_\xi \qquad (17)$$

where τ_ξ is the relaxation time of a single blob (containing a length of chain l_e) and $\alpha \equiv l_e/\bar{L}$ as before. Thus an average

(28) Safran, S. A., Turkevich, L. and Pincus, P. *J. Phys. (Paris), Lett.* **1984**, *45*, L19.

chain consists of α^{-1} blobs; the curvilinear friction increases like the number of blobs, as does the curvilinear distance that the chain must diffuse to escape completely from the tube. Since the mean squared curvilinear displacement increases linearly with time, τ_{rep} varies like α^{-3}. If we assume that hydrodynamic effects are only screened for distances greater than ξ, we may estimate τ_ξ by the Zimm time of a single blob, which varies[23] as the cube of the blob size ξ. We note that ξ and l_e are related by the usual excluded-volume random walk statistics $l_e \sim \xi^{1/\nu}$. Hence τ_{rep} can be written in terms of L and ξ only

$$\tau_{rep} \simeq L^3 \xi^{3(1-1/\nu)} \tag{18}$$

Scaling arguments[22] predict the following dependence for ξ (with $\nu = 0.588$)

$$\xi \sim \phi^{\nu/(1-3\nu)} \sim \phi^{-0.77} \tag{19}$$

which is in close agreement with a variety of experiments on systems of wormlike micelles.[1] Using this result and (15) we find, from (18), that τ_{rep} scales as follows:

$$\tau_{rep} \sim \phi^{3.4} \tag{20}$$

We note that the scaling of α with ϕ can also be calculated using (15), (19), and the relationship $l_e \sim \xi^{1/\nu}$.

$$\alpha \sim \phi^{-1.9} \tag{21}$$

Combining (16) and (20) we find $\zeta \sim \phi^{-5.0}$. This result, together with (21) above, allows us to use (13) to determine the scaling of τ with ϕ for bond-interchange reactions

$$\tau \sim \begin{cases} \phi^{3.4} & \text{for } \zeta \gtrsim 1, \text{ "unbreakable" chains} \\ \phi^{1.7} & \text{for } \alpha^{3/2} \lesssim \zeta \lesssim 1, \text{ reptative regime} \\ \phi^{1.2} & \text{for } \alpha^4 \lesssim \zeta \lesssim \alpha^{3/2}, \text{ breathing regime} \end{cases} \tag{22}$$

In order to calculate the scaling of the zero-shear viscosity η with ϕ, we use the following relationship[23] between η, τ, and the plateau modulus G_o

$$\eta \simeq G_o \tau \tag{23}$$

The plateau modulus is predict to scale like the density of entanglements[22]

$$G_o \sim \xi^{-3} \sim \phi^{2.3} \tag{24}$$

which is in close agreement with various experiments on micellar systems.[2] Using these results, and with $\tau \sim \phi^x$, the zero-shear viscosity is given by $\eta \sim \phi^{x+2.3}$.

We now compare these results with those for end-interchange and reversible scission. First we recall that our model for end-interchange reactions (section 1) implies $\tau_{break} \propto \phi^{-1}$. Combining this with (20) we find $\zeta \sim \phi^{-4.4}$ which, together with (21) above, allows us to use (14) to determine the scaling of τ (and hence η) with ϕ for end-interchange reactions

$$\tau \sim \begin{cases} \phi^{3.4} & \text{for } \zeta \gtrsim 1, \text{ "unbreakable" chains} \\ \phi^{1.2} & \text{for } \alpha \lesssim \zeta \lesssim 1, \text{ reptative regime} \\ \phi^{0.58} & \text{for } \alpha^3 \lesssim \zeta \lesssim \alpha, \text{ breathing regime} \end{cases} \tag{25}$$

We recall that our model for reversible scission reactions (section 1) implies that $\tau_{break} \propto 1/L$. Hence $\tau_{break} \sim \phi^{-0.6}$, which is in rough agreement with recent experiments, where τ_{break} is estimated via T-jump measurements.[4]

Combining this result with (20), we find $\zeta \sim \phi^{-4.0}$. Using (21) and (14), we determine the scaling of τ (and thus η) with ϕ for reversible scission reactions

$$\tau \sim \begin{cases} \phi^{3.4} & \text{for } \zeta \gtrsim 1, \text{ "unbreakable" chains} \\ \phi^{1.4} & \text{for } \alpha \lesssim \zeta \lesssim 1, \text{ reptative regime} \\ \phi^{0.88} & \text{for } \alpha^3 \lesssim \zeta \lesssim \alpha, \text{ breathing regime} \end{cases} \tag{26}$$

5. Monomer Diffusion in the Regime of Rapid Micelle Reactions

In the regime of rapid reactions $\tau_{break} \ll \tau_{rep}$ the micelles only have transient identity and it is meaningless to discuss their center of mass diffusion. However, we may consider the spatial motion of a single labeled monomer.

In order to calculate the monomer displacement in the breathing and reptative regimes, we first introduce a length $\hat{L}$ which is the length of tube along which the chain travels before a reaction occurs somewhere on this same length. The time for the chain to move the curvilinear distance $\hat{L}$ is equivalent to the waiting time for a reaction to occur on $\hat{L}$ and is defined as $\hat{\tau}$. When such a reaction occurs, the monomer we are tracing will be diverted along another tube uncorrelated with the first.[29] For $\tau_R \lesssim \hat{\tau} \lesssim \tau_{rep}$ the chain motion is reptative, with the following expression for $\hat{L}$ (3)

$$\hat{L}^2 \simeq L^2(\hat{\tau}/\tau_{rep}) \tag{27}$$

while for $\tau_e \lesssim \hat{\tau} \lesssim \tau_R$ the chain motion is dominated by breathing modes and, according to (8), $\hat{L}$ obeys

$$\hat{L}^2 \simeq L^2\alpha(\hat{\tau}/\tau_R)^{1/2} \tag{28}$$

In both cases $\hat{\tau}$ is given by

$$\hat{\tau} \simeq (\hat{L}/L)\tau_{break} \tag{29}$$

These relationships are independent of which reaction scheme is present. We can thus view the motion of the monomer as a series of random steps with a root mean squared *spatial* extent $\hat{R}$ given by the usual random walk statistics for a string of blobs[22]

$$\hat{R}^2 \simeq (\hat{L}/l_e)\xi^2 \tag{30}$$

We note that for times $t \gtrsim \hat{\tau}$ the mean-squared spatial displacement of a monomer $R(t)^2$ obeys the diffusion relation

$$R(t)^2 \simeq D_{mon} t \tag{31}$$

This equation defines the monomer diffusion constant D_{mon}, which is independent of the reaction scheme present. We may now solve for D_{mon} at $t = \hat{\tau}$, $R = \hat{R}$, using (27) or (28), (29), and (30). For the reptative regime $\tau_R \lesssim \hat{\tau} \lesssim \tau_{rep}$, corresponding to $\alpha^{3/2} \lesssim \zeta \lesssim 1$, we find[9]

$$D_{mon} \simeq \alpha^{-1}\zeta^{-1/3}\xi^2\tau_{rep}^{-1} \tag{32}$$

while for the breathing regime $\tau_e \lesssim \hat{\tau} \lesssim \tau_R$, $\alpha^4 \lesssim \zeta \lesssim \alpha^{3/2}$, we find

$$D_{mon} \simeq (\alpha\zeta)^{-3/5}\xi^2\tau_{rep}^{-1} \tag{33}$$

For $\hat{\tau} \gtrsim \tau_{rep}$ the chains are essentially unbreakable. In this case the chain takes random steps of mean squared extent $\alpha^{-1}\xi^2$ on a time scale τ_{rep} and we obtain

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(29) Strictly speaking one requires some number of reactions, of order 1, to occur before the new tube is completely uncorrelated with the first. This factor is unimportant here since we are interested only in scaling results and not the associated numerical prefactors.

Table I. Scaling of the Stress Relaxation Time τ, the Zero-Shear Viscosity η, and the Monomer Diffusion Constant D_{mon} with ϕ[a]

		Unbreakable chains	Reptative regime	Breathing regime
		$\zeta \geq 1$	$1 \leq \zeta \leq \alpha$	$\alpha \leq \zeta \leq \alpha^3$
Reversible Scission	τ	$\phi^{3.4}$	$\phi^{1.4}$	$\phi^{0.88}$
	η	$\phi^{5.7}$	$\phi^{3.7}$	$\phi^{3.2}$
End-interchange	τ	$\phi^{3.4}$	$\phi^{1.2}$	$\phi^{0.58}$
	η	$\phi^{5.7}$	$\phi^{3.5}$	$\phi^{2.9}$

			$\zeta \geq 1$	$1 \leq \zeta \leq \alpha^{3/2}$	$\alpha^{3/2} \leq \zeta \leq \alpha^4$
Bond-interchange		τ	$\phi^{3.4}$	$\phi^{1.7}$	$\phi^{0.3}$ (*)
		η	$\phi^{5.7}$	$\phi^{4.0}$	$\phi^{2.6}$ (*)
D_{mon}	Bond-interchange		$\phi^{-3.0}$	$\phi^{-1.4}$	$\phi^{-0.8}$
	Reversible Scission		$\phi^{-3.0}$	$\phi^{-1.7}$	$\phi^{-1.4}$
	End-interchange		$\phi^{-3.0}$	$\phi^{-1.6}$	$\phi^{-1.2}$

[a] The results for each of the three reaction schemes are shown, in all three regimes. An asterisk indicates the scaling due to tube evaporation (see section 6).

$$D_{mon} = D_{chain} \simeq \alpha^{-1}\xi^2\tau_{rep}^{-1} \qquad (34)$$

The scaling of D_{mon} with ϕ is given in Table I.

These results for the diffusion constant are, in effect, based on a mean-field picture which assumes that the transport of individual monomers is not dominated by rare events. This assumption breaks down, leading to anomalous diffusion phenomena,[30] if the diffusion constant of an unbreakable chain has too strong a dependence on chain length ($D(L) \sim L^{-\kappa} > 2$), in which case the weight average diffusion constant is unbounded. The reptation theory in fact corresponds to the marginal case ($\kappa = 2$) for which the anomaly can be ignored provided the chain length is sufficient.[30]

6. Validity of the Tube Model

A polymer undergoing diffusive motion in a concentrated solution has its lateral motion restricted by the steric constraints of the neighboring chains. The entanglements of a chain with its neighbors can be thought of as providing the tube along which the chain moves. This is the well-known tube model.[22,23] As has already been mentioned bond-interchange reactions allow chains to pass through one-another via the four-armed intermediate state. This process leads to "tube evaporation" (entanglement removal) in a way which cannot occur in other polymer-like systems, even those in which reversible scission or end-interchange reactions are present. In this section we suggest that the stress relaxation model of section 3, based on the idea of permanent entanglements, may be retained for systems where ζ is larger than some critical value ζ_c. In order to see this, we assume that the tube model remains appropriate up to the point when one bond-interchange reaction has taken place per entanglement length; this occurs after a time τ_{tube}

(30) Bouchaud, J. P.; Ott, A.; Langevin, D.; Urbach, W. *J. Phys. II* 1991, *1*, 1465.

$$\tau_{tube} = \zeta\alpha^{-1}\tau_{rep} \qquad (35)$$

At this point most of the original entanglements will have disappeared. We assume that the stress relaxation model used in section 3 remains appropriate whenever $\tau_{tube} \gtrsim \tau$. Using (13) and (35) we find that this is the case for $\zeta \lesssim \zeta_c$, with $\zeta_c = \alpha^{3/2}$. Tube evaporation is therefore predicted to be unimportant throughout the reptative regime. This verifies our results in that regime, and also the validity of recent numerical work on stress relaxation in such systems.[14] However the process of tube evaporation may *dominate* stress relaxation throughout the breathing regime. In this case we argue that the effective stress relaxation time scales like τ_{tube}. This is because after a time τ_{tube} each entanglement length has undergone one reaction and has been able to adopt an equilibrium conformation.

Finally we consider the process of "tube renewal" which arises from the fact that each entanglement point disappears when the end of the polymer providing the *entanglement* passes by. Hence the tube itself evolves in time as these constraints disappear.[14,31-33] Tube renewal occurs regardless of the reaction scheme present while tube evaporation can only occur in the presence of bond-interchange reactions. We assume that each entanglement point disappears when the end of the polymer providing it passes by.[34] Thus each entanglement (and therefore the original tube itself) has the same average lifetime τ as the original tube segment introduced in section 3. We now assume that the stress associated with each tube segment can disappear according to one of two processes: (i) The end of the chain passes through the tube segment (the mechanism considered in section 3) or (ii) the entanglement(s) providing the tube segment dissappear by an exactly similar process. Since both of these events take place on the same time scale τ, the *effective* stress relaxation time must itself scale like τ and the scaling results of sections 3 and 4 above are unaffected by tube renewal considerations.

In summary, for the case of bond interchange reactions *only*, there is a second relevant time scale for stress relaxation τ_{tube} which only becomes important when $\zeta \lesssim \zeta_c$. This is due to the effect we call tube evaporation. Using (35) and the earlier scaling results for ξ (19) and α (21), we have

$$\tau_{tube} \sim \phi^{0.3} \qquad (36)$$

If we assume that this time scale dominates stress relaxation, then (23) and (24) give the following scaling for η

$$\eta \sim \phi^{2.6} \qquad (37)$$

These results are quoted in Table I, where an asterisk is used to denote the fact that they arise from tube evaporation and not from the stress relaxation model of section 3. We note that there exists a large regime $\zeta \gtrsim \zeta_c$ (corresponding to the reptative regime) where the effects of bond-interchange reactions can be detected in the scaling results of section 4 or in the shape of the stress relaxation function,[13,14] without a total breakdown of the tube model.

(31) Viovy, J. L.; Monnerie, L.; Tassin, J. F. *J. Polym. Sci., Polym. Phys. Ed.* 1983, *21*, 2427. Viovy, J. L. *J. Polym. Sci., Polym. Phys. Ed.* 1985, *23*, 2423.
(32) Marucci, G. *J. Polm. Sci., Polym. Phys. Ed.* 1985, *23*, 159.
(33) Des Cloizeaux, J. *Europhys. Lett.* 1988, *5*, 437.
(34) We know that (a) new entanglements appear on roughly the same time scale as old ones disappear and (b) entanglements consist of more than one chain. However these factors do not affect our scaling predictions, only the associated prefactors.

Finally we remark that our expressions for D_{mon}, derived in section 5 above, should remain unaffected by tube evaporation and renewal. The basic diffusive step occurs when any reaction takes place within the characteristic length $\hat{L} \gg l_e$; the time scale $\hat{\tau}$ for this is always much shorter than τ_{tube} defined above.

7. Conclusions

We have shown that bond-interchange reactions cannot modify the MWD after an arbitrary material conserving perturbation. This result is important since it allows one to ignore the effect of bond-interchange reactions in experiments which measure the relaxation of the MWD after such a perturbation, e.g. T-jump.

We have derived new results for the scaling of τ, η, and D_{mon} in the presence of bond- and end-interchange reactions in the limit of rapid chain reactions. These results, along with the corresponding results for reversible scission, are summarized in Table I. They provide, in principle, a method for identifying which reaction scheme is present in a given system.

Finally the validity of the tube model was discussed: Tube evaporation arises from the fact that bond-interchange reactions allow chains to pass through one another. We suggest that this only becomes important for very rapid reactions, when the chain motion is no longer reptative on the lifetime of the chain end.