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Proposal to Solve the Time−Stress Discrepancy of Tube Models

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ABSTRACT: Recently, Liu et al. (Macromolecules **2006**, *39*, 3093) showed a systematic discrepancy of tube model predictions for describing the apparent plateau modulus of short (weakly entangled) linear chains while predicting very accurately their terminal relaxation times. In the present article, we investigate the origin of this problem, which we call "time-stress discrepancy", by confronting our time-marching algorithm (TMA) with experimental viscoelastic data of nearly monodisperse linear polymers. We show that the contour length fluctuations of the outer molecular segments are overestimated, not taking into account the fact that a chain needs a short but essential time to be considered in equilibrium in its tube. Indeed, tube models consider that stress relaxation by reptation or contour length fluctuations starts at time $t = 0$ after an imposed small deformation, whereas in reality, there is a proceeding fast Rouse relaxation, which is especially important for shorter chains. Therefore, we propose to use a new segment coordinate system for describing the contour length fluctuations process, which restores the consistency with the tube definition and ensures that the necessary time for reaching an equilibrated system is equal to the relaxation time of an entanglement segment, τ_e. Results obtained with the so-corrected TMA model show a very good agreement with experimental data. In particular, the molecular-weight dependence of the apparent plateau modulus, the zero-shear viscosity, and the terminal relaxation time are now correctly predicted.

I. Introduction

To explain the relaxation of linear chains, Doi and Edwards have developed the tube model,[1] based on the "reptation" concept introduced by de Gennes.[2] On the basis of a 1D curvilinear diffusion of the chain along its primitive path, the initial model predicts that the zero-shear viscosity, η_0, and the terminal relaxation time, τ_d, of a monodisperse linear polymer scale with the third power of its molecular weight (M). However, this result was not supported by experiments, which rather show a $M^{3.4}$ scaling.[3,4] This discrepancy was solved by Doi, who introduced the contour length fluctuations (CLFs) concept, which allows the chain length to fluctuate around the equilibrium length and thus to relax faster than with pure reptation[5]

$$\eta_0^{(F)} = \eta_0^{(NF)}[1 - \mu(1/Z)^{1/2}]^3 \tag{1}$$

$$G_{N,\,app}^{0(F)} = G_{N,\,app}^{0(NF)}[1 - \mu(1/Z)^{1/2}] \tag{2}$$

$$\tau_d^{(F)} = \tau_d^{(NF)}[1 - \mu(1/Z)^{1/2}]^2 \tag{3}$$

where superscripts (F) and (NF) describe values with and without fluctuations, $Z = M/M_e$ is the number of entanglement segments of the observed chain (M_e being the molecular weight between entanglements), $G^0_{N,app}$ is the apparent plateau modulus, and μ is a prefactor, which gives more or less importance to the fluctuations process.[6] Whereas with these equations, the η_0 scaling could be corrected, Liu et al.[6] have recently shown that the Z dependence of $G^0_{N,app}$ predicted by a state-of-the-art tube model, which has been proposed by Likhtman and McLeish[7] (LM model), remains inconsistent when compared with experimental data, questioning the validity of eqs 1−3. Whereas the relaxation time is adequately described by the theory, a much stronger dependence on Z is predicted for the apparent plateau modulus as compared with experiments. Whereas this discrepancy is not crucial for the overall quality of the predictions, it suggests an overestimation of the fluctuations process. However, if the contribution of fluctuations is artificially reduced by reducing the value of μ (see eq 1−3), terminal relaxation times no longer follow the $M^{3.4}$ scaling, questioning the origin of this 3.4 power.

The objective of the present article is to clarify the origin of this time−stress discrepancy by investigating the individual role of each mechanism, which takes place in the relaxation of a linear chain, and consistently, to propose a way to improve tube models. To this end, we use the time-marching algorithm (TMA) that we developed for predicting the linear viscoelastic (LVE) properties of linear and branched polymers.[8,9] On the basis of a approach similar to the model proposed by Milner and McLeish,[10,11] it presents the advantage of clearly distinguishing the different contributions to the polymer relaxation.[9] This allows us to isolate the effect of the different relaxation mechanisms.

The article is organized as follows: Section II.1 presents the linear samples used in this work as well as their rheology. Section II.2 briefly describes the TMA applied to linear chains. Then, in Section III.1, we test this model and determine the origin of the time-stress discrepancy. In Section III.2, we propose a correction of the initial model, and in Section III.3, results obtained with the corrected model are compared with representative sets of experimental data. Conclusions are presented in Section IV.

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Table 1. Monodisperse Linear PBD Samples: Molecular Characteristics

sample	M_w [g/mol]	M_n [g/mol]	H
PBD8	9.1k	8.8k	1.04
PBD21	22.8k	21.7k	1.05
PBD37	38.4k	36.6k	1.05
PBD47	51.8k	46.7k	1.11
PBD75	78.8k	75k	1.05
PBD165	155k	148k	1.05
PBD326	365k	326k	1.12

II. Materials and Methods

II.1. Linear Viscoelastic Properties of Linear Polybutadienes. The linear rheology of a series of monodisperse linear polybutadienes (1,4 addition > 90%) was measured. Their molecular characteristics are listed in Table 1. All samples were obtained from Polymer Source, Canada, except for PBD165, which was synthesized by Roovers[12]. The rheological measurements were conducted on a TA (formerly Rheometric Scientific) strain-controlled rheometer (ARES 2KFRTN1) in the parallel plate geometry (8 mm diameter, about 1 mm sample thickness) with a temperature control of ±0.1 °C (achieved via an air/nitrogen convection oven and a liquid nitrogen Dewar) under a nitrogen environment to reduce the risk of degradation. Testing the reproducibility of the measurements and comparing the zero-shear recoverable compliance against old data[12] served as the check of a sample's condition). Dynamic rheological measurements were carried out in the temperature range of −90 to 80 °C. Dynamic time sweep and strain sweep experiments were conducted to ensure thermal equilibrium of the sample and determine the LVE region for the frequency sweeps (small amplitude oscillatory shear). The time−temperature superposition principle was used to combine frequency sweep experiments at different temperatures and create the master frequency spectrum at 25 °C. The data were first vertically shifted by a vertical shift factor (common for all data), which was determined from the change of density with temperature $b_T = (\rho(T_{\mathrm{ref}})T_{\mathrm{ref}})/(\rho(T)T)$. Note that the used temperature dependency of the density is $\rho(T) = 1.0547 - (5.6 \times 10^{-4})T$ (T in kelvin).[13] Subsequently, the data were shifted along the frequency axis, and the horizontal shift factors for all samples were fitted with a single set of parameters of the WLF equation.[14]

II.2. Time-Marching Algorithm for Monodisperse Linear Chains. According to the tube theory, each entangled molecule in a polymer melt can be pictured as if it were confined by a virtual tube.[1,2] The tube represents the entanglement constraints on the observed molecule by the surrounding chains. To relax after a deformation, a test molecule has to move out of its original (oriented) tube. This relaxation process is described by the relaxation function $F(t)$ of the polymer, which accounts for the fact that each molecular segment can relax by three different ways: reptation, CLFs, or constraint release (CR).[15−17] We determined the unrelaxed fraction of the polymer at time t by multiplying the survival probabilities related to these three mechanisms, $p_{\mathrm{rept}}(x,t)$, $p_{\mathrm{fluc}}(x,t)$, and $p_{\mathrm{CR}}(x,t)$, over all segments x of the polymer (from 0 at the extremities, to 1 in the middle of the chain)[8]

$$F(t) = \int_0^1 (p_{\mathrm{rept}}(x,t) \cdot p_{\mathrm{fluc}}(x,t) \cdot p_{\mathrm{CR}}(x,t))\, \mathrm{d}x \tag{4}$$

Reptation and fluctuations processes will disorient the molecular segments, from the chain extremities toward the middle. They are governed by the reptation and fluctuations times of a segment, τ_{rept} and τ_{fluc} (M,t)

$$p_{\mathrm{rept}}(x,t) = \sum_{p\,\mathrm{odd}} \frac{4}{p\pi} \sin\left(\frac{p\pi x}{2}\right) \exp\left(\frac{-p^2 t}{\tau_{\mathrm{rept}}(M,t)}\right) \tag{5}$$

$$p_{\mathrm{fluc}}(x,t) = \exp\left(\frac{-t}{\tau_{\mathrm{fluc}}(x,t)}\right) \tag{6}$$

On the other hand, CR considers that at times longer than its relaxation time a segment will act as a solvent, and it has the same effect on all molecules, still oriented or not, leading to a renormalization of the equilibrium state values of the polymer[16]

$$M_{\mathrm{e}}(t) = M_{\mathrm{e},0}/\Phi(t)^{\alpha} \tag{7}$$

$$L_{\mathrm{eq}}(M,t) = L_{\mathrm{eq},0}(M) \cdot (\Phi(t))^{\alpha/2} \tag{8}$$

where L_{eq} is the equilibrium length of a chain M, α is the dilution exponent, and $\Phi(t)$ is the unrelaxed polymer fraction (either by reptation or by CLF) at time t

$$\Phi(t) = \int_0^1 (p_{\mathrm{rept}}(x,t) \cdot p_{\mathrm{fluc}}(x,t))\, \mathrm{d}x \tag{9}$$

As explained in ref 9, this renormalization of the equilibrium values also influences the reptation and CLF processes through the dynamic tube dilution (DTD) process.[16] However, in the particular case of a monodisperse linear chain, the "solvent effect" of the relaxed part of the polymer on the reptation time of the chain can be neglected

$$\tau_{\mathrm{rept}}(t,M) = \tau_{\mathrm{rept},0}(M) = 3\tau_{\mathrm{e}}\left(\frac{M}{M_{\mathrm{e}}(t)}\right)^3 \tag{10}$$

where τ_{e} is the Rouse time of an entanglement segment. The value of $\Phi(t)$ in eqs 7 and 8 is determined at each time step without the need for an explicit analytical description. By using such a TMA, the viscoelastic properties of complex molecules can be predicted easily.[18,19]

Note that in eq 4, reptation and CLF are considered to be independent processes, with the exception of the DTD process; when the latter is operative, it affects and links both mechanisms. Indeed, because in general, the motions by CLF of the chain extremities cannot be considered to be fast compared with the reptation process (especially with short chains), we have to consider that the contour length for reptation is the entire chain length and not the contour length reduced to the part that is not relaxed by fluctuations.[9]

The consequence of this definition on the description of the terminal relaxation process of the polymer is discussed in Section III.3.

Using the physical ingredients of the model proposed by Milner and McLeish,[10] the formulation of eq 4 has the advantage of being simple and easily applicable to more complex polymers or blends of polymers. Indeed, for linear polymers, by employing the same definition of the relaxation times as in ref 20, we obtain identical results.[11]

III. Results and Discussion

III.1. Time-Marching Algorithm: LVE Predictions for Weakly Entangled Polymers. As described in ref 6, tube models are known to predict poorly the linear viscoelasticity of weakly entangled linear polymers (typically, $Z < 10$). To identify eventual discrepancies and provide possible remedies using our TMA, we investigated the rheology of a set of PBD linear samples listed in Table 1. The parameters of the models were chosen consistently with previous publications:[8,11,18] the molar mass between two entanglements was fixed to $M_{\mathrm{e}} = 1600$ g/mol.[21,22] We used a value of 1.2 MPa for the plateau modulus, which is consistent with rubber elasticity predictions $G_N^0 = 4\rho RT/5M_{\mathrm{e}}$, where the density is

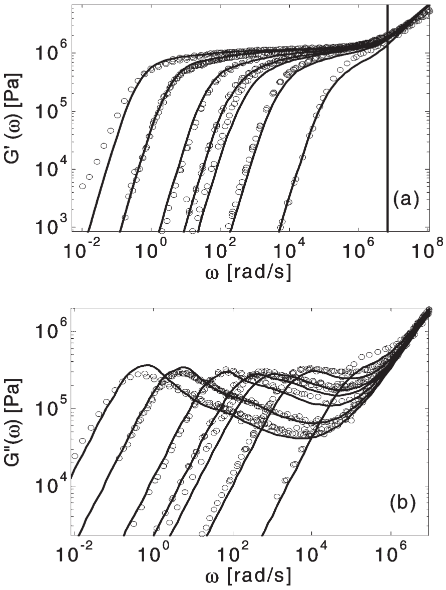

Figure 1. (a) Storage and (b) loss modulus of samples described in Table 1 from PBD8 (left) to PBD326 (right): comparison between theoretical (—) and experimental (○○) results. The vertical line corresponds to $\omega = 1/\tau_e$.

$\rho = 0.895$ g/mL. The Rouse time of an entanglement segment at $T = 25$ °C was fixed to $\tau_e = 1.6 \times 10^{-7}$ s. As in our previous publications,[9,18,19] the dilution exponent α was fixed to 1.

In Figure 1, predictions of the storage modulus obtained with these material parameters are compared with experimental results. Note that in this article all predictions of the storage and loss moduli are obtained by including the fast Rouse relaxation process at high frequencies, determined as proposed in ref 18. Whereas the agreement between theory and experiments is relatively good (especially at higher M), the plateau modulus is poorly described for shorter chains, as already observed by Liu et al.,[6] who used the LM tube model.[7] In particular, we observe that the storage modulus corresponding to the inverse of the Rouse time of an entanglement segment, $1/\tau_e$, is strongly molecular-weight-dependent. Because the equilibrium values at time τ_e (as for example, M_e) do not depend on the polymer molecular weight of architecture, the validity of this prediction is indeed questionable.

To discuss this discrepancy, the molar mass dependence of the apparent value of the plateau modulus is presented in Figure 2, where experimental data from the literature[23-28] and the polymers of Table 1 are collected. Results obtained with the LM tube model and same material parameters are also shown. For molar masses higher than 25 kg/mol, the apparent value of the plateau modulus has been determined for both experimental and theoretical data by the "minimum method", that is, by taking the value of G' at the frequency $\omega_{\min}$ where G'' reaches a minimum.[6,21] For shorter molecular weights, where there is no clear minimum in the G'' curve, the value of G' at the minimum of the loss angle tangent, tan(δ), was taken as the apparent value of $G^0_{\mathrm{N,app}}$. The dotted line indicates the theoretical asymptotic value of the plateau modulus, which has been fixed to 1.2 MPa. (See Section III.1.)

Whereas for well-entangled chains, the TMA predictions are in good agreement with experimental data, as expected from Figure 1, a large discrepancy appears for short chains. Because reptation and CLF are not a priori cumulative in the TMA model (Section II.2), this effect is slightly less pronounced than with the tube model based on the Doi and Edwards theory (eq 2) as, for example, with the LM tube model.[6] Next, the importance of CR and CLF processes has been tested with the TMA model by comparing results obtained with and without taking into account these mechanisms. To remove the CR (CLF) influence, the survival probability $p_{\mathrm{CR}}(x,t)$ ($p_{\mathrm{CLF}}(x,t)$) in eq 4 has been fixed to 1. As shown in Figure 3a, removing the CR process slightly improved the description of the apparent plateau modulus. However, as shown in Figure 3b, at the same time, the predicted terminal relaxation time of the chains is shifted toward lower frequencies: relaxation of the chains becomes twice as slow. Removing the CLF effect in the model leads to a more interesting result when compared with the initial predictions: as shown in Figure 3c, consistently with experiments, the plateau modulus becomes nearly constant, and the predicted storage modulus does not depend on molar mass at a frequency of $1/\tau_e$. (See Figure 3d.) Furthermore, this modification does not affect the terminal relaxation times of the long chains. (See Figure 3d.) Of course, removing the CLF effect completely is certainly too strong of a condition, especially for short chains because they mainly relax by this process. However, this test gives a good indication of how to correct tube models: from a theoretical point of view, it seems that CLF influence is overestimated. This goes in the same direction as the work of Liu et al.[6] and is also supported by Figure 4, where the fluctuations times of the molecular segments are plotted as a function of their localization x for chains of 10 and 100 kg/mol, that is, of 6.5 and 65 entanglements, respectively. The Rouse time of an entanglement segment, τ_e, is indicated by the dotted line. Whereas at this time the long chain is still almost fully oriented, 17% of the shorter chain has already relaxed by fluctuations (i.e., τ_{fluc} $(x = 0.17) = \tau_e$). This means that according to the model, a large polymer fraction is allowed to relax from its "equilibrium state" (described by G^0_{N} and M_e) before having even reached this state, that is, before that molecules feel any topological constraint. This indeed seems to be in contradiction with the tube picture.[16,17]

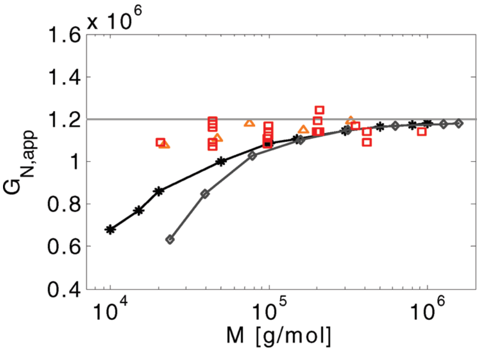

Figure 2. Apparent plateau modulus versus the molecular weight determined with the TMA model (∗∗) or with the LM model (◇◇) and compared with experimental data (□) from refs 23−28 and from samples of Table 1 (△△). Dotted line indicates the value of the plateau modulus used in the model.

III.2. CLF: Description of the Early Fluctuations. As shown in Section III.1, the theory overestimates the CLF influence for linear chains at short times. This comes from the fact that the "equilibrium state" of a chain is assumed to be reached at time $t = 0$. Indeed, the tube model does not take into account that first, the chains partially relax according to the Rouse process (until $t = \tau_e$), and only for $t > \tau_e$ can other relaxation mechanisms such as reptation or CLF take place. Whereas this assumption is negligible for long chains, it can strongly affect the relaxation of shorter molecules.

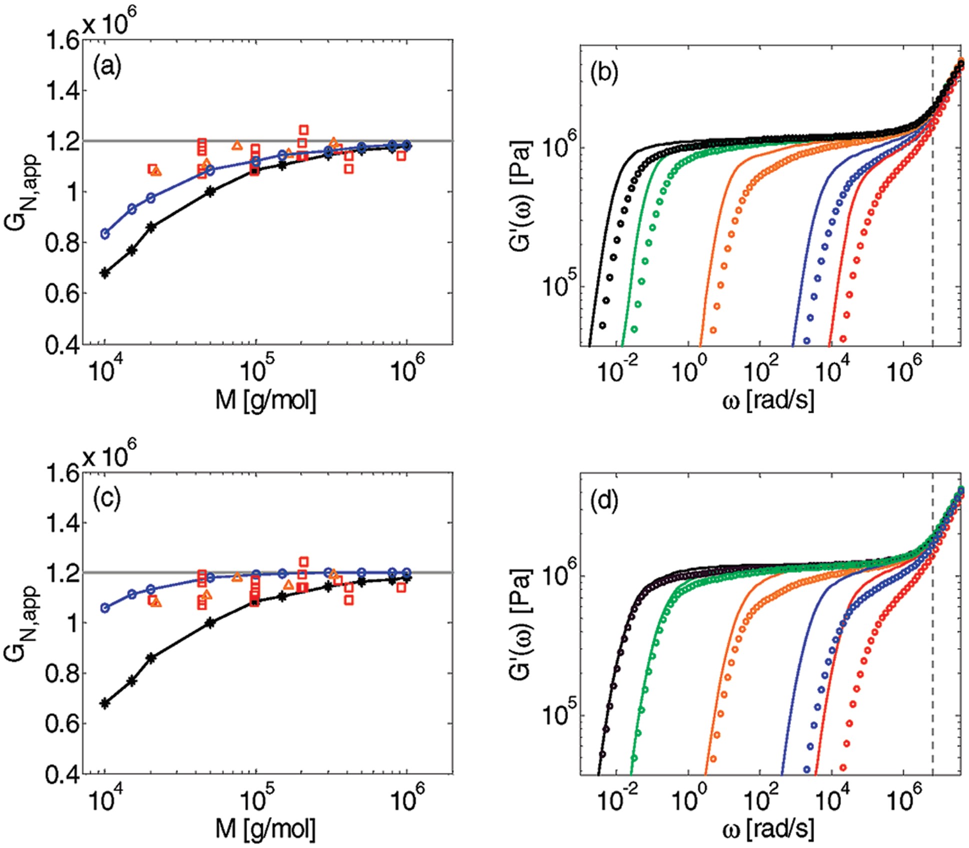

Figure 3. (a) Apparent plateau modulus versus M_w: Experimental data (□, Δ)[23−28] or data obtained with the TMA model with (∗∗) and without (○○) considering the CR effects. (b) Predicted storage modulus for monodisperse linear chains of M_w of, from right to left, 10, 20, 100, 500, and 1000 kg/mol with (○) and without (—) consideration of the CR effects. (c,d) Same as parts a and b but with and without considering the CLF effect. The vertical line corresponds to $\omega = 1/\tau_e$.

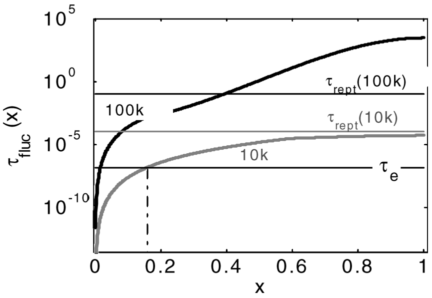

Figure 4. Predicted fluctuations times (thick curves) versus the segment localization for a linear polymer of 10 (---) or 100 kg/mol (—). The dotted line indicates the Rouse time relaxation of an entanglement segment, τ_e. The thin lines indicate the initial reptation times of the two chains.

Correcting this problem is not trivial. For example, adding a constant τ_e to the actual fluctuations times strongly alters the shape of the loss modulus (with a new maximum at $\omega = 1/\tau_e$), and at the same time, because of its very short value, its effect on G' soon becomes negligible. Therefore, this method does not allow the molar mass dependence of the plateau modulus to be improved. Multiplying the actual fluctuation times by a constant will affect the terminal relaxation time of the polymer, which does not have any physical meaning.

To correct the model, we use similar arguments as in refs 9 and 19 for describing the motions of the inner part of a pom-pom molecule while keeping the continuity of the CLF process at the branching point. In the case of a linear chain,

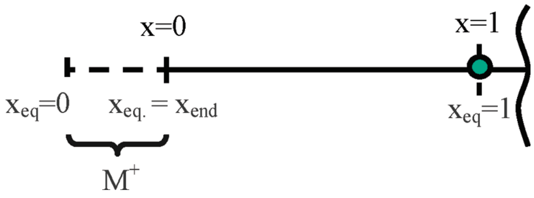

Figure 5. Illustration of real and equivalent coordinate systems for describing the fluctuations times of a linear molecule. (See the text.)

after its deformation, the relaxation of a molecule can be described by a Rouse process until a time τ_e, where the chain motions become constrained by the entanglements with its neighboring chains. At this time, the polymer has reached its equilibrium state, and the tube starts playing a role. Therefore, from a modeling point of view, we should impose that the fluctuation time of the molecular segment $x = 0$ is equal to τ_e instead of 0. To this end, we define an "equivalent molecule", longer than the real one by a mass M^+ at each extremity, in such a way that the fluctuation time of M^+ is equal to τ_e. This is illustrated in Figure 5, where x represents the real coordinate system and x_{eq} is related to the equivalent molecule. Therefore, the mass M^+ is defined such that

$$\tau_{\text{fluc}}(x = 0) = \tau_{\text{fluc}}(x_{\text{eq}} = M^+) = \tau_e \qquad (11)$$

For the PBD samples analyzed in this work, M^+ is equal to 767 kg/mol. As the early fluctuations process, it does not depend on the molar mass of the sample. While negligible for long polymers, this value becomes important compared with the molar mass of weakly entangled polymers.

Therefore, to ensure that a molecule is not relaxing before τ_e, the fluctuations time of a molecular segment x is determined by using the equivalent coordinate system rather than the original one. The fluctuation times obtained with this method are shown in Figure 6 and compared with the previous results. They are physically meaningful because in addition to slowing down the relaxation of the outer molecular segments, using the equivalent coordinates does not affect the relaxation of deeper segments for well-entangled molecules. As expected, the relaxation of the longer chains is not sensitive to this correction. The molar mass dependence of the plateau modulus as well as the storage modulus predicted by using the equivalent coordinate system are depicted in Figure 7. Now, this M dependence of the plateau is indeed in better agreement with experiments, also for small M. Nevertheless, a slight decrease in the apparent value of the plateau modulus is still observed. This mainly comes from the tan(δ) method used for determining $G_{N,app}^0$ at low molecular weights. Note that in this range experimental data were determined by the G'' integration method,[14] which cannot be applied to the predictions because the results will be identical to the imposed G_N^0, by definition.

As shown in Figure 7b, the use of this equivalent coordinate system affects the storage modulus prediction in the right direction: the M effect in the intermediate region is much less pronounced, without affecting the terminal relaxation time of the chains. Only very short molecules are predicted to relax slightly slower, which seems to be reasonable.

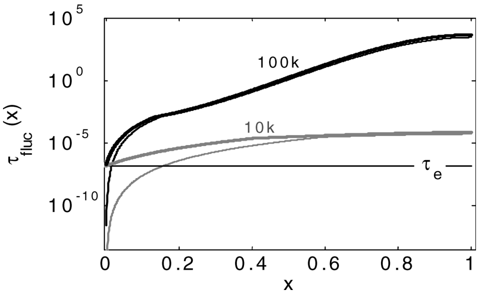

Figure 6. Predicted fluctuation times versus the segment localization for a linear polymer of 10 kg/mol (---) or 100 kg/mol (—) with the usual coordinate system (thin curves) or with the equivalent coordinate system (thick curves). The dotted line indicates the Rouse time relaxation of an entanglement segment, τ_e.

This result shows the extreme sensitivity of the data to a good description of the relaxation at very short times.

III.3. TMA Model with the New Coordinate System: Comparison to Experimental Data. *III.3.1. Frequency Spectra.* Having proposed a way to correct the discrepancy observed at short time for the relaxation of the linear polymers, we now confront the corrected model to experimental data. To this end, different sets of experiments on polybutadiene (PBD) linear samples are used. The materials parameters, M_e, G_N^0, and τ_e are kept constant for all samples, respectively, equal to 1600 g/mol, 1.2 MPa, and 1.6×10^{-7} s at $T = 25$ °C.

The data set from Table 1 was already tested with the initial model. (See Figure 1.) Results obtained with the new coordinate system are shown in Figure 8. The agreement between theory and experiment is indeed much better in the intermediate frequency region. Note that the description of the loss moduli of the highest-M sample exhibits some discrepancy, probably because of the higher polydispersity of the sample.

In Figure 9, the corrected model is tested on a set of PBD samples from Liu et al.[29] (See the Figure caption for their description.) Again, the model describes the data very well.

The last set of data, which is proposed here, is the set of PBD samples from Baumgaertel et al.[27] (See their description in the caption of Figure 10.) As shown in Figure 10a, the corrected model captures the polymer behavior in the transition region quite well. In ref 7, the ML model was tested on the same samples, showing indeed a larger discrepancy in this region. This confirms again how important the correction of the CLF of external segments is. In this specific case, we should also note that discrepancies between theory and experiments are sometimes due to experimental issues. As an example, Figure 10b compares experimental data for two PBD samples of same molar mass (97 kg/mol), measured by Liu et al.[29] or by Baumgaertel et al.[27] A large difference is observed in the loss modulus curves, but elucidating its origin is beyond the scope of this work.

III.3.2. Molar Mass Dependence of the Zero-Shear Viscosity. As explained in Section II.2, the reptation time of a chain is defined in the TMA model by considering the diffusion of the center of mass of the chain along its whole equilibrium length (eq 10) and not along the chain fraction not relaxed by CLF. The reptation time is thus only renormalized

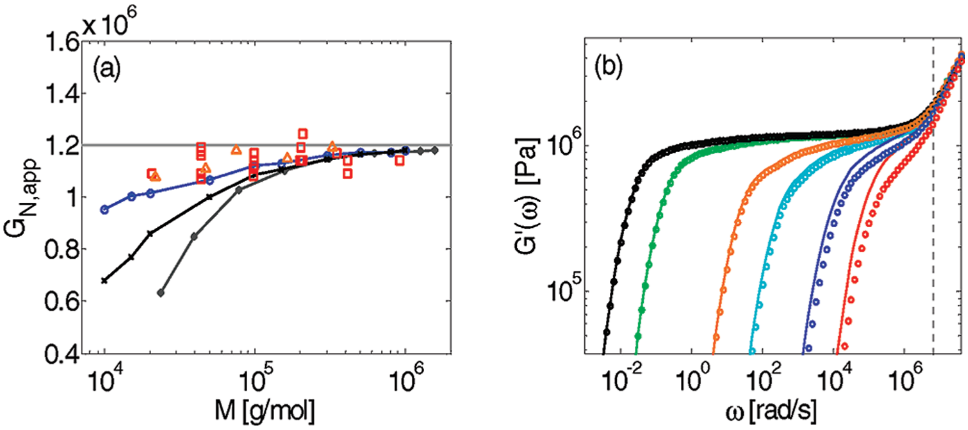

Figure 7. (a) Apparent plateau modulus versus M_w. The experimental data (□,△) are compared with data obtained with the LM model (◇◇) or with the TMA model using the standard (××) or the equivalent (○○) coordinate system. (b) Predicted storage modulus for monodisperse linear chains of M_w of, from right to left, 10, 20, 50, 100, 500, and 1000 kg/mol with the standard TMA model (○) or by using the equivalent coordinate system (—). The vertical line corresponds to $\omega = 1/\tau_e$.

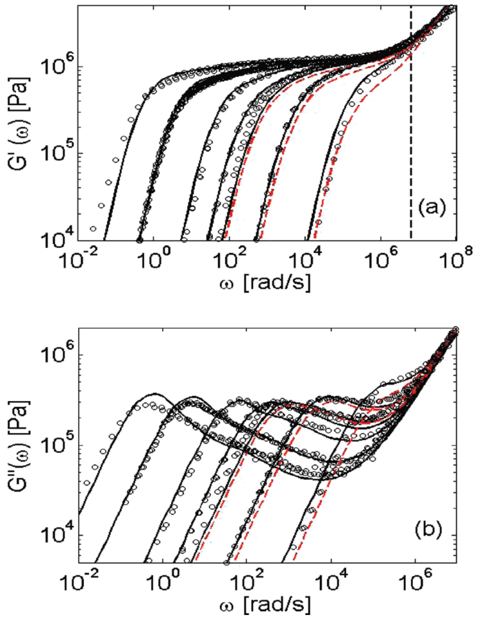

Figure 8. (a) Storage and (b) loss moduli of the PBD samples listed in Table 1: comparison between theoretical (—) and experimental (○) results. The theoretical results account for the proposed correction. For comparison, results obtained without the correction are also shown for the three shorter samples. (See the dashed curves.)

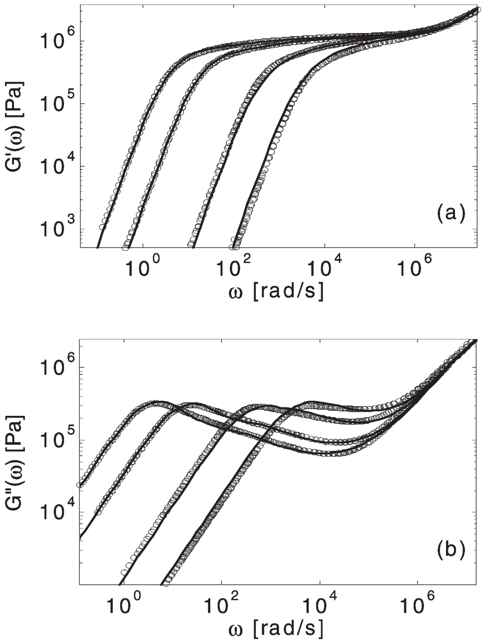

Figure 9. (a) Storage and (b) loss moduli of the PBD samples (ref 29), with M_w equal to 22.8 (H = 1.07), 38.6 (H = 1.07), 98.8 (H = 1.07), and 163 kg/mol (H = 1.07). Comparison between theoretical (after correction) and experimental (○○) results.

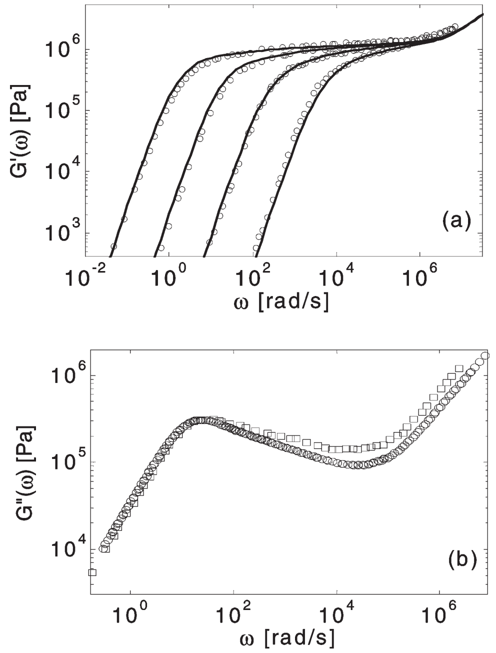

Figure 10. (a) Storage modulus of nearly monodisperse PBD samples from ref 27, with M_w equal to 20.7, 44.1, 97, and 207 kg/mol. Comparison between theoretical (after correction) and experimental (○○) results. (b) Experimental loss modulus of a linear PBD of M_w = 97 kg/mol from Liu et al. (○○) or from Baumgaertel et al. (□□).

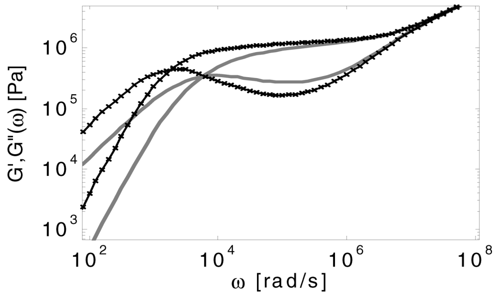

Figure 11. Predicted storage and loss moduli of a monodisperse linear PBD sample of M_w equal to 22 kg/mol, with (—) or without (++) consideration of the effect of CLF.

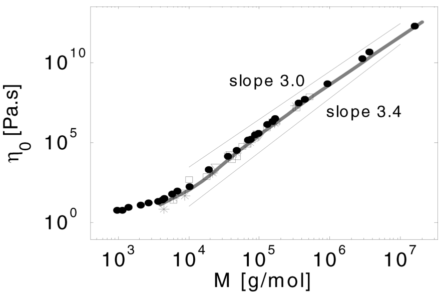

Figure 12. Zero-shear viscosity as a function of M_w. Theoretical data (thick continuous curve) and experimental data from Liu[6] (∇∇), Colby[26] (●●), and Archer[30] (□□) and from the samples of Table 1 (**). The thin lines indicate a 3 and 3.4 power law.

through the DTD process ($L_{eq}(t) = L_{eq,0}\phi^{\alpha}$). The effect of CLF is taken into account in eq 4, which allows a chain segment to be disoriented by CLF, by reptation or by both processes at the same time. It is important to note that even if the reptation time is considered to be constant, the terminal relaxation time of short linear polymers will depend on both reptation and CLF. This is illustrated in Figure 11 for a PBD sample of M_w = 22 kg/mol, where the storage and loss moduli are predicted with and without taking into account the CLF effect. Therefore, as shown in Figure 12, the expected log dependence of the zero-shear viscosity versus the M_w of the chain is recovered, with a slope of 3.4 at lower M_w toward a slope of 3 at higher M_w, consistently with the experimental data.[6,26,30] Therefore, when taking into account the CLF effect in a separated term, as in eq 4, the rescaling of the reptation time as proposed by Doi and Edwards[1] as eq 3 is not needed anymore to observe the correct molar mass dependence of the terminal relaxation time. Furthermore, with the proposed definition, the plateau modulus, the zero-shear viscosity, and the terminal relaxation time can be correctly described at the same time for a large range of molar masses. We also observe a better relationship between the values of G_N^0 and M_e.[7,11,21] This suggests that the influence of CLF on the reptation time is indeed better described with this approach, without overestimating its effect.

IV. Concluding Remarks

Recently, Liu et al. have shown a systematic deviation of tube model predictions for the plateau modulus of short linear chains.[6] In the present work, we confronted our TMA to experimental viscoelastic data of monodisperse linear polymers to investigate the origin of this discrepancy. We analyze the contribution of each relaxation process to the global relaxation of the polymer and conclude that CLFs of the outer molecular segments are overestimated. Indeed, tube models do not take into account the fact that a chain needs a short but essential time, fixed to τ_e, to be considered in equilibrium.

Using a renormalization of segment coordinates similar to the motion of the branching point of a pom-pom polymer,[9,19] we work with "equivalent molecules", which ensure that the necessary time for reaching an equilibrated system is indeed equal to τ_e. Results obtained with the corrected model are in very good agreement with experimental data. In particular, the molar mass dependence of the plateau modulus, the zero-shear viscosity as well as the terminal relaxation time is now correctly predicted.

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References and Notes

(1) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: New York, 1986.
(2) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.
(3) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(4) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(5) Doi, M. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 265 ; *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 667.
(6) Liu, C. Y.; He, J. S.; Keunings, R.; Bailly, C. *Macromolecules* **2006**, *39*, 3093.
(7) Likhtman, A. E.; McLeish, T. *Macromolecules* **2002**, *35*, 6332.
(8) van Ruymbeke, E.; Keunings, R.; Bailly, C. *J. Non-Newtonian Fluid Mech.* **2005**, *128*, 7.
(9) van Ruymbeke, E.; Bailly, C.; Keunings, R.; Vlassopoulos, D. *Macromolecules* **2006**, *39*, 6248.
(10) Milner, S. T.; McLeish, T. C. B. *Phys. Rev. Lett.* **1998**, *81*, 725.
(11) van Ruymbeke, E.; Liu, C. Y.; Bailly, C. Quantitative Tube Model Predictions for the Linear Viscoelasticity of Linear Polymers. In *Rheology Reviews*; Binding, D. M., Hudson, N. E., Keunings, R., Eds.; The British Society of Rheology, 2007; pp 53−134.
(12) Roovers, J. *Polymer J.* **1986**, *18*, 153.
(13) *Standard Pressure−Volume−Temperature Data for Polymers*; Zoller, P., Walsh, D., Eds.; Technomic Publishing: Lancaster, PA, 1995.
(14) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: London, 1980.
(15) des Cloizeaux, J. *Europhys. Lett.* **1988**, *5*, 437.
(16) Marrucci, G. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 159.
(17) (a) Ball, R. C.; McLeish, T. C. B. *Macromolecules* **1989**, *22*, 1911. (b) McLeish, T. C. B. *J. Rheol.* **2003**, *47*, 177.
(18) van Ruymbeke, E.; Orfanou, K.; Kapnistos, M; Iatrou, H; Pitsikalis, M; Hadjichristidis, N; Lohse, D. J.; Vlassopoulos, D. *Macromolecules* **2007**, *40*, 5941.
(19) van Ruymbeke, E.; Kapnistos, M.; Knauss, D. M.; Vlassopoulos, D. *Macromolecules* **2007**, *40*, 1713.
(20) Park, S. J.; Larson, R. G. *Macromolecules* **2004**, *37*, 597.
(21) Liu, C. Y.; van Ruymbeke, E.; Keunings, R.; Bailly, C. *Polymer* **2006**, *47*, 4461.
(22) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639 .
(23) Struglinski, M. J.; Graessley, W. W. *Macromolecules* **1985**, *18*, 2630.
(24) Colby, R. H.; Fetters, L. J.; Graessley, W. W. *Macromolecules* **1987**, *20*, 2226.
(25) Raju, V. R.; Menezes, E. V.; Marin, G.; Graessley, W. W. *Macromolecules* **1981**, *14*, 1668.
(26) Colby, R. H.; Fetters, L. J.; Funk, W. G.; Graessley, W. W. *Macromolecules* **1991**, *24*, 3873.
(27) Baumgaertel, M.; De Rosa, M. E.; Machado, J.; Masse, M.; Winter, H. H. *Rheol. Acta* **1992**, *31*, 75.
(28) Wang, S.; Wang, S. Q.; Halasa, A.; Hsu, W. L. *Macromolecules* **2003**, *36*, 5355.
(29) Liu, C. Y.; Halasa, A. F.; Keunings, R.; Bailly, C. *Macromolecules* **2006**, *39*, 7415.
(30) Juliani; Archer, L. A. *J. Rheol.* **2001**, *45*, 691.