Mechanical Properties of SBS Block Copolymers. I. Effect of Structure and Selective Solvent Casting on Dynamic Viscoelasticity

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Synopsis

Thermomechanical spectra of poly(styrene–*b*–butadiene) copolymers were obtained at 110 Hz and between −120 and 120°C. The molecular parameters studied were the styrene content (35%–45%) and, at constant composition (39% styrene), the length of the copolymer blocks. The films studied were cast from selective solvents, methyl ethyl ketone (MEK), cyclohexane, and toluene, a common solvent. MEK- and toluene-cast films were quite similar in their dynamic viscoelasticity and more rigid than the corresponding cyclohexane-cast films. Solvent differentiation was more evident at the higher styrene content. No evidence of a relaxation due to a mixed interphase was obtained. At constant composition a morphological transformation takes place when the length of the blocks exceeds a certain limit; this affected the dynamic modulus of the cyclohexane-cast films. The results were analyzed using two-phase models proposed by the composite theory. For some samples results on the effect of annealing and prestretching are also reported.

INTRODUCTION

A considerable amount of research activity has been directed in the last decade to the elucidation of the structure–property relationships of SBS copolymers, where the elastomeric polybutadiene segment (B) is reinforced by the glassy polystyrene block (S). Much of this work up to 1971 has been summarized by Dawkins.[1] Subsequent investigations in this area dealt with the effect of terminal chains on their dynamic mechanical properties,[2-4] their viscoelastic and dielectric behavior,[5] and the use of various optical techniques to elucidate their deformation mechanism.[6] The realization that the mixed interphase between the blocks plays a significant role in determining their mechanical properties stimulated further experimental and theoretical activity.[7-12]

The present experimental study examines the dynamic viscoelastic behavior of a series of SBS block copolymers at various styrene compositions, as a function of block length at constant composition, and cast from different solvents. Previous studies[9,13,14] indicated that the morphology of these two-phase systems is significantly affected by the selective solvent power of cyclohexane for polybutadiene, the methyl ethyl ketone for polystyrene, and the mutual solubility of the PS and PB blocks in toluene. Solution casting, in addition to a morphological differentiation, ensures under suitable conditions absence of residual stresses in the polymer film produced. In some samples the effect of annealing and mechanical pretreatment was also examined.

EXPERIMENTAL

Materials and Specimens Preparation

The SBS block copolymers were experimental products prepared by the anionic "living polymer" techniques[15] at the Research and Development Div., Polymer Corp., Sarnia, Ontario, Canada. Their composition and structure is given in Table I. The styrene content was confirmed by NMR analysis[16] which also gave the content of the polybutadiene 1,4- and 1,2-isomers. A Varian A60 NMR spectrometer was used and a 5% polymer solution in CCl_4. The NMR spectra also indicated that the synthesis was successful and no random or "transitional" random-block copolymers were formed.[16]

Films were prepared from 4% solutions in purified toluene, cyclohexane, and methyl ethyl ketone by casting over a mercury surface. The Teflon-coated pans containing the solutions were covered and left for evaporation to take place slowly (approx. 2 ml/hr) at room temperature. The dry films were subsequently vacuum dried for a week at room temperature. In the following discussion the samples will be designated as in Table I and the solvents used by M (methyl ethyl ketone, MEK), T (toluene), and C (cyclohexane); e.g., B(T) will refer to a triblock 14S–44B–14S cast from toluene.

Thermomechanical Testing

Isochronal measurements at 110 Hz were carried out between -120 and $120°C$ with the Rheovibron viscoelastometer Model DDV-II (Toyo-Baldwin, Co. Ltd., Tokyo, Japan). The heating rate was approximately $1°C/min$, and specimens dimensions were $3.0 \times 0.2 \times 0.02$ cm^3. During the measurements a flow of precooled nitrogen prevented moisture condensation in the chamber and oxidation of the samples at elevated temperatures. In calculating $|E^*|$, the correction due to clamp extension was applied.

RESULTS AND DISCUSSION

Effect of Solvent

The following qualitative remarks are based on the visual film inspection which were, in general, transparent. Film A(M) was nonflexible and had a "frosty" texture. During the transition from A(M) to E(M) the frosty texture goes through a maximum and the glassy character increases. Films A(T) to E(T) were highly transparent and had a smooth surface texture and an increasing rigidity from A to E. Films A(C) and B(C) were also highly transparent and more elastic than the corresponding samples cast from MEK and toluene. In film C(C) and more so in D(C), the existence of a two-phase system became apparent and their flexibility decreased. In film E(C), phase discontinuity was more evident and the film had a leather-like feel and a slightly rough surface.

Morphological studies of such copolymers[1,17] demonstrate that in this composition range when a nonselective solvent (toluene) is used, the microphase structure consists of alternating lamellae (of pure components) parallel to the film surface. The use of selective solvents MEK (for PS) and cyclohexane (for PB) gives in the first case a more irregular lamellar structure. In the latter case the PS domains take the form of rods or spheres in a PB matrix.

TABLE I
Composition and Microstructure of Triblock Copolymers

| Polymer sample | Styrene, wt-% | | PB isomers 1,4-1,2, wt-% | Block sequence length $\times 10^{-3}$, g/mol | PS (comp.) Φ_{PS}[a] | PS (pure) Φ'_{PS}[b] | PS-PB (mix. int.) Φ_I |
	Feed ratio	NMR					
A	35	35.9	56.4-7.7	16S-60B-16S	0.319	0.239	0.103
B	39	40.5	51.2-8.3	14S-44B-14S	0.358	0.257	0.131
C	39	40.9	50.1-9.0	17S-54B-17S	0.356	0.273	0.107
D	39	41.7	50.1-8.2	20S-62B-20S	0.361	0.289	0.093
E	45	46.2	48.6-5.2	20S-50B-20S	0.412	0.330	0.106

[a] PS volume fraction calculated from the overall copolymer composition.
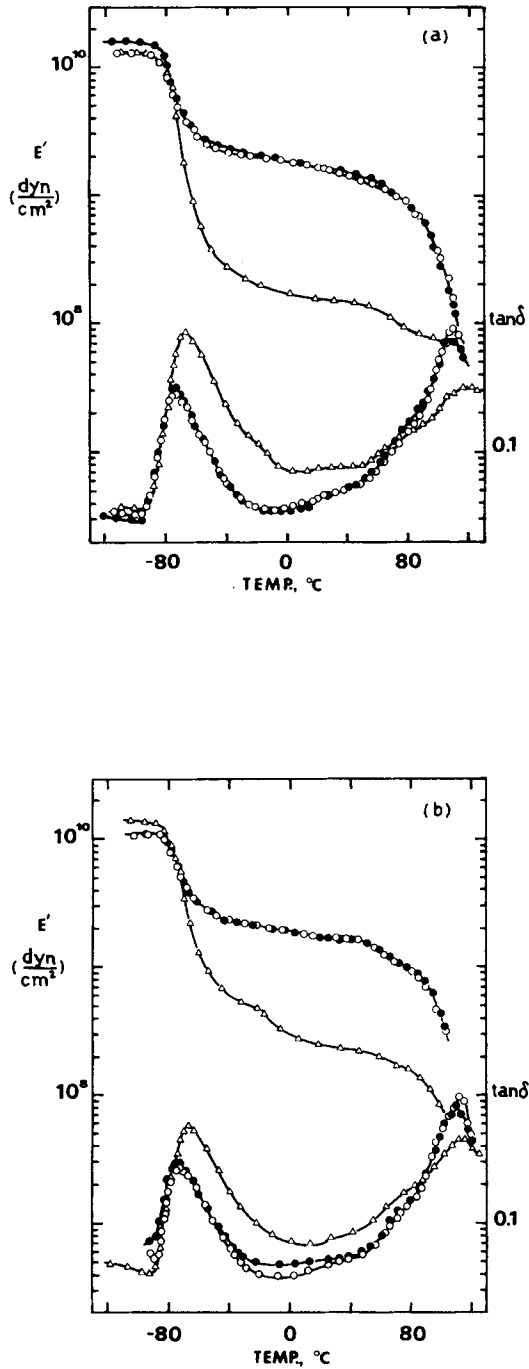[b] Pure PS domain volume fraction taking into account interphase formation, Ref. 7.

Fig. 1. Effect of solvent casting on the thermomechanical spectra of polymer samples: (O) from MEK; (●) from toluene; (△) from cyclohexane; (a) sample A; (b) sample B; (c) sample D; (d) sample E.
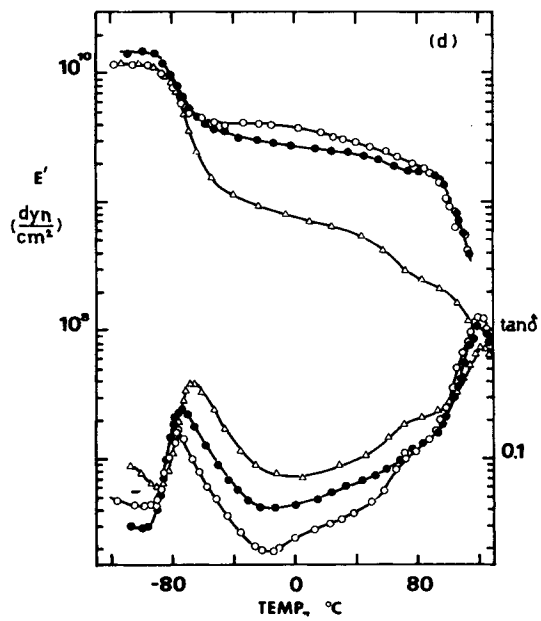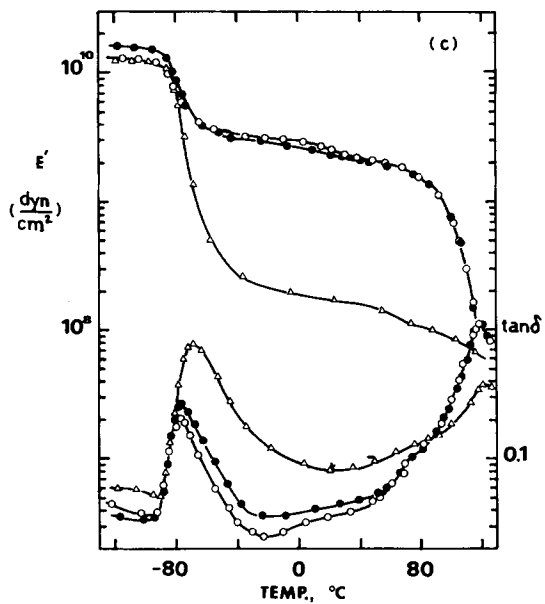
Fig. 1. (*Continued from previous page.*)

In Figures 1(a) to 1(d) and Table II, the experimental results on the dynamic mechanical properties under isochronal conditions are summarized. In general, solvent differentiation is more evident at the higher styrene contents and at constant composition as the length of the blocks increases (samples B and D). Most significant differences are indicated by the cyclohexane-cast films. The polybutadiene relaxation is shifted to a higher temperature (see Table II), and the E' value in the plateau region is about an order of magnitude less than in the MEK- and toluene-cast films. It is proposed that the $T_{g,PB}$ shift is attributed to an antiplasticization effect caused by a stronger PS–PB interaction. This suggestion is supported by the fact that at longer block lengths where the volume fraction of the mixed phase Φ_I is smaller (see Table I), the $T_{g,PB}$ shift is also reduced. Also, recent experimental results[17(a)] on the effect of repeated shearing on the dynamic viscoelasticity of HIPS shows that, as the degree of cycling increases, the $T_{g,PB}$ shifts to higher temperatures. At the higher PS contents (sample E), a differentiation between E(T) and E(M) is also evident, the relative E' values changing in the order E(M) > E(T) > E(C). At this composition the hard domains form interconnections, giving stiffer MEK-cast films.

Effect of Composition and Structure

The previous data were redrawn to demonstrate the effect of the above molecular parameters (Figs. 2 and 3). The mechanical spectra of films cast from MEK and toluene were essentially the same, so only those cast from MEK are compared. For the latter (Fig. 2) at constant overall $\overline{M}_n$, the storage modulus E' increases with the styrene content [samples A(M) and E(M)]. At constant composition, E' increases with the PS block length [samples B(M) and D(M)]. This explains why A(M) and B(M) have the same modulus at room temperature even though B has a higher styrene content. Inspection of Table II (E'' values) shows that both relaxations $T_{g,PS}$ and to a lesser extent $T_{g,PB}$ depend on the block length. However, the relationship[18]

$$T_g = T_{g\infty} - K_g M^{-1} \tag{1}$$

with $K_g = 20 \times 10^4$ and M the MW of the PS endblock, had limited success. The ΔT_g predicted for polymers B and D is 4.3°C. This is not verified by B(T) and D(T), where the ΔT_g determined was 10°C. This is possibly connected with the fact that in the B(M)–D(M) system the PS domains have a more distinct character than in the samples cast from a common solvent. It has been reported[13] that casting an SBS triblock (30% PS) from selective solvents (MEK, ethyl acetate) causes an additional relaxation to appear at around 10°C. On the basis of the $\Delta H^{\ddagger}$ reported, this would appear at 10°C. No such peak was observed. A shoulder was detected around 70°C. Examination of the mechanical spectra reported in the literature[19] suggests that it can be attributed to the β relaxation of the PS domain. For the cyclohexane-cast samples, an anomaly in the modulus–composition trend is observed at the 39% styrene composition (B to D). The C(M) and D(M) E' values constitute a minimum, in contrast to the other series, cast from toluene and MEK. This anomaly is undoubtedly associated with the morphological changes which take place at this composition and solvent. It is suggested that at these compositions [C(C) and D(C)], the distribution of particle sizes (PS domains) changes from monodisperse to poly-

TABLE II
Temperatures of Relaxations Maxima Observed (°C)

Polymer sample	Methyl ethyl ketone (M)				Toluene (T)				Cyclohexane (C)			
	$T_{g,PB}$		$T_{g,PS}$		$T_{g,PB}$		$T_{g,PS}$		$T_{g,PB}$		$T_{g,PS}$	
	tan δ	E''	tan δ	E''	tan δ	E''	tan δ	E''	tan δ	E''	tan δ	E''
A	−74	−78	109	103	−75	−77	109	90	−67	−75	110	95
B	−72	−76	96	96	−74	−78	110	94	−66	−72	110	—a
C	—b	—b	110	99	—b	—b	—	105	—a	—b	—	114
D	−77	−80	118	99	−76	−78	119	104	−69	−78	120	—
E	−77	−80	119	105	−74	−79	121	110	−68	−72	121	112
					Annealed Samples							
A					−72	−77	94	81	−72	−76	109	96
D					−74	−77	117	107	−72	−78	121	108
E					−73	−76	118	102				
					Stretched and Relaxedc Samples							
A	−72	−75	112	92					−67	−75	—	—

a Could not accurately locate.
b Not measured.
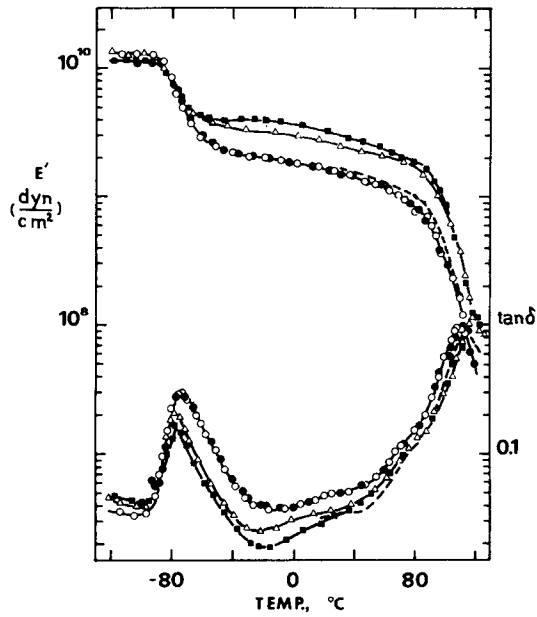c A(M), λ (permanent set) = 1.33; A(C), λ (permanent set) = 1.12.

Fig. 2. Effect of copolymer structure on thermomechanical spectra of MEK-cast films: (O) sample A; (●) sample B; (- -) sample C; (△) sample D; (■) sample E.
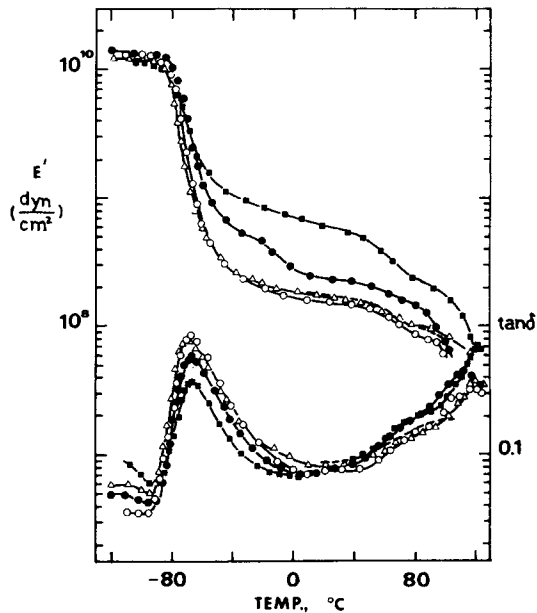

Fig. 3. Effect of copolymer structure on thermomechanical spectra of cyclohexane-cast films: (O) sample A; (●) sample B; (- -) sample C; (△) sample D; (■) sample E.

disperse.   Mixtures of different particle sizes can pack more densely than monodisperse particles.   A high packing fraction Φ_m (see below), results leading to a lower modulus.[20]   This is only a tentative explanation since direct morphological evidence is lacking at present.   This change could be a result of a

sphere-to-lamellar morphological transformation predicted on the basis of Meier's theory.[21] In this respect it should be pointed out that this change is taking place at a constant ratio of block molecular weights to PS composition. What does change from B to D is the total $\overline{M}_n$ of the triblock. This would change the kinetic barrier (diffusional transport) to these transformations, and indeed it is recognized[10] that thermodynamics alone cannot establish *a priori* the morphology of these systems. In Table I the volume fraction of the PS domains and of the mixed interphase Φ_I are reported assuming the validity of Kaelble's model.[7] It is seen that for the same composition (B to D) Φ'_{PS} is changing while Φ_{PS} (based on overall composition) is essentially constant. The Φ_I is also changing (decreasing) with increasing block length. These changes would influence the morphology and the modulus of these samples. The fact it does not do so in the case of MEK- and toluene-cast films indicates that the selective solvation by the cyclohexane is a more important parameter.

The modulus–composition data were analyzed on the basis of the available for such systems composite theory.[20] The results are summarized in Figure 4. These materials fall into two groups, the MEK-, toluene-, and the cyclohexane-cast films. The former give moduli values E' which could be best correlated with the generalized Halpin–Tsai equation for an inverted system (rubber in a PS
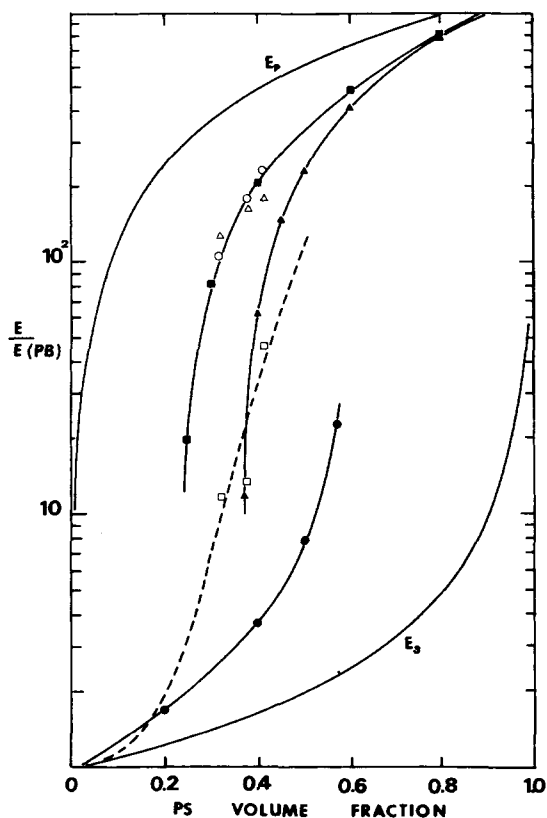

Fig. 4. Comparison of calculated and experimental E (copolymer)/E(PB) values at 35°C: (O) MEK; (△) toluene; and (□) cyclohexane-cast film; (-●-) eq. (2) with a rubber matrix, $\Phi_m = 0.60$; (-■-) eq. (2) with a PS matrix, $\Phi'_m = 0.77$; (-▲-) $\Phi'_m = 0.64$; (- -) eq. (3) with $n = 4.0$. (At 39% styrene, data of sample D are used.)

matrix).   The equation has the form

$$E/E_2 = (1 - B\Psi\Phi_2)/(1 + AB\Phi_2) \qquad (2)$$

with $A = (8 - 10\nu_1)/(7 - 5\nu_1)$, $B = [(E_1/E_2) - 1]/[(E_1/E_2) + A]$ and $\Psi = 1 + [(1 - \Phi'_m)(\Phi_2/\Phi'_m)]$, where E, E_1, E_2 are the moduli (E') of the composite, the rigid, and the soft phase, respectively; ν_1 = Poisson ratio of the rigid phase; Φ_2 = volume fraction of the soft phase; and Φ'_m = maximum packing fraction of the soft phase dispersed in the rigid matrix.   The pure component data used were[22] $E_1 = 16,666$ kg/cm^2, $E_2 = 13.6$ kg/cm^2, and $\nu_1 = 0.33$, and the best fit was obtained with $\Phi'_m = 0.77$.   This would indicate a close packing of rubbery spheres in a rigid matrix ($\Phi'_m = 0.740$).   The same type of eq. (2) using a model with a dispersed rigid phase in a rubbery matrix gave unsatisfactory results (see Fig. 4).   The results for cyclohexane-cast films could be correlated using eq. (2) only for the D and E compositions and $\Phi'_m = 0.637$.   This characterizes an inverted system with random close packing of the rubbery spheres.

For this system the relationship proposed by Coran and Patel[23] was also applied:

$$E = \Phi_1^n(n\Phi_2 + 1)(E_p - E_s) + E_s \qquad (3)$$

where subscripts 1 and 2 refer to hard and soft phases, respectively; E_p and E_s refer to the parallel and series connection of the phases, respectively; and n is a fitting parameter taken as 4.0 (instead of the 4.5 proposed[23]).   This equation predicts the moduli of the above system for the lower styrene compositions as well, however, the significance of the numerical value of n with regard to morphology is uncertain.   To conclude, the mechanics models that correlate the data best predict that the morphology of the MEK- and toluene-cast films is that of an inverted system at all the PS compositions, while for the cyclohexane system
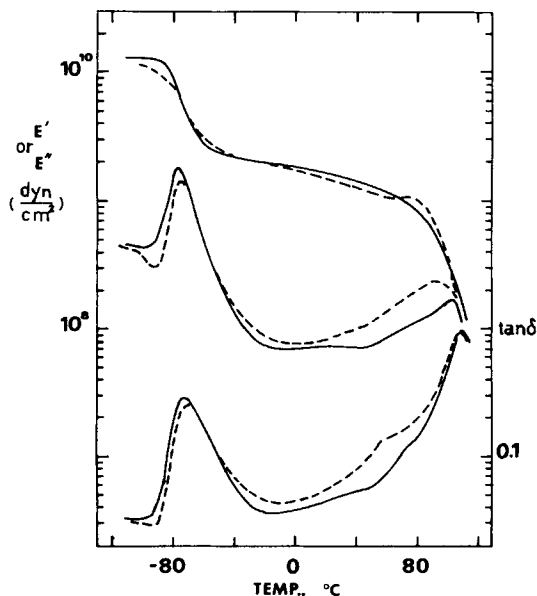

Fig. 5. Effect of prestretching on thermomechanical spectra of sample A(M):   (—) unstretched; (- -) prestretched ($\lambda_{\text{permanent set}} = 1.33$).

this model is applicable only at the higher styrene compositions. The above analysis points to the fact that mechanics models cannot reliably predict the morphological features of such two-phase systems since the results are not in agreement with the morphological features revealed by the electron microscopy.[1,17]

A limited study was also made on the effect of stretching and annealing. The stretched samples ($\lambda_{max} = 7.0$) were allowed to relax at room temperature and the mechanical spectra obtained (see Fig. 5 and Table II). The results for film A(M) indicate some disruption of the PS network (decrease in E') and an increase of the lossy region. This is attributed to an increase in the mixed interphase which could be the result of some PS domain disruption during the cold drawing of the material. There is experimental evidence[17(a)] that repeated reprocessing of HIPS with its attendant PS–PB entanglements breakdown and phase mixing gives rise to a weak relaxation in the same region as given in Figure 5. Comparison of the mechanical spectra of annealed (1 hr at 100°C, in nitrogen atmosphere) and nonannealed A(T) and E(T) samples (not reported here) show no significant differences. The E' of the A(T) annealed was decreased, and the $T_{g,PS}$ was displaced to lower temperatures. Heating at higher temperatures can conceivably increase the amount of mixed interphase associated with the PS domains.

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