3706 *Macromolecules* **1992,** *25,* 3706-3714

Rheological Behavior of Binary Mixtures of a Block Copolymer and a Homopolymer

Deog Man Baek and Chang Dae Han*

Department of Chemical Engineering, Polytechnic University, Brooklyn, New York 11201

Received October 15, 1991; Revised Manuscript Received March 11, 1992

ABSTRACT: The rheological behavior of binary mixtures of a block copolymer and a homopolymer was studied. For the study, polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymers having molecular weights of 3900S-93300I-3900S and 7400S-99000I-7400S, respectively, and a series of homopolymer polystyrenes (PS) having molecular weights of 1000, 1300, 1500, 2000, and 3000, respectively, were synthesized via anionic polymerization, and various mixtures were prepared. For each block copolymer/homopolymer system, a phase diagram was constructed using the combined results of dynamic viscoelastic measurements and turbidity measurements. Rheological properties were measured for (a) single-phase mixtures (H), (b) microphase-separated block copolymer (M_1) into which added homopolymer PS is solubilized, (c) two-phase mixtures consisting of microphase-separated block copolymer (M_1) into which added homopolymer is solubilized and macrophase-separated homopolymer PS (L_2), and (d) two-phase mixtures consisting of disordered block copolymer (L_1) and macrophase-separated homopolymer PS (L_2). The rheological properties measured were interpreted using information on the morphological state of the materials studied.

Introduction

The morphology of microdomains in a block copolymer depends, among other factors, upon the block length ratio, total molecular weight, and temperature. A block copolymer with microdomains (also referred to as a microphase-separated block copolymer) can be made homogeneous by raising the temperature above a certain critical value, referred to as the order-disorder transition temperature (T_r) (or microphase-separation transition temperature),[1-6] or by adding a low molecular weight homopolymer.[7-13] A homogeneous block copolymer may also be synthesized by keeping the block molecular weights below certain critical values, which in turn depend on the chemical structure of the constituent blocks.[1,14,15] Conversely, one can induce the formation of microdomains in a homogeneous block copolymer by adding a low molecular weight homopolymer.[16,17] This may be accompanied by a morphological transition,[18-25] with the resulting phase equilibria being very complicated.[7-13,25]

Earlier, we reported on the rheological behavior of block copolymers in the disordered state,[26] as well as in the ordered state,[27-29] and cited therein previous studies that dealt with the same subject. To date, however, relatively little has been reported on the rheological behavior of binary mixtures of a block copolymer and a homopolymer. This subject is of fundamental and practical importance to the development of, for instance, pressure-sensitive and hot-melt adhesives.

In this paper we report our recent study on the rheological behavior of mixtures of a homogeneous block copolymer and a homopolymer and the rheological behavior of mixtures of a microphase-separated block copolymer and a homopolymer. This paper is organized as follows. We shall present first phase diagrams for (a) mixtures of a homogeneous block copolymer and a homopolymer polystyrene and (b) mixtures of a microphase-separated block copolymer and a homopolymer polystyrene. Next, we shall present (a) the rheological behavior of binary mixtures of a *homogeneous* block copolymer and a homopolymer polystyrene and then (b) the rheological behavior of binary mixtures of a *microphase-separated* block copolymer and a homopolymer polystyrene.

Experimental Section

Materials. In the present study we synthesized, via anionic polymerization, polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS triblock) copolymers and a series of homopolymer polystyrenes (PS). Table I gives sample codes for the SIS triblock copolymers and homopolymers (PS) synthesized and their molecular characteristics. In the polymerization of the SIS triblock copolymers, *sec*-butyllithium was used as initiator to first polymerize styrene monomer anionically and then to initiate isoprene monomer with this "living" polystyrene to form a living polystyrene-*block*-polyisoprene (SI diblock) copolymer. The latter was reacted with a stoichiometric amount of 1,2-dibromoethane to couple the SI diblock copolymers into linear SIS triblock copolymers.

The gel permeation chromatograms of the samples indicated that there were some uncoupled diblocks, which were estimated to comprise about 20 wt %, and a very small amount of "dead" polystyrene homopolymer, which was estimated to be less than 1 wt %. Nuclear magnetic resonance (NMR) spectroscopy indicated that the polyisoprene consisted of about 6 wt % 3,4-polyisoprene, about 94 wt % 1,4-polyisoprene, and no detectable amount of 1,2-polyisoprene in the SIS block copolymer.

Sample Preparation. Samples for light scattering and rheological measurements were prepared by first dissolving a predetermined amount of block copolymer (or a block copolymer and a homopolymer polystyrene) in toluene (10 wt % of solid in solution) in the presence of an antioxidant (Irganox 1010, Ciba-Geigy Group) and then slowly evaporating the toluene. The evaporation of toluene was carried out initially in a fume hood at room temperature for a week and then in a vacuum oven at 40 °C for 3 days. The last trace of solvent was removed by drying the samples in a vacuum oven at elevated temperature by gradually raising the oven temperature up to 110 °C. The drying of the samples was continued until there was no further change in weight. Finally, the samples were annealed at 130 °C for 10 h.

Rheological Measurement. A Model R16 Weissenberg rheogoniometer (Sangamo Control Inc.) in the cone-and-plate mode (25 mm diameter plate and 4° cone angle with a 160-μm gap between the cone tip and the plate) was used to measure the dynamic storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, as functions of angular frequency (ω) at various temperatures. Data acquisition was accomplished with the aid of a microcomputer interfaced with the rheometer. The temperature control was satisfactory to within ±1 °C. In the rheological measurements a fixed strain was used at a given temperature. Specifically, the strain was varied from 0.03 to 0.3% depending on temperature, so that measurements were taken well within the linear viscoelastic range of the block copolymer investigated. All experiments

0024-9297/92/2225-3706$03.00/0

Table I
Molecular Characteristics of the Block Copolymers and Homopolymer Polystyrene Synthesized

(A) SIS Triblock Copolymer

sample code	block molecular weight	PS, wt %	microdomain morphology
SIS-A	7400S–99000I–7400S	13	spheres
SIS-D	3900S–93300I–3900S	7	no microdomains

(B) Homopolymer Polystyrene

sample code	M_w	M_w/M_n	sample code	M_w	M_w/M_n
PS10	1000	<1.05	PS20	2000	<1.05
PS13	1300	<1.05	PS30	3000	<1.05
PS15	1500	<1.05			

were conducted under a nitrogen atmosphere to avoid oxidative degradation of the samples.

Turbidity Measurement. Turbidity (or cloud point) was measured for mixtures of a block copolymer and a homopolymer polystyrene, using a light scattering apparatus, which was constructed in our laboratory. The apparatus consisted of (a) a He–Ne laser light source, (b) a photodiode, (c) a sample holder for two glass plates, between which a sample was placed, and (d) a programmable temperature controller. Cloud point was determined by heating the sample at the rate of 2 °C/min.

Hot-Stage Microscopy. A hot-stage microscope (Nippon Kogaku) with a light source, camera, temperature programmer, and photomicrographic attachment was used to take micrographs of a sample when it exhibited macrophage separation. The sample was heated at a rate of 2 °C/min. During the heating period, the temperature was recorded continuously on a chart recorder.

Results and Discussion

Phase Equilibria in Mixtures of a Block Copolymer and a Homopolymer. Since we are here interested in the rheological behavior of mixtures of a block copolymer and a homopolymer, before rheological measurements are presented, let us first consider phase equilibria in the various mixtures that we dealt with. Figure 1 gives cloud point curves for various mixtures of the *homogeneous* block copolymer SIS-D and homopolymer PS, which were obtained from turbidity measurements. In Figure 1, H denotes a single-phase mixtures of SIS-D and homopolymer PS, and L_1 and L_2 inside the cloud point curve denote SIS-D and homopolymer PS, respectively, which form a two-phase mixtures. We have shown in a previous paper[30] that the block copolymer SIS-D has no microdomains (i.e., homogeneous) at temperatures above 30 °C, as determined by dynamic viscoelastic measurement and small-angle X-ray scattering, respectively. Note in Figure 1 that the SIS-D/PS mixtures exhibit an upper critical solution temperature (UCST), the miscibility window becomes smaller as the molecular weight of added homopolymer PS is increased, and the UCST increases with increasing molecular weight of added homopolymer PS.

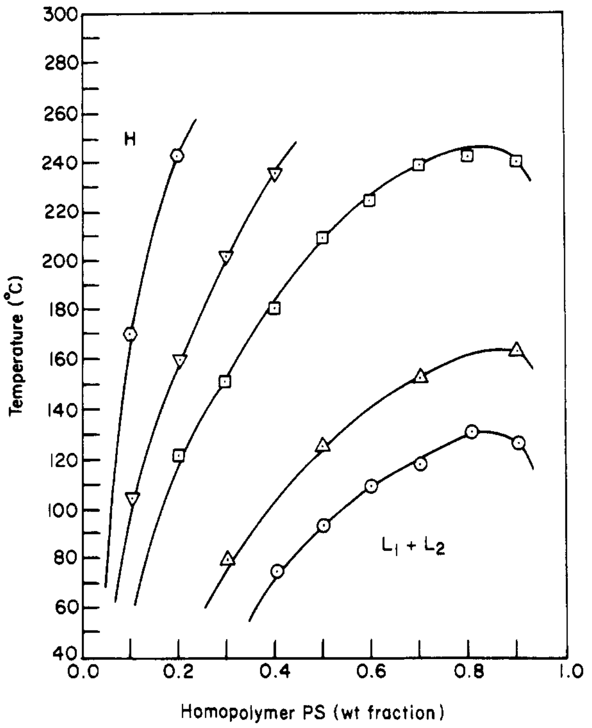

Figure 1. Cloud point curves for (⊙) SIS-D/PS10 mixtures, (▲) SIS-D/PS13 mixtures, (⊡) SIS-D/PS15 mixtures, (▼) SIS-D/PS20 mixtures, and (⊙) SIS-D/PS30 mixtures. H denotes the region which has a single-phase mixture of SIS-D and homopolymer PS, and ($L_1 + L_2$) denotes the region which has a two-phase mixture consisting of the homogeneous block copolymer SIS-D (L_1) and homopolymer PS (L_2).

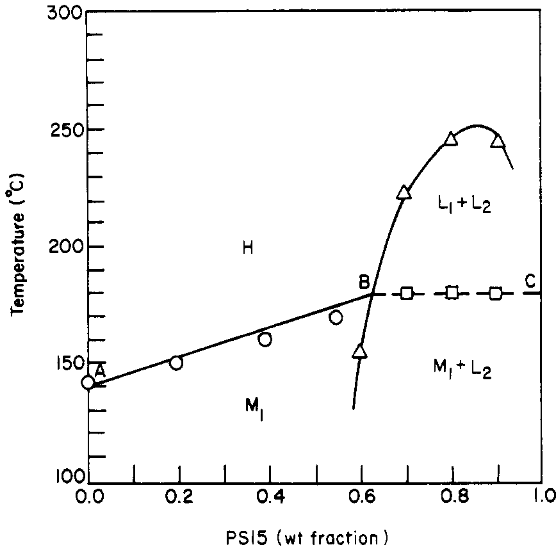

Figure 2. Phase diagram for the block copolymer SIS-A/homopolymer PS15 mixtures. H denotes the region which has a single-phase mixture of disordered SIS-A and PS15, M_1 denotes the the region where the mesophase contains the entire amount of added PS15 that has been solubilized, ($M_1 + L_2$) denotes the region where the mesophase (M_1) containing a portion of added PS15 and the macrophase-separated PS15 (L_2) coexist, and ($L_1 + L_2$) denotes the region where disordered SIS-A (L_1) and macrophase-separated PS15 (L_2) coexist.

Figure 2 gives a phase diagram for mixtures of the *microphase-separated* block copolymer SIS-A and homopolymer PS15, where (a) the region denoted by H represents a single-phase mixture of SIS-A and PS15, (b) the region denoted by M_1 represents the mesophase in which the entire amount of added homopolymer PS15 has been solubilized, (c) the region denoted by ($M_1 + L_2$) represents the mixture consisting of the mesophase (M_1) and the macrophase-separated homopolymer PS15 (L_2), and (d) the region denoted by ($L_1 + L_2$) represents the mixture consisting of the disordered block copolymer (L_1) and the macrophase-separated PS15 (L_2). Note that (i) the block copolymer SIS-A has spherical microdomains at temperatures below about 140 °C,[31] (ii) mesophase M_1 inside the cloud point curve, i.e., region ($M_1 + L_2$), contains a portion of added PS15 that has been solubilized, and (iii) the microdomain structure of mesophase M_1 in this region may not be the same as that in region M_1 adjacent to the cloud point curve. This is because the addition of a homopolymer to a microphase-separated block copolymer may bring about a morphological transition.[18-25] A further discussion of this subject is beyond the main theme of this paper.

In reference to Figure 2, curve AB separating the region M_1 and the region H was obtained by dynamic viscoelas-

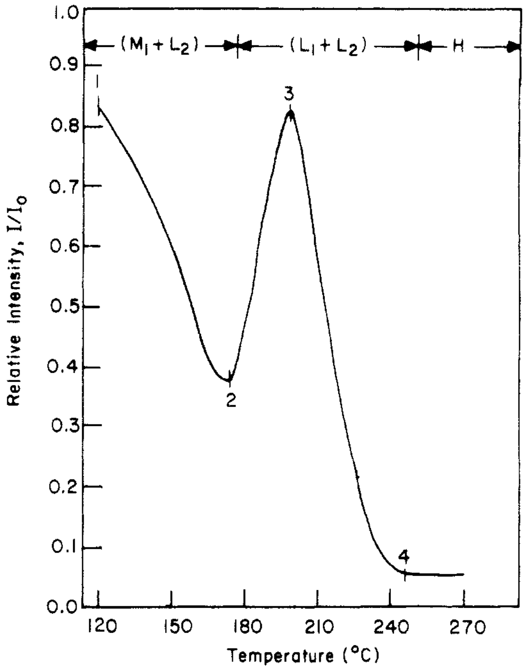

Figure 3. Trace of the intensity of scattered light for the 20/80 SIS-A/PS15 mixture as it was heated from 120 to 270 °C.

tic measurements, the details of which are described elsewhere.[11-13] The phase boundary between regions M_1 and (M_1 + L_2), the phase boundary between regions H and (L_1 + L_2), and the phase boundary between regions (M_1 + L_2) and (L_1 + L_2) were determined by turbidity measurements. The horizontal broken line BC was obtained by noticing a sudden increase in the turbidity as the temperature increased. For illustration purposes, a trace of the intensity of scattered light is given in Figure 3 as the 20/80 SIS-A/PS15 mixture was heated from 120 to 270 °C. It can be seen in Figure 3 that the intensity of scattered light inside region (M_1 + L_2) initially decreased as the temperature was increased, passing through a minimum at about 178 °C, and then increased with increasing temperature until it passed through a maximum at about 205 °C inside region (L_1 + L_2), and finally the intensity of scattered light did not change anymore with increasing temperature in region H. Therefore, the temperature corresponding to the horizontal broken curve BC in Figure 2 was determined from location 2 indicated in Figure 3.

Rheological Behavior of Binary Mixtures of a Homogeneous Block Copolymer and a Homopolymer Polystyrene. In this section we shall first discuss the rheological behavior of binary mixtures of the homogeneous block copolymer SIS-D and homopolymer PS in two separate regions, namely, in reference to Figure 1, (a) region H in which a single-phase mixture of SIS-D and homopolymer PS exists and (b) region (L_1 + L_2) in which a two-phase mixture of SIS-D and homopolymer PS exists. Then we shall discuss the differences in the rheological behavior between the single-phase and two-phase mixtures, as affected by the morphological state in the two-phase mixture.

Figure 4 give logarithmic plots of dynamic viscosity η' vs angular frequency ω for the 70/30 SIS-D/PS10 mixture at various temperatures, and Figure 5 gives similar plots for the 30/70 SIS-D/PS10 mixture at various temperatures. We also obtained results, similar to Figures 4 and 5, for other blend compositions, but space limitation here does not permit us to present them. According to the phase diagram given in Figure 1, the 70/30 SIS-D/PS10 mixture forms a single phase at temperatures above 30 °C (i.e., in region H), whereas the 30/70 SIS-D/PS10 mixture forms two phases at temperatures below 115 °C (i.e., in region (L_1 + L_2)) but forms a single phase at temperatures above 115 °C (i.e., in region H). Plots of zero-shear viscosity (η_0) vs blend composition for SIS-D/PS10 mixtures at various temperatures are given in Figure 6, in which open symbols refer to the data in region H and solid symbols refer to the data in region (L_1 + L_2). Note that the values of η_0 given in Figure 6 (also in other figures given) were calculated from the measured values of $G''(\omega)$ using the well-known relationship, $\eta_0 = \lim_{\omega \to 0} G''(\omega)/\omega$. The vertical line on each curve of Figure 6 represents the blend composition at which the SIS-D/PS10 mixture undergoes liquid–liquid phase separation. It is of interest to observe

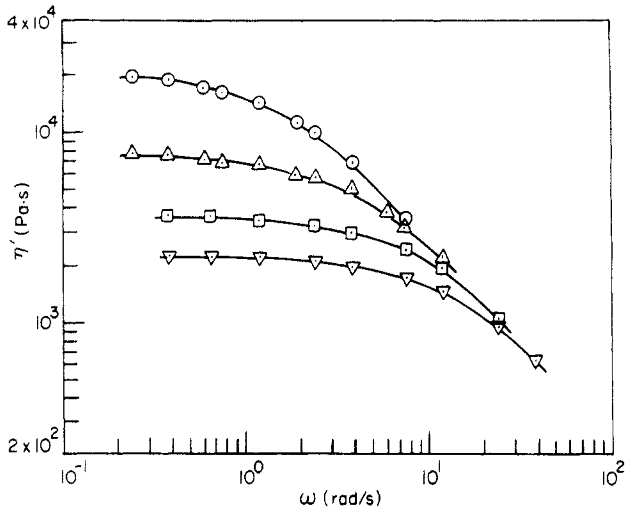

Figure 4. Plots of log η' vs log ω for the 70/30 SIS-D/PS10 mixture at various temperatures: (⊙) 50 °C; (▲) 60 °C; (⊡) 70 °C; (▼) 80 °C.

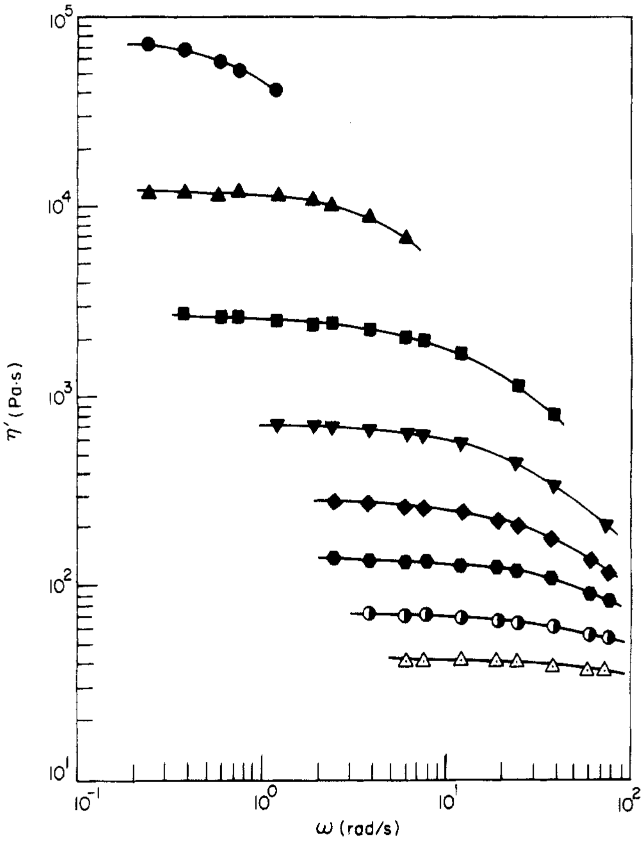

Figure 5. Plots of log η' vs log ω for the 30/70 SIS-D/PS10 mixture at various temperatures: (●) 50 °C; (▲) 60 °C; (■) 70 °C; (▼) 80 °C; (◆) 90 °C; (●) 100 °C; (◑) 110 °C; (▲) 120 °C.

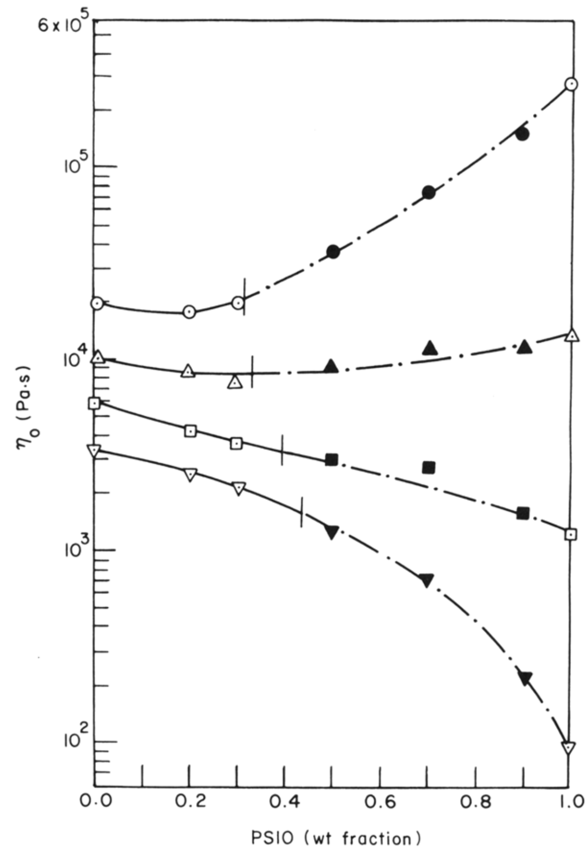

Figure 6. Plots of log η_0 vs blend composition for SIS-D/PS10 mixtures at various temperatures: (⊙, ●) 50 °C; (◬, ▲) 60 °C; (⊡, ■) 70 °C; (▽, ▼) 80 °C. Open symbols represent single-phase mixtures, and solid symbols represent two-phase mixtures.

in Figure 6 that the dependence of η_0 on blend composition does not appear to exhibit any anomaly as the mixture undergoes phase separation.

Plots of log G' vs log G'' are given in Figure 7 for the 50/50 SIS-D/PS10 mixture at various temperatures. Notice in Figure 7 that log G' vs log G'' plots for the mixture show temperature dependency at temperatures 80 °C and lower (denoted by solid symbols) but show a temperature-independent correlation at temperatures 90 °C and higher (denoted by open symbols). It should be mentioned that log G' vs log G'' plots for flexible homopolymers (or random copolymers) are *virtually* independent of temperature.[32-35] It is of interest to observe further in Figure 7 that log G' vs log G'' plots move toward the solid line, representing the plot for a single-phase mixture, as the temperature approaches 90 °C. In accordance with the phase diagram given in Figure 1, the 50/50 SIS-D/PS10 mixture forms two phases at temperatures below 90 °C and a single phase at temperatures above 90 °C. It can thus be concluded that plots of log G' vs log G'' are very sensitive to the morphological state of the mixture.

To facilitate our discussion here, we present micrographs in Figure 8 for the 50/50 SIS-D/PS10 mixture at various temperatures and in Figure 9 for the 30/70 SIS-D/PS10 mixture at various temperatures. Note in Figures 8 and 9 that the dark area represents the homopolymer PS10 and the white area represents the block copolymer SIS-D. We observe in Figure 8 that the 50/50 SIS-D/PS10 mixture becomes homogeneous as the temperature approaches 95 °C, and we observe in Figure 9 that the 30/70 SIS-D/PS10 mixture becomes homogeneous as the temperature approaches 120 °C. (See also the phase diagram given in Figure 1.) This observation reinforces our view that plots of log G' vs log G'' are very sensitive to the morphological state of mixtures consisting of a block copolymer and a homopolymer and that truly homogeneous mixtures would exhibit a temperature-independent correlation in log G'

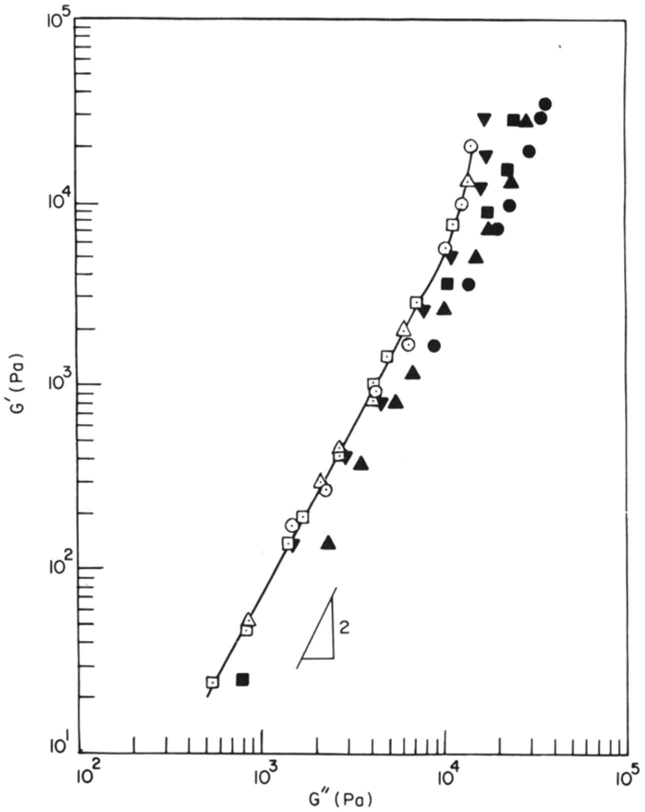

Figure 7. Plots of log G' vs log G'' for the 50/50 SIS-D/PS10 mixture at various temperatures: (●) 50 °C; (▲) 60 °C; (■) 70 °C; (▼) 80 °C; (⊙) 90 °C; (◬) 100 °C; (⊡) 110 °C. Solid symbols represent two-phase mixtures, and open symbols represent single-phase mixtures.

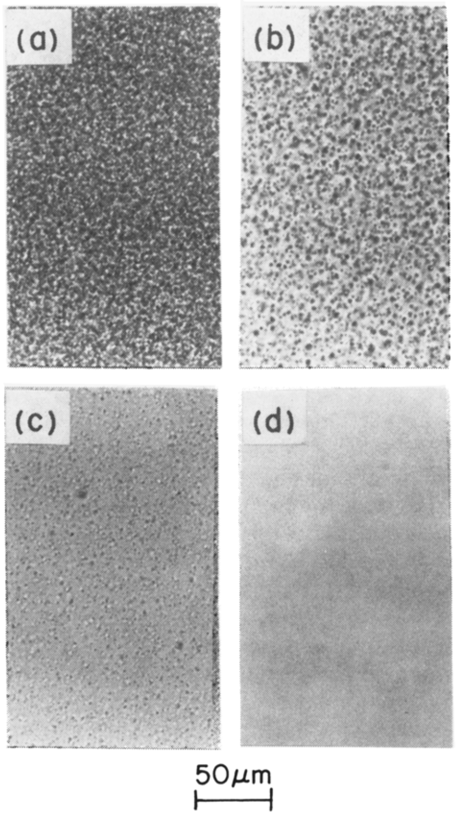

Figure 8. Micrographs for the 50/50 SIS-D/PS10 mixture at various temperatures: (a) 65 °C; (b) 85 °C; (c) 90 °C; (d) 95 °C.

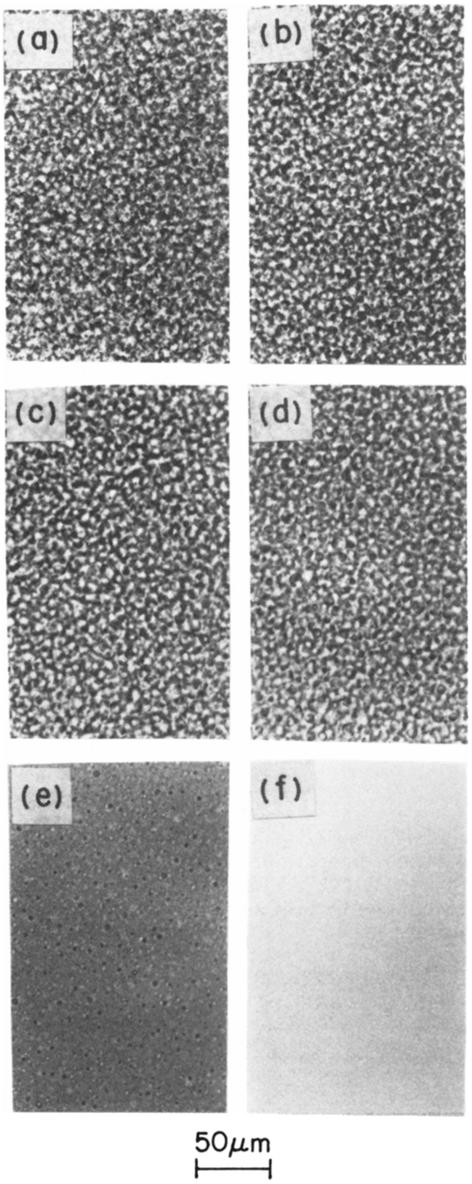

Figure 9. Micrographs for the 30/70 SIS-D/PS10 mixture at various temperatures: (a) 70 °C; (b) 90 °C; (c) 100 °C; (d) 110 °C; (e) 115 °C; (f) 120 °C.

vs log G'' plots.

The dependence of log G' vs log G'' plots on blend composition is given in Figure 10 for the SIS-D/PS10 mixtures at 50 °C and in Figure 11 for the SIS-D/PS30 mixtures at 100 °C. It can be seen in Figure 10 that log G' vs log G'' plots for the 80/20 and 70/30 SIS-D/PS10 mixtures, which form single phases (the region H in Figure 1), lie slightly above those for the block copolymer SIS-D, whereas log G' vs log G'' plots for the 50/50, 30/70, and 10/90 SIS-D/PS10 mixtures, which form two phases (the region ($L_1 + L_2$) in Figure 1), lie between those for the constituent components, the block copolymer SIS-D and homopolymer PS10. This observation suggests that the elasticity of single-phase mixtures, which consist of the homogeneous block copolymer SIS-D and homopolymer PS10, is greater than that of the constituent components and, also, is greater than that of the two-phase mixtures. It should be remembered that the dynamic storage modulus G' represents the energy stored in the fluid (thus an elastic property) and the dynamic loss modulus G'' represents the energy dissipated (thus a viscous property) during oscillatory shear flow.[36] On the other hand, it can be seen in Figure 11 that log G' vs log G'' plots for the 80/20, 60/40, and 40/60 SIS-D/PS30 mixtures lie between those of the constituent components. Notice that, according to the phase diagram given in Figure 1, these mixtures form two phases at 100 °C. We thus conclude from Figure 11 that the elasticity of SIS-D is greater than that of PS30 and that the elasticity of the two-phase mixtures approaches that of the block copolymer as the amount of SIS-D increases.

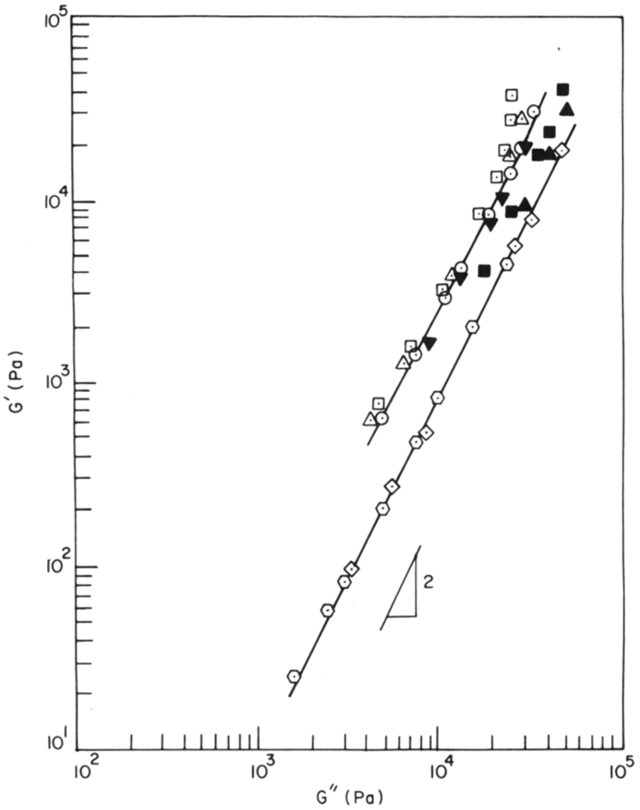

Figure 10. Plots of log G' vs log G'' for SIS-D/PS10 mixtures: (⊙) SIS-D at 50 °C; (◈) PS10 at 60 °C; (⊙) PS10 at 70 °C; (△) 80/20 SIS-D/PS10 mixture at 50 °C, forming a single phase; (⊡) 70/30 SIS-D/PS10 mixture at 50 °C, forming a single phase; (▼) 50/50 SIS-D/PS10 mixture at 50 °C, forming two phases; (■) 30/70 SIS-D/PS10 mixture at 50 °C, forming two phases; (▲) 10/90 SIS-D/PS10 mixture at 50 °C, forming two phases.

Rheological Behavior of Binary Mixtures of a Microphase-Separated Block Copolymer and a Homopolymer Polystyrene. In this section, we shall discuss the rheological behavior of mixtures of the block copolymer SIS-A and homopolymer polystyrene in the three separate regions shown in Figure 2, namely (a) region H in which a single-phase mixture of SIS-A and PS15 exists, (b) region M_1 where the entire amount of added homopolymer PS15 has been solubilized in the microphase-separated block copolymer SIS-A, and (c) region ($M_1 + L_2$) in which mesophase M_1 and macrophase-separated homopolymer PS15 (L_2) coexist. Note that the mesophase M_1 in region ($M_1 + L_2$) contains a portion of the added PS15 that has been solubilized. Since the rheological behavior of the two-phase mixture consisting of *disordered* (homogeneous) block copolymer SIS-A (L_1) and homopolymer PS15 (L_2) is expected to be very similar to that for the two-phase mixture consisting of *homogeneous* block copolymer SIS-D and homopolymer PS15 discussed above, to avoid repetition, we shall not discuss below the rheological behavior of the two-phase mixture in region ($L_1 + L_2$). When presenting the phase diagram given in Figure 2, we indicated that the block copolymer SIS-A has spherical microdomains at temperatures below 140 °C and becomes homogeneous at temperatures above 140 °C.

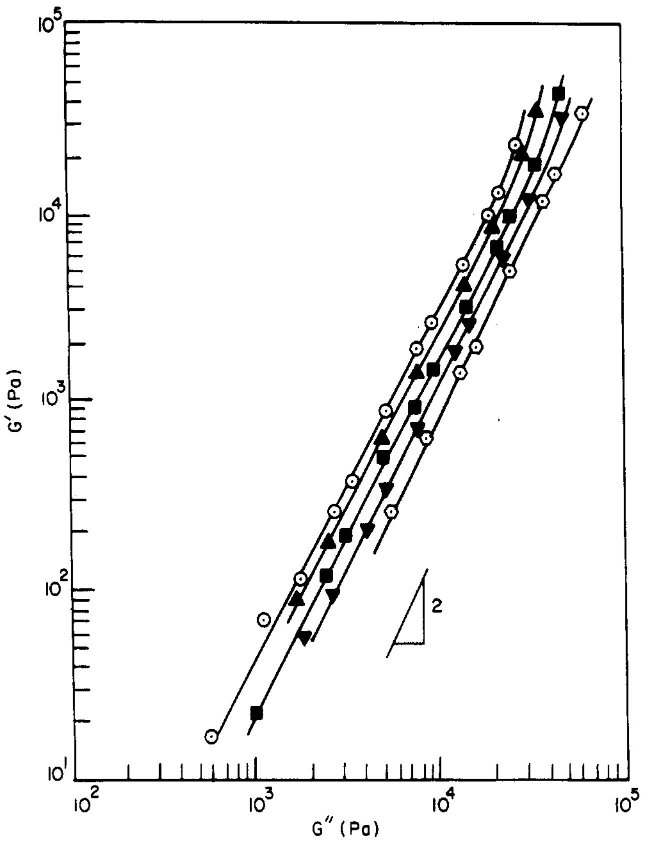

Figure 11. Plots of log G' vs log G'' for the SIS-D/PS30 mixtures at 100 °C: (⊙) SIS-D; (○) PS30; (▲) 80/20 SIS-D/PS30 mixture; (■) 60/40 SIS-D/PS30 mixture; (▼) 40/60 SIS-D/PS30 mixture. All three mixtures form two phases.

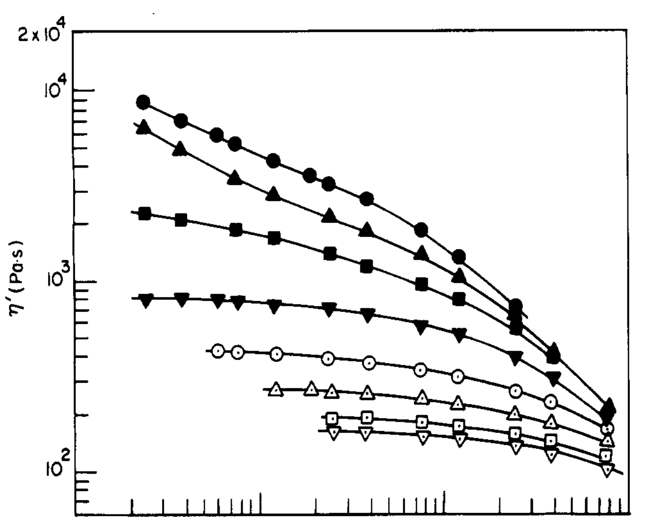

Figure 12. Plots of log η' vs log ω for the 60/40 SIS-A/PS15 mixture at various temperatures: (●) 120 °C; (▲) 130 °C; (■) 140 °C; (▼) 150 °C; (⊙) 160 °C; (△) 170 °C; (⊡) 180 °C; (▽) 190 °C.

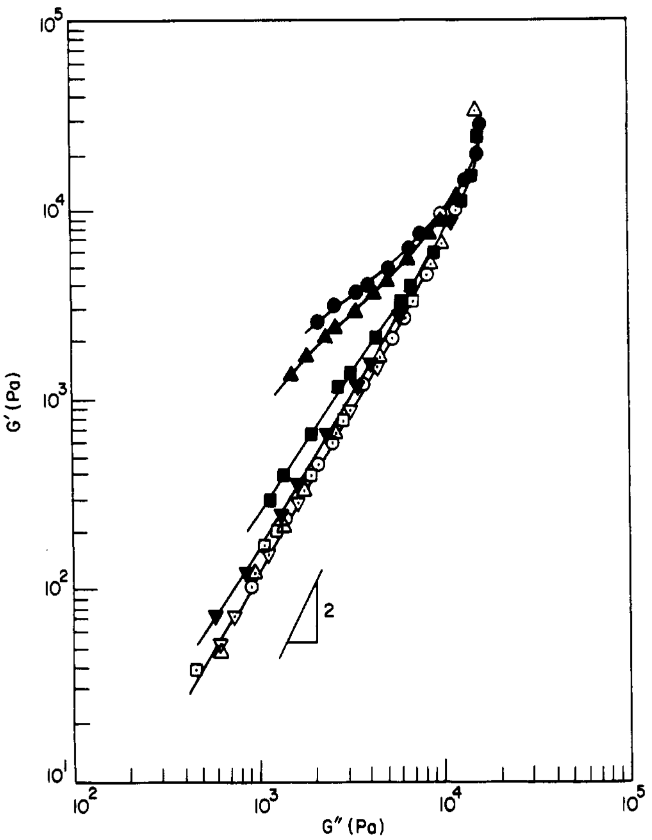

Figure 13. Plots of log G' vs log G'' for the 60/40 SIS-A/PS15 mixture at various temperatures. Symbols are the same as in Figure 12.

Figure 12 gives logarithmic plots of η' vs ω for the 60/40 SIS-A/PS15 mixture at various temperatures, describing variations of the viscosity with temperature, in reference to Figure 2, in regions H (solid symbols) and M_1 (open symbols), respectively. Notice in Figure 12 that as the temperature is decreased from 190 °C, at a certain critical temperature the 60/40 SIS-A/PS15 mixture begins to exhibit an apparent "yield stress" behavior at low values of ω, which is often observed in highly filled molten polymers, concentrated suspensions, or cross-linked polymers. By comparing Figure 12 with Figure 5, we observe that at low values of ω the temperature dependence of η' for the 60/40 SIS-A/PS15 mixture in the region M_1 (see Figure 2) is quite different from that for the 30/70 SIS-D/PS10 mixture (see Figure 1). This difference stems from the contrasting morphologies between the two mixtures in that the 60/40 SIS-A/PS15 mixture contains spherical microdomains of polystyrene having dimensions less than 0.1 μm, while the 30/70 SIS-D/PS10 mixture has droplets of PS10 having dimensions greater than 1 μm (although this depends on temperature).

Figure 13 gives plots of log G' vs G'' for the 60/40 SIS-A/PS15 mixture at various temperatures. It can be seen in Figure 13 that such plots give rise to temperature dependency at temperatures of 150 °C and lower but a single correlation at temperatures of 160 °C and higher. A similar observation has been reported for neat block copolymers by Han and co-workers,[27-29] who then suggested that a critical temperature, at which log G' vs log G'' plots cease to vary with temperature, be regarded as the order–disorder transition temperature (T_r), i.e., the temperature at which microdomains in a block copolymer completely disappear, forming a single phase, as the temperature is increased. Notice in Figure 13 that the slope of log G' vs log G'' plots at temperatures of 160 °C and higher is about 2, which is expected for flexible homopolymer melts or random copolymer melts. We observe from Figure 13 that addition of homopolymer PS15 by 40 wt % has increased the T_r of SIS-A by 20 °C. Earlier, similar observations were also reported by other investigators.[9-13,22-25] It should be mentioned that whether the addition of a homopolymer increases or decreases the T_r of a block copolymer depends on the molecular weight of added homopolymer relative to the molecular weight of the block copolymer and block copolymer composition.

Let us now examine the rheological behavior of the 30/70 SIS-A/PS15 mixture which, in reference to Figure 2, is in region (M_1 + L_2). It should be remembered that this

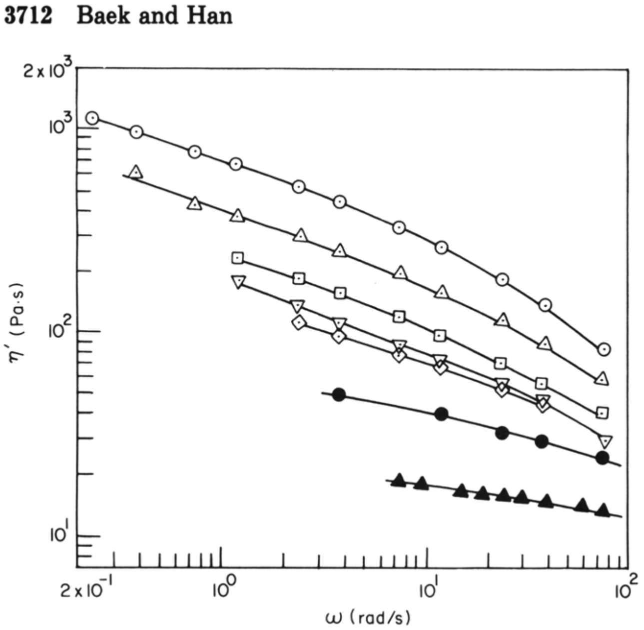

Figure 14. Plots of log η' vs log ω for the 30/70 SIS-A/PS15 mixture at various temperatures: (⊙) 120 °C; (△) 130 °C; (⊡) 140 °C; (▽) 150 °C; (◇) 160 °C; (●) 170 °C; (▲) 180 °C.

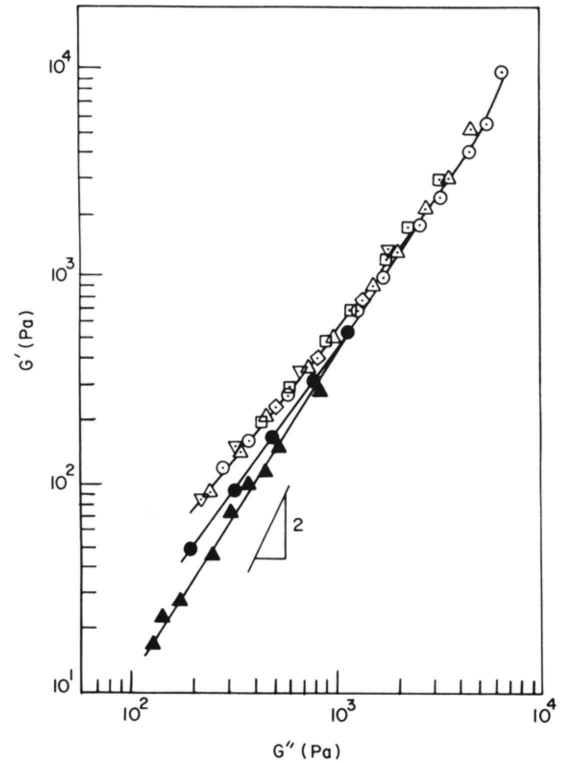

Figure 15. Plots of log G' vs log G'' for the 30/70 SIS-A/PS15 mixture at various temperatures. Symbols are the same as in Figure 14.

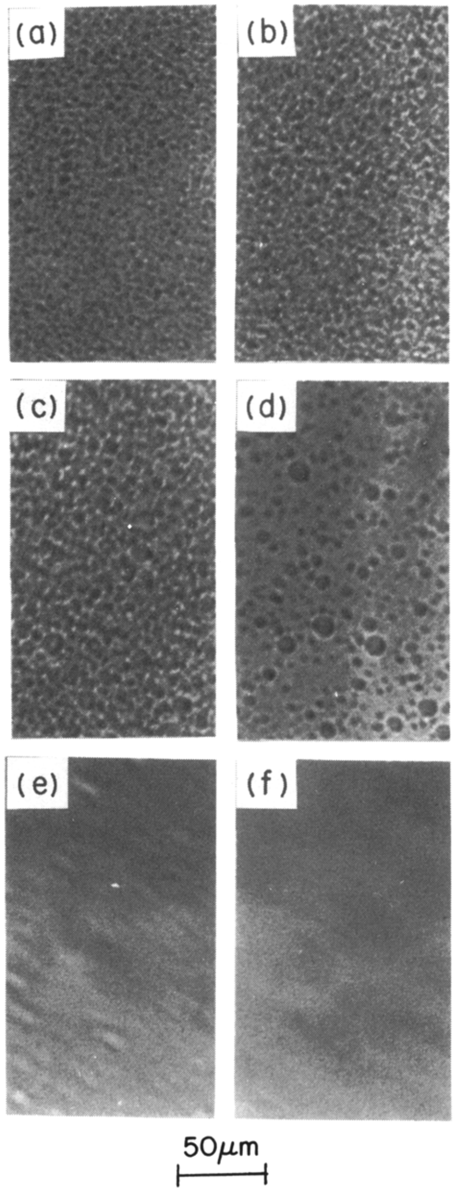

Figure 16. Micrographs for the 30/70 SIS-A/PS15 mixture at various temperatures: (a) 120 °C; (b) 180 °C; (c) 190 °C; (d) 210 °C; (e) 220 °C; (f) 230 °C.

mixture consists of mesophase M_1 and macrophase-separated homopolymer PS15 (L_2). Figure 14 gives plots of log η' vs log ω, and Figure 15 gives log G' vs log G'', for the 30/70 SIS-A/PS15 mixture at various temperatures ranging from 120 to 180 °C. The following observations are worth noting in Figures 14 and 15: (a) Over the entire range of temperatures investigated, *no* Newtonian behavior can be seen in Figure 14, although the dependency of η' on ω becomes weaker as the temperature is increased from 150 to 180 °C. This attests to the fact that the mixture contains microdomains throughout the entire range of temperatures investigated (see Figure 2). (b) Plots of log G' vs log G'' appear to stay on a single curve at temperatures ranging from 120 to 160 °C and then show temperature dependency as the temperature is increased from 160 to 170 to 180 °C. Notice in Figure 2 that at about 180 °C mesophase M_1 in region ($M_1 + L_2$) transforms into a disordered phase L_1. Therefore, we can surmise that the contribution of microdomains to the rheology of the 30/70 SIS-A/PS15 mixture diminishes as the temperature approaches 180 °C. The above observation indicates that plots of log G' vs log G'' are very sensitive to the morphology of a mixture consisting of a block copolymer and a homopolymer.

Micrographs for the 30/70 SIS-A/PS15 mixture at temperatures ranging from 120 to 230 °C are given in Figure 16, in which the dark area represents the homopolymer PS15 and the white area represents the block copolymer SIS-A. In Figure 16, a change in the morphological state of the mixture is hardly discernible as the temperature is increased from 120 to 190 °C, and the two-phase mixture becomes a single phase as the temperature approaches 230 °C. In accordance with Figure 2, the order–disorder transition temperature of an SIS-A/PS15 mixture increases as the PS15 is added. Also, a morphological transition of the block copolymer SIS-A from spheres to cylinders to lamellae is expected to take place, if the solubility limit

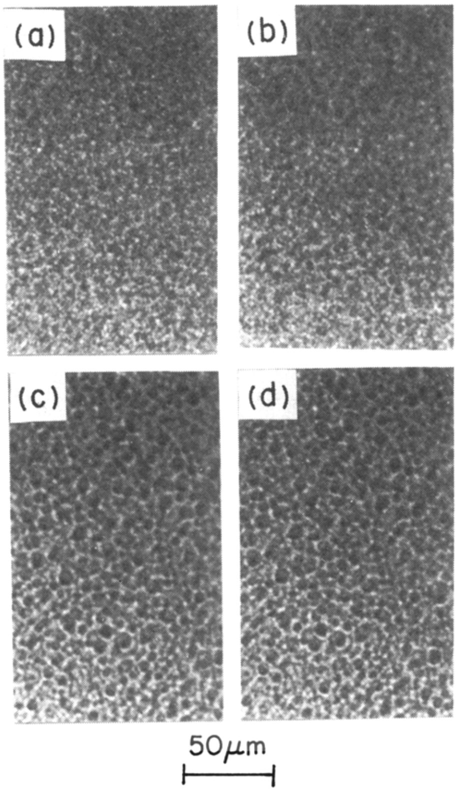

Figure 17. Micrographs for the 30/70 SIS-D/PS10 mixture: (a) at 70 °C at the beginning of the experiment; (b) 30 min later at 70 °C; (c) at 100 °C at the beginning of the experiment; (d) 30 min later at 100 °C.

is not encountered, as the amount of added PS15 is increased.[23-25] Since the sizes of the microdomains are so small (ca. 10–50 nm) compared to those of the macrophase-separated PS15, for the magnification of the micrographs shown in Figure 16 we cannot discern the presence of the microdomains of the block copolymer SIS-A.

Stability of Mixtures of a Block Copolymer and a Homopolymer. In presenting above the results of rheological measurements, we implicitly assumed that the mixture below the cloud point curve is stable, such that the composition does not change during rheological measurement. If the assumption is proven to be invalid, the interpretation presented above of the rheological behavior of mixtures of a block copolymer and a homopolymer below the cloud point curve are of little physical significance. To test the validity of the assumption, using hot-stage microscopy we conducted a separate experiment to investigate how fast the morphological state of the samples might change with time. For this, we prepared samples using the same procedure as that for the rheological measurements described under Experimental Section.

Figure 17 gives micrographs for the 30/70 SIS-D/PS10 mixture, which were taken at 70 °C at an interval of 30 min (see micrographs a and b) and at 100 °C at an interval of 30 min (see micrographs c and d). Note in Figure 17 that the dark area represents the homopolymer PS10 and the white area represents the homogeneous block copolymer SIS-D. It can be seen in Figure 17 that no discernible change in morphology occurred over a period of 30 min. In the present study, rheological measurements of a given composition were completed within 30 min.

Figure 18 gives micrographs for the 30/70 SIS-A/PS15 mixture, which were taken at 140 °C at an interval of 30 min (see micrographs a and b) and at 200 °C at an interval of 30 min (see micrographs c and d). Note in Figure 18 that the dark area represents the homopolymer PS15 and the white area represents the microphase-separated block copolymer SIS-A in which part of the added homopolymer PS15 is solubilized. Similar micrographs were taken for other blend compositions and also at different temperatures, but the place limitations here do not allow us to present them. It can be seen in Figure 18 that no

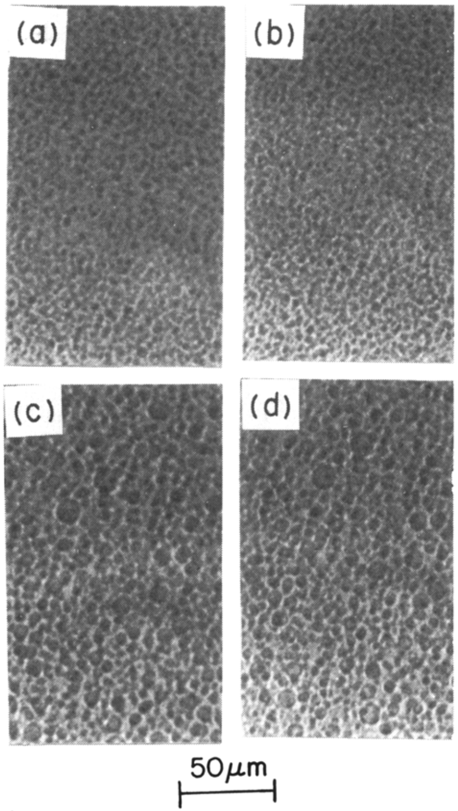

Figure 18. Micrographs for the 30/70 SIS-A/PS15 mixture: (a) at 140 °C at the beginning of the experiment; (b) 30 min later at 140 °C; (c) at 200 °C at the beginning of the experiment; (d) 30 min later at 200 °C.

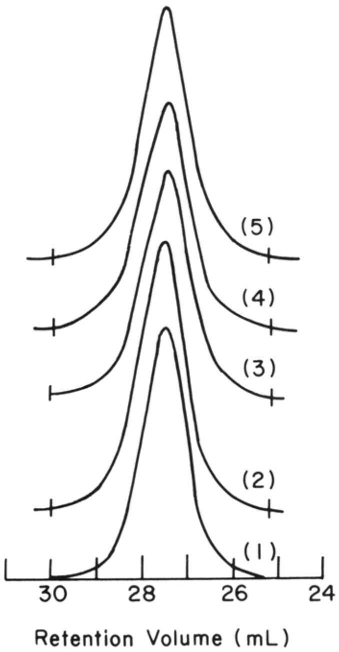

Figure 19. Traces of the GPC chromatograms for polyisoprene samples, which received heat treatment under a nitrogen atmosphere: (1) without heat treatment; (2) annealed at 140 °C for 30 min; (3) annealed at 160 °C for 30 min; (4) annealed at 180 °C for 30 min; (5) annealed at 200 °C for 30 min.

discernible change in morphology can be detected between the two micrographs, which were taken at an interval of 30 min. The above observations indicate that indeed the morphological state of the samples was stable during our rheological measurements, which lasted less than 30 min.

We also performed an experiment for testing thermal stability of homopolymer polyisoprene when subjected to temperatures above 140 °C.[37] For this, we prepared samples of homopolymer polyisoprene using the same procedure as that described under Experimental Section; i.e., we used 0.5 wt % of an antioxidant (Irganox 1010, Ciba-Geigy) in a polyisoprene having the weight-average molecular weight of 78 000, which was synthesized by anionic polymerization. Samples were first annealed at elevated temperatures under a nitrogen atmosphere for 30 min in a differential scanning calorimeter (DSC) cell, and then the molecular weights of the samples were measured, via gel permeation chromatography (GPC), to determine whether or not there might be a discernible change in molecular weight and molecular weight distribution after heat treatment at an elevated temperature. Figure 19 gives traces of the GPC chromatograms for five samples, each being subjected to different heat treatment, namely (1) without heat treatment, (2) annealed at 140 °C for 30 min, (3) annealed at 160 °C for 30 min, (4) annealed at 180 °C for 30 min, and (5) annealed at 200 °C for 30 min. Note that rheological measurements of a given composition presented above lasted less than 30 min. From Figure 19, we can conclude that there is no discernible change in molecular weight and molecular weight distribution under the conditions of heat treatment employed. If there had been cross-linking taking place during the heat treatment, we would expect to observe a noticeable change in the GPC chromatogram. In a recent study, Kim and Han[38] performed experiments, similar to those described above, for poly(α-methylstyrene)-*block*-polystyrene copolymers and concluded that there was little thermal degradation, within the first 1 h, of the sample containing an antioxidant when it was subjected to an elevated temperature under a nitrogen atmosphere.

Concluding Remarks

In this paper we have shown that the rheological behavior of mixtures of a block copolymer and a homopolymer is intimately related to their morphological state, which in turn depends on, among many other factors, blend ratio, molecular weight of added homopolymer relative to the molecular weight of the block copolymer, and temperature. The present paper emphasizes the importance of relating rheological measurements of mixtures of a block copolymer and a homopolymer to their morphological state. This study suggests that when the rheological behavior of mixtures of a block copolymer and a homopolymer is investigated, the phase diagram of the mixtures must be constructed, in conjuction with the rheological measurements.

References and Notes

(1) (a) Meier, D. J. *J. Polym. Sci., Part C* **1969**, *26*, 81. (b) Meier, D. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1970**, *11* (2), 400. (c) Meier, D. J. In *Thermoplastic Elastomers*; Legge, N. R., Holden, G., Schroeder, H. E., Eds.; Hanser: Munich, 1987; Chapter 2.

(2) (a) Hashimoto, T.; Tsukahara, Y.; Kawai, H. *J. Polym. Sci., Polym. Lett.* **1980**, *18*, 585. (b) Hashimoto, T.; Shibayama, M.; Kawai, H.; Watanabe, H.; Kotaka, T. *Macromolecules* **1983**, *16*, 361.

(3) Roe, R. J.; Fishkis, M.; Chang, J. C. *Macromolecules* **1981**, *14*, 1091.

(4) Leibler, L. *Macromolecules* **1980**, *13*, 1602.

(5) Ohta, T.; Kawasaki, K. *Macromolecules* **1986**, *19*, 2621.

(6) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1976**, *9*, 897; **1978**, *11*, 960; **1980**, *13*, 994.

(7) Hong, K. M.; Noolandi, J. *Macromolecules* **1983**, *16*, 1083.

(8) Whitmore, M. D.; Noolandi, J. *Macromolecules* **1985**, *18*, 2486.

(9) Roe, R. J.; Zin, W. C. *Macromolecules* **1984**, *17*, 189.

(10) Nojima, S.; Roe, R. J. *Macromolecules* **1987**, *20*, 1866.

(11) Kim, J.; Han, C. D.; Chu, S. G. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 677.

(12) Han, C. D.; Kim, J.; Baek, D. M. *J. Adhes.* **1989**, *28*, 201.

(13) Han, C. D.; Kim, J.; Baek, D. M.; Chu, S. G. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 315.

(14) Robeson, L. M.; Matzner, M.; Fetters, L. J.; McGrath, J. E. In *Recent Advances in Polymer Blends, Grafts and Blocks*; Sperling, L. H., Ed.; Plenum Press: New York, 1974; p 281.

(15) Hansen, D. R.; Shen, M. *Macromolecules* **1975**, *8*, 903.

(16) Hong, K. M.; Noolandi, J. *Macromolecules* **1983**, *16*, 1083.

(17) Cohen, R. E.; Torrada, J. M. *Macromolecules* **1984**, *17*, 1101.

(18) Toy, L.; Ninomi, M.; Shen, M. *J. Macromol. Sci., Phys.* **1975**, *B11* (3), 281.

(19) Ninomi, M.; Akovali, G.; Shen, M. *J. Macromol. Sci., Phys.* **1977**, *B13* (1), 133.

(20) Zin, W. C.; Roe, R. J. *Macromolecules* **1984**, *17*, 183.

(21) Quan, X.; Gancarz, I.; Koberstein, J. T.; Wignall, G. D. *Macromolecules* **1987**, *20*, 1431.

(22) Hashimoto, T.; Tanaka, H.; Hasegawa, H. In *Molecular Conformation and Dynamics of Macromolecules in Condensed Systems*; Nagasawa, M., Ed.; Elsevier: Amsterdam, 1988; p 257.

(23) Hashimoto, T.; Tanaka, H.; Hasegawa, H. *Macromolecules* **1990**, *23*, 4378.

(24) Tanaka, H.; Hasegawa, H.; Hashimoto, T. *Macromolecules* **1991**, *24*, 240.

(25) Han, C. D.; Baek, D. M.; Kim, J.; Kimishima, K.; Hashimoto, T. *Macromolecules* **1992**, in press.

(26) Han, C. D.; Baek, D. M.; Kim, J. K.; Chu, S. G. *Polymer* **1992**, *33*, 294.

(27) Han, C. D.; Kim, J. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 1741.

(28) Han, C. D.; Kim, J.; Kim, J. K. *Macromolecules* **1989**, *22*, 383.

(29) Han, C. D.; Baek, D. M.; Kim, J. K. *Macromolecules* **1990**, *23*, 561.

(30) Han, C. D., Baek, D. M., Kim, J. K.; Hashimoto, T.; Okamoto, S. *Macromolecules* **1991**, *24*, 5408.

(31) The T_r of 140 °C reported here for block copolymer SIS-A is lower than that reported in ref 29, because the "dead" homopolymer PS has been fractionated from the sample that had been used in the previous study (ref 29). In view of the fact that addition of the homopolymer PS having a molecular weight of 1500 has increased the T_r of the block copolymer SIS-A (see Figure 2), the presence of a small amount of dead homopolymer PS having a molecular weight of 7400 must have contributed to the higher value of T_r (180 °C) reported in ref 29.

(32) Han, C. D.; Lem, K. W. *Polym. Eng. Rev.* **1983**, *2*, 135.

(33) Han, C. D.; Chuang, H. K. *J. Appl. Polym. Sci.* **1985**, *30*, 2431.

(34) Han, C. D.; Jhon, M. S. *J. Appl. Polym. Sci.* **1986**, *32*, 3809.

(35) Han, C. D. *J. Appl. Polym. Sci.* **1988**, *35*, 167.

(36) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.

(37) This experiment was performed to address the issue, which was raised by an anonymous reviewer, expressing a concern about the possibility of having cross-linking when polyisoprene is exposed to temperatures above about 160 °C.

(38) Kim, J. K.; Han, C. D. *Macromolecules* **1992**, *25*, 271.

Registry No. SIS, 105729-79-1; PS, 9003-53-6.