structural groups of the pure components are the real driving force for miscibility, this conclusion may well be valid for a large class of systems.

Concluding Remarks

The main objective of this study was to investigate in some detail the effect of the intramolecular repulsion on the chain conformations for mixtures of polymers. A new aspect turned out to be the reorganization of the random copolymer into "micellelike" structures, a feature already observed experimentally. There are strong indications that the shape of the polymers is influenced as well. At present this is investigated in detail.[30]

Another interesting observation concerns the possibility that polymers that are immiscible in three dimensions become miscible in two dimensions. This is due to the fact that the number of segmental interactions that one chain has with all other chains is proportional to the number of segments, N, per chain in the first case, whereas in two dimensions this number is proportional to the square root of N, because in two dimensions segregation dominates at least as long as the interactions are slightly unfavorable, which is the relevant situation to consider. Monte Carlo simulations to study the influence of crossover from three dimensions to two dimensions on the miscibility and the conformations of polymers have been started.

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Thermal Characterization of Block Copolymer Interfaces

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ABSTRACT: A thermal technique to determine the volume fraction of interfacial material in microphase-separated block copolymers is described. By measurement of the enthalpy relaxation that results from annealing at a temperature between the glass transition temperatures of the blocks, the total content of interfacial material can be determined. The technique assumes that the interface can be modeled as a series of discrete fractions with glass transition temperatures (T_g's) between the T_g's of the blocks which contribute independently to the excess enthalpy observed in a differential scanning calorimetry experiment. Several examples involving block copolymers and block copolymers blended with homopolymers are given to illustrate the utility of the method, which also may be extended to study other microphase-separated systems, such as filled composites and semicrystalline polymers.

Introduction

Interfacial or "interphase" material plays an important role in the mechanical properties of microphase-separated block copolymer systems. This is true especially for weakly segregated systems where the interfacial volume fraction is high. Due to conformational constraints on the polymer chains, the thickness of interfacial regions in polymer systems is large compared to those in low molecular weight mixtures and is generally on the order of a few nanometers.[1] However, the regions become much thicker, on the order of tens of nanometers and approaching the size of the microdomains, as the interaction energy and micro-

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Table I
Description of Polymers and Blends

sample	description[a]	M_n,[b] kg/mol	M_w/M_n[b]
BB2[c]	1,4-PB/1,2-PB	26–31	1.03
BB7[c]	1,4-PB/1,2-PB	40–44	1.05
SIS-1	SIS	31–24–31	1.07
SIS-7	SIS	6–6–6	1.12
H7-1	SIS-1/PI (90/10 w/w)	85/3.28	1.07/1.08
H7-2	SIS-1/PI (80/20 w/w)	85/3.2,	1.07/1.08
H7-4	SIS-1/PI (90/10 w/w)	85/10.2	1.07/1.11
H7-5	SIS-1/PI (90/10 bw)	85/16.5	1.07/1.06
H7-8	SIS-1/PI (90/10 w/w)	85/305	1.07/1.05

[a] PB, polybutadiene block; S, styrene block; I, isoprene block; PI, polyisoprene. [b] Values obtained from supplier. [c] Samples obtained from F. S. Bates.

phase separation between the different monomeric species decrease.[1,2] The effect of these regions of mixed composition can be seen in dynamic mechanical measurements where the loss tangent of block copolymers may show additional features attributed to interfacial material.[3] Models similar to those used to describe multiphase polymer composites indicate that properties of these materials can be correlated with the interphase volume fraction.[4,5]

Many techniques have been used to determine the fraction of material contained in the mixed regions between microphases. Porod analysis of small-angle X-ray or neutron scattering data can be used to estimate the width of the interface.[6] However, experimental difficulties of the method and competing effects have been discussed fully by a number of authors,[6-8] and uncertainty in the value obtained by this analysis can be high. Dynamic mechanical[3,9] data can be modeled by assuming interfacial profiles, but this method requires large interface volume fractions. A technique that yields both interfacial width and profile is transmission electron microscopy, and results from highly ordered systems have been obtained that are in good agreement with small-angle X-ray and dynamic mechanical measurements.[10] However, preparation of appropriately ordered samples for which this technique may be used can be difficult.

Recently, several thermal techniques have been developed to estimate the volume fraction of interfacial material.[11-13] Two methods use the change in heat capacity due to the glass transition of each block relative to the corresponding values for the parent homopolymers to estimate the material in the microphases.[11,12] However, due to difficulties in accurately determining the heat capacities, particularly of the block with the higher T_g, there can be much uncertainty in this calculation. A technique developed in this laboratory, which does not need the external standards of the parent homopolymers, stems from enthalpy relaxation of the mixed composition material.[13] This paper describes the method in detail.

Experimental Section

Differential scanning calorimetry (DSC) experiments have been performed on the block copolymer systems described in Table I. Except as shown in the table, the polymer samples were obtained from Polysciences (Warrington, PA). All polymers were polymerized by anionic polymerization and had low polydispersities as measured by size exclusion chromatography. For the styrene–diene systems, films were prepared from both pure block copolymers and block copolymer/homopolymer blends by solvent casting from dichloromethane.

A Perkin-Elmer DSC-4 scanning calorimeter was used with a heating rate of 30 °C/min and a nominal cooling rate of 320 °C/min. For most of the work, a two-stage mechanical refrigerator was used to provide cooling, although liquid nitrogen cooling was utilized in some experiments. The base line was initially flattened and then corrected by Perkin-Elmers' SAZ technique.[14] DSC traces for most samples (approximately 10 mg) were obtained after heating them above the upper glass transition temperature, quenching to a temperature between the glass transition temperatures of the microphases, annealing in situ, and finally quenching to −70 °C. The data were transferred to an ISI microcomputer for analysis. The scans were compared against scans taken after quenching directly to −70 °C after heating above the upper glass transition temperature to erase the thermal history.

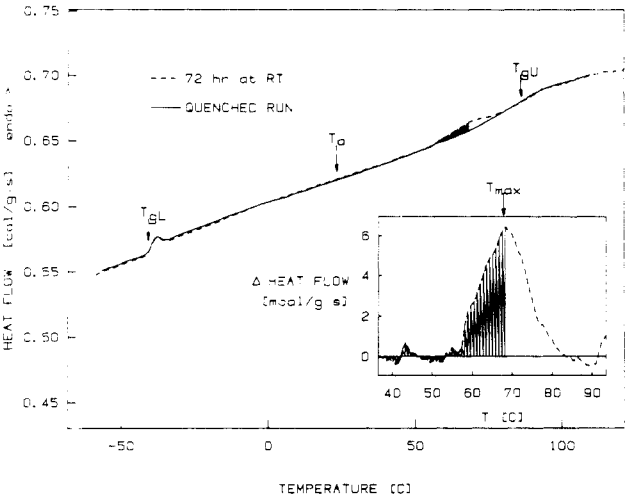

Figure 1. DSC trace of sample H7-8 annealed for 72 h at 23 °C. The inset indicates the difference between traces of the same sample after annealing (dashed line) and after quenching (solid line). The glass transition temperatures of the styrene- and isoprene-rich microphases are indicated by T_{gU} and T_{gL}, respectively. The annealing temperature, T_a, and the peak temperature, T_{max}, are also shown. The peak area used to determine the excess enthalpy due to physical aging is indicated by crosshatching in the inset.

Results and Discussion

Enthalpy relaxation, often referred to as physical aging, is the response of a glass annealed below its glass transition temperature, T_g.[15] As a melt is cooled through T_g, the relaxation times of the molecules become extremely long, and the material cannot respond to further decreases in temperature, even though the molecules are not packed into an equilibrium conformation. However, if the temperature is held constant at T_a, a temperature below T_g, rearrangement and densification can slowly occur, since the relaxation times are long but finite. As discussed previously,[13] this densification process can be exploited to probe the interfacial regions of microphase-separated materials since different portions of the sample will respond to different annealing conditions.

The method used to determine the degree of enthalpy relaxation for a block copolymer under a particular annealing condition is illustrated in Figure 1. The inset shows the difference between the endotherm formed by annealing at room temperature (23 °C) for 72 h and that from the quenched run. Taking the area of this difference up to the peak temperature, T_{max}, as shown, allows the calculation of the excess enthalpy, ΔH_e, recovered from the annealing process of the interfacial material. This in turn is related to the volume fraction of interfacial material, F, as discussed below.

The interfacial annealing technique is based on the premise that the composition and T_g of material within the interface vary between those of the microphases. We further assume that portions of the interface with different glass transition temperatures undergo enthalpy relaxation independently. In this work, the interface is modeled by a linear gradient of glass transition temperatures. Thus,

the portion of the interface, f_i, that has a T_g in the range of T_{gi} to $T_{gi} + dT_i$ is related to the total fraction of material contained in the interface, F, and the difference in the T_g's of the microphases, ΔT_g.

$$f_i = \frac{F}{T_{gU} - T_{gL}} dT_i = \frac{F}{\Delta T_g} dT_i \quad (1)$$

The total amount of enthalpy, ΔH_∞, that can be recovered by a sample that has relaxed from a quenched state to its equilibrium configuration at the annealing temperature, T_a, is assumed to be directly related to the difference between the glass transition temperature of the sample undergoing relaxation and T_a.

$$\Delta H_\infty = k_H(T_g - T_a) \quad (2)$$

The constant k_H can be determined experimentally[15,16] by measuring the enthalpy relaxation observed as a function of time and extrapolating to an asymptotic value for long times. It can also be related to the difference in heat capacities of the glassy and liquid states.

The amount of enthalpy recovered from a given fraction of interfacial material with T_{gi} is the product of eq 1 and 2 if the fraction has completely relaxed to its equilibrium state. By summation of the contributions of each portion of the interface that is fully relaxed, i.e., integration of the product of eq 1 and 2 with respect to temperature, an expression for the total excess enthalpy, ΔH_e, is obtained. In this integration, it is assumed that only material with $T_{gi} \leq T_{max}$ is fully relaxed. It must be pointed out that the endotherm peak observed in this experiment is not equivalent to the peak due to the enthalpy relaxation of a simple glass, since it is composed of the contributions of a number of fractions that are at different stages of relaxation. Thus it might be expected that changes in T_{max} do not correspond directly to the behavior observed in the physical aging of homopolymers.

Equation 3 can be obtained by rearranging the expression for ΔH_e to determine the total fraction of interfacial material:

$$F = \frac{2}{k_H} \frac{\Delta T_g}{(\Delta T)^2} \Delta H_e \quad (3)$$

$\Delta T = T_{max} - T_a$, and ΔH_e is the excess enthalpy determined as shown in Figure 1. This expression implicitly assumes that k_H is the same constant for all materials, i.e., that the same amount of enthalpy is ultimately recovered in relaxing to the equilibrium state after quenching to a given temperature below T_g, regardless of the composition of the material or the experimental conditions. In this work, we have used a value of 0.073 (cal/g)/°C for k_H, which was obtained for poly(vinyl acetate).[16] Similar values have been obtained for polystyrene[11,15] and other polymers,[11] and although there has been recent evidence that k_H depends on chemical structure (strongly enough to use differences in k_H to determine miscibility in blends where the components have similar T_g's[17]), we feel the error will be small in these calculations.

The endotherm shown in Figure 1 is not due simply to sub-T_g annealing of microphases with a high glass transition temperature, T_{gU}. Figure 2 shows the effect of annealing polystyrene homopolymer and a styrene–isoprene–styrene block copolymer under identical annealing conditions of 1 h at 30 °C. Within experimental error, no annealing is observed for the homopolymer. Under the same annealing conditions, however, a pronounced endotherm is observed for the block copolymer. Figure 2 shows it is decidedly not the polystyrene-rich microphases

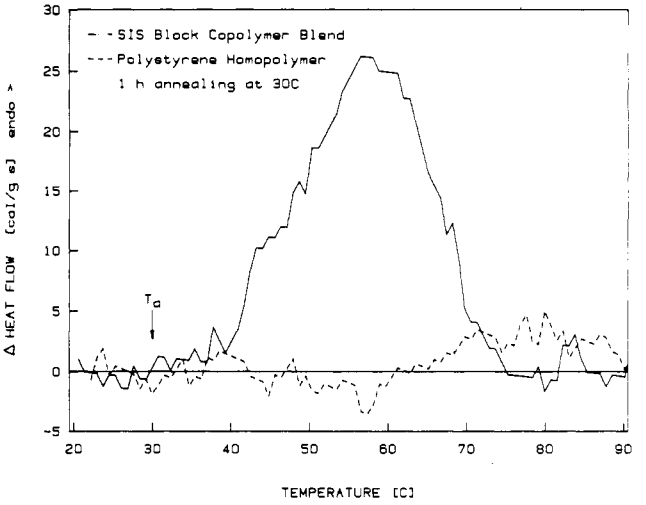

Figure 2. Comparison of annealing behavior of sample H7-2, a styrene–isoprene–styrene block copolymer (70% styrene) blended with 10% w/w polyisoprene homopolymer, and a polystyrene homopolymer (dotted line) after 1 h of annealing at 30 °C. The styrene glass transition temperature in each case is approximately 100 °C. The isoprene glass transition temperature for the blend is approximately −50 °C.

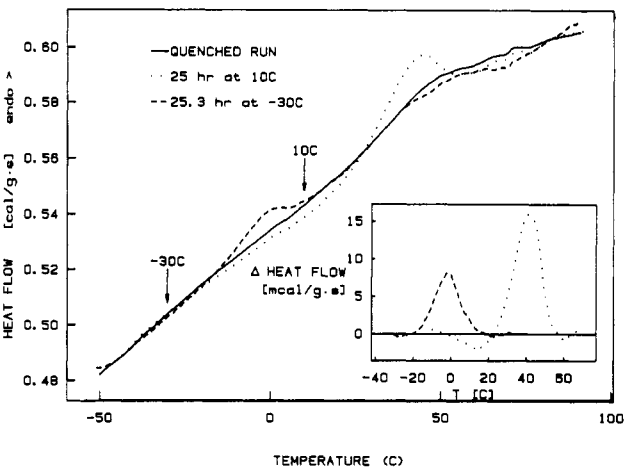

Figure 3. DSC trace of sample SIS-7 after annealing for 25 h at 10 °C (dotted line) and −30 °C (dashed line). Inset shows the difference between annealed and quenched runs.

Table II
Effect of Annealing Temperature[a]

T_a, °C	ΔH_e, cal/g	T_{max}, °C	F
−25	2.41×10^{-2}	−2.5	0.18
−25	2.45×10^{-2}	0.5	0.14
−25	2.73×10^{-2}	6	0.11
5	2.92×10^{-2}	32	0.15
30	5.95×10^{-2}	58	0.29

[a] Blend H7-2 after 1 h of annealing. $\Delta T_g = 90 - (-49) = 139$ °C.

that are responding to the annealing conditions. Since enthalpy relaxation cannot take place above T_g, where the sample is presumably in its equilibrium conformation, the effect is also not due to the polyisoprene-rich regions. Thus we must be observing the physical annealing of regions with intermediate values of T_g, such as the interface.

However, if the annealing temperature of the block copolymer systems is close to the glass transition of the higher temperature microphases, some of the material in these microphases also relaxes and the observed endotherms are anomalously large (Figures 3 and 4). When the temperatures are well below T_{gU}, the areas under the endotherms are approximately equal (Figure 4), supporting

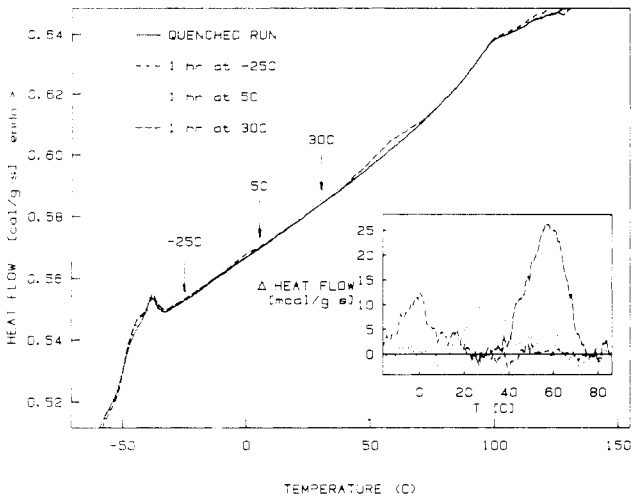

Figure 4. DSC traces of blend H7-2 showing the effect of annealing temperature after 1 h. Data obtained from this plot are summarized in Table II.

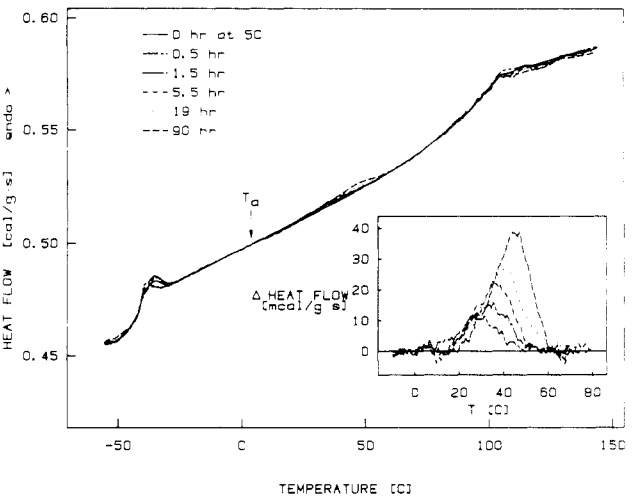

Figure 5. Effect of annealing time at 5 °C on blend H7-5. Data obtained from this plot are summarized in Table III.

Table III
Effect of Annealing Time[a]

time at 5 °C, h	ΔH_e, cal/g	T_{max}, °C	F
0.57	2.12×10^{-2}	32	0.11
1.75	3.92×10^{-2}	36	0.15
5.5	3.94×10^{-2}	36.5	0.15
15	5.04×10^{-2}	39.5	0.16
41.33	6.69×10^{-2}	43	0.17
90	7.67×10^{-2}	45	0.18

[a] Blend H7-5. $\Delta T_9 = 94 - (-42) = 136$ °C.

the assumption of a linear gradient of T_g's within the interface. Table II lists excess enthalpy, annealing parameters, and interfacial volume fraction for the blend in Figure 4 after 1 h of annealing at each annealing temperature. Since there can be some participation of material in the higher T_g microphases for relatively high annealing temperatures, $T_a \approx T_{gU} - 50$ °C, care must be taken in this analysis to avoid long annealing times. Enthalpy relaxation has been observed at $T_g - T_a \geq 50$ °C in homopolymers,[18] but the effect is extremely small for short annealing times. However, the advantage gained by minimizing the relaxation of the microphases is counterbalanced by the fact that short annealing times for samples with low values of F can lead to considerable scatter in the data as seen in Table II.

In all cases, the endotherms observed for the block copolymer systems are observed to grow and shift to higher temperatures with time (Figure 5). ΔH_e and F are listed in Table III as a function of annealing time at 5 °C. Figure 5 shows that the contribution of material that has not fully relaxed is small below T_{max}. The difference peaks shown in the inset essentially coincide at temperatures below T_{max}; i.e., further relaxation does not occur at these temperatures with further annealing. Thus, the excess enthalpy determined by $\Delta T = T_{max} - T_a$ is due only to fully relaxed material, and eq 2 may be used. From the results in Table III, the assumption appears fully justified, since essentially the same value for the interfacial volume fraction is obtained for all annealing times. The slight increasing trend may perhaps be accounted for by a more detailed analysis of the kinetics of the relaxation process.

Trends observed in Tables IV andV, on the other hand, are due to real differences in the interfacial content of the samples. To vary the degree of microphase separation in a block copolymer system at any given temperature, one can vary either the degree of polymerization or the composition of the block copolymer.[19] In Table IV, interfacial volume fractions for two different block copolymer systems where the degree of polymerization has been varied are summarized. Different annealing conditions are given. The reproducibility of the technique is indicated by a standard deviation of 15% for five analyses of sample BB7 using the same annealing conditions. Table V shows the effect of changing the composition of a block copolymer system by introducing a homopolymer diluent that has the same chemical structure as the midblock of the copolymer. In both cases, the effect is to drive the system closer to the microphase-separation transition to increase the fraction of interfacial material.

The importance of the annealing conditions is clear in Table IV, where it is seen that it may be inappropriate to use the same annealing temperatures for block copolymers with similar composition but different molecular weights. As described above, miscibility increases as the degree of polymerization decreases. Enhanced mixing in the microphases lowers T_{gU} (and raises T_{gL}) to increase the possibility of including some of the material in those microphases in the annealing study, leading to the complications displayed in Figures 3 and 4. Annealing temperatures must be carefully chosen for each molecular weight to ensure that only the interfacial material is sampled.

Table IV
Effect of Block Copolymer Molecular Weight

sample	M_w, kg/mol	% PS	annealing	F	T_{gL}, °C	T_{gU}, °C	T_{max}, °C
SIS-1	85	72	25 h, 10 °C	0.16	−33	95	46.5
SIS-7	18	69	25 h, 10 °C	0.54	−38	32	41
			25 h, −30 °C	0.30			−2
BB7	84		3.3 h, −45 °C	0.42	−91	−7	−25.5
			0.5 h, −80 °C	0.36			−64
BB2	57		3.3 h, −45 °C	0.67–0.89[a]	−88	−28, −8	−26

[a] Range is due to different definitions of T_{gU}.

Table V
Effect of Homopolymer Molecular Weight and Content

blend	HP M_w, kg/mol	F^a
SIS-1	0	0.13
H7-1	3.28	0.18
H7-4	10.2	0.15
H7-5	16.5	0.15
H7-8	305	0.11
blend	**HP content, % w/w**	**F^b**
SIS-1	0	.13
H7-1	10	.18
H7-2	20	.22

[a] Blends containing 10% by weight polyisoprene homopolymer; annealed at 5 °C for 5.5 h. [b] Blends containing 3.28 kg/mol polyisoprene homopolymer; annealed at 5 °C for 5.5 h.

From Table IV, it is clear that the volume fraction of interface increases as miscibility increases. If the values of F for the styrene–isoprene–styrene samples are considered, the magnitude of the change in F is in good agreement with estimates for this system using Helfand and Wasserman's approximations for interfacial thickness and domain spacing.[1,20] The model would predict values of 0.12 and 0.35 for SIS-1 and SIS-7, respectively, using the parameters given in the reference. This is in good agreement with the experimentally obtained values of 0.16 and 0.30, respectively. It should be noted, however, that the model used to estimate F only holds in the narrow interphase limit and really is not applicable to all of the block copolymers used in this work.

The values obtained for the 1,4-polybutadiene/1,2-polybutadiene diblock copolymers are also worth consideration. First, unlike our previous work[13] and most of the current work, these are not styrene–diene (or styrene–hydrogenated diene) systems, showing the widespread applicability of the technique. Also, the value obtained for sample BB7 is in reasonable agreement with the value of $F = 0.3$ estimated from heat capacity measurements.[21] The value obtained for sample BB2, while it has a large uncertainty because of the difficulty in determining the upper and lower T_g values, is much higher, as expected for a material near the microphase-separation transition.

F is seen to increase with miscibility in Table V, where the concentration of homopolymer diluent has been increased to decrease the degree of microphase separation. A low molecular weight homopolymer has been used to avoid exclusion of the homopolymer from the microphases. This phenomenon of macrophase separation may explain why, in the second part of Table V, the sample containing a high molecular weight homopolymer has an interfacial volume fraction less than that of the pure block copolymer. This result implies that sample H7-8 is at least as strongly segregated as the pure block copolymer, even in the presence of a homopolymer diluent.

Although the differences between the values in Table V are small, there is an indication that the content of interfacial material increases as the molecular weight of the diluent is decreased. This is in qualitative agreement with the literature where more homopolymer is dissolved within a styrene–hydrogenated diene block copolymer matrix as the molecular weight is decreased.[22]

The values obtained for F by this technique are consistent with the behavior expected for material contained in interfacial regions of block copolymer systems. There is good agreement, where available, with measurements made using other techniques and with theoretical estimates. However, the annealing conditions must be chosen such that only interfacial material responds to the annealing conditions. This can be done by comparing the results for different annealing times and temperatures. It is possible that the technique can be extended to microphase-separated systems other than block copolymers such as semicrystalline materials and filled composites, since the latter systems also exhibit a range of glass transition temperatures in the interfacial regions.[4,23,24] In fact, a thermal analytical method using heat capacities has been used to determine not only the amount of interfacial material but the thickness of the interface in metal-filled epoxy resins using appropriate standards.[4] Thus, the technique described here could be widely applicable.

Conclusions

We find that the volume fraction of interfacial material in microphase-separated systems can be determined by a thermal technique. An endotherm is observed in DSC experiments on block copolymers that have been annealed at temperatures well below the upper glass transition temperature, but above the lower T_g. It is not observed when the sample is quenched directly from a temperature above the upper glass transition temperature. The effect is due to enthalpy relaxation of material in the interfacial regions of the microphase-separated block copolymer rather than enthalpy relaxation of the microphases. The interface can be modeled as discrete fractions with T_g values between those of the blocks, and each fraction contributes independently to the excess enthalpy observed in the DSC experiment. The amount of excess enthalpy due to fractions that have relaxed to the equilibrium state can be related to the total content of interfacial material.

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Registry No. (S)(I) (block copolymer), 105729-79-1; PB, 9003-17-2; PI, 9003-31-0.

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