Phase Behavior in PS-*b*-PMMA Block Copolymer by Enthalpy Relaxation

C. Tsitsilianis* and G. Staikos

Department of Chemical Engineering, University of Patras, 26110 Patras, Greece

Received June 10, 1991; Revised Manuscript Received September 19, 1991

ABSTRACT: The enthalpy relaxation method for investigating miscibility in polymer blends in which the glass transition temperatures, T_g, of the components are similar has been applied to the investigation of phase behavior of polystyrene–poly(methyl methacrylate) block copolymer in the solid state. Two methods were used for the preparation of the samples: solution casting and precipitation. It is demonstrated that a partial phase mixing is evidenced which is strongly dependent on the choice of the solvent and/or the precipitant. On the contrary, the respective polymer blend shows complete immiscibility irrespective the solvent and/or the precipitant used. Furthermore, some new aspects concerning the enthalpy relaxation method and its applicability in partially mixed polymer systems, as is the case of block copolymers, are also discussed.

Introduction

One of the main topics of research in block copolymers deals with the phase behavior of these polymeric species in the solid state which finally determines their ultimate properties. The question to be answered is whether microdomain structure can be formed and how much is the amount of the mixed phase located at the domain boundary. In fact this is a problem of polymer–polymer miscibility which in the case of block copolymers is affected by the architecture of the macromolecule.

When the investigation of phase behavior is based upon the single glass transition temperature, T_g, criterion, differential scanning calorimetry, DSC, or dynamic mechanical analysis, DMA, are usually the suitable techniques for this purpose. These methods fail to give reliable results when the T_g regions of the pure components are overlapped.

Recently a new method has been developed to study the miscibility in polymer blends and the morphology of block copolymers using DSC combined with the physical aging phenomena which occur when a polymer is subjected to annealing at temperatures below their T_g.[1–5]

It is well established that polymer glasses undergo physical aging arising from their nonequilibrium thermodynamic state.[6–9] In a DSC thermogram this phenomenon is revealed by an endothermic peak at the T_g region which is related to the enthalpy relaxation of the material. The position and the magnitude of this peak are affected by a number of factors concerning the thermal history of the material (e.g., cooling rate, annealing temperature, etc.) as well as the structure characteristics of the polymeric glass itself.

The method dealing with the polymer miscibility investigation relies on the inspection of the position of the peak maximum, T_{max}, and the onset, T_{ons}, of the enthalpy relaxation peak of the blend with respect to those of the pure components. *In a phase-separated blend it is possible* to generate two endothermic peaks, the positions of which approach those of the pure components. On the other hand, in a miscible blend a single peak is generated at an intermediate position between those of the pure components.[1–3] However, the situation is more complicated as the appearance or not of the two peaks depends upon the enthalpy relaxation kinetics and the difference between the T_g's of the pure components.

In this paper another approach of the enthalpy relaxation method to the investigation of the phase behavior in block copolymers has been attempted. The copolymer studied is a polystyrene–poly(methyl methacrylate), PS-*b*-PMMA, diblock copolymer for which the classical DSC method cannot be applied as the T_g regions of the two homopolymers are overlapped.

The samples investigated were prepared following two methods: by solvent casting and by selective precipitation from different solvents. As has been reported, the choice of the solvent in both cases is important and affects the phase behavior of the copolymers.[10–14]

Another attempt to use the enthalpy relaxation method for the investigation of the phase behavior of PMMA-*b*-PS-*b*-PMMA triblock copolymer cast from different conditions has been reported recently.[15]

Simultaneously with the investigation of the copolymer a PS–PMMA blend of the same composition, the same molecular weights of the parent homopolymers, and the same sample preparation method has also been investigated. The aim of the above procedure was to compare the phase behavior between the blend and the respective block copolymer.

Experimental Part

The polymer samples used in this work have been synthesized via an anionic polymerization technique according to the classical procedure. Their polydispersity is lower than 1.15, as has been shown by gel permeation chromatography. The diblock copolymer PS-*b*-PMMA has a weight-average molecular weight obtained by light scattering equal to 83 000 and a PS content of 67% by weight. The PS sample is the precursor of the diblock copolymer, and the PMMA sample has a molecular weight equal to 29 000, which is about the same as the molecular weight of the PMMA block of the copolymer.

DSC measurements were performed using a Du Pont 910 calorimeter equipped with a 99 thermal analyzer. The samples amounted to about 15 mg, and the heating rate was 20 °C/min. Measurements have been made with PS and PMMA homopolymers, PS-*b*-PMMA copolymer, and a PS–PMMA blend with a component ratio equal to that of the copolymer (67/33).

Two series of samples were prepared in film form by solvent casting. Solutions (8%) from tetrahydrofuran (THF) and/or carbon tetrachloride (CCl_4) were evaporated in a Teflon container covered with glass to control the rate of evaporation at 20 °C. Four other series were derived by precipitation from THF and/or CCl_4 solution using as nonsolvents methanol (MeOH) or petroleum ether (PE). All the samples were dried under vacuum for 5 days at gradually increasing temperature up to 100 °C to ensure the best possible removal of the solvent.

Results and Discussion

A series of samples—PS and PMMA homopolymers, PS-*b*-PMMA block copolymer, and a PS–PMMA blend—

0024-9297/92/2225-0910$03.00/0

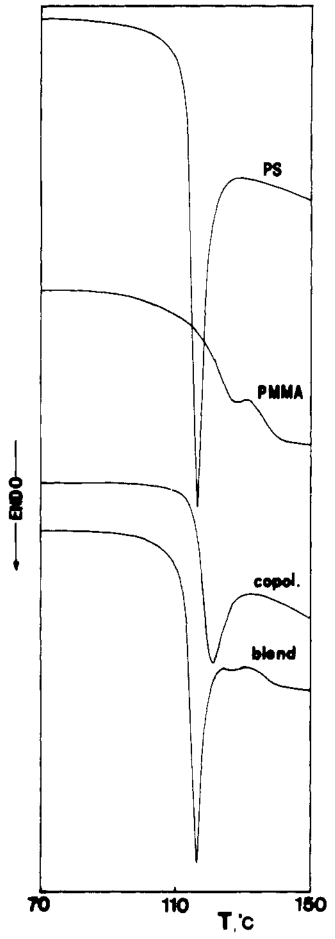

Figure 1. DSC thermograms of PS, PMMA, PS-*b*-PMMA copolymer, and PS–PMMA blend, precipitated from THF solutions with PE and annealed at 92 °C for 24 h.

derived by precipitation from THF solutions in excess PE were heated at 150 °C for 15 min to erase any thermal history. Next these were annealed for 24 h at 92 °C, which is a temperature lower than the T_g of both homopolymers, 106 and 126 °C for PS and PMMA, respectively. In Figure 1 DSC thermograms of the above-mentioned samples are illustrated. Obviously, the observed endothermic peaks correspond to the enthalpy relaxation of the glassy amorphous materials. At first sight it seems that the block copolymer exhibits one-phase morphology, as one single enthalpy relaxation peak can be observed. On the other hand, the corresponding blend exhibits phase separation as two enthalpy relaxation peaks are evidenced, the positions of which resemble those of the pure components. The magnitude of the PMMA peak is very weak as the annealing temperature T_a is 34 °C below the T_g of the homopolymer, and therefore the aged glass is far apart from the equilibrium. To overcome this problem that could obscure the conclusions concerning the phase behavior of the system, the following procedure has been undertaken.

Keeping the annealing time constant at 24 h, we have subjected all the samples to annealing at various temperatures approaching the T_g of PMMA.

At temperatures higher than 103 °C the single peak of the copolymer is eliminated while a new peak in the vicinity of the position of the peak of PMMA homopolymer is generated. These two peaks must be attributed to a PS-rich phase and a PMMA-rich phase, respectively.

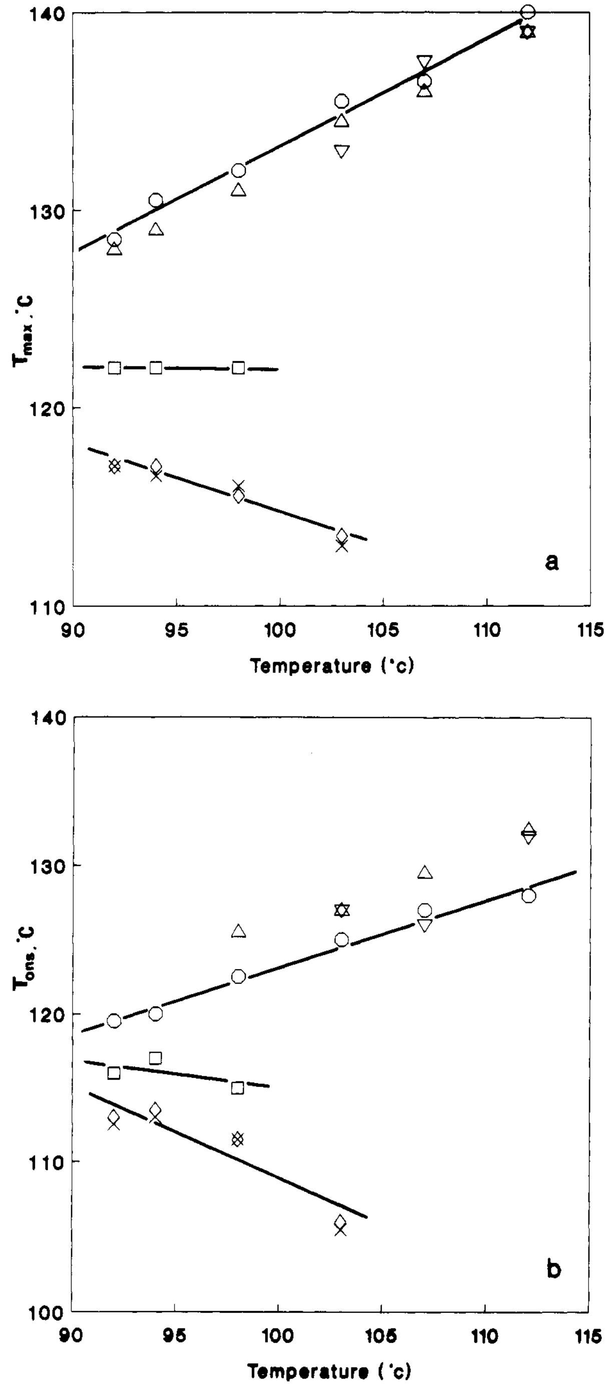

Figure 2. T_{max} (a) and T_{ons} (b) as a function of annealing temperature for the same as in Figure 1 samples annealed for 24 h: $\mathrm{PMMA_{hom}}$ (○), $\mathrm{PMMA_{bl}}$ (△), $\mathrm{PMMA_{cop}}$ (▽), $\mathrm{PS_{hom}}$ (◇), $\mathrm{PS_{bl}}$ (×), $\mathrm{PS_{cop}}$ (□).

In Figure 2 the T_{max} and the T_{ons} of the peaks for the copolymer, the blend, and the parent homopolymers are presented as a function of annealing temperature T_a. It is known that the T_{max} increases approximately linearly with T_a provided that the aged glass is not too close to equilibrium.[8] This is the case for the PMMA homopolymers, as is shown in Figure 2a. A peculiar behavior is evidenced in the case of the PS homopolymer. The T_{max} decreases with T_a as the aged glass approaches the equilibrium. This result has been reproduced in all the systems investigated in this work. It seems that the T_{max} should pass through maxima as a function of T_a. Such a behavior needs further investigation, as to our knowledge it has not been observed so far. It follows that the distance between the peaks of the two homopolymers is enhanced by increasing T_a. Consequently, the procedure of annealing at different temperatures approaching T_g may be proven useful in order to select the optimum annealing temper-

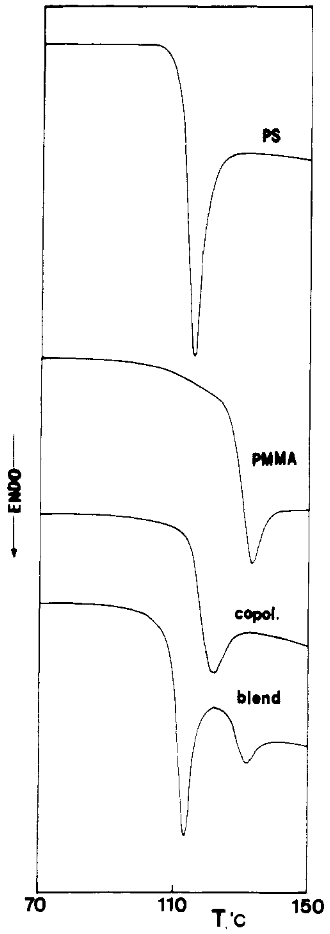

Figure 3. DSC thermograms of the same as in Figure 1 samples annealed at 98 °C for 320 h.

ature when enthalpy relaxation experiments are performed as a function of annealing time. The polymer blend appears to be completely immiscible, as two distinct peaks are evidenced, the positions of which lie almost exactly on the positions of the peaks corresponding to the pure components. In both plots of Figure 2, T_{max} and T_{ons} vs T_a, the points concerning the different components of the blend fit approximately the lines corresponding to the respective homopolymers. The image for the copolymer differs remarkably from that of the blend. The T_{max} and the T_{ons} of the first peak lie at intermediate positions between the respective peaks of the two homopolymers. The T_{max} and the T_{ons} of the second peak which is revealed only at high T_a lie on the line corresponding to the PMMA homopolymer. These results suggest that the system mainly consists of two phases. One PS-rich phase into which PMMA has been dissolved and a pure PMMA phase.

Another experiment using the annealing time, t_a, as a variable at T_a equal to 98 °C has been carried out. This annealing temperature has been chosen after the results presented in Figure 2, for two reasons. First, at this temperature the two peaks are most separated, and, second, it is closer to the T_g of PMMA.

In Figures 3 and 4 DSC thermograms of samples annealed at 98 °C for 320 h and the T_{max} and the T_{ons} of the peaks as a function of the logarithm of t_a are depicted. From these results it is clearly demonstrated that the blend provides two distinct peaks which are located at the same positions as those of the pure components. On the contrary, the copolymer shows only one enthalpy relaxation peak lying between the peaks of the respective homopolymers though the annealing time has been adequately prolonged (320 h). The absence of a second peak related to the PMMA-rich phase together with the strong shift of the peak related to the PS-rich phase toward intermediate temperatures suggest that a large amount of the PMMA has been dissolved into the PS phase and the remaining pure quantity is not detectable using the above annealing conditions. In the following the estimation of the amount of PMMA which has been dissolved in the PS-rich phase is attempted.

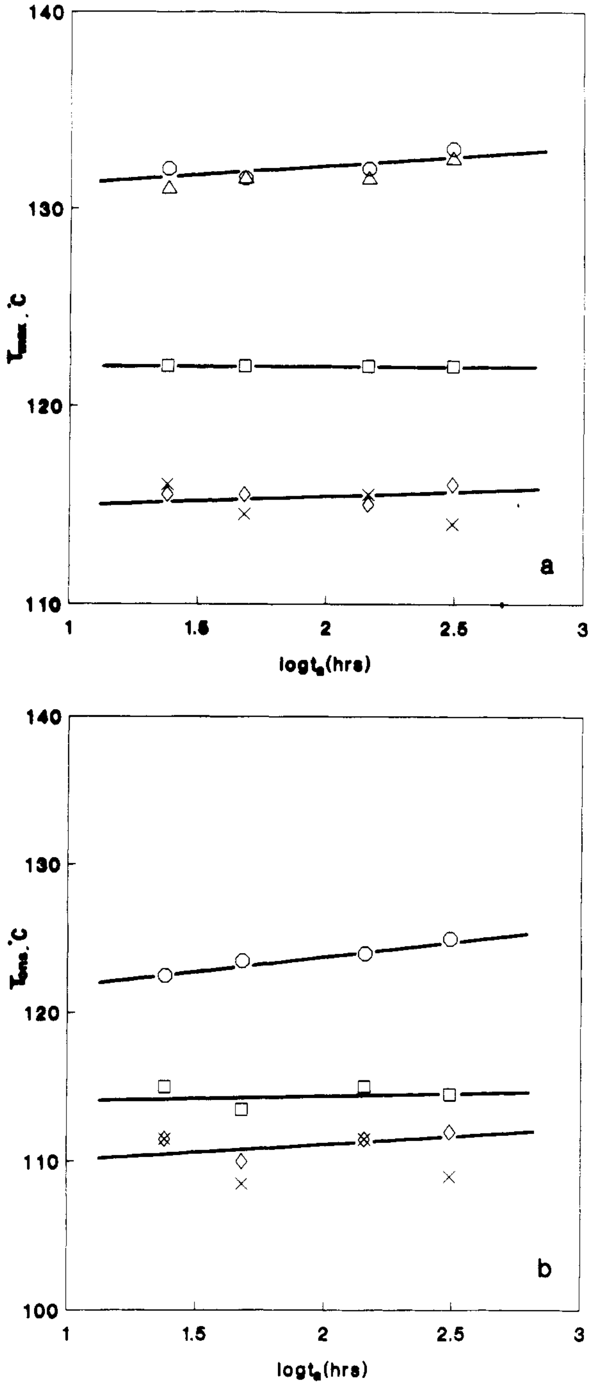

Figure 4. T_{max} (a) and T_{ons} (b) as a function of the logarithm of annealed time, log t_a, for the same as in Figure 1 samples annealed at 98 °C. Symbols as in Figure 2.

Figure 5 shows the T_{max} and the T_{ons} for the same polymer samples as a function of T_a. In this case the samples have been produced by solvent casting in THF at room temperature. The annealing time was again 24 h. As shown, the phase behavior of the blend remains the same as in the previous case, i.e., T_{max} and T_{ons} of the two

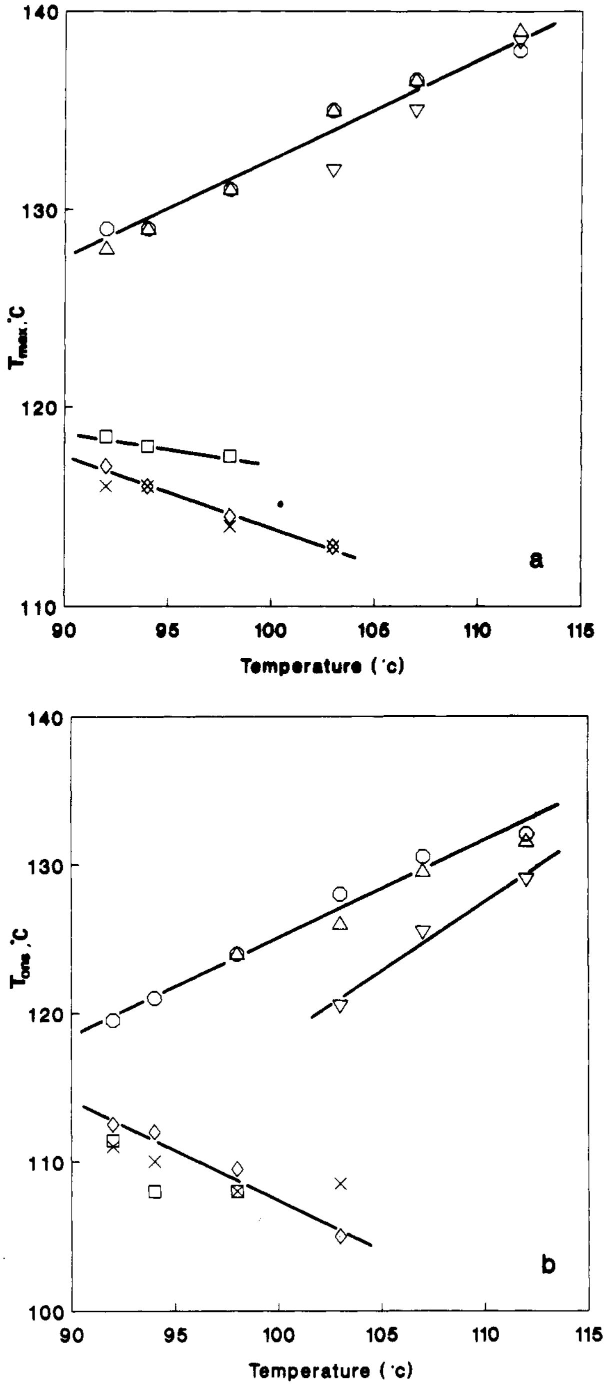

Figure 5. T_{max} (a) and T_{ons} (b) as a function of annealing temperature for PS, PMMA, PS-b-PMMA copolymer, and PS–PMMA blend, cast from THF. Annealing time was 24 h. Symbols as in Figure 2.

peaks appear at the same positions as those of the respective homopolymers (solid lines).

The phase behavior of the copolymer is remarkably different compared to that presented by the samples produced by precipitation (see Figure 2). The shift of T_{max} of the PS-rich phase with respect to that of the homopolymer is now less pronounced (Figure 5a) while the T_{ons} remains unchanged (Figure 5b). On the other hand, the T_{ons} of the peaks for the PMMA-rich phase have been shifted toward lower temperatures (Figure 5b). The above results suggest that in the copolymer sample taken by precipitation there is a pronounced miscibility between the two phases as both T_{max} and T_{ons} have been shifted toward intermediate positions while a small pure PMMA phase is still present.

A different morphology is evidenced in the case of the samples produced by solvent casting. The slight shift of the T_{max} of PS together with the fact that the T_{ons} remains the same with respect to that of the homopolymers demonstrates a lesser miscibility. Moreover, the lowering of the T_{ons} of the PMMA, which suggests a broadening of the PMMA T_g region, must be attributed to a contamination of the pure PMMA phase by a small amount of PS. In other words, the shift of the T_{max} toward intermediate positions must be considered as a stronger evidence of miscibility effects than that of T_{ons}.

In order to detect the solvent effect on the phase morphology of the cast film, we have prepared a series of films cast in CCl_4, which is a selective solvent of the two homopolymers (poor solvent of PMMA and good solvent of PS). The obtained results showed a behavior similar to that presented in Figure 5. However, the shift of T_{max} for the PS-rich phase in the copolymer is now slightly more pronounced for the samples cast in CCl_4 than those in THF. This unexpected difference could be attributed to the different rate of solvent evaporation and not to the quality of the solvent. As is known, a common good solvent favors miscibility.[16,17] On the contrary, the quality of the solvent has a more pronounced effect on the morphology of the copolymer when the samples are prepared by precipitation.[14] However, the choice of the precipitant is critical, as will be demonstrated in the following.

Parts a and b of Figure 6 show T_{max} as a function of T_a (for t_a = 24 h) and of log t_a (at T_a = 98 °C) correspondingly for the polymer samples precipitated from THF and CCl_4 using MeOH and/or PE as nonsolvent. As shown, T_{max} of the PMMA-rich phase of the copolymer coincide with those of the respective homopolymer whereas T_{max} of the PS-rich phase are higher than those of the respective homopolymer. Considering that the shift of T_{max} of the PS-rich phase toward intermediate positions implies miscibility, the following remarks could be drawn.

In the case where PE is used as a precipitant, miscibility is favored when the samples are precipitated from THF compared with the samples precipitated from CCl_4. THF as a common good solvent favors the contacts between the two kinds of segments of the copolymer, implying better miscibility,[16,17] whereas CCl_4 as a selective solvent favors segregation. However, this miscibility improvement does not occur when the precipitant is MeOH. Then T_{max} of the PS-rich phase corresponding to the two solvents coincide.

The different behavior of the samples precipitated from THF must be attributed to the selectivity of the precipitants.[14] The selectivity of MeOH for precipitating PS is larger than that for precipitating PMMA, due also to hydrogen-bonding interactions, whereas the selectivity of PE is approximately the same for both blocks. Consequently, by precipitating in a nonselective precipitant, the miscibility or the segregation of the two blocks in the solution is maintained in the solid state, whereas by precipitating in a selective precipitant, any miscibility of the two blocks in the solution is raised in the solid state.

In order to avoid thermal history effects, we have heated all the samples at 150 °C for 15 min. This time is sufficient to allow local rearrangements and to destroy the differences between the different produced samples. Since the differences in behavior still exist after this thermal treatment, it has to be concluded that long-distance effects relative to the mutual interaction between blocks of different nature are involved.

The results concerning the blend show that miscibility effects are not evidenced: the samples are taken from

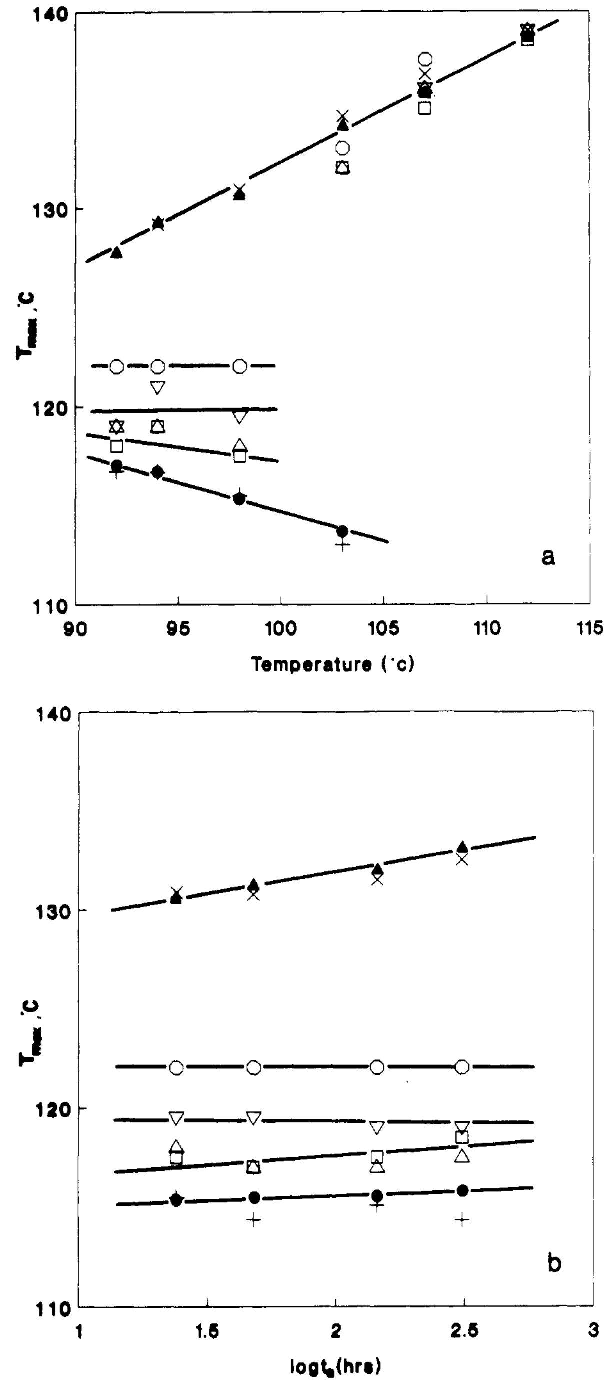

Figure 6. T_{max} as a function of annealing temperature (a) (t_a = 24 h) and as a function of the logarithm of the annealing time, log t_a (b) (T_a = 98 °C) for PS_{hom} (●), $PMMA_{hom}$ (▲), PS_{bl} (+), and $PMMA_{bl}$ (×), precipitated from THF and or CCl_4 in MeOH and or PE (average values) and PS-*b*-PMMA precipitated from THF–MeOH (□), THF–PE (○), CCl_4–MeOH (△), and CCl_4–PE (▽).

either solvent casting or precipitation irrespective of the quality of the solvent and/or the precipitant, contrary to observations taken in other systems.[18-20] This behavior reflects the incompatibility between PS and PMMA, which is partially counterbalanced in the case of the PS-*b*-PMMA copolymer where two chains are covalently joined together.

Our DSC results (Figure 6) show that T_{max} of the PMMA-rich phase in the block copolymer, as well as in the blend, fit the line corresponding to the T_{max} of the PMMA homopolymer. This implies that the PMMA-rich phase in the block copolymer and/or the blend is roughly a pure PMMA phase. This behavior induced us to use the enthalpy relaxation, ΔH, of PMMA in order to estimate the degree of phase mixing (DPM), in a manner analogous to that in which the heat capacity change in the T_g region, Δc_p, has been used.[21,22] It is obvious that the enthalpy loss of the pure component in the blend or the copolymer is related to the amount of the material which has been located at the interface.

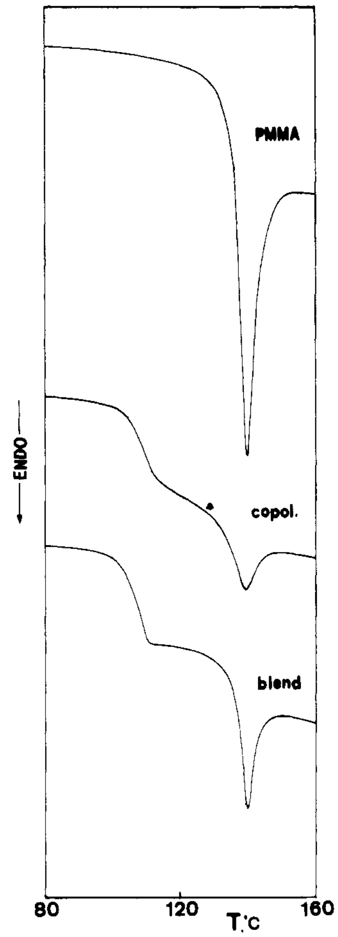

Figure 7. DSC thermograms of PMMA, PS-*b*-PMMA copolymer, and PS–PMMA blend annealed at 112 °C for 240 h.

Table I
T_{max} and T_{ons} of the PMMA-Rich Phase in Copolymer, Blend, and PMMA Homopolymer Annealed at 112 °C for 240 h

	T_{max}, °C			T_{ons}, °C		
preparation method	co-polym	blend	PMMA homo-polym	co-polym	blend	PMMA homo-polym
THF[a]	140	140	140	133	135.5	135
CCl_4[a]	139	141	141	130	136.5	136.5
THF-PE[b]	142	140	141.5	133	134	136.5
CCl_4-PE[b]	140	140.5	141	131	135	135.5
THF-MeOH[b]	139.5	140	141	130	135	136
CCl_4-MeOH[b]	140	139.5	142	131	134.5	136

[a] Solvent casting. [b] Precipitation.

In order to enhance the magnitude of the enthalpy relaxation peaks and therefore the sensitivity of the method, the samples were annealed at 112 °C for 240 h, where equilibrium conditions have been considerably approached. Figure 7 shows the DSC thermograms of the PMMA homopolymer, the blend, and the copolymer where the enthalpy relaxation peaks of the PMMA phase are exhibited.

Table I contains the T_{max} and the T_{ons} of the PMMA phase in all systems investigated. It is observed that the

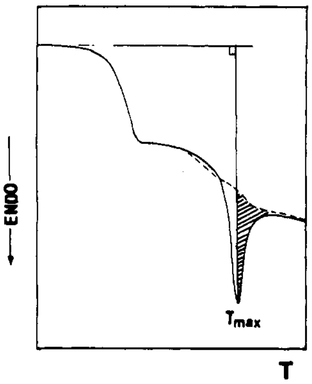

Figure 8. Schematic illustration for the calculation of the enthalpy relaxation of the pure PMMA phase in the copolymer and the blend: aged sample (—), quenched sample (- -).

Table II
DPM (%) of the PS-*b*-PMMA Copolymer and PS–PMMA Blend

preparation method	copolymer	blend
THF[a]	25.4	6.2
CCl_4[a]	48.2	4.6
THF-PE[b]	43.9	3.2
CCl_4-Pe[b]	40.0	10.9
THF-MeOH[b]	40.9	13.5
CCl_4-MeOH[b]	32.4	8.9

[a] Solvent casting. [b] Precipitation.

T_{max} of the PMMA phase in the copolymer and in the blend coincide with that of the homopolymer. However, this coincidence is not observed in the T_{ons} (Figure 5b), reflecting a broad interfacial region.

This behavior induced us to consider the right half of the enthalpy recovery peak, defined in Figure 8 by the shadowed section of the peak area, as a more reliable measure of the quantity of the pure PMMA phase in the copolymer. It has been adopted that, even if the whole enthalpy recovery peak is due to the relaxation of the pure PMMA phase, it should be affected by the existence of an interfacial region. We consider that the influence of the interface is restricted in the left half of the peak area, as is suggested by T_{ons} shift and T_{max} stability. In this way it is assured that the determined enthalpy difference (right half of the peak) is attributed to the pure PMMA phase of the copolymer while the relaxation process for the phase is considered to be similar to that of the parent homopolymer.

The DPM in the copolymer is calculated by the equation

$$\mathrm{DPM} = [1 - (\Delta H/\Delta H')] \times 100\%$$

where ΔH and $\Delta H'$ are the enthalpy differences at $T > T_{max}$ of the PMMA-rich phase in the copolymer and the parent PMMA homopolymer, respectively. The same method has also been used for the blend.

In Table II the DPM values of the blend and the copolymer samples obtained by different methods are summarized. The results seem to be reasonable, as the average DPM value for the blend is low enough, 8%, while for the copolymer it is much higher, 38.5%. These results are in a satisfactory agreement with those drawn from the inspection of T_{max} shifts.

In fact the high values of DPM of the copolymer are always accompanied by a T_{max} shift of the PS-rich phase, whereas this shift is not observed for the blend whose DPM is very low. This characteristic coherence between the DPM values and the T_{max} shift is also evidenced by comparing the behavior of the copolymer obtained from THF solution by casting and/or by precipitation in PE. The higher DPM value in the later case, 45.9%, against 25.4% in the former case is reflected by a more pronounced T_{max} shift as observed by comparing Figures 2 and 5.

The enthalpy relaxation method used in this work seems to give reliable results concerning the phase behavior of the PS–PMMA system. The Flory–Huggins interaction parameter χ between PS and PMMA is equal to 0.041 (at 20 °C), as has been calculated according to Russell et al.[23] Roughly the same value, 0.046, has been derived from viscometric results in THF solution by Dondos and Benoit.[24] According to the predictions of the Leibler theory,[25] a diblock copolymer containing N monomer units has a critical χ value equal to $10.5/N$. It is also known that the mixture of the corresponding homopolymers separates at $\chi_c = 4/N$ when each of the homopolymers has $N/2$ monomer units. Provided that $N = 805$, we expect that our system should exhibit two-phase morphology, which is consistent with the results presented herein. The partial mixing observed in the copolymer should be attributed to the copolymer structure itself and the solvent effects.

In light of the present findings, it is worthwhile to comment on related results reported recently.[15] In the investigation of the phase morphology of a PMMA-*b*-PS-*b*-PMMA triblock copolymer, the sharpness of the enthalpy relaxation peak had been used as a miscibility criterion. It must be noted here that this criterion is valid only when it is accompanied by a shift of the position of the peak toward intermediate temperatures. Indeed, this condition is fulfilled in work corroborating the conclusions derived therein.

Concluding Remarks

The results of this work demonstrate that the enthalpy relaxation method, proposed by ten Brinke and Ellis for the investigation of miscibility in polymer blends[1,3] and block copolymers[4] with similar glass transition temperatures, can be applied to the investigation of the phase behavior of a PS-*b*-PMMA block copolymer.

This investigation showed miscibility effects depending on the preparation conditions. It has been demonstrated that the choice of the solvent for samples obtained by solvent casting and the choice of the solvent and the precipitant for samples obtained by precipitation are critical. The phase mixing is most favored when the solvent of the solution is a common good solvent (THF) and the precipitant is not a selective nonsolvent for the parent homopolymers (PE).

On the contrary, the study of the miscibility in the respective polymer blend, PS–PMMA, showed almost complete phase separation irrespective of the solvent or precipitant used.

Moreover, we have pointed out some new remarks concerning the enthalpy relaxation method and its application to partially mixed systems, as is the case of block copolymers. First, it seems that it is useful to investigate the enthalpy relaxation of the aged glass as a function of the annealing temperature at constant annealing time. In the case studied here, this procedure showed a greater sensitivity compared to the alternative procedure in which annealing time is the variable at constant temperature. Second, the fact that T_{max} of one phase in the copolymer coincides with that of the respective homopolymer gives the possibility to estimate the degree of phase mixing by comparing the magnitude of the respective enthalpy recovery peaks.

References and Notes

(1) Bosma, M.; ten Brinke, G.; Ellis, T. S. *Macromolecules* **1988**, *21*, 1465.
(2) Jorda, R.; Wilkes, G. L. *Polym. Bull.* **1988**, *20*, 479.
(3) Grooten, R.; ten Brinke, G. *Macromolecules* **1989**, *22*, 1761.
(4) Ellis, T. S. *Macromolecules* **1990**, *23*, 1494.
(5) ten Brinke, G.; Grooten, R. *Colloid Polym. Sci.* **1989**, *267*, 992.
(6) Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, The Netherlands, 1978.
(7) Kovacs, A. J.; Aklonis, J. J.; Hutchinson, T. M.; Ramos, A. R. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1097.
(8) Petri, S. E. B. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 1255.
(9) Hodge, I. M. *Macromolecules* **1983**, *16*, 898.
(10) Beecher, J. F.; Marker, L.; Bradford, R. D.; Aggarwal, S. L. *J. Polym. Sci., Part C* **1969**, *26*, 117.
(11) Beamish, A.; Goldberg, R. A.; Hourston, D. J. *Polymer* **1977**, *18*, 49.
(12) Kalfoglou, N. *J. Appl. Polym. Sci.* **1979**, *23*, 2385.
(13) Cowie, J. M. G.; Lath, D.; McEwen, I. J. *Macromolecules* **1979**, *12*, 52.
(14) Sohn, J.; Ree, T. *J. Appl. Polym. Sci.* **1984**, *29*, 4237.
(15) Tsitsilianis, C.; Staikos, G.; Dondos, A.; Lutz, P.; Rempp, P.; Benoit, H. *Makromol. Chem.* **1990**, *191*, 2309.
(16) Hugelin, C.; Dondos, A. *Makromol. Chem.* **1969**, *126*, 206.
(17) Zeman, L.; Patterson, D. *Macromolecules* **1972**, *5*, 513.
(18) Saldanha, M. J.; Kyn, T. *Macromolecules* **1987**, *20*, 2840.
(19) Chiou, J. S.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1459.
(20) Bui, V. T.; Baril, D.; Vu, T. L. *Makromol. Chem., Macromol. Symp.* **1988**, *16*, 267.
(21) Pascault, J. P.; Camberlin, Y. *J. Polym. Sci. Polym. Chem. Ed.* **1983**, *21*, 415.
(22) Feng, D.; Wilkes, L. G.; Grivello, J. V. *Polymer* **1989**, *30*, 1800.
(23) Russell, T. P.; Hjelm, R. P.; Seeger, P. A. *Macromolecules* **1990**, *23*, 890.
(24) Dondos, A.; Benoit, H. *Makromol. Chem.* **1968**, *118*, 165.
(25) Leibler, L. *Macromolecules* **1980**, *13*, 1602.

Registry No. (PS)(PMMA) (block copolymer), 106911-77-7; PS, 9003-53-6; PMMA, 9011-14-7; THF, 109-99-9; CCl_4, 56-23-5; MeOH, 67-56-1.