described by the above theory.

Depletion Regime ($\delta \simeq +1$). The profile is assumed to obey the scaling structure $\phi(z) = \phi_b(z/\xi_b)^m$ together with condition 1. The change in interfacial tension is

$$\Delta\gamma = \frac{kT}{a^2}\left(\phi_s\frac{\delta}{a^2} + \frac{1}{{\xi_b}^3}(\xi_b - D)\right)$$

The second term is due to the creation of the depletion layer of thickness $\xi_b \simeq D$ (cf. Figure 6). Writing that this expression should be independent of the molecular mass of the polymer leads to $m = {}^5/_3$ and $D = a\delta^{-3/2}$ and finally

$$\Delta\gamma = \frac{kT}{a^2}({\phi_b}^{3/2} + {\phi_b}^{9/4}(D/a))$$

As $D \simeq a(\delta \simeq 1)$ and $\phi_b < 1$, the leading term is

$$\Delta\gamma = \frac{kT}{a^2}{\phi_b}^{3/2}$$

Special Transition. Close to the adsorption–depletion transition, $|\delta| \simeq 0$ (if T_a is the transition temperature, $\delta \propto (T - T_a)/T_a$). This case has been addressed by Eisenriegler, Kremer, and Binder[10,11] by mapping the polymer adsorption problem to the half-infinite spin problem with a short-range attractive term due to the surface. It is a multicritical problem with two associated correlation lengths: $\xi_b = (g^{-1})^{-\nu}$ ("bulk" critical length; g is the number of monomers per blob, $g = {\Phi_b}^{-5/4}$); ξ_c $(=D)$ $= |\delta|^{-\nu/\varphi}$ ("surface" critical length), where ν is the usual exponent of critical phenomema ($\simeq 0.6$) and φ is a crossover exponent. A simple physical meaning of φ can be given for a single chain: if this chain has N links, the number M of adsorbed links is $M = N^{\varphi}$. φ has been computed from scaling arguments and Monte Carlo simulations[10] and $\epsilon = 4 - d$ expansions to the second order:[12] it appears that $\varphi \simeq \nu$ (in ref 2, $\varphi \simeq 1 - \nu$). This gives now $D = a|\delta|^{-1}$. The resulting concentration profiles and surface tension[13] are given in Figures 7 and 8. The peculiar behavior associated with singular profiles can be qualitatively understood on the basis of the competition for polymers in the semidilute regime between the attraction by the wall and excluded volume effects. Notice that the first approach is a subcase of the second one for $|\delta| \rightarrow 1$ (adsorption or depletion) because then $|\delta|^{-1} = |\delta|^{-3/2} = 1$ and $D = a$.

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Dielectric Study of the Concentration Dependence of the End-to-End Distance and Normal-Mode Relaxation Time of Polyisoprene in Moderately Good Solvents

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ABSTRACT: The dielectric normal-mode process was studied for semidilute and concentrated solutions of *cis*-polyisoprene (*cis*-PI) in moderately good solvents, hexadecane (C16) and eicosene (C20). The mean-square end-to-end distance $\langle r^2 \rangle$ was determined and compared with our previous data on $\langle r^2 \rangle$ in good solvents, benzene and toluene, and those in a Θ solvent, dioxane. In dilute solutions, the values of $\langle r^2 \rangle$ in C16 and C20 were between those in the good and Θ solvents. From the expansion factor of the *cis*-PI molecules in dilute solutions, the interaction parameter χ was estimated based on the Flory theory. The double-logarithmic plot of $\langle r^2 \rangle/M$ against concentration C indicated four regimes: dilute (I), semidilute (II), semiconcentrated (II′), and concentrated (III). The C dependences of $\langle r^2 \rangle$ in regimes II and II′ were explained on the basis of the scaling theory by Daoud and Jannink and the mean-field theory by Edwards, respectively. A phase diagram classifying these regimes was obtained by plotting the crossover concentrations C^* on the solvent quality vs C diagram. The double-logarithmic plot of the relaxation time τ against C indicated that τ is independent of C in the dilute regime (I), but log τ is proportional to log C in the semidilute region (II). The dynamic crossover concentration C_τ coincided with the static crossover concentration C^* between regimes I and II.

Introduction

In our previous papers we reported that *cis*-polyisoprene (*cis*-PI) exhibits a dielectric normal-mode process due to fluctuation of the end-to-end distance.[1-3] The data of the normal-mode process provide us information on the mean-square end-to-end distance $\langle r^2 \rangle$ as well as the dynamic properties such as the relaxation time τ for the fluctuation of the end-to-end vector $\mathbf{r}$ of *cis*-PI.

Concentration C dependences of $\langle r^2 \rangle$ and τ in semidilute and concentrated solutions are recent main subjects of polymer physics.[5-11] However, τ and $\langle r^2 \rangle$ have never been measured directly by a method other than dielectric

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Table I
Characteristics of *cis*-Polyisoprene

code	$10^{-3}M_w$	M_w/M_n
PI-32	31.6	1.05
PI-101	101	1.09
PI-102	102	1.18
PI-164	164	1.17

spectroscopy,[12] though these quantities frequently appear in the literature of polymer physics. Most of the experimental studies were conducted by measuring the radius of gyration,[13-15] thermodynamic properties,[16] viscosity,[17-19] and diffusion coefficient.[20]

Daoud and Jannink[6] classified polymer solutions into three regimes according to the magnitude of intra- and intermolecular excluded-volume effects: the dilute regime (I), the semidilute regime (II), and the concentrated regime (III). In regime II, the dimension of the polymer molecules decreases with C in proportion to $C^{(2\nu-1)/(3\nu-1)}$, where ν is the Flory excluded-volume parameter. However, Edwards and Muthukumar[8] reported a theory based on the mean-field theory and predicted the existence of a new regime, in which the C dependence of $\langle r^2 \rangle$ is different from the scaling law. In the regime III, the excluded volume effect is completely screened out and $\langle r^2 \rangle$ is the same as that in the unperturbed state.

To test these theoretical predictions, we used the dielectric normal-mode method and reported the C dependence of $\langle r^2 \rangle$ of *cis*-PI in a good solvent, benzene (Bz), and a Θ solvent, dioxane (Diox).[2,3]

This paper is an extension of the previous studies[2,3] to solutions of *cis*-PI in moderately good or marginal solvents, hexadecane (C16) and eicosene (C20). The previous studies[2,3] indicated the existence of two regimes, II and II′, in which $\langle r^2 \rangle$ was proportional to ca. $C^{-1/5}$ and ca. $C^{-0.4}$, respectively. The latter behavior cannot be explained by the Daoud–Jannink theory,[6] since the absolute value of the exponent, 0.4, is larger than the predicted maximum value of $^1/_4$. We explained the behavior on the basis of the mean-field theory proposed by Edwards.[7,8] In regime III, $\langle r^2 \rangle$ in Bz solutions was close to the value in the bulk state. To confirm this behavior, we will use data on toluene solutions reported recently.[21]

An objective of this study was to examine whether the C dependence curve of $\langle r^2 \rangle$ in marginal solvents also exhibits the regime II′. We also intended to construct a phase diagram by plotting the crossover concentrations on a solvent quality versus the C plane from the set of data on the C dependence of $\langle r^2 \rangle$ in good, marginal, and Θ solvents. Besides these static properties, we also studied the dynamical properties of *cis*-PI in these solvents. The effect of the solvent quality on the relaxation time for the fluctuation of the end-to-end vector of *cis*-PI was also examined.

Experimental Section

The samples of *cis*-PI used in this study were prepared by anionic polymerization and characterized by gel permeation chromatography as described previously.[1,2] In the present study, we used *cis*-PI with the weight-average molecular weight M_w of 1.01×10^5 (PI-101). For the sake of comparison, the data of Bz, toluene (Tol), and Diox solutions of PI-164, PI-102, and PI-32 are also employed.[2,3,21] The characteristics of the samples are summarized in Table I.

Hexadecane (C16) and eicosene (C20) were purchased from Wako Pure Chemicals Ltd. and used without further purification, since the direct-current conduction of as-received solvents was negligible. We determined the polymer concentration, C (g mL^{-1}), from the weight fraction of *cis*-PI in the solution, assuming the additivity of the density of the solvent and *cis*-PI.

Table II
Weight Fraction w, Concentration C, Relaxation Strength $\Delta\epsilon$, Values of $\Delta\epsilon/C$, and the Mean-Square End-to-End Distance $\langle r^2 \rangle$ of *cis*-PI in C16 and C20 at 308.2 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	$10^{11}\langle r^2 \rangle$, cm^2
		PI-101/C16			
0.70	0.54	0.088		0.168	1.24
1.45	1.17	0.186		0.165	1.22
1.86	1.45	0.284		0.172	1.27
3.19	2.48	0.459		0.174	1.38
4.85	3.78	0.629		0.166	1.23
10.36	8.16	1.21	1.34	0.156	1.16
15.97	12.68	1.73	1.93	0.145	1.07
30.12	24.43	3.02	3.10	0.125	0.93
49.87	41.72	4.46	4.56	0.108	0.80
		PI-101/C20			
0.70	0.55	0.085		0.156	1.15
1.50	1.18	0.184		0.158	1.16
2.50	1.96	0.338		0.159	1.18
5.00	3.40	0.633		0.161	1.19
9.97	7.90	1.23	1.10	0.148	1.09
14.64	11.68	1.65	1.69	0.143	1.06
25.07	20.30	2.72	2.85	0.137	1.02
39.72	32.87	4.03	4.50	0.130	0.96

[a] From the area under the ϵ'' curve. [b] From the Cole–Cole plot.

Measurements of the dielectric constant ϵ' and loss factor ϵ'' were made at 308 K. A capacitance cell and bridges were the same as those described previously.[2,3]

Intrinsic viscosities of PI-101 in C16 and C20 were determined at 308 K to be 46.1 and 41.5 g^{-1} mL, respectively.

Results and Discussion

Dielectric Relaxation Strength and End-to-End Distance. Dielectric relaxation strength $\Delta\epsilon$ of *cis*-PI solutions was determined from the area under their dielectric loss ϵ'' curves and also from the Cole–Cole plots. For dilute solutions, the ϵ'' curves extended into the high-frequency range beyond the maximum attainable frequency of the bridges employed here. In such a case, we estimated the high-frequency tail assuming the same shape of the loss curve as that for PI-164 reported previously.[2] The results are given in Table II.

The relaxation strength for the normal-mode process is given by[4]

$$\Delta\epsilon/C = 4\pi N_A \mu^2 \langle r^2 \rangle F/(3k_B TM) \qquad (1)$$

where C is the concentration in wt/vol, N_A, the Avogadro constant, M, the (weight-average) molecular weight, μ ($=4.80 \times 10^{-12}$ cgs esu), 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 to external field strengths.

As is well-known, the dipole moment of a simple molecule is usually determined on the basis of the internal field proposed by Lorentz or by Onsager.[22,23] Thus, we have to express F for the normal-mode process as a function of the dielectric constant of the medium surrounding the *cis*-PI molecules. However, in the case of the normal-mode process, we found experimentally that F is independent of the solvent polarity.[4] We also discussed the validity of $F = 1$ in our previous paper.[2] Even if the above assumption is not valid, the C dependence of F is expected to be very small in the present systems, because the dielectric constants of C16 and C20 are close to the high-frequency dielectric constant of bulk *cis*-PI. Thus, on the basis of the assumption of $F = 1$, $\langle r^2 \rangle$ was determined from $\Delta\epsilon/C$ for the C16 and C20 solutions with varying C. The results are summarized in Table II and Figure 1.

The error in the determination of $\Delta\epsilon/C$ is estimated to be ca. 10% in the concentrated regime, but it increases

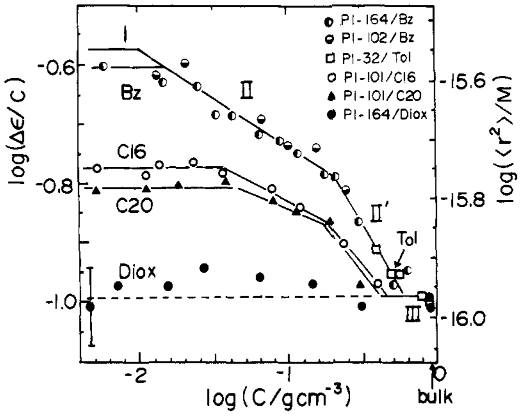

Figure 1. Concentration C dependence of the dielectric relaxation strength $\Delta\epsilon$ divided by C and the mean-square end-to-end distance $\langle r^2 \rangle$ divided by molecular weight M for solutions of *cis*-PI.

Table III
Values of $(\alpha^5 - \alpha^3)/2M^{1/2}$, V_1, C_M, $^1/_2 - \chi$, and ν at Temperature T

soln	$10^3(\alpha^5 - \alpha^3)/2M^{1/2}$	V_1	10^2C_M	$^1/_2 - \chi$	ν^a	ν^b	T, K
PI-102/Bz	8.14	89	2.34	0.35	0.578	0.58	298.2
PI-101/C16	1.86	290	0.72	0.26	0.563	0.54	308.2
PI-101/C20	1.33	360	0.58	0.22	0.557	0.52	308.2
PI-164/Diox	0.0	87	2.40	0	0.5	0.5	308.2

[a] From α with eq 5. [b] From the slope of $\langle r^2 \rangle$ vs C plot in regime II.

with decreasing C since $\Delta\epsilon$ becomes small. We estimated the error in the dilute regime to be 20%.[1]

Expansion Coefficient and the Quality of the Solvent. Before analyzing the C dependence of $\langle r^2 \rangle$, we assess the solvent quality using the expansion coefficient α^2 ($= \langle r^2 \rangle / \langle r^2 \rangle_0$) in dilute solutions. The subscript 0 denotes the unperturbed state. According to Flory,[24] α is given by

$$(\alpha^5 - \alpha^3)/2M^{1/2} = C_M \Psi_1 (1 - \Theta/T) \tag{2}$$

Here Θ is the Θ temperature, Ψ_1 is a constant, and C_M is given by

$$C_M = 0.8572(v^2/V_1 N_A)(M/\langle r^2 \rangle_0)^{3/2} \tag{3}$$

with v being the specific volume of the polymer, and V_1, the molar volume of the solvent. The interaction parameter χ between the polymer and the solvent is given by

$$\tfrac{1}{2} - \chi = \Psi_1 (1 - \Theta/T) \tag{4}$$

The parameter $^1/_2 - \chi$ was determined from the observed values of α. Table III lists the values of the left-hand side of eq 2 and $^1/_2 - \chi$ with the values of C_M and V_1. In this calculation, we used $v = 1.10$ cm^3 g^{-1} and $\langle r^2 \rangle_0 / M = 8.8 \times 10^{-17}$ cm^2.[1] The results indicate that C16 and C20 are moderately good solvents for *cis*-PI and that C16 is a slightly better solvent than C20.

We also determined the Flory excluded-volume parameter ν using the following relation:[24]

$$\nu = (3\alpha^4 - 2\alpha^2)/(5\alpha^4 - 3\alpha^2) \tag{5}$$

As is well-known, the limiting value of ν is 0.6 in a good solvent and 0.5 in a Θ solvent. The values of ν are also listed in Table III.

Concentration Dependence of $\langle r^2 \rangle$ in the Semidilute Region. In Figure 1, the C dependence of $\langle r^2 \rangle / M$ of *cis*-PI in Bz, Tol, C16, C20, and Diox solutions are compared. As pointed out previously,[2,3] the double-logarithmic plot of $\langle r^2 \rangle / M$ vs C for Bz solutions exhibited four different regimes: dilute (I), semidilute (II), semiconcentrated (II′), and concentrated (III). On the other hand, $\langle r^2 \rangle / M$ for Diox solutions was independent of C within the experimental error. Although the data points are scattered, we recognize the existance of the regime II′ as well as regimes I and II for C16 and C20 solutions. Therefore, we conclude that the solutions in marginal solvents also exhibit behavior similar to those in a good solvent.

Daoud and Jannink[6] proposed the C dependence of $\langle r^2 \rangle$ in semidilute solutions as

$$\langle r^2 \rangle = \langle r^2 \rangle_I (C/C^*)^{-(2\nu-1)/(3\nu-1)} \tag{6}$$

where $\langle r^2 \rangle_I$ is the mean-square end-to-end distance in the dilute regime of the given solvent, C^*, the crossover concentration between regimes I and II, and ν, the Flory excluded-volume exponent. We estimated ν from the slope of the log $\langle r^2 \rangle$ vs log C plot in the regime II and compared with ν determined from α in Table III. It is seen that for C16 and C20 solutions the values of ν do not agree each other.

The slopes in the regime II′ for Bz, C16, and C20 solutions are −0.45, −0.35, and −0.35, respectively. These slopes are steeper than the maximum slope of −0.25 predicted by eq 6. Thus, the scaling theory cannot explain the behavior in this range of C. In our previous work[1,2] we compared the regime II′ behavior in Bz solutions with the mean-field theory proposed by Edwards:[7]

$$\langle r^2 \rangle = \langle r^2 \rangle_0 [1 + KC^{-1/2}] \tag{7}$$

Here K is a constant given by

$$K^2 = a^2 w M_0 / (6 l^4 N_A) \tag{8}$$

where a and w are constants, l, the Kuhn step length, and M_0, the molecular weight of the repeating unit. When K has a value of the order of unity, the slope of the log $\langle r^2 \rangle$ vs log C becomes higher than the maximum slope predicted by the scaling theory. Previously we evaluated K to be 0.55 for *cis*-PI in Bz.[2] The values of K for C16 and C20 solutions are calculated to be 0.26 and 0.22, respectively, from the data of $\alpha^5 - \alpha^3$. The K value of 0.26 gives the slope at $C = 0.5$ of ca. −0.25, which is too small to explain the observed high slope in the regime II′.

In the regime III, the scaling theory predicts that the excluded-volume effect is completely screened and that $\langle r^2 \rangle$ is equal to the unperturbed value $\langle r^2 \rangle_0$. To test this, we used the data of Tol solutions of PI-32 instead of PI-101.[21] This is because the relaxation time for PI-101 in the high-concentration region became too long and the whole ϵ'' curve could not be observed at 308 K with the capacitance bridge used in this study. To collect low-frequency data, it was necessary to raise the temperature or to use a transient current method.[2] Both methods caused error in determining the relaxation strength $\Delta\epsilon$.

In the high-concentration range the excluded-volume effect acts within the correlation length, and hence $\langle r^2 \rangle / M$ is expected to be independent of molecular weight.[5] Therefore, the data for the relatively low-molecular-weight *cis*-PI can be used to examine the behavior in regime III. We also expect that the solvent quality of Tol is similar to Bz. Thus, we plotted $\langle r^2 \rangle / M$ for the PI-32/Tol system with square symbols in Figure 1. We see that $\langle r^2 \rangle$ decreases to the unperturbed value around $C = 0.6$.

Here we consider whether the molecular weight of *cis*-PI employed in this study is sufficiently high for applying scaling laws that assume extremely high molecular weight. Obviously the main factor that affects the dimension of a polymer chain is the number of atoms Z in the main chain. For PI-101, Z is ca. 5900. We may consider that this number is not too small for the argument of scaling laws, though it is not sufficiently high. Scaling laws have

Table IV
Crossover Concentration[a]

system	theor C^*	obsd C^*	obsd C^+	obsd C^{++}
PI-102/Bz	0.0041	0.014	0.21	0.55
PI-101/C16	0.0074	0.035	0.17	0.39
PI-101/C20	0.0082	0.041	0.15	

[a] In g cm^{-3}.

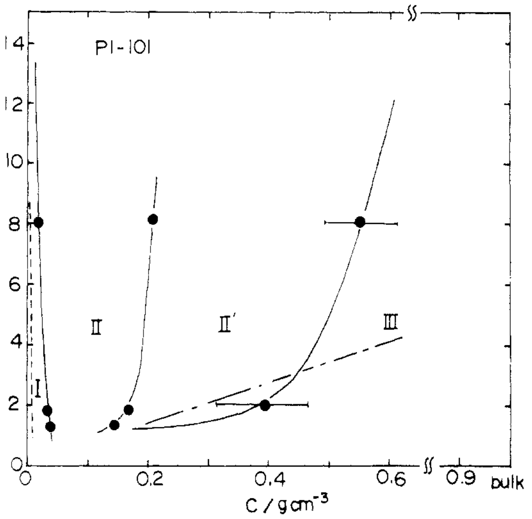

Figure 2. Phase diagram classifying the various regimes of PI-101 solutions. The dashed line indicates eq 9, and the dash-dot line eq 10 calculated with $C_M = 0.0234$ and $\Psi_1 = 0.3$.

been most frequently tested for polystyrene. With respect to Z, PI-101 corresponds to polystyrene with a molecular weight of 3.1×10^5.

Crossover Concentrations and Phase Diagram. According to the scaling theory,[5,6] the crossover concentration C^* between regimes I and II is written as

$$C^* = (3/4\pi)M/(S^3N_A) \qquad (9)$$

where S is the average radius of gyration in regime I. As is well-known, C^* cannot be determined in an unambiguous manner, i.e., the value of C^* changes by a factor of ca. 3 depending on the choice of the front factor of eq 9, which is $3/4\pi$ in the present equation but often assumed to be unity. We estimated roughly the theoretical C^* from the experimental values of $\langle r^2 \rangle$ in dilute solutions assuming $S^2 = \langle r^2 \rangle/6$, though this relation as well does not hold in a good solvent.[25] Due to the error in measurement of $\Delta\epsilon/C$ in dilute regime, theoretical C^* includes an error of 30%.

The two horizontal lines drawn for Bz solutions in regime I represent the $\langle r^2 \rangle/M$ for PI-164 and PI-102. Since the data points are few, the levels were determined by interpolating our previous data of the M_w dependence of $\langle r^2 \rangle/M$ in dilute solutions.[1] From the cross points of the dilute and semidilute lines, C^* was determined to be 0.013 and 0.017 for PI-164 and PI-102, respectively. The observed C^* thus estimated is compared with the theoretical value of eq 9 in Table IV. The crossover concentration C^+ between II and II' and that C^{++} between II' and III are also estimated graphically as the cross points of the lines representing $\langle r^2 \rangle/M$ in the respective regimes. These results are listed in Table IV.

The phase diagram is shown in Figure 2 where the crossover concentrations C^*, C^+, and C^{++} are plotted on the $(\alpha^5 - \alpha^3)/M^{1/2}$ vs C plane. We see from eq 2 that the ordinate is proportional to $(T - \Theta)/T$. The theoretical C^* is shown by the dashed line. According to the theory by Daoud and Jannink,[6] semidilute regime II transforms into concentrated regime III at the crossover concentration C^{**} given by

$$C^{**} = (T - \Theta)/\Theta \qquad (10)$$

where Θ is the Θ temperature. Since T is close to Θ, C^{**} is approximately equal to $(^1/_2 - \chi)/\Psi_1$. For cyclohexane solutions of polyisobutylene, Ψ_1 is reported to be 0.3.[26] We roughly plotted C^{**} in Figure 3 assuming $\Psi_1 = 0.3$ and using the value of C_M for Bz. We see that the experimental phase diagram is quite different from that predicted by the scaling theory.

As an alternative quantity for the ordinate of the phase diagram, one may use $^1/_2 - \chi$. However, we consider that this quantity is not adequate for the present purpose. The reason is as follows. In the lattice theory, Flory–Huggins assumed that each solvent molecule occupies one lattice point.[24] However, C16 and C20 have a flexible chain structure, and hence we should evaluate $^1/_2 - \chi$ taking into account the oligomer-like properties of the C16 and C20 molecules which occupy more than two sites.[27] Using $^1/_2 - \chi$ thus evaluated, we obtain a phase diagram similar to that in Figure 2.

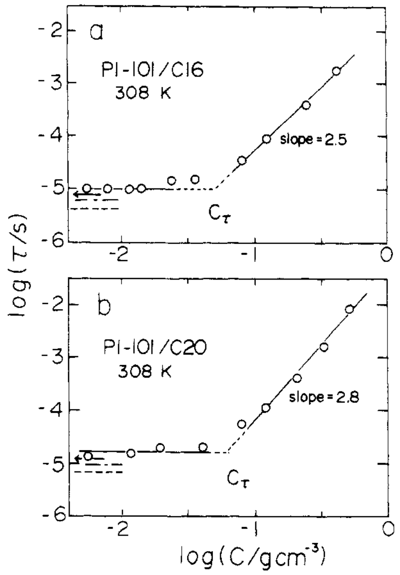

Figure 3. Concentration dependence of the relaxation time τ for solutions of PI-101 in C16 (a) and C20 (b). The arrows indicate the relaxation time at infinite dilution extrapolated by the Muthukumar plot. The dashed line and dot–dash lines indicate the theoretical τ calculated with Zimm and Rouse theories, respectively.

Dynamic Behavior. Now we turn our attention toward the C dependence of the dynamic properties of *cis*-PI solutions. Figure 3 shows the C dependence of the relaxation time τ in C16 and C20 solutions. In the dilute regime, the Rouse–Zimm theory predicts

$$\tau = KM\eta_s[\eta]/RT \qquad (11)$$

where η_s is the solvent viscosity and K is a constant equal to 1.22 for the free-draining model of Rouse[28] and 0.85 for nondraining model of Zimm.[29] Figure 3 shows the theoretical τ calculated with the data of the intrinsic viscosity given in the Experimental Section and those reported in the literature.[30] We extrapolated log τ to infinite dilution by plotting log τ with respect to $C[\eta]$ as shown in Figure 4. The linearity in the log τ versus $C[\eta]$ plot was confirmed by Lodge et al. by oscillatory-flow birefringence.[18] This linear relationship was also derived theoretically by Muthukumar and Freed.[31,32]

For each solution shown in Figure 3 the relaxation time τ_0 at infinite dilution is indicated by the arrow. We see

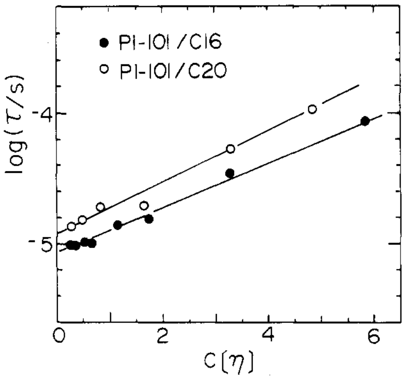

Figure 4. Muthukumar plot for C16 and C20 solutions of PI-101.

that τ_0 for C16 and C20 solutions are longer by factors of 2.0 and 1.6, respectively, than the theoretical relaxation times predicted by the Zimm theory.

According to Muthukumar,[32] the slope A of the ln τ vs C plot is given by

$$A = \pi N_A l l_1^{3/2}/(12M_0^2 q)^{1/2} \qquad (12)$$

where N_A is the Avogadro number, l, the Kuhn step length, l_1, the renormalized step length, M_0, the molecular weight for the step, and $q = 2\pi/L$. Here L is the contour length of the chain. From the data of $\langle r^2 \rangle$ in the dilute regime, we estimated l and l_1 and then calculated A to be 170 and 152 for C16 and C20 solutions, respectively. On the other hand, the experimental value of A was determined from the slope of log τ vs $C[\eta]$ to be 17.2 and 17.1 for C16 and C20 solutions, respectively. These values are ca. 1 order smaller than the theoretical ones calculated above.

With increasing concentration, the polymer molecules entangle each other more and more frequently, and accordingly the relaxation time becomes longer. In the range log $C > -1$, log τ increases in proportion to 2.5 log C. The dynamic crossover concentration C_τ between the dilute and semidilute regimes is estimated to be 0.04 as the intersect of the two straight-line portions of the curves in the both regimes. The C_τ is nearly the same as the observed static crossover concentration C^*. In Bz solutions, a similar coincidence was observed: for PI-102, $C^* = 0.014$ and $C_\tau = 0.016$. This behavior is different from that found in the rheological behavior: Noda et al. reported the crossover concentration for toluene solutions of poly(α-methylstyrene) from the C dependence of the osmotic pressure[16] and the viscosity.[17] They found that their dynamic crossover concentration is ca. 5 times higher than the static C^* of the same system.[17]

According to the dynamic scaling theory of de Gennes,[9] the C dependence of τ in the semidilute regime is given by

$$\tau \propto \eta_s (C/C^*)^{\beta(1-\nu)/(3\nu-1)} \qquad (13)$$

where β is a constant equal to 2 for the free-draining model and 3 for the nondraining model.

Previously, we determined the C dependence of the relaxation time τ_ζ reduced to the isofriction coefficient state for Bz and Diox solutions of PI-164.[2] To calculate τ_ζ, we need the data of either the relaxation time for the segmental motion or the relaxation time for the normal-mode process for the low-molecular-weight *cis*-PI. Since these data are not available for C16 and C20 solutions, we analyze the present data without reducing τ into the isofriction state.

We determined the slope of the log τ vs log C plot in the semidilute regime to be 2.5 ± 0.2 and 2.8 ± 0.2 for C16 and C20 solutions, respectively. To test eq 13, we use two sets of the data of ν: One is the set of ν determined from α with eq 5 and the other from the C dependence of $\langle r^2 \rangle$ in the regime II. The values of β calculated from the former and the latter are denoted as β_1 and β_2, respectively, and are listed in Table V. We see that β_1 for the good and moderately good solvents is ca. 4 but changes to 2.5 in the Θ solvent. On the other hand, β_2 varies monotonously from 4.2 for the good solvent to 2.5 for the Θ solvent. On average, these values are close to the nondraining model. However, the dynamic scaling law does not agree quantitatively with the experimental data.

Table V
Comparison of β_1 and β_2

soln	β_1	β_2
PI-102/Bz	4.2	4.2
PI-101/C16	4.0	3.4
PI-101/C20	4.2	3.3
PI-102/Diox	2.5	2.5

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