Miscibility, Microstructure, and Dynamics of Blends Containing Block Copolymer. 3. Molecular Motion in Homopolystyrene and Polystyrene/Four-Arm Styrene–Butadiene Star Block Copolymer Blends

Hanqiao Feng* **and Zhiliu Feng**

Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

Liangfang Shen

Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics, Chinese Academy of Sciences, Wuhan 430071, People's Republic of China

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ABSTRACT: The proton spin–spin relaxation times (T_2(H)) at different temperatures (from 160 to 390 K) have been determined for polystyrene (PS) and four-arm star styrene–butadiene block copolymer (SB-4A) and its blends with PS of different molecular weights (M_{PS}). The results indicate that for PS these exists a crystallinelike structure in its bulk resulting from the microsegregation of phenyl groups, and the transition behavior of PS chains in the "crystalline" state is quite different from that in the "noncrystalline" state; for SB-4A there is a low critical temperature, below which both PS block and PBD chain motions are frozen in, exhibiting characteristics similar to that of an "ideal solid"; for PB/SB-4A blends there is a high critical temperature, above which diffusion of the PS chains into the PBD microdomains was observed. The lower the M_{PS} of PS added, the larger its diffusivity D under the same condition. Meanwhile, both the high and low transition temperatures of PS and PBD blocks in the blends strongly depend on the M_{PS} of PS added, indicating the effect of molecular weight of PS on the miscibility and molecular motions of PS/SB-4A blends.

Introduction

This is the third part of a series of studies of the miscibility, morphology, and dynamics of two block copolymers, SB-4A (a styrene–butadiene four-arm star block) and SBS (SB triblock), and their blends with homopolystyrene (PS) of different molecular weights (M_{PS}). In part 1,[1] the miscibilities of PS/SB-4A and PS/SBS blends were studied by dynamic mechanical analysis (DMA) and ^{13}C CPMAS NMR techniques. Some interesting results were obtained: (1) the dependence of their miscibilities on the M_{PS} but very little on the molecular architecture of the SB block copolymer as long as the blocks corresponding to the homopolymer added are at the outer ends of the blocks copolymer chains; (2) the existence of an optimum range of M_{PS}, giving rise to well-improved mechanical properties, resulting from intermolecular "entanglement" interactions as suggested; (3) detectable quantities of PS chains solubilized in polybutadiene (PBD) block domains, even when the M_{PS} is as high as 1.0×10^6; (4) the unusual miscibility of these blends at M_{PS}/M_{bPS} ratios as high as 1.2 for PS/SB-4A and 1.5 for PS/SBS and even a partial miscibility when M_{PS} is much higher than M_{bPS}. In part 2,[2] the microstructures of these two blends were quantitatively investigated by small-angle X-ray scattering (SAXS) and proton spin-diffusion measurements. Several important conclusions have been drawn: (1) Ordered microstructures were observed for SB-4A and SBS and their blends with PS of different M_{PS}. Quantitative analysis of the SAXS data indicates that the interdomain distance in the miscible blends increases with M_{PS} of PS added, but not the partially miscible blends. (2) Results from proton spin-diffusion measurement for pure block copolymer are in good agreement with those from SAXS, but not so good for their blends. However, the NMR data are in excellent agreement with those from DMA. (3) The molecular architecture of the studied SB block copolymers has little effect on the morphological structures of their blends with PS.

In this part, the molecular motion of SB-4A and its blends with PS of different M_{PS} has been studied by proton spin–spin relaxation times (T_2(H)) at different temperatures (from 160 to 390 K). Some novel results have been obtained.

Experimental Section

The polymers and the blends of PS/SB-4A used in this work were the same as those used in our previous work.[1,2] The molecular characteristics of PS and SB-4A are listed in Table 1.

Proton spin–spin relaxation times at different temperatures (from 160 to 390 K) were determined with a SXP 4–100 pulsed spectrometer. The ^{1}H resonance frequency was 90.21 MHz, while a 2.5-μs 90° pulse was used and the delay time was 2 s.

Results and Discussion

Proton spin–spin relaxation times, T_2(H), within a temperature range of 160 to 390 K for PS2 and PS/SB-4A blends are shown in Figures 1 and 2(a–d), respectively. From Figure 1, it is clearly seen that there are two groups of molecules with markedly different rates of motion in the homopolystyrene PS2, one with relatively high rate, i.e., with longer T_2(H), and the other with lower rate, i.e., with shorter T_2(H). It is well-known that the molecules in relatively more mobile domains will have a longer T_2(H) than those in the rigid domains.[3] It has been found that there exists an

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* To whom correspondence should be addressed. Present address: Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics, Chinese Academy of Sciences, Wuhan 430071, People's Republic of China.

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Table 1. Molecular Characteristics of Homopolystyrenes and SB-4A

sample	$M_n \times 10^{-4}$	M_w/M_n	T_g (K)
PS03	0.34	1.05	339.3
PS2	2.16	1.04	369.2
PS12	12.5	1.06	371.8
SB-4A[a]	15.43		

[a] PS blocks locate at the outer end of the block copolymer chains and the weight ratio of S/B = 45/55.

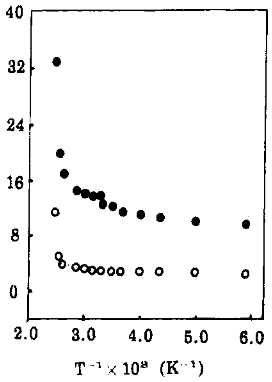

Figure 1. Plot of T_2(H) values vs $1/T$ (K^{-1}) for PS2.

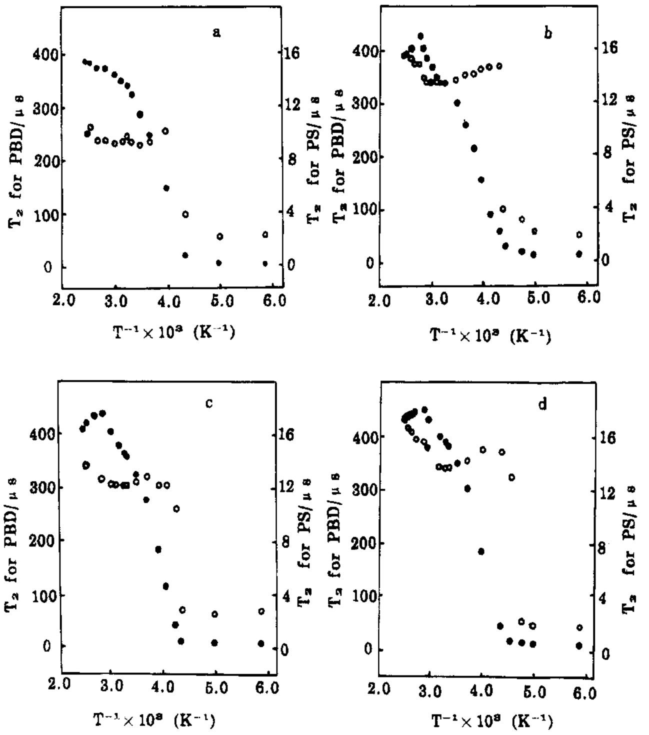

Figure 2. Plot of T_2(H) values vs $1/T$ (K^{-1}) for (a) SB-4A, (b) PS03/SB-4A, (c) PS2/SB-4A, and (d) PS12/SB-4A; (●) for PBD; (○) for PS. PS/SB-4A: 20/80 by weight.

unusual crystallinelike structure resulting from the microsegregation of phenyl groups in homopolystyrene (PS).[4] Therefore, the PS molecules with shorter T_2(H) may be assigned to the molecules whose phenyl groups form crystallinelike structure through microsegregation, which severely hinders the motions of the PS chains, and the molecules with longer T_2(H) belong to those in the "noncrystalline" state. It is interesting to find that the molecules with different motion characteristics have markedly different transition behaviors with increasing temperature. For the molecules with shorter T_2(H), their T_2(H) value remains constant with increasing temperature until a sharp transition occurs near 370 K. This transition temperature is in good agreement with the glass transition temperature T_g (369.2 K) of the same PS obtained with differential scanning calorimetry (DSC). For the molecules with longer T_2(H), there are three transitions on their T_2(H) curve: a weak low-temperature transition from 9 to 11 μs near 230 K, a medium transition from 12 to 14 μs near 305 K, and a strong transition from 17 to 33 μs near 350 K. As reported in the literature, a β peak at 243 K was found by Martin et al. for pure PS,[5] Illers[6] found a dynamic loss peak for PS in the region 25–60 °C. Kosfeld[7] ascribed the β process to the motion of the phenyl side group by his study with X-ray and NMR techniques; the broad, intense tan(−δ), β transition (1 Hz at −60 to +20 °C) for PS was assigned to cooperative ring- and main-chain oscillations.[8] Therefore, the transitions near 230 and 305 K on the T_2(H) curve can be assigned to the crankshaft motion[9] and the motion of the phenyl groups, and the transition near 350 K is the glass transition temperature of the PS molecules in the "noncrystalline" state. It is worthwhile to point out that the difference between the transition temperature of the molecules in the "crystalline" state and those in the "noncrystalline" state is as high as 20 K, indicating that the intermolecular interaction in the "crystalline" state is much stronger than that in the noncrystalline state. This, on the other hand, could be taken as evidence for the theory that PS consists of two kinds of structures. Besides, it is also found that the relative quantity of PS molecules in the "crystalline" state decreases with increasing temperature. These are quite reasonable. However, even when the temperature is as high as 390 K there are still great quantities of PS molecules in the "crystalline" state. This means that even when the temperature is 20 K higher than the glass transition temperature T_g of PS the PS system is still heterogeneous.

For the T_2(H) vs $1/T$ plot of SB-4A (Figure 2a), there are several features worth mentioning: (1) The T_2(H) values of both blocks of PS and PBD indicate that there is a critical temperature below which both PS block and PBD segment motions become frozen and exhibit the characteristics of an "ideal solid", i.e., the decays of their free induction decay (FID) are Gaussian and both PS blocks and PBD chains move with almost the same and a much slower rate. (2) There are two strong transitions on the PBD T_2(H) curve, one from 4 μs at 160 K to 50 μs at 240 K and the other from 290 μs at 285 K to 350 μs at 305 K. After the transition at the higher temperature the T_2(H) vlaues of PBD chains increase with an increase in temperature. (3) There are three transitions on the PS block T_2(H) curve. The strong low-temperature transition from 3 μs at 190 K to 10 μs at 240 K indicates the transition from a completely frozen state to a relatively mobile state. The other two transitions are near 300 and 350 K. It should be kept in mind that the decay of the PS block FID should be at least biexponential, as mentioned above, a slower process and a faster process. The measured T_2(H) values should be the overlapping of the T_2(H) values of these two processes. The overlapping effect of the T_2(H) values smears the transition which should be clear, especially at the glass transition temperature (370 K). However, it is clearly seen that there exist on the PS block T_2(H) curve three transitions similar to those of PS (Figure 1). However, it is reasonable that the positions of these three transitions of the PS block in SB-4A are slightly different from those of the three transitions of PS, due to the effect of the motion of the PBD block. The T_2(H) curves of PS/SB-4A blends give

Table 2. Change of T_2(H) Values of SB-4A and Its Blends[a] with PS in the Temperature Range of 340–390 K

material	T^b (K)	T_2(H) (μs)	T (K)	T_2(H) (μs)	ΔT^c (μs)
SB-4A	340	374.0	390	384.2	+10.3
PS03/SB-4A	340	424.1	390	389.5	−34.6
PS2/SB-4A	340	436.9	390	408.4	−28.5
PS12/SB-4A	340	448.7	390	438.7	−10.0

[a] Composition of PS/SB-4A 20/80 by weight. [b] The temperature of PBD T_2(H) maximum in blends. [c] "−" means T_2(H) decreases with increasing temperature.

a very different picture from those of pure PS and pure SB-4A. On the PBD T_2(H) curves of the blends, there are three transitions. The two lower-temperature transitions near 190 and 300 K are similar to those of the PBD blocks in pure SB-4A, and the highest-temperature transition near 350 K, which appears due to the addition of PS, may be attributed to the transition of PBD microdomains containing a certain amount of diffused PS chains. Hashimoto et al. have studied the mutual diffusion of block copolymers (SI) and homopolymer (PS).[10] They found that the mutual diffusivity D of PS and PI spherical microdomains depends on the molecular weight of PS (M_{PS}) and the amount of PS (Ψ_{PS}) initially solubilized into SI microdomains. For a given block copolymer SI, the larger the Ψ_{PS} value and the smaller the M_{PS} value, the larger the D value.

In this work, the diffusion of PS into the PBD microdomains has been observed because the T_2(H) of the PBD block decreases with an increase in temperature beyond a certain temperature due to the addition of PS (see Table 2). Meanwhile, the difference of the PBD T_2(H) values at two fixed temperatures markedly depends on the molecular weight of the PS added, i.e., the higher the M_{PS} of PS, the smaller the effect of PS on the molecular motions of the PBD block. Possible explanations for these are as follows: First, when the temperature is high enough, the free PS chains will diffuse into the PBD microdomains, which certainly will hinder the motions of PBD blocks. The higher the temperature, the more the PS chains will diffuse into the PBD microdomains and hence the greater its interference on PBD's motions. Therefore, the PBD T_2(H) values in the blends will decrease with elevation of temperature when the temperature is high enough. On the other hand, there is no free PS in the pure SB-4A copolymer; therefore, the PBD T_2(H) values increase with temperature due to the absence of the interference of PS molecules. Besides, as reported by Hashimoto et al.,[10] the higher the molecular weight of PS, the smaller its diffusivity D. Therefore, under the same conditions, the amount of PS diffused into PBD microdomains is inversely proportional to the M_{PS} of PS added. Its result is that the lower the M_{PS} of the added PS, the bigger the difference of the PBD T_2(H) values at two fixed temperatures.

The PS T_2(H) curves of the blends are rather complicated, indicating the existence of complicated molecular motions of PS chains. There are three transitions in the PS T_2(H) values of the blends, which all depend on the M_{PS} of the added PS. The lower the M_{PS} of PS, the lower the transition temperature. It is reasonable to suggest that these three transitions are corresponding to the transitions of the pure bPS phase, the pure PS phase, and the mixed phase of bPS and PS, respectively. Meanwhile, it should be pointed out that there is a minimum PS T_2(H) value near 305 K for all the blends; its origin has to be further investigated, although we consider that it is most probably the transition of PS blocks, since they are connected with PBD blocks, which have a much lower glass transition temperature.

Conclusions

From the results of T_2(H) values of the studied polymer systems at different temperatures the following conclusions may be drawn:

(1) The PS molecules with markedly different rates of motion exist in two different aggregation states; one is of crystallinelike structure arising from the microsegregation of phenyl groups, and the other is noncrystalline. It is also found that the transition behavior of the molecules in the "crystalline" state is quite different from that of the molecules in the "noncrystalline" state. This is the first time of discovering the existence of two glass transition temperatures in pure PS with a temperature difference of 20 K.

(2) For SB-4A, there is a critical temperature below which both PS block and PBD block motions are frozen in and exhibit characteristics similar to that of "ideal solids".

(3) When the temperature is high enough, diffusion of PS molecules in PBD microdomains is observed, and the smaller the molecular weight of the added PS, the larger its diffusivity D under the same conditions.

(4) The temperatures of both low- and high-temperature transitions of PBD blocks and PS blocks strongly depend on the M_{PS} of PS added, indicating that there are different quantities of PS chains solubilized into PS and PBD microdomains, respectively.

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References and Notes

(1) Part 1: Feng, H.; Feng, Z.; Yuan, H.; Shen, L. *Macromolecules*, previous paper in this issue.
(2) Part 2: Feng, H.; Feng, Z.; Shen, L. *Macromolecules*, previous paper in this issue.
(3) Cheung, T. T. P.; Gerstein, B. C. *J. Appl. Phys.* **1981**, *52*, 5517.
(4) Feng, H.; Feng, Z.; Yuan, H.; Shen, L. *Macromolecules* **1992**, *25*, 5981.
(5) Martin, G. M.; Rogent, S. S.; Mandelkern, L. *J. Polym. Sci.* **1956**, *20*, 580.
(6) Illers, K. H. *Z. Elektrochem.* **1961**, 65, 679.
(7) Kosfeld, V. R. *Kolloid* **1960**, *2*, 172, 182.
(8) Schaefer, J.; Sefcik, M. D.; Stejskal, E. O.; McKay, R. A.; Dixon, W. T.; Cais, R. E. *Macromolecules* **1984**, *17*, 1107.
(9) Boyer, R. F. *Polym. Eng. Sci.* **1968**, *8*, 161.
(10) Koizumi, S.; Hasagawa, H.; Hashimoto, T. *Macromolecules* **1990**, *23*, 2955.