

Microdomain Structure and Dynamic Mechanical Properties of Polystyrene–Poly(*t*-butyl acrylate) Diblock Polymers

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ABSTRACT: Polystyrene–poly(*t*-butyl acrylate) diblock polymers (PS–PTBA) were prepared by sequential anionic polymerization with *s*-butyllithium as the initiator and tetrahydrofuran at -78°C as the solvent. The microdomain structures of these polymers observed by electron microscopy were two coexisting microphases consisting of PS blocks and PTBA blocks. Linear dynamic mechanical responses of the block polymers exhibited two primary dispersions typical of two-phase polymer systems. Primary dispersions of PTBA microdomains and of PS microdomains shifted respectively toward higher and lower temperatures with increasing PTBA fraction. These shifting cannot be explained as the effect of molecular weight of the block chains *i.e.*, the effect of the excess free volume of free chain ends. The shift of the PTBA primary dispersion was attributed to the excess free volume in the PTBA microdomains frozen-in during the solidification process and/or to the domain-boundary relaxation effect. The shift of the PS primary dispersion was considered to arise from domain-boundary relaxation effect, *i.e.*, the effect of dynamical interactions of the chains in the respective domains at the domain-boundary interphase on mechanical relaxation behavior. The greater the specific surface area of the interfaces or the volume fraction of the interphase, the larger is the shift of PS and PTBA primary dispersions.

KEY WORDS Polystyrene–Poly(*t*-butyl acrylate) Block Polymer / Microdomain Structure / Microphase Separation / Dynamic Mechanical Properties / Glass Transition Temperature / Transition Map / Excess Free Volume / Domain–Boundary Relaxation / Mechanical Relaxation /

Recently, a great deal of interest has been aroused in regard to the structure and properties of multi-component polymers or polymeric alloys. Block polymers are one of the most important class of *polymeric alloys*. In the equilibrium state, they usually form microdomain structures whose sizes correspond to the unperturbed chain dimensions of the block chains,^{1–10} when the constituent block chains are incompatible. The microdomain structure is responsible for the unique physical properties found in thermoplastic elastomers and rubber reinforced plastics.¹¹

In this paper, we report the microdomain structures and linear dynamic mechanical properties of polystyrene–poly(*t*-butyl acrylate) (PS–PTBA) di-

block polymers. This polymer may be unique in the following points. (i) Upon saponification, the PTBA block may be converted into a polyacid and the resultant block polymer becomes “amphiphilic,” consisting of hydrophilic and hydrophobic block chains; (ii) It is possible to obtain various degree of “amphiphilicity” by changing the degree of esterification or saponification. The degree of neutralization of acidic group can also be altered.

SYNTHESIS OF BLOCK POLYMERS

The monomer *t*-butyl acrylate (TBA) was prepared by esterification of acrylic acid with isobutene

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Table I. Characterization of block polymers of PS-PTBA

Sample code	$M_n \times 10^{-5}$ ^a total	$M_n \times 10^{-4}$ TBA	TBA content ^b	M_w/M_n ^c	Density ^d
			wt%		
STBA-1	3.4	2.4	7	1.21	1.054
STBA-2	1.1	3.1	28	1.23	1.046
STBA-3	2.1	5.9	28	1.46	1.045
STBA-4	2.3	14.3	62	1.57	1.038
PTBA	1.7	17.0	100	1.80	1.025

^a Determined by a membrane osmometer in toluene.

^b Determined by oxygen wt% from elemental analysis.

^c Determined by GPC.

^d Determined by the density gradient method at 25°C (methanol-ethylene glycol).

and was dried with calcium hydride and distilled *in vacuo*. TBA was further distilled through a glass tube coated with a sodium mirror and finally purified with a diglyme solution of triphenylmethyl-sodium. The details appeared in a paper of Kitano *et al.*¹²

A styrene monomer of commercial grade was washed in a 10 wt% sodium hydride, and distilled *in vacuo*. The monomer was then purified several times with a tetrahydrofuran (THF) solution of the sodium salt of benzophenone. The THF was dried with metal sodium and distilled *in vacuo*, then purified by the sodium salt of α -methyl styrene tetramer for one week.

The anionic block-polymerization of TBA and styrene was carried out at -78°C in a high vacuum line by the sequential method, in which styrene was first allowed to polymerize and TBA was added following the consumption of the styrene monomer. *s*-Butyllithium was used as the initiator and THF as the solvent. Since the rate of anionic polymerization of TBA is fast, a shower nozzle and a fritted glass filter were inserted in the polymerization apparatus. The monomer concentration was chosen below 0.2 mol l^{-1} for ensuring homogeneous polymerization. The polymerization of TBA was carried out for about 30 min and terminated with methanol. The polymerization products were poured into a large volume of a methanol-water mixture, and the resulting precipitate was dried *in vacuo* for at least one week before use.

Table I summarizes the characteristics of the obtained PS-PTBA diblock polymers (coded STBA-1 to 4) and PTBA homopolymers.

MICRODOMAIN STRUCTURE

STBA block polymers were cast from 10 wt% toluene solutions. The films were embedded in epoxy resin and sectioned normal to the surface by LKB ultramicrotome to a thickness of several ten nanometers. The morphology of the microdomain structure was investigated by transmission electron microscopy without using a staining agent such as osmium tetroxide.

Figure 1 shows typical electron micrographs of unstained ultrathin-sectioned specimens for (a) STBA-3 and (b) STBA-4. The bright and dark domains in the micrographs were confirmed to consist of PS and PTBA block chains, respectively by solubilization experiment. In this experiment, it was found that homopolystyrene when mixed with STBA-4, came to be solubilized into the domains consisting of PS block chains, giving rise first to thickened bright lamellar domains and eventually to dark domain dispersed in the matrix of white domains as the fraction of homopolystyrene increased.

Block polymers STBA-1 to 3 formed spherical microdomains of PTBA block chains in the matrix of PS block chains, while STBA-4 formed alternating lamellar microdomains consisting of PS block chains and PTBA chains. The average radius of the spherical domains for STBA-3 was about 20 nm, and the average lamellar identity period for STBA-4 was about 100 nm, whose domain size was about equal to that of a polystyrene-polyisoprene (PS-PI) diblock polymer. The average radius of PI spheres for the PS-PI diblock polymer having a PI block

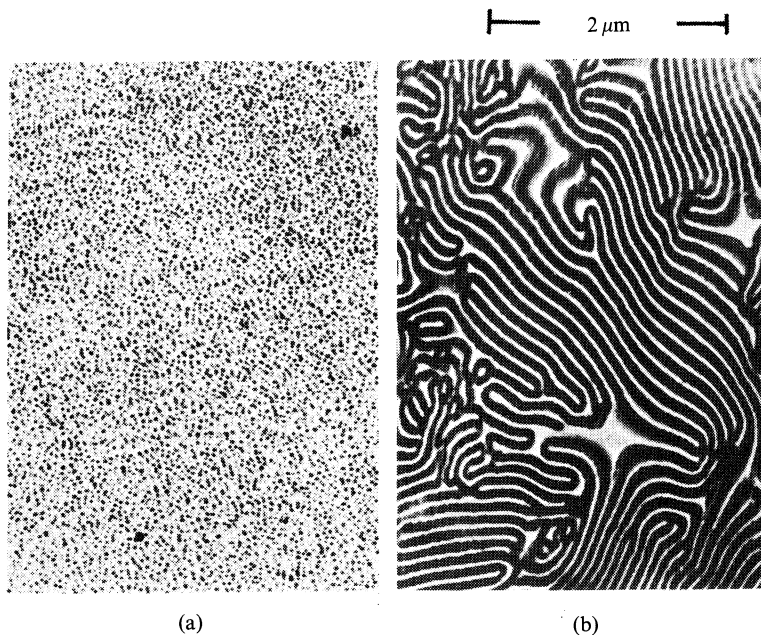


Figure 1. Transmission electron micrographs of unstained, ultrathin-sectioned specimens of STBA-3(a) and STBA-4(b).

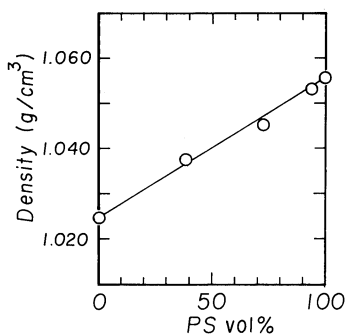


Figure 2. Densities of homo and block polymers as a function of volume percent of polystyrene block in the block polymer.

chain with a number-average molecular weight $M_n = 5.9 \times 10^4$ was about 20 nm, and the lamellar identity period for the PS-PI diblock polymer of a number-average molecular weight of 2.3×10^5 was about 90 nm.

Figure 2 shows the density of the block polymers as a function of the volume percent of the PS component. It can be seen that the density ρ of a block polymer is approximately equal to the volume average of those of the corresponding homo-

polymers (the straight line in Figure 2), *i.e.*,

$$\rho = \rho_1 \phi_1 + \rho_2 \phi_2 \quad (1)$$

where ρ_i and ϕ_i are the density of pure *i*-polymer and the volume fraction of domains composed of *i*-polymer, respectively. This suggests that the PS and PTBA domains are almost pure, containing little or no PTBA and PS segments, respectively, as is the case for block polymer of strongly segregating components.¹⁻¹⁰

LINEAR DYNAMIC MECHANICAL RESPONSE

Figure 3 shows the temperature-dependence of isochronal storage modulus (E') and loss tensile modulus (E'') at 10 Hz for block polymers STBA-1, 2, and 4. The specimens were cast from 10 wt% toluene solutions and dried under vacuum for several days until their weights became constant. The as-cast films were further annealed for 2 h at 90°C prior to the dynamic mechanical test.

In Figure 3, each block polymer shows two primary dispersions, indicating a two-phase structure: one at about 50°C corresponding to the primary dispersion of PTBA microdomains and the

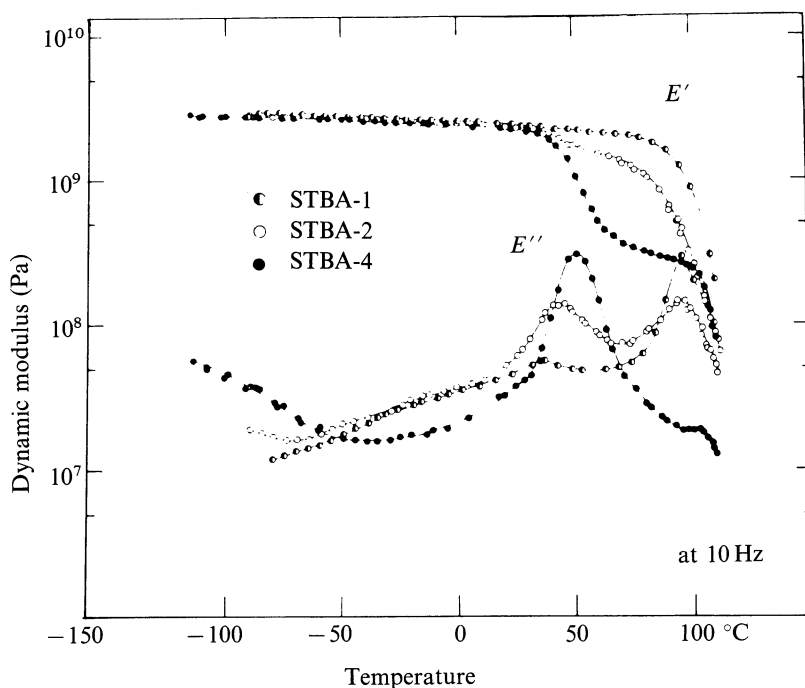


Figure 3. Temperature-dependence of isochronal storage modulus (E') and loss tensile modulus (E'') at 10 Hz for block polymers STBA-1, 2, and 4.

other at about 100°C corresponding to the primary dispersion of PS microdomains. The dispersion shifts with composition of the block polymer, *i.e.*, the peak of E'' for the PTBA dispersion and that for the PS dispersion shift toward a higher and a lower temperature, respectively with increasing PTBA fraction.

The matrix phases in STBA-1 and 2 are comprised of PS block chains. Consequently, these polymers have high E' at temperatures between the above-mentioned two primary dispersions. The area under the peak of E'' for the PTBA domain increased and that for the PS domain decreased as the fraction of PTBA increased.

The frequency and temperature dependence of the two primary dispersions of a block polymer may be illustrated by contour maps of the loss tangent. Figures 4 to 6 show the contour plots of the loss tangent $\tan \delta = E''/E'$ against $1/T$ (K^{-1}) and the logarithmus of frequency ν for block polymers STBA-1, 3, and 4, respectively. In these figures, the loci of the loss tangent maxima for the PTBA domains are shown by dotted lines. The maxima of

the loss tangent for the PS domains appear at the bottom left corner of each contour map.

These contour maps clearly indicate that the block polymers are “*thermorheologically complex*.” The simple time-temperature superposition principle cannot be applied to the block polymers. The dispersion of each domain has a different time and temperature dependence and a different apparent activation energy. With increasing PTBA fraction, the loss tangent of the primary dispersion of PTBA domains increases, and the locus of loss tangent maxima shifts toward higher temperature and lower frequency as in Figure 3. The loss tangent of the primary dispersion of PS domains decreases with increasing PTBA fraction.

SHIFT OF PRIMARY DISPERSIONS WITH COMPOSITION

Figure 7 shows the loss tangents of block polymers STBA-1, 3, and 4 at three different frequencies as a function of temperature. At each frequency, it is clear that the temperature correspond-

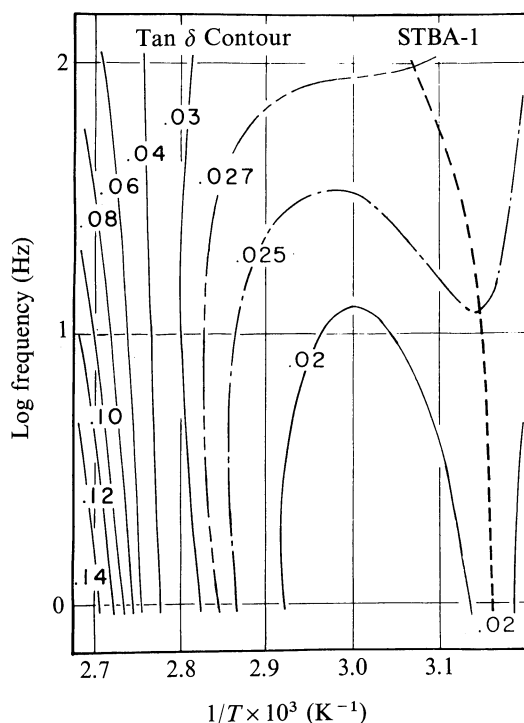


Figure 4. Contour plot of the loss tangent $\tan \delta = E''/E'$ against $1/T$ (K^{-1}) and logarithms of frequency ν for block polymer STBA-1.

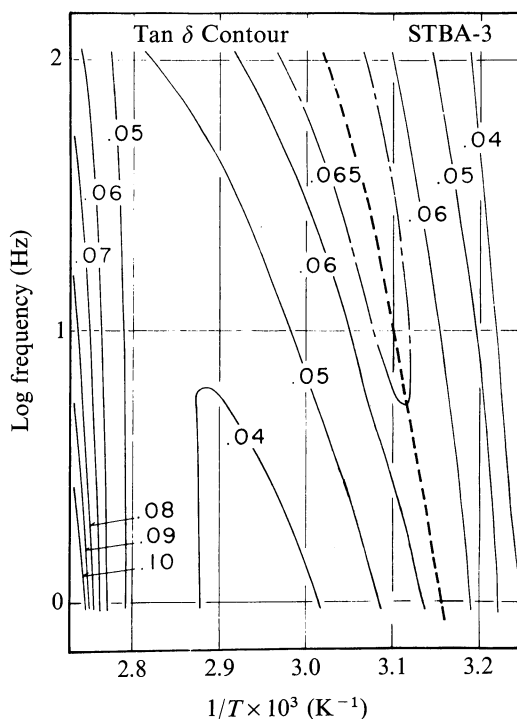


Figure 5. Contour plot of the loss tangent $\tan \delta = E''/E'$ against $1/T$ (K^{-1}) and $\log \nu$ for block polymer STBA-3.

ing to the maximum loss tangent for the PTBA domains shifts toward lower temperature with decreasing PTBA fraction.

This temperature decrease is much larger than that which may be attributed to the excess free volume of chain ends,^{13,14} *i.e.*,

$$T_g = T_{g\infty} - K/M \quad (2)$$

where T_g and $T_{g\infty}$ are the glass transition temperature of PTBA having molecular weight M and infinitely large molecular weight, respectively. When $K = 1.1 \times 10^5$ degree g mol⁻¹, one half of the value reported for poly(methyl methacrylate) homopolymer,¹⁵ K/M equals 4.6, 1.9 and 0.8 for STBA-1, 3, and 4, respectively. This choice for the K value was made because a PTBA block has only one free end. Thus a temperature-decrease as large as 3.8°C with variation on copolymer composition can be expected. The apparent glass transition temperatures measured from the peak-temperature of loss tangent were 38, 42, and 50°C at 1 Hz, 42, 47,

and 55°C at 10 Hz, 50, 55, and 62°C at 100 Hz for STBA-1, 3, and 4, respectively. Thus, the observed temperature decrease is much greater than that expected from the molecular weight dependence of the glass transition temperature.

Frozen-in Excess Free Volume

The shift of the PTBA primary dispersion temperature may be attributed to one or both of following mechanisms: (i) "excess free volume" incorporated into the PTBA domains during the solidification process ("frozen-in excess free volume"), and (ii) a mixing of unlike segments in the interphase between the two coexisting domains ("domain-boundary relaxation"). First, the effect of "frozen-in excess free volume" is discussed. During the solidification process of a block polymer caused by lowering the temperature or solvent evaporation, the domain morphology (*i.e.*, the size and shape of the domain) should be fixed when the temperature is below the T_g of the polystyrene microdomains or

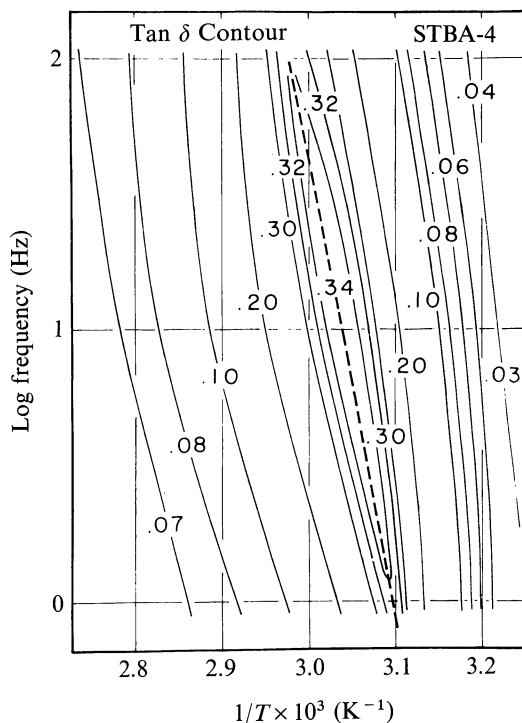


Figure 6. Contour plot of the loss tangent $\tan \delta = E''/E'$ against $1/T$ (K^{-1}) and $\log \nu$ for block polymer STBA-4.

when the solvent concentration is sufficiently low to permit the T_g of the polystyrene solution to reach an ambient temperature. When the solvent is further evaporated or the temperature is further lowered, each domain tends to shrink so as to take on a density equal to that of the corresponding homopolymer. Such shrinkage may easily take place when the PTBA block chains form a continuous matrix throughout which PS domains are dispersed, but, not easily so when the PTBA domains are dispersed in the matrix of PS block chains so that there is an excess free volume in the dispersed PTBA domains.

Since STBA-4 has alternating lamellar microdomains, the PTBA domains are more or less continuous. Therefore, the fraction of the excess free volume is small compared with that for STBA-1 and STBA-3. On the other hand, STBA-1 and 3 have the spherical domains of PTBA block chains dispersed in the matrix of the PS block chains. Hence, the PTBA spheres may have an appreciable amount of

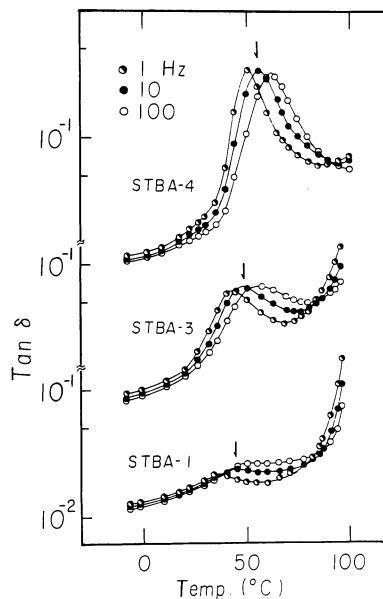


Figure 7. Loss tangent of block polymers STBA-1, 3, and 4 as a function of temperature at three different frequencies.

excess free volume so that the primary dispersion temperature is shifted toward a temperature lower than that of STBA-4. The difference in dispersion temperature between STBA-1 and 3 may be accounted for in consideration of the molecular weight effect.^{13,14} Thus, if corrected for the molecular weight effect according to eq 2, the apparent glass transition temperatures of the PTBA domains for STBA-1, 3, and 4 are, respectively, 43, 44, and 50°C at 1 Hz, 47, 49, and 56°C at 10 Hz, and 55, 57, and 63°C at 100 Hz. Thus, the difference in the dispersion temperature between STBA-1 and 3 is negligible compared with that between STBA-3 and 4.

Domain-Boundary Relaxation

Now the second effect, *i.e.*, the "domain-boundary relaxation" effect will be considered. This effect may involve the shift of the primary dispersion of the PS domain as well as that of the PTBA domain. The primary dispersions of PS and STBA domains may be influenced by dynamical interactions of the chains in the soft and hard microphases at the interphase. Thus, the *chain connectivity* between PS and PTBA blocks may cause *cooperative molecular dynamics*. The molecular motions of the

PTBA blocks generally affect some of the molecular motion of the PS blocks, probably producing an excess free volume in the PS domains. This cooperative molecular dynamics also causes the shift of the PTBA dispersion toward higher temperature for the following reason.

The chain connection between the two blocks prevents the PS and PTBA chains from separating in macroscopic dimension but rather confines the separation to their molecular dimensions, resulting in a microphase separation of submicroscopic scale dimensions. The relationship between the molecular dimension and the size of the microphase-separated domain has already been clarified both experimentally^{9,10,16} and theoretically.¹⁻⁸ Owing to this microphase separation, the block polymers generally have an interfacial area, a surface-to-volume ratio (S/V), and a volume fraction of the interphase, all of which are much larger than those of the interphase in polymer blend systems. This condition enhances dynamical interactions between the chains at the interphase of the domains. Thus, the chain connection between PS and PTBA is important also in this respect. The larger the values S/V , the larger is the dynamical interactions and hence the larger the shift of the respective primary dispersions (PTBA and PS dispersions are shifted toward higher and lower temperatures, respectively). The dynamical interactions between the chains in the respective domains may exist even in systems having sharp interphases.¹⁷ However, the diffuse interphase further enhances the dynamical interactions between the two blocks. In some of our papers, we have defined "domain-boundary relaxation"^{18,19} (sometimes "grain-boundary relaxation"²⁰) as a general effect of the dynamical interactions between chains at the interphase (sharp or diffuse) on the mechanical relaxation behavior.

It has been shown both experimentally and theoretically that, in the strong segregation limit, two block chains are mixed only in a narrow interfacial region¹⁻¹⁰ whose "characteristic thickness" t is about 2 nm for polystyrene-polyisoprene and polystyrene-polybutadiene block polymers.^{9,10,21} Here t is defined by the equation

$$t = 1 / |d\bar{\rho}(z)/dz|_{\rho=1/2} \quad (3)$$

and is roughly one half of the full thickness of the interphase. In eq 3, $\bar{\rho}(z)$ is the relative electron density distribution in the direction normal to the

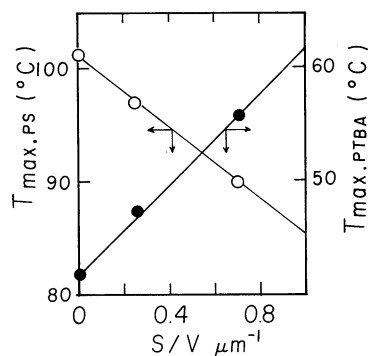


Figure 8. PS dispersion temperature $T_{\text{max,PS}}$ (open circles) and PTBA dispersion temperature $T_{\text{max,PTBA}}$ (solid circles) as a function of the surface-to-volume ratio S/V (10 Hz).

interface (z -direction) and varies from 0 to 1 when going from one domain to another. The mixing of unlike segments and the gradual variation in segment composition with z at the interphase enhances the dynamical interactions such that the dispersion temperature gradually changes from that of the pure PTBA phase to that of the pure PS phase when the interphase is traversed from the PTBA to the PS domain.^{18,19,22-24} This effect, defined as a "domain-boundary mixing" effect in one of our papers,¹⁹ tends to displace the primary dispersion of PTBA domains toward higher temperature and that of PS domain toward lower temperature.^{18,19,24}

Figure 8 shows that the PS dispersion temperature $T_{\text{max,PS}}$ (open circles) and the PTBA dispersion temperature $T_{\text{max,PTBA}}$ (solid circles) vary linearly with the surface-to-volume ratio S/V estimated from the electron micrographs of the samples. This is consistent with the findings of Bares.²⁵ Since the characteristic interfacial thicknesses t of block polymers are about the same^{9,10,21} it may be concluded that the two dispersion temperatures shift linearly with the "interfacial volume fraction."

We conclude in summary that the shift of the PS dispersion temperature is due to the "domain-boundary relaxation effect" and that the shift of the PTBA dispersion temperature is due to the domain-boundary relaxation effect and/or the "frozen-in excess free volume" of PTBA domains, the excess free volume of chain ends playing only a minor role.

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