our experiment has low molecular weight, which does not satisfy the condition assumed in the theory.

Conclusion

1. In dilute blends, the high molecular weight component has an expanded conformation, and the expansion factor α^2 is proportional to $P_2^{1/5}P_1^{-2/5}$, where P_1 and P_2 are the degree of polymerization of the low molecular weight and high molecular weight components, respectively.
2. In semidilute blends, $P_1^{1/4}\alpha^2$ is independent of P_2.

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References and Notes

(1) Flory, P. J. *J. Chem. Phys.* **1947**, *17*, 303.
(2) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
(3) Joanny, J. F.; Grant, G.; Turkevich, L. A.; Pincus, P. *J. Phys. (Les Ulis, Fr.)* **1981**, *42*, 1045.
(4) Joanny, J. F.; Grant, G.; Pincus, P.; Turkevich, L. A. *J. Appl. Phys.* **1981**, *52*, 5943.
(5) Kirste, P.; Lehnen, B. *Makromol. Chem.* **1976**, *177*, 1137.
(6) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539.
(7) Adachi, K.; Kotaka, T. *Macromolecules* **1985**, *18*, 466.
(8) Adachi, K.; Okazaki, H.; Kotaka, T. *Macromolecules* **1985**, *18*, 1486.
(9) Adachi, K.; Kotaka, T. *Macromolecules* **1988**, *21*, 157 and references cited therein.
(10) Imanishi, Y.; Adachi, K.; H.; Kotaka, T. *J. Chem. Phys.* **1988**, *89*, 7585.
(11) Jones, A. A.; Stockmayer, W. H.; Molinari, R. J. *J. Polym. Sci., Polym. Symp.* **1976**, *54*, 227.
(12) Huggins, M. L. *J. Chem. Phys.* **1941**, *9*, 440.
(13) Kuhn, W. *Kolloid Z.* **1936**, *76*, 258.
(14) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(15) Daoud, M.; Cotton, J. P.; Frarnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.
(16) King, J. S.; Boyer, W.; Wignall, G. D.; Ullman, R. *Macromolecules* **1985**, *18*, 709.
(17) Hayashi, H.; Flory, P. J.; Wignell, G. D. *Macromolecules* **1983**, *16*, 1328.
(18) McAlea, K. P.; Schulz, J. M.; Gardner, K. H. *Macromolecules* **1985**, *18*, 447.

Dielectric Normal Mode Process in Binary Blends of Polyisoprene. 2. Dynamic Behavior

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ABSTRACT: The dielectric behavior was studied on binary blends through observation of the normal mode relaxation time τ_n of a small amount of a test chain component blended with a matrix component, both of which were narrow molecular weight *cis*-polyisoprenes (*cis*-PIs). The test chain was a low molecular weight component (lmc) and the matrix a high molecular weight component (hmc) and vice versa. The τ_n of the lmc test chain was somewhat increased from that of its pure undiluted state: when the molecular weight M_w of the lmc test chain was higher than 3000, the τ_n was proportional to $M_w^{3.0}$. The behavior is in agreement with the original tube theory proposed by de Gennes. For the binary blends composed of an hmc test chain and an lmc matrix, the τ_n of the hmc test chain was first corrected for the excluded volume effect by using the data of the expansion factor reported in part 1. The slope of the resulting double logarithmic plot of τ_n vs M_w of the hmc test chain was 1.9 in the lmc matrix of $M_w = 1600$, while the slope decreased to 1.6 for the lmc matrix with $M_w \leq 1000$. The results suggest that the hydrodynamic nondraining effect becomes significant in the lmc matrix of $M_w < 1000$. The widths of the loss curves reflecting the distribution of relaxation times of the test components were almost the same among the two types of the blends as well as those of the corresponding monodisperse *cis*-PIs.

Introduction

In part 1 of this series,[1] the preceding paper in this issue, we reported the effect of excluded volume in binary blends of narrow distribution *cis*-polyisoprenes (*cis*-PIs) by observing the end-to-end distance of high molecular weight (hmc) *cis*-PI in a matrix of low molecular weight (lmc) *cis*-PI. In this article, we study the dynamic behavior of the same blends by observing the dielectric normal mode relaxation time of the test component that can be either an hmc or lmc.

For monodisperse *cis*-PIs, we reported[2-4] that when the molecular weight M is less than the characteristic molecular weight M_c of *cis*-PI ($\simeq$10 000), the dielectric normal mode relaxation time τ_n is proportional to $M^{2.0}$, while in the range $M > M_c$ τ_n is proportional to $M^{3.7}$–$M^{4.0}$.

While the former behavior is in accordance with the theory of Rouse,[5] which describes the dynamics of unentangled free-draining linear chains, the latter behavior of entangled linear chains is explained on the basis of the tube theory proposed by de Gennes[6] and developed later by Doi and Edwards.[7,8] The original tube theory predicted the longest (viscoelastic) relaxation time τ being proportional to $M^{3.0}$, which is obviously too low to explain the experimental results of both viscoelastic and the dielectric normal mode relaxation times. The original theory has thus been modified by Doi and others incorporating various other factors such as the contour length fluctuation[9]

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and the constraint release through tube renewal[10-14] reflecting a possibility that the tube itself deforms as the surrounding chains move.

To clarify these features, many authors[15-18] including ourselves studied viscoelastic relaxation behavior of binary blends of narrow molecular weight distribution polymers.[15-18] Usually in such experiments, a small amount of high molecular weight component (hmc) was dissolved as the test chain in a medium of low molecular weight component (lmc). The idea is that since the tubelike constraint imposed by the matrix lmc disintegrates much faster than the tube disengagement or reptation time of the hmc test chain, the tube renewal effect rather than repetation becomes the rate-determining mechanism of the dynamics of the test chain in such blends as long as their molecular weights are well separated. In the corresponding monodisperse system of the hmc alone, this is not necessarily the case. On the other hand, in the dynamics of the lmc test chain in an hmc matrix the reverse is expected: reptation rather than tube renewal should overwhelm the dynamics of the lmc test chain.

However, the reverse case is difficult to examine through viscoelastic spectroscopy, because the contribution of the lmc test chain to the viscoelastic functions is overwhelmed by the contribution of the Rouse mode[5] of the hmc matrix. Such systems thus have been studied only through measuring diffusion coefficient[19-21] or more recently through infrared dichroism.[22] We expect that through dielectric normal-mode spectroscopy we can clearly resolve the dielectric loss curves of the two components in either type of the blends, if the molecular weights of the hmc and lmc are well separated. Thus, one of the objectives of this study is to examine in detail the relaxation behavior of the lmc test chain in the hmc matrix through the dielectric normal mode spectroscopy on such binary blends of *cis*-PIs.

The second objective is to clarify whether or not the hydrodynamic effect of the lmc matrix chains does exert influence on the dynamics of the hmc test chain. Obviously, if the lmc matrix chains have M close to that of the monomer, they may act as an ordinary solvent in dilute solution, in which the non-free-draining model proposed by Zimm[23] prevails over the Rouse free draining model. However, with increasing M of the lmc matrix chains, the dynamics of the hmc test chain tends to be governed by the free-draining model.[5] Thus the M dependence of the relaxation time changes from the $M^{1.5}$ to $M^{2.0}$ power law dependence with increasing molecular weight of the lmc matrix. To test this expectation, we study here the dynamic behavior of narrow molecular weight distribution *cis*-PI binary blends composed of the hmc test chain in the lmc matrix as well.

Theory

Relaxation Time in Nonentangled Matrix. When the molecular weight of matrix chains is lower than the characteristic molecular weight M_c ($\simeq 2M_e$), they are not entangled with each other. Here M_e is the molecular weight between entanglements. The dynamics of a test chain in such a matrix is described by the Rouse and Zimm theories,[5,23] which assume the unperturbed conformation of the test chain. However, as reported in part 1, the hmc molecules in a blend have an expanded conformation when the molecular weight of the matrix is low.[1] Thus, it is necessary to extend the Rouse and Zimm theories to those including the excluded volume effect.

For this purpose, Doi and Edwards proposed a dynamical scaling law.[8] This law assumes that if the number of beads N is changed into N/λ and at the same time the separation of the beads b is changed into $\lambda^{\nu} b$, a dynamical quantity A becomes $\lambda^{x} A$, where ν is the exponent characterizing the molecular weight dependence of the dimension of the polymer molecule. On the basis of the scaling arguments, we expect that the excluded volume effect causes increase of the relaxation time τ_R for the Rouse model and increase of τ_Z for the Zimm model by α^2 and α^3 times, respectively, where α is the expansion factor of the test chain.

Combining the result of the dynamical scaling law and the free draining model,[5] we write the relaxation time τ_R for the first normal mode of the Rouse model as

$$\tau_R = \alpha^2 \zeta N^2 b^2/(3\pi^2 k_B T) \tag{1}$$

where ζ is the friction constant per bead, N the number of beads of the test chain, b the average distance between the beads, and $k_B T$ the thermal energy.

Similarly, the relaxation time τ_Z for the first mode of the Zimm model[23] is given by

$$\tau_Z = \alpha^3 \pi^{3/2} \eta_s b^3 N^{3/2}/(12^{1/2} k_B T \lambda_1) \tag{2}$$

where η_s is the viscosity of matrix and λ_1 the first eigenvalue.[24]

Relaxation Time in Entangled Matrix. When the molecular weight of matrix chains is higher than M_c ($\simeq 2M_e$), the dielectric relaxation time τ_n for the normal mode process may be described by the tube theory.[6-8] We consider the case where a test chain with molecular weight M_1 is dissolved in matrix chains with molecular weight M_2 ($>M_1$).

The original tube theory predicts that τ_n is equal to the relaxation time τ_d for the tube disengagement process:[7,8]

$$\begin{aligned}\tau_d &= \zeta N^3 b^4/(\pi^2 a^2 k_B T) \\ &= 3\tau_R(M_e) M^3/M_e^3\end{aligned} \tag{3}$$

where a is the diameter of the tube, M_e the molecular weight between entanglements, and $\tau_R(M_e)$ the Rouse relaxation time of the chain with $M = M_e$. The second equation is derived from the assumption that the diameter of the tube, a, is equal to the average end-to-end distance of the chain with $M = M_e$.[7]

Theories of constraint release predict that the time scale of the constraint release is proportional to the third power of the matrix molecular weight. Therefore, when the molecular weight of a test chain is lower than that of matrix chains, the effect of the constraint release is negligibly small.

On the other hand, the contour length fluctuation is expected to occur irrespective of the matrix molecular weight. Doi[9] expressed the longest relaxation time τ_1 assuming that the contour length of a test chain in the tube fluctuates according to the Rouse model. An approximate expression is

$$\tau_1 \simeq \tau_d[1 - 1.47(M_e/M)^{1/2}]^2 \tag{4}$$

Effect of constraint release on the dynamic behavior in binary blends was studied theoretically by Daoud and de Gennes[13] and Doi et al.[14] for reverse cases where a test chain has higher molecular weight than the matrix.

Constraint Release in Monodisperse System. To compare the relaxation times in the blends and those in the monodisperse system, we review the theory in the monodisperse system. Klein[10] first modified eq 3 by considering constraint release. For the monodisperse system, the longest relaxation time τ_1 is given by

$$\tau_1 = \tau_R + (1 - M_e^2/M^2)\tau_d \tag{5}$$

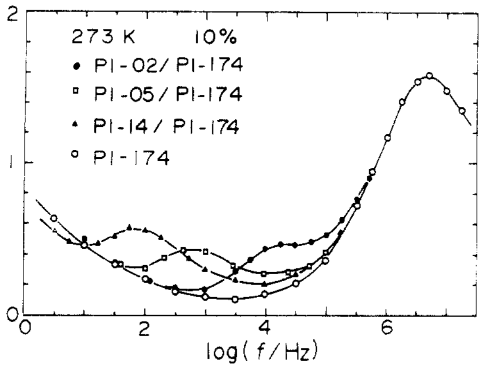

Figure 1. Frequency dependence of dielectric loss factor of blends consisting of 10% low molecular weight components and PI-174. Open circle indicates the ϵ'' curve for monodisperse PI-174.

where M_e is the molecular weight between entanglements.

Graessley[11] developed another theory of constraint release: the relaxation time τ_{cr} for motions of a chain due to the constraint release is given by

$$\tau_{cr} = (2\Lambda M^2/\pi^2 M_e^2)\tau_d \tag{6}$$

$$\Lambda \simeq (\pi^2/12)^z/z \tag{7}$$

where z is the number of the constraints per cell. The longest relaxation time τ_1 is determined as a competition between the reptation and the constraint release:

$$\tau_1 = 1/(\tau_d^{-1} + \tau_{cr}^{-1}) \tag{8}$$

$$\tau_1 = \tau_d[1 + \pi^2 M_e^2/(2\Lambda M^2)]^{-1} \tag{9}$$

Recently, Watanabe and Tirrell[12] also proposed a theory of constraint release assuming that the rate of tube deformation depends on its configuration. Their results indicate that τ_1 is given by eq 9, but the distribution of relaxation times is different from that calculated on the Graessley model.[11]

So far no theory has been proposed to consider both the constraint release and the contour length fluctuation at the same time.

Experimental Section

Details of the sample preparation and characterization were described in part 1.[1] The number in the sample codes represents the weight-average molecular weight M_w in units of kg/mol. The methods of dielectric measurements were also described in part 1 and elsewhere. The error in determination of the relaxation time is estimated to be less than 10%.

Results and Discussion

Dielectric Loss Curves of *cis*-PI Binary Blends. Figure 1 shows representative master curves of dielectric loss factor ϵ'' at 273 K for the blends containing 10% lmc *cis*-PIs in PI-174 matrix. The increase of ϵ'' with decreasing frequency f is due to the normal mode of hmc PI-174 matrix, while the small bumps seen in the audio frequency range are due to the lmc *cis*-PIs. Examples of the ϵ'' curves for the blends consisting of a small amount of hmc test chain and a lmc matrix were shown in part 1.[1] The contribution of the minor components was determined with a simple additivity law as described in part 1.

The normal mode relaxation time τ_n of the test components was evaluated with $\tau_n = 1/(2\pi f_m)$ from the loss maximum frequency f_m. If the distribution of relaxation times is given by either the Rouse theory[5] or the original tube theory of de Gennes,[6] the theoretical loss curve exhibits the loss maximum at a frequency equal to $1.03/(2\pi\tau_1)$, where τ_1 is τ_R or τ_d given in the theoretical section. We therefore regard that τ_n thus determined corresponds approximately to $0.97\tau_1$. The results are summarized in Table I.

Table I
Relaxation Time τ of Minor Component in Blends of *cis*-PI

blend system	concn[a]	log τ	log (τ/α^2)
PI-12/PI-0.5	5.0	-5.15	-5.26
PI-32/PI-0.5	5.0	-4.40	-4.65
PI-53/PI-0.5	5.0	-3.80	-4.03
PI-174/PI-0.5	5.0	-2.70	-2.93
PI-12/PI-01	5.0	-4.50	-4.44
PI-53/PI-01	5.0	-3.28	-3.45
PI-174/PI-01	5.0	-2.32	-2.50
PI-12/PI-02	5.0	-3.70	-3.60
PI-32/PI-02	5.0	-3.08	-3.13
PI-53/PI-02	5.0	-2.40	-2.48
PI-101/PI-02	0.50	-2.13	
PI-101/PI-02	1.3	-2.10	
PI-101/PI-02	2.5	-2.04	
PI-101/PI-02	5.0	-1.93	
PI-02/PI-174	10.0	-4.90	
PI-03/PI-174	10.0	-4.37	
PI-05/PI-174	10.0	-3.60	
PI-14/PI-174	10.0	-2.60	
PI-02/PI-234	5.0	-4.85	
PI-03/PI-174	5.0	-4.30	
PI-05/PI-174	5.0	-3.55	
PI-06/PI-234	5.0	-3.45	
PI-12/PI-234	5.0	-2.55	
PI-32/PI-234	5.0	-1.20	

[a] Volume concentration of hmc in percent.

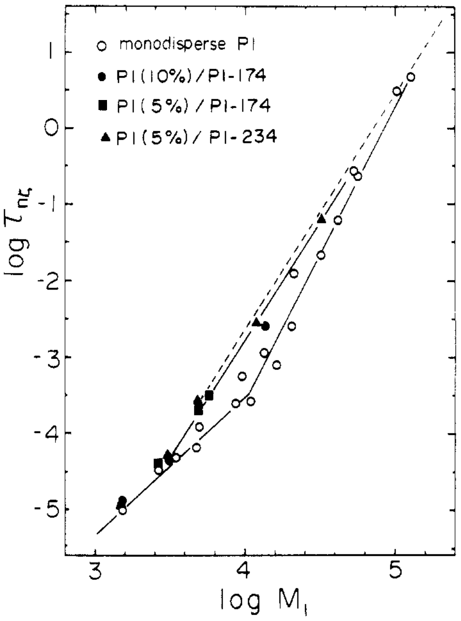

Figure 2. Molecular weight dependence of relaxation time in the isofriction state at 273 K. Closed symbols indicate the relaxation time of low molecular weight component in PI-174 and PI-234. Open circle indicates the relaxation time of monodisperse *cis*-PI. Dashed line represents the theoretical value calculated with the tube theory (eq 3) with M_e = 5000.

Short Chains in Long-Chain Matrix. Molecular Weight Dependence of Relaxation Time. Figure 2 shows the relaxation time τ_n(lmc) of the lmc test chain plotted against its molecular weight M_l for the blends containing 5% or 10% lmc in PI-174 or PI-234 matrix. For the sake of comparison, the τ_n for monodisperse *cis*-PIs was also plotted against their own M_w.

As reported previously,[3,4] the friction coefficient ζ of eqs 1 and 3 for the monodisperse *cis*-PI is independent of M_w in the range $M_w > 4000$. However, it decreases in the range $M_w < 4000$ since the chain ends create more free volume with decreasing M_w. Assuming the friction coefficient ζ is proportional to the segmental mode relaxation time τ_s, we reduced τ_n of the lmc *cis*-PI to the values $\tau_{n\zeta}$ of the isofriction state, in which ζ is equal to that of hmc *cis*-PIs.

Before discussing the data in more detail, we note that the relaxation time of an lmc in the blends depends only slightly on the matrix molecular weights of 174 000 and 234 000. We also note that the difference in $\tau_{n\zeta}$ between 5% and 10% blends is also small. In the following discussion, we thus neglect these factors.

In Figure 2, we see that the $\tau_{n\zeta}$ of lmc in the blends is longer than that of the corresponding monodisperse *cis*-PI. Qualitatively, this behavior may be explained as a result of constraint release. In these blends, the hmc matrix chains surround the lmc test chain, and hence the constraint release (due to reptation of the hmc matrix) hardly occurs during the time span of τ_d for the lmc. On the other hand, in the monodisperse systems, the constraint release may occur at a rate much faster than in the blend. Thus the relaxation time of lmc in the blends approximately corresponds to the relaxation time in a fixed network.

As is seen in Figure 2, the slope of $\tau_{n\zeta}$(lmc) vs M_1 changes at $M_1 = 3000$. The results may imply that the short chains are already entangled with the matrix chains in the range $3000 < M_1$. The slope in this range is 3.0 in contrast to 3.7 for the monodisperse *cis*-PI. On the other hand, in the range $M_1 < 3000$, the slope is ca. 2.0 and agrees with the Rouse theory.[5]

The original Doi–Edwards[7] theory predicts that τ_d is given by eq 3. The dashed line represents eq 3 calculated by using the experimental value of τ_R given in the same figure and $M_e = 5000$. The slope and the absolute values of the τ_n of the lmc test chains agree well with this simple theory. As far as the present data are concerned, we thus conclude that in the $\tau_n \propto M^\beta$ relation for entangled monodisperse systems the dominant factor leading to the power β of 3.5–4.0 higher than 3.0 of the original tube model is presumably a manifestation of the constraint release effect.

This view is, however, not in harmony with our previous data of the normal mode relaxation times of *cis*-PIs trapped in cross-linked natural rubber and polybutadiene networks.[25–27] In those systems, the slope of the double logarithmic plot of the $\tau_{n\zeta}$ of the guest *cis*-PI vs M_w was, depending on the cross-link density of the networks, 3.6–4.2, which is much higher than 3.0. It is natural to expect that the cross-linked networks and the hmc matrix polymers both act as a similar obstacle against short test chains. Since the networks were cross-linked by γ-ray irradiation,[25,26] one may consider that irregular distribution of cross-links and the irregular structure of the resulting networks greatly differing from an ideal model network might be a reason for this discrepancy between the two systems. In this connection, Ferry et al. previously reported viscoelastic relaxation times of guest molecules in networks prepared from telechelic polymers with narrow molecular weight distribution[28,29] (MWD). Their data, however, also exhibited a power higher than 3.0.[27] Consequently, we tentatively conclude that the dynamics of lmc test chains in binary blends and in networks are quite different. We cannot explain these puzzling results on β in the τ_n vs M relations at present time.

As to the problem of the extent of enhancement in the terminal relaxation times of the lmc test chain in an hmc matrix, Kornfield et al.[22] recently reported observation of relaxation behavior of lmc in binary blends composed of polyisoprene and hydrogenated polyisoprene by a rheooptical method. They found that with decreasing lmc content in the blends the terminal relaxation time of the lmc increased by as much as ca. 1 decade. This behavior is qualitatively similar to, but does not agree quantitatively with, our present data. In their experiments, an lmc with $M_w = 5.3 \times 10^4$ was used. As is seen in Figure 2, the present data indicate that the difference of the relaxation time between the blend and monodisperse *cis*-PI in only 0.1–0.2 decades, which is much smaller than their result. They suggested that the prolonged relaxation time is due to nematic-like interactions proposed by Jarry and Monnerie.[30,31]

In the range $3000 < M_w < 10\,000$, the monodisperse systems exhibit Rouse behavior with a power law index of 2, but surprisingly, for the lmc in the blends, the ideal tube model behavior has an index of 3. An additional question arising here is why is this so? According to the Doi–Edwards theory,[7] the motions of a chain confined in tube are governed by wiggling motions of the chain described by the Rouse theory. Thus, the chain cannot move faster than the characteristic rate given by the Rouse theory. For the monodisperse systems in the range $M_w < 10\,000$, the (hypothetical) tube reptation time with constraint release might become shorter than the intrinsic Rouse relaxation time τ_R, implying that the monodisperse *cis*-PIs with $M_w < M_c$ are forced to conform the Rouse relaxation mode. On the other hand, even for the lmc test chain with M_w as low as 3000–10 000 in the blends, the ideal tube reptation mode is still prevailing because of the absence of the constraint release mode.

Now we turn our attention to the effect of contour length fluctuation and whether it exerts influence on the relaxation time of an lmc test chain in an hmc matrix of the blends. In our previous paper, we compared eq 4 with the M_w dependence of τ_n for monodisperse *cis*-PIs[4] and suggested that eq 4 explains qualitatively the observed exponent β. We expect that contour length fluctuation should appear in the blends as well. However, the present blend data show no such tendency as far as the observed power-law index of the M_w dependence of τ_n is concerned.

Constraint Release in Monodisperse System. Figure 3 shows a double logarithmic plot of the ratio of the relaxation time of the lmc test chain τ_n(lmc) in the blends to that, τ_n(mono), in the matrix of itself (the monodisperse *cis*-PI) against the number of entanglements N ($=M/M_e$) per test chain. Here we used $M_e = 5000$, although the present data suggest that M_e might be lower than 5000. The data points indicate the ratio of τ_n(lmc) determined from the smoothed line shown in Figure 2 to the corresponding τ_n(mono) values. If constraint release is prevailing in the monodisperse system but does not occur in the blend, τ_n(lmc) and τ_n(mono) should correspond respectively to the theoretical relaxation times τ_d and τ_1 given by Graessley (eq 9) or by Klein (eq 5). The solid line shows τ_d/τ_1 calculated from eq 9 with $z = 4.0$, and the dashed line eq 5. We see that the observed ratios of $\tau_n(\mathrm{lmc})/\tau_n(\mathrm{mono})$ agree fairly well with the Graessley theory[11] but not with the Klein theory.[10]

Long Chain in Short Chain Matrix. Hydrodynamic Effect of the Low Molecular Weight *cis*-PI. In this section, we analyze the relaxation time τ_n(hmc) of hmc test chains of molecular weight M_2 in the lmc matrices of M_1. The M_1 of all the lmc is less than the molecular weight between entanglement M_e ($\simeq$5000 for

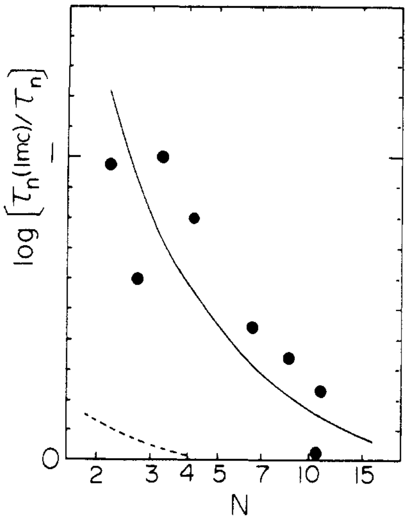

Figure 3. Ratio of the relaxation time of the low molecular weight component in PI-174 or in PI-234 to that of monodisperse *cis*-PI. N represents the number of entanglements per chain and is equal to M_w/M_e. Solid and dashed lines show the Graessley theory (eq 9) with $z = 4$ and the Klein theory (eq 5), respectively.

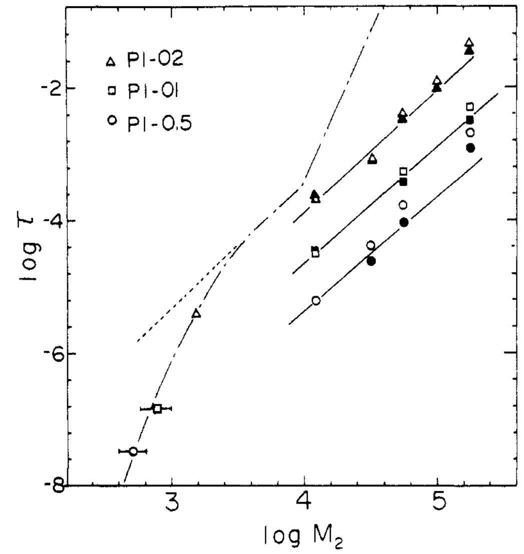

Figure 4. Molecular weight M_2 dependence of relaxation time of high molecular weight component in the matrix of low molecular weight component (PI-02, PI-01, and PI-0.5) at 273 K. Dash-dot line indicates the relaxation time of monodisperse *cis*-PI. The dashed line shows the relaxation time of monodisperse *cis*-PI reduced to isofriction state. The solid symbols indicate the relaxation time reduced to the unperturbed state.

cis-PIs), and hence the dynamics of the hmc is expected to obey the Rouse[5]–Zimm[23] theory.

Figure 4 shows the double logarithmic plot of τ_n(hmc) vs M_2 for the blends consisting of 5% hmc and 95% PI-02, PI-01, or PI-0.5 as the matrix lmc. The dash-dot line represents the relaxation times for monodisperse *cis*-PIs plotted without reduction to the isofriction state. On the other hand, the dashed line with the slope 2 show the relaxation time reduced to the isofriction state.

The plots of log τ_n(hmc) vs log M_2 shift to the short-time side with decreasing M_1 of the lmc matrix. This indicates that the friction coefficient decreases with decreasing the matrix molecular weight M_1. The friction coefficient for hmc in the blends of the same matrix *cis*-PI is expected to be the same since the hmc content is fixed to 5%.

As reported in part 1, the hmc chains in these blends have an expanded conformation. We reduced the observed relaxation times into those in unperturbed state using eqs 1 and 2. Equation 1 for the free-draining model indicates that τ_R is proportional to α^2, but eq 2 for the non-draining model predicts $\tau_Z \propto \alpha^3$. Since the behavior of the blends is expected to be close to the free-draining behavior, we corrected the relaxation time assuming the α^2 dependence of τ_n(hmc) with the data of α^2 reported in the part 1. The values of $\tau_n(\mathrm{hmc})/\alpha^2$ are listed in Table I and plotted in Figure 4 with solid symbols.

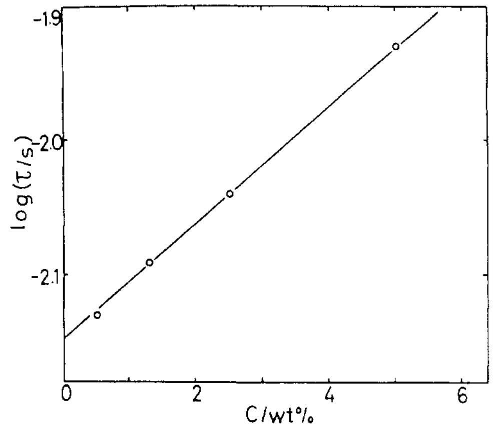

Figure 5. Concentration dependence of the relaxation time at 273 K for PI-101/PI-02 system.

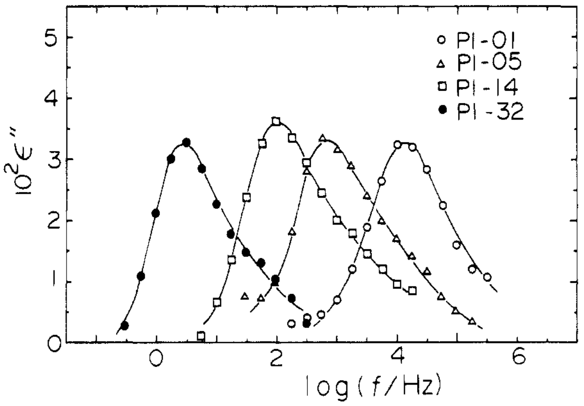

Figure 6. Contribution of low molecular weight component (lmc) to dielectric loss ϵ'' of blends consisting of the lmc (5%) and PI-174 or PI-234.

As shown in Figure 4 the values of $\tau_n(\mathrm{hmc})/\alpha^2$ at the highest molecular weight (PI-174) deviate upward. This is probably due to the entanglement effect, since M_e of 5% solutions of *cis*-PI is estimated to be 1×10^5 with an empirical relation $M_e \propto C^{-1}$. Thus, we omitted the data of PI-174 to determine the slope of the log τ_n vs log M_2 plots. The slopes thus determined for the blends of lmc matrices of PI-02, PI-01, and PI-0.5 are 1.9 ± 0.1, 1.7 ± 0.2, and 1.7 ± 0.1, respectively. If we correct the relaxation time assuming the α^3 dependence, the slope for the PI-0.5 blends becomes 1.5 ± 0.1.

Equations 1 and 2 indicate that at the limits of non-draining and free-draining, τ_n is proportional to $M_w^{1.5}$ and $M_w^{2.0}$, respectively. The above results indicate that in the matrices of PI-01 and PI-0.5 the slope is close to the Zimm behavior. The slope decreases with decreasing M_1 of the matrix as expected. We may say that in the matrix of *cis*-PI with $M_w = 1600$ (PI-02) the hydrodynamic interactions are almost shielded, but in the matrix of PI-0.5 with $M_n = 450$ the effect is not shielded. Thus, the critical molecular weight for the onset of hydrodynamic shielding is estimated to be ca. 1000 for *cis*-PI.

Concentration Dependence of Relaxation Time. In the above discussion, we neglected the concentration dependence of the relaxation times τ_n(hmc). Figure 5 shows the results on PI-101/PI-02. According to Muthukumar and Freed,[33,34] the concentration (C) dependence of the relaxation time τ_p of the pth normal mode is

$$\tau_p \simeq \tau_p^0(1 + CAp^{-\kappa}) \qquad (10)$$

where τ_p^0 is the relaxation time at infinite dilution and A and κ are parameters depending on the molecular weight and the excluded volume effect. In the present case, τ_n corresponds to τ_1, and hence τ_n(hmc) is linear to CA. The result shown in this figure is in good agreement with eq 10. From Figure 5, we find that the logarithm of τ_n(hmc) at $C = 5\%$ is longer than τ_1^0 by 0.22 decade. Since A is proportional to $M^{3\nu-1}$, we can correct the relaxation times plotted in Figure 4 to the values at infinite dilution, where ν is the excluded volume parameter. However, the correction is small and unimportant for lmc with $M_1 < 50\,000$.

Previously, the value of A was determined to be 10.1 for solutions of PI-101 in moderately good solvents, and for hexadecane and eicosene A was estimated to be 17.2 and 17.1, respectively.[35] The value of A in the PI-02 blends is smaller than those in moderately good solvents. This is in harmony with the Freed–Muthukumar theory, which predicts that A increases with the solvent quality.

Distribution of Relaxation Times. Figure 6 shows representative loss curves for the lmc/hmc blends. The ϵ'' of the lmc is reduced to the value of the pure state. The tails of the loss curves are somewhat ambiguous because of unavoidable experimental errors. The half-widths of these loss curves are in the range from 1.5 to 1.85 and are approximately the same as those for monodisperse samples of reasonably narrow molecular weight distribution.[4] We conclude that the distribution of relaxation times may not be seriously affected by a change in environment. Recently, Watanabe and Tirrell[12] indicated that the distribution of relaxation times $g(\tau)$ is independent of constraint release on the basis of their model of configuration-dependent constraint release. The present result is in harmony with their theory.

Conclusions

1. In the blends in which a small amount of short *cis*-PI chains with $M > M_e$ is dissolved in matrices of long chains, the normal mode relaxation time τ_n of the short chains is proportional to $M^{3.0}$, which conforms to the original tube theory.

2. The relaxation times of the short chain in the matrices of long chains are enhanced several times longer than that for the corresponding monodisperse short-chain *cis*-PI. This enhancement can be ascribed due mainly to the absence of constraint release effect in such blends. The Graessley theory approximately explains this behavior, especially the increase in the relaxation times.

3. On the other hand, when a small amount of long-chain *cis*-PI is blended with short-chain *cis*-PI with $M = M_1$, hydrodynamic interactions appear to prevail when $M_1 < 1000$. Otherwise, the long chains conform to the Rouse behavior.

4. The distribution of relaxation times of a small amount of short-chain *cis*-PIs in binary blends with long-chain *cis*-PIs is almost the same as that for the monodisperse *cis*-PIs.

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References and Notes

(1) Adachi, K.; Nishi, I.; Itoh, S.; Kotaka, T. *Macromolecules* Preceding paper in this issue.
(2) Adachi, K.; Kotaka, T. *Macromolecules* **1984**, *17*, 120.
(3) Adachi, K.; Kotaka, T. *Macromolecules* **1985**, *18*, 466.
(4) Imanishi, Y.; Adachi, K.; Kotaka, T. *J. Chem. Phys.* **1988**, *89*, 7585, 7593.
(5) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(6) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(7) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818.
(8) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.
(9) Doi, M. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 667.
(10) Klein, J. *Macromolecules* **1978**, *11*, 852.
(11) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 68.
(12) Watanabe, H.; Tirrell, M. *Macromolecules* **1989**, *22*, 927.
(13) Daoud, M.; de Gennes, P.-G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1971.
(14) Doi, M.; Graessley, W. W.; Helfand, E.; Pearson, D. S. *Macromolecules* **1987**, *20*, 1900.
(15) Masuda, T.; Kitagawa, K.; Inoue, T.; Onogi, S. *Macromolecules* **1970**, *2*, 116.
(16) Montfort, J. P.; Marin, G.; Monge, P. *Macromolecules* **1984**, *17*, 1551.
(17) Watanabe, H.; Sakamoto, T.; Kotaka, T. *Macromolecules* **1985**, *18*, 1008, 1436.
(18) Struglinski, M. J.; Graessley, W. W. *Macromolecules* **1985**, *18*, 2630.
(19) Antonietti, M.; Coutandin, J.; Sillescu, H. *Macromolecules* **1986**, *19*, 793.
(20) Green, P. F.; Kramer, E. J. *Macromolecules* **1986**, *19*, 1108.
(21) Antonietti, M.; Sillescu, H. *Macromolecules* **1985**, *18*, 1162.
(22) Kornfield, J. A.; Fuller, G. G.; Pearson, D. S. *Macromolecules* **1989**, *22*, 1343.
(23) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(24) Zimm, B. H.; Roe, G. L.; Epstein, L. F. *J. Chem. Phys.* **1956**, *24*, 279.
(25) Poh, B. T.; Adachi, K.; Kotaka, T. *Macromolecules* **1985**, *20*, 2568, 2574.
(26) Adachi, K.; Nakamoto, T.; Kotaka, T. *Macromolecules* **1989**, *22*, 3111.
(27) Adachi, K.; Kotaka, T. *Polymer Yearbook*, in press.
(28) Nelb, G. W.; Pedersen, S.; Taylor, C. R.; Ferry, J. D. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 645.
(29) Granick, S.; Pedersen, S.; Nelb, G. W.; Ferry, J. D.; Macosko, C. W. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1745.
(30) Jarry, J.-P.; Monnerie, L. *Macromolecules* **1979**, *12*, 316.
(31) See references cited in ref 18.
(32) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303.
(33) Muthukumar, M.; Freed, K. F. *Macromolecules* **1978**, *11*, 843.
(34) Muthukumar, M. *Macromolecules* **1984**, *17*, 971.
(35) Adachi, K.; Imanishi, Y.; Shinkado, T.; Kotaka, T. *Macromolecules* **1989**, *22*, 2391.