

Phase Behavior for Blends of Styrene Containing Triblock Copolymers with Poly(2,6-dimethyl-1,4-phenylene oxide)

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Synopsis

The extent to which the styrene end-blocks of three commercially available triblock copolymers can mix with a particular poly(2,6-dimethyl-1,4-phenylene oxide) ($M_n = 22,600$ and $M_w = 34,000$) or PPO has been examined by investigation of the glass transition behavior of the PPO and polystyrene (PS) portions of the blends using differential scanning calorimetry. Each block copolymer has a butadiene-based mid-block which was hydrogenated for two of these materials, but not the third. The three copolymers differ substantially in overall molecular weight and in molecular weight of the blocks. However, in analogy with the literature on blends of homopolymer polystyrene with styrene-based block copolymers, the molecular weight of the PS block should be the principal factor affecting the phase behavior in the present blends. Mixtures of the PPO with the block copolymers having PS blocks with $M = 14,500$ (nonhydrogenated midblock) and with $M = 29,000$ (hydrogenated mid-block) exhibited single composition-dependent T_g 's for the hard phase, indicating complete mixing of PS segments with the PPO, for all proportions. On the other hand, the block copolymer having a PS block with $M = 7,500$ and a hydrogenated mid-block exhibited two separate hard phase T_g 's corresponding to an essentially pure PPO phase and a PS-rich phase. For blends of homopolymer PS with styrene-based block copolymers, the similar two-phase behavior of the glassy portion can be readily explained by entropic considerations. For the present case, the favorable enthalpic contribution for mixing PPO and PS is an additional factor which seems to influence the restrictions on molecular weight for complete mixing; however, additional work is needed to develop a more quantitative assessment of this new issue.

INTRODUCTION

In the bulk state, block copolymers generally segregate into phases consisting essentially of each individual segment type.¹⁻⁴ The sharpness of the interface between phases, domain size, phase morphology, and the placement of individual chains in this structure depend on the number and sequencing of the blocks per molecule, the length of each block, overall molecular weight, and the interactions between segments forming the various blocks. There is an extensive body of experimental and theoretical work concerning blends of homopolymers with phase-separated block copolymers having a block chemically identical with the homopolymer.^{5,6} In principle, this is a simple means of continuously varying the proportions of the phases in the composite and morphology. Simple notions of mixing would lead one to expect the homopolymer to be incorporated into a phase composed of the same type of segments; however, it is now well-known that satisfying simultaneously the constraints of placing the junction of the block copolymer near the interface

and achieving uniform segment densities within each phase defines a relation between domain size and block length and restricts the size of homopolymer molecules that can be incorporated into these domains.⁵ Because of these issues, it is generally believed that significant solubilization of a homopolymer into a like domain of a block copolymer cannot occur if the homopolymer is much larger in molecular size than the corresponding block of the copolymer.^{7,8}

A related problem which has received much less attention is the mixing of block copolymers with a chemically different homopolymer which forms miscible blends with a polymer made up of segments identical to those in one of the blocks of the copolymer. We refer specifically to the situation where this miscibility stems from an exothermic heat of mixing, that is, a favorable segment-segment interaction, which contrasts with the former case where mixing is athermal since the segments are identical. This case raises some interesting scientific questions such as how the strength of the favorable interaction affects size restrictions of homopolymer molecules that can be incorporated into block copolymer domains of any given dimensions. When solubilization does occur, this situation offers an attractive route for tailoring the properties of this domain, for example, its glass transition temperature (T_g).

An obvious example of the latter type is when the homopolymer is poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and one of the blocks of the copolymer is polystyrene (PS) since this pair of homopolymers forms miscible blends which have been thoroughly studied.^{9,10} Schultz and Beach¹¹ have examined the glass transition behavior of blends of PPO with a poly(styrene-*b*-butadiene-*b*-styrene) copolymer (SBS) and aside from the rubber phase T_g , they found a single, composition-dependent T_g corresponding to PPO-PS mixtures, suggesting that the PPO is completely incorporated into the PS domains. Related work by Kambour¹² showed that by addition of PPO the heat distortion temperature of the block copolymer could be significantly increased without substantial loss in its elastomeric behavior. Meyer and Tritscher¹³ reported related work on a more complex system involving poly(styrene-*b*-isoprene-*b*-styrene) copolymers blended with a modified PPO. Hansen¹⁴ has shown that the service temperature of adhesives based on styrene containing block copolymers can be increased by the addition of a low molecular weight PPO while a higher molecular weight PPO gave no such advantage. This observation apparently relates to the question of relative size restrictions mentioned earlier.

In response to the questions and opportunities indicated above, we have initiated a detailed study of the characteristics and properties of blends of styrene-based block copolymers with homopolymers known to interact exothermically with polystyrene. This first report is concerned only with PPO although other candidate polymers are known. All of the block copolymers examined are of the SBS type with primary emphasis on those where the butadiene midblock is hydrogenated since elimination of the diene unsaturation results in better thermal and oxidative resistance for processing with PPO and the possibility to take advantage of any higher use temperature which might be achieved by blending. The goal is to learn more about the restrictions on the length of the styrene blocks for complete incorporation of a PPO with a fixed molecular weight. This is accomplished by evaluation of the glass

TABLE I
Summary of triblock copolymers containing styrene end-blocks used in this work

Designation used here	Commercial designation	MW of PS end-block	Weight % PS ^a	PS Block T_g
SBS	Kraton 1101	14,500 ^b	28.8	88°C ^c
SEBS-H	Kraton G1651	29,000 ^d	33.3	103°C ^c
SEBS-L	Kraton G1652	7,500 ^d	28.6	70°C ^e

^a Calculated from molecular weight information.

^b See Ref. 11.

^c From DSC, midpoint at 40°C/min.

^d See Ref. 15.

^e Estimated from Fig. 1, could not be detected by DSC.

transition behavior of the blends using differential scanning calorimetry (DSC).

EXPERIMENTAL

The PPO used was provided to us through the courtesy of Dr. Joseph C. Golba, Jr. of the General Electric Co. Molecular weight characterization by gel permeation chromatography with a light scattering detection system gave $M_n = 22,600$; $M_w = 34,000$; and $M_z = 57,200$.

The triblock copolymers are commercial products of the Shell Chemical Co. provided by the courtesy of G. Holden and are described in Table I.¹⁵ Various information about these polymers were obtained from the literature as noted. Each copolymer has styrene end-blocks which differ in molecular weight rather considerably. For the latter two, the butadiene mid-block is hydrogenated resulting in a structure equivalent to an ethylene/butene (EB) random copolymer which is essentially amorphous. For convenience, these polymers are designated further by H and L to indicate the high and low molecular weight of their styrene blocks.

Blends of each of the three copolymers with PPO were prepared by making solutions containing 5% by weight of total polymer in a mixture of solvents consisting of 75% toluene and 25% chloroform on a weight basis. The polymer was recovered by precipitation from this solution using an excess of methanol. The precipitated polymer was dried at room temperature without vacuum for at least two days. Final solvent removal was accomplished in a vacuum oven at elevated temperature (60 to 110°C) over a period of two days. This protocol was judged adequate since DSC results showed that the pure polymers had the same T_g as the as-received materials while for blends, repeated DSC runs on the same sample gave little variation in T_g .

For SEBS-L, blends with PPO were prepared in two additional ways. Films were cast from a solution containing 5% polymer in trichloroethylene. Drying and testing for solvent removal was done in the same manner described above. In addition, melt mixing was done in a Brabender Plasti-Corder for 5 to 10 minutes at 260°C to 270°C. These samples were subsequently compression molded in a heated hydraulic press.

Thermal analysis for glass transition behavior was done at 40°C/min with a nitrogen purge using a Perkin-Elmer DSC-2 equipped with a Thermal Analysis Data Station. Samples ranging in weight from 8 to 20 mg were sealed in aluminum pans. Between heats, the samples were quenched at a programmed rate of 320°C/min using a mechanical intercooler. Base line subtraction improved the quality of thermograms and facilitated their interpretation. The thermogram from the first heat was usually not reproducible owing to differences in sample history and was therefore discarded. The glass transition behavior reported here was obtained from subsequent heats.

Thermograms were interpreted as follows. In the vicinity of each T_g , tangent lines were drawn through the glassy portion, through the transition or inflection portion, and through the rubbery or melt portion of the trace. The intersections of these three lines define the onset, T_1 , and the end, T_2 , of the transition region. The midpoint between T_1 and T_2 was defined as T_g while $\Delta T_g = T_2 - T_1$ was used as a measure of the breadth of the transition. The change in the heat capacity, ΔC_p , was calculated from the difference in the extrapolated glass and melt tangent lines at the T_g as defined above.

For SEBS-L and its blends containing small amounts of PPO, it was difficult and often impossible to detect the glass transition for the hard phase. Others^{16,17} have noted similar problems. It has been suggested¹⁸ that large samples and fast heating rates improve instrument sensitivity while smaller samples and slower heating rates improve resolution. Since the size of the preformed sample pans limits the size of the sample, the relatively high heating rate of 40°C/min was chosen to enhance detection of these difficult transitions.

RESULTS AND DISCUSSION

Glass Transitions for PS End-Blocks

The glass transition temperature observed for polystyrene end-block domains in the neat copolymer will be influenced by several factors. First, it will depend on the heating rate used; specifically, the value for 40°C/min will be higher than that at 10°C/min. Using four monodisperse polystyrene standards from Pressure Chemical Company, with relatively low molecular weights, we found an average increase in T_g of 5°C as the heating rate was raised from 10°C/min to 40°C/min. The T_g will also depend on the molecular weight of the segment, and this is a very strong dependence at low molecular weights. Finally, it has been observed by Krause and Iskandar¹⁹ that PS microphases in various diblock and triblock copolymers have lower T_g s than polystyrene homopolymers of the same molecular weight. This difference is about 10°C in most cases, but below end-block molecular weights of about 12,000 the difference becomes even more pronounced.

With the help of the compilation of data by Krause and Iskandar, we estimated the probable T_g for PS domains of copolymers using data for polystyrene homopolymers. For molecular weights of 14,500 and 29,000, the depression in T_g is approximately 10°C while for a molecular weight of 7,500, it is approximately 20°C. We assume that these differences will remain the same for other heating rates as well. Figure 1 shows glass transition tempera-

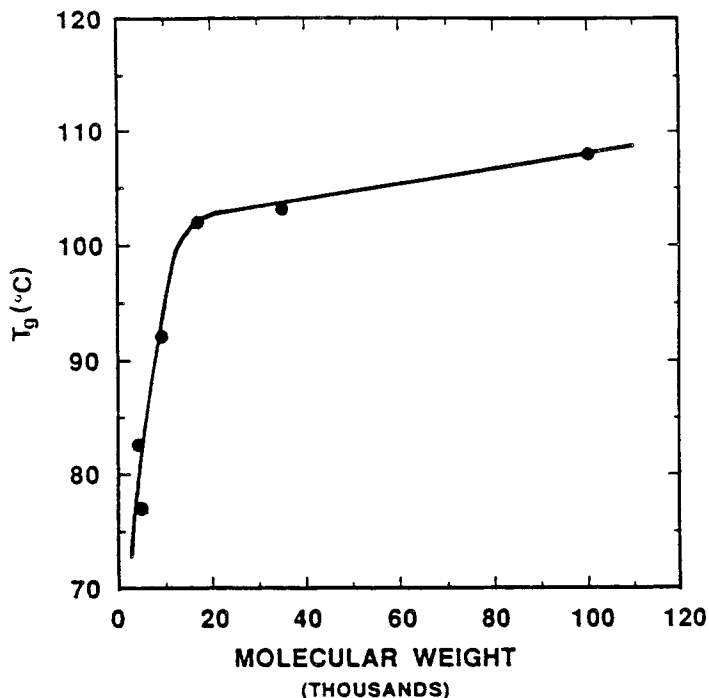


Fig. 1. Glass transition temperature of various polystyrene standards (Pressure Chemical Company) as determined by differential scanning calorimetry at 40°C/min.

tures as a function of molecular weight for several PS standards obtained from Pressure Chemical Company for a heating rate of 40°C/min. From this curve for homopolystyrene, we have estimated the glass transition temperature of the polystyrene domains in the SEBS-L copolymer to be 70°C as stated in Table I. We were not able to detect this T_g by DSC owing to the breadth of this transition and the broad melting endotherm from residual crystallinity of the mid-block which masks its onset. The estimate of 70°C is supported by dynamic mechanical analysis by which we were able to detect clearly the T_g for SEBS-L. For comparison, the estimated T_g s for PS domains in SBS and SEBS-H are 90°C and 94°C, while our DSC values are 88°C and 103°C, respectively. The agreement is reasonable for SBS, but it appears that for SEBS-H the T_g value has approached that of the polystyrene homopolymer. The estimated value of T_g for SEBS-L and the experimental values for SBS and SEBS-H are used to estimate the T_g of blends via the Fox equation²⁰ as described later.

Blends with SBS

As mentioned above, Shultz and Beach¹¹ have examined the glass transition behavior of PPO blends with an SBS block copolymer using a thermal optical analysis (TOA) technique. We have repeated these experiments using DSC with essentially equivalent materials to verify our techniques, and we obtained the results shown in Figure 2. Here we report the T_g for the hard phase as a function of the weight fraction of PPO added excluding the

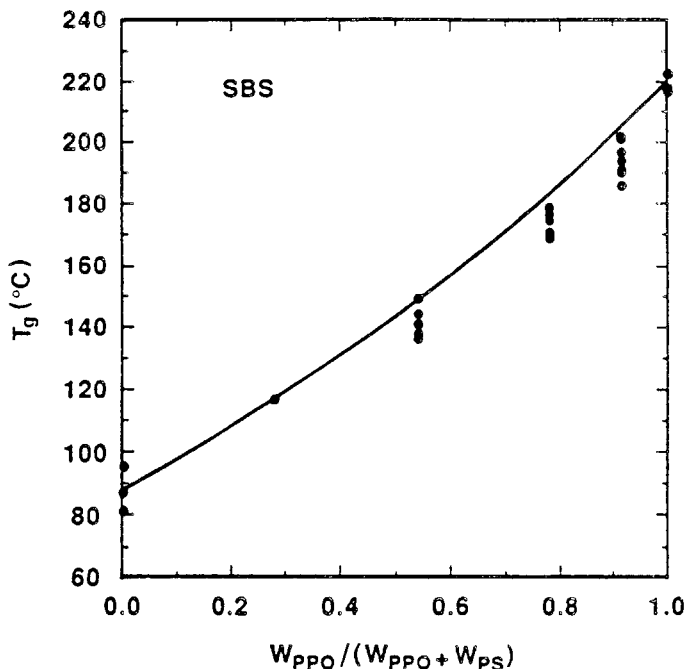


Fig. 2. Hard phase glass transition temperature for SBS/PPO blends prepared by precipitation (DSC, 40°C/min). The solid line represents the Fox prediction for T_g .

rubbery phase of the copolymer midblock, that is, the fraction of PPO in the hard phase of the blend. There is only one T_g in the region expected for PS and PPO which varies continuously with PPO content. The solid line drawn in Figure 2 was computed from the Fox equation using experimental values for T_g at the two composition extremes. The observed values of T_g for blends agree with this prediction rather well except for high PPO contents where the measured results fall slightly below the prediction. Shultz and Beach noted a similar trend. In general, our data compare well with the values obtained by Shultz and Gendron⁹ for PPO/PS blends using DSC (onset method for T_g at 20°C/min) and TOA (end-point method for T_g at 10°C/min) and for PPO/SBS blends¹¹ using TOA (end-point method for T_g at 10°C/min) when appropriate allowances are made for the differences from our technique of defining T_g as the midpoint and a heating rate of 40°C/min. Based on the above, the PPO and the PS end-blocks appear to form a single, molecularly mixed hard phase which is the conclusion reached by Shultz and Beach.

The multiple points shown in Figure 2 and subsequent plots represent results from different runs on the same sample and runs for different samples. The scatter in these data will be discussed later.

From the DSC thermograms we also computed the breadth of the glass transition region, ΔT_g , and the change in the heat capacity, ΔC_p , over this interval. These results are shown in Figures 3 and 4. The measured values of ΔT_g lie consistently above the dashed tie line drawn between those for PPO and PS domains of the copolymer. The ΔT_g for PPO is comparable to that reported by others.²¹ The ΔT_g for the polystyrene phase of the pure block

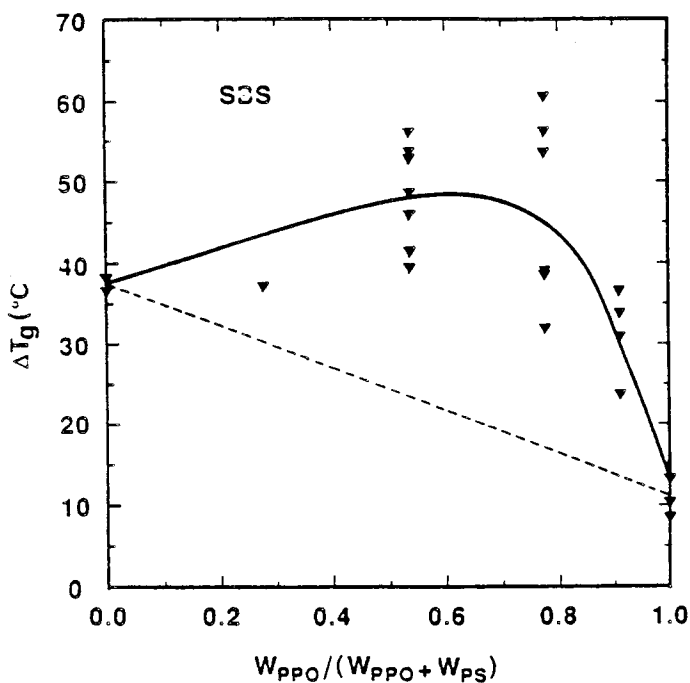


Fig. 3. Breadth of glass transition for SBS/PPO blends.

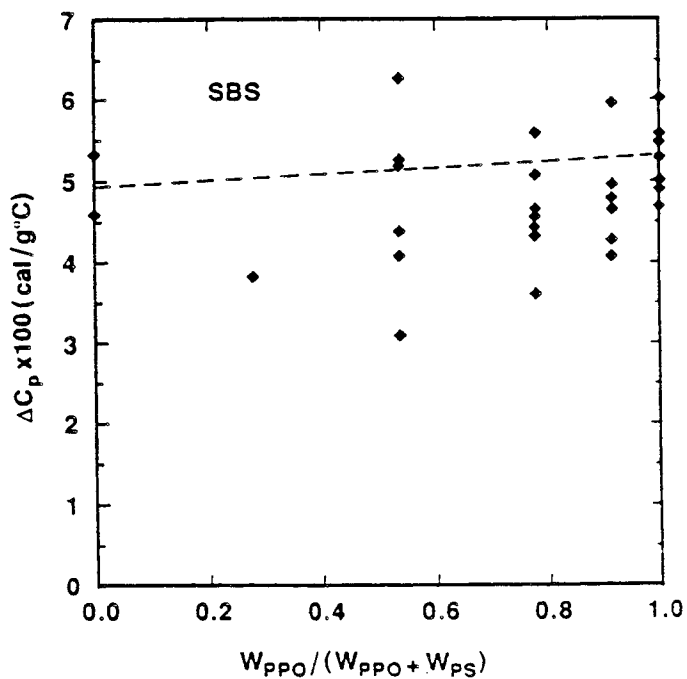


Fig. 4. Heat capacity change through the T_g for SBS/PPO blends.

copolymer is also consistent with values in the literature;²² however, it is considerably larger than that expected for bulk polystyrene homopolymer of comparable molecular weight. The latter may be attributed to interfacial effects.^{23,24} Such a result would be expected based on the commonly accepted view that the interface between phases is not sharp owing to a certain amount of mixing of the two types of chain segments.²⁵ In addition, Gaur and Wunderlich²⁴ have shown that emulsion particles of polystyrene homopolymer have broader T_g 's than the corresponding material in the bulk state. The extent of this effect increases with the surface to volume ratio. The glass transition region for miscible blends of homopolymers is often found to be broader than expected from those of the pure homopolymers which may be attributed to composition fluctuations.²⁶ In fact, Fried and Hanna²⁷ have shown such broadening for PPO-PS mixtures which appears to be greatest in the PPO-rich region as also noted in Figure 3 for blends with SBS. Of course, the extent of broadening is greater here. Based on the above, the results in Figure 3 follow a reasonable pattern with several factors contributing to the rather significant broadening of this transition. More will be said later about the scatter in these data.

The change in heat capacity upon traversing the glass transition region, based on mass of hard phase, for PPO-SBS blends falls below the dashed tie line as shown in Figure 4. The ΔC_p noted here for pure PPO is comparable to values in the literature.²¹ The value for the polystyrene domains of the SBS copolymer is below that reported for homopolystyrene.²¹ Gaur and Wunderlich²⁴ report similar observations for block copolymers and for emulsion particles of PS homopolymer with the value of ΔC_p depending on the surface to volume ratio of the particles in either case. Krause et al.¹⁷ have reported larger values of ΔC_p for copolymers than bulk homopolymer which they felt may result from incorporation of some midblock segments into the styrene domains. In miscible blends of homopolymers, values for ΔC_p typically follow the tie line, but values lower than the tie line have also been noted.²⁸ This has been attributed to not accounting for all of the material actually present. Because of the complexity of PPO-SBS blends and the conflicting results for simpler systems, further interpretation of Figure 4 seems rather dubious at this time.

Blends with SEBS-H

Attention is now focused on the copolymers having hydrogenated midblocks described in Table I. The one with the higher molecular weight PS end-block, SEBS-H, resulted in blends with PPO that have a single, composition-dependent glass transition for the nonrubbery portion of mixture, as shown in Figure 5, using the same composition axis as before. The line drawn was computed from the Fox equation which describes the experimental data rather well. In contrast to the SBS/PPO system where the experimental values fall slightly below the calculated curve on the PPO-rich end, the data for this pair fall slightly above the Fox equation prediction in this region. The result is a slight tendency towards a sigmoidal shape for the T_g -composition relation. Similar shapes have been noted for other blend systems.²⁶ From the

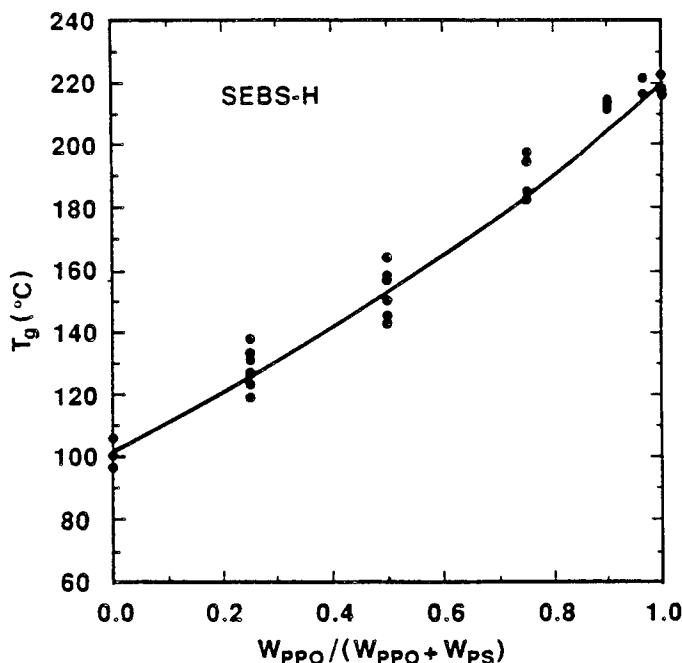


Fig. 5. Hard phase glass transition temperature for SEBS-H/PPO blends prepared by precipitation (DSC, 40°C/min). The solid line represents the Fox prediction for T_g .

single T_g we conclude that PPO and the PS end-blocks form a single, miscible hard phase like that for the SBS/PPO pair.

Figure 6 shows the breadth of the hard phase glass transition region. As noted for the SBS/PPO pair, the transition breadth for blends falls considerably above the tie line shown as a dashed line between values for PPO and the PS transition in SEBS-H. The breadth for this copolymer is greater than that for bulk PS homopolymer but is significantly smaller than that for SBS. Two factors are most likely responsible for the latter. First, the PS block in SEBS-H has a higher molecular weight than in SBS by nearly a factor of two which leads to significantly larger PS domains for the former. Second, hydrogenation of the mid-block results in segments less likely to mix with PS segments based on solubility parameter differences.²⁹ Thus, the interface in SEBS copolymers is expected to be much sharper than in SBS copolymers.

Very likely, the significant T_g broadening shown in Figure 6 is the result of composition fluctuations or gradients within the mixed PPO-PS hard phase of these composites.

Figure 7 shows the change in heat capacity (based on mass of hard phase only) upon traversing the glass transition region for the nonrubbery portion of these materials. The value of ΔC_p for SEBS-H is lower than that for both homopolystyrene and SBS. Based on surface area to volume considerations alone, we would expect the value for SEBS-H to fall between that for the homopolymer and SBS. This discrepancy could arise from the difference in the sharpness of the interface for the two copolymers. The computed ΔC_p for

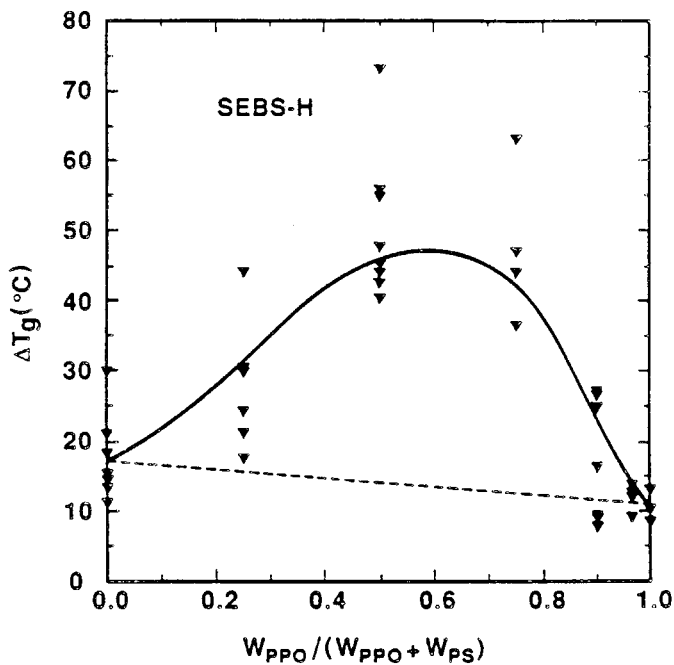


Fig. 6. Breadth of glass transition for SEBS-H/PPO blends.

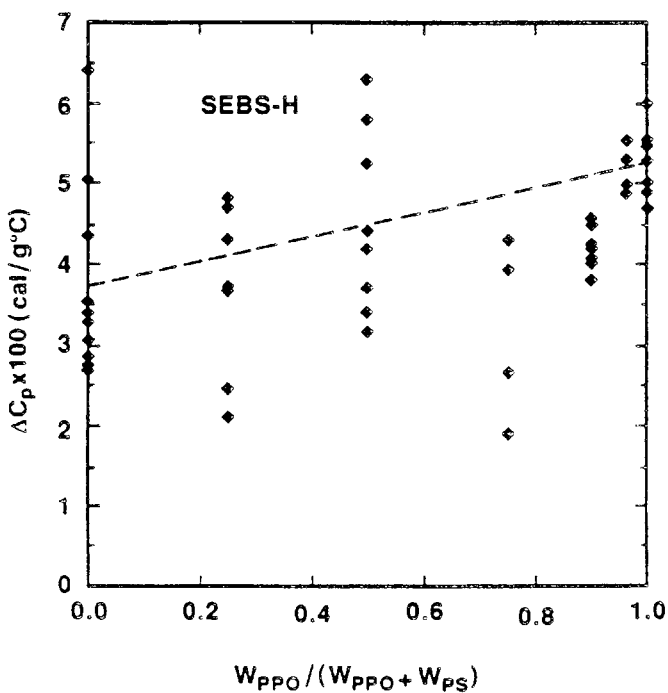


Fig. 7. Heat capacity change through the T_g for SEBS-H/PPO blends.

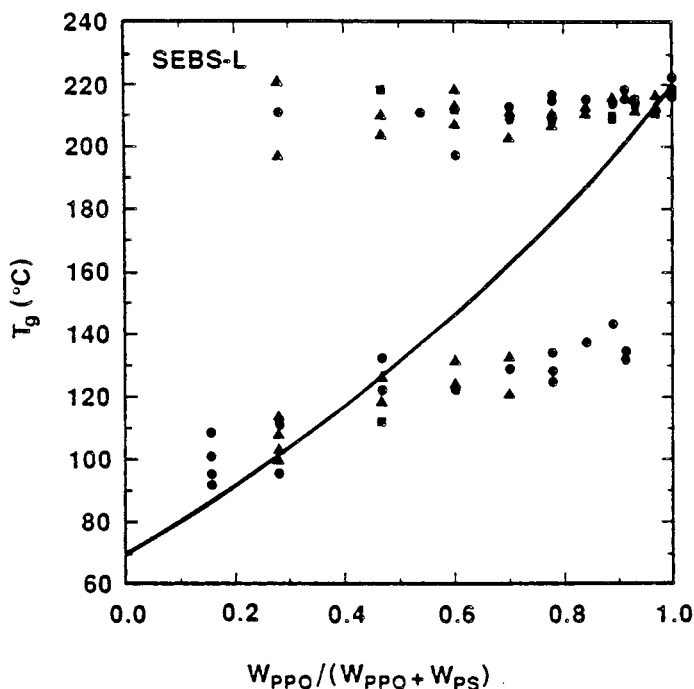


Fig. 8. Hard phase glass transition temperature for SEBS-L/PPO blends prepared by precipitation (Δ), melt mixing (\bullet), and solvent casting (\blacksquare); (DSC, $40^\circ\text{C}/\text{min}$). The solid line represents the Fox prediction for T_g .

SBS reflects more strongly the incorporation of mid-block into the interphase than does the value for SEBS-H. In effect, ΔC_p for both SBS and SEBS-H account for material in the interphase which is mixed with the PS, but the SBS, having a more diffuse interface accounts for a greater fraction of this material. Although there is a great deal of scatter in the data, it is clear that values for the blends fall below the tie line, congruent with previous results for SBS/PPO mixtures. The product $T_g \Delta C_p$ has been found to be essentially independent of polymer type for homopolymers, including PPO and PS, and also independent of composition for blends of PPO with homopolymer PS.³⁰ Clearly this is not the case for PS in block copolymers since the T_g and ΔC_p for these domains are both lower than for homopolystyrene, or for blends of PPO with either SBS or SEBS-H since both T_g and ΔC_p generally fall below the tie line.

Blends with SEBS-L

In contrast to the results described above, blends of PPO with SEBS-L exhibit two distinct glass transitions, as seen in Figure 8, for the nonrubbery portion of these mixtures. To establish that this behavior represents an equilibrium situation and is not the result of preparation technique, the three different methods described earlier (melt blending, solvent casting, and precipitation method) were used to make blends. The three techniques give essentially the same results as may be seen. We therefore conclude that this

PPO cannot completely mix with the PS phase of this copolymer but rather two separate hard phases form. Evidently, this is due to the rather low molecular weight of the PS end-blocks for SEBS-L relative to those of SBS or of SEBS-H (see Table I).

The higher T_g occurs at about the same temperature as the T_g for PPO, indicating that these blends contain an essentially pure PPO phase. The lower T_g evidently corresponds to a mixed phase rich in PS segments. As explained earlier, we expect the PS phase of pure SEBS-L to exhibit a T_g near 70°C although this transition cannot be observed directly by DSC. Upon adding PPO, a transition at a somewhat higher temperature becomes evident, and the location of this transition shifts to even higher temperatures as more PPO is added. For blends containing 50% or more PPO on a rubber-free basis, this transition is in the range of 120 to 140°C which is much higher than one could ever expect for pure PS domains regardless of size or segment molecular weight. Therefore, it seems quite clear that some PPO is incorporated into the PS domains of SEBS-L. At low PPO contents, we were only able to detect the lower T_g . The manner in which this lower T_g depends on composition in this region suggests that perhaps there is only one hard phase with all of the PPO incorporated in it. However, we regard this possibility as unproven at the present time. Failure to detect a PPO-rich phase in this region may be because the amount of this phase is below the limits of detection by DSC—recall that this composition scale excludes the rubber phase, so the absolute fraction of PPO in the sample is much less than shown here.

The breadth of the upper T_g at each blend composition is about the same or only slightly larger than that of pure PPO while the lower T_g s have breadths comparable to those found for blends of SBS and SEBS-H with PPO. These results are summarized in Figure 9 where, for simplicity, only averages of several data points are shown. As in other cases, these data contain considerable scatter; however, this seems to be independent of method of preparation. In general, these results support the notion that the upper T_g corresponds to a

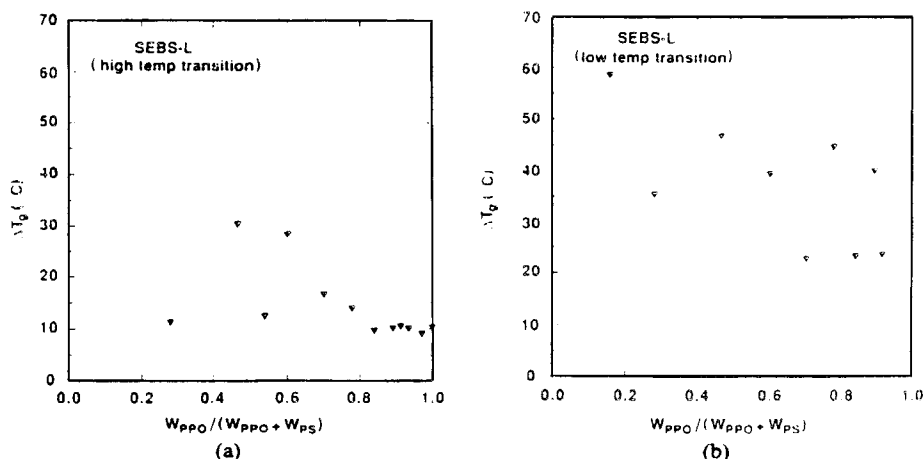


Fig. 9. (a) Breadth of glass transition for PPO-rich phase of SEBS-L/PPO blends (average values); (b) Breadth of glass transition for PS-rich phase of SEBS-L/PPO blends (average values).

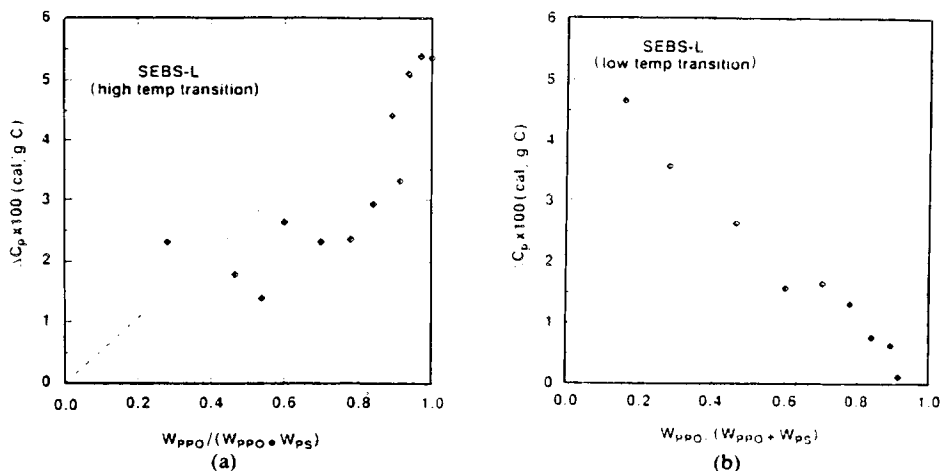


Fig. 10. (a) Heat capacity change through T_g of PPO-rich phase of SEBS-L/PPO blends (average values); (b) Heat capacity change through T_g of PS-rich phase of SEBS-L/PPO blends (average values).

phase consisting mostly of PPO while the lower T_g corresponds to a mixture of PPO and PS segments.

Figure 10 shows the change in heat capacity at each of the two hard phase glass transitions noted for these blends. For clarity, only average values from several thermograms are shown. The dashed line in Figure 10(a) is the expected result if all of the PPO formed a separate pure phase and none mixed with the polystyrene phase. The fact that the experimental points generally fall well below this expectation suggests that not all of the PPO is accounted for at the higher transition and, therefore, some PPO must be present in the PS-rich phase which gives rise to the lower temperature transition. Figure 10(b) shows that ΔC_p at the lower temperature transition appears to be proportional to the amount of PS present; however, a detailed analysis is not possible in this case since no value could be obtained for the PS portion of the neat SEBS-L material. In any case, the information available seems to support the notion that at least a small portion of the added PPO does mix with the PS end-blocks of SEBS-L.

Statistical Analysis of Data

As mentioned above, we observed significant scatter in the three quantities T_g , ΔT_g , and ΔC_p deduced from the DSC thermograms for these blends. Since the extent of this scatter is greater than normally encountered in similar studies for blends not involving block copolymers, further comments regarding the nature and origin of these variations in the data are in order. During the course of this work, several batches of most compositions were prepared, and for one system, SEBS-L, three different methods of preparation were used. For each batch, DSC runs were made for several different samples while multiple runs were made on each sample. While the number of replications of each type was not extensive enough to merit a complete statistical analysis, we were able to reach some general and useful conclusions. For each quantity determined, the mean values did not vary significantly from run to run, from

sample to sample, from batch to batch, or from method to method. The deviations about these means or standard deviations were severalfold larger from sample to sample, whether from the same batch or not, than from run to run on the same sample. Variations in ΔT_g and ΔCp are apparently larger than for the value of T_g as might be expected; however, there is no simple percentage basis for normalizing the latter as there is for the former such that a direct comparison can be made.

Before going further, it is important to remember that in the present work we are examining the transition behavior of only the hard phase for materials that contain significant amounts of rubber. At best, this proportionately reduces the magnitude of the thermal response observed per unit mass of sample. Additional problems relating to the potentially small size of phase domains and the diffuseness of the interfaces between them further diminish the sharpness and/or magnitude of these measured quantities as noted in the literature^{16,17} for simple block copolymers. All of these factors compromise the precision with which information can be extracted from thermograms. However, we feel that because of the complex, multiphase nature of these materials that some of the variability noted may arise for reasons beyond these obvious difficulties. It appears that there is some variability in the actual nature of the mixtures from point to point in a given batch (samples of a few milligrams as commonly used in thermal analysis) probably caused by differences in the local history of each sample. At this point, we are not prepared to speculate about the nature of the differences. If this were the case, measurements on much larger samples, for example, dynamic mechanical properties, might show consistently broad transitions but less variation from sample to sample. Annealing might remove some of the variability although preliminary experiments along these lines have not proved conclusive.

SUMMARY AND CONCLUSIONS

The results described above demonstrate that the PPO employed in this work mixes completely with the PS phases of the block copolymers SBS and SEBS-H to form a single hard phase regardless of the amount of PPO added. However, this does not occur for the copolymer SEBS-L having shorter PS end-blocks. In this case, two separate hard phases occur regardless of the method of blend preparation. One of these phases appears to contain only PPO while the other apparently contains some PPO mixed with PS segments. The mixed phases have rather broad glass transitions in all cases which may result from composition fluctuations within domains of the hard phase, from composition variation from domain to domain, or from very diffuse domain interfaces. Characteristics of the hard phase glass transition region vary considerably from sample to sample, but this variability does not compromise the main conclusions mentioned above.

From these observations, it is clear that there are molecular weight limitations on formation of a single hard phase from the PS segments of block copolymers and PPO even though homopolymers of PPO and PS mix uniformly regardless of their molecular weights. The reasons for this are qualitatively the same as those restricting solubilization of homopolymer PS into the domains of PS in block copolymers. Theories have been developed^{31,32} for

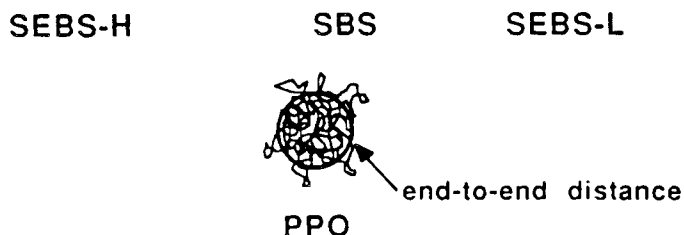


Fig. 11. Schematic diagram of predicted PS domain radii and size of PPO molecule. Circle within domains represents end-to-end distance of a PS molecule with the same MW as the end-block.

predicting the dispersed phase domain dimensions in block copolymers which agree well with experimental evidence. The predicted radii for the PS domains (assuming they are spherical) are 17.7 nm for SEBS-H; 12.5 nm for SBS; and 9 nm for SEBS-L. These domains are represented schematically to scale in Figure 11. The smaller concentric circles in each of the domain representations correspond to the approximate size of a randomly coiled PS molecule with the same molecular weight as the PS end-block of that molecule. A polystyrene molecule larger than this would be presumed immiscible with the corresponding PS domain. A comparison with the approximate size of a single, randomly coiled PPO molecule is also made in Figure 11. The circle shown corresponds to the rms end-to-end distance, 15 nm, of a PPO molecule (estimated from a group contribution method³³) having a molecular weight corresponding to the M_w for the PPO used. Since the PPO is polydisperse, this is only a typical size with a large fraction of the chains being smaller than this. The pure PS domains for SEBS-H and SBS are larger than this coil while those for SEBS-L are not, which qualitatively explains the results found. To place a PPO chain into the PS domain of SEBS-L requires a substantial compression of the PPO coil which lowers the entropy of the system. However, unlike incorporating a similar homopolymer of PS, there is some lowering of the system-free energy in the present case because of the exothermic mixing of PPO and PS segments. In the absence of a quantitative theory for this situation, no assessment can be made at this time of how this enthalpic contribution affects the size limits for solubilization compared to the homopolymer PS case where it does not exist.

The present work does not address the issue of morphology for these blends, that is the spatial arrangement of the hard and soft phases. At low PPO contents, it seems clear that the hard phase in SEBS-H and SBS blends would

be dispersed in a similar manner as in the neat copolymers. In fact, we found such blends to retain the elastomeric nature of the pure copolymers; although, we expect a higher modulus because of the larger fraction of hard phase and a higher softening temperature owing to the PPO contained therein. We also might expect the usual progression to hard phases having the shapes of rods and lamellae as more PPO is added. Finally, at the PPO-rich end of the scale, the hard phase should become continuous with a finely dispersed phase of rubber.

In addition to morphology, future work could profitably focus on a number of other issues such as mechanical behavior. The latter should include both large and small deformations with temperature as a variable. A more refined experimental definition of the size restrictions for forming a single hard phase is planned using other block copolymers with a wider range of PS block lengths (including diblocks) and a series of PPO polymers varying in molecular weight. The role of segmental interactions could be explored experimentally using polymers other than PPO which are miscible with PS. It would be ideal to employ monodisperse polymers for this purpose since, in principle, molecular size fractionation may occur when two hard phases are formed with a polydisperse homopolymer, for example, blends of PPO with SEBS-L.

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