Transient Conformational Change of Bead−Spring Ring Chain during Creep Process

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ABSTRACT: The bead−spring model is the fundamental model in the field of polymer physics, but its conformational dynamics under stress-controlled conditions had not been analyzed so far. For completeness of the model, this dynamics was recently analyzed for linear and star bead−spring chains during the creep process under a constant stress. In this paper, the analysis is extended to the bead−spring ring chain having no free end. Since all segments of the ring chain are equivalent (due to the lack of the chain end) and the orientational anisotropy summed over these segments corresponds to the stress (stress−optical rule), the segments have the same, time-independent anisotropy throughout the creep process. In other words, no retardation occurs for the segment anisotropy. However, the ring chain exhibits the retarded creep behavior (delay in achieving the steady flow state), as similar to the behavior of the linear chain. The analysis of the conformational dynamics reveals that this retardation of the ring corresponds to growth of the orientational correlation between different segments with time. The analysis also indicates a difference between the ring and linear chains that the ring segments have either positive or negative correlations depending on their separation along the chain backbone while the correlation is always positive for the segments of the linear chain.

1. Introduction

The bead−spring model of the flexible chains is the very important, fundamental model of polymer dynamics and has been widely utilized so far.[1−5] The dynamics of the bead−spring chains of various topological structure under the *strain-controlled* condition such as the rate-controlled flow has been fully analyzed in the literature,[1−9] and the corresponding linear viscoelastic properties (such as the relaxation modulus) have been formulated with no ambiguity.[1−5]

Nevertheless, no conformational analysis was made in the literature for the dynamics of the bead−spring chains under the *stress-controlled* condition. This lack of the analysis was quite surprising to the current authors when they thought about the fundamental importance of the bead−spring model. Thus, for completeness of the model, they recently made this analysis for monodisperse systems and blends of linear chains[10−14] (Rouse chains) as well as for monodisperse systems of star chains[15] (Rouse−Ham chains), both in the absence of hydrodynamic interaction. The analysis indicated that the eigenmodes of different orders defined for the position of the chain segments, being independent under the strain-controlled condition, have correlated amplitudes during the stress-controlled creep process.[10,12,14,15] The correlation also emerges for long and short chain components in the blends during the creep process.[13] These correlations naturally result from the constant-stress requirement that forces the orientational anisotropy summed over all segments to be kept constant during the creep process. Furthermore, the analysis gave an analytic expression of the creep compliance as a byproduct.[10−15]

The above analysis also revealed that the linear and star bead−spring chains have a uniform distribution of the orientational anisotropy along the chain backbone (corresponding to the affine deformation) on sudden imposition of a stress at the onset of creep.[11,14,15] During the creep process, the anisotropies of the segments near and far from the chain end decrease and increase, respectively, thereby achieving a nonuniform anisotropy distribution in the steady flow state. This transient change in the anisotropy distribution (partly) contributes to the retardation in achieving the steady flow state described by the creep compliance.

The above change in the anisotropy distribution occurs because the segments near the chain end can relax more quickly compared to the segments far from the end and the former segments compensate for a delay in the anisotropy growth for the latter. In relation to this point, we expect an interesting feature for a bead−spring *ring* chain: Since all segments of the ring chain are equivalent, we note, even without any detailed analysis, that the anisotropies of these segments should be the same and time-independent during the creep process. At the same time, the creep compliance of the ring chain is similar to that of the linear chain and exhibits the retardation. Thus, we naturally ask a question: How does this retardation emerge under the time-independent, uniform distribution of the orientational anisotropy of the segments?

We have addressed this interesting question by solving the equation of motion for the bead−spring ring chain and making a full analysis of the orientational correlation of the ring segments. The analysis indicates that the retardation seen for the creep compliance reflects a growth of this correlation with time (while keeping the same anisotropy for respective segments). Details of these results are presented in this paper.

2. Results

2.1. The Model. We consider a monodisperse system of bead−spring ring chains. No hydrodynamic interaction is considered and thus our system corresponds to melts of low molecular weight, nonentangled chains. Each chain is composed of N segments having the friction coefficient ζ. Neighboring segments are connected with the Gaussian spring of the equilibrium length a and spring constant $\kappa = 3k_BT/a^2$, with k_B = Boltzmann constant, T = absolute temperature. We consider

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the continuous limit for $N \to \infty$ where the analysis of the conformational dynamics is greatly simplified. (In this limit, we can neglect a difference between N and N-1 whenever necessary.)

We arbitrarily choose a segment in the chain and assign it as zeroth segment. Then, we can specify the remaining segments of the ring with the segment index n running from 1 to N, where the Nth segment is identical to the zeroth segment. The orientational correlation of two segments under a shear field is quantified by an isochronal orientational correlation function defined by

$$S_2(n,n',t) \equiv \frac{1}{a^2}\langle u_x(n,t)u_y(n',t)\rangle \quad \text{with} \quad u_\xi(n,t) = \frac{\partial r_\xi(n,t)}{\partial n} \tag{1}$$

Here, $r_\xi(n,t)$ and $u_\xi(n,t)$ are the ξ components ($\xi = x, y$) of the spatial position $\mathbf{r}(n,t)$ and bond vector $\mathbf{u}(n,t)$ ($= \partial\mathbf{r}/\partial n$ in the continuous treatment) of the nth segment at time t, and $\langle\cdots\rangle$ represents an average over all chains in the system. In eq 1 and hereafter, the shear and shear gradient directions are chosen to be the x- and y-directions, respectively. Note that the expression of $S_2(n,n',t)$ derived later (eqs 22 and 25) is independent of our choice of the zeroth segment and has a generality.

The orientational anisotropy of respective segments is described by an orientation function

$$S(n,t) = S_2(n,n,t) = \frac{1}{a^2}\langle u_x(n,t)u_y(n,t)\rangle \tag{2}$$

The stress−optical rule, generally valid for slow viscoelastic processes of uniform polymeric liquids,[16] allows us to relate the shear stress of the ring chain system at time t to this $S(n,t)$ as[3−5]

$$\sigma(t) = 3\nu k_B T\int_0^N S(n,t)\,dn \tag{3}$$

Here, ν is the number density of the chains in the system.

The time evolution of $S_2(n,n',t)$ and $S(n,t)$ is determined by the equation of motion of the chain. In the continuous treatment, this equation is written as[3−5]

$$\zeta\left\{\frac{\partial\mathbf{r}(n,t)}{\partial t} - \mathbf{V}(\mathbf{r}(n,t))\right\} = \kappa\frac{\partial^2\mathbf{r}(n,t)}{\partial n^2} + \mathbf{F}(n,t) \tag{4}$$

Here, κ is the spring constant, and $\mathbf{F}(n,t)$ is the Brownian force acting on nth segment at time t: $\mathbf{F}(n,t)$ is modeled as a white noise characterized with the dyadic average[3]

$$\langle\mathbf{F}(n,t)\mathbf{F}(n',t')\rangle = 2\zeta k_B T\delta(n-n')\delta(t-t')\mathbf{I} \quad \text{with} \quad \mathbf{I} = \text{unit tensor} \tag{5}$$

The $\mathbf{V}(\mathbf{r}(n,t))$ term appearing in eq 4 indicates the flow velocity of the frictional medium for the chain motion at the position $\mathbf{r}(n,t)$. In the linear viscoelastic regime of our interest, the shear field is uniform in the system and $\mathbf{V}(\mathbf{r}(n,t))$ can be written, in terms of the strain rate $\dot\gamma(t)$ at time t, as[4]

$$\mathbf{V}(\mathbf{r}(n,t)) = \begin{pmatrix}\dot\gamma(t)r_y(n,t)\\ 0\\ 0\end{pmatrix} \tag{6}$$

2.2. Eigenmode Analysis. The position of the ring segment, $\mathbf{r}(n,t)$, should be a continuous and smooth function of n and thus satisfy the boundary condition,[9]

$$\mathbf{r}(0,t) = \mathbf{r}(N,t),\ \left[\frac{\partial\mathbf{r}(n,t)}{\partial n}\right]_{n=0} = \left[\frac{\partial\mathbf{r}(n,t)}{\partial n}\right]_{n=N} \tag{7}$$

Considering this condition, we can expand $\mathbf{r}(n,t)$ with respect to the sine and cosine eigenfunctions associated with eq 4:[9]

$$\mathbf{r}(n,t) = \sum_{p=1}^{N/2}\mathbf{B}_S(t;p)\sin\left(\frac{2p\pi n}{N}\right) + \sum_{p=0}^{N/2}\mathbf{B}_C(t;p)\cos\left(\frac{2p\pi n}{N}\right) \tag{8}$$

Here, $\mathbf{B}_\xi(t;p)$ with ξ = S and C represent the stochastic amplitude vectors of the pth order sine and cosine eigenmodes at time t. In eq 8, the upper limit of the summation of the mode index p is set to be $N/2$ so that the total number of modes coincides with the number of segments. However, in the continuous treatment for $N \to \infty$, this factor of $N/2$ can be replaced by ∞ in most of the calculation steps explained below.

As noted from eqs 1 and 8, the orientational correlation function $S_2(n,n',t)$ is expressed in terms of the xy component of the dyadic averages of the eigenmode amplitudes, $\langle\mathbf{BB}\rangle_{xy}$. These averages can be calculated from the equation of motion (eq 4) rewritten for $\mathbf{B}_\xi$:

$$\dot{\mathbf{B}}_\xi(t;p) = -\frac{p^2}{2\tau_{\text{ring}}}\mathbf{B}_\xi(t;p) + \begin{pmatrix}\dot\gamma(t)Y_\xi(t;p)\\ 0\\ 0\end{pmatrix} + \frac{1}{\zeta}\hat{\mathbf{F}}_\xi(t;p) \quad \text{with} \quad \xi = \text{S, C}\ (p = 1, 2, ...) \tag{9}$$

where $\dot{\mathbf{B}}_\xi(t;p)$ is the time derivative of $\mathbf{B}_\xi(t;p)$, $Y_\xi(t;p)$ represents the y component of $\mathbf{B}_\xi(t;p)$, and τ_{ring} denotes the longest viscoelastic relaxation time of the bead−spring ring chain:

$$\tau_{\text{ring}} = \frac{\zeta}{2\kappa}\left(\frac{N}{2\pi}\right)^2 = \frac{\zeta a^2N^2}{24\pi^2k_BT} \tag{10}$$

In eq 9, $\hat{\mathbf{F}}_\xi(t;p)$ with ξ = S and C represent the pth order sine− and cosine−Fourier components of the Brownian force defined by

$$\hat{\mathbf{F}}_S(t;p) = \frac{2}{N}\int_0^N dn\,\mathbf{F}(n,t)\sin\left(\frac{2p\pi n}{N}\right) \quad (p = 1, 2,...) \tag{11}$$

$$\hat{\mathbf{F}}_C(t;p) = \frac{2}{N}\int_0^N dn\mathbf{F}(n,t)\cos\left(\frac{2p\pi n}{N}\right) \quad (p = 1, 2, ...) \tag{12}$$

Equation 9 is formally identical to the time evolution equation for the eigenmode amplitudes of the linear chain and can be solved with the standard method.[10,14,15] Specifically, from eqs 5 and 9, we find that the x and y components of $\mathbf{B}_\xi$, designated by X_ξ and Y_ξ, have the averages given by

$$\langle X_\xi(t;p)Y_{\xi'}(t;q)\rangle = \delta_{\xi\xi'}\delta_{pq}\left(\frac{a^2N}{6\pi^2p^2}\right)\int_0^t dt\,\dot\gamma(t')\exp\left(-\frac{p^2(t-t')}{\tau_{\text{ring}}}\right) \quad (p, q = 1, 2, ...) \tag{13}$$

In derivation of eq 13, we have utilized the dyadic averages at equilibrium, $\langle\mathbf{B}_\xi(p)\mathbf{B}_{\xi'}(q)\rangle^{\text{eq}} = \delta_{\xi\xi'}\delta_{pq}a^2N\mathbf{I}/6\pi^2p^2$ with $\mathbf{I}$ = unit tensor. (This $\langle\mathbf{BB}\rangle^{\text{eq}}$ is calculated from the equilibrium distribution function,[3,5,15,17] $\Psi(\{\mathbf{B}\}) \propto \exp(-E/k_BT)$ with E = elastic free energy = $(\kappa/2)\int_0^N \{\partial\mathbf{r}/\partial n\}^2\,dn$.)

2.3. Calculation of $S_2(n,n',t)$. From eqs 1, 8, and 13, we find a compact equation that determines the isochronal orientational correlation function:

$$S_2(n,n',t) = \frac{2}{3N}\int_0^t dt'\,\dot\gamma(t')g_2(n,n',t-t') \tag{14}$$

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Table 1. Low Order Eigenvalues for Creep Process of Bead−Spring Ring Chain

p	1	2	3	4	5
θ_p/π	1.430	2.459	3.471	4.477	5.482

with

$$g_2(n,n',t) = \sum_{p=1}^{N/2} \exp\left(-\frac{p^2 t}{\tau_{\rm ring}}\right)\cos\left(\frac{2p\pi(n-n')}{N}\right) \quad (15)$$

For the strain-controlled processes, $\dot\gamma(t)$ is known and eq 14 straightforwardly gives $S_2(n,n',t)$.[18] However, for the stress-controlled creep process, $\dot\gamma(t)$ is not known in advance but self-consistently determined in a way that the stress sustained by the chains always coincides with the applied stress σ_0. As noted from eqs 1−3 and eqs 14 and 15, this constant-stress requirement gives an equation that determines $\dot\gamma(t)$ for the ring system[19]

$$\sigma_0 = 2\nu k_B T\int_0^t {\rm d}t'\,\dot\gamma(t')\left\{\sum_{p=1}^{\infty}\exp\left(-\frac{p^2(t-t')}{\tau_{\rm ring}}\right)\right\} \quad (16)$$

(In eq 16, we have made the continuous treatment to set the upper limit of the summation of p to ∞, instead of $N/2$.) This equation can be solved with the previously utilized Laplace transformation method[4,14,15] that is briefly summarized in Appendix A. The results can be conveniently written in the form of the creep compliance $J(t)$:

$$J(t) \equiv \frac{\gamma(t)}{\sigma_0} = \frac{t}{\eta_0^{\rm ring}} + \frac{2}{\nu k_B T}\sum_{q=1}^{\infty}\frac{1}{\theta_q^{\,2}}\left\{1-\exp\left(-\frac{t}{\lambda_q^{\rm ring}}\right)\right\} \quad (17)$$

with

$$\eta_0^{\rm ring} = \frac{\nu k_B T\pi^2\tau_{\rm ring}}{3} \quad \text{(zero-shear viscosity of ring)} \quad (18)$$

and

$$\lambda_q^{\rm ring} = \frac{\pi^2\tau_{\rm ring}}{\theta_q^{\,2}} \quad \text{(qth retardation time of ring)} \quad (19)$$

The factor θ_q appearing in eqs 17 and 19 is the qth eigenvalue for the creep process determined from

$$\tan\theta_q = \theta_q \quad (q = 1, 2, ...; \pi < \theta_1 < \theta_2 < ...) \quad (20)$$

(The θ_q values for low order eigenmodes are summarized in Table 1.) These θ_q are identical to those for the linear chain and satisfy the summation rules[4,14,15] (cf. Appendices A and B),

$$\sum_{q=1}^{\infty}\frac{1}{\theta_q^{\,2}} = \frac{1}{10}, \quad \sum_{q=1}^{\infty}\frac{1}{p^2-\theta_q^{\,2}/\pi^2} = -\frac{3}{2\pi^2} \quad (p = \text{integer}) \quad (21)$$

Substituting the strain rate $\dot\gamma(t) = \sigma_0\dot J(t)$ specified by eq 17 into eq 14, we can calculate the orientational correlation function of the ring chain with the method explained in Appendix B. The results are summarized as

$$S_2(n,n',t) = \frac{\sigma_0}{\nu N k_B T}\left\{Q_0(n,n') + \sum_{q=1}^{\infty}Q_q(n,n')\exp\left(-\frac{t}{\lambda_q^{\rm ring}}\right)\right\} \quad (22)$$

with

$$Q_0(n,n') = \frac{1}{2}\left\{1-\frac{2|n-n'|}{N}\right\}^2 - \frac{1}{6} \quad (23)$$

and

$$Q_q(n,n') = \frac{2}{3\theta_q^{\,2}}\left\{1-\frac{\cos\theta_q\left(1-\dfrac{2|n-n'|}{N}\right)}{\cos\theta_q}\right\} \quad (24)$$

An equivalent expression of $S_2(n,n',t)$ can be obtained from Fourier analysis of the right-hand side of eq 22 (cf. Appendix B),

$$S_2(n,n',t) = \frac{\sigma_0}{\nu N k_B T}\sum_{p=1}^{\infty}A_p(t)\cos\left(\frac{2p\pi(n-n')}{N}\right) \quad (25)$$

with

$$A_p(t) = \frac{2}{p^2\pi^2} + \frac{4}{3\pi^2}\sum_{q=1}^{\infty}\frac{1}{p^2-\theta_q^{\,2}/\pi^2}\exp\left(-\frac{t}{\lambda_q^{\rm ring}}\right) \quad (p = 1, 2, ...) \quad (26)$$

This $A_p(t)$ is identical to the normalized anisotropy of the pth eigenmode amplitude common to sine and cosine eigenmodes; $A_p(t) \equiv \{4\nu k_B T p^2\pi^2/a^2 N\sigma_0\}\,\langle X_\xi(t;p)Y_\xi(t;p)\rangle$ with ξ = S and C. Equation 26 indicates that $A_p(t)$ is associated with infinite number of characteristic times $\lambda_q^{\rm ring}$ because of the correlation of the eigenmodes due to the constant-stress requirement during the creep process.

For the bead−spring linear chain (Rouse chain) composed of N segments, the orientational correlation function $S_2^{\rm lin}(n,n',t)$ is also defined by eq 1, with n, $n' = 0$ and N indexing the segments at the chain ends. For convenience of comparison with the ring chain, we have calculated $S_2^{\rm lin}(n,n',t)$ in a way similar to that for the ring chain. The results are summarized in Appendix C.

3. Discussion

3.1. Conformational Behavior of Ring Chain. As noted from eqs 22 and 25, the orientational correlation function $S_2(n,n',t)$ of the ring chain is not separately dependent on n and n' but only on an interval between the indices of the two segments, $\Delta n = n - n'$ (more accurately, on $|\Delta n|$). This result means that the expression of $S_2(n,n',t)$ given by eqs 22 and 25 is a general expression not affected by our arbitrary choice of the zeroth segment.

Figure 1 shows plots of the normalized correlation function, $S_2^\circ(n,n',t) \equiv \{\nu N k_B T/\sigma_0\}\,S_2(n,n',t)$, against the normalized time, $t/\lambda_1^{\rm ring}$. The numbers indicate the segment interval Δn. We first note that the normalized orientation function $S^\circ(n,t)$ ($\Delta n = 0$; thick curve) does not change with t. In fact, $S^\circ(n,t)$ is dependent on neither t nor n and has a value of $^1/_3$ (cf. eq 22−24 with $n = n'$), confirming that all segments of the ring chain are equivalent and have the same orientational anisotropy. We also note that different segments have no orientational correlation at short times ($S_2^\circ(n,n',t) = 0$ for $n \neq n'$ at $t \to 0$) but the correlation represented by nonzero $S_2^\circ(n,n',t)$ grows with increasing t; see thin curves. Thus, the ring chain exhibits a transient conformational change during the creep process even though the anisotropies of respective segments ($S^\circ(n,t)$) are kept

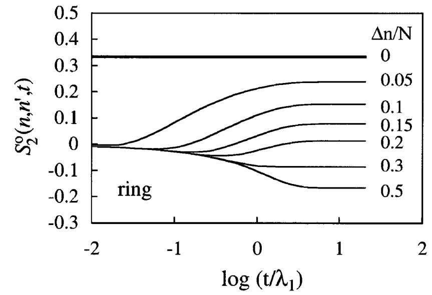

Figure 1. Time evolution of the normalized, isochronal orientational correlation function $S_2^\circ(n,n',t)$ for the bead−spring ring chain during the creep process. The numbers indicate the interval of the segment induces, $\Delta n = n - n'$. $S_2^\circ(n,n',t)$ with $\Delta n = 0$ (thick curve) is identical to the normalized orientation function $S^\circ(n,t)$.

constant in this process. This conformational change results in the retardation behavior seen for the creep compliance $J(t)$ (eq 17).

Here, we examine some details of this transient conformational change. At equilibrium just before the onset of creep, the bond vectors $\mathbf{u}(n,t)$ of the chain segments have the isotropic orientation characterized with a dyadic average[3,5] $\langle \mathbf{u}^{eq}(n)\mathbf{u}^{eq}(n')\rangle = \{a^2/3\}\ \mathbf{I}\delta_{nn'}$. If an affine shear deformation of a magnitude γ_a (represented by a displacement tensor $\mathbf{D}$) is applied to these bond vectors, the dyadic average becomes

$$\langle \mathbf{u}(n)\mathbf{u}(n')\rangle = \langle\{\mathbf{D}\cdot\mathbf{u}^{eq}(n)\}\ \{\mathbf{D}\cdot\mathbf{u}^{eq}(n')\}\rangle = \frac{a^2}{3}\delta_{nn'}\begin{pmatrix}1+{\gamma_a}^2 & \gamma_a & 0\\ \gamma_a & 1 & 0\\ 0 & 0 & 1\end{pmatrix} \quad (27)$$

The correlation function corresponding to the *xy* component of this $\langle \mathbf{u}(n)\mathbf{u}(n')\rangle$ is given by $S_2 = \gamma_a\delta_{nn'}/3$ (cf. eq 1). Thus, the nonnormalized correlation function of the ring chain at $t \rightarrow 0$, $S_2 = \{\sigma_0/\nu Nk_BT\}S_2^\circ = \{\sigma_0/\nu Nk_BT\}\delta_{nn'}/3$ (cf. Figure 1), coincides with that for the affine deformation of the magnitude $\gamma_a = \sigma_0/G(0)$, with $G(0) = \nu Nk_BT$ being the initial modulus of the ring chain system.[18] This affine deformation requires no relaxational motion of the chain thereby enabling the chain to instantaneously respond to the applied stress σ_0.[11,14,15] At $t > 0$, the chain exhibits this motion to change its conformation to the nonaffine conformation having the orientational correlation of different segments. Thus, the transient conformational change seen in Figure 1 can be classified as a change from the affine to the nonaffine state.

For the ring chain, this conformational change is associated with no change in the orientational anisotropies of *respective* segments ($S^\circ(n,t)$ = constant; cf. Figure 1). However, the same conformational change induces a change in the anisotropy for a larger portion of the chain (and leads to the retardation behavior of $J(t)$). As an example, we focus on the anisotropy for an end-to-end vector of a half portion of the ring chain backbone, $\Delta\mathbf{r}(t) = \mathbf{r}(N/2,t) - \mathbf{r}(0,t)$. The orientation function quantifying this anisotropy is calculated from $S_2(n,n',t)$ as

$$S_{\Delta\mathbf{r}}(t) \equiv \frac{1}{\langle\Delta\mathbf{r}^2\rangle^{eq}}\langle\Delta r_x(t)\Delta r_y(t)\rangle = \frac{4}{N}\int_0^{N/2} dn\int_0^{N/2} dn' S_2(n,n',t) \quad (28)$$

Here, $\langle\Delta\mathbf{r}^2\rangle^{eq}$ $(= Na^2/4)$[17] is the mean square end-to-end distance of this portion at equilibrium. In Figure 2, the normalized orientation function, $S_{\Delta\mathbf{r}}^\circ(t) \equiv \{\nu k_BT/\sigma_0\}\ S_{\Delta\mathbf{r}}(t)$ calculated with the aid of eqs 22 and 25, is shown with the solid curve. This $S_{\Delta\mathbf{r}}^\circ(t)$ increases with t, confirming the growth of the orientational anisotropy of the half portion of the chain (larger than the segment). This increase is exclusively due to the growth of the correlation between segments, as easily noted from a discrete expression of the orientation function, $S_{\Delta\mathbf{r}}(t) = \{4/N\}\ \Sigma_n S(n,t) + \{4/N\}\ \Sigma_{n,n'\neq n} S_2(n,n',t)$ with $S(n,t)$ = constant for the ring chain.

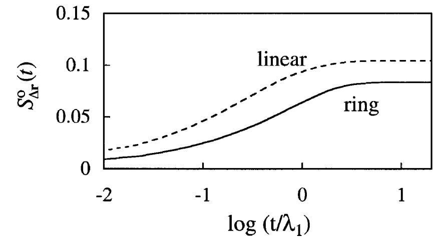

Figure 2. Time evolution of the normalized orientation function $S_2^\circ(t)$ for the half portion of the backbone of the bead−spring ring and linear chains during the creep process.

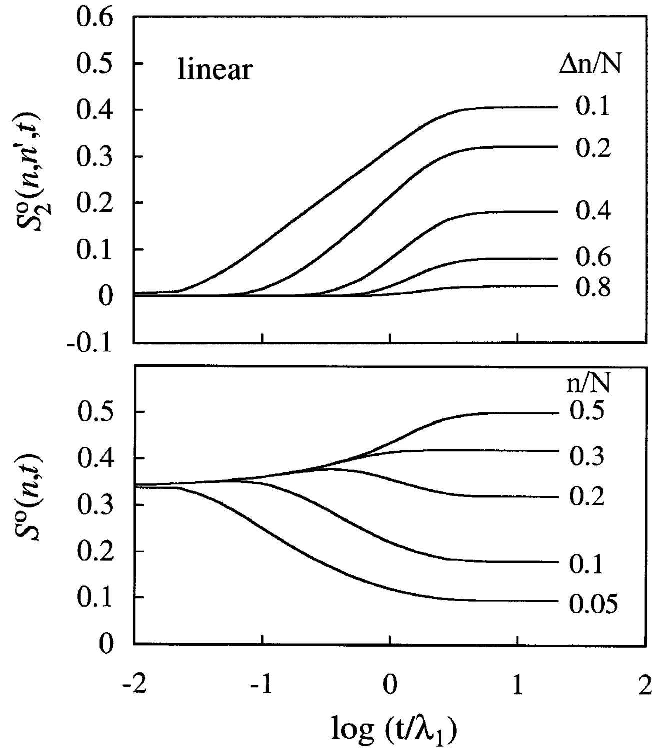

Figure 3. Time evolution of the normalized, isochronal orientational correlation function $S_2^\circ(n,n',t)$ (top panel) and normalized orientation function $S^\circ(n,t)$ $(=S_2^\circ(n,n,t)$; bottom panel) for the bead−spring linear chain during the creep process. For $S_2^\circ(n,n',t)$, *n*th and *n*′th segments are located symmetrically with respect to the chain center ($n = N/2 + \Delta n/2$ and $n' = N/2 - \Delta n/2$), and the interval of the segment indices, $\Delta n = n - n'$, is increased from $0.1N$ to $0.8N$.

3.2. Similarities/Differences between Ring and Linear Chains. Now, we focus on similarities/differences between the ring and linear chains. For the linear chain composed of N segments, the expression of $S_2(n,n',t)$ is given in Appendix C. The corresponding normalized correlation function, $S_2^\circ(n,n',t) \equiv \{\nu Nk_BT/\sigma_0\}\ S_2(n,n',t)$ is shown in the top panel of Figure 3: The *n*th and *n*′th segments are located symmetrically with respect to the chain center ($n = N/2 + \Delta n/2$ and $n' = N/2 - \Delta n/2$), and their interval Δn is varied from $0.1N$ to $0.8N$. The bottom panel shows the normalized orientation function $S^\circ(n,t) \equiv \{\nu Nk_BT/\sigma_0\}\ S_2(n,n,t)$ for the n values as indicated. The normalized anisotropy of the end-to-end vector $\Delta\mathbf{r}(t) = \mathbf{r}(N/2,t) - \mathbf{r}(0,t)$ of the half portion of the linear chain, $S_{\Delta\mathbf{r}}^\circ(t) \equiv \{\nu k_BT/\sigma_0\}\ \langle\Delta r_x(t)\Delta r_y(t)\rangle/\langle\Delta\mathbf{r}^2\rangle^{eq}$ with $\langle\Delta\mathbf{r}^2\rangle^{eq} = Na^2/2$ for this portion, is shown in Figure 2 with the dotted curve. (This

$S^{\circ}_{\Delta\mathbf{r}}(t)$ is calculated from $S_2(n,n',t)$ of the linear chain through an equation similar to eq 28.)

Figure 3 demonstrates that at $t \to 0$ $S^{\circ}_2(n,n',t) = 0$ for $n \neq n'$ and $S^{\circ}(n,t) = {}^1/_3$ irrespective of the n value. This short time behavior of the linear chain, corresponding to the affine deformation against the applied stress, is identical to that of the ring chain. In addition, the orientational correlation of the segments (top panel of Figure 3) and the anisotropy of the half portion of the chain[22] (Figure 2) grow with t. These features of the linear chain are qualitatively similar to those of the ring chain.

However, we also note an important difference: For the ring chain, $S^{\circ}(n,t)$ is independent of n and t throughout the creep process (Figure 2) because of the equivalence of all segments therein. In contrast, for the linear chain, $S^{\circ}(n,t)$ at $n \cong N/2$ monotonically increases from the affine value of 1/3 to the steady-state value ($>{}^1/_3$), while $S^{\circ}(n,t)$ at n well bellow $N/2$ exhibits a overshoot and then decreases to its steady-state value ($<{}^1/_3$), and the magnitude of this overshoot is reduced as n approaches 0; see bottom panel of Figure 3. This behavior of the linear chain reflects the nonequivalence of its segments: The relaxation can occur more quickly and the steady-state orientation is smaller for the segment closer to the chain end. Thus, under the constant-stress requirement, the segments near the chain end compensate for a delay in the anisotropy growth at around the chain center and approach the steady state together with the segments near the center. This compensation results in the overshoot and decrease of $S^{\circ}(n,t)$ explained above.

The other type of difference is noted for the orientational correlation of the segments specified by $S^{\circ}_2(n,n',t)$ with $\Delta n = n-n' > 0$. For the ring chain, $S^{\circ}_2(n,n',t)$ exhibits the transient increase and decrease from the initial value ($= 0$) for $\Delta n \cong 0$ and $N/2$, respectively, and its steady-state value can be either positive or negative according to the Δn value; cf. Figure 1. In contrast, for the linear chain, $S^{\circ}_2(n,n',t)$ is positive for all Δn values at $t > 0$; cf. top panel of Figure 3.[23]

The behavior of the ring chain is a natural consequence of the lack of the chain end: This lack gives a constraint for the segment bond vectors, $\Sigma_{n'=0}{}^N\mathbf{u}(n',t) = \mathbf{0}$, which results in a zero-sum rule, $\Sigma_{n'=0}{}^N\langle\mathbf{u}(n,t)\mathbf{u}(n',t)\rangle_{xy} = a^2\Sigma_{n'=0}{}^N S_2(n,n',t) = 0$. Since $S(n,t)$ ($= S_2(n,n,t)$) is positive for all ring segments during the creep process and the chain connectivity requires neighboring segments (with small Δn) to have positive $S_2(n,n',t)$ close to this $S(n,t)$, the segments far apart along the ring backbone ($\Delta n \cong N/2$) are forced to have negative $S_2(n,n',t)$ to satisfy the zero-sum rule. In contrast, the segments of the linear chains are not subjected to this rule and tend to be oriented in the same direction to have the positive $S_2(n,n',t)$ during the creep process. For this case, an increase of Δn just results in a decrease of $S_2(n,n',t)$ to zero.

4. Concluding Remarks

We have solved the equation of motion for the bead−spring ring chain to analyze its conformational dynamics during the creep process. Since all segments of this chain are equivalent, the orientational anisotropy during this process is the same for all segments and independent of time. In other words, no retardation occurs for the segment anisotropy. However, the ring chain exhibits retardation behavior in its creep strain. The conformational analysis indicated that this retardation of the ring chain corresponds to growth of the orientational correlation of different segments with time.

This correlation was found to be different for the ring and linear chains. For the ring chain, the two segments near and far along the chain backbone have positive and negative correlations, respectively, while any two segments of the linear chain have the positive correlation. This difference is a natural consequence of the lack of the end for the ring chain.

McKenna et al.[24] reported the zero-shear viscosity data of ring and linear polystyrenes (PS) melts in a wide range of the molecular weight M. The viscosity ratio r_η of nonentangled ring and linear PS of the same M evaluated from their data is close to the ratio deduced from the bead−spring model, $r_\eta = \eta_0^{\text{ring}}/\eta_0^{\text{linear}} = 1/2$ at the iso-segmental friction state (cf. eqs 10, 18, C1, and C3). Thus, this model seems to work for the linear and ring PS chains in the nonentangled regime.[25] However, we should note that the viscosity (and other viscoelastic properties such as the dynamic modulus) just corresponds to the orientational anisotropy *averaged over all segments* and thus the details of the bead−spring model (motion of *respective* segments) have not been verified even for the ring and linear PS. It is of interest to rheooptically examine if the low-M ring and linear polymers exhibit the detailed conformational features deduced from the current analysis. This test, to be made for partially labeled polymers to detect the dynamics of respective segments, is considered as an important subject of future work.

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APPENDIX A. Calculation of Creep Compliance of Ring Chain

For calculation of the strain $\gamma(t)$ during the creep process of the ring chain, we can focus on the Laplace transformation of $\gamma(t)$, $\Gamma(s) \equiv \int_0^\infty \gamma(t)\exp(-st)\,dt$. Considering the initial condition $\gamma(0) = 0$ (no strain just before the onset of creep) and making the Laplace transformation for both sides of eq 16, we find

$$\frac{\sigma_0}{s} = 2\nu k_B T\left\{\sum_{p=1}^{\infty}\frac{1}{s + p^2/\tau_{\text{ring}}}\right\}s\Gamma(s) \qquad \text{(A1)}$$

With the aid of the mathematical formula,[20,21] $\Sigma_{p=1}^{\infty}\{p^2 + x^2\}^{-1} = (\pi/x)\coth(\pi x) - 1/2x^2$, eq A1 is rewritten as

$$\Gamma(s) = \frac{\sigma_0}{s^2\eta_0^{\text{ring}}} + \Gamma_R(s) \qquad \text{(A2)}$$

with

$$\Gamma_R(s) = \left(\frac{\sigma_0}{\nu k_B T}\right)\frac{3 + \pi^2 s\tau - 3\pi\sqrt{s\tau}\coth\pi\sqrt{s\tau}}{\pi^2 s^2\tau\{\pi\sqrt{s\tau}\coth\pi\sqrt{s\tau} - 1\}},\ \tau = \tau_{\text{ring}} \qquad \text{(A3)}$$

Here, η_0^{ring} ($= \nu k_B T\pi^2\tau_{\text{ring}}/3$: eq 18) and τ_{ring} ($= \zeta a^2N^2/24\pi^2k_BT$; eq 10) are the zero-shear viscosity and longest viscoelastic relaxation time of the ring system, and $\Gamma_R(s)$ is the Laplace transformation of the recoverable strain. $\Gamma_R(s)$ has the first-order poles at $s = 0$ (with a residue $[s\Gamma_R(s)]_{s\to 0} = \sigma_0/5\nu k_B T$) and at $s = s_p = -\theta_p{}^2/\pi^2\tau_{\text{ring}}$ (with a residue $[(s - s_p)\Gamma_R(s)]_{s\to s_p} = -2\sigma_0/\nu k_B T\theta_p{}^2$), where θ_p is the pth eigenvalue for the creep process determined from

$$\tan\theta_p = \theta_p \qquad \text{(A4)}$$

Considering the above results, we can make the Laplace inversion of eq A2 to find

$$\gamma(t) = \sigma_0\left\{\frac{t}{\eta_0^{\text{ring}}} + J_\text{R}(t)\right\} \tag{A5}$$

Here, $J_\text{R}(t)$ is the recoverable compliance given by

$$J_\text{R}(t) = \frac{1}{5\nu k_\text{B}T} - \frac{2}{\nu k_\text{B}T}\sum_{q=1}^{\infty}\frac{1}{\theta_q^{\ 2}}\exp\left(-\frac{t}{\lambda_q^{\text{ring}}}\right) \tag{A6}$$

with

$$\lambda_q^{\text{ring}} = -\frac{1}{s_q} = \frac{\pi^2\tau_\text{ring}}{\theta_q^{\ 2}} \quad (q\text{th retardation time}) \tag{A7}$$

From eq A6, $\dot{J}_\text{R}(t)$ is written as $\{2/\nu k_\text{B}T\}\ \Sigma_{q=1}^{\infty}\{1/\theta_q^{\ 2}\lambda_q^{\text{ring}}\}\exp(-t/\lambda_q^{\text{ring}})$ and thus its integral is given by

$$\int_0^\infty \dot{J}_\text{R}(t)\,\text{d}t = \frac{2}{\nu k_\text{B}T}\sum_{q=1}^{\infty}\frac{1}{\theta_q^{\ 2}} \tag{A8}$$

Since the system of the ring chains with large N ($\to \infty$) has an infinitely large initial modulus[18] $G(0) = \nu N k_\text{B}T$ ($\to \infty$) and the corresponding infinitesimal initial compliance $J_\text{R}(0) \to 0$, we find that the same integral can be also written as

$$\int_0^\infty \dot{J}_\text{R}(t)\text{d}t = J_\text{R}(\infty) - J_\text{R}(0) = J_\text{R}(\infty) = \frac{1}{5\nu k_\text{B}T} \tag{A9}$$

(Here, we have utilized eq A6 to specify the $J_\text{R}(\infty)$ value). Comparison of eqs A8 and A9 indicates that θ_p satisfy the summation rule,[10,14,15]

$$\sum_{q=1}^{\infty}\frac{1}{\theta_q^{\ 2}} = \frac{1}{10} \tag{A10}$$

From eqs A6 and A10, we find a compact expression of the creep compliance $J(t)$ shown in eq 17.

Appendix B. Expression of $S_2(n,n',t)$ for Ring Chain

B-1. Calculation of $S_2(n,n',t)$. Considering the initial condition for the strain in the creep process, $\gamma(0) = 0$, we can express the Laplace transformation of the strain rate for the ring chain as

$$\int_0^\infty \dot{\gamma}(t)\exp(-st)\text{d}t = s\int_0^\infty \gamma(t)\exp(-st)\text{d}t = s\int_0^\infty \sigma_0 J(t)\exp(-st)\text{d}t = \sigma_0 s\tilde{J}(s) \tag{B1}$$

Here, $\tilde{J}(s)$ is the Laplace transformation of the creep compliance given by

$$\tilde{J}(s) = \frac{1}{\nu k_\text{B}Ts\{\pi\sqrt{s\tau_\text{ring}}\coth\pi\sqrt{s\tau_\text{ring}} - 1\}} \tag{B2}$$

(This $\tilde{J}(s)$ is obtained from eqs A2 and A3; $\tilde{J}(s) = \Gamma(s)/\sigma_0$.) Thus, from eqs 14 and 15, the Laplace transformation of the correlation function, $\tilde{S}_2(n,n',s) \equiv \int_0^\infty S_2(n,n',t)\exp(-st)\,\text{d}t$, is obtained as

$$\tilde{S}_2(n,n',s) = \frac{2}{3N}\sigma_0 s\tilde{J}(s)\tilde{g}_2(n,n',s) \tag{B3}$$

Here, $\tilde{g}_2(n,n',s)$ is the Laplace transformation of $g_2(n,n',t)$ (eq 15) given by

$$\tilde{g}_2(n,n',s) \equiv \int_0^\infty \text{d}t g_2(n,n',t)\exp(-st) = \tau_\text{ring}\sum_{p=1}^{\infty}\frac{1}{p^2 + s\tau_\text{ring}}\cos\left(\frac{2p\pi(n-n')}{N}\right) \tag{B4}$$

With the aid of the mathematical formula[20,21]

$$\sum_{p=1}^{\infty}\frac{\cos px}{p^2+\beta^2} = \frac{\pi\cosh\beta(\pi - x)}{2\beta\sinh(\pi\beta)} - \frac{1}{2\beta^2}, \quad \text{for } 0 \le x \le 2\pi,$$

we can rewrite this $\tilde{g}_2(n,n',s)$ as

$$\tilde{g}_2(n,n',s) = \frac{\pi\tau\cosh\left(\pi\sqrt{s\tau}\left\{1 - \frac{2|n-n'|}{N}\right\}\right)}{2\sqrt{s\tau}\sinh(\pi\sqrt{s\tau})} - \frac{1}{2s} \quad \text{with } \tau = \tau_\text{ring} \tag{B5}$$

As can be noted from eqs B2, B3, and B5, $\tilde{S}_2(n,n',s)$ has first-order poles at $s = s_0 = 0$ and $s = s_q = -\theta_q^2/\pi^2\tau_\text{ring} = -1/\lambda_q^{\text{ring}}$, with θ_q being the eigenvalue determined by eq A4. The residues at these first-order poles ($=[(s - s_q)\tilde{S}_2(n,n',s)]_{s\to s_q}$) are given by the following equations.

At $s_0 = 0$:

$$\text{residue} = \left(\frac{\sigma_0}{\nu N k_\text{B}T}\right)Q_0(n,n') \quad \text{with}$$

$$Q_0(n,n') = \frac{1}{2}\left\{1 - \frac{2|n-n'|}{N}\right\}^2 - \frac{1}{6} \tag{B6}$$

At $s_q = -1/\lambda_q^{\text{ring}}$:

$$\text{residue} = \left(\frac{\sigma_0}{\nu N k_\text{B}T}\right)Q_q(n,n') \quad \text{with}$$

$$Q_q(n,n') = \frac{2}{3\theta_q^{\ 2}}\left\{1 - \frac{\cos\theta_q\left(1 - \frac{2|n-n'|}{N}\right)}{\cos\theta_q}\right\} \tag{B7}$$

Thus, the Laplace inversion of eq B3 gives the expression of $S_2(n,n',t)$ shown in eq 22.

B-2. Fourier Expression of $S_2(n,n',t)$. As noted from eqs 22−24 as well as eq B4, $\tilde{S}_2(n,n',s)$ is a function of $n - n'$ and can be expanded with respect to $\cos\{2p\pi(n-n')/N\}$. Thus, we can decompose the right-hand side of eq 22 into the Fourier components (by conducting the integral shown below) to find the Fourier expression of $S_2(n,n',s)$

$$S_2(n,n',t) = \frac{\sigma_0}{\nu N k_\text{B}T}\sum_{p=1}^{\infty}A_p(t)\cos\left(\frac{2p\pi(n-n')}{N}\right) \tag{B8}$$

with

$$A_p(t) = \frac{2\nu k_\text{B}T}{\sigma_0}\int_0^N \text{d}\{n-n'\}\,S_2(n,n',t)\cos\left(\frac{2p\pi(n-n')}{N}\right) = \frac{2}{p^2\pi^2} + \frac{4}{3\pi^2}\sum_{q=1}^{\infty}\frac{1}{p^2 - \theta_q^{\ 2}/\pi^2}\exp\left(-\frac{t}{\lambda_q^{\text{ring}}}\right) \quad (p = 1, 2, ...) \tag{B9}$$

This $A_p(t)$ is identical to the normalized anisotropy of the pth eigenmode amplitude, $A_p(t) \equiv \{4\nu k_\text{B}Tp^2\pi^2/a^2N\sigma_0\}\ \langle X_\xi(t;p)Y_\xi$-

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$(t;p)\rangle$ with ξ = S and C. As noted from eq 13, $A_p(t)$ can be also calculated from the derivative of the creep compliance, $\dot{J}(t)$ (= $\dot{\gamma}(t)/\sigma_0$) specified by eq 17:

$$A_p(t) = \frac{2\nu k_B T}{3}\int_0^t dt' \dot{J}(t) \exp\left(-\frac{p^2(t-t')}{\tau_{ring}}\right) = \frac{2}{p^2\pi^2}\left\{1-\exp\left(-\frac{p^2 t}{\tau_{ring}}\right)\right\} + \frac{4}{3\pi^2}\sum_{q=1}^{\infty}\frac{1}{p^2-\theta_q^{\,2}/\pi^2} \times \left\{\exp\left(-\frac{t}{\lambda_q^{ring}}\right) - \exp\left(-\frac{p^2 t}{\tau_{ring}}\right)\right\} \quad (B10)$$

Comparing eqs B9 and B10, we find a summation rule for the eigenvalues θ_q,

$$\sum_{q=1}^{\infty}\frac{1}{p^2-\theta_q^{\,2}/\pi^2} = -\frac{3}{2\pi^2} \quad (p = \text{integer}) \quad (B11)$$

Appendix C. Expression of $S_2(n,n',t)$ for the Linear Chain

For a monodisperse system of the linear Rouse chain composed of N segments, we define the isochronal orientational correlation function $S_2^{lin}(n,n',t)$ by eq 1, with n, n' = 0, N indexing segment at the chain end. We can utilize the method explained in Appendix B to calculate this $S_2^{lin}(n,n',t)$ in the following way.

Since the end segments of the linear chain is subjected to the spring force only from the inner segments, the segment position for this chain, $\mathbf{r}(n,t)$, can be expanded with respect to the cosine eigenfunctions,[3−6] $\cos(p\pi n/N)$. Considering this expansion form, we can make the eigenmode analysis similar to that for the ring chain and find that $S_2^{lin}(n,n',t)$ is determined by eq 14 with the $g_2(n,n',t)$ term therein being replaced by

$$g_2^{lin}(n,n',t) = \sum_{p=1}^{N}\exp\left(-\frac{p^2 t}{\tau_{lin}}\right)\sin\left(\frac{p\pi n}{N}\right)\sin\left(\frac{p\pi n'}{N}\right) \quad \text{with} \quad \tau_{lin} = \frac{\zeta a^2 N^2}{6\pi^2 k_B T} \quad (C1)$$

The other term included in eq 14, $\dot{\gamma}(t')$, is calculated from the creep compliance (obtained in the previous work):[10,14,15]

$$J^{lin}(t) = \frac{t}{\eta_0^{lin}} + \frac{4}{\nu k_B T}\sum_{q=1}^{\infty}\frac{1}{\theta_q^{\,2}}\left\{1-\exp\left(-\frac{t}{\lambda_q^{lin}}\right)\right\} \quad (C2)$$

with

$$\eta_0^{lin} = \frac{\nu k T \pi^2 \tau_{lin}}{6}, \lambda_q^{lin} = \frac{\pi^2 \tau_{lin}}{\theta_q^{\,2}} \quad (q\text{th retardation time}) \quad (C3)$$

The eigenvalues for the creep process, θ_q appearing in eqs C2 and C3, are determined by eq A4. Namely, the eigenvalues for the linear chain are identical to those for the ring chain and thus $J^{lin}(t)$ (eq C2) is similar to $J(t)$ of the ring chain (eq 17).

The Laplace transformation of $J^{lin}(t)$ is written as[10]

$$\tilde{J}^{lin}(s) = \frac{2}{\nu k_B T s\{\pi\sqrt{s\tau_{lin}}\coth\pi\sqrt{s\tau_{lin}} - 1\}} \quad (C4)$$

With the method explained in Appendix B, the Laplace transformation of $g_2^{lin}(n,n',t)$ is obtained as

$$\tilde{g}_2^{lin}(n,n',s) = \frac{\pi^2\tau_{lin}}{4z\sinh(z)}\left[\cosh\left(z\left\{1-\frac{|n-n'|}{N}\right\}\right) - \cosh\left(z\left\{1-\frac{(n+n')}{N}\right\}\right)\right] \text{ with } z = \pi\sqrt{s\tau_{lin}} \quad (C5)$$

Analyzing the poles of the Laplace transformation of the orientational correlation function, $\tilde{S}_2^{lin}(n,n',s) = 2\sigma_0 s\tilde{J}^{lin}(s)\tilde{g}_2^{lin}(n,n',s)/3N$, we find a compact expression of this function:

$$S_2^{lin}(n,n',t) = \frac{\sigma_0}{\nu N k_B T}\left\{Q_0^{lin}(n,n') + \sum_{q=1}^{\infty}Q_q^{lin}(n,n')\exp\left(-\frac{t}{\lambda_q^{lin}}\right)\right\} \quad (C6)$$

with

$$Q_0^{lin}(n,n') = \frac{n+n'}{N} - \frac{|n-n'|}{N} - \frac{2nn'}{N^2} \quad (C7)$$

and

$$Q_q^{lin}(n,n') = \frac{2}{3\theta_q\sin\theta_q}\left[\cos\left\{\theta_q\left(1-\frac{n+n'}{N}\right)\right\} - \cos\left\{\theta_q\left(1-\frac{|n-n'|}{N}\right)\right\}\right] \quad (C8)$$

As noted from eq 14 and eq C1, $S_2^{lin}(n,n',t)$ is expanded with respect to $\sin(p\pi n/N)\sin(p\pi n'/N)$. Thus, we can decompose the right-hand side of eq C6 into the Fourier components to find the Fourier expression of $S_2^{lin}(n,n',t)$ equivalent to eq C6:

$$S_2^{lin}(n,n',t) = \frac{2\sigma_0}{\nu N k_B T}\sum_{p=1}^{\infty}A_p^{lin}(t)\sin\left(\frac{p\pi n}{N}\right)\sin\left(\frac{p\pi n'}{N}\right) \quad (C9)$$

with

$$A_p^{lin}(t) = \frac{2\nu k_B T}{\sigma_0 N}\int_0^N dn\int_0^N dn' S_2^{lin}(n,n',t)\sin\left(\frac{p\pi n}{N}\right)\sin\left(\frac{p\pi n'}{N}\right) = \frac{2}{p^2\pi^2} + \frac{4}{3\pi^2}\sum_{q=1}^{\infty}\frac{1}{p^2-\theta_q^{\,2}/\pi^2}\exp\left(-\frac{t}{\lambda_q^{lin}}\right) \ (p = 1, 2, ...) \quad (C10)$$

The orientation function obtained from eq C9, $S(n,t) = S_2^{lin}(n,n,t)$, is identical to that derived in the previous work.[10]

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(17) Combining eq 8 (with $N/2 \rightarrow \infty$) and the expression of the dyadic averages of the eigenmode amplitudes at equilibrium, $\langle \mathbf{B}_{\xi}(p)\mathbf{B}_{\xi'}(q)\rangle^{\text{eq}} = \delta_{\xi\xi'}\delta_{pq}a^2N\mathbf{I}/6\pi^2p^2$ (p, $q \geq 1$), and utilizing the mathematical formula[20,21] $\sum_{p=1}^{\infty} p^{-2}\sin^2 px = x(\pi - x)/2$, we recover the well-known expression of the mean square distance between nth and n'th segments of the ring chain at equilibrium:[9] $\langle\{\mathbf{r}(n) - \mathbf{r}(n')\}^2\rangle^{\text{eq}} = 2a^2N/\pi^2 \sum_{p=1}^{\infty} p^{-2} \sin^2(p\pi(n - n')/N) = a^2(n - n')\{1 - (n - n)/N\}$.
(18) From eq 14, $S_2(n,n',t)$ of the ring chain under the step strain ($\dot{\gamma}(t) = \gamma_0\delta(t)$) is obtained as $S_2(n,n',t) = \{2\gamma_0/3N\} \sum_{p=1}^{N/2} \exp(-p^2t/\tau_{\text{ring}})\cos\{2p\pi(n - n')/N\}$. Utilizing this $S_2(n,n',t)$ in eq 3, we obtain the relaxation modulus, $G(t) = 2\nu k_BT\sum_{p=1}^{N/2} \exp(-p^2t/\tau_{\text{ring}})$ for the ring chains. Similarly, we obtain $S_2^{\text{lin}}(n,n',t) = \{2\gamma_0/3N\} \sum_{p=1}^{N} \exp(- p^2t/\tau_{\text{lin}})\sin(p\pi n/N)\sin(p\pi n'/N)$ and $G^{\text{lin}}(t) = \nu k_BT\sum_{p=1}^{N} \exp(-p^2t/\tau_{\text{lin}})$ for the linear chain composed of N segments. For both of the ring and linear chains, the initial modulus is given by $G(0) = \nu Nk_BT$.
(19) Equation 16 is equivalent to the linear viscoelastic constitutive equation under a condition of zero strain at time < 0, $\sigma(t) = \int_0^t \mathrm{d}t'\, \dot{\gamma}(t')G(t - t')$ with $G(t)$ being the relaxation modulus.
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(22) For the linear chain, the growth of $S_{\Delta\mathbf{r}}^{\circ}(t)$ seen in Figure 2 is contributed from time-dependent changes in both of the orientational correlation of different segments and the orientational anisotropy of respective segments.
(23) The difference in the orientational correlation of the segments of the ring and linear chains is not limited to the stress-controlled creep process but also observed for the start-up process of constant rate flow. In both processes, positive and negative correlations grow for the ring segments with $\Delta n \cong 0$ and $N/2$ while the positive correlation grows for all segments of the linear chain.
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