Full-Chain Dynamics of Entangled Linear and Star Polymers

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ABSTRACT: The full-chain dynamics and the linear viscoelastic properties of monodisperse, entangled linear and star polymers are simulated consistently via an equilibrium stochastic algorithm, based on a recently proposed full-chain reptation theory that is able to treat self-consistently mechanisms of chain reptation, chain-length fluctuations, and constraint release. In particular, it is the first time that the full-chain simulation for star polymers is performed without subjecting to the great simplifications usually made. To facilitate the study on linear viscoelasticity, we employ a constraint release mechanism that resembles the idea of tube dilation, in contrast to the one used earlier in simulating flows, where constraint release was performed in a fashion similar to double reptation. Predictions of the simulation are compared qualitatively and quantitatively with experiments, and excellent agreement is found for all investigated properties, which include the scaling laws for the zero-shear-rate viscosity and the steady-state compliance as well as the stress relaxation and dynamic moduli, for both polymer systems. The simulation for linear polymers indicates that the full-chain reptation theory considered is able to predict very well the rheology of monodisperse linear polymers under both linear viscoelastic and flow conditions. The simulation for star polymers, on the other hand, strongly implies that double reptation alone is insufficient, and other unexplored mechanisms that may further enhance stress relaxation of the tube segments near the star center seem crucial, in explaining the linear viscoelasticity of star polymers. © 2000 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 38: 248–261, 2000

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INTRODUCTION

The linear viscoelasticity (LVE) of monodisperse entangled linear polymers is well described by the reptation model proposed by de Gennes and extended by Doi–Edwards. However, effects such as segment connectivity, chain-length fluctuations, chain retraction, and constraint release (CR) that were neglected in the original Doi–Edwards model have been found to be very important in describing the LVE of polydisperse and branched polymer systems as well as the flow rheology of monodisperse linear polymers. After all these effects have been implemented rigorously in a recently proposed full-chain reptation theory, the tube model was shown to be extremely successful in predicting the rheology of monodisperse linear polymers under several different types of shearing flows. In spite of these achievements, the theory has not been investigated in detail for its ability to predict the linear viscoelasticity due to the expensive simulation effort involved.

We note that the LVE of entangled polymers has seldom been investigated by using a full-chain model, especially in modeling branched
polymers such as the star polymer for which the process that a star arm retracts its free end back along the primitive path is usually treated as if a Brownian particle were diffusing in a specified potential well.\textsuperscript{3,10,11,16} It has been shown that the effect of full chain is very important in explaining several distinct features observed for entangled linear polymers under double-step strain and simple shear flows.\textsuperscript{14,15} Although it is not clear whether such an effect is also important in describing the linear viscoelasticity, it is worthwhile studying the LVE at the full-chain level, for then mechanisms of chain reptation and chain-length fluctuations can be treated rigorously so that the effect of CR can be well discriminated.

Despite its well-known importance for the tube model, the CR mechanism has been relatively less agreed on its implementation. The major problems that remain to be resolved are (1) the existing theories that proved successful in explaining the linear viscoelasticity, such as double reptation\textsuperscript{7,8} and tube dilation\textsuperscript{5} theories, cannot be easily extended to the flow conditions, and (2) for branched polymers, the effect of CR is not so well understood as for linear polymers. To facilitate making progress on these aspects, it seems vital for a tube model to bear the following features:

1. The model must be able to account for CR at the levels of both linear viscoelasticity and fast flows, and consistent predictions may be required according to the well-known experimental rules, such as the Cox–Merz rule.\textsuperscript{17}

2. The model employs as less approximations or assumptions as possible so that the effect of CR can be well discriminated from others.

To step toward these goals, we wish in this work to study the LVE of two very basic entangled systems—monodisperse linear and star polymers—by using the previously proposed full-chain reptation theory that employs no approximations for chain connectivity, chain reptation, chain retraction, and chain-length fluctuations. The theory can be applied easily to any kind of flow field as well as the linear viscoelastic condition. We here are particularly interested in the simulation of star, for it is the first time that such a study is performed at the full-chain level so that arm retraction can be accurately mimicked.

The goals of this paper are twofold. On the one hand, we wish to examine the ability of the previously proposed full-chain theory to predict the LVE of linear polymers. Because the theory is primarily constructed for simulating flows and is not very efficient for studying the linear viscoelasticity, we propose a more efficient equilibrium algorithm based on the same theory, except that a different CR mechanism that best fits the current scheme is adopted. On the other hand, we wish to study the LVE of star polymers based on the full-chain simulation without subjecting to the great simplifications usually made, thereby exploring features of CR essential in explaining the observed linear viscoelastic properties of star polymers.

This article is organized as follows: We first briefly review the full-chain reptation theory used to construct the simulation algorithm. Then a detailed description of the simulation procedures is given, along with extensive discussions concerning various theories of constraint release and its implementation in the current simulation. After, simulation results are shown and compared to experiments, and we discuss possible implications of the simulation results as well as the essential features of CR for the two polymer systems considered, followed by a summary of this work.

**THEORY**

It is well known that all the linear viscoelastic properties can be obtained from a single function, $G(t)$, called the “relaxation modulus”. For example, one can find the zero-shear properties, such as the zero-shear-rate viscosity, $\eta_0$, and the steady-state compliance, $J'_0$, as well as the storage and loss moduli, $G'$ and $G''$, via the following relations:\textsuperscript{3}

\begin{align}
\eta_0 &= \int_0^\infty G(t) \, dt, \\
J'_0 &= \frac{1}{\eta_0} \int_0^\infty tG(t) \, dt, \\
G'(\omega) &= \omega \int_0^\infty G(t)\sin(\omega t) \, dt,
\end{align}
\[ G^*(\omega) = \omega \int_0^\infty G(t) \cos(\omega t) \, dt. \] (4)

In modeling the LVE of polymer liquids, one usually has two options. The first is to use directly the definition of \( G(t) \) in a single-step strain flow with a vanishing strain:

\[ G(t) = \lim_{\gamma \to 0} -\frac{\tau_{xx}}{\gamma}, \] (5)

where \( \gamma \) is the magnitude of strain, and \( \tau_{xx} \) is the shear stress. This approach is preferred as long as an analytical expression of \( G(t) \) can be deduced in a step-strain experiment. In stochastic simulations, however, it is usually very difficult to retrieve a sufficiently smooth curve for \( G(t) \) via eq 5 because of the usually drastic noise-signal ratio, unless a significant amount of CPU time is devoted to simulating a huge number of realizations.

An alternative way of obtaining \( G(t) \) in a stochastic simulation is to take advantage of linear response theory\(^{18} \) that relates the linear relaxation of a nonequilibrium physical property, like stress or temperature, to the decay of the auto-correlation function of the same quantity at equilibrium. It turned out that this could be a more efficient way to evaluate \( G(t) \) in the stochastic simulation of polymer liquids (see ref. 19 for example). When polymer melts are concerned, another choice is available, though.

An important assumption employed in the original Doi–Edwards model is that the stress remaining at time \( t \) following a small step-strain at \( t = 0 \) is proportional to the tube survival probability, \( \psi(t) \). That is, one can write\(^{9} \)

\[ G(t) = G_{0(N)}^0 \psi(t), \] (6)

where \( G_{0(N)}^0 \) is the plateau modulus. It is important to note that whereas the stress relaxation is strictly a nonequilibrium property, the tube survival probability can be evaluated at equilibrium from the chain-diffusion process. The situation is analogous to that of applying linear response theory; however, the idea behind eq 6 only applies to the tube model for concentrated systems.

To explain the \( M_1^{N,\lambda} \) molecular weight dependence of \( \eta_0 \), Ketzmerick and Öttinger\(^{20} \) applied a non-Markovian stochastic simulation for a Rouse chain confined in a tube with chain-length fluctuations accounted for. In their theory, the basic quantity calculated and used to compute the linear viscoelastic properties is the mean tube survival probability \( \langle L(t) \rangle / \langle L(0) \rangle \), where \( \langle L(t) \rangle \) is the mean length of the part of the original tube that has not been visited by either of the chain ends up to time \( t \). Here, we wish to calculate a similar quantity for linear polymers using a simpler equilibrium, Markovian stochastic scheme for the full-chain reptation model proposed in ref. 1 with both chain-length fluctuations and constraint release included. Furthermore, we wish to extend the simulation to the simplest branched system—the star-shaped polymer for which effects of chain-length fluctuations and constraint release were both found to be extremely important.\(^{10} \) The benefits of using an equilibrium scheme instead of the nonequilibrium one employed in ref. 1 will be discussed in a later section. Below, we introduce the theory used to construct the simulation algorithm.

In a recently proposed, self-consistent, full-chain reptation theory,\(^1 \) a linear polymer in the entangled system is modeled as a Rouse (or FENE) chain confined in a tube. The Rouse chain consists of \( N \) chain segments connecting the \( (N + 1) \) beads. The position of the \( i \)th bead is characterized by a scalar \( s_i \), measured along the tube contour from an arbitrarily chosen origin on the tube. Each bead of the chain is subjected to a sum of forces, including the Stokes-drag hydrodynamic force, the Hookean (or FENE) elastic force, and a random Brownian force. One then can write down a set of \( (N + 1) \) equations of motion for the \( (N + 1) \) beads, subject to the imposed flow field, with bead inertia neglected. Based on these equations, one can further construct another set of \( N \) equations describing the motion of the \( N \) chain segments, plus one for the reptative motion at one end of the chain. This is simply done by subtracting the equation of motion for the \( (i + 1) \)th bead from that for the \( i \)th bead, while keeping the one for the first bead unchanged. The resulting discretized equations for a linear polymer chain employing first-order, Eulerian forward schemes are\(^1 \)

\[ \Delta s_i = \frac{H}{\xi} Q_i \Delta t + \sqrt{\frac{2kT}{\xi}} \sqrt{\Delta t} \zeta_i, \]

\[ Q_i(t + \Delta t) = Q_i(t) + (v_\gamma(s_2) - v_\gamma(s_1)) \Delta t \]
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\[
+ \frac{H}{\zeta} (Q_1 - 2Q_i) \Delta t + \frac{2kT}{\zeta} \sqrt{\Delta t} (\xi_1 - \xi_i),
\]

\[
Q_i(t + \Delta t) = Q_i(t) + (v_T(s_{i+1}) - v_T(s_i)) \Delta t + \frac{H}{\zeta} (Q_{i+1} - 2Q_i + Q_{i-1}) \Delta t + \frac{2kT}{\zeta} \sqrt{\Delta t} (\xi_{i+1} - \xi_i),
\]

\[
i = 2, \ldots, N-1,
\]

\[
Q_N(t + \Delta t) = Q_N(t) + (v_T(s_{N+1}) - v_T(s_N)) \Delta t + \frac{H}{\zeta} (-2Q_N + Q_{N-1}) \Delta t + \frac{2kT}{\zeta} \sqrt{\Delta t} (\xi_{N+1} - \xi_N),
\]

where \( \Delta s_1 \) determines the reptation of the chain at one end in a given timestep \( \Delta t \), and \( Q_i \) is the segmental length of the \( i \)th chain segment; \( H \) is the Hookean spring constant, \( kT \) is the Boltzmann constant times the absolute temperature, and \( \zeta \) is the Stokes-drag coefficient; \( v_T(s) \) is the tube velocity at the position \( s_i \) and \( \xi_i \) is a random number whose distribution satisfies zero mean and unit variance. An excluded-volume potential is specified that prevents two beads from passing through each other, which results in an average equilibrium chain length proportional to the number of chain segments \( N \), and thus no Maxwell demons are needed to keep the polymer chain at a certain equilibrium length.

In examining eq 7, one sees that the equations of motion for a chain are coupled with those for the tube via the tube velocity terms \( v_T(s_i) \) and the boundary condition imposed at the tube ends. The tube is assumed to be deformed affinely by flow and convected with flow, plus a possible random process of tube-segment constraint release. Note that effects of chain connectivity, chain reptation, chain retraction, chain-length fluctuations, and constraint release are all self-consistently incorporated into eq 7. This theory can be, in principle, applied to any kind of flow field, and no approximations usually associated with a tube model are needed to solve the model. Note that because the tube is assumed to completely determine the orientation of the confined chain, no possible lateral motions, such as the Rouse-like motions, of polymer chains can be accounted for in the theory. For a more detailed introduction of the theory, the reader is referred to ref. 1.

Of particular concern here is how the CR mechanism was executed. In the theory, when a tube segment is abandoned by chain reptation, chain retraction or chain-length fluctuations, one randomly picks a constraint formed by two adjacent tube segments on another chain in the ensemble to be released; but no CR will result if the selected tube segment is older than the abandoned one (see discussions in ref. 1). The greatest advantage of such a CR scheme is that it can be applied easily to general flow fields, unlike most of the previous schemes that were either restricted to the linear viscoelastic properties,4–11 or only applied to fast flows.12,13 Note that the idea of the above CR scheme is very similar to the double reptation theory of des Cloizeaux,8 which is restricted to the equilibrium condition, however. We shall examine in a later section whether such a CR scheme is able to lead to satisfactory predictions for the LVE of linear and star polymers.

SIMULATION ALGORITHM

To calculate the tube survival probability for a polymer chain whose dynamics is governed by the set of equations in eq 7 is straightforward when CR is excluded. The procedures are depicted in the following for linear polymers:

1. We first assume that the tube is intact at the beginning of simulation, that is, \( \langle \psi(t = 0) \rangle = 1 \), where \( (\cdots) \) represents the ensemble average. For each chain in the ensemble, we specify the one-dimensional coordinates of its two ends as follows: the left one starts at a coordinate of \( S_1(t = 0) = 0 \) and the right equal to its initial chain length, denoted by \( S_r(t = 0) = \sum_{i=1}^{N} Q_i(t = 0) \). The initial distribution of \( Q_i \) is assumed to satisfy the Maxwell–Boltzmann relation, which results in an ensemble average of \( \sqrt{2kT/\pi H} \) for \( Q_i \).

2. In each timestep, we calculate \( \Delta s_i(t + \Delta t) \) and the new positions along the tube of segments \( Q_i(t + \Delta t) \) for \( i = 1 \) to \( N \) from eq 7 without the tube velocity terms. The new coordinates of \( S_1 \) and \( S_r \) can be found by \( S_1(t + \Delta t) = S_1(t) + \Delta s_1(t + \Delta t) \) and \( S_r(t + \Delta t) = S_r(t + \Delta t) + \sum_{i=1}^{N} Q_i(t + \Delta t) \).

3. The mean tube survival probability \( \langle \psi(t) \rangle \) is obtained by

\[
\langle \psi(t) \rangle = \left( \frac{L(t)}{L(0)} \right) = \left( \frac{S_{r, \text{min}}(t) - S_{1, \text{max}}(t)}{L(0)} \right),
\]
where \( S_{r,\text{min}}(t) \) and \( S_{l,\text{max}}(t) \) are the minimum and maximum values for \( S_r \) and \( S_l \), respectively, up to time \( t \). The values of \( S_{l,\text{max}} \) and \( S_{r,\text{min}} \) may be updated after each timestep when compared to the most recent values of \( S_l \) and \( S_r \), and the value of \( L(t) \) is set to be zero when \( S_{l,\text{max}} \geq S_{r,\text{min}} \), when the original oriented tube is totally evacuated. Note that the way the mean tube survival probability \( \langle \psi(t) \rangle \) is defined here differs slightly from that in ref. 20; nevertheless, no discernible differences of the simulation results are found based on either definition.

The corresponding procedures for star polymers are nearly the same as those depicted above, except that we shall artificially keep the left end of a chain, which now represents the star center (or branch point), fixed at all times (i.e., \( \Delta s_1 = 0 \) for all \( t \)), as is usually treated for a star polymer. Although the motion of the star center was believed to be unimportant for the linear relaxation of star polymers,\(^{21} \) we would rather regard such a treatment as a theoretical expediency in modeling star polymers. Because the usual reptative motion is prohibited, a star can only relax stress by withdrawing its arm back along the primitive path; in other words, only chain-length fluctuations will contribute to the stress relaxation if the effect of CR were not considered. For this case, \( \Delta s_1 \) is defined here differs slightly from that in ref. 20; nevertheless, no discernible differences of the simulation results are found based on either definition.

A different choice for the ratio \( G(\gamma) \) to be introduced later, whose actual value is of no practical interest in the present work. In other words, any important conclusion that might be drawn from this work should be essentially independent of the choices of \( N / Z \) and \( C^* \) within reasonable ranges.

Now we shall address how constraint release can be incorporated in the previously prescribed procedures. Apparently there are many possibilities that it can be done according to numerous reptation theories proposed so far. Thus it is instructive to start with a brief review on earlier studies related to this issue: Marrucci\(^5 \) first proposed the idea of tube dilation to account for the swelling of tube diameter in the course of stress relaxation for entangled linear polymers. This idea was later extended by Ball and McLeish\(^{10} \) in explaining the scaling law for the zero-shear-rate viscosity of star polymers. Rubinstein and Colby\(^9 \) as well as some earlier workers\(^{4,6} \) considered the stress relaxation modulus as a product of two relaxation functions: one accounts for the usual chain reptation, the other for tube constraint release; the stress relaxation due to constraint release was treated as the Rouse-like relaxation of a random copolymer with various relaxation rates. Des Cloizeaux\(^8 \) proposed an idea of double reptation and obtained a very successful mixing rule of...
G(t) for a set of binary blends that had been considered earlier by Rubinstein and Colby. A similar result for mixing was also reached by Tsengoglou who accounted for the effect of CR by the destruction of temporary networks. Öttinger added a stochastic term in the dynamic equation of a tube segment for the Doi–Edwards model to mimic the effect of constraint release, and he obtained an improved prediction of the power law index of steady-state viscosity in simple shear flow. In the full-chain reptation theory currently proposed by Hua and Schieber, constraint release was performed in a fashion similar to the double reptation mechanism of des Cloizeaux, but is more general; because stochastic schemes were employed, more complicated causes of constraint release, such as chain retraction under fast flows, can also be treated consistently in their theory.

As can be seen from this brief review, there exists a variety of schemes that constraint release can be executed at the linear viscoelastic level, and to date no definitive conclusions can be drawn regarding the way constraint release should be performed. Before more conclusive remarks can be made, any theoretical or experimental (ref. 23 for example) investigation that may help further understanding of the actual roles of CR in various entangled systems should be imperatively important. In the following, we propose a very simple, yet consistent, CR mechanism for implementation in the current simulation that resembles the idea of tube dilation and results in predictions well in accord with all the observed linear viscoelastic properties of both linear and star polymers.

Recognizing the fact, in the mean field sense, that whenever stress relaxation by chain retraction or chain-length fluctuations occurs, corresponding stress relaxation by CR must also result because of tube reorganization, we assume that the stress relaxation by CR can be accounted for in a self-consistent manner plausible for monodisperse systems:

\[ \Delta \langle \psi^\prime(t) \rangle = C^* \Delta \langle \psi^\prime(t) \rangle, \]
\[ \Delta \langle \psi^\prime(t) \rangle := \langle \psi(t) \rangle - \langle \psi(t + \Delta t) \rangle \quad \text{(without CR)}, \quad (10) \]

where \( \Delta \langle \psi(t) \rangle \) and \( \Delta \langle \psi^\prime(t) \rangle \) are the negative of the changes of tube survival probability caused by CR and by reptation and/or chain-length fluctuations, respectively, during a timestep \( \Delta t \), and \( C^* \) is a proportional constant denoted as the “CR parameter”. Naively, one might expect the value of \( C^* \) to be close to but below one according to double reptation theory, because there is a certain possibility that two entangled polymer chains are reptating away at almost the same time, and thus no CR should result. However, the value of \( C^* \) can also depend on how eq 10 is executed.

Of course, one may also adopt directly results from the double reptation principle by taking the square of the average tube survival probability evaluated for polymer chains in a permanent network (i.e., no CR):

\[ \frac{G(t)}{G^0(\infty)} = \langle \psi^\prime(t) \rangle^2, \]
\[ \langle \psi^\prime(t) \rangle := \langle \psi(t) \rangle \quad \text{(without CR)}. \quad (11) \]

However, such a procedure cannot be applied accordingly under flow conditions. Moreover, as one will see that predictions based on eq 11, which was believed to hold for both linear and star polymers, turn out to be unsatisfactory for the star system.

Partly motivated by the success of the tube dilation theory employed by Ball and McLeish in explaining the LVE of star polymers, we propose below a CR mechanism similar to tube dilation that eq 10 can be executed in the current simulation.

In each timestep, we calculate the change of the average tube survival probability by reptation and/or chain-length fluctuations, \( \Delta \langle \psi^\prime(t) \rangle \). According to eq 10, decrease of \( \langle \psi^\prime(t) \rangle \) caused by CR by an amount of \( C^* \Delta \langle \psi^\prime(t) \rangle \) must accompany. The latter can be performed by first evaluating the average tube length to be evacuated by CR, \( \Delta L^c \):

\[ \Delta L^c = \Delta \langle \psi^\prime(t) \rangle \times \langle L(0) \rangle = C^* \Delta \langle \psi^\prime(t) \rangle \times \langle L(0) \rangle. \quad (12) \]

Then, for linear polymers, for each tube in the ensemble we specify a portion of the tube with a distance \( \Delta L^c \) to be indicated as “elastically inactive” due to constraint release, and the inactive tube region expands outwardly in both directions from the tube center, as illustrated in Figure 1. For the case of star, the corresponding region expands from the star center towards the free end, as also indicated in Figure 1. The above
procedure for CR is performed at the end of each timestep. The average tube survival probability $^c t \langle t \rangle$ is obtained by evaluating the ratio $L(t) / L(0)$, where $L(t)$ is the portion of the original tube that has not been evacuated by any of the three relaxation mechanisms (i.e., reptation, chain-length fluctuations, and constraint release) up to time $t$.

The CR scheme depicted above resembles the idea of tube dilation in that the effective primitive path length (which is inversely proportional to the tube diameter in order to keep the mean square of the polymer end-to-end distance constant) is decreasing during stress relaxation, but it differs from the double reptation concept that allows CR to take place in any point of the tube and leads to no change of the tube diameter (and thus the primitive path length). However, in the original tube dilation theory for linear polymers, the tube diameter swells inversely to the square root of the average tube survival probability, and thus the effective entangled distance reduces to $\langle \psi(t) \rangle^2 \times \langle L(0) \rangle$ at time $t$, whereas the current CR scheme does not lead to the same square dependence of $\langle \psi(t) \rangle^2$ that is believed to be necessary in explaining the LVE of polydisperse systems. Nonetheless, as we shall see that the current CR scheme seems sufficient for both linear and star polymers of monodispersity, while predictions based on eq 11 alone is unsatisfactory for the star system. Even though it is possible here to construct a CR mechanism that can be naturally extended to the polydisperse conditions, the current scheme appears to be the simplest one that is sufficient to meet our tentative concerns in this work.

In the following section, we shall examine the performance of the full-chain model, based on the proposed CR mechanism, in predicting the linear viscoelasticity. From the simulation results we should be able to gain insight into the essential features of the CR mechanism for these two polymer systems, especially for the star system.

RESULTS AND DISCUSSION

Results shown in this section are obtained by simulating an ensemble size of 3,000 polymer chains with the number of chain segments $N$ varying from 11 to 101 for linear polymers, and $N_a$ from 3 to 19 for star polymers, where $N_a$ is the number of chain segments for a star arm. Because we will consider only the case of $N/Z = 1$, we may replace $N$ and $N_a$ by the numbers of entanglements $Z$ and $Z_a$, respectively. The reptation time constant for a linear polymer with $N$ chain segments is defined as

$$\tau_d(N) := \frac{2}{\pi^2} N^3 \lambda_H,$$

(13)

where $\lambda_H := \zeta H$ is the relaxation time constant associated with the Hookean springs. Note that the definition given here for the reptation time constant is the same as in ref. 1, but it differs from that in the Doi–Edwards model by a factor of two. The terminal relaxation time for a star with $N_a = N$ is typically much longer than that given by
eq 13 for linear polymers. In order to see better the effect of molecular weight and to compare more conveniently the simulation results for these two polymer systems, we tend to choose a single time constant, say \( t_{d} \) \((N = 21)\), to make time dimensionless for all simulation results. Because a first-order Eulerian scheme is used, the effect of discrete timestep size is another important issue to address. For linear polymers, we find that the choice of \( \Delta t/\lambda_{H} = 0.4 \) is sufficient for all purposes. The errors for \( \eta_{0} \) and \( J_{0}^{\eta} \) due to discrete time simulation are estimated to be a few percent for the range of \( N \) simulated. For the case of star polymers, much larger errors are found, however, based on the same timestep size. The error due to the use of a discrete timestep size comes from the unobserved visiting of the chain’s free ends during a given timestep, which can be accounted for, though, by solving exactly the first-passage-time problem.\(^{22}\) Because the time required for a star arm to retract back a distance \( s \) along the primitive path and thereby relax stress held by the portion of the tube behind it depends exponentially on \( s \), any small error associated with such unobserved visiting of the free end might lead to significant errors in evaluating the linear viscoelastic properties of star polymers.

In Figure 2 we show a typical plot for the computed zero-shear-rate viscosity as functions of timestep size for star polymers. We find that the estimated value of \( \eta_{0} \) at zero timestep size can be approximated very well by performing a linear extrapolation at the interval \( \Delta t/\lambda_{H} = 0.2 \) to 0.6. A similar situation is found for the steady-state compliance, but not shown here. Hence, we try extrapolating directly the result of \( G(t) \) by performing in parallel one simulation with two different timestep sizes: \( \Delta t/\lambda_{H} = 0.25 \) and 0.5. The result compares favorably with that obtained by using a much smaller timestep size \( \Delta t/\lambda_{H} = 0.01 \). A significant amount of simulation time can be saved by performing such extrapolations.

Before we formally proceed with the simulation results, it is of interest to make a direct comparison between the equilibrium (using eq 6) and nonequilibrium (using eq 5) simulations for the prediction of \( G(t) \). Note that both simulations are based on the same set of governing equations, eq 7, except that the tube velocity terms drop in the equilibrium simulation and two different CR schemes are employed respectively. Because here we have assumed a ratio for \( N/Z \) \((= 1)\) different from that used in the nonequilibrium simulation \((= 3)\), we must make comparisons based on the number of chain segments \( N \) only. In Figure 3, we show comparison of \( G(t) \) for three different chain lengths: \( N = 11, 21, \) and 31 without constraint release. One sees that the predictions from these two schemes coincide as \( N \) becomes large. The differences observed for short chains could be due to the effect of discrete tube segments used in the nonequilibrium simulation, and such an effect be-

![Figure 2](image1.png)

**Figure 2.** The computed zero-shear-rate viscosity as functions of timestep size for star polymers with arm length \( Z_{a} = 13 \) predicted by the simulation (square points). The solid line is the linear extrapolation using data points at \( \Delta t/\lambda_{H} = 0.5 \) and 0.25.

![Figure 3](image2.png)

**Figure 3.** The relaxation modulus as functions of time for three different chain lengths: \( N = 11, 21, \) and 31 from the equilibrium (solid lines) and nonequilibrium (dotted lines) simulations without constraint release (i.e., \( C^{*} = 0 \)).
comes unimportant as the number of tube segments becomes large for a relatively long chain. A similar comparison with CR included is made in Figure 4. We find that the equilibrium simulation results for $C^* = 0.4$ mimic very well those obtained from the nonequilibrium simulation. The agreement between these two schemes enables us to evaluate the performance of the full-chain representation theory considered in predicting the linear viscoelasticity via the current equilibrium scheme that is much more efficient.

We must point out that in the above comparisons, while only 3,000 chains are simulated by the equilibrium algorithm, ten times more chains are used to obtain the still much noisier curves by the nonequilibrium simulation. The agreement between these two schemes enables us to evaluate the performance of the full-chain reptation theory considered in predicting the linear viscoelasticity via the current equilibrium scheme that is much more efficient.

In Figure 5 we show predictions of the zero-shear-rate viscosity as functions of chain length for linear polymers with and without constraint release. From the plots we see that the simulation is able to predict very closely the experimentally observed $Z^{3.4}$ dependence of $\eta_0$, and such a prediction seems to be independent of the CR mechanism employed here. This result agrees well with the usual understanding that mechanisms of reptation and chain-length fluctuations are sufficient to account for the experimentally observed $Z^{3.4}$ dependence of $\eta_0$.

It was found experimentally that the steady-state compliance of entangled linear polymers is quite independent of the molecular weight, and the product $J_0^e G^e(N)$ was found to fall around 2 (see ref. 24 and others referred therein). These observations are also verified by the simulation, as shown in Figure 6.

For star polymers, the Doi–Edwards model predicts $\eta_0 \propto (Z_o)^b \exp[\nu Z_o]$, where $b$ and $\nu$ are two scaling parameters with $b = 2$ and $\nu = 15/8$.
given by their model. The previous dependence was found to be too strong for the experimental data. Rather, \( n = 0.5 \) with \( b \) somewhat arbitrarily chosen between 0.5 and 2 was found for a variety of numbers and lengths of star arms for several different polymer species. In Figure 7 we plot the zero-shear-rate viscosity curve for star polymers, where \( b = 1.5 \) is used. One sees that the simulation is able to predict the correct dependence of \( \eta_0 \) on \( Z_a \) (i.e., \( n = 0.5 \)) based on the same value of \( C^* \) as for linear polymers. We, however, do not regard it is important to have such coincidence for the value of \( C^* \), and it is simply a best fit consistent with the choice of \( N / Z = 1 \). What might be important is to see if consistent predictions are obtainable for other linear viscoelastic properties to be examined in the following.

In Figure 8 we plot the steady-state compliance curve for star polymers. The steady-state compliance is found to scale linearly with \( Z_a \), and the slope of the curve is found to be about 0.96. These predictions are in excellent agreement with the experimental findings, although in ref. 16 a smaller value (= 0.6) for the slope of the compliance curve was reported; nevertheless, this disparity should be unimportant considering that their compliance data are so widely scattered.

As shown earlier for linear polymers that the equilibrium simulation results follow closely those of the nonequilibrium simulation, despite that the CR mechanisms employed are very different. It is therefore of interest to see if the same situation also applies to the star system. In Figure 9 we compare the predictions of \( G(t) \) from both schemes. This time we, however, do not see the accordance found earlier for linear polymers. We also find that the zero-shear-rate viscosity obtained by the nonequilibrium simulation scales in a much stronger way with \( Z_a \) than observed experimentally. The discrepancy has important implications and may be understood more easily via double reptation theory, which is similar to the CR mechanism performed in the nonequilibrium simulation.
According to the double reptation theory of des Cloizeaux, the stress held by a stress point, which is formed by two chain segments of different chains, can be relaxed only if one of the two entangled chains diffuses away. Because there is a certain probability that chain segments near the star center are entangled with others located at a similar position, the double reptation mechanism will not help to relax in time the stress held by these stress points before the star’s free ends can effectively reach them by arm retraction. Based on the CR mechanism proposed here, a star arm only needs to withdraw an average distance of $1/(1 + C^*) \langle L(0) \rangle$, rather than the full distance $\langle L(0) \rangle$ to relax the stress held by the original tube. For time scales comparable to the longest relaxation time of a star in such a system, if instead double reptation were used for the CR mechanism, the fraction of tube segments that cannot be evacuated by either arm retraction or double reptation would be about $[C^*/(1 + C^*)]^2$ (≈8% for $C^* = 0.4$). It is this small fraction of tube segments near the star center that would greatly lengthen the longest relaxation time of a star system. In this case, one would expect an unrealistic long lasting plateau of $G(t)$ at intermediate times when stress relaxation by both arm retraction and double reptation is apparently slowed down due to the significant entropic potential barrier encountered by the star’s free ends. Indeed, this is what we found in the nonequilibrium simulation for star that results in a much stronger scaling law of $\eta_0$ than observed in experiments.

Based on the above observations, we believe that other mechanisms that could possibly help to relax the stress held by those tube segments near the star center must be explored, if double reptation is to remain valid for the star system. Of course, it is possible to introduce the stress dilution mechanism adopted by Ball and McLeish or other similar theories to resolve this problem, where the entropic forces acting on the chain ends were assumed to be diluted by the relaxed tube segments served as solvents, resulting in a rapid reduction of the primitive path length and fast stress relaxation of the unrelaxed tube segments near the star center. We, however, would rather leave it as an open question as to whether it is necessary to “dilute” the spring potential of a full-chain model in order to account for the effect of constraint release in branched systems.

One of the distinct features found for star polymers is the shape of the loss modulus curve. It was found that after the intersecting point of $G'$ and $G''$, the $G''$ of a monodisperse linear polymer starts dropping, whereas it remains climbing up for a star polymer. In Figures 10 and 11 we plot the dynamic moduli $G'$ and $G''$ for linear and star polymers, respectively, and compare them to two sets of experimental data. Note that the selection of the data sets is based on the consideration that they are typical of the systems we wish to compare. From the plots one can see that the simula-

**Figure 9.** Comparison of the relaxation modulus for star polymers predicted by the equilibrium (solid line) and nonequilibrium (dotted line) simulations. A long-lasting plateau is observed at intermediate times for the nonequilibrium simulation result.

**Figure 10.** The dynamic moduli as functions of frequency for a linear polymer obtained from the simulation (solid lines) and experiment (points). The parameter values used in the simulation are $Z = 51$ and $C^* = 0.4$, and the data are reproduced from ref. 24.
tion is capable of exhibiting the signatures of these two polymer systems.

In Figure 10, the plateau modulus and the reptation time constant are fitted to be \( G_0(N) = 1.25 \times 10^7 \text{ dynes/cm}^2 \) and \( \tau_d(N=51) \approx 10 \alpha_T \text{ s} \), respectively, where \( \alpha_T \) is the time–temperature superposition factor. Note that the fitted value of \( G_0(N) \) is in close agreement with the reported value \((= 1.15 \times 10^7 \text{ dynes/cm}^2)\). For linear polymers, we find that the quality of fitting of the dynamic moduli is rather insensitive to the choice of \( Z \). Hence, the value of \( Z \) chosen here to make the comparison, \( Z = 51 \), should not necessarily imply anything about the actual number of entanglements for the sample. In Figure 11, the longest relaxation time of the system is estimated to be 550 s; the plateau modulus is fitted to be \( 4.54 \times 10^6 \text{ dynes/cm}^2 \), again in close agreement with the reported value \((= 4.34 \times 10^6 \text{ dyn/cm}^2)\). For star polymers, we find that the height of the intersecting point of \( G'_9 \) and \( G'_0 \) depends apparently on the arm molecular weight (or \( Z_a \)), in contrast to the linear polymer system where the corresponding height is quite independent of \( Z \) and is about 0.4 \( G'_0(N) \). Such a difference was also observed in experiments. Based on the above observations, we believe that the current CR mechanism employed in this work is able to lead to remarkable agreement with experimental observations for all linear viscoelastic properties investigated. The success found for linear polymers is not too surprising, because the effect of CR will only modify slightly the predicted LVE of monodisperse linear polymers, and other relaxation mechanisms have already been included rigorously in the model. Nonetheless, for its remarkable performance in predicting the LVE of star polymers, we believe that the current CR mechanism must have already captured the essential features of the linear relaxation of the star system. In order to retain the validity of double reptation, which naturally takes care of the effect of polydispersity and is more likely to be implemented rigorously in the full-chain model in simulating flows, other mechanisms that may further enhance stress relaxation of the tube segments near the star center must be explored. Without subjecting to ad hoc stress dilution mechanisms, one possibility is to account for the motion of the star center, which could play important roles when the usual CR mechanism, say double reptation, makes it easier for a star center to change its position without requiring first to retract any of its arms fully back to the star center. In this case, a star arm would not have to withdraw its free end all the way down to the star center in order to relax the full stress held by the arm, as suggested by the current CR scheme, because then the motion of the star center would “share” the responsibility in relaxing stress. Indeed,
stress relaxation due to the motion of the star center has been considered earlier by Klein, but his study was restricted to a system of permanent networks. Theoretical or experimental investigations that may help to clarify this issue are eagerly awaited. On the other hand, the Rouse-like CR motion active in the process of tube dilation that has been neglected in the current simulation may also play important roles in the linear stress relaxation. For monodisperse systems, we suspect that such a motion could be important only in the star system where tube dilation seems more relevant. However, if the star center were to be nailed in space, the Rouse-like motion of the confined chain near the star center would also be highly suppressed, and thus it cannot contribute much either to the stress relaxation of the tube segments near the star center. Hence, it appears that in addition to the double reptation mechanism, an ideal reptation theory for star or other branched polymers should also be able to account for both the motion of the branch points and the Rouse-like CR motion, and their relative importance to the linear stress relaxation should be an interesting future work.

CONCLUSIONS

We here investigate the linear viscoelastic properties of entangled linear and star polymers via a recently proposed full-chain reptation theory. Because stochastic schemes are employed, the dynamics of the full chain can be easily tracked; and because mechanisms of chain reptation and chain-length fluctuations can be treated rigorously, the effect of CR can be well discriminated. Focus is on the full-chain simulation of the star polymer, and it is the first time that such a study is performed without involving the great simplifications usually made.

In order to be more efficient in studying the linear viscoelasticity, we propose an equilibrium algorithm that inherits all rigorous features of the previous full-chain theory, while employing a different CR mechanism that resembles the idea of tube dilation and fits best the current equilibrium scheme. We find that the current simulation is able to predict excellently all the investigated linear viscoelastic properties, including the scaling laws for the zero-shear-rate viscosity and the steady-state compliance, as well as the relaxation and dynamic moduli, for both polymer systems.

The simulation for linear polymers indicates that the full-chain reptation theory considered, besides its already successful features in predicting the nonlinear flow rheology, is able to predict satisfactorily the LVE of monodisperse linear polymers. For star polymers, the current study strongly implies that double reptation alone is insufficient and other unexplored mechanisms, such as the positioning fluctuations of the star center and the Rouse-like CR motion in a swelling tube that may further enhance stress relaxation of the tube segments near the star center, seem crucial in predicting the LVE of star polymers.

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REFERENCES AND NOTES

1. Hua, C. C.; Schieber, J. D. J Chem Phys 1998, 109, 10018. Several typographical errors exist in eq 17 of this manuscript, which have been corrected in the eq 7 of this article.