2550 *Macromolecules* 1990, *23*, 2550–2554

Dielectric Normal Mode Process in Binary Blends of Polyisoprene. 1. Excluded Volume Effect in Undiluted Binary Blends

Keiichiro Adachi,* Isao Nishi, Shigeru Itoh, and Tadao Kotaka

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received June 16, 1989; Revised Manuscript Received October 28, 1989*

ABSTRACT: The excluded volume effect in chemically homologous polymer blends was studied by dielectric normal mode spectroscopy on binary blends of narrow molecular weight distribution *cis*-polyisoprenes (*cis*-PI). Dielectric measurements of the mean-square end-to-end distance $\langle r^2 \rangle$ of the high molecular weight *cis*-PI component (hmc) were carried out on the blends containing 0.5–5% hmc with the degree of polymerization (DP) = P_2 in low molecular weight *cis*-PI (lmc) with DP = P_1. In dilute blends of $P_2^{1/2}/P_1$ being larger than unity, $\langle r^2 \rangle$ of hmc was greater than the unperturbed value, as predicted earlier by Flory. In some semidilute blends containing 5% hmc of $P_2 > 300$, the expansion factor α^2 of $\langle r^2 \rangle$ became independent of P_2. This behavior was qualitatively in agreement with the theory of Joanny et al.

Introduction

Polymer chains in the undiluted state are known to assume the conformation of the unperturbed state.[1,2] However, in a binary mixture of polymers of chemically same species but with different molecular weight (MW) M_1 and M_2 ($M_1 < M_2$), we expect that this does not necessarily hold under all conditions. When M_1 and M_2 are widely separated but M_1 is still sufficiently large relative to the monomer unit, the low molecular weight component (lmc) conceivably works as an athermal solvent, and therefore the high molecular weight component (hmc) could have an expanded conformation due to the excluded volume effect. On this problem, Flory[1] proposed as early as the 1940s that the lmc acts as a good solvent when $M_2^{1/2}/M_1$ exceeds a certain critical value. Recently, Joanny et al.[3,4] applied a scaling concept to describe the concentration dependence of the dimension of hmc in the dilute to semidilute blends. However, few experimental studies have been reported on this problem except that of Kirste and Lehnen in 1974.[5]

We reported previously that *cis*-polyisoprene (*cis*-PI) has the component of dipole moment aligned in the same direction parallel to the chain contour and is thereby classified as a type-A polymer[6] that exhibits dielectric normal mode relaxation.[7–10] From the relaxation strength of *cis*-PI of known MW, we thus can determine the mean-square end-to-end distance $\langle r^2 \rangle$.[8,9,11] In 1976, Jones, Stockmayer, and Molinari[11] first observed the excluded volume effect by the dielectric method for dilute solutions of poly(ϵ-caprolactone). This method was developed by us recently.[8,9] Since the normal mode relaxation time depends strongly on MW, we can observe the dielectric relaxations of the two components in the blend in widely separated frequency ranges. Then, from the area under the loss curve for the hmc, we can determine its $\langle r^2 \rangle$. In this paper, we report the expansion factor for the end-to-end distance of hmc in binary blends of narrow MW *cis*-PIs.

Theory

Excluded Volume Effect in Binary Blends. Flory calculated the dimension of hmc based on the Flory–Huggins lattice model[1,2,12] assuming a balance between the elastic free energy F_{el} of the hmc and the free energy of mixing F_{mix} of the hmc and lmc present inside of the random coil of the hmc.

We consider a binary blend in which a small amount of hmc of index 2 is dissolved in lmc of index 1. The expansion factor α of the hmc molecule is defined as

$$\alpha^2 = \langle r^2 \rangle / \langle r^2 \rangle_0 \tag{1}$$

where $\langle r^2 \rangle_0$ is the mean-square end-to-end distance in the unperturbed state. According to Flory,[1,2] α is written as

$$\alpha^5 - \alpha^3 = 2C_{\mathrm{M}}(1/2 - \chi)M_2^{1/2} \tag{2}$$

where χ is the interaction parameter between the both components and C_{M} is given by

$$C_{\mathrm{M}} = (Kv^2/N_{\mathrm{A}}V_1)(\langle r^2 \rangle_0/M_2)^{-3/2} \tag{3}$$

where N_{A} is the Avogadro number, K a constant equal to $27/(2^{5/2}\pi^{3/2})$, v the specific volume of the hmc, and V_1 the molar volume of the lmc. When the hmc and lmc are of chemically the same kind, $\chi = 0$, and eq 2 becomes

$$\alpha^5 - \alpha^3 = (Kv/N_{\mathrm{A}}M_0^{1/2})(\langle r^2 \rangle_0/M_2)^{-3/2}(P_2^{1/2}/P_1) \tag{4}$$

where M_0 is the molecular weight of the repeat unit and P the degree of polymerization. When α is sufficiently large, the term α^3 is neglected, and eq 4 predicts

$$\alpha^2 \simeq K' P_2^{1/5} P_1^{-2/5} \tag{5}$$

where K' is a constant independent of the molecular weight of the components. Since the excluded volume effect expressed by eq 5 is limited in the range $\alpha \geq 1$, eq 5 provides a criterion for the occurrence of excluded volume effect of the hmc and is written as

$$P_2^{1/2}/P_1 > K'^{-1} \tag{6}$$

Joanny et al.[3,4] pointed out that K' is of the order of unity.

Semidilute Regime. Joanny et al.[3,4] extended the Flory theory to include the concentration dependence of the radius of gyration S of hmc in binary blends. Their results are summarized as follows. When the mass concentration C ($=\rho\phi_2$, with ρ being the density) of the hmc is lower than the overlapping concentration C^* (the critical threshold) given by[14]

$$C^* = 3M/(4\pi N_{\mathrm{A}} S^3) \tag{7}$$

with N_{A} being the Avogadro constant, the blend is said to be in the dilute regime, for which the expansion fac-

0024-9297/90/2223-2550$02.50/0

Table I
Characteristics of *cis*-Polyisoprene

code	$10^{-3}M_w$	$10^{-3}M_n$	M_w/M_n
PI-0.5	0.63	0.45	1.39
PI-01	1.01	0.72	1.40
PI-02	1.55	1.40	1.11
PI-03	2.62	2.42	1.09
PI-05	4.80	4.52	1.07
PI-06	5.80	5.47	1.06
PI-12	12.0	11.01	1.09
PI-32	31.6	30.1	1.05
PI-53	52.9	40.0	1.08
PI-101	101	92.7	1.09
PI-174	174	154	1.13

tor α ($=\alpha_{\text{dil}}$) is already given by eqs 4 and 5.

On the other hand, in the concentration range $C^* < C < \rho P_1^{-1}$, the blend is in the semidilute regime, where α^2 is proportional to $\alpha_{\text{dil}}^2(C^*/C)^{1/4}$. From the equations given above, we see that α^2 in the semidilute regime is independent of P_2 and given by

$$\alpha^2 \propto C^{-1/4}P_1^{-1/4} \tag{8}$$

Finally, in the range $C > \rho P_1^{-1}$, which is the concentrated regime, the hmc assumes the unperturbed conformation: $\alpha = 1$.

Dielectric Relaxation Strength. From the relaxation strength $\Delta\epsilon$ of the dielectric normal mode process for *cis*-PI solutions of concentration C, $\langle r^2\rangle$ of *cis*-PI of M_w can be determined by[8,9]

$$\Delta\epsilon/C = 4\pi N_A\mu^2\langle r^2\rangle/(3k_BTM_w) \tag{9}$$

where μ is the dipole moment per unit contour length of *cis*-PI and is equal to 4.80×10^{-12} esu.

When eq 9 is applied to determine $\langle r^2\rangle$, the effects of the internal electric field and concentration should be considered. As to the former effect, it has been discussed fully in our previous papers.[8,9] To summarize, the reaction field for the type-A dipole of an overall molecule is expected to be very small, and hence the ratio of the internal field to the external field is close to unity.

The effect of concentration was also discussed previously.[9] In semidilute or concentrated solutions, we expect that type-A dipoles orient antiparallel due to their dipole–dipole interaction. Such interaction causes a decrease in $\Delta\epsilon$ with increasing concentration even if $\langle r^2\rangle$ is independent of concentration. However, as far as polyisoprene is concerned, the electric interaction between the type-A dipoles is negligibly small, as is evidenced by the observation that $\Delta\epsilon/C$ in the Θ solvent dioxane is almost independent of concentration.[9]

Thus, we apply eq 9 to both dilute and semidilute blends of *cis*-PI. If the contribution $\Delta\epsilon$ of hmc to the dielectric normal mode strength of the blend is estimated separately from that of lmc, eq 9 holds for that of the hmc by replacing M_w with M_2 and C with $\rho\phi_2$, where ρ is the density of bulk *cis*-PIs.

As discussed above, the type-A dipoles of *cis*-PI molecules are electrically independent each other. Therefore, we expect the linear blending law of the dielectric loss factor ϵ'':

$$\epsilon''_{\text{blend}} = \phi_1\epsilon''_1 + \phi_2\epsilon''_2 \tag{10}$$

where ϕ_i may be either the volume fraction or the weight fraction of the component i in the blends.

Experimental Section

Samples of *cis*-PIs were prepared by anionic living polymerization with *sec*-butyllithium in *n*-heptane at about 20 °C. Some samples reported previously[10] were also used. The weight-average molecular weight M_w of *cis*-PIs with $M_w > 5000$ was determined by low-angle light scattering. For low MW *cis*-PIs, on the other hand, we determined the number-average molecular weight M_n from freezing point depression in benzene. The M_w/M_n ratio was determined by gel permeation chromatography. The characteristics of the samples are summarized in Table I, in which the number in the sample codes indicates the M_w in kg/mol.

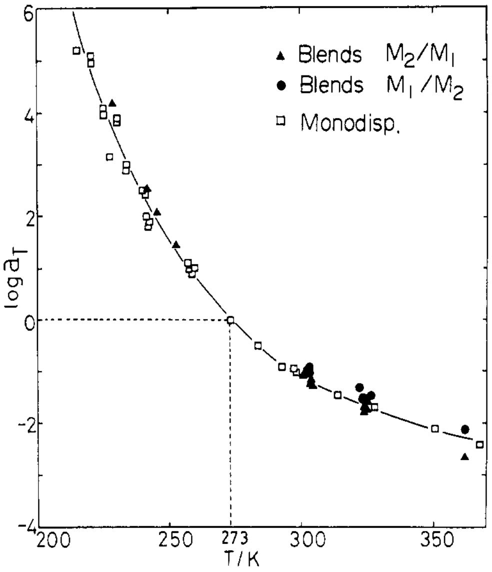

Figure 1. Shift factor for binary blends of *cis*-PI (solid symbols) and that for monodisperse cis-PI (open square) reported previously.[10]

Blends were prepared by dissolving prescribed amounts of the two components in benzene to make approximately 10 wt % solution, and then the solvent benzene was removed thoroughly by evaporation in vacuo at 340 K for 12 h. The content of the hmc in each blend was controlled to be 0.5–5%. These blends are coded as PI-12/PI-01, which represents a mixture of the minor component PI-12 dissolved in PI-01.

The capacitance cell and cryostat used were reported previously.[10] Dielectric measurement was carried out in the frequency range from 20 Hz to 50 kHz with a transformer bridge (General Radio 1615A). Since the available frequency range is limited, we constructed master curves at 273 K. Figure 1 shows the shift factor a_T versus T relation for the blends. The values of a_T agree with those for monodisperse bulk *cis*-PIs.[7,8]

The relaxation strength $\Delta\epsilon$ of the hmc was determined from the area of the ϵ_2'' curve:

$$\Delta\epsilon = (2/\pi)\int_0^\infty \epsilon_2''\, \mathrm{d}\ln f \tag{11}$$

Since the values of ϵ'' of the pure lmc and that of the blend are known, ϵ_2'' is calculated with eq 10. However, in some cases the value of ϵ_2'' thus calculated had a negative value or constant positive values at a frequency far from the loss maximum. This is due to the error in measurements of ϵ_1'' and ϵ''(blend). In such cases, we extrapolated smoothly the portion of the ϵ_2'' curve around the loss maximum to the frequency range of the tail. The error in determination of $\Delta\epsilon$ is estimated to be within 30% but mostly ca. ±10%.

Results and Discussion

Dielectric Loss Curves of *cis*-PI Binary Blends. Figure 2 shows master curves of ϵ'' at 273 K for three blends, all of which contain 5% hmc *cis*-PIs dissolved in the matrix PI-0.5. The loss maxima around 10^7 Hz are assigned to the loss peaks due to PI-0.5 (and small contribution from the segmental mode of hmc). Unlike *cis*-PIs with $M_w > 2000$, which exhibit two distinct loss maxima due to the normal and segmental modes, the matrix lmc PI-0.5 exhibits only one loss peak into which presumably the two modes have been merged. The small

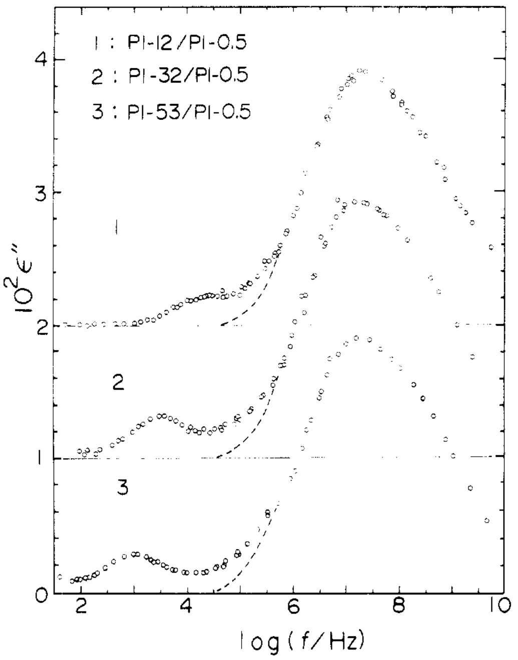

Figure 2. Master curves of the frequency (f) dependence of loss factor ϵ'' at 273 K for blends of PI-12, PI-32, and PI-53 dissolved in PI-0.5. Concentration of the high molecular weight component is 5.0%. Curves 1 and 2 are shifted upward by 0.02 and 0.01, respectively. Dashed line indicates ϵ'' for pure PI-0.5.

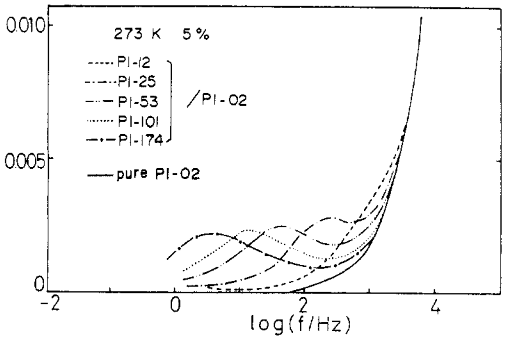

Figure 3. Master curves of the loss factor ϵ'' at 273 K for blends containing 5.0% of the high molecular weight component in the matrix of PI-02. Solid line represents ϵ'' for pure PI-02.

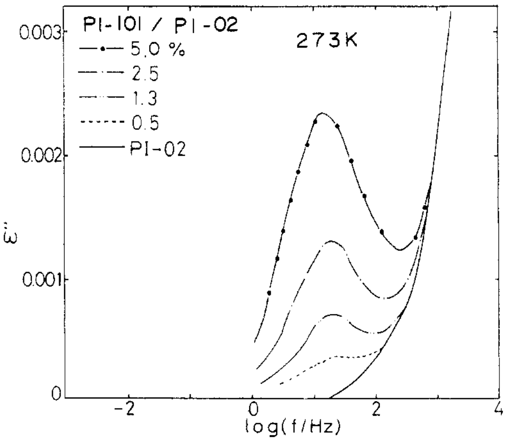

Figure 4. Concentration dependence of the master curves of ϵ'' for the PI-101/PI-02 system at 273 K. Solid line represents the ϵ'' curve of pure PI-02.

bump seen for each blend in the audio frequency range is due to the normal mode process of the hmc, whereas the dashed line indicates the low-frequency tail of the loss curve for pure PI-0.5.

Table II
Expansion Factor α^2 in Binary Blends of *cis*-PI

blend system	concn[a]	$P_2^{1/2}/P_1$	$\Delta\epsilon/C$	$\langle r^2\rangle$	α^2
PI-12/PI-0.5	5.0	1.96	0.139	1.08	1.28
PI-32/PI-0.5	5.0	2.80	0.192	3.94	1.77
PI-53/PI-0.5	5.0	4.06	0.191	6.57	1.71
PI-12/PI-01	5.0	1.21	0.099	0.77	0.89
PI-53/PI-01	5.0	2.53	0.165	5.67	1.48
PI-12/PI-02	5.0	0.67	0.091	0.70	0.80
PI-32/PI-02	5.0	1.02	0.128	2.62	1.13
PI-53/PI-02	5.0	1.30	0.153	5.26	1.21
PI-101/PI-02	0.50	1.79			
PI-101/PI-02	1.30	1.79	0.146	9.58	1.31
PI-101/PI-02	2.50	1.79	0.148	9.71	1.33
PI-101/PI-02	5.0	1.79	0.137	8.98	1.23
PI-174/PI-02	5.0	2.31	0.156	17.6	1.40

[a] Concentration of hmc in percent by volume.

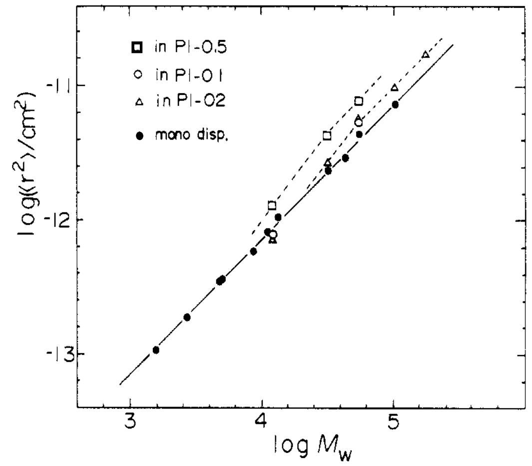

Figure 5. Molecular weight dependence of mean-square end-to-end distance $\langle r^2\rangle$ for monodisperse *cis*-PI (solid circle) and $\langle r^2\rangle$ of the high molecular weight component (hmc) in binary blends. Concentration of hmc in blends is 5.0%.

Figure 3 shows similar loss curves for PI-02 matrix blends which contain 5% of an hmc in the matrix of lmc PI-02. The steep increase in ϵ'' above the 1-kHz range is due to the normal mode of PI-02, while the small bumps below the 1-kHz range are due to the hmc. Figure 4 shows the loss curves of PI-101/PI-02 blends containing different amount of the hmc. From these ϵ'' curves for *cis*-PI blends, the contribution of hmc was determined by eq 10. The relaxation strength of the hmc is determined with eq 11 and listed in Table II.

Molecular Weight Dependence of End-to-End Distance. The $\langle r^2\rangle$ data of hmc in the blends are compared in Figure 5 with those for monodisperse *cis*-PIs reported previously.[7,10] The $\langle r^2\rangle_0$ data of the monodisperse system are proportional to M_w in agreement with the theoretical prediction.[6-9] The solid line passing through the data points for the monodisperse systems in Figure 5 is expressed as

$$\log \langle r^2\rangle_0 = \log M_w - 16.14 \qquad (12)$$

Several authors have already pointed out that they have confirmed by small-angle neutron scattering (SANS) on blends of deuterated and undeuterated polystyrenes that the radii of gyration of undiluted polymers are equal to their unperturbed values.[15-18]

On the other hand, the data points for hmc of the blends deviate upward from eq 12 beyond a certain value of M_w ($=M_2$), indicating the onset of the excluded volume effect taking place. For example, the $\langle r^2\rangle$ of hmc in the 5% hmc/PI-02 blends deviates from the unperturbed value at $\log M_2 \simeq 4.2$: $\langle r^2\rangle$ increases with the slope of 1.2 ± 0.1. With further increase in M_2 beyond $\log M_2 \simeq 4.7$,

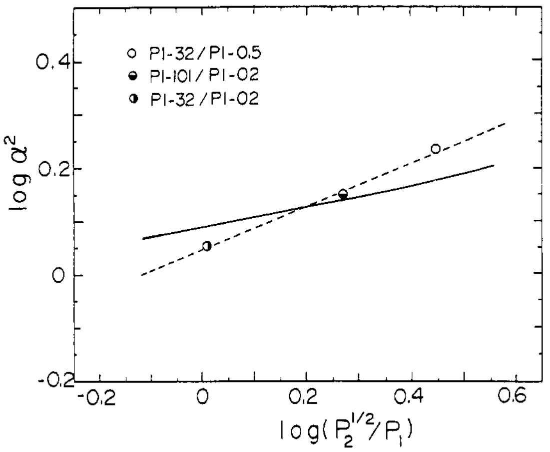

Figure 6. Double logarithmic plot of expansion factor α^2 versus $P_2^{1/2}/P_1$ for *cis*-PI blends in dilute regime. The solid line indicates eq 4 and the dashed line eq 5 with $K' = 1.35$.

however, the plot again becomes almost parallel to that of eq 12. This result suggests that the excluded volume effect in the hmc in the blends becomes independent of M_2.

This behavior qualitatively agrees with the theoretical prediction of eq 8.[1-4] When M_2 of the hmc in the 5% blends is relatively low, eq 6 is not satisfied, and hence $\langle r^2 \rangle$ of the hmc in the blends is close to the unperturbed value. In the range where eq 6 is satisfied, $\langle r^2 \rangle$ increases with increasing M_2 with a higher exponent than unity. In these blends, the exponent is 1.2 ± 0.1, as given by eq 5. However, with further increase in M_2 at a fixed concentration of hmc (5% in this case), random coils of the hmc begin to overlap and thus begin to obey the behavior of semidilute solutions as given by eq 8.

Using eq 7, we estimated the overlapping concentration C^* $(=\rho\phi_2^*)$ of hmc for PI-12, PI-32, and PI-53 to be 8.6%, 5.3%, and 4.1%, respectively. Thus, at the concentration of 5% employed in this study, the blends containing an hmc with $M_w >$ about 30 000 ($\log M_w = 4.5$) are in the semidilute regime. The value of $\log M_w = 4.5$ thus estimated is in agreement with the observed $\log M_w$ of 4.7, at which the M_w dependence of $\langle r^2 \rangle$ becomes parallel to the line given by eq 12.

Expansion Factor. From the estimated crossover concentration, C^*, of hmc in each blend, we may assume that the blend containing 5% PI-32 is just in the crossover region between the dilute and semidilute blends. Thus, the blend containing 5% PI-32 and that containing 1.3% PI-101 is in the dilute regime. The values of α^2 of these dilute blends are plotted against $P_2^{1/2}/P_1$ in Figure 6. In Table II, we see that the PI-12/PI-01 and PI-12/PI-02 blends are also dilute blends. However, as seen in Figure 3, the ϵ'' curve for PI-12 heavily overlaps the loss peak of the lmc over a wide range of frequency, and hence the area of the ϵ'' curve for PI-12 determined by resolving the ϵ'' curve of the PI-12 blends includes relatively large error. We thus neglected the data for PI-12 hmc blends in constructing the plot of Figure 6.

To compare these data with the theory, we calculated eq 4 with the experimental values of $\langle r^2 \rangle_0$ given by eq 12 and plotted in Figure 6 with the solid line. Here v is taken to be 1.10 cm³/g. The theoretical value for eq 5 is also plotted with $K' = 1.35$ with the dashed line. As is seen in Figure 6, eq 4 predicts the slope of the plot much lower than the limiting value of 0.4 in the range of $P_2^{1/2}/P_1$ covered in this experiment. We see that the present experimental slope is higher than that given eq 4 and agrees well with eq 5. Thus, we conclude that α in the binary blends is described with eq 5 rather than eq 4.

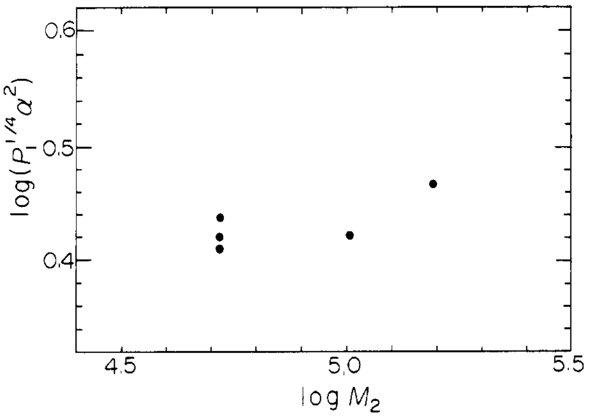

Figure 7. Double logarithmic plot of $\alpha^2 P_1^{1/4}$ vs molecular weight M_2 of the high molecular weight component in semidilute blends.

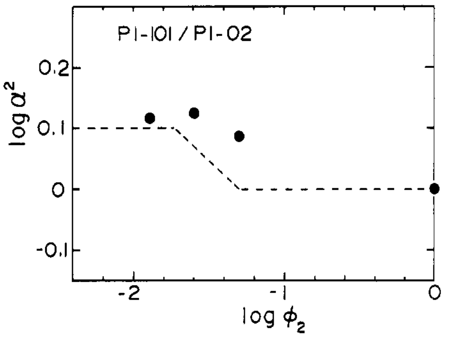

Figure 8. Dependence of expansion factor α^2 of PI-101 on its volume fraction ϕ_2 in PI-101/PI-02 system. Dashed line represents the theoretical prediction by Joanny et al.[3]

Semidilute Blends. When blends are in the semidilute regime, eq 8 predicts that $P_1^{1/4}\alpha^2$ is independent of P_2 as long as the concentration of the hmc is fixed to be a certain value. Figure 7 shows a test of this prediction for all the blends containing 5% hmc. As is seen in Figure 7, $P_1^{1/4}\alpha^2$ is almost independent of P_2. This result is equivalent to the fact that the M_2 dependene of $\langle r^2 \rangle$ of hmc becomes parallel with that for the monodisperse samples, as already seen in Figure 5. Thus we conclude the experimental result in the semidilute regime agrees with eq 8.

Strictly speaking, however, we see a trend that $P_1^{1/4}\alpha^2$ increases slightly with increasing M_2. This is explained by considering the behavior of crossover of a real system as follows. Since the crossover from the dilute to semidilute takes place over a certain concentration range, the value of α^2 in the crossover concentration region is slightly smaller than the theoretical one, which assumes a sharp crossover at C^*. In Figure 7, the hmc coils at lower M_2 region are still in a crossover region, but those at higher M_2 are not. Thus $P_1^{1/4}\alpha^2$ increases slightly with increasing M_2.

Figure 8 shows the dependence of $\log(\langle r^2 \rangle / \langle r^2 \rangle_{\text{bulk}})$ of hmc PI-101 on the volume fraction ϕ_2 in the four PI-101/PI-02 blends containing 1.3–5% PI-101. The $\langle r^2 \rangle_{\text{bulk}}$ is the value for pure undiluted PI-101. The dashed line in the figure represents the prediction of the theory of Joanny et al.[3] We see that the concentration dependence of $\langle r^2 \rangle$ is much weaker than expected from eq 8. We also see that the crossover concentration from the semidilute to concentrated regime appears to be higher than $1/P_1$ expected from the Joanny theory. This disagreement may be explained as follows. The scaling theory assumes that even if $P_1 \ll P_2$ the lmc has a high degree of polymerization. On the other hand, the lmc in 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.

Acknowledgment. This work was supported in part by the Grant-in-Aid for Scientific Research by the Ministry of Education, Science and Culture (6055062). A support from the Institute of Macromolecular Research (Osaka University) is also gratefully acknowledged.

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

Keiichiro Adachi,* Shigeru Itoh, Isao Nishi, and Tadao Kotaka

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received June 16, 1989; Revised Manuscript Received August 10, 1989*

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]

0024-9297/90/2223-2554$02.50/0