lower ΔT or at a much earlier stage.

Registry No. PS, 9003-53-6; PVME, 9003-09-2.

References and Notes

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(29) The borderlines in Figure 9 correspond to the critical time t_c at $q = q_m$.

Structure and Properties of Tapered Block Polymers. 4. "Domain-Boundary Mixing" and "Mixing-in-Domain" Effects on Microdomain Morphology and Linear Dynamic Mechanical Response

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ABSTRACT: A series of tapered block polymers of styrene–butadiene (S and P series) and styrene–isoprene (K series) were prepared by anionic polymerization, and the effects of composition variation along the main chain in the tapered block polymers on microdomain structure and on linear dynamic mechanical response were investigated. It was found that the effects are generally twofold: (i) enhancement of mixing of unlike segments in the interfacial region ("interphase") between two coexisting microphases ("domains") (i.e., enlargement of the interphase), designated as "domain-boundary" effect, and (ii) enhancement of mixing of unlike segments in the domains (or domain centers), designated as "mixing-in-domain" effect. The domain morphology and linear dynamic mechanical response were found to be predicted in terms of the two effects, the relative contribution being dependent upon the primary chemical structure. The morphological and mechanical behaviors of the ideal block polymer and S series can be predicted in terms of the domain-boundary effect, while those of the P and K series are dominantly affected by the mixing-in-domain effect.

I. Introduction

Zelinski and Childers[1] reported a large degree of control over monomer sequence distribution can be achieved by anionic copolymerization of butadiene and styrene. For example, when mixtures of butadiene and styrene are copolymerized with lithium alkyls in nonpolar hydrocarbon media, block polymers are formed in which the first block is a copolymer rich in butadiene and the second is one rich in polystyrene. An addition of ether such as diethyl ether to the reaction medium results in the block polymer in which styrene and butadiene monomers are more extensively mixed along the chains.[2-7]

In this paper we define "tapered block polymer" as the block polymers in which composition of one component varies along the main chain. The "ideal block polymer" prepared by a sequential polymerization of styrene and butadiene monomers is effectively a special type of tapered block in which the styrene fraction jumps stepwise from unity to zero along the main chain. The ideal random copolymer in which the comonomers follow each other in statistically random fashion along the chain may be regarded as another extreme of the tapered block in that the fraction of one comonomer averaged over many chains is uniform along the main chain. The effects of the monomer

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Table I
Sample Characterization of S-Series Block Polymers Composed of Styrene and Butadiene

sample	molecular weight $M_n \times 10^{-4}$ [a]	molecular weight M_w/M_n [b]	total styrene,[c] wt %	architecture S-S_m/B_m-B,[d] wt %	polybutadiene microstructure, %[e] cis-1,4	trans-1,4	vinyl
S-1	9.6	1.58	65	65-(0/0)-35	50	38	12
S-2	8.6	1.35	65	60-(5/5)-30	46	41	13
S-3	9.0	1.66	65	55-(10/5)-30	46	41	13

[a] Membrane osmometry. [b] GPC. [c] Elementary analysis. [d] As charged. [e] Infrared spectroscopy.

Table II
Sample Characterization of P-Series Block Polymers Composed of Styrene and Butadiene

sample	molecular weight $M_n \times 10^{-4}$ [a]	molecular weight M_w/M_n [b]	total styrene,[c] wt %	architecture S_m/B_m-S,[d] wt %	polybutadiene microstructure,[e] % cis-1,4	trans-1,4	vinyl
P-1	7.2	1.10	25	8/75-17	39	51	10
P-2	13.5	1.13	40	18/60-22	39	51	10
P-3	11.9	1.13	69	26/31-43	27	58	15
P-4	9.3	1.13	70	20/30-50	31	53	16

[a] Membrane osmometry. [b] GPC. [c] Elementary analysis. [d] Chemical analysis (ASTM D3314-74). [e] Infrared spectroscopy.

sequence distribution or the composition variation along the main chains on the properties of the tapered block polymers were qualitatively discussed by Kraus et al.[3,4] and some others[7] in relation to various anionic copolymerization techniques. The theme of this series of our studies on tapered block polymers is on the same line and is to investigate quantitatively the effect on the domain morphology and properties.

We investigated a series of styrene–butadiene block polymers, designated as the S and P series, and styrene–isoprene block polymers, designated as the K series, all prepared by anionic polymerization. The synthesis, characterization, and techniques we employed here are described in section II. In section III we will give some considerations on primary structure of these S-, P-, and K-series specimens (section III-1). We will discuss its effect on the morphology of microdomains (sections III-2 and III-3) and on mixing of unlike segments in the domain-boundary region ("domain-boundary" effect) and in the domains (or domain centers) as well ("mixing-in-domain" effect) (section III-4). In section IV we will present some results of the linear dynamic mechanical response of the specimens. The behaviors of ideal block polymers and the S series will be shown to be dominantly affected by the "domain-boundary" effect (section IV-1) while those of the P and K series will be affected by the "mixing-in-domain" effect (section IV-2). Finally in section IV-3 we will present some results on simulations of the mechanical response with a composite model. The present studies are an extension of former studies on the structure and properties of tapered block polymers of styrene and isoprene.[8]

II. Experimental Methods

1. Polymerization of the S, P, and K Series of Tapered Block Polymers. The S series of styrene–butadiene block polymers were prepared by anionic polymerization, in a nitrogen atmosphere rather than under high vacuum, with cyclohexane as a polymerization solvent and *n*-butyllithium as an initiator at 60 °C. A small amount of tetrahydrofuran (THF) was added to all the reaction systems. Almost 100% conversion was obtained for all the specimens. The block polymerization was carried out in sequential order, i.e., the prescribed amount of styrene monomers (defined as S in wt %) was first polymerized, then the prescribed amount of a mixture of styrene and butadiene (each containing S_m and B_m wt %, respectively), and finally the prescribed amount of butadiene monomers (defined as B wt %). THF was added as a randomizer for simultaneous copolymerization of the comonomers in the second step. Thus S-series specimens have the molecular architecture of a styrene block sequence, connected by a short sequence of more or less random mixture of the comonomers, which is further linked by a butadiene block sequence. This architecture is designated as S–S_m/B_m–B for the sake of convenience, where S, S_m/B_m, and B designate the styrene block sequence, the short sequence of the random mixture of the comonomers, and the butadiene sequence, respectively. The weight fractions of S, S_m, B_m, and B are summarized in Table I. The specimen S-1 is an ideal block polymer, while S-2 and S-3 contain the short random sequence between the polystyrene and polybutadiene block chains. The total styrene weight fraction was fixed to be 0.65 and the total molecular weight was also estimated to be about the same.

The specimens of the P series were received from Phillips Petroleum Co., Bartlesville, OK, by the courtesy of Dr. G. Kraus. The general scheme of the polymerization procedure is described in the patent literature, example II by Zelinski,[2], and in the paper by Zelinski and Childers.[1] The specimens were prepared by a simultaneous copolymerization of styrene and butadiene monomers in cyclohexane at 50 °C. *n*-Butyllithium was used as an initiator, but no ether such as THF and diethyl ether was present in the reaction system. The polymerization is suggested to produce "tapered" block polymers containing two blocks, the molecular architecture being designated as S_m/B_m–S. The first block is a butadiene–styrene copolymer containing a small amount of styrene (designated as S_m/B_m) while the second block is a styrene homopolymer (designated as S). Table II summarizes the molecular weight and wt % of total styrene (S + S_m), block styrene S, nonblock styrene S_m, and the microstructure.

The specimens of K series are tapered block polymers of styrene and isoprene, the polymerization procedures of which were described in detail elsewhere.[8] The characterization of the primary structure in terms of ^{1}H NMR spectroscopy and pyrolysis gas chromatography as well as characterization of the microdomain structure and analysis of dynamic mechanical properties were described[8] and will be described elsewhere.[9] The K-2 and K-3 specimens here correspond to the TB-2 and TB-3 specimens in those papers.[8,9] The K-1 specimen is an ideal block polymer prepared by the sequential polymerization of styrene and then isoprene monomers in THF at −78 °C under high vacuum (10^{-6} torr) with *sec*-butyllithium as an initiator. The specimens K-2 and K-3 are the tapered block polymers prepared by simultaneous copolymerization of the two monomers with *sec*-butyllithium as an initiator in benzene at 25 °C. A small amount of THF was added to the reaction system as a randomizer. It will be shown later from morphological and dynamic mechanical studies that the tapered block has a molecular architecture of an isoprene-rich block connected with a styrene-rich block. Incorporation of styrene monomers in an isoprene-rich block seems to be smaller than that of isoprene monomers in a styrene-rich block, giving rise to the architecture approximately equal to I–S_m/I_m, as will be discussed later. The characterization of the K series is summarized in Table III.

Table III
Sample Characterization of K-Series Block Polymers Composed of Styrene and Isoprene[a]

sample	molecular weight		total styrene,[d] wt %	polybutadiene microstructure,[e] %		
	$M_n \times 10^{-4}$ [b]	M_w/M_n [c]		1,4 linkage	3,4 linkage	1,2 linkage
K-1	10.6	1.05	45	3	63	34
K-2	6.3	1.08	48	6	72	22
K-3	10.6	1.09	45	3	76	21

[a] K-2 and K-3 have an architecture of isoprene-rich block linked with styrene-rich block as a first approximation (see text). [b] Membrane osmometry. [c] GPC. [d] Elementary analysis. [e] Infrared spectroscopy.

2. Characterization. The number-average molecular weight, $\bar{M}_n$, was measured by membrane osmometry, the heterogeneity index, M_w/M_n, by gel permeation chromatography, the total styrene weight fraction by elementary analysis, and the microstructure of polydienes by infrared spectroscopy. The weight percentage S of block styrene in the tapered block polymers of P series (see Table II) was determined by the chemical analysis proposed by Kolthoff, Lee, and Carr.[10] It is based on the degradation of the butadiene portion of the molecule by *tert*-butyl hydroperoxide in *p*-dichlorobenzene, catalyzed by osmium tetraoxide. In section III-1 we will analyze this from conversion data.

3. Small-Angle X-ray Scattering (SAXS). The SAXS profiles were measured with a rotating-anode X-ray generator as a high-flux X-ray source (12 kW) and a position-sensitive linear detector. The details of the apparatus and data treatment were described elsewhere[11,12] and will not be repeated here.

4. Linear Dynamic Mechanical Response. Isochronal dynamic mechanical responses in the linear range of the tensile deformation were measured (with a static tensile strain of 0.5% and a dynamic strain amplitude of 0.05%) at 10 Hz as a function of temperature from about −150 to 100 °C (with a dynamic mechanical spectrometer, Iwamoto Seisakusho, Kyoto, Japan).

III. Primary Structure and Effects of Domain-Boundary Mixing and Mixing in Domain on Microdomain Structures

1. Primary Structure. The primary structure, i.e., the composition variation along the main chain of the tapered block polymers, is of great importance in understanding their physical properties. Such information is especially important for the P- and K-series specimens, while the primary structure of S-series specimens is more or less obvious from the polymerization procedures. The structure of the P- and K-series specimens may be analyzed from the conversion data, which, however, were not obtained for any of the specimens to be studied here. Kraus and Rollmann, however, reported the conversion data for the polymer designated as E in their paper,[4] which had been prepared in the same manner as the P-series polymers in this paper. Thus we will present an analysis of the composition variation along the chain for the polymer E as a representative of the general scheme for polymers of the P series. It was reported that the polymer contains a total styrene wt % of 30.0. It has $\bar{M}_n = 1.47 \times 10^5$ and $\bar{M}_w/\bar{M}_n = 1.17$. Figure 1 shows the reported conversion data on $\tilde{W}_2$ as a function of x where x is the fractional conversion by weight and $\tilde{W}_2$ the weight fraction of styrene in polymer sampled at x.

As proposed by Kraus and Rollmann[4] one can estimate the instantaneous composition of styrene w_2 in the polymer formed at x by eq 1. The function $w_2(x)$ is the quantity

$$w_2 = \tilde{W}_2 + x(\mathrm{d}\tilde{W}_2/\mathrm{d}x_2) \qquad (1)$$

that characterizes the composition variation along the chain. Figure 1 includes also the estimated function $w_2(x)$ for the sample E (solid line with solid circles) and for the ideal block (broken line). It is shown that up to 50 wt % conversion the polymer E has a sequence of nearly ideal random copolymer with a small content of styrene monomers, after which styrene incorporation is suddenly increased to 100% at about 80 wt % conversion. Consequently a sharp tapering of the composition is seen from 60 to 80 wt % conversion for this particular polymer. The block styrene percent as estimated from the conversion data is in fairly good agreement with the value 21.8% obtained by the chemical method of Kolthoff et al.[10] (see Table I of ref 4).

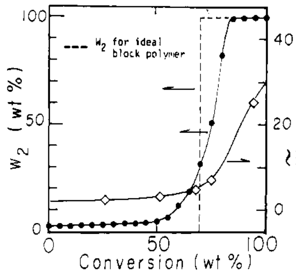

Figure 1. Variation of the instantaneous weight percent of styrene units w_2 as a function of conversion x, which was calculated from Kraus–Rollmann data[4] on $\tilde{W}_2(x)$.

The general features of the composition variation for the polymer E will be well representative of those for the P-series tapered block polymers, which were prepared under equivalent conditions to the polymer E. Thus as a first-order approximation, the P-series polymers may be considered to be a block polymer composed of a block styrene sequence (S) and the rest of the chains (S_m/B_m) (i.e., a random copolymer of nonblock styrene and butadiene), thus having the architecture of S_m/B_m–S (see Table II).

Although we do not have the conversion data for the K-series polymers, the general scheme of the composition variation along the chain is considered to be the same as that of the P series. In fact we concluded that the K-2 and K-3 polymers can be approximated as the block polymers composed of a "styrene-rich" block and "isoprene-rich" block from their dynamic mechanical responses and critical temperature (as observed by SAXS) at which the microdomains are dissolved into a homogeneous mixture.[8,9,13] Judging from the shifts of the glass transition temperature we may further advance the speculation that the fraction of styrene monomers in the isoprene-rich block is less than that of isoprene monomers in the styrene-rich block. Thus the K-series polymers may have the architecture of I–I_m/S_m as a approximation, as willl be discussed later.

2. Microdomain Morphology As Observed by Electron Microscopy. Microdomain morphology of the tapered block polymers was investigated under transmission electron microscopy with a conventional fixation and staining technique with osmium tetraoxide followed by ultra-thin sectioning.

Figure 2 shows the domain morphology of the P-series polymers. Polymers P-1 and P-2 have the microdomain structure of a "polystyrene cylinder" dispersed in a "polybutadiene matrix", while polymers P-3 and P-4 have "alternating lamellar domains". Polymers P-3 and P-4 should form cylindrical microdomains of polybutadiene dispersed in the matrix of polystyrene judging from total styrene content if they were the ideal block polymers.

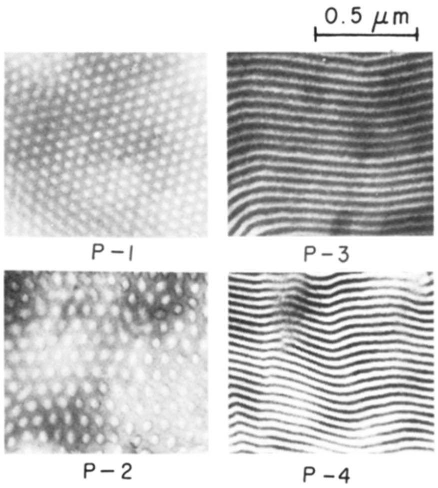

Figure 2. Microdomain structure of P-series polymers observed by transmission electron microscopy on ultra-thin sections stained by OsO_4.

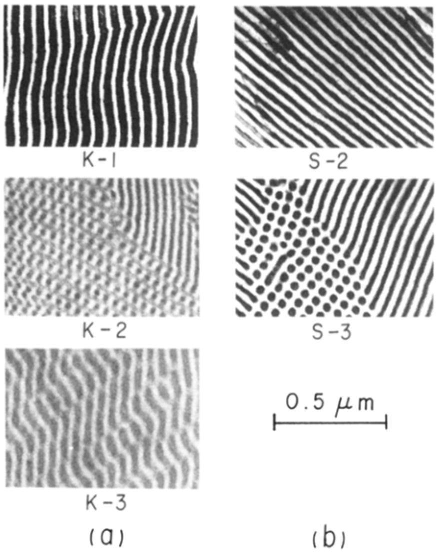

Figure 3. Microdomain structure of K-series polymers (a) and S-series polymers (b) observed by transmission electron microscopy on ultra-thin sections stained by OsO_4.

Despite this fact, they take the "alternating lamellar domains", which may be best understood as a consequence of the microphase separation between the block styrene and the rest of the chain (i.e., more or less random sequence of styrene and isoprene). This hypothesis will be further confirmed by SAXS results (section III-3) and dynamic mechanical studies (section IV-2).

The quotation marks such as "polybutadiene matrix", "polystyrene cylinder", and "alternating lamellar domains" refer to the respective terms, which are different from those for the ideal block polymers. That is, the "polybutadiene matrix" and "polybutadiene lamellar domains" do contain an appreciable amount of styrene units. "Polystyrene cylinder" and "polystyrene lamellar domains" may also contain some butadiene units, the amount of which may be much less than that of styrene units in the "polybutadiene domains", as will be clarified later (section IV-2).

Figure 3 shows the microdomain morphology for the K-series (a) and S-series (b) polymers. The polymer K-1 is an ideal block polymer having 55 wt % polyisoprene, and consequently it has the morphology of alternating lamellar microdomains, each domain being composed mostly of its own polymer segments and mixing of the unlike segments preferentially occurring in the interphase between the two coexisting phases.[14] In contrast to K-1, the tapered block polymers have extremely weak contrast between the two phases under transmission electron microscopy, indicating that a considerable amount of mixing of unlike segments occurs in each domain. The mixing of the unlike segments is considered to reduce the contrast between the domains even on the stained ultra-thin section. Polymer K-2 has the morphology of "polyisoprene cylinders", while K-3 may be "alternating lamellar" or "cylindrical" morphology. The fact that K-2 has the cylindrical polyisoprene domains may be a consequence of the architecture as discussed in section III-1: the isoprene monomers are incorporated into the styrene-rich block much more than the styrene monomers in the isoprene-rich block, resulting in a shorter "isoprene-rich" block compared with "styrene-rich" block.

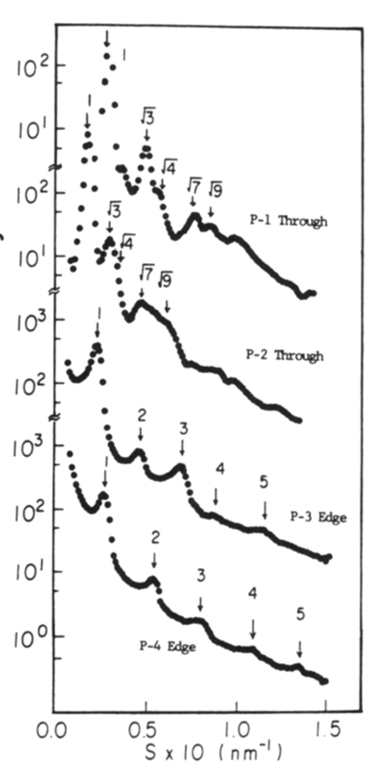

Figure 4. SAXS intensity profiles of the P-series polymers, $S = (2 \sin \theta)/\lambda$, where 2θ and λ are the scattering angle and wavelength of X-ray.

All the S-series polymers have a contrast as high as that of the ideal block polymer K-1. The ideal block polymer S-1 and the tapered block polymer S-2 have alternating lamellar microdomains, while S-3 has polybutadiene cylinders in the polystyrene matrix. Although the variation of the morphology with the architecture is not well understood at present, it may be clear and common to all the S polymers that the mixing of unlike segments may occur only in the interphase, from the SAXS results to be discussed in next section (section III-3). The thickness of the interphase may increase with increase in the random sequence S_m/B_m between the two blocks S and B.

3. Domain Morphology and State of Mixing of Unlike Segments As Analyzed by SAXS. Figure 4 shows typical SAXS profiles for the series of P polymers. The scattered intensity distributions from P-1 and P-2 are nearly isotropic and have maximum intensities at the relative angular positions approximately equal to $1:3^{1/2}:4^{1/2}:7^{1/2}:9^{1/2}$ as shown by the arrows. These maxima are typical of the interparticle interference maxima for the cylindrical particles in the hexagonally close-packed array. The arrays themselves are oriented nearly randomly. Thus

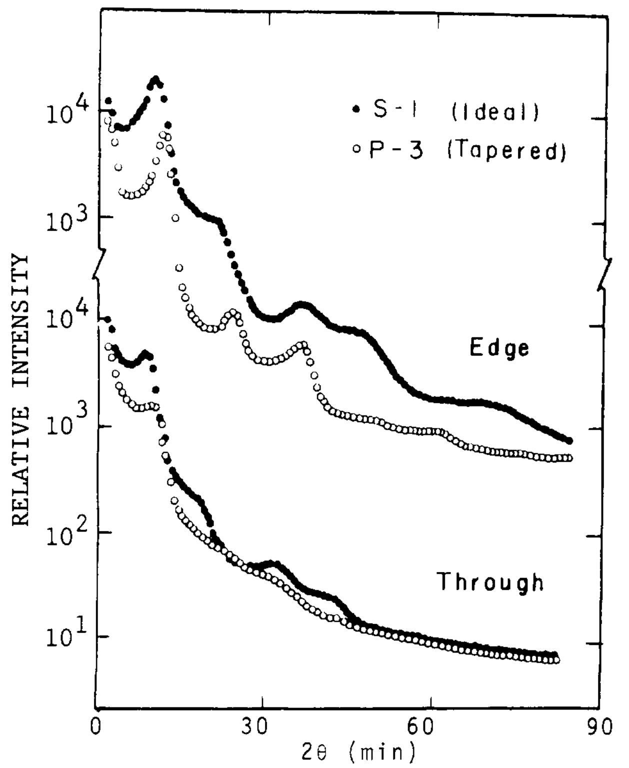

Figure 5. SAXS intensity profiles for S-1 (ideal SB block polymer) and P-3 (tapered SB block polymer) taken with "edge radiation" (top two curves) and "through radiation" (bottom two curves).

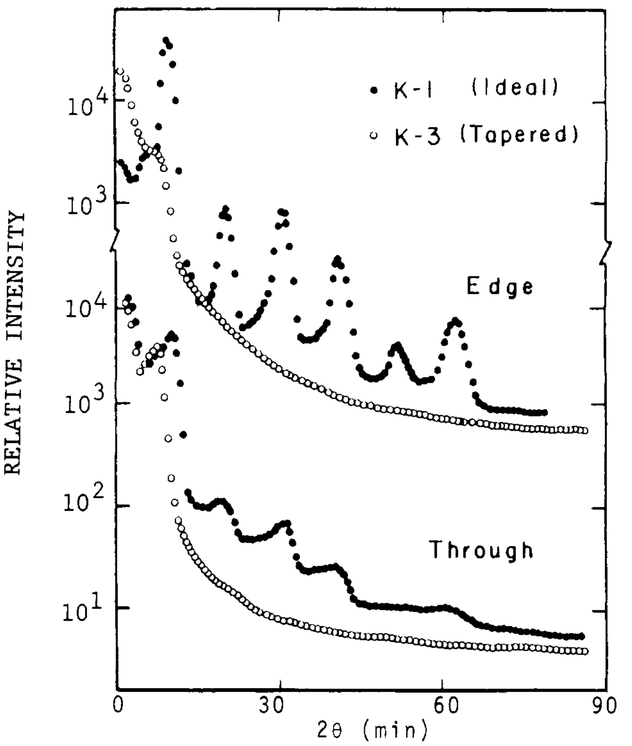

Figure 6. SAXS intensity profiles for K-1 (ideal SI block polymer) and K-3 (tapered SI block polymer) taken with "edge radiation" (top two curves) and "through radiation" (bottom two curves).

the micrographs for P-1 and P-2 in Figure 2 just correspond to a view cut nearly normal to the cylindrical axes.

On the other hand the scattering profiles from the P-3 and P-4 specimens exhibit scattering maxima at the relative angular positions of 1:2:3:4:5 as shown by the arrows, typical to the scattering from alternating lamellar microdomains. Thus the SAXS results confirm those obtained in Figure 2. When the incident beam is irradiated parallel to the film surface (designated as "edge radiation"), the scattering from P-3 and P-4 appears normal to the film surface. The intensity is much stronger than the scattered intensity observed under the condition that the incident beam is irradiated normal to the film surfaces (designated as "through" radiation). These facts further suggest that the lamellar domains are highly oriented with their boundaries parallel to the film surfaces, as is generally common with the lamellar microdomains in the solvent-cast films.[14]

Figures 5 and 6 indicate that the scattering power with the "edge" radiation is higher than that with the "through" radiation for the S-1, P-3, and K-1 specimens. The figures give important information on "state of mixing" of the unlike segments in the domain. The ideal S–B block polymer S-1 has a much higher scattering power than the tapered S–B block polymers P-3 (see Figure 5). The ideal S–I block polymer K-1 has a much higher scattering power than the tapered S–I block polymers K-3. Since the scattering power depends on mean-squared electron-density fluctuations $\langle\eta^2\rangle$, it decreases with increases degree of mixing of the unlike segments in each domain.

For example, for a two-phase system where the unlike segments S and B are mixed in a volume fraction ϕ_{S1} and ϕ_{B1}, respectively, in phase 1 and in ϕ_{S2} and ϕ_{B2} in phase 2, $\langle\eta^2\rangle$ is given by

$$\langle\eta^2\rangle = (\rho_1 - \rho_2)^2\phi_1(1 - \phi_1) \qquad (2)$$

$$(\rho_1 - \rho_2)^2 = (\phi_{S1} - \phi_{S2})^2(\rho_S{}^\circ - \rho_B{}^\circ)^2 \qquad (3)$$

where ρ_K and ϕ_K are the average electron density and volume fraction of K phase (K = 1 or 2), respectively, and $\rho_K{}^\circ$ is the electron density of pure K polymer (K = S or B). A complete uniform mixing of the unlike segments gives $\phi_{S1} = \phi_{S2}$ and hence $\langle\eta^2\rangle = 0$, while a complete segregation gives $(\phi_{S1} - \phi_{S2})^2 = 1$ and hence a maximum scattering power. Consequently it becomes obvious that the lower scattering power of the tapered block polymers directly results from the higher degree of mixing of the unlike segments in each domain or in one of the domains. The conclusion is consistent with that deduced from the primary structure (section III-I) and electron microscopic observations (Section III-2).

4. Mixing in Domain and in Domain Boundary. Comparisons of SAXS from the block polymers of the S, K, and P series show that the scattering power increases in the order

$$\text{K-2} \simeq \text{K-3} < \text{P-1} \simeq \text{P-2} \simeq \text{P-3} \simeq \text{P-4} < \text{S-2} \simeq \text{S-3} < \text{K-1} \simeq \text{S-1} \qquad (4)$$

Consequently the degree of mixing of the unlike segments decreases in that order, and the results obtained in section III may be summarized schematically in Figure 7.

Figure 7 presents models on spatial distribution of reduced segment density, $\tilde{\rho}_k(r) \equiv \rho_k(r)/\rho_k{}^\circ$ ($\rho_k(r)$ being the number density of the K unit (K = S, B, or I) at r and $\rho_k{}^\circ$ being the number density of bulk k polymer) for polymer blend (a), ideal block polymers S-1 and K-1 (b), S-series tapered block polymers (c), P-series tapered block polymers (d), and K-series tapered block polymers (e). From (a) to (c) the mixing of the unlike segments should dominantly occur in the "domain boundary". The more or less random short sequence of S_m/B_m between S and B blocks in the S-2 and S-3 polymers may increase the interfacial thickness λ_3 compared with λ_1 and λ_2.

The model of Figure 7c for the S series was deduced from the fact that the SAXS powers from S-2 and S-3 are about the same as that of S-1, thus $\langle\eta^2\rangle$ for S-2 and S-3

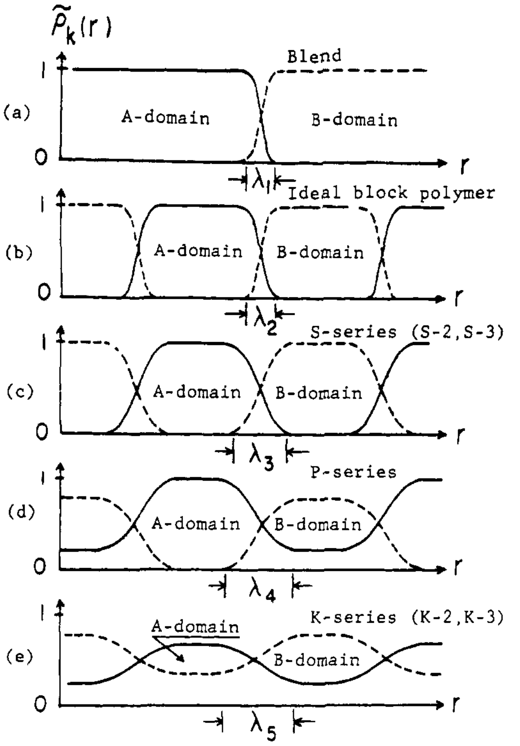

Figure 7. Schematic representation of models on spatial distribution of a reduced segment density $\tilde{\rho}(\mathbf{r})$ for polyblend (a), ideal block polymers (b), S-series tapered block polymers (c), P-series tapered block polymers (d), and K-series tapered block polymers (e).

being approximately equal to $\langle\eta^2\rangle$ for S-1. A slight increase of the interfacial thickness, which may be caused by a presence of the short sequence of S_m/B_m, should generally decrease $\langle\eta^2\rangle$. For example, for the trapezoidal electron density distribution[15]

$$\langle\eta^2\rangle = (\rho_1 - \rho_2)^2[\phi_1(1 - \phi_1) - \lambda S/6V] \quad (5)$$

where λ is the interfacial thickness and S/V is the surface-to-volume ratio. If the λ_3 is not very much larger than λ_2, the effect of λ on the scattering power may not easily be resolved.

Statistical mechanical theories of the interphase[16-18] will predict that the interfacial thickness of polymer blend in the high molecular weight limit is primarily determined by statistical segment length b_k and Flory–Huggins[19] interaction parameter χ between the polymers: the larger the value b_k and the smaller the value χ, the larger the value λ_1. The theories[18,20] predict also that λ_1 is equal to or less than λ_2 for the ideal block polymer. The "characteristic interfacial thickness" of the ideal block polymers K-1 and S-1 was found to be typically about 2 nm.[14,21,22]

For the P-series and K-series tapered block polymers, the mixing of unlike segments extensively occurs in one type of the domain (B domains for the P series; Figure 7d) and in both types of the domains (I and S domains for the K series; Figure 7e) as well as in the domain-boundary region. For the K series there are not phases that are pure, although the degree of mixing of the unlike segments in each domain is not symmetric, being slightly greater in the S domain than in the I domain. The interfacial thicknesses λ_4 and λ_5 are presumably larger than λ_1 and λ_2, since the mixing of the unlike segments in the primary structure reduces the effective χ parameter between the two blocks. That is, if the two blocks (numbered 1 and 2) contain A monomers in fractions of f_{A1} and f_{A2} and B monomers in f_{B1} and f_{B2}, respectively, the effective χ parameter χ_{12} between the two blocks is given by, from the χ parameter between A and B (χ_{AB}),

$$\chi_{12} = \chi_{AB}(f_{A1} - f_{A2})^2 = \chi_{AB}(f_{B1} - f_{B2})^2 \quad (6)$$

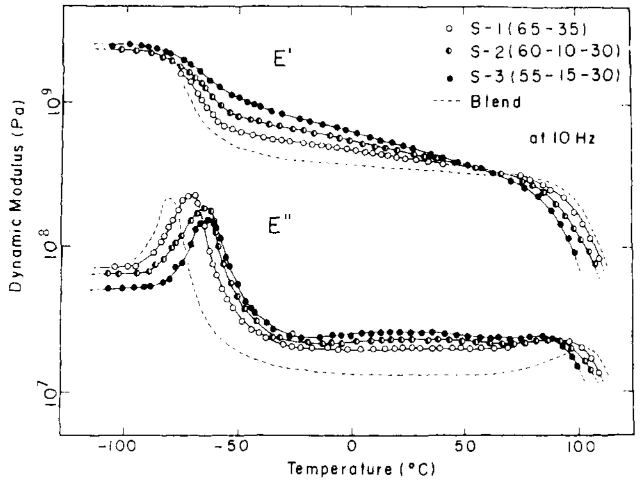

Figure 8. Temperature dependence of isochronal dynamic tensile moduli, E' (real part) and E'' (imaginary part), at 10 Hz for the S-series block polymers and the polymer blend of PS and PB.

IV. Linear Dynamic Mechanical Response and Effects of Domain-Boundary Mixing and Mixing in Domain

In this section we will discuss the effects of domain-boundary mixing (section IV-1) and of mixing-in-domain (section IV-2) on the linear dynamic mechanical response. From the preceding section it may be obvious that the domain-boundary mixing effect may be effectively studied by comparing the responses of the S-2 and S-3 specimens with those of S-1 and polyblend.

On the other hand the mixing-in-domain effect may be effectively studied from the responses of the P-series and K-series polymers.

1. "Domain-Boundary Mixing" Effect. Figure 8 shows the real, E', and the imaginary, E'', parts of linear dynamic mechanical moduli as a function of temperature at a fixed frequency, 10 Hz, for the polystyrene (PS) and polybutadiene (PB) blend (broken line) and for the S-series polymer. The homopolymers PS and PB have number-average molecular weights of 1.23×10^5 and 6.2×10^4, respectively, and the microstructure of PB is similar to that of B in block polymers, i.e., having 46%, 45%, and 9% cis, trans, and vinyl linkages, respectively. The weight fraction of PS in the blend was 0.5.

The polyblend exhibits two primary dispersions, corresponding to the dispersions of PB and PS. The ideal block (S-1) also exhibits the two dispersions, but there exist some quantitative differences in the responses between the polyblend and S-1; (i) the two dispersions of the ideal block, corresponding to B and S domains, are shifted to higher and lower temperatures in comparison with those of the polyblend, and (ii) temperature dependence of E' and the level of E'' between the two dispersion temperatures are greater for the ideal block polymer than for the polyblend. We ascribe these differences to the "domain-boundary relaxation" effect, i.e., the effect of "domain-boundary mixing" giving rise to the characteristic differences as described above.

The interfacial thickness of the microdomains of the block polymers is generally a function of molecular weight:[18,20] the larger the molecular weight, the thinner the interphase. The interfacial thickness of a polymer blend should be equal to a limiting value of the block polymer at high molecular weight limit and hence generally

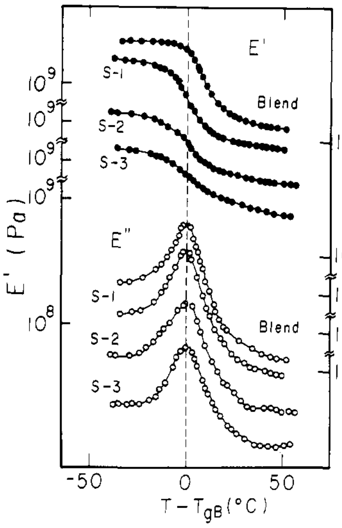

Figure 9. Temperature dependence of isochronal dynamic tensile moduli, E' (real part) and E'' (imaginary part), at 10 Hz, near the primary-dispersion region corresponding to the rubbery domains, for the polymer blend of PS and PB and for the S-series block polymers. T_{gB} is the temperature at which E'' in the primary dispersion of "butadiene-rich" domains becomes maximum.

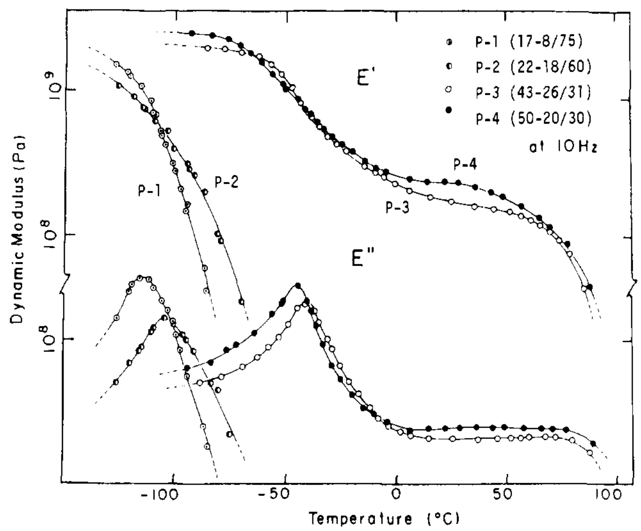

Figure 10. Temperature dependence of isochronal dynamic tensile moduli, E' (real part) and E'' (imaginary part), at 10 Hz for the P-series polymers.

smaller than that of block polymers. A series of our SAXS studies of the domain-boundary interphase has shown that the "characteristic interfacial thickness" is about 20 Å for the SI ideal block polymers and is almost independent of the total molecular weight of block polymers covered in the experiments (greater than 21 000 for lamellar domains and 80 000 for spherical domains).[14,21,22] Since the Flory–Huggins interaction parameter between PS and PB is nearly identical with that between PS and PI, the results obtained for SI may be applied to SB block polymers with a good accuracy. Judging from molecular weights of the polyblend and S-1, their characteristic interfacial thickness should be approximately identical with each other.

Although the interfacial thickness of the polyblend is nearly equal to that of S-1, the volume fraction of the interphase of the polyblend should be negligibly small compared with that of S-1, since the domain size of the polyblend (order of μm) is orders of magnitude larger than that of S-1 (order of 10 nm). Thus the domain-boundary effect is negligible for the polyblend but is appreciable for the ideal block S-1. Moreover, it is shown from Figure 8 (data for S-2 and S-3) that the domain-boundary effect is increasingly enhanced with increasing fraction of the random portion of S_m/B_m between S and B blocks. The concept and the effect of the "domain-boundary relaxation" will be presented more explicitly in section IV-3 on the basis of computer simulation of the response with a composite model.

Figure 9 shows E' and E'' in the region of the primary dispersion of the polybutadiene phase as a function of a reduced temperature $T - T_{gB}$ at 10 Hz for the polyblend and the S-series block polymers, where T_{gB}'s are the glass transition temperatures of polybutadiene domains. It is clearly shown that the primary dispersion of PB becomes broader in the order of polyblend, ideal block S-1, S-2, and S-3.

2. "Mixing-in-Domain" Effect. Figure 10 shows temperature dependence of the isochronal Young's moduli E' and E'' at 10 Hz for the P-series polymers. For P-1 and P-2 the matrix phase is composed of polybutadiene chains (more rigorously block chain composed of butadienes and nonblock styrenes, see section III) so that their moduli at temperatures above the glass transition of the matrix phase become too low to be detected. On the other hand for P-3 and P-4, the lamellae composed of polystyrene blocks form the continuous phase, giving rise to a high modulus level even at temperatures above the glass transition of the "polybutadiene-rich" lamellar domains.

The dispersion temperatures corresponding to "butadiene-rich" domains dramatically vary with the specimens, while those corresponding to polystyrene domains do not. The large shift is a consequence of a mixing of the "nonblock" styrenes in polybutadiene blocks, which in turn gives rise to a mixing of styrene segments into the "butadiene-rich" domains. A minor shift of the dispersion temperature corresponding to polystyrene domains indicates that butadiene segments are not incorporated much into the styrene-rich domains. Thus the dynamic mechanical response can be well predicted from the molecular and structural picture as discussed in section III and typically given by Figure 7.

Moreover one can show that the dispersion temperature T_{gB} corresponding to the "butadiene-rich" domains systematically shifts with weight fraction of "nonblock" styrene W_{NBS} in the butadiene-rich domains. The quantity W_{NBS} was estimated from the primary chemical structure (see Table II).

$$W_{NBS} = S_m/(S_m + B_m) \tag{7}$$

The quantity W_{NBS} is the weight fraction of styrene segments in the butadiene-rich domains in cases where the microphase separation occurs between a "nonblock-styrene" sequence and the rest of the chain. Figure 11 shows the variation of $1/T_{gB}$ (K^{-1}) with W_{NBS} (%). The straight line is drawn according to the Fox equation[23] for a random copolymer

$$\frac{1}{T_{gB}} = \frac{1 - W_{NBS}}{T_{gB}{}^\circ} + \frac{W_{NBS}}{T_{gS}{}^\circ} \tag{8}$$

where $T_{gB}{}^\circ$ and $T_{gS}{}^\circ$ are the glass transition temperature for polybutadiene and polystyrene homopolymers, respectively.

If one takes into account a small variation of polybutadiene microstructure within the P series, T_{gB}'s variation with W_{NBS} can be well approximated by eq 8. This also indicates that the styrene segments are randomly mixed in the "butadiene-rich" domains, at least, as a first-order approximation. In addition to this "mixing-in-domain" effect, there exists also the "domain-boundary mixing" effect on the dynamic mechanical response of the

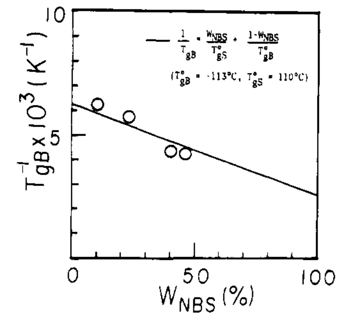

Figure 11. Shift of T_{gB}, the temperature at which E'' in the primary dispersion of "butadiene-rich domains" becomes maximum, with W_{NBS}, weight percent of "nonblock" styrene units in the sequence of nonblock styrenes and butadienes.

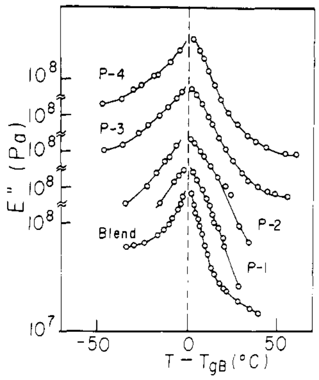

Figure 12. Temperature dependence of isochronal dynamic tensile moduli E'' (imaginary part), near the primary-dispersion region corresponding to the rubbery domains, for P-series polymers and the polyblend of PS and PB. T_{gB} is the temperature at which E'' in the primary dispersion of "butadiene-rich" domains becomes maximum.

P-series samples as observed for the S-series polymer.

Figure 12 shows temperature dependence of E'' at 10 Hz in the primary dispersion region of the "butadiene-rich" phase, a reduced temperature $T - T_{gB}$ being used. The P-series polymers have much broader dispersion than the S-series polymers. This is because for the P series the mixing-in-domain effect as well as the domain-boundary mixing effect broadens the dispersion, while for the S series only the latter broadens the dispersion. The broadness of the dispersion increases with increasing W_{NBS}, i.e., with increasing "mixing-in-domain" effect.

Figure 13 shows isochronal tensile moduli at 10 Hz for the K series polymers and polymer blend of PS and PI. The number-average molecular weights $\bar{M}_n$ of PS and PI are 2.77 × 10^5 and 4.9 × 10^5 g/mol, respectively, and equal weights of each are mixed. The microstructure of PI is the same as that of K-1, ideal block polymer. The tapered block polymer K-3 (and K-2 as well, though its data are not shown here) exhibits roughly a single broad dispersion maximum, despite the fact that they have alternating lamellar microdomain structure.

In the tapered block polymers K-2 and K-3, the dispersions corresponding to PI and PS phases of the polyblend and ideal block polymer are shifted toward higher and lower temperatures, respectively, so that the two dispersions overlap each other, resulting in the single broad maximum. The shift of the dispersion temperatures and the broadening of the dispersion are again a consequence of the mixing-in-domain effect. The effect seems to be more symmetric and stronger for the K series than for the P series, for which only the primary dispersion associated with the "butadiene-rich" phase is affected. However, closer observation of the respons will lead to a conclusion that the fraction of the unlike segments in the styrene-rich domains is slightly larger than that in the isoprene-rich domains, since the shift of PS-dispersion is slightly larger than that of PI-dispersion (see Figure 7e). In the case of K-2 and K-3, the domain-boundary mixing effect is buried in the dominant contribution of the mixing-in-domain effect.

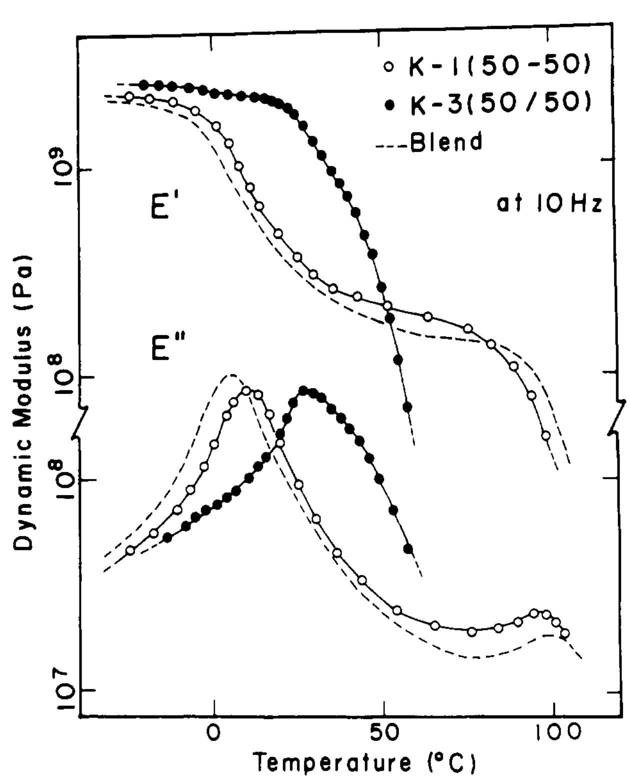

Figure 13. Temperature dependence of isochronal dynamic tensile moduli E' and E'' at 10 Hz for the K-series polymers and the polyblend of PS and PI.

3. Simulation with a Composite Model. In this section we will present some results of computer simulation of the two effects on the dynamic mechanical response with a composite model (Takayanagi's model).[24] We used basically the same technique as that employed by Kraus and Rollmann[25] (KR) to calculate temperature dependence of the isochronal tensile modulus at 10 Hz. Figure 14 defines various quantities required for calculations.

When the stress is applied parallel to the interfaces of the domains (e.g., lamellar domains), the composite mechanical model gives a complex modulus of the system at temperature T ($E_p^*(T)$) (eq 9) on the basis of the additivity

$$E_p^*(T) = \frac{2}{D}\int_{-D/4}^{D/4} E^*(z;T)\,dz \tag{9}$$

of the partial stress of each sublayer, where z is the coordinate normal to the lamellar interface, D is the identity period, and $E^*(z;T)\,dz$ is a contribution of the sublayer at $z \sim z + dz$ to the total complex modulus at T. We assume, as in the treatment of KR,[25] that $E^*(z;T)$ is identical with the complex modulus of pure polybutadiene at T', $E_i^*(T')$, which, in turn, can be estimated by knowing weight fraction of styrene segments at the sublayer, $W_s(z)$.

$$E^*(z;T) = E_i^*(T') \tag{10}$$

$$T' = T + T_{gi} - T_g(z) \tag{11}$$

$$\frac{1}{T_g(z)} = \frac{1 - W_s(z)}{T_{gi}} + \frac{W_s(z)}{T_{gs}} \tag{12}$$

$T_g(z)$ is the glass transition temperature of the sublayer

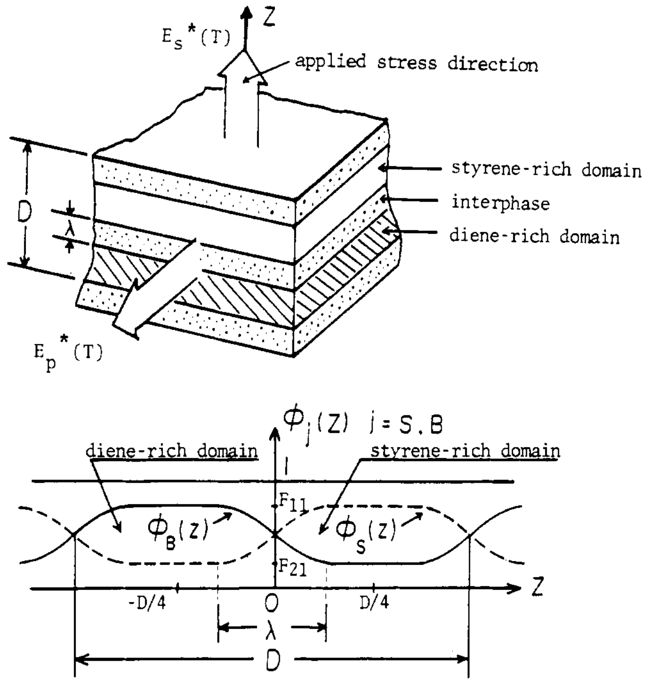

Figure 14. Model describing spatial distribution of styrene, $\phi_s(z)$, and diene segments, $\phi_B(z)$ (fractional volume), for computer simulation of the dynamic mechanical responses with a composite mechanical model.

at a given frequency (e.g., 10 Hz) estimated by using Fox's rule for the random mixture. T_{gi} and T_{gs} are the glass transition temperatures of pure polyisoprene (or polybutadiene) and polystyrene, respectively, at the given frequency.

When the stress is applied perpendicular to the interface, the composite mechanical model gives the complex compliance of the system at $T(J_s^*(T))$ as

$$J_s^*(T) = 1/E_s^*(T) = \frac{2}{D}\int_{-D/4}^{D/4} J^*(z;T)\,\mathrm{d}T \tag{13}$$

$$J^*(z;T) = J_i^*(T') \tag{14}$$

on the basis of additivity of the partial strain of each sublayer at $z \sim z + \mathrm{d}z$. If there is orientation distribution of the lamellar domains, then the modulus of the system $E^*(T)$ lies between $E^*_p(T)$ and $E^*_s(T)$ depending upon the average orientation. Here we use the approximation employed by KR:[25]

$$E'(T) = [E_p'(T)]^{\alpha}[E_s'(T)]^{1-\alpha} \tag{15}$$

$$E''(T) = [E_p''(T)]^{\alpha}[E_s''(T)]^{1-\alpha} \tag{16}$$

α is an orientation parameter ($0 \leq \alpha \leq 1$).

One can calculate $E'(T)$ and $E''(T)$ if one knows the spatial distribution of styrene and butadiene (or isoprene) units. We assume that

$$\begin{aligned} \phi_s(z) &= F_{21} \qquad \text{for } -D/4 \leq z \leq -\lambda/2 \\ &= \left(\frac{F_{11} - F_{21}}{2}\right) \sin\left(\frac{\pi Z}{\lambda}\right) + \left(\frac{F_{11} + F_{21}}{2}\right) \qquad \text{for } |z| = \lambda/2 \\ &= F_{11} \qquad \text{for } \lambda/2 \leq z \leq D/4 \end{aligned} \tag{17}$$

where $\phi_s(z)$ is the volume fraction of styrene segments in the sublayer located at z, from which $W_s(z)$ can be estimated. Here we consider a case where mixing of the unlike segments in each domain is symmetric: F_{11} and F_{21} are the volume fractions of styrene segments in "styrene-rich" domains and "butadiene-rich" or "isoprene-rich" domains, respectively.

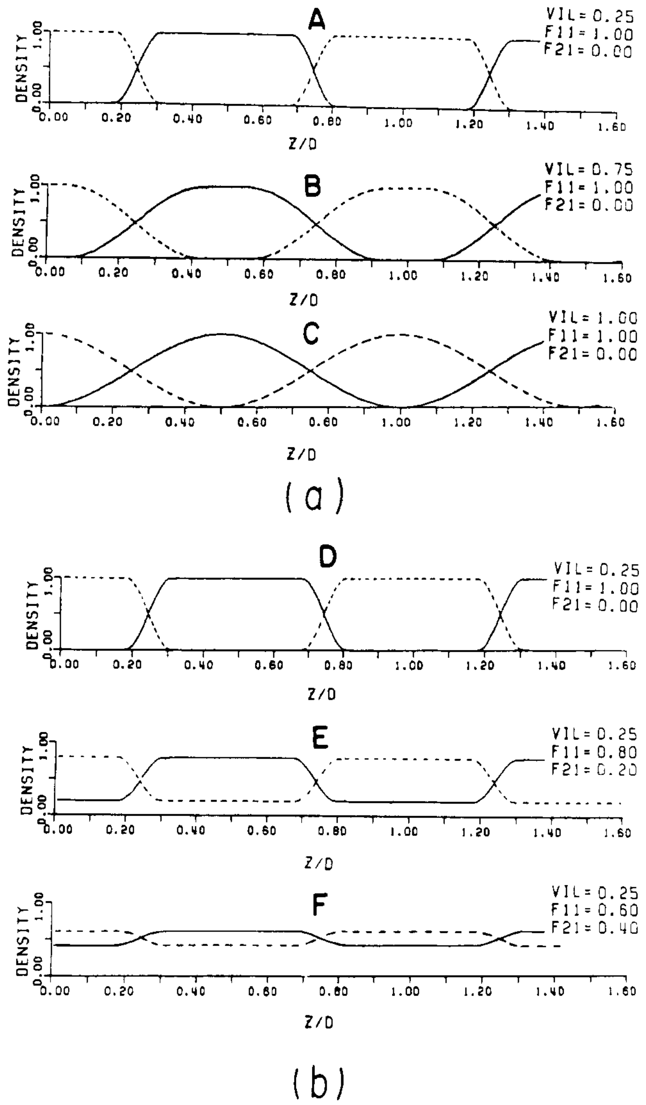

Figure 15. Spatial distribution of styrene and diene segments: (a) "domain-boundary mixing" increasing in the order of A to C, and (b) "mixing-in-domain" increasing in the order of D to F, V_{IL} being the volume fraction of the interphase and F_{11} and F_{21} being defined in Figure 14.

We will separately investigate the two effects on the mechanical response: (i) "domain-boundary mixing" effect (Figure 15a) and (ii) "mixing-in-domain" effect (Figure 15b). In Figure 15a the mixing in domain is negligible ($F_{11} = 1$ and $F_{21} = 0$), but the mixing occurs only in the interphase whose volume fraction $V_{IL} \equiv 2\lambda/D$ increases from 0.25 to 1 (designated as cases A–C, respectively). On the other hand, in Figure 15b the volume fraction of the interphase is kept constant, 0.25, but the mixing of the unlike segments in each domain progressibly increases in the order of D to F (F_{21} varying from 0, 0.2, and 0.4, respectively). The cases A and D are identical and correspond to the ideal block polymers S-1 and K-1.

Figure 16a shows the results of computer simulation of the "domain-boundary mixing" effect on the dynamic mechanical response. The effect gives (i) only slight shifts of the dispersion maxima of E'' corresponding to a "diene-rich" phase and a "styrene-rich" phase toward higher and lower temperatures, (ii) greater temperature dependence of E' and the higher level of E'' between the

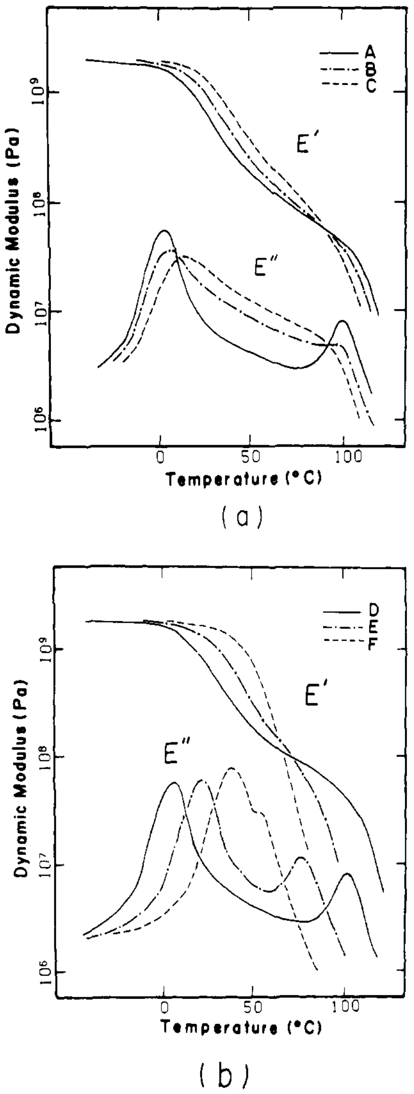

Figure 16. Computer-simulated dynamic mechanical responses at 10 Hz based upon the composite mechanical model. (a) and (b) are the results obtained for a spatial distribution of each segments as described in Figure 15, parts a and b, respectively.

two primary dispersion temperatures, and (iii) broadening of E'' peaks. This effect is exactly identical with what is observed for the S specimens. Thus molecular origin of the "domain-boundary relaxation" may now become clear.

It may be very important to note that there is a possibility of the structure being changed from A to C during the isochronal measurements. If this is the case, the dynamic response continuously shifts from A to C with temperature. This structure change may happen if the critical temperature (at which the microdomain structures is dissolved into homogenous mixture) is low as in the cases of low molecular weight block polymers and block polymers whose blocks have low thermodynamic interaction parameters χ_{12} (see eq 6).

Figure 16b shows the "mixing-in-domain" effect. The effect gives extensive shifts of the primary dispersions, eventually resulting in a single broad dispersion. In the intermediate mixing as in case E, the effect might appear similar to the effect of the domain-boundary mixing. A close observation of E'', however, reveals substantial differences between the two effects, especially in the amount of peak shift and shape of E'' between the two dispersion peaks. This effect is identical with what is found for the P and K series. In the P series the "mixing-in-domain" is asymmetric, giving rise to a large shift of the PB dispersion and a small shift of the PS dispersion. It is also important to consider a possibility of the state of the mixing in domain being changed from D to F during the isochronal measurements. If this is the case the dynamic mechanical response continuously shifts from D to F with temperature.

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Registry No. Butadiene–styrene copolymer, 9003-55-8; isoprene–styrene copolymer, 25038-32-8.

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