Viscoelastic Behavior of Mixtures of a Block Copolymer and a Homopolymer

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ABSTRACT: The viscoelastic behavior of mixtures of a block copolymer and a homopolymer was investigated. For the investigation, polystyrene-*block*-polybutadiene-*block*-polystyrene copolymer (Kraton D-1102, Shell Development Co.) and polystyrene-*block*-polyisoprene-*block*-polystyrene copolymer (Kraton D-1107, Shell Development Co.) were used. In order to prepare mixtures with each of these block copolymers, a series of nearly monodisperse poly(α-methylstyrene)s (PαMS) with molecular weight ranging from 1200 to 8000 were synthesized via anionic polymerization. The Rheometrics Dynamic Mechanical Spectrometer was used to measure the dynamic storage modulus, G', dynamic loss modulus, G'', and loss tangent, tan δ, of the various block copolymer and homopolymer mixtures. It was observed that the plateau modulus of the 70/30 Kraton 1102/PαMS mixture increased steadily, whereas the plateau modulus of the 70/30 Kraton 1107/PαMS mixture first increased and then decreased, as the molecular weight of PαMS was increased from 1200 to 8000. An independent investigation of phase morphology, using both optical and transmission electron microscopies, revealed that the 70/30 Kraton 1107/PαMS mixture with the PαMS having molecular weight 8000 underwent macrophase separation at room temperature, while no macrophase separation had occurred in the 70/30 Kraton 1102/PαMS mixture with the same PαMS. This observation has lead us to conclude that the solubility limit of PαMS, in terms of its molecular weight, is much lower in Kraton 1107 than in Kraton 1102. We have predicted the solubility limits of PαMS in Kraton 1102 and Kraton 1107 from phase diagrams predicted by Noolandi's theory and interpreted the experimental results.

Introduction

Among the synthetic elastomers, the diene-based block copolymers, namely, polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS), polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS), and polystyrene-*block*-poly(ethylenebutylene)-*block*-polystyrene (SEBS) copolymers, have steadily gained wide acceptance for use in pressure-sensitive and hot-melt adhesives. Their unique combination of elasticity and thermoplasticity makes them suitable for use in such applications. The reason is that these block copolymers have a unique structure, where the polystyrene end block attached to the polydiene midblock undergoes microphase separation to form polystyrene microdomains, thereby creating a physically cross-linked network structure at the service temperatures.[1,2]

Since the elastomer alone is not sufficient to give rise to the desired levels of adhesion and tack, one usually adds a low-molecular-weight resin, in order to improve its wettability and contact strength properties. When a low-molecur-weight resin is added to an SIS or SBS triblock copolymer, a distinction must be made between one which associates (or is compatible) with the rubbery midblock of the block copolymer and one which associates (or is compatible) with the end block (i.e., polystyrene microdomains) of the block copolymer. It has been reported that the addition of a midblock-associating resin tends to soften the mixtures by decreasing the modulus of the polydiene midblock.[3-5] On the other hand, the addition of an end-block-associating resin tends to increase the modulus of block copolymer due to the increased volume of end block.[5] Also reported in the literature is the observation that the molecular weight of the added resin plays an important role in either increasing or decreasing the modulus of a given block copolymer.[5] Specifically, when the low-molecular-weight resin has a molecular weight above a certain critical value, it becomes incompatible with either of the blocks, forming a separate phase in the mixture. Under such circumstances, the mixture of block copolymer and low-molecular-weight resin does not function as an effective adhesive.[6]

Table I
Molecular Characteristics of the Block Copolymers Investigated[a]

sample	structure	segment molec wt × 10^{-3}	polystyrene wt %	triblock/diblock
Kraton D-1102	SBS	10S-50B-10S	28	80/20
Kraton D-1107	SIS	10S-120I-10S	14	80/20

[a] Supplied to us by the Shell Development Co.

Due to its high glass transition temperature and good solubility with polystyrene, poly(α-methylstyrene) (PαMS) is regarded as an effective end-block-associating resin for SBS or SIS block copolymer. Very recently, we synthesized a series of low-molecular-weight PαMSs, mixed them with SIS or SBS block copolymer, and then investigated their dynamic viscoelastic behavior.

In this paper we will first report on the experimental results of the viscoelastic behavior of SBS/PαMS and SIS/PαMS mixtures and then explain the differences observed in the viscoelastic behavior between the two sets of mixtures, through phase diagrams constructed with the statistical thermodynamic theory developed by Noolandi and co-workers.[7,8]

Experimental Section

Materials. The block copolymers employed were polystyrene-*block*-polybutadiene-*block*-polystyrene copolymer (Kraton D-1102, Shell Development Co.) and polystyrene-*block*-polyisoprene-*block*-polystyrene copolymer (Kraton D-1107, Shell Development Co.). Table I summarizes the molecular characteristics of the block copolymers investigated.

A series of low-molecular-weight poly(α-methylstyrene)s (PαMS) were synthesized via anionic polymerization. The reagent grade α-methylstyrene monomer was obtained from Scientific Polymer Products, Inc. The polymerization was carried out with tetrahydrofuran (THF) as solvent by adapting the capped-bottle procedure of Hsieh.[9] The initiator used was *sec*-butyl lithium. We followed the procedure described in the literature[10] for purifying the solvent and the monomer. Basically, the polymerization was carried out in a 300-mL flat-bottom flask, equipped with a magnetic stirring bar, which had been soaked for 1 week in solvent,

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Table II
Molecular Weights and T_g's of the Poly(α-methylstyrene) Synthesized

sample	$(M_w)_{GPC}$	$(M_w/M_n)_{GPC}$	$10^2[\eta]_{THF}$	T_g, °C
PαMS1	1200	≈1.3	3.41	54
PαMS2	1900	≈1.3	4.05	76
PαMS3	3400	≈1.3	5.09	128
PαMS4	4200	≈1.3	5.78	132
PαMS5	4600	<1.3	6.37	140
PαMS6	5000	<1.3	6.41	144
PαMS7	8000	<1.2	7.42	159

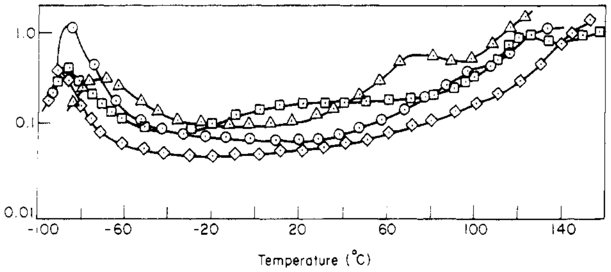

Figure 1. tan δ versus temperature for mixtures of Kraton 1102 with homopolymer: (⊙) Kraton 1102; (▲) Kraton 1102/PαMS1 mixture; (▣) Kraton 1102/PαMS4 mixture; (◇) Kraton 1102/PαMS7 mixture. All mixtures have 70/30 (by weight) blend composition.

dried overnight at 150 °C, and sealed with a rubber septum. The septum was tightly wired and the flask was evacuated with a syringe needle connected to a vacuum line. The flask was heated over a flame while being evacuated. The needle was removed after about 1 h of evacuation. Table II summarizes the molecular characteristics of the poly(α-methylstyrene) synthesized.

Sample Preparation. All samples for the rheological measurements were prepared by the solution-casting method. Predetermined amounts of block copolymer (Kraton 1102 or Kraton 1107), PαMS homopolymer, and antioxidant (Irganox 1010, Ciba-Geigy Group) were dissolved in toluene (10% solid in toluene). The solution was cast onto a piece of Teflon releasing paper and allowed to evaporate at room temperature for a week. The mixture was then transferred to a vacuum oven and dried for 3 days at 40 °C. The temperature of the vacuum oven was raised gradually up to 110 °C and the mixture was dried at this temperature until no weight loss was observed, confirming the absence of solvent. Finally, the sample was annealed at 150 °C for 2 h.

Measurement of Dynamic Viscoelastic Properties. A Dynamic mechanical spectrometer (Rheometrics Inc.) operated in the parallel plate mode (8-mm diameter plates with a 2-mm gap) was used to measure the dynamic viscoelastic properties of mixtures of block copolymer and end-block resin. For a temperature scan (from about −100 to 140 °C) at a fixed angular frequency 10 rad/s, the dynamic storage modulus (G'), loss modulus (G''), and loss tangent (tan δ) defined as G''/G' were plotted.

Microscopy. In order to examine the morphological details of some selected samples, transmission electron microscopy was used to take photomicrographs of the samples, following the standard procedure for staining ultrathin sections of samples with osmium tetroxide. Additionally, an optical microscope was used to investigate the phase morphology of some selected samples.

Experimental Results

Viscoelastic Behavior of Mixtures of Kraton 1102 and Poly(α-methylstyrene). Figure 1 gives temperature scans of the loss tangent (tan δ) for the pure block copolymer Kraton 1102 and 70/30 Kraton 1102/PαMS mixtures at a fixed frequency, 10 rad/s. In this paper, we regard the temperature at which tan δ goes through a maximum as the glass transition temperature (T_g). It can be seen in Figure 1 that (1) Kraton 1102 exhibits a sharp peak in tan δ at about −84 °C, which represents the T_g of the polybutadiene midblock, and a broad peak at about 95 °C, which represents the T_g of the polystyrene end block; (2) the PαMS1, which has the lowest molecular weight of the seven PαMSs used, associates with both the midblock and end block of Kraton 1102, as evidenced by the shifts of the peaks in tan δ toward higher temperatures in the lower transition region and toward lower temperatures in the upper transition region; (3) when the molecular weight of PαMS is increased, it associates only with the end block and not with the midblock of Kraton 1102; and (4) the peak in tan δ in the upper transition region is shifted steadily toward higher temperatures as the molecular weight of PαMS is increased but the values of the peaks in tan δ for the Kraton 1102/PαMS mixtures correspond to neither the T_g of the Kraton 1102 nor the T_g of added PαMS. This indicates to us that when the molecular weight of PαMS is less than about 8000, it associates with (or enters into) the end block of Kraton 1102 (i.e., microdomains of polystyrene in Kraton 1102).

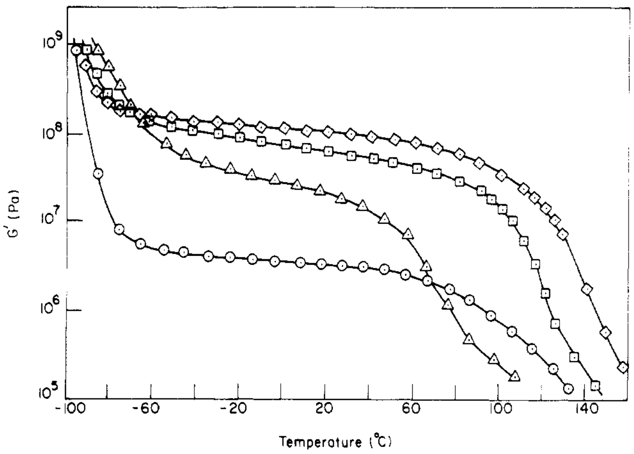

Figure 2. log G' versus temperature for Kraton 1102/PαMS mixtures. Symbols are the same as in Figure 1.

It is of interest to observe in Figure 1 that a very broad tan δ peak appears in the region between the two primary tan δ peaks for the Kraton 1102/PαMS4 mixture, but not for the Kraton 1102/PαMS7 mixture. Note further in Figure 1 that the height of the broad tan δ peak increases as the molecular weight of added PαMS increases from 1200 to 4200, but it decreases as the molecular weight of added PαMS increases further from 4200 to 8000. This observation leads us to the conclusion that the molecular weight of added homopolymer has much to do with the existence of such a broad tan δ peak appearing in the region between the two primary tan δ peaks. Further discussion of this and its physical implications will be postponed until more of such evidence is presented below for other mixtures.

Figure 2 gives temperature scans of the dynamic storage modulus (G') for the pure block copolymer Kraton 1102 and 70/30 Kraton 1102/PαMS mixtures. It can be seen in Figure 2 that Kraton 1102 exhibits almost a constant value of G' in the plateau region, hereafter referred to as the plateau modulus, extending from about −60 to 40 °C and that the addition of PαMS to Kraton 1102 increases significantly the value of the plateau modulus. Notice that the plateau modulus of the Kraton 1102/PαMS mixtures increases with increasing molecular weight of the PαMS. The observed increase in plateau modulus for the Kraton 1102/PαMS mixtures suggests to us that the added homopolymer has associated with the end block (i.e., polystyrene microdomains) of Kraton 1102.

Viscoelastic Behavior of Mixtures of Kraton 1107 and Poly(α-methylstyrene). Figure 3 gives temperature scans of tan δ for the 70/30 Kraton 1107/PαMS mixtures at a fixed angular frequency, 10 rad/s. It can be seen in Figure 3 that the addition of PαMS1 or PαMS2 broadens

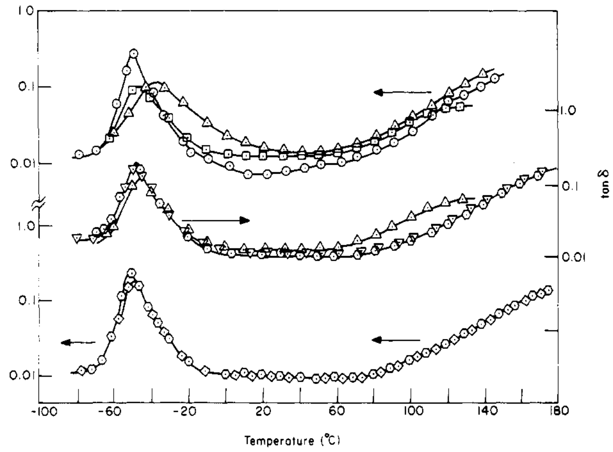

Figure 3. tan δ versus temperature for Kraton 1107/PαMS mixtures: (⊙) Kraton 1107; (▲) Kraton 1107/PαMS1 mixture; (⊡) Kraton 1107/PαMS2 mixture; (▼) Kraton 1107/PαMS3 mixture; (⊙) Kraton 1107/PαMS6 mixture; (◇) Kraton 1107/PαMS7 mixture. All mixtures have 70/30 (by weight) blend composition.

the tan δ peak of Kraton 1107 in the lower transition region and also shifts it toward higher temperatures, although this effect is not significant for the Kraton 1107/PαMS2 mixture. This observation indicates to us that the PαMS1 and PαMS2 associate with the midblock (i.e., polyisoprene phase) of Kraton 1107. However, as the molecular weight of PαMS is increased, the corresponding mixtures with Kraton 1107 do not see a shift in the tan δ peak in the lower transition region, indicating that the PαMS with molecular weight greater than about 2000 no longer associates with the midblock of Kraton 1107. This observation is very similar to that made for the Kraton 1102/PαMS mixtures (see Figure 1). Notice in Figure 3 that *no* tan δ peak representing the T_g of the polystyrene phase, which is about 100 °C, can be observed. This is attributable to the relatively small amounts of polystyrene microdomains (about 14 wt %) present in Kraton 1107. Figure 4 gives temperature scans of G' for the 70/30 Kraton 1107/PαMS mixtures at a fixed angular frequency, 10 rad/s. It is of interest to observe in Figure 4 that the plateau modulus of the mixture first increases and then decreases as the molecular weight of PαMS is increased from 1200 to 8000. If the entire amount of added PαMS7 has entered into (or has associated with) the microdomains of polystyrene in Kraton 1107, the plateau modulus of the Kraton 1107/PαMS7 mixture would be expected to be larger than that of the Kraton 1107/PαMS1 mixture. Since this is not the case, we speculate that *macrophase* separation might have taken place in the Kraton 1107/PαMS7 mixture. This speculation is based on the expectation that when macrophase separation takes place, the plateau modulus of a mixture of block copolymer and homopolymer would be lower than that of a mixture without macrophase separation taking place.

It is worth mentioning that the theoretical studies by Noolandi and co-workers[7,8] indicate that for a fixed amount of added homopolymer, there exists a critical value of molecular weight ratio, M_H/M_C, at and above which macrophase separation occurs, where M_H is the molecular weight of homopolymer and M_C is the molecular weight of block copolymer. Later in this paper we will present phase diagrams, constructed with Noolandi's theory,[7,8] for mixture of Kraton 1102 with PαMS and mixtures of Kraton 1107 with PαMS for different values of the molecular weight of PαMS, and explain the differences observed on the dependence of the molecular weight of

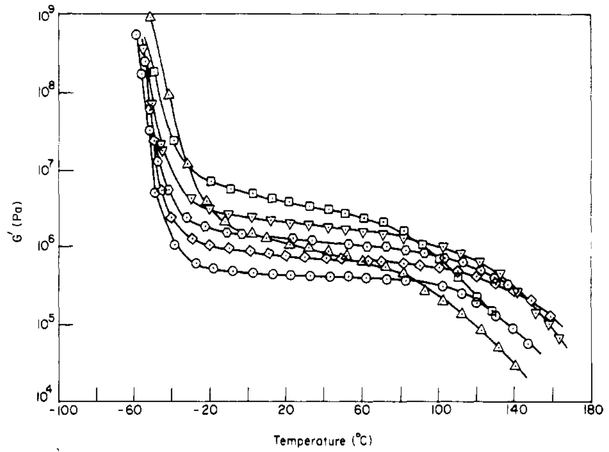

Figure 4. log G' versus temperature for Kraton 1107/PαMS mixtures. Symbols are the same as in Figure 3.

PαMS on the plateau modulus of the respective mixtures, shown in Figures 2 and 4.

Discussion of Experimental Results

We have observed in Figures 1 and 3 that when mixed with either Kraton 1102 or Kraton 1107, PαMS1 associates with both the polystyrene microdomains and polydiene phase in the block copolymer. This can be discussed in a more quantitative fashion by calculating the amounts of PαMS1 that have associated with the respective phases of the block copolymer, using the following expression:[11]

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \qquad (1)$$

where T_g, T_{g1}, and T_{g2} are the glass transition temperatures of the mixture and the constituent components, respectively, and w_1 and w_2 are the weight fractions of the constituent components. Our calculation shows that about 51 wt % of PαMS1 in the 70/30 Kraton 1102/PαMS1 mixture has associated with the polybutadiene phase and the rest (i.e., 49 wt %) with the polystyrene microdomains. It should be pointed out that eq 1 assumes that there exists *no* interface between the polystyrene microdomains and polybutadiene phase, and consequently our calculation assumes that *no* PαMS1 is present at the interface. On the other hand, there is experimental evidence[12-16] suggesting that an interface does indeed exist in block copolymers. Thus, the use of eq 1 is not entirely justified, but it does give us an idea as to how a homopolymer, when its molecular weight is sufficiently low, can be distributed into the respective phases of the block copolymer.

It should be remembered that (1) a broad tan δ peak appears in the region between the two primary tan δ peaks of the Kraton 1102/PαMS mixtures and the height of this peak first increases and then decreases as the molecular weight of added PαMS increases from 1200 to 8000 (see Figure 1), while no such broad tan δ peak appears in the Kraton 1107/PαMS mixtures (see Figure 3), and (2) the plateau modulus of the Kraton 1102/PαMS mixtures increases as the molecular weight of added PαMS increases from 1200 to 8000 (see Figure 2), while the plateau modulus of the Kraton 1107/PαMS mixtures first increases and then decreases as the molecular weight of added PαMS increases (see Figure 4). In order to expound upon these experimental observations, we investigated the effect of the amount of PαMS on the viscoelastic behavior of the Kraton 1102/PαMS mixtures, with emphasis on the nature of the broad tan δ peak appearing in the region between the two primary tan δ peaks.

Figure 5 gives temperature scans of tan δ, and Figure 6 gives temperature scans of G', for three different con-

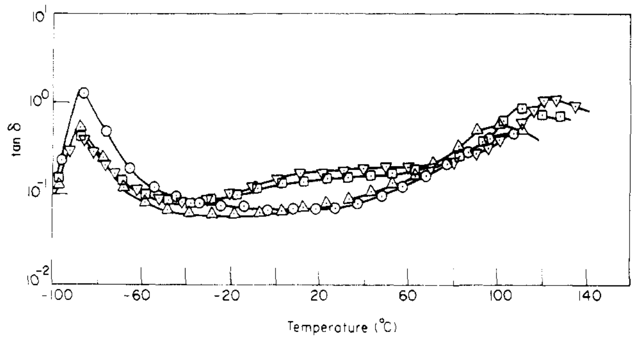

Figure 5. Effect of blend composition on tan δ for the Kraton 1102/PαMS4 mixtures: (⊙) Kraton 1102; (▲) 90/10 Kraton 1102/PαMS4 mixture; (⊡) 80/20 Kraton 1102/PαMS4 mixture; (▼) 70/30 Kraton 1102/PαMS4 mixture.

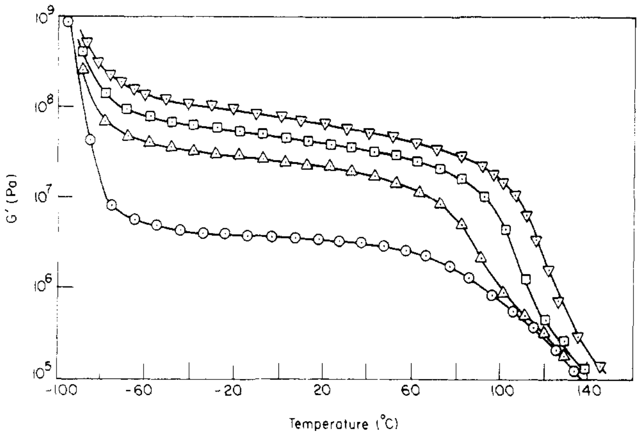

Figure 6. Effect of blend composition on G' for the Kraton 1102/PαMS4 mixtures. Symbols are the same as in Figure 5.

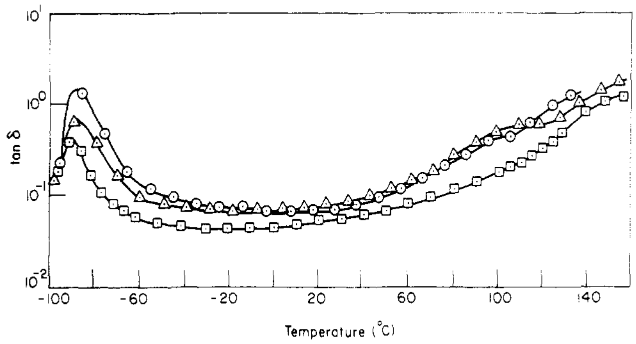

Figure 7. Effect of blend composition on tan δ for the Kraton 1102/PαMS7 mixtures: (⊙) Kraton 1102; (▲) 90/10 Kraton 1102/PαMS7 mixture; (⊡) 70/30 Kraton 1102/PαMS7 mixture.

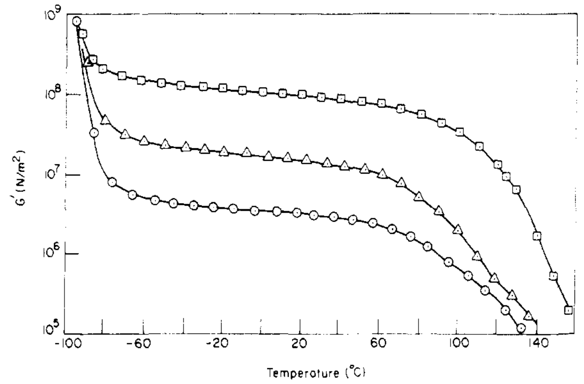

Figure 8. Effect of blend composition on G' for the Kraton 1102/PαMS7 mixtures. Symbols are the same as in Figure 7.

centrations of the Kraton 1102/PαMS4 mixture. The following observations are worth noting in Figures 5 and 6: (1) There is no shift in the tan δ peak in the lower transition region with concentration of PαMS4 for all three mixtures, implying that PαMS4 has a molecular weight too high to be associated with the polybutadiene phase of Kraton 1102; (2) the tan δ peak in the upper transition region is shifted toward higher temperatures with concentration of PαMS4, implying that the added PαMS4 has associated with the polystyrene microdomains of Kraton 1102; (3) a broad tan δ peak appears in the middle of the two primary tan δ peaks in the 80/20 and 70/30 Kraton 1102/PαMS4 mixtures, while no such broad tan δ peak appears in the 90/10 Kraton 1102/PαMS4 mixture; and (4) the plateau modulus of the Kraton 1102/PαMS4 mixture increases with increasing amounts of PαMS4, implying that the added PαMS4 has associated with the polystyrene microdomains of Kraton 1102.

The question can then be raised: why does a broad tan δ peak appear in the middle of the two primary tan δ peaks as the amount of PαMS4 in the Kraton 1102/PαMS4 mixture exceeds 10 wt % (see Figure 5)? Before we answer the question, let us look at the temperature scans of tan δ given in Figure 7 and the temperature scans of G' given in Figure 8, for the 90/10 and 70/30 Kraton 1102/PαMS7 mixtures. Note that the molecular weight of PαMS7 is 8000 and that the molecular weight of PαMS4 is 4200. It can be seen in Figure 7 that no broad tan δ peak appears in the region between the two primary tan δ peaks for the Kraton 1102/PαMS7 mixtures and the values of tan δ in the intermediate region decrease as the amount of PαMS7 in the mixture increases from 10 to 30 wt %. On the other hand, as can be seen in Figure 8, the plateau modulus of the Kraton 1102/PαMS7 mixtures increased as the amount of PαMS7 in the mixture increased from 10 to 30 wt %. This observation rules out the possibility that macrophase separation occurred in the Kraton 1102/PαMS7 mixture as the amount of PαMS7 in the mixture increased from 10 to 30 wt %.

At this juncture it is worth mentioning that in the measurements of dynamic viscoelastic properties of tapered block copolymers, Hashimoto et al.[17] observed a broad peak in the dynamic loss modulus (G'') in the region between the two primary dispersion temperatures, one corresponding to the T_g of the end block and the other corresponding to the T_g of the midblock, of the block copolymer investigated. They attributed the observed broad peak of G'' to a "domain-boundary mixing" effect, i.e., to the existence of an interface between the end block and midblock of the block copolymer.

We therefore hypothesize that the height of the broad tan δ peak appearing in between the two primary tan δ peaks in the Kraton 1102/PαMS mixtures (see Figures 1 and 5) is related to the interfacial thickness in the block copolymer. It is worth proving (or disproving) this hypothesis by conducting small-angle X-ray scattering experiments in the future. We suppose further that the interfacial thickness of a mixture of block copolymer and homopolymer may be affected by the molecular weight ratio of homopolymer to block copolymer, M_H/M_C, and the amount of homopolymer in the mixture.

Figure 9 gives transmission electron microscopy (TEM) photomicrographs of Kraton 1102 and Kraton 1107. It can be seen in Figure 9 that Kraton 1102 has a cylindrical microdomain structure and Kraton 1107 has a spherical microdomain structure. Taking into consideration the fact that Kraton 1102 has about 28 wt % of polystyrene and Kraton 1107 has about 14 wt % of polystyrene, the TEM photomicrographs corroborate the results of earlier experimental investigations[18,19] and also confirm theoretical

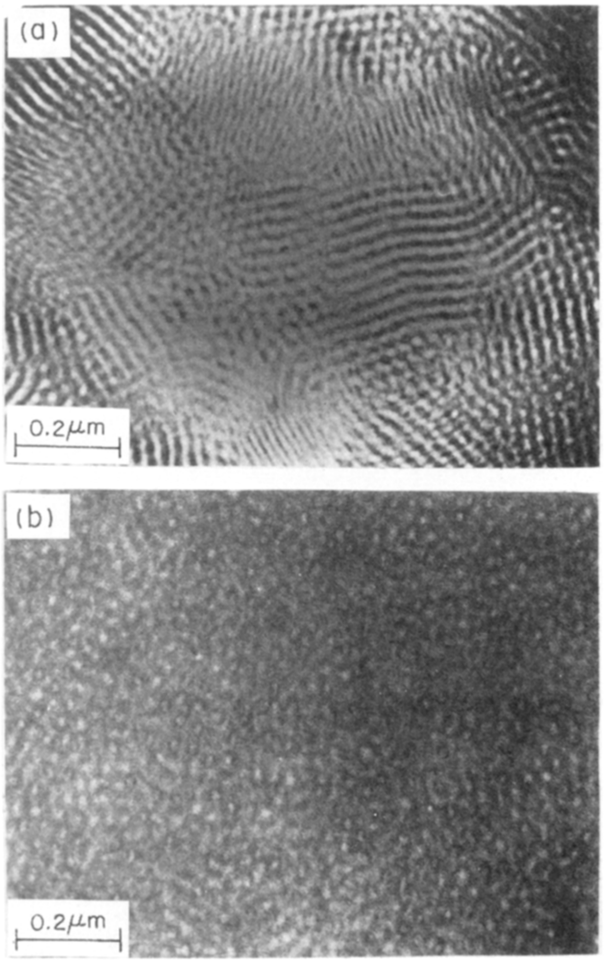

Figure 9. TEM photomicrographs of (a) Kraton 1102 and (b) Kraton 1107.

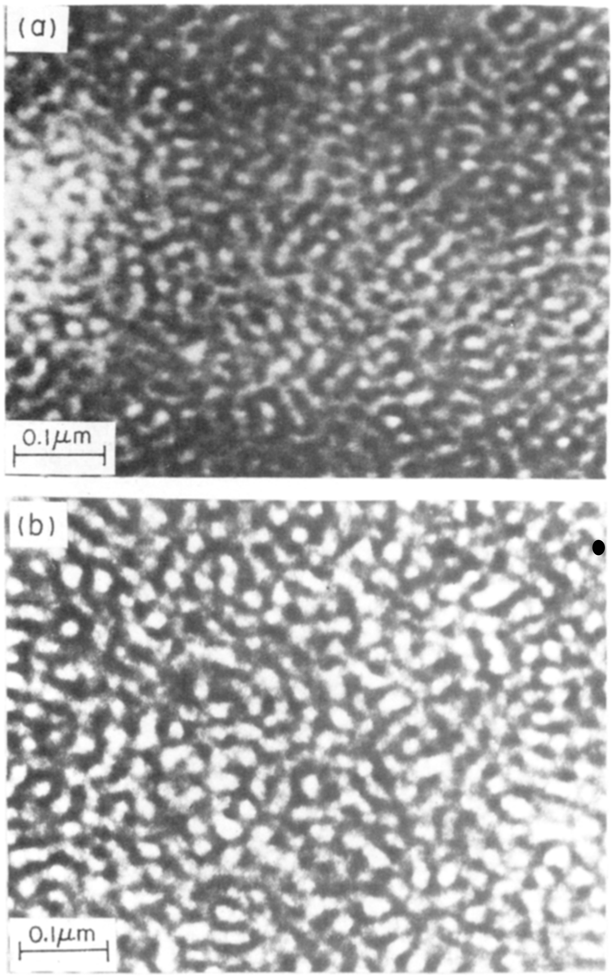

Figure 10. TEM photomicrographs of (a) 70/30 Kraton 1107/PαMS1 mixture and (b) 70/30 Kraton 1107/PαMS2 mixture.

predictions by various investigators.[20,21]

Figure 10 gives TEM photomicrographs of the 70/30 Kraton 1107/PαMS1 and 70/30 Kraton 1107/PαMS2 mixtures. Notice that the magnification of the photomicrographs given in Figure 10 is one half of that in Figure 9. It can be seen in Figure 10 that when PαMS1 or PαMS2 is added to Kraton 1107, the microdomain structure of the polystyrene remains more or less unchanged, but the microdomain size of the 70/30 Kraton 1107/PαMS2 mixture is larger than that of the 70/30 Kraton 1107/PαMS1 mixture. This observation supports the hypothesis made above when discussing the results of the viscoelastic behavior of the mixtures (see Figure 4), that part of the added PαMS1 has associated with the rubbery midblock of Kraton 1107 and thus lesser amounts of the added PαMS1 have become available that can be associated with the microdomains of polystyrene in Kraton 1107, whereas the entire amount of the added PαMS2 has associated with the microdomains of polystyrene in Kraton 1107. In view of the fact that the molecular weights of PαMS1 and PαMS2 are 1200 and 1900, respectively (see Table II), we can conclude from the above observation that as the molecular weight of the added PαMS is increased, the chances for it to be associated with the polydiene midblock of a block copolymer will become less.

Figure 11 gives photomicrographs of the 70/30 Kraton 1102/PαMS7 and 70/30 Kraton 1107/PαMS7 mixtures. It should be remembered that the molecular weight of PαMS7 is 8000 (see Table II). It can be seen in Figure 11 that *macrophase* separation occurred in the 70/30 Kraton 1107/PαMS7 mixture but *not* in the 70/30 the Kraton 1102/PαMS7 mixture. Notice the difference in the magnifications between parts a and b of Figure 11. Figure 11a suggests that mixtures of Kraton 1102 and PαMS with molecular weights of up to, at least, 8000 do *not* give rise to macrophase separation. Under such circumstances, the plateau modulus of 70/30 Kraton 1102/PαMS mixtures would be expected to increase as the molecular weight of added PαMS is increased to about 8000. This is precisely what has been observed from the dynamic viscoelastic measurements given in Figure 2. On the other hand, when *macrophase* separation occurred in the 70/30 Kraton 1107/PαMS7 mixture, as evidenced in Figure 11b, its plateau modulus at temperatures below about 60 °C was smaller than the plateau moduli of the 70/30 Kraton 1107/PαMS1 and 70/30 Kraton 1107/PαMS2 mixtures (see Figure 4). It should be remembered that *no* macrophase separation occurred in either the 70/30 Kraton 1107/PαMS1 or 70/30 Kraton 1107/PαMS2 mixtures, as indicated in the TEM photomicrographs of Figure 10. It can then be concluded that the values of plateau modulus in mixtures of block copolymer and homopolymer are greatly influenced by the morphological state of the mixture.

Theoretical Interpretation of Experimental Results

We have shown above that the plateau modulus of mixtures of a block copolymer and a homopolymer is greatly influenced by whether or not *macrophase* separation has taken place in the mixture, which in turn is dependent upon the molecular weight of the homopolymer

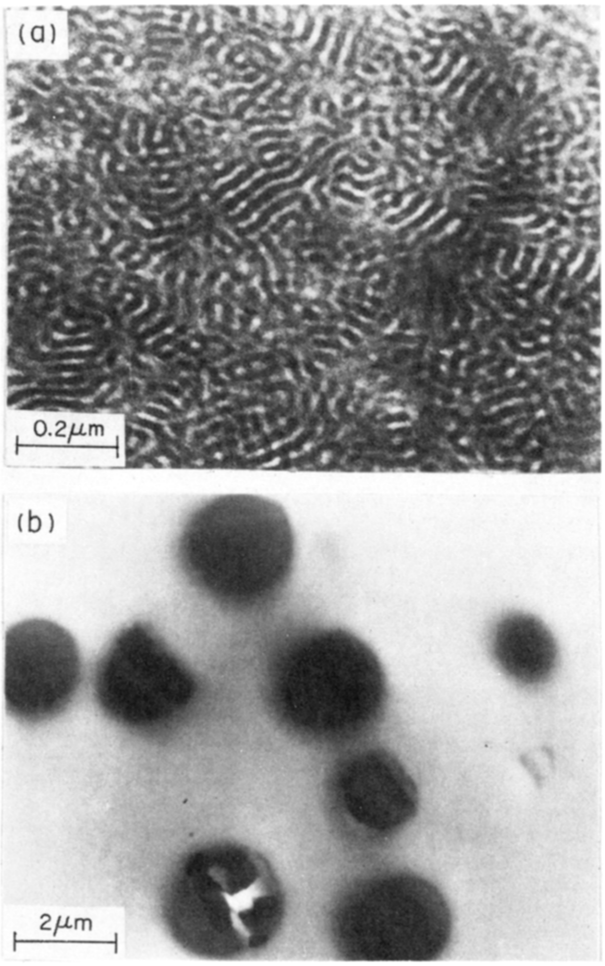

Figure 11. TEM photomicrographs of (a) 70/30 Kraton 1102/PαMS7 mixture and (b) 70/30 Kraton 1107/PαMS7 mixture.

added. Since experimental investigations to find relationships between the molecular weight of homopolymer and the onset of macrophase separation are very time consuming, it is highly desirable to be able to develop such relationships theoretically. As a matter of fact, a statistical thermodynamic theory due to Noolandi and co-workers[7,8] is available, which allows one to find such relationships. In this section we will first review very briefly Noolandi's theory and then use it to interpret the experimental results presented above, by constructing phase diagrams for the Kraton 1102/PαMS and Kraton 1107/PαMS mixtures for different values of the molecular weight of PαMS.

Noolandi's Theory. Noolandi and co-workers[7,8] have developed a statistical thermodynamic theory, which allows one to predict the spinodal temperature (T_s) of microphase separation in mixtures of a block copolymer and a homopolymer, the chemical structure of which may be *different* from that of one of the blocks. Note that the experimental systems (Kraton 1102/PαMS and Kraton 1107/PαMS mixtures) investigated in this study have the homopolymer PαMS whose chemical structure is different from that of the constituent components of the block polymers employed.

Using functional integral formalism, Noolandi and coworkers[7,8] derived an expression for the free energy of an inhomogeneous mixture of a block copolymer and a homopolymer and suggested that the T_s of mixtures of a block copolymer and a homopolymer can be determined by satisfying the following relation:

$$\lambda_-(q^*) = 0 \qquad (2)$$

where q^* is the value of the wave vector q that minimizes λ_-, which is defined by

$$\lambda_-(q) = (1/2)[c(q) + a(q) - \Delta(q)] \qquad (3)$$

where

$$\Delta(q) = [(c(q) - a(q))^2 + 4b^2(q)]^{1/2} \qquad (4)$$

$$a(q) = \frac{g_{AA}^{-1}(q)}{r_C\phi_C} + \frac{1}{r_H\phi_H g_H(q)} - 2\chi_{AH} \qquad (5)$$

$$b(q) = \frac{g_{AB}^{-1}(q)}{r_C\phi_C} + \frac{1}{r_H\phi_H g_H(q)} + \chi_{AB} - \chi_{AH} - \chi_{BH} \qquad (6)$$

$$c(q) = \frac{g_{BB}^{-1}(q)}{r_C\phi_C} + \frac{1}{r_H\phi_H g_H(q)} - 2\chi_{BH} \qquad (7)$$

where subscripts A, B, C, and H refer to block A, block B, copolymer, and homopolymer, respectively; χ_{AB}, χ_{AH}, and χ_{BH} are interaction parameters; r_C is equal to V_C/V_r and r_H is equal to V_H/V_r, where V_r is the reference volume and V_C and V_H are the molecular volumes of the block copolymer and homopolymer, respectively; ϕ_C and ϕ_H are the volume fractions of the block copolymer and homopolymer, respectively, in the mixture; and $g_H(q)$ is equal to $g(x_h)$, which is defined by

$$g(x_j) = (2/x_j^2)[x_j + \exp(-x_j) - 1] \qquad (8)$$

in which x_j (j = 1, 2, h) are defined by

$$x_1 = q^2R_1^2/6; \qquad x_2 = q^2R_2^2/6; \qquad x_h = q^2R_H^2/6 \qquad (9)$$

where R_1, R_2, and R_H are the root-mean-square end-to-end distances of block A, block B, and homopolymer, respectively. In eq 5–7, $g_{AA}^{-1}(q)$, $g_{BB}^{-1}(q)$, and $g_{AB}^{-1}(q)$ are elements of the inverse of matrix $\|\mathbf{g}\|$, defined by

$$\left\|\begin{matrix} g_{AA}(q) & g_{AB}(q) \\ g_{BA}(q) & g_{BB}(q) \end{matrix}\right\| = \left\|\begin{matrix} S_{11}(q)/N & S_{12}(q)/N \\ S_{12}(q)/N & S_{22}(q)/N \end{matrix}\right\| \qquad (10)$$

For an ABA-type block copolymer, the expressions for $S_{11}(q)$, $S_{12}(q)$, and $S_{22}(q)$ appearing in eq 10 are given by[22]

$$S_{11} = N[g_1(f_1,x) + g_1(f_2,x) + g_1(f_3,x) + g_1(1,x) - g_1(1-f_3,x) - g_1(1-f_1,x)] \qquad (11)$$

$$S_{22} = Ng_1(f_2,x) \qquad (12)$$

$$S_{12} = (N/2)[g_1(1-f_1,x) + g_1(1-f_3,x) - g_1(f_1,x) - g_1(f_3,x) - 2g_1(f_2,x)] \qquad (13)$$

where $g_1(f,x)$ is equal to $f^2g(x_j)$, $g(x_j)$ being defined by eq 8; f_1, f_2, and f_3 are the volume fractions of each block sequence in the ABA-type triblock copolymer, for which $f_1 = f_3$ and thus $2f_1 + f_2 = 1$; and N is the polymerization index of the block copolymer.

It should be noted that eq 2–7 contain three interaction parameters, χ_{AB}, χ_{AH}, and χ_{BH}, which in turn depend on temperature. Therefore, one must find the temperature which satisfies the condition given by eq 2. A computational procedure that can be used to determine the spinodal temperature T_s of *microphase* separation is presented in the Appendix. Note that when the chemical structure of the homopolymer is *identical* with that of one of the blocks, it can be shown that Nooland's theory reduces to Leibler–Benoit's theory[23] (see Appendix).

Construction of Phase Diagram. The spinodal decomposition for *macrophase* separation occurs at a temperature that satisfies eq 2 at the wave vector $q^* = 0$ (or $x^* = 0$). The construction of a binodal curve for an inhomogenous system is much more difficult. In the present study, we have constructed binodal curves by following the computational procedures described by Noolandi and co-

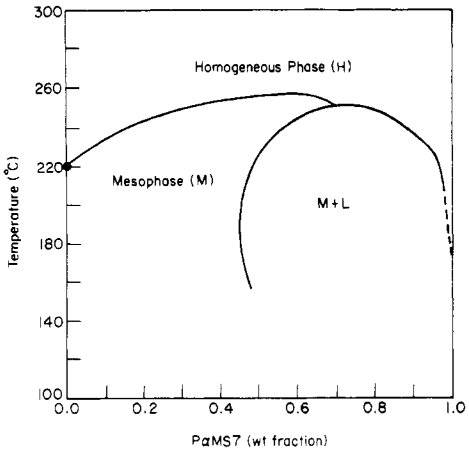

Figure 12. Phase diagram for mixtures of Kraton 1102 and PαMS7 having a molecular weight of 8000.

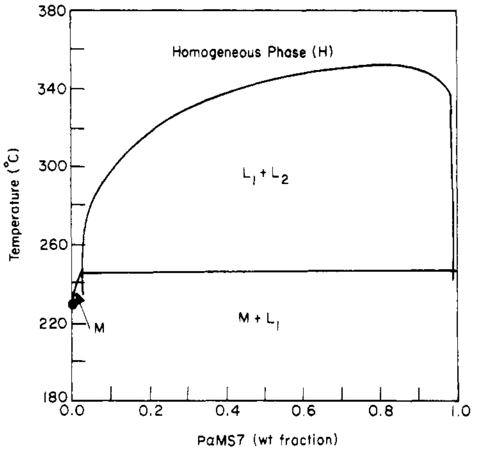

Figure 13. Phase diagram for mixtures of Kraton 1107 and PαMS7 having a molecular weight 8000.

workers,[7,8] who considered, in addition to the homogeneous free energy (i.e., Flory–Huggins free energy), the second- and fourth-order terms in the expansion of the inhomogenous free energy. The binodal curves thus constructed are valid only for the *lamellar* microdomain structure in a block copolymer. When a block copolymer has a spherical or cylindrical microdomain structure, which is the case investigated by us, the third-order term, as well as the second- and fourth-order terms, must be included in the expansion of the inhomogeneous free energy when constructing binodal curves. Since solutions for the expansion of the inhomogeneous free energy that include the second-, third- and fourth-order terms are not available at the present time, in this study we have constructed phase diagrams from (a) the spinodal temperature T_s of microphase separation, determined by the procedure given in the Appendix, and (b) the binodal curve by following the procedures mentioned above. The phase diagrams thus constructed are given in Figures 12–14 for the Kraton 1102/PαMS and Kraton 1107/PαMS mixtures. Although these phase diagrams may not be highly accurate, we believe that they can help us to interpret, at least qualitatively, the experimental results presented above.

In the construction of phase diagrams we used the expreessions for interaction energy density given in Table III and the expressions for specific volume given in Table IV. It should be mentioned that in the numerical computations we used the interaction energy density Λ, as advocated by Roe and co-workers,[15] which is related to the Flory–Huggins interaction parameter χ by $\Lambda = \chi RT/V_r$, where R is the universal gas constant, T is the absolute temperature, and V_r is the reference volume. We have found that the use of Λ has an advantage over the use of χ, in that the necessity for determining the reference volume V_r and the polymerization index N can be avoided.[31]

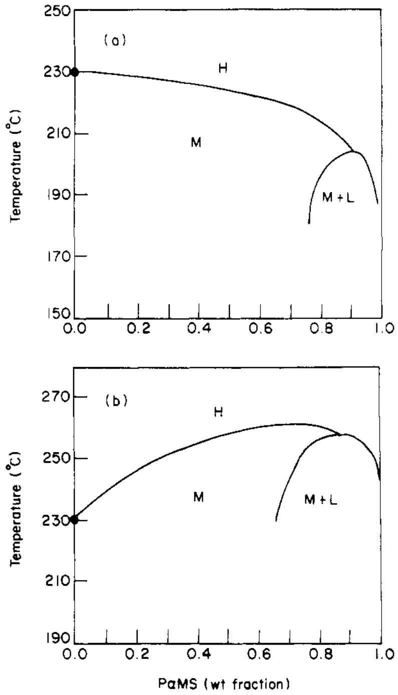

Figure 14. Phase diagrams for (a) mixtures of Kraton 1107 and PαMS1 having molecular weight of 1200 and (b) mixtures of Kraton 1107 and PαMS2 having molecular weight of 1900.

Table III
Expressions for the Interaction Energy Density of the Polymers Investigated

polymer pair	interaction energy density, cal/cm³
polystyrene/polybutadiene[24,25]	$\Lambda_{PS/PB} = 1.573 - 0.0021T + 0.09\phi_{PS}$
polystyrene/poly(α-methylstyrene)[25]	$\Lambda_{PS/P\alpha MS} = 0.0608 - 0.56 \times 10^{-4}T + 0.0018\phi_{P\alpha MS}$
polybutadiene/poly(α-methylstyrene)[25]	$\Lambda_{PB/P\alpha MS} = 1.276 - 0.00183T - 0.021\phi_{PB}$
polystyrene/polyisoprene[26]	$\Lambda_{PS/PI} = 1.663 - 0.00234T$
polyisoprene/poly(α-methylstyrene)[26]	$\Lambda_{PI/P\alpha MS} = 1.681 - 0.0026T$

[a] T is the absolute temperature. [b] ϕ is the volume fraction.

Table IV
Expressions for the Specific Volumes of the Polymers Investigated

polymer	specific volume, cm³/g
polystyrene[27]	$v_{PS} = 0.9199 + 5.098 \times 10^{-4}(T - 273) + 2.354 \times 10^{-7}(T - 273)^2 + (32.46 + 0.1017(T - 273))/M_{w,PS}$
polybutadiene[28]	$v_{PB} = 1.1138 + 8.24 \times 10^{-4}(T - 273)$
poly(α-methylstyrene)[29]	$v_{P\alpha MS} = 0.87 + 5.08 \times 10^{-4}(T - 273)$
polyisoprene[30]	$v_{PI} = 1.0771 + 7.22 \times 10^{-4}(T - 273) + 2.46 \times 10^{-7}(T - 273)^2$

[a] T is the absolute temperature. [b] $M_{w,PS}$ is the molecular weight of polystyrene.

Figure 12 gives a phase diagram for mixtures of Kraton 1102 and PαMS7 having a molecular weight (M_w) of 8000. Note in Figure 12 that (a) the closed circle at 220 °C represents the microphase separation transition temperature (T_r) of Kraton 1102, which was determined experimentally in a previous study;[32] (b) the curve separating the homogeneous phase (H) and mesophase (M) was obtained by determining the temperature T_s that satisfied eq A4;

and (c) the binodal curve, which separates the mesophase (M) and the macrophase-separated liquid phase (L), was constructed by the procedures described above.

According to Figure 12, macrophase separation does not take place in Kraton 1102/PαMS7 mixtures containing less than about 40 wt % of PαMS7. This observation supports the result of the TEM photomicrograph, given in Figure 11a, showing no evidence of macrophase separation for the Kraton 1102/PαMS7 containing 30 wt % of PαMS7. This further confirms our conclusion drawn above, in reference to Figure 2, that the steady increase of the plateau modulus for the 70/30 Kraton 1102/PαMS mixtures with increasing molecular weight of PαMS up to 8000 was attributed to the fact that the entire amount of PαMS added had entered into the microdomains of the polystyrene phase. In order to confirm the theoretically predicted phase diagram given in Figure 12, we have conducted light-scattering experiments for the various concentrations of Kraton 1102/PαMS7 mixtures. We indeed have confirmed that the Kraton 1102/PαMS7 mixtures containing more than 50 wt % of PαMS7 show turbidity, indicating that those mixtures undergo *macrophase* separation.

Figure 13 gives a phase diagram for mixtures of Kraton 1107 and PαMS7 having a M_w of 8000. Note in Figure 13 that the closed symbol represents the T_r of Kraton 1107, which was determind experimentally in a previous study.[32] Figure 13 suggests that macrophase separation can occur when the amount of PαMS7 in the mixture exceeds about 4 wt %. This observation then supports the result of the TEM photomicrograph, given in Figure 11b, showing macrophase-separated domains of PαMS7 for the 70/30 Kraton 1107/PαMS7 mixture. Note that the horizontal line in Figure 13 separates two regions: (a) region M + L_1, which consists of mixtures of Kraton 1107 in the mesophase state (M) and macrophase-separated PαMS7 (L_1), and (b) region L_1 + L_2, which consists of mixtures of macrophase-separated PαMS7 (L_1) and Kraton 1107 in the disordered state (L_2). According to Roe and Zin,[33] the intensity of turbidity increases when crossing the horizontal line from region M + L_1 to region L_1 + L_2.

Figure 14 gives phase diagrams (a) for mixtures of Kraton 1107 and PαMS1 having a M_w of 1200 and (b) for mixtures of Kraton 1107 and PαMS2 having a M_w of 1900. It is of interest to note in Figure 14 that the T_s of *microphase* separation in Kraton 1107/PαMS1 mixtures decreases steadily with increasing amount of PαMS1, but the T_s of *microphase* separation in Kraton 1107/PαMS2 mixtures increases with increasing amount of PαMS2. Figure 14 suggests that *macrophase* separation would *not* occur for the Kraton 1107/PαMS mixture when it contains an amount of PαMS1 less than about 75 wt % or when it contains an amount of PαMS2 less than about 60 wt %. These observations support the results of the TEM photomicrographs, given in Figure 10, which showed no evidence of macrophase separation in the respective mixtures. The phase diagrams given in Figures 13 and 14 appear to support our conclusion drawn above, in reference to Figure 4, that the plateau modulus for the 70/30 Kraton 1107/PαMS mixture would first increase with increasing molecular weight of PαMS and then decrease, due to the occurrence of macrophase separation, when the molecular weight of PαMS exceeds a certain critical value.

Although our experimental results are explained at least qualitatively by the phase diagrams given in Figures 12–14, more accurate phase diagrams could have been constructed had the third-order term in the expansion of the inhomogeneous free energy been also included in the computation. In the absence of a suitable theory at the present time, we were not able to do this. Further theoretical work is needed in this area.

Concluding Remarks

It was shown from experimental study that the linear viscoelastic properties of a mixture of block copolymer and homopolymer are greatly influenced by the molecular weight of the homopolymer. It was observed that for a given block copolymer there exists a critical value of molecular weight of homopolymer added at which macrophase separation takes place and that the plateau modulus of mixtures of a block copolymer and a homopolymer decreases with increasing molecular weight of homopolymer, once macrophase separation has taken place. The occurrence of macrophase separation in a mixture of block copolymer and homopolymer is related to the solubility limits for a given pair of homopolymer and block copolymer. The solubility limits in turn depend on the molecular weight ratio of homopolymer to block copolymer, M_H/M_C, and also on the composition of the block copolymer itself.

We can now explain why, when the PαMS7 having a M_w of 8000 was added to Kraton 1102 and Kraton 1107, the 70/30 Kraton 1107/PαMS7 mixtures underwent *macrophase* separation (see Figure 11b), while the 70/30 Kraton 1102/PαMS7 mixtures did not (see Figure 11a). It should be remembered that Kraton 1102 has about 28 wt % and Kraton 1107 about 14 wt % of polystyrene (see Table I). Thus, Kraton 1102 can be mixed with greater amounts of PαMS7 than can Kraton 1107, before the mixtures reach solubility limits. Note that solubility limits would decrease as M_H/M_C increases. This now explains why no macrophase separation was observed in the 70/30 Kraton 1107/PαMS mixtures containing PαMS having molecular weights up to 1900 (see Figure 10), while macrophase separation took place when the molecular weight of PαMS was increased to 8000 (see Figure 11b).

However, the experimental determination of solubility limits for mixtures of a block copolymer and a homopolymer, in terms of the molecular weight ratio of homopolymer to block copolymer and the composition of a block copolymer, would require an enormous amount of effort. Thus, it is highly desirable for one to be able to predict the conditions at which macrophase separation takes place in mixtures of a block copolymer and a homopolymer, in terms of those variables referred to above. Such predictions would greatly help one to prepare various formulations for use, for instance, in pressure-sensitive and hot-melt adhesives.

We have demonstrated above that indeed such predictions are possible, using the currently held statistical thermodynamic theory.[7,8] However, the existing theory assumes that the block copolymer has a lamellar microdomain structure. Therefore, further theoretical study is needed, which will enable one to construct phase diagrams for mixtures of a block copolymer and a homopolymer, where the block copolymer can have spherical or cylindrical microdomain structures. It should be emphasized that accurate predictions of equilibrium phase behavior of mixtures of a block copolymer and a homopolymer require reliable information on the interaction parameter and specific volume for a given polymer pair.

Appendix

We will describe below the computational procedure for determining the spinodal temperature (T_s) of microphase separation for mixtures of an ABA-type triblock copolymer and a homopolymer, using Noolandi's theory. We must first determine the value of the wave vector q^* which satisfies eq 2. Note that from eq 3 and 4 we have

$$a(q^*)c(q^*) = b^2(q^*) \tag{A1}$$

where a, b, and c are defined by eq 5, 6, and 7, respectively. The components of the inverse of matrix $\|\mathbf{g}\|$, g_{AA}^{-1}, g_{AB}^{-1}, and g_{BB}^{-1}, which appear in eq 5–7, are defined by

$$g_{AA}^{-1} = g_{BB}/D; \qquad g_{AB}^{-1} = -g_{AB}/D; \qquad g_{BB}^{-1} = g_{AA}/D \tag{A2}$$

where D is defined by

$$D = g_{AA}g_{BB} - g_{AB}^2 \tag{A3}$$

and g_{AA}, g_{BB}, and g_{AB} are given by eq 11–13, respectively.

Substitution of eq 5–7 into eq A1 gives

$$\begin{aligned}&[(1 - a_0 - b_0)^2 - 4a_0b_0](\chi_{AB}r_C\phi_C)^2 + \\ &\quad 2\left[\left(g_{AB}^{-1} + \frac{1}{A}\right)(1 - a_0 - b_0) + a_0\left(g_{BB}^{-1} + \frac{1}{A}\right) + b_0\left(g_{AA}^{-1} + \frac{1}{A}\right)\right]\chi_{AB}r_C\phi_C + \\ &\left[\left(g_{AB}^{-1} + \frac{1}{A}\right)^2 - \left(g_{AA}^{-1} + \frac{1}{A}\right)\left(g_{BB}^{-1} + \frac{1}{A}\right)\right] = 0\end{aligned} \tag{A4}$$

where

$$A = \frac{r_H\phi_H}{r_C\phi_C}g_H; \qquad a_0 = \chi_{AH}/\chi_{AB}; \qquad b_0 = \chi_{BH}/\chi_{AB} \tag{A5}$$

Note that the interaction parameters χ_{AB}, χ_{AH}, and χ_{BH} depend on temperature. Therefore, one must find the temperature T_s which satisfies eq A4, using an iterative procedure. It can be seen from eq A4 that for a given copolymer composition, $\chi_{AB}r_C$ ($=\chi_{AB}N_C$) is dependent upon V_H/V_C, ϕ_H, χ_{AH}/χ_{AB}, and χ_{BH}/χ_{AB}.

When the chemical structure of the homopolymer is identical with that of block A (i.e., $\chi_{AH} = 0$ and $\chi_{BH} = \chi_{AB}$), eq A4 reduces to

$$2(\chi_{AB})_s r_C = \frac{\phi_H(r_H/r_C)g_H + \phi_C(g_{AA} + g_{BB} + 2g_{AB})}{\phi_C\phi_H(r_H/r_C)g_Hg_{BB} + \phi_C^2(g_{AA}g_{BB} - g_{AB}^2)} \tag{A6}$$

where the subscript s on the variable χ_{AB} refers to the transition condition. On the other hand, when the chemical structure of the homopolymer is identical with that of block B (i.e., $\chi_{BH} = 0$ and $\chi_{AH} = \chi_{AB}$), eq A4 reduces to

$$2(\chi_{AB})_s r_C = \frac{\phi_H(r_H/r_C)g_H + \phi_C(g_{AA} + g_{BB} + 2g_{AB})}{\phi_C\phi_H(r_H/r_C)g_Hg_{AA} + \phi_C^2(g_{AA}g_{BB} - g_{AB}^2)} \tag{A7}$$

We can now show that eq A6 or eq A7 is identical with the expression that can be derived from Leibler–Benoit's theory,[23] which is applicable to situations only where the chemical structure of the homopolymer is identical with that of one of the blocks.

As a matter of fact, Nojima and Roe[34] used Leibler–Benoit's theory[23] to determine the spinodal temperature T_s for a mixture consisting of an AB-type diblock copolymer and a homopolymer, which had an identical chemical structure with that of block A, by finding the value $q = q^*$, which minimized $Q(q)$ defined by eq 2 of ref 34:

$$2(\Lambda/kT)_s = Q(q^*) = \frac{S_{11}(q^*) + S_{22}(q^*) + 2S_{12}(q^*)}{S_{11}(q^*)S_{22}(q^*) - S_{12}^2(q^*)} \tag{A8}$$

where the subscript s on the variable Λ/kT refers to the transition condition, k is the Boltzmann constant, Λ is the interaction energy density, which is related to the interaction parameter χ by

$$\Lambda = \chi RT/V_r \tag{A9}$$

where V_r is a reference volume, R is the universal gas constant, and T is the absolute temperature.

Substituting eq 4–6 of ref 34 into eq A8, one obtains

$$2(\Lambda/kT)_s V_C = \frac{\phi_H(r_H/r_C)g_H + \phi_C(g_{AA} + g_{BB} + 2g_{AB})}{\phi_C\phi_H(r_H/r_C)g_Hg_{BB} + \phi_C^2(g_{AA}g_{BB} - g_{AB}^2)} \tag{A10}$$

where, in terms of the variables appearing in ref 34, we have

$$g_{AA} = f_1^2g(x_1) \tag{A11}$$

$$g_{BB} = f_2^2g(x_2) \tag{A12}$$

$$g_{AB} = f_1f_2[1 - \exp(-x_1)][1 - \exp(-x_2)]/x_1x_2 \tag{A13}$$

It can be seen that eq A10 is identical with eq A6, since $(\Lambda/kT)_s V_C = \chi_s V_C/V_r = \chi_s r_C$.

Registry No. PαMS, 25014-31-7; (I)(S) (copolymer), 105729-79-1.

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