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Dielectric Normal Mode Process in Semidilute and Concentrated Solutions of *cis*-Polyisoprene

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ABSTRACT: The dielectric normal mode process was studied for semidilute and concentrated solutions of *cis*-polyisoprene (*cis*-PI) dissolved in a good solvent, benzene, and a Θ solvent, dioxane. The mean-square end-to-end distance $\langle r^2 \rangle$ of *cis*-PI was determined from the dielectric relaxation strength. In dioxane solutions, $\langle r^2 \rangle$ was almost independent of concentration C. On the other hand, $\langle r^2 \rangle$ in benzene solutions decreased with increasing C in proportion to $C^{-1/5}$ in the semidilute region of $0.01 < C < 0.25$ and in proportion to about $C^{-1/3}$ in the region $0.25 < C <$ ca. 0.5. The relaxation time in solutions of low molecular weight *cis*-PI (PI-09) with weight-average molecular weight M_w of 8.6×10^3 was converted to the friction coefficient ζ per monomeric unit by using the Rouse theory. Using ζ thus estimated, we reduced the relaxation times in solutions of *cis*-PI (PI-164) with $M = 1.64 \times 10^5$ to those, $\tau_{n\zeta}$, at an isofriction coefficient state. In benzene and dioxane solutions, $\tau_{n\zeta}$ was proportional to $C^{1.3}$ and $C^{1.6}$, respectively, in the semidilute range. The exponent for benzene solutions was slightly higher than that predicted by the dynamic scaling theory proposed by de Gennes, while the exponent in dioxane solutions was lower than the theoretical value. The widths of the loss curves for solutions of PI-164 increased with increasing concentration. The factors affecting the breadth of the loss curve are discussed.

Introduction

The study on dynamic and static properties of polymer molecules in semidilute and concentrated solutions is one of the most active area in the polymer research for the last 10 years.[1] In our recent studies,[2,3] we demonstrated that dielectric spectroscopy is a powerful technique for studying these properties if accurate measurement is made on type-A polymers having the dipole moment aligned parallel in the same direction along the chain contour.[4-8] *cis*-Polyisoprene (*cis*-PI) is a type-A polymer, which exhibits dielectric normal mode process due to fluctuation of the end-to-end polarization vector.[9-12] From the study of the normal mode process, we can determine not only the relaxation times but also the mean-square end-to-end distance $\langle r^2 \rangle$. In fact, we already reported the concentration C dependences of $\langle r^2 \rangle$ as well as the relaxation time τ_n for the normal mode process over a wide range of C from infinite dilution to undiluted state for benzene solutions of *cis*-PI.[2,11] The present article is an extension and refinement of this study.

We have three objectives in mind. The first objective is a static problem to compare the C dependences of $\langle r^2 \rangle$ in a good and a Θ solvent. In the previous study,[2] we observed two concentration regions having different C dependences of $\langle r^2 \rangle$ for benzene (good solvent) solutions of *cis*-PI (PI-102) with weight-average molecular weight $M_w = 102 \times 10^3$: $\langle r^2 \rangle$ is proportional to $C^{-1/5}$ in the semidilute solutions and to $C^{-1/2}$ in the semiconcentrated region. The $C^{-1/5}$ dependence was explained by the scaling law proposed by Daoud and Jannink,[13] and the $C^{-1/2}$ region by the mean field theory by Edwards.[14,15] At present, no theoretical and experimental works showed coexistence of the two semidilute regions.[16-18]

One may suspect that the C dependence of $\langle r^2 \rangle$ determined by the dielectric method does not reflect the true change in the chain dimension but merely reflects a feature specific to the dipole–dipole interactions. If such is the case, $\Delta\epsilon$ should depend on C even in a Θ solvent in which $\langle r^2 \rangle$ is independent of C. This was tested by using dioxane as a Θ solvent for *cis*-PI. The reproducibility of the C dependence of $\langle r^2 \rangle$ in a good solvent, benzene, has been also reexamined in this study.

The second objective is a dynamic problem to clarify the C dependence of the relaxation time τ_n for the normal mode process. Since τ_n is close to the viscoelastic longest relaxation time of the same polymer, τ_n in dilute solutions is described by a bead–spring model originally proposed by Rouse[19] and developed by Zimm.[20] With increasing C, the random coils overlap one another, and hence τ_n increases on account of entanglement. According to the dynamic scaling law proposed by de Gennes,[21] the C dependence of τ_n may change depending on the solvent quality. In this study, we compared the C dependences of τ_n in benzene and dioxane.

We expect that τ_n is written as $\tau_n = \zeta f(M,C)$, where ζ is the monomeric friction coefficient and f the structural factor dependent on the architecture of the polymer molecules, molecular weight M, and C.[22,23] Usually, theories of polymer dynamics in semidilute solutions are concerned only with $f(M,C)$, and ζ is implicitly assumed to be a parameter independent of C. However, in actual systems, ζ depends strongly on C, and hence we must separate the C dependences of ζ and $f(M,C)$ to obtain a complete picture of the C dependence of the relaxation times due to the entanglement effect.

Since *cis*-PI also has the components of the dipole moment perpendicular to the chain contour, it exhibits the segmental mode process due to local motions.[10] To estimate the C dependence of ζ, we are able to employ two methods: One is from the relaxation time ζ_s for the segmental mode process[24] assuming τ_s is proportional to ζ but independent of $f(M,C)$ and the other from τ_n for *cis*-PI with M less than the characteristic molecular weight M_c for entanglement. In the present study, we estimated ζ by the latter method.

The third objective is to clarify the C dependence of the width of the loss curves or the distribution of relaxation times of the normal mode process. Previously, we reported for solutions of *cis*-PI with $M = 102 \times 10^3$ that the width of the loss curve increased with C. We attempted to explain this behavior by a 3-τ model,[2,10] assuming three modes of motions of an entangled chain confined in a "tubelike" constraint.[25,26] Although this model agreed with the experiment semiquantitatively, it is necessary to check the mechanisms of broadening of the loss curves more carefully by taking into account other factors such as the distribution of molecular weight and the excluded volume effect. Thus, we examined the width of the loss curves for solutions of *cis*-PI dissolved in benzene and dioxane.

Theory

The complex dielectric constant ϵ^* of a macroscopic system may be given by Fourier–Laplace transform of the time (t) derivative of the normalized response function Φ

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for the dielectric polarization $\mathbf{M}$ of the system:[27-29]

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_\infty + \Delta\epsilon\int_0^\infty(-\mathrm{d}\Phi/\mathrm{d}t)\exp(-i\omega t)\,\mathrm{d}t \quad (1)$$

where ϵ_∞ is the unrelaxed dielectric constant; $i^2 = -1$; ω, the angular frequency; and $\Delta\epsilon$, the relaxation strength. The response function Φ is defined by

$$\Phi(t) = \langle\mathbf{M}(0)\cdot\mathbf{M}(t)\rangle/\langle\mathbf{M}(0)^2\rangle \quad (2)$$

where $\langle\ \rangle$ denotes the ensemble average and $\mathbf{M}$ is the vectorial sum of both the permanent and induced moments of all the dipoles existing in the system.

We consider a solution of monodisperse type-A polymer with degree of polymerization n in a nonpolar solvent. The system involves the N_p polymer molecules with the running index i and the N_s solvent molecules with index s. We use index j to distinguish the repeat units in the polymer molecule. Each polymer molecule has the permanent dipole moment $\mathbf{Q}_i(t)$ which is the vectorial sum of the parallel $\mu_{ij}^{\parallel}$ and perpendicular $\mu_{ij}^{\perp}$ components of the dipole moment of the repeat units. For the sake of later discussion, we also define the dipole moment $\mathbf{p}_i$ due to the parallel component of the polymer molecule by $\mathbf{p}_i = \sum\mu_{ij}^{\parallel}$. The induced dipole moments of the repeat units are denoted as $\mathbf{q}_{ij}$ and those of the solvent molecules as $\mathbf{q}_s$. Putting the vector sum of these dipoles in eq 2, we obtain Φ as the sum of the many cross-correlation functions between the different dipoles such as $\langle\mu_{ij}^{\parallel}(0)\cdot\mu_{kl}^{\perp}(t)\rangle$. Since such an equation is too complex to apply to the practical system, we simplify it by considering that the dipoles except the parallel components have a relaxation time much shorter than the time scale of interest.

Before considering the contribution of the cross terms, we derive the complex dielectric constant $\epsilon^*(\omega)$ from eq 1, assuming that some of these cross-correlation functions are negligible. This is shown in the Appendix.[30] We see that Φ is composed of the contributions of the parallel and perpendicular components as expected.

Now confining ourselves to the low frequency range, we consider the cross-correlation functions. As shown in the Appendix, the type-A dipoles $\mathbf{p}_i$ cause the dielectric normal mode process. The normalized molecular correlation function γ_1 for $\mathbf{p}_i$ is given by eq A9 if the cross-correlations are ignored. In the following we attempt to express γ_1 without ignoring them.

The perpendicular dipoles and solvent dipoles $\mu_{kj}^{\perp}$, $\mathbf{q}_{kj}$, and $\mathbf{q}_s$ move much faster than $\mu_{ij}^{\parallel}$ or $\mathbf{p}_i$. Therefore the parallel dipoles are subjected to a mean field from them as the result of the dipole–dipole interactions. Since it is difficult to estimate the contributions of μ_{ij}, $\mathbf{q}_{ij}$, and $\mathbf{q}_s$ to the mean field separately, we denote these dipoles merely as $\mathbf{m}_{kl}$ without distinguishing them.

We assumed that all $\mathbf{p}_i$ dipoles are equivalent. Then, taking an arbitrary type-A dipole as the representative dipole $\mathbf{p}$, we may express $\gamma_1(t)$ as

$$\gamma_1(t) = \frac{\langle\mathbf{p}(0)\cdot\mathbf{p}(t)\rangle + \sum\langle\mathbf{p}(0)\cdot\mathbf{p}_i(t)\rangle + \sum\sum\langle\mathbf{p}(0)\cdot\mathbf{m}_{kl}(t)\rangle}{\langle\mathbf{p}(0)\cdot\mathbf{p}(0)\rangle + \sum\langle\mathbf{p}(0)\cdot\mathbf{p}_i(0)\rangle + \sum\sum\langle\mathbf{p}(0)\cdot\mathbf{m}_{kl}(0)\rangle} \quad (3)$$

where $\sum$ indicates the sum over all $\mathbf{p}_i$ other than $\mathbf{p}$ and $\sum\sum$ over $\mu_{ij}^{\perp}\mathbf{q}_{ij}$ and $\mathbf{q}_s$. The contribution of $\langle\mu_{ij}^{\parallel}(0)\cdot\mu_{ij}^{\perp}(0)\rangle$ to γ is zero, because the parallel and perpendicular components are always orthogonal. However, $\mu_{ij}^{\parallel}(0)$ and $\mu_{ij}^{\perp}(t)$ are generally not orthogonal.

We may consider that the terms $\langle\mathbf{p}(0)\cdot\mathbf{m}_{kl}(t)\rangle$ act to enhance the internal electric field for $\mathbf{p}$, which is independent of time t in the time scale of interest. This may cause an effect as if the dipole moment $\mathbf{p}$ becomes greater by a factor of $F^{1/2}$ than that in vacuum.[31]

The factor F is a function of the dielectric constant of the medium surrounding the representative dipole and is usually expressed by the Onsager[28] or Lorentz[29] fields. However, only the term $\langle\mathbf{p}(0)\cdot\mathbf{p}_k(t)\rangle$ cannot be regarded as a mean field being independent of time since its correlation time is similar to that of the autocorrelation function. Thus, eq 3 may be given by

$$\gamma_1(t) = \frac{F\langle\mathbf{p}(0)\cdot\mathbf{p}(t)\rangle + F\sum\langle\mathbf{p}(0)\cdot\mathbf{p}_k(t)\rangle}{F\langle\mathbf{p}(0)\cdot\mathbf{p}(0)\rangle + F\sum\langle\mathbf{p}(0)\cdot\mathbf{p}_k(0)\rangle} \quad (4)$$

Since F appears for every term, eq 4 may be reduced to the correlation function of the same form as that for the one-component system.[27,29]

For one-component systems, Cole[27] and Nee and Zwanzig[28] proposed the theories of ϵ^* in terms of the autocorrelation function of the representative dipole. These theories indicate that the contribution of the cross term is small when the relaxation strength $\Delta\epsilon$ is small. These theories may also hold approximately for solutions. Since $\Delta\epsilon$ for *cis*-PI is small, we may expect that the cross terms for *cis*-PI solutions are also small.

The type-A dipole moment $\mathbf{p}_i$ due to the parallel component is proportional to the end-to-end vector $\mathbf{r}_i$ of the ith molecule:

$$\mathbf{p}_i = \mu\mathbf{r}_i \quad (5)$$

where μ is the dipole moment per unit length of the stretched chain. From eq 4 and 5, $\gamma_1(t)$ for the normal mode process is rewritten as

$$\gamma_1(t) = \frac{\langle\mathbf{r}(0)\cdot\mathbf{r}(t)\rangle + \langle\mathbf{r}(0)\cdot\sum\mathbf{r}_k(t)\rangle}{\langle\mathbf{r}(0)\cdot\mathbf{r}(0)\rangle + \langle\mathbf{r}(0)\cdot\sum\mathbf{r}_k(0)\rangle} = \frac{\langle\mathbf{r}(0)\cdot\mathbf{r}(t)\rangle + \psi(t)}{\langle r^2\rangle + \psi(0)} \quad (6)$$

where $\mathbf{r}$ is the end-to-end vector of the representative molecule.

The denominator of eq 6 multiplied by μ^2F is proportional to the relaxation strength $\Delta\epsilon_n$ for the normal mode process. For isolated polymer molecules in a dilute solution, $\langle\mathbf{r}(0)\cdot\mathbf{r}_i(0)\rangle = 0$. In this case, $\Delta\epsilon_n$ was derived through various routes:[5,20,3]

$$\Delta\epsilon_n/C = 4\pi N_A\mu^2\langle r^2\rangle F/(3k_BTM) \quad (7)$$

where C is the concentration in weight/volume; N_A, Avogadro's constant; and M, the (weight-average) molecular weight.[5,20] This equation can be also derived from the Guggenheim equation[33] as given in part II of the Appendix.[34] We note that eq 7 is similar to the relation between the intrinsic viscosity and the mean-square radius of gyration $\langle s^2\rangle$ of the polymer chain. The comparison between these equations was reported in our previous paper.[11]

Previously, we investigated the interactions between the parallel components of the polymer and the solvent dipoles using dilute solutions of poly(2,6-dichloro-1,4-phenylene oxide).[3] The result indicated that the internal field F for the normal mode process is close to unity. Thus, we assume $F = 1$ in eq 7.

In a more concentrated system, the end-to-end polarizations might be correlating between the neighboring molecules. Then, $\psi(t)$ and $\psi(0)$ might not vanish, and $\Delta\epsilon$ should be given by

$$\Delta\epsilon_n/C = 4\pi N_A\mu^2[\langle r^2\rangle + \psi(0)]/(3k_BTM) \quad (8)$$

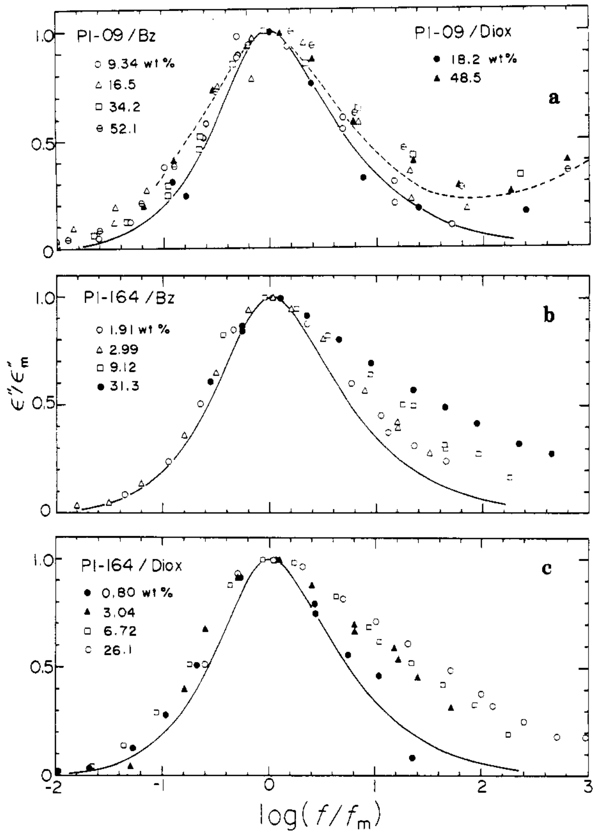

Figure 1. Representative normalized ϵ'' curves for semidilute and concentrated solutions: (a) benzene and dioxane solutions of PI-09; (b) benzene solutions of PI-164 (298 K); (c) dioxane solutions (308 K) of PI-164. Dashed line indicates the ϵ'' curve for bulk PI-09.

In such a case, the absolute value of $\psi(0)$ might increase with C. Therefore, $\Delta\epsilon/C$ of a solution of a Θ solvent might change with C, even if $\langle r^2 \rangle$ is independent of C. On the other hand, if $\psi(0)$ is negligible with respect to $\langle r^2 \rangle$, $\psi(t)$ is also negligible, because it has a magnitude of similar order to $\psi(0)$. In this case, ϵ^* for the normal mode process is simply given by

$$\frac{\epsilon^*(\omega) - \epsilon_{\infty l}}{C} = \frac{4\pi N_A \mu^2 \langle r^2 \rangle}{3k_B T M} \int_0^\infty -\frac{d}{dt}\left[\frac{\langle \mathbf{r}(0)\mathbf{r}(t)\rangle}{\langle r^2 \rangle}\right] e^{-i\omega t}\, dt \tag{9}$$

where $\epsilon_{\infty l}$ is the unrelaxed dielectric constant for the normal mode process.

Experimental Section

Samples of *cis*-PI were prepared by anionic polymerization, and characterized by gel permeation chromatography as described previously.[1,9] In this study, *cis*-PI of $M = 1.64 \times 10^5$ (PI-164) and $M = 8.6 \times 10^3$ (PI-09) were employed. The ratio of the weight- to number-average molecular weight M_w/M_n was 1.17 for PI-164 and 1.29 for PI-09.

Solvents, benzene and dioxane, were purified by vacuum distillation. Special care to prevent contamination by moisture was taken in preparing and handling the dioxane solutions as described previously.[11]

Measurements of the dielectric constant ϵ' and loss factor ϵ'' were made at 298 and 308 K for benzene and dioxane solutions, respectively. The capacitance cell and bridges were the same as described previously.[2,3] For concentrated solutions of PI-164, the dielectric dispersion occurred in the range of frequency lower than 3 Hz which was the lowest frequency available for the present bridge. For these concentrated solutions, we measured the relaxation strength by a transient method by using a current amplifier (Keithley Model 427) and a digital transient recorder (Kawasaki Electronica Co Ltd, TM-1410).

Table I
Dielectric Relaxation Strength $\Delta\epsilon$ and Relaxation Time τ_n in s for the Normal Mode Process for Solutions with Weight Fraction *w* of the Polymer and Concentration *C* in g/cm³

10^2w	10^2C	$\log_{10}(\Delta\epsilon/C)$	$\log_{10}\tau_n$
	PI-09/Bz (298 K)		
5.10	4.50	−0.83	−7.25
9.34	8.22	−0.87	−7.04
16.5	14.6	−0.89	−6.95
34.2	30.5	−0.90	−6.42
52.1	46.9	−0.91	−6.00
74.2	67.2	−0.93	−5.60
100	91.1	−1.03	−4.68
	PI-164/Bz (298 K)		
0.50	0.44	−0.614	−5.03
1.91	1.68	−0.666	−4.75
2.99	2.62	−0.668	−4.60
4.80	4.22	−0.703	−4.40
9.14	8.05	−0.686	−3.79
13.1	11.6	−0.730	−3.49
20.7	18.4	−0.730	−2.80
31.3	27.9	−0.817	−2.45
56.0	50.0	−1.03	
100	91.1	−0.99	
	PI-09/Diox (308 K)		
5.56	5.61	−0.89	−7.0
8.37	8.43		−6.8
12.1	12.1	−1.01	−6.7
28.4	27.9	−1.04	−6.4
48.5	46.5	−0.92	−6.0
	PI-164/Diox (308 K)		
0.528	0.537	−0.97	−5.05
0.802	0.815	−0.96	−5.10
1.48	1.50	−0.98	−4.95
1.59	1.62		−5.05
3.04	3.08	−0.91	−4.70
6.72	6.78	−0.92	−4.10
16.3	16.3	−0.94	−3.35
26.1	25.7	−0.98	−3.10

Results

Figure 1 shows representative ϵ'' versus frequency f curves for benzene and dioxane solutions of PI-164 and PI-09. For convenience, the curves are reduced by dividing ϵ'' by the maximum value ϵ''_m of the loss factor and the loss maximum frequency f_{mn} for the normal mode process. The solid lines show the Zimm theory as a reference. In the top part of the figure (a), the dashed line shows $\epsilon''/\epsilon''_{max}$ for bulk PI-09, in which the loss maximum frequency f_{ms} for the segmental mode process was seen at 3.8 decades above f_{mn}. In our recent study for toluene solutions of *cis*-PI, the separation between f_{mn} and f_{ms} was almost independent of C. Therefore, we consider that the increase in the ϵ'' curve for PI-09 solutions in the range of $f/f_{mn} > 2.5$ is due to the segmental mode process similar to that of the bulk PI-09. On the other hand, the separation between the normal and segmental modes of PI-164 is more than 6 decades,[10] and hence the influence of the segmental mode process is not seen in parts b and c of Figure 1.

We determined the dielectric relaxation strength $\Delta\epsilon$ for the normal mode process from the area under the ϵ'' curve. The relaxation time τ_n for the normal mode process was determined as $\tau_{mn} = 1/(2\pi f_{mn})$. The data are listed in Table I. As is seen in Figure 1a, data points for PI-09 solutions are scattered because ϵ'' was measured in the megahertz region where the sensitivity of our bridge is relatively low. In spite of this scattering, we see the width of the ϵ'' curve increases only slightly with increasing C. In contrast, for solutions of PI-164, remarkable broadening of the ϵ'' curve is seen for solutions of PI-164. This be-

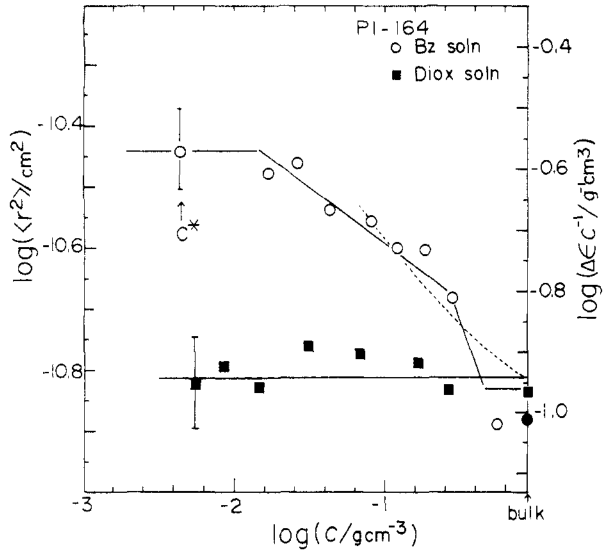

Figure 2. Concentration C dependence of the dielectric relaxation strength $\Delta\epsilon$ divided by C for benzene (good solvent) and dioxane (Θ solvent) solutions of PI-164. The dotted line shows eq 11 divided by $(1 + K)$. The solid lines are for the guide of the eyes.

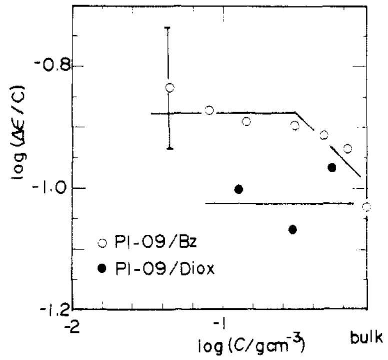

Figure 3. Double-logarithmic plot of $\Delta\epsilon/C$ versus C for benzene and dioxane solutions of PI-09.

havior was observed also in the benzene solutions of PI-102.[2] Although not shown in Figure 1, we observed that ϵ''_m/C for benzene solutions of PI-164 decreased with increasing C. This is due to both the broadening of the ϵ'' curve and the decrease in $\Delta\epsilon/C$ with increasing concentration as discussed below.

Discussion

Cross-Correlation Function in Solutions of *cis*-PI. Figures 2 and 3 show double-logarithmic plots of $\Delta\epsilon/C$ versus C for benzene and dioxane solutions of PI-164 and PI-09, respectively. Using either eq 7 or 8, we can correlate $\Delta\epsilon/C$ to $\langle r^2 \rangle$. Before doing so, we have to estimate the magnitude of the cross term $\psi(0)$ in eq 8. As described below, we may neglect this term for two reasons.

First, we note that in dioxane (Θ) solutions the values of $\Delta\epsilon/C$ are almost independent of C. Since $\langle r^2 \rangle$ in a Θ solvent is expected to be independent of C, this result indicates strongly that the contribution of $\psi(0)$ in eq 8 is less than the experimental uncertainty.

Second, we estimate the order of the dipole–dipole interaction energy U between two PI-164 molecules. The average dipole moment $\mathbf{p}$ of this molecule due to the parallel dipole is given by $\mu\langle r^2 \rangle^{1/2}$, where μ defined by eq 5 is equal to 4.80×10^{-12} cgs esu.[10] As shown in Figure 2, the end-to-end distance of PI-164 in the Θ state is 3.8×10^{-6} cm, and hence $\mathbf{p}$ is about 1.8×10^{-17} cgs esu. If we assume that the dipole is a point dipole, U/k_BT for two PI-164 molecules separated by 10 nm is only 4×10^{-3} at 300 K, which is much smaller than unity. If we assume that the vector sum of the parallel dipoles is equivalent to that of a molecule which has a charge of $\pm q$ ($=\pm 4.8 \times 10^{-12}$ esu) on the head and tail of the chain, U/k_BT is only 6×10^{-2} even when the distance of the two charges is 0.1 nm. Thus, as far as *cis*-PI molecules are concerned, the dipole–dipole interaction and hence $\psi(0)$ are negligible.

Concentration Dependence of the Relaxation Strength. On the basis of the above results, we converted $\Delta\epsilon/C$ into $\langle r^2 \rangle$ assuming $\psi(0) = 0$. The values of $\langle r^2 \rangle$ thus calculated are indicated on the oridinate of the left-hand side in Figure 2. As is seen in Figure 2, the PI-164 molecules in dilute benzene solutions have an expanded dimension. With increasing C, the polymer coils overlap each other causing a decrease in the excluded volumes and hence in $\langle r^2 \rangle$.

According to the scaling theory by Daoud and Jannink,[13] the C dependence of $\langle r^2 \rangle$ is given by

$$\langle r^2 \rangle \propto C^{(2\nu-1)/(1-3\nu)} \tag{10}$$

where ν is the excluded volume exponent equal to $^3/_5$ in a good solvent and $^1/_2$ in a Θ solvent. Thus, $\langle r^2 \rangle$ in a good solvent should be proportional to $C^{-1/4}$ in the semidilute region. As seen in Figure 2, the slope of the log $\langle r^2 \rangle$ versus log C plot for benzene solutions of PI-164 is -0.20 ± 0.03 in the range $0.02 < C < 0.25$. This value corresponds to eq 10 with $\nu = 0.57 \pm 0.02$, slightly smaller than $^3/_5$.

In the higher concentration region, the slope becomes steeper than $-^1/_5$. Although the data points are sparse, we see that the slope is about -0.3 to -0.5. This behavior is similar to the behavior in the semiconcentrated region in benzene solutions of PI-102.[2]

According to Muthukumar and Edwards,[14,15] the C dependence of $\langle r^2 \rangle$ in a good solvent in the relatively low concentration region is given by the same scaling form as eq 10, but in the limit of high concentration, it is written as

$$\langle r^2 \rangle = \langle r_0^2 \rangle (1 + KC^{-1/2}) \tag{11}$$

$$K = (\alpha^2 w M_0 / 6 l^4 N_A)^{1/2} \tag{12}$$

where $\langle r_0^2 \rangle$ is the mean-square end-to-end distance in the unperturbed state; α, the constant depending on the structure of the polymer; w, the parameter depending on the excluded volume; l, the Kuhn step length; and M_0 the molecular weight of the monomer unit. Here the monomer density in the original paper is replaced by CN_A/M_0. If the value of K is an order of unity, eq 11 predicts that the slope of log $\langle r^2 \rangle$ versus log C plot is steeper than $-^1/_4$. We estimated αw to be 1.44×10^{-7} (cgs unit) based on eq 1.9 of ref 30, using the experimental data of $\langle r^2 \rangle$ in the dilute region of benzene and dioxane solutions. Assuming $\alpha = 12/\pi$, we obtained K to be 0.549.

Here, we encounter a problem that in the bulk state, i.e.. at $C \simeq 1$, eq 11 predicts $\langle r^2 \rangle / \langle r_0^2 \rangle = 1.56$. This is unreasonable and may be due to the neglect of the higher order terms in eq 11. In order to compare the slope of log $\langle r^2 \rangle$ versus log C plot with the theoretical slope given by eq 11, we shifted eq 11 by a factor of $(1 + K)^{-1}$ and plotted the data in Figure 2. This equation with $K = 0.55$ explains qualitatively the trend that the slope in concentrated solutions becomes steeper than that in semidilute region. However, eq 11 cannot explain the slope quantitatively, which seems to be steeper than the prediction of eq 11.

In contrast to the PI-164 solutions, PI-09 does not show the regions in which $\Delta\epsilon/C$ is proportional to $C^{-1/5}$. This is due to the weak excluded-volume effect for PI-09 having low molecular weight. We recognize that the crossover concentration C^* for benzene solutions of PI-09 is about

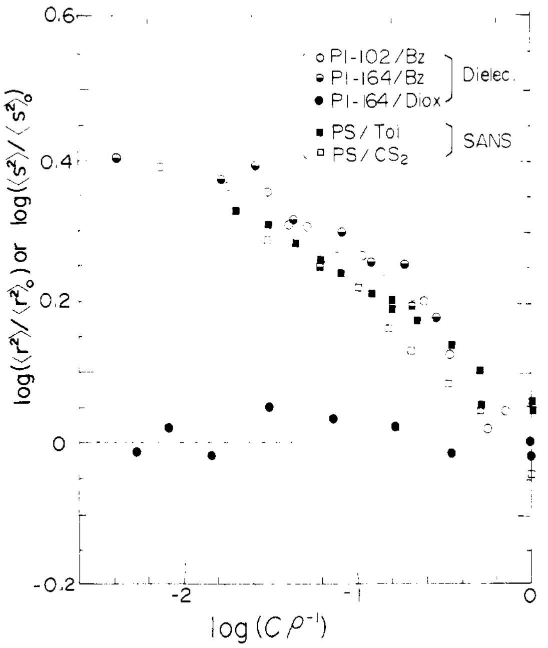

Figure 4. Comparison of the concentration dependence of the expansion coefficient determined from dielectric data and the data of small-angle neutron scattering (SANS). (□) From SANS for CS_2 solutions of polystyrene with $M = 10 \times 10^4$ (Daoud et al.[16]); (■) from SANS for toluene solutions of PS with $M = 11 \times 10^4$ (King et al.[17]); (○) from dielectric data for benzene solutions of PI-102;[2] (⊖) present data for benzene solutions of PI-164; (●) present data for dioxane solutions of PI-164.

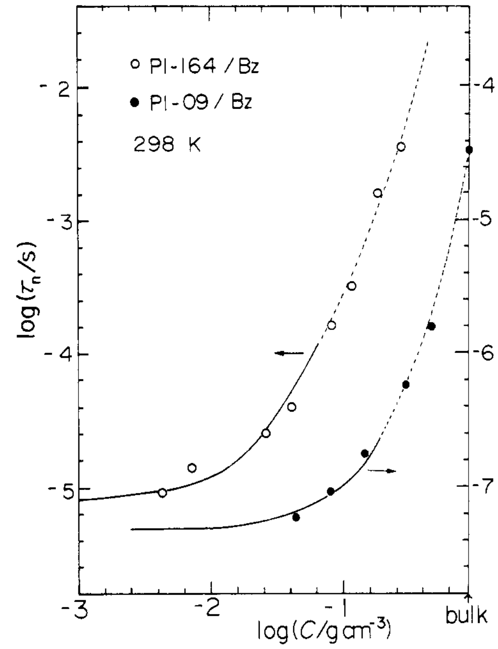

Figure 5. Double-logarithmic plot of the relaxation time for the normal mode process τ_n versus concentration C for benzene solutions of PI-164 and PI-09. The solid lines are drawn by using the Muthukumar theory.[11,31]

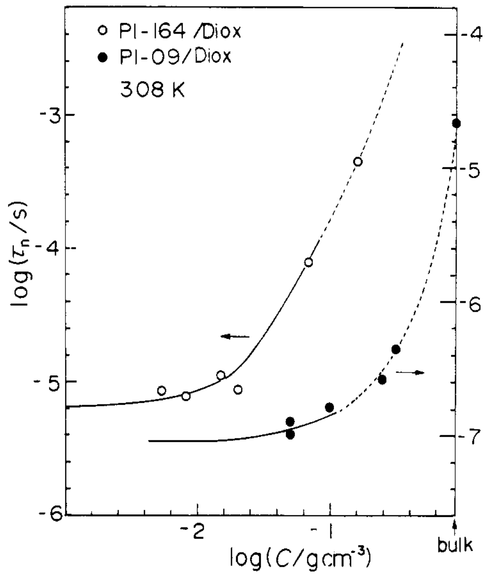

Figure 6. Double-logarithmic plot of τ_n versus concentration C for dioxane (Θ) solutions of PI-164 and PI-09. The solid lines are drawn on the basis of the Muthukumar theory.[11,31]

0.2, while C^* for PI-164 is about 0.015. The scaling theory[13] predicts that C^* is proportional to $M^{-(1-3\nu)}$, and hence the ratio of C^*(PI-09) and C^*(PI-164) should be 8.1 for $\nu = 0.57$. This agrees roughly with the observed ratio of ca. 13.

Comparison of the Concentration Dependence of $\langle r^2 \rangle$ with Data of Small-Angle Neutron Scattering. It is interesting to see whether or not other polymer systems also show behavior conforming to eq 11. There are only two sets of data of small-angle neutron scattering (SANS) on the C dependence of the mean-square *radius of gyration* $\langle s^2 \rangle$: One is reported by Daoud et al.[16] and the other by King et al.[17] These data are compared with our data in Figure 4 where $\langle s^2 \rangle / \langle s_0{}^2 \rangle$ and $\langle r^2 \rangle / \langle r_0{}^2 \rangle$ are plotted against C/ρ. Here, the subscript 0 indicates the unperturbed state and ρ is the density of the bulk polymer. For $\langle s_0{}^2 \rangle$ of polystyrene, we used the average values reported in the literatures.[35]

Both Daoud et al.[16] and King et al.[17] determined $\langle s^2 \rangle$ for solutions of polystyrene with molecular weight of ca. 10^5 and concluded that $\langle s^2 \rangle$ obeys eq 10 from the semidilute region to the bulk state. However, as is seen in Figure 4, it appears that SANS data also indicate a steep slope similar to the dielectric data in the range $C > 0.3$. In Figure 4, we note that $\langle r^2 \rangle$ determined from our dielectric data is slightly larger than $\langle s^2 \rangle$ from SANS data. This suggests that the expansion ratio for $\langle r^2 \rangle$ might be larger than that for $\langle s^2 \rangle$ although the scaling theory predicts that polymer coils in semidilute solutions have a Gaussian conformation, and thus $\langle r^2 \rangle / \langle r_0{}^2 \rangle$ should be equivalent to $\langle s^2 \rangle / \langle s_0{}^2 \rangle$.

Concentration Dependence of Relaxation Time. As is seen in Figure 1, the ϵ'' curves in the frequency range below f_{mn} are close to the Debye distribution curve because the ϵ'' curve for the Zimm theory given by the solid line is close to the Debye curve in this region. This indicates that τ_n $(=1/2\pi f_{mn})$ corresponds to the longest relaxation time. The C dependence of τ_n in benzene and dioxane solutions are shown in Figures 5 and 6, respectively. The values of τ_n at infinite dilution were reported in the preceding paper,[11] and the value is replotted in the same figure. We note that τ_n for PI-164 increases more steeply than that for PI-09. This is clearly due to the entanglement effect.

de Gennes[21] discussed the C dependence of the longest relaxation time τ_d in semidilute solutions based on a model that a chain composed of "blobs" moves in a tube whose diameter is equal to the correlation length ξ. Two extreme cases were assumed: One is a free draining model in which solvent molecules go through the blob and the other is the nondraining model. In the free draining model, the frictional force for motion of one blob is proportional to the number of the monomer unit in the blob, and τ_d is given by

$$\tau_d \propto \zeta C^{2(1-\nu)/(3\nu-1)} \tag{13}$$

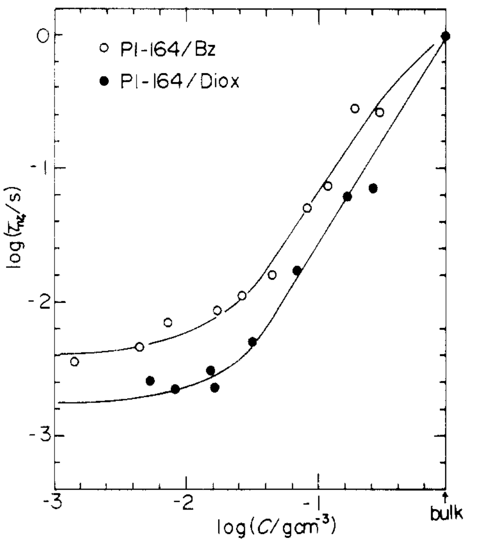

Figure 7. Concentration dependence of the relaxation time $\tau_{n\zeta}$ reduced to the isofriction coefficient state for benzene and dioxane solutions of PI-164.

where ν is defined in eq 10. On the other hand, τ_d in a nondraining model is given by

$$\tau_d \propto C^{3(1-\nu)/(3\nu-1)} \tag{14}$$

de Gennes assumed that the friction coefficient ζ_b per one blob is given by the Stokes equation[21]

$$\zeta_b = 6\pi\eta_0\xi \tag{15}$$

where η_0 is the viscosity of the medium.

To compare with experiment, it is necessary to express eq 14 by a form of $\zeta f(C)$. The C dependence of ξ and the number g of the monomeric units in the blob is given by

$$\xi = \langle r^2\rangle^{1/2}(C/C^*)^{\nu/(1-3\nu)} \tag{16}$$

$$g = N(C/C^*)^{1/(1-3\nu)} \tag{17}$$

where N is the degree of polymerization. Thus the friction coefficient ζ per monomer unit (ζ_b/g) is given by

$$\zeta = (6\pi\eta_0\langle r^2\rangle^{1/2}/N)(C/C^*)^{(\nu-1)/(1-3\nu)} \tag{18}$$

From eq 14 and 18, we note that if we express τ_d by a form of $\zeta(C)f(C)$, $f(C)$ has the same C dependence as the free draining model (eq 13). In other words, the two models, in spite of their difference, predict the same C dependence of τ_n through $f(C)$ as long as the experimental relaxation time reduced to an isofriction state is concerned.

It is known that the entanglement effect is observed only in the polymers having molecular weight M higher than the characteristic molecular weight M_c. We reported previously that M_c for bulk *cis*-PI is 1×10^4. Since M_c increases with decreasing C, we can safely regard that the PI-09 molecules meet this criterion; that is, they are not entangled at all concentrations. In order to reduce τ_n to the isofriction state, the C dependence of ζ was estimated by using the relaxation time for the PI-09 solutions. For the nonentangled polymers in concentrated solutions, the longest relaxation time is described by the Rouse theory.[19]

$$\tau_R = \zeta N\langle r^2\rangle/(3\pi^2k_BT) \tag{19}$$

Thus, if we further assume that $\langle r^2\rangle$ is independent of C and that τ_n for the PI-09 solutions satisfies eq 19, we may estimate the C dependence of ζ because the change in τ_n of PI-09 is totally due to the change of ζ. Thus, the ratio of τ_n in the PI-164 solutions to τ_n in PI-09 is proportional to the relaxation time in the isofriction state, $\tau_{n\zeta}$, which should reflect $f(C)$ of the PI-164 solutions.

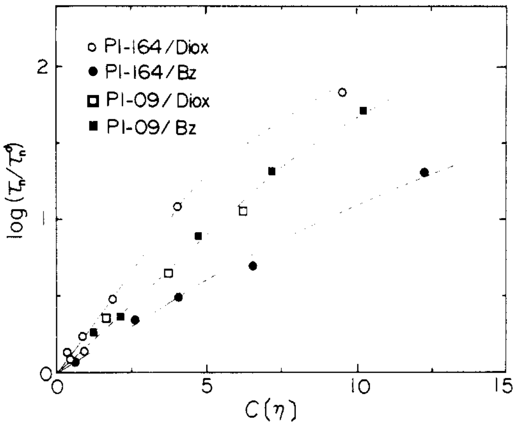

Figure 8. log (τ_n/τ_n^0) versus $C[\eta]$ plot for solutions of PI-164 and PI-09 in benzene and dioxane. The values of $[\eta]$ are calculated to be 155 mL/g for PI-164/Bz, 59 mL/g for PI-164/Diox, 15.6 mL/g for PI-09/Bz, and 13.4 mL/g for PI-09/Diox.

In a relatively low concentration range, it is a difficult problem to evaluate whether the Rouse model or the Zimm model is a better approximation for unentangled solutions. However, Zimm theory also predicts that τ_n for PI-09 is proportional to ζ, and thus, we may eliminated $\zeta(C)$ from τ_n for the PI-164 solutions based on the same procedure as mentioned above. Figure 7 shows the C dependence of $\tau_{n\zeta}$ thus determined for the PI-164 solutions. We reduced τ_n to the state in which ζ is the same as the bulk state.

In Figure 7, we notice that the C dependence of $\tau_{n\zeta}$ is almost straight line in the semidilute region. The slope in benzene solutions is 1.3 and that in dioxane solutions, 1.6. As mentioned above, these values should be compared with eq 13 which predicts the slopes in good and Θ solvents are 1.0 and 2.0, respectively. The observed slope in benzene solutions is larger than the theoretical prediction by 0.3, but in dioxane solutions, the slope is 0.4 smaller than theory. Thus, de Gennes's theory[21] explains qualitatively the difference of the slope in benzene and dioxane solutions but cannot explain the slope quantitatively.

In the crossover region between the dilute and semidilute regions, the C dependence of the relaxation time τ_p for the pth normal mode is described by the Muthukumar–Freed theory:[36,37]

$$\tau_p = \tau_p^0[1 + CAp^{-\kappa} - 2^{0.5}(CAp^{-\kappa})^{1.5} + 2(CAp^{-\kappa})^{2.0} + ...] \tag{20}$$

where τ_p^0 is the relaxation time at infinite dilution, A the constant proportional to $M^{(3\nu-1)}$, and κ the constant equal to $3\nu - 1$. It is noted that A is proportional to the intrinsic viscosity $[\eta]$. For the analysis of τ_n, we set $p = 1$ since τ_n is close to τ_1. Previously we determined graphically the value of A to be 47 and 41 for solutions of PI-164 in benzene and in dioxane, respectively.[11] We also determined τ_n^0 for solutions of *cis*-PI samples including PI-164 and PI-09. The solid lines in Figures 5 and 6 show the theoretical curves based on the Muthukumar theory corresponding to these values of A. We see that experimental results agree well with eq 20 in the low concentration range.

If CA is sufficiently small compared with unity, eq 20 predicts that log τ_n is proportional to CA and hence to $C[\eta]$.[36] Before eq 20 was proposed, Jones et al.[8] used this relation to extrapolate τ_n to infinite dilution for solutions of poly(ϵ-caprolactone) and found that log τ_n is linear to $C[\eta]$. For solutions of PI-164, we tested this relation in Figure 8. The value of $[\eta]$ was calculated based on the Mark–Houwink–Sakurada equation reported by Poddubnyi and Ehrenberg.[38] Although the data points are slightly scattered, we see that log τ_n is linear to $C[\eta]$ in the range

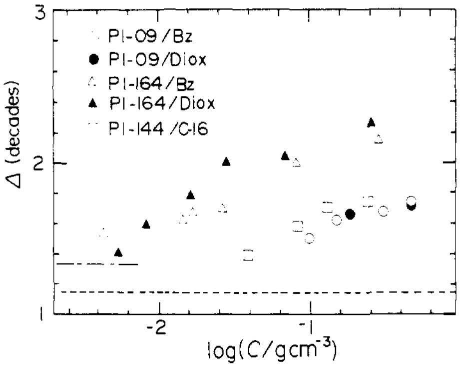

Figure 9. Concentration C dependence of the half-width Δ of the loss curves for solutions of PI-09, PI-144, and PI-164 in benzene (Bz) and dioxane (Diox). The dot–dash line and dashed lines represent the width given by the Zimm and Debye theories, respectively.

$C[\eta] < 5$. This linear relation was also seen in solutions of poly(2,6-dichloro-1,4-phenylene oxide).[39] As is seen in Figure 8 the slope of the plot depends on both the molecular weight and solvent quality.

The Shape of the Loss Curve. In the previous paper, we showed that the loss curve becomes broad with increasing either C or M. The width is broader than that predicted by the Rouse theory for nonentangled systems or by the tube theory for entangled systems. As shown in Figure 1b,c, this trend is also seen in the loss curves of the PI-164 solutions.

We expect that several factors would affect the broadening of the ϵ'' curve. They are (1) entanglement, (2) excluded volume effect, (3) hydrodynamic interaction, and (4) distribution of molecular weight.

Previously, we assumed that the broadening of the ϵ'' curve is mainly due to the entanglement effect and explained the width of the ϵ'' curve in terms of the tube model.[25,26] We assumed a 3-τ model which involves three kinds of motions of the chain confined in a tube: (1) motion of the chain end of size M_e, (2) stretching of the chain, and (3) reptation. This model explained the broadening behavior qualitatively as reported for PI-102 ($M_w/M_n = 1.18$) solutions.[2] However, our recent data[12,40] for solutions of PI-144 ($M_w/M_n = 1.09$) having C narrower molecular weight distribution than PI-164 ($M_w/M_n = 1.17$) indicates that the breadth is affected considerably by the molecular weight distribution. Therefore, it is necessary to check the factors listed above more carefully.

As shown in Figure 9, the C dependence of the width Δ of the ϵ'' curves for the dioxane solutions of PI-164 is slightly larger than that in the benzene solutions. In the case of PI-09 solutions, the difference in Δ between benzene and dioxane (Θ) solutions is very small. These data indicate that the excluded volume effect does not affect Δ strongly. The same conclusion was also drawn by comparison of the Cole–Davidson parameter β for these solutions.[12] We can test the strength of the effect of the hydrodynamic interactions on Δ by using the data for PI-09 solutions. As mentioned above, PI-09 is not entangled at any C. In low C, the motions are described by a nondraining model but in high C by free draining model. Thus, hydrodynamic effect varies with C. As shown in Figure 9, Δ increases slightly with C. Therefore, the hydrodynamic effect also affects slightly the breadth of the ϵ'' curve.

The values of Δ for the hexadecane (C-16) solutions of PI-144 is also shown in Figure 9, indicating that distribution of molecular weight affects Δ considerably. In the entangled state, the relaxation time increases in proportion to $(C/C^*)^{1.3}$ to $(C/C^*)^{1.6}$ and C^* is proportional to $M^{(1-3\nu)}$. Therefore, the ratio of the relaxation times for fractions with different molecular weights increases with increasing C. It is necessary to estimate Δ for the polymer with a single distribution by extrapolating the values of Δ for the samples with various M_w/M_n ratios.

Appendix

I. Autocorrelation Function.[30] The relationship between ϵ^* and the response function $\Phi(t)$ is given by eq 1 and 2. We consider a dilute solution of monodisperse type-A polymer. As described in the text, the polarization $M(t)$ of the system is the vector sum of all the dipoles:

$$\mathbf{M}(t) = \sum \mathbf{Q}_i(t) + \sum \mathbf{q}_{ij} + \sum \mathbf{q}_s \qquad \text{(A1)}$$

where $\mathbf{Q}_i$ is the permanent dipole moment of the individual chains. If the time-independent term and the cross-correlations between i- and kth chains can be ignored, $\Phi(t)$ becomes equal to the molecular autocorrelation function as given by

$$\Phi(t) = \langle \mathbf{Q}_i(0)\cdot\mathbf{Q}_i(t)\rangle / \langle \mathbf{Q}_i(0)^2\rangle \qquad \text{(A2)}$$

$\mathbf{Q}_i$ is the vector sum of the dipole moment μ_j of the repeat units. We decompose it into the components parallel $\mu^{\parallel}$ and perpendicular $\mu^{\perp}$ to the chain contour. Thus $\mathbf{Q}_i$ is written as

$$\mathbf{Q}_i(t) = \sum[\mu_{ij}{}^{\parallel}(t) + \mu_{ij}{}^{\perp}(t)] \qquad \text{(A3)}$$

Hence $\langle \mathbf{Q}_i(0)\cdot\mathbf{Q}_i(t)\rangle$ is the sum of four kinds of summations

$$\langle \mathbf{Q}_i(0)\cdot\mathbf{Q}_i(t)\rangle = \sum\sum\langle \mu_{ij}{}^{\parallel}(0)\cdot\mu_{il}{}^{\parallel}(t)\rangle + \sum\sum\langle {}^{\circ}\mu_{ij}{}^{\parallel}(0)\cdot \mu_{il}{}^{\perp}(t)\rangle + \sum\sum\langle \mu_{ij}{}^{\perp}(0)\cdot\mu_{il}{}^{\parallel}(t)\rangle + \sum\sum\langle \mu_{ij}{}^{\perp}(0)\cdot\mu_{il}{}^{\perp}(t)\rangle \qquad \text{(A4)}$$

Let $\mathbf{b}_{ij}(t)$ the bond vector of the jth repeat unit of the ith molecule, then $\mu_{ij}{}^{\parallel}(t)$ is written as

$$\mu_{ij}{}^{\parallel}(t) = \mu\mathbf{b}_{ij}(t) \qquad \text{(A5)}$$

where μ is the constant having the meaning of the parallel dipole moment per unit contour length. Then the first term of eq A4 is rewritten as

$$\sum\sum\langle \mu_{ij}{}^{\parallel}(0)\cdot\mu_{il}{}^{\parallel}(t)\rangle = \mu^2\sum\sum\langle \mathbf{b}_{ij}(0)\cdot\mathbf{b}_{il}(t)\rangle \qquad \text{(A6)}$$

Since the end-to-end vector $\mathbf{r}_i(t)$ is equal to the vector sum of the bond vector, the right-hand side of eq A6 is equal to $\mu^2\langle \mathbf{r}_i(0)\cdot\mathbf{r}_i(t)\rangle$.

On the other hand, the fourth term of eq A4 is simply the autocorrelation function of the perpendicular component of the dipole moment. We further ignore the cross terms between the parallel and perpendicular components, i.e., the second and the third terms of eq A4. Thus $\Phi(t)$ is rewritten as

$$\Phi(t) = \frac{\mu^2\langle \mathbf{r}_i(0)\cdot\mathbf{r}_i(t)\rangle + \sum\sum\langle \mu_{ij}{}^{\perp}(0)\cdot\mu_{il}{}^{\perp}(t)\rangle}{\mu^2\langle \mathbf{r}_i(0)\cdot\mathbf{r}_i(0)\rangle + \sum\sum\langle \mu_{ij}{}^{\perp}(0)\cdot\mu_{il}{}^{\perp}(0)\rangle} \qquad \text{(A7)}$$

We note that $\Phi(t)$ has two components, one due to the end-to-end vector motion and the other due to the perpendicular components. Since the relaxation times for these components are much separated, $\Phi(t)$ may be written as the sum of two terms well separated in the time domain:

$$\Phi(t) = a_1\gamma_1(t) + a_2\gamma_2(t) \qquad \text{(A8)}$$

where $\gamma_1(t)$ and $\gamma_2(t)$ are the normalized molecular-correlation functions for the parallel and perpendicular components, respectively, and a_1 and a_2 are the weighing factor. From eq A7 and A8, we express $\gamma_1(t)$ as

$$\gamma_1(t) = \langle \mathbf{r}_i(0)\cdot\mathbf{r}_i(t)\rangle / \langle r^2\rangle \qquad \text{(A9)}$$

Thus, the complex dielectric constant in the low frequency region is simply given by[29]

$$\frac{\epsilon^*(\omega) - \epsilon_{\infty 1}}{\epsilon_0 - \epsilon_{\infty 1}} = 1 - i\omega\mathcal{L}(\psi_1(t)) \qquad \text{(A10)}$$

where $\mathcal{L}$ denote the Laplace transform and $\epsilon_{\infty 1}$ the dielectric constant at a frequency which is sufficiently high for the normal mode process but is sufficiently low for the segmental mode process.

II. Relaxation Strength for the Normal Mode Process.[34] The next step is to express $\Delta\epsilon = \epsilon_0 - \epsilon_{\infty 1}$. According to Guggenheim, the dipole moment p of a simple molecule is given by

$$p^2 = (3k_BT/4\pi N)[9/(\epsilon_1 + 2)(n_1^2 + 2)]\ (\Delta\epsilon) \qquad \text{(A11)}$$

where N is the number of dipoles in unit volume; ϵ_1 and n_1 are the static dielectric constant and the refractive index of the solution, respectively. The factor given by [ ] corresponds to $1/F$. We also note that in the rigid simple molecules, $\mathbf{p}^2$ is independent of time but $\mathbf{p}^2$ for the type-A polymer fluctuates with time. Thus we should take the ensemble average of $\mathbf{p}_i^2$ over many molecules. The parallel dipole moment $\mathbf{p}_i$ under the Θ condition is given by

$$\langle \mathbf{p}_i^2 \rangle = n\mu^{\parallel 2} = n\mu^2\mathbf{b}^2 \qquad \text{(A12)}$$

where n is the degree of polymerization. Since $n\mathbf{b}^2$ is equal to the mean-square end-to-end distance $\langle r^2 \rangle$, we obtain

$$\Delta\epsilon = \epsilon_0 - \epsilon_{\infty 1} = 4\pi N\mu^2\langle r^2\rangle F/(3k_BT) \qquad \text{(A13)}$$

From eq A10 and A13 we can express the complex dielectric constant in the low frequency region by eq 9 of the text.

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Registry No. Polyisoprene, 9003-31-0; benzene, 71-43-2; dioxane, 123-91-1.

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