Properties of Low Molecular Weight Block Copolymers. 3. Mixtures of Styrene–Dimethylsiloxane Diblock Copolymers with Polystyrene

Zhong-he Lu,[1] Sonja Krause,* and Magdy Iskandar[2]

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181.

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ABSTRACT: The glass transition temperatures of mixtures of styrene–dimethylsiloxane (S–DMS) diblock copolymers with polystyrene (PS) were studied by refractive index–temperature (n–T) measurements. Some mixtures were also studied by differential scanning calorimetry (DSC). A single glass transition temperature (T_g) was observed in all mixtures using n–T measurements; all these T_g's were between that of the PS sample and that of the S microphase whether the molecular weight of the PS was greater or less than that of the S block in the S–DMS sample with which it was mixed. The T_g's of these mixtures obeyed the Fox equation within 1 K except when the mixtures had either very large or very small ratios of PS molecular weight to S block molecular weight, either ≥ 2.5 or ≤ 0.23. DSC data, on the other hand, gave a T_g for each mixture that was close to either that of the PS sample or that of the S microphase in the S–DMS sample comprising the mixture. The results are discussed.

Experimental studies of mixtures of microphase-separated block copolymers with one of the corresponding homopolymers[3-5] generally indicate that homopolymers whose molecular weight is equal to or less than that of the corresponding block in the block copolymer are solubilized into the microphase comprised of the corresponding block. When the molecular weight of the added homopolymer is much higher than that of the corresponding block, on the other hand, the block copolymer acts as if it were incompatible with the added homopolymer, and the homopolymer forms separated domains within the microphase-separated block copolymer sample. Inoue et al.[3] studied the morphology of mixtures of styrene–isoprene (S–I) diblock copolymers with polystyrene (PS) and with polyisoprene (PI) using electron microscopy and concluded that PS of molecular weight 1.8×10^5 was solubilized into styrene (S) microphases in an S–I sample with an S block molecular weight, $\bar{M}^S$, of 2.1×10^5 and that PS of molecular weight 3.34×10^4 was solubilized but that PS samples of molecular weights 6.0×10^4 and 1.8×10^5 were not solubilized and formed separate phases in an S–I sample with $\bar{M}^S = 5.1 \times 10^4$. A PI sample with molecular weight 4.0×10^4 was solubilized into the I microphase of the latter S–I sample, whose I block molecular weight, $\bar{M}^I$, was 2.27×10^5. Toy et al.[4] investigated the morphology of a styrene–butadiene–styrene (S–B–S) triblock copolymer after mixing with a polybutadiene (PB) sample with $\bar{M}_w = 3.30 \times 10^5$, $\bar{M}_w/\bar{M}_n = 2.4$ (sample H), and with a PB sample with $\bar{M}_w = 10^4$, $\bar{M}_w/\bar{M}_n = 1.2$ (sample L), also using electron microscopy. The B blocks in the S–B–S sample had $\bar{M}^B = 7.8 \times 10^4$; sample L was incorporated into the B microphases while sample H formed separate domains. Hashimoto et al.[5] analyzed the small-angle X-ray scattering data of some mixtures of S–I block copolymers with PS and PI, both of which had molecular weights considerably lower than those of the corresponding blocks in the block copolymers and again concluded that these low molecular weight homopolymers were solubilized into their corresponding microphases.

In those cases in which added homopolymer is solubilized into the corresponding microphase in a block copolymer, one should expect the mixture to exhibit a glass transition temperature, T_g, between that of the homopolymer and that of the corresponding unmixed microphase. On the other hand, when the added homopolymer forms a separate phase in the mixture, one should expect the mixture to exhibit both the T_g of the homopolymer, perhaps somewhat perturbed by the large surface-to-volume ratio of the homopolymer domains, and the T_g of the corresponding microphase. In the present work, only a single T_g was discovered by n–T measurements in all mixtures of sytrene–dimethylsiloxane (S–DMS) diblock copolymers with PS that were investigated, no matter what the ratio of PS molecular weight to S block molecular weight. In most cases, differential scanning calorimetry (DSC) gave similar results.

Experimental Section

Polymers. The polystyrene samples were anionically polymerized standard samples purchased from ARRO Chemical Co., Joliet, Ill.; all samples had $\bar{M}_w/\bar{M}_n \leq 1.1$. The S–DMS diblock copolymers were anionically polymerized samples from different sources; characterization data on these samples have been provided and discussed in paper 1 of this series.[6] DSC data on the PS samples and on the S–DMS diblock copolymers were discussed in paper 1,[6] n–T data on the PS samples were discussed by Krause and Lu,[7] and n–T data on the S–DMS samples were discussed in paper 2 of this series.[8]

n–T Measurements. Sample films were prepared from the polymer mixtures in 5 wt % solution in toluene; the solutions were allowed to evaporate at room temperature and were then dried further in a vacuum oven at room temperature for 3 days and finally at 100–120 °C for 2 h. A Bausch and Lomb precision refractometer was used to measure the refractive indices, starting at a temperature well above T_g of each mixture and then lowering the temperature at intervals of 5 °C up to about 10 °C above T_g, then at intervals of 2.5 °C in the vicinity of T_g, and again at 5 °C intervals starting 10 °C below T_g. The temperature was controlled to ±0.1 °C below 100 °C and to ±0.2 °C above 100 °C. At all temperatures except those in the vicinity of T_g, refractive index equilibrium was established in about 15 min, but at least 1 h was needed for equilibrium to be established in the vicinity of T_g. All measurements were made using the sodium D line. Although many of the mixtures were noticeably turbid at room temperature, it was nevertheless possible to measure their refractive indices at elevated temperatures. These very turbid samples are so designated in Table I.

DSC. Sample films were prepared as for n–T measurements, except that the films were dried in a vacuum oven at room temperature. The data were obtained on a DuPont thermal analyzer, run in the DSC mode, in the laboratory of Professor B. Wunderlich. The calibration of this instrument has been described previously.[6] All polymer mixtures weighed 5–25 mg and were run at equal heating and cooling rates, 10 K min^{-1}, under a stream of N_2. The first heat of each sample was discarded and the averages of the second and third heating cycles are reported in Table I. The value of T_g was taken as the temperature at which half of the heat capacity change during the glass transition, ΔC_p,

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Table I
Data on S–DMS Diblock Copolymer Mixtures with PS

mix no.	block copolymer: sample	block copolymer: $\overline{M}_n^S \times 10^{-3}$	block copolymer: wt % S	homopolymer mol wt × 10^{-3}	mixture % PS	n–T measurements: T_g, K	n–T: $-dn/dT \times 10^{-4}$ K^{-1}: $T < T_g$	n–T: $-dn/dT \times 10^{-4}$ K^{-1}: $T > T_g$	DSC data: T_g, K	DSC data: T_{g_1}, K	DSC data: T_{g_2}, K
1	I23	2.33	86		0	305	2.4	3.7	317 ± 1	308 ± 1	329 ± 5
2	I23	2.33	86	2.0	25	310	2.0	3.7			
3	I23	2.33	86	2.0	50	314	1.8	3.7			
4	I23	2.33	86	2.0	75	320	1.8	3.7			
5	I23	2.33	86	4.0	50	324	1.8	3.7			
6	I23	2.33	86	10.3	50	333	1.8	3.7			
7	I23	2.33	86	20.4[a]	50	336	1.8	3.7			
8	I23	2.33	86	51.0[a]	50	345	1.8	3.7			
9	I24	3.34	86		0	313	2.5	3.7	322 ± 0.5	312 ± 1	330 ± 0.5
10	I24	3.34	86	2.0	50	318	1.8	3.7			
11	I24	3.34	86	4.0	50	328	1.8	3.7			
12	I24	3.34	86	10.3	50	337	1.8	3.7			
13	I24	3.34	86	20.4[a]	50	340	1.8	3.7			
14	R13	8.2	54		0	350	3.0	3.7	358 ± 4	342 ± 4	370 ± 4
15	R13	8.2	54	4.0	25	348	2.6	3.7	360 ± 0.5	354 ± 0.5	366 ± 0.5
16	R13	8.2	54	20.4[a]	50	358	2.2	3.7	379 ± 0.5	376 ± 0.5	385 ± 0.5
17	D1	17.6	88		0	365	2.0	3.7	370 ± 0.5	361 ± 2	378 ± 3
18	D1	17.6	88	2.0	50	338	1.8	3.7			
19	D1	17.6	88	4.0	50	348	1.8	3.7			
20	D1	17.6	88	10.3	50	363	1.8	3.7			
21	D1	17.6	88	20.4	50	366	1.8	3.7			
22	R15	39.0	47		0	369	2.0	3.7	377 ± 0.5	371 ± 4	384 ± 3
23	R15	39.0	47	20.4[a]	25[b]	368	2.2	3.7	380 ± 0.5	377 ± 0.5	383 ± 0.5
24	R8	105	60		0	372	2.0	3.7	378 ± 0.5	374 ± 0.5	384 ± 2
25	R8	105	60	4.0	25	361	2.0	3.7	348 ± 6	337 ± 5	358 ± 6
26	R8	105	60	4.0	75	352	2.0	3.7	340 ± 2	321 ± 4	350 ± 0.5
27				2.0	100	323	1.4	3.6	331	328	334
28				4.0	100	343	1.4	3.5	347	344	350
29				10.3	100	361	1.3	3.4	368	366	371
30				20.4	100	368	1.3	3.3	373	369	375
31				51.0	100	371	1.3	3.3	377	374	379

[a] Sample was visibly turbid at room temperature. [b] Traces of a second transition were seen at 328 ± 2 K (see Figure 1).

had occurred. The lower end of the glass transition interval, T_{g_1}, was defined as the point of intersection of the extrapolated glassy base line with the tangent to the inflection point on the DSC trace at the glass transition, while the upper end of the glass transition interval, T_{g_2}, was defined as the point of intersection of the extrapolated rubbery base line with the same tangent. The definitions of T_g, T_{g_1}, and T_{g_2} are shown on a figure in paper 1 of this series.[6] Limits of error shown in Table I are mean deviations.

Results

Table I shows both n–T and DSC data on the block copolymers, the homopolymers, and the block copolymer/homopolymer mixtures discussed in this work. The column headed $\overline{M}_n^S$ refers to the $\overline{M}_n$ of the S block in the block copolymer. The data on the pure S–DMS block copolymer samples were taken from papers 1[6] and 2[8] of this series, while the data on the homopolymers were taken from paper 1[6] and work of Krause and Lu.[7] Refractive index–temperature plots all showed only a single, sharp transition and looked like those shown previously for the pure homopolymers[7] and for the pure block copolymers.[8] The DSC data, except in the case of mix 23 (Figure 1a), showed a single, relatively broad transition in the temperature region expected for the PS and for the S microphases. When the mixtures contained up to 50% PS, as in Figure 1b, very little hysteresis was noted in the DSC curves as was noted in the pure block copolymers earlier;[6] when the mixtures contained 75% PS, however,

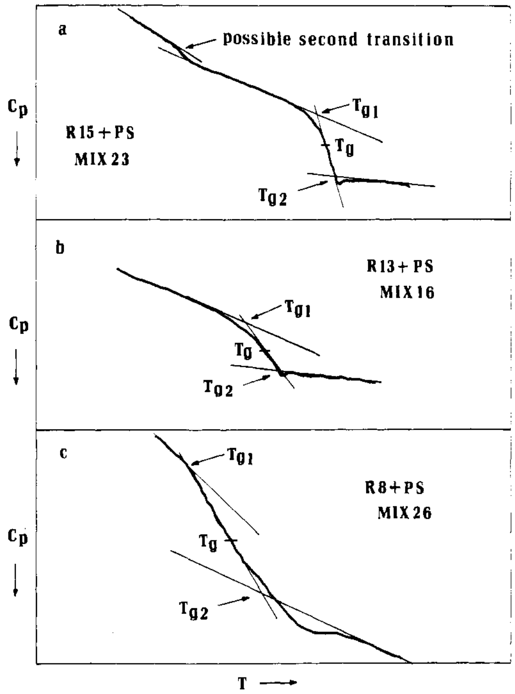

Figure 1. Some representative DSC traces of S-DMS/PS mixtures.

Table II
Comparison of T_g's of Mixtures with Theoretical Calculations

	T_g, K		
mix no.	n-T data	eq 1	eq 2
2	310	310	310
3	314	315	314
4	320	319	319
5	324	326	324
6	333	335	333
7	336	339	336
8	345	341	337
10	318	318	318
11	328	329	329
12	337	339	337
13	340	343	340
15	348	347	347
16	358	362	361
18	338	343	341
19	348	353	353
20	363	363	363
21	366	367	367
23	368	369	369
25	361	348	361
26	352	362	348

as in Figure 1c, hysteresis comparable to that observed in pure PS[6] was observed.

Discussion

The T_g's obtained for our S-DMS block copolymer/PS mixtures using n–T measurements (Table I) were all single valued and between that of the S microphase in the pure block copolymer and that of the PS sample with which it was mixed, no matter whether the PS molecular weight was greater or less than that of the relevant S microphase. This indicates relatively good mixing of all the homopolymers into the S microphases. This mixing seems to have occurred whether the mixtures were clear or turbid, and even when the PS molecular weight was over 5 times that of the S microphase with which it was mixed (mixes 6, 7, 8, and 13). It was of interest to see whether the T_g's of these mixtures obeyed either the Gordon–Taylor equation[9] in the form

$$T_g = w_A T_{g_A} + w_B T_{g_B} \tag{1}$$

or the Fox[10] equation

$$T_g = T_{g_A} T_{g_B} / (w_A T_{g_B} + w_B T_{g_A}) \tag{2}$$

Wall et al.[11] found that the Gordon–Taylor equation, as modified by Wood[12]

$$T_g = T_{g_B} - k(T_{g_A} - T_g) w_A (1 - w_A)^{-1} \tag{3}$$

with the value of $k = 0.45$, described the T_g's of mixtures of anionically polymerized polystyrenes as measured by DSC.

In eq 1–3, T_{g_A} and T_{g_B} are the T_g's of the two components of the mixture, respectively, w_A and w_B are the weight fractions of these two components, respectively, and k is a constant. Differences between the thermal expansion coefficients of the components of the mixture have been removed from the Gordon–Taylor equation (eq 1) since we are discussing mixtures only of polystyrenes; Fox and Flory found no trends with molecular weight of the thermal expansion coefficients of polystyrenes.[13]

Table II compares the T_g's of the homopolymer/block copolymer mixtures as obtained by n–T measurements with those calculated by eq 1 and 2. The T_g calculated by eq 1 and 2 is within 1 K of the experimental T_g for 9 and 15, respectively, of the 20 T_g's investigated. Equation 2, the Fox equation, therefore predicts 75% of the experimentally determined T_g's within 1 K; the five mixtures for which these predictions deviate from 3 to 8 K are some of those which have either very large or very small ratios of PS molecular weight to S block molecular weight, this ratio being either ≥ 2.5 or ≤ 0.23.

The single T_g, located between the T_g's of the constituents of each mixture, that was found by n–T measurements indicates that all the PS samples dissolved in all the S microphases, no matter what the ratio of PS molecular weight to S block molecular weight. This seems to contradict the morphological data quoted above.[3-5] It does not seem possible that the PS formed phases separate from the S microphases in those mixtures in which the PS molecular weight was considerably larger than the S block molecular weight even while the mixtures exhibited only a single intermediate T_g (mixes 5–8, 12, 13, and 16). Before discussing a possible cause for this contradiction, it will be useful to look at the DSC data in Table I. First, it should be noted that the DSC T_g's of none of the mixes are intermediate between those of the PS and S microphase constituents. The DSC T_g's of mixes 15 and 23 are close to those of the respective constituent S microphases while the DSC T_g's of mixes 16, 25, and 26 are close to those of the respective homopolymers. The n–T data and the DSC measurements are therefore not consistent, especially since in the case of the pure PS samples, n–T measurements yielded T_g's 3–7 K below those obtained from DSC data.[7] Also, in the case of the pure S–DMS diblock copolymers, theT_g's from n–T measurements were 6–8 K below those obtained from DSC data when $\bar{M}_n^S \geq 8.2 \times 10^3$, but at lower S block molecular weights, the T_g from n–T measurements varied from 12 K below to 13 K above that obtained from DSC data. This discrepancy at low S block molecular weight was assumed to be connected with the extremely broad S microphase glass transition interval, $T_{g_2} - T_{g_1}$, that was observed in these samples by DSC.

The discrepancy between the n–T and DSC data in the case of mixes 15, 16, 23, 25, and 26 does not appear to be entirely connected with the broadness of the DSC glass transition interval. We suspect that the discrepancy is connected either with the difference in pretreatment, e.g., drying temperature, or with the difference in time scale between the two types of measurements; the latter hypothesis was invoked earlier[8] to help explain why n–T T_g's were so sharp in comparison to the diffuseness of some of the DSC T_g's of pure block copolymers. Before each DSC measurement, the cooling rate of each sample from above the styrene T_g was 10 K min^{-1}, while the n–T measurements were performed during or after a cooling cycle in which the cooling rate was 10–20 K h^{-1} far from T_g and 2.5 K h^{-1} near T_g. Glassy samples are never at true equilibrium, but quickly cooled samples can be expected to be farther from equilibrium than slowly cooled samples. If, at high temperature, there were a tendency for the PS to separate out from the S microphases in our samples and to form separate PS phases, while the equilibrium morphology at lower temperatures consisted of PS mixed into the S microphases, then we could rationalize our data. On slow cooling, a close-to-equilibrium morphology could be attained and its T_g would be observed by n–T measurements. On fast cooling, most of the high-temperature morphology would be retained and the PS-phase T_g and/or the S-microphase T_g would be observed by DSC measurements. The observation of only one of the two expected T_g's is not as disturbing as it might be; it has been noted several times[14,15] that DSC data sometimes reveal only one of two expected T_g's in block copolymer samples since the other transition may be broadened so much that it is not observed on the DSC trace. The possible second transition seen in mix 23 is at too low a temperature to be associated with the types of styrene phases considered here. If our S–DMS diblock copolymer/PS mixtures can exist either with a mixed styrene phase or with S microphases and separate PS phases, depending on temperature, then our data can be rationalized. There appears to be no way, at present, of predicting the morphology of other block copolymer/homopolymer mixtures. The S–I/PS, the S–I/PI, and the S–B–S/PB mixtures observed by others using different methods may well have a different room-temperature morphology than our samples. Furthermore, the cooling history of these other samples is not known to us.

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References and Notes

(1) On leave from the Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou, People's Republic of China.
(2) Present address: Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Va. 24061. DSC data obtained in partial fulfillment of the requirements for the Ph.D., Rensselaer Polytechnic Institute.
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Properties of Block Copolymers and Homopolymer Blends Comprised of 1,2-Polybutadiene and 1,4-Polybutadiene

Robert E. Cohen* and D. E. Wilfong

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received September 4, 1981*

ABSTRACT: Four diblock copolymers, each comprised of a 1,2-polybutadiene block (99% 1,2) and a 1,4-polybutadiene block (36% cis, 51% trans, 13% 1,2), were examined along with several blends of the corresponding homopolymers. Dynamic mechanical tests, differential scanning calorimetry, and transmission electron microscopy were used to determine the homogeneous or heterogeneous character of each material. The overall trends of the present results combined with extensive data obtained previously on another set of double-diene materials are explained in a unified fashion with a type of phase diagram in which three separate regions can be identified—(i) a high molecular weight region in which block copolymers and the corresponding polymer blends are heterogeneous materials, (ii) a low molecular weight region in which blocks and blends are homogeneous materials, and (iii) an intermediate region, spanning a range of at least a factor of 5 in molecular weight, in which a block copolymer is homogeneous but its corresponding blend is heterogeneous. It is in this third interesting and largely unexplored region in which most of the polymers of the present study lie.

Introduction

Diblock copolymers and two-component polymer blends in which both constituents are rubbery at room temperature offer certain advantages in a research program aimed at establishing connections between molecular structure, morphology, and physical properties of multicomponent polymer systems. The rubbery nature of the constituents helps to minimize various nonequilibrium effects, which can influence the behavior of glassy/rubbery and glassy/glassy systems. In addition, if the rubbery constituents are based on diene monomers, chain microstructure can be used to vary molecular architecture while leaving chemical composition unchanged. The diblock copolymers[1] and homopolymer blends of 1,2-polybutadiene (1,2B) and 1,4-polybutadiene (1,4B) described in this paper represent one example of this type of two-component polydiene system.

Previous work[2–6] in this laboratory showed that diblock copolymers of 1,4-polybutadiene (45% cis, 45% trans, 10% 1,2) and *cis*-1,4-polyisoprene (1,4I) are homogeneous materials in the range of 250 000 molecular weight. On the other hand, the corresponding homopolymer blends of *cis*-1,4-polyisoprene and 1,4-polybutadiene are heterogeneous in essentially all proportions;[2,5] binary and ternary blends of a 1,4I/1,4B diblock with one or both of the corresponding homopolymers may be homogeneous or heterogeneous, depending upon the composition of the blend and the relative segment lengths of the copolymer.[2,4,5] In the previous work, the two components 1,4I and 1,4B differed both in microstructure and in chemical composition. Examination of homopolymer blends of 1,4I with polybutadienes of various microstructures[6] indicated that both of these variables affect the structure and properties of the materials. On the basis of these observations it appeared that copolymers and blends of 1,4-polybutadiene and 1,2-polybutadiene would be suitable for examining the role of chain microstructure alone and would lead to useful comparisons with the 1,4I/1,4B system studied earlier.

Experimental Section

Materials. The block copolymers and homopolymers used in this study were synthesized by Dr. Adel F. Halasa of the Firestone Tire and Rubber Co. A novel feature of this set of polymers is the unusually high vinyl content (99%) of the atactic

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