

End-evaporation kinetics in living-polymer systems

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(Received 17 May 1993; accepted 21 July 1993)

We study theoretically the process of “end-evaporation” in living polymer systems, such as wormlike surfactant micelles. End-evaporation occurs when single monomers either break away from, or join onto, a chain end, the rates being described by the (mean-field) rate constants k and k' , respectively. Thus the chains can exchange material with one-another via a bath of free monomers. The relaxation of a system of living polymers after a small temperature jump (T -jump) is studied theoretically. The effect of a T -jump is to prepare the system with the wrong mean chain length, which relaxes to its equilibrium value \bar{L} by end-evaporation. It is found that the number of free monomers in the system relaxes almost completely in a time of order $1/k\bar{L}$, while the weight-average chain length, which is the quantity measured in light scattering experiments, relaxes on a time scale $\tau_D = 4\bar{L}^2/k$, which is three powers of \bar{L} longer. We also predict that the stress relaxation after a step strain is dominated by end-evaporation whenever $\tau_D \lesssim \tau_{\text{rep}}$, where τ_{rep} is the reptation (disengagement) time for a chain of length \bar{L} . In this case the stress relaxation is found to be “stretched exponential” for times smaller than τ_D and single exponential for longer times.

I. INTRODUCTION

Living polymers are linear self-assemblies of monomers which can break and recombine. They are known to exist in a wide variety of systems, ranging from surfactant solutions to liquid sulphur and selenium.^{1,2} The breakage-recombination process allow the macromolecules to exchange material (length). This results in an intrinsic, annealed polydispersity of the chain lengths, which is exponential, with an average chain size \bar{L} (Ref. 1),

$$c(L) = \frac{\phi}{\bar{L}^2} \exp\left(-\frac{L}{\bar{L}}\right). \quad (1)$$

In this expression $c(L)$ is the number density of chains of length L and ϕ is (in suitable units) the total volume fraction of monomers. These quantities are related by the conservation equation $\phi = \int_0^\infty Lc(L)dL$. The two basic ingredients which give the exponential distribution of chain lengths are (i) the translational entropy of the chains, and (ii) the energy cost E of a pair of chain end-caps. The associated average chain-length \bar{L} ,

$$\bar{L} = \sqrt{\phi} \exp\left(-\frac{E}{2k_B T}\right) \quad (2)$$

depends only on the equilibrium thermodynamic quantities of the system, being insensitive to the kinetic mechanism by which the chains exchange material. Although irrelevant for the static properties of the living polymer system, the kinetic mechanism determines its dynamic behavior. In particular, the viscoelastic response of the polymer solution is significantly different under different kinetic mechanisms.³⁻⁷ In the past attention has been given to three distinct mechanisms (i) the *scission-recombination* process in which two smaller chains may be created by breaking a chain, and the reverse process whereby a large chain may

be created by the end-to-end combination of two smaller chains; (ii) the *end-interchange* reaction in 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; (iii) the *bond-interchange* mechanism whereby two chains collide at random positions along their arc lengths, forming a transient four-armed star which then decays into two new chains of different lengths. Each of these three reactions is characterized by a primitive rate constant, denoted k_s , k_e , and k_b , respectively. The characteristic time τ for a reaction to occur on a typical chain depends on these rate constants, the average length of the chains and on the monomer volume fraction. For these three mechanisms we have $\tau_s = 1/(\bar{L}k_s)$, $\tau_e = 1/(\phi k_e)$ and $\tau_b = 1/(\phi \bar{L}k_b)$, respectively. The terminal times of the viscoelastic response for each of these mechanisms are combinations of the reaction times $\tau_i (i=s,e,b)$, and of the reptation time of the polymers.^{1,4} In principle an independent, direct measurement of the reaction times τ_i can be made in a temperature-jump (T -jump) experiment. In this experiment one monitors the relaxation of the average length of the chain distribution, following a sudden change in temperature. However only reactions such as scission-recombination, which allow for a change in the chain number, can contribute to the relaxation after T -jump.⁴ Consequently only the reaction time for the scission-recombination process is measured in such experiments. The results agree remarkably well with the data for τ_s derived by analyzing the viscoelastic spectrum.⁸

In this paper we consider in detail a further kinetic mechanism which also allows the average chain length to relax after a T -jump, we call this end-evaporation kinetics. This reaction proceeds by the addition or removal of a single monomer from the extremity of a chain.⁹ End-

evaporation is thought to be an important reaction mechanism in certain liquid sulphur systems² and may also be present in surfactant systems containing wormlike micelles and/or self assembled aggregates of certain dyes.¹⁰ In the next section we present analytical results for the evolution of the chain-length distribution under end-evaporation kinetics, after a sudden small change in temperature. We present a tractable exact solution for the problem as a function of frequency (the conjugated variable of time by a Laplace transformation). In Sec. III we solve numerically the kinetic equations and obtain the time evolution of several relevant quantities (number of free monomers, chain-number, and the weight average of the length). The last section is devoted to a discussion on the experimental relevance of the model.

II. THE KINETIC MODEL FOR END-EVAPORATION

In this section we study the response of a living polymer system to a temperature jump, assuming that monomer exchange in the system is exclusively due to end-evaporation reactions. There are two distinct reactions which modify the number of chains of length L (measured in units of the monomer size or micelle diameter). The first is evaporation of one monomer from the end of a chain, the second is condensation of one monomer onto a chain end. We introduce a rate constant k for the evaporation process (the probability per unit time of a given chain losing a monomer from *either* end) and a second rate constant k' for condensation (the probability per unit free monomer density, per unit time of a given chain gaining a monomer at *either* of its two ends). Each of these reactions can contribute either to an increase or to a decrease in the number of chains of a given length L . At the mean-field level we write the following rate equation for $c(L)$:

$$\frac{dc(L)}{dt} = k[c(L+1) - c(L)] + k'c(1)[c(L-1) - c(L)]. \quad (3)$$

The positive terms on the right-hand side of this equation refer to events that increase the number of chains of length L (evaporation of one monomer from a chain of size $L+1$, or condensation of one monomer onto a chain of size $L-1$), while negative terms correspond to the events which decrease the number of chains of size L (evaporation from, or condensation onto a chain of size L). This equation only applies to chains with two or more monomers ($L \geq 2$). To see this note that (i) a monomer (chain of size 1) cannot break into two smaller chains; (ii) when a monomer is shed from a chain of size 2 *two* chains of size 1 are formed; (iii) the number of free monomers can be reduced by recombination with chains of *any* length, and not only by reaction with other monomers; and (iv) when two free monomers combine the total number of monomers is reduced by 2. The kinetic equation for the free monomers thus reads

$$\frac{dc(1)}{dt} = k \left[c(2) + \sum_{L=2}^{\infty} c(L) \right] - k'c(1) \left[2c(1) + \sum_{L=2}^{\infty} c(L) \right]. \quad (4)$$

This relation can also be directly obtained from Eq. (3) by imposing monomer conservation

$$c(1) + \sum_{L=2}^{\infty} Lc(L) = \phi. \quad (5)$$

The stationary solution of Eqs. (3) and (4) is the thermodynamic equilibrium distribution given by Eq. (1), provided that detailed balance holds. Detailed balance actually implies that the evaporation and the condensation rates are not independent variables but are instead related by $k' = k\bar{L}^2/\phi$. Note that for algebraic simplicity, all these results assume a large average length $\bar{L} \gg 1$.

We now study the time evolution of the chain-length distribution for a sudden small change in temperature, occurring at (say) time $t=0$. For times prior to zero, the distribution has an average length \bar{L}_0 . For large times the chain distribution will tend asymptotically to the new equilibrium distribution of average length \bar{L} that corresponds to the new temperature. We monitor the evolution of the difference $\Delta(L,t) = c(L,t) - c(L,\infty)$, a function which has, for small temperature changes, the initial value⁵

$$\Delta(L,0) = \frac{\epsilon}{\bar{L}^2} \left(\frac{L}{\bar{L}} - 2 \right) \exp\left(-\frac{L}{\bar{L}}\right) \quad (6)$$

and which vanishes in the limit of very long times. The magnitude of the change induced by T -jump can be characterized by the relative difference of the initial and the final average chain-lengths, $\epsilon = (\bar{L} - \bar{L}_0)/\bar{L}$. In the limit of small ϵ we can linearize Eqs. (3) and (4) which then read

$$\frac{1}{k} \frac{d\Delta(L)}{dt} = \Delta(L+1) - \Delta(L) \left[1 + \exp\left(-\frac{1}{\bar{L}}\right) \right] + \left[\exp\left(-\frac{1}{\bar{L}}\right) \right] \Delta(L-1) + \Delta(1) \times \left[\exp\left(\frac{1}{\bar{L}}\right) - 1 \right] \exp\left(-\frac{L}{\bar{L}}\right), \quad (7)$$

$$\frac{1}{k} \frac{d\Delta(1)}{dt} = -\exp\left(-\frac{1}{\bar{L}}\right) \left[\frac{4 - 3 \exp\left(-\frac{1}{\bar{L}}\right)}{1 - \exp\left(-\frac{1}{\bar{L}}\right)} \right] \Delta(1) + \Delta(2) + \left[1 - \exp\left(-\frac{1}{\bar{L}}\right) \right] \sum_{L=2}^{\infty} \Delta(L). \quad (8)$$

The initial decay rates of the quantities of interest can be directly obtained by inserting the initial values of $\Delta(L)$ into expressions (7) and (8). One gets, in the limit of large

average chain lengths \bar{L} , the following values for the excess free monomer number $\Delta(1)$, the excess chain density $\Delta(L)$, the excess total chain number $n = \Delta(1) + \sum_{L=2}^{\infty} \Delta(L)$ and the mass averaged length of the excess chains, $L_2 = \langle L^2 \rangle = \Delta(1) + \sum_{L=2}^{\infty} L^2 \Delta(L)$, the following results:

$$\begin{aligned} \frac{1}{\Delta(1)} \frac{d\Delta(1)}{dt} \Big|_{t=0} &= -k\bar{L}, \\ \frac{1}{\Delta(L)} \frac{d\Delta(L)}{dt} \Big|_{t=0} &= -k \frac{2}{\bar{L}} \left[\frac{L}{\bar{L}} - 2 \right]^{-1}, \\ \frac{1}{n} \frac{dn}{dt} \Big|_{t=0} &= -k\bar{L}, \\ \frac{1}{L_2} \frac{dL_2}{dt} \Big|_{t=0} &= -\frac{2k}{\bar{L}}. \end{aligned} \quad (9)$$

The larger initial decay rate is the monomer decay rate; after one time step $t \approx k^{-1}$ almost all the chains have lost or gained at least one monomer. Since there are ϕ/\bar{L} chains reacting (compare to ϕ/\bar{L}^2 monomers) the rate is given by $k\bar{L}$. It is important to stress that the monomer population behaves very differently from the population of any other chain length. For instance there are two powers of \bar{L} between the initial relaxation rates of unimers and of dimers. The density of chains of characteristic size \bar{L} decays initially with a rate which is also two powers of \bar{L} slower than the monomer decay rate. The initial decay rate of the chain number n is $k\bar{L}$ because at this stage the variation of the number of the chains is dominated by the variation of the number of monomers.

Equations (7) and (8) represent an infinite set of coupled linear differential equations which can be solved by performing a Laplace transformation in time coordinates and then solving the resulting recurrence equations. The solution has the form

$$\begin{aligned} \Delta(L) &= \alpha(\omega, \bar{L}) X(\omega, \bar{L})^L + \beta(\omega, \bar{L}) \exp\left(-\frac{L}{\bar{L}}\right) \\ &\quad + \frac{\epsilon}{\bar{L}^2} \frac{1}{\omega} \frac{L}{\bar{L}} \exp\left(-\frac{L}{\bar{L}}\right), \end{aligned} \quad (10)$$

where X is the physical solution of the quadratic equation

$$X^2 - \left[\omega + 1 + \exp\left(-\frac{1}{\bar{L}}\right) \right] X + \exp\left(-\frac{1}{\bar{L}}\right) = 0 \quad (11)$$

and β is given by

$$\begin{aligned} \beta &= -\frac{\epsilon}{\bar{L}^2} \frac{1}{\omega} \left\{ 2 + \frac{1}{\omega \bar{L}} \left[1 - \exp\left(-\frac{1}{\bar{L}}\right) \right] \right\} \\ &\quad - \Delta(1) \frac{1}{\omega} \left[1 - \exp\left(-\frac{1}{\bar{L}}\right) \right]. \end{aligned} \quad (12)$$

Both the frequency ω and the jump amplitude ϵ are here expressed in units of k . Inserting expression (10) into Eqs. (7) and (8) gives two equations for α and $\Delta(1)$. In prin-

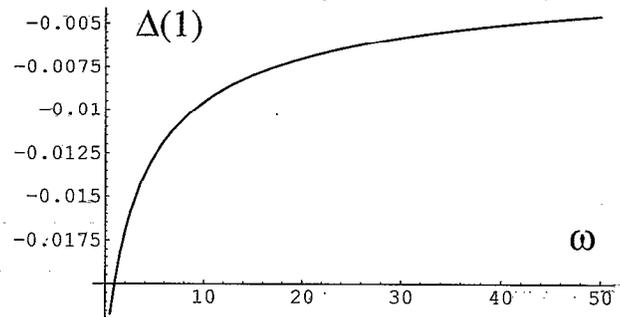


FIG. 1. The frequency response of the unimer concentration $\Delta(1)$ after a T -jump. The frequency and the concentration are normalized by the characteristic frequency $1/\tau_D$.

ciple the evaluation of these coefficients can be straightforwardly performed, although the number of algebraic transformations is quite large. We have found it convenient to use a symbolic computation package for calculating the quantities of interest. Details of this, and the numerical routine used in Sec. III, can be provided on request (marques@janus.u-strasbg.fr). We plot in Figs. 1–3 the frequency response for the excess monomer number $\Delta(1)$, the excess chain-number n , and the mass averaged length of excess chains L_2 .

In principle the time dependence of these quantities can be obtained by performing a numerical inverse Laplace transform. However there is no single characteristic frequency in the expressions for $\Delta(1)$, n or L_2 and a better insight into the relaxation mechanism is provided by the continuous version of Eqs. (5) and (7). In these equations we take the limit of large \bar{L} and expand to second order in $1/\bar{L}$,

$$\begin{aligned} \frac{d\Delta(L)}{dt} &= k \frac{\partial^2 \Delta(L)}{\partial L^2} + \frac{k}{\bar{L}} \frac{\partial \Delta(L)}{\partial L} \\ &\quad + \left(\frac{k}{2\bar{L}^2} + \frac{k}{\bar{L}} \right) \Delta(0) \exp\left(-\frac{L}{\bar{L}}\right) \end{aligned} \quad (13)$$

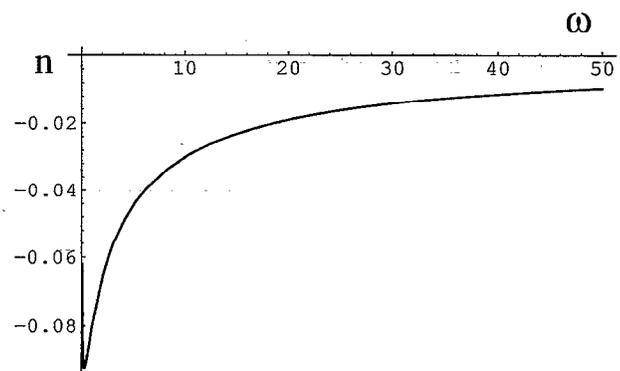


FIG. 2. The frequency response of the chain-number density n after a T -jump. The frequency and the concentration are normalized by the characteristic frequency $1/\tau_D$. Moreover the concentration is also normalized by an extra factor \bar{L} .

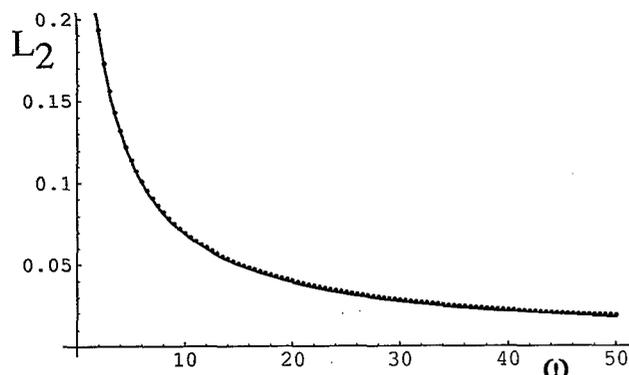


FIG. 3. The frequency response of the average chain-length L_2 after a T -jump. The frequency and the concentration are normalized by the characteristic frequency $1/\tau_D$. Moreover the concentration is also normalized by an extra factor \bar{L}^3 . Dots correspond to the numerical results of Sec. III (L_2'), while the continuous line represents the analytical results of Sec. II.

$$\Delta(0) + \int_0^\infty L \Delta(L) dL = 0, \quad (14)$$

where $\Delta(0)$ denotes the free monomer density which is in general different from $\lim_{L \rightarrow 0} \Delta(L)$. To first order in $1/\bar{L}$ the two preceding equations give $\Delta(0, t) = \Delta(0, t=0) \times \exp(-k\bar{L}t)$ as an approximation for the initial time-evolution of the number of free monomers, which holds for times $t \ll \log(\bar{L})/(k\bar{L})$. However, for longer times, one needs to proceed to second order in $1/\bar{L}$. The structure of the $O(\bar{L}^{-2})$ terms in Eq. (14) reveals the two main relaxation mechanisms of the excess chain density. The first term on the right-hand side of Eq. (14) is a diffusive term and it would correspond to a purely random evaporation/condensation of free monomers from/into the chain ends (the diffusion constant is k in our units where the size of the monomer is taken to be unity). However, because the equilibrium chain length distribution is exponential, the diffusion is biased towards the small chain lengths. The second term on the right-hand side of Eq. (14) is the manifestation of this bias, and has the structure of a convective term with a drift velocity k/\bar{L} . The $O(\bar{L}^{-2})$ correction to the source term of the rate equation can be neglected. Equation (13) has a green function of the form $\sqrt{1/(4\pi kt)} \exp[-(L + kt/\bar{L})^2/(4kt)]$. The decay process of this function for a given length L is predominantly diffusive for times $t \ll \bar{L}L/k$ and predominantly convective for times $t \gg \bar{L}L/k$. In any case one can define a characteristic decay time for the typical chain as

$$\tau_D = 4 \frac{\bar{L}^2}{k}. \quad (15)$$

However, due to the presence of the source term on the right-hand side of Eq. (13) and of the constraint (14), the overall decaying process cannot be described only by a single decay time. In particular the source term which is proportional to the free monomer density, varies on a much smaller time scale. This mixture of frequencies results in a rather complicated time-evolution which we now study numerically by solving the rate equations.

III. NUMERICAL STUDY

In this section we will discuss the results of a numerical study of the kinetics of end-evaporation. This involves solving Eqs. (3) and (4) numerically, subject to the boundary condition (5). We choose $\phi=1$ without loss of generality.

We suppose, as before, that the length distribution $c(L)$ is prepared with the "wrong" mean length \bar{L}_0 at $t=0$. The distribution $c(L)$ then relaxes to the final distribution which will have a mean length \bar{L} . Our numerical routine employs a discrete version of $c(L)$ and calculates solutions to the equations iteratively in time. A record is kept of $c(L)$ for all integer values of $L \leq \nu \bar{L}$, where $\nu \gg 1$ (we take $\nu=40$ below). This array is repeatedly updated after time steps of duration δt , chosen so that the probability of any given monomer reacting in one time step is not too large. This probability is roughly given by $p \approx k\bar{L}\delta t$ (we explicitly choose p , not δt). The routine calculates the array c at time $t + \delta t$ given the values at t by expanding c as a Taylor series in time using Eqs. (3) and (4) and keeping only terms to order δt . One cannot apply the kinetic Eq. (3) for the largest L -value stored since, for this element, the contribution from breaking chains of length $L+1$ is unknown. We choose arbitrarily a scheme for updating this element; for large enough ν any sensible choice should suffice. Finally at each time step various moments of the distribution are calculated and stored. We checked explicitly that an exponential length distribution provides a steady-state solution, that the routine conserves total material ϕ and that the results are relatively insensitive to the precise choice of ν .

The routine was initially implemented on a PC over 1000 time steps using the following parameter values $\bar{L}=5$, $\epsilon=-0.01$, $\nu=40$, and $p=1$ (hence $\delta t = \tau_D/500$). The computational time required for this routine scales like \bar{L}^3 (at fixed p); for $\bar{L}=5$, 1000 time steps corresponds to a real time of only $2\tau_D$. When the results are transformed to frequency space they are reliable only for frequencies that probe this time scale, i.e., in the present case $\omega \gg \omega_D/2$. The mass averaged length of the excess chains is defined as $L_2'(t) = |\langle L(t)^2 \rangle - \langle L(\infty)^2 \rangle| / |\langle L(0)^2 \rangle - \langle L(\infty)^2 \rangle|$ with similar definitions for n' and $\Delta'(1)$, $\langle \dots \rangle$ denoting an average over all chains. In the limit of small perturbations these expressions coincide with the definitions L_2 , n , and $\Delta(1)$ given earlier [this identification neglects $O(\epsilon^2)$ terms]. Results are shown in Figs. 4(a)–6(a). The quantity $L_2'(t)$ can be transformed to frequency space via a Laplace transform and the resulting $\tilde{L}_2'(\omega)$ compared with the analytical prediction of Sec. II, see Fig. 3. The modest parameter values taken here do seem to be adequate to give excellent agreement with the analytical results of Sec. II.

The numerical routine provides verification of other features predicted in Sec. II, such as the extremely rapid equilibration of monomers. In order to study this process the routine was prepared with $p=0.01$ (all other parameters unchanged). The number of excess monomers in the system was observed to fall by 80%–90% within roughly p^{-1} time steps, corresponding to a real time of $1/k\bar{L}$, see

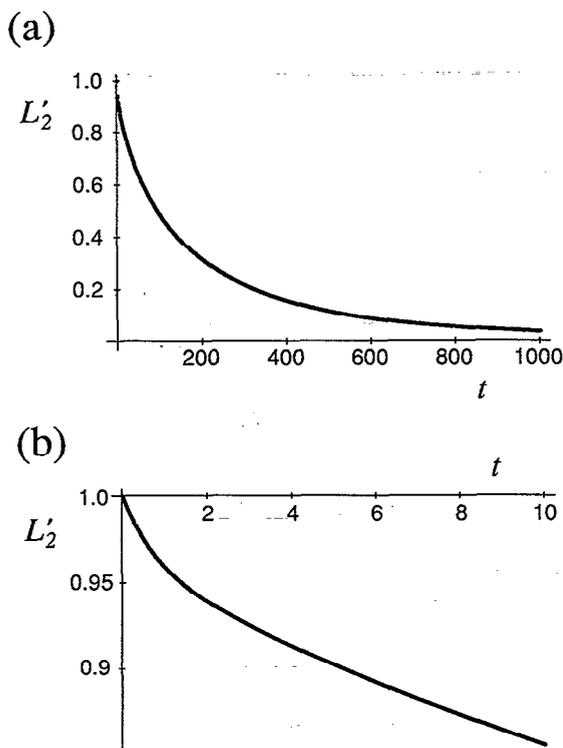


FIG. 4. The normalized change in the second moment L'_2 as a function of time, in units of $1/k\bar{L}$, for $\bar{L}=5$, $\epsilon=-0.01$, $\nu=40$, and $p=1$ (a) or $p=0.01$ (b). In these units the monomer relaxation time is predicted to be of order 1 and $\tau_D=500$.

Fig. 6(b). This is the time taken for the average number of reactions per monomer to reach of order 1. As predicted in Sec. II this initial rapid relaxation shows up strongly in the variation of the excess chain number $n'(t)$ with time, but much more weakly in the higher moment $L'_2(t)$, see Figs. 5(b) and 4(b), respectively.

IV. VISCOELASTIC RESPONSE

We now study the viscoelastic properties of a semidilute living polymer system, in which the dynamics is dominated by end-evaporation reactions. Assuming that this is the only reaction present, we find that the evaporation process dominates over reptation whenever $\tau_D \ll \tau_{\text{rep}}$, where τ_{rep} is the reptation time for a polymer of length \bar{L} (the time taken for a polymer of this length to disengage completely from its initial tube by curvilinear diffusion). Here τ_D is the characteristic time for evaporation defined earlier.

When a step strain is applied to a semidilute polymer solution (at $t=0$) each deformed into a new, nonequilibrium, conformation. Each chain is modeled as confined within a tube made up of the entanglements with neighboring chains.¹¹ In a classical polymer solution (containing unbreakable chains) the stress associated with the “unhappy” polymer conformations relaxes as the polymers diffuse out of their original tubes and into a new equilibrium tube. Such stress relaxation due to reptation results in¹¹

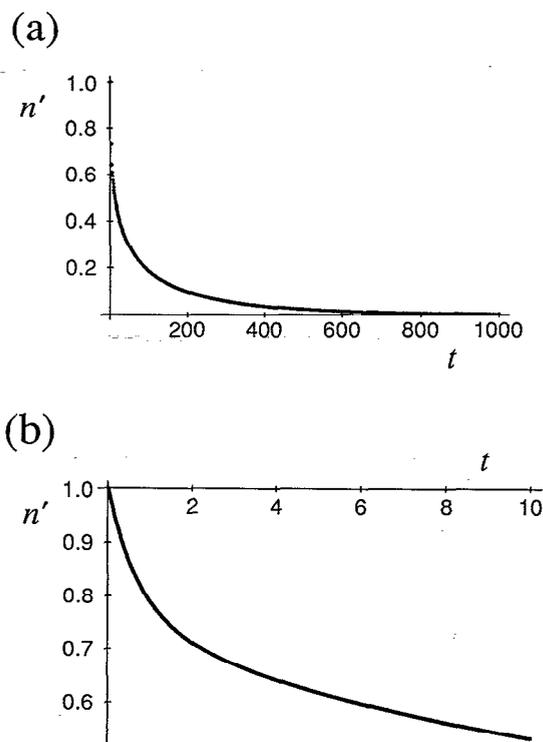


FIG. 5. The normalized change in the total chain number n' as a function of time, in units of $1/k\bar{L}$, for $\bar{L}=5$, $\epsilon=-0.01$, $\nu=40$, and $p=1$ (a) or $p=0.01$ (b). In these units the monomer relaxation time is predicted to be of order 1 and $\tau_D=500$.

$$\mu(t) \propto \sum_{p,\text{odd}} \frac{8}{p^2 \pi^2} e^{-p^2 t / \tau_{\text{rep}}}, \quad (16)$$

where $\mu(t)$ is the fraction of stress remaining at time t . It is known that the presence of chain reactions, such as reversible scission, end-interchange or bond-interchange, can significantly alter the stress relaxation, leading to single exponential stress relaxation in the limit of rapid chain reactions.³

We now wish to estimate the stress relaxation function in the presence of end-evaporation reactions. We first neglect the reptative motion of the chains (we will later determine just how slow reptation must be for end-evaporation to dominate the stress relaxation). End-evaporation reactions allow “stressed” monomers to be shed from the end of a chain. These monomers then later combine onto another chain end, creating a new (unstressed) piece of chain. The stress remaining at some later time is proportional to the number of “original” monomers (those that have not been shed from a chain end) that still exist. In what follows we are interested only in scaling results and neglect all numerical prefactors.

Crudely speaking the contour length of “original” polymer which has evaporated 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

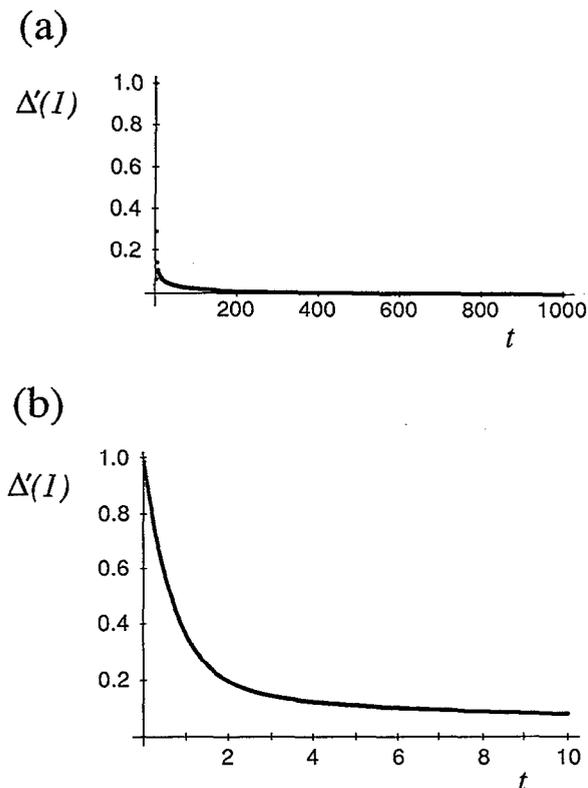


FIG. 6. The normalized change in the number of monomers $\Delta'(1)$ as a function of time, in units of $1/k\bar{L}$, for $\bar{L}=5$, $\epsilon=-0.01$, $\nu=40$, and $p=1$ (a) or $p=0.01$ (b). In these units the monomer relaxation time is predicted to be of order 1 and $\tau_D=500$.

each chain undergoes an evaporation reaction in a time $1/k$ and a condensation reaction in a time $\exp\{1/\bar{L}\}/k$. This is a diffusion-convection process with a small bias towards small chain lengths. Hence

$$\hat{L}(t)^2 \approx \begin{cases} \bar{L}^2 t / \tau_D & \text{for } t \lesssim \tau_D \\ L^2 (t / \tau_D)^2 & \text{for } t \gtrsim \tau_D \end{cases} \quad (17)$$

The stress is proportional to the number of "original" monomers remaining at time t , which scales like

$$\mu(t) \sim \int_{L=\hat{L}}^{\infty} (L - \hat{L}) e^{-L/\bar{L}} dL, \quad (18)$$

where we have neglected numerical factors of order unity. Hence

$$\mu(t) \approx \mu(0) \begin{cases} \exp[-\gamma(t/\tau_D)^{1/2}] & \text{for } t \lesssim \tau_D \\ \exp[-\gamma' t / \tau_D] & \text{for } t \gtrsim \tau_D \end{cases}, \quad (19)$$

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 time scale of order $\tau_D = 4\bar{L}^2/k$, the same as that predicted in Sec. II for relaxation following a T -jump. For times much larger than τ_D the stress relaxation approaches a single exponential with the same characteristic decay rate. Whenever $\tau_D \lesssim \tau_{\text{rep}}$ 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 (16) and (19).

We also remark that $\tau_D/\tau_{\text{rep}} \sim 1/\bar{L}$ 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.

V. CONCLUSIONS

We have studied the relaxation of a system of living polymers after a small temperature jump (T -jump) assuming that these polymers exchange material by end-evaporation. We find that the number of monomers in the system relaxes almost completely in a time of order $1/k\bar{L}$, while the weight-average chain length, which is the quantity measured in light scattering experiments, relaxes on a time scale $\tau_D = 4\bar{L}^2/k$, which is longer by three powers of \bar{L} .

We also predict that, in semidilute polymer systems undergoing end-evaporation, the stress relaxation after a step strain is dominated by end-evaporation whenever $\tau_D \lesssim \tau_{\text{rep}}$, where τ_{rep} is the reptation (disengagement) time for a chain of length \bar{L} . In this case the stress relaxation is "stretched exponential" for times smaller than τ_D and single exponential for longer times.

The end-evaporation reaction considered here takes into account the evaporation and condensation of single unimers from the chain ends. The exact size of the unimer (i.e., the number of surfactant molecules shed) is accounted for in the theory by the lower cutoff length of the chains. There may be some variation in the size of unimers between shedding events but this merely means that we must choose an "effective" unimer size (an average of the distribution of unimer sizes). The important point is that the unimer size is small compared to the chain length. Large shedding events, involving a significant fraction of the total chain length, are unlikely to be distinct from the random scission-recombination scheme, where the chain randomly breaks anywhere along its length and recombines with its neighbors.³⁻⁷ This is because all points along the chain, other than the ends are equivalent. In other words we expect breaking-recombination reactions to occur either very close to the chain ends, leading to end-evaporation, or everywhere along the chains, leading to random scission-recombination; noting that both of these two reaction schemes may be present in a single sample.

End-evaporation reactions may be important in systems other than liquid sulphur, where crown shape S_8 rings (the free monomers) coexist with a broad distribution of large polymerized chains.² Though not the general case, there are also certain systems containing living wormlike micelles where evidence suggests that macromolecular scission-recombination reactions, as distinct from end-evaporation, are absent or at least highly suppressed.^{12,13} This is important since it leaves end-evaporation as a possible reaction scheme for relaxation following a T -jump. Moreover, end-evaporation is also a candidate mechanism

to describe self-assembled aggregates of rigid, polarizable polyaromatic compounds in water,¹⁰ such as certain dyes.

ACKNOWLEDGMENTS

We thank Professor S. J. Candau (Strasbourg) for very helpful comments. Financial support from the British French join program Alliance is gratefully acknowledged.

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