Nonlinear Stress Relaxation of H-Shaped Polymer Melt Revisited Using a Stochastic Pom-Pom Model

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ABSTRACT: A versatile, stochastic version of the pom-pom model is proposed and employed to reexamine the nonlinear stress relaxation of a nearly monodisperse H-shaped polyisoprene melt. Since the current simulation model requires less assumptions and approximations to solve the stretch relaxation of entangled H-polymer chains, the pom-pom model proposals can be tested independently and rigorously. Detailed comparisons are made among the current stochastic simulation, the predictions of the original model, and a set of stress relaxation data. At short times right after the imposition of a large strain sufficient to induce complete arm withdraw, the proposals concerning an initial partial cross-bar retraction are well supported by showing close agreement between the simulation and the nonlinear relaxation data. On intermediate time scales when a renormalized cross-bar retraction was predicted to set in, the essential properties of stress relaxation are also largely consistent with the early theories that considered drag-strain coupling along with a dumbbell-like cross-bar retraction. The most obvious discrepancy is found for the nonlinear relaxation at long times, where the data begin to exhibit systematic deviations from the predictions assuming complete cross-bar retraction near the renormalized Rouse time. The last finding is discussed in conjunction with recent experimental observations regarding the possibility of a partial stretch relaxation upon the Rouse time.

I. Introduction

Encouraging progress has recently been made in molecular modeling of the rheology of entangled branched polymers based on the framework of the tube model.[1,2] The pom-pom molecular theory established by McLeish and Larson[3] and developed by subsequent workers[4,5] has been demonstrated to capture many essential linear and nonlinear viscoelastic properties of entangled branched polymers.[3−9] As a further scrutiny into the central proposals of the theory, McLeish and co-workers[4] lately conducted simultaneously rheological measurements and small-angle neutron scattering for a series of nearly monodisperse H-shaped polyisoprene melts, and close agreement between theoretical predictions and experimental data was generally observed, particularly for the linear viscoelastic properties. The corresponding investigations on nonlinear viscoelasticity were not as conclusive, however. For example, for nonlinear stress relaxation following large step-strain deformations, an extra adjustable parameter had to be introduced to obtain a reasonable fit of the data. More importantly, since no direct comparisons have been carried out for strains that are large enough to induce complete arm withdraw or partial cross-bar retraction, the case in which all possible retraction modes for an entangled H-polymer chain are perturbed, the test of the theory was strictly incomplete. Since the pom-pom model was primarily designed for simulating fast flows, and since the related constitutive equations have recently become a very popular tool for studying complex flows of entangled branched polymers, it is important to conduct further investigations on the fundamental proposals of the theory, particularly for those concerning cross-bar retraction that has been believed to be the key to several peculiar nonlinear rheological properties of this class of polymers.

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To perform an independent, theoretical test of the pom-pom model proposals, we here construct a stochastic version of the pom-pom model that is able to fulfill more faithfully the central proposals in the original theory concerning nonlinear viscoelasticity, by avoiding unnecessary physical assumptions and mathematical approximations in solving the nonlinear chain dynamics. Indeed, the ability to obtain more realistic predictions of the tube model based on stochastic schemes has recently been demonstrated in modeling the rheology of entangled linear polymers.[10−12] On the other hand, the success of recently developed numerical schemes that allow molecular theories to be directly incorporated into the simulation of complex flows (for example, the CONNFFESSIT approach[13,14] and many of its descendants) also encourages the establishment of stochastic schemes for simulating the rheology of entangled branched polymers. To the best of our knowledge, so far no stochastic schemes have been constructed for this purpose.

In the following sections, we first review briefly the basic formulation of the pom-pom model, and then we describe the stochastic schemes for simulating the model. Afterward, we proceed with detailed comparisons among the current simulation, the predictions of the original model, and an existing set of stress relaxation data on an H-shaped polyisoprene melt. During the comparisons, we reexamine the central proposals of the original theory based on a more rigorous simulation scheme; other molecular effects essential for describing the nonlinear relaxation data are also explored. Finally, we supply proper interpretation and discussion for the central findings, followed by a summary and conclusion.

II. Theoretical Background

II.A. The Pom-Pom Molecular Theory. For an entangled H-polymer, McLeish[15] was the first to recognize that while the arm material bears no fundamental

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difference from a usual star arm in the essential polymer dynamics, the linear relaxation of the cross-bar material may be viewed as governed by a process similar to reptation of an entangled linear chain. In particular, the main effect of the branch points was proposed to rescale the effective frictional drag on the cross-bar molecules, and such a renormalized feature would, in general, bring in a wide spectrum of relaxation time scales characteristic of an entangled polymer with long-chain branching. Along with a subsequent proposal that accounted for the cooperative stress relaxation due to dynamic dilation of the unrelaxed tube segments,[16] the following expressions of the relaxation time scales for an entangled H-polymer were arrived in the recently developed pom-pom molecular theory:[3,4]

$$\tau_a(x) = \tau_0 S_a^{1.5} \exp\left\{\frac{15}{4} S_a \left[\frac{(1-x)^2}{2} - (1-w_b)\frac{(1-x)^3}{3}\right]\right\} \quad (1)$$

$$\tau_b = 2\tau_a(0) w_b^2 S_b^2 \quad (2)$$

where S_a and S_b are the numbers of entanglements for the arm and cross-bar materials, respectively; τ_0 is the Rouse time of one entanglement ($= 2\lambda_H$ in this work, where λ_H is the Hookean spring time constant); $\tau_a(0)$ and τ_b are the terminal relaxation times of the arm and cross-bar materials, respectively; w_b is the weight fraction of the cross-bar material; and x is the normalized distance measured from the branch point toward the free end of an arm. Note that the above, already simplified, formulas do not account for the effect of chain-length fluctuations or a more sophisticated dynamic dilution, and thus their expressions differ slightly from the ones given in ref 4.

In addition, another important proposal in the pom-pom model was a novel segmental retraction mechanism for the cross-bar polymer. By considering the entropic barrier involved, it was proposed that cross-bar retraction would be entropically favorable only if the elastic tension acting on the cross-bar chain is greater than twice the equilibrium one (i.e., sum of the equilibrium tensions exerting by the two attached arms on each side); otherwise, it must wait for the branch point to make a diffusive hop on the time scale of arm orientation relaxation. Thus, right after a step-strain deformation, the cross-bar chain may not be able to retract at all or can only execute partial retraction, depending on the extent of the cross-bar stretching. Consequently, the time for complete cross-bar retraction must scale with the terminal relaxation time of the arm as[4]

$$\tau_s = 5\tau_a(0) w_b S_b \quad (3)$$

Experimental evidence of the prescribed cross-bar retraction and its rheological consequences have been discussed in, for example, refs 3−6; direct evidence for a partial cross-bar retraction based on the stress relaxation data is still absent, however. Similarly, the expression of τ_s given in eq 3 essentially implies that a simplified dynamic dilution mechanism (i.e., double reptation) is assumed.

At this point, it is important to point out that, in contrast with a near cubic dependence on the polymer molecular weight, the terminal cross-bar orientation relaxation time given in eq 2 bears a quadratic dependence on the cross-bar molecular weight; a similar observation applies to the cross-bar retraction, as can be seen in eq 3. The relatively weaker dependencies of the two terminal relaxation times on the cross-bar molecular weight are, in fact, an important consequence of the proposal that the frictional drag on the cross-bar molecules is concentrated on the branch points;[3] in other words, the diffusive motion of a cross-bar chain is mainly controlled by the branch points at both ends. In parallel with this essential proposal, it was argued that segmental retraction of the cross-bar polymer must then be dumbbell-like, with the observation that a Hookean dumbbell has exactly two frictional points. Accordingly, the following expression was adopted in the original pom-pom model for describing the renormalized cross-bar retraction (to be contrasted with a possible partial cross-bar retraction at initial times) after a step deformation:

$$\frac{L(t)}{L_{eq}} = 1 + [\langle|\mathbf{E}\cdot\mathbf{u}|\rangle_{eq} - 1] \exp\left(\frac{-t}{\tau_s}\right) \quad (4)$$

where $L(t)$ denotes the mean instantaneous length of the primitive chain, $\mathbf{E}$ is the displacement gradient tensor of the Finger strain tensor, $\mathbf{u}$ is the unit orientational vector of a polymer segment, and $\langle ... \rangle$ represents the ensemble average. It is important to realize that although eq 4 has typically been employed as a simple approximation to the Rouse retraction for an entangled linear chain, it was argued to legalize exceptionally for the cross-bar retraction due to the proposal mentioned above. Note also that eq 4 should not be directly applied to the case $\langle|\mathbf{E}\cdot\mathbf{u}|\rangle_{eq} > 2$ when complete arm withdraw occurs. A recent modification that further accounted for an enhanced cross-bar retraction, or the so-called "drag-strain coupling", due to branch-point displacement driven by the local chain tension yielded the following equation:[5]

$$\frac{1}{L_{eq}}\frac{\partial L(t)}{\partial t} = -\frac{L(t)/L_{eq} - 1}{\tau_s} \exp\left[\nu^*\left(\frac{L(t)}{L_{eq}} - 1\right)\right] \quad (5)$$

with the initial condition $L(t=0^+)/L_{eq} = \langle|\mathbf{E}\cdot\mathbf{u}|\rangle_{eq}$, where ν^* is a parameter related to the property of the local potential well for branch-point displacement. Note that eq 4 is recovered by letting $\nu^* = 0$, and a theoretical value $\nu^* = 1$ was suggested for H-polymers. Finally, it should be mentioned that the basic formulations and assumptions introduced above remain typical in the later-developed pom-pom constitutive equations. Although the treatment of the orientation relaxation involves several simplifications, it should be sufficient for most of the purposes in the investigations of nonlinear viscoelasticity.

II.B. Stochastic Reformulation. Since this is probably the first time that a stochastic scheme is directly employed to simulate the rheology of an entangled branched polymer, we introduce in detail how the simulation algorithm is constructed. Also, since the orientation and stretch relaxations are simulated independently, we divide the introduction into two subsections.

II.B.1. Orientation Relaxation. In simulating the linear relaxation, eqs 1 and 2 are employed in conjunction with the double-reptation mechanism for stress dilution. Below, we describe how these two equations together with the effect of double reptation can be reformulated in terms of stochastic processes. Primarily

on the basis of the consideration of numerical efficiency, Öttinger has developed stochastic schemes for simulating single-segment tube models for entangled linear polymers.[17−19] To mimic the linear relaxation, he suggested two independent Wiener processes—one for the reptative motion of the primitive chain the other for tube constraint release or double reptation. In fact, this idea can be easily generalized to a polymer system where the full relaxation spectrum has been known theoretically or experimentally. For the present case, this is achieved by differentiating a relaxation spectrum into discrete relaxation (or "reptational") modes, each with a specific relaxation time given by eq 1 or 2 according to its representative position measured along the primitive path, and the number of relaxation modes per chain is chosen here to be the same as the number of entanglements. As an example, the following Wiener process is employed to mimic the diffusive motion of a jth reptational mode ($j = 1$ to $S_a + S_b$) that has a characteristic relaxation time τ_j:

$$dS_t = \sqrt{\frac{c_1}{\tau_j}}\, dW_t, \quad \text{if } S_t \in (-1, 1) \tag{6}$$

where W_t represents a one-dimensional Wiener process that is completely specified by its first moment and correlation function: $\langle W_t \rangle = 0$ and $\langle W_t W_{t'} \rangle = \min(t,t')$. The implementation and physical interpretation of eq 6 in single step-strain flows are as follows. A large ensemble of reptational modes, each with an initial orientation determined by affine deformation for a randomly selected, uniformly distributed unit vector, are being tracked for their respective one-dimensional coordinates S_t (which is made dimensionless by a certain average length) according to eq 6. Initially, S_t is set to be zero for all modes. When S_t assumes a value out of the above-specified range indicating that the corresponding reptational mode has just escaped from the deformed tube (what actually happens is that a particular tube segment has just been reached by either of the chain ends), we then replace its early orientation by a random unit vector; otherwise, it remains unchanged. The constant c_1 ($=1/3$) is chosen such that eq 6 mimics the usual reptative process with a reptation time τ_j. To further simulate double reptation, we assume binary contact for each entanglement, and the chain segment entangling with a jth reptational mode is assigned a mean lifetime $\hat{\tau}_j$, which is chosen statistically among those of the existing reptational modes and is independent of the choice of τ_j. Then, stress relaxation due to double reptation or constraint release is treated as if the tube segment itself were able to perform reptative or Brownian motions:

$$d\mathbf{u}_j = \sqrt{\frac{c_2}{\hat{\tau}_j}}\, d\mathbf{W}_t, \quad \mathbf{u}_j(t + \Delta t) = \frac{\mathbf{u}_j(t) + d\mathbf{u}_j}{|\mathbf{u}_j(t) + d\mathbf{u}_j|} \tag{7}$$

where c_2 ($=1/6$) is chosen such that the usual result of double reptation can be mimicked, and $\mathbf{W}_t$ is a random vector formed by three independent Wiener processes. In summary, in single step-strain flows, an ensemble of prescribed relaxation modes first deform affinely and subsequently proceed with orientational relaxation via either the reptative motion, tracked by eq 6, or double reptation, dictated by eq 7. Note that, as in the original theory, the orientation relaxation is assumed here to be unaffected by the stretch relaxation.

Because of the usually associated, broad relaxation spectrum for an entangled H-polymer, two numerical strategies are further employed to reduce the computational effort considerably. The first utilizes the scheme of control varieties, first introduced by Öttinger for the stochastic simulations of polymer kinetic theories,[18,20] to reduce the statistical deviations (or the so-called "noise") associated with a finite, usually very limited, size of polymer ensemble. The implementation is that one simulates in parallel two processes at one time—one for equilibrium and the other for flow conditions. After the numerical value of a particular average quantity (strictly, only for those having a zero mean at equilibrium) for the equilibrium system is directly subtracted, considerable reduction of the statistical noise can usually be achieved for the same quantity for the flow system. This procedure turns out to be crucial in order to retrieve a sufficiently smooth curve for the linear relaxation modulus $G(t)$, which in turn is essential in order to achieve a smooth transformation to the dynamic moduli G' and G''. Although considerable computational effort may be saved via the variance reduction scheme, a broad relaxation spectrum still poses severe challenge for direct stochastic simulations. Fortunately, this difficulty can be easily resolved for the case of single step-strain flows. From a physical point of view, it appears plausible to assume that whenever a polymer segment has completely relaxed its stress during linear relaxation, it will not contribute any more to the system stress and will serve only as a background Newtonian solvent. This property can be utilized to enlarge adaptively the simulation time step size whenever stress relaxations of the faster relaxation modes are complete. Such an adjustment turns out to lead to a dramatic reduction in the simulation time and makes it possible here to simulate the stress relaxation of entangled H-polymers with almost arbitrary molecular weights.

II.B.2. Stretch Relaxation. As has been introduced earlier, it was proposed in the pom-pom model that for an entangled H-polymer the cross-bar chain may be seen as it would retract in a renormalized frictional field when the elastic tension on it is less than twice the equilibrium one; otherwise, the cross-bar chain would retract in a usual way as does an entangled linear chain, except that its two ends are now subjected to twice the equilibrium chain tension (strictly, this is true only if instantaneous arm retraction is assumed). Thus, for the case that the cross-bar chain is initially stretched to above twice the equilibrium length, the cross-bar chain must then go through both a Rouse-like (for the initial partial retraction) and subsequently a renormalized, strictly dumbbell-like, retractions. Note that this is the case that has not been directly investigated in ref 4 and will be the focus of the current simulation. Below, we introduce how an existing stochastic, full-chain reptation model may be applied to the case of entangled H-shaped polymers, so that the rather complicated retraction mechanisms mentioned above may be simulated more rigorously.

In simulating an entangled H-polymer chain, one must pay extra attention to the distinct natures of frictional drag that could be experienced by the arm and cross-bar molecules. In other words, one must be able to treat arm retraction as usual, while accounting for the renormalized feature of cross-bar retraction when the more usual retraction is prohibited. Below, we

describe how segmental retractions of both materials may be modeled within a one-dimensional Rouse chain, which has been formulated in a full-chain reptation model.[10] For the Rouse beads corresponding to the cross-bar polymer, a renormalized frictional field may be accounted for by renormalizing the usual Rouse time for an entangled linear chain, $\tau_R \approx 18/\pi^2 S_b^2 \lambda_H$ (where we have assumed the relationship $N_b = 3S_b$, with N_b being the number of Rouse beads for the cross-bar polymer), to be the theoretical cross-bar retraction time derived in the pom-pom model, $\tau_s = 5\tau_a(0) w_b S_b$. An essential step before equating these two expressions is to replace first the fundamental time constant in the Rouse model, λ_H, by the renormalized one, λ_b, owing to a renormalized frictional drag. Then, we obtain an expression of the renormalized time constant, $\lambda_b \approx {}^5/_2 w_b \tau_a(0)/S_b$, which plays a similar role as does λ_H in the usual Rouse model. Namely, the two time constants λ_H and λ_b serve analogously as the fundamental time constants in the Langevin equations of motion for the arm and cross-bar polymers, respectively, so that the retraction processes of both materials can be simulated rigorously. Note, however, that the new time constant λ_b should be introduced for the cross-bar polymer only when it fails to retract in the usual way, i.e., when the elastic tension on the cross-bar is less than or equal to twice that on the attached arm; otherwise, only a single time constant λ_H should be used throughout (this is the case for the initial partial cross-bar retraction at $\gamma >$ 4). Indeed, there are several important advantages of the current formulation of chain retraction. First, we do not need to neglect the contribution from arm stretching, as usually done in the original model (see, for example, eq 12 in ref 4), and thus a Rouse-like, partial cross-bar retraction encountered at large strains and initial times can be executed rigorously according to the *instantaneous* chain tensions acting on the arm and cross-bar polymers, respectively. This is obviously a painstaking procedure for the original mean-field model that, however, can be easily treated in a stochastic model. Second, the above-mentioned criterion and adjustment can be applied to *each individual* H-polymer chain rather than accounted for in an average manner. These novel features make it possible here to carry out a rigorous test of the pom-pom model proposals against the nonlinear relaxation data for arbitrary strain magnitudes.

Finally, we consider a stress tensor expression that is consistent with the current implementation of the pom-pom model:

$$\boldsymbol{\sigma} = -3nkT\langle (1 - w_b) T_a \sum_{i=1}^{S_a} \mathbf{u}_i \mathbf{u}_i + w_b T_b \sum_{i=S_a+1}^{S_a+S_b} \mathbf{u}_i \mathbf{u}_i \rangle,$$

$$T_a = \frac{1}{N_a} \sum_{j=1}^{N_a} H Q_j^2, \quad T_b = \frac{1}{N_a} \sum_{j=N_a+1}^{N_a+N_b} H Q_j^2 \qquad (8)$$

where n is the number density of the H-polymer chain and H is the Hookean spring constant; Q_j is the segmental length of the jth chain segment, as defined and formulated in ref 10; $\mathbf{u}_i$ is the unit orientational vector of the ith tube segment, and $N_{a,b}$ (=$3S_{a,b}$) is the number of chain segments per arm or cross-bar. The brackets in eq 8 indicate that the stress is evaluated by the ensemble average of the simulated H-polymer chains.

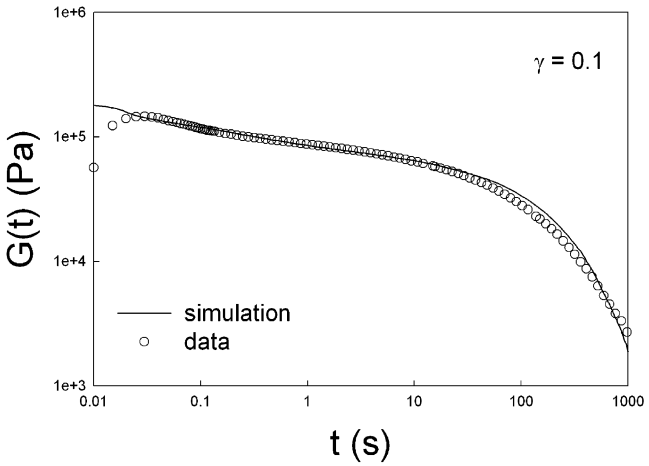

Figure 1. Comparison of the linear stress relaxation between experiment (points; ref 4) and the simulation (solid line) for an H-polymer melt with $S_a = 4$ and $S_b = 22$.

III. Results and Discussion

III.A. Stress Relaxation. In this work, we focus on the case $S_a = 4$ and $S_b = 22$, for which a set of stress relaxation data is available.[4] For the case of linear relaxation, an ensemble size of 40 000 polymer chains is used in the simulation, and the statistical error is mostly below 1%; the simulation time is about 20 min on a Pentium 4 personal computer. The excellent quality of signal-to-noise ratio as well as the relatively short simulation time is ascribed to the use of variance reduction and adaptive time step size, as described earlier. The statistical noise for G' and G'' is somewhat amplified after a numerical Fourier transform, however. For the nonlinear stress relaxation, an ensemble size of 5000 chains is used, and the statistical errors are generally found to fall below a few percent for the time interval of primary interest. The simulation time for this case, however, is much longer (about 2 h) due to the need to simulate one-dimensional Rouse chains.

Since we here focus on the nonlinear relaxation experiment, several simplifications are made in simulating the linear relaxation. Among them, we mention in particular the neglect of the effects of chain-length fluctuations and a slight polydispersity in the molecular weight distribution. For the first, choosing a smaller prefactor (=2) in eq 2 in comparison with that given in ref 4 (≈8) is found to be necessary to lead to a reasonable fit of $G(t)$ at long times. (Such an adjustment is nevertheless consistent with the fact that chain-length fluctuations would reduce the primitive path length left to be relaxed by chain reptation.) As for the second, aside from a slight change in the shapes of the dynamic moduli, the main consequence appears to be a rescaling of the fundamental time constant.[4] Figure 1 shows the comparison of the linear stress relaxation for the case $\gamma = 0.1$. One sees that the simulation is able to mimic reasonably well the experimental data, particularly for short and intermediate times. Because of the current simplifications, however, a few slight disparities are clearly seen in Figure 2 for the comparison of the dynamic moduli between two theoretical predictions. For instance, the dip observed at high frequencies for the stochastic simulation is because no short-time Rouse modes are accounted for; a lump at intermediate frequencies for G'' created by the stochastic simulation, on the other hand, might be attributed to both the effect of statistical errors and the use of discrete relaxation

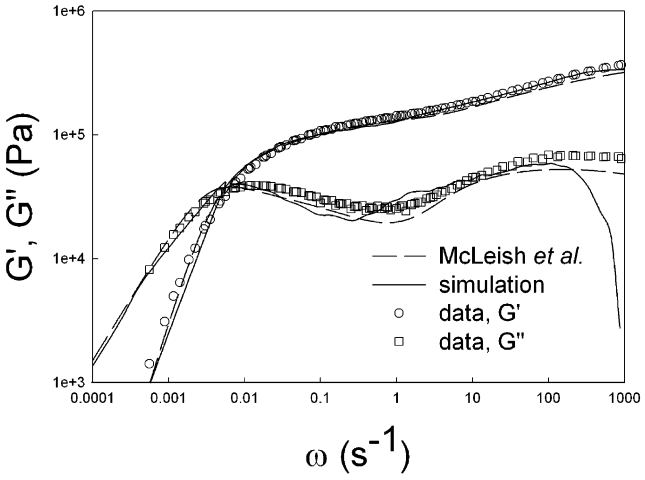

Figure 2. Comparison of the dynamic moduli between experiment (points; ref 4), the prediction of the original pom-pom model (dashed lines), and the current simulation (solid lines).

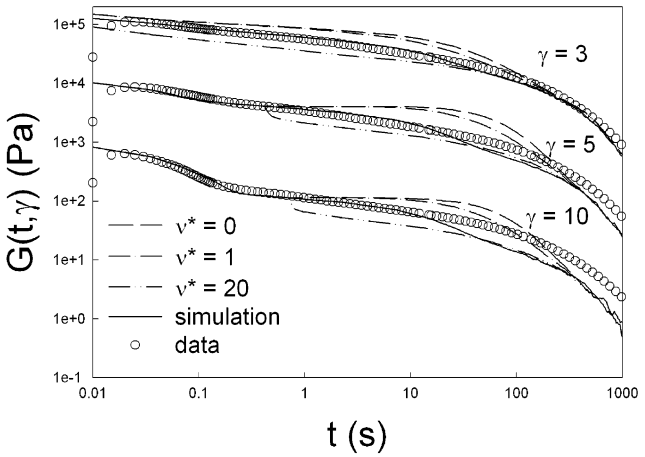

Figure 3. Comparison of the nonlinear stress relaxation between experiment (points; ref 4), the predictions of the original pom-pom model (dashed lines; see comments in the text), and the current simulation (solid lines). Note that the results for $\gamma = 5$ and 10 have been shifted downward for clarity.

modes. Nevertheless, the agreement currently achieved in Figure 1 or 2 should be sufficient for the subsequent investigations of the nonlinear stress relaxation.

For the set of experimental data considered, consistency check indicated good reproducibility of the data up to a strain $\gamma = 10$;[4] moreover, since the step strain was reported to be imposed within 0.1 s, only the data beyond the average imposition time, $t \sim 0.05$ s, should be considered in the following comparisons. Below, we focus on the comparisons for three large strains: $\gamma = 3$, 5, and 10. Recall that complete arm withdraw or partial cross-bar retraction is predicted above a critical strain of about 4, but no direct comparisons have been made for this case in the early investigation. To better see the effect of chain retraction, the linear viscoelastic prediction of the original pom-pom model is supplied by the current stochastic simulation; only cross-bar retraction is simulated differently. Moreover, since the effect of partial cross-bar retraction is very difficult to simulate within the original model, the predictions (for times up to about 1 s and for the cases $\gamma = 5$ and 10) are also provided by the stochastic simulation.

Figure 3 shows the comparisons of the nonlinear stress relaxation, where the predictions based on eq 5 for three different choices of ν^* are plotted together with the stochastic simulation results. For the case $\gamma = 3$, at which no partial cross-bar retraction is predicted, it was found in ref 4 that a parameter as large as $\nu^* = 20$ is necessary for a reasonable fit of the data. This property is confirmed in the current comparison. On the other hand, the stochastic simulation based on a renormalized 1-D Rouse model for chain retraction appears to exhibit a better agreement with the data. To clarify whether the preaveraging approximation employed for arriving at eq 5 is responsible for the remaining disparity, we have also simulated the original model using an ensemble of H-polymer chains that bear a realistic distribution of chain stretching. In this case, each polymer chain follows the same affine deformation but stretches differently according to its chain configuration at equilibrium, and the subsequent individual chain retraction is still dictated by eq 5. Except for a minor difference within a short time interval (~1 s) for the case $\nu^* = 20$, no discernible differences are found between the predictions with and without the preaveraging approximation.

For the cases $\nu^* = 5$ and 10, when partial cross-bar retraction is predicted, one can see from Figure 3 that the data between the imposition time, $t \sim 0.05$ s, and that partial cross-bar retraction ceases, $t \sim 1$ s, are mimicked quite closely by the stochastic simulations that assume a characteristic chain retraction as that has been proposed in the original model. Thus, the comparisons indeed appear to support a Rouse-like, partial cross-bar retraction at initial times and large strains.

At times after partial cross-bar retraction is complete, a renormalized cross-bar retraction is predicted to take over in the time interval $t \sim 1-100$ s. For the strain magnitudes considered here (i.e., $\gamma = 5$ and 10), it may be inferred from the early argument in ref 4 that eq 5 together with a parameter value much smaller than $\nu^* = 20$ should describe the essential stress relaxation in this time interval. That is, a far less significant drag-strain coupling was expected when branch-point displacement is highly restricted by a larger chain tension. The comparisons made in Figure 3 indeed seem to favor smaller values for ν^* at large strains, although the overall comparison is still not quite satisfactory unless probably ν^* is treated as fully adjustable. Similar to the case for $\gamma = 3$, closer agreement appears to be achieved by the simulations based on the 1-D Rouse model without considering drag-strain coupling. As has been discussed earlier, the preaveraging assumption employed in the original model cannot be responsible for the observed disparity; the effects of other essential assumptions, such as the neglect of CCR, remain to be explored. Although the reason for the improvement achieved by the 1-D Rouse model is not clear at the current stage, it undoubtedly indicates that the cross-bar chain bears a broad stretch relaxation not entirely captured by existing theories.

A remaining and obvious discrepancy observed in Figure 3 is concerned with the stress relaxation at long times. The long-time stress relaxation at large strains appears to be considerably slower than what predicted based on eq 3, independent of the chain retraction mechanisms employed; furthermore, such a tendency becomes more pronounced as the strain magnitude is increasing (note that this observation essentially implies that there should be no time-strain separability for $G(t,\gamma)$ at least up to time $t = 1000$ s, as verified by the

experiment in ref 4). It is important to point out that a similar deviation at long times is not observed for the linear relaxation, as can be seen from Figure 1, or for other smaller strains (not shown here) at which chain stretching remains insignificant. Recall that, as in the original theory, the simulation has so far neglected any possible coupling effect between the stretch and orientation relaxations. Two existing molecular theories that are however against this assumption are concerned with an enhanced stress relaxation due to constraint release by chain retraction (i.e., the CCR mechanism[21,22]) and a somewhat opposite effect of only a partial stretch relaxation at the Rouse time (i.e., the PSE mechanism[23]). Aside from the observation that its effect should become unimportant at long times, the CCR mechanism should further expedite rather than slow down the stress relaxation and thus cannot be responsible for the current discrepancy (because the stress relaxation is already overestimated). Before we shall discuss the second effect, we mention in particular two other nonlinear effects—finite extensibility in chain connectors and a possible nonaffine deformation for the tube—that have not been considered either in the current simulation. Similarly, finite extensibility cannot be important for the long-time stress relaxation when chain retraction is nearly complete; the close agreement already established for the stress relaxation at short and intermediate times as well as the long-time behavior of the "damping function" reported in ref 4 (which is close to the prediction of the Doi−Edwards model that assumes affine deformation) seems to preclude the importance of a nonaffine deformation. A plausible explanation that is consistent with the current findings is hence the effect of partial strand extension (or PSE), recently proposed by Archer and co-workers based on both scaling arguments[23] and phenomenology.[6,24] According to their recent experimental findings for both entangled linear and branched polymers, the time for the nonlinear relaxation modulus to start exhibiting time-strain separability appears to scale closely with the terminal orientation relaxation time instead of the usual Rouse time, which had long been believed to mark complete chain retraction for an entangled chain. In fact, the above observation is consistent, at least in part, with the experimental finding in ref 4 that no time-strain separability was observed at the Rouse time or later for the H-polymer sample considered here. Below, we address how the effect of PSE in the nonlinear stress relaxation may be investigated within the current formulation of the pom-pom model.

An existing scaling argument[23] suggested a two-stage retraction mechanism for an entangled linear chain following a step deformation: an initial Rouse retraction, followed by a slower retraction that bears a characteristic relaxation time close to that for orientation relaxation. It was further proposed that the second stage of chain retraction commences when the primitive chain has retracted to the square root of its initially deformed length. In order not to introduce extra adjustable parameters, we here assume that the cross-bar retraction time is modified by PSE at the second stage to be equal to the terminal orientation relaxation time. Such an adjustment can be easily implemented in the current stochastic simulation in a way as in modeling previously a renormalized cross-bar retraction, except that the theoretical retraction time τ_s is now replaced by τ_b. We contrast in Figure 4 the predictions with and

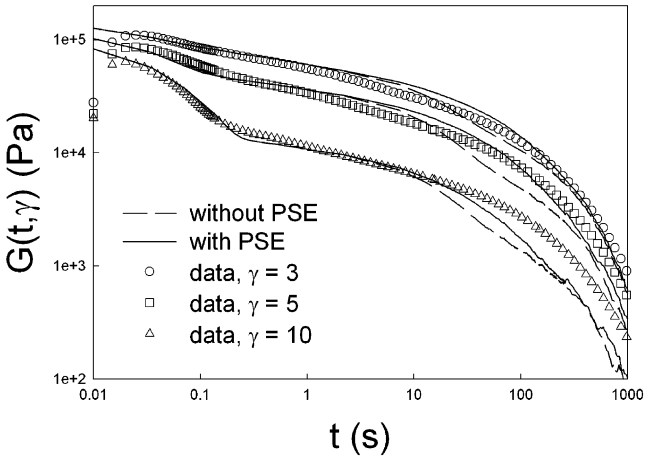

Figure 4. Comparison of the predicted stress relaxation with (solid lines) or without (dashed lines) considering the effect of PSE, along with the experimental data (points; ref 4).

without including PSE. One sees that the comparisons on intermediate time scales can indeed be improved considerably by accounting for such an effect; the remaining disparity might be ascribed to the crudeness of the previous scaling argument in accounting for the real, probably quite complicated, coupling between chain retraction and tube renewal. It must be noted, however, that the theory of PSE strictly remains debatable, and hence conclusive remarks must await further investigations on the nonlinear stress relaxation for well-characterized entangled linear or branched polymers. Furthermore, since the comparisons in Figure 3 together with the early finding in ref 4 do not seem to suggest there is time-strain separability for $G(t,\gamma)$ even at times much longer than τ_b ($\approx$300 s), other molecular effects might also be responsible for the discrepancies currently observed.

III.B. The Damping Function. Early experimental data (see the review in ref 25) appear to indicate that the damping functions for branched polymer melts are less strain-thinning in comparison with those for entangled linear polymers, for which the predictions of the Doi−Edwards theories apply rather well in general. The current simulation, however, displays no such difference, as shown in Figure 5. An early explanation of the weaker damping function for branched polymer melts ascribed it to the effect of partial cross-bar retraction (see, for example, ref 26); namely, extra stresses should be held if certain polymer segments are unable to achieve complete retraction. This proposal is partly consistent with a recent experimental finding for a three-arm pom-pom polymer, which indicated that whereas the damping function at low strains is less strain-thinning in comparison with the prediction of the Doi−Edwards model, the large-strain behavior appears to approach it.[6] On the other hand, we note that if the nonlinear relaxation modulus would exhibit time-strain separability only when complete chain retraction is achieved, the detail of chain retraction should not actually affect the form of the damping function, at least not directly. In fact, the damping function reflects mainly the strain dependence of the extent of polymer alignment, instead of the extent of chain stretching, induced by the step deformation. For comparison, we also plot the simulation result for $G(t,\gamma)/G(t)$ at a short time $t = \tau_a(0)$ when the cross-bar has just completed a partial retraction and has begun to proceed with a

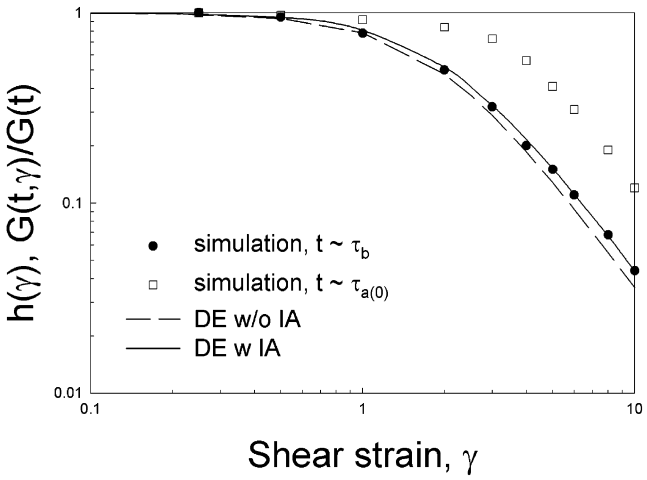

Figure 5. Comparison of the strain dependence of the nonlinear relaxation modulus divided by the linear relaxation modulus obtained from the simulation at a time before (square points) or after (circle points) complete cross-bar retraction. The damping functions $h(\gamma)$ predicted by the Doi−Edwards theories with (solid line) or without (dashed line) the assumption of independent alignment are also plotted for comparison.

renormalized one. Notably, this quantity appears to behave more like the damping functions reported earlier for entangled branched polymers; similar short- and long-time responses of the "damping function" were also reported by McLeish and co-workers from their recent experiments.[4] Thus, it can be questioned whether the damping functions reported earlier for entangled branched polymers might have been evaluated on the basis of incomplete chain retraction. Apparently, our understanding of the damping function for entangled branched polymers is incomplete, and further theoretical and experimental investigations are necessary to draw definitive conclusions.

III.C. Scaling Arguments for PSE. Despite the fact that the proposal of PSE deserves further verifications, we here consider its molecular origin based on scaling arguments. Although the following discussion is restricted to entangled linear polymers, it should apply equally well to the cross-bar chain of an entangled branched polymer. We first summarize an existing argument.[23] For an entangled linear chain and within the physical picture of the tube model, the Gaussian statistics dictates that the mean square of the polymer end-to-end distance at equilibrium should be equal to L_0a_0, where a_0 is the tube diameter at equilibrium. Following a step deformation, if the primitive chain is stretched by a factor $\lambda(\lambda > 1)$, i.e., $L = \lambda L_0$, the tube diameter must shrink accordingly to $a = \lambda^{-1/2}a_0$ (a heuristic explanation of this result is that the tube volume is preserved during the deformation).[23] If the primitive chain must subsequently retract in the previous shrunk tube, it can be shown that the mean square of the polymer end-to-end distance will resume its equilibrium value upon a critical chain retraction $L = \lambda^{1/2}L_0$ (i.e., on this occasion the value of La returns to that of L_0a_0). It was argued by Mhetar and Archer[23] that from then on the usual Rouse retraction would cease and would be replaced by a much slower retraction with a characteristic relaxation time similar to that of the orientation relaxation.

A probably more instructive point of view is to consider a polymer chain being confined in a straight tube with a diameter d which is greater than the polymer bond length but much smaller than the radius of gyration of the polymer chain at equilibrium. Extending the scaling argument of de Gennes[27] to the case of a Gaussian chain, the static (equilibrium) length of the tube l that would be occupied by the confined chain can be argued to scale with the tube diameter as $l \propto d^{-1}$. For example, if the tube diameter shrinks by a factor $\lambda^{-1/2}$, the static tube length occupied by the same confined polymer chain will increase by a factor $(\lambda^{-1/2})^{-1} = \lambda^{1/2}$. It is important to realize that such an extension in the primitive path length may be viewed as being due to an extra pressure arising from the confinement potential of the shrunk tube that acts on the confined chain laterally and forces it to expand axially. In fact, the above argument for the effect of tube diameter on the primitive chain length has been verified by a recent Monte Carlo simulation for the case of good solvents.[28] Now consider that the confined chain is suddenly stretched in the axial direction by a factor λ from its static state, and the diameter of the confining tube shrinks at the same time by a factor $\lambda^{1/2}$ and remains at the shrunk state. Since the new axial chain length (i.e., λl_0) is greater than the favorable static one in the currently deformed tube (i.e., $\lambda^{1/2}l_0$), the polymer chain would naturally proceed with a Rouse retraction until its axial length reaches the favorable static one, $l = \lambda^{1/2}l_0$, at which severe restriction on the lateral movement of the confined chain begins to induce pressure to resist further axial chain retraction. From then on, further retraction back to the original chain length (i.e., $l = l_0$) must rely on the confined chain to explore new regions of larger tube diameters via, say, the reptative motion or constraint release. This argument also explains the existence and the characteristics of a two-stage retraction for confined polymers, as first pointed out by Mhetar and Archer.[23] Note that in applying a static scaling argument to the stretch relaxation of an entangled chain, we simply utilize the central idea that the primitive chain cannot return to its original static length in a tube which is already shrunk.

IV. Summary and Conclusion

In an attempt to further test the pom-pom model proposals for the description of the nonlinear relaxation of entangled H-polymer chains, we construct a stochastic version of the pom-pom model that, while relying on a simplified treatment of the linear relaxation, allows the stretch relaxation to be simulated more rigorously. For instance, since we do not need to neglect the effect of arm stretching or employ preaveraging approximation to solve the chain dynamics, the whole retraction process encountered at a large strain ($\gamma > 4$) can be simulated rigorously, so that existing theoretical proposals can be better tested against experimental data. However, as in the original theory, the current simulation assumes affine deformation for the tube and essentially neglects any coupling effect between the stretch and orientation relaxations (e.g., the effect of CCR). In the current reexamination of the nonlinear stress relaxation of an H-polymer melt, we focus on the case of large strain deformations that are sufficient to induce complete arm withdraw or partial cross-bar retraction. In this respect, the early investigation was strictly incomplete for definitive conclusions to be drawn. Detailed comparisons are made among the current stochastic simulation, the predictions of the original pom-pom model, and an existing set of stress relaxation data on a nearly monodisperse H-shaped

polyisoprene melt. At times right after the imposition of a large strain when a Rouse-like, partial cross-bar retraction is predicted, close agreement between stochastic simulations and the data is generally observed, indicating a characteristic cross-bar retraction as that has been proposed in the original theory. At intermediate times when partial cross-bar retraction ceases and a renormalized frictional field sets in, the essential features of stress relaxation are also largely consistent with the early theories that considered drag-strain coupling along with a dumbbell-like cross-bar retraction, despite the observation that the data clearly exhibit a broader stretch relaxation in comparison with the theoretical predictions. Curiously, the predictions based on a renormalized 1-D Rouse model without drag-strain coupling appear to exhibit closer agreement with the data in this time interval. The most obvious discrepancy observed during the comparisons is concerned with the long-time stress relaxation at large strains, where the data exhibit a much slower relaxation in comparison with the theoretical predictions based on a theoretical retraction time considerably shorter than that of the terminal orientation relaxation. Part of this discrepancy is linked to the mechanism of PSE, whose effect has been roughly investigated on the basis of an existing scaling theory; in addition, a new scaling argument illustrating the molecular origin of PSE is proposed. Consistent with an early finding but contrary to the usual understanding, the currently retrieved damping function for an entangled H-polymer appears to conform well to the Doi−Edwards theory without exhibiting a weaker dependence on strain.

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