Properties of Low Molecular Weight Block Copolymers. 2. Refractive Index–Temperature Measurements of Styrene–Dimethylsiloxane Diblock Copolymers

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ABSTRACT: The glass transition temperature, T_g, of the styrene microphase in a series of phase-separated styrene–dimethylsiloxane (S–DMS) diblock copolymers was obtained by refractive index–temperature (n–T) measurements and was compared with T_g's obtained by the same procedure on standard polystyrene (PS) samples. The results were similar to those obtained using T_g's from differential scanning calorimetry (DSC); the T_g's of the S microphases fell on the T_g vs. molecular weight curve defined by the PS standards when S block molecular weights were $\geq 1.76 \times 10^4$ and fell below this curve when S block molecular weights were $\leq 0.82 \times 10^4$. All T_g's obtained from n–T measurements were sharply defined, even though the T_g's obtained from DSC for samples with S block molecular weights $\leq 0.82 \times 10^4$ were very broad and diffuse.[2] Possible implications of these results are discussed.

Introduction

Paper 1 of this series[2] concerned the differential scanning calorimetry (DSC) of some styrene–dimethylsiloxane (S–DMS) diblock copolymers. In that work, 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 for both microphases in these diblock copolymers and were compared with the same quantities obtained on the corresponding homopolymers. In S–DMS samples with styrene (S) block molecular weights $\geq 3.90 \times 10^4$, the S phases had properties very similar to those of S homopolymer. When the S block molecular weights were $\leq 0.82 \times 10^4$, the S microphases had T_g's lower than those of PS of comparable molecular weight and ΔT_g's that varied from 3 to 8 times that of polystyrene; that is, the glass transition range became very broad. It was of interest to study the properties of the S microphases in these block copolymers by a different method in order to shed further light on these results. Refractive index–temperature (n–T) measurements were chosen for three reasons: (1) only a small sample, ~100 mg, is needed, (2) the time scale of the measurements is several orders of magnitude greater than that of DSC, and (3) we had a precision refractometer available.

Experimental Section

Polymers and Sample Preparation. The S–DMS diblock copolymers studied in this work have been described in paper 1 of this series. Data pertinent to the present paper are repeated in Table I. Sample films were prepared from 5% polymer solutions 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.

Refractive Index–Temperature Measurement. 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 at any temperature, but at least 1 h was needed for equilibrium to be established in the vicinity of T_g. All measurements were made by using the sodium D line.

Results

The first three columns of Table I show the block copolymer identification as explained in paper 1,[2] the number-average molecular weight of the S block ($\bar{M}_n^S$) as obtained from gel permeation chromatography,[2] and the weight percent S in each sample obtained by NMR.[2] The T_g values in the fourth column of Table I are taken from plots of n_D vs. temperature; three representative plots are shown in Figure 1. The values in Table I of dn/dT, both below and above T_{g_1}, and of n_D at T_g are also taken from such plots. The last three columns in Table I are some of the DSC data on the styrene microphase glass transition taken from paper 1, namely, the values of T_g, the beginning of the glass transition region, T_{g_1}, and the end of the glass transition region, T_{g_2}. Definitions of T_g, T_{g_1}, and T_{g_2} are given in paper 1.[2]

Figure 2 shows the variation of the n–T T_g values with S molecular weight in the S–DMS diblock copolymers and with polystyrene (PS) molecular weight in standard homopolymers for block and homopolymer molecular weight $<2.5 \times 10^4$. On the figure, the solid curve is drawn through the PS T_g's, which were obtained by the same method in our laboratory.[3]

Discussion

If the data on Figure 2 were continued up to $\bar{M}_n^S = 1.15 \times 10^5$, the highest S block molecular weight investigated in this work, it would be found that the data for all S microphases with S block molecular weights $>1.76 \times 10^4$ fall on the PS curve. Using refractive index–temperature data, in other words, it appears that the T_g of the S microphases in S–DMS diblock copolymers with $\bar{M}_n^S > 1.76 \times 10^4$ is consistent with that of PS standard samples of comparable molecular weight. The T_g of the S microphase in the S–DMS block copolymer with $\bar{M}_n^S = 1.54 \times 10^4$ lies as far below the PS standard curve as one of the $\bar{M}_n^S = 1.76 \times 10^4$ samples, while the T_g's of all S–DMS block copolymers with $\bar{M}_n^S \leq 8.2 \times 10^3$ lie 8–30 K below the PS standard curve. The data in Figure 2 are consistent with the DSC data shown on a similar diagram in paper 1. The DSC T_g's of the S microphases, however, agreed with those of PS standard samples down to $\bar{M}_n^S = 1.54 \times 10^4$, where the n–T data show a slight discrepancy. The DSC data on the S microphases indicated that the S–DMS block copolymers could be divided into three groups: (1) a high molecular weight group, $\bar{M}_n^S \geq 3.90 \times 10^4$, in which the S microphases have T_g equal to that of PS of comparable molecular weight but the width of the glass transition region, $\Delta T_g = T_{g_2} - T_{g_1}$, is about twice that of PS; (2) a low molecular weight group, $\bar{M}_n^S \leq 0.82 \times 10^4$, in which the S microphases have T_g's lower than that of PS of comparable molecular weight and ΔT_g's greater than those of the high molecular weight group; and (3) an intermediate molecular weight group in which the changes in properties

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Table I
Refractive Index-Temperature Data on S-DMS Diblock Copolymers

sample	$\bar{M}_n^S \times 10^{-4}$ (GPC)	[S], wt %	T_g, K	$dn/dT \times 10^4$, K		n_D at T_g	DSC data[2]		
				$T < T_g$	$T > T_g$		T_g, K	T_{g_1}, K	T_{g_2}, K
I23	0.233	86	305	−2.4	−3.7	1.5546	317 ± 1	308 ± 1	329 ± 5
I25	0.307	78	311	−2.4	−3.7	1.5418	323 ± 0.5	313 ± 2	332 ± 0.5
I24	0.334	86	313	−2.5	−3.7	1.5493	322 ± 0.5	312 ± 1	330 ± 0.5
I15	0.519	59	333	−3.0	−3.7	1.4997	320 ± 9	290 ± 12	342 ± 10
I26	0.58	79	339	−2.4	−3.7	1.5336	346 ± 3	332 ± 7	354 ± 1
I29	0.63	29	335	−3.1	−3.8	1.4384	335	304	360
R13	0.82	54	350	−3.0	−3.7	1.4876	358 ± 4	342 ± 4	370 ± 2
D2	1.54	84	362	−2.0	−3.7	1.5483	370 ± 1	357 ± 2	381 ± 3
D1	1.76	88	365	−2.0	−3.7	1.5567	370 ± 0.5	361 ± 2	378 ± 3
R14	1.76	57	363	−2.0	−3.7	1.4900	374 ± 0.5	368 ± 3	382 ± 2
R15	3.90	47	369	−2.0	−3.7	1.5241	377 ± 0.5	371 ± 4	384 ± 3
R8	10.5	60	372	−2.0	−3.7	1.5240	378 ± 0.5	374 ± 0.5	384 ± 2
R5	11.5	74	373	−2.0	−3.7	1.5235	379 ± 0.5	373 ± 2	384 ± 2

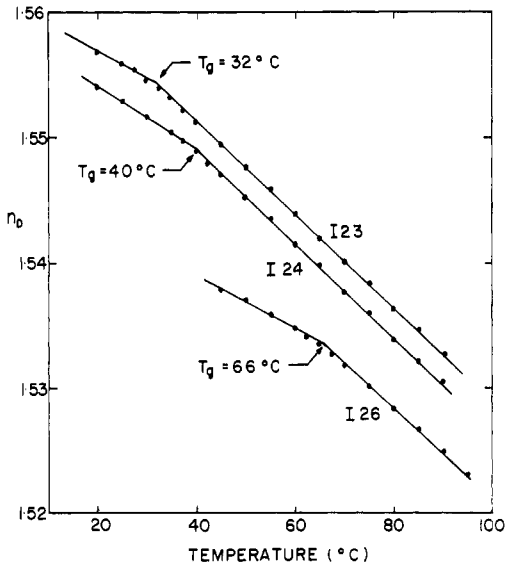

Figure 1. Refractive index vs. temperature data of three S-DMS diblock copolymers.

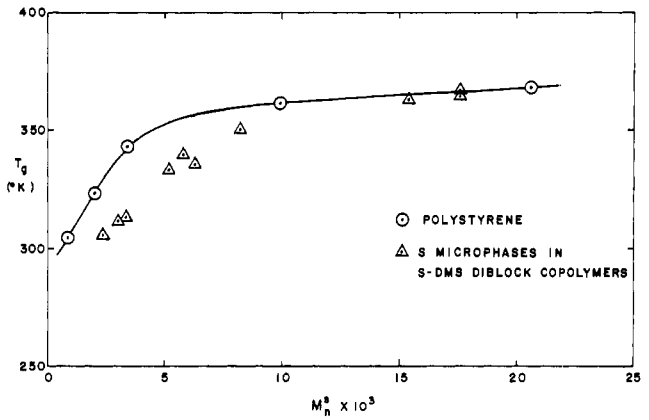

Figure 2. T_g, obtained by n–T measurements, vs. molecular weight of the styrene block in S–DMS diblock copolymers and vs. homopolymer molecular weight of PS standards. The solid curve is drawn through the PS data.

from the high to the low molecular weight group are somewhat sporadic and gradual. The n–T data in Table I and Figure 2, however, indicate only two groups: (1) a high molecular weight group with $\bar{M}_n^S \geq 1.76 \times 10^4$, in which the S microphase T_g's are comparable to those of standard PS samples of comparable molecular weight; and (2) a low molecular weight group with $\bar{M}_n^S \leq 0.82 \times 10^4$, in which the S microphase T_g's are less than those of standard PS samples of comparable molecular weight. It is not possible to say into which of these groups the S–DMS sample with $\bar{M}_n^S = 1.54 \times 10^4$ belongs.

Table I shows that the T_g values obtained for the various S microphases from n–T measurements are 6–8 K below those obtained from DSC data when $\bar{M}_n^S \geq 0.82 \times 10^4$. This is similar to the results obtained for the PS standards;[3] here, n–T measurement yielded T_g's 3–7 K below those obtained from DSC data. For the S–DMS samples with $\bar{M}_n^S \leq 0.63 \times 10^4$, however, T_g from n–T measurements varies from 12 K below to 13 K above that obtained from DSC data. This is probably connected with the very large ΔT_g's obtained on these low S block molecular weight samples using DSC. This makes the exact location of the DSC T_g within the glass transition interval somewhat uncertain.

Although the DSC ΔT_g for the S microphase glass transition in the S–DMS diblock copolymers varied from 10 to 56 K, all the n–T T_g's were very sharp; all n–T data looked like the three samples shown in Figure 1. This is a major discrepancy between the n–T and the DSC data and it must have something to do with the differences between the two types of measurements. Refractive index–temperature measurements are performed very slowly, over at least an 8-h period, while the sample is being cooled; a relatively large area of the sample is illuminated by the light beam. The DSC measurements were performed very quickly, while the sample was being heated at 10 K min^{-1} after the sample had been cooled at 10 K min^{-1}. DSC measurements also probe a relatively large sample volume but may find heat capacity changes that occur in smaller volume elements than the refractive index changes that are found using n–T measurements. It is nevertheless hard to say why the n–T T_g's of the S microphases should be so sharp while the DSC T_g's of the lower molecular weight S microphases should be so diffuse. The discrepancy is most likely to be connected with the large difference in cooling rates used in the two types of measurements. In a microphase-separated block copolymer sample, it should be much easier to freeze in high-temperature conformations of chains and high-temperature changes in segment mixing at microphase interfaces at the cooling rate of 10 K min^{-1} in DSC measurements than at a cooling rate that averaged 2.5 K h^{-1} near T_g in n–T measurements. For this reason, the sharp T_g's from n–T measurements, which indicate a relatively uniform S microphase structure, probably are more informative about the "equilibrium" behavior of the sample than the diffuse DSC T_g's obtained on the same samples.

The dn/dT values for these samples, in Table I, above T_g are all about the same, -3.7×10^{-4}, somewhat greater than those found for PS standards,[3] -3.3×10^{-4} to -3.6×10^{-4}, increasing with decreasing molecular weight; the PS standards varied in molecular weight from 9×10^2 to 10^5.

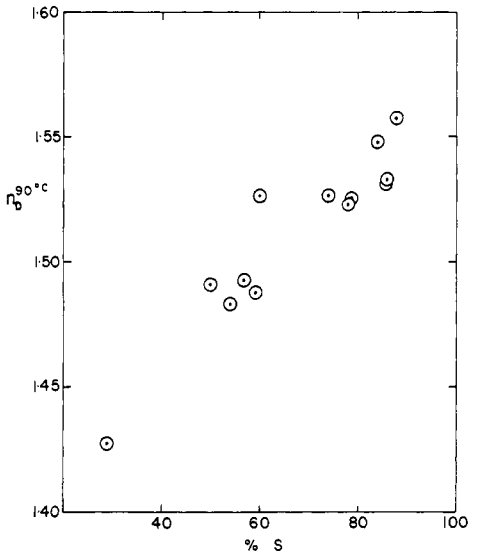

Figure 3. n^{90}_D vs. percent S in the S–DMS diblock copolymers. When T_g of the S microphase was >90 °C, the n^{90}_D was extrapolated from data taken above T_g.

This increase in $|dn/dT|$ for $T > T_g$ of the block copolymer samples probably reflects the presence of the DMS in the block copolymers, especially since sample I29, the sample with the highest percent DMS, has the highest $|dn/dT|$, $T > T_g$.

It is tempting to try to use the refractive index values of these copolymers at a representative temperature as a method for determining their percent composition. But this will not work as can be seen in Figure 3, in which the points are the refractive indices of the block copolymers at 90 °C vs. percent S for all block copolymers with $T_g \leq$ 90 °C; for the five samples with $T_g >$ 90 °C, the high-temperature refractive index line was extrapolated back to 90 °C so that all refractive indices referred to fully rubbery polymers. As can be seen in Figure 3, there is only an imperfect correlation between n^{90}_D and percent S. There would be no improvement in this correlation if one picked n^{30}_D, where all the S microphases are below their T_g. This imperfect correlation is exactly what should be expected since rubbery polymers have refractive indices that are quite molecular weight dependent. It was found previously that the refractive index of the PS standards above T_g increased with molecular weight at each temperature,[3] reaching an asymptotic value at a molecular weight between 5×10^4 and 10^5. In addition, although we found no molecular weight dependence for the refractive index of PS below T_g,[3] Fechner et al.[4] found a molecular weight dependence for the refractive index of PDMS up to a molecular weight 5.8×10^4 near room temperature, that is, well above the PDMS T_g. The molecular weight dependence of the refractive index of both PS and PDMS perturbs the correlation that may have been expected in Figure 3, while, at 30 °C, only the molecular weight dependence of the PDMS refractive index would perturb such a correlation. Therefore, at reasonable temperatures, refractive index cannot be used to determine percent composition in S–DMS diblock copolymers.

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References and Notes

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Optical Behavior and Polymorphism in Poly(ethylene sebacate). 1. Morphology and Optical Properties

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ABSTRACT: Depending upon crystallization temperature, poly(ethylene sebacate) crystallizes from the melt to form spherulites of three distinct types. Two of these, one unringed and one showing double extinction rings of the kind often found in spherulites of biaxial polymers, are comprised of crystals having the known monoclinic structure but with different preferred orientations. However, the third type, which shows uniformly spaced extinction rings, comprises crystals having a previously unknown structure. The new polymorph is metastable and, on heating, spherulites transform to the known stable form but with little visual evidence of the change other than a striking increase in magnitude of birefringence. The structure of this polymorph is closely related to that of the monoclinic form, and the transformation is accomplished without change in orientation of principal crystallographic axes. Optical properties of the two polymorphs have been studied in detail. It is shown that accurate alignment of the optic normal along the radius in double-ringed spherulites is the result of an averaging of electrical polarizabilities over two approximately equal populations of monoclinic crystals with opposite tilting of molecular chains with respect to the radius (a polymer analogue of mimetic twinning in simpler crystalline materials). Quantitative analyses of birefringences in ringed spherulites (including the change in birefringence accompanying transformation between the polymorphic forms) strongly reinforce the view, which has been challenged in some recent papers, that the crystallographic orientation averaged over neighboring lamellar crystals in these spherulites twists uniformly about the radius. Other properties of the new polymorph are described in a companion paper (part 2).

Introduction

Linear aliphatic polyesters prepared by condensation of dibasic acids with ethylene glycol were among the first crystalline polymers to be subjected to systematic structural investigation by X-ray diffraction.[1-3] Members of the homologous series prepared from acids having an odd number of carbon atoms crystallize with orthorhombic unit cells, and those prepared from acids having an even number of carbon atoms crystallize with monoclinic unit cells. With the exception of poly(ethylene succinate), all share

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