Swelling Equilibrium of Solution Cross-Linked Polybutadiene Networks in Polyisoprene Solutions

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ABSTRACT: Solution cross-linked polybutadiene networks (BR) were prepared by irradiation with γ-rays to *cis*-polybutadiene in toluene solution, and their swelling behavior in benzene solutions of *cis*-polyisoprene (*cis*-PI) was investigated. The swelling ratio q ($=1/v_2$) and the absorption ratio A ($=1 + v_3/v_2$) increased strongly with decreasing cross-linking concentration C_x, where v_2 and v_3 denote the volume fractions of the network and *cis*-PI, respectively. The absorption ratio A also increased with decreasing molecular weight of *cis*-PI. The behavior was analyzed on the basis of the Flory–Rehner assumption that the network is in the most stable state when $q = 1/C_x$. The theoretical q and A agreed semiquantitatively with the observed values, if we assume that the interaction parameter χ_{23} between BR and *cis*-PI is equal to 0.022 for *cis*-PI with molecular weight $M_w = 2.6 \times 10^3$ and $\chi_{23} = 0.014$ for $M_w = 3.16 \times 10^4$. The diagram of A vs concentration ϕ of *cis*-PI solutions exhibited a maximum. This behavior was ascribed to the effect of the repulsive interaction between BR and *cis*-PI.

Introduction

Although many studies have been made on the swelling of polymer networks,[1-6] only a few of them are concerned with the swelling in bulk polymers or in polymer solutions.[3-5] A polymer network placed in an undiluted polymer barely swells, since the entropy of mixing of the polymers is very small. Recently we studied the swelling and absorption behavior of natural rubber (NR) cross-linked in the solution state[5] and found that the solution cross-linked NR networks exhibit relatively high degrees of absorption toward *cis*-polyisoprene (*cis*-PI), which is chemically the same kind as the network. So far the properties of solution cross-linked networks have been studied only by a few authors,[7-11] in contrast to those of ordinary networks prepared in the absence of solvents. High swellability of solution cross-linked networks has not been well understood.

The theory of rubber elasticity has been developed by Flory and co-workers[12-16] and by others.[17-19] According to the phantom network model proposed by James and Guth,[20,21] the tensile force f_{ph} for a network prepared by cross-linking in a solution of concentration C_x and then dried completely is given by[16]

$$f_{ph} = (\xi k_B T / L_{i,v}) C_x^{2/3} (\alpha - \alpha^{-2}) \quad (1)$$

where ξ is the effective number of the strands in the specimen and is called cycle rank, $L_{i,v}$ is the length of the network in the dry state, and α is the linear expansion coefficient. Flory and Erman[14,15] proposed a theory on a network with the junctions subject to strain dependent constraints and expressed the tensile force f as

$$f = f_{ph}(1 + f_c/f_{ph}) \quad (2)$$

where f_c is a function of α, representing the contribution of the force from the effects of constraints on the fluctuation of the network junctions.

As mentioned in our previous paper,[5] however, the Flory–Erman theory is rather complicated to analyze the experimental data for the purpose of understanding the high swellability of the solution cross-linked networks in polymer solutions. The theory predicts that in highly swollen networks f_c/f_{ph} is negligibly small.[14] Therefore, we analyzed our previous data[5] on the basis of the primitive theory proposed by Flory and Rehner.[22] We ascribed the major factor of the high swellability to the front factor $C_x^{2/3}$ which appears in eq 1. This factor reflects the lowered conformational entropy of the network strands by a factor of $\langle r^2 \rangle / \langle r^2 \rangle_0$, where $\langle r^2 \rangle$ and $\langle r^2 \rangle_0$ are the mean-square end-to-end distance of the strand in the dry state and that in the as cross-linked network including the solvent, respectively.

On the basis of these assumptions, we calculated the content of the free polymer v_3 in the swollen NR network as a function of the concentration C_x of NR in the solution which had been subjected to γ-ray irradiation for cross-linking.[5] To our surprise, the experimental results agreed semiquantitatively with the Flory–Rehner theory.[5]

The basic assumption of the Flory–Rehner theory is that the mixing and elastic free energies are separable. This hypothesis was doubted by Yen and Eichinger.[23] Recently Neuburger and Eichinger[24] investigated the swelling of poly(dimethylsiloxane) networks in benzene and cyclohexane vapor. They found that the reduced swellability, which should be independent of the solvent if the mixing and elastic free energies are separable, depended strongly on the chemical nature of the solvent. Thus they concluded that the Flory–Rehner theory needs some modification.[24]

The result of Neuburger and Eichinger suggests that the swelling behavior of the solution cross-linked networks by chemically different polymers are quite different from the systems composed of networks and free polymers of the same kind. If this is the case, the agreement between the previous experiment[5] and the Flory–Rehner theory was only accidental, and the swelling behavior in the chemically different system will not agree with the Flory–Rehner theory.

One of the objectives of this study is to check this point. For this purpose we studied the swelling behavior of *cis*-polybutadiene (*cis*-PB) networks (BR) toward *cis*-polyisoprene (*cis*-PI) in bulk and in solution. Since *cis*-PB and *cis*-PI are partially miscible,[25,26] we anticipate that solution cross-linked BR networks absorb *cis*-PI to an extent less but not much less than that the solution cross-linked NR networks did.[5] We compare the present system with the previous NR/*cis*-PI system to see the effect of the interaction between the chemically different network and the polymer.

Experimental Section

Preparation of Networks. Polybutadiene (*cis*-PB) supplied by Japan Synthetic Rubber Co., Ltd., was purified by reprecipitation from benzene solution in methanol. The weight-average molecular weight M_w was determined to be 7.5×10^5 on a gel permeation chromatograph (Tosoh, Model HLC-801A) equipped with a low-angle light-scattering monitor (Tosoh, LS-8). The polydispersity index M_w/M_n was 3.3. The microstructure of the

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Table I
Characteristics of Networks

code	C_x	q	E, MPa	$10^{-3}M_{xs}$	$10^{-3}M_{xE}$
BR(0.1:40)	0.13	16.3	0.20	11.1	7.3
BR(0.2:40)	0.19	12.7		9.6	
BR(0.4:40)	0.39	8.4		7.5	
BR(0.7:40)	0.66	6.4		6.4	
BR(0.8:40)	0.82	4.5		3.5	
BR(1:40)	1	3.1	1.98	1.6	3.5
BR(0.1:20)	0.10	19.7	0.17	13.3	8.7
BR(0.2:20)	0.20	15.2	0.35	19.6	19.6
BR(0.5:20)	0.50	10.4	0.86	14.5	5.0
BR(1:20)	1	3.5	1.29	2.1	5.3
BR(1:10)	1	4.7	1.08	4.6	6.4
BR(1:5)	1	6.2	0.75	8.5	9.2
BR(1:2)	1	10.3	0.49	24.2	14.0

cis-PB was determined by high-hresolution ^{13}C NMR spectroscopy according to Clague et al.[27] The contents of cis-1,4-, trans-1,4-, and 1,2-vinyl linkages were 94, 4, and 2%, respectively.

To prepare cross-linked BR samples for swelling experiments, we sealed toluene solutions of *cis*-PB or bulk *cis*-PB in glass ampules under vacuum at liquid nitrogen temperature and irradiated with ^{60}Co γ-rays in situ at room temperature. We also prepared BR films so that we can do experiments on the samples characterized by both the swelling ratio and Young's modulus. To prepare films, the solutions were sandwiched between glass plates with a Teflon O-ring spacer. The concentration C_x (in volume fraction) of each solution was determined from the weight by assuming the additivity of *cis*-PB (ρ = 0.92 g cm^{-1}) and toluene (ρ = 0.87 g cm^{-1}). Reagent-grade toluene was used as the cross-linking solvent without further purification.

Irradiation was carried out at an ambient temperature with a dosage of 2–40 Mrd. After irradiation no syneresis was found in the samples. All the irradiated samples were immersed in benzene at room temperature for 3 days to extract the sol fraction. We confirmed that after 3 days sol could no longer be extracted by further extraction. The networks thus treated were dried at 50 °C in vacuo until a constant weight was reached. The networks were coded as BR (C_x:dosage in megarads).

Characteristics of Networks. Usually the average molecular weight M_x of the network strands has been estimated from either the swelling ratio or the elastic modulus. We define the M_x determined from the swelling ratio and that from the Young's modulus as M_{xs} and M_{xE}, respectively. For swelling, Flory proposed a theory based on the same model as eq 2.[13] However, it is rather difficult to apply this theory to calculate M_x from the data of swelling ratio. We use the Flory–Rehner equation as a working definition of M_{xs}:[7,19]

$$-\ln(1-v_2) - v_2 - \chi_{12}v_2^2 = (\rho/M_{xs})V_s C_x^{2/3}(v_2^{1/3} - v_2/2) \quad (3)$$

where χ_{12} is the interaction parameter between polybutadiene and benzene, v_2 is the volume fraction of the network, ρ is the density, and V_s is the molar volume of the solvent. Several authors reported the value of χ_{12}.[28-31] Among these data, we employed χ_{12} = 0.39 reported by Bhatnager.[29] It is noted that in eq 1 the cycle rank ξ for unit volume of a network is equal to $\rho N_A/M_{xs}$, where N_A is the Avogadro number.

Young's modulus E was measured at elongation ratio of 1.1–1.2 by reading the elongation with a cathetometer after loading a weight. Measurements of E were made within 10 min after loading the weight. Appreciable stress relaxation was not seen. It is desirable to determine the Young's modulus E of the solution cross-linked network by eq 2. However, the factor f_c in eq 2 is usually determined from the stress–strain curve. Since we do not have the required data, we again use the classical theory written as[5]

$$E = (3\rho RT/M_{xE})C_x^{2/3} \quad (4)$$

Again this equation is a working definition of M_{xE} of a solution cross-linked network. Table I shows M_{xs} and M_{xE} calculated with eq 3 and 4, respectively, for the networks used in this study.

***cis*-Polyisoprene.** Narrow distribution samples of *cis*-polyisoprene (*cis*-PI) were prepared by anionic polymerization and characterized as reported previously.[32] They were coded as *cis*-PI with the weight-average molecular weight M in kilograms per mole. Their characteristics are shown in Table II. Reagent grade benzene was used for swelling experiments without further purification. To estimate the volume fraction of the free polymer in the solution and network phases, we assumed the additivity in the volumes and used ρ = 0.91 g cm^{-3} for *cis*-PI and 0.88 g cm^{-3} for benzene.

Table II
Characteristics of *cis*-Polyisoprene

code	$10^{-3}M_w$	$10^{-3}M_n$	microstructure 1,4-cis	1,4-trans	3,4-vinyl
PI-02	1.6	1.4	83.1	13.5	3.4
PI-03	2.6	2.4	82.5	14.3	3.2
PI-05	4.8	4.5	80.3	15.1	4.6
PI-14	13.5	12.5	82.3	14.2	4.1
PI-32	31.6	30.1	81.8	13.5	3.5

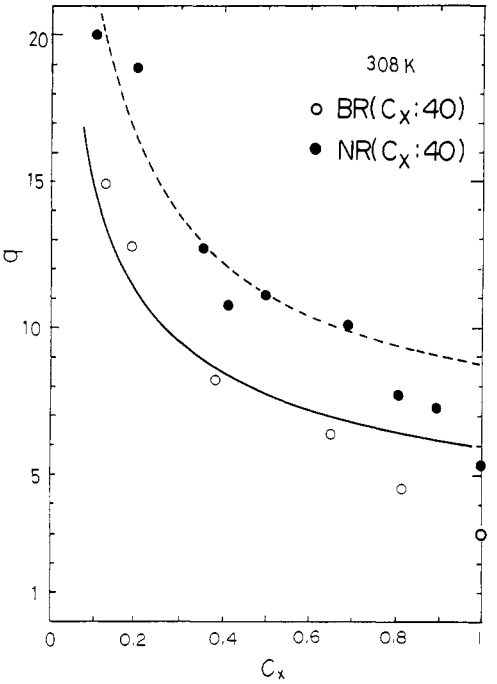

Figure 1. C_x dependence of the swelling ratio q in pure benzene for networks BR(C_x:40) cross-linked by a 40-Mrd dose and natural rubber NR(C_x:40) prepared under the same condition as BR. Solid and dashed lines represent eq 5 for BR and NR calculated with q_0 = 6.0 and 8.7, respectively.

Measurement of Swelling Ratio. Swelling ratio was determined by measuring the size of the swollen network by a travelling microscope. The content of the *cis*-PI in the networks was determined by weighing after drying in vacuo. To establish the time required for the network reaching a swelling equilibrium in free polymer solutions, we measured the time dependence of the absorption ratio A defined as $(v_2 + v_3)/v_2$ for BR(0.2:40) soaked in the solutions of PI-32 in benzene. We confirmed that the equilibrium absorption was achieved ca. 200 h after soaking in the solutions. A much shorter time was sufficient in the case of PI-03 solutions. We therefore regarded the values of q and A at t = 200 h as the equilibrium values throughout the experiment.

Results and Discussion

Swelling in Benzene. Figure 1 shows the C_x dependence of the swelling ratio q in pure benzene for BR(C_x:40) and natural rubber NR(C_x:40) cross-linked at a 40-Mrd dose reported previously.[5] The swelling ratio q (=$1/v_2$) increases with decreasing C_x. It is seen that C_x dependences of q for the both networks are quite similar. The C_x dependence of q may be ascribed to the following four factors: (1) the effect of the front factor of $C_x^{2/3}$ in eq 1, (2) the C_x dependence of the cross-link density ν, (3) the C_x dependence of the functionality f of the cross-link

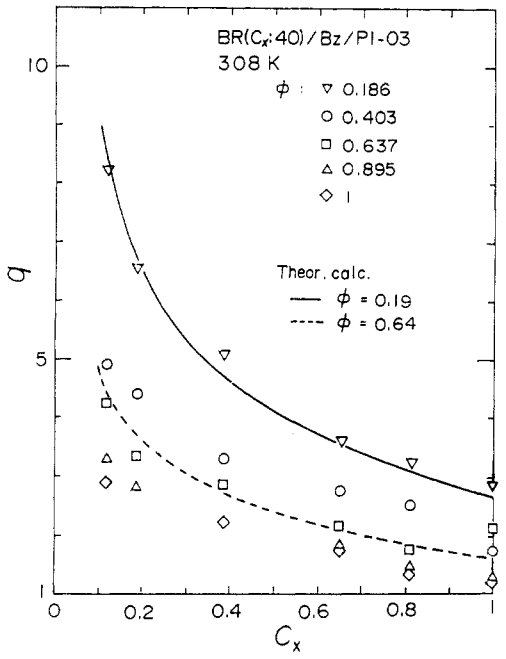

Figure 2. C_x dependence of q of BR(C_x:40) in benzene solutions of PI-03. Solid and dashed lines indicate the Flory–Rehner equation at $\phi = 0.19$ and 0.64, respectively. Here, calculation was made with $\chi_{23} = 0.22$, $\chi_{12} = 0.39$, $\chi_{13} = 0.21$, and M_{xs} listed in Table I.

points, and (4) the change in the contents of the trapped entanglement.

In our previous paper,[5] we ascribed the strong C_x dependence of q to the factor (1). This factor is obviously most important among these factors. However, it is necessary to check other factors carefully. As seen in Table I, M_x ($\propto \xi^{-1}$) increases with decreasing C_x, indicating that the cycle rank $\xi = \nu(f-2)/2$ decreases with decreasing C_x provided that the dose of γ-rays is the same. Therefore, the C_x dependence of q is partly ascribed to the factors (2) and (3) and hence to the change in the cycle rank ξ. As to the factor (3), Van der Hoff[33] reported that the functionality of BR networks cross-linked with peroxide is as high as 12. Since γ-rays induce radicals,[34] the functionality in the presence BR samples might have a similar functionality to those cross-linked with peroxide. There is a possibility that such a high value of the functionality changes with C_x. As shown in Figure 1, the ratio of q(NR) to q(BR) increases from 1.2 at $C_x = 0.1$ to 1.7 at $C_x = 1$. This behavior may be ascribed to the differences in the C_x dependence of ξ between the NR and the BR. However, we cannot distinguish the contributions of the factors (2) and (3). Mark[19] indicated that the factor (4) is significant to explain the C_x dependence of the elastic modulus of the solution cross-linked network.

When q is large, eq 3 predicts

$$q/q_0 = C_x^{-2/5} \tag{5}$$

where q_0 is the swelling ratio of the bulk cross-linked network ($C_x = 1$) with the same M_x as the solution cross-linked network. To compare the experimental data with eq 5, we need the data of q for the samples with same M_x. As is seen in Table I, M_x varies with C_x. Therefore we attempted to compare the data with eq 5 in the low-C_x range assuming that q_0 is an adjustable parameter. The solid line and the dashed line in Figure 1 indicate eq 5 for BR(C_x:40) and NR(C_x:40) with $q_0 = 6.0$ and $q_0 = 7.5$ for the BR and NR, respectively. In the low-C_x range, observed q agrees well with eq 5 although M_x of the samples are different, indicating that the $C_x^{2/3}$ term governs the

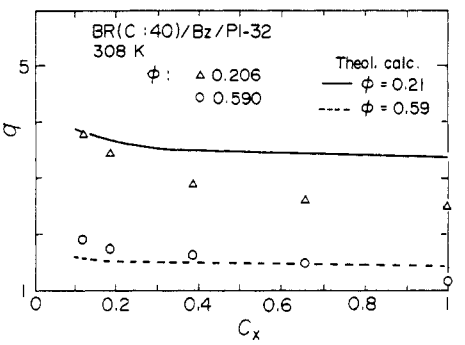

Figure 3. C_x dependence of q of BR(C_x:40) in benzene solution of PI-32. Solid and dashed lines indicate the Flory–Rehner equation at $\phi = 0.21$ and 0.59, respectively. Calculation was made similarly to Figure 2 with $\chi_{23} = 0.014$.

Table III
Swelling Ratio q of BR(C_x:40) in Bulk PI-03 and Interaction Parameter χ_{23}

code	C_x	$10^{-3}M_{xE}$	q	χ_{23}
BR(0.1:40)	0.13	11.1	2.89	0.020
BR(0.2:40)	0.19	9.6	2.57	0.020
BR(0.4:40)	0.39	7.5	2.24	0.013
BR(0.7:40)	0.66	6.4	1.81	0.012
BR(0.8:40)	0.82	3.5	1.38	0.016
BR(1:40)	1	3.1	1.23	0.022

C_x dependence of q. As pointed out previously,[5] the M_x dependence of q at constant C_x is small compared with the C_x dependence of q at constant M_x.

Swelling Ratio in Solutions of Free *cis*-PI. Figure 2 shows the C_x dependence of q in PI-03 benzene solutions with different ϕ. We see that the behavior for the BR(C_x:40) networks is similar to that in pure benzene. The swelling ratio q decreases with increasing concentration ϕ of the free polymer solution. This is the deswelling phenomenon of the gel due to the increase in the chemical potential of the solvent in the solution phase.[4]

Figure 3 shows the C_x dependence of q for the BR(C_x:40) networks in PI-32 solutions. The values of q are much smaller than those in PI-03 solutions, reflecting the difference in the coordination entropies of the free *cis*-PI molecules of 10 times higher molecular weight.

To compare these results with the theoretical prediction, we calculated the theoretical q vs C_x curves with eq 7–10 of ref 5 using M_{xs} for the corresponding networks. The details of the calculation were described previously.[5] In the calculation, the interaction parameters between the solvent and the two polymers were taken to be $\chi_{12} = 0.39$ and $\chi_{13} = 0.21$ according to the values reported by Bhatnager[29] and Hays,[35] respectively. We estimated the polymer–polymer interaction parameter χ_{23} from the swelling ratio of the BR(C_x:40) networks in bulk PI-03 with eq 7–10 of ref 5. The value of χ_{23} thus determined changed slightly from one sample to another as shown in Table III. Here, we used $\chi_{23} = 0.022$ for the BR/Bz/PI-03 systems but $\chi_{23} = 0.014$ for the BR/Bz/PI-32 systems. The tendency that χ_{23} increases with decreasing molecular weight is usually observed.[11]

Using these parameters, we calculated q for BR(C_x:40) with the corresponding value of M_{xs} given in Table I at different C_x. In Figures 2 and 3, the solid and dashed lines indicate the smoothed curves of the theoretical q at $\phi =$ ca. 0.2 and 0.6, respectively. As is seen in these figures, the theoretical values agree semiquantitatively with the experimental values.

Absorption Ratio of Guest Polyisoprenes. Figures 4 and 5 show the C_x dependence of the absorption ratio $A = (\upsilon_2 + \upsilon_3)/\upsilon_2$ for BR(C_x:40) in PI-03 and PI-32 solutions

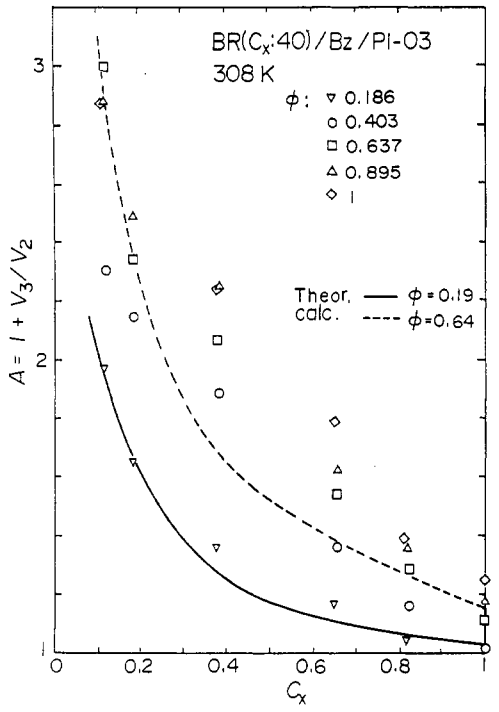

Figure 4. C_x dependence of the absorption ratio A ($=1 + v_2/v_3$) for BR(C_x:40) in benzene solutions of PI-03. Theoretical values calculated by the Flory–Rehner equation are indicated by solid and dashed lines for $\phi = 0.19$ and 0.64, respectively. The conditions of the calculation are the same as in Figure 2.

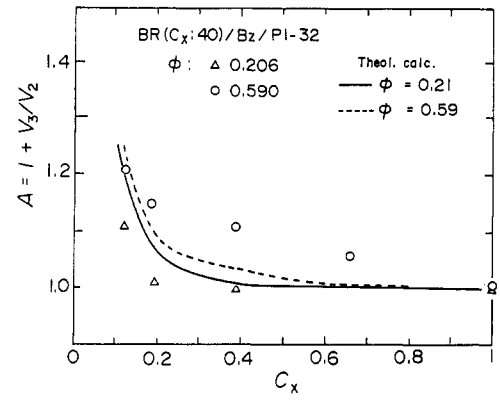

Figure 5. C_x dependence of A for BR(C_x:40) in benzene solutions of PI-32. Solid and dashed lines indicate the Flory–Rehner equation for $\phi = 0.21$ and 0.59, respectively, calculated with the same conditions as Figure 3.

of concentration ϕ, respectively. The ratio A is relatively high for PI-03 solutions compared to that for PI-32 solutions. As seen in Figure 5, the ratio A of PI-32 for the network cross-linked at $C_x = 1$ is essentially unity in agreement with our previous results on NR networks,[5] but the networks cross-linked at low C_x absorb a substantial amount of PI-32. This is a clear manifestation of the effect of solution cross-linking. The filled symbols in these figures indicate the theoretical values calculated with $\chi_{23} = 0.022$ for the BR/PI-03 system and 0.014 for the BR/PI-32 system. We see that the computed A values are in rough agreement with the experimental data. This agreement indicates that the theory based on the classical Flory–Rehner model works as well for the chemically different pair of the network/free polymer systems as for the chemically similar pair of the systems given in our previous paper.[5]

To summarize the swelling data, we plotted the composition of the swollen networks on a triangular diagram shown in Figure 6a and 7, where the data of BR(C_x:40) in PI-03 and PI-32 solutions are given, respectively. From such diagrams, we can determine the swelling ratio q ($=1/v_2$) and the absorption ratio A ($=1 + v_3/v_2$) in the manner depicted in Figure 6b. To read q for a given data point P, we only need to determine v_2 according to the definition of the diagram. To read A, on the other hand, we first draw a line passing through the point P and the solvent apex (1), and read $v_2' = v_2/(v_2 + v_3)$ as the intersect of the line P–1 and the BR–PI side (2–3). Furthermore, the line connecting a given data point and a point S corresponding to ϕ of the free polymer solution in which the network has been equilibrated represents a tie line.

As is seen from these figures, we can control the composition of the network phase for a given BR/*cis*-PI/Bz system in a definite range by choosing the *cis*-PI solution of an appropriate concentration ϕ. However, the controllable range depends strongly on the molecular weight of *cis*-PI as contrasted in Figures 6a and 7.

Figure 8 reproduces the ϕ dependence of the absorption ratio A for the PI-03 solutions, although the information is already implicitly given in Figure 6a. For the networks cross-linked at high C_x, the ratio A increases monotonously with increasing ϕ, but for those at low C_x, the ratio A exhibits a maximum or a plateau at high ϕ. This behavior can be explained by the effect of the repulsive interaction between the network and the free polymer. As shown in the figure, the experimental values of A roughly agree with the theoretical calculation, when we employ $\chi_{23} = 0.022$.

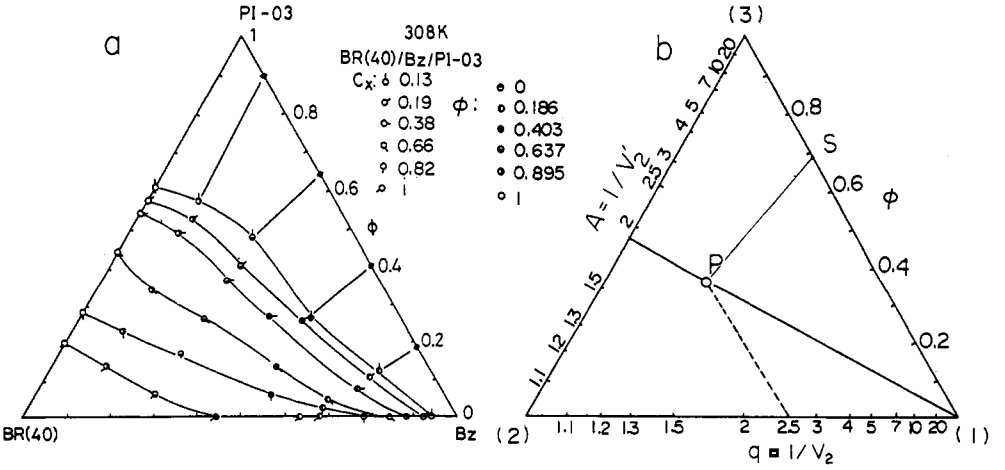

Figure 6. (a) Composition of BR(C_x:40) swollen in PI-03/Bz solutions. (b) Diagram representing the method to read swelling ratio q ($=1/v_2$) and absorption ratio A ($=1 + v_2/v_3$) for the each data point.

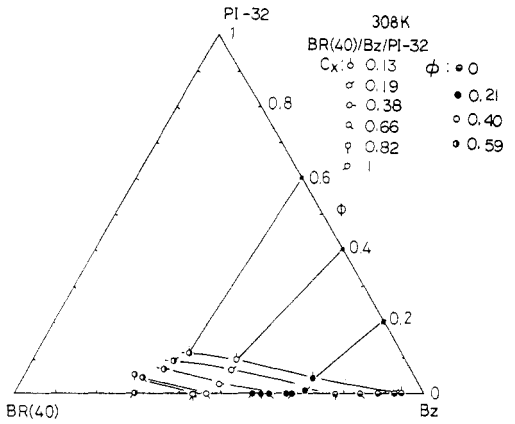

Figure 7. Composition of BR(C_x:40) swollen in PI-32/Bz solutions.

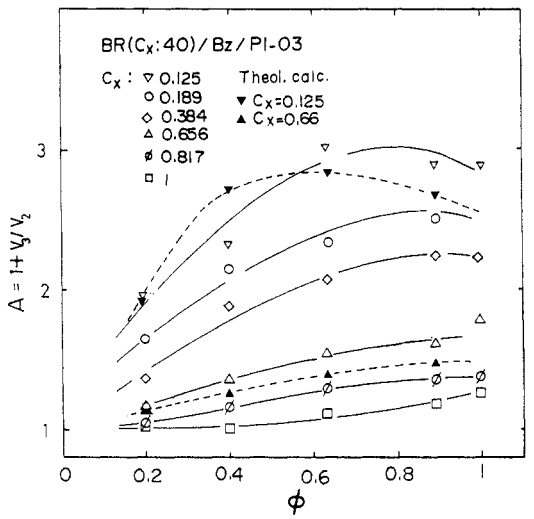

Figure 8. Dependence of absorption ratio A on the concentration ϕ of the PI-03 solutions for BR(C_x:40). The dashed line indicates the theoretical value calculated with $\chi_{23} = 0.022$.

When the BR(0.1:40) network is equilibrated in PI-03 solution of $\phi = 0.2$ and then dried, it contains more free polymer molecules than the same network which is equilibrated in bulk PI-03($\phi = 1$). Therefore, the former network/free polymer system must be in a nonequilibrium state, and the network should eventually deswell. We, however, observed neither elimination of the excess free polymer molecules nor opacity even after the sample was allowed to stand at room temperature for about 3 months. Therefore, the deswelling must be a very slow process, taking a much longer period. However, at the moment it is not clear whether microphase separation is taking place within the networks or not.

Total Polymer Concentration in Swollen Networks. For *cis*-PI with the degree of polymerization y, eq 9 and 10 in ref 5 give

$$\ln (v_1) + \chi_{12}v_2 + \chi_{13}v_3 - \chi_{13}v_1 \simeq F(\phi,y) \qquad (6)$$

where $F(\phi,y)$ denotes a function of ϕ and y. Here we neglected $(1/y)$ ln v_3 and $\chi_{23}v_2$ because y is much larger than unity and χ_{23} is close to 0. This equation indicates that if $\chi_{12} = \chi_{13}$, the total polymer content $v_2 + v_3$ ($=1 - v_1$) is uniquely given by eq 6 and hence is indepencent of C_x. In the present systems, we expect that $v_2 + v_3$ depends weakly on C_x since χ_{12} and χ_{13} are different. Figure 9 shows a test of this prediction for the BR(C_x:40) networks equilibrated in 20 and 60% solutions of PI-03. For the other systems, we see in Figures 6a and 7 that v_1 and hence $v_2 + v_3$ for constant ϕ is almost independent of C_x. We also note that $v_2 + v_3$ ($=A/q$) is approximately equal to

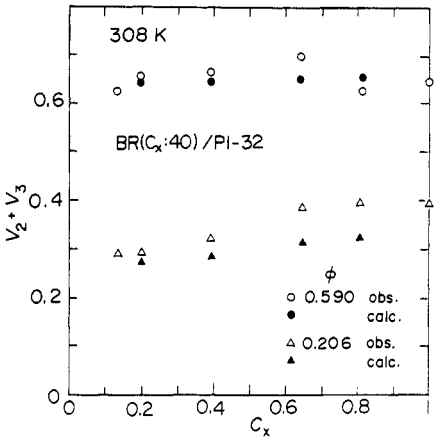

Figure 9. C_x dependence of the total polymer concentration $v_1 + v_2$ in the network phase for the BR(C_x:40)/PI-03 systems. The filled symbols indicate the theoretical values calculated with $\chi_{23} = 0.014$.

ϕ. Thus, although q and A increase steeply with decreasing C_x, the ratio A/q remains almost independent of C_x. As shown in Figure 9, the theoretical $v_2 + v_3$ agrees fairly well with the experiment. This agreement again indicates that the Flory–Rehner theory works well.

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Registry No. *cis*-PB, 9003-17-2; *cis*-PI, 9003-31-0.

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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 $\pm$ 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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