Dielectric Relaxation of Type-A Rouse Chains
Undergoing Reversible End-Adsorption and Desorption

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Theoretical analysis was made for dielectric relaxation of model chains, linear Rouse chains having type-A dipoles and being end-adsorbed (tethered) and desorbed at equilibrium, with an attempt to find a clue for investigation of the adsorbed chain dynamics in polymer nanocomposites. Expanding the bond vector of those chains with respect to the Rouse eigenfunctions, we obtained analytical expressions of the normalized complex dielectric permittivity and the first-moment average relaxation time of those chains. The adsorbed and desorbed chains, respectively, were found to exhibit retarded and accelerated relaxation due to motional coupling activated by their mutual conformation transfer.

Key Words: Reversible end-adsorption / Rouse dynamics / Type-A dipole / Dielectric relaxation

1. INTRODUCTION

Properties of polymer nanocomposites (PNCs) reflect not only those of polymer matrix and nanoparticles but also the behavior of the interface therein1). The structure and dynamics of interfacial layers between the bulk polymer phase and the particle surface have been studied with the aid of molecular dynamics simulation2) and various experimental techniques, for example, small angle x-ray scattering3), nuclear magnetic resonance4), and broadband dielectric spectroscopy5). A decrease of the segmental mobility in those layers, revealed from the simulation and experiments, suggests that the segments adsorb, either physically or chemically, on the particle surface thereby affecting the relaxation of the adsorbed chains in the interfacial layer6).

Previous work often considered very strong adsorption of the segments, which is equivalent to an assumption of the chains attached to the particle surface through strong bonds. Obviously, this assumption should fail for the adsorption occurring through weak physical and chemical bonding (for example, hydrogen bonding)7). In fact, Holt et al.8) found weaker suppression of the interfacial segmental motion in PNCs containing physically adsorbed chains than in PNCs containing chains grafted via covalent bonds, and interpreted this result in relation to the local chain stretch at the interface. However, for the case of weak adsorption, a dynamic exchange should occur between the adsorbed and desorbed chains in a detectable time scale. This dynamic exchange would strongly affect the behavior of PNCs, but this effect has not been fully understood.

Thus, with an attempt to find a clue for investigation of the effect of the dynamic exchange on the PNC relaxation, we have made a theoretical analysis for dielectric relaxation of model chains, linear chains having type-A dipoles and undergoing reversible end-adsorption and desorption. For chains in melts and solutions, combination of the Rouse or reptation dynamics and the association/dissociation reaction kinetics has been successfully formulated on the basis of the eigenfunction expansion8-11). We have extended this formulation to end-adsorbed and desorbed chains having so-called type-A dipoles parallel along the chain backbone to analytically obtain their dielectric relaxation function. For simplicity, we assumed that the chains are not entangled. Furthermore, we also assumed that the chain is adsorbed on a fixed point in space, not on the repulsive particle surface, to extract the
effect of the dynamic exchange of the adsorbed and desorbed chains on the relaxation in the absence of the wall effect\textsuperscript{12} on the chain conformation and dynamics. This assumption is reasonable in PNCs wherein the particle size is well below the average end-to-end distance of the chain\textsuperscript{13}, but not in PNCs containing larger particles. Nevertheless, we adopted this assumption in order to extract the effect of the dynamic exchange in the clearest form.

With the above assumptions, the chains obey the Rouse dynamics as the intrinsic dynamics without a disturbance on their conformation from the particle surface (namely, without stretching). It turned out that the free (desorbed) and adsorbed chains, respectively, exhibit retardation and acceleration of their dielectric relaxation compared to the pure Rouse case due to the dynamic exchange of their conformations. Details of this result are presented in this article.

2. THEORY

2-1 System

We consider an equilibrium system of free and end-adsorbed Rouse chains, the latter being equivalent to a chain grafted to a fixed point in space, as illustrated in Fig. 1. Each chain is composed of $N$ Rouse segments, and the adsorbed and desorbed chain ends are indexed with $n_g = 0$ and $n_f = 0$, respectively. The chains have the type-A dipoles parallel to the segmental bond vector $\mathbf{u}(n_j, t)$, with $j = g$ and $f$ standing for the grafted (end-adsorbed) and free chains. For convenience of distinguishing these chains, Fig. 1 also shows a hypothetical, permeable surface that has no effect on the chain conformation and dynamics.

The adsorption and desorption are modeled as a chemical reaction obeying the simplest first-order kinetics giving the following rate equations at equilibrium.

\begin{align}
\frac{d}{dt}[F]_{eq} &= 0 = -k[F]_{eq} + k'[G]_{eq} \\
\frac{d}{dt}[G]_{eq} &= 0 = k[F]_{eq} - k'[G]_{eq}
\end{align}

The equilibrium molar concentrations of the free and grafted chains, $[F]_{eq}$ and $[G]_{eq}$, are mutually correlated through the reaction rate constants, $k$ and $k'$, as

\begin{equation}
K = \frac{[F]_{eq}}{[G]_{eq}} = \frac{k}{k'} = \frac{\tau_{ads}}{\tau_{des}} = \frac{1}{k'} = \frac{\tau_{des}}{k}
\end{equation}

where $\tau_{ads}$ and $\tau_{des}$ indicate the corresponding adsorption and desorption time constants, respectively. These $\tau$'s are not of purely chemical nature but contributed from the local chain motion (triggered by the chemical reaction), as fully discussed in a previous study\textsuperscript{10}. Despite this contribution, those $\tau$'s are independent of time $t$ and can be utilized as the basic time constants in our analysis\textsuperscript{10}.

As shown in Fig. 1, the free chain is converted into the grafted chain on adsorption thereby transferring its conformation described by $\mathbf{u}(n_f, t)$ to the grafted chain. On the other hand, the grafted chain becomes the free chain on desorption to transfer its $\mathbf{u}(n_g, t)$ to the free chain. As noted from Fig. 1, this mutual conformation transfer is described by a simple mapping rule,

For created free chain

\begin{equation}
\mathbf{u}^{(\text{created})}(n_f, t) = \mathbf{u}^{(f)}(n_f, t) \quad (0 < n_f < N)
\end{equation}

For created graft chain:

\begin{equation}
\mathbf{u}^{(\text{created})}(n_g, t) = \mathbf{u}^{(g)}(n_g, t) \quad (0 < n_g < N)
\end{equation}

This mapping rule plays a key role in our analysis of the conformational evolution of the free and grafted chains, as explained later in detail.

2-2 Definition of dielectric quantities

On application of an electric field $E$ in $y$ direction over an interval of time $-\infty < t < 0$, the free and grafted chains are oriented in that direction. In a continuous treatment of the segment index $n_j$, the average polarization in $y$ direction is expressed in terms of the $y$ component of the segmental bond vector $\mathbf{u}_y$ as $\langle P_y(t) \rangle = \mu \langle \mathbf{u}_y(n_j, t) \rangle dn_j$, where $\mu$ is the magnitude of type-A dipole per unit length of the bond vector and $\langle \cdots \rangle$ indicates the averages taken for an ensemble of the free or grafted chains ($j = f$ or $g$). After removal of the electric field at $t = 0$, thermal motion of those chains (affected by the adsorption/desorption kinetics) results in a decay of this polarization, which is observed as the macroscopic dielectric relaxation. The normalized dielectric relaxation functions of the free and grafted chains are expressed as
The initial value, \( \langle u^y_j(n_j, 0) \rangle \), is calculated from the elastic and electrostatic energies of the segment as \(^9, 10\)

\[
\langle u^y_j(n_j, 0) \rangle = \frac{E b^2}{3 k_B T} \text{ with } b^2 = \langle u^2 \rangle \quad (j = f, g)
\]

where \( k_B \) and \( T \) represent the Boltzmann constant and absolute temperature, respectively, and \( b^2 \) is the mean-square segment size at equilibrium. This initial value is not dependent on \( j \) and \( n_j \); namely, both free and grafted chains are uniformly oriented along their backbone by the electric field applied at \(-\infty < t < 0\).

The normalized decrease of the dynamic dielectric constant and the normalized dielectric loss defined in measurements in the angular frequency (\( \omega \)) domain,

\[
\Delta \varepsilon^\prime_j(\omega) = \frac{\varepsilon^\prime_j(0) - \varepsilon^\prime_j(\omega)}{\Delta \varepsilon_j} \quad \text{and} \quad \Delta \varepsilon^\prime\prime_j(\omega) = \frac{\varepsilon^\prime\prime_j(\omega)}{\Delta \varepsilon_j}
\]

with \( \Delta \varepsilon_j \) being the dielectric relaxation intensity of the chain \( j \) (= f, g), is related to the Laplace transformation of the normalized dielectric relaxation function, \( \tilde{\Phi}_j(s) = \int_0^{\infty} \Phi_j(t) \exp(-st)dt \), as \(^10, 11\)

\[
\Delta \tilde{\varepsilon}_j^\prime(\omega) = -\omega \text{ Im} \left[ \tilde{\Phi}_j(s) \right]_{s=\omega}
\]

\[
\Delta \tilde{\varepsilon}_j^\prime\prime(\omega) = \omega \text{ Re} \left[ \tilde{\Phi}_j(s) \right]_{s=\omega}
\]

The first moment average dielectric relaxation time is straightforwardly obtained from eq 6b \(^10, 11\):

\[
\langle \tau_j \rangle_n = \left[ \frac{\Delta \tilde{\varepsilon}_j^\prime(\omega)}{\omega} \right]_{s=0}
\]

### 2-3 Calculation of time evolution of segmental bond vector and dielectric quantities

As clearly noted from eq 4, the normalized dielectric relaxation function is determined by the time evolution of the averaged \( y \) component of the bond vector of the chain, \( \langle u^y_j(n_j, t) \rangle \). For the free and grafted chains, this evolution is described by the Rouse equation modified with the adsorption/desorption kinetics \(^9, 11\),

For free chain:

\[
\frac{\partial}{\partial t} \langle u^y_j(n_j, t) \rangle = D_j \frac{\partial^2}{\partial n_j^2} \langle u^y_j(n_j, t) \rangle - \frac{1}{\tau_{ads}} \langle u^y_j(n_j, t) \rangle + \frac{1}{\tau_{ads}} \langle u^y_j(n_j, t) \rangle_{\text{initial}}
\]

\[
(0 < n_j < N)
\]

For grafted chain:

\[
\frac{\partial}{\partial t} \langle u^y_j(n_j, t) \rangle = D_j \frac{\partial^2}{\partial n_j^2} \langle u^y_j(n_j, t) \rangle - \frac{1}{\tau_{ads}} \langle u^y_j(n_j, t) \rangle + \frac{1}{\tau_{ads}} \langle u^y_j(n_j, t) \rangle_{\text{initial}}
\]

\[
(0 < n_j < N)
\]

Here, \( \tau^* \) is the end-to-end fluctuation time (dielectric relaxation time) of the free chain in the absence of reaction.

In eqs 8 and 9, the first terms show the decay of orientation through the diffusive Rouse mechanism, and the second terms indicate the decay due to conversion of the free chain into the grafted chain (eq 8) and the inverse conversion (eq 9) occurring with the time constants \( \tau_{ads} \) and \( \tau_{des} \), respectively. The third terms show the growth of orientation due to creation of the free chain (via desorption of the grafted chain; cf. eq 8) and of the grafted chain (via adsorption of the free chain; cf. eq 9). \( \langle \epsilon_i \rangle_{\text{initial}} \) of the created chain appearing in the third terms is specified by the mapping rule, eqs 3a and 3b.

A comment needs to be made for the desorption time constant (free chain creation time constant) appearing in the third term of eq 8. If this time constant is defined for the grafted chain having the equilibrium concentration \([G]_{eq}\), it is given by \( \tau_{des} \) (cf. eqs 1a and 2). However, eq 8 is defined for the free chain having \([F]_{eq}\), so that the time constant therein has been normalized to \( \tau_{des} \times \frac{[F]_{eq}}{[G]_{eq}} = \tau_{ads} \) (cf. eq 2). Similarly, the adsorption time constant for the third term in eq 9 has been normalized to \( \tau_{ads} \times \frac{[G]_{eq}}{[F]_{eq}} = \tau_{des} \). In fact, necessity of this normalization of the time constants can be easily noted for a hypothetical case of no Rouse relaxation (for a case of \( D_f = D_g = 0 \)). The free and grafted chains have the same initial orientation (cf. eq 5), so that they just exchange the same orientation to exhibit no orientational relaxation if the Rouse mechanism is quenched. Equations 8 and 9 having the normalized time constants correctly reproduce this behavior for the case of \( D_f = D_g = 0 \).

Equations 8 and 9 are coupled through the creation terms (third terms) but are linear with respect to \( \langle u^y_j \rangle \) and \( \langle \epsilon_i \rangle \), so that they can be solved analytically with appropriate initial and boundary conditions. The initial condition, common for eqs 8 and 9, has been specified by eq 5. The boundary conditions are expressed as
For free chain:
\[ \langle u_y^{(i)}(n, t) \rangle = 0 \quad \text{for} \quad n_i = 0, N \] (11)

For grafted chain:
\[ \langle u_y^{(i)}(n, t) \rangle = r_{y_0} \quad \text{for} \quad n_g = 0 \] (12a)
\[ \langle u_y^{(i)}(n, t) \rangle = \langle \partial_y u_y^{(i)}(n, t) / \partial n_i \rangle = 0 \quad \text{for} \quad n_g = N \] (12b)

Equation 11 represents random orientation at both ends of the free chain being subjected to no external force at \( t > 0 \). This condition also applies to the free end of the grafted chain (cf. eq 12b). For this chain, the grafted end is fixed on an adsorbing point located at position \( r_0 \), and the boundary condition for this end is specified for its position vector as shown in eq 12a. Considering these boundary conditions, we can expand \( \langle u_y \rangle \) of the free and grafted chains with respect to sinusoidal Rouse eigenfunctions as

For free chain:
\[ \langle u_y^{(i)}(n, t) \rangle = \sum_{p>0} \theta_p(t) \sin \left( \frac{p \pi n_i}{N} \right) \quad (0 < n_i < N) \] (13)

For grafted chain:
\[ \langle u_y^{(i)}(n, t) \rangle = \sum_{p>0} \psi_p(t) \cos \left( \frac{(2p-1) \pi n_i}{2N} \right) \quad (0 < n_i < N) \] (14)

Equation 14 is obtained by first considering eqs 12a and 12b to expand the \( y \) component of the segmental position vector as \( \langle u_y^{(i)}(n_i, t) \rangle = r_{y_0} + \sum_{p>1} (2N/(2p-1) \pi) \psi_p(t) \sin((2p-1) \pi n_i/2N) \), and then convert this expansion for \( \langle u_y^{(i)}(n_i, t) \rangle = \langle \partial_y u_y^{(i)}(n_i, t) / \partial n_i \rangle \).

Substituting eqs 13, 14, and eq 3 (mapping rule) into eqs 8 and 9 and then making Fourier integral of both sides of eqs 8 and 9, we find time evolution equations for the expansion coefficients \( \theta_p(t) \) and \( \psi_p(t) \) appearing in eqs 13 and 14. Then, these equations are solved for Laplace-transformed coefficients, \( \tilde{\theta}_p(s) = \int_0^\infty \theta_p(t) \exp(-st) dt \) and \( \tilde{\psi}_p(s) = \int_0^\infty \psi_p(t) \exp(-st) dt \), and these coefficients are used to calculate the Laplace-transformed dielectric relaxation functions, \( \tilde{\Phi}_j(s) \). This calculation involves kernel calculation for densely coupled \( \tilde{\theta}_p(s) \) and \( \tilde{\psi}_p(s) \), and can be conducted in a way explained in previous studies\( ^{10,11} \). Some detail of the calculation is explained in Appendix A, and the expression of \( \tilde{\Phi}_j(s) \) thus obtained is summarized below.

For free chain:
\[ \Phi_j(\omega) = \frac{8}{\pi^2} \left\{ f_j^{(x)} + \frac{W_j^2}{4} f_j^{(x)} \right\} \left\{ f_j^{(x)} + \frac{8}{\pi} \text{cosh}\left( \frac{\pi W_j^2}{4} \right) \right\} \]
(15)
\[ \text{with} \]
\[ f_j^{(x)} = \frac{\pi^2}{8} \left( \frac{1}{P_j^2 - P_j^2} \right) \left\{ \text{tan}\left( \frac{\pi P_j}{2} \right) - \text{tan}\left( \frac{\pi P_j}{2} \right) \right\} \]
(16a)
\[ f_j^{(x)} = \frac{\pi^2}{8} \left( \frac{1}{P_j^2 - P_j^2} \right) \left\{ \frac{\pi P_j}{2} - \frac{\pi P_j}{2} \right\} \]
(16b)
\[ f_j^{(x)} = \frac{1}{8} \left( \frac{1}{P_j^2 - P_j^2} \right) \left[ \frac{4}{\pi^2} \left( \frac{1}{r_{y_0}} \frac{\pi W_j^2}{4} \right) \frac{1}{\pi W_j^2} \right] \left( \frac{1}{\pi W_j^2} \right) \]
(17)

and
\[ \tilde{\theta}_p(s) = \int_0^\infty \theta_p(t) \exp(-st) dt \]
(18a)
\[ \tilde{\psi}_p(s) = \int_0^\infty \psi_p(t) \exp(-st) dt \]
(18b)
\[ \tilde{\psi}_p(s) = \frac{1}{4} \left( \frac{1}{P_j^2 - P_j^2} \right) \left[ \frac{1}{4P_j^2 + W_j^2} \left( \frac{1}{\pi W_j^2} \right) \left( \frac{1}{\pi W_j^2} \right) \left( \frac{1}{\pi W_j^2} \right) \left( \frac{1}{\pi W_j^2} \right) \right] \]
(18c)
\[ \tilde{\theta}_p(s) = \frac{1}{2P_j^2} \left( \frac{1}{2P_j^2} \right) \left( \frac{1}{P_j^2 - P_j^2} \right) \left[ \frac{1}{4P_j^2 + W_j^2} \left( \frac{1}{\pi W_j^2} \right) \left( \frac{1}{\pi W_j^2} \right) \right] \]
(18d)

For grafted chain:
\[ \tilde{\Phi}_j(s) = \frac{32}{\pi^2} f_j^{(x)} + \frac{128}{\pi^2} \left( \frac{W_j^2}{P_j^2} \right) f_j^{(x)} + \frac{32}{\pi} \left( \frac{1}{\pi} \left( \frac{1}{\pi} \right) \left( \frac{1}{\pi} \right) \right) \left( \frac{1}{\pi} \right) \left( \frac{1}{\pi} \right) \left( \frac{1}{\pi} \right) \]
(19)
\[ \text{with} \]
\[ f_j^{(x)} = \frac{\pi^2}{32} \left( \frac{1}{P_j^2 - P_j^2} \right) \left\{ \text{tan}\left( \frac{\pi P_j}{2} \right) - \text{tan}\left( \frac{\pi P_j}{2} \right) \right\} \]
(20a)

For free chain:
The basic parameters appearing in the above expression of $\Phi_j(s)$ are defined by

$$r_{ax} = \frac{r_j}{r_{ax}}, \quad r_{ax} = \frac{r_j}{r_{ax}}$$

$$W_p(s) = \sqrt{s + r_{ax}}, \quad W_p(s) = 2\sqrt{s + r_{ax}}$$

$$P_0(s) = \frac{1}{2}\left[-\left(W_p^2 + \frac{W_p^2}{4}\right) + \sqrt{W_p^2 - \frac{W_p^2}{4}} + 4r_{axs}^2\right]\quad (23a)$$

$$P_0(s) = \frac{1}{2}\left[-\left(W_p^2 + \frac{W_p^2}{4}\right) + \sqrt{W_p^2 - \frac{W_p^2}{4}} + 4r_{axs}^2\right]\quad (23b)$$

The first-moment average dielectric relaxation time $\langle \tau_j \rangle_0$ (eq 7), we can make the calculation explained above but with the Laplace transformation variable fixed to $s = 0$. Some detail of this calculation is explained in Appendix B, and the results are summarized below as a ratio of $\langle \tau_j \rangle_0$ to the first-moment average relaxation time of the free chain.

For free chain:

$$\frac{\langle \tau_j \rangle_0}{\langle \tau_j \rangle_0} = f_j^{(i)} + 9\pi f_j^{(i)}$$

with

$$f_j^{(i)} = \frac{48r_{axs}^2}{\pi^2 r_{ax}^4} \left[\left(\tanh\left(\frac{\pi}{\sqrt{s + r_{ax}}}ight)\right) - \frac{\pi}{\sqrt{s + r_{ax}}} \tanh\left(\frac{\pi}{\sqrt{s + r_{ax}}}ight)\right]\left(H_{\pi}^{(i)}\right)^{f_j^{(*)}}$$

and

$$H_{\pi}^{(i)} = 1 - \frac{12}{\pi^2} \left(\tan\left(\frac{\pi}{\sqrt{s + r_{ax}}}ight)\right)^2$$

$$H_{\pi}^{(i)} = \frac{\pi^2}{8\left(\tau_{axs} + r_{axs}\right)} \tanh\left(\frac{\pi}{\sqrt{s + r_{ax}}}ight)\left(\tau_{axs} + r_{axs}\right)$$

For grafted chain:

$$\frac{\langle \tau_j \rangle_0}{\langle \tau_j \rangle_0} = f_j^{(i)} + 9\pi f_j^{(i)}$$

with

$$f_j^{(i)} = \frac{48r_{axs}^2}{\pi^2 r_{ax}^4} \left[\left(\tanh\left(\frac{\pi}{\sqrt{s + r_{ax}}}ight)\right) - \frac{\pi}{\sqrt{s + r_{ax}}} \tanh\left(\frac{\pi}{\sqrt{s + r_{ax}}}ight)\right]\left(H_{\pi}^{(i)}\right)^{f_j^{(*)}}$$

and

$$H_{\pi}^{(i)} = 1 - \frac{12}{\pi^2} \left(\tan\left(\frac{\pi}{\sqrt{s + r_{ax}}}ight)\right)^2$$

$$H_{\pi}^{(i)} = \frac{\pi^2}{8\left(\tau_{axs} + r_{axs}\right)} \tanh\left(\frac{\pi}{\sqrt{s + r_{ax}}}ight)\left(\tau_{axs} + r_{axs}\right)$$

For calculation of the first-moment average dielectric relaxation time $\langle \tau_j \rangle_0$ (eq 7), we can make the calculation explained above but with the Laplace transformation variable fixed to $s = 0$. Some detail of this calculation is explained in Appendix B, and the results are summarized below as a ratio of $\langle \tau_j \rangle_0$ to the first-moment average relaxation time of the free chain.

$$\frac{\langle \tau_j \rangle_0}{\langle \tau_j \rangle_0} = f_j^{(i)} + 9\pi f_j^{(i)}$$

with
3. DISCUSSION

3-1 Overview

Figures 2 and 3, respectively, show the normalized decrease of dynamic dielectric constant $\Delta\tilde{\varepsilon}_1^{(j)}(\omega)$ and the normalized dielectric loss $\tilde{\varepsilon}_2^{(j)}(\omega)$ of the free and grafted chains (cf. eqs 15-22 and eq 6) plotted against the normalized frequency, $\omega\tau_f$. The reduced adsorption and desorption rates, $r_{a,f}$ and $r_{d,f}$ (cf. eq 23), were set identical to each other, which corresponds to the equimolar condition for the free and grafted chains (cf. eq 2). Black curves show the pure Rouse behavior of the free and grafted chains in the absence of adsorption/desorption.

As noted in Fig. 2, the dielectric relaxation of the free chain is a little retarded (compared to the pure Rouse behavior) on an increase of $r_{d,f}$ from 0.01 to 1 and then accelerated on a further increase of $r_{d,f}$. Correspondingly, the relaxation of the grafted chain is monotonically accelerated with increasing $r_{d,f}$ from 0.01 to 100 (cf. Fig. 3). These changes of the relaxation rate is most clearly noted in Fig. 4 where the first-moment average relaxation times of the free and grafted chains, $\langle \tau_f \rangle_n$ and $\langle \tau_g \rangle_n$ (cf. eqs 26-33), are normalized by $\langle \tau_f \rangle_n$ of the free Rouse chain and plotted against $r_{d,f}$ ($= r_{a,f}$).

It should be noted that the changes of $\langle \tau_f \rangle_n$ and $\langle \tau_g \rangle_n$ with $r_{d,f}$ (Fig. 4) are accompanied by changes of the dielectric relaxation mode distribution. For the free chain, the mode distribution first broadens and then narrows to approach the distribution in the absence of adsorption/desorption with increasing $r_{d,f}$ (normalized desorption rate; cf. eq 23), as most clearly noted for the dielectric loss $\tilde{\varepsilon}_2^{(f)}(\omega)$ in the bottom panel of Fig. 2; see the broadening of the $\tilde{\varepsilon}_2^{(f)}(\omega)$ curve for $r_{d,f} = 1$ (red curve) in the range of $\omega\tau_f^0 = 0.3 - 3$. In contrast, for the grafted chain, Fig. 3 clearly shows that the terminal mode distribution first narrows ($\tilde{\varepsilon}_2^{(g)}(\omega)$ peak sharpens; see the red curve (for $r_{d,f} = 1$) in the bottom panel) and then broadens to approach the distribution in the absence of adsorption/desorption. In the fast adsorption/desorption limit ($r_{d,f} = r_{a,f} \to \infty$), the relaxation mode distribution and relaxation time of the free and grafted chains commonly approach those of the free Rouse chain in the absence of adsorption/desorption.

The changes of the dielectric mode distribution with $r_{d,f}$
reflect the dense coupling of the expansion coefficients $\hat{\theta}_p(s)$ and $\hat{\psi}_d(s)$ for the free and grafted chains explained earlier for eqs 13 and 14. The corresponding dynamic coupling of these chains, being activated by the adsorption/desorption, is the essential factor underlying the changes of the dielectric mode distribution and relaxation time with $r_{a,f} (= r_{a,g})$ noted in Figs. 2-4.

3-2 Separate roles of adsorption and desorption in relaxation

It is informative to separately examine roles of the adsorption and desorption processes in the dielectric relaxation behavior. For this purpose, changes of the normalized relaxation time $\langle\tau\rangle_n / \langle\tau\rangle_n^0$ with $r_{a,f}$ (for fixed $r_{a,d}$) and with $r_{a,d}$ (for fixed $r_{a,f}$) are separately shown in Figs. 5a and 5b, respectively. Figure 5c shows 3D plots of $\langle\tau\rangle_n(= \langle\tau\rangle_n^0)$ against $r_{a,f}$ and $r_{a,d}$, where $\langle\tau\rangle_n = \tau_{free} + \tau_{g}$ is the relaxation time of the system as a whole obtained as an average for the free and grafted chains having the volume fractions $v_i$ and $v_g$, respectively.

Figures 5a and 5b demonstrate that $\langle\tau\rangle_n$ of the free and grafted chains (solid and dashed curves) agree with each other if one of $r_{a,f}$ and $r_{a,d}$ is much larger than unity irrespective of the value of the other, namely, if the adsorption or desorption is much faster than the pure Rouse motion of the chains. For example, $\langle\tau\rangle_n$ of the free chain approaches $\langle\tau\rangle_n^0$ for the pure Rouse relaxation of the grafted chain on an increase of $r_{a,f}$ (>> fixed $r_{a,d}$; cf. Fig. 5a) or on a decrease of $r_{a,d}$ (<< fixed $r_{a,f}$; cf. Fig. 5b). Namely, $\langle\tau\rangle_n$ in the limit of $r_{a,f} >> r_{a,d}$ is longer, by a factor of 4, than $\langle\tau\rangle_n^0$ for the pure Rouse relaxation of the free chain. This behavior is quite different from the behavior for the cases of $r_{a,f} = r_{a,d}$ shown in Fig. 4, which reflects a difference in the concentration ratio of the free and grafted chains, $[F]_{eq}/[G]_{eq}$. As noted from eqs 2 and 23, $[F]_{eq}/[G]_{eq} = 1$ for the case of $r_{a,f} = r_{a,d}$ ($r_{ads} = r_{des}$) whereas $[F]_{eq}/[G]_{eq} << 1$ in the limit of $r_{a,f} >> r_{a,d}$ ($r_{ads} << r_{des}$). For the case of $r_{a,f} = r_{a,d} >> 1$, the free chain can fully relax through its Rouse motion to have $\langle\tau\rangle_n$ approaching $\langle\tau\rangle_n^0$ even though it is dynamically coupled with the grafted chain having $[G]_{eq} = [F]_{eq}$, because $\langle\tau\rangle_n$ of the grafted chain approaches $\langle\tau\rangle_n^0$ for this case; cf. Fig. 4. In contrast, in the limit of $r_{a,f} >> r_{a,d}$ each free chain is at equilibrium with much more concentrated grafted chains so that the conformational transfer from the grafted chains (third term in eq 8) dominates the dielectric relaxation of the free chain. For this reason, $\langle\tau\rangle_n$ of the free chain approaches $\langle\tau\rangle_n^0$ of the grafted chain (that is negligibly affected by the dilute free chain). In all panels a-c, these situations can be noted also for the $\langle\tau\rangle_n$ of the system that is dominated by the major component in the system.

4. CONCLUDING REMARKS

For linear Rouse chains having type-A dipoles and undergoing reversible end-adsorption to a fixed point, we have theoretically formulated the dielectric relaxation function through conformational mapping between the free and grafted (end-adsorbed) chains at equilibrium with the aid of eigenfunction expansion. When the end-adsorption and desorption occur at the same rate, the free and grafted chains have the
same concentrations. For this case, dynamic coupling between these chains (occurring through mutual conformation transfer) yields many additional dielectric modes not emerging in the intrinsic Rouse dynamics, thereby retarding and accelerating the dielectric relaxation of the free and grafted chains. On the other hand, when the end-adsorption is much faster than the desorption, the free chain is much more dilute compared to the grafted chain. In this case, the dielectric relaxation of the free chain is dominated by the conformation transfer from the grafted chain and thus occurs at a rate for the pure Rouse relaxation of the grafted chain. These findings would serve as a starting clue for future investigation of the relaxation of polymer nanocomposites wherein the particle surface serves as the reversible end-adsorbing site for the polymer chains and also affects the intrinsic chain dynamics and conformation\textsuperscript{12}).

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**APPENDIX A. METHOD OF CALCULATION OF DIELECTRIC RELAXATION FUNCTIONS**

Considering the mapping rule (eq 3) to substitute eqs 13 and 14 in eqs 8 and 9 and make the Fourier integral of both sides of eqs 8 and 9, we find time evolution equations for the expansion coefficients defined in eqs 13 and 14. The results can be summarized as

for free chain:
\[
\frac{d}{dt} \theta_p(t) = -\left( \frac{p^2}{\tau_{f0}} + \frac{1}{\tau_{f0}} \right) \theta_p(t) + \frac{8p}{\pi \tau_{f0} \rho} \sum_{m=1}^{\infty} \frac{1}{4p^m - (2q - 1)} \psi_p(t) \quad (p \geq 1)
\] (34a)

and for grafted chain:
\[
\frac{d}{dt} \psi_p(t) = -\left( \frac{1}{\tau_{g0}} + \frac{1}{4p^m - (2q - 1)} \right) \psi_p(t) + \frac{8}{\pi \tau_{g0} \rho} \sum_{m=1}^{\infty} \frac{q}{4p^m - (2q - 1)} \theta_p(t) \quad (p \geq 1)
\] (34b)

where \( \tau_{f0} \) is the end-to-end Rouse relaxation time of the free chain, and \( \tau_{g0} \) and \( \tau_{f0} \) are the adsorption and desorption time constants, respectively. The creation terms in eqs 8 and 9 strongly couple the coefficients \( \theta_p(t) \) and \( \psi_p(t) \), as noted in eqs 34a and 34b. Despite this coupling, we can analytically solve eqs 34a and 34b through a simple (though lengthy) calculation explained in the previous study\textsuperscript{10}). For convenience of this calculation, we can rewrite eqs 34a and 34b for the Laplace-transformed coefficients \( \tilde{\theta}_p(s) \) and \( \tilde{\psi}_p(s) \) as

\[
\left \{ s + \frac{p^2}{\tau_{f0}} + \frac{1}{\tau_{f0}} \right \} \tilde{\theta}_p(s) = \theta_p(0) + \frac{8p}{\pi \tau_{f0} \rho} \sum_{m=1}^{\infty} \frac{1}{4p^m - (2q - 1)} \tilde{\psi}_p(s) \quad (35a)
\]

\[
\left \{ s + \frac{(2p - 1)^2}{4p^2} + \frac{1}{\tau_{g0}} \right \} \tilde{\psi}_p(s) = \psi_p(0) + \frac{8}{\pi \tau_{g0} \rho} \sum_{m=1}^{\infty} \frac{q}{4p^m - (2q - 1)} \tilde{\theta}_p(s) \quad (35b)
\]

where \( \theta_p(0) \) and \( \psi_p(0) \) are the initial values of \( \theta_p(t) \) and \( \psi_p(t) \). These values are straightforwardly obtained from the initial condition for the bond vector of the free and grafted chains, eq 5, as

\[
\theta_p(0) = \frac{2\left(1 - \cos(p\pi)\right)}{p\pi} C_0 \quad (36a)
\]

\[
\psi_p(0) = -\frac{4\cos(p\pi)}{(2p - 1)\pi} C_0 \quad (36b)
\]

with

\[
C_0 = \frac{E \mu b^2}{3k_B T} \quad (37)
\]

\( E \) is the intensity of the electric field applied at \(-\infty < t < 0\), \( \mu \) is the magnitude of type-A dipole per unit length of segmental bond vector, \( b^2 \) is the mean-square size of the bond vector at equilibrium, and \( k_B T \) denotes the thermal energy.

From eqs 35a and 35b, we can find two equations, each involving only \( \tilde{\theta}_p(s) \) or \( \tilde{\psi}_p(s) \) but with all indices \( \alpha \geq 1 \). For example, the equation for \( \tilde{\theta}_p(s) \) is summarized as

\[
\left \{ s + \left( p^2 + \frac{W_p^2}{4} \right) \left( p^2 + \frac{W_p^2}{4} \right) \right \} - \tau_f r_{s, f} \tilde{\theta}_p(s) = \tau_f r_{s, f} \left[ \cos(p\pi) - \frac{1}{p} \right] - \frac{4p}{W_p^2} \left[ \frac{1}{\cosh(pW_p^2/2) - 1} \right] + 2 \tau_{s, f} r_{s, f} \left[ \frac{W_p^2}{2} \right] \quad (38a)
\]

with

\[
K_\theta = \sum_{\alpha \geq 1} \frac{\alpha}{\alpha^2 + W_p^2} \tilde{\theta}_p(s) \quad (38b)
\]

In eq 38, \( r_{s, f} \) and \( r_{s, f} \) denote the normalized association and dissociation rates (cf. eq 23), and the parameters \( W_p \) and \( W_p \) are specified by eq 24. \( K_\theta \) is a kernel for obtaining an explicit
functional form of \( \tilde{\theta}(s) \), as similar to the situation explained in the previous study\(^{10} \). An equation corresponding to eq 38 is obtained for \( \tilde{\psi}(s) \), and an explicit functional form of \( \tilde{\psi}(s) \) is obtained with the aid of kernel calculation.

As noted from eq 4 in the main text, the Laplace-transformed dielectric relaxation functions of the free and grafted chains are expressed in terms of these \( \tilde{\theta}(s) \) and \( \tilde{\psi}(s) \) as

For free chain:

\[
\tilde{\Phi}_f(s) = \frac{1}{C_\theta} \sum_{p=0}^{\infty} \frac{2}{p\pi} \tilde{\theta}_f(s)
\]  

(39a)

For grafted chain:

\[
\tilde{\Phi}_g(s) = -\frac{1}{C_\theta} \sum_{p=0}^{\infty} \frac{2\cos(p\pi)}{(2p-1)p\pi} \tilde{\psi}_f(s)
\]  

(39b)

Utilizing the explicit functional forms of \( \tilde{\theta}(s) \) and \( \tilde{\psi}(s) \) explained above, we can conduct the summation in eqs 39a and 39b to find the expression of \( \tilde{\Phi}(s) \). The results are summarized in eqs 15-22 in the main text.

**APPENDIX B. METHOD OF CALCULATION OF TERMINAL RELAXATION TIME**

Starting equations for calculation of the first-moment average dielectric relaxation time \( \langle \tau \rangle_n \), being identical to eqs 35 and 39 but with the Laplace-transformation variable set as \( s = 0 \), are summarized as

\[
(p^2 + r_s) \tilde{\theta}_f(0) + r_s \tilde{\theta}_f(0) + \frac{8p}{\pi} \sum_{q=0}^{\infty} \frac{1}{4p^2 - (2q - 1)^2} \tilde{\psi}_f(0)
\]  

(40a)

\[
(2p - 1)^2 + r_s \tilde{\psi}_f(0) = 4r_s \tilde{\psi}_f(0) + \frac{32p}{\pi} \sum_{q=0}^{\infty} \frac{q}{4q^2 - (2p - 1)^2} \tilde{\theta}_f(0)
\]  

(40b)

\[
\langle \tau \rangle_n = \frac{1}{C_\theta} \sum_{p=0}^{\infty} \frac{2}{p\pi} \tilde{\psi}_f(0)
\]  

(41a)

\[
\langle \tau \rangle_n = -\frac{2}{\pi C_\theta} \sum_{p=0}^{\infty} \frac{\cos(p\pi)}{2p-1} \tilde{\psi}_f(0)
\]  

(41b)

After making the kernel calculation similar to that explained for eq 38, we obtain an explicit expression of \( \langle \tau \rangle_n \). The results are summarized in eqs 26-33 in the main text.

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13) If the particle in a polymer nanocomposite (PNC) has the radius well below the average size of the chains, the particle and the end-adsorbed chains thereon (say \( q \) chains) as a whole would behave similarly to a star chain. A friction of the branching point of this star chain, \( \zeta_b \), should be given by a sum of the particle friction \( \zeta_P \) and \( q \zeta_s \), with \( \zeta_s \) being the segmental friction in the star arm, so that \( \zeta_b \gg \zeta_s \) and the branching point would be effectively fixed in space in the time scale of the arm relaxation unless both \( \zeta_b \) and \( q \) are small. Thus, the end-adsorption on a spatially fixed point seems to be a reasonable approximation for the chains in such PNC.