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Dynamics of living polymers and flexible surfactant micelles : scaling laws for dilution

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Résumé. — On étend au régime semidilué un modèle théorique introduit récemment pour décrire la dynamique de rupture et de recombinaison de chaînes polymériques. On sait que, dans ce régime, la statistique de volume exclu du système peut différer considérablement de celles de polymères indissociables, à cause de la formation d'anneaux fermés. Ces changements affectent aussi les exposants des lois d'échelles qui décrivent la dépendance en concentration de la viscosité et de la diffusion des monomères. En général, la gamme de concentrations où on attend un comportement d'échelle plutôt que de champ moyen est assez étroite.

Abstract. — A theoretical model, recently introduced to describe the dynamics of reversibly breakable polymer chains at high density, is extended to the semidilute regime. It is known that, in this regime, the excluded volume statistics of the system can differ significantly from those of unbreakable polymers of comparable molecular weight (because of the presence of closed rings). These changes also affect the scaling exponents for the concentration dependence of the viscosity and monomer diffusion constant. In general, the range of concentrations over which scaling (as opposed to mean-field) behaviour can be expected is probably rather small.

1. Introduction.

In a recent article [1] the author proposed a simple model to describe the dynamical properties (stress-relaxation, monomer diffusion, etc.) in entangled systems of living polymers. These are long linear-chain polymers that can break and recombine reversibly, and so are in equilibrium with respect to their molecular weight distribution. (This contrasts with ordinary polymers, for which the molecular weight distribution is fixed by the conditions prevailing at the time of synthesis.)

The model makes three basic assumptions :

- (i) that chain breakage occurs with a fixed uniform probability per unit length anywhere along the chemical sequence ;
- (ii) that successive breakage and recombination events are uncorrelated, in the sense that a newly-created chain end is not much more likely to recombine with its « partner » from the preceding dissociation than with the end of another chain ;
- (iii) that the dynamics of a chain end, on the time scale of its recombination, is predominantly that of reptation [2-4].

A detailed discussion of each assumption, and of the conditions under which it is valid, is given in reference [1]. That paper also describes how assumption (iii) may be relaxed to allow for fluctuation modes and/or Rouse motion that control the dynamics of a chain end at short times. This modification is expected to be important in some systems (notably in the case of polymeric liquid sulfur [5], whose behaviour seems to be very well described by the resulting, modified, theory) but will be left out of the present investigation in the interests of simplicity.

Under melt conditions, the equilibrium molecular weight distribution $c(L)$ is exponential with some mean \bar{L} . (We choose units so that L is a large integer equal to the number of monomers on a chain). Then it is helpful to introduce two characteristic times to describe the dynamics : (a) τ_{rep} , the reptation time of a (hypothetical) unbreakable chain of length \bar{L} ; and (b) τ_{break} , the average time before such a chain breaks into two pieces as a result of the reversible scission process. By detailed balance, this is comparable to the life-time of a free chain end before recombination [1, 5].

There follows a brief summary of the results of reference [1] :

(i) when τ_{break} is long compared to τ_{rep} , the dynamics of stress relaxation or monomer diffusion approaches that of a « quenched » system, in which there is a fixed (exponential) distribution of chain lengths, but no scission processes. The terminal time, viscosity, and monomeric diffusion constant are all within factors of order unity of their values for a monodisperse, unbreakable, system of comparable mean molecular weight. However, the stress relaxation function, $\mu(t)$ (which denotes the fraction of shear stress remaining at time t after a small step strain is applied at time zero) is very different from that a monodisperse polymers ; roughly speaking, one finds

$$\mu(t) \sim \exp[-(t/\tau_{\text{rep}})^{1/4}] \quad (1)$$

as opposed to an almost pure exponential decay [3] in the monodisperse case ;

(ii) more interesting is the behaviour when $\tau_{\text{break}} \ll \tau_{\text{rep}}$. In this regime, the terminal time for stress relaxation is neither τ_{rep} nor τ_{break} , but instead

$$\tau \approx (\tau_{\text{break}} \tau_{\text{rep}})^{1/2} . \quad (2)$$

This result is found as follows. In the reptation picture, each chain is confined by a « tube » of topologically constraining strands. The fraction of stress $\mu(t)$ remaining at time t after a step strain is applied at time zero, is simply the fraction of the original ($t = 0$) tube which has not been relaxed by the passage of a chain end through it, during that interval. Focussing on a randomly chosen segment of tube, the characteristic time τ for passage of a chain end turns out to be the waiting time for a break in the chain to occur within a distance λ of that segment along the chemical sequence, where λ is the typical curvilinear displacement of a reptating chain end in the time available ($\sim \tau_{\text{break}}$) before it recombines with the end of another chain. A simple calculation, supported by a numerical study of the coupled reaction/diffusion process, shows that this τ obeys equation (2), and that the stress relaxation function in this regime reverts to an almost pure exponential form. Correspondingly the viscosity η obeys

$$\eta \sim \eta_{\text{rep}} \zeta^{1/2} \quad (\zeta \ll 1) \quad (3)$$

whereas the monomer diffusion constant is predicted to obey

$$D \sim D_{\text{rep}} \zeta^{-1/3} \quad (\zeta \ll 1) . \quad (4)$$

In these expressions we have defined

$$\zeta \equiv \tau_{\text{break}}/\tau_{\text{rep}} ; \quad (5)$$

the subscript rep in equations (3), (4) denotes the

equivalent quantity calculated in the reptation model without explicitly allowing for breakage reactions.

Subject to the original assumptions of the model, the results 3 and 4 should be applicable under semi-dilute conditions as well as in melts and concentrated solutions (described by mean field theory). This is fortunate as there are several experimental surfactant systems in which living polymers appear to give highly entangled behaviour even at very low concentrations [6-11]. The observation of a pure exponential decay in the stress relaxation function [8, 9] is very strongly suggestive that $\zeta \ll 1$; this is also supported by measurements of D [10]. It is therefore desirable to translate the results embodied in equations (3), (4) into a concrete prediction for, say, the concentration dependence of the viscosity (which is observed to be very strong).

This is nontrivial for two main reasons. Firstly, there can be a strong dependence of the average chain length on concentration which is inadequately described by mean field theory. Even the scaling theory as applied to ordinary (monodisperse) polymers is inapplicable due to the effects of ring formation. These effects have been studied extensively by Petschek, Pfeuty and Wheeler (PPW) [12], and their implications for dynamics are considered in this paper.

The second complication is that in many of the experimental systems studied so far (polymer-like surfactant micelles in water) there is a strong *salt effect* [6-10] which may mean that parameters such as the energy for creating a chain end are also concentration dependent. These additional complications are beyond the scope of the present work. It would be most interesting to study polymer-like *reverse micelles* in oil, for which they would, presumably, be absent.

2. Static equilibrium considerations.

2.1 MEAN-FIELD THEORY. — We start at the level of a Flory-Huggins or mean field theory. We choose units so that $k_B T = 1$, and assume that no closed rings are present [11-13]. (This assumption is valid at high enough density [12].) For a system of linear chains, inscribed for convenience on a unit lattice, the free energy may then be written as

$$F = \sum_L c(L) [\log c(L) + E] + (1 - \phi) \log (1 - \phi) \quad (6)$$

where the number density of chains of length L is denoted by $c(L)$; E is the scission energy of the chain (as required to create two new chain ends) and we have defined the total volume fraction

$$\phi = \sum_L Lc(L) . \quad (7)$$

In the first term of equation (6) we have, without loss of generality, set equal to zero the part of the free energy per chain that is extensive in chain length; since the term in ϕ also is extensive (it depends only on the total concentration) we may absorb this term, too, leaving finally

$$F = \sum_L c(L) [\log c(L) + E]. \quad (8)$$

Minimizing with respect to $c(L)$ (paying attention to the constraint of equation (7)) yields immediately

$$c(L) \propto \exp[-L/\bar{L}] \quad (9a)$$

$$\bar{L} \simeq \phi^{1/2} e^{E/2}. \quad (9b)$$

2.2 SCALING THEORY : NO RINGS PRESENT. — It is simple to extend this analysis to the case of a semidilute solution of chains *again assuming that no rings are present* [11]. This assumption turns out to be incorrect [12], but the analysis is nonetheless instructive. In semidilute solution we know that a mean-field approach remains valid [13] so long as the basic « monomer » entering the analysis is replaced by a « blob » of size

$$\xi \sim \phi^{\nu_0/(1-\nu_0 d)}. \quad (10)$$

Here d is the dimension of space, and ν_0 is the correlation length exponent of the n -vector model in the limit $n \rightarrow 0$.

Thus we may write (again omitting an osmotic term that depends only on the overall concentration, ϕ)

$$F = \sum_L c(L) [\log c'(L) + E']. \quad (11)$$

In this expression,

$$c'(L) = c(L) \xi^d \quad (12)$$

denotes the number density of L -chains measured in coarse-grained « blob » units, and

$$E' = E - (d + \theta) \log \xi \quad (13)$$

where $\theta = (\gamma_0 - 1)/\nu_0$. In equation (13) the first term is, as before, the scission energy of a bond. The second is more subtle: it is the free energy change resulting from the *gain in entropy* when a chain breaks so that the two new ends can explore a volume ξ . (The entropy associated with separation beyond this distance is already included in the coarse-grained Flory-Huggins expression.) This entropy gain is enhanced by the fact that the excluded volume repulsion on scales less than ξ is also reduced by breaking the chain; this effect is accounted for by the term θ in the prefactor of $\log \xi$ [14].

Now minimizing equation (11) at fixed ϕ gives

$$c(L) \propto \exp[-L/\bar{L}] \quad (14a)$$

$$\bar{L} \simeq e^{E/2} \phi^{\gamma_0} \quad (14b)$$

$$\gamma_0 = \frac{1}{2} [1 + (\gamma_0 - 1)/(\nu_0 d - 1)] \simeq 0.6. \quad (14c)$$

Thus the concentration dependence of the mean molecular weight \bar{L} is described by an exponent γ_0 that differs from the one predicted by simple mean-field theory ($\gamma = 1/2$, Eq. (9b)). Note that equation (14a) is clearly invalid for those chains which are short enough to be smaller than the blob size; however, in the semidilute regime these chains are in a minority. Their statistics are those of dilute equilibrium chains without rings [14, 15]

$$c(L) \sim L^{\gamma_0 - 1}, \quad (L \ll L_{\text{blob}} = \xi^{1/\nu_0}) \quad (15)$$

and indeed by demanding a crossover from this behaviour to an exponential distribution at $L \simeq L_{\text{blob}}$, one can easily recover the prediction of equation (14c) for the exponent γ_0 .

2.3 SCALING THEORY WITH RINGS. — The scaling theory when rings are present is far more complicated. The details have been worked out by PPW [12]; here we select only a minority of their results, which are directly relevant to the discussion of dynamics in the next section. The presentation is somewhat less technical than that of the original papers.

It is essential to recognise that, in equilibrium, there is no independent control of whether rings occur: the system makes this choice for itself. Under these conditions, it is found theoretically [12] that rings are invariably present, and that they *qualitatively* change the scaling behaviour from that described in the previous subsection.

Perhaps the biggest change is as follows. In the absence of rings, there is a broad semidilute regime spanning the range $\phi^* \ll \phi \ll 1$. Here ϕ^* is the volume fraction at which chains first start to overlap. Since, by equation (14), the chains at any given ϕ can be made longer by increasing E , ϕ^* becomes extremely small when the scission energy E is large. This gives a very wide range of semidilute scaling behaviour. When rings are allowed, this ceases to be true. At low concentrations, the very long chains that would exist (for large E) can gain entropy by fragmenting into numerous smaller rings. Such rings pay an entropy penalty for closure but they gain entropy of mixing, without having to pay the high price in scission energy (E) that would be needed to make linear chains of the same length.

As a result, the effective « overlap threshold » ϕ^* is pushed to a much higher value, in principle of

order unity. This value may be substantially reduced if rings smaller than a certain size are unfavorable ; for example if the chains are relatively stiff so that ring closure is difficult for short chains. But in that case, there is every reason to expect excluded volume interactions to be relatively weak (the virial coefficient between sections of relatively stiff chain is much reduced from its value in the fully flexible case [16]). Hence it is probably valid to use the simple mean-field results (Eqs. (8, 9)) for all $\phi \gg \phi^*$. Correspondingly, the qualitative agreement between experimental measurements of the collective diffusion constant and osmotic pressure for entangled worm-like micelles at low volume fractions [6, 7, 9], and the semidilute scaling predictions for the same quantities calculated in the absence of rings [11], is actually rather hard to understand.

In the presence of rings, the « overlap threshold » ϕ^* can be better described as a polymerization transition ; for $\phi \leq \phi^*$ there are mainly rings present, whereas for $\phi > \phi^*$ there is also a condensate of very long chains. (The length of these diverges as $E \rightarrow \infty$; in that limit, only, is there a true phase transition at ϕ^*). Exactly at the transition point, there is a power law distribution of ring sizes

$$c_{\text{ring}}(L) \simeq L^{-\psi} \quad (16)$$

where ψ is a certain exponent (discussed below). Note that $\psi > 2$ so that the total volume fraction, $\sum_L L c_{\text{ring}}(L)$ is finite (and equal to ϕ^*). As indicated

above, ϕ^* can be made small by excluding rings smaller than a certain size ; but this has no effects on the universal critical behaviour near the transition.

The presence of rings of all sizes leads to considerable subtlety in regard to the screening of excluded volume effects. As explained in quite general terms in reference [17], a power law distribution of molecular weights can lead to a new value of the size exponent, as a result of « self-similar screening » of excluded volume. The work of reference [12] shows that this indeed occurs in the present system, and that the chain obey a mass/radius relation

$$L \sim R^D \quad (17)$$

where D is *not* equal to the value $1/\nu_0$ that applies for linear chain polymers in the absence of rings.

Instead, PPW find [12] that

$$D = \phi_1/\nu_1 \quad (18)$$

$$\psi = 1 + d/D \quad (19)$$

(see also Ref. [17]), where ϕ_1 and ν_1 are respectively the quadratic anisotropy crossover exponent and the correlation length exponent for the n -vector model, in the limit $n \rightarrow 1$ (rather than $n \rightarrow 0$ as for ordinary

polymers). The numerical values of ψ and D are about 2.72 and 1.75 respectively, in three dimensions (when $\phi_1 \simeq 1.08$ and $\nu_1 \simeq 0.63$).

At $\phi > \phi^*$ there is a range of concentration over which scaling behaviour is expected. There is, as usual, a certain correlation length ξ which can be thought of as defining a « blob » for one of the long linear chains that are present in this regime. But the structure within the blob is quite different than for polymers without rings ; the piece of linear chain is « decorated » by a power law cascade of smaller rings, which partially screen its excluded volume interactions. Thus the correlation length ξ obeys

$$\xi^{D-d} \sim \phi_c \quad (20)$$

where $\phi_c \neq \phi$ is the volume fraction of material *in the form of long linear chains*. The remainder of material, $\phi_r = \phi - \phi_c$, is in the form of rings ; ϕ_r decreases rapidly for $\phi > \phi^*$ [12]. Indeed, the transition proceeds largely by the amalgamation of rings into long chains. As ϕ is raised beyond ϕ^* , the range of concentrations over which this process can continue is limited : clearly ϕ_c cannot exceed about ϕ^* before all the rings are used up. This fixes the semidilute scaling regime to lie between ϕ^* and roughly $2\phi^*$. If, as found experimentally in surfactant living polymer systems, ϕ^* is very small [6-10], then so is the range of validity of the $n = 1$ scaling behaviour.

At higher concentrations than this, one might hope to revert to the $n = 0$ scaling regime for which rings can be ignored but excluded volume is strong. This would explain the success of the $n = 0$ theory in matching the collective diffusion and osmotic pressure data seen in experiments on CTAB (cetyltrimethyl ammonium bromide) [6, 7, 9, 10]. However, as mentioned above, it is probably more realistic to expect only simple mean-field exponents in this regime. There is perhaps some evidence of mean-field exponents (e.g., in the plateau modulus) for the CPySal (cetyl pyridinium salicylate) systems studied in reference [8].

Finally, there is the question of how ϕ_c varies with ϕ , and how the average chain length \bar{L} depends on ϕ_c . (Note that the chain length distribution is exponential, as before [12].) For the latter, one expects a further (small) shift in the exponent y from that calculated in the absence of rings (Eq. (14c)) to reflect the power-law screening of excluded volume. PPW find

$$\phi_c \sim (\phi - \phi^*)^s \quad (21a)$$

$$s = (2 - \alpha_1 - \phi_1)/(1 - \alpha_1) \simeq 0.9 \quad (21b)$$

where $\alpha_1 = 2 - d\nu_1$. From the work of PPW we also find after a little algebra (and correcting a misprint in Eq. (5.20) of Ref. [12])

$$\bar{L} \sim e^{E/2} \phi_c^{1-(2-\alpha_1-\gamma_1)/[2(2-\alpha_1-\phi_1)]} \sim e^{E/2} (\phi - \phi^*)^{\gamma_1} \quad (22a)$$

$$\gamma_1 = \frac{2 - \alpha_1 + \gamma_1 - 2\phi_1}{2(1 - \alpha_1)} \simeq 0.55. \quad (22b)$$

Here $\gamma_1 \simeq 1.3$ has its usual meaning in terms of the $n = 1$ (Ising) model. Note that these results reduce to those in the absence of rings (Eqs. (14b, c)) if one sets $\phi^* \rightarrow 0$ and replaces the exponents ν , α , γ , ϕ of the $n = 1$ vector model with those for the $n = 0$ case [12].

3. Dynamics.

Given the results of the previous section, some progress can be made in calculating the reptation time τ_{rep} in a hypothetical system of unbreakable chains having mean molecular weight \bar{L} . The calculated result can then be inserted into equations (2)-(4) to give a prediction of how the terminal time τ varies with concentration.

3.1 MEAN-FIELD REGIME. — For monodisperse chains at moderately high concentrations, there is an empirical relation [3] between the plateau modulus G , and the volume fraction ϕ ,

$$G \sim \phi^x; x \simeq 2. \quad (23)$$

This relation remains largely unexplained [3, 18]. It implies a dependence of the entanglement length on ϕ as

$$L_e \sim \phi^{-1}. \quad (24)$$

The reptation time τ_{rep} may be estimated as

$$\tau_{\text{rep}} \simeq \tau(L_e) (\bar{L}/L_e)^3 \quad (25)$$

where $\tau(L_e)$ is the relaxation time of a section of chain of length L_e , and the factor $(\bar{L}/L_e)^3$ comes from the usual reptation argument. That is, the chain is constructed as a string of units, each of length L_e ; the curvilinear friction on the whole chain is increased by a factor of order \bar{L}/L_e from that of a single unit, and the curvilinear distance that the chain must diffuse to escape from its tube is also increased by this factor. Since the mean-square curvilinear displacement increases linearly with time, this gives three powers of \bar{L}/L_e in total.

Unfortunately it is not completely clear how to estimate the concentration dependence of $\tau(L_e)$ itself in this mean-field regime. We assume of the empirical law, equation (24), insofar as it can be applied at fairly low ϕ (as might be the case for rather inflexible chains [18]) that the entanglement length L_e is much larger than the length L_h of chain whose radius corresponds to the hydrodynamic screening length [3],

$$L_h^{1/2} \sim \xi_h \sim \phi^{-1/(d-2)}. \quad (26)$$

Thus the motion of a chain on the scale of L_e is Rouse-like, with a relaxation time

$$\tau(L_e) \sim (L_e/L_h)^2 \tau(L_h) \quad (27a)$$

$$\tau(L_h) \sim \eta_0 L_h^{d/2}. \quad (27b)$$

The latter expression is the Zimm-time of an unscreened sub-segment of chain of length L_h ; η_0 is the solvent viscosity.

This manipulation yields the estimate (in $d = 3$)

$$\tau(L_e) \sim \eta_0 \phi^{-1}. \quad (28)$$

Using also equation (25) one has

$$\tau_{\text{rep}} \sim \eta_0 \bar{L}^3 \phi^2 \sim \phi^{7/2} \quad (29)$$

(where Eq. (9b) was used to give the last form.) A different approach, possibly more appropriate at high concentrations ϕ , is to argue that L_h is of order one (complete hydrodynamic screening) from which one finds $\tau_{\text{rep}} \sim \eta_0 \bar{L}^3 \phi$. This approach was taken in reference [5] when calculating the viscosity of polymeric liquid sulfur. However for the case of polymeric surfactant micelles the volume fractions of interest seem to be quite small [6-10], and hence we adopt equation (29).

Finally to estimate the terminal time τ in the presence of breakage, we make the further assumption that the chain breaking reaction is unimolecular (so that the breaking rate per unit length is independent of concentration). This gives

$$\tau_{\text{break}} \propto 1/\bar{L} \quad (30)$$

and inserting this and equation (29) into equation (2) we find

$$\tau \sim \bar{L} \phi. \quad (31)$$

Recalling at last that $\bar{L} \sim \phi^{1/2}$ (Eq. (9b)) we obtain

$$\tau \sim \phi^{3/2}, \quad (32)$$

and, using equation (23),

$$\eta \simeq G\tau \sim \phi^{7/2}. \quad (33)$$

This contrasts with the dependence $\eta \sim \phi^{11/2}$, that would be predicted by exactly parallel arguments, in the case when breakage was negligibly slow on the time scale of reptation ($\xi \equiv \tau_{\text{break}}/\tau_{\text{rep}} \gg 1$).

A similar analysis for the real-space monomeric diffusion constant, D , yields

$$D_{\text{rep}} \sim \bar{L}/\tau_{\text{rep}} \sim \phi^{-3} \quad (34a)$$

$$D \sim D_{\text{rep}} \xi^{-1/3} \sim \phi^{-5/3}. \quad (34b)$$

3.2 SCALING ANALYSIS IN THE ABSENCE OF RINGS. In this case, there is only one length scale, the semidilute correlation length ξ which obeys equation (10). The entanglement length L_e is just $\xi^{1/\nu}$; the relaxation time $\tau(L_e)$ of an entanglement unit is the Zimm time of a blob [4, 13]

$$\tau(L_e) \simeq \eta_0 \xi^d. \quad (35)$$

For the reptation time we have, as before [4]

$$\tau_{\text{rep}} \simeq (\bar{L}/L_e)^3 \tau(L_e); \quad (25)$$

since from equation (14) $\bar{L} \sim \phi^{y_0}$, we find

$$\tau_{\text{rep}} \sim \phi^{3y_0 + (d\nu_0 - 3)/(1 - \nu_0 d)} \simeq \phi^{3.4}. \quad (36)$$

Finally, if we again assume that chain breaking is unimolecular (there is no ϕ dependence of the rate constant per monomer), and use the relation $\tau_{\text{break}} \propto 1/\bar{L}$, we find for the terminal time (using Eq. (2))

$$\tau \simeq (\tau_{\text{rep}} \tau_{\text{break}})^{1/2} \simeq \phi^{y_0 + (d\nu_0 - 3)/[2(1 - \nu_0 d)]} \sim \phi^{1.4}. \quad (37)$$

Using the fact that the plateau modulus is proportional to the density of blobs ($G \sim \xi^{-d}$ [13, 14]), we find for the viscosity

$$\eta \sim \phi^{y_0 - (3 + \nu_0 d)/[2(1 - \nu_0 d)]} \sim \phi^{3.7} \quad (38)$$

as opposed to $\eta_{\text{rep}} \sim \phi^{3y_0 - 3/(1 - \nu_0 d)} \sim \phi^{5.8}$ as would occur in the limit where the breaking/recombination dynamics were negligibly slow on the time scale of reptation ($\xi \gg 1$). In a similar way, the monomeric diffusion constant D may be found to obey

$$D_{\text{rep}} \sim (\bar{L}/L_e) \xi^2 / \tau_{\text{rep}} \sim \phi^{-2y_0 + [2 + (2 - d)\nu_0]/(1 - \nu_0 d)} \sim \phi^{-3.1} \quad (39a)$$

$$D \sim D_{\text{rep}} \xi^{-1/3} \sim \phi^{-[2y_0 - (6\nu_0 + 3 - 2d\nu_0)/(1 - \nu_0 d)]/3} \sim \phi^{-1.7}. \quad (39b)$$

It should be noted that in all cases (Eqs. (35-39)) the exponents characterizing the ϕ -dependence are close to those given in equations (29)-(34) for the simple mean-field calculation (that is, to within 10-15 %). Experimentally it would be quite difficult to distinguish the two sets of predictions.

3.3 SCALING THEORY IN THE PRESENCE OF RINGS. As mentioned in section 2.3, the semidilute regime is, with rings present, probably rather narrow, especially in systems where the volume fraction ϕ^* at which polymerization occurs is itself small. Moreover, the general scaling expectation is for power law dependences on $(\phi - \phi^*)$, rather than powers of ϕ itself.

The entanglement length L_e of the long linear chains (whose volume fraction is ϕ_c) should now obey

$$L_e \simeq \xi^D \quad (40)$$

where ξ is the correlation length (obeying Eq. (20)) and D is the mass/radius dimension (Eq. (18)). Since the variation of \bar{L} with ϕ is given by equation (22), the only further ingredient required to calculate $\tau(L_e)$ is the relaxation time $\tau(L_e)$ of a single « blob ». Here we run into a difficulty, since the presence of a cascade of rings within the blob can cause partial screening of hydrodynamics, as it did for excluded volume. This problem is intractable, but discussed in detail in reference [19], where it is found that

$$\tau(L_e) \sim L_e^z \quad (41a)$$

$$d/D \leq z \leq 2. \quad (41b)$$

These bounds on z correspond to unscreened (Zimm-like) and fully screened (Rouse-like) motion, respectively. A more accurate estimate of z would require a dynamical renormalization group calculation which is beyond our scope.

The reptation time τ_{rep} of a long linear chain should still obey equation (25), so long as the new dependence on ξ of the friction within a blob is taken into account (Eqs. (41)). Using also equations (18, 21, 25, 40), we find after some simple algebra

$$\tau_{\text{rep}} \sim \tau(L_e) (\bar{L}/L_e)^3 \sim (\phi - \phi^*)^t \quad (42a)$$

$$t = 3y_1 + \frac{s(z-3)D}{(D-d)} \simeq 2.9-3.3. \quad (42b)$$

Using also equation (22) (assuming as before that the breaking of a chain is unimolecular so that $\tau_{\text{break}} \propto 1/\bar{L}$) we obtain finally

$$\tau \sim (\phi - \phi^*)^u \quad (43a)$$

$$u = y_1 + \frac{s(z-3)D}{2(D-d)} \simeq 1.1-1.4. \quad (43b)$$

To calculate the corresponding viscosity, we assume that the plateau modulus G is dominated by the contribution of the long linear chains. [Above the transition there are relatively few large rings [12]; the small rings would contribute to the effective elastic modulus at very short times, but we expect these to be predominantly unentangled [19] so that their relaxation time is very short and they do not contribute significantly to the viscosity.] In this case, the relevant plateau modulus is $G \sim \xi^{-d}$ ($k_B T$ per blob, as in ordinary semi-dilute polymer solutions) and the corresponding viscosity obeys

$$\eta \sim (\phi - \phi^*)^v \quad (44a)$$

$$v = u - \frac{ds}{(D-d)} \simeq 3.3-3.6 \quad (44b)$$

as opposed to $v \approx 5.0-5.5$ which would be predicted from a pure reptation theory. All of these numerical values for the exponents must be treated with caution since ϕ_1 is not known to great accuracy in three dimensions [12]. It should again be emphasized that the predictions are anyway only valid for ϕ in a narrow range near ϕ^* ; at higher ϕ one expects equations (29)-(34) from the mean-field treatment to be more appropriate. Note also that in the scaling regime, it is likely that the monomeric diffusion constant D is dominated by the contribution from (unentangled) small rings, which is not readily calculable within the present framework.

4. Discussion.

The above analyses extend the model of reference [1] for the dynamics of concentrated living polymer systems to cover the semidilute regime. This was a lengthy procedure because the equilibrium chain statistics are themselves rather complicated.

In predicting the concentration dependences of viscosities, etc., it was assumed that chain scission proceeds by a unimolecular reaction whose rate (per unit length of chain) remains independent of the polymer volume fraction ϕ . This is a natural assumption, but it may be argued that in some systems the breakage of one chain is mediated by, e.g. the free end of another (a « chain-end interchange » reaction) [20]. This would alter the various ϕ -dependences calculated above.

Another competing reaction involves the preferential « shedding » from a chain end, of a certain fixed number of monomers. [For example, in polymeric sulfur a chain end will preferentially shed exactly eight atoms, which can form an S_8 ring.] This corresponds to a breaking probability that, in contrast to the assumptions of the model, is not uniform along the chemical sequence. However, unless such a reaction is extremely rapid, it has little effect on stress relaxation [1, 5, 20]. Were such a reaction to dominate, the relaxation of a tube segment would require the « diffusion » of a chain end (by shedding of material) along the chemical sequence until the given tube segment was reached. The typical time for this process is strongly dependent on chain length; this would lead to pronounced departures from exponential behaviour in the stress relaxation function $\mu(t)$ (one would have roughly $\mu(t) \approx \exp[-t^{1/3}]$.) Thus the experimental observations of pure exponential decay [8, 9] in surfactant-based living polymer systems strongly support the uniform breaking mechanism originally proposed.

Unfortunately these surfactant systems offer much weaker experimental support for any of the predictions given above concerning the concentration

dependence of the terminal time τ , viscosity η , [9] or monomer diffusion constant D [10]. As mentioned in the introduction, the experimentally observed behavior seems strongly dependent on salt concentration; in some systems, the viscosity at fixed salt level is even non-monotonic as a function of ϕ [8]. These complications make quantitative comparison with experimental data difficult at present; even if their effects on equilibrium statistics were fully understood (which they are not) they could also lead to concentration dependences in the activation energy for breaking (for example) which would enter the model in a nontrivial way.

It should nevertheless be mentioned that in the CTAB system of Candau *et al.*, for which the terminal time, viscosity, etc. show evidence of power law scaling with concentration ϕ , the observed exponents are closer to those predicted in sections 3.1, 3.2 for *pure reptation* (without breaking) than those predicted by taking the reversible scission process into account. This would of course be quite consistent, were the breaking to be slow on the time-scale of reptation ($\xi \gg 1$) — but this possibility is effectively ruled out by the observation of near pure-exponential stress decay in these systems. Similarly the monomer diffusion measurements of Chatenay *et al.* [10] appear to give a stronger dependence on ϕ than predicted by the present model (although the measured slope approaches that predicted in Eq. (34b) at high salt levels). It remains to be seen whether these discrepancies are mainly associated with the complications of salt dependence, mentioned above, or whether there is something more fundamentally wrong with the model. One possibility is that the model is basically correct, but that the treatment of the frictional forces on a chain (which is an ingredient in calculating τ_{rep}) is inadequate — the true friction might increase faster with ϕ than envisaged, as a result of increasing inter-chain contacts, etc., which are not fully reflected in the equations (27)-(29) that describe $\tau(L_e)$ in the mean-field regime. Another possibility, already raised above, is that for one reason or another the pre-exponential factor (attempt frequency) for the scission reaction is itself a decreasing function of ϕ . To help answer these questions, it would be very useful to perform experiments on oil-based surfactant solutions (or indeed non-surfactant living polymers) for which the complexities of the salt-dependence would, presumably, disappear.

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