Miscibility, Microstructure, and Dynamics of Blends Containing Block Copolymer. 1. Miscibility of Blends of Homopolystyrene with Styrene–Butadiene Block Copolymers

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Received August 31, 1993; Revised Manuscript Received August 30, 1994®

ABSTRACT: The miscibilities of blends of homopolystyrene/styrene–butadiene/styrene (PS/SBS) and PS/SB-4A (4-arm star block copolymer) have been studied by dynamic mechanical analysis (DMA) and ^{13}C CPMAS NMR techniques. The results indicate that the miscibilities of these two blends depend on the molecular weight of PS (M_{PS}) and are almost independent of the molecular architecture of the studied block copolymers. It is also found that there exists an optimum range of M_{PS} which will give rise to well-improved mechanical properties of the blends. The reason suggested for this phenomenon is that the intermolecular entanglement interaction plays a critical role. It is also found that even when the ratio value of M_{PS}/M_{bPS} (molecular weight of PS block in SB block copolymers) is as high as 1.2 for PS/SB-4A and 1.5 for PS/SBS, PS is still miscible with the PS block microdomains very well. Meanwhile, when M_{PS} is much higher than M_{bPS}, the blends of PS/SBS and PS/SB-4A are still partially miscible.

Introduction

Recently much attention has been paid to the miscibility and morphology of blends comprised of a homopolymer and a block copolymer. Many new microstructures, such as "mesh" and "strut" structure[1] and the ordered bicontinuous double diamond (OBDD) structure, etc.,[2] have been discovered in such blends. The effect of the molecular weight of the homopolymer on the ordered structure of the blends consisting of a block copolymer and a homopolymer has been systematically studied by some authors.[3–6] Some common experimental evidences have been found: (1) The molecules of the homopolymers of lower molecular weight will cause, more or less, the microdomains of the block corresponding to the homopolymer to swell. (2) The swelling generally changes the microdomain morphology. (3) The solubilization behavior of homopolymers in the microdomains of block copolymer strongly depends on both the molecular architecture of the block copolymer and the location of the blocks corresponding to the homopolymer. Different ratio values of the molecular weight of the homopolymer to that of the corresponding block in the copolymer (M_{PS}/M_{bPS}) are required for block copolymers of different architectures in the case of that the corresponding block is in the center of the block copolymer.

However, as compared to the attention paid to the morphology of the homopolymer/block copolymer blends, it seems that not enough attention has been paid to the molecular motion and mechanical properties of blends of such type. Besides, almost all the studies on the morphology of these blends have been made by means of transmission electron microscopy (TEM) and/or small-angle X-ray scattering (SAXS), which cannot provide the structural information on a molecular level. Therefore, the "real" microstructure of such blends remains unknown. In order to understand the origin of and hence to control the unique properties of such blends, this study is of both academic and technical significance.

Table 1. Molecular Characteristics of Homopolystyrenes

sample	$M_n \times 10^{-4}$	M_w/M_n	T_g (K)
PS03	0.32	1.05	339.3
PS1	0.97	1.03	367.0
PS2	2.16	1.04	369.2
PS12	12.5	1.06	371.8
PS100	97.4	1.08	374.5

It is well-known that NMR techniques can provide information about miscibility, molecular motion, and heterogeneity (morphology) of polymer blends on a molecular level.[7–9] The purpose of this work is to explore the relationship between the microstructure of homopolymer/block copolymer blends and their mechanical properties. The blends of two styrene-butadiene block copolymers (SB) with different molecular architectures and homopolystyrene (PS) of different molecular weights (M_w's) have been investigated by NMR and dynamic mechanical analysis (DMA) techniques.

Experimental Section

The polymers used in this study were all commercial products. PS with different M_w's were obtained from Nanjing University; triblock (SBS) and four-arm star block (SB-4A) copolymers were obtained from the Synthetic Rubber Factory of Baling Petro-Chemical Co. and were purified before use. Solution blending was used in this study, using toluene as solvent and a solution concentration of 5% (w/v).

Film specimens of PS/SBS and PS/SB-4A (20:80 by weight) were cast from the solution at 40 °C and then dried under vacuum at 60 °C until a constant weight was attained. The characteristic data of the polymers are listed in Tables 1 and 2.

DMA experiments were done on a dynamic viscoelastometer (Rheovibron DDV-II-EA) at a heating rate of 3 °C/min from −120 to +140 °C. The vibration frequency was 3.5 Hz. The specimens used were about 2.6 × 0.44 × 0.015 cm.

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® Abstract published in *Advance ACS Abstracts,* October 15, 1994.

0024-9297/94/2227-7830$04.50/0

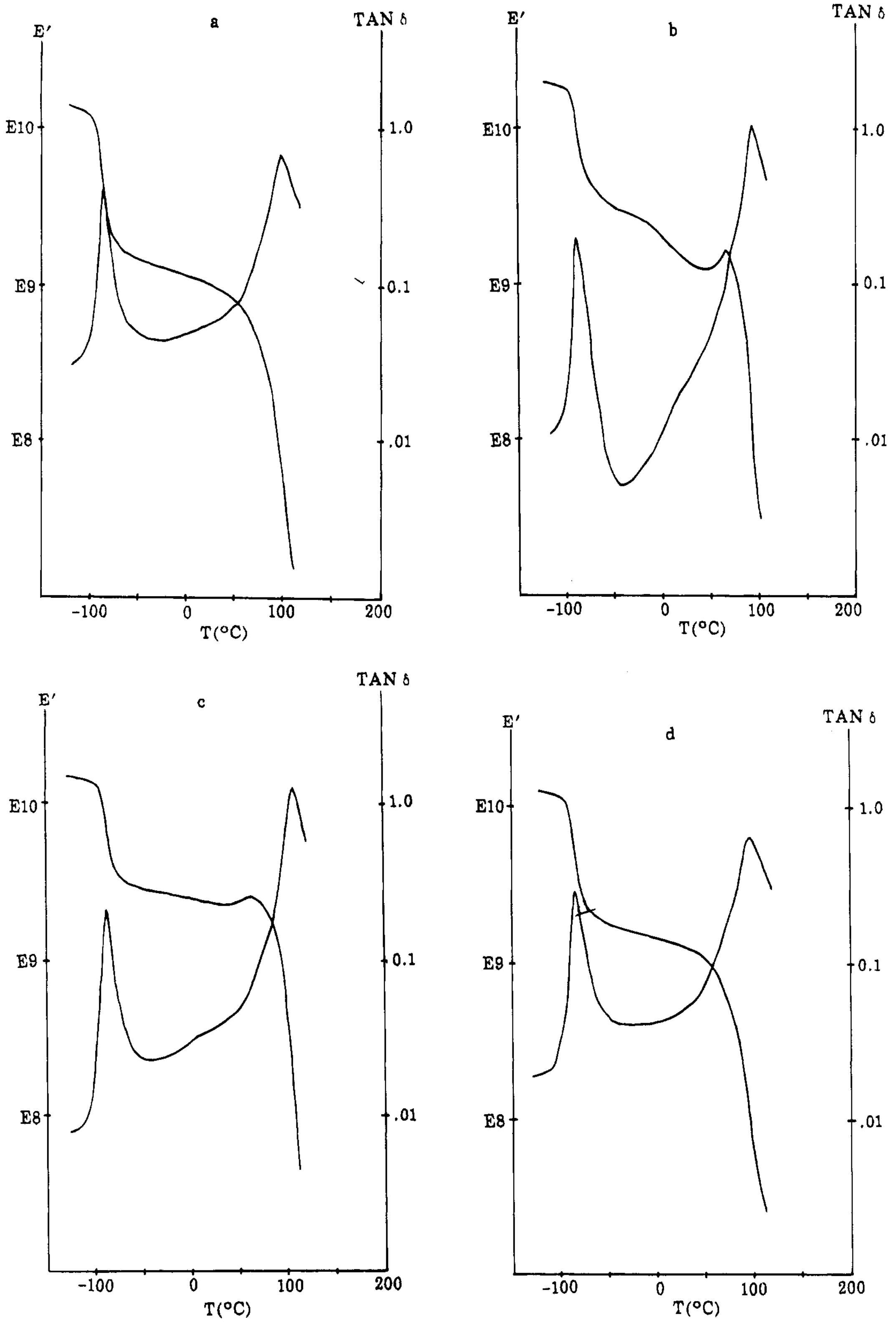

Figure 1. DMA curves of SB-4A and its blends with PS; (a) SB-4A; (b) PS03/SB-4A; (c) PS1/SB-4A; (d) PS100/SB-4A.

Table 2. Molecular Characteristics of Block Copolymers

sample	$M_n \times 10^{-4}$ [a]	S/B[b] (w/w)	PS $M_n \times 10^{-4}$
SBS	6.70	44/56	1.47
SB-4A[c]	15.43	45/55	1.73

[a] Determined by membrane osmometry in toluene at 37 °C. [b] Determined by ^{13}C NMR. [c] PS blocks locate at the outer ends of the copolymer chains.

Proton spin–lattice relaxation times in the rotating frame, $T_{1\rho}$, were measured on a Bruker MSL-400 NMR spectrometer at 298.0 K. The TOSS method was used for suppressing the spinning side band. The carbon resonance frequency was 100.63 MHz, and the proton resonance frequency was 400.13 MHz. A 4.8-μs 90° pulse for the ^{13}C nucleus and a 5.1-μs 90° pulse for ^1H were used. The Hartmann–Hahn cross-polarization matching field was about 49 kHz. The contact time (CT) was 1.0 ms. The delay time was 2 s.

Results and Discussion

A. Results of DMA. Shown in Figure 1a–d are plots of E' vs T and tan δ vs T of SB-4A and its blends with PS of different M_w's. All the blends have the same composition with 80 wt % of SB-4A. The glass transi-

Table 3. T_g's of SB-4A and Its Blends[a] with PS

material	T_{g^1} (°C)	T_{g^2} (°C)
SB-4A	−86.9	+99.1
PS03/SB-4A	−90.2	+93.2
PS1/SB-4A	−88.6	+106.1
PS2/SB-4A	−88.9	+106.0
PS12/SB-4A	−86.0	+97.1
PS100/SB-4A	−84.2	+97.1

[a] Blend composition: PS/SB-4A 20/80 by weight. $T_{g^1} = T_g$ of PBD; $T_{g^2} = T_g$ of PS.

Table 4. T_g's of SBS and Its Blends[a] with PS

material	T_{g^1} (°C)	T_{g^2} (°C)
SBS	−87.0	+98.9
PS03/SBS	−87.5	+93.2
PS1/SBS	−85.9	+105.1
PS2/SBS	−86.0	+105.1
PS100/SBS	−86.0	+97.1

[a] Blend composition: PS/SBS 20/80 by weight. $T_{g^1} = T_g$ of PBD; $T_{g^2} = T_g$ of PS.

tion temperatures (T_g) of SB-4A and its blends with PS of different M_w's are listed in Table 3.

It is noticed that the films of SB-4A and its blends with PS03, PS1, or PS2 are all transparent, but the film of the PS12/SB-4A blend shows distinct phase separation; the film of the PS100/SB-4A blend is opaque, but its domains are not big enough to be seen by the naked eye. Obviously, the miscibility of these blends is quite different. The dynamic mechanical properties of these blends, obtained by measurements of their viscoelasticity, have several features deserving mention: (1) For pure SB-4A, two T_g values, −86.9 and +99.1 °C, are observed, which are assigned to the glass transition temperatures of polybutadiene (PBD) and PS chains, respectively. (2) For the blends whose films are transparent, blending results in a decrease in T_g of PBD and an increase in T_g of PS with the exception of PS03/SB-4A. (3) On the contrary, for the blends giving opaque films, mixing of the two polymers gives rise to an increase in PBD T_g and a decrease in PS T_g. (4) At the same time, with the increase in temperature for PS03/SB-4A and PS1/SB-4A there appears an increase in the storage modulus (E') right before their final sharp drop.

The above results of the blends may be explained as follows: (1) As the M_w of PS03 is very low, when it is mixed with SB-4A, most of the PS03 molecules solubilize in the microdomains of the PS block, resulting in an increase in the size of the PS block microdomains with low M_w PS molecules free to more; hence, the T_g of the PS block domain decreases. At the same time, there are detectable quantities of PS03 molecules dispersing in the microdomains of the PBD block, which also has two effects on the PBD domains; i.e., increasing the size of the PBD domains and lowering the T_g value of the PBD block, but the pure PBD domains become smaller. The reason for the decrease in T_g of the PBD block may be ascribed to the increase in its motion freedom which originates from the addition of PS03 with bulky pendant groups. (2) For the blend of SB-4A with PS1 or PS2, the situation is somewhat different. As can be seen from Table 3, for both PS1/SB-4A and PS2/SB-4A, the lowering of the T_g values of the PBD block is not as much as that of PS03/SB-4A, while their T_g's of the PS block increase much more than that of PS03/SB-4A. A possible explanation for both cases is the increase in M_w's of the PS components, which decreases the solubility of the PS chains in the PBD domains and especially results in the existence of entanglements between the PS blocks and the PS polymer chains. The entanglements can be considered as intermolecular interferences to the translational and rotational motion of the whole coils or large portions of them (for flexible polymers) or whole rodlike macromolecules (for rigid polymers).[10−12] According to Aharoni,[10,11] for undiluted PS the characteristic molecular weight between intermolecular entanglements, M_c, is 7650 and the spatial distance between intermolecular entanglements, R_c, is 31.18 Å. For the PS/SB-4A blends, there exist at least two possible entanglement interactions between the PS1 (or PS2) and PS block chains. They are the entanglements between the PS chains and the PS block in SB-4A within the PS domains and the entanglements between them locating at the interface of the PS domains and the PS block domains. In this situation, some PS chains may go through two or more PS block domains, while some may even bridge two PS block domains separated by a PBD domain. The latter is similar to "strut" structure observed by Hashimoto et al.[1] It is the entanglement interactions that seriously hinder the molecular motions of the PS block chains, resulting in an increased PS T_g of the blends. It is these entanglement interactions which make the storage modulus of the blends have an increase near the glass transition temperature. The reason for decreased PBD T_g's of PS1/SB-4A and PS2/SB-4A is similar to that of the PBD block in PS03/SB-4A. (3) For blends of PS12/SB-4A and PS100/SB-4A, inward shifts of both the T_g's of the PBD block and the PS block are observed, which implies that partial miscibility occurs between the PS and SB-4A polymers, in spite of the rather high molecular weight of PS. Moreover, it can be seen that the effect of PS100 on the T_g of the PBD block is greater than that of PS12. A possible explanation for this is that more entanglements exist between the PS chains and the PBD and PS blocks in the blends. It is easy to understand that the higher the M_w's of PS, the more the number of the entanglements and hence the greater the effect of PS on the segment motions of both kinds of blocks. Of course, the effects of the M_w of PS are not infinite; the entanglement effects only improve the miscibility of the PS/SB-4A blends to some degree, within a certain range of the M_{PS}/M_{bPS} ratio. According to the DMA results, it is found that both miscibility and mechanical properties of the SB-4A blends are strongly dependent on the molecular weight of PS. Obviously, for blends of a fixed composition there exists an optimum range of PS M_w's which will effectively improve the mechanical properties of the blends, including the enhancement of the storage modulus and the broadening of its temperature range. It is interesting to point out that the miscibility of PS03/SB-4A is better than that of the blends of SB-4A with PS1 and with PS2, respectively, but its mechanical properties are poorer than that of the latter. The main reason is that there exist entanglement interactions in the latter cases but not in the former, because the molecular weight of PS03 (3400) is much smaller than the characteristic molecular weight between entanglements, M_c, of PS which is 7650. Therefore, it is seen that the mechanical properties of the blends depend on their morphology as well as the chain entanglement interactions in the blends.

Interestingly, according to the results of DMA, the miscibility of PS/SBS blends is similar to that of the PS/SB-4A blends. The glass transition temperatures of SBS and its blends, measured under the same conditions as used for the PS/SB-4A blends, are listed in Table 4. In comparison with the T_g values of SB-4A and

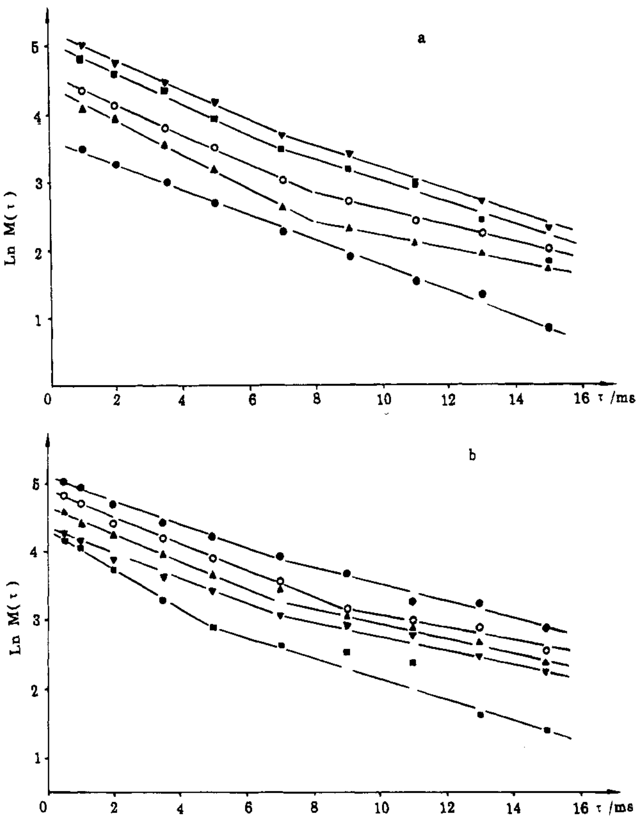

Figure 2. Plots of logarithmic ^{13}C resonance intensity vs time of proton spin-locking of the PS/SB-4A blends: (●) SB-4A; (○) PS03/SB-4A; (▲) PS1/SB-4A; (▼) PS12/SB-4A; (■) PS100/SB-4A. (a) PS in the blends; (b) PBD in the blends.

its blends, the effects of the addition of PS on the low-temperature T_g's of PBD in PB/SBS blends are less. The possible explanation is that the amount of PS dissolved in the PBD microdomains in SBS is less than that dissolved in the PBD microdomains in SB-4A. In fact, the addition of PS has almost no effect on the low-temperature T_g's of PBD in SBS within experimental error. The high-temperature PS T_g values of the PS/SBS blends are similar to those of the PS/SB-4A blends. Therefore, from the DMA results, it may be concluded that the added PS molecules mainly solubilize in PS block domains and the effect of molecular architecture of block copolymers on the miscibility of homopolymer and block copolymer blends is very small, so long as the blocks corresponding to the homopolymer locate at the outer ends of the block copolymer chains. This is in good agreement with the work of Zhao.[6]

B. Results of $T_{1\varrho}$(H) Measurements. Usually, a single $T_{1\varrho}$(H) value will be observed for a homogeneous polymer system,[7-9,13] which has been used as a criterion for the miscibility of polymer blends. A single $T_{1\varrho}$ value means that spin diffusion via strong coupling between protons, which depends on the spatial mixing of polymeric chains, is efficient enough to damp out nonequilibrium magnetization in any part of the proton spin system. However, when the size of the separated phases is larger than the maximum displacement resulting from spin diffusion during a time t, a single $T_{1\varrho}$ value may be also observed.[14,15] In this case, a single $T_{1\varrho}$ is invalid as a criterion for the miscibility of polymer blends. This situation occurs in pure SB-4A copolymer.

Table 5. $T_{1\varrho}$'s[a] (ms) and Percentages of SB-4A and Its Blends[b] with PS

	PS chains				PBD chains			
material	$T_{1\varrho}(1)$	%	$T_{1\varrho}(2)$	%	$T_{1\varrho}(1)$	%	$T_{1\varrho}(2)$	%
SB-4A			4.8	100	15.5	82.4	1.4	17.6
PS03/SB-4A	16.9	15.1	3.4	84.9	16.5	72.0	2.4	28.0
PS1/SB-4A	21.2	13.0	3.8	87.0	19.7	67.0	3.7	33.0
PS12/SB-4A	10.4	15.8	3.9	84.2	18.5	76.4	2.1	23.6
PS100/SB-4A	10.6	12.1	4.9	87.9	15.4	64.9	2.6	35.1

[a] Estimated error <±10%. [b] Blend composition: PS/SB-4A 20/80 by weight.

Shown in parts a and b of Figure 2 are plots of logarithmic ^{13}C resonance intensity vs proton spin-locking time for PS chains and PBD chains, respectively, in SB-4A and its blends with PS. The $T_{1\varrho}$(H) values of them as well as their corresponding percentages are listed in Table 5. Some very important results can be obtained from Figure 2 and Table 5: (1) The decay of PS magnetization in pure SB-4A is exponential, but the decay of PBD magnetization is biexponential. However, it is known that SB-4A is a multiphase polymer system with microphase separation. A single $T_{1\varrho}$(H) value means that the size of the homogeneous PS domain is larger than 4 nm (calculated from $L = (6Dt)^{1/2}$ with spin diffusion coefficient $D = 4.0 \times 10^{-12}$ cm^2/s and $t = T_{1\varrho}$(H) = 5.0 ms). The biexponential decay of PBD magnetization suggests that there exist two kinds of PBD domains with different molecular motions; one is the homogeneous PBD domain with longer $T_{1\varrho}$(H), and the other is the interfacial domain with shorter $T_{1\varrho}$(H). (2) The addition of PS has different effects on the decays of PBD and PS magnetization. First, addition of PS gives rise to a biexponential decay of PS magnetization, and both $T_{1\varrho}$(H) values and their corresponding percentages of PS chains depend on the molecular weight of PS. Second, the addition of PS has almost no effect on the $T_{1\varrho}$(H) values of PBD chains but has a distinct effect on the relative amount of PBD locating in the homogeneous PBD domains and the interfacial domains. The addition of PS results in a decrease in the amount of PBD chains in the homogeneous PBD domains. For PS the biexponential decay implies that not all the added PS solubilize in the PS block domains, and the amount of PS solubilized in the PS block domains depends on the M_w's of PS. For PBD the decreased amount of PBD chains locating in the homogeneous PBD domains unambiguously indicates that there are some PS chains solubilized in the pure PBD domains, even when the M_w's of PS are as high as 1.0×10^6. Of course, the solubilized amount and mechanism of solubilization of PS in PBD domains are different for PS with different M_w's, as mentioned in the above section. (3) The addition of PS has a more obvious effect on the decay of PS magnetization than that of PBD magnetization; this means that most of the added PS solubilizes in or locates between the PS block domains. It is noteworthy to point out that, for the blends with PS of much higher M_w's, the decays of their magnetization are more complicated than those of the other blends, indicating that the phase behavior of the former are more complicated than those of the latter.

Similar results were obtained for the proton spin-lattice relaxation times in rotating frame, $T_{1\varrho}$, of SBS and its blends with PS.

Conclusion

The miscibilities of PS/SB-4A and PS/SBS blends have been studied by DMA and ^{13}C CPMAS NMR techniques. Some novel conclusions have been drawn by combination of the DMA and NMR results.

(1) It is found that the miscibility of PS/SB-4A and PS/SBS blends strongly depends on the molecular

weight of PS, M_{PS}, and has almost nothing to do with the molecular architecture of the two SB block copolymers used in this work.

(2) There exists an optimum range of M_{PS} which will give rise to well-improved mechanical properties of the blends as compared with those of the pure block copolymers. It is suggested that the intermolecular entanglement interactions play a key role in this case.

(3) Most of the added PS solubilizes in or locates between the PS block domains. However, there are detectable amounts of PS which solubilizes in PBD domains, even when the M_w's of PS are as high as 1.0×10^6.

(4) It is found that even when the ratio value of the molecular weight of PS (M_{PS}) to that of the PS block (M_{bPS}), M_{PS}/M_{bPS}, is as high as 1.2 for PS/SB-4A and 1.5 for PS/SBS, PS is still very miscible with the PS block microdomains.

(5) When M_{PS} is much higher than M_{bPS}, the PS/SB-4A and PS/SBS blends are still partially miscible.

(6) The NMR results for these blends are in good agreement with those from DMA measurements.

Acknowledgment. The authors are grateful for the financial support granted by the National Basic Research Project—Macromolecular Condensed State, the National Natural Science Foundation of China, and the Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics, Chinese Academy of Sciences.

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