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A Dielectric Study of the Dynamics of Polyisoprene Trapped in Polybutadiene Networks

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ABSTRACT: The dielectric normal-mode process was studied on *cis*-polyisoprene (*cis*-PI) trapped in solution cross-linked *cis*-polybutadiene (*cis*-PB) networks (BR). The relaxation time τ for fluctuation of the end-to-end vector decreased with decreasing weight fraction w of the guest *cis*-PI due to the changes in the monomeric friction coefficient ζ and in the entanglement effect. The w dependence of ζ was estimated from τ of *cis*-PI with the molecular weight M lower than that between entanglements M_e of *cis*-PB ($\simeq 2700$) trapped in a loose BR network with the molecular weight between cross-links $M_x > M_e$, by assuming that the w dependence of τ of such a system was totally ascribed to the change in ζ. On the basis of this w dependence of ζ, the τ's of other BR/*cis*-PI systems were reduced to that, τ_ζ, in an isofriction state. For *cis*-PI with $M > 5000$ in the BR with $M_x > M_e$, the τ_ζ increased with decreasing w. This may be attributed to the following: (1) the change in the topological constraint being determined by the competition of the diffusible *cis*-PI chains and undiffusible network strands (the tube renewal effect); (2) the change in the effective M_e for *cis*-PI. From the w dependence of τ_ζ for *cis*-PI with $M = 32\,000$, the M_e at the limit of $w = 0$ was estimated to be 1700 ± 600. The increase in τ_ζ with decreasing w due to the diminishing tube renewal effect was most remarkably observed for the guest *cis*-PI with $M = 14\,000$, which was close to the characteristic molecular weight M_c of *cis*-PI. The M dependence of τ_ζ of *cis*-PI at $w = 0.05$ indicated that the τ_ζ in the BR networks increased by a factor of ca. 10 over that of the bulk *cis*-PI. The mean-square end-to-end distance $\langle r^2 \rangle$ of the trapped *cis*-PI evaluated from the normal-mode relaxation strength decreased with decreasing w.

1. Introduction

Among several theories on the effect of entanglement on polymer dynamics, the tube model provides a simple and straightforward picture. The original theory proposed by de Gennes[1] and by Doi and Edwards[2] assumed that polymer molecules around a test chain work as its obstacles fixed in space. However, in reality since the molecules forming the tube also move, the tube itself gradually disintegrates.[3] Klein called the process "tube renewal".[3] However, in a network/guest polymer system, the network chains do not diffuse away. Therefore, such a system should provide information on the effect of entanglement free from the complex effect of tube renewal. Motivated by this view, we studied dynamics of guest *cis*-polyisoprene (*cis*-PI) molecules trapped in cross-linked natural rubber (NR) networks, examining their dynamic Young's moduli[4] and dielectric normal-mode processes.[5] From the latter, we determined the relaxation time for fluctuation of the end-to-end vector and the mean-square end-to-end distance of the trapped *cis*-PI molecules.[6-8] Ferry and coworkers have reported viscoelastic studies on several network/guest polymer systems.[9-14]

de Gennes[15] proposed a dynamic-state diagram classifying the mobility of guest molecules in networks of the same kind into three regimes, I-III, according to the molecular weight M of the guest molecules, the molecular weight M_e between entanglements, and the molecular weight M_x between cross-links.

In regime I where $M < M_e$ and $M < M_x$, the guest molecules are free from the entanglement effect: the free-draining regime. In regime II where $M > M_e$ and $M_x > M_e$, the entanglement effect is the same as that in the uncross-linked bulk polymer system: the reptation regime. In regime III where $M > M_e > M_x$, the trapped chains suffer severe constraints from the network: the strangulation regime. Recently, we classified the data reported by Ferry et al.[9-14] and by ourselves[4,5] based on the de Gennes state diagram and reviewed the dynamics of the guest polymer in networks.[16]

In our recent paper,[17] we reported that solution cross-linked *cis*-polybutadiene networks BR exhibit relatively high absorbance toward *cis*-PI. In this paper, we report results on the dielectric normal-mode process of *cis*-PI trapped in BR networks. For dynamics in such systems, we face two problems:[18,19] what is the molecular weight between entanglements and what is the monomeric friction coefficient in such a heterogeneous system? The objective of this study is to clarify the effects arising from such a different polymer pair on the dynamics. So far only one different-polymer-pair system was reported by Ferry et al. employing a BR/styrene–butadiene copolymer system.[12]

Studying dynamics of guest PI in BR networks by the dielectric normal-mode method has a few advantages. First, since *cis*-polybutadiene (*cis*-PB) does not exhibit the dielectric normal-mode process, we expect a very low background level of the dielectric loss factor. Second, we can determine the longest relaxation time of the guest polymers with low molecular weight. This is a difficult task by the mechanical method.[18] Third, the dielectric method makes it possible to estimate the mean-square end-to-end distance $\langle r^2 \rangle$ of the guest PI molecules as well.[6-8]

Taking such advantages of the dielectric method, we attempted to clarify the dynamic and conformational properties of guest *cis*-PI molecules in BR networks.

2. Experimental Section

Polybutadiene networks (BR) were prepared by irradiation by γ-rays to solutions of *cis*-polybutadiene (*cis*-PB). Narrow distribution samples of *cis*-polyisoprene (*cis*-PI) were prepared by anionic polymerization. Details of the preparation and characterization have been described in our recent paper.[17] The same

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Table I
Molecular Weight M_x between Cross-Links for BR and Weight-Average Molecular Weight M_w and Polydispersity M_w/M_n of *cis*-PI

code	$10^{-3}M_{xs}$[a]	$10^{-3}M_{xE}$[b]	$10^{-3}M_x$[c]	$10^{-3}M_w$	M_w/M_n
BR(0.1:20)	13.3	8.7	11.0		
BR(0.2:20)	19.6	19.6	19.6		
BR(0.5:20)	14.5	5.0	9.8		
BR(0.7:40)	6.4[d]				
BR(1:40)	1.6	3.5	2.6		
BR(1:20)	2.1	5.3	3.7		
PI-02				1.6	1.14
PI-03				2.6	1.08
PI-05				4.8	1.07
PI-14				13.5	1.08
PI-32				31.6	1.05

[a] M_x from the swelling ratio. [b] M_x from the Young's modulus. [c] Average of M_{xs} and M_{xE}. [d] M_x was determined only from the swelling ratio.

sample code BR(*x*:*y*) is used here: *x* represents the volume fraction of *cis*-PB in the solution irradiated and *y* the dose of γ-rays in Mrd. The molecular weight M_x between cross-links was determined from the swelling ratio in benzene and from the Young's modulus. The former and the latter are denoted as M_{xs} and M_{xE}, respectively, and are listed in Table I together with their averages. The number of the sample code of *cis*-PI indicates the weight-average molecular weight in kilograms per mole. The characteristics of *cis*-PI are also listed in Table I.

The BR films were soaked in *cis*-PI/benzene solutions for 1–3 days. The concentration ϕ of the solutions and the period of soaking were adjusted to get an appropriate content *w* of the guest molecules where *w* is the weight fraction of *cis*-PI in the absence of any solvents.[17] After they were soaked, the specimens were washed quickly with pure benzene and dried at 70 °C in vacuo until constant weight was reached. All the network/guest systems were optically transparent.

The dielectric constant ϵ' and loss factor ϵ'' were measured by a transformer capacitance bridge (General Radio 1615 A) in the frequency range from 20 Hz to 50 kHz. In the case where the ϵ'' curve over wide frequency *f* range was required, measurements were carried out at 273, 295, and 320 K, and then the master curve of ϵ'' at 273 K was constructed by shifting the log ϵ'' vs log *f* curves at 295 and 320 K both in the horizontal and vertical directions. In some cases, the reference temperature was taken to be 295 K when the 273 K data does not exhibit a clear loss maximum. The logarithm of the horizontal shift factor vs temperature curves is almost straight in the range from 273 to 320 K. The apparent activation energy is approximately the same for all the samples measured and is 22.6 ± 2.6 kJ/mol.

As reported in the previous paper, we can estimate the friction coefficient for the normal-mode process from the relaxation time τ_s for the segmental-mode process. However, τ_s was not measured since BR crystallizes in the temperature range where the segmental-mode process is observed.

To characterize the thermal behavior, we used a differential scanning calorimeter (Seiko Instruments & Electronics Ltd. SSC 580/DSC-20). Figure 1 shows typical DSC thermograms for pure BR(0.1:20), pure PI-03, and BR(0.1:20)/PI-03 ($w = 0.24$). All these systems exhibit a single glass transition T_g, which varied from 160 K for BR to 200 K for pure *cis*-PI with increasing *cis*-PI content. The pure BR and BR/*cis*-PI systems exhibit a sharp endothermic peak around 265 K due to the melting of BR crystallites.

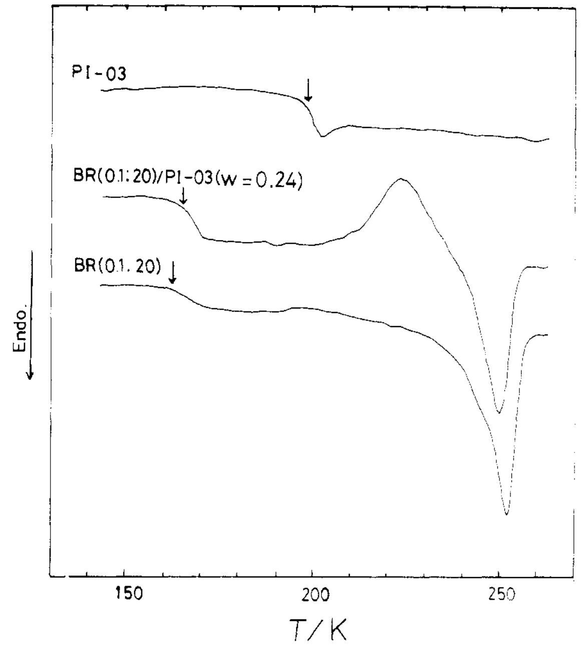

Figure 1. DSC thermograms for pure BR(0.1:20), pure PI-03, and BR(0.1:20)/PI-03 ($w = 0.24$). The arrows indicate the glass transition temperature.

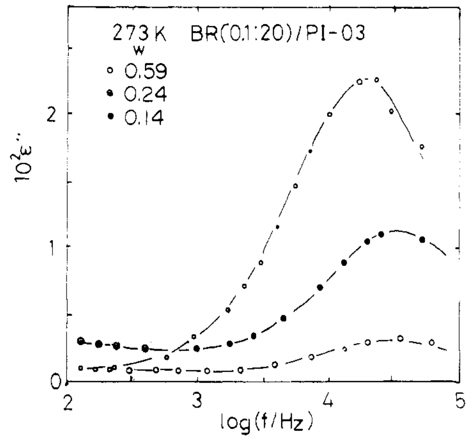

Figure 2. Frequency dependence curves of ϵ'' for the BR(0.1:20)/PI-03 system with varying content *w* of PI-03.

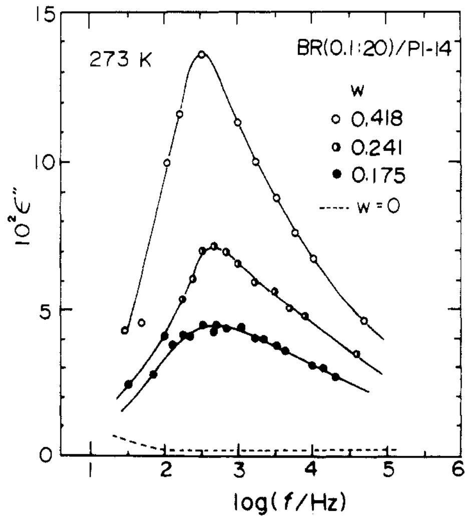

Figure 3. Frequency dependence curves of ϵ'' at 273 K for the BR(0.1:20)/PI-14 system with varying content of the guest PI-14. The dashed line indicates the ϵ'' curve for BR(0.1:20).

3. Results and Discussion

3.1. Frequency Dependence of ϵ''. Figures 2 and 3 show representative ϵ'' curves for BR(0.1:20) containing PI-03 and PI-14, respectively. In each curve a clear ϵ'' peak is seen in the audio-frequency range, where the values of ϵ'' for pure BR are less than 3×10^{-3} at $T > 250$ K. Therefore, the relaxation peak observed is essentially the contribution of the guest molecules alone. The loss-maximum frequency f_m increases with decreasing molecular weight *M* of the guest *cis*-PI. Evidently, these loss peaks can be assigned to the normal-mode process of the guest

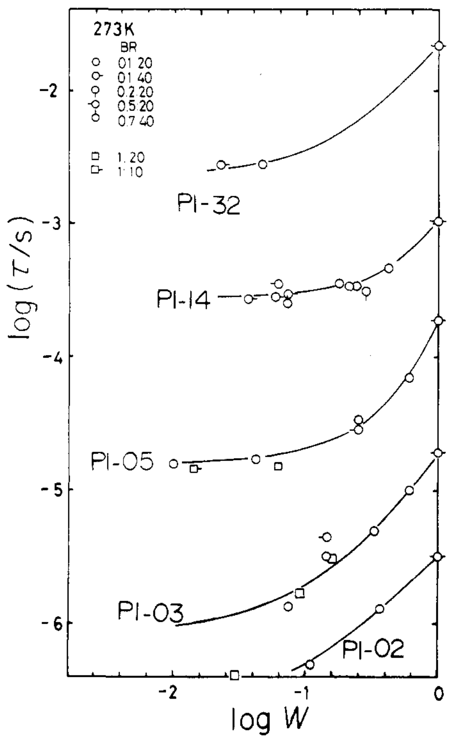

Figure 4. Double-logarithmic plot of the relaxation time τ of *cis*-PI trapped in the BR networks versus the weight fraction w of *cis*-PI.

cis-PI trapped in the BR networks. The loss maxima shift to the high-frequency side with decreasing weight fraction w of the guest *cis*-PI molecules. From f_m, the relaxation time τ is determined with a relation $\tau = (2\pi f_m)^{-1}$. As discussed by Jones et al., τ thus determined can be regarded as the longest relaxation time within the error of 3%.[19]

The data shown above are for the BR network with $M_x = 11.0 \times 10^3$, which is higher than the M_e (=5000) of *cis*-PI[20] and that (=2700) of *cis*-PB.[20] We still have been unable to obtain dielectric data for the BR network with low M_x. For example, the bulk cross-linked network BR(1:20) absorbed PI-14 and PI-32 only 1.5% and 0.5%, respectively.[17] Due to this small *cis*-PI content, we could not obtain reliable dielectric data for these systems.

3.2. Concentration Dependence of Friction Coefficient. Figure 4 shows the w dependence of $\tau = 1/(2\pi f_m)$ for various guest *cis*-PI trapped in BR(0.1:20). The most striking feature seen in Figure 4 is that τ decreases with decreasing w. This trend is the reverse of the behavior in the *cis*-PI/natural rubber system.[5] Since BR has lower T_g than *cis*-PI, the *cis*-PI molecules surrounded by the BR strands are more mobile than in bulk *cis*-PI. The monomeric friction coefficient ζ decreases with decreasing w. However, careful observation indicates that the w dependence of τ depends on the molecular weight of the guest *cis*-PI molecules. This complex behavior suggests that the w dependence of τ may be ascribed to changes not only in the monomeric friction coefficient ζ but also in the density of entanglement couplings.

Generally, the relaxation time for the large scale motion can be expressed as[21]

$$\tau = \zeta f(M,w) \tag{1}$$

Here, f(M,w) is the structural factor that depends on the architecture and molecular weight of the polymer molecule.

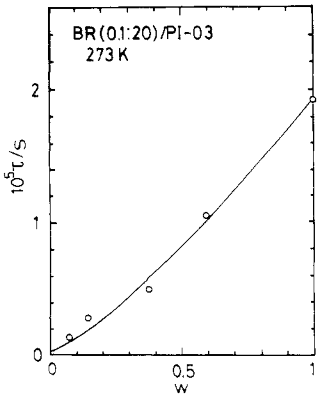

Figure 5. Weight fraction w dependence of the relaxation time τ of guest PI-03 in the BR(0.1:20) network. The solid line indicates eq 2.

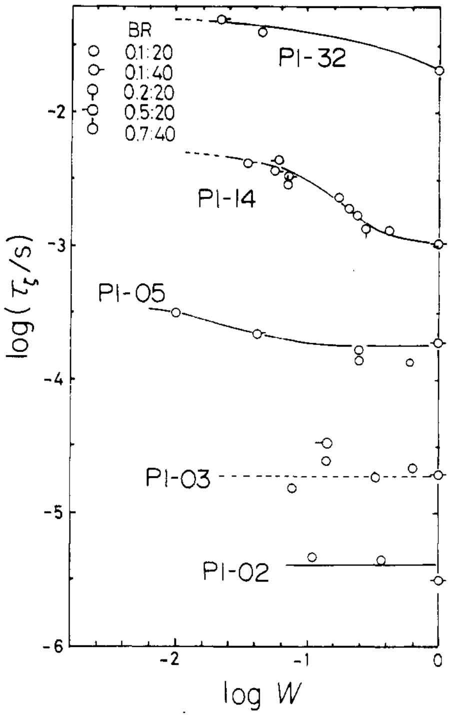

Figure 6. w dependence of relaxation time τ_ζ corrected to an isofriction coefficient state of w = 1.

To separate the contributions of ζ and $f(M,w)$, we first consider a system in which guest chains do not entangle either with themselves or with the network strands. We assume that the w dependence of τ of PI-03 in the BR(0.1:20)/PI-03 system totally reflects the change in ζ. This is rationalized since the molecular weight of PI-03 is lower than M_e of both *cis*-PI (=5000) and *cis*-PB (=2700)[20] and also lower than M_x of BR(0.1:20) (=1.4×10^4).

For guest PI-03 trapped in BR(0.1:20), τ is given as a function of the weight fraction w of *cis*-PI:

$$10^5\tau = 0.084 + 1.090w + 0.766w^2 \tag{2}$$

The best fit curve thus determined is compared with the observed τ in Figure 5. This equation represents the ratio of ζ for any *cis*-PI in any BR network to that of the *cis*-PI in bulk.

3.3. Concentration Dependence of Entanglement Effect. Now we turn our attention to the w dependence of $f(M,w)$. To do this we calculated the relaxation time τ_ζ corrected to an isofriction coefficient state using eq 2. Here, we reduced τ to a state that is the same as bulk *cis*-PI. The result is plotted in Figure 6. The ratio τ_ζ/τ(bulk PI) increases with decreasing w for the guest *cis*-PI with M higher than 5000.

The following two different mechanisms may be responsible for this behavior: the tube renewal effect and the *w* dependence of M_e effective for the guest *cis*-PI molecules.

In the introductory section, we mentioned that the constraint for the *cis*-PI chain trapped in the network is stronger than in bulk *cis*-PI, because in terms of the tube theory the tube-forming chains in the uncross-linked system can disentangle by their own motion. This effect is called the tube renewal effect. Klein[3] has expressed the longest relaxation time τ_d^{ren} in such a system with $M > M_e$ as

$$\tau_d^{ren} = \tau_R + (1 - M_e^2/M^2)\tau_d \qquad (3)$$

where τ_R is the longest relaxation time given by the Rouse theory,[22] and τ_d, the relaxation time for the tube disengagement process in the original tube theory.[1,2] Thus, the τ_d corresponds to the relaxation time for a test chain in a fixed tube. This equation (3) predicts that the ratio of τ_d/τ_d^{ren} increases with decreasing *M*.

In actual uncross-linked systems, we observe the entanglement effect for the molecules with *M* higher than the characteristic molecular weight M_c ($=2M_e$).[18,20] Thus, roughly speaking, the tube renewal effect may become prevailing for the polymer molecules with $M \simeq M_c$. Applying this model to our systems, we expect the following situations. When *w* is relatively high, one *cis*-PI molecule is surrounded by the same *cis*-PI molecules, which can diffuse away, and therefore it should possess τ close to τ_d^{ren}. On the other hand, when *w* is low, the *cis*-PI molecule is surrounded by BR strands whose ends are fixed at the cross-links. Thus, the frequency of tube reorganization increases with increasing *w*. This causes the *w* dependence of τ_ζ.

Another mechanism we have to consider is the *w* dependence of M_e. It is reminded that M_e of *cis*-polybutadiene is 2700 and that of PI is 5000.[20] We thus expect that the effective M_e for the *cis*-PI chains trapped in the network decreases with decreasing *w*. This also causes the increase in τ_ζ with decreasing *w*.

Turning to the experimental results shown in Figure 6, we see that the *w* dependence of the τ_ζ for PI-14 is stronger than that for PI-32. Since the M_c of bulk *cis*-PI is 10 000, we consider that the *w* dependence of τ_ζ for PI-14 is due to both origins described above. Equation 3 indicates that when $M/M_e = 6$, the difference of τ_d^{ren} and τ_d is only about 3% of τ_d. Therefore, we assume that the *w* dependence of τ_ζ for PI-32 is due only to the change in M_e.

From the data for PI-32, we estimated the *w* dependence of M_e as follows. The tube theory[2] predicts that the longest relaxation time τ_d is proportional to M^3/M_e. Therefore, we expect that τ_ζ is inversely proportional to M_e

$$\tau_\zeta(w) = \tau_\zeta(1)[M_e(1)/M_e(w)] \qquad (4)$$

where $\tau_\zeta(w)$ and $M_e(w)$ represent the corresponding quantities for *cis*-PI at the concentration *w* and $M_e(1)$ is the M_e for bulk *cis*-PI i.e. at $w = 1$. As shown in Figure 6, log τ_ζ for PI-32 at the limit of $w = 0$ is estimated to be -1.20 ± 0.15, while log τ_ζ for the bulk PI-32 is -1.68. From these data and $M_e(1) = 5000$ for the bulk *cis*-PI, eq 4 leads to the M_e at the limit of $w = 0$ to be 1700 ± 600. This value is smaller than the M_e of *cis*-PB in bulk. At present, no theory is available to estimate the value of M_e in such a heterosystem.

Having estimated the *w* dependence of M_e, we now analyze the τ_ζ for PI-14. The difference in log τ_ζ between the states of $w = 0$ and 1 is estimated to be 0.68 from the data shown in Figure 6. If we simply subtract the contribution of the M_e change ($=0.48 \pm 0.15$) from this value, the enhancement in log τ_ζ due to the tube renewal effect amounts to 0.20 ± 0.15. On the other hand, eq 3 predicts log τ_d/τ_d^{ren} for PI-14 to be 0.06, in agreement within the experimental error. Obviously, we need data in the region of low *w* for PI-32 for the further quantitative discussion.

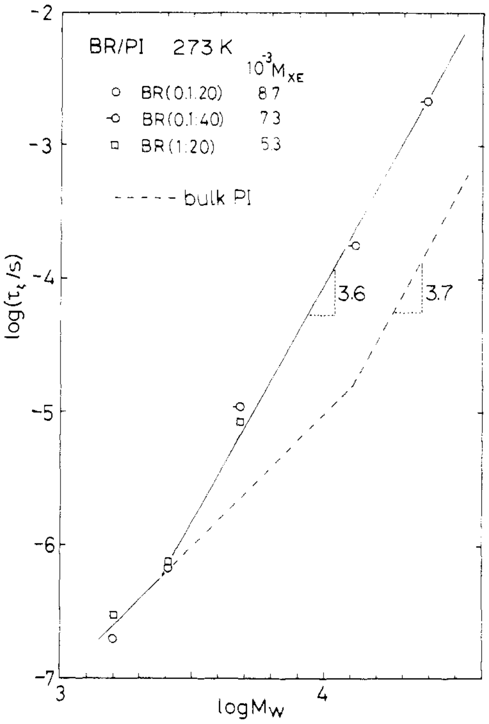

Figure 7. Weight-average molecular weight M_w dependence of τ_ζ corrected to the isofriction state of $w = 0.05$. The dashed line indicates the τ_ζ of bulk *cis*-PI.

Finally, we comment briefly on the behavior of PI-05. As shown in Figure 6, the τ_ζ of PI-05 is almost independent of *w* in the range of $w > 0.1$ but increases with decreasing *w* in the range of $w < 0.1$. This behavior is explained as follows: In the range of $w > 0.1$, PI-05 is in the nonentangled state since M_c of *cis*-PI is 10 000. Below $w = 0.1$, however, the PI-05 molecules entangle with the BR strands due to the decrease in M_e.

3.4. Molecular Weight Dependence of Relaxation Time. To examine the dependence of τ on the guest molecular weight in the isofriction state, we determined τ at $w = 0.05$ by interpolation or extrapolation of the τ vs *w* plots shown in Figure 4. Figure 7 shows τ_ζ at $w = 0.05$ plotted against log (guest M_w) for the networks with M_x much higher than M_e of both *cis*-PI and *cis*-PB. In such systems ζ depends only on *w*, and thereby, the values of τ thus collected are those in the isofriction state at $w = 0.05$.

To compare these plots with the values of τ for bulk *cis*-PI, we reduced the values of τ for bulk *cis*-PI to the friction coefficient at $w = 0.05$ by using eq 2. The result is shown by the dashed line in Figure 7. Figure 7 thus shows the M_w dependence of τ_ζ reduced to $w = 0.05$ for *cis*-PI trapped in the BR networks and *cis*-PI in bulk.

The slope of the log τ_ζ vs log M_w plot for the guest *cis*-PI in BR(0.1:40) is determined to be 3.6 ± 0.3 for $M > 3 \times 10^3$. In the range $M_w < 3 \times 10^3$, it is difficult to determine precisely the slope since the number of the data points is limited. However, we see that the slope is approximately 2 if the average of the two values of log τ_ζ at log $M_w = 3.2$ is taken.

The dielectric[6] as well as viscoelastic[18,20] relaxation times τ for bulk *cis*-PI are known to be divided into two regions: In the range of $M < M_c$ ($\simeq 10^4$), τ is proportional to M^2 while in the range of $M > M_c$, τ is proportional to $M^{3.7}$.

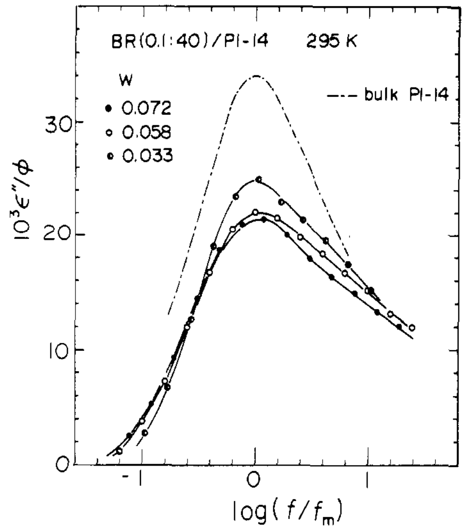

Figure 8. Master curves of ϵ'' at 295 K for the BR(0.1:40)/PI-14 system normalized with the volume fraction ϕ of *cis*-PI. Smoothed values are plotted. The dash–dot line indicates the ϵ'' curve for the bulk PI-14.

The M^2 dependence is common to any unentangled polymer systems and is described by the Rouse theory,[22] while the latter dependence is characteristic of entangled polymer systems.[6] Comparing the behavior of PI in the pure bulk state and in the BR networks, we can conclude that the PI molecules of $M > 3 \times 10^3$ in BR(0.1:40) are in the entangled state. The characteristic molecular weight M_c for this system was estimated to be about 3×10^3.

In the previous section, we estimated M_e for the BR/guest *cis*-PI systems at infinite dilution to be 1700 ± 600. If we assume that the empirical law $M_c = 2M_e$ is applicable to the network/guest systems,[18,20] M_c becomes 3400. This value agrees approximately with M_c estimated in Figure 7.

We have discussed the behavior in the systems having M_x much higher than the M_e of *cis*-PB. Thus, the above data show the behavior in regime II of the dynamic-state diagram proposed by de Gennes.[15] Unfortunately, we could not yet obtain reliable data for the present systems in the regime III, as mentioned earlier.

3.5. Relaxation Strength. For determination of the relaxation strength for the normal-mode process, measurement of the complex dielectric constant over a sufficiently wide frequency range is necessary. Since the available frequency range was restricted in the range of 200 Hz to 50 kHz, we attempted to superpose the data at three different temperatures. Figure 8 shows the master curves for BR(0.1:40) containing PI-14 with w = 0.072, 0.058, and 0.033. Since there are many data points, we plotted the smoothed values. The dot–dash line shows the ϵ'' of bulk PI-14.

From the area under the master curve, we evaluated the dielectric relaxation strength $\Delta\epsilon$. To do so, the ϵ'' curves in the high-frequency range were estimated by linear extrapolation of log ϵ'' vs log f curve. The error in $\Delta\epsilon$ is estimated to be ±20%. Figure 9 shows the w dependence of $\Delta\epsilon$ of PI-14 in BR(0.1:20) and BR(0.1:40). As shown previously, $\Delta\epsilon/C$ is proportional to the mean-square end-to-end distance $\langle r^2\rangle/M^7$

$$\Delta\epsilon/C = 4\pi N_A\mu^2\langle r^2\rangle/(3k_BTM) \tag{5}$$

where C is the concentration in w/v of the polymer, N_A is the Avogadro constant, M is the (weight average) molecular weight, and μ (=4.80×10^{-12} cgs esu for *cis*-PI) is the dipole moment per unit contour length. Although data points are rather scattered, we see a systematic decrease in $\langle r^2\rangle$ with decreasing w. This suggests that $\langle r^2\rangle$ of *cis*-PI in the BR network is smaller than that of pure *cis*-PI or that in a Θ solvent. This behavior may be attributed to the repulsive thermodynamic interaction between *cis*-PI and BR.

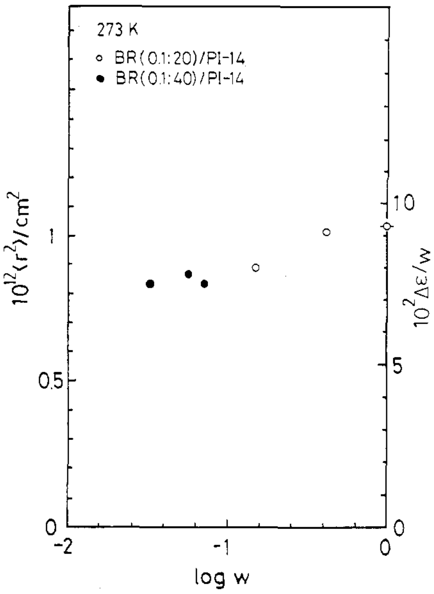

Figure 9. w dependence of the dielectric relaxation strength $\Delta\epsilon$ of the guest PI-14 in the BR networks at 273 K. The values of $\Delta\epsilon$ at 295 K for BR(0.1:40)/PI-14 were converted to those at 273 K by multiplying the vertical shift factor 1.20.

Table II
Half-Width Δ of the Loss Curve for Bulk PI-14 and BR/PI-14 Systems

system	w	Δ
PI-14(bulk)	1	1.69
BR(0.1:20)/PI-14	0.418	1.98
BR(0.1:20)/PI-14	0.175	2.00
BR(0.1:40)/PI-14	0.072	2.15
BR(0.1:40)/PI-14	0.058	2.18
BR(0.1:40)/PI-14	0.033	1.90

3.6. Distribution of Relaxation Times. The shape of the ϵ'' curves, such as shown in Figures 2, 3, and 8, primarily reflects the difference in the distribution of relaxation times, which in turn reflects the change in the mode of molecular motions. In Table II we summarize the half-width Δ of the ϵ'' peaks. The half-width Δ exhibits a maximum around w = 0.06. Overlapping of the tails of the loss peaks due to the normal-mode and segmental-mode processes might be partly responsible to this broadening of the ϵ'' peaks. However, the overlapping effect is rather small in the present systems, and nevertheless the ϵ'' curve for *cis*-PI in the network is still considerably broader than that for pure *cis*-PI.

We speculate on the mechanism of the broadening as follows. Since the present network was prepared by irradiation with γ-rays, the distribution of M_x is very broad. Although the BR sample used in the present experiment has M_x higher than M_e, there exist network strands shorter than the average size. Such short strands will cause greater confinement on the motions of the guest molecules. This causes the wider distribution of the relaxation time than in the pure *cis*-PI.

Conclusions

(1) The relaxation time τ for the normal-mode process of the guest *cis*-PI molecules trapped in the BR networks changes through the following factors: (i) the friction coefficient ζ, (ii) the molecular weight M_e between entan-

glement, and (iii) the extent of the topological confinement on *cis*-PI due to the surrounding chains (*cis*-PI and the network strands depending on w). The M_e in the infinite dilution state was estimated to be 1700, which is lower than the M_e in pure *cis*-polybutadiene.

(2) The relaxation time of the guest *cis*-PI trapped in BR reduced to the isofriction coefficient state was longer than the bulk *cis*-PI, indicating that the guest *cis*-PI molecules in the network were confined more strongly than in the bulk state.

(3) The relaxation strength of the guest *cis*-PI molecules in BR is smaller than that in the bulk state. This indicates that their mean-square end-to-end distance is smaller than the unperturbed dimension.

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Use of Gas Chromatography To Determine the Degree of Cross-Linking of a Polymer Network

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ABSTRACT: The technique of finite-concentration inverse gas chromatography has been used to estimate the relative cross-link density of ethylene–propylene rubbers that had been cross-linked by using ^{60}Co radiation. The solvent activity in networks swollen with hexane was treated in terms of the Flory–Rehner equation.

Introduction

Over the past two decades, gas chromatography has been used to study a wide range of polymer properties such as glass transition and melting temperatures, crystallinity, and diffusion coefficients.[2,3] In particular, it has been applied to solution studies where measurements of activity coefficients, enthalpies of mixing and of solution, and interaction and solubility parameters may be made rapidly over a wide range of conditions. The purpose of this article is to introduce its use in the characterization of cross-linked polymer networks.

Solutions of linear polymers are usually treated in terms of the Flory–Huggins theory[4,5] for the thermodynamic activity of the solvent, a_1:

$$\ln a_1 = \ln \phi_1 + [1 - (1/r)]\phi_2 + \chi\phi_2^2 \qquad (1)$$

where ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer, respectively, r is a parameter representing the size ratio of polymer and solvent segments, and χ is the Flory–Huggins interaction parameter which accounts for energetic and noncombinatorial contributions to the free energy of mixing.

Equation 1 was extended to apply to polymer networks by Flory and Rehner,[6] who assumed an additional, additive contribution due to the elastic free energy of deforming the network on swelling with the solvent:

$$\ln a_1 = \ln \phi_1 + [1 - (1/r)]\phi_2 + \chi\phi_2^2 + V_1\nu_e/v_2[\phi_2^{1/3} - (\phi_2/2)] \qquad (2)$$

where V_1 and v_2 are the molar volume of solvent and specific volume of polymer. ν_e represents the effective number of cross-links per gram of polymer, i.e., the reciprocal of the molecular weight of the polymer chain between cross-links, M_c.

In characterizing polymer networks, ν_e is usually measured by determining the amount of solvent absorbed in an equilibrium swelling experiment,[7,8] although techniques such as vapor sorption have also been used.[9] There has been considerable debate on the question of the additivity of the various contributions to the free energy of mixing,[10,11] and eq 2 is now recognized to be at best an approximation to the behavior of real systems (much as in the case of the original Flory–Huggins treatment) in that it tends to overestimate the degree of cross-linking. However, despite this, its use remains widespread in polymer chemistry.

Gas chromatography (GC), as usually used to study polymers, often referred to as inverse gas chromatography (IGC), is performed at inifinite dilution of solvent. As long

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