

Nonlinear stress relaxation of entangled polymer chains
in primitive chain network simulation

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CHAPTER 1

Introduction

1-1. Background

Dynamics of entangled polymer chains is one of the most important issues in the field of polymer science¹⁾ and polymer processing industry.²⁾ Under large strain/fast flow, the motion and conformation of polymer chains are significantly different from those at equilibrium. This difference is reflected in nonlinear viscoelastic properties of polymers. Some industrial products such as highly elastic fibers and films benefitically utilize the polymer-specific features (nonlinear elasticity and toughness for this case), and the polymer processing is designed in a way enhancing those features in the products.³⁾ Therefore, understanding of polymer dynamics and rheology under large strain/fast flow is strongly demanded. In fact, theoretical and experimental efforts have been made extensively to achieve this understanding.

In particular, nonlinear viscoelastic responses of entangled polymeric liquids,^{1), 2), 4) - 6)} the target of this thesis, have been the subject of extensive researches. Those responses reflect non-equilibrium motion of the polymer chains under large strain/fast flow and cannot be described within Boltzmann's superposition framework. For this reason, the nonlinear responses have been investigated individually for each type of deformation. The following sections first summarize nonlinear features of linear entangled chains experimentally observed under shear and then explain the theoretical framework being developed to describe/understand those features.

1-2. Nonlinear viscoelastic behaviors of linear entangled polymers

1-2-1. Stress relaxation under large step shear

On application of large step shear strain γ at $t = +0$, the shear stress $\sigma_s(t, \gamma)$ exhibits nonlinear relaxation. This behavior is characterized by the nonlinear shear relaxation modulus $G(t, \gamma)$ defined as

$$G(t, \gamma) = \frac{\sigma_s(t, \gamma)}{\gamma} \quad (1.1).$$

Extensive experiments^{8) - 12)} revealed that $G(t, \gamma)$ shows characteristic damping. As shown in Fig. 1-1, $G(t, \gamma)$ data of an entangled linear polystyrene (PS) solution¹²⁾ decrease with an increase of $\gamma > 0.57$ and exhibit a two-step relaxation. At times t longer than the characteristic time τ_k , the $G(t, \gamma)$ data vertically shifted by an adequate factor $h(\gamma)^{-1}$ can be superposed on the linear relaxation modulus $G(t)$. This behavior can be cast in a factorized form,¹²⁾

$$G(t, \gamma) = h(\gamma)G(t) \quad (1.2).$$

The vertical shift factor $h(\gamma)$ is referred to as the shear damping function. Figure 1-2 shows typical $h(\gamma)$ data for entangled linear PS solutions. In an early study, Osaki et al.¹²⁾ possibly adopted a criterion of superposition within ~ 10 % uncertainty to conclude that τ_k is considerably shorter than the terminal relaxation time τ_d and close to $4.5\tau_R$ (with τ_R being the Rouse time explained later). However, recent experiments^{13), 14)} adopting a severer criterion (within a few % uncertainty) demonstrated that τ_k is close to τ_d rather than τ_R .

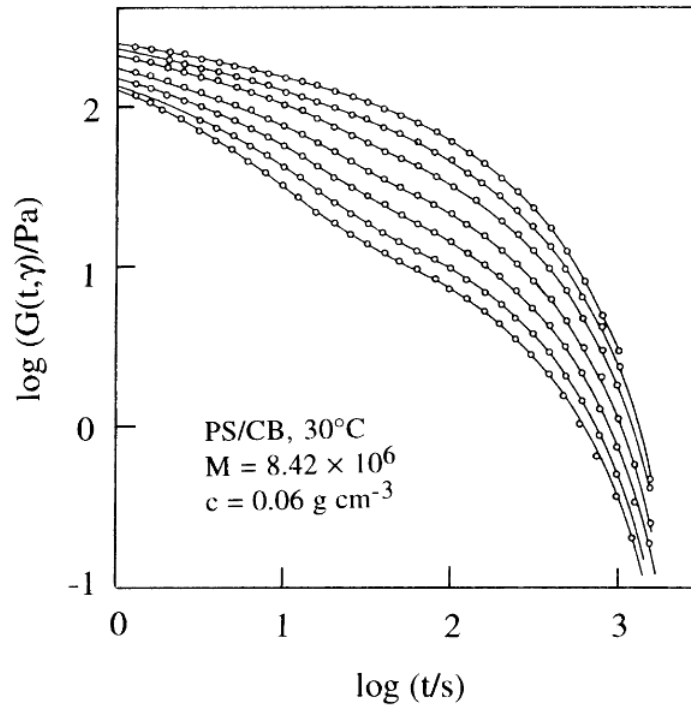


Figure 1-1 Nonlinear relaxation modulus $G(t, \gamma)$ of an entangled linear PS solution in chlorinated biphenyl. The shear strain γ is 0.57, 1.25, 2.06, 3.04, 4.0, 5.3, and 6.1 from top to bottom.¹²⁾

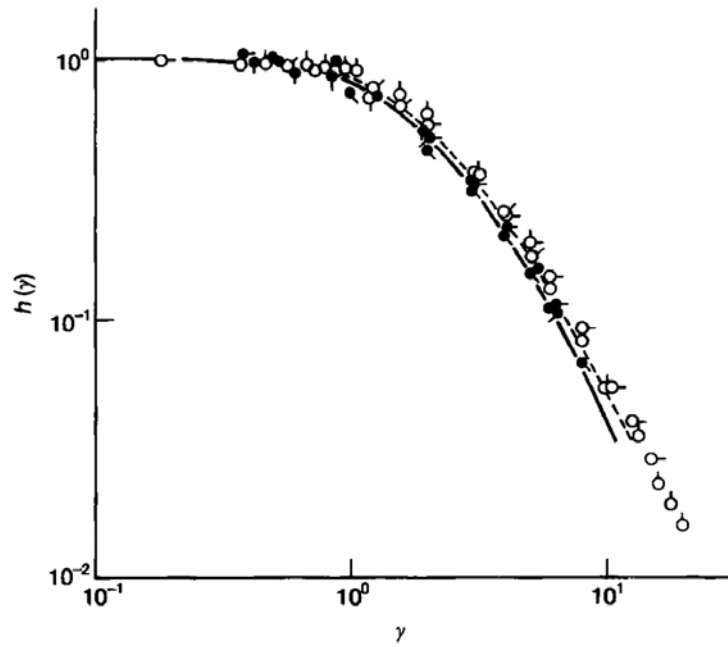


Figure 1-2 Shear damping function $h(\gamma)$. Symbols indicate experimental data of entangled linear PS solutions.¹²⁾ Dashed and solid curves represent the theoretical predictions of the Doi-Edwards model with and without the Independent Alignment Approximation (IAA), respectively (see Section 1-3-1).

Osaki¹¹⁾ classified the damping behavior into three types A, B, and C according to the $h(\gamma)$ values, as shown in Fig. 1-3. Moderately entangled polymers exhibit type-A damping that is associated with $h(\gamma)$ being close to the prediction of the Doi-Edwards (DE) model explained in the next section. Scarcely entangled polymers exhibit type-B behavior associated with larger $h(\gamma)$ (weaker nonlinearity), as first found by Takatori et al.¹⁶⁾ for linear PS solutions and later by Inoue et al.¹⁷⁾ (for linear PS solutions) and by Vega et al.¹⁸⁾ (for linear PS melts). In contrast, highly entangled polymers show the type-C behavior associated with much smaller $h(\gamma)$ under moderate strains. Type-C behavior was suggested to be an experimental artefact due, for example, to an interfacial slip between the measuring assembly and sample,¹⁵⁾ although a theoretical analysis suggested that the type C behavior is related to an elasticity instability intrinsic to highly entangled polymers.¹⁹⁾

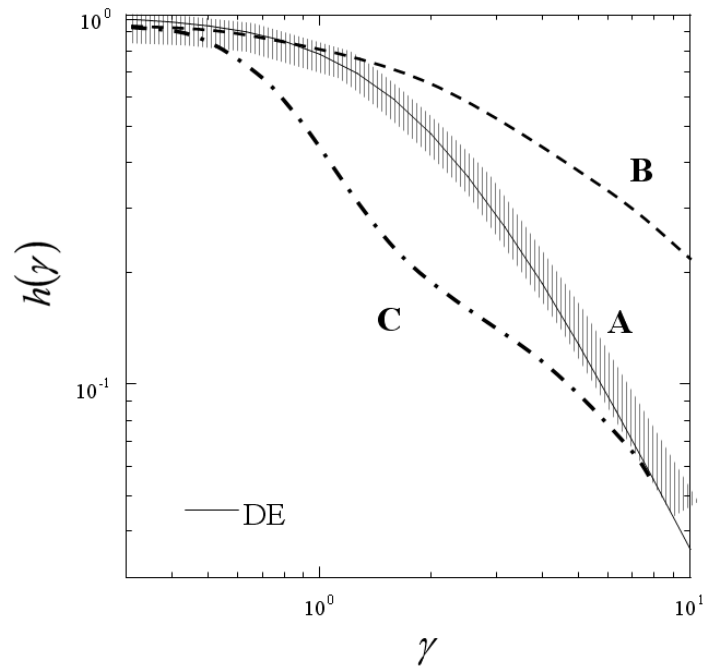


Figure 1-3 Classification of damping function by Osaki.¹¹⁾ Solid curve indicates the prediction of DE model. Type-A behavior (hatched area) matches the DE prediction. Type-B behavior is associated with weaker strain dependence of the damping function (dashed curve), whereas type-C behavior (dot-dashed curve) shows stronger strain dependence.

1-2-2. Steady and transient behavior under shear flow

Under steady shear, the viscosity $\eta(\dot{\gamma})$ of entangled polymers decreases with an increase of shear rate $\dot{\gamma}$. An example of this *shear-thinning* behavior is shown in Fig. 1-4 for linear PS solutions,²⁰⁾ where the viscosity and the shear rate are reduced by the zero-shear viscosity, η_0 , and the shear rate at the onset of shear thinning, $1/\tau_\eta$, respectively. At high shear rates, $\eta(\dot{\gamma})$ can be described by a power-law relationship,

$$\eta(\dot{\gamma}) \sim \dot{\gamma}^{-\beta} \quad (\beta \cong 0.8) \quad (1.3).$$

Before reaching to the steady state, entangled polymers exhibit complicated transient behavior¹⁾ characterized by the viscosity growth function,

$$\eta^+(t, \dot{\gamma}) = \frac{\sigma_s(t, \dot{\gamma})}{\dot{\gamma}} \quad (1.4).$$

An example is shown in Fig. 1-5 for a linear polybutadiene (PB) solution.²¹⁾ $\eta^+(t, \dot{\gamma})$ agrees with the linear viscosity growth function $\eta^+(t)$ at short t but deviates downward from $\eta^+(t)$ at long t to reach the steady state. For relatively small $\dot{\gamma}$, the peak of $\eta^+(t, \dot{\gamma})$ corresponding to this downward deviation emerges at a time, $t_{\text{peak}} \cong 2/\dot{\gamma}$, which indicates that the peak emerges when the flow imposes a constant strain, $\gamma_{\text{peak}}^0 \cong 2$. In contrast, for large $\dot{\gamma}$, the peak strain γ_{peak} increases with increasing $\dot{\gamma}$, as shown in Fig. 1-6²²⁾ where the normalized strain $\gamma_{\text{peak}}/\gamma_{\text{peak}}^0$ is plotted against the normalized shear rate $\dot{\gamma}\tau_k$ (with τ_k being the onset time for the time-strain factorization of $G(t, \gamma)$ explained in Section 1-2-1). The data are well described by the theory of Pearson et al.²³⁾ explained later.

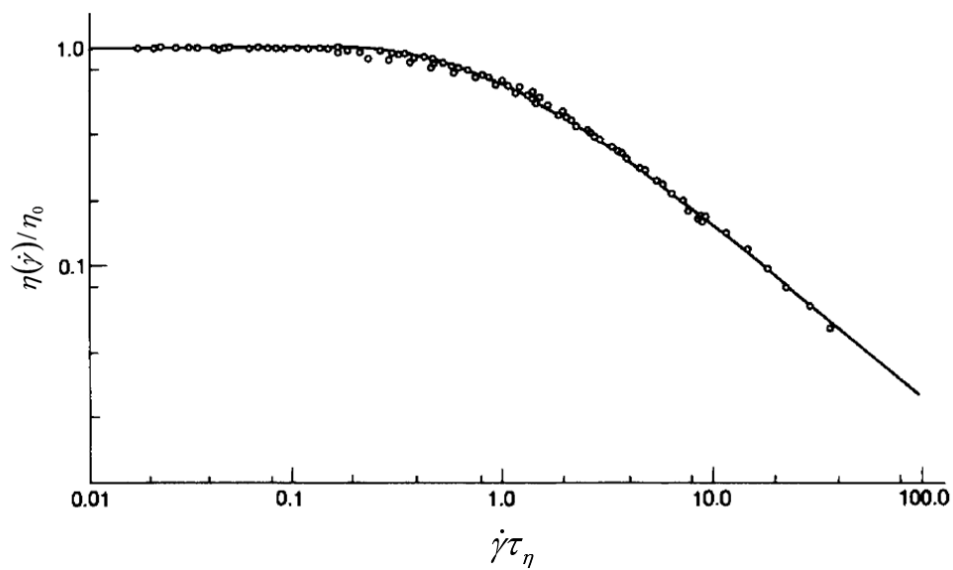


Figure 1-4 Reduced plot of steady shear viscosity for linear PS solution.²⁰⁾

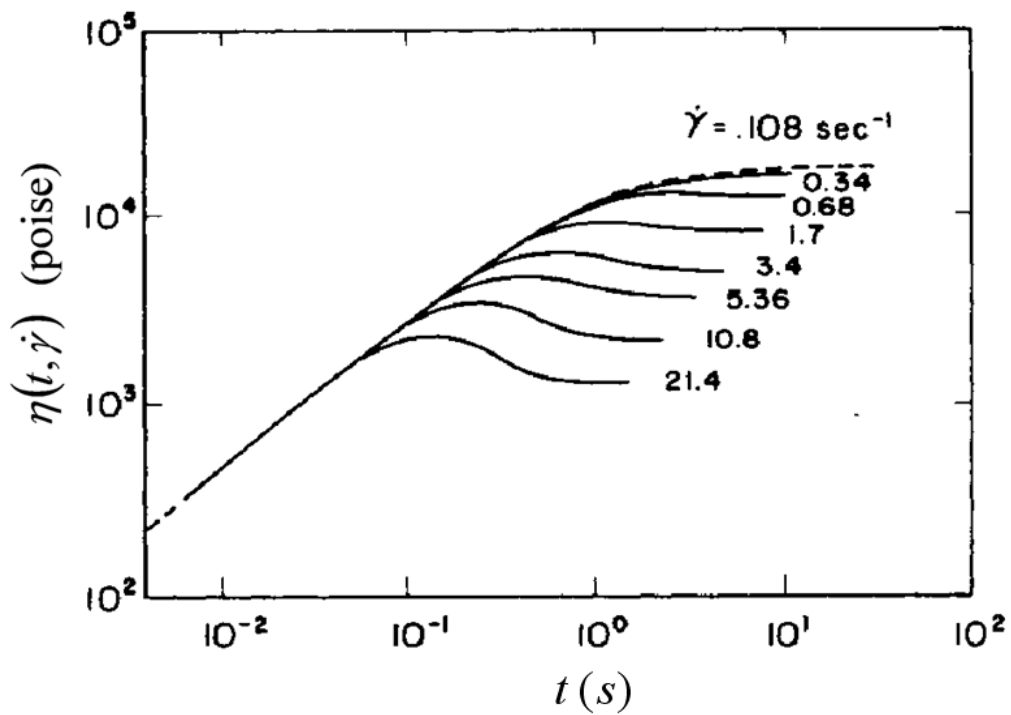


Figure 1-5 Shear stress growth function at various $\dot{\gamma}$ for linear PB solution.²¹⁾ Solid curves show experimental data. The dashed curve indicates the linear response calculated from linear viscoelastic data.

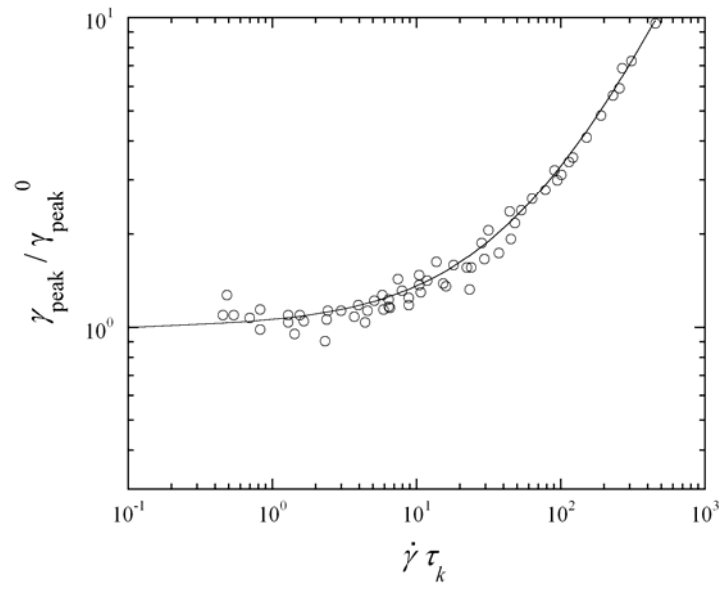


Figure 1-6 $\dot{\gamma}$ dependence of normalized γ_{peak} of the viscosity growth function.²²⁾ Solid curve indicates the theory of Pearson et al.²³⁾

1-3. Theoretical models for nonlinear behavior of linear entangled polymers

Nonlinear viscoelastic features of entangled polymers summarized in the previous section reflect the non-equilibrium chain dynamics under large strain/fast flow. This dynamics has been frequently discussed on the basis of the tube model proposed by Doi and Edwards (DE),⁵⁾ a sophisticated extension of de Gennes's reptation model⁴⁾ that proposed reduction of multi-chain dynamics into a single-chain dynamics in a dynamic mean field. The DE model is believed to capture an essence of entanglement dynamics but also misses some basic aspects of entanglement itself. Thus, theoretical efforts have been made to refine the model. This section summarizes the features of the DE model and its refinements.

1-3-1. Doi-Edwards model

Adopting the main concept in de Gennes's reptation model, the DE model represents the effect of entanglement as a “tube” that topologically allows the *large-scale* chain motion only along the tube axis (referred to as primitive path⁵⁾), as shown in Fig. 1-7. The tube radius, a , is taken to be the end-to-end length of an entanglement segment of the molecular weight M_e (evaluated from the entanglement plateau modulus $G_N^{(0)}$),¹⁾ so that the entanglement effect considered in the model emerges only for chains having the molecular weights $M > M_e$. Thus, the chain length is measured as the number of entanglement segments per chain,

$$Z_e = \frac{M}{M_e} \quad (1.5).$$

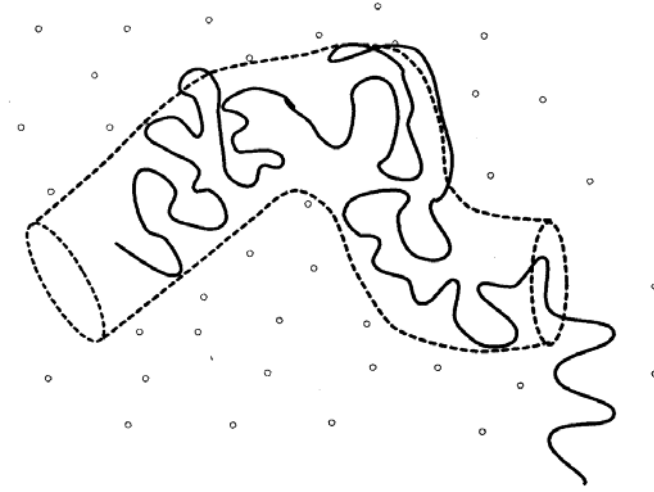


Figure 1-7 A tube-like constraint around a polymer chain.⁷⁾

The expression of the stress tensor $\boldsymbol{\sigma}$ in the DE model is equivalent to that deduced from the stress-optical rule,²⁴⁾

$$\boldsymbol{\sigma} = 3\nu k_B T \left\{ \left\langle \frac{\mathbf{r}\mathbf{r}}{nb^2} \right\rangle - \frac{\mathbf{I}}{3} \right\} \quad (1.6).$$

Here, ν is the number density of submolecules, $\mathbf{r}$ is the end-to-end vector of the submolecule, n is the number of Kuhn segments per submolecule, b is the step length of the Kuhn segment, and $\langle \dots \rangle$ denotes the ensemble average over the submolecules. k_B and T are the Boltzmann constant and absolute temperature, respectively, and $\mathbf{I}$ is the identity tensor. Equation 1.6 gives $\boldsymbol{\sigma} = \mathbf{0}$ at equilibrium where the submolecules have the isotropic Gaussian distribution of $\mathbf{r}$ characterized by $\langle \mathbf{r}\mathbf{r} \rangle_{\text{eq}} = (nb^2/3) \mathbf{I}$.

The DE model assumes that the tube axis (primitive path) and the chain trapped in the tube are affinely oriented and stretched on application of an instantaneous strain (step strain) at $t = +0$. On this affine deformation, the end-to-end vector of the entanglement segment (submolecule adopted in the DE model) changes from $\mathbf{r}_{\text{eq}}$ at equilibrium to $\mathbf{r} = \mathbf{E} \cdot \mathbf{r}_{\text{eq}}$, with $\mathbf{E}$ being the deformation gradient tensor for the step strain. The corresponding stress is given by Eq. 1.6 utilizing this $\mathbf{r}$.

However, in a very short time scale, the entanglement points fluctuate to reduce the stress by a factor of $4/5$.²⁵⁾ The stress after this fluctuation, $\boldsymbol{\sigma}(+0) = (12 \nu k_B T / 5) \{ \langle (\mathbf{E} \cdot \mathbf{r}_{eq}) (\mathbf{E} \cdot \mathbf{r}_{eq}) / nb^2 \rangle - \mathbf{I} / 3 \}$, is the initial stress adopted in the DE model.

The model considers the chain to relax from this initial state in two steps,⁵⁾ as shown in Fig. 1-8. The first step is the contraction of the chain back to its equilibrium “contour length”, aZ_e , that completes at the Rouse time, τ_R . (In the DE model, the length equilibration time τ_{eq} is assumed to be equal to τ_R .) The stress tensor after the contraction can be written as

$$\boldsymbol{\sigma}(\tau_R) = 3 \nu k_B T \mathbf{Q}(\mathbf{E}) \quad \text{with} \quad \mathbf{Q}(\mathbf{E}) = \frac{1}{\langle |\mathbf{E} \cdot \mathbf{u}_{eq}| \rangle} \left\langle \frac{(\mathbf{E} \cdot \mathbf{u}_{eq}) (\mathbf{E} \cdot \mathbf{u}_{eq})}{|\mathbf{E} \cdot \mathbf{u}_{eq}|} \right\rangle - \frac{\mathbf{I}}{3} \quad (1.7).$$

Here, $\mathbf{u}_{eq} = \mathbf{r}_{eq} / |\mathbf{r}|$ is the unit tangential vector of the entanglement segment at equilibrium, and $\mathbf{Q}(\mathbf{E})$ is the DE universal orientation tensor (measure of chain strain) determined by $\mathbf{E}$. In Eq. 1.7, the factor $1 / \langle |\mathbf{E} \cdot \mathbf{u}_{eq}| \rangle$ represents the decrease of the number of entanglement segments per chain, and the other factor $1 / |\mathbf{E} \cdot \mathbf{u}_{eq}|$ included in the second average term represents an increase of the number of the Kuhn segments per entanglement segment, both being induced by the chain contraction. With the Independent Alignment Approximation (IAA) considering the chain to preserve its shape on contraction, the expression of $\mathbf{Q}(\mathbf{E})$ (Eq. 1.7) reduces to

$$\mathbf{Q}^{IAA}(\mathbf{E}) = \left\langle \frac{(\mathbf{E} \cdot \mathbf{u}_{eq}) (\mathbf{E} \cdot \mathbf{u}_{eq})}{|\mathbf{E} \cdot \mathbf{u}_{eq}|^2} \right\rangle - \frac{\mathbf{I}}{3} \quad (1.8).$$

The second step of relaxation is the disengagement from the deformed tube through the diffusion along the primitive path referred to as *reptation*. This disengagement process completes at $t = \tau_d$ (reptation time being proportional to M^3).

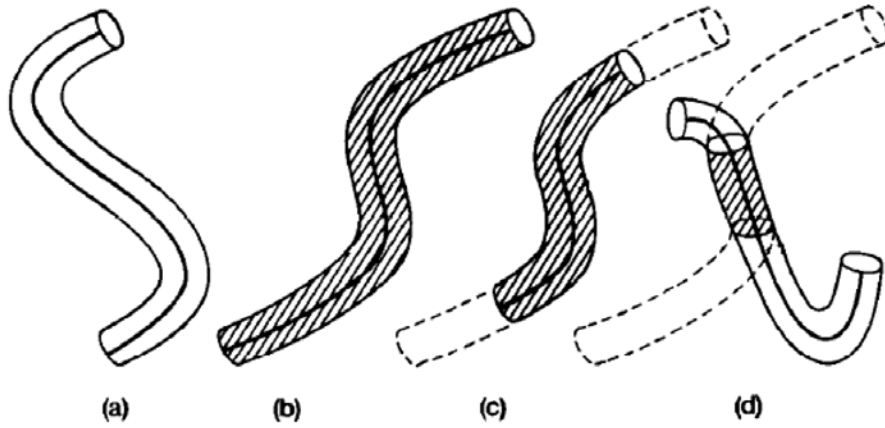


Figure 1-8 Stress relaxation after large step strain. (a) Before the deformation ($t = +0$), the chain is at equilibrium. (b) Immediately after the deformation ($t = +0$), the tube and chain therein are deformed affinely. (c) The chain contracts along the tube to recover the equilibrium contour length at $t \cong \tau_R$. (d) At $t > \tau_R$, the chain escapes from the deformed tube by reptation. The oblique lines indicate the deformed part of the tube.⁵⁾

From the above molecular picture of the DE model, the shear damping function is naturally calculated without any adjustable parameter as

$$h(\gamma) = \frac{\sigma_{12}(\tau_R)}{\sigma_{12}(+0)} = \frac{Q_{12}(\gamma)}{4\gamma/15} \quad (1.9)$$

where the subscript “12” stands for the shear component. Of course, Eq. 1.9 gives $h(\gamma) \rightarrow 1$ for $\gamma \rightarrow 0$ ($[Q_{12}]_{\gamma \rightarrow 0} = 4\gamma/15$). This DE prediction, shown in Fig.1-2 with the solid and dashed curves (without and with IAA), is in good agreement with the data, which has been believed to be the evidence supporting the DE model.

The DE expression of the stress under the step strain (Eq. 1.7) can be extended to a constitutive equation that describes the stress activated by a strain of arbitrary history. The chain has the equilibrium contour length at any time under relatively slow flow/deformation at the strain rate $< 1/\tau_R$, because the contraction freely occurs for this case. Doi and Edwards⁵⁾ focused on such slow flow/deformation to derive the constitutive equation. They argued that a stress $d\sigma(t, t')$ at time t , being activated by a small deformation in a short interval of time from t' ($< t$) to $t'+dt$, exhibits the contraction and relaxation, the latter occurring in the interval from t' to t

through reptation. From Eq. 1.7 with $\mathbf{Q}(\mathbf{E})$ therein being replaced by $\mathbf{Q}^{\text{IAA}}(\mathbf{E})$ (Eq. 1.8), the damping part of $d\boldsymbol{\sigma}(t, t')$ can be expressed as $d\boldsymbol{\sigma}^{\text{[damping]}}(t, t') = 3\nu k_B T d\mathbf{Q}^{\text{IAA}}[\mathbf{E}(t, t')]$ $= 3\nu k_B T \{-\partial \mathbf{Q}^{\text{IAA}}[\mathbf{E}(t, t')]/\partial t'\} dt$, where $\mathbf{E}(t, t')$ is the deformation tensor at t measured from the past time t' , and the minus sign appears in the $\{-\partial \mathbf{Q}^{\text{IAA}}/\partial t'\}$ term because $\mathbf{Q}$ (and $\mathbf{E}$) decreases with increasing t' . This $d\boldsymbol{\sigma}^{\text{[damping]}}(t, t')$ relaxes through reptation, so that $d\boldsymbol{\sigma}(t, t')$ is expressed as $d\boldsymbol{\sigma}(t, t') = d\boldsymbol{\sigma}^{\text{[damping]}}(t, t') \psi(t - t')$ where $\psi(t)$ is the reptation relaxation function specified below. Accumulation of $d\boldsymbol{\sigma}(t, t')$ in the whole range of t' ($< t$) gives the stress at time t as

$$\boldsymbol{\sigma}(t, \mathbf{E}) = 3\nu k_B T \mathbf{S}(t, \mathbf{E}) \quad (1.10)$$

$$\mathbf{S}(t, \mathbf{E}) = -\int_{-\infty}^t dt' \psi(t - t') \left\{ \frac{\partial}{\partial t'} \mathbf{Q}^{\text{IAA}}[\mathbf{E}(t, t')] \right\} = \int_{-\infty}^t dt' \left\{ \frac{\partial}{\partial t'} \psi(t - t') \right\} \mathbf{Q}^{\text{IAA}}[\mathbf{E}(t, t')] \quad (1.11)$$

with

$$\psi(t) = \sum_{p:\text{odd}} \frac{8}{p^2 \pi} \exp\left(-\frac{p^2 t}{\tau_d}\right) \quad \text{with} \quad \tau_d = \text{reptation time} \quad (1.12)$$

(The integration by parts was made in Eq. 1.11.)

The DE constitutive equation with IAA, Eqs. 1.10 - 1.12, is phenomenologically classified as the K-BKZ type²⁶⁾ constitutive equation. This DE equation fails to describe the stress data under double step strains with reversed directions^{27), 28)} because IAA is invalid under this condition. However, the rigorous DE constitutive equation based on Eq. 1.7 without IAA can successfully describe those data, given that the empirically determined $\psi(t)$ is utilized instead of the reptation relaxation function, Eq. 1.12.²⁷⁾ The rigorous DE equation also describes the Weissenberg effect as well.^{29), 30)}

Nevertheless, the DE constitutive equation, Eqs. 1.10 - 1.12, severely fails under steady shear flow. For this case, no reversal of deformation direction occurs and IAA involved in this

equation is a harmless approximation. The steady state shear stress $\sigma_s(\dot{\gamma})$ calculated from the DE equation decreases in proportion to $\dot{\gamma}^{-1/2}$ on an increase of the shear rate $\dot{\gamma}$ above the reptation rate $1/\tau_d$ (see solid curve in Fig. 1-9).⁵⁾ This physically unrealistic prediction results from the over-orientation of the entanglement segments in the flow direction deduced from the DE molecular picture, the affine deformation of the tube with respect to the deformation at every time and the chain contraction and reptative relaxation along the axis of this deforming tube. (In fact, $\sigma_s \sim Q_{12}$ vanishes when those segments are fully oriented in the flow direction.)

The failure of the DE model due to the over-orientation of the segments cannot be improved by the extension of the model for chain stretching. In the original DE model, the contour length is assumed to remain a constant. This assumption is apparently not correct if the deformation rate is higher than the contraction rate, i.e., for $\dot{\gamma} > 1/\tau_R$. In such a condition the chain is stretched and the contour length becomes larger than the equilibrium value. This chain stretching is an important mechanism to describe the viscoelasticity under fast flows. For instance, under the condition $\dot{\gamma} > 1/\tau_R$, the shear stress starts to increase with an increase of shear rate due to the chain stretch (see dashed curve in Fig. 1-9). Marrucci and Grizzuti³¹⁾ extended the DE model by considering this chain stretching (their model is referred to as DEMG model). Later, Pearson et al.³²⁾ proposed a simplified model where the orientation and the stretch are decoupled in the stress expression. The average orientation tensor in their model is common to the DE equation with IAA (Eq. 1.11). On the other hand, the time evolution of chain stretch ratio λ is described by

$$\frac{d\lambda}{dt} = \lambda \mathbf{k} : \mathbf{S} - \frac{1}{\tau_{eq}}(\lambda - 1) \quad \text{with } \lambda = \frac{L(t)}{\langle L \rangle_{eq}} \quad (1.13)$$

where $\mathbf{k}$ is the velocity gradient tensor, $L(t)$ is the chain contour length at the time t , $\langle L \rangle_{eq}$ is the equilibrium value of L , and τ_{eq} is the relaxation time of chain stretch assumed to be given by $2\tau_R$. The first term on the right-hand side of Eq. 1.13 corresponds to the stretch due to the affine

deformation. The second term represents the relaxation of the stretch. The stress tensor is expressed as

$$\boldsymbol{\sigma}(t, \mathbf{E}) = 3 \nu k_B T \lambda^2 \mathbf{S}(t, \mathbf{E}) \quad (1.14).$$

This expression is reduced to the DE expression (Eq. 1.10) for the unstretched condition ($\lambda = 1$). Pearson et al.²³⁾ also proposed another refined model to investigate the chain stretching effect in transient shear flow. Their model²³⁾ well describes the stress overshoot in transient shear flow. Specifically, their model correctly predicts the peak position of the stress overshoot as a function of shear rate (as shown in Fig. 1-6). However, these models considering the effect of chain stretch^{23), 31), 32)} still predict the flow curve exhibiting the peak of shear stress at $\dot{\gamma} \cong 1/\tau_d$, as shown in Fig. 1-9. This failure is rational because the chain stretching affects the stress only at $\dot{\gamma} > 1/\tau_R$ and no effect is conceptually expected for the over-orientation of the segment that results in the peak at $\dot{\gamma} \cong 1/\tau_d$.

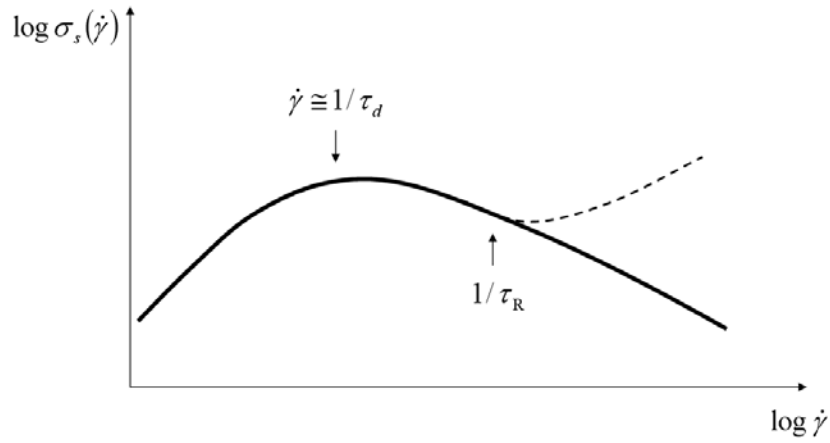


Figure 1-9 Steady state shear stress vs shear rate. Solid curve represents the DE prediction. Dashed curve indicates a prediction of the refined model considering the chain stretching.^{23), 31), 32)}

1-3-2. Convective Constraint Release (CCR)

Extensive theoretical efforts have been made to remove the flaws of the DE model due to the over-orientation of the segments. Specifically, the mechanism called constraint release is in focus below.

The immobility of tube (assumed in the DE model) is a crude approximation and indeed, the tube can move according to the relative motion of the surrounding chains. At equilibrium, this tube motion is referred to as the thermal constraint release (CR). Figure 1-10 shows the molecular picture of the thermal CR.^{33) - 36)} When a chain forming entanglement with the test chain diffuses away (as shown for the unfilled chain in the left panel in Fig. 1-10), the conformation of the test chain changes through a local jump of the released segment (middle panel in Fig. 1-10). Because the entanglement density at equilibrium (which determines the entanglement plateau modulus $G_N^{(0)}$) is unchanged, this jumping segment is entangled by another chain after a certain time (right panel in Fig. 1-10). Accumulation of such local jumps lateral to the chain backbone leads to a global motion of the test chain. This test chain motion can be taken into account in the DE model via the tube dynamics. For example, Graessley³³⁾ proposed CR-Rouse dynamics where the configurational dynamics of the tube is described by the Rouse dynamics with the friction of beads being replaced by the waiting time of disentanglement. These improvements have been reported to give better predictions in linear viscoelastic regime.^{6), 33)}

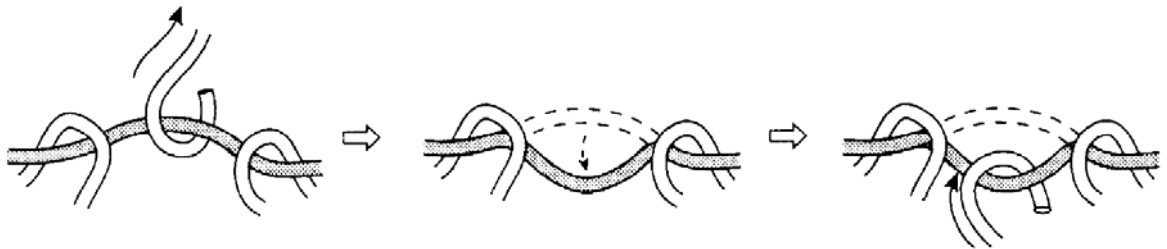


Figure 1-10 Schematic picture of the thermal constraint release.⁶⁾

Under large strain/fast flow, the tube behaves differently from that under equilibrium. Marrucci³⁷⁾ proposed such a CR mechanism activated in the nonlinear regime. He considered two entangling chains under a steady shear flow at the shear rate $\dot{\gamma} > 1/\tau_d$, and assumed that the center of mass positions of the chains are separated by a distance of $R_{ee} = |\mathbf{R}_{ee}|$ (the end-to-end distance of the chain). For this situation, the relative velocity between the chains is ca. $\dot{\gamma} R_{ee}$ and the time required to separate these two chains can be estimated as $R_{ee}/(\dot{\gamma} R_{ee}) = \dot{\gamma}^{-1}$ (see Fig. 1-11). This separation time corresponds to the disentanglement time for these chains. With the other assumption where the separation time is common for any pair of the entangled chains, the renewal rate of entanglement for the convection-induced disentanglement is thus estimated as $\dot{\gamma}$. Further assuming that the convection-induced entanglement renewal is independent of the thermal motion, Marrucci proposed that the terminal relaxation time can be given by

$$\frac{1}{\tau} = \frac{1}{\tau_d} + \dot{\gamma} \quad (1.15).$$

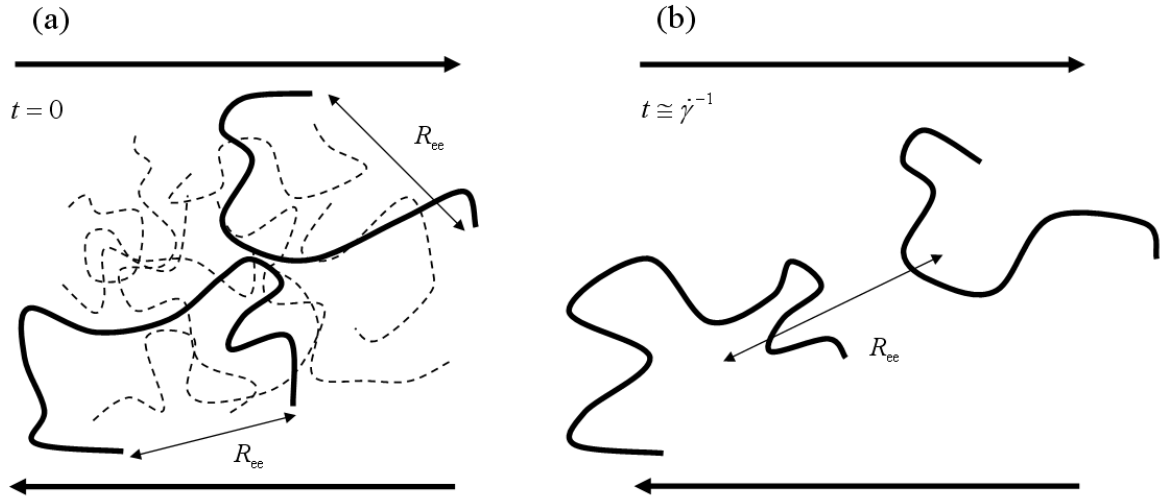


Figure 1-11 Schematic picture of the Marrucci's convection-induced constraint release.³⁷⁾ (a) Representative two chains (thick solid curves with a mean end-to-end distance R_{ee}) are neighboring at $t = 0$. These chains are surrounded by the other chains (thin dashed curves). (b) Under steady shear flow, the center of mass of these chains has a relative velocity $\dot{\gamma} R_{ee}$, and these chains are separated in a time of order $R_{ee}/(\dot{\gamma} R_{ee}) = \dot{\gamma}^{-1}$.³⁷⁾

Following the above work by Marrucci,³⁷⁾ Ianniruberto and Marrucci³⁸⁾ introduced in the tube model the mechanism of Convective Constraint Release (CCR). CCR is defined as the reduction of topological constraints due to the flow.³⁸⁾ This “flow” includes not only the steady and unsteady flows but also large step deformations. However, Ianniruberto and Marrucci³⁸⁾ focused on only the formulation of CCR under the steady flow. As mentioned above, the convection term in Eq. 1.15 (the second term on the right-hand side) is derived from the simple argument that only considers the relative velocity between center-of-mass positions. This idea can be extended to deformation of the chain, as schematically illustrated in Fig. 1-12. When the test chain is transiently stretched under a shear flow at the shear rate $\dot{\gamma} < 1/\tau_R$, it contracts to recover the equilibrium contour length. (The contraction process considered here is similar to that considered in the DE model (Fig. 1-8), but the DE model only gives the chain conformation after the contraction and does not discuss the transient behavior.) Under the flow specified by the velocity gradient tensor $\mathbf{k}$, the chain ends move inward along the tube with the average velocity $\langle V \rangle = L \mathbf{k} : \mathbf{S} / 2$, where L is the chain contour length and $\mathbf{S}$ is the average orientation tensor. This end motion removes entanglements between the test chain and the surrounding chains, and thus, the disentanglement rate is proportional to $\mathbf{k} : \mathbf{S}$. Ianniruberto and Marrucci³⁸⁾ formulated the terminal relaxation time for the test chain exposed to this process as

$$\frac{1}{\tau} = \frac{1}{\tau_d} + \beta_{\text{CCR}} \mathbf{k} : \mathbf{S} \quad (1.16)$$

where β_{CCR} is a numerical parameter adjusting the intensity of CCR. Replacing the reptation time of the original DE model by τ given by Eq. 1.16 and setting $\beta_{\text{CCR}} > 2.76$, Ianniruberto and Marrucci³⁸⁾ showed that the shear stress monotonically increases with an increase of shear rate even at high shear rates $\dot{\gamma} > 1/\tau_d$.

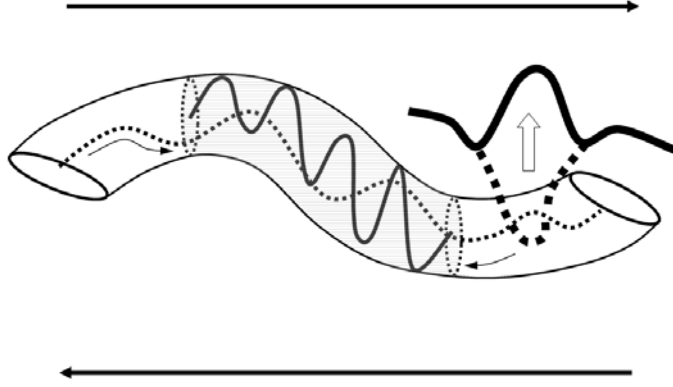


Figure 1-12 Schematic illustration of the convective constraint release (CCR) under fast flow.

Mead-Larson-Doi (MLD) model³⁹⁾ further elaborately considered the effect of chain conformation on CCR. In their model, the terminal relaxation time is given by

$$\frac{1}{\tau} = \frac{1}{\lambda^2 \tau_d} + f(\lambda) \left(\mathbf{k} : \mathbf{S} - \frac{1}{\lambda} \frac{d\lambda}{dt} \right) \quad (1.17).$$

In the first term on the right-hand side of Eq. 1.17, λ^2 represents an increase of the reptation time due to the chain stretch. The second term represents the acceleration induced by CCR and $f(\lambda)$ is the stretch dependent intensity for this acceleration. In the parentheses, the first term comes from Eq. 1.16, and the second term is the correction that the constraint release by the chain contraction is decelerated by the chain elongation at a rate $d(\ln \lambda)/dt = (d\lambda/dt)/\lambda$. Under steady shear flow at an intermediate shear rate between $1/\tau_d$ and $1/\tau_R$, the MLD model gives a constant stress eliminating the over-orientation in the DE model. However, the MLD model underpredicts the relaxation modulus after large step shear strain due to the correction term in Eq. 1.17, because this term affects, even in the absence of flow, the relaxation as long as the chain is stretched.

1-3-3. local-CCR

Effects of the CCR on the relaxation time have not been fully elucidated yet. In the models mentioned in the previous subsection, the effect of CCR is embedded only in the change of the relaxation time of the chain as a whole (terminal relaxation time). However, the change of the terminal relaxation time is achieved through accumulation of local relaxation of segment, which is induced by local disentanglement due to the flow. The implementations of CCR such as Eqs. 1.16 and 1.17 are crude approximations as long as the detail of the local relaxation of segment is unknown. Specifically, the single segment models,^{38) - 43)} averaging the distribution of the contour variables into representative values, cannot describe changes of the distribution function induced by local disentanglement. In this thesis hereafter, this local disentanglement due to “flow” (that includes step strain in addition to usual steady/transient flow) is abbreviated as local-CCR.

To clarify the detail of local-CCR theoretically, a full-chain model (not smearing details along the chain contour) is desired. For example, the GLaMM model⁴⁴⁾ is a full-chain model that can describe the distribution of chain stretch along the contour, thereby giving good agreements with experiments for shear viscosity growth curve. However, this model considers the single chain dynamics in a dynamic mean field, so that it requires a certain relaxation mechanism representing local-CCR. In the GLaMM model, the local relaxation of segment induced by local-CCR is cast into the CR-Rouse dynamics with the friction of the Rouse bead being given by the rate of local-CCR. For the local-CCR rate, an adjustable parameter is introduced to fit to the experiment. These artificial treatments in the single chain models can be avoided if the motion of the focused chains is traced in an ensemble of many interacting chains. Thus, the details of local-CCR can be best examined by a full-chain model for such multi-chain ensemble.

To avoid any artificial treatment concerning local-CCR, the ideal choice is the full-atomistic molecular dynamics simulation. However, this choice is impractical due to its heavy

computational cost. To reduce the cost, there have been developed coarse-grained molecular models^{45) - 50)} describing only the slow variables. The choice of the coarse-grained level is arbitrary and it is required to choose a model not averaging out the local-CCR process. In this respect, the Primitive Chain Network (PCN) simulation⁵⁰⁾ is a reasonable option. In the PCN simulation, many chains are distributed in 3-D space and the chain consists of consecutive segments. Each segment is bundled by sliplink to the other segment in pair. The time development of the position of sliplinks is traced according to the equation of motion that takes into account the local balance among elastic force, drag force, osmotic force, and thermal Brownian force. The sliplink is created and destructed around the chain ends due to the relative motion of the connected chains (induced by both thermal and convective motions). In this treatment, local-CCR event is naturally traced without any a priori assumption, except the assumption that the entanglement is a binary event and is represented by the sliplink.

1-4. Scope of this thesis

This thesis investigates the nonlinear features of linear entangled chains under large strain using the PCN simulation.⁵⁰⁾ The main focus is placed on the relationship between nonlinear rheological properties and the collective mechanisms between chains including local-CCR. This thesis consists of six chapters including this introduction as the first chapter.

Chapter 2 describes details of the PCN simulation utilized in this thesis. The governing equations and algorithms in the PCN simulation are presented.

Chapter 3 investigates the stress relaxation process under large step strain, and the relative contribution of local-CCR and elastic force balance around entanglements to the damping behavior is tested. The relaxation mechanism at short times is focused to investigate the actual deformation of the polymer network.

Chapter 4 investigates the stress relaxation process in detail. Especially, the long time region where the time-strain separability of the nonlinear relaxation modulus holds is focused to investigate the molecular origin of the delicate failure of this separability at $t \cong \tau_R$ (which contradicts to the DE prediction) in terms of local-CCR.

Chapter 5 examines the molecular weight dependence of nonlinear stress relaxation. Especially, the transition from type-A to type-B damping behavior is focused, and the relationship between local-CCR and this transition is discussed.

Finally, Chapter 6 gives a summary of the findings of this thesis.

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CHAPTER 2

Primitive chain network simulation

2-1. Overview

Under large strain/fast flow, the nonlinear response reflects the non-equilibrium motion and conformation of the entangled chains. Direct experimental observation of the motion/conformation of entangled chains is almost impossible with the current methodologies. However, the primitive chain network (PCN) simulation¹⁾ serves as a platform for this observation, given that the conformation in large length scales (entanglement length) are to be focused. Thus, the nonlinear rheology of entangled polymers can be understood precisely by the analysis of results of the simulation. The details of the PCN simulation utilized in this thesis are presented in this chapter.

2-2. Model

In the PCN simulation,¹⁾ the entangled polymers are represented as a network consisting of sliplinks (network nodes), subchains (network strands) and dangling ends. The polymer chain is depicted as a series of consecutive subchains and two dangling ends connected at both ends. On the basis of the binary assumption of entanglement, two chains are bundled at each sliplink (so that 4 subchains converge to one sliplink), as schematically shown in Fig. 2-1.

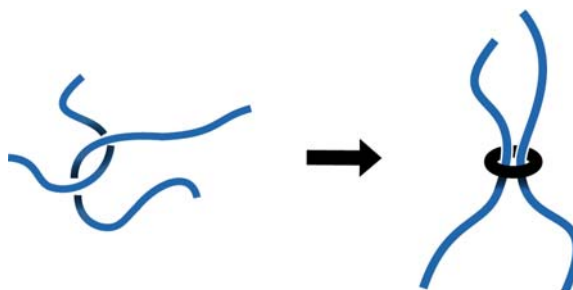


Figure 2-1 The binary contact assumption of sliplink.

The dynamics of the network is described by the 3-D motion of sliplinks, the 1-D monomer transport between adjacent subchains, and the topological change of network around the chain ends. The state variables for description of this dynamics are position vector of the sliplinks $\{\mathbf{R}\}$, number of monomers in each subchain $\{n\}$, and number of subchains in each chain $\{Z\}$. The governing equations for the set of state variables are written below in a dimensionless form utilizing unit of length $a = n_0^{1/2}b$, unit of energy $k_B T$, and unit of time $\tau_0 = \zeta a^2 / 6k_B T$, where n_0 is the mean equilibrium value of monomer number in the subchain, and ζ is the friction coefficient of the sliplink. In addition, $\{n\}$ is normalized by taking the ratio to n_0 . n_0 is related to the unit of molecular weight M_0 , which is comparable to the entanglement molecular weight M_e .²⁾ The average number of Z at equilibrium is obtained as $\langle Z \rangle_{\text{eq}} = M / M_0$.

The equation of motion for $\{\mathbf{R}\}$ is written as

$$\dot{\mathbf{R}} - \mathbf{k} \cdot \mathbf{R} = \frac{1}{2} \sum_j \frac{\mathbf{r}_j}{n_j} - \frac{1}{3} \nabla \mu + \mathbf{F} \quad (2.1).$$

On the left-hand side, the drag force is proportional to the relative velocity between the sliplink and the surrounding continuum. Here $\mathbf{k}$ is the velocity gradient tensor of the continuum. The first term on the right-hand side shows the tension for subchains having the end-to-end vector $\mathbf{r}_j$ and being connected to the sliplink. The second term is the osmotic term suppressing the density fluctuation in the system. μ is the chemical potential derived from the local free energy A given by,

$$A = \begin{cases} \varepsilon \left(\frac{\phi(\mathbf{R})}{\langle \phi \rangle} - 1 \right)^2 & \text{for } \phi(\mathbf{R}) > \langle \phi \rangle \\ 0 & \text{for } \phi(\mathbf{R}) \leq \langle \phi \rangle \end{cases} \quad (2.2).$$

Here $\phi(\mathbf{R})$ is the local sliplink density and $\langle \phi \rangle$ is the average over the system (and fixed at $\langle \phi \rangle = 10$ in this thesis). ε is a numerical parameter (fixed at 0.5). These values of $\langle \phi \rangle$ and ε

reproduce linear and nonlinear viscoelasticity for entangled polymeric liquids.³⁾ The third term in Eq. 2.1 is the thermal Brownian force obeying $\langle \mathbf{F} \rangle = 0$ and $\langle \mathbf{F}(t) \mathbf{F}(t') \rangle = \delta(t - t') \mathbf{I}$. The dynamics of sliplinks described by Eqs. 2.1 and 2.2 is illustrated in Fig. 2-2(a).

The time evolution equation of $\{n\}$ is given by

$$\rho_i^{-1} \dot{n}_i = \left(\frac{r_i}{n_i} - \frac{r_{i-1}}{n_{i-1}} \right) - \frac{1}{3} \nabla \mu + f \quad (2.3).$$

Here, $\dot{n}_i$ is the rate of change of monomer number in i -th subchain according to the monomers transported from $i-1$ -th subchain. ρ_i is the averaged linear monomer density given by

$$\rho_i = \frac{1}{2} \left(\frac{n_i}{r_i} + \frac{n_{i-1}}{r_{i-1}} \right) \quad (2.4).$$

Here r is the subchain length. The first term on the right-hand side in Eq. 2.3 is the tension difference between two subchains. The second term is the osmotic term where the gradient of chemical potential is taken along the chain. The third term is the thermal Brownian force obeying $\langle f \rangle = 0$ and $\langle f(t) f(t') \rangle = (2/3) \delta(t - t')$. The motion of monomer along the primitive chain described by Eqs. 2.3 and 2.4 is illustrated in Fig. 2-2(b).

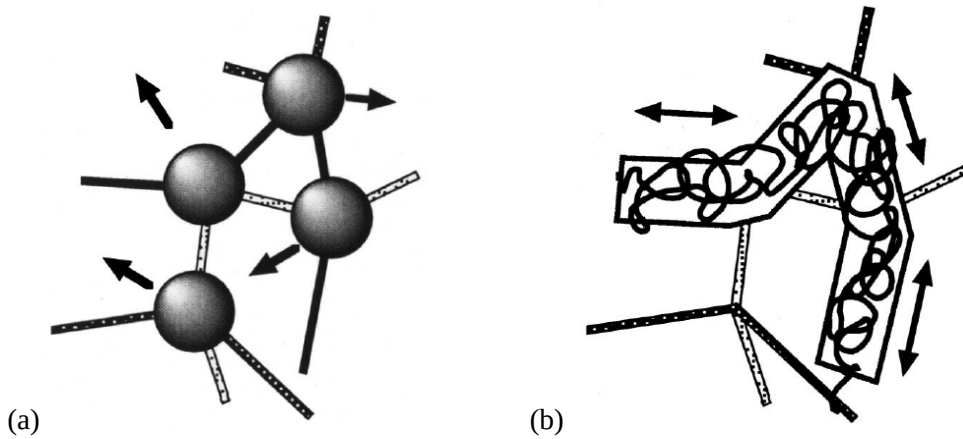


Figure 2-2 Schematic representation of dynamics of primitive chain network simulation.¹⁾ (a) 3-D motion of the sliplinks and (b) 1-D motion of monomer along the primitive chain.

The change of $\{Z\}$ is induced by the creation/destruction of the sliplinks due to the hooking/unhooking around the chain ends. If the monomer number at the end subchain exceeds a certain upper threshold ($= 1.5$), the subchain randomly searches one of the surrounding subchains to create a new sliplink. The new partner subchain is chosen randomly within a sphere of radius a . The geometrical details of hooking are shown in Fig. 2-3. One half the monomer of the parent subchain is partitioned to each newly created subchain. On the contrary, if the monomer number falls below a lower threshold ($= 0.5$), the subchain unhooks the partner subchain to remove the sliplink bundling these two subchains, and then the two subchains of the partner chain merge into one, as shown in Fig. 2-4.

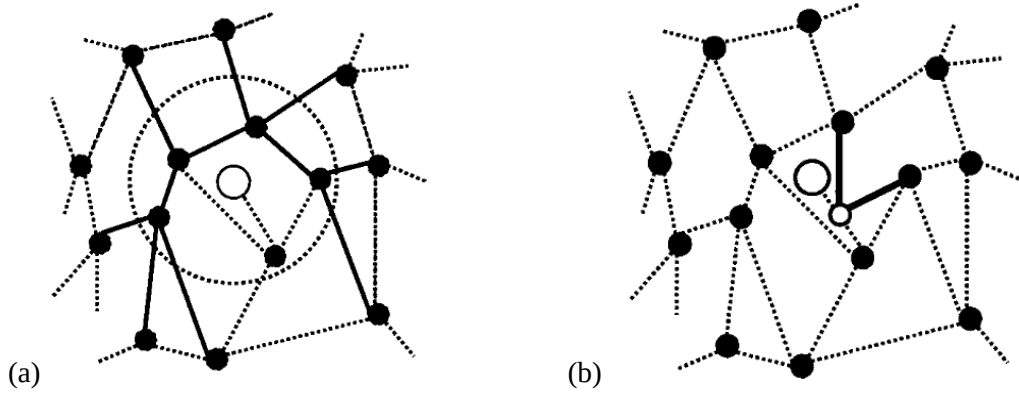


Figure 2-3 Schematic representation of the hooking procedure.¹⁾ (a) The chain end, which is indicated by an unfilled circle, selects the partner to make a new sliplink from the area within dotted circle with radius a . Candidates for the partner are indicated by solid lines. (b) The selected partner hooks at the middle point of the end subchain. The new sliplink and the renewed subchains are indicated by small unfilled circle and thick solid lines, respectively.

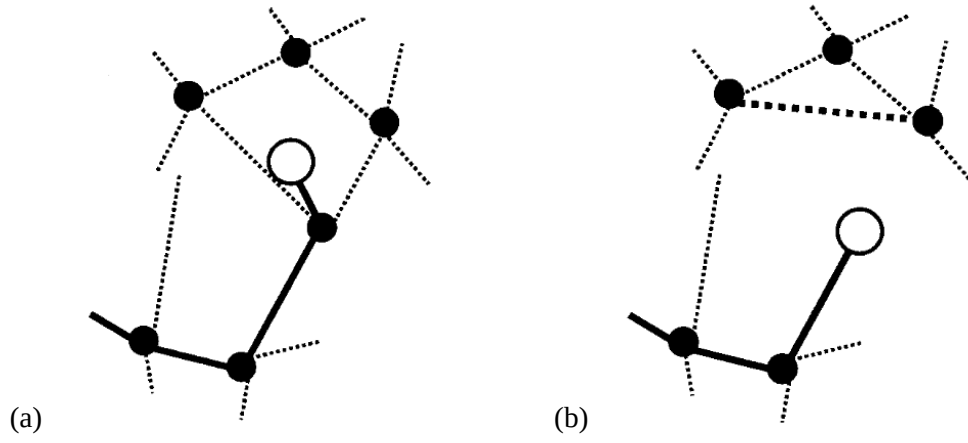


Figure 2-4 Schematic representation of the unhooking procedure.¹⁾ (a) Before destruction of sliplink and (b) after destruction.

Based on the stress optical law,⁴⁾ the stress tensor of PCN simulation is written as (in the dimensionless form)

$$\boldsymbol{\sigma} = 3 \langle \mathbf{r} \mathbf{r} / n \rangle \quad (2.5).$$

The osmotic stress (corresponding to the second term on the right-hand side of Eqs. 2.1 and 2.3) is not taken into account, because it is small compared to the stress given by Eq. 2.5.

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CHAPTER 3

Polymer orientation and stretch under large step deformation

3-1. Introduction

Molecular models for entangled polymer dynamics developed from the tube theory¹⁾ are based on the assumption of affine deformation. This assumption has not been frequently challenged but mostly adopted.²⁾⁻⁵⁾ It is well known that the affine deformation of a network of Gaussian chains gives a stress proportional to the Finger tensor $\mathbf{C}^{-1} (= \mathbf{E}^T \mathbf{E} : \mathbf{E} = \text{deformation gradient tensor})$, whereas the affine deformation of the tubes (after chain contraction), a stress proportional to the DE $\mathbf{Q}$ tensor (Eq. 1.7). However, the local balance of elastic force around entanglements is not fulfilled in the DE case. For this problem, Marrucci et al.^{6), 7)} proposed an ad hoc model (called the three-chain model) where all chain strands are aligned to the 3 principal axes of the deformation, one third of them to each axis, and the affine deformation and the local balance of elastic force are reconciled. After chain contraction, this model is characterized with a new simple deformation tensor $\tilde{\mathbf{Q}}$ which is linked to the square root of the Finger tensor, $\mathbf{C}^{-1/2}$, i.e., $\mathbf{C}^{-1} = (\mathbf{C}^{-1/2})^2$. The damping function predicted by the three-chain model (with this $\tilde{\mathbf{Q}}$) is in reasonable agreement with the experimental data. Ianniruberto and Marrucci (IM)⁸⁾ proposed a constitutive equation that considers an effect(s) of CCR^{9), 10)} on the relaxation time and adopt the $\tilde{\mathbf{Q}}$ tensor to fulfill the local balance of elastic force around entanglements. Thus, the IM model assumes the separate influences of CCR and elastic force balance on the chain dynamics.

Although the IM model qualitatively describes the nonlinearities of entangled polymer, contributions of CCR and elastic force balance to the stress relaxation have not been well separated. The IM model assumes no CCR effect on the chain orientation, which is convenient for a single segment model where the elastic force balance and CCR cannot be straightforwardly coupled to

each other. However, this assumption may fail because local-CCR could disturb the local balance of elastic force and the deformation.

This problem is addressed in this chapter. Specifically, the PCN simulation is utilized as a platform for analyzing the stress relaxation data under large step strain to resolve the interplay between the local-CCR and the local balance of elastic force around entanglements in actual entangled systems. In addition, the models so far proposed (DE model, three-chain model, etc) are examined on the same platform to check if their assumptions are valid.

3-2. Simulations

In the simulation, a periodic boundary condition with the Lees-Edwards modification for shear was used, with a cell dimension of 16^3 . The model parameters were obtained from fit of the linear dynamic moduli data with the simulated results (obtained after 3 period of oscillatory strain at the amplitude of 0.3). The nonlinear stress relaxation was simulated for the system deformed at $t = +0$, and the resulting nonlinear relaxation modulus $G(t, \gamma)$ was analyzed (in comparison with the data). In the simulation, over 30 independent runs each starting from sufficiently equilibrated state at $t = -0$ were conducted, and $G(t, \gamma)$ was obtained as an average of those runs.

3-3. Results and discussion

3-3-1. Simulation parameters

The simulation was conducted for a nearly monodisperse linear PS melt of $M = 330000$ examined by Ferri and Greco.¹¹⁾ The simulation parameters were determined from comparison of the simulated dynamic moduli $G^* (= G' + i G'')$ with the data, as explained below.

Figure 3-1 shows G^* simulated for $\langle Z \rangle_{\text{eq}} = 30$ with the data.¹¹⁾ The chosen simulation parameters, $G_0 = \nu k_B T = 0.33 \text{ MPa}$ and $\tau_0 = 3.2 \times 10^{-4} \text{ s}$, allow satisfactory fitting of the data. This G_0 value agrees with that determined for the other PS melt samples,¹²⁾ whereas the τ_0 value differs from the previously determined value (because of a difference of temperatures). The molecular mass M_0 between consecutive sliplinks is obtained from the G_0 value as $M_0 = \rho RT / G_0 = 11000$, where ρ is the polymer density and R is the gas constant.

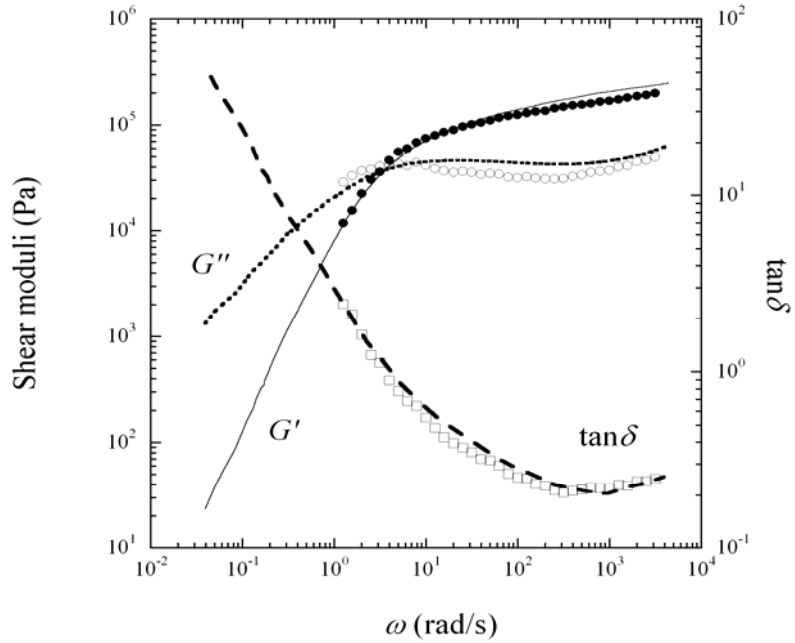


Figure 3-1 Linear viscoelasticity simulation results (symbols) compared with experimental data (curves) for a PS melt at 200 °C.¹¹⁾

3-3-2. Nonlinear relaxation moduli

Figure 3-2(a) compares the nonlinear relaxation modulus $G(t, \gamma)$ obtained from the PCN simulation (utilizing $G_0 = 0.33$ MPa, $\tau_0 = 3.2 \times 10^{-4}$ s, and $\langle Z \rangle_{\text{eq}} = 30$) and the data for PS melt of $M = 330000$.¹¹⁾ The simulation satisfactorily reproduces the data in the entire range of strain ($\gamma = 0.5 - 5$), confirming that the PCN simulation serves as the platform for analyzing the molecular dynamics underlying the nonlinear relaxation process.

For the simulated $G(t, \gamma)$, the time-strain separability is examined in Fig. 3-2(b) where $G(t, \gamma)$ for the smallest examined γ ($= 0.5$) is utilized as the linear $G(t)$ and the $G(t, \gamma)$ curves for larger γ are vertically shifted to be superposed on this $G(t)$ at long t . The onset time for the time-strain separability determined from this shift, $\tau_k \sim 0.32$ s, agrees well with τ_k (~ 0.3 s) separately estimated for the experimental data. The τ_k value was insensitive to the type of deformation (shear, uniaxial elongation, etc), as demonstrated in Appendix 3A.

In the PCN simulation, the Rouse time τ_R is related to τ_0 as $\tau_R = \tau_0 \langle Z \rangle_{\text{eq}}^2 / 2\pi^2$ (cf. Appendix 3B). Thus, τ_R is estimated from the above τ_0 value as $\tau_R = 1.4 \times 10^{-2}$ s (which is rather close to an estimate obtained from the zero-shear viscosity data.¹³⁾) This τ_R is significantly smaller than τ_k , confirming the results reported in several papers (e.g. Ref. 11). This large difference between τ_R and τ_k can be related to the coupling of the chain contraction and orientational relaxation induced by local-CCR, as discussed in the next chapter.

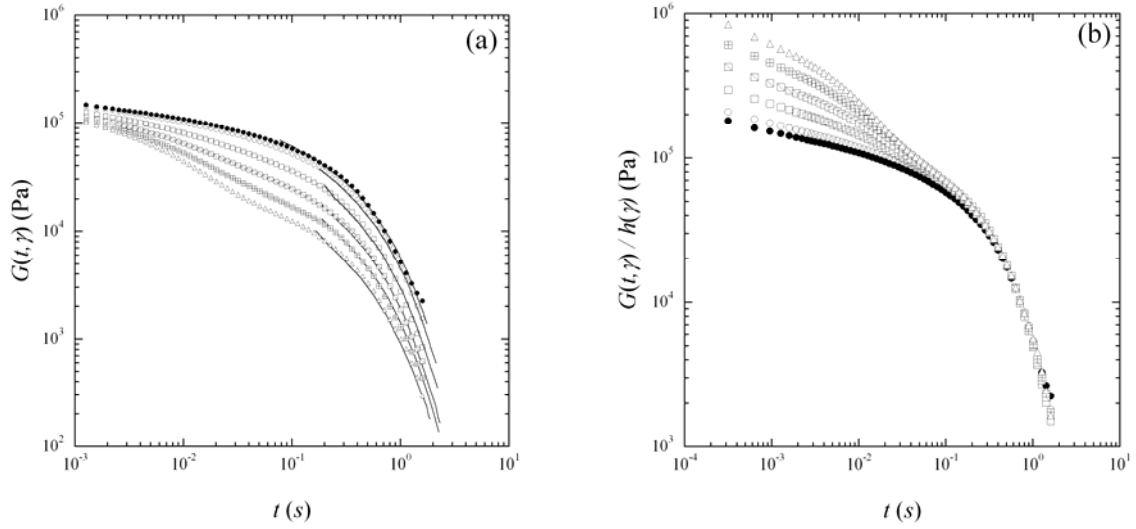


Figure 3-2 (a) Relaxation modulus $G(t, \gamma)$ of step shear strain for various strains ($\gamma = 0.5, 1.0, 2.0, 3.0, 4.0, 5.0$) obtained from the PCN simulation (symbols). Solid curves are the experimental data.¹¹⁾ (b) Test of the time-strain separability for $G(t, \gamma)$ from the simulation.

3-3-3. Damping function

Figure 3-3 shows the damping function $h(\gamma) (= G(t, \gamma)/G(t))$ at long t) obtained from the PCN simulation and experimental data (cf. Fig. 3-2). For comparison, Fig. 3-3 also shows $h(\gamma)$ deduced from the DE model,¹⁾ the three-chain model,⁷⁾ Greco's model²⁾ (incorporating detailed Gaussian statistics), and the MLD model⁴⁾ incorporating CCR.¹⁴⁾ The $h(\gamma)$ of the DE model is a little smaller whereas $h(\gamma)$ of the PCN simulation and the three-chain model are moderately larger than the $h(\gamma)$ data. The agreement between the PCN result and the three-chain model on $h(\gamma)$ suggests the dominance of the elastic force balance (considered in both calculations) in the long time range. In other words, the effect of the other forces in the PCN, i.e., drag force, osmotic force and Brownian force, smears out in this time range. The $h(\gamma)$ of Greco's model calculated for the number of Kuhn steps in the segment, $n_0 = 25$,¹¹⁾ agrees with the data but approaches $h(\gamma)$ of the PCN simulation on an increase of n_0 .¹¹⁾ Finally, $h(\gamma)$ of the MLD model is considerably smaller than the $h(\gamma)$ data. Similar differences between the models and PCN simulation were found also

for non-shear deformations, as summarized in Appendix 3A.

It is informative to remember that the MLD model exhibits over-damping (giving $h(\gamma)$ smaller than the data) because the CCR mechanism incorporated therein accelerates the orientational relaxation in the quiescent state under large step strain (cf. Chapter 1). Consequently, lack of the over-damping in the PCN simulation suggests that the orientational relaxation (at $t < \tau_k$) is hardly accelerated by the local-CCR and the force balance mechanisms incorporated in the simulation and thus the chain contraction and orientational relaxation are not strongly coupled at short times even in the presence of local-CCR. The agreement of $h(\gamma)$ of the PCN simulation and the three-chain model lends support to this argument. Thus, the dynamics in actual PS melt at $t < \tau_k$ appears to be governed by the elastic force balance as well.

The above lack of the coupling between the contraction and orientational relaxation can be further examined if the stress obtained from the simulation/models is (approximately) decoupled in the stretch and orientation terms and respective terms are analyzed separately. The following subsections are devoted for the analysis of those terms at short times $t \leq \tau_0$.

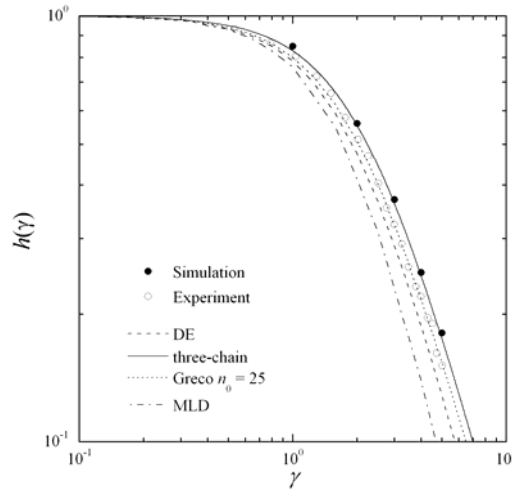


Figure 3-3 Damping function of step shear deformation from the PCN simulation with $\langle Z \rangle_{eq} = 30$ is compared with theories and experiments. Filled circles are simulation results, dashed curve is the DE model without IAA, solid curve is the three-chain model, dotted curve is Greco's model, and dot-dashed curve is the MLD model. Experimental data¹¹⁾ are indicated by unfilled circles.

3-3-4. Subchain stretch

In the models and PCN simulation, the average subchain stretch ratio λ is defined as:

$$\lambda = \left\langle \left| \mathbf{E} \cdot \mathbf{u}_{\text{eq}} \right| \right\rangle \quad (\text{Affine deformation}) \quad (3.1)$$

$$\lambda = \frac{1}{3} \text{tr} \mathbf{C}^{-1/2} \quad (\text{three-chain model}) \quad (3.2)$$

$$\lambda = \frac{\langle r \rangle}{\langle r \rangle_{\text{eq}}} \quad (\text{PCN simulation}) \quad (3.3).$$

Derivation of Eq. 3.2 is given in Appendix 3C. For various chain lengths, Figs. 3-4 (a) - (c) show plots of λ against the step shear strain γ . In the PCN simulation, all subchains are affinely deformed at $t = +0$ and their λ is fully described by Eq. 3.1. Then the PCN results show relaxation of λ according to the local dynamics involved in the PCN simulation. The short time relaxation of λ seen in Fig. 3-4 is similar to the process X proposed by Lin¹⁵⁾ within the framework of the fixed tube model. For long chains ($\langle Z \rangle_{\text{eq}} = 30$ and 9.2) in Figs. 3-4(a) and (b), the simulated λ at $t = \tau_0$ is close to the three-chain prediction. This result suggests that the short time contraction (decay of λ) in the PCN simulation is dominated by the local balance of elastic force around entanglement, which is commonly incorporated in the simulation and the three-chain model. Indeed, in the relaxation of λ , the contribution from the other forces (drag force, osmotic force and thermal Brownian force) can be averaged out, as shown in Appendix 3D. In addition, since the total sliplink number per chain $\langle Z(t) \rangle$ retains its equilibrium value up to $t = \tau_0$, the local-CCR incorporated only in the simulation (not in the model), does not affect this short time contraction. Indeed, as shown in the next chapter, the local-CCR is significantly activated only at long $t \sim \tau_R$. Because the three-chain model assumes that the tension along the chain is uniform and such situation is not realized in this short time region, the quantitative agreement between two models is rather coincidence, though. For short chain ($\langle Z \rangle_{\text{eq}} = 4.7$), λ

decays within τ_0 to become smaller than λ of the three-chain model as shown in Fig. 3-4(c). This rapid decay is dominated by the dangling (unconstrained) subchains at the chain ends. Such dangling subchains affect the damping function of short chains, as discussed later in Chapter 5.

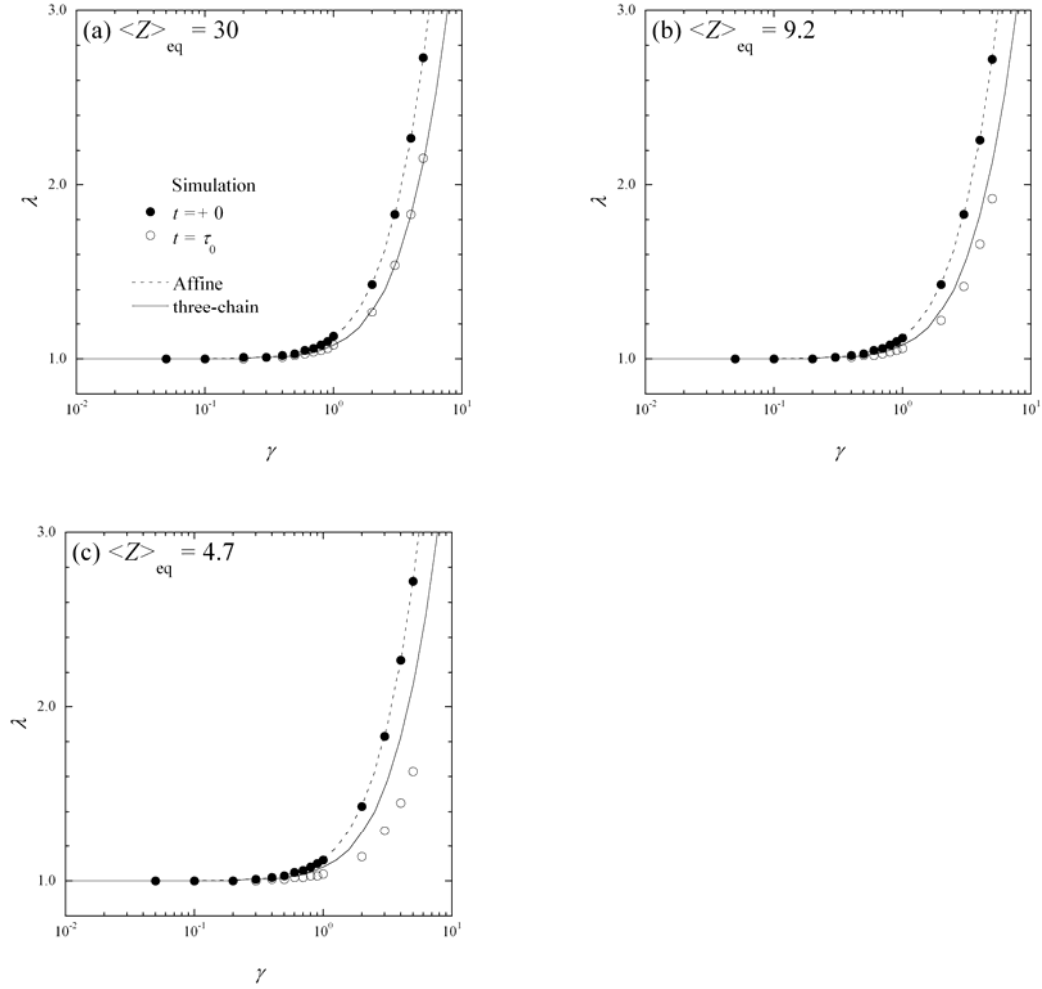


Figure 3-4 Subchain stretch as a function of strain for (a) $\langle Z \rangle_{eq} = 30$, (b) $\langle Z \rangle_{eq} = 9.2$ and (c) $\langle Z \rangle_{eq} = 4.7$. Filled and unfilled circles are from the PCN simulation at $t = +0$ and $t = \tau_0$, respectively. Dashed curve corresponds to affine deformation, and solid curve is the three-chain model.

3-3-5. Subchain orientation

In the models and PCN simulation, the orientation tensor $\mathbf{S}$ is defined as:

$$\mathbf{S} = \frac{\langle (\mathbf{E} \cdot \mathbf{u}_{\text{eq}}) (\mathbf{E} \cdot \mathbf{u}_{\text{eq}}) \rangle}{\text{tr} \langle (\mathbf{E} \cdot \mathbf{u}_{\text{eq}}) (\mathbf{E} \cdot \mathbf{u}_{\text{eq}}) \rangle} \quad (\text{Affine deformation}) \quad (3.4)$$

$$\mathbf{S} = \frac{\mathbf{C}^{-1/2}}{\text{tr} \mathbf{C}^{-1/2}} (= \tilde{\mathbf{Q}}) \quad (\text{three-chain model}) \quad (3.5)$$

$$\mathbf{S} = \frac{\langle \mathbf{r} \mathbf{r} \rangle}{\langle r^2 \rangle} \quad (\text{PCN simulation}) \quad (3.6).$$

Derivation of Eq. 3.5 is given in Refs. 6 and 7 as well as in Appendix 3C. For various chain lengths, Figs. 3-5 (a) - (c) show the shear component S_{12} of the orientation tensor. In the PCN simulation, all subchains are affinely deformed at $t = +0$, and S_{12} is described by Eq. 3.4. For all chain lengths, the simulated S_{12} deviates from the affine deformation in a short interval of time up to $t = \tau_0$. The deviation of S_{12} from the affine deformation is due to the relaxation mechanisms in the PCN simulation as discussed for the subchain stretch. However, unlike the subchain stretch, the decay of S_{12} is less than the three-chain prediction. These features suggest that the elastic force balance does not significantly affect the short time orientational relaxation in comparison to that of subchain stretch, but affects the long time orientation relaxation at t up to τ_k . The slow local-CCR activated at such long times also contributes to the orientational relaxation in addition to the elastic force balance but has a secondary effect on the damping behavior.

In addition, S_{12} for the short chain ($\langle Z \rangle_{\text{eq}} = 4.7$) in Fig. 3-5(C) decays rapidly. This rapid decay is dominated by the dangling (unconstrained) subchains at the chain ends, again in accord to the behavior seen for the subchain stretch.

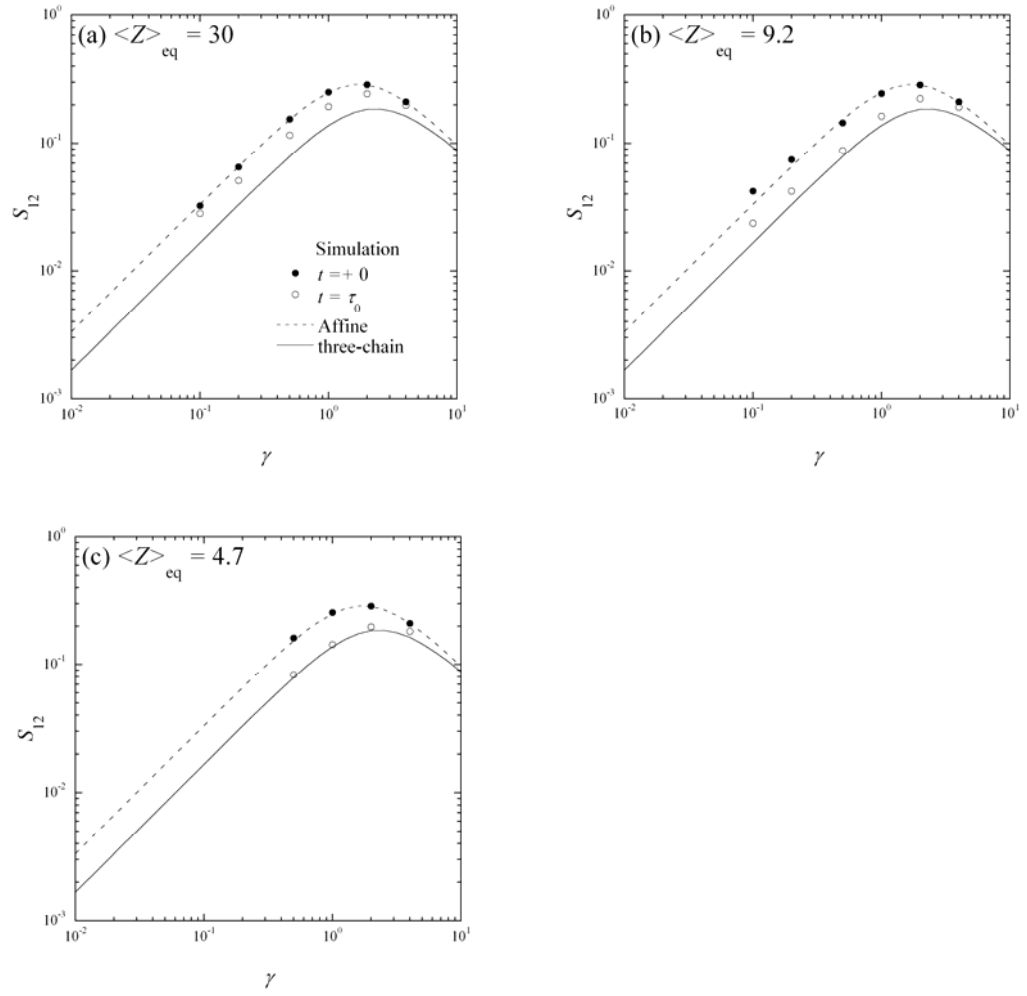


Figure 3-5 Shear component of the orientation tensor for (a) $\langle Z \rangle_{eq} = 30$, (b) $\langle Z \rangle_{eq} = 9.2$ and (c) $\langle Z \rangle_{eq} = 4.7$. Filled and unfilled circles are from the PCN simulation at $t = +0$ and $t = \tau_0$, respectively. Dashed curve corresponds to affine deformation, and solid curve is the three-chain model.

3-4. Conclusions

The contributions of local-CCR and the elastic force balance to the stress relaxation after large step deformation were investigated. The damping function obtained from the PCN simulation was very close to that deduced from the three-chain model. This fact suggests that the damping behavior (due to chain contraction) is governed by the local balance of elastic force around the entanglements. The short time dynamics of entangled chain is also dominated by the elastic force balance and is not affected by the local-CCR. In other words, the local-CCR is slowly activated and has just a secondary effect on the damping behavior.

Appendix 3A. Nonlinear stress relaxation for various deformation modes

Figure 3A-1 examines time-strain separability of nonlinear relaxation modulus obtained from the PCN simulation for a chain with $\langle Z \rangle_{\text{eq}} = 9.2$ being subjected to shear, uniaxial, biaxial, and planar step deformations. The $\tau_k (= 30\tau_0)$ is insensitive to the type of deformation and significantly larger than $\tau_R (= 4.3\tau_0)$ as mentioned in Section 3-3-2. Figure 3A-2 summarizes the damping functions obtained from those simulated moduli together with the damping functions deduced from the DE model, the three-chain model, Greco's model, and the MLD model. Clearly, the PCN results are close to those expected from the three-chain model.

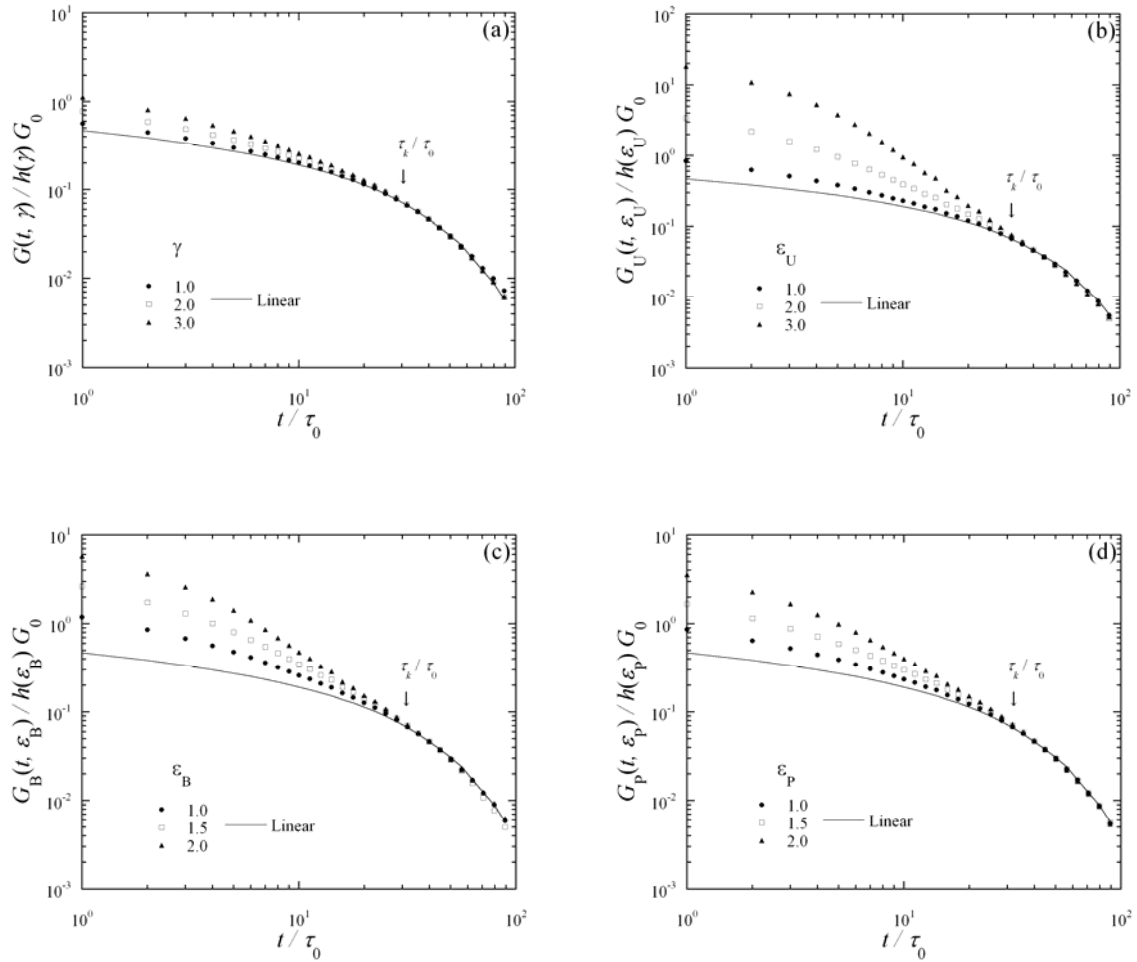


Figure 3A-1 The tests of time-strain separability for (a) shear, (b) uniaxial, (c) biaxial, and (c) planar deformations. The respective strains are γ , ϵ_U , ϵ_B , and ϵ_P . Solid curve is the linear relaxation modulus. Time τ_k indicates the characteristic value below which the time-strain separability is not satisfied.

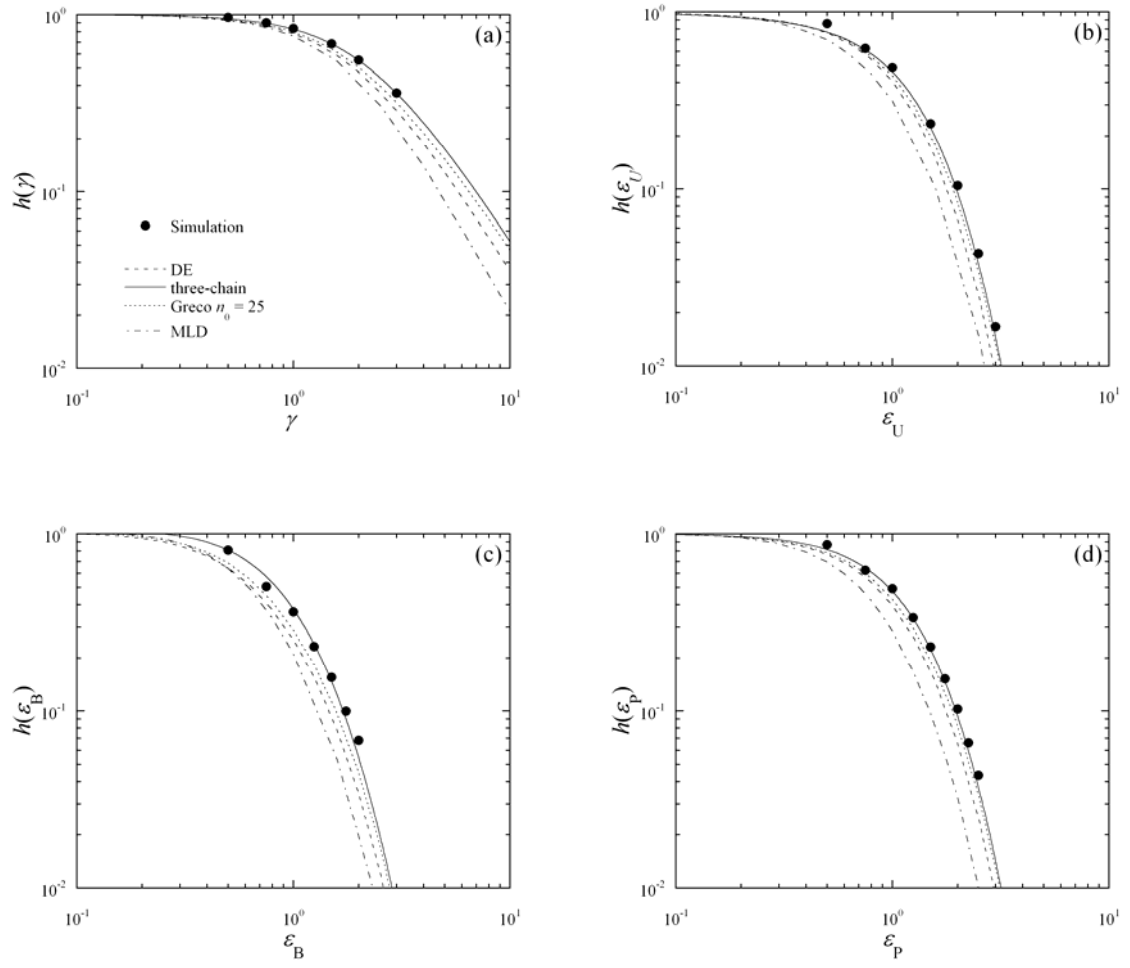


Figure 3A-2 Damping functions for (a) shear, (b) uniaxial, (c) biaxial, and (c) planar deformations. Filled circles are the simulation results, dashed curve is the DE model without IAA, solid curve is the three-chain model, dotted curve is Greco's model, and dot-dashed curve is the MLD model.

Appendix 3B. The Rouse time of PCN simulation

The Rouse time for stress relaxation (half of the end-to-end vector relaxation time) can be written as¹⁾

$$\tau_R = \frac{\zeta_m N^2 b^2}{6\pi^2 k_B T} \quad (3B.1)$$

where ζ_m is the friction coefficient of a “monomer” (taken to be the Kuhn segment), N is the total monomer number per chain. The unit time τ_0 used in the simulation is defined as:

$$\tau_0 = \frac{\zeta n_0 b^2}{6k_B T} \quad (3B.2).$$

Here, ζ is the friction coefficient associated to one node of the network. With the aid of relations $\zeta = 2n_0 \zeta_m$ and $\langle Z \rangle_{eq} = N/n_0$, Eqs. 3B.1 and 3B.2 give the Rouse time τ_R written in the form:

$$\tau_R = \frac{1}{2\pi^2} \left(\frac{N}{n_0} \right)^2 \tau_0 = \frac{\langle Z \rangle_{eq}^2}{2\pi^2} \tau_0 \quad (3B.3).$$

Appendix 3C. Derivation of $\tilde{\mathbf{Q}}$ tensor for the three-chain model

The deformation gradient tensor is conveniently factorized as $\mathbf{E} = \mathbf{C}^{-1/2} \cdot \mathbf{W}$, where $\mathbf{W}$ is the rotational tensor representing the rigid body rotation of the material and $\mathbf{C}^{-1/2}$ is the square root of Finger tensor representing net (real) deformation of the material.¹⁶⁾ From this factorization, the Doi-Edwards $\mathbf{Q}$ tensor without IAA¹⁾ is written in the form

$$\begin{aligned} \mathbf{Q} &= \frac{1}{\langle |\mathbf{E} \cdot \mathbf{u}_{\text{eq}}| \rangle} \left\langle \frac{(\mathbf{E} \cdot \mathbf{u}_{\text{eq}})(\mathbf{E} \cdot \mathbf{u}_{\text{eq}})}{|\mathbf{E} \cdot \mathbf{u}_{\text{eq}}|} \right\rangle \\ &= \frac{1}{\langle |\mathbf{C}^{-1/2} \cdot \mathbf{W} \cdot \mathbf{u}_{\text{eq}}| \rangle} \left\langle \frac{(\mathbf{C}^{-1/2} \cdot \mathbf{W} \cdot \mathbf{u}_{\text{eq}})(\mathbf{C}^{-1/2} \cdot \mathbf{W} \cdot \mathbf{u}_{\text{eq}})}{|\mathbf{C}^{-1/2} \cdot \mathbf{W} \cdot \mathbf{u}_{\text{eq}}|} \right\rangle \end{aligned} \quad (3C.1).$$

For chains aligned on a simple cubic lattice as assumed in the three-chain model,^{6), 7)} the orientational distribution of bond vectors at equilibrium is given by

$$f(\mathbf{u}_{\text{eq}}) = \frac{1}{3} \{ \delta(\mathbf{u}_{\text{eq}} - \mathbf{i}) + \delta(\mathbf{u}_{\text{eq}} - \mathbf{j}) + \delta(\mathbf{u}_{\text{eq}} - \mathbf{k}) \} \quad (3C.2)$$

where δ is Dirac delta function, and $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ are the normalized principal vectors of the lattice.

From Eq. 3C.2, the average terms included in Eq. 3C.1 can be written as

$$\begin{aligned} &\langle |\mathbf{E} \cdot \mathbf{u}_{\text{eq}}| \rangle \\ &= \int d\mathbf{u}_{\text{eq}} f(\mathbf{u}_{\text{eq}}) |\mathbf{E} \cdot \mathbf{u}_{\text{eq}}| \\ &= \frac{1}{3} \int d\mathbf{u}_{\text{eq}} |\mathbf{C}^{-1/2} \cdot \mathbf{W} \cdot \mathbf{u}_{\text{eq}}| \{ \delta(\mathbf{u}_{\text{eq}} - \mathbf{i}) + \delta(\mathbf{u}_{\text{eq}} - \mathbf{j}) + \delta(\mathbf{u}_{\text{eq}} - \mathbf{k}) \} \\ &= \frac{1}{3} \{ (\mathbf{C}^{-1/2} \cdot \mathbf{W})_{11} + (\mathbf{C}^{-1/2} \cdot \mathbf{W})_{22} + (\mathbf{C}^{-1/2} \cdot \mathbf{W})_{33} \} \\ &= \frac{1}{3} \text{tr}(\mathbf{C}^{-1/2} \cdot \mathbf{W}) \end{aligned} \quad (3C.3)$$

$$\begin{aligned}
& \left\langle \frac{(\mathbf{E} \cdot \mathbf{u}_{\text{eq}})(\mathbf{E} \cdot \mathbf{u}_{\text{eq}})}{|\mathbf{E} \cdot \mathbf{u}_{\text{eq}}|} \right\rangle \\
&= \int d\mathbf{u}_{\text{eq}} f(\mathbf{u}_{\text{eq}}) \frac{(\mathbf{C}^{-1/2} \cdot \mathbf{W} \cdot \mathbf{u}_{\text{eq}})(\mathbf{C}^{-1/2} \cdot \mathbf{W} \cdot \mathbf{u}_{\text{eq}})}{|\mathbf{C}^{-1/2} \cdot \mathbf{W} \cdot \mathbf{u}_{\text{eq}}|} \\
&= \frac{1}{3} \left\{ \frac{(\mathbf{C}^{-1/2} \cdot \mathbf{W})_{11}^2 \mathbf{i}\mathbf{i}}{(\mathbf{C}^{-1/2} \cdot \mathbf{W})_{11}} + \frac{(\mathbf{C}^{-1/2} \cdot \mathbf{W})_{22}^2 \mathbf{j}\mathbf{j}}{(\mathbf{C}^{-1/2} \cdot \mathbf{W})_{22}} + \frac{(\mathbf{C}^{-1/2} \cdot \mathbf{W})_{33}^2 \mathbf{k}\mathbf{k}}{(\mathbf{C}^{-1/2} \cdot \mathbf{W})_{33}} \right\} \\
&= \frac{1}{3} \mathbf{C}^{-1/2} \cdot \mathbf{W}
\end{aligned} \tag{3C.4}.$$

For $\mathbf{W} = \mathbf{I}$ (identity tensor), Eqs. 3C.3 and 3C.4 reduce to

$$\left\langle |\mathbf{E} \cdot \mathbf{u}_{\text{eq}}| \right\rangle = \frac{1}{3} \text{tr } \mathbf{C}^{-1/2} \tag{3C.5}$$

$$\left\langle \frac{(\mathbf{E} \cdot \mathbf{u}_{\text{eq}})(\mathbf{E} \cdot \mathbf{u}_{\text{eq}})}{|\mathbf{E} \cdot \mathbf{u}_{\text{eq}}|} \right\rangle = \frac{1}{3} \mathbf{C}^{-1/2} \tag{3C.6}$$

which gives the $\tilde{\mathbf{Q}}$ tensor of the three-chain model:

$$\tilde{\mathbf{Q}} = \frac{\mathbf{C}^{-1/2}}{\text{tr } \mathbf{C}^{-1/2}} \tag{3C.7}.$$

Appendix 3D. Time evolution equation of subchain stretch

From Eq. 3.3, the time evolution equation for square of subchain stretch is written as

$$\frac{d\lambda^2}{dt} = \frac{d}{dt} \left(\frac{\langle r \rangle}{\langle r \rangle_{\text{eq}}} \right)^2 \approx \frac{d}{dt} \frac{\langle r^2 \rangle}{\langle r \rangle_{\text{eq}}^2} = \frac{2}{\langle r \rangle_{\text{eq}}^2} \left\langle \mathbf{r} \cdot \frac{d\mathbf{r}}{dt} \right\rangle \quad (3D.1)$$

where $\mathbf{r}$ is the end-to-end vector of subchain connecting p -th and q -th sliplink. The position vectors of these sliplinks are written as $\mathbf{R}_p$ and $\mathbf{R}_q$. On the basis of Eq. 2.1, time development part in Eq. 3D.1 can be written as

$$\begin{aligned} \left\langle \mathbf{r} \cdot \frac{d\mathbf{r}}{dt} \right\rangle &= \left\langle \mathbf{r} \cdot \frac{d}{dt} (\mathbf{R}_q - \mathbf{R}_p) \right\rangle \\ &= \frac{1}{2} \left\langle \mathbf{r} \cdot \left[\left(\sum_{j=1}^4 \frac{\mathbf{r}_j}{n_j} \right)_q - \left(\sum_{j=1}^4 \frac{\mathbf{r}_j}{n_j} \right)_p \right] \right\rangle \end{aligned} \quad (3D.2).$$

For the derivation of Eq. 3D.2, the convection is neglected (under step strain) and the following averages are assumed.

$$\langle \mathbf{r} \cdot \nabla \mu \rangle = 0 \quad (3D.3)$$

$$\langle \mathbf{r} \cdot \mathbf{F} \rangle = 0 \quad (3D.4).$$

From Eqs. 3D.1 – 3D.4, the time evolution equation for λ^2 is obtained as

$$\frac{d\lambda^2}{dt} = \frac{1}{\langle r \rangle_{\text{eq}}^2} \left\langle \mathbf{r} \cdot \left[\left(\sum_{j=1}^4 \frac{\mathbf{r}_j}{n_j} \right)_q - \left(\sum_{j=1}^4 \frac{\mathbf{r}_j}{n_j} \right)_p \right] \right\rangle \quad (3D.5).$$

The summation terms in Eq. 3D.5 represent the difference of the elastic force between the adjacent sliplinks. Thus, it so appears that the time development of λ is dominated by the local elastic force balance and the effects of the other forces are smeared out.

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CHAPTER 4

Chain contraction and nonlinear stress damping

4-1. Introduction

The DE model¹⁾ reasonably describes entangled polymer dynamics after step deformation assuming that the chain contraction and the orientational relaxation occur independently. However, recent experiments suggested that the chain contraction and orientational relaxation are coupled with each other. For example, Sanchez-Reyes and Archer²⁾ measured the stress relaxation of linear PS solutions and found that the onset time of time-strain separability is close to the terminal relaxation time, τ_d (rather than τ_R). Inoue et al.³⁾ also measured stress relaxation of PS solutions and reported that the relaxation modulus involves a secondary, weak relaxation with a characteristic time much longer than τ_R .

A molecular picture that may rationalize the coupling of the chain contraction and the orientational relaxation has been proposed in relation to the tube deformation in a direction lateral to the chain contour. Mhetar and Archer proposed a Partial Strand Extension (PSE) model⁴⁾ where the chain does not fully contract to the equilibrium length at $t \sim \tau_R$ because of the lateral squeezing on the chain due to deformation of the tube. They considered that this squeezing effect vanishes and the chain recovers its equilibrium length only after the chain escapes the deformed tube and thus the time-strain separability becomes valid only at $t \sim \tau_d$ ($\gg \tau_R$). A similar squeezing effect was pointed out earlier by Marrucci and de Cindio.⁵⁾

Another idea rationalizing the coupling of the chain contraction and orientational relaxation is the local-CCR mechanism. The contraction under step strain releases the entanglement constraints thereby affecting the orientational relaxation process. This local-CCR effect can be easily examined with the sliplink simulation. Chen et al.⁶⁾ simulated the stress relaxation with a

single chain sliplink simulation proposed by Hua and Schieber.⁷⁾ In spite of the coupling between the chain contraction and orientational relaxation incorporated in their model, the simulated results systematically deviated from experimental data with increasing time from τ_R to τ_d . They suggested that nonaffine deformation due to local balance of elastic force around entanglement, being not considered in their mean-field single-chain simulation, may improve the prediction. Indeed, they adopted the three-chain model⁸⁾ to demonstrate the nonaffine deformation of the chains subjected to the step strain due to this force balance. However, the chain contraction itself and the coupling between the chain contraction and orientational relaxation were not fully examined.

Therefore, this chapter focuses on the effects of coupling of the chain contraction and orientational relaxation on the delicate failure of time-strain separability at $t \cong \tau_R$. Although this coupling due to local-CCR is weak as mentioned in Chapter 3, it turned out that local-CCR reduces the chain tension at chain center compared to the DE prediction. This tension reduction leads to the retarded chain contraction and the limited validity of rigorous time-strain separability (at $t \geq \tau_d$). Utilizing the PCN simulation as a platform for analyzing the stress relaxation in actual entangled polymers, this chapter presents details of these results and discusses a mechanism(s) leading the retarded chain contraction.

4-2. Simulations

Simulations were performed with a periodic shear boundary condition on the basis of the Lees-Edwards method in a box of size 16^3 . The system was affinely step-sheared at $t = +0$, and the relaxing stress was calculated as the average over 50 independent runs. The linear relaxation modulus $G(t)$ was calculated from autocorrelation of a microscopic shear stress (microscopic momentum transfer) at equilibrium under no strain (see Appendix 4A).

4-3. Results

4-3-1. Overview of nonlinear damping behavior

The simulation was conducted for a PS/arclor solution examined by Osaki et al.⁹⁾ Their experiment shows the clear nonlinear damping behavior under large step strain. Figure 4-1(a) compares the data of the nonlinear relaxation modulus $G(t, \gamma)$ (curves)⁹⁾ with $G(t, \gamma)$ obtained from the PCN simulation (symbols) with the parameters $G_0 = 34000$ Pa, $M_0 = 29700$, and $\tau_0 = 0.9$ s. (These parameters were evaluated by fitting the $G(t)$ data with the simulation as performed in the previous chapter.) The parameters G_0 and M_0 are related to each other as

$$G_0 = \frac{cRT}{M_0} \quad (4.1)$$

where c ($=0.4$ g/cm³) is the polymer concentration. From M_0 , the average number of Z at equilibrium is obtained as $\langle Z \rangle_{\text{eq}} = M / M_0 = 23$, where M ($=670000$) is the molecular weight of the PS sample. As seen in Fig. 4-1(a), the simulated $G(t, \gamma)$ agrees quantitatively with the data except at long times (where the polydispersity of the PS sample $M_w / M_n = 1.1$ needs to be considered to reproduce the data). Figure 4-1(b) examines the time-strain separability for the measured and simulated $G(t, \gamma)$. The $G(t, \gamma)$ curves for different γ values are excellently superposed when reduced by an appropriate damping function, which confirms the time-strain

separability at long $t > 300$ s. The simulation reproduces the nonlinear relaxation of PS solution quantitatively, so that the PCN model gives detailed information on the failure of time-strain separability at $t = \tau_R = 24$ s (cf. Appendix 3B) through the analysis of chain dynamics. As mentioned in Chapter 3, the onset time of time-strain separability is significantly larger than τ_R . This large difference between the onset time and τ_R can be related to the effect of local-CCR, as discussed in the next section.

Figure 4-2 shows the γ dependence of $h(\gamma)$ giving the superposition of $G(t, \gamma)$. The simulated $h(\gamma)$ agrees with the $h(\gamma)$ data, and the γ dependence of simulated $h(\gamma)$ is close to the prediction of the three-chain model.⁸⁾

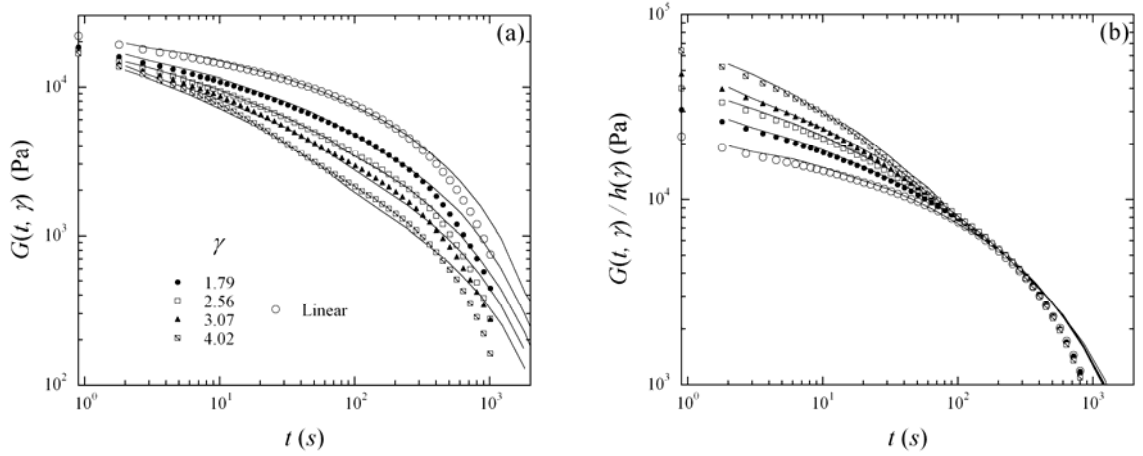


Figure 4-1 Comparison of simulation results and the experimental data for PS solution.⁹⁾ (a) Relaxation modulus for various strains; (b) test of time-strain separability. Symbols and solid curves indicate the simulation results and experimental data, respectively.

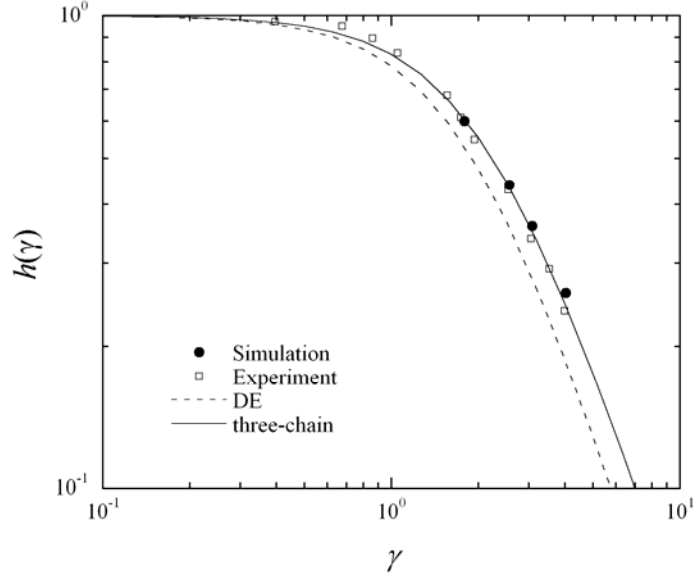


Figure 4-2 Damping function obtained from the simulation (filled circle), experiments (unfilled square),⁹⁾ the DE model without IAA (dashed curve),¹⁾ and the three-chain model (solid curve).⁸⁾

4-3-2. Detailed feature of time-strain separability

The limited validity of time-strain separability at $t = \tau_R$ can be further characterized by a time-dependent damping function,

$$h(t, \gamma) \equiv \frac{G(t, \gamma)}{G(t)} \quad (4.2).$$

The experimentally obtained and simulated $h(t, \gamma)$ are shown in Fig. 4-3 (symbols). For analysis of $h(t, \gamma)$, it can be cast in an approximate but rather general form proposed by Takahashi et al.:^{10), 11)}

$$h(t, \gamma) = h(\gamma) [1 + \{ \alpha(\gamma) - 1 \} f(t, \gamma)]^2 \quad (4.3).$$

Here, $\alpha(\gamma)$ is the stretch ratio of the chain at $t = +0$ (immediately after the deformation) and $f(t, \gamma)$ is a relaxation function. $h(\gamma)$ and $\alpha(\gamma)$ appearing in Eq. 4.3 can be assumed to be analytically expressed in a form deduced from the three-chain model,⁸⁾

$$h(\gamma) = \frac{6}{4 + \gamma^2 + \sqrt{4 + \gamma^2}} \quad (4.4)$$

$$\alpha(\gamma) = \frac{1 + \sqrt{4 + \gamma^2}}{3} \quad (4.5).$$

In fact, $h(\gamma)$ obtained from the simulation and experiments are excellently described by Eq. 4.4, as noted in Fig. 4-2 (compare solid curve and symbols). The quantity $1 + \{\alpha(\gamma) - 1\}f(t, \gamma)$ in Eq. 4.3 can be regarded as a certain average of the stretch ratio of the chain contour.¹¹⁾ Thus, the nonlinear feature of chain contraction process can be examined for the relaxation function $f(t, \gamma)$ appearing in Eq. 4.3.

This $f(t, \gamma)$ should relax through several modes. Specifically, the data and simulation results suggest that $f(t, \gamma)$ relaxes with three modes as

$$f(t, \gamma) = \varphi_1 \exp\left(-\frac{t}{\tau_1}\right) + \varphi_2 \exp\left(-\frac{t}{\tau_2}\right) + \varphi_3 \exp\left(-\frac{t}{\tau_3}\right) \quad (4.6).$$

Here, the indices 1, 2, and 3 representing the fast, intermediate, and slow modes. The fractional intensities φ_i change with γ but satisfy a relationship $\varphi_1 + \varphi_2 + \varphi_3 = 1$ to fulfill a requirement of $f(t = +0, \gamma) = 1$. The fast and intermediate relaxation times are set to be independent of γ and have known values, $\tau_1 = \tau_0$ (unit time of simulation) = 0.9 s and $\tau_2 = \tau_R$ (longest Rouse time of simulation) = 24 s. Thus, the $h(t, \gamma)$ data shown in Fig. 4-3 are fitted with Eqs. 4.3 - 4.6 with τ_3 and φ_i being utilized as the fitting parameters. Good fitting was achieved with the three-mode form of $f(t, \gamma)$ (Eq. 4.6), and the best fit results, shown in Fig. 4-3 with the dashed curves, were obtained with a γ -independent $\tau_3 = 230$ s and γ -sensitive φ_i . This τ_3 value is close to the value of the terminal relaxation time in the linear regime, 400 s.

The γ -independence of τ_3 naturally results in the time-strain separability at long $t > \tau_3$, and the change of φ_3 with γ corresponds to the damping function $h(\gamma)$. However, the time-strain separability begins to hold approximately at shorter $t < \tau_3$ (at $t > \tau_2 = \tau_R$) if the slow mode hardly contributes to $h(t, \gamma)$. The absolute magnitude of φ_3 is considerably smaller than that of φ_2 : $(\varphi_2, \varphi_3) = (0.62, 0.17)$ for $\gamma = 1.79$ (not very far from the linear viscoelastic regime), $(\varphi_2, \varphi_3) = (0.67, 0.11)$ for $\gamma = 2.56$, $(\varphi_2, \varphi_3) = (0.67, 0.07)$ for $\gamma = 3.07$, and $(\varphi_2, \varphi_3) = (0.73, 0.06)$ for $\gamma = 4.02$ (well in the nonlinear regime). Thus, the slow mode contribution to $h(t, \gamma)$ is minor compared to the intermediate mode contribution and the time-strain separability holds even at $t \sim \tau_2$ ($= \tau_R$) within an uncertainty of $\pm 10\%$ and in particular for large γ (> 2.56). This is the result reported earlier,¹²⁾ which suggested that the time-strain separability being valid after completion of the longitudinal Rouse mode at $t \sim \tau_R$.¹²⁾ However, the slow mode contribution to $h(t, \gamma)$ is small but detectable, in particular for small γ , as already noted by Sanchez-Reyes and Archer²⁾ and Inoue et al.³⁾ Thus, rigorously speaking, the nonlinear damping occurs mainly through the longitudinal Rouse mode (intermediate mode) but also through the terminal, reptation-like mode (slow mode) at $t \sim \tau_3$ and the separability rigorously holds only after completion of this terminal mode. In other words, chain contraction process involves a secondary, slow relaxation governed by the reptation-like mode.

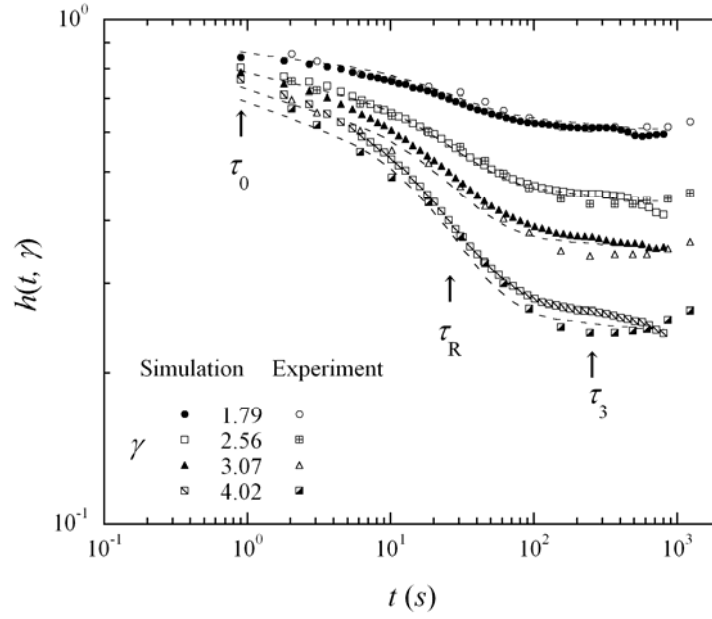


Figure 4-3 Time-dependent damping functions obtained from simulations and the experiments.⁹⁾ Dashed curves show the behavior deduced from Eq. 4.3. Arrows indicate the unit time τ_0 , the Rouse time τ_R and the longest relaxation time τ_3 defined in Eq. 4.6.

4-4. Discussion

The nonlinear damping under step shear strain has been attributed to the contraction of the chain along the array of entanglements. Thus, the finding of the previous studies,^{2), 3)} rigorous validity of the time-strain separability only in the time scale of terminal relaxation (time scale of τ_3 seen in the PCN simulation), may reflect the retardation of chain contraction compared to the Rouse equilibration at $t \sim \tau_R$. Therefore, a possible origin of this retarded contraction can be related to local relaxation induced by local-CCR. The remaining part of this chapter examines quantities that specify the chain contraction and then discusses the origin of the retarded validity of time-strain separability in relation to perturbation of contour variables due to local-CCR.

4-4-1. Quantities specifying the chain stretch/contraction

The chain stretch/contraction can be quantified by the following relaxation functions.

For chain contour length (L):

$$F_{\text{chain}}(t, \gamma) = K_1 \left[\frac{\langle L(t) \rangle}{\langle L \rangle_{\text{eq}}} - 1 \right] \quad (4.7)$$

For subchain length (r):

$$F_{\text{subchain}}(t, \gamma) = K_2 \left[\frac{\langle r(t) \rangle}{\langle r \rangle_{\text{eq}}} - 1 \right] \quad (4.8)$$

For subchain stretch ratio defined with respect to *quasi-equilibrium* reference:

$$\Lambda_{\text{subchain}}(t, \gamma) = K_3 \left[\left\langle \frac{r(t)^2}{b^2 n(t)} \right\rangle^{1/2} - 1 \right] \quad (4.9).$$

In Eqs. 4.7 – 4.9, $\langle \rangle$ and $\langle \rangle_{\text{eq}}$ represent the ensemble average at a given time t under strain γ and at equilibrium, respectively: $\langle L \rangle_{\text{eq}} = \langle r \rangle_{\text{eq}} \langle Z \rangle_{\text{eq}}$ and $\langle r \rangle_{\text{eq}} = b \langle n \rangle_{\text{eq}}^{1/2}$. K_i ($i = 1 \sim 3$) are the normalization constants ensuring $F_{\text{chain}} = F_{\text{subchain}} = \Lambda_{\text{subchain}} = 1$ at $t = +0$. The average monomer number per subchain $\langle n(t) \rangle$ at time t is different from the equilibrium number $\langle n \rangle_{\text{eq}}$, and a *quasi-equilibrium* size of the subchain composed of $\langle n(t) \rangle$ monomers is given by $b \langle n(t) \rangle^{1/2}$. Thus, the function $\Lambda_{\text{subchain}}(t, \gamma)$ specifies the subchain stretch defined with respect to this *quasi-equilibrium* reference characterized by $\langle n(t) \rangle$. In contrast, $F_{\text{chain}}(t, \gamma)$ and $F_{\text{subchain}}(t, \gamma)$ specify the ratios of the chain and subchain lengths to their real equilibrium lengths. The distributions of the subchain length and its stretch along the chain contour are smeared in the averages taken for all subchains, $F_{\text{subchain}}(t, \gamma)$ and $\Lambda_{\text{subchain}}(t, \gamma)$.

From the simulated values of $r(t)$ and $n(t)$ at each time t during the stress relaxation process, the relaxation functions defined above are evaluated. In Fig. 4-4, these functions are plotted against the reduced time t / τ_R (symbols). The dashed curves denote the DE prediction (cf. Appendix 4B). The terminal relaxation times of $F_{\text{chain}}(t, \gamma)$, $F_{\text{subchain}}(t, \gamma)$ and $\Lambda_{\text{subchain}}(t, \gamma)$ are insensitive to γ , and the time evolution of the chain and subchain lengths is well characterized

by these functions.

As noted in Fig. 4-4(a), the chain length recovers its equilibrium value (i.e., $F_{\text{chain}}(t, \gamma)$ decays to zero) via three steps. The fast step occurring at $t \sim \tau_0$ results from the local balance of elastic force which has been discussed in Chapter 3. The intermediate process occurring at $t \sim \tau_R$ is due to the intrinsic, longitudinal Rouse motion of the chain as considered in the DE model. The recovery of the equilibrium chain length completes up to $\sim 90\%$ through this intrinsic Rouse process, but the recovery of the remaining 10% requires the slow process occurring in a time scale of τ_3 defined for the time-dependent damping function (Fig. 4-3). Thus, the retarded chain contraction, corresponding to the retarded validity of the time-strain separability, is directly confirmed for $F_{\text{chain}}(t, \gamma)$.

In contrast to this behavior of the chain length, the relaxation of $F_{\text{subchain}}(t, \gamma)$ and $\Lambda_{\text{subchain}}(t, \gamma)$ proceeds almost in one-step and completes at $t \sim \tau_3$; cf. Figs. 4-4(b) and 4-4(c). Thus, the dominant part of the length equilibration is slower for the subchain than for the whole contour of the chain, as noted from comparison of $F_{\text{chain}}(t, \gamma)$ and $F_{\text{subchain}}(t, \gamma)$. This difference is discussed later in relation to local-CCR and the tension distribution along the chain contour.

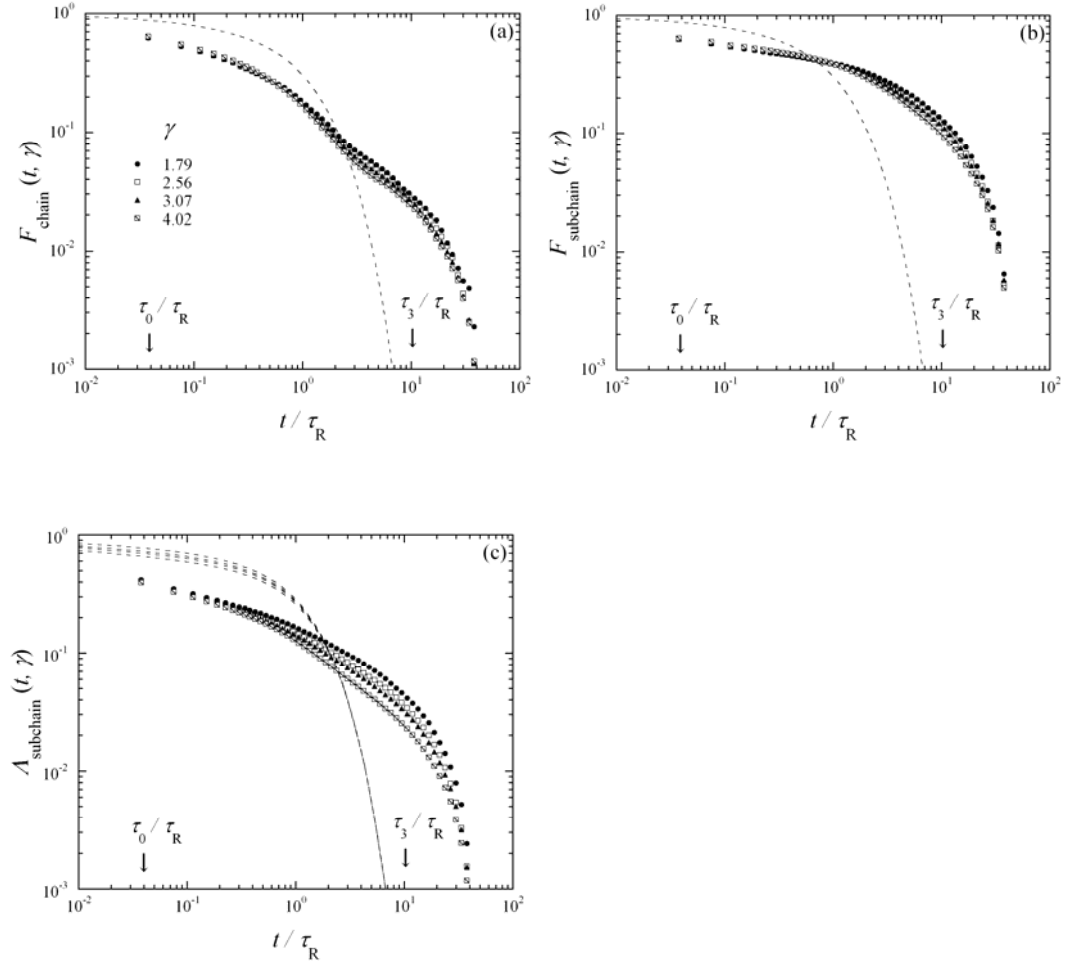


Figure 4-4 Relaxation of (a) contour length of the chain, (b) subchain length, and (c) subchain stretch defined with respect to the quasi-equilibrium reference (based on the monomer number in the subchain at respective times). Dashed curves indicate the prediction of the DE model (see Appendix 4B).

For specifying the dominant mechanism of the slow equilibration of the subchain length, the simulation was conducted for various chain lengths to evaluate $F_{\text{subchain}}(t, \gamma)$. The results were very similar to those seen in Fig. 4-4(b) (and not shown here), and the terminal relaxation time τ_3' defined for $F_{\text{subchain}}(t, \gamma)$ was evaluated. In Fig. 4-5, this τ_3' is reduced by the unit time of simulation τ_0 and plotted against the equilibrium entanglement number per chain, $\langle Z \rangle_{\text{eq}}$ (that is proportional to the total monomer number per chain, N). For comparison, the characteristic time

τ_3 of the slow mode involved in the time-dependent damping function $f(t, \gamma)$ (cf. Eq. 4.6) and the terminal relaxation time τ_d in the linear viscoelastic regime are also shown. These characteristic times are close to each other and proportional to $\langle Z \rangle_{\text{eq}}^{3.4}$. This result confirms that the reptative motion of the chain dominates the recovery of the subchain length (as well as the onset of the rigorous time-strain separability of $G(t, \gamma)$).

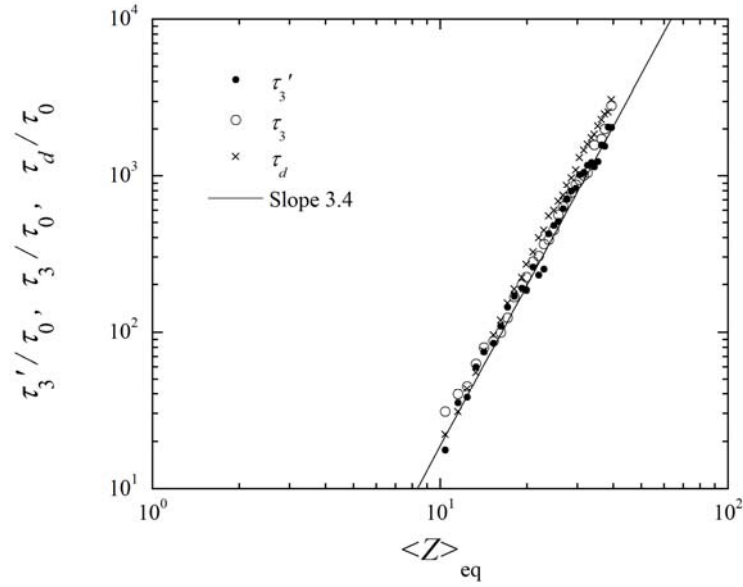


Figure 4-5 Chain length dependence of the relaxation time τ'_3 extracted from the subchain length relaxation function. For comparison, the characteristic time τ_3 of the slow mode involved in the time-dependent damping function and the terminal relaxation time τ_d in the linear viscoelastic regime are also shown.

4-4-2. Origin of the slow length equilibration

This subsection examines the origin of the slow equilibration of the subchain length through the analysis of contour variables affected by local-CCR. The chain length has been almost equilibrated at $t = \tau_R$ ($\langle L(t = \tau_R) \rangle \cong 1.1 \langle L \rangle_{\text{eq}}$ for $\gamma \cong 3$) but the subchain length equilibration is retarded to $t \sim \tau_d$; cf. Figs. 4-4(b) and 4-4(c). This retardation is intimately related to the time-evolution of the total sliplink number per chain and the sliplink density along the chain. In Fig. 4-6(a), the total sliplink number per chain $\langle Z(t) \rangle = N / \langle n(t) \rangle$ at respective t is reduced by its

equilibrium value, $\langle Z \rangle_{\text{eq}}$, and plotted against the reduced time t/τ_R . Figures 4-6(b) and 4-6(c) show similarly reduced plots for the sliplink density $\langle Z(s,t) \rangle'$ at a reduced curvilinear coordinate $s = x/\langle L(t) \rangle$, where x is the curvilinear distance of the sliplink measured from one end of the chain and $\langle \rangle'$ indicates an average taken for all subchains at the given coordinate s . The $\langle Z(t) \rangle / \langle Z \rangle_{\text{eq}}$ ratio decreases with increasing t up to $2\tau_R$. This decrease is attributable to accumulation of local-CCR, i.e., the removal of sliplinks for a given chain due to the contraction of surrounding chains that occurs through the intrinsic, longitudinal Rouse mode. Detailed features of this process are noted for $\langle Z(s,t) \rangle'$: The sliplink density first decreases at portions near chain ends (at $s \sim 0.1$ and 0.9), and this decrease propagates to the chain center ($s \sim 0.5$) at intermediate $t \sim \tau_R$. Finally, the equilibrium sliplink density is recovered at the center and end portions, with the recovery being faster for the latter.

For further discussion of the slow recovery of the total number and density of the sliplink seen above, the average length of the subchain $\langle r(t = \tau_R) \rangle$ at the time τ_R can be conveniently rewritten as,

$$\langle r(\tau_R) \rangle \cong \frac{\langle L(\tau_R) \rangle}{\langle Z(\tau_R) \rangle} = \frac{\langle L(\tau_R) \rangle}{\langle L \rangle_{\text{eq}}} \times \frac{\langle Z \rangle_{\text{eq}}}{\langle Z(\tau_R) \rangle} \times \langle r \rangle_{\text{eq}} \quad \text{with} \quad \langle r \rangle_{\text{eq}} = \frac{\langle L \rangle_{\text{eq}}}{\langle Z \rangle_{\text{eq}}} \quad (4.10).$$

Thus, $\langle r(t) \rangle$ remains considerably larger than $\langle r \rangle_{\text{eq}}$ (by a factor of 1.4 for $\gamma \cong 3$; cf. Fig. 4-4(b)) due to the $\langle Z \rangle_{\text{eq}} / \langle Z(\tau_R) \rangle$ factor even at $t \sim \tau_R$ where the intrinsic Rouse contraction is completed and the chain length has been almost equilibrated ($\langle L(\tau_R) \rangle / \langle L \rangle_{\text{eq}} \cong 1$). In other words, the increase of $\langle n(t) \rangle$ ($= N / \langle Z(t) \rangle$) due to accumulation of local-CCR is one of the factors that leads to the retarded equilibration of the subchain length. The full equilibration of the subchain length requires full reformation of the sliplinks which occurs through the large-scale reptative motion in the time scale of $\tau_3' \cong \tau_d$, as noted for $F_{\text{subchain}}(t, \gamma)$ (Fig. 4-4(b)).

In relation to the above argument, the subchain stretch $\Lambda_{\text{subchain}}(t, \gamma)$ has only

moderately relaxed at $t \sim \tau_R$ where $\langle n(t) \rangle$ begins to decrease ($\langle Z(t) \rangle$ begins to increase); compare Figs. 4-4(c) and 4-6(a). Namely, the increase of $\langle n(t) \rangle$ is not the only factor that retards the subchain length equilibration. The other factor resulting in this retardation can be found in relation to the subchain tension, as discussed below.

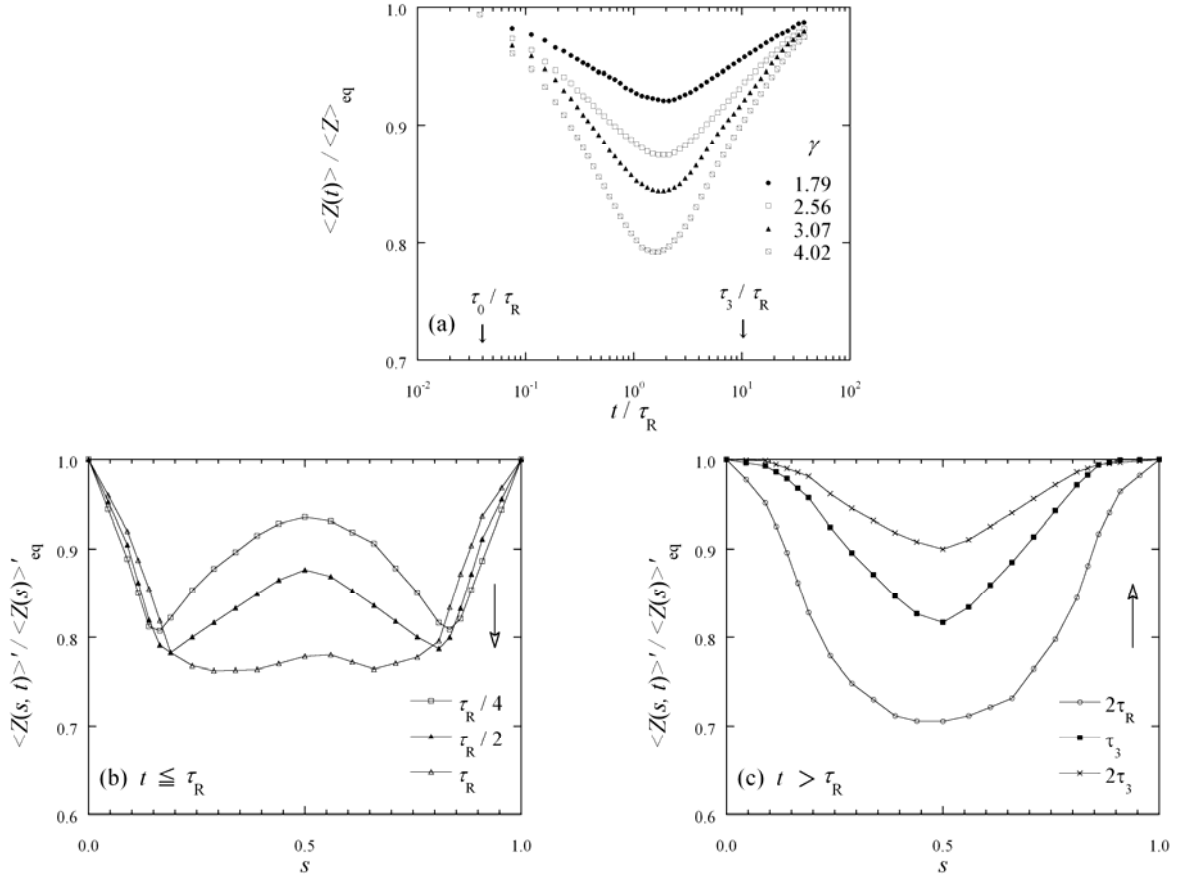


Figure 4-6 Time-evolution of the sliplink number under step strain: Reduced total sliplink number per chain for various strains (part a) and curvilinear sliplink density at $\gamma = 4.02$ for $t \leq \tau_R$ (part b) and $t > \tau_R$ (part c). Arrows in parts b and c indicate the direction of time evolution.

As can be noted from Fig. 4-6(a), the average monomer number per subchain, $\langle n(t) \rangle \cong \langle n \rangle_{\text{eq}} \langle Z \rangle_{\text{eq}} / \langle Z(t) \rangle$, is larger than $\langle n \rangle_{\text{eq}}$ due to accumulation of local-CCR. Thus, the average spring constant of the subchain, $\langle \kappa(t) \rangle \propto 1 / \langle n(t) \rangle$, is smaller than that at equilibrium and the subchain tension, the driving force of the chain contraction, is weaker than that expected for the intrinsic Rouse contraction considered in the DE model. This weak tension leads to the retarded equilibration of the chain/subchain length. For more quantitative argument, it should be noted that the chain contracts because the tension is larger at around the chain center than at the chain ends. In other words, the retarded equilibration reflects a distribution of the subchain tension along the chain contour. The tension at the curvilinear coordinate s and time t is given by

$$\langle T(s, t) \rangle' \cong \left\langle \frac{r(s, t)}{n(s, t)} \right\rangle, \quad (4.11).$$

In Fig. 4-7(a), $\langle T(s, t) \rangle'$ is normalized by the equilibrium tension $\langle T \rangle_{\text{eq}}$. For comparison, $\langle T(s, t) \rangle'$ deduced from the DE model (for the Rouse contraction along the fixed tube axis; cf. Appendix 4B) is shown in Fig. 4-7(b). For both of PCN simulation and DE model, the tension is larger at around the chain center than at the chain ends to activate the chain contraction. More importantly, this tension gradient along the chain backbone is less significant for simulations throughout the stress relaxation process. In other words, the tension at around the chain center is smaller in the PCN simulation than in the DE model in particular at $t \leq \tau_R$, as most clearly seen for the $\langle T(s, t) \rangle' / \langle T(s, t) \rangle'_{\text{DE}}$ ratio (Fig. 4-7(c)). The weak tension at around the chain center is due to a reduction of the spring constant (a rise of the monomer number per segment) in this part of the chain, corresponding to the minimum of the sliplink density shown in Figs. 4-6 (b) and 4-6(c). This reduction of the tension at around the chain center due to local-CCR, is the dominant factor that results in the retarded equilibration of the subchain length in the PCN simulation.

In relation to this point, it should be emphasized that the relaxation of the subchain stretch $\Lambda_{\text{subchain}}(t, \gamma)$ is slower in the PCN simulations than in the DE model; cf. Fig. 4-4(c). Enhancement of the chain tension due to this retarded relaxation of $\Lambda_{\text{subchain}}(t, \gamma)$ is overwhelmed by the softening of the subchain (decrease of the spring constant) due to increase of $\langle n(t) \rangle$ (cf. Fig. 4-6) thereby giving a net decrease of the chain tension at around the chain center to retard the subchain length equilibration.

Finally, it should be emphasized that the dominant part of the chain length equilibration (contraction) is faster than the subchain length equilibration and occurs at $t \sim \tau_R$. Cancellation between the increase of subchain length $\langle r(t) \rangle$ (due to the increase of $\langle n(t) \rangle$ and the subchain stretch) and the decrease of $\langle Z(t) \rangle$, both due to accumulation of local-CCR, allows the chain length $\langle L(t) \rangle = \langle r(t) \rangle \langle Z(t) \rangle$ to be almost equilibrated at $t \sim \tau_R$, although the subchains have not been equilibrated at such short t . Furthermore, the softening of the subchains (due to the increase of $\langle n(t) \rangle$) tends to help completion of the nonlinear damping of the stress, which results in the approximate validity (within $\pm 10\%$) of the time-strain separability at $t \sim \tau_R$. At the same time, the delicate failure of this separability at $t \sim \tau_R$ reflects the nonlinear dynamics of the chain under step shear, which is mainly driven by distribution of tension along the chain contour due to local-CCR.

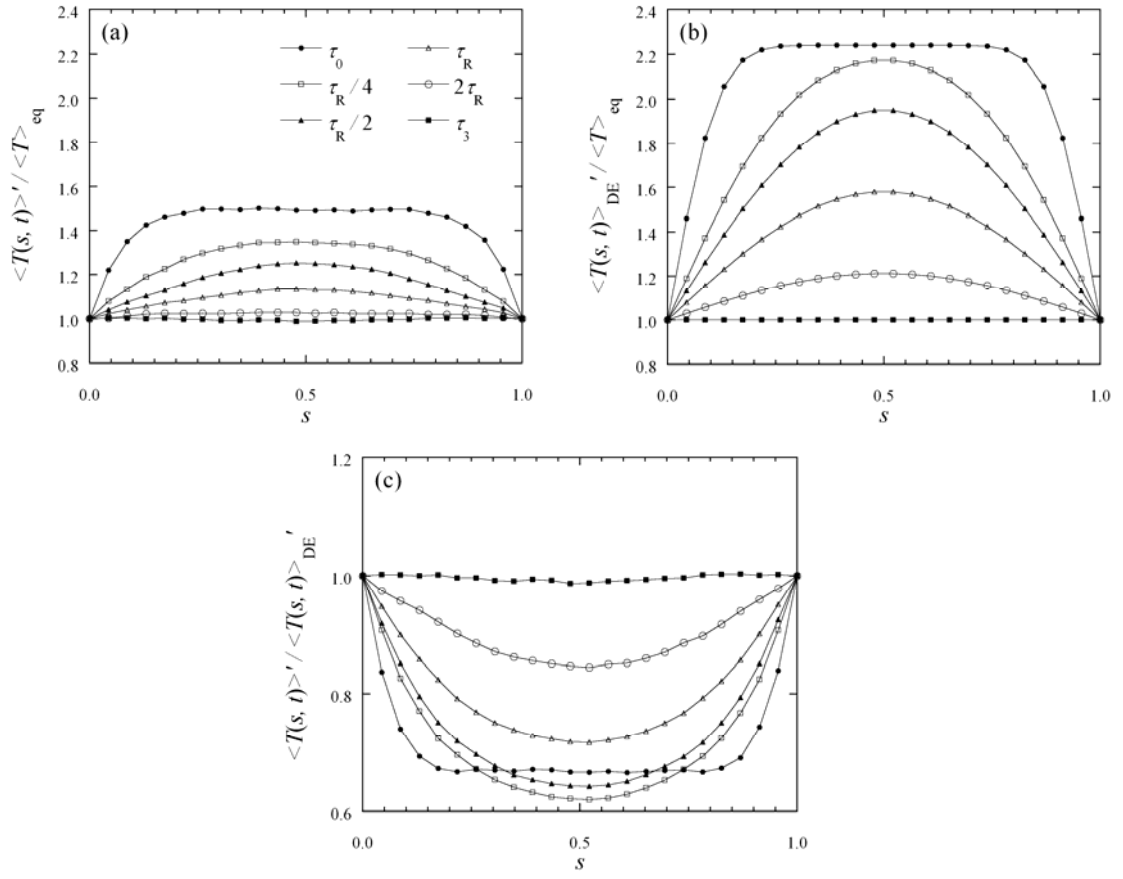


Figure 4-7 Curvilinear distribution of normalized subchain tension under step strain $\gamma = 4.02$ obtained from (a) simulation in this study and (b) the DE model. Part (c) shows a ratio of the stress obtained from the simulation to that deduced from the DE model.

4-5. Conclusions

The molecular origin of delicate failure of time-strain separability at $t \cong \tau_R$ was investigated in terms of coupling of the chain contraction and orientational relaxation through local-CCR. Specifically, the impact of local-CCR on the distribution of tension along the chain contour was focused. Due to local-CCR, the tension around the chain center is reduced and becomes weaker than the DE prediction. This tension reduction leads to the retarded chain contraction and the limited validity of rigorous time-strain separability (found only at $t \geq \tau_d$). This conclusion was also deduced from the examination of the relaxation functions specifying the chain contraction, which are affected by the slow reptative mode. These results suggest that the retarded time-strain separability seen for the $G(t, \gamma)$ data of actual entangled polymers is mainly attributed to the retarded length equilibration induced by local-CCR.

Appendix 4A. Autocorrelation of microscopic shear stress

Linear relaxation modulus $G(t)$ is given by the stress correlation function (Green-Kubo relation) in equilibrium condition:¹³⁾

$$G(t) = \frac{V}{k_B T} \langle \sigma_{xy}(t) \sigma_{xy}(0) \rangle_{\text{eq}} \quad (4A.1)$$

where V is the volume of system, σ_{xy} is the shear component of stress tensor defined as $\sigma_{xy} = 3 \nu k_B T \langle r_x r_y / n \rangle$, and $\langle \rangle_{\text{eq}}$ is an ensemble average in equilibrium.

Appendix 4B. 1-D Rouse motion in Doi-Edwards model

In the 1-D Rouse model proposed in ref. 1, the curvilinear coordinate of the n -th segment $s_n(t)$ at time t is written as

$$s_n(t) = Y_0(t) + 2 \sum_{p=1}^{\infty} Y_p(t) \cos\left(\frac{p\pi n}{N}\right) + \frac{\langle L \rangle_{\text{eq}}}{N} n \quad (4B.1)$$

where $Y_p(t)$ is normal mode amplitude defined by

$$Y_0(t) \equiv \frac{1}{N} \int_0^N dn s_n(t) \quad (4B.2)$$

$$Y_p(t) \equiv \frac{1}{N} \int_0^N dn \cos\left(\frac{p\pi n}{N}\right) \left(s_n(t) - \frac{\langle L \rangle_{\text{eq}}}{N} n \right) \quad \text{for } p = 1, 2, \dots \quad (4B.3).$$

The first and second moments of the normal modes after step strain are provided by Wen and Hua¹⁴⁾

$$\langle Y_p(t) \rangle = -\frac{2(\alpha-1)}{p^2 \pi^2} \langle L \rangle_{\text{eq}} \exp\left(-\frac{p^2 t}{\tau_R}\right) \quad \text{for odd } p, \quad \langle Y_p(t) \rangle = 0 \quad \text{for even } p \quad (4B.4)$$

$$\langle Y_p(t)^2 \rangle = \frac{N(\alpha-1)^2}{2p^2 \pi^2} \langle L \rangle_{\text{eq}}^2 \exp\left(-\frac{2p^2 t}{\tau_R}\right) \quad (4B.5)$$

where $\alpha \equiv \langle \mathbf{E} \cdot \mathbf{u}_{\text{eq}} \rangle$ with $\mathbf{E}$ = deformation gradient tensor and $\mathbf{u}_{\text{eq}}$ = unit vector at equilibrium.

From Eqs. 4B.1 and 4B.4, the mean contour length of chain can be calculated as

$$\begin{aligned}\langle L(t) \rangle &= \langle s_N(t) - s_0(t) \rangle = \langle L \rangle_{\text{eq}} - 4 \sum_{p:\text{odd}}^{\infty} \langle Y_p(t) \rangle \\ &= \langle L \rangle_{\text{eq}} \left[1 + (\alpha - 1) \sum_{p:\text{odd}}^{\infty} \frac{8}{p^2 \pi^2} \exp\left(-\frac{p^2 t}{\tau_R}\right) \right]\end{aligned}\quad (4B.6).$$

Thus, relaxation function for the whole contour length $F_{\text{chain}}(t, \gamma)$ defined by Eq. 4.7 is given by

$$F_{\text{chain}}^{\text{DE}}(t) = \frac{\langle L(t) \rangle - \langle L \rangle_{\text{eq}}}{\langle L(t=+0) \rangle - \langle L \rangle_{\text{eq}}} = \sum_{p:\text{odd}}^{\infty} \frac{8}{p^2 \pi^2} \exp\left(-\frac{p^2 t}{\tau_R}\right) \quad (4B.7).$$

In the DE model, the average subchain length is given by $\langle r(t) \rangle = \langle L(t) \rangle / N$ and thus the relaxation function for the subchain length $F_{\text{subchain}}(t, \gamma)$ defined by Eq. 4.8 is identical to $F_{\text{chain}}^{\text{DE}}(t)$.

The mean-square subchain length is expressed as

$$\begin{aligned}\langle r(t)^2 \rangle &= \frac{1}{N} \sum_{n=1}^N \langle (s_{n+1}(t) - s_n(t))^2 \rangle = \frac{1}{N} \int_0^N dn \left\langle \left(\frac{\partial s_n}{\partial n} \right)^2 \right\rangle \\ &= \frac{1}{N} \sum_{p=1}^N \frac{2p^2 \pi^2}{N} \langle Y_p(t)^2 \rangle - \frac{8}{N} \frac{\langle L \rangle_{\text{eq}}}{N} \sum_{p:\text{odd}}^{\infty} \langle Y_p(t) \rangle + \left(\frac{\langle L \rangle_{\text{eq}}}{N} \right)^2 \\ &= \left(\frac{\langle L \rangle_{\text{eq}}}{N} \right)^2 \left[1 + (\alpha - 1)^2 \frac{1}{N} \sum_{p=1}^N \exp\left(-\frac{2p^2 t}{\tau_R}\right) + 2(\alpha - 1) \sum_{p:\text{odd}}^{\infty} \frac{8}{p^2 \pi^2} \exp\left(-\frac{p^2 t}{\tau_R}\right) \right]\end{aligned}\quad (4B.8).$$

Thus, the subchain stretch ratio defined by Eq. 4.9 is readily obtained as

$$\Lambda_{\text{subchain}}^{\text{DE}}(t, \gamma) = \frac{1}{\alpha - 1} \left[\left\{ 1 + (\alpha - 1)^2 \frac{1}{N} \sum_{p=1}^N \exp\left(-\frac{2p^2 t}{\tau_R}\right) + 2(\alpha - 1) \sum_{p:\text{odd}}^{\infty} \frac{8}{p^2 \pi^2} \exp\left(-\frac{p^2 t}{\tau_R}\right) \right\}^{1/2} - 1 \right] \quad (4B.9).$$

Finally, the tension at the curvilinear coordinate $s = n / N$ can be calculated as

$$\begin{aligned}\langle T(s, t) \rangle_{\text{DE}} &= \frac{3k_B T}{b^2} \left\langle \frac{\partial s_n(t)}{\partial n} \right\rangle \\ &= \frac{3k_B T}{b^2} \left[-2 \sum_{p=1}^{\infty} \langle Y_p \rangle \frac{p\pi}{N} \sin\left(\frac{p\pi n}{N}\right) + \frac{\langle L \rangle_{\text{eq}}}{N} \right] \\ &= T_{\text{eq}} \left[1 + 4(\alpha - 1) \sum_{p:\text{odd}}^{\infty} \frac{1}{p\pi} \sin(p\pi s) \exp\left(-\frac{p^2 t}{\tau_R}\right) \right]\end{aligned}\quad (4B.10).$$

Here, $T_{\text{eq}} = (3k_B T / b^2) (\langle L \rangle_{\text{eq}} / N) = 3k_B T / a$ (= independent of s).

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CHAPTER 5

Nonlinear stress relaxation of scarcely entangled chains

5-1. Introduction

The γ dependence of the shear damping function $h(\gamma)$ for scarcely entangled polymers^{1) - 3)} having $M_C \sim 2M_e$ is considerably weaker than the DE prediction.⁴⁾ This weak damping was classified as the type-B behavior.⁵⁾ A couple of theoretical attempts have been made for explaining the origin of type-B damping behavior. Kapnistos et al.⁶⁾ have reported weak damping of $h(\gamma)$ using their slip-spring model⁷⁾ where a Rouse chain is confined in a tube shaped parabolic potential. The confinement is modeled by some springs having one end anchored in space and the other end connected to the chain. The spring end connected to the chain slides along the chain backbone to mimic the entanglement. Kapnistos et al. reported that the γ dependence of $h(\gamma)$ is weakened if the number of slip-springs on the chain, which reflects the number of entanglement per chain, is decreased. Because a free Rouse chain exhibits no damping, it is rather natural that the strain dependence of $h(\gamma)$ becomes weaker when the number of springs on the chain becomes smaller. Kapnistos et al. discussed that their simulation results are consistent with that for comb polymers with a small number of backbone-backbone entanglements.

Another explanation of the type-B behavior was given by Kharlamov et al.⁸⁾ They derived the distribution function of the end-to-end vector of a whole chain $\mathbf{R}_{ee}$ after the chain contraction along the primitive chain, and then calculated the stress from the second moment of $\mathbf{R}_{ee}$. In this stress calculation, they implicitly assumed that the entanglements on the primitive chain relax during chain contraction while the orientation of $\mathbf{R}_{ee}$ is preserved. In general, this molecular picture is inconsistent with their first assumption on the calculation of distribution function of $\mathbf{R}_{ee}$, where the contraction occurs along the primitive chain and after that the entanglement disappears.

(For instance, in the DE model, the relaxation time of $\mathbf{R}_{ee}$ is identical to that of the entanglements on the chain.) However, similar situations may be realized in some cases where the $\mathbf{R}_{ee}$ relaxes slow enough compared to the relaxation of entanglements on the chain. For example, Kharlamov et al.⁶⁾ stated that multiple branch polymers may be in this situation if the relaxation of chain backbone between branch points is much slower than that of entanglements between the backbone and the dangling arms.

Osaki⁵⁾ claimed that the transition from the type-A to type-B behavior is likely to occur gradually with decreasing molecular weight. However, there has been no theoretical explanation for the transitional behavior of $h(\gamma)$ with the molecular weight. Kapnistos et al.⁶⁾ showed the reasonable change of $h(\gamma)$ with the change of constraint on the chain. However, they did not report simulation result for well-entangled chains. For the longest chain they examined, the damping is much weaker than the DE prediction. This weak damping may be due to their model construction conserving the total number of slip-springs along the chain, which neglects disentanglement due to the chain contraction (local-CCR). The theory by Kharlamov et al.⁸⁾ predicts no molecular weight dependence of $h(\gamma)$, and the condition to realize their assumption is unknown.

As discussed in Chapter 4, the coupling between chain contraction and orientational relaxation induced by local-CCR leads to the reduction of the subchain tension at around the chain center. This reduction of tension is expected for short chains as well. However, the magnitude of the tension reduction for the short chains may be different from the long chains because of the larger fraction of the dangling end-subchains for shorter chains. Indeed, these dangling end-subchains accelerate the relaxation of both stretch and orientation as seen in Chapter 3. In this chapter, the mechanism of transition from the type-A to type-B damping behavior is examined by utilizing the PCN simulation as a platform for investigating the molecular weight dependence of

$h(\gamma)$ in actual scarcely entangled polymers. In particular, the importance of local-CCR and recovery of entanglement network structure in this weak damping mechanism is discussed.

5-2. Simulations

For monodisperse linear polymers having various chain lengths, $Z_0 = M / M_0 = 1 \sim 30$, the simulation was conducted with the Lees-Edwards periodic shear boundary condition for the unit cell dimension of 16^3 . Linear viscoelastic modulus $G^*(\omega)$ was evaluated under two complete cycles of dynamic shear strain with the amplitude $= 0.3$ in the stationary state. Nonlinear relaxation modulus $G(t, \gamma)$ was obtained as the average of more than 50 independent runs under step shear strain affinely applied at $t = +0$. Linear relaxation modulus $G(t)$ was calculated from the auto-correlation function of the microscopic shear stress at equilibrium (see Appendix 4A).

5-3. Results and discussion

5-3-1. Nonlinear viscoelasticity

The simulation of nonlinear stress relaxation was conducted for $\langle Z \rangle_{\text{eq}} = 4 \sim 9.2$. This range of $\langle Z \rangle_{\text{eq}}$ includes the scarcely entangled regime. Specifically, this scarcely entangled regime emerges at around $4 \leq \langle Z \rangle_{\text{eq}} < 7$, which is identified from the chain length dependence of zero-shear viscosity η_0 . The critical chain length corresponding to the critical molecular weight M_C is $Z_C^\eta \sim 4$ (as explained in Appendix 5A).

Figure 5-1 shows the nonlinear relaxation modulus $G(t, \gamma)$ simulated for representative $\langle Z \rangle_{\text{eq}}$ values. $G(t, \gamma)$ for $\langle Z \rangle_{\text{eq}} = 9.2$ exhibits a strong damping, which is similar to the behavior of $G(t, \gamma)$ simulated for well-entangled chains with $\langle Z \rangle_{\text{eq}} = 23$ and 30 (that agreed with the $G(t, \gamma)$ data for a PS melt in Fig. 3-2 and a PS solution in Fig. 4-1, respectively). On the other hand, $G(t, \gamma)$ for $\langle Z \rangle_{\text{eq}} = 4.7$ exhibits weaker damping.

The difference between the cases of $\langle Z \rangle_{\text{eq}} = 9.2$ and 4.7 can be clearly seen in Fig. 5-2, where $G(t, \gamma)$ reduced by the damping function $h(\gamma)$ is compared with the linear $G(t)$. The arrows indicate the onset time τ_k for the time-strain separability, the longest relaxation time τ_L , and the longest Rouse relaxation time τ_R . For both cases, τ_k is longer than τ_R by a factor of 6 and close to τ_L (in particular for the case of $\langle Z \rangle_{\text{eq}} = 4.7$). As discussed in Chapter 4, the considerable difference between τ_k and τ_R , noted experimentally for well-entangled cases,^{9), 10)} is related to the reduction of the chain tension at the chain center due to local-CCR.

Figure 5-3 shows the damping function $h(\gamma)$ evaluated from the simulated $G(t, \gamma)$. For well entangled chains, the results of previous chapters indicate that $h(\gamma)$ obtained from the PCN simulation is insensitive to $\langle Z \rangle_{\text{eq}}$ (which is in harmony with the experimentally observed type-A behavior).⁵⁾ This $h(\gamma)$ for the well entangled chains is close to the prediction of the three-chain model¹¹⁾ as shown in Fig. 5-3 with the solid curve. (This result is consistent with that shown in previous chapters.) The $h(\gamma)$ for $\langle Z \rangle_{\text{eq}} = 6.6$ (filled square) falls in this category. However, $h(\gamma)$ increases with decreasing $\langle Z \rangle_{\text{eq}}$ below 7 to exhibit the type-B behavior.⁵⁾ Specifically, $h(\gamma)$ for $\langle Z \rangle_{\text{eq}} = 4$ (filled circles) is close to the data for the PS solution with $M = 1.9M_e$ (unfilled circles).²⁾ According to the above observation, a critical chain length for the transition between type-A and type-B behaviors can be estimated to be $Z_C^h = 7$. This Z_C^h value corresponds to the upper bound of scarcely entangled regime, as confirmed from the 3.4th power-law behavior of η_0 seen for $\langle Z \rangle_{\text{eq}} \geq Z_C^h$ (see Appendix 5A).

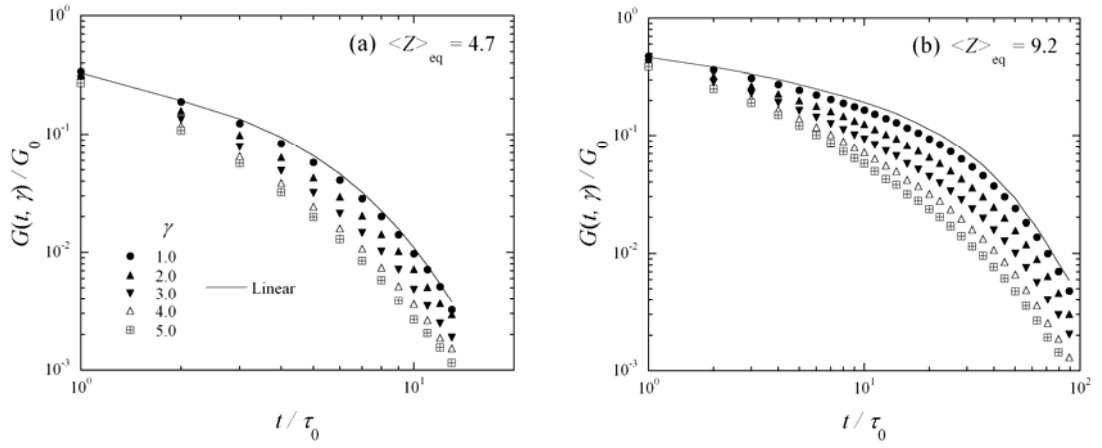


Figure 5-1 Normalized nonlinear relaxations modulus $G(t, \gamma)/G_0$ for (a) $\langle Z \rangle_{\text{eq}} = 4.7$ and (b) $\langle Z \rangle_{\text{eq}} = 9.2$. Solid curve shows the linear relaxation modulus $G(t)$.

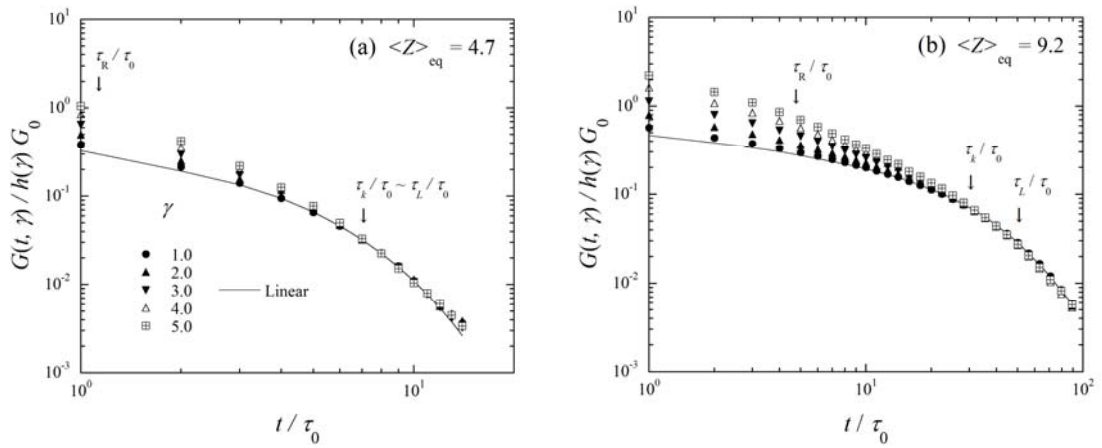


Figure 5-2 Test of time-strain separability for (a) $\langle Z \rangle_{\text{eq}} = 4.7$ and (b) $\langle Z \rangle_{\text{eq}} = 9.2$. Solid curve shows the linear relaxation modulus $G(t)$. The arrows indicate the onset time τ_k for the separability, the longest relaxation time τ_L , and the longest Rouse relaxation time τ_R , respectively.

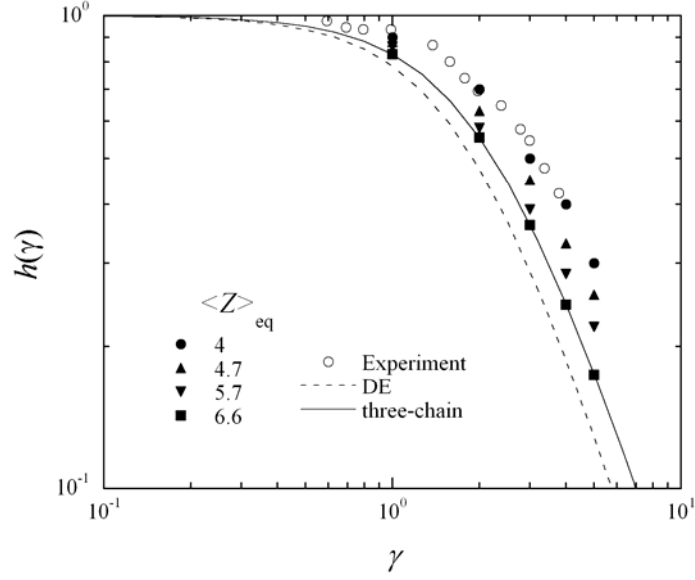


Figure 5-3 Damping function $h(\gamma)$ for various chain lengths. Filled symbols are simulation results, dashed curve is the DE model without IAA,⁴⁾ and solid curve is the three-chain model.²³⁾ Experimental data of PS solution with $Z_e = M/M_e = 1.9$ taken from Inoue et al.²⁾ are indicated by unfilled circles.

5-3-2. Molecular picture

In this subsection, the molecular weight dependence of $h(\gamma)$ is analyzed on the basis of local-CCR and the entanglement network recovery. For short chains, the entanglement network recovery is different from those for long chains, reflecting a qualitative difference in the recovering process. Figure 5-4 shows the time evolution of reduced total sliplink number per chain $\langle Z(t) \rangle / \langle Z \rangle_{eq}$. As discussed in Chapter 4, $\langle Z(t) \rangle / \langle Z \rangle_{eq}$ decreases with time until $t = 2\tau_R$, because the loss of sliplinks corresponding to accumulation of local-CCR overwhelms the creation of the sliplinks. In $t > 2\tau_R$, $\langle Z(t) \rangle / \langle Z \rangle_{eq}$ increases to recover the equilibrium value. Comparison of the behavior between the long and short chains suggests that this feature is common for the long and short chains. Indeed, the relaxational part of $\langle Z(t) \rangle / \langle Z \rangle_{eq}$, reformulated as $F_Z(t, \gamma)$ defined by Eq. 5.1, satisfies the time-strain separability, as can be noted in Fig. 5-5.

$$F_Z(t, \gamma) = 1 - \langle Z(t) \rangle / \langle Z \rangle_{eq} \quad (5.1).$$

The separability of $F_Z(t, \gamma)$ emerges because the mode of relaxation (reptation) at the long times is insensitive to γ (as similar to the DE situation) even for the short chains. On the other hand, the γ dependence of $F_Z(t, \gamma)$ is different between the long and short chains. Specifically, for the short chains, $F_Z(t, \gamma)$ at $t = \tau_k$ is more weakly dependent on γ than that for the long chains, (Similar trend is noted for the minimum $\langle Z(t) \rangle / \langle Z \rangle_{\text{eq}}$ value at $t = 2\tau_R$ in Fig. 5-4). This weak γ dependence of $F_Z(t, \gamma)$, corresponding to the weak nonlinearity of $h(\gamma)$, is attributable to a difference in the tension equilibration process at the short times ($t < \tau_k$). For the long chains, the tension equilibration is achieved by the chain contraction as discussed in Chapter 4. In contrast, for the short chains, the dominant relaxation mechanism appears to be the constraint renewal process by surrounding chains because the dangling end-subchain density is considerably large.

The above difference in the tension equilibration process is clearly observed also for the tension distribution along the chain contour. As an example, Fig. 5-6 shows the tension distribution, $\langle T(s, t) \rangle'$ for the long and short chains. For the long chain (discussed in Chapter 4) the equilibration of tension has not completed even at $t = \tau_R$. On the other hand, for the short chain, the inhomogeneity of tension along the chain has been smeared at $t \sim \tau_R$ due to the fast recovery of entanglement network structure.

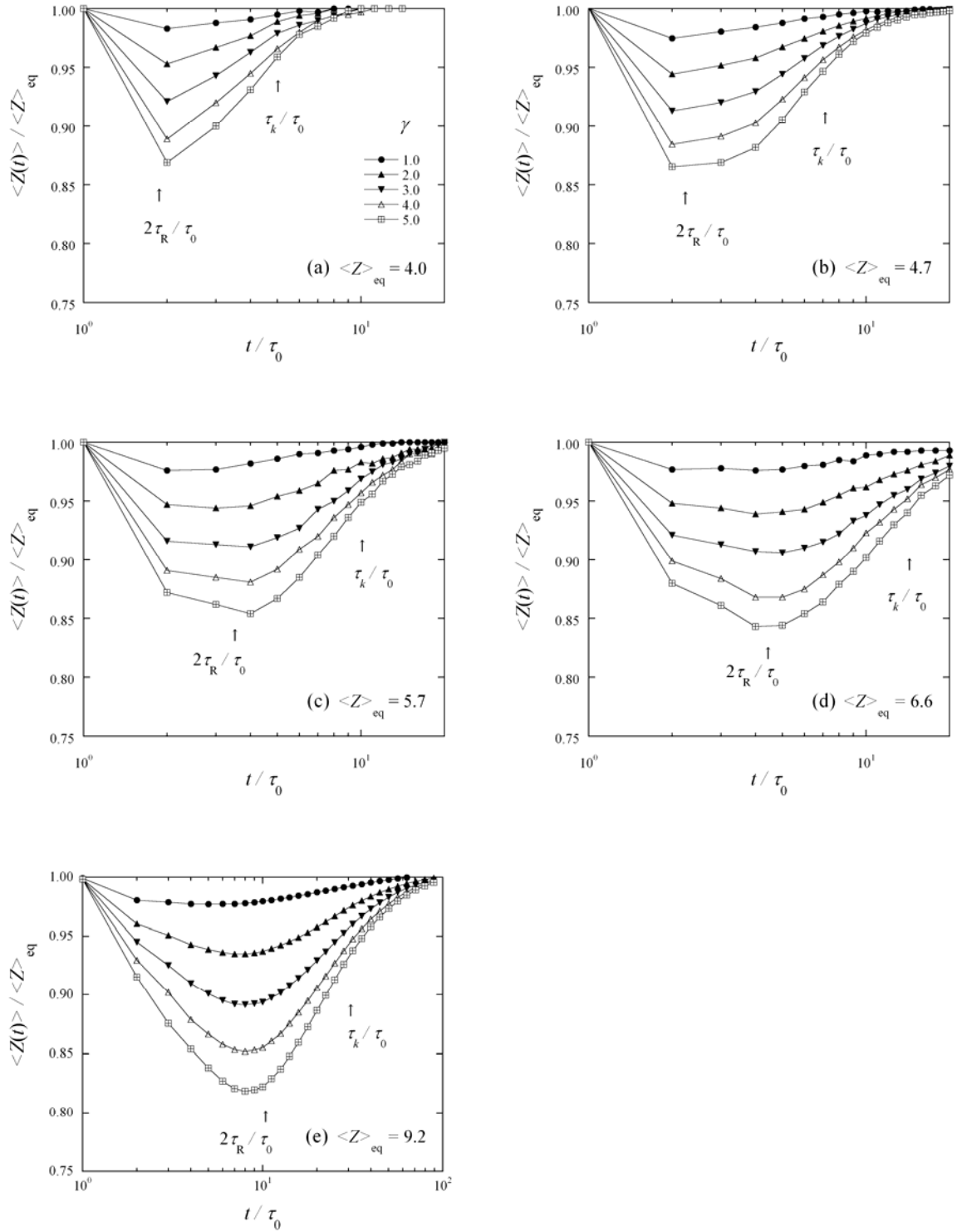


Figure 5-4 Time-evolution of the reduced total sliplink number per chain under step strain for various strains. (a) $\langle Z \rangle_{eq} = 4.0$, (b) $\langle Z \rangle_{eq} = 4.7$, (c) $\langle Z \rangle_{eq} = 5.7$, (d) $\langle Z \rangle_{eq} = 6.6 \sim Z_C^h$, and (e) $\langle Z \rangle_{eq} = 9.2$. Arrows indicate the onset time for the time-strain separability, τ_k , and the minimum of $\langle Z(t) \rangle / \langle Z \rangle_{eq}$ at $t = 2 \tau_R$.

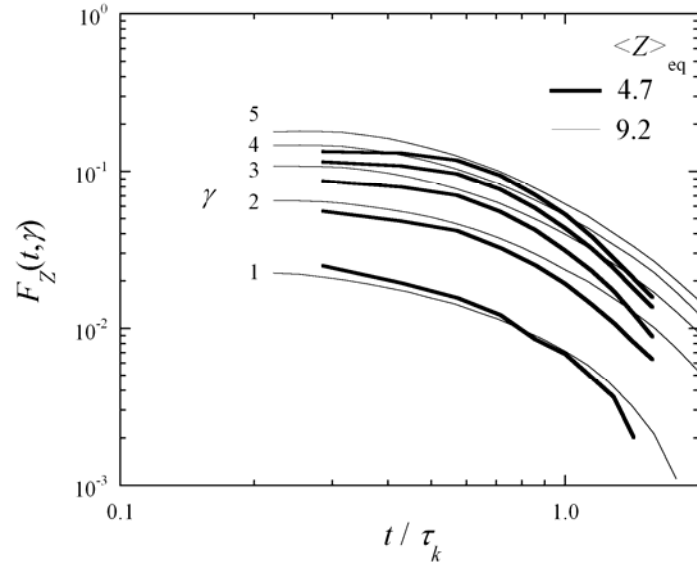


Figure 5-5 Relaxation of total sliplink number per chain for $\langle Z \rangle_{\text{eq}} = 4.7$ (thick curves) and $\langle Z \rangle_{\text{eq}} = 9.2$ (thin curves). Applied strain is $\gamma = 5 \sim 1$ from top to bottom.

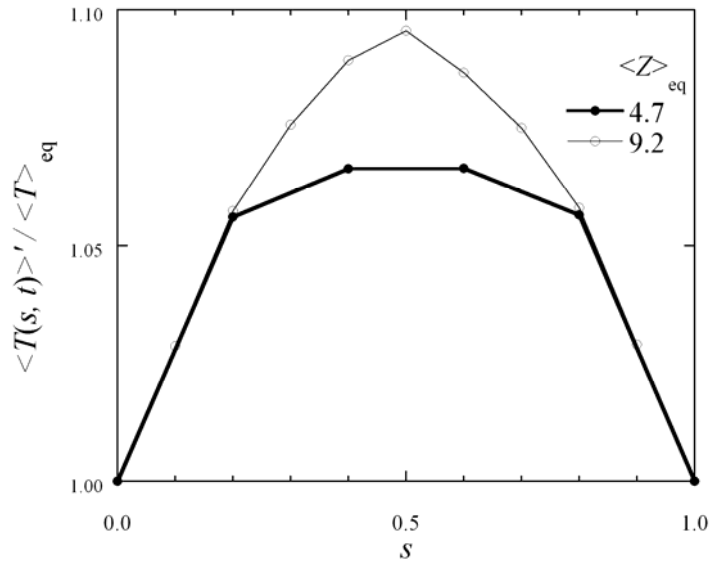


Figure 5-6 Curvilinear distribution of normalized subchain tension under step strain $\gamma = 3$ at $t = \tau_R$ for $\langle Z \rangle_{\text{eq}} = 4.7$ and 9.2 .

5-4. Conclusions

The mechanism realizing the type-B damping behavior was discussed according to the local-CCR and the entanglement network recovery. The molecular weight dependence of recovery process is different between the long and short chains, whereas the local-CCR is essentially common for the long and short chains. For the short chains showing the type-B behavior, the recovery of the total number of sliplink per chain $\langle Z(t) \rangle$ is faster than that for longer chain because of enhanced constraint renewal due to large concentration of end-subchains. This fast recovery process of $\langle Z(t) \rangle$ weakens inhomogeneity of tension along the chain contour (induced by the local-CCR) and reduces the magnitude of damping. The transition from the type-A to type-B behavior can be attributed to the difference of recovering rate of entanglement network structure. In other words, the effect of local-CCR, which induces the distribution of contour variables, becomes less significant with decreasing the chain length below Z_c^h . These results suggest that the molecular weight dependence of $h(\gamma)$ in actual scarcely entangled polymers reflects the fast recovering process of entanglement network.

Appendix 5A. Identification of scarcely entangled regime

The scarcely entangled regime in the PCN simulation was determined from the chain length dependence of zero-shear viscosity η_0 for $Z_0 = M/M_0 = 1 \sim 30$. Figure 5A-1 shows storage and loss moduli, G' and G'' , simulated for the chains of various $\langle Z \rangle_{\text{eq}}$. Only representative results are shown for clarity of the plot. $\langle Z \rangle_{\text{eq}}$ is close but not identical to Z_0 due to the distribution of Z .¹²⁾

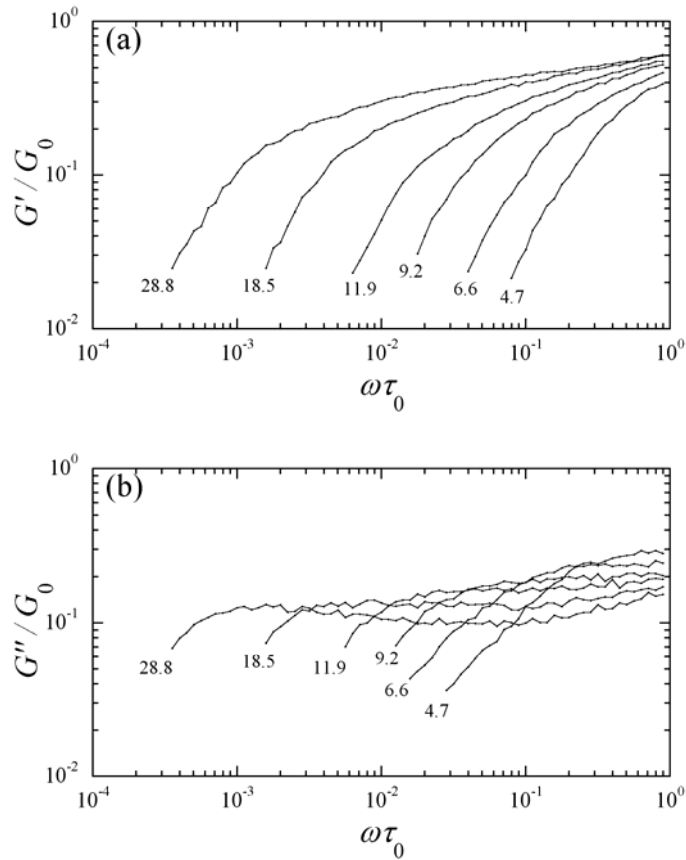


Figure 5A-1 Linear viscoelasticity obtained from the PCN simulation for various chain lengths, $\langle Z \rangle_{\text{eq}} = 4 \sim 30$. (a) Normalized storage modulus G'/G_0 and (b) normalized loss modulus G''/G_0 .

The chain length dependence of zero-shear viscosity η_0 ($= [G''/\omega]_{\omega \rightarrow 0}$) is summarized in Fig. 5A-2. For chains with $\langle Z \rangle_{\text{eq}} > 7$, η_0 is proportional to $\langle Z \rangle_{\text{eq}}^{3.4}$ (thin solid line in Fig. 5A-2), which is attributed to entanglements. Thick solid line and dashed curve shown in Fig. 5A-2 are the continuous and discrete Rouse predictions, respectively.

$$\text{Discrete Rouse} \quad \frac{\eta_0}{G_0 \tau_0} = \frac{1}{12} \left(\langle Z \rangle_{\text{eq}} + \frac{2}{n_0} \right) \quad (5A.1)$$

$$\text{Continuous Rouse} \quad \frac{\eta_0}{G_0 \tau_0} = \frac{1}{12} \langle Z \rangle_{\text{eq}} \quad (5A.2).$$

Some details of the derivations of Eqs. 5A.1 and 5A.2 are given in Appendix 5B. For the discrete Rouse model for PS, $n_0 = M_0 / M_K = 13$ is used, where M_0 ($= 11000$)¹³⁾ is the unit molecular weight in the PCN simulation and M_K ($= 840$)¹⁴⁾ is the molecular weight of the Kuhn segment. (The smallest Rouse segment and Kuhn segment are close in their molecular weights.)¹⁴⁾ On a decrease of $\langle Z \rangle_{\text{eq}} \leq 7$, the simulated η_0 exhibits deviation from the 3.4th power law behavior and approaches the discrete Rouse viscosity. The crossover between the Rouse viscosity and the entanglement viscosity (the 3.4th power law behavior) occurs at $\langle Z \rangle_{\text{eq}} \sim 4$. Thus, the critical molecular weight for η_0 in the PCN simulation can be estimated as $Z_C^\eta \sim 4$. This Z_C^η value is consistent with the fact that the unit molecular weight M_0 of the PCN simulation is ca. 60% of the entanglement molecular weight M_e .^{12), 13)} Because the PCN simulation focuses on entangled polymers, the chains with $\langle Z \rangle_{\text{eq}} < Z_C^\eta$ are not well-defined within this simulation. Nevertheless, the scarcely entangled regime being available in the PCN simulation certainly exists at around $Z_C^\eta \leq \langle Z \rangle_{\text{eq}} < 7$.

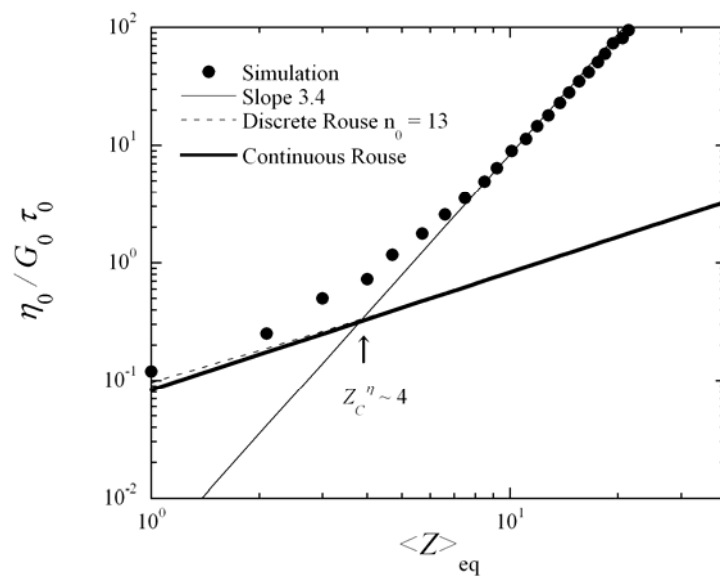


Figure 5A-2 Normalized zero-shear viscosity $\eta_0/G_0\tau_0$ as a function of chain length, $\langle Z \rangle_{eq}$, calculated from the simulated G' and G'' . Thin solid line indicates slope of 3.4. Thick solid line and dashed curve indicate the prediction of continuous and discrete Rouse models, respectively. The critical molecular weight for the transition of scaling exponent, Z_C^η , is indicated by arrow.

Appendix 5B. Zero-shear viscosity of discrete Rouse model

Zero-shear viscosity of the discrete Rouse model with $N + 1$ beads¹⁵⁾ is given by

$$\eta_0 = \nu_{\text{chain}} k_B T \sum_{p=1}^N \tau_p^{[\text{R,G}]} \quad (5\text{B.1})$$

where ν_{chain} is number density of the chain and $\tau_p^{[\text{R,G}]}$ is relaxation time of the p -th Rouse mode:

$$\tau_p^{[\text{R,G}]} = \frac{\zeta_m b^2}{24 k_B T} \sin^{-2} \left\{ \frac{p\pi}{2(N+1)} \right\} \quad (5\text{B.2}).$$

In Eq. 5B.2, ζ_m is the friction coefficient of the Rouse bead, which is related to the sliplink friction as $\zeta = 2 n_0 \zeta_m$ (see Appendix 3B). With the unit time τ_0 and the unit modulus $G_0 = \nu k_B T = \nu_{\text{chain}} n_0 N k_B T$, the normalized zero-shear viscosity is given by^{16), 17)}

$$\frac{\eta_0}{G_0 \tau_0} = \frac{1}{8 n_0 N} \sum_{p=1}^N \sin^{-2} \left\{ \frac{p\pi}{2(N+1)} \right\} = \frac{1}{12} \frac{N+2}{n_0} \quad (5\text{B.3}).$$

Eq. 5A.1 is derived from Eq. 5B.3 with $\langle Z \rangle_{\text{eq}} = N / n_0$. Eq. 5A.2 is obtained from Eq. 5A.1 for $N \gg n_0$.

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Eq. 5B.3 can be expressed as $\sum_{p=1}^N \sin^{-2}\{p\pi / 2(N+1)\} = 2N(N+2)/3$.

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CHAPTER 6

Summary

Following the general introduction (Chapter 1) and the description of theoretical background for primitive chain network (PCN) simulation (Chapter 2), the results and discussion on the simulations for nonlinear stress relaxation are presented in Chapters 3 to 5. The findings in these chapters are summarized below.

In Chapter 3, the contributions of the local-CCR and the elastic force balance to the stress relaxation after large step deformations were investigated. The damping function obtained from simulation was close to that deduced from the three-chain model. This fact suggests that the damping behavior is governed by the local balance of elastic force around the entanglements. The short time dynamics of actual entangled chain is also dominated by the elastic force balance and is not affected by the local-CCR. The local-CCR is slowly activated and has a secondary effect on the damping behavior.

In Chapter 4, the delicate failure of time-strain separability at $t \cong \tau_R$ was investigated in relation to the local-CCR. The local-CCR induces the coupling between the chain contraction and orientational relaxation through the local relaxation of segment. This coupling weakens the tension around the chain center and leads to the retarded validity of time-strain separability (becoming valid at $t \sim \tau_d$). This fact was also supported by the analysis of the relaxation functions for the chain contraction, which are affected by the slow reptative mode.

In Chapter 5, the mechanism of the transition from type-A to type-B damping was investigated in relation to the local-CCR and the entanglement network recovery. The local-CCR is common for the long and short chains. In contrast, the recovery process of entanglement network is different between the long and short chains. For the short chains, the recovery of network structure is

faster than that for the long chains because this recovery is enhanced by rapidly moving subchains at the chain end. This fast recovery reduces inhomogeneity of tension along the chain contour and the nonlinearity (magnitude of damping). Consequently, the transition from the type-A to type-B behavior can be attributed to the difference of recovery rate of entanglement network.

List of publications

I. Publications included in this thesis

1. Entangled polymer orientation and stretch under large step shear deformations in primitive chain network simulations

Kenji Furuichi, Chisato Nonomura, Yuichi Masubuchi, Hiroshi Watanabe,

Giovanni Ianniruberto, Francesco Greco, Giuseppe Marrucci

Rheologica Acta, 47, 591 (2008).

2. Primitive chain network simulations of damping functions for shear, uniaxial, biaxial and planar deformations

Kenji Furuichi, Chisato Nonomura, Yuichi Masubuchi, Giovanni Ianniruberto,

Francesco Greco, Giuseppe Marrucci

Nihon Reoroji Gakkaishi (J. Soc. Rheol., Jpn.), 35, 73 (2007).

3. Chain contraction and nonlinear stress damping in primitive chain network simulations

Kenji Furuichi, Chisato Nonomura, Yuichi Masubuchi, Hiroshi Watanabe

Journal of Chemical Physics, 133, 174902 (2010).

4. Nonlinear stress relaxation of scarcely entangled chains in primitive chain network simulations

Kenji Furuichi, Chisato Nonomura, Yuichi Masubuchi, Hiroshi Watanabe

Nihon Reoroji Gakkaishi (J. Soc. Rheol., Jpn.), 41, 13 (2013).

II. Other related publication

1. Primitive chain network simulations for entangled DNA solutions

Yuichi Masubuchi, Kenji Furuichi, Kazushi Horio, Takashi Uneyama, Hiroshi Watanabe,

Giovanni Ianniruberto, Francesco Greco, Giuseppe Marrucci

Journal of Chemical Physics, 131, 114906 (2009).

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March 2013

Kenji Furuichi