



ELSEVIER

Journal of Non-Crystalline Solids 172-174 (1994) 1168-1172

JOURNAL OF
NON-CRYSTALLINE SOLIDS

Relaxation mechanisms in worm-like micelles

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Abstract

Aqueous solutions of surfactants such as CTAC/NaSal and CTAB/KBr, certain dye molecules, S_8 rings in plastic sulphur or the α form of polymethylstyrene are thought to self-assemble reversibly into long, linear flexible chains. The fascinating properties of these systems arise from their propensity to randomly destroy or create connections between chains, a labile character which allows for exchange of material from chain to chain. As a consequence they exhibit a unique dynamic behaviour, which reflects both the kinetics of exchange of material from chain to chain and the dynamic properties of polymers. In this paper four types of reaction that have been proposed as candidates for describing the kinetics in these systems are reviewed. The implications of these mechanisms on the viscoelastic behaviour of the living polymer materials are also discussed.

1. Introduction

The kinetic mechanisms allow the linear living polymers to exchange material [1-6]. This results in an intrinsic, annealed polydispersity of the chain lengths. A simple description of the polydispersity [1] leads to an exponential chain-length distribution

$$c(L) = (\phi/\bar{L}^2) \exp[-L/\bar{L}] \quad (1)$$

with an average length \bar{L} given by $\bar{L} = \phi^{1/2} \exp\{(E+1)/2\}$, where ϕ is the monomer volume

fraction and E is the energy cost of creating two chain caps. This mean-field result can be modified to take into account the effect of excluded volume interactions: in the scaling picture, the cutoff size is replaced by the correlation length of the semidilute solution ($\xi \sim \phi^{-3/4}$), which leads to the new average length $\bar{L} \sim \phi^{0.6}$ [1].

2. Reversible scission

In this reaction scheme it is assumed that a chain can only change mass either by breaking into two new shorter chains or by recombining with another to form a new, larger chain [5,6]. This scheme provides an integro-differential equation for the

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time evolution of $c(t, L)$:

$$\begin{aligned} \frac{dc(t, L)}{dt} = & -kLc(t, L) + 2k \int_L^\infty c(t, L') dL' \\ & + (k'/2) \int_0^L c(t, L')c(t, L - L') dL' \\ & - k'c(t, L) \int_0^\infty c(t, L') dL', \end{aligned} \quad (2)$$

where k and k' are respectively the scission and recombination rate constants. The length distribution (1) is a stationary solution of the rate equation (2) under the condition $\phi k' = 2kL^2$ (detailed balance).

In a T -jump experiment, a technique widely used to determine the exchange rates in micellar solutions, a sudden perturbation (a step-change in the temperature) is imposed on the system [7]. The system will then relax to the new equilibrium length distribution with average length, \bar{L}_r . The relaxation can be calculated from the rate equation (2) for any amplitude of the temperature jump, because the exponential function $c(t, \bar{L}) = \phi/\bar{L}^2(t) \exp\{-L/\bar{L}(t)\}$ is a non-linear eigenfunction of the rate equation with the time-dependent average length obeying

$$L(t) = \bar{L}_r^{-1} \coth\left[\frac{(t + t_0)}{2\tau_b}\right] \quad (3)$$

for a positive t -jump (increase of the temperature) [8]. The constant t_0 depends on the amplitude of the temperature jump and the characteristic relaxation rate, τ_b , is given by $\tau_b = 1/(2k\bar{L}_r)$. Note that in the perturbative limit where $(\bar{L} - \bar{L}_r)/\bar{L}_r \ll 1$ the decay is simply exponential with decay rate τ_b .

The viscoelastic behaviour of entangled polymers is described by the tube model which considers that the pathway for stress relaxation after an imposed small step strain, is provided by the diffusion of the macromolecules along the tube formed by the wrapping entanglements of the other chains. The stress relaxation function $\mu(L, t)$ associated with this description is given by [9].

$$\mu(L, t) \propto \sum_{p:\text{odd}} \frac{8}{p^2 \pi^2} e^{-p^2 t / \tau_{\text{rep}}(L)}. \quad (4)$$

When the characteristic time for a chain to disentangle from its tube (known as the reptation time, τ_{rep}) is much smaller than the breaking time, the chains behave as unbreakable chains and the terminal time for relaxation in a viscosity measurement is simply $\tau_b \sim \bar{L}^3$. Because of the polydispersity of length distribution, the resulting stress relaxation function is a strongly stretched exponential,

$$\begin{aligned} \mu(t) = & 1/\bar{L}^2 \int_0^\infty L \exp\{-L/\bar{L}\} \mu(L, t) dL \\ & \propto \exp\{- (t/\tau_{\text{rep}})^{1/4}\}. \end{aligned} \quad (5)$$

In the opposite limit where the chains can break and recombine many times before the chain is able to reptate out of its tube, the reactions need to be incorporated into the diffusion process. In order to do so, one considers a length, λ , that a chain can diffuse before it recombines with another end. This length is given by $\lambda^2 \sim D(\bar{L})\tau_b$, where $D(\bar{L}) \sim \bar{L}$ is the curvilinear diffusion coefficient of a chain of average length. The relaxation time, τ , is then the time for a break to appear within a distance, λ , which is given by $\tau = \tau_b(\bar{L}/\lambda)$. This leads to a relaxation time given by [5].

$$\tau \sim (\tau_b \tau_{\text{rep}})^{1/2}. \quad (6)$$

Another consequence of the fast breakage-recombination process is that the relaxation function, $\mu(t)$, becomes single exponential. For surfactant solutions one can calculate the volume fraction dependence of the terminal time, τ , by replacing in Eq. (6) the average lengths by their values as a function of the volume fraction. One obtains $\tau \sim \phi^{1.4}$ for reactions faster than the reptation time and $\tau \sim \phi^{3.4}$ in the other limit.

3. End interchange

The end-interchange mechanism is a reaction by which the end of one chain collides with a second chain at a random position along its length, forming a transient three-armed star which then decays into two new chains of different lengths [10]. The equation for the time evolution of

$c(t, L)$ is now given by

$$\begin{aligned} \frac{dc(t, L)}{dt} = & -k_e L c(t, L) \int_0^\infty c(L') dL' \\ & - k_e C(L) \int_0^\infty L' c(t, L') dL' \\ & + k_e \int_0^L dL' \int_{L-L'}^\infty dL'' C(L') C(L'') \\ & + k_e c(t, L) \int_0^\infty c(t, L') dL', \end{aligned} \quad (7)$$

where k_e is the reaction rate constant. Because the reaction conserves the chain number, it cannot relax the length distribution after a T -jump. Indeed, it can be verified by inspection that the rate equation (7) has a solution for any $C(L)$ of the form (1). Still, we can define a characteristic time for an interchange event to occur on a chain of the typical length $\tau_e = 1/(\phi k_e)$.

We can calculate the viscoelastic response for a system where end-interchange reactions are present along the same lines of the calculation for reversible scission. In fact, the end-interchange reaction can be viewed as a scission or a recombination process, activated by a collision with or from a second chain. Then, in the regime where the breaking time is much smaller than the reptation time, one still has $\tau \sim (\tau_e \tau_{\text{rep}})^{1/2}$ and a mono-exponential decay for the stress relaxation function [6]. Note however, that the scaling of τ_e with the volume fraction is different, leading to a terminal time which scales as $\tau \sim \phi^{1.2}$.

4. Bond interchange

This reaction involves two reactant chains which come into contact at some random point along their arc lengths, form a transient four-armed star and decay into two new chains of different lengths. Let $L_A = L_1 + L_2$ and $L_B = L_3 + L_4$ be the lengths of the two chains, with the reaction occurring at a distance L_1 from one end of chain A and at a distance L_3 from one end of chain B.

Then, the rate equation for this reaction is:

$$\begin{aligned} \frac{dc(t, L)}{dt} = & k_i \int_0^L dL_1 \int_0^\infty dL_2 \int_0^L dL_3 \int_0^\infty dL_4 \\ & \times \delta(L_1 + L_3 - L) c(L_1 + L_2) c(L_3 + L_4) \\ & - k_i \int_0^L dL_1 \int_0^L dL_2 \int_0^\infty dL_3 \int_0^\infty dL_4 \\ & \delta(L_1 + L_2 - L) c(L_1 + L_2) c(L_3 + L_4), \end{aligned} \quad (8)$$

where k_i is the reaction rate. As far as the T -jump technique is concerned, the situation is similar to end-interchange: because chain number is conserved in the reaction, it does not provide a path for the chain relaxation of the chain-length distribution. It can also be checked that the any-exponential distribution is a stationary solution of the rate equation. The characteristic reaction time is now given by $\tau_i = 1/(\phi \bar{L} k_i)$.

The terminal time for the stress relaxation is calculated again by considering: (i) the distance, λ , over which a chain is expected to diffuse without making any reaction and (ii) the time it takes to a chain end to appear at a distance, λ , from the end. Note that both quantities differ from their analogues of the reversible-scission reaction by a factor \bar{L}/λ because not only a reaction needs to occur at a distance λ from the end, but the added piece of the chain needs also to be smaller than λ . This leads to the relaxation time [4]

$$\tau \sim \tau_i^{1/3} \tau_{\text{rep}}^{2/3} \quad (9)$$

which scales with concentration as $\tau \sim \phi^{1.7}$.

5. End evaporation

When the reactions are confined to the terminal region of the chains, the resulting kinetics can be described by the evaporation/condensation mechanism [11], which is described by the rate equations

$$\begin{aligned} \frac{dc(L)}{dt} = & k_D [c(L+1) - c(L)] \\ & + k'_D c(1) [c(L-1) - c(L)] \end{aligned} \quad (10)$$

for all the chains with length $L \geq 2$ and

$$\frac{dc(1)}{dt} = k_D \left[c(2) + \sum_{L=2}^{\infty} c(L) \right] - k'_D c(1) \left[2c(1) + \sum_{L=2}^{\infty} c(L) \right] \quad (11)$$

for the monomers. One of the important points in considering end evaporation is that it does provide a way to relax the chain length distribution. It is thus a serious candidate for the systems where evidence suggests the scission recombination to be absent [12]. After a T -jump, there is a fast initial process by which almost every chain can lose or gain by an order of one monomer, thus allowing the monomer density to relax much faster to its final (equilibrium) value than any other population of chain lengths. It can be checked, for instance, that there is a difference of two powers of \bar{L} in the initial decay times of the monomers and of the dimers. Different moments of the distribution relax here with different characteristic times, and the average length does not decay exponentially (even for small perturbations) to its final equilibrium value. The rate equations can be solved numerically for any T -Jump amplitude. For instance, in the case of small amplitudes, the second moment of the distribution (the average sampled for instance in a light scattering experiment) relaxes with a characteristic time $\tau_D = 4\bar{L}^2/k_D$.

In order to determine the viscoelastic behaviour in systems where end evaporation is the dominant mechanism, we note that, crudely speaking, the contour length of ‘original’ polymer which has evaporated at time, t , from each chain, $\hat{L}(t)$, is determined by the extent of a simple one-dimensional biased random walk, corresponding to the evaporation and condensation of monomers. Thus chains with a contour length $\lesssim \hat{L}$ will have completely evaporated; longer chains will have lost $\sim \hat{L}$ of their original monomers. On average, each chain undergoes an evaporation reaction in a time $1/k_D$ and a condensation reaction in a time $\exp\{1/\bar{L}\}/k_D$. This is a diffusion convection process with a small bias towards small chain lengths.

Hence

$$\hat{L}(t)^2 \simeq \begin{cases} \bar{L}^2 t / \tau_D & \text{for } t \lesssim \tau_D \\ \bar{L}^2 (t / \tau_D)^2 & \text{for } t \gtrsim \tau_D. \end{cases} \quad (12)$$

The stress is proportional to the number of ‘original’ monomers remaining at time t , which scales like $\mu(t) \sim \int_{L=\hat{L}}^{\infty} (L - \hat{L}) e^{-L/\bar{L}} dL$ where we have neglected numerical factors of order unity. Hence

$$\mu(t) \simeq \mu(0) \begin{cases} \exp\{-\gamma(t/\tau_D)^{1/2}\} & \text{for } t \lesssim \tau_D \\ \exp\{-\gamma' t / \tau_D\} & \text{for } t \gtrsim \tau_D, \end{cases} \quad (13)$$

where γ and γ' are constants of order unity. We see that the stress relaxation is stretched exponential for times smaller than τ_D with a characteristic timescale of order $\tau_D = 4\bar{L}^2/k_D$. For times much larger than τ_D , the stress relaxation approaches a single exponential with the same characteristic decay rate. Whenever $\tau_D \lesssim \tau_{rep}$, we expect stress relaxation by way of end evaporation to dominate over that resulting from reptative motion, and vice versa. For intermediate times, we expect some smooth interpolation between the two limiting cases. We also remark that $\tau_D/\tau_{rep} \sim 1/\bar{L}$ and so for long enough chains end-evaporation reactions (if present) will dominate the process of stress relaxation. The difference of one power of \bar{L} merely arises from the fact that the curvilinear diffusion constant for reptation scales as $D_c \sim \bar{L}$, whereas individual end-evaporation reactions lead to an effective diffusion constant of chain ends (relative to the tube) that is insensitive to chain length.

6. Conclusions

We have described four reaction mechanisms which may account for the kinetic and dynamic response of living polymers systems. Only two of these mechanisms (reversible scission and evaporation condensation) are able to relax their chain-length distribution under a sudden change of the thermodynamic conditions (T -jump). The evaporation–condensation reaction leads to relaxation times for the average length, three powers of \bar{L}

larger than the corresponding time under reversible scission reactions.

The stress relaxation functions depend strongly on the ratio of the characteristic time for each reaction to the reptation time. When the reptation time is much smaller than this typical time, the chain behaves as a classical solution (or melt) of polydisperse unbreakable chains. When the reptation time is the largest time in the system, the chains can react many times before they disentangle from their original tube. This leads to a much faster relaxation time, which is a combination of the breaking and reptation times for the three first described mechanisms, and independent of reptation for end evaporation. In this regime of fast reactions, the first three mechanisms also lead to a monoexponential decay of the stress function, while the fourth is only monoexponential at times larger than the reaction time, τ_D .

References

- [1] M.E. Cates and S.J. Candau, *J. Phys.: Condens. Matter* 2 (1990) 6869.
- [2] T.K. Attwood, J.E. Lydon, C. Hall and G.J. Tiddy, *Liq. Cryst.* 7 (1990) 657.
- [3] F. Boué, J.P. Ambroise, R. Bellissent and P. Pfeuty, *J. Phys. (Paris)* 2 (1984) 725.
- [4] M.S. Turner, C.M. Marques and M.E. Cates, *Langmuir* 9 (1993) 695.
- [5] M.E. Cates, *Macromolecules* 20 (1987) 2289.
- [6] M.S. Turner and M.E. Cates, *J. Phys. (Paris)* 51 (1990) 307.
- [7] S.J. Candau, F. Merikhi, G. Waton and P. Lemaréchal, *J. Phys. (Paris)* 51 (1990) 977.
- [8] C.M. Marques and M.E. Cates, *J. Phys. II (Paris)* 1 (1991) 489.
- [9] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).
- [10] M.S. Turner and M.E. Cates, *Langmuir* 7 (1991) 1590.
- [11] C.M. Marques, M.E. Turner and M.E. Cates, *J. Chem. Phys.* 99 (1993) 7260.
- [12] H. Rehage and H. Hoffmann, *Molec. Phys.* 74 (1991) 933.