Microphase Separation in Low Molecular Weight Styrene–Isoprene Diblock Copolymers Studied by DSC and ^{13}C NMR

B. Morèse-Séguéla, M. St-Jacques, J. M. Renaud, and J. Prud'homme*

Department of Chemistry, University of Montreal, Montreal, Quebec, Canada H3C 3V1.

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ABSTRACT: Differential scanning calorimetry (DSC) and ^{13}C NMR line width measurements have been carried out on a series of 1:1 styrene–isoprene diblock copolymers of low molecular weight in order to gain new information on the nature of the domain boundary in phase-separated block copolymers. The DSC data together with the NMR line width data contribute some additional evidence that there are strong dynamical interactions at the interface between the chains in the soft and the hard microphases. It is shown that these interactions are responsible for the abnormal decrease of the glass transition temperature, T_g, of the polystyrene microphase rather than a mixing of the two components at the domain boundary.

The study of the microphase separation in AB and ABA block copolymers, particularly those prepared from styrene and diene (isoprene or butadiene), has received much attention in recent years. A particular aspect that has been of interest is the nature of the domain boundaries. In fact, many of the theories of phase separation in block copolymers are based on the concept of a three-phase system consisting of regions of pure A, pure B, and an interdomain region of mixed A and B.[1–3] If such an interlayer of mixed A and B exists at the domain boundary, at constant composition, its volume fraction in the system should increase with decreasing molecular weight, owing to the greater dispersion. Specific investigations considering this problem have appeared in the literature.[4–6] Kraus and Rollmann[4] have reported a thermomechanical dynamic study of a series of SIS, SBS, and BSB block copolymers having the same composition but varying molecular weight. This study showed that the glass transition temperature, T_g, of the hard phase in the block copolymers decreased much more rapidly with decreasing molecular weight than predicted for homopolystyrene. On the other hand, it was observed that the T_g of the soft phase remained at about the same value, close to that of the homopolydienes. Similar behaviors have been observed by Kumler et al.[5] for various block copolymer systems, using the spin probe ESR technique. Both of these groups concluded that the abnormal shift of T_g of the hard phase toward low temperatures was due to an increasing amount of the mixed phase. But both studies failed to detect the presence of a third phase, even though the experimental methods used for these investigations were expected to discriminate the individual behavior of each phase present in the material.

Broad band proton pulsed NMR also has been applied by Wardell et al.[6] for studying the molecular motions in the microphases of SBS block copolymers. Spin–spin relaxation times, T_2, and spin–lattice relaxation times, T_1, were measured as a function of temperature for both the hard and soft phases. The T_2 data indicated restriction of motion in the soft microphase as compared with homopolybutadiene but no appreciable shift of T_g for this phase. On the other hand, the T_2 data measured for the hard microphase showed lower T_g as compared to homopolystyrene. As first suggested by Bianchi et al.,[7] who had reported a similar decrease of T_g for the hard phase in the same system, Wardell et al. interpreted this latter behavior as a consequence of premature molecular motions in the polystyrene microphase induced by the highly mobile chains in the polybutadiene microphase.

In view of these two different interpretations given in the literature for explaining the abnormal lowering of T_g for the hard phase in block copolymers, it is clear that further investigations are required for clarifying this problem. In the present study, a series of styrene–isoprene diblock copolymers of low molecular weight M_n in the range 2.7×10^3–1.3×10^4, and styrene weight fraction close to 0.50, were investigated, using both DSC and ^{13}C NMR techniques. It was shown by Toporowski and Roovers[8] that for sufficiently low molecular weight, SI and SIS copolymers can form a single phase. Therefore, the present low molecular weight material was studied in expectation of covering the range from microphase separation to miscibility and having a better insight on the mixed phase, if the latter does exist in the system. The DSC results showed the presence of two phases for all of the samples studied but very low T_g for the harder phase. The line widths of the ^{13}C resonances of some individual carbons in the polyisoprene units were measured at 333 K, a temperature where it was possible to observe high-resolution NMR spectra of the polyisoprene moiety. It is shown that the NMR data together with the DSC data contribute some additional evidences that there are strong dynamical interactions between the chains in the hard and the soft phases and that these interactions are responsible for the abnormal decrease of T_g of the polystyrene phase.

Experimental Section

Materials and Molecular Characterizations. The diblock copolymers, a series of five samples designated as SI-1 to SI-5, were prepared anionically at 298 K by a previously described procedure.[9] The initiator was *sec*-butyllithium, and the solvent was benzene. The number average molecular weights, M_n, were determined with a Perkin-Elmer Hitachi vapor-pressure osmometer, using benzene as solvent at 310 K. The instrument calibration was performed with benzil. The gel-permeation chromatography measurements were recorded using a Waters Associates Model 200 instrument with a series arrangement of four Waters Styragel columns with upper porosity designations of 10^6, 10^5, 10^4, and 10^3 Å. The mobile phase was reagent grade toluene at 310 K, and its flow rate was 1 mL min^{-1}. A 2-mL portion of solution, 2.5×10^{-3} g cm^{-3} concentration, was injected.

DSC Measurements. The calorimetric measurements were conducted in the heating mode with a Perkin-Elmer DSC-1-B differential scanning calorimeter. Sample sizes were in the range 17–26 mg. A helium atmosphere was provided by flushing the dried gas through the sample holder at a constant rate of 20 cm^3 min^{-1}. The low-temperature device filled with liquid nitrogen was used for all of the measurements, including those on the homopolystyrene samples. The temperature scale of the instrument was calibrated by measuring melting points of *n*-octane (216.3 K), benzene (278.7 K), and naphthalene (353.4 K), at a heating rate of 1.25 K min^{-1}. The heat capacity calibration was made according to the standard technique,[15] using alumina disks of known weights.

^{13}C NMR Measurements. The carbon-13 proton noise-decoupled spectra were measured in the bulk at 333 K and 22.6 MHz,

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Table I
Molecular Characteristics and DSC Results of the Material Samples Studied in the Present Work

sample	$10^{-3} M_n$	w_s	$T_{g,1}$, K	$\Delta c_{p,1}$, J K^{-1} g^{-1}	$T_{g,2}$, K	$\Delta c_{p,2}$, J K^{-1} g^{-1}
SI-1	12.6	0.50	214	0.38	338	0.25
SI-2	11.0	0.50	216	0.36	332	0.23
SI-3	8.5	0.50	219	0.38	304	0.17
SI-4	4.8	0.51	224	0.39	276	0.11
SI-5	2.7	0.51	227	0.61	250	0.10
PI	7.0	0	209	0.39		
PS-1	9.6	1.00			375	0.31
PS-2	3.1	1.00			360	0.31

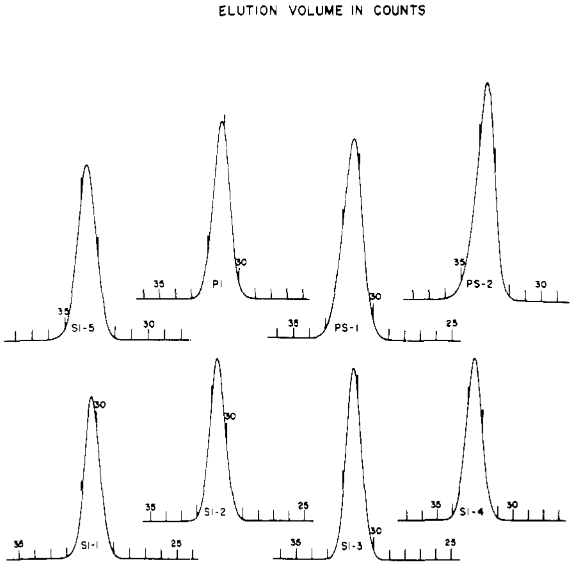

Figure 1. GPC elution curves of the styrene-isoprene diblock copolymers SI-1 to SI-5, the polyisoprene sample PI, and the Waters polystyrene standards PS-1 and PS-2. Sample PS-2 has a known polydispersity of M_w/M_n = 1.04.

using a Bruker WH-90 spectrometer. The samples were allowed to flow into 10-mm NMR tubes by gently heating the tubes at 333 K in a water bath. A 5-mm NMR tube containing a 1:1 mixture of D_2O and ethylene glycol was inserted concentrically in the 10-mm tube for external locking and reference. The instrumental conditions were as follows: pulse width, 4 μs (corresponding to a flip angle of 30°); spectral sweep width, 2300 Hz; acquisition time, 1.8 s; number of pulses, 1000.

Results and Discussion

The number average molecular weights, M_n, and the styrene weight fractions, w_s, of the block copolymers used for this study are listed in the second and third columns of Table I, respectively. Also described in Table I are a low molecular weight polyisoprene sample prepared anionically, using the same initiator-solvent system as that used for the diblock copolymers, and two low molecular weight polystyrene samples obtained from Waters Associates Co. The microstructure of the polyisoprene sample determined by ^{1}H NMR spectroscopy is 71% cis-1,4, 22% trans-1,4, 7% 3,4, and 0% 1,2. The same microstructure is expected for the polyisoprene blocks in the copolymers. As shown in Figure 1, the GPC curves of all of the diblock copolymers indicate unimodal molecular weight distributions and low polydispersities. This latter characteristic can be observed by comparing the GPC curves of the diblock copolymers with those of the polystyrene standards also shown in Figure 1.

DSC Study. Figure 2 shows the DSC curves measured on the diblock copolymers at a heating rate of 40 K min^{-1}. This relatively high heating rate was chosen in order to enhance the singularities of the curves. Also shown in Figure 2 are the DSC curves measured on the polyisoprene sample ($M_n = 7.0 \times 10^3$) and the polystyrene sample of the lowest molecular weight ($M_n = 3.1 \times 10^3$). All of the samples but the polyisoprene sample had been previously annealed for 15 min at 400 K, cooled to room temperature at a rate of 5 K min^{-1}, and stored for a month at this latter temperature. The DSC curves in Figure 2 were measured on the first heating runs. Immediately before the scanning runs, the samples were cooled to 173 K at a constant rate of 5 K min^{-1}.

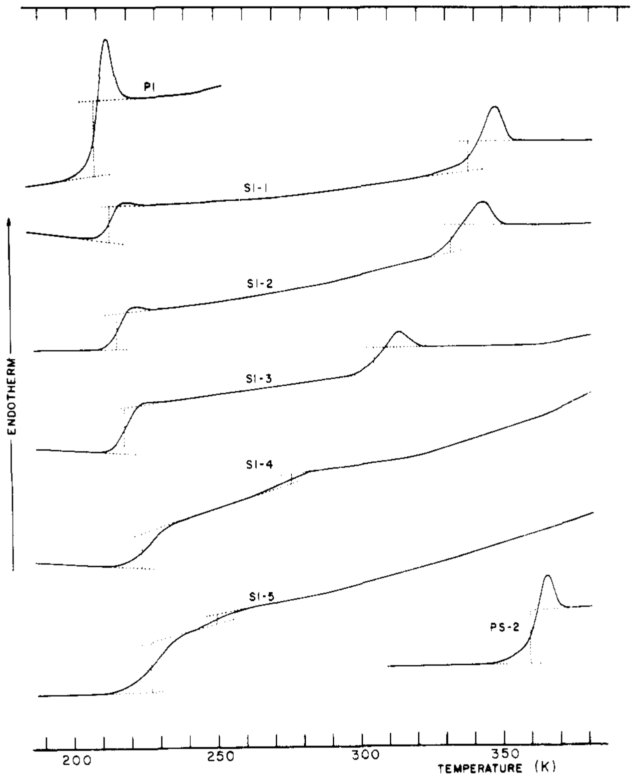

Figure 2. DSC curves of the polyisoprene sample PI (19.3 mg), the styrene-isoprene diblock copolymers SI-1 (19.6 mg), SI-2 (20.9 mg), SI-3 (26.3 mg), SI-4 (18.0 mg), and SI-5 (17.3 mg), and the polystyrene sample PS-2 (17.3 mg), measured at 40 K min^{-1} after cooling from room temperature at 5 K min^{-1}.

From Figure 2 one can see that all of the diblock copolymers exhibit two distince steps in their DSC curves, indicating microphase separation. The step occurring at the glass transition of the softer phase appears at a temperature slightly higher than that observed for the polyisoprene sample and moves slightly toward higher temperatures with decreasing molecular weight between samples SI-1 and SI-5. This behavior contrasts with the opposite trend normally observed for homopolymers and explained, in this case, by an increase of free volume associated with the chain ends. Another feature of the step occurring at the lowest T_g is the absence of a pronounced endothermic peak, as observed for the polyisoprene sample.

Inspection of the second step occurring in the DSC curves of the block copolymers in Figure 2 shows that the T_g of the harder phase decreases markedly with decreasing molecular weight. From comparison with the DSC curve of the polystyrene sample and data in the literature,[10] it is obvious that the free volume effect associated with the chain ends cannot account for the large shift of T_g observed between samples SI-1 and SI-5. From Figure 2 one can also see that the samples whose T_g of the harder phase is above room temperature show a substantial endothermic

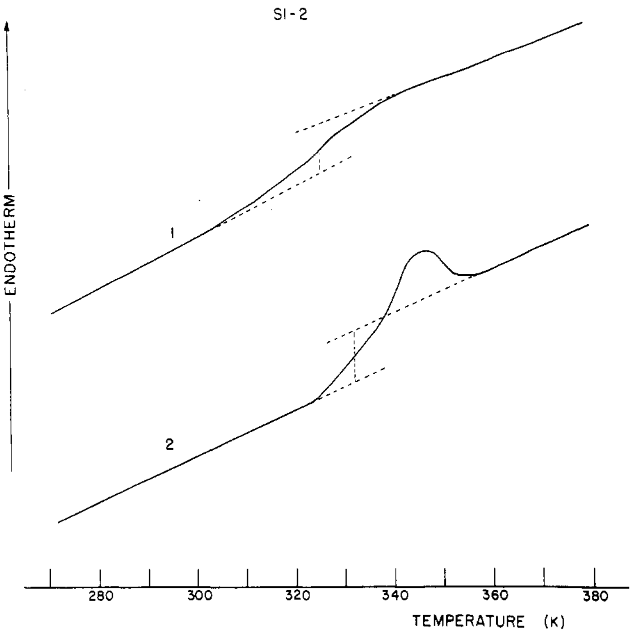

Figure 3. DSC curves measured on sample SI-2 at 40 K min^{-1} immediately after the first run of Figure 2 (curve 1) and 2 weeks later (curve 2).

peak at this transition. In contrast, the samples whose T_g of the harder phase is below room temperature do not show any endothermic peak. Also observed was the fact that once a given sample which shows an endothermic peak in Figure 2 had been heated to 400 K and cooled to 173 K (or room temperature) at a rate of 5 K min^{-1}, it did not exhibit an endothermic peak at the T_g of the harder phase in the consecutive heating run, but only a more diffuse sigmoid step which appeared at a somewhat lower temperature. This is illustrated in Figure 3 in which curves 1 and 2 are examples of DSC curves measured immediately after the first heating run of Figure 2 and 2 weeks later, respectively. It is, therefore, not surprising that the lowest molecular weight samples SI-4 and SI-5, whose two T_g's are below room temperature, showed only a diffuse step at their highest T_g in the DSC curves of Figure 2. Actually, for these two samples, the situation was exactly that which corresponds to the situation of curve 1 in Figure 3. Note that this phenomenon is a characteristic of the block copolymers only. It has not been observed for the low molecular weight polystyrene samples.

For homopolymers, the occurrence of an endothermic peak at the glass transition is a general characteristic of the DSC curves measured in the heating mode after slow cooling from temperatures above T_g.[11,12] Also observed for homopolymers is an increase of both the magnitude of the endothermic peak and its temperature when the samples have been annealed at a temperature below but close to T_g.[12-15] Both of these phenomena have been explained qualitatively by kinetic considerations based on the freezing-in model for the vitrification process.[11,12] According to this model, an amorphous polymer in the rubbery or the viscous state may be considered as a substance which reaches thermodynamic equilibrium readily at a given pressure and temperature. Thus, at temperatures above T_g, the extensive properties such as enthalpy or volume are well defined by the two variables P and T only. This is illustrated schematically by curve 1 in the isobar diagrams of Figure 4. These properties are intimately related to the molecular motions in the system. These include small-amplitude motions such as vibrations and rotations of the elementary groups of the polymer chains as well as cooperative large-amplitude motions of chain segments. Upon cooling through T_g, the large-ampitude segmental motions become so slow that the system is frozen in a state whose enthalpy and volume decrease with temperature at a slower rate than that predicted by the equilibrium curve. This is illustrated by curve 2 in Figure 4. The temperature range at which the freezing-in process is observed depends on the cooling rate. The slower the cooling rate the lower the temperature at which freezing-in is observed.

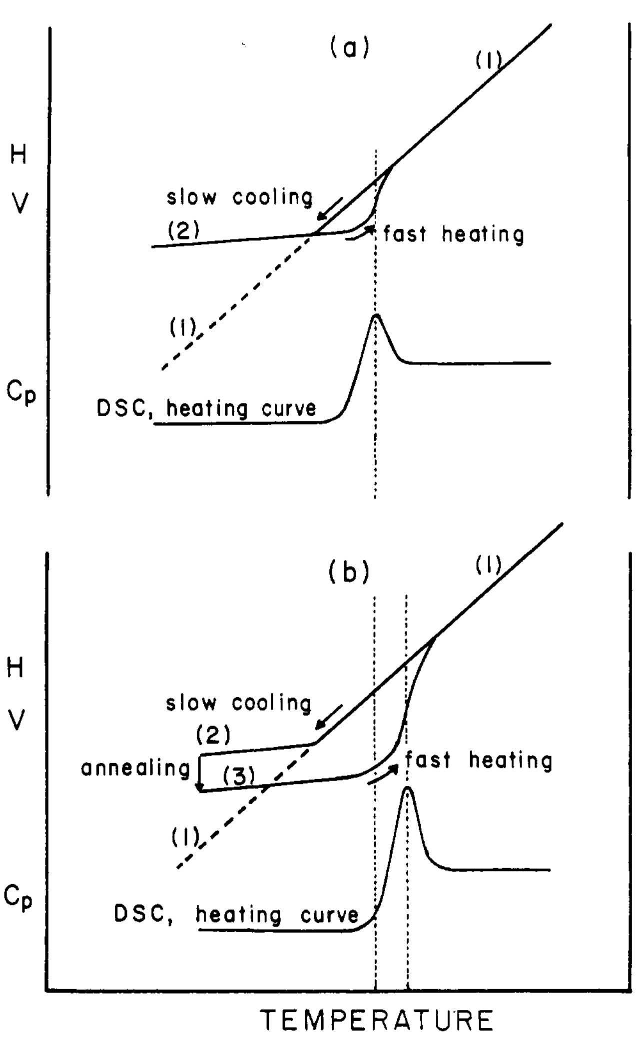

Figure 4. (a) Diagram illustrating the changes of enthalpy, H (or volume, V), and the corresponding heat capacity curve, c_p, on fast heating subsequent to a slow cooling. (b) Diagram illustrating the changes of the same quantities after annealing at a temperature below but close to T_g.

The abrupt change in c_p observed by DSC during the subsequent heating corresponds to the onset of segmental motions. As for the freezing-in process, the temperature range at which the release of these motions is observed in the heating mode depends on the time scale of the measurement. The faster the heating rate the higher the temperature at which a change in c_p is observed. When, as illustrated in Figure 4a, the heating rate is such that the return toward equilibrium in the rubbery or viscous state takes place at a temperature above that at which the system was frozen during the cooling process, the transition is accompanied by a step increase in the enthalpy curve of the system. This gives rise to the endothermic peak observed at T_g on the DSC curve.

The effect of annealing at a temperature below but close to T_g is illustrated in Figure 4b. The initial material which has greater enthalpy or volume than that predicted by the equilibrium curve slowly relaxes toward equilibrium. This process is the result of both slow molecular rearrangements and strong intersegmental forces within the material. It leads to a contracted system having more internal cohesion than the initial material. The enthalpy or volume temperature dependence of the partially relaxed glassy system is now given by curve 3 in Figure 4b. Upon subsequent heating, due to the greater cohesion within the annealed material, the onset of the large-amplitude segmental motions occurs at a higher temperature than that for the unannealed material. As illustrated in Figure 4b, coupled to this shift of T_g toward higher temperature is a higher enthalpy step increase at T_g. This results in a greater endothermic peak on the DSC curve.

The above considerations concerning homopolymers should also apply to block copolymer systems, but the thermal behavior of the latter should, in addition, depend on their microphase structure. The extensive properties of a given microphase might be influenced in some way by the presence of the other microphase, particularly because there are chemical links between the chains which belong to both phases. Curves 1 and 2 in Figure 3 suggest that vitrification of block copolymers by slow cooling, from a temperature above T_g of the harder phase, leads to glassy domains of the harder phase in which there is more freedom of movement than in the corresponding system annealed for several days at a temperature below but near the T_g of the harder phase. Comparison with the behavior of low molecular weight polystyrenes indicates that the rate of relaxation of the harder microphase in the glassy state is considerably slower than that one can observe in the absence of the rubbery microphase. Such a situation is not surprising since this relaxation process which involves a contraction of the harder microphase is hindered by the motion of the polyisoprene chains in the softer microphase. On the other hand, the absence of a substantial endothermic peak at the T_g of the softer microphase in the DSC curves of Figure 2 suggests a premature immobilization of the polyisoprene chains upon cooling at 5 K min^{-1} as compared with homopolyisoprene. This effect obviously arises from hindrance to motion due to the polystyrene glassy domains.

A better insight on both the microphase composition and the anticipated dynamic interactions between the unlike microphases can be obtained from a quantitative analysis of the DSC curves in Figure 2. From these curves, one can establish the variation of the T_g of each phase as a function of the block copolymer molecular weight. Also, one can estimate the heat capacity increase, Δc_p, associated with the glass transition of either phase. As will be shown below, comparison of the latter data with those of the corresponding homopolymers reveals some other interesting features of the system.

The heat capacity increase, Δc_p, associated with the glass transition of each phase in the block copolymers has been evaluated by measuring the difference in height between the extrapolated base lines recorded before and after the transition, at the temperature which corresponds to the half-height of the base line shift. This is illustrated by the broken lines in Figure 2. The same temperature has been arbitrarily chosen for characterizing the glass transition temperature, T_g, of each phase. The values of $T_{g,1}$ and $\Delta c_{p,1}$ associated with the soft phase, together with those of $T_{g,2}$ and $\Delta c_{p,2}$ associated with the hard phase, are listed in Table I. Also listed in Table I are the values of T_g and Δc_p similarly evaluated for the homopolymer samples. For the sake of comparison, the values of Δc_p evaluated for each phase in the block copolymers are quoted per gram of the respective block (polyisoprene or polystyrene) in the material.

From Table I, one can see that the values of $\Delta c_{p,1}$ associated with the glass transition of the softer phase in the block copolymers are close to 0.38 J K^{-1} g^{-1} for all of the samples but that of the lowest molecular weight (sample SI-5, $M_n = 2.7 \times 10^3$). This value is only 3% lower than that measured for the low molecular polyisoprene sample. If one assumes that the magnitude of $\Delta c_{p,1}$ is a measure of the weight fraction of the material involved in the softer phase, one can conclude that there is no significant miscibility of the two components in the present diblock copolymers of styrene and isoprene, at least for molecular weights as low as that of sample SI-4 ($M_n = 4.8 \times 10^3$). In fact, only the sample having the lowest molecular weight (sample SI-5, $M_n = 2.7 \times 10^3$) contrasts with this behavior and shows a substantially higher value of $\Delta c_{p,1}$. This may indicate extensive mixing of both components in the softer phase of this copolymer. But another explanation would be a superimposition of the Δc_p associated with the glass transitions of the two microphases present in the sample. Evidence for this latter explanation is the closeness of the two steps one can observe on the DSC curve of this sample.

Turning to the glass transition of the harder phase, the values of $\Delta c_{p,2}$ listed in Table I appear to be much lower than the value of 0.31 J K^{-1} g^{-1} measured for the polystyrene samples. They also show a substantial decrease with decreasing molecular weight. This suggests that only a fraction of the polystyrene component takes part in the glass transition observed at $T_{g,2}$. One plausible explanation for this behavior would be that the polystyrene chain segments located near the interphase boundary do not take part in the transition observed at $T_{g,2}$ but experience onset of large-amplitude motions over a wide range of temperature between $T_{g,1}$ and $T_{g,2}$. We suggest that the decrease of $\Delta c_{p,2}$ with decreasing molecular weight can be explained if it is assumed that a uniform state of segment density is achieved only for the polystyrene segments which are beyond a critical distance from the polyisoprene microdomains, and that a gradient of density occurs for the segments located between this critical distance and the microdomain interface.

For the present diblock copolymers, whose styrene weight fractions, w_s, are close to 0.50, a lamellar morphology of the microdomains is expected. For such lamellar systems, it has been observed that the thickness, t_s, of the polystyrene lamellae is close to 1.6 ± 0.15 times the unperturbed root-mean-square end-to-end distance, $\langle r_0^2\rangle^{1/2}$, of a homopolystyrene chain of the same molecular weight as the polystyrene block in the copolymer.[16] Since $\langle r_0^2\rangle = 0.67M^{1/2}$ Å for bulk homopolystyrene,[17] one can derive the following empirical relationship between t_s and the molecular weight, M_s, of the polystyrene block:

$$t_s = 1.1 \pm 0.1M_s^{1/2} \qquad (1)$$

Assuming that the weight fraction of the polystyrene chain segments located in the interfacial layer, and not taking part in the glass transition process observed at $T_{g,2}$, is given by the quantity $[1 - (\Delta c_{p,2}/\Delta c_{p,s})]$ where $\Delta c_{p,s}$ is the heat capacity increase at T_g for homopolystyrene, the thickness, t_s', of the interfacial layer in either side of the polystyrene lamella can be written as:

$$t_s' = (t_s/2)[1 - (\Delta c_{p,2}/\Delta c_{p,s})] \qquad (2)$$

The values of t_s and t_s' estimated from eq 1 and 2, respectively, are listed in Table II. Inspection of the data shows that the t_s' values range from 8 to 17 Å, with a definite trend to increase with decreasing M_s. This trend suggests values of t_s' lower than 8 Å for polystyrene blocks

Table II
Estimated Thickness, t_S, of the Total Polystyrene Lamella and Estimated Thickness, t_S', of the Polystyrene Interfacial Layer Not Taking Part in the Glass Transition Process Observed at $T_{g,2}$

sample	t_S, Å	t_S', Å
SI-1	87	8
SI-2	82	11
SI-3	72	16
SI-4	54	17
SI-5	41	14

having higher molecular weights than those of the present material. Interestingly, an estimate of the thickness of the global interfacial region from small-angle X-ray scattering data by Hashimoto et al.[18] suggested a value of 19 Å for an annealed styrene–isoprene diblock copolymer of lamellar morphology, having a styrene weight fraction w_s = 0.59 and $M_n = 1.05 \times 10^5$. The value of 19 Å estimated by Hashimoto et al. is about twice as much as that estimated for the thickness of the interfacial layer in the polystyrene microphase of sample SI-1, i.e., the highest molecular weight sample studied in the present work. Thus, like the X-ray scattering analysis, the present analysis based on DSC results suggests a relatively thin interlayer at the domain boundary. Note that Hashimoto et al. related this interlayer to a zone of partial mixing of the unlike chains, but their analysis which is based on a model allowing electron density variation across an interfacial diffuse boundary should also apply to a chemically sharp boundary surrounded by zones where a gradient of segment density occurs in each microphase.

Figure 5 shows the variation of both $T_{g,1}$ and $T_{g,2}$ as a function of the copolymer molecular weight, M_n. From this figure one can see that both T_g's exhibit a linear dependence on M_n. Furthermore, extrapolations of both T_g's to zero molecular weight give a nearly common intercept close to 230 K. This suggests that the dynamic interactions between the unlike chains increase with decreasing chain lengths up to a point where both types of chains show a common behavior dictated by a combination of their respective large-amplitude motions. That this means that phase separation persists at very low molecular weights ($M_n < 2 \times 10^3$) seems unreasonable. Conceivably, there must exist a molecular weight limit below which styrene–isoprene diblock copolymers of the present composition should become homogeneous. From the above results based on DSC measurements, it is clear that this limit is not attained for the present material, even though the lowest molecular weight sample studied here has a M_n as low as 2.7×10^3. Thus, the limiting behavior depicted in Figure 5 has no real significance. It just describes what would happen if phase separation could remain down to very small molecular weights.

^{13}C NMR Line Width Study. Recent ^{13}C NMR studies have shown that high-resolution spectra can be measured on bulk elastomers such as natural rubber,[19] synthetic *cis*- and *trans*-polyisoprene,[19,20] polyisobutylene,[21] and various random or alternating copolymers.[22] In these experiments, well-resolved spectra were obtained from normal free induction decays, using the conventional proton decoupling technique. An important feature of the ^{13}C NMR method is its ability to allow molecular motion probing through the relaxation parameters of different individual carbon atoms in the polymer chains.[20–23] For that reason, most of the works mentioned above have been oriented toward a better understanding of molecular motions of polymer chains in the bulk. Also studied was the effect of fillers such as carbon black[20] or that of crystalline regions[23] on the dynamical behavior of the amorphous moiety in *cis*-polyisoprene. In both of these latter studies, a significant increase in line widths was observed for the heterogeneous materials as compared with the corresponding unfilled completely amorphous polyisoprenes. Schaefer[20] has interpreted the ^{13}C NMR line widths of *cis*-polyisoprene, assuming that not all of the spatial orientations are readily accessible to the chain units as a result of restrictions imposed on the segmental motions, particularly by chain entanglements. Such restrictions would produce, in contrast with small organic molecules, rapid but incomplete motional narrowing of the line widths. The increase of line widths observed for filled or semicrystalline *cis*-polyisoprene was attributed to the additional source of entanglements produced by the filler or the crystallites.[20,23] For the carbon black filled polyisoprene, this interpretation was substantiated by the use of the magic-angle spinning technique, which produced substantial line narrowing of all of the resonances observed in the nonspinning measurements.[24]

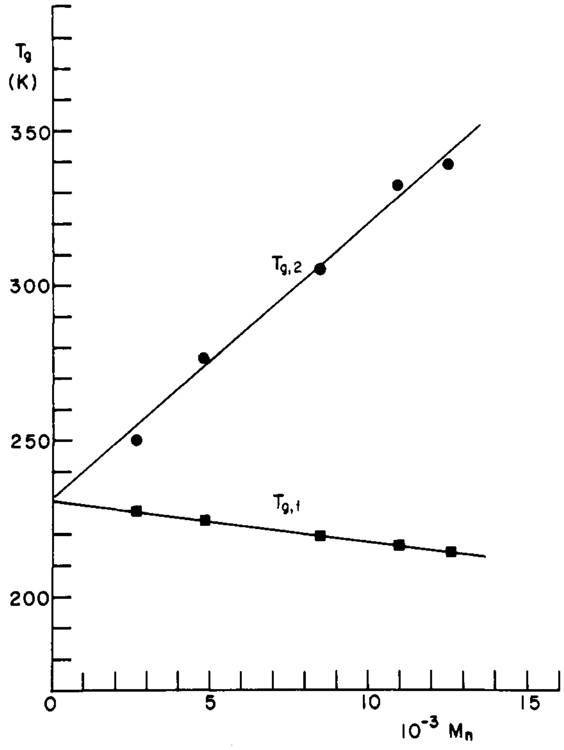

Figure 5. Observed glass transition temperatures, $T_{g,1}$ and $T_{g,2}$, of the soft and the hard phases, respectively, as a function of the molecular weight, M_n, of the block copolymers.

In view of these studies on *cis*-polyisoprene, it was tempting to perform a similar investigation on the present diblock copolymers of styrene and isoprene, particularly to gain some complementary information on the dynamics of the rubbery microphase in the material. As a preliminary investigation, ^{13}C NMR spectra were recorded at 333 K on the bulk for all of the block copolymer samples previously studied by DSC. At this temperature, all of the spectra showed well-resolved resonances for the carbon atoms of the polyisoprene chains, but no signal was observed for those of the polystyrene chains. The present study was confined to the spectral region ranging from 10–50 ppm downfield from tetramethylsilane (Me_4Si). In this region, the resonances of the sp^3 carbons only are observed.

An example of the high-resolution bulk spectra obtainable at 333 K is depicted in Figure 6. Spectra measured on the block copolymer sample SI-2 and the polyisoprene

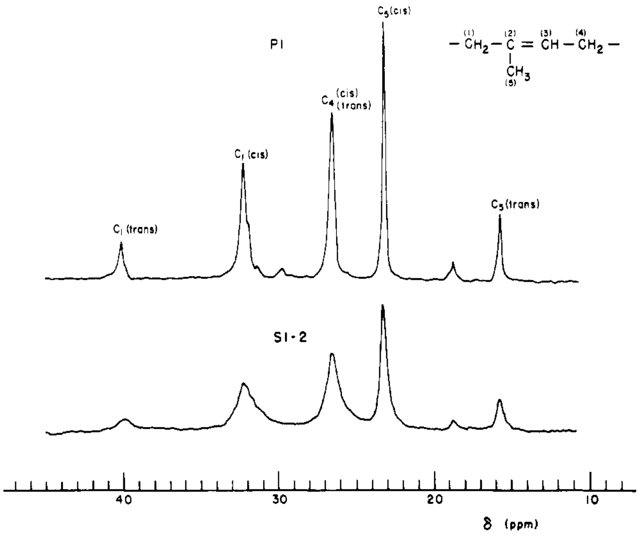

Figure 6. Proton noise-decoupled 22.6 MHz ^{13}C NMR spectra measured on the bulk, at 333 K, for the polyisoprene sample PI and the block copolymer sample SI-2. Chemical shifts are in ppm downfield from Me_4Si, with assignments made according to Duch and Grant.[19]

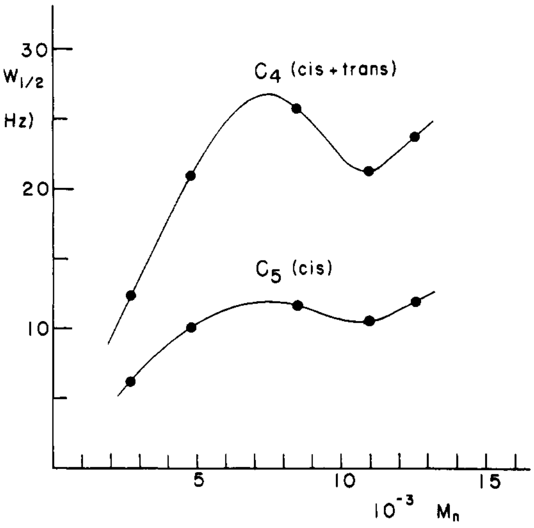

Figure 7. Observed line widths, $W_{1/2}$, of the methyl C_5 (cis) and the methylene C_4 (cis + trans) resonances plotted as a function of the molecular weight, M_n, of the block copolymers.

sample are shown in this figure. Also shown in Figure 6 are the line assignments made according to Duch and Grant.[19] The line widths at half-height, $W_{1/2}$, were measured directly from the plotted spectra. In each case, the measurements were repeated on two or three independent spectra. The accuracy was ±7%.

Figure 7 shows the observed line widths of both the methyl C_5 (cis) and methylene C_4 (cis + trans) resonances plotted as a function of molecular weight, M_n, of the block copolymers. The corresponding line widths measured on the polyisoprene spectra were 4.5 and 9 Hz for the methyl C_5 and the methylene C_4 resonances, respectively. From Figure 7, one can see that either series of data points can be described by a curve which first increases with molecular weight, passes through a maximum at $M_n \simeq 7 \times 10^3$, then decreases to a minimum at $M_n \simeq 11 \times 10^3$, and shows a further rise after passing through the minimum. At $M_n \simeq 7 \times 10^3$, the values of $W_{1/2}$ are greater than those of the polyisoprene sample by a factor of 3, approximately. The maxima and minima in the curves of Figure 7 suggest that the polyisoprene units located near the microdomain interface are more severely immobilized than those removed from the interface. At very low molecular weights, the thickness of the polyisoprene microdomains is so small that almost all of the polyisoprene carbon atoms experience an additional incomplete motional narrowing due to the junctions with the less mobile polystyrene phase. As molecular weights increase, the line widths increase owing to the greater rigidity of the polystyrene phase. However, parallel to this effect, an increasing amount of the polyisoprene units is removed from the interface. Since the carbon atoms of these units experience less partial motional narrowing than those near the interface, the combination of these two effects results in the maximum observed in the curves of Figure 7. The further rise observed at higher molecular weights results from both the greater rigidity of the polystyrene phase and the increasing amount of chain entanglements in the polyisoprene phase. Note that previous studies on bulk polyisobutylene[21] and molten poly(ethylene oxide)[25] indicated that ^{13}C line widths smoothly increased with molecular weight toward a limiting value attained at molecular weights of the same order of magnitude as those found in bulk viscosity curves for the critical molecular weight, M_c, for one chain entanglement per molecule. Obviously, this limiting behavior is not attained for the low molecular weight polysioprene chains of the present block copolymer series.

Conclusion

In summary, we have shown that the abnormal decrease of $T_{g,2}$ observed for the hard phase in styrene-isoprene block copolymers can be explained by assuming that the observed T_g reflects the onset of segmental motions in the region of the polystyrene microdomains where a nearly uniform state of segment density has been achieved. This region is located in the core of the microdomains and is separated from the interface by a second region where a gradient of segment density occurs. The response of the first region, only, is detected by DSC and presumably by the other techniques such as Rheovibron and spin probe ESR. The temperature at which $T_{g,2}$ is observed depends not only on the molecular weight of the polystyrene block, but to a greater extent on the mobility of the polyisoprene chains in the soft microphase. The segmental motions occurring in the polyisoprene microdomains are cooperatively transmitted to the chains in the polystyrene microdomains and thereby lower the freezing-in temperatue of the latter. It is suggested that, due to these dynamic interactions between the unlike phases, the polystyrene segments located near the interface undergo freezing-in at lower temperatures than those in the core of the microdomains. Their motion onset upon heating spreads over a large range of temperatures between $T_{g,2}$ and $T_{g,1}$ and for that reason cannot be detected by the current techniques used for detecting T_g. Similarly, it is suggested that the glassy polystyrene microdomains impart some restrictions to the segmental motions of the polyisoprene segments located near the interface. This description is consistent with the observation of a maximum in the ^{13}C NMR line widths plotted as a function of molecular weight.

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Fourier Transform Infrared Thermal Analysis of a Segmented Polyurethane

G. A. Senich and W. J. MacKnight*

Materials Research Laboratory, Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003. *Received August 13, 1979*

ABSTRACT: Fourier transform infrared spectroscopy (FTIR) has been used to study the extent of hydrogen bonding and its temperature dependence in a segmented polyurethane elastomer synthesized from 2,6-toluene diisocyanate, 1,4-butanediol, and poly(tetramethylene oxide) of 2060 number average molecular weight. It is found that the ratio of the molar extinction coefficient for the hydrogen bonded to the free amine stretching vibration is 4.6 and that this ratio is 1.05 for the hydrogen bonded to the free carbonyl stretching vibration. The temperature dependence of the concentration of hydrogen bonded groups is without any discontinuity at the hard segment glass transition temperature, and the enthalpy and entropy of hydrogen bond dissociation are 29 kJ mol^{-1} and 64 J mol^{-1} K^{-1}, respectively. An additional absorption band in the carbonyl stretching region at 1726 cm^{-1} is attributed to an oxidation product of the polyether segment formed during initial sample preparation and subsequent thermal treatment.

Segmented polyurethanes are generally composed of a polyether or polyester soft segment and a polyurethane hard segment. The composition of the latter varies, but it frequently involves the reaction product of an aromatic diisocyanate and an aliphatic diol. Such polyurethanes are capable of forming several kinds of hydrogen bonds. In all cases, the hydrogen atom of the N-H group in the urethane linkage is the donated proton, while the acceptor groups may include the carbonyl and adjacent oxygen atom in the urethane linkage as well as those of the ester linkage when a polyester soft segment is present or the ether oxygen when a polyether soft segment is present. Hydrogen bonding in polyurethanes has been the subject of numerous investigations using infrared spectroscopy. It is manifested by shifts in the N—H and C=O stretching frequencies to lower values than those observed when these groups are not hydrogen bonded.[1] The temperature dependence of hydrogen bonding is also amenable to examination by the infrared technique. In a previous study from these laboratories,[2] a series of model hard segment polyurethanes based on the reaction products of 2,4-toluene diisocyanate (TDI) or *p,p'*-diphenylmethane diisocyanate (MDI) with α,ω diols were examined. It was found that these polyurethanes are hydrogen bonded to the extent of 75% or less below their glass transition temperatures (T_g) and that the integrated absorbances of the N-H stretching vibration showed discontinuities at temperatures corresponding to the T_g or melting point (T_m) of the polymers.

The relationship between hydrogen bonding and thermal transitions in segmented polyurethanes is not clear. In a study of polyether–TDI segmented polyurethanes, Paik Sung and Schneider[3] concluded that the temperature dependence of hydrogen bonding is not correlated to T_g or T_m. They found that measurable dissociation of hydrogen bonded N—H and C=O groups began at about 65 °C for 2,6-TDI polyurethanes independent of hard segment content. In the case of 2,4-TDI polyurethanes, hydrogen bonded N-H began to dissociate between 40 and 60 °C, while hydrogen bonded C=O underwent little change to temperatures in excess of 150 °C.

Segmented polyurethanes are generally considered to exhibit microphase separation due to incompatibility between the hard segment and the soft segment. The degree of interurethane hydrogen bonding and the enthalpy of hydrogen bond dissociation have been used as indicators of phase separation in MDI polyurethane segmented elastomers.[4] In this study it was found that the extent of interurethane hydrogen bonding and the enthalpy of hydrogen bond dissociation increase as phase separation becomes pronounced.

Previous studies of the temperature variation of the hydrogen bonding equilibrium in segmented polyurethanes have required curve-resolving techniques for the separation of overlapping absorption bands, a method which entails the assumption of a Gaussian or Lorentzian shape for the contributing absorptions. Several symmetric absorption

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