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Application of Scaling Laws to the Dielectric Normal Mode Process of *cis*-Polyisoprene in Solutions of Infinite Dilution to the Bulk

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ABSTRACT: The dielectric relaxation due to the "normal mode process" originating from fluctuation of the end-to-end vector was investigated at 298 K for solutions of a *cis*-polyisoprene (of the weight-average molecular weight = 102×10^3) in benzene over the entire range of concentration C. The relaxation time τ_n for the normal mode process and the mean-square end-to-end distance $\langle r^2 \rangle$ determined from the dielectric relaxation strength were analyzed in terms of dynamic and static scaling laws, respectively. In the dilute range of C less than 0.02 g cm^{-3}, τ_n coincided approximately with the theoretical relaxation time calculated by the Rouse–Zimm theory. In the semidilute range of $0.03 < C < 0.25$, τ_n reduced to the isofriction state was proportional to $C^{1.0}$–$C^{1.6}$, in agreement with the prediction by the tube model by de Gennes on semidilute solutions in good solvents. In the range of $0.3 < C$, τ_n increased with a high power of C because of the increase in local friction. The width of the distribution of the relaxation times for the normal mode process also increased with C and was explained in terms of the tube model by assuming that the molecular weight between entanglements is proportional to C^{-1}. In addition to the dilute and concentrated regions, two regions, designated as II and IIA, were identified by the difference in the C dependence of $\langle r^2 \rangle$, where $\langle r^2 \rangle$ varied in proportion to $C^{-1/5}$ and $C^{-1/2}$, respectively. The C dependence of $\langle r^2 \rangle$ was compared with the prediction by scaling laws and mean field theories.

Introduction

Recently, we reported a series of studies on the dielectric relaxation due to fluctuation of the end-to-end vector,[1,2] termed the "dielectric normal mode process".[3–7] In such a study on undiluted *cis*-polyisoprenes (*cis*-PI),[4,5] we found that the molecular weight M dependence of the dielectric relaxation time τ_n for the normal mode process was entirely different between high molecular weight, entangled systems and low molecular weight, unentangled systems.[1–3,8–12] For the latter, τ_n was proportional to M^2, and the behavior was explained in terms of the bead–spring model by Rouse and Zimm.[13–16] However, for the former with M above the characteristic molecular weight M_c (=10 000), τ_n increased in proportion to $M^{3.7}$. This behavior was similar to the 3.4 power law for the viscoelastic behavior of entangled systems.[17–19] We explained the behavior in terms of the tube theory, in which τ_n was considered to correspond to the relaxation time τ_d for the tube disengagement process proposed by de Gennes[20,21] and by Doi and Edwards.[22] We also showed for the solutions of poly(2,6-dichloro-1,4-phenylene oxide) that the relaxation strength $\Delta\epsilon$ for the normal mode process is proportional to the mean square end-to-end distance $\langle r^2 \rangle$.[7] The present study is an extension of these studies to the solutions of *cis*-PI in benzene with an objective to elucidate the effect of entanglement on τ_n and $\langle r^2 \rangle$ as a function of concentration C.

A theory for the C dependence of τ_d in semidilute solutions has been proposed by de Gennes,[23] who assumed that the distance between entanglements corresponds to the correlation length ξ (screening length) beyond which the excluded volume effect is screened. Later, dynamic scaling theories have been developed by several authors,[24–27] by taking into account[27] the various types of the C dependence of ξ and the fluctuation of the contour length of primitive chains proposed by Doi.[28] In concentrated solutions, where the excluded volume effect vanishes, the molecular weight M_e between entanglement is empirically known to exhibit C^{-1} dependence. Doi[29] calculated the tube diameter as a function of C and suggested C^{-2} dependence of M_e. We compare these theories with the C dependence of τ_n found in this study.

Previously, the distribution of the relaxation times for the normal mode process in bulk *cis*-PI was explained[5] in terms of the tube model, in which the relaxation times were scaled by M/M_e. Since M_e in concentrated solutions is empirically known to be proportional to C^{-1}, the dielectric relaxation spectrum of *cis*-PI with molecular weight M in a solution of concentration C should have the same shape as that for undiluted *cis*-PI having molecular weight CM. To test this relationship, we have compared the spectra for the solutions and corresponding bulk polymers.

Although the C dependence of $\langle r^2 \rangle$ has been discussed extensively in terms of static scaling laws[21,31] and with mean field theories,[32,33,47] only a few experimental studies have been conducted by means of elaborate small-angle neutron-scattering (SANS) techniques[34–38] to determine the C dependence of the chain dimension. Strictly, however, one can determine the mean-square radius of gyration, $\langle s^2 \rangle$, by SANS, but not $\langle r^2 \rangle$ directly. As pointed out previously, the dielectric method provides a convenient and relatively easy method for determining the dimension, especially $\langle r^2 \rangle$, of the polymer coil in condensed systems.[7] We have illustrated this dielectric method by comparing the C dependence of $\langle r^2 \rangle$ determined from $\Delta\epsilon$ with the theories.

Experimental Section

A *cis*-PI sample (coded as PI-102) reported previously was used.[4,5] The weight- and number-average molecular weights were 102×10^3 and 86×10^3, respectively. The content of cis, trans, and vinyl linkages was determined by ^{13}C NMR based on the assignment by Sato et al.[39] as 78.3, 18.7, and 3.0%, respectively. The solvent was highly pure benzene dried with calcium hydride and distilled under vacuum.

Dielectric measurements were made at 298.2 ± 0.3 K in the frequency range from 3 Hz to 100 MHz. Methods of measurement have been described previously.[4,5]

The density ρ of the solutions with concentration below 60 wt % was measured at 298 K with a small pipette (1 mL) by weighing, while the density of the solutions above 60 wt % was measured by a float method in water and methanol mixtures. The accuracy was estimated to be 2%. The density data in g/cm^3 were expressed approximately by the quadratic equation

$$\rho = 0.875 + 0.060w - 0.024w^2 \qquad (1)$$

where w denotes the weight fraction of *cis*-PI.

Results and Discussion

1. Overview. Frequency dependence of the dielectric loss factor ϵ'' at 298.2 K divided by w is shown in Figure

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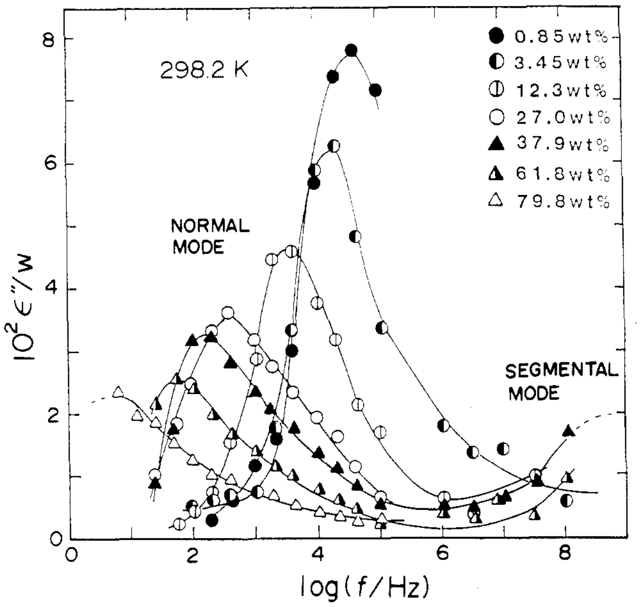

Figure 1. Frequency dependence of dielectric loss factor ϵ'' divided by weight fraction w of *cis*-PI at 298.2 K. Concentrations for the solutions are given in the figure.

1. The main loss peak seen below 10 kHz shifts to the lower frequency with increasing w and approaches the frequency f_{mn} of the loss maximum for the normal mode process of undiluted PI-102 (f_{mn} = 0.5 Hz at 298 K). Therefore, these main peaks were assigned to the normal mode process. As seen in Figure 1, ϵ''/w for solutions of relatively high concentration increases with frequency above 10 MHz. Since the loss maximum frequency f_{ms} for the segmental mode process in undiluted PI-102 was 62 MHz at 298 K,[4,5] the high-frequency process of the solutions can be assigned to the segmental mode process. However, f_{ms} should appear above the highest frequency (100 MHz) covered in this study because of the dilution effect. As seen in Figure 1, the maximum value of ϵ''/w for the normal mode process decreases with increasing concentration, while the half-width increases. This behavior is similar to the molecular weight dependence of the shape of the loss curve in undiluted *cis*-PI.[4,5]

2. Analysis of Dynamic Properties. Concentration Dependence of Relaxation Times. The values of τ_n were determined from f_{mn} as $\tau_n = 1/(2\pi f_{mn})$ and are plotted against C on a double logarithmic scale in Figure 2. In the dilute solutions, τ_n is given by the longest relaxation time τ_1 and τ_1' of the Rouse[14] and Zimm[15] theories, respectively. In the case of the free-draining model by Rouse, τ_1 is written as[14]

$$\tau_1 = \frac{12M\eta_s[\eta]}{\pi^2RT} \tag{2}$$

where η_s is the solvent viscosity, $[\eta]$ the intrinsic viscosity, and R the gas constant. On the other hand, τ_1' for the nondraining model by Zimm[15] is given by

$$\tau_1' = \frac{2M\eta_s[\eta]}{0.586RT\lambda_1'} \tag{3}$$

where λ_1' is the eigenvalue for the first normal mode. By use of reported values[40,41] of $[\eta]$ and η_s, τ_1 and τ_1' were calculated to be 3.23 × 10^{-6} and 2.24 × 10^{-6} s, respectively. In Figure 2 these values are compared with the experimental data. It is seen that τ_n in the dilute region (I) ($C < 0.02$) agrees roughly with τ_1 and τ_1'.

With increasing C, τ_n increases because of the increase in both the number of entanglement points and the local friction constant for motions of the segments. Similar C dependence of the maximum relaxation times have been observed by Schrag and co-workers[42-45] by means of oscillatory flow birefringence. The results were explained in terms of the theory proposed by Muthukumar and Freed.[46] In this paper, we have analyzed the data by scaling laws.

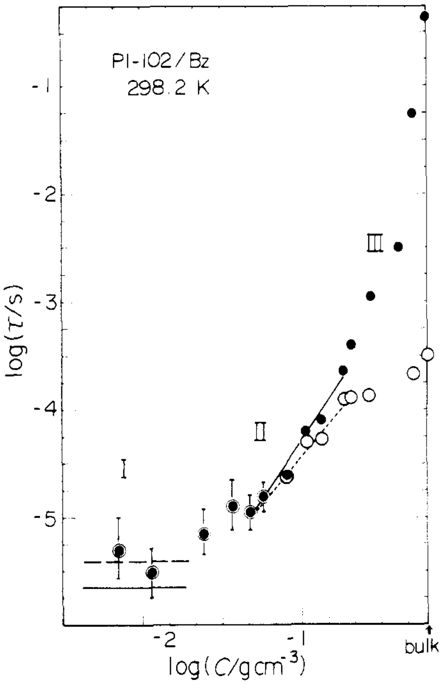

Figure 2. Double logarithmic plot of the relaxation time for the normal mode process vs. concentration C in g cm^{-3}: ●, experimental results of τ_n; ○, the relaxation time, $\tau_{n\zeta}$, reduced to the condition that the friction constant is the same as that in dilute solutions. The dashed and solid lines in region I represent eq 2 and 3, respectively.

Before analyzing the data, it is necessary to estimate the C dependence of the local friction constant ζ per monomeric unit. Recently, we estimated[47] the C dependence of ζ in toluene solutions of *cis*-PI by assuming ζ is proportional to $1/f_{ms}$. We reduced τ_n into the relaxation time $\tau_{n\zeta}$ under the isofriction state by using the relation $\tau_n \propto \zeta\tau_{n\zeta}$. Although the validity of this assumption has not been fully tested, it is plausible that the segmental mode is an elementary process prescribing the rate of molecular motions of a chain. The fact that the value of f_{ms}/f_{mn} in bulk *cis*-PI[4,5] was almost independent of temperature supports this assumption. We failed to determine f_{ms} for the present solutions at 298 K because of the limitation in the highest attainable frequency (100 MHz). Unfortunately, we also failed in determination of f_{ms} at low temperatures where $f_{ms} < 100$ MHz, because benzene crystallized below 278 K. Since the solvent qualities of benzene and toluene are similar, we assumed that the C dependence of ζ in benzene solutions is the same as that in toluene solutions. In this way, $\tau_{n\zeta}$ under a condition that ζ is the same as that in dilute solutions is estimated and plotted in Figure 2 (shown by open circles).

de Gennes[23] expressed the C dependence of τ_d in semidilute solutions by assuming that the distance between entanglements is equal to the screening length ξ. In the case of the free-draining model, τ_d is given by[23]

$$\tau_d = \left(\frac{\zeta XS^2}{k_BT}\right)\left(\frac{C}{C^*}\right)^{(3-3\nu)/(3\nu-1)} \tag{4}$$

where X is the number of the segments in the chain, ν is the exponent representing the molecular weight dependence of the radius of gyration S $(=\langle s^2\rangle^{1/2})$ in the dilute solution, and C^* is the crossover concentration between the dilute and semidilute regions. On the other hand, the nondraining model predicts[23]

$$\tau_d = \left(\frac{6\pi\eta_s S^3}{k_B T}\right)\left(\frac{C}{C^*}\right)^{(3-3\nu)/(3\nu-1)} \qquad (5)$$

For *cis*-PI/benzene, we assumed $\nu = 3/5$, since benzene is a good solvent for *cis*-PI as indicated by the exponent ($\alpha = 0.78$) in the Mark–Houwink–Sakurada equation.[40] Hence eq 4 and 5 predict that $\tau_d \propto C$ and $\tau_d \propto C^{1.5}$, respectively.

Jamieson and Telford[24] and Takahashi and Masuda[25] proposed the C dependence of τ_d and zero-shear viscosity based on the unified scaling theory by Schaefer, Joanny, and Pincus.[26,27] In these theories, fluctuation of the chain length proposed by Doi[28] was taken into account. This modifies the exponent of (C/C^*) in eq 4 and 5 into $(2.4 - 2\nu)/(3\nu - 1)$ and $(3.4 - 3\nu)/(3\nu - 1)$, respectively. With $\nu = 3/5$, the free-draining model with the fluctuation of chain length preducts $\tau_d \propto C^{1.5}$ and the nondraining model, $\tau_d \propto C^{2.0}$.

In Figure 2, we recognize that $\tau_{n\zeta} \propto C^{(1.3\pm0.3)}$ as indicated by the dotted line in region II ($0.03 < C < 0.25$). Thus, $\tau_{n\zeta}$ is in approximate agreement with the predictions of the nondraining model (eq 5) or the free-draining model with chain length fluctuation. If the C dependence of ζ is not corrected, τ_n is proportional to $C^{(1.8\pm0.3)}$ in region II. Martel et al.[45] measured the longest relaxation time τ_1 for semidilute solutions of polystyrene and poly(dimethylsiloxane). Their data indicate that τ_1 is also proportional to the power of 1.8 ± 0.3. It should be emphasized that since the crossover occurs gradually over a relatively wide C range, it is difficult to judge whether these values of exponent reflect a feature of the semidilute region or not.

In region III ($C > 0.3$), τ_n increased with a high power of C due to increase in ζ, but $\tau_{n\zeta}$ depends moderately on C as is known for the C dependence of mechanical relaxation times in an isofree volume state. $\tau_{n\zeta}$ is approximately proportional to C, reflecting that M_e is proportional to C^{-1} in concentrtaed solutions.[30]

Dielectric Relaxation Spectra. In Figure 1, we observe that C and M affect similarly the shape of the loss curve. Therefore, we may explain this behavior in the same manner as for undiluted *cis*-PI. In the previous analysis,[5] we used the tube theory assuming the existence of three kinds of motions for the chain in a tube: (i) motion of the chain ends with the size of M_e, (ii) stretching of the chain in the tube, and (iii) reptation. The relaxation times for these modes were expressed as a function of the number of the entanglement points N $(=M/M_e)$:

$$\tau_e = 4\tau_R(M_e) \qquad (6)$$

$$\tau_{eq} = N^2\tau_R(M_e) \qquad (7)$$

$$\tau_d = N^3\tau_R(M_e) \qquad (8)$$

where suffixes e, eq, and d represent modes i, ii, and iii, respectively, and $\tau_R(M_e)$ is[5] the longest relaxation time in the Rouse theory with $M = M_e$. The intensities of the modes per molecule were scaled by the intensity $2P_0$ of the mode (i) to give

$$P_{eq} = P_0(N - 2)/N^{1/2} \qquad (9)$$

$$P_d = P_0(N - 2)(1 - 1/N^{1/2}) \qquad (10)$$

In these equations, we assumed that the intensity for mode ii is proporational to $N^{-1/2}$, as proposed by Doi.[28]

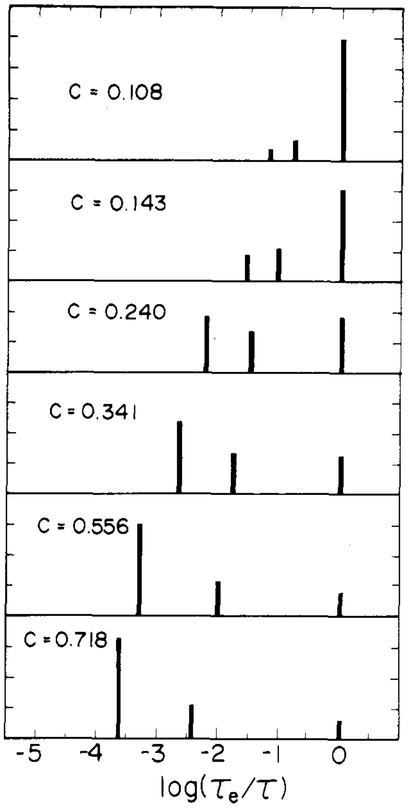

Figure 3. Dielectric relaxation spectra for the normal mode process calculated with eq 6–10.

In order to apply this model to the relaxation spectra for solutions, it was necessary to estimate the C dependence of N. In region III, it is known both theoretically and experimentally that M_e is proportional to C^{-1}. On the other hand, the dynamic scaling law predicts that M_e is proportional to $C^{-1.5}$ in semidilute solutions in a good solvent. For the sake of simplicity, we assumed that M_e is proportional to C^{-1} over the whole concentration range and calculated the spectra as shown in Figure 3.

On the basis of these spectra, we further calculated the theoretical loss curves by assuming that each mode is represented by a Debye-type loss curve and that the sum of the relaxation strengths for the three modes is equal to the experimental value of $\Delta\epsilon/C$. The relaxation time for the motion of the chain end τ_e was used as an adjustable parameter to fit the theoretical curve to the experimental curve. In Figure 4, the loss curves are compared with the experimental loss curves for some typical solutions. Each theoretical curve has a fine structure, but the experimental curves do not. A similar discrepancy was also seen in the spectra for the bulk samples[5] and may be due to the oversimplified model used. However, the model explains the features of the C dependence of the loss curves at least semiquantitatively.

These results imply that the dielectric relaxation spectra for the normal mode process are a function of M/M_e alone. Thus, the shape of the loss curve for the solutions should be the same as that for an undiluted *cis*-PI with a molecular weight CM. This idea is tested in Figure 5, in which the normalized loss curves $\epsilon''/\epsilon''_{max}$ vs. $\log(f/f_m)$ plots are compared between the solutions and corresponding bulk samples. For 12.3 and 16.2 wt % solutions, the agreement is excellent. But for 37.9 and 61.8% solutions, the loss curves for the solutions are slightly narrower than those of the corresponding bulk samples. One of the origins for this disagreement may be a wider distribution in molecular

Table I

Weight Fraction w, Concentration C, Relaxation Strength $\Delta\epsilon$ Determined (a) from Cole–Cole Plots and (b) from the Area under the Loss Curve, $\Delta\epsilon$ Divided by C, the Mean Square End-to-End Distance $\langle r^2\rangle$, and Relaxation Time τ_n for the Normal Mode Process at 298 K

10^2w	10^2C, g cm^{-3}	$10^2\Delta\epsilon$[a]	$10^2\Delta\epsilon$[b]	$\Delta\epsilon/C$, g^{-1} cm^3	$10^{12}\langle r^2\rangle$,[c] cm^2	τ_n, s
0.852	0.741	0.190	0.166	0.24	19.4	3.2×10^{-6}
2.091	1.82	0.41	0.41	0.21	18.2	7.1×10^{-6}
3.45	3.04	0.69	0.66	0.22	17.7	1.3×10^{-5}
4.57	4.02	0.81	0.79	0.199	16.0	1.1×10^{-5}
5.81	5.11	1.07	0.95	0.198	15.9	1.6×10^{-5}
8.68	7.64	1.50	1.31	0.184	14.8	2.5×10^{-5}
12.30	10.82	2.00	1.87	0.179	14.4	6.3×10^{-5}
16.21	14.26	2.49	2.37	0.170	13.7	7.9×10^{-5}
23.13	20.59	3.31	3.16	0.157	12.6	2.3×10^{-4}
27.0	24.0	3.75	3.70	0.155	12.5	4.0×10^{-4}
37.9	34.1	4.6	4.27	0.130	10.4	1.1×10^{-3}
61.8	55.6	5.7	5.65	0.102	8.2	3.2×10^{-3}
79.8	71.8		7.8	0.109	8.8	5.6×10^{-2}
100.0	91.1		8.9	0.098	7.9	3.4×10^{-1}

[a] From the Cole–Cole plot. [b] From the area of loss curve. [c] From $\Delta\epsilon/C$ with $\mu = 4.80 \times 10^{-12}$ (cgs) and $F = 1$.

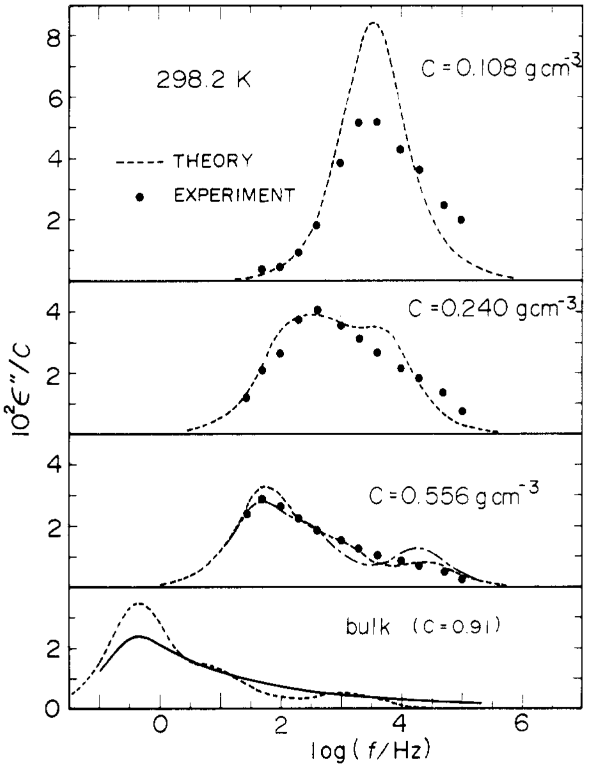

Figure 4. Comparison between the calculated (dashed line) and the experimental loss factor for the representative solutions.

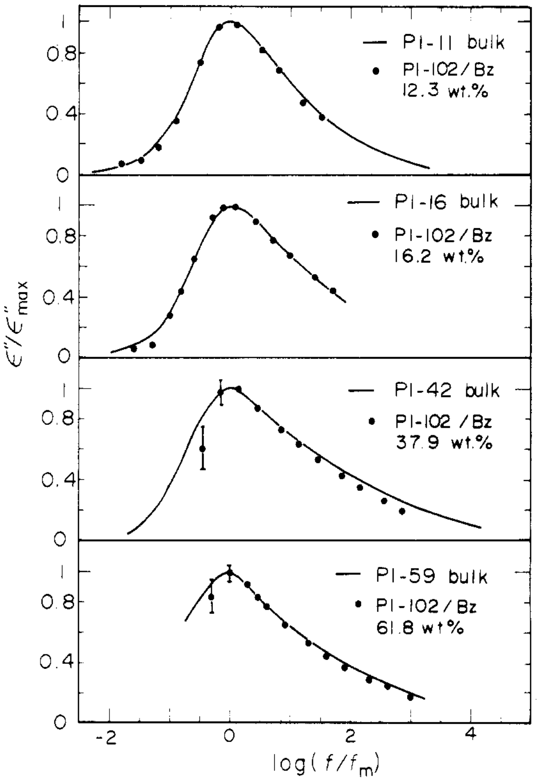

Figure 5. Comparison of the shape of the loss curve for the normal mode process between the *cis*-PI solution, in which the molecular weight of the solute is M and concentration is C, and the corresponding undiluted *cis*-PI with the molecular weight CM.

weight for PI-42 and PI-59 than for PI-102. These results suggest that the spectra for the solutions having the same CM are at least approximately the same.

3. Relaxation Strength. Concentration Dependence of $\langle r^2\rangle$. The dielectric relaxation strength $\Delta\epsilon$ was determined from the Cole–Cole plot and the area of the loss curve. Since the values from the two methods coincide fairly well, as seen in Table I, the average of the two values was used for the later analysis.

The value of $\Delta\epsilon/C$ for the normal mode process is given by[13,15]

$$\frac{\Delta\epsilon}{C} = \left(\frac{4\pi N_A\mu^2F}{3k_BT}\right)\left(\frac{\langle r^2\rangle}{M}\right) \tag{11}$$

where μ is the dipole moment per unit contour length; $\langle r^2\rangle$, the mean square end-to-end distance; and F, the ratio of the internal and external electric fields. In our recent paper,[7] we showed that eq 11 holds irrespective of the conformation of the chain and that F is closer to unity than to the values given by the Lorentz or the Onsager equations. We also estimated the direction and the magnitude of the dipole moment of the monomeric unit of *cis*-PI. A calculation of the electron density in terms of the molecular orbital theory indicated that the C=C double bond has a relatively strong bond moment (0.54 D) and —C(CH$_3$)= group is charged positively.[5] The value of μ was estimated to be 4.80×10^{-12} cgs esu from the relaxation strength of bulk *cis*-PI with $F = 1$.

Using the value of μ thus estimated experimentally and $F = 1$, we calculated $\langle r^2\rangle$ for the solutions. The results are shown in Figure 6 and Table I. It should be noted that since the dielectric constant of benzene (=2.276) and the unrelaxed dielectric constant of bulk *cis*-PI (=2.34) are approximately the same, we may take F, if not unity, independent of C for the present system. Therefore $\Delta\epsilon/C$

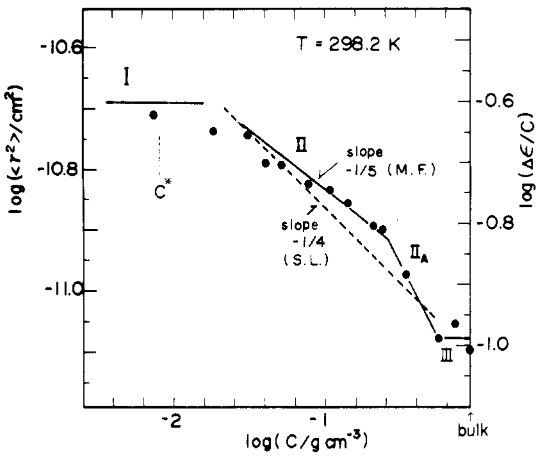

Figure 6. Concentration dependence of the mean square end-to-end distance at 298.2 K.

differs from $\langle r^2 \rangle$ only by a constant factor, and the plot of log ($\Delta\epsilon/C$) vs. log C should reflect, at least, a correct C dependence of $\langle r^2 \rangle$.

In Figure 6, we recognize a rather gradual change of $\langle r^2 \rangle$ with C. None of the existing theories can explain unequivocally such a C dependence of $\langle r^2 \rangle$. However, we may divide the curve into four concentration regions in which the C dependence of $\langle r^2 \rangle$ differs: namely, regions I ($C < 0.01$), II ($0.01 < C < 0.20$), IIA ($0.2 < C < 0.5$), and III ($0.5 < C$). We call region IIA the semiconcentrated region after Richards et al.[37] The crossover concentration C^* between the I and II regions was estimated to be 0.007 g/cm^3 from the relation

$$C^* = 3M/4\pi S^3 N_A \tag{12}$$

where S $(=\langle s^2 \rangle^{1/2})$ was estimated from the largest value of $\langle r^2 \rangle$ in the dilute region by assuming $\langle s^2 \rangle = \langle r^2 \rangle/6$. As seen in Figure 6, log $\langle r^2 \rangle$ decreases linearly with log C, and we can draw a line wiht a slope of $-^1/_5$ in the region of C from 0.03 to 0.2 (region II).

According to Daoud and Jannink,[31] the C dependence of $\langle r^2 \rangle$ in the semidilute region is expressed by a scaling form:

$$\langle r^2 \rangle \propto C^{-(2\nu-1)/(3\nu-1)} \tag{13}$$

If we assume $\nu = 3/5$ for the *cis*-PI/benzene system, $\langle r^2 \rangle$ should be proportional to $C^{-1/4}$. If we combine regions II and IIA as one semidilute region, the average slope of log $\langle r^2 \rangle$ vs. log C becomes–1/4, as shown by the dashed line in Figure 6. Thus, the scaling theory explains approximately the C dependence of $\langle r^2 \rangle$.

With a mean field theory, Edwards[32] proposed for the C dependence of $\langle r^2 \rangle$

$$\langle r^2 \rangle \propto 1 + KC^{-1/2} \tag{14}$$

where K is a constant. Edwards and Jeffers[33] indicated that there exists an additional semidilute region in which $\langle r^2 \rangle$ is proportional to $C^{-1/5}$, which is in agreement with the observed C dependence in region II ($0.03 < C < 0.25$). However, the recent theory by Muthukumar and Edwards[48] does not indicate the existence of this region. They indicate that eq 14 is valid at the limit of high concentration.

We tested our data against the $C^{-1/2}$ dependence as shown in Figure 7. Again, we observe a rather gradual change in $\langle r^2 \rangle$ with $C^{-1/2}$. However, in the limited region (IIA) of $0.2 < C < 0.5$, we recognize that $\langle r^2 \rangle$ is linear in $C^{-1/2}$. Therefore, this region may be assigned to the region conforming to eq 14. With further increase of C, $\langle r^2 \rangle$ becomes independent of concentration. Thus region III is assigned to the concentrated state.

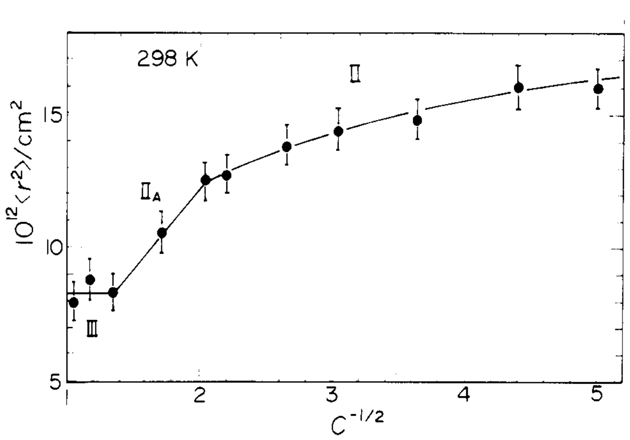

Figure 7. Plot of the mean-square end-to-end distance $\langle r^2 \rangle$ vs. $C^{-1/2}$ to test the applicability of eq 14.

To date, only a few experimental data on the C dependence of polymer dimensions have been reported. All of these studies were made on $\langle s^2 \rangle$ rather than $\langle r^2 \rangle$ for solutions of deuterated polystyrene by SANS.[34-38] Richards et al.[37] showed that the C dependence of $\langle s^2 \rangle$ in cyclohexane solutions of polystyrene conformed to eq 14. However, they did not observe the coexistence of regions II and IIA. The data by Daoud et al.[34] on carbon disulfide solutions of polystyrene also indicated the existence of only one semidilute region, II, in a range of $0.02 < C$. Since the experimental error in the determination of the dielectric relaxation strength is estimated to be about 15%, we need to confirm the existence of the IIA region by more precise measurements.

Crossover Concentrations. Schaefer et al. studied the C dependence of the screening length ξ by taking into account the local rigidity of the chain.[26,27] They proposed the existence of five concentration regions in which the C dependence of ξ changes, namely the dilute (I′), semidilute–good (II′), semidilute–marginal (III′), semidilute-θ (IV′), and concentrated (V′) regions.[26,27] Schaefer et al. considered that the C dependence of ξ in region III′ can be described by the mean field theory of Edwards.[32] Therefore, the IIA region in Figure 7 may correspond to region III′ by their theory. The volume fraction $\tilde{\phi}$ at the crossover between II′ and III′ and ϕ^+ between III′ and IV′ are expressed by using the interaction parameter χ and the parameter $n = C_\infty/6$, where C_∞ denotes the characteristic ratio:

$$\tilde{\phi} = \frac{3}{4\pi}\,\frac{1-2\chi}{n^3} \tag{15}$$

$$\phi^+ = 1 - 2\chi \tag{16}$$

The value of C_∞ for *cis*-PI is reported[49] to be 4.7, resulting in $n = 0.78$. Using this value, we find the ratio $\tilde{\phi}/\phi^+$ to be 2.0, in approximate agreement with the ratio of the crossover concentration between II and IIA to that between IIA and III. However, we should note that the theory is not in harmony with the present result in two aspects. First, we need to assume a relatively low value of χ (=0.25) if we regard the crossover between IIA and III regions as corresponding to ϕ^+. But χ is reported to be 0.44 for the system *cis*-PI/benzene.[41,50] Second, they considered that $\langle r^2 \rangle$ is independent of C in the region III′, while the value of $\langle r_2 \rangle$ in the region IIA still depends on C.

Finally, we compare in Table II the crossover concentrations determined from $\langle r^2 \rangle$ with those from the C dependence in τ_n. The crossover concentrations from the

Table II
Comparison of the Various Concentration Regions in the *cis*-PI Solutions Observed by the C Dependences of the Relaxation Time τ_n and by the Relaxation Strength $\Delta\epsilon$ (or $\langle r^2 \rangle$)

	I, dil	II, semidilute	IIA, semiconcentrated	III, concd
τ_n	$C < 0.02$	$0.03 < C < 0.25$		$0.25 < C$
$\Delta\epsilon$	$C < 0.01$	$0.01 < C < 0.2$	$0.2 < C < 0.5$	$0.5 < C$

static and dynamic properties coincide fairly well. At the present stage, it is not clear whether the C dependence of τ_n in the IIA region is different from that in region III.

Conclusions

The relaxation time for the normal mode process in the isofriction state increased with C with the power of 1.3 ± 0.3 in the semidilute region. This C dependence agrees with the prediction of dynamic scaling law based on the nondraining model or the free-draining model with fluctuation of the chain length in a tube.

The distribution of the relaxation times became broader with C and could be semiquantitatively explained as a function of M/M_e by the tube model.

The solutions having the same value of CM exhibited the same distribution of the relaxation times with the bulk sample with M.

The solutions may be split into four groups having different C dependence of the mean-square end-to-end distance $\langle r^2 \rangle$. The C dependence of $\langle r^2 \rangle$ was in approximate agreement with the prediction by the scaling law and the mean field theory.

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