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Dielectric Relaxation of Dipole-Inverted *cis*-Polyisoprene in Solutions: Concentration Dependence of the Second-Mode Relaxation Time

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cis-Polyisoprene (PI) chains have dipoles aligned along the chain contour (type A dipoles;[1] see Figure 1). These dipoles enable us to detect the global motion of the PI chains as slow dielectric relaxation.[1−10] Fundamental features of this relaxation are described by a local correlation function that represents orientational correlation of two segments at two separate times:[7−9]

$$C(n,t;m) = \frac{1}{a^2}<\mathbf{u}(n,t)\cdot\mathbf{u}(m,0)> \qquad (1)$$

Here, $\mathbf{u}(n,t)$ is a bond vector for the nth segment at time t, and $a^2 = <\mathbf{u}^2>$. For a PI chain composed of N segments, $C(n,t;m)$ can be decomposed into its *eigenmodes* at long time scales of the global motion:[7−9]

$$C(n,t;m) = \frac{2}{N}\sum_{p=1}^{N} f_p(n) f_p(m)\exp(-t/\tau_p) \qquad (2)$$

where $f_p(n)$ and τ_p are the eigenfunction and relaxation time for the pth eigenmode ($\tau_1 > \tau_2 > \tau_3 ...$). Correspondingly, at low frequencies (ω) where the global relaxation takes place, the dielectric loss $\epsilon''(\omega)$ of the PI chain is decomposed into dielectric modes:[7−9]

$$\epsilon''(\omega) = \sum_{p=1}^{N} g_p\frac{\omega\tau_p}{1+\omega^2{\tau_p}^2},\ g_p \propto [\int_0^N \xi(n) f_p(n)\,\mathrm{d}n]^2 \qquad (3)$$

Here, $\xi(n)$ is a parameter specifying the direction of the type A dipole of the nth segment with respect to the bond vector $\mathbf{u}(n,t)$: $\xi(n) = 1$ and -1 for the dipole being parallel and antiparallel to $\mathbf{u}$. Specifically, $\xi(n) = 1$ for $0 \le n \le N$ for *regular* PI chains having no inversion of dipoles (Figure 1a), while for PI chains having *dipole inversion* at the n^*th segment (Figure 1b) $\xi = 1$ for $0 \le n \le n^*$ and $\xi = -1$ for $n^* \le n \le N$. As noted in eq 3, the relaxation time of the pth dielectric mode is identical to τ_p of the pth eigenmode of $C(n,t;m)$, while the intensity g_p of the pth dielectric mode is determined by $f_p(n)$ for the pth eigenmode and the dipole alignment (ξ). τ_p and $f_p(n)$ are determined by the chain dynamics. Thus $\epsilon''(\omega)$ reflects features of chain dynamics through τ_p and $f_p(n)$.

The chain dynamics in solutions is governed by hydrodynamic, excluded volume, and entanglement interactions. These interactions change with the concentration c, and the corresponding changes in the chain dynamics have been dielectrically studied for PI solutions in moderately good (marginal) solvents: Isopar-G,[5] heptane,[6] and oligobutadiene ($M_\mathrm{n} = 711$).[9] For regular PI chains having no inversion of dipoles ($\xi(n) = 1$ for $n = 0-N$), only odd modes having symmetric $f_p(n)$ ($=f_p(N-n)$) contribute to $\epsilon''(\omega)$, and the end-to-end vector fluctuation is dielectrically detected. (g_p values vanish for even modes having antisymmetric eigenfunctions, $f_p(n) = -f_p(N-n)$.) For those chains, Patel and Takahashi[5] and Urakawa et al.[6] found that the dielectric mode distribution (observed as the ω dependence of ϵ'') is broadened with increasing c. They also found that the c dependence of the longest relaxation time τ_1 in dilute to semidilute solutions is well described by a theory of Muthukumar[11] considering changes in the hydrodynamic and excluded volume interactions with c:[5,6]

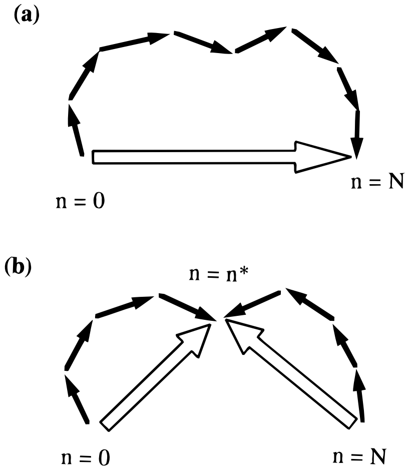

Figure 1. Schematic representation of PI chains. The small arrows indicate type A dipoles: (a) regular PI and (b) dipole-inverted PI.

$$\tau_p = \tau_{p,0}[1 + cAp^{-\kappa} - 2^{0.5}(cAp^{-\kappa})^{1.5} + 2(cAp^{-\kappa})^2 + ...] \qquad (4)$$

Here, $\tau_{p,0}$ is the relaxation time for the pth mode at infinite dilution, A is a constant proportional to the intrinsic viscosity $[\eta]$, and $\kappa = 3\nu - 1$ with ν being the Flory exponent for a chain dimension: κ is close to the Mark−Houwink−Sakurada (MHS) exponent for the intrinsic viscosity $[\eta]$. (The theory[11] leads to $f_p \propto \sin(p\pi n/N)$ and $g_p \propto p^{-2}$ irrespective of c within the approximation involved in it.)

As noted from eq 3, the dielectric mode distribution is determined by both τ_p span (τ_p/τ_1 ratio) and g_p distribution (g_p/g_1 ratio). The data for regular type A chains are not sufficient to specify whether the observed broadening of the mode distribution is due to changes in the τ_p span or g_p distribution (or both) with c. Nevertheless, for solutions of regular poly(ϵ-caprolactone) chains having no dipole inversion in a marginal solvent (benzene), Urakawa et al.[12] concluded, without examining the τ_p span and the g_p distribution experimentally, that the broadening at relatively low c (up to $c[\eta] = 3$) is explained with the Muthukumar theory if molecular weight distribution is taken into account. In other words, they concluded that the broadening at those c values is essentially due to changes in the τ_p span with c (cf. eq 4).

Watanabe et al.[9] posed a serious question for this conclusion. They examined dielectric relaxation for a series of specially synthesized PI chains having almost identical M_w ($\cong$50K) but different location of the dipole inversion point, n^* (cf. Figure 1b).[7−9] After a very minor

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Table 1. Characteristics of PI Samples

code	$10^{-3}M_w$	M_w/M_n
Without Dipole Inversion		
I-222	222	1.07
I-542	542	1.06
I-743	743	1.07
I-1230	1230	1.07
With Symmetrical Dipole Inversion		
I-I 415-415	828[a]	1.08

[a] Prepared via head-to-head coupling of precursor PI anions (M_w = 415K) and successive fractionation.

correction for small differences in M_w, τ_p and f_p of the local correlation function (eq 2) are identical for those PI chains. However, ϵ'' values of the PI chains are quite different[7-9] because of the difference in n^* (difference in the dipole alignment ξ in eq 3). Watanabe et al.[7-9] utilized those differences in ϵ'' to evaluate τ_p and integrated eigenfunctions, $F_p(n) = (\sqrt{2/N}) \int_0^n f_p(n')\,dn'$, for the lowest three eigenmodes ($p = 1-3$) in a purely experimental way. For solutions of the PI chains in a marginal solvent, an oligobutadiene with $M_n = 711$, they found that the τ_p span changes with c only a little (much less significantly than predicted from the Muthukumar theory[11]) and the broadening of the dielectric mode distribution is essentially due to changes in the g_p distribution resulting from changes in the functional form of $F_p(n)$ (or $f_p(n)$) with c.[9] This experimental fact suggested necessity of reexamination of the conclusion of Urakawa et al.[12] who attributed the broadening to changes in the τ_p span without experimental evaluation of this span.

On the basis of this background, we here examine the c dependence of the τ_1/τ_2 ratio for high molecular weight (=828K) PI chains in cyclohexane. The intrinsic viscosity in this solvent is[13]

$$[\eta] = 1.59 \times 10^{-2} M_w^{0.747}\ (\mathrm{cm^3/g}) \qquad (5)$$

As noted from this large MHS exponent, 0.747, cyclohexane is a good solvent in which the prediction of the Muthukumar theory for the τ_p/τ_1 ratio is most strongly dependent on c.

Table 1 shows molecular characteristics of the PI samples. The regular PI chains (without dipole inversion) were synthesized previously.[10] The I-I 415-415 sample having symmetrically inverted type A dipoles ($n^* = N/2$) was synthesized in this study with an anion-coupling method. Details of this method were described elsewhere.[4]

$\epsilon''(\omega)$ values were measured at 25 °C for cyclohexane solutions of those PI chains in a range of c, $0.6 \le c[\eta] \le 17$. For the regular PI chains, only odd eigenmodes of $C(n,t;m)$ contribute to ϵ'', and the slowest mode ($p = 1$) dominates sharp ϵ'' peaks. Thus, τ_1 was evaluated as a reciprocal of the peak frequency. For the dipole-inverted I-I 415-415 chain, $\xi(n) = 1$ for $0 \le n \le N/2$ and $\xi(n) = -1$ for $N/2 \le n \le N$ (cf. eq 3), and only even eigenmodes contribute to ϵ''. As before,[4,7-9] τ_2 was evaluated as the reciprocal of the ϵ'' peak frequency for I-I 415-415.

The τ_1 and τ_2 of the PI solutions were extrapolated to $c = 0$ to evaluate $\tau_{1,0}$ and $\tau_{2,0}$ at infinite dilution. (Plots of log $\tau_1(c)$ and log $\tau_2(c)$ against c were used in this extrapolation.) Figure 2 shows plots of $\tau_{1,0}$ and $\tau_{2,0}$ against M_w. $\tau_{1,0}$ obeys a power law type empirical equation, $\tau_{1,0} = 8.7 \times 10^{-15} M_w^{1.73}$ (in s; solid line). This exponent, 1.73, is close to the exponent for a product $[\eta]M_w$, 1.747. These exponents characterize the relaxation of an isolated chain in a good solvent. We also note that $\tau_{1,0}$ of I-I 415-415 evaluated from the empirical equation is 3.4 times longer than the measured $\tau_{2,0}$. This $\tau_{1,0}/\tau_{2,0}$ ratio, 3.4, is larger than the ratio for the Zimm model (without the excluded volume interaction; $\tau_{1,0}/\tau_{2,0} = 3.17$)[14,15] and close to a ratio deduced from nondraining bead spring models considering this interaction (for example, $\tau_{1,0}/\tau_{2,0} = 3.31$ for the Tschoegl model with a chain expansion parameter $\epsilon = 0.2$).[15-17]

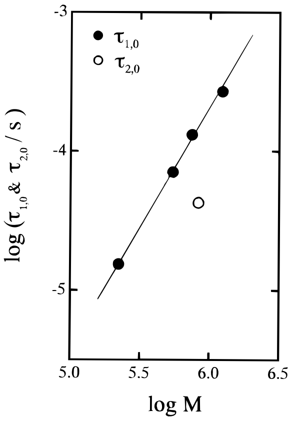

Figure 2. Molecular weight dependence of $\tau_{1,0}$ and $\tau_{2,0}$ of PI chains in infinitely dilute cyclohexane solutions at 25 °C.

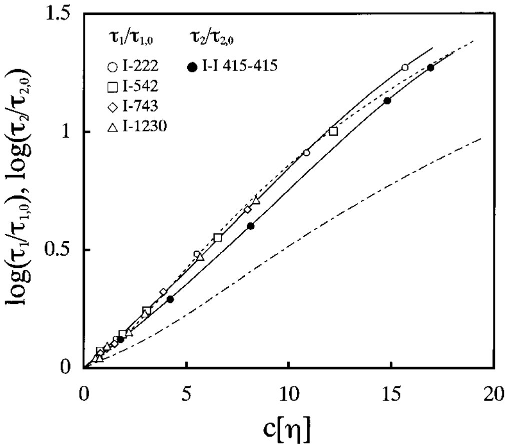

Figure 3. Comparison of the $\tau_1/\tau_{1,0}$ and $\tau_2/\tau_{2,0}$ ratios for the PI chains in cyclohexane at 25 °C. The solid curves are empirical curves smoothly connecting the data points. The dotted and dash–dot curves indicate the prediction of the Muthukumar theory for $\tau_1/\tau_{1,0}$ and $\tau_2/\tau_{2,0}$.

Figure 3 shows plots of $\tau_1/\tau_{1,0}$ and $\tau_2/\tau_{2,0}$ against $c[\eta]$. The PI chains are mostly in the nonentangled, semidilute regime, except the I-222, I-542, and I-I 415-415 chains at $12 < c[\eta]$ (<17) where small effects of entanglements may emerge and the monomeric friction ζ may increase with c. The $\tau_1/\tau_{1,0}$ ratio is universally dependent on $c[\eta]$ irrespective of M_w, as also found in previous studies.[5,6] We also note that the $c[\eta]$ dependence of the $\tau_2/\tau_{2,0}$ ratio is a little weaker than that of the $\tau_1/\tau_{1,0}$ ratio for small $c[\eta]$, but this small difference vanishes for large $c[\eta]$ (as most clearly seen later in Figure 4).

To examine the validity of the Muthukumar theory,[11] we fitted the $\tau_1/\tau_{1,0}$ data by eq 4 with κ taken to be the MHS exponent, 0.747 (eq 5). The best fit was achieved for $A = 0.204[\eta]$, as shown in Figure 3 by the dotted curve. ($[\eta]$ given in eq 5 was used.) The corresponding prediction for the $\tau_2/\tau_{2,0}$ ratio, *evaluated from the same set of* κ *and* A, is shown with the dash–dot curve.

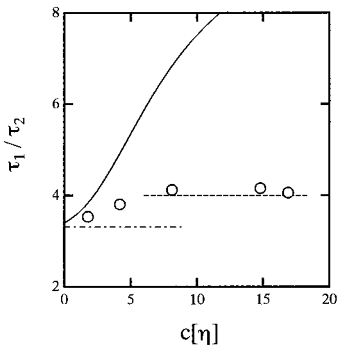

Figure 4. Dependence of the τ_1/τ_2 ratio for I-I 415-415 in cyclohexane at 25 °C on the reduced concentration $c[\eta]$. The solid curve indicates the prediction of the Muthukumar theory. The horizontal dash−dot and dotted lines indicate the τ_1/τ_2 ratio deduced from the Tschoegl and Rouse/reptation models (with the chain expansion parameter $\epsilon = 0.2$ for the former).

In Figure 3, we note good agreements between the observed and calculated $\tau_1/\tau_{1,0}$ at $c[\eta] \leq 12$. For $c[\eta] > 12$, the $\tau_1/\tau_{1,0}$ data are more strongly dependent on $c[\eta]$ than the theory possibly due to increases in ζ with c and small entanglement effects not considered in the theory. The theory appears to be valid for describing the $\tau_1/\tau_{1,0}$ ratio in the nonentangled, semidilute regime of $c[\eta]$ ($\leq$12). However, in this regime the theoretical $\tau_2/\tau_{2,0}$ ratio (dash−dot curve) is much less c-dependent than the data. Similar results were found also in our previous work.[9]

As explained above, the $\tau_1/\tau_{1,0}$ ratio exhibits universal dependence on $c[\eta]$ in the range of $c[\eta]$ examined. This enabled us to use the empirical curve smoothly connecting $\tau_1/\tau_{1,0}$ data points (solid curve in Figure 3) and evaluate the $\tau_1/\tau_{1,0}$ values for the solutions of the I-I 415-415 chain. From those $\tau_1/\tau_{1,0}$ values, the measured $\tau_2/\tau_{2,0}$ data (filled circles in Figure 3), and the $\tau_{1,0}/\tau_{2,0}$ ratio at infinite dilution (=3.4; cf. Figure 2), we evaluated the τ_1/τ_2 ratio for those solutions. Figure 4 shows dependence of the τ_1/τ_2 ratio for the I-I 415-415 chain on $c[\eta]$. The solid curve indicates the prediction of the Muthukumar theory (eq 4) that is to be compared with the data in the nonentangled, semidilute regime ($c[\eta] \leq 12$). Clearly, the $c[\eta]$ dependence in this regime is much weaker for the data than for the theoretical prediction.

As demonstrated in Figures 3 and 4, the changes in the τ_p span with c are not described by the Muthukumar theory. This experimental fact enables us to conclude that the agreement between the theoretical and experimental ϵ'' curves claimed by Urakawa et al.[12] merely reflects the width of the assumed molecular weight distribution but does not mean the validity of the theory.

The results of this study are in harmony with our previous conclusion[9] that the broadening of the dielectric mode distribution with increasing c is essentially due to changes in the dielectric intensities g_p. Concerning this fact, we note in Figure 4 that the measured τ_1/τ_2 ratio increases from the ratio expected for the Tschoegl model ($\tau_1/\tau_2 = 3.31$; dash−dot line) to that expected for the Rouse/reptation models[18] ($\tau_1/\tau_2 = 4$; dotted line). From this result, one might tend to simply attribute the changes in the dynamics of the I-I 415-415 chain with c to screening of excluded volume and hydrodynamic interactions considered in the framework of these bead spring models and further to onset of reptative motion. However, our previous work[9] indicated that the changes in the chain dynamics are associated with changes in the eigenfunctions f_p (cf. eq 2) not deduced from those models. These changes, not attributable to the simple screening effect and onset of reptation,[19] and their effects for dielectric as well as viscoelastic relaxation[20] deserve further attention.

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