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Properties of Low Molecular Weight Block Copolymers. 4. Differential Scanning Calorimetry and Refractive Index–Temperature Measurements on Styrene–Butadiene Diblock Copolymers and Styrene–Butadiene–Styrene Triblock Copolymers[1]

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ABSTRACT: The glass transition temperatures (T_g) and related properties of the styrene (S) and butadiene (B) microphases in styrene–butadiene (S–B) diblock and styrene–butadiene–styrene (S–B–S) triblock copolymers with low molecular weight S blocks were examined by refractive index–temperature (n–T) and differential scanning calorimetry (DSC) measurements. In all block copolymers investigated, having S block molecular weights $\leq 2.2 \times 10^4$, the S-phase T_g's obtained by either n–T or DSC measurements were at least 18 K less than those of S homopolymers with molecular weights comparable to those of the S blocks. The change in specific heat at the T_g of the S microphase (ΔC_p^S) was always equal to or greater than that of S homopolymer. These results suggest that some B segments are mixed into most of the S microphases examined, in contrast to earlier results on styrene–dimethylsiloxane (S–DMS) diblock copolymers, where mixing was postulated only at S block molecular weights $\leq 0.82 \times 10^4$.

In the first paper in this series, we reported differential scanning calorimetry (DSC) studies of styrene–dimethylsiloxane (S–DMS) diblock copolymers.[4] The glass transition temperature (T_g), the width of the glass transition interval (ΔT_g), and the change in specific heat at T_g (ΔC_p) were obtained on all styrene (S) microphases and on those dimethylsiloxane (DMS) microphases that were fully amorphous and were compared with the same quantities obtained on S and DMS homopolymers of comparable molecular weight. The S microphases could be divided into three groups. The high molecular weight group, having $\bar{M}_n^S \geq 3.90 \times 10^4$ ($\bar{M}_n^S \equiv$ molecular weight of the styrene block), contains S microphases that have T_g and ΔC_p equal to those of polystyrene (PS) of comparable molecular weight, but ΔT_g is about double that of PS. The low molecular weight group, $\bar{M}_n^S \leq 0.82 \times 10^4$, contains S microphases that have T_g lower than that of PS of comparable molecular weight, ΔT_g's greater than those of the high molecular weight group, and ΔC_p's either larger or smaller than that of PS. There is an intermediate molecular weight group in which the changes in properties from the high to the low molecular weight group are somewhat sporadic and gradual. No trends with percent composition of the samples were found although the copolymers varied between 24 and 86% S by weight. Since many of the low molecular weight S microphases had ΔC_p values greater than those of PS, we postulated that those S microphases probably contained admixed DMS segments. The fact that some of the low molecular weight S microphases had ΔC_p's less than that of PS indicates that admixing of DMS segments, if that hypothesis is correct, is not the only thing that affects ΔC_p. There is probably also an effect from the connectedness of the S blocks with the DMS blocks across the interface between microphases and/or a general effect of the large surface-to-volume ratio of the microphases made up of very low molecular weight blocks.

Small differences between the T_g's of the DMS microphases and of DMS homopolymers agreed qualitatively with the differences expected from considerations of thermal stresses in phase-separated block copolymers according to Paterno[5] and Wang and Sharpe.[6]

The results of refractive index–temperature (n–T) studies on the S–DMS block copolymers in the temperature range near T_g of the S microphases have been reported in paper 2 of this series.[7] The n–T T_g's of the S microphases were again equal to those of PS[8] having molecular weight comparable to the S blocks when $\bar{M}_n^S \geq 1.76 \times 10^4$ and were less than those of PS[8] having molecular weight comparable to the S blocks when $\bar{M}_n^S \leq 0.82 \times 10^4$. All T_g's obtained from n–T measurements were sharply defined, even though the T_g's obtained from DSC for samples with $\bar{M}_n^S \leq 0.82 \times 10^4$ were very broad and diffuse. It was postulated that the very slow rate at which the S–DMS samples were cooled during n–T measurements allowed the samples to come closer to their equilibrium states than they were allowed to come with the 10 K min^{-1} cooling rate between DSC runs. In the equilibrium state, therefore, the T_g's of the S microphases are sharply defined.

The S blocks in the S–DMS diblock copolymers should be and are extremely incompatible; even hexamers of S and of DMS are not miscible and have an upper critical solution temperature above 35 °C.[9] It was of interest to study a somewhat more compatible system in which relatively monodisperse block copolymers could be prepared and in which the T_g's of the microphases remained widely separated. The system we have begun to study is styrene–butadiene, a system in which homopolymer standards are available and in which it was possible to obtain some diblock and triblock copolymers relatively quickly. In an earlier paper[10] in which we had compared DSC T_g's of the S microphases in a number of different phase-separated diblock and triblock copolymers obtained by many different workers using different instruments, it appeared that the T_g's of all S microphases depended only on $\bar{M}_n^S$ and not on the chemical nature of the other block or blocks or the percent composition of the block copolymers. It seemed useful to compare data obtained in the same laboratory by the same workers on the same instruments. As will be seen below, both similarities and differences have been observed between the properties of the S microphases in styrene–butadiene (S–B) diblock, in styrene–butadiene–styrene (S–B–S) triblock, and in S–DMS diblock copolymers.

We are certainly not the first to study glass transitions in low molecular weight styrene–butadiene block copolymers. Kraus et al.[11] studied S–B diblock and S–B–S triblock copolymers, both dilatometrically and by dynamic mechanical methods. Styrene microphase T_g's determined dilatometrically decreased with decreasing $\bar{M}_n^S$ when $\bar{M}_n^S$ was near 2×10^4 and were all less than that of high molecular weight PS. Styrene microphase T_g's determined

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Table I
Polybutadiene Standards (Vendor's Characterization)

sample	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	% trans-1,4	total % 1,4	% 1,2
B1	420[a]	1.17[b]	50[c]	80[c]	20[c]
B2	960[a]	1.07[b]	49[c]	85[c]	15[c]
B3	2 350[a]	1.13[b]	53[d]	94[d]	6[d]
B4	16 100[e]	1.06[f]	49.1[d]	92.6[d]	7.4[d]
B5	135 000[e]	1.26[f]	44.5[d]	91.6[d]	8.4[d]
B6	206 000[e]	1.32[f]	43.5[d]	93.3[d]	6.7[d]
B7	226 000[e]	1.47[f]	43.6[d]	92.3[d]	7.7[d]
B8	286 000[e]	1.48[f]	41.7[d]	93.4[d]	6.6[d]

[a] By vapor pressure osmometry. [b] By gel permeation chromatography. [c] By NMR. [d] From the infrared spectrum. [e] By membrane osmometry. [f] Using $\bar{M}_w$ determined by light scattering.

from dynamic mechanical loss peaks decreased from 104 to 60 °C when styrene block length decreased by a factor of 4 ($\bar{M}_n^S$ values were not given). Matsuo et al.[12] found that the heat distortion temperature (HDT) of S–B, S–B–S, B–S–B, and S–B–S–B block copolymers decreased with decreasing $\bar{M}_n^S$; HDT is related to the T_g of the styrene microphases in these block copolymers. The HDT was not equal to that of high molecular weight PS even when $\bar{M}_n^S$ exceeded 10^5. Using DSC measurements, Ikeda et al.[13] found variations from 99 to 105 °C in the T_g's of the S microphases in S–B–S and B–S–B triblock copolymers with $\bar{M}_n^S$ from 5×10^4 to 9.7×10^4, but the T_g's did not show a trend with $\bar{M}_n^S$. Kraus and Rollmann[14] in a dynamic mechanical study of S–B–S and B–S–B triblock copolymers found that the T_g of the S microphases decreased as $\bar{M}_w$ decreased from 3.5×10^4 to 4×10^3, was virtually independent of whether the S blocks were in S–B–S or B–S–B block copolymers, and was less than that expected for PS of comparable molecular weight. Unfortunately, none of these results could be directly compared with our S–DMS block copolymer data. It is known that different measurement techniques give somewhat different results; even the DSC data cited above[13] were taken on a different instrument and at a different heating rate from that used in our work, were evaluated differently, and were not as complete. It was therefore necessary to work on new samples of styrene–butadiene block copolymers with our own methods.

Experimental Section

Homopolymers. The characterization and properties of the anionically polymerized PS standards, purchased from ARRO Co., have been presented previously.[4,8] All samples have $\bar{M}_w/\bar{M}_n <$ 1.1 and ranged from 600 to 1.8×10^6 in molecular weight. The polybutadiene (PB) standards were purchased from Scientific Polymer Products, Inc., and from Goodyear Chemicals. The characterization data on these samples as provided by the vendors are given in Table I.

Block Copolymers. Tables II and III show characterization data on all block copolymer samples used in this work. Values labeled "nominal" were provided by others (see below). The three S–B diblock copolymers were sent to us by R.-J. Roe, University of Cincinnati; he received them from H. L. Hsieh, Phillips Petroleum Co., who also provided the "nominal" characterization data. The nominal weight percent S of these samples was determined from the monomer ratios, the microstructure was obtained from IR analysis, and the molecular weights were determined from gel permeation chromatography (GPC).[15] The five S–B–S triblock copolymers whose designations start with TR were given to us by C. I. Chung of our Materials Engineering Department; he received these from Shell Development Co. The three samples labeled TR-41 were prepared by sequential polymerization, the nominal styrene contents and butadiene microstructures were obtained from IR spectra, and the nominal molecular weights were calculated from the intrinsic viscosity of the S segment that was polymerized first and from the S contents of the S–B moiety and of the final S–B–S triblock copolymer as obtained from their IR spectra.[16] The two samples designated TRW-6 were made by coupling S–B diblock copolymers and are stated to contain about 15 wt % uncoupled S–B diblock copolymer.[16] We have no information on how the nominal molecular weights and compositions were obtained on these samples. The S–B–S triblock copolymers labeled V1 through V7 were prepared for C. I. Chung by E. Vanzo, Scientific Polymer Products, Inc. The nominal compositions and molecular weights of these samples were presumably calculated from the polymerization conditions.

Characterization. NMR spectra of the block copolymers were obtained on a Varian T60A NMR spectrometer. Solutions of 10 wt % polymer in CCl_4 containing tetramethylsilane as an internal standard were used. Percent S and percent 1,2 addition of the B monomers were calculated by the procedure of Senn[17] from the aromatic peak at 7.2 ppm and the olefinic peaks at 5.4 ppm. A planimeter was used to obtain peak areas.

IR spectra were obtained with a Perkin-Elmer 928 IR spectrometer. Areas under the peaks at 964–977 (trans 1,4), 908–916 (1,2), 675–729 (cis 1,4), and 699 cm^{-1} (S) were used to calculate the B microstructures after the 699-cm^{-1} band intensity had been subtracted from the 675–729-cm^{-1} band intensity. Block copolymer films were cast from toluene solution, allowed to dry, and dried further in a vacuum oven at room temperature for 48 h. Since film samples were used and since base lines were difficult to construct, the method used[18] was checked against several of the PB standards; our microstructures averaged ±3 (in weight percent units) of the microstructures shown in Table I.

Gel permeation chromatographs (GPC) of all PS and PB standard samples and of all block copolymers were obtained in toluene solution at 45 °C with a Knauer high-pressure GPC

Table II
Structural Characterization of Styrene–Butadiene Block Copolymers

		wt % S		B, % trans-1,4		B, total % 1,4			B, % 1,2		
sample	type	nominal	NMR	nominal	IR	nominal	IR	NMR	nominal	IR	NMR
52110	S–B	25	27	42	45	70	73	70	30	27	30
52111	S–B	50	53 ± 8[a]	45	47	69	70	70	31	30	30
52112	S–B	80	78	48	51	72	72	76	28	28	24
TR-41-2445	S–B–S	25	24	50	47	90	89	86	10	11	14
TR-41-2443	S–B–S	28	31	49	48	89	87	90	11	13	10
TR-41-2446	S–B–S	33	36	34	26	59	66	59	41	34	41
TRW-6-1086	S–B–S	28	27		49		91	80		9	20
TRW-6-1087	S–B–S	30	27		49		89	65		11	35
V1	S–B–S	25	31		45		85	84		15	16
V2	S–B–S	14	11		50		83	85		17	15
V3	S–B–S	27	35		46		83	81		17	19
V4	S–B–S	42	45		47		89	83		11	17
V5	S–B–S	19	6		45		85	85		15	15
V6	S–B–S	39	57		47		82	84		18	16
V7	S–B–S	24	16		49		86	85		14	15

[a] The weight percent S of sample 52111 was much less reproducible than those of the other samples. The mean deviation of three measurements is reported.

Table III
Molecular Weight Characterization of Styrene-Butadiene Block Copolymers

sample	nominal mol wt × 10^{-4}	main GPC peak × 10^{-4} as PS	as PB	as block	fast peak × 10^{-4} as PS	as PB	as block	slow peak × 10^{-4} as PS	as PB	as block	$\overline{M}_w/\overline{M}_n$[d]
52110	2.8[a] 2.7[b]	4.8	1.8	2.6							1.04
52111	2.6[a] 2.5[b]	3.8	1.45	2.6				0.64	0.21	0.44	1.86
52112	2.2[a] 2.1[b]	2.7	1.00	2.3				1.06	0.37	0.91	1.17
TR-41-2445	5.7[c]	10.5	4.4	7.4							1.06
TR-41-2443	11.8[c]	21.0	8.7	12.5				1.25	0.46	0.70	1.08
TR-41-2446	12.6[c]	19.8	8.0	12.3							1.09
TRW-6-1086	7.1	13.7	5.6	7.8				7.6	3.0	4.2	1.26
TRW-6-1087	10.0	19.8	8.0	11.2				11.0	4.5	6.3	1.17
V1	5.7	7.2	2.9	4.2	15.0	6.1	8.9	3.5	1.3	2.0	1.52
V2	6.9	11.6	4.6	5.4	24.0	9.5	11.1				1.17
V3	3.7	7.0	2.8	4.3	13.5	5.4	8.2				1.03
V4	3.3	6.4	2.6	4.3	13.5	5.4	9.0	2.5	0.90	1.62	1.77
V5	6.3	24.0	9.5	10.4							1.18
V6	3.1	3.9	1.5	2.9	7.8	3.2	5.8	0.25	0.12	0.18	2.60
V7	6.7	14.0	5.8	7.2							1.11

[a] $\overline{M}_w$ from GPC.[10] [b] $\overline{M}_n$ from GPC.[10] [c] Molecular weights calculated from measurement of the intrinsic viscosity of the first S block and from the S contents of the S-B fragment first synthesized and of the final S-B-S triblock copolymer.[11] [d] See text. This is a minimum value for $\overline{M}_w/\overline{M}_n$.

apparatus, Utopia Instrument Co., with a differential refractometer as detector. The calibration curves for the PS and for the PB standards at a flow rate of 1 mL min^{-1} are shown in Figure 1. The S shapes of the calibration curves are probably normal for this type of apparatus.[18]

***n*-*T* Measurements.** Sample films were prepared from 15 wt % polymer in toluene solutions; the solutions were allowed to evaporate at room temperature and were then dried further in a vacuum oven 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 sample 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 with the sodium D line.

DSC. The data were obtained in the laboratory of B. Wunderlich with a DuPont 990 thermal analyzer run in the DSC mode. The calibration of this instrument has been described previously.[4] All samples weighed 15–30 mg; all but samples V1–V7 were run "as received". Samples V1–V7 were received in toluene solution, and films were cast on Al dishes at room temperature, left to evaporate for 24 h, and then placed in a vacuum oven at room temperature for 3 days. All samples except those that were run after quenching in liquid N_2 from 460 K were run at equal heating and cooling rates, 10 K min^{-1}, under a stream of N_2. Data were recorded only for heating cycles that followed the appropriate cooling cycle. The values of T_g were taken as the temperature at which half of the specific heat change during the glass transition, ΔC_p, 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. These definitions of T_g, T_{g_1}, and T_{g_2} are shown on a figure in paper 1 of this series.[4] Limits of error shown in Tables IV and V are mean deviations.

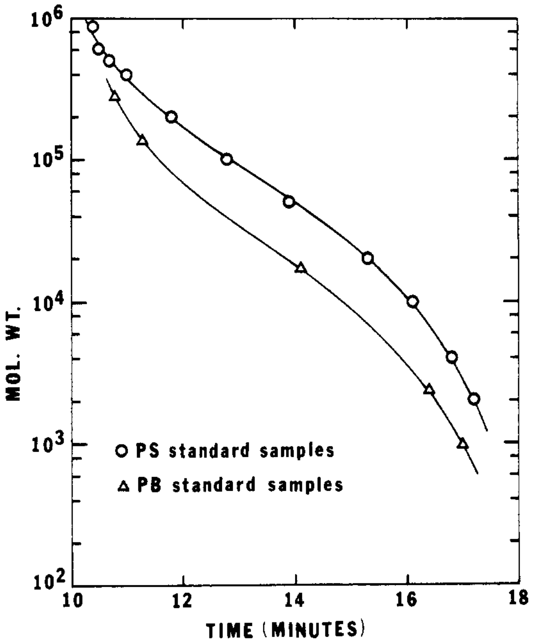

Figure 1. GPC calibration plot.

Results

Table II shows the IR and NMR structural characterization of our block copolymer samples. The meanings of the numbers in the "nominal" columns are explained in the Experimental Section. Table III shows the molecular weight characterization of our block copolymers. The nominal molecular weights in this table that are not footnoted were simply taken from the suppliers' data. In order to understand Table III, it is necessary to see the shapes of some of the GPC peaks (Figure 2). The main GPC peak in Figure 2 is always denoted by an arrow and, as can be seen, the various chromatograms contained slower and/or faster peaks. Very slow peaks, corresponding to molecular weights lower than those of the standards shown in Figure 1, are designated L on Figure 2. Some of these peaks correspond to antioxidant that is present in some of the samples, and others may connote the presence of residual monomer, oligomers, or polymer whose molecular weight was less than that of samples on the calibration curve. None of these L peaks was considered in our calculations. The diblock copolymers said to be present in the two TRW-6 samples by the supplier can be clearly seen as shoulders on the main GPC peaks in Figure 2a. Since the three TR-41 samples had similar GPC

Table IV
Glass Transition Data of the S Microphases in S-B and S-B-S Samples

sample	$\overline{M}^S \times 10^{-3}$	*n*-*T* data			DSC data				no. of runs
		T_g, K	$-dn/dt \times 10^4$, K^{-1}						
			$T < T_g$	$T > T_g$	T_g, K	T_{g_1}, K	T_{g_2}, K	ΔC_p, J g^{-1} K^{-1}	
V2	3.0	327.5	3.4	3.5	334 ± 2	322 ± 2	360 ± 6	1.01 ± 0.03	2
					342	324	366	1.50	1[a]
V5	3.1	327.5	3.4	3.5	316 ± 2	302 ± 2	354 ± 6	0.74 ± 0.05	2
					320 ± 3	306 ± 2	348 ± 2	0.76 ± 0.12	2[a]
V7	5.8	333	3.3	3.5					
V1	6.5	331.5	3.3	3.5		321	369		1
					348 ± 6	310 ± 4	358 ± 0.5	0.46 ± 0.21	2[a]
52110	7.0	329.5	3.3	3.5	310 ± 4	290 ± 4	326 ± 4	0.58 ± 0.20	4
V3	7.5	331	3.3	3.5	335	285	352	0.45	1
					340 ± 2	289 ± 3	358 ± 0.5	0.64 ± 0.12	2[a]
V6	8.3	334	3.3	3.5	336 ± 0.5	325 ± 0.5	348 ± 2	0.29 ± 0.01	2
					336 ± 4	324 ± 0.5	346 ± 5	0.29 ± 0.01	2[a]
TR-41-2445	8.9	331	3.3	3.5	338	302	350	0.55	1
V4	9.7	335	3.3	3.5	338 ± 9	318 ± 0.5	368 ± 12	0.50 ± 0.08	2
					340 ± 6	324 ± 4	368 ± 9	0.75 ± 0.17	2[a]
TRW-6-1086	10.5	338	3.3	3.5					
52111	13.5	335	3.1	3.5	340 ± 2	306 ± 3	353 ± 0.5	0.49 ± 0.04	3
TRW-6-1087	15.0	343	3.2	3.5					
52112	17.9	338	2.2	3.4	353 ± 0.5	339 ± 0.5	361 ± 0.5	0.27 ± 0.01	2
					338 ± 7	302 ± 0.5	352 ± 0.5	0.59 ± 0.03	2[a]
TR-41-2443	19.0	343	3.3	3.5					
TR-41-2446	22.0	349	3.2	3.5					

[a] Run after quenching in liquid N_2 from 460 K.

Table V
DSC Data of the B Microphases in S-B and S-B-S Samples

sample	$\overline{M}^B \times 10^{-4}$	T_g, K	T_{g_1}, K	T_{g_2}, K	ΔC_p, J g^{-1} K^{-1}	no. of runs
52111	1.25	194 ± 1	191 ± 1	196 ± 1	0.61 ± 0.02	3
V6	1.25	221 ± 0.5	208 ± 1	221 ± 1	0.53 ± 0.005	2
		215 ± 2	208 ± 1	221 ± 2	0.52 ± 0.02	2[a]
52110	1.90	193 ± 0.5	190 ± 0.5	196 ± 1	0.71 ± 0.005	3
V4	2.4	208 ± 2	200 ± 2	212 ± 2	0.78 ± 0.02	2
		207 ± 1	202 ± 0.5	212 ± 2	0.80 ± 0.04	2[a]
V3	2.8	206 ± 0.5	202 ± 0.5	209 ± 0.5	0.70 ± 0.02	2
		206 ± 0.5	201 ± 1	209 ± 0.5	0.66 ± 0.02	2[a]
V1	2.9	211 ± 0.5	204 ± 0.5	215 ± 1	0.74 ± 0.04	2
		207 ± 1	203 ± 1	212 ± 1	0.71 ± 0.06	5[a]
V2	4.8	199 ± 0.5	195 ± 0.5	202 ± 0.5	0.70 ± 0.02	2
		199 ± 0.5	196 ± 1	202 ± 0.5	0.70 ± 0.02	2[a]
TR-41-2445	5.6	190	187	192	0.75	1
		195 ± 0.5	193 ± 0.5	195 ± 0.5	0.67 ± 0.005	2[a]
V5	9.8	200 ± 0.5	195 ± 1	201 ± 1	0.80 ± 0.02	2
		200 ± 0.5	197 ± 0.5	202 ± 0.5	0.66 ± 0.20	2[a]

[a] Run after quenching in liquid N_2 from 460 K.

traces, only one of these is shown. The time at which each peak appeared was noted at least three times, and the corresponding molecular weight was calculated as if the sample were pure PS, pure PB, or a copolymer having the actual average composition of the sample. The pure PS and pure PB calculations were made because some of the peaks could or should correspond to such components in some of the samples and also in order to provide absolute limits to the molecular weight to which the peak corresponds. The "as-block" molecular weight calculated for each peak was calculated simply as (weight fraction of S)(molecular weight as PS) + (weight fraction of B)(molecular weight as PB). Considering all of the errors involved in this evaluation, this procedure probably gives reasonable results. If other procedures are used, slightly different values will be obtained. The $\overline{M}_w/\overline{M}_n$ values shown in Table III were calculated in the usual way, using the GPC peaks not labeled L and assuming that the whole sample had its average composition; these $\overline{M}_w/\overline{M}_n$ are for general comparison only and should be taken as lower limits for their real values. We show results on even the most polydisperse samples from Figure 2b in order to study the magnitude of the effect of polydispersity on our measurements.

Table IV shows the *n*–*T* and DSC data for the S-microphase T_g in our block copolymers. The molecular weight of each S block in each block copolymer was calculated by using our NMR weight percent S and the molecular weight calculated for the main GPC peak taken as block copolymer. This was done because the main GPC peak is the one most likely to represent the nominal block copolymer that we received in each case. Table V shows the DSC data for the B-microphase T_g in our block copolymer samples. The molecular weight of the B block in each block copolymer was calculated in the same way as for each S block as discussed above.

Discussion

Sample Characterization. Table II shows that, in most cases, the composition and microstructure deter-

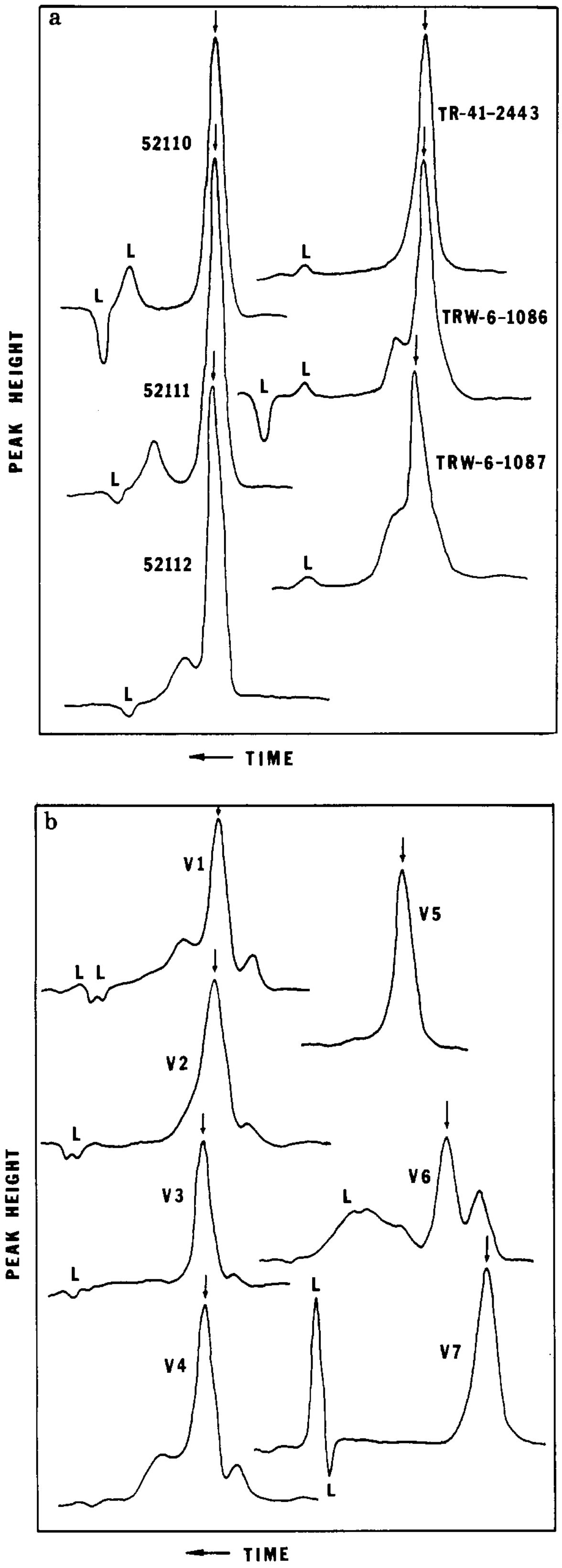

Figure 2. GPC data for the block copolymers. The arrow designates the main GPC peak and the letter L designates peaks that eluted after 17 min.

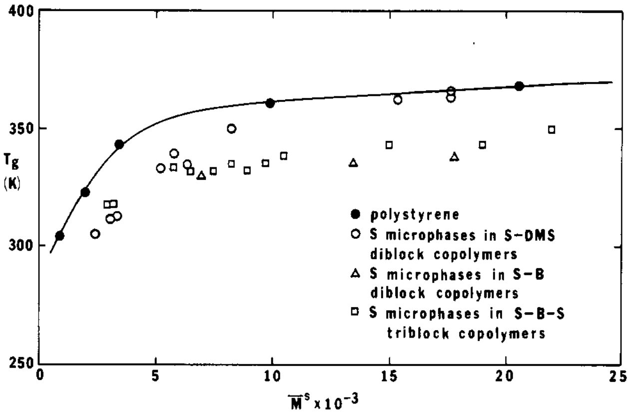

Figure 3. n–T glass transition temperatures of PS samples and of S microphases in S–DMS, S–B, and S–B–S block copolymers vs. molecular weight per S block or of PS homopolymer. The curve is drawn through the PS T_g's.

mined in this work are very close to the nominal values. Exceptions occur in the percent composition of samples V1, V3, V5, V6, and V7. Some of these samples showed many peaks in their GPC data (see Figure 2b), so it is clear that these samples are not the pure triblock copolymers that we hoped to use. The microstructures measured by NMR and by IR agreed well with each other and with the nominal microstructures. All the block copolymers contained ≤41% 1,2-added B units, and all but one sample has 45–59% trans-1,4-added B units. It is reasonable, therefore, to compare data on these samples without worrying very much about variations in the microstructures of the B blocks.

Figure 2 and Table III show that only a few of the block copolymers can be considered reasonably monodisperse. Some of the block copolymers, like V7, that appear relatively monodisperse in Table III can be seen to contain a substantial amount of low molecular weight material in Figure 2. Some of the slow peaks on the GPC traces shown in Figure 2b can be assigned to styrene homopolymer terminated before or while the butadiene was added to the polymerization mixture. Other slow peaks and the fast peaks are hard to assign. All that can be said about samples like V1, V4, and V6 is that they are extremely polydisperse, probably because of impurities that were present during their polymerization.

Properties of the S Microphase. Table IV shows the properties of the S microphases as measured by n–T and DSC techniques. The method used to calculate $\bar{M}_n^S$ has been described above. Obviously, the calculated value of $\bar{M}_n^S$ is closest to the correct value in the most monodisperse samples. In spite of the problems encountered in the calculation of $\bar{M}_n^S$ and in spite of the different polydispersities of the block copolymers, the T_g values obtained from n–T measurements and even the values obtained for the very polydisperse samples V1, V4, and V6 increase almost monotonically with $\bar{M}_n^S$. Figure 3 shows these T_g values plotted vs. $\bar{M}_n^S$ and compared with n–T T_g's obtained earlier on PS[8] and on the S microphases in S–DMS diblock copolymers.[7] It is important to emphasize here that $\bar{M}_n^S$ in the triblock S–B–S copolymers refers to the molecular weight of each block and not to the total molecular weight of S per molecule. A number of conclusions can be drawn from Figure 3. First, the n–T T_g's of all the S microphases in the S–B and S–B–S block copolymers are at least 18 K below the expected T_g of PS of molecular weight equal to $\bar{M}_n^S$. Figure 3 also shows that the n–T T_g's of the S microphases in all the block copolymers shown, S–DMS, S–B, and S–B–S, are very close to each other when $\bar{M}_n^S \leq 6.5 \times 10^3$. At higher values of $\bar{M}_n^S$, the T_g's of the S microphases in S–DMS diblock copolymers move closer to those of PS of molecular weight equal to $\bar{M}_n^S$, becoming equal at $\bar{M}_n^S > 1.76 \times 10^4$, while the T_g's of the S microphases in S–B and S–B–S block copolymers remain low. Differences in polydispersity do not change the T_g

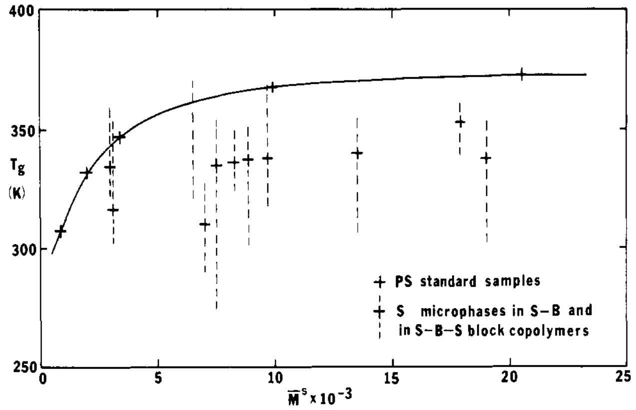

Figure 4. DSC glass transition temperature and glass transition ranges of S-B and of S-B-S block copolymers and of PS samples vs. molecular weight per S block or of PS homopolymer. The curve is drawn through the PS T_g's.

behavior of the S microphases in the S-B and S-B-S block copolymers. In the future, when S-B and/or S-B-S block copolymers with higher molecular weight S blocks become available it will be interesting to determine whether the n-T T_g's of microphases in these block copolymers approach that of PS of equal molecular weight at some value of $\bar{M}_n{}^S$. Some of the DSC data obtained by Ikeda et al.[13] suggest that the T_g's of the microphases in B-S-B and in S-B-S triblock copolymers do not reach PS values even when $\bar{M}_n{}^S \approx 10^5$. These data, as mentioned above, are difficult to compare with our own since Ikeda et al. used the value that we call T_{g_1} for T_g and since their DSC heating rate was 30 °C min^{-1} after a liquid N_2 quench of their samples.

The DSC data on our samples confirm the n-T data in the sense that all the S microphases had low T_g's and very broad glass transition regions; Figure 4 compares our DSC T_g's and ΔT_g's ($\Delta T_g = T_{g_2} - T_{g_1}$) on the S-B and S-B-S samples to those obtained earlier on PS.[4] We had shown earlier[4] that the DSC T_g's of the S microphases in S-DMS diblock copolymers approach those of PS of molecular weight equal to $\bar{M}_n{}^S$ at values of $\bar{M}_n{}^S$ similar to those shown in Figure 3 for n-T T_g's. The DSC ΔT_g's of the S microphases in the S-DMS diblock copolymers, however, remained about double those of PS, even at large values of $\bar{M}_n{}^S$. Figure 5 shows schematically a few of the block copolymer DSC data; it can be seen that the phase transition regions of the S microphases are extremely broad, so broad that the values of T_g taken from these data should not be taken too seriously. The n-T T_g's of all samples were, however, very sharp and can be considered more trustworthy. Figure 5 shows the DSC data on three of the block copolymers very schematically; the temperature scale is not the same for the three samples. Most samples showed DSC plots similar to that of sample 52111, but samples V5 and V6 had DSC plots like that of sample V4, showing a kink in their DSC plots at temperatures below those of the main transition region of the S blocks; sample V2 showed an exaggerated version of such a kink. Picking base lines was rather difficult even for samples with plots like that of sample 52111 but was even more difficult for samples V2, V4, V5, and V6. Some of these samples had multipeaked GPC data, but sample V5 did not. Sample V1, which had a DSC plot similar to that of sample 52111, on the other hand, had a multipeaked GPC plot. It is therefore hard to say whether the kinks in the DSC plots of samples V2, V4, V5, and V6 can be considered a glass transition for another phase, presumably a mixed phase or interphase containing both S and B segments. Because of the peculiarities of the DSC data, the ΔC_p values in Table IV are also only approximate. One may note, however, that all ΔC_p's except those of sample V6 and of nonquenched sample 52112 are much larger than that measured previously[4] on PS, 0.288 ± 0.006 J g^{-1} K^{-1}. This could be an indication of extensive mixing of B segments into the S microphases, just as similar data for S microphases in S-DMS diblock copolymers with $\bar{M}_n{}^S \leq 8.2 \times 10^3$ were interpreted as mixing of DMS segments into the S microphases. We may note, then, that elevated values of ΔC_p and T_g values more than 10 K below those of PS samples of molecular weight equal to $\bar{M}_n{}^S$ occur in S-DMS diblock copolymers only when $\bar{M}_n{}^S \leq 8.2 \times 10^3$ but occur in S-B-S triblock copolymers *at least* up to $\bar{M}_n{}^S = 2.2 \times 10^4$ and in S-B diblock copolymers *at least* up to $\bar{M}^S = 1.8 \times 10^4$. This major difference between S-containing block copolymers containing DMS or B as the rubbery block is most probably caused by differences in the compatibility of PS with PDMS vs. PS with PB. In general, PS is considered to be much more compatible with PB than with PDMS, and the present results tend to confirm this. It is also possible, however, that these differences are connected with the different temperature intervals between the T_g's of the S microphases and the rubbery microphases in the two systems: T_g = 141-160 K for DMS microphases[4] while T_g = 194-221 K for B microphases (Table V).

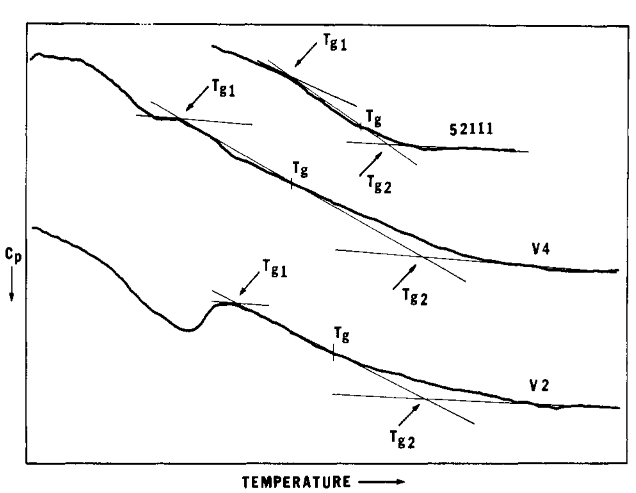

Figure 5. DSC data for the S-microphase glass transition in some of the block copolymers.

Roe et al.[19] have indicated that sample 52110 had a broad transition centered around 70-80 °C by DSC. This temperature range is higher than our n-T T_g and even the T_{g_2} obtained by DSC in this work. This discrepancy may be caused by major differences in heating and cooling rates in the two DSC measurements. A broad transition was, however, observed in both sets of measurements.

Although most of our ΔC_p values were greater than that of PS, Ikeda et al.[13] must have found ΔC_p values equal to that of PS for their samples with $\bar{M}_n{}^S$ from 5×10^4 to 10^5. This can be surmised from the fact that they could use their ΔC_p values per gram of sample to calculate the percent S in their samples. It seems, therefore, that mixing of B segments into S microphases ceases when $\bar{M}_n{}^S > 5 \times 10^4$.

Table IV indicates that there are no major differences between the DSC data when one of the block copolymers is quenched in liquid N_2 and after cooling at 10 K min^{-1}. We reported some data on sample TR-41-2445 earlier[20] in which it turned out that a film of this material, after being quenched in liquid N_2 from 460 K and then being placed in a DSC pan, had an S microphase glass transition that was so diffuse that only T_{g_2} could be determined. This indicated that some mixing of B segments into the S microphases probably occurred at 460 K and that this mixing could be frozen in by very fast quenching. Again, as in the case of S–DMS block copolymers, cooling rate appears to affect glass transition data. This is especially apparent in the very broad transition regions noted in our DSC data either after quenching in liquid N_2 or after cooling at 10 K min^{-1} vs. the narrow glass transition region in our n–T measurements of the same samples during slow cooling. It is possible that phase separation in these samples becomes more perfect during slow cooling.

There is considerable evidence in the literature that S–B–S triblock copolymers may become homogeneous on heating. Chung and co-workers[21–23] and Gouinlock and Porter[24] found that sample TR-41-2445 when heated above 423 K had a melt rheological transition from highly nonlinear viscous behavior to linear viscous behavior when measured at very low shear with a Weissenberg rheogoniometer. These melt rheological transitions were assumed to be a consequence of a morphological transition from a multiphase structure to a single-phase structure. Our previous DSC data on the same sample,[20] mentioned above, indicate a more gradual transition to a structure in which the microphases became less pure; that is, more and more B segments enter the S microphase. Pico and Williams[25] found that the clarity of films of S–B–S triblock copolymers increased on heating; this also points to increased mixing of the microphases at higher temperatures.

Roe et al.,[19] who specifically studied samples 52110 and TR-41-2445 by small-angle X-ray diffraction (SAXS) as a function of temperature, found that intermixing of block segments in the different microphases increased as the temperature was raised above room temperature with no change in the thickness of the interface between microphases. In other words, they found that the microphases persisted at elevated temperatures but that more and more segment mixing occurred as the temperature increased, with complete disappearance of the microphases at 200 °C. It is of interest to note that Roe et al.[19] also found that samples that had been quenched in liquid N_2 from 200 °C had the same SAXS patterns as those that had been cooled more slowly. The mixing–demixing phenomenon appeared to occur very quickly in their films. Thus, there are many data that indicate increased mixing of the microphases in S–B–S triblock copolymers at higher temperatures. It is a moot point, however, because of conflicting data, whether this mixed state can actually be frozen into the samples during fast cooling.

Properties of the B Microphases. Table V shows that the glass transition range, ΔT_g for the B microphases was quite narrow, 2–13 K, thus making it relatively easy to determine the T_g's. The T_g's of the B microphases vary from 190 to 221 K. Unfortunately, these variations correlate neither with $\bar{M}^B$, with microstructure of B units, nor with percent composition, that is, morphology. Microstructure certainly affects the T_g of PB; for example, Dainton et al.[26] calorimetrically determined that T_g = 165 K for 94% cis-1,4-PB–3% trans-1,4-PB–3% 1,2-PB and 190 K for 96.2% trans-1,4-PB–3.8% 1,2-PB. Kraus et al.[11] used dilatometrically determined T_g's on PB samples of different microstructure to estimate that T_g = 159 K for pure cis-1,4-PB, T_g = 171 K for pure trans-1,4-PB, and T_g = 266 K for pure atactic 1,2-PB. They also determined that the T_g's of the various PB samples could be expressed by using an extension of the Gordon–Taylor[27] equation to three components. Kraus et al.'s values[11] for these T_g's indicate that the B microphases with the highest 1,2 contents should have the highest T_g's. This is not so in our samples. A correlation with composition might have been expected because morphology of the sample changes with composition, but no such correlation has been found. In the triblock copolymers, there is a partial correlation of the T_g of the B microphase with polydispersity. The greater $\bar{M}_w/\bar{M}_n$, the higher this T_g. This suggests that styrene segments may mix into the B microphases in the more polydisperse samples or that the true $\bar{M}_n{}^S$ values of these samples are higher than those that we calculated.

Little can be said about our ΔC_p values because, again, these can be expected to vary with microstructure of the B microphases. The data of Ikeda et al.[13] can be analyzed to give ΔC_p = 0.55 J g^{-1} K^{-1} (using our ΔC_p for PS of 0.288 J g^{-1} K^{-1}) for 90% 1,2-PB–10% trans-1,4-PB. This is not far from our reported values.

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