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Monomer-mediated relaxation in living polymers

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We study the relaxation kinetics in living polymer systems, such as poly(α-methylstyrene), where association-dissociation processes are monomer mediated, so that the molecular weight distribution adapts reversibly to the new thermodynamic parameters by monomer exchange at active sites at chain ends. Using both a system of rate equations for the concentration of l-mers, which is solved numerically, and Monte Carlo simulations in terms of a bond fluctuation model, we find a good description of the dynamic response of the system to large deviations from equilibrium in terms of a single relaxation time $\tau_L \propto L^5$, where L is the average chain length in equilibrium. The response itself is found to decay with time t as t^{-1} in the late stages of relaxation. In contrast to wormlike micelles with scission-recombination kinetics, the average lifetime τ_l of chains of length l is found to be practically independent of l for $l \gg 1$ for a given rate of dissociation which may essentially determine the dynamics of such systems. [S1063-651X(97)08408-0]

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I. INTRODUCTION

Systems in which polymerization is believed to take place under conditions of chemical equilibrium between the polymers and their respective monomers are termed ''living polymers.'' These polymers are long linear-chain macromolecules or threadlike giant micelles that can break and recombine reversibly so that they are in equilibrium with respect to their molecular weight distribution (MWD). A number of examples have been studied recently, including liquid sulfur [1–3] and selenium [4], wormlike micelles [5], poly(α-methylstyrene) [6–9], and protein filaments [10].

Due to experimental difficulties [5,8] the properties of living polymers still pose a number of questions. Theoretical descriptions are formulated predominantly within the framework of the mean field approximation (MFA), and some very recent computer simulation studies [11–14] support most of the MFA predictions. Thus it has been confirmed that equilibrium polymerization proceeds through a phase transition [11], and the macromolecules in a polydisperse system of living polymers are characterized by an equilibrium exponential length distribution, n_l^{eq},

$$n_l^{\mathrm{eq}}(T) = \frac{\phi}{L^2} \exp\left(-\frac{l}{L}\right), \tag{1}$$

where L is the mean chain length. L depends on the thermodynamic variables of the system, such as temperature T, pressure, and total monomer density $\phi = \Sigma l n_l$:

$$L \propto \sqrt{\phi} \exp\left(\frac{J}{2k_BT}\right), \tag{2}$$

and grows exponentially with increasing ratio $J/2k_BT$ where J denotes the energy to create a chemical bond along the backbone of the polymer, and k_B is the Boltzmann constant [12,13].

While these equilibrium properties are insensitive to the kinetic mechanism by which the chains exchange material, the dynamical behavior of a living polymer system is governed entirely by its kinetics. Thus in the case of a *scission-recombination* mechanism a chain may break anywhere along its backbone into two smaller chains, and the reverse process of end-to-end association of smaller species into a larger chain takes place as well. For such systems the characteristic nonlinear thermodynamic relaxation upon a T jump (temperature change) in living polymer systems, for which the MFA kinetic equation can be solved exactly [15], has been shown to be in excellent agreement with results of computer experiments [14].

In the present study we focus on the dynamic response of living polymers, characterized by a different mechanism, namely, *monomer-mediated* equilibrium polymerization in which only single monomers may participate in the mass exchange. For this no analytic solution, even in terms of MFA, seems to exist yet [16]. Monomer-mediated equilibrium polymerization (MMEP) is typical for systems such as poly(α-methylstyrene) [6–8] in which a reaction proceeds by the addition or removal of a single monomer at the active end of a polymer chain after a radical initiator has been added to the system so as to start the polymerization. The attachment and/or detachment of single monomers at chain ends is believed to be important also for certain liquid sulfur systems [17] as well as for self-assembled aggregates of certain dyes [18] where chain ends are thermally activated radicals.

We point out an important difference in MMEP systems as compared to giant micelles with scission-recombination relaxation kinetics: the insensitivity of a chain lifetime to the length of the macromolecule, or to the average chain length of the polydisperse system. Thus the average lifetime of a MMEP chain should be determined predominantly by the rate of dissociation, F, at a given temperature, and for the *same F* this lifetime is expected to be much larger than that

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of a giant surfactant micelle. This difference could have implications for the polymer dynamics too.

In the present investigation we treat the problem as a system of coupled rate equations for a thermally activated polymerization-depolymerization process, which we solve numerically in Sec. II. We argue that despite some differences (in the rate equation for active monomers only) in systems with and without initiator, the relaxation towards equilibrium as well as the MWD, established in equilibrium, are the same. We compare results from the numerical solution of the system of rate equations to those from our Monte Carlo simulations, using a modified bond-fluctuation algorithm [13], described in Sec. III. In this way we check for the importance of transport properties of the medium (not accounted for in the system of rate equations) and demonstrate that both approaches produce almost identical results. In the final section we briefly summarize our results.

II. RATE-EQUATION ANALYSIS OF THE MMEP MODEL

A. The system of rate equations without initiator

Assuming that the probability distribution of cluster sizes n_l (chains of length l) is governed exclusively by MMEP, each chain may gain or lose a monomer at the chain end, which is considered to be the only active site of the macromolecule. The kinetics will be described then by two rate constants, K for coagulation and F for fragmentation, denoting the probability per unit time that a single monomer is attached or detached at the end of a given l chain through the following reaction mechanism:

$$n_l+n_1 \overset{K,F}{\Leftrightarrow} n_{l+1}. \tag{3}$$

Using a Smoluchowski rate-equation approach [19] we can write a system of nonlinear differential equations:

$$\begin{aligned}
\dot{n}_1&=-2Kn_1^2-Kn_1\sum_{l=2}^{\infty} n_l+2Fn_2+F\sum_{l=3}^{\infty} n_l,\\
\dot{n}_2&=Kn_1^2-Kn_1n_2+Fn_3-Fn_2,\\
\dot{n}_3&=Kn_1n_2-Kn_1n_3+Fn_4-Fn_3,\\
&\vdots\\
\dot{n}_l&=-Kn_1(n_l-n_{l-1})+F(n_{l+1}-n_l).
\end{aligned} \tag{4}$$

The constants of 2 in the first of Eqs. (4) follow from the fact that when two free monomers combine, the total number of monomers n_1 is reduced by 2, similarly when a dimer breaks, 2 chains of size 1 are formed.

From the conservation of mass in the system,

$$\sum_{l=1}^{\infty} n_l=\phi V, \tag{5}$$

where V is the system's volume, and the total number of clusters (chains) $N(t)$ at time t is

$$N(t)=\sum_{l=1}^{\infty} n_l(t). \tag{6}$$

The average chain length at time t after the system is moved out of equilibrium is given by $L(t)=\phi VN(t)^{-1}$. It can readily be checked that a summation over l in Eqs. (4) yields

$$\dot{N}=(F-Kn_1)N-Fn_1. \tag{7}$$

The first of Eqs. (4) for the free monomers then becomes $\dot{n}_1=-Kn_1^2+(F-Kn_1)N+F(n_2-n_1)$. Thus Eq. (7) depends on the number of free monomers, n_1, which in turn is coupled to the number of dimers, n_2, and so on, and the system of Eqs. (4) cannot be represented in a closed form.

B. The system of rate equations with initiator

In this case there is a fixed and constant number of initiators I_0 and thus a fixed number of active species in the system. Propagation of polymerization proceeds by attaching or detaching an inert monomer to or from an active chain:

$$n_l+M \overset{K,F}{\Leftrightarrow} n_{l+1}. \tag{8}$$

Thus the total number of polymer chains $N=\Sigma n_l$ (including the *active* monomers, n_1) is eternally fixed and $N=I_0$. This means that for the case of initiators we have $\dot{N}=0$ for all times. Besides the relative concentration of chains of length l, the quantity that changes with time in this case is the number of inert monomers M since part of them are consumed by the growing polymer chains. The system of rate equations can be written [20–22] under involvement of the number of inert monomers M as

$$\begin{aligned}
\dot{n}_1&=-KMn_1+Fn_2,\\
\dot{n}_2&=KMn_1-KMn_2+Fn_3-Fn_2,\\
\dot{n}_3&=KMn_2-KMn_3+Fn_4-Fn_3,\\
&\vdots\\
\dot{n}_l&=-KM(n_l-n_{l-1})+F(n_{l+1}-n_l).
\end{aligned} \tag{9}$$

Because of the mathematical similarity to the system with all monomers active (no initiator), Eqs. (4), below we consider the latter more thoroughly.

C. The molecular weight distribution in equilibrium

An analytical solution for n_l appears possible only in equilibrium: setting the left hand side of Eqs. (4) equal to zero, it can be represented as a recurrence relation,

$$n_{l+1}=(a+1)n_l-an_{l-1}, \tag{10}$$

where we have set $a=n_1K/F$. One can then easily verify that the resultant distribution of chain lengths for a MMEP system is given by

$$n_l=\frac{F}{K}a^l \quad (0<a<1), \tag{11}$$

just as in the case of scission-recombination kinetics; see Eq. (2). With the equilibrium distribution, Eq. (11), one finds $N=(F/K)a/(1-a)$ and $\phi V=(F/K)a/(1-a)^2$ so that the mean length $L_{\mathrm{eq}}=\phi V/N=(1-a)^{-1}$, or, for the MWD one obtains

$$n_l=\frac{F}{K}\exp(l\ln a)\approx\frac{F}{K}\exp\left(-\frac{l}{L_{\mathrm{eq}}}\right),$$

$$L_{\mathrm{eq}}^{-1}=\frac{F}{2K\phi V}\left(\sqrt{1+\frac{4K\phi V}{F}}-1\right)\approx\sqrt{\frac{F}{K\phi V}}. \tag{12}$$

Following Lequeux [23], we can estimate the average lifetime τ_l of a chain of length l in a MMEP system by suppressing the terms n_{l+1} and n_{l-1} in Eqs. (4). Then $\dot{n}_l=-(F+Kn_1)n_l=-F(1+a)n_l\equiv-n_l/\tau_l$, which yields for the lifetime

$$\tau_l^{-1}=F\left(2-\frac{1}{L_{\mathrm{eq}}}\right). \tag{13}$$

Thus it turns out that the lifetime of sufficiently long polymers $L_{\mathrm{eq}}\gg1$ in a MMEP system is practically independent of chain length, contrary to the case of scission-recombination kinetics [23], where it depends both on l and on the mean chain length L_{eq},

$$\tau_l^{-1}=F(l+2L_{\mathrm{eq}}). \tag{14}$$

Of course, this is to be expected since a micelle has an L-times larger probability to break than a MMEP chain has.

An important implication of this result concerns stress relaxation. In a dense system of entangled ''dead'' polymer chains, diffusion is expected to be determined by their *reptational* movement, and stress at points of entanglement is relaxed only after a chain has traveled out of the ''tube,'' occupied during characteristic time, τ_{rep}, and entered a new tube. As it has been shown recently by Cates [5] and O'Shaughnessy [24], long enough chains of wormlike micelles, $L_{\mathrm{eq}}\gg1$, could have $\tau_l\ll\tau_{\mathrm{rep}}$ [cf. Eq. (14)] and, therefore, by breaking into smaller fractions, effectively shorten the initial ''tube'' and release the stress faster than a conventional reptation mechanism would imply. In contrast, for the same F as in Eq. (14), from the present investigation, Eq. (13), one could conclude that in a MMEP system *all* chains will be sufficiently long lived and the conventional reptation mechanism of stress relaxation will take place. If F, however, is large enough (e.g., at high temperature) the chains will quickly disintegrate so that this mechanism will not be the dominating one.

The general case, Eqs. (4), can be solved analytically exactly if only *irreversible* aggregation is considered, $F=0$, which is relevant in the case when the binding energy J is much larger than the thermal energy k_BT. The rate equations (4) then reduce to

$$\dot{N}=-Kn_1N,$$

$$\dot{n}_1=-Kn_1^2-Kn_1N. \tag{15}$$

In this case the time evolution of N is given implicitly by

$$Kt=E_1(\ln N), \tag{16}$$

where E_1 is the exponential integral function, $E_1(x)=\int_x^\infty t^{-1}\exp(-t)dt$.

Closing this general consideration of the system of rate equations, it appears appropriate to note the differences between the two cases of MMEP with and without an initiator. It is immediately evident from the last of Eqs. (4) that the generic equation for all polymer chains (except for n_1) is identical to that of Eq. (9), whereby in the right-hand side of Eq. (9) n_1 is simply replaced by M. Mathematically the only difference between systems with and without an initiator, as a comparison of Eqs. (9) and (4) shows, pertains to the time evolution of active monomers n_1, albeit in both cases the corresponding equations contain contributions from binary and linear terms only. Practically, the difference (if of any significance since eventually the MWD will be determined by the longer chains) is most easily seen again for the exact solution of the case of no fragmentation, $F=0$. Instead of the integral exponent, obtained in Eq. (16), in the case of an initiator one can readily verify that the number of inert monomers decreases exponentially, that is, somewhat faster with time.

D. Numerical solution of the rate equations

We consider now a numerical study of the MMEP kinetics, as described by the system of nonlinear differential equations (4) subject to mass conservation, Eq. (5). Most of the calculations are carried out over 1000 equations, so that the total number of monomers $M=\phi V=1000$. A record is kept of $n_l(t)$ for $1\leqslant l\leqslant50$ over some 10000 time steps, and we employ an integration scheme with self-adjusting integration step δt. We also calculate the evolution of the mean chain length $L(t)$ and the number of chains $N(t)$.

As an initial length distribution we use an equilibrium MWD, Eq. (11), or a δ distribution, $\delta(l-2)$, starting with an initial system of dimers. The system then evolves in time until a new equilibrium is reached, characterized by a mean length L_∞.

In Fig. 1 we plot in log-log coordinates the time variation of the number of clusters of size l after a quench from an initial equilibrium MWD into a final state with $L_\infty=10$ is performed. In contrast to a previous work [16], where very small deviations from equilibrium were considered, $(1-L^0/L_\infty)=-0.01$, here we are interested in deviations that are nearly two orders of magnitude larger.

It is immediately clear from Fig. 1 that during relaxation to a new equilibrium state the temporal MWD does not preserve its exponential form. Clearly, the change in the number of free monomers in the system takes place much faster than that of clusters with larger l. In the late stages of relaxation the number of long chains still varies significantly whereas the shorter species have already attained equilibrium values. However, even at late times n_1 still keeps changing, contributing thus to the overall slow relaxational kinetics of MMEP.

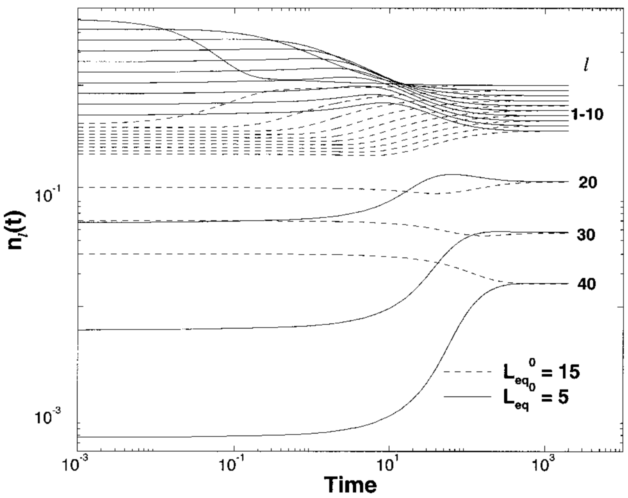

FIG. 1. Numerical solution for the evolution of the number of chains of length l (given as a parameter) from an initial equilibrium MWD with $L_{\rm eq}^0=15$ (dashed lines), and $L_{\rm eq}^0=5$ into a new equilibrium state with $L_\infty=10$.

Thus a substitution of a constant $n_1^{\rm eq}$ instead $n_1(t)$ in Eq. (6) would produce an exponentially fast relaxation of $N(t)$ with time in contrast to the results of numerical integration.

It is also evident from Fig. 1 that the variation of the number of clusters of a given size is not symmetric with respect to the direction of the T jump when the initial deviations from equilibrium are equal.

In Fig. 2(a) we show the time evolution of a system consisting initially of only dimers, towards an exponential equilibrium MWD. The nonlinear relaxation of $L(t)$ (cf. inset) is clearly seen. The variation of $L(t)$ with time is reasonably interpolated for all times t by the function

$$L(t)/L_\infty = 1 - \left(\frac{L_\infty}{L_\infty - L_0} + \frac{t}{2} \right)^{-1}$$

with $L_0=2$ and $L_\infty=5$. In Fig. 2(b) we replot the data from Fig. 2(a) in terms of n_l versus l for several times elapsed after the quench. Evidently, at $t=0.10$ s, shortly after the quench, the initial δ-like distribution broadens and transforms into a Poisson distribution, which later changes into a Gaussian distribution (at $t=0.50$ s) and ends eventually as an exponential distribution after $t=30$ s. Thus our numerical results for a system without an initiator exactly follow the scenario, predicted by Taganov [20] for a MMEP *with* an initiator and even the form of the MWD for various times after the quench is the same as in his Fig. 2 [20], derived in terms of a continuum approximation to the system of Eqs. (9). It appears indeed that MMEP systems with and without an initiator undergo qualitatively the same relaxational process.

It turns out that a rather simple description of this nonlinear relaxation in terms of a *single* relaxation time, τ_{L_∞}, depending on the final average chain length L_∞ is suggested by a scaling plot of $L(t)$ for different L_∞, as shown in Fig. 3 for an initial exponential MWD. It is evident from Fig. 3 that the response curves, $L_\infty - L(t)$, for different L_∞ may be collapsed on to a single ‘‘master’’ curve, $1-L(t)/L_\infty = f(t/\tau_{L_\infty})$ if time t is measured in units of a single relaxation time τ_{L_∞}. For the case of an exponential initial MWD we find $\tau_{L_\infty}=(0.33L_\infty)^5$. The scaling is also observed for an initial δ distribution, Fig. 4, where we obtain $\tau_{L_\infty}=(1.3L_\infty)^5$. We also find for the scaling function, $f(x)$, where $x=t/\tau_{L_\infty}$, $f(x)=x^{-1}$ for $x\to\infty$.

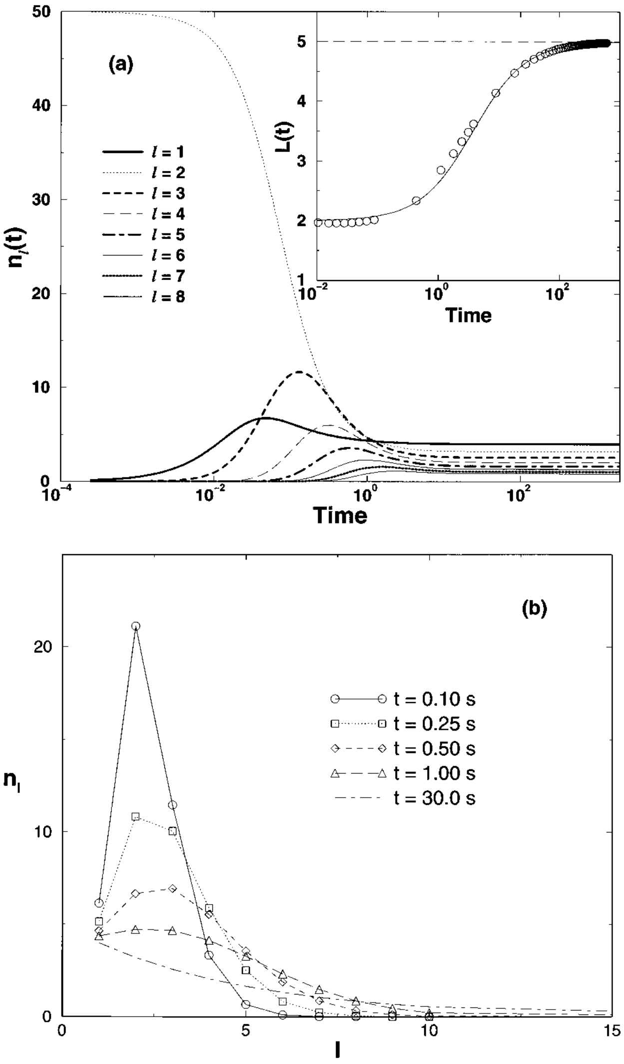

FIG. 2. (a) Numerical solution for the change in the number of chains of length l with time after a quench from an initial δ-like distribution of chains with $L=2$. In the inset the variation of the average chain length $L(t)$ with time is shown (empty circles). The solid line denotes an interpolation by

$$L(t)/L_\infty = 1 - \left(\frac{L_\infty}{L_\infty - L_0} + \frac{t}{2} \right)^{-1}$$

with $L_0=2$ and $L_\infty=5$. (b) The same data plotted as n_l vs l for different times after the quench.

III. MONTE CARLO SIMULATION OF THE MMEP MODEL

A. The algorithm

In the Monte Carlo simulation of the MMEP kinetics of relaxation we use a modified algorithm [13], based on the

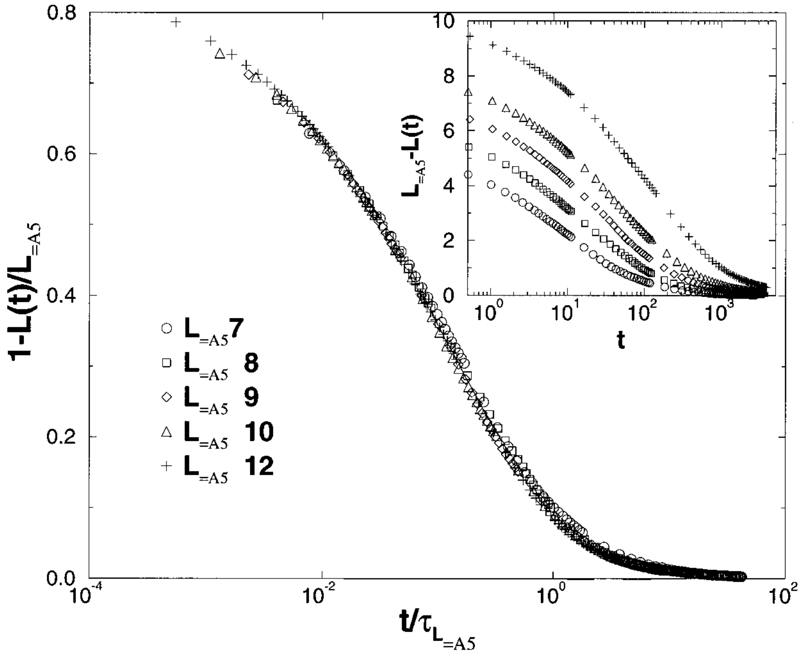

FIG. 3. Scaling plot of $L(t)$ from the numerical solution of the rate equations for quenches to different equilibrium states from an initial exponential MWD with $L=2$. The final mean lengths, L_∞ are given in the legend. The inset shows the original $L(t)$ vs t data. Here $\tau_{L_\infty}=(0.33L_\infty)^5$.

highly efficient bond fluctuation model [25], which is known to be very reliable in reproducing both static and dynamic properties of polymer chains in melts and solutions. The bond fluctuation model is a coarse-grained model of polymer chains, in which an ‘‘effective monomer’’ consists of an elementary cube whose eight sites on the hypothetical cubic lattice are blocked for further occupation. This defines the largest possible density of the polymer solution, which in terms of occupied to total volume is 0.5. A polymer chain is made by effective monomers joined by bonds. A bond corresponds to the end-to-end distance of a group of $3-5$ successive chemical bonds and can *fluctuate* in some range. It is represented by vectors $\mathbf{l}$ of the set $P(2,0,0)$, $P(2,1,0)$, $P(2,1,1)$, $P(3,0,0)$, and $P(3,1,0)$, which guarantee that intersections of the polymer chain with other chains, or with itself, are virtually impossible. All lengths are measured here in units of the lattice spacing and the symbol P stands for all permutations and sign combinations of the Cartesian coordinates (l_x,l_y,l_z), which yields a total of 108 permissible bonds. The modified bond fluctuation model allows now for a changing number of chains and chain lengths due to monomer attachment and/or detachment events in the course of the MMEP process. In the course of the simulation the ends of polymer chains are not allowed to bind together so that formation of rings is impossible.

Time is measured, as usual, in Monte Carlo Steps (MCS) per monomer of the system and a MCS is organized as follows: (i) A monomer is chosen at random and allowed to perform a move according to the bond fluctuation model algorithm; i.e., a random jump on a cubic lattice is carried

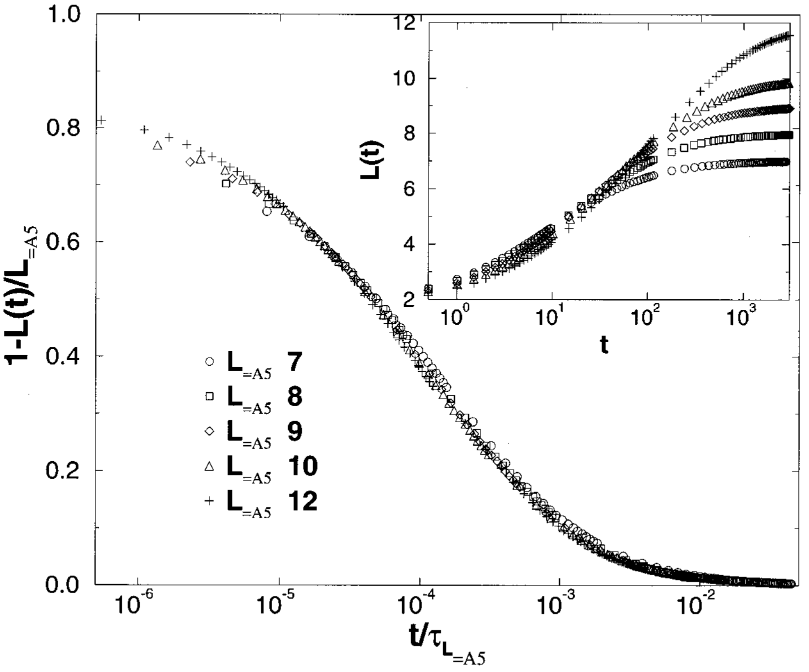

FIG. 4. The same as in Fig. 3 for an initial monodisperse system of dimers and $\tau_{L_\infty}=(1.3L_\infty)^5$.

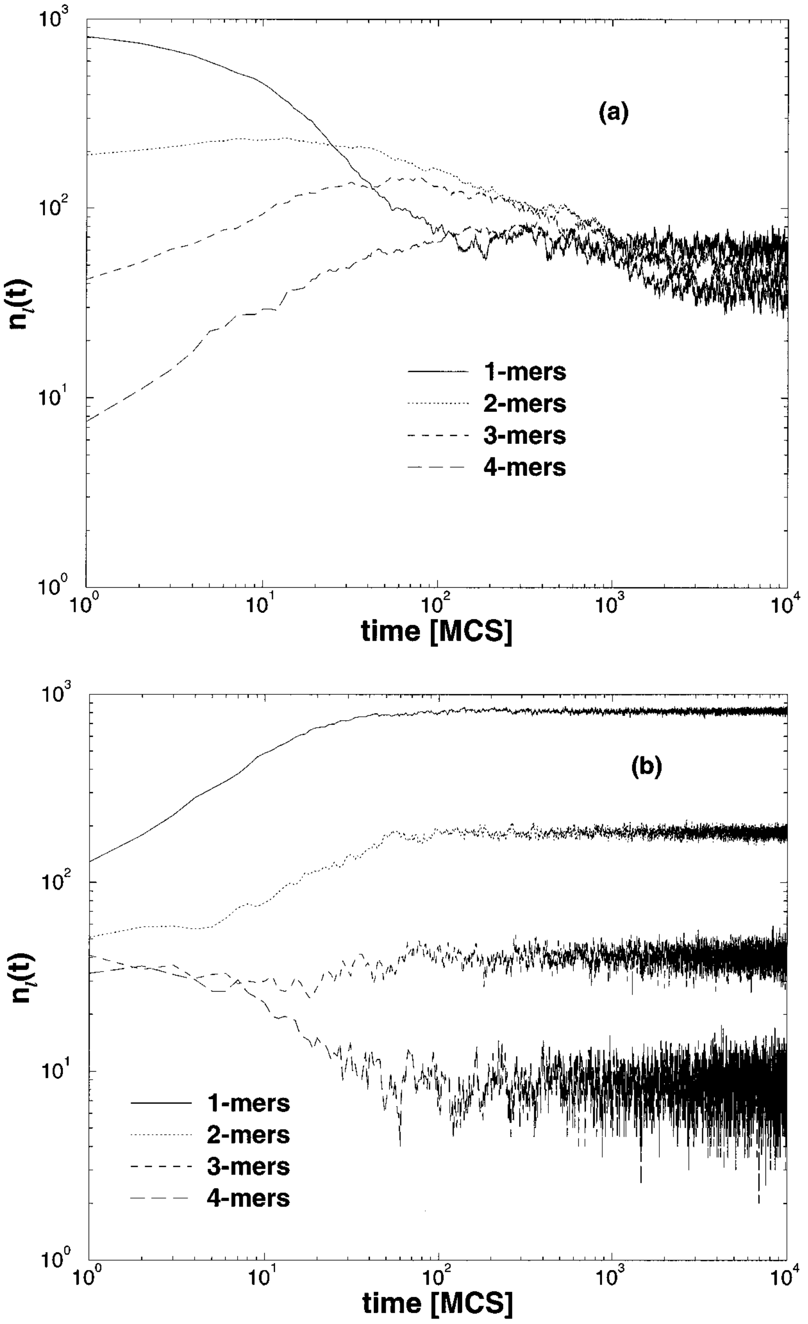

FIG. 5. (a) Monte Carlo results for the time evolution of $n_l(t)$ for $l=1,2,3,4$ after a T jump from $T_0=1.0$ with $L_0=1.289$ to $T=0.35$ with $L_\infty=4.280$. (b) The same for a heating from $T_0=0.35$ to $T=1.0$.

out so that chains do not intersect other chains or themselves. (ii) If a monomer happens to be an end of a chain, an attempt is made to detach it from the chain; i.e., its bond is broken if the value of a random number between 0 and 1 is smaller than the Boltzmann constant $\exp(-J/k_BT)$. (iii) If a free monomer exists within the range of permissible bond lengths from a chain end, it is associated with the chain and a new bond is created.

During one MCS one carries out these three steps as many times as there are monomers in the system. The simulations have been done on a $30\times30\times30$ cubic lattice with periodic boundary conditions. In the regime of dense polymer solution with $\phi=0.4$, which we keep throughout the present investigation, the system box accommodates a total of 1350 monomers. Finite size effects have been found earlier to disappear [13] for system sizes larger than $15\times15\times15$, however, in order to ensure good average values, the mean chain length L has been kept rather small—less than 1% of the total number of monomers in the system, which significantly restricts the choice of the lowest temperature. Usually, we have performed 30 runs for a given T jump whereby the initial, T_0, and the final, T, temperatures, have been chosen so as to ensure a larger change in the MWD.

B. Simulational results

In Fig. 5(a) we show the evolution of the number of chains of different length after cooling of the system from $T_0=1.0$ to $T=0.35$, and in Fig. 5(b) the same is shown for the reverse process of heating from $T_0=0.35$ to $T=1.0$. Obviously, the simulational curves, representing the change of $n_l(t)$ with time are almost identical to those of Fig. 1, although in the MFA rate equations (4), transport properties of the medium have been completely ignored. This comparison

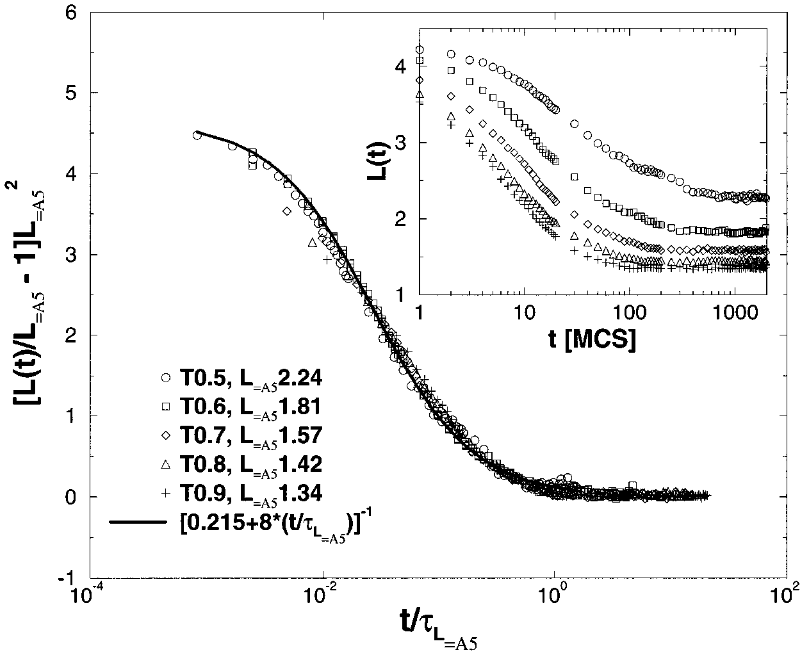

FIG. 6. Scaling plot for the relaxation of the mean chain length $L(t)$ after a T jump from $T_0=0.35$ to a series of final temperatures, given as a parameter along with the respective L_∞'s. The same Monte Carlo results as in Fig. 5 are used. Full line denotes the scaling function $f(x=t/\tau_{L_\infty})=(2.215+9x)^{-1}$. In the inset the evolution of $L(t)$ with time, measured in MCS is shown.

suggests that most of the conclusions, derived from the MFA approach, could be found to be still valid in the case of our computer experiment. Certainly, this might not be too surprising since mean field treatments work best at high densities; in any case, however, it shows that a treatment in terms of a system of differential rate equations appears reasonable.

In the case of very low densities, however, the situation could be more complex. The relaxation kinetics could involve additionally a characteristic "diffusion time," needed by the free monomers to find a chain end in the solution. This time would compete with the fragmentation rate and possibly, if too large, slow down the evolution toward equilibrium. A simulational study of the limit of very low densities would imply dealing with very large systems at sufficiently low temperature so that one still has $L_{\mathrm{eq}} \gg 1$, and thus require substantial computational efforts—we envisage this as a task for future work.

The behavior of the mean chain length is shown in Fig. 6 as a raw data (inset) and in a scaled form, $[L(t)/L_\infty - 1]L_\infty^2 = f(t/\tau_{L_\infty})$, representing a sudden heating of the system from initial temperature $T_0=0.35$ to a series of higher temperatures, $T=0.5$, 0.6, 0.7, 0.8, and 0.9. Despite some statistical fluctuations at late times after the T jump, it is evident from Fig. 6 that the different curves collapse on a single one if time is scaled by a single τ_{L_∞}. As for the system of rate equations (4), we again find $\tau_{L_\infty}=(1.85L_\infty)^5$, where the power 5 is determined with an accuracy of $\pm 2\%$. An interpolation formula for the scaling function $f(x=t/\tau_{L_\infty})=(2.215+9x)^{-1}$ appears to account well for the observed relaxation kinetics.

IV. SUMMARY

We have studied the relaxation kinetics of a system in a state of monomer-monomer equilibrium polymerization, as in sulfur and some dyes, in which association-dissociation processes involve single monomers only. It appears that a different MMEP process, as in poly(α-methylstyrene) where the polymerization involves an initiator, evolves qualitatively in the same way. For both, as in the case of wormlike micelles with scission-recombination kinetics, the equilibrium MWD is shown to be exponential, characterized by an average chain length L.

Within a MFA approach, describing the time variation of the number of l chains after a temperature jump towards new equilibrium, we find that the mean lifetime τ_l does not depend essentially on l, which might have important implications for the dynamics of MMEP systems.

From the numerical solution of the nonlinear coupled system of rate equations, we conclude that during the dynamic response of the system to a strong perturbation, the MWD does not retain its exponential form, as in the case for wormlike micelles with scission-recombination kinetics. Starting with an initial δ-like MWD, the system evolves into a Poisson, and later into a Gaussian distribution, the latter relaxing eventually into an exponential distribution at equilibrium. It appears possible to describe MMEP relaxation in terms of a single characteristic time that varies as the fifth power of the equilibrium average chain length. During the asymptotic (late) stages of relaxation the mean chain length approaches its equilibrium value as t^{-1}.

A Monte Carlo simulation of the relaxation kinetics in a MMEP system yields results that agree remarkably well with the MFA treatment in terms of rate equations, suggesting that at higher density transport processes do not significantly limit the relaxation. Both the variation of the number of chains of a given length with time as well as the evolution of the mean chain length $L(t)$ support the MFA conclusions and demonstrate that the initial deviation from equilibrium decays asymptotically as t^{-1} and is described by a single characteristic time $\tau_L \propto L^5$.

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