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Study of Subchain Dynamics by Dielectric Normal-Mode Spectroscopy: Butadiene-Isoprene Block Copolymers

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ABSTRACT: Dielectric measurements were carried out on homogeneous (not microphase-separated) samples of butadiene (B)-isoprene (I) block copolymers of the BI diblock and BIB triblock types in bulk and in toluene solution. The I block has the component of the dipole moment aligned in the same direction parallel to the chain contour, but the B block does not. We thus were able to investigate dynamics of the I subchains through observation of the dielectric normal-mode process of the I blocks. The nominal relaxation times τ_n of the block copolymers were determined as the inverse of loss maximum frequencies. They strongly depended on the molecular weight and the location of the I block as well as on the molecular weight of the whole chain. For BIBs the τ_n were close to that for homopolyisoprene (homo-PI), with the molecular weight the same as BIBs. The loss curves of BIs and BIBs were much broader than that of homo-PIs. To analyze the behavior, we reduced the molecular weight, the molecular weight between entanglement, and the friction coefficient of the B block to those equivalent with the PI block. Using these reduced molecular weights, we can reasonably well explain the longest relaxation times τ_1, the nominal times τ_n, and the distribution of dielectric relaxation times by the bead-spring model or the tube model.

I. Introduction

Now it is well-known that *cis*-polyisoprene (PI) is a typical type A polymer,[1] having the dipole moment aligned in the same direction parallel to the chain contour, and thus exhibits a dielectric normal-mode process.[2-9] If dielectric spectroscopy is applied to a block copolymer containing such a type A chain linked to another block chain(s) without such dipoles, we can obtain information on the dynamics of only the type A labeled portion of the block copolymer chains. Three quantities may be obtained through such studies: (1) the average relaxation time for fluctuation of the end-to-end vector of the subchain; (2) the distribution of the dielectric relaxation modes, and (3) the mean-square end-to-end distance of the subchain.

In the present study, we attempted to examine the dynamics of a subchain incorporated into a prescribed position of such a block copolymer that is in turn in a homogeneous, not microphase-separated, state. Although block copolymers often undergo microphase separation,[10,11] we found in our previous dielectric study on PI/polybutadiene (PB) blends and PI trapped in PB networks that PI and PB are reasonably well miscible especially when the molecular weights are less than ca. 30 000.[6] Thus, we have chosen polybutadiene-*cis*-polyisoprene diblock (BI) and triblock (BIB) copolymers as the samples.

Another reason for making this choice was that PB chains possess a symmetrical structure in the monomer unit and do not exhibit normal-mode processes. Both PI and PB blocks have dipole moments perpendicular to the chain contour (type B dipoles)[1] and thus exhibit a segmental-mode process due to their local motion related to the glass transition. The segmental modes, however, usually appear in the frequency range far higher than that of the normal modes of PI subchains. These features allow us to detect signals from PI subchains quite effectively. Still another reason is that both PI and PB have relatively low glass transition temperatures, T_g, and thus the global motion of the whole block chains is active under the ambient condition where most of the measurements have been made.

For microphase-separated block copolymers, we recently reported dielectric behavior of styrene-*cis*-polyisoprene diblock (SI) copolymers.[12] However, so far few studies have been reported on the dynamics of subchains incorporated into linear block copolymers in a homogeneous state. Osaki et al.[13] reported results of birefringence and stress-strain relations in concentrated solutions of methyl methacrylate (M)-styrene-methyl methacrylate triblock (MSM) copolymers in which MSM chains are not microphase separated but are certainly entangled among one another. They found that the birefringence due to the mid-S blocks agreed with a reptation picture derived from the tube theory of Doi and Edwards,[22] when the strain level was low. In the present study we use the dielectric method to study the dynamics of I subchains in BI diblock and BIB triblock copolymers in a homogeneous entangled state.

II. Theory

II-1. Nonentangled Regime. When block copolymer chains are not entangled with other chains in the bulk state and/or in dilute solution, the bead-spring models proposed by Rouse[14] and Zimm[15] are applicable to describe their dynamics including the dielectric relaxation behavior. We consider a chain consisting of N springs and $N + 1$ beads consecutively numbered from 0 to N, as shown in the Appendix. The springs connecting the nth to mth beads are labeled with type A dipoles in such a way that the spring dipole vector connecting the j and $(j + 1)$th beads is $\mu(\mathbf{R}_{j+1} - \mathbf{R}_j)$. Here μ is the dipole moment per unit contour length of the A-type subchain, and $\mathbf{R}_j$, the coordinate of the jth bead. Then the dipole moment $\mathbf{P}(t)$ of the molecule at time t is given by

$$\mathbf{P}(t) = \mu[\mathbf{R}_n(t) - \mathbf{R}_m(t)] \tag{1}$$

The complex dielectric constant, ϵ^*, is given by the Fourier-Laplace transform of the autocorrelation function, $\phi(t)$, of the molecular polarization vector $\mathbf{P}(t)$ as[16]

$$\phi(t) = \langle \mathbf{P}(0)\cdot\mathbf{P}(t)\rangle / \langle \mathbf{P}(0)\cdot\mathbf{P}(0)\rangle \tag{2}$$

If we assume that the friction coefficient for the nth to mth bead is the same as that for other beads, $\phi(t)$ and ϵ^* for the block copolymer chain are calculated as described

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in the Appendix. The result for ϵ^* reads

$$\frac{\epsilon^* - \epsilon_\infty}{\Delta\epsilon} = \frac{8N}{(m-n)\pi^2}\sum_{p=1}^{N}\left[\sin^2\left\{\frac{p\pi(n+m)}{2N}\right\} \times \sin^2\left\{\frac{p\pi(m-n)}{2N}\right\}\frac{1}{p^2 + i\omega\tau_1}\right] \quad (3)$$

where ω is the angular frequency, ϵ_∞, the high-frequency dielectric constant, $\Delta\epsilon$, the dielectric relaxation strength defined in eq 5 below, p, the number of the mode ($p = 1, 2, ..., N$), and τ_1, the longest (normal-mode) relaxation time. For the free-draining Rouse model,[14] τ_1 is given by

$$\tau_1 = \zeta N^2 b^2 / 3\pi^2 k_B T \quad (4)$$

where ζ is the friction coefficient per bead, and b, the average distance between the two adjoining beads or the average length of the spring.

More general calculations of the normal modes and the eigenvalues were made for nonentangled AB block copolymers by Hansen and Shen,[17] Hall and De Wames,[18] Stockmayer and Kennedy,[19] and Wang.[20] They calculated the normal modes to explain the bulk viscosity of AB block copolymers of which the average segment lengths and the friction coefficients for the A and B blocks are different. Unfortunately their results cannot be expressed by analytical functions. The theory of Stockmayer and Kennedy[19] is briefly summarized in the Appendix.

The relaxation strength, $\Delta\epsilon$, is given by[2,3]

$$\Delta\epsilon / C_b = 4\pi N_A \mu^2 \langle r_{nm}^2 \rangle / 3k_B T M_b \quad (5)$$

where N_A is Avogadro's constant, $\langle r_{nm}^2 \rangle$, the mean-square distance between the nth and mth beads (or the mean-square length of the type A subchain), C_b, the weight fraction of the subchains in unit volume of the whole system, and M_b, the molecular weight of the subchain. Using eq 5, we can determine the mean-square length of the subchains.

For a homo-PI chain with $n = 0$ and $m = N$, eq 3 reduces to the well-known form,[1-4] in which all the even-numbered modes vanish and the fundamental ($p = 1$) mode dominates. The $\langle r_{nm}^2 \rangle$ obviously reduces to the mean-square end-to-end distance of the whole chain. The *nominal* relaxation time τ_n, operationally defined as $\tau_n = (1/2\pi f_{max})$, the reciprocal of the loss maximum frequency f_{max}, is virtually equal to τ_1, the longest relaxation time. However, for a block copolymer chain containing type A segments from the nth to the mth beads of the total N beads, the τ_1 depends only on N, but the distribution of dielectrically active relaxation modes that determines the shape of the dielectric loss ϵ'' curve and the ratio of the longest to the observable relaxation times τ_1/τ_n are complex functions of the block copolymer composition, $(m - n)/N$, and the relative location of the type A subchain, n/N. Some typical examples of the *dielectrically active* mode distributions of block copolymers of the same length but different architectures are shown in the Appendix.

II-2. Entangled Regime. When block copolymer chains entangle, the tube model may be applied.[21-23] We assume a test block copolymer chain is confined in a tube with the diameter a. The block copolymer chain is now remodeled, as shown in the Appendix, as a chain composed of $N + 1$ beads connected with N springs of average length a, of which springs connecting with nth to mth beads possess type A dipoles.

Table I
Characteristics of BI and BIB Block Copolymers[a]

code	$10^{-3}M_w$				M_w/M_n
	PB$_1$ block	PI block	PB$_2$ block	total	
B(15)	15.0			15.0	1.03
BI(15–16)	15.0	16.2		31.2	1.06
BI(15–14)	15.0	14.1		29.1	
BI(44–18)	44	18		62	
BI(40–105)	40	105		145	
BIB(15–16–22)	15.0	16.2	21.7	52.9	1.06
BIB(15–14–45)	15.0	14.1	45.0	74.1	1.04

[a] The microstructure (in mol %) of *cis*-PI blocks and that of PB blocks prepared in this study are supposed to be 56–30% cis-1,4, 37–62% trans-1,4, and 7–8% vinyl.[23]

For such a model, the Doi–Edwards theory[22,23] can be applied to calculate the autocorrelation function $\phi(t)$ of the polarization vector $\mathbf{P}(t)$ of the subchain. From $\phi(t)$ we can calculate $\epsilon^*(\omega)$ by the same way as we have done for the Rouse chain. We see that $\epsilon^*(\omega)$ has exactly the same form as eq 3 for the nonentangled chain, except a difference in the expression of the longest relaxation time τ_1 given as

$$\tau_1 = a^2 L^2 / D_c \pi^2 \quad (6)$$

where D_c is the curvilinear diffusion coefficient of the chain along the tube of contour length L.

Regardless of the entanglement effect, $\Delta\epsilon$ is given by eq 5 since $\Delta\epsilon$ is the static quantity.

Obviously the *dielectrically active* relaxation mode distribution relative to τ_1 is the same for the Rouse and tube models, provided $(m - n)/N$ and n/N are the same. This means that, for a given block copolymer, the shape of the reduced loss curve, $\epsilon''/\epsilon_{max}''$ versus f/f_{max}, and the τ_1/τ_n ratio should be independent of the copolymer concentration C.

III. Experimental Section

All block copolymer samples were prepared by anionic polymerization with *sec*-butyllithium in *n*-heptane at 20 °C. First a prescribed amount of butadiene was allowed to polymerize, and then isoprene was introduced to react with living polybutadienyl anions. The living BI chains were terminated with methanol. In some cases a part of the living BI sample was saved and further reacted with butadiene to obtain a BIB triblock copolymer. The weight-average molecular weight, M_w, and the polydispersity index, M_w/M_n, of these samples were determined on a gel permeation chromatograph (GPC; Tosoh HLC 801A) equipped with a low-angle light-scattering photometer (Tosoh LS-8000). The characteristics of the samples are summarized in Table I. The samples are coded with the block molecular weight M_w in kilograms per mole.

Thermograms of differential scanning calorimetry of BI and BIB samples exhibited a single glass transition point. We thus concluded that the samples used here were homogeneously mixed to a molecular level.

Dielectric measurements were carried out with a tranformer bridge (General Radio 1615A) in the frequency range from 20 Hz to 50 kHz according to our laboratory routine with a condenser cell as reported previously.[5]

IV. Results

IV-1. Toluene Solutions of BI and BIB. Figure 1 shows typical master curves reduced at 273 K for toluene solutions of BI(44–18) with the concentration C = 10 and 40 wt %. On the other hand, Figure 2 shows the ϵ'' curves at 273 K for toluene solutions of BIB(15–16–22) and BIB(15–14–45) at the concentrations indicated.

The loss peaks for each sample shown in Figures 1 and 2 were assigned to the normal-mode process. Although the results are not shown here, the data were cast into a normalized form, $\log \epsilon''\phi^{-1}$ versus $\log f/f_{max}$. The resulting normalized ϵ'' curves became somewhat broader as C

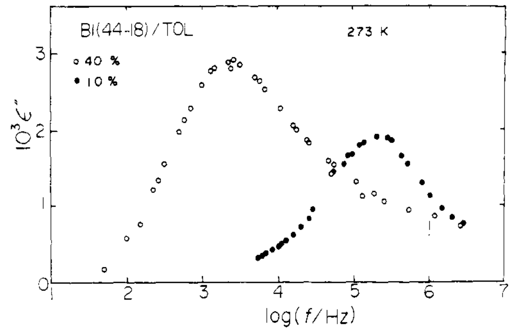

Figure 1. Master curves of ϵ'' at 273 K for toluene solutions of BI(44–18) with concentrations 10 and 40 wt %.

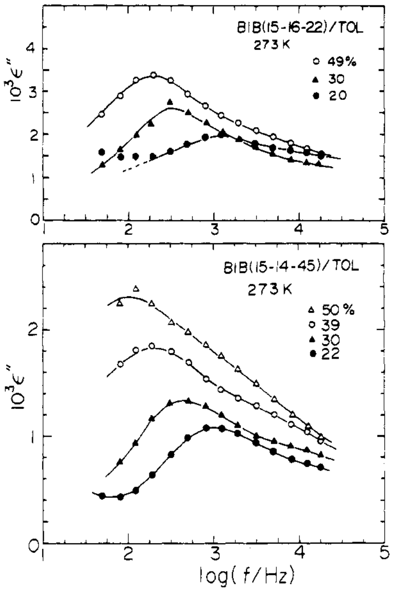

Figure 2. Frequency dependence of dielectric loss factor ϵ'' for concentrated solutions of BIB(15–16–22) and BIB(15–14–45) in toluene at 273 K.

decreased, as opposed to the tendency expected from eq 3 with eq 4 or eq 6.

On the other hand, the loss peaks due to the segmental modes are observed in the frequency range of 100 Hz to 10 kHz around 150–170 K depending on the polymer concentration C.

The *nominal* relaxation times, τ_n for BI and BIB solutions were plotted in Figures 3 and 4, respectively, with solid circles against concentration C. In these figures the τ_n (equal to τ_1) for some homo-PI samples are also plotted for the sake of comparison. This will be discussed later.

IV-2. Undiluted BI and BIB. The ϵ'' curves for bulk BI and BIB samples at various temperatures were first superposed at 273 K to obtain master curves.[24,25] Figure 5 shows the results. We see that BI samples exhibit two peaks: The loss peak seen in the low-frequency region is assigned to the normal-mode process of the PI blocks, because the order of f_{max} is the same as that of *cis*-PI, with the M_w the same as that of the block copolymer.[2,5] On the other hand, the loss peak around 100 MHz is due to the segmental modes of both PI and PB blocks. For BIB samples the loss peak due to the normal modes locates in the frequency range below our experimental window. We thus cannot observe the whole shape of the curves.

In Figure 5, the loss maximum frequency for the segmental mode of BI(15–16) is 0.6 decades lower than that of BI(15–16). This is due to the change in the friction coefficient as discussed below.

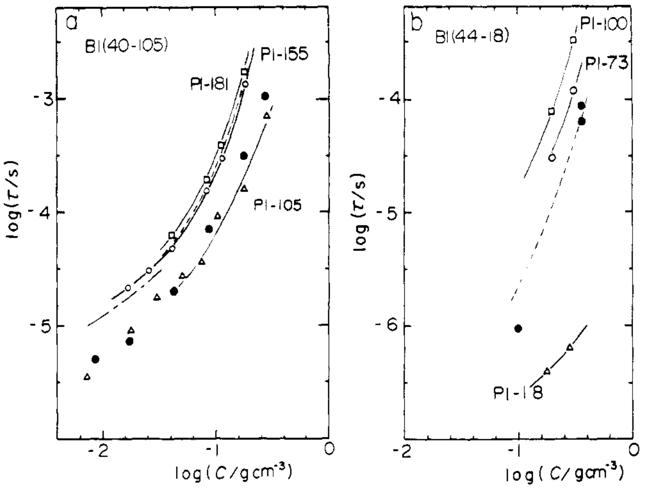

Figure 3. Concentration dependence of the observed nominal relaxation times for (a) BI(40–105) and (b) BI(44–18). Closed circles indicate the nominal relaxation time for BI. Three solid lines and data points with open keys indicate τ_1^{PI}, τ_1°, and τ_1^{e} (see text). The dashed line indicates the semitheoretical nominal relaxation time given by eq 12.

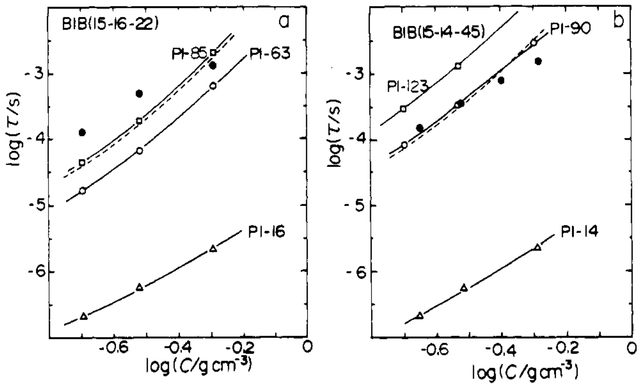

Figure 4. Concentration dependence of the observed nominal relaxation times for (a) BIB(15–16–22) and (b) BIB(15–14–45). Keys and lines indicate the same meaning as Figure 3.

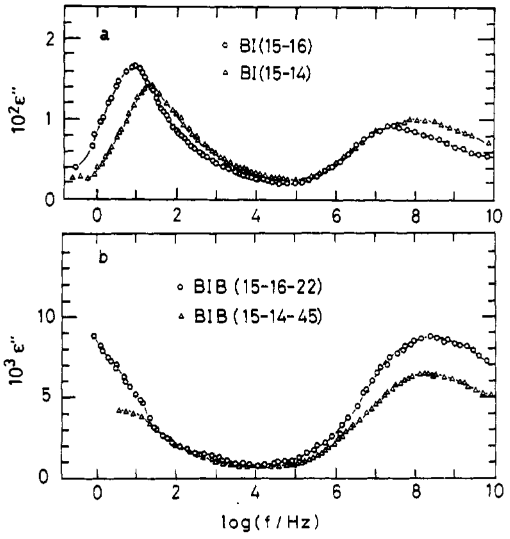

Figure 5. Master curves of the ϵ'' for (a) undiluted BI and (b) BIB.

By selecting the reference temperature T_0 as 273 K for bulk PI, 263 K for BI(15–16), 258 K for BI(15–14), 251 K for BIB(15–16–22), and 238 K for BIB(15–14–45), we can cast the shift factors, a_T, of these samples into a common form such as shown in Figure 6. The solid line represents the shift factor for bulk PI with T_0 = 273 K. Thus

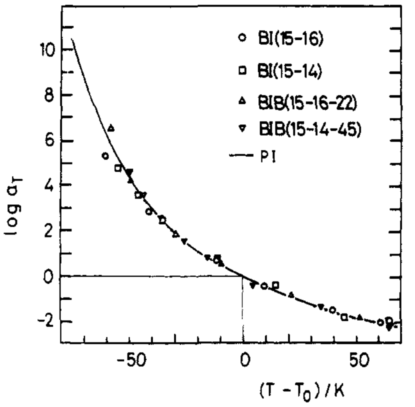

Figure 6. Shift factor for BI and BIB block copolymers. The solid line is the shift factor for *cis*-PI. The reference temperatures T_0 were taken for *cis*-PI, BI(15–16), BI(15–14), BI(15–16–22), and BIB(15–14–45) to be 273, 263, 258, 251, and 238 K, respectively.

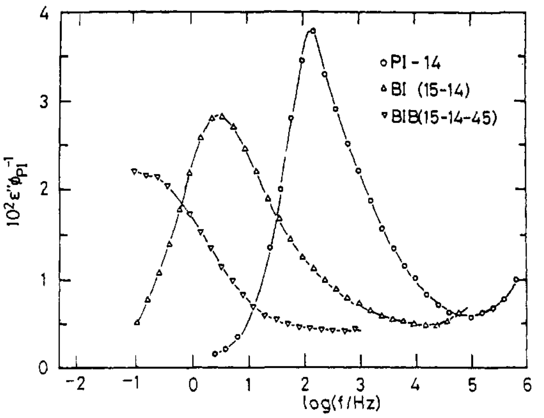

Figure 7. Comparison of the ϵ'' curves in the isofriction state for undiluted PI-14, BI(15–14), and BI(15–14–45).

determined reference temperatures, T_0 are lower for the sample with a higher PB content, indicating that the friction coefficient decreases with decreasing PI content, ϕ_{PI}, of the block copolymer, as reported previously for PI/PB blends.[6]

Figure 7 shows the ϵ'' master curves for PI-14, BI(15–14), and BIB(15–14–45) reduced again to their respective reference temperatures, T_0, and normalized by their PI contents, ϕ_{PI}. Among these samples the molecular weights M(PI) of the PI blocks are the same. As seen in Figure 7, the peak height decreases but the width increases as the total chain length increases. Obviously the nominal relaxation time, τ_n, and the dielectrically active mode distribution (as revealed by the shape of the ϵ'' curve) are strongly influenced by both the total molecular weight and the location of the subchain in the molecules. For toluene solutions of BI and BIB, we also compared their ϵ'' curves (reduced at 273 K) with those of homo-PI/toluene solutions reported previously.[7] We found a trend for the solutions quite similar to that shown in Figure 7 for the undiluted systems.

V. Discussion

V-1. Normal-Mode Process of Subchains.

To make a quantitative comparison of the dielectric normal-mode process of PI subchains in BI, BIB, and homo-PIs with the theories given by eqs 3, 4, and 6, we need to define the total segment number N, the block composition $(m-n)/N$, and the starting point of the subchain n/N. Because we only know the block molecular weights $M = M(\mathrm{PI}) + M(\mathrm{PB})$ of the samples, we need to reduce the following quantities to those equivalent of PI chains: (1) the molecular weight M(PB) and (2) the molecular weight between entanglements M_e(PB) of PB chains in the block copolymers. We also need to know (3) the monomeric or segmental friction coefficient ζ_0[25–27] of the PB segment relative to that of the PI segment. Strictly speaking, this last factor may change the dynamics of block copolymer chains, as discussed before for unentangled chains.[17–20] However, the change should be small for the present case because of the reasons mentioned later. We thus will postpone detailed discussion of this problem in future work.[29]

At this point we consider the reduced molecular weight for the block copolymer $M_r = M(\mathrm{PI}) + M_r(\mathrm{PB})$, with M(PB) reduced to M_r(PB) relative to that of M(PI). The simplest way to find M_r(PB) is to use the degree of polymerization

$$M_r(\mathrm{PB}) = M(\mathrm{PB})\,M_0(\mathrm{I})/M_0(\mathrm{B}) \qquad (7)$$

where M_0(I) and M_0(B) are the molar masses of the isoprene and butadiene units, respectively.

Another way to estimate M_r(PB) for nonentangled systems may be to employ the Fox–Allen parameter[27] X used by Berry and Fox[28] to scale the molecular weight versus melt viscosity relations of homopolymers: $X \equiv Z(S_{g0}^2/M)\rho$, where Z is the number of chain atoms in the molecular backbone, S_{g0}^2, the mean-square radius of gyration of unperturbed molecules of molecular weight M, and ρ, the density of the polymer. This procedure is equivalent to scaling the PB block length with the characteristic ratio C_∞ for PI chains.

The value of C_∞ for high *cis*-polyisoprene is reported to be 5.3,[30,31] while the C_∞ of PB with a microstructure of cis/trans/vinyl = 50/40/10 is 5.4.[31] As shown Table I, the microstructures of these PI and PB samples are nearly the same as those samples. This means that the values of X/Z for the PI and PB blocks are the same. Thus, this procedure should be the same as eq 8 to scale M(PB).

For entangled homopolymer systems dynamical properties may be described with the chain length scaled by the tube diameter a or the molecular weight between entanglements M_e. For a multicomponent entangled system, however, to make an adequate choice of M_e poses a difficult problem. We know that the values of M_e for PI and PB in the undiluted state ($M_e°$) are 5000 and 2700, respectively, and for the solutions of concentration C we take $M_e = M_e°/C$. Then what is the effective M_e for the PI and PB chains in the multicomponent but homogeneous solutions?

Here we assume a simple tube model picture that demands the diameter of the tube confining a test chain to be determined by its environment. For the environment we further assume that the contributions from all the components, PI and PB blocks and the solvent toluene, are smeared out. Then M_e of the present block copolymer solutions with concentration C may be given by

$$1/M_e(\mathrm{block}) = C/M_e°(\mathrm{block}) = C\{\phi/M_e(\mathrm{PI}) + (1-\phi)/M_e°(\mathrm{PB})\} \qquad (8)$$

where $M_e°$(block) represents the value of a block copolymer of the PI volume fraction ϕ in the bulk state. Then the reduced molecular weights, M_r', in the entangled state (both in bulk and in solution) are given by

$$M_r'(\mathrm{PI}) = M(\mathrm{PI})[M_e°(\mathrm{PI})/M_e°(\mathrm{block})] \qquad (9)$$

$$M_r'(\mathrm{PB}) = M(\mathrm{PB})[M_e°(\mathrm{PI})/M_e°(\mathrm{block})] \qquad (10)$$

Table II lists the total reduced molecular weights M_r(to-

Table II
Reduced Molecular Weight M_r, Molecular Weight between Entanglement M_e, and log τ_1/τ for BI and BIB Samples

code	$10^{-3}M_r$(total)	$10^{-3}M_r'$(total)	$10^{-3}M_e$	log τ_1/τ
BI(15–16)	35	44	3.5	0.30
BI(15–14)	33	41	3.5	0.40
BI(44–18)	73	100	3.1	0.90
BI(40–105)	155	181	4.0	0.07
BIB(15–16–22)	63	85	3.1	0.06
BIB(15–14–45)	90	123	3.0	0.66

tal) and M_r'(total) estimated by eqs 8–10 for BI and BIB in unentangled and entangled states.

A still better approximation may be derived from the hypothesis of Graessley and Edwards[31] on the plateau modulus $G_N°$ of a polymer solution of the volume fraction ϕ, which reads

$$(G_N°)_0\phi^\beta = G_N° = Kk_BT(\nu Ll^2)^\beta \qquad (11)$$

where $(G_N°)_0$ is the value for the bulk polymer, K, a universal constant, ν, the number of chains per unit volume, L, the chain contour length, and l, the Kuhn step length of the polymer. From eq 11, the M_e can be calculated as $M_e = CkT/G_N°$. The exponent β lies in the range of 2–2.3, varying slightly with the polymer species. For an AB block copolymer we may take $L = L_A + L_B$, with $(m - n)/N = L_A/L$ as the simplest assumption. Then, if we further take β to be 2, the M_e from eq 11 reduces to eq 8.

The next step is the reduction of the friction coefficient, ζ_0. Previously we estimated ζ_0(PI) for PI chains in PI/PB blends, simply assuming the additivity in the free volumes.[6] In the present systems, it is also necessary to estimate ζ_0(PB) for PB blocks per reduced chain segment in the mixed state. This is a rather complex problem. However, in solutions that are far above the glass transition, we may assume that the ζ_0 governed mostly by the solvent free volumes may be the same for PI and PB segments. Thus, we first analyze the solution data without reducing ζ_0.

V-2. Nominal Relaxation Times in Solution. Here we first compare the nominal τ_n of BI and BIB solutions with τ_1 ($=\tau_n$) of homo-PI chains with $M_w = M$(PI) of the PI blocks, both in solutions with the same C. The latter data referred to here as τ_1^{PI} were taken from our previous homo-PI toluene solution results, which are shown in Figures 3 and 4 with open triangles.

Then we compared τ_n with τ_1 as follows. As given in eqs 4 and 6, we see that the τ_1 of a block copolymer can be estimated simply by comparing it with that of a homo-PI chain with the same N or with M_W the same as M_r or M_r' of the block copolymer. Thus we picked up τ_1 ($=\tau_n$) data of homo-PI chains with $M_w = M_r$ (or M_r') in toluene solutions of the same C from our previous work.[7] For the former, we take the value M_r derived from eq 8 and thus referred to as $\tau_1°$; and for the latter, we take the M_e-based value M_r' derived from eq 10 and thus referred to as τ_1^e. The results are shown in Figures 2 and 3 with circles and squares, respectively.

We see that for all the cases $\tau_1^{PI} < \tau_1° < \tau_1^e$ and that the τ_n for the block copolymers are longer than τ_1^{PI} but mostly shorter than $\tau_1°$ and τ_1^e. For BI, the τ_n are between τ_1^{PI} and $\tau_1°$ ($<\tau_1^e$): Especially for BI(40–105) τ_n is quite close to τ_1^{PI}. For BIB, however, the τ_n are always much longer than τ_1^{PI} and rather close to $\tau_1°$ and/or τ_1^e. This indicates that the relaxation of the central portion of the chain is somehow synchronized with that of the overall molecule, or, more precisely, the slowest and the strongest mode of the central subchain reflects the fundamental ($p = 1$) mode of the whole molecule, as implied by eq 3.

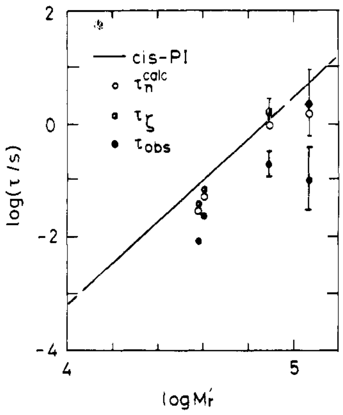

Figure 8. Nominal relaxation times τ for BI(15–16), BI(15–14), BIB(15–16–22), and BIB(15–14–45) plotted against reduced molecular weight M_r' (solid circles). Half-filled circles and open circles indicate τ_ζ and τ_n^{calcd}, respectively. The solid line indicates τ for pure *cis*-PI.

In Figure 4a, we are surprised to see that the τ_n for BIB(15–16–22) is even longer than the corresponding τ_1^e. Since the τ_n must be shorter than τ_1, this must be an artifact. In fact, a more precise analysis discussed below shows that τ_1/τ_n is very close to unity. This might be within experimental error.

For a more precise comparison of τ_n with the theories, we estimated the ratios of τ_n/τ_1 using the relaxation mode distribution given by eq 3. We determined this ratio $(\tau_{max}/\tau_1)^{grph}$ from the graphs of the theoretical ϵ'' curves given by eq 3 and then calculated nominal τ_n^{calc} of PI blocks for entangled systems as

$$\tau_n^{calc} = \tau_1^e(\tau_n/\tau_1)^{grph} \qquad (12)$$

and for unentangled systems simply by replacing τ_r^e by $\tau_r°$. The values of log τ_n^{calc} are plotted with the dashed lines in Figures 3 and 4. We see that the nominal τ_n are close to the dashed lines, except for BI(40–105) shown in Figure 3a. The result implies the Rouse model and/or the Doi–Edwards theory[22,23] modified for block copolymers reasonably well describe the dynamics of block copolymer subchains.

V-3. Behavior of Undiluted Systems. The nominal relaxation times τ_n for undiluted BI and BIB are plotted against M_r' in Figure 8. Those for BIB samples were estimated by assuming that the shapes of the ϵ'' curves for the undiluted BIB and its solution are the same, since the loss maxima were not observed.

Then assuming that $\zeta_0(PI) = \zeta_0(PB) \equiv \zeta_0$ in the homogeneous systems at their respective T_0, we estimated the change in ζ_0 from the shift factor a_T shown in Figure 6 by taking the difference Δlog a_T between the values of log a_T at $T = T_0$ of the block copolymer and at T_0 (=273 K) of homo-PI (that is taken as T_0 in Figure 6). This difference Δlog a_T corresponds to the ratio of ζ_0 between the copolymers and bulk PI at 273 K. Thus we reduced the observed τ_n to the value at an isofriction state, in which ζ is supposed to be the same as that of bulk-PIs:

$$\tau_\zeta = [\zeta_0(PI)/\zeta_0(copolymer)]\tau_n \qquad (13)$$

The values of the relaxation times reduced to the isofriction states τ_ζ are plotted in Figure 8 with half-filled circles. In Figure 8 the solid line represents τ_1 ($=\tau_n$) for bulk PIs plotted against M_r'. For undiluted samples, we also estimated the τ_n/τ_1 ratio and then calculated semitheoretical longest relaxation time τ_n^{calc} and plotted it in Figure 8 with open circles, which agree fairly well with the

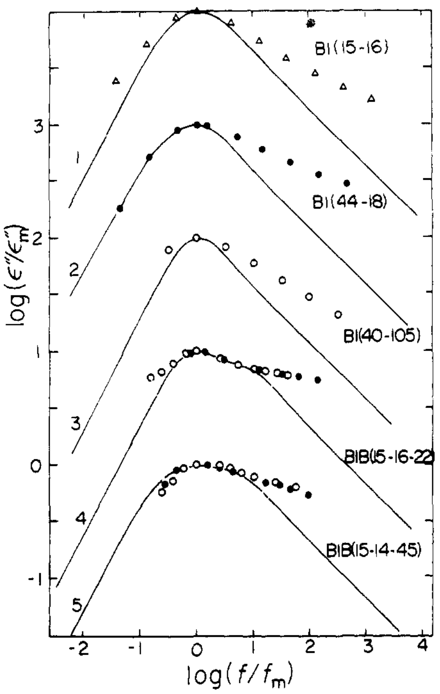

Figure 9. Double-logarithmic plot of the normalized ε'' curves. Solid lines indicate theoretical ε'' curves calculated with eq 3.

corresponding values of τ_ζ (the half-filled circles) and τ_1 of bulk PIs (the solid line).

V-4. Shape of ε'' Curves. We compare the shape of the ε'' curves with the theory given by eq 3. Figure 9 shows the normalized ε'' curves, in which f is normalized with $f_{\max}$, and ε'', with the $\epsilon_{\max}''$. For solutions we have chosen data at $C = 30$ or 40%.

As seen in Figure 9, the observed normalized ε'' curves are broader especially in the high-frequency side than the theoretical ones indicated by the solid curves. Although quantitatively the agreement is not extremely good in any examples shown in Figure 9, we notice a qualitative agreement, however. For example, in Figures 2 and 5 for BIB, we notice a shoulder or a bump around the frequency 1 decade higher than the $f_{\max}$. This behavior might reflect the prediction of eq 3 as seen in Figure 9.

Here we also compare the normalized ε'' curve with the theory of Stockmayer and Kennedy[19] for unentangled systems, which is described briefly in the Appendix. As discussed in the above sections, the $\zeta_{\rm PI}$ for the PI block may be higher than that, $\zeta_{\rm PB}$, for the PB block, but the contour length is approximately the same, provided the degrees of polymerization of the PI and PB blocks are the same. In terms of the Stockmayer–Kennedy theory, these conditions correspond to $K_{\rm A} = K_{\rm B}$ and λ [$=(\zeta_{\rm B}/\zeta_{\rm A})^{1/2}$] being higher than unity. In parts B and D of Figure 12 the ε'' curves for such cases are calculated and plotted in these figures. We see that the ε'' curves become slightly narrower but not broader with increasing λ than the unmodified curves.

V-5. Relaxation Strength. Finally we examine the relaxation strength Δε(block) of BI and BIB samples to compare the mean-square length $\langle r_{\rm nm}^2\rangle$ of the PI blocks with eq 5. Our interest here is to examine the expansion coefficient α^2 of the subchain

$$\alpha^2 = \langle r_{\rm nm}^2\rangle/\langle r^2\rangle_0 = [\Delta\epsilon({\rm block})/\Delta\epsilon({\rm PI})](\rho/C_{\rm b}) \quad (14)$$

where $\langle r^2\rangle_0$ is the mean-square end-to-end distance given by Δε(PI) of undiluted homo-PI with $M_{\rm w} = M({\rm PI})$ of the block copolymer, and ρ, the density of undiluted PI.

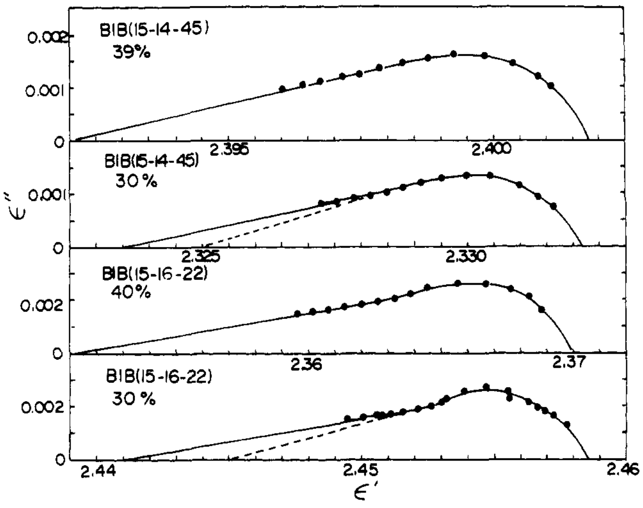

Figure 10. Cole–Cole plots for BIB solutions.

Table III
Relaxation Strength Δε, Δε/C, and Expansion Factor α^2 for BI

code	C(wt %)	$10^3\Delta\epsilon$	$\Delta\epsilon/C_{\rm b}$	α^2
BI(15-16)	100	56	0.109	1.09
BI(15-14)	100	51	0.106	1.06
BI(44-18)	40	12.1	0.103	1.03
BIB(15-16-22)	30	15 ± 3	0.17 ± 0.2	1.7 ± 0.2
	40	19	0.15	1.5
BIB(15-14-45)	30	7.8 ± 0.7	0.13 ± 0.3	1.3 ± 0.2
	40	9.6	0.13	1.3

We calculated Δε for BI from the area under the ε'' curve since the data of ε'' over the wide frequency range were available. For BIB solutions, however, we estimated Δε by using Cole–Cole plots shown in Figure 10, because the area under the ε'' curve data is not available. The values thus calculated are normalized with the content $C_{\rm b}$ of PI in the unit volume of the sample. The results are listed in Table III.

The values of α^2 for undiluted BI and a 40% solution of BI(44-18) are close to unity, indicating that the I block chains assume a Gaussian conformation. This is consistent with the classical theory of conformation. On the other hand, the α^2 of BIB samples are higher than unity. This suggests that the middle part of the chain is expanded. However, this interesting result is still not conclusive because of possible errors involved in the extrapolation of the Cole–Cole plots.

VI. Conclusions

(1) The nominal relaxation times of BI and BIB are in agreement with the calculated relaxation times from the data for homo-PI with the same reduced molecular weight.

(2) The ε'' curves for BI and BIB are broader than the theoretical ones calculated with the tube theory.

(3) The end-to-end distance of the I blocks of BI is close to the unperturbed value, but that of BIB might be expanded due to the excluded volumes within the chain.

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Appendix

On the basis of the models described in the theoretical section, we calculate the correlation function $\phi(t)$ of the total dipole moment $P(t)$ defined by eq 2. In the nonentangled state $N + 1$ beads are connected with springs

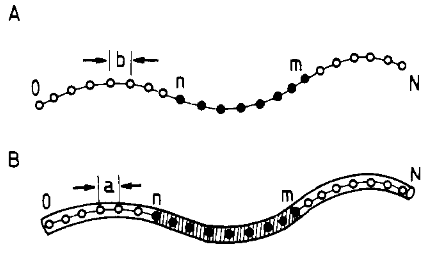

Figure 11. Bead–spring model (A) and tube model for a block copolymer (B). Open circles show the nonpolar beads and filled circles with type A dipole. In B the subchain in the hatched region is oriented to the direction of the external electric field.

as shown in Figure 11A, and at the limit of free draining,[14,23] the coordinate $R_j(t)$ of the jth bead is expressed with the normal modes $X_p(t,j,N)$

$$R_j(t) = 2\sum_{p=1}^{N} X_p \qquad \text{(A1)}$$

$$X_p(t,j,N) = A_p(t)\cos(p\pi j/N) \qquad \text{(A2)}$$

where p is the number of the normal mode and A_p the amplitude of the pth mode. From eqs 1, 2, and A1, we obtain $\phi(t)$

$$\phi(t) = \frac{8N}{(m-n)\pi^2}\sum_{p=1}^{N}\left[\sin^2\left\{\frac{p\pi(n+m)}{2N}\right\}\times \sin^2\left\{\frac{p\pi(m-n)}{2N}\right\}\exp\left(-\frac{p^2t}{\tau_1}\right)\right] \qquad \text{(A3)}$$

where ζ is the friction coefficient per bead and the longest relaxation time τ_1 is given by eq 4. By Fourier transform of eq A2, we obtain eq 3.

Stockmayer and Kennedy proposed a general theory of the normal modes for symmetrical triblock copolymers ABA and diblock copolymers AB in which the friction coefficients for the beads of the A block, ζ_A, is different from those in the B block, ζ_B. Moreover, the force constant, K_A, in the A block is different from that, K_B, in the B block. In their theory the index j of the beads is replaced by the continuous contour variable s. For triblock copolymers, s is defined by

$$s = (2j/N) - 1 \qquad \text{(A4)}$$

Then the normal modes for the A and B blocks are written by a form

$$X_A = \exp(-t/\tau_1)[C_A \sin \alpha s + D_A \cos \alpha s] \qquad \text{(A5)}$$

$$X_B = \exp(-t/\tau_1)[C_B \sin \alpha\lambda_s + D_B \cos \alpha\lambda s] \qquad \text{(A6)}$$

where λ^2 is equal to ζ_B/ζ_A. The parameters C_A, D_A, C_B, D_B, and α are functions of the index of the mode p but are not expressed by analytical functions. For even modes $C_B = 0$, and for odd modes D_B equals 0. From the conditions of continuity at the junction points of the A and B blocks and the condition of $\partial X/\partial s = 0$ at the chain ends, eqs A5 and A6 are solved numerically. The normal modes of the diblock copolymers become equivalent to those of the even modes of the triblock copolymers. The theoretical ϵ'' curves for di- and triblock copolymers are shown in parts B and D of Figure 12 in which the solid and dash-dot lines indicate the ϵ'' curves for $\lambda = 2$ and 3, respectively. In the calculation, we assumed $K_A = K_B$.

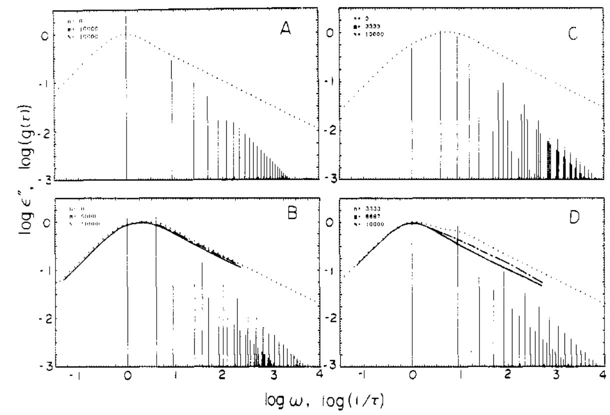

Figure 12. Theoretical relaxation spectra $g(\tau)$ and ϵ'' curves plotted against angular frequency ω and $1/\tau$, respectively. The histograms indicate $g(\tau)$ and the dotted lines the ϵ'' curves for chains with $N = 10\,000$ and (A) $n = 0$, $m = 10\,000$; (B) $n = 0$, $m = 5000$; (C) $n = 0$, $m = 3333$; (D) $n = 3333$, $m = 6667$. The solid and dot-dash lines indicate the ϵ'' curves calculated with the Stockmayer–Kennedy theory.[19] The histograms of $g(\tau)$ are shifted upward by 0.5 decades.

When chains are entangled, the tube model may be applied.[21–23] We consider the relaxation of the polarization of the test chain confined in a tube as shown in Figure 11B. The chain has been subjected to a direct current (dc) electric field and then the field is switched off at time $t = 0$. The subchain composed of the beads with indices n to m is polarized and is oriented in the direction of the field, but the other part of the tube is not. When the subchain goes out of the tube with indices n to m (hatched part of the tube in Figure 11B), the subchain is depolarized. However, the subchain does not completely lose the memory of polarization if it is still in the original tube from 0 to N because the bead has a probability to go back to the polarized tube region n to m. Doi and Edwards[22,23] calculated the probability $\Psi(\xi,t;s)$ that the bead with the index s is still in the tube when it has moved ξ along the tube

$$\phi(\xi,t;s) = \sum_{p=1}^{N}\frac{2}{N}\sin\left(\frac{p\pi s}{N}\right)\sin\left\{\frac{p\pi(s-\xi)}{N}\right\}\exp\left(-\frac{p^2t}{\tau_1}\right) \qquad \text{(A7)}$$

where τ_1 is the longest relaxation time given by eq 5. Then the probability that the segment s is still in the tube region from n to m is given by

$$\phi(s,t) = \int_{s-m}^{s-n} d\xi\ \Psi(\xi,t;s) \qquad \text{(A8)}$$

The correlation function $\phi(t)$ for polarization is equal to the sum of ϕ for all s with the indices n to m. Thus, after integration of $\phi(s,t)$ from n to m, we finally obtain $\phi(t)$ having exactly the same form as eq A3. Fourier Laplace transformation of eq A3 gives the angular frequency dependence of the complex dielectric constant written as eq 3.

Some examples of the relaxation spectra and the corresponding ϵ'' curves are shown in Figure 12.

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Registry No. BI (block copolymer), 109264-12-2; PI (homopolymer), 9003-31-0.