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Pre-Averaged Sampling On the Entanglement Kinetics for Polymer Dynamics

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Summary: A new model for entangled polymer dynamics based on pre-averaged sampling of the entanglement structure is proposed. Although it has been reported that sliplink simulations are powerful and promising to predict entangled polymer dynamics, it is still unpractical to calculate polymers with many entanglements. In the present study, a possible approach to achieve fast calculation is proposed by pre-averaged sampling of entanglement structure with skipping detail kinetics of entanglements dominated by chain ends in conventional sliplink models. To achieve time development of the chain conformation and entanglement structure, i) number of entanglement per chain and number of monomers for each segment are randomly obtained from the equilibrium distribution proposed by Schieber [*J. Chem. Phys.* **2003**, *118*, 5162] and ii) the renewed entanglement structure is mechanically equilibrated. The established power-laws on molecular weight dependence of chain dimension, the longest relaxation time and self-diffusion coefficient were reasonably reproduced. Comparison on linear viscoelastic response is also discussed.

Keywords: entanglement; modeling; polymer dynamics; rheology; stochastic method

1. Introduction

The present work is intend to propose a novel model for entangled polymer dynamics with further coarse-grained time step than conventional sliplink simulations.[1–4] It has been established that entangled polymer dynamics can be described by the reptation model[5,6] with additional relaxation modes such as constraint release[7] and contour length fluctuation.[6,8] To take account more detailed dynamics and multi-body effects sliplink simulations have been developed. As molecular simulation, the sliplink approaches have apparent advantage on calculation cost over coarse-grained molecular dynamics.[9,10] However, the calculation time is not practically reachable for polymers with many entanglements such as polyolefins in industrial use. To overcome the problem, Yaoita *et al.*[11] proposed a method utilizing dynamic tube dilation picture[12–14] where long time behavior of long chains shows similarity to short chain dynamics. In this study another approach is examined with skipping detail kinetics of entanglements at chain ends. In the sliplink models, polymer diffusion is achieved by rearrangement of the entanglement network and the network rearrangement is conventionally performed by creation and destruction of sliplink (or entanglement) around chain ends. The rearrangement events are performed by monitoring chain ends and hence the time unit is consistently chosen to τ_e which is Rouse time of one entanglement segment. Such τ_e based algorithms are inadequate for long polymers since detail kinetics of blinking short-lifetime entanglements is time consuming and it is not essential in long time region if the dynamic tube dilation picture by Yaoita *et al.*[11] is accepted. One possible idea to skip the detail

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kinetics is pre-averaging of the entanglement rearrangement by a given probability distribution of the entanglement network. We examine such an attempt with the distribution proposed by Schieber.[15]

2. Model

Following the sliplink approach, number of entanglement per chain, Z, monomer numbers assigned to the entanglement segments, N_i, and position of each entanglement, $\mathbf{R}$, are chosen as state variables. Let us consider a model of polymer dynamics based on renewal time for Z and N_i to skip frequent blinking of entanglements with short-lifetime locating around chain ends. It is certain that the renewal time for Z and N_i is somewhere in between the renewal time of whole tube, τ_d, and the shortest lifetime of the blinking entanglement, τ_e. Hereafter we assume that the renewal time for Z and N_i is comparable to Rouse relaxation time of the chain inside of the tube, τ_R, since the equilibration time for Z and N_i is dominated by sliding motion of the chain and contour-length fluctuation of the surrounding chains. Time development of chain conformation is performed by three steps. In the first step, Z and N_i are renewed by statistical sampling from an equilibrium distribution.[15] In the second step, increments or decrements of Z is reflected to chain conformation by a certain rule. Finally the renewed chain conformation is mechanically equilibrated. Detail description of each step is presented in the following sections.

2.1 Renewal of Z and N_i

A joint probability of Z and N_i for monodispersed linear chains has been proposed by Schieber[15] as

$$p_{\mathrm{eq}}(N_i, Z) = \frac{\exp(-Z_0)}{(Z-2)!N_{\mathrm{e}}}\left(Z_0 - \frac{N_i}{N_{\mathrm{e}}}\right)^{Z-2}, \tag{1}$$

where Z_0 and N_e are the average number of Z and N_i. From Eq. (1), independent probability distribution for Z is obtained by integration for N_i from zero to total monomer number of the chain, N_{tot}, as

$$p_{\mathrm{eq}}(Z) = \frac{\exp(-Z_0)}{(Z-1)!} Z_0^{z-1}. \tag{2}$$

Similarly independent probability distribution for N is derived by infinite series of Eq. (1) forZ as

$$p_{\mathrm{eq}}(N) = N_{\mathrm{e}}^{-1} \exp\left(-\frac{N}{N_{\mathrm{e}}}\right). \tag{3}$$

For the renewal of Z and N_i, firstly Z for each chain is determined by Eq. (2) and after that N_i for each segment is obtained by Eq. (3). To conserve total monomer number per chain, N_{tot} is rescaled by

$$\tilde{N}_i = N_i \frac{N_{\mathrm{tot}}}{\sum_{i=1}^{Z} N_i}. \tag{4}$$

In addition, for the mechanical equilibration of $\mathbf{R}$ described below, a minimum cut-off for N_i is employed and set to 0.05. In spite of the above mentioned modifications, the distribution of Eq. (3) is fairly reproduced.

2.2 Change of Z on chains

As mentioned above we assume that the change of Z is due to the short time blinking of entanglements. Hence the change of Z is realized by perturbation to the original chain. When the newly assigned Z is smaller than the original one, necessary number of entanglements are removed from the chain. On the contrary, when the renewed Z is larger than the original, demanded number of entanglements are added to the chain. For the destruction and the creation of entanglements, two different methods are examined. In model, occurring position of the destruction and the creation on the chain is randomly chosen. In the case of increase, one segment is randomly chosen and the position of a new entanglement is on the sphere from a center of the chosen segment with the radius of the average segment length. In the case of decrease, randomly chosen entanglements are removed. In model 2, the occurrence position is restricted to chain ends. In the case of increase, new segments are added to the chain end via random walk manner while in the case of decrease, segments are removed from the ends.

2.3 Equilibration of the renewed networks

Because Z, N_i and $\mathbf{R}$ are renewed independently, the renewed chain is mechanically frustrated. The frustration is removed by changing $\mathbf{R}$ obeying the following equation.

$$\zeta\dot{\mathbf{R}} = \mathbf{F}^{\mathrm{E}} + \mathbf{F}^{\mathrm{T}} + \mathbf{F}^{\mathrm{R}}, \tag{5}$$

where ζ is friction coefficient of the node. The first term on the right hand side, $\mathbf{F}^{\mathrm{E}}$ is the elastic force by connected segments.

$$\mathbf{F}^{\mathrm{E}} = \frac{3kT}{b^2}\left(\frac{\mathbf{r}_i}{N_i} - \frac{\mathbf{r}_{i-1}}{N_{i-1}}\right), \tag{6}$$

where kT is the thermal energy, b is the monomer length and $\mathbf{r}_i$ is the end-to-end vector of i^{th} chain segment. The second term $\mathbf{F}^{\mathrm{T}}$ is tube constraint force based on the tube potential for single chain model proposed by Likhtman.[4] Since we assume that the renewal of Z and N_i is presented by perturbation to chain conformation, memory of the original conformation should be retained in the renewed conformation somehow. One simple option is to fix the position of the conserved entanglements. However, due to the tension described in Eq. (6) with renewed N_i, the original position does not fulfill the force balance. Hence to retain the memory of the chain shape, each segment except ends is supposed to exist in a parabolic potential.[4]

$$\mathbf{F}^{\mathrm{T}} = \frac{3kT}{N_{\mathrm{e}}b^2}(\mathbf{X}_i - \mathbf{R}_i), \tag{7}$$

where $\mathbf{X}_i$ is the centre position of the potential set to the previous position of the segment. Note that the anchoring point $\mathbf{X}_i$ is created with a newly added segment and vanishes when the connected segment is removed. The third term $\mathbf{F}^{\mathrm{R}}$ is Gaussian random force of zero means suffusing the fluctuation dissipation theorem[16] as

$$\left\langle \mathbf{F}^{\mathrm{R}}(t) \cdot \mathbf{F}^{\mathrm{R}}(t') \right\rangle = 6kT\zeta\delta(t - t'). \tag{8}$$

The equation for the network equilibration is expressed in nondimensional variable by unit length a_0 which is average length between nearby entanglements, and unit time $\tau_{\mathrm{e}} = \zeta a_0^2/2kT$ which is Rouse time of average chain segment. In the two models, since created entanglement node is distant from about average segment length, τ_{e} is employed as an equilibration time confirming the fact that the longer equilibration time does not affect the results.

3. Results and Discussions

3.1 Chain dimension

Fig. 1 shows the mean square end-to-end distance, $\left\langle \mathbf{P}^2 \right\rangle$, as a function of Z. Both models are in good agreement with the established power law with the exponent of 1.0 with distribution of $\left\langle \mathbf{P}^2 \right\rangle$ and Z.

3.2 Linear viscoelastic response

Relaxation modulus $G(t)$ was obtained through the autocorrelation function of the shear stress σ_{xy}.

$$\sigma_{xy} = \left\langle \frac{r_x r_y}{N} \right\rangle, \tag{9}$$

$$G(t) \propto \left\langle \sigma_{xy}(t + t') \cdot \sigma_{xy}(t') \right\rangle. \tag{10}$$

Fig. 2 is logarithmic plot of $G(t)$ versus t/τ_{d} for $Z_0 = 20$ with the prediction of the reptation theory.[6] Note that $G(t)$ is normalized by $G(t = 1)$ because the relaxation between

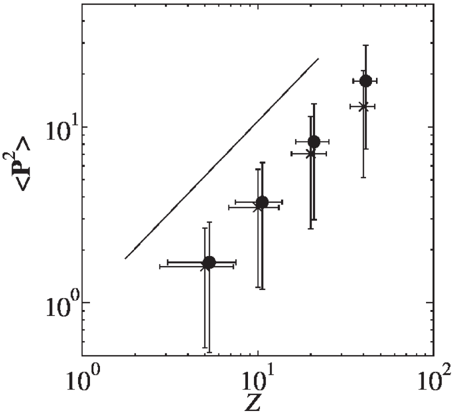


Figure 1.
Average square end-to-end distance $\left\langle \mathbf{P}^2 \right\rangle$ plotted against Z for model 1 (×) and for model 2 (●). Solid line shows $\left\langle \mathbf{P}^2 \right\rangle = Z$.

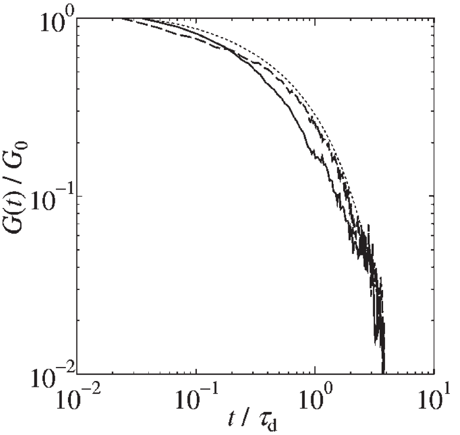


Figure 2.
Relaxation modulus $G(t)/G_0$ plotted against τ_d. Dotted curve is based on the reptation theory.[2] Solid and dashed lines are model 1 and model 2 for $Z_0 = 20$.

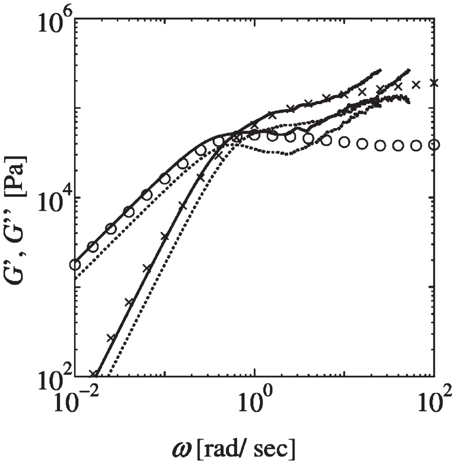


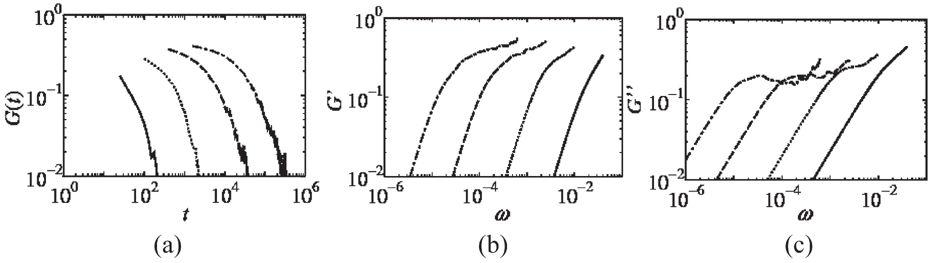
Figure 4.
$G'(\omega)$ and $G''(\omega)$ compared with monodisperse polystyrene melt (symbols). Z_0 is 20. Solid and dashed lines are for model1 and for model2 respectively.

$t = 0$ and 1 involves fast relaxation modes out of the level of coarse-graining of this study.

Fig. 3(a) shows $G(t)/G(t=1)$ for various Z_0. Notice that following the assumption where the entanglement renewal time is comparable to Rouse time, unit time of each Z is assumed to be proportional to Z^2. Storage and loss modulus, $G'(\omega)$ and $G''(\omega)$, obtained from $G(t)$ are also shown in Fig. 3(b) and (c). Plateau region of $G'(\omega)$ and relaxation peak of $G''(\omega)$ are observed for longer chains consistently with experiments. It is noted that Rouse mode like upturns observed especially in $G''(\omega)$ are artifact reflecting the fact that the uniformity of tension along chain is not achieved and hence local stretch the chain remains. Even when the equilibration in Sec 2.3 is performed for longer calculation time, the upturn behavior is not removed since in our model change of N_i during the equilibration according to slip motion of the chain is not considered for the mechanical equilibration.

Fig. 4 shows comparison with polystyrene melt[17] for $Z_0 = 20$. The simulation result is vertically shifted by the rubber theory;[18]

$$G_{\text{shift}} = \frac{\rho RT}{M_w} Z_0, \tag{10}$$



(a) (b) (c)

Figure 3.
(a) Relaxation modulus $G(t)/G_0$, (b) storage modulus $G'(\omega)/G_0$ and (c) loss modulus $G''(\omega)/G_0$. From top to bottom the value of Z_0 are 40, 20, 10 and 5.

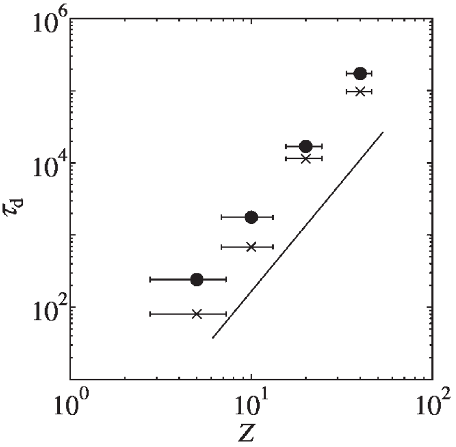


Figure 5.
Molecular weight dependence of the longest relaxation time, τ_d for model 1 (×) and for model 2 (●). Solid line indicates power of 3.

where ρ is 959 $kg \cdot m^{-3}$, R is 8.31 $JKmol^{-1}$, T is 453 K and M_w is 275 k. The horizontal shift factor is determined to reproduce the cross point of $G'(\omega)$ and $G''(\omega)$. Eliminating the artificial upturns in $G'(\omega)$ and $G''(\omega)$, the prediction of model1 is fairly reasonable.

Fig. 5 shows the longest relaxation time, τ_d, obtained from the cross-point frequency of $G'(\omega)$ and $G''(\omega)$ plotted against Z_0. Note again that the unit time for each Z_0 is assumed to be proportional to the Rouse time. The power exponent is around 3.5 and 3.2 for model1 and model2 respectively and both results are consistent with the earlier results.

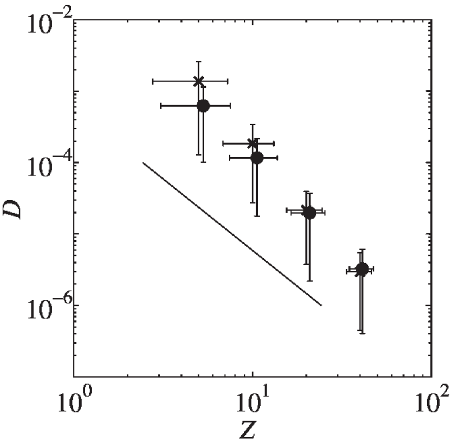


Figure 6.
Molecular weight dependence of self-diffusion coefficient, D for model 1(×) and for model 2 (●). Solid line indicates power of -2.

3.3 Self-diffusion coefficient

Fig. 6 shows molecular weight dependence of self-diffusion coefficient D. The power exponent is in between -2 and -3 which is consistent with the earlier results[19] within the distribution of Z and statistics for D.

4. Conclusions

A new model for dynamics of entangled polymers based on pre-averaged sampling of the entanglement structure has been proposed. Using the probability distribution for monodisperse linear polymers proposed by Schieber,[15] linear viscoelastic response above Rouse time is reasonably predicted. Assuming that the renewal time of the entanglement structure is comparable to Rouse time, the established power laws against molecular weight for the longest relaxation time and diffusion coefficient are reproduced. It is certain that to extend the model to polydispersed systems, branch polymers, polymer under flow, etc., modified probability distribution for the entanglement structure is required. Such a distribution can be provided by sliplink simulations based on the detail kinetics of the entanglement rearrangement around chain ends. Combined has been being investigated and results shall be presented elsewhere.

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