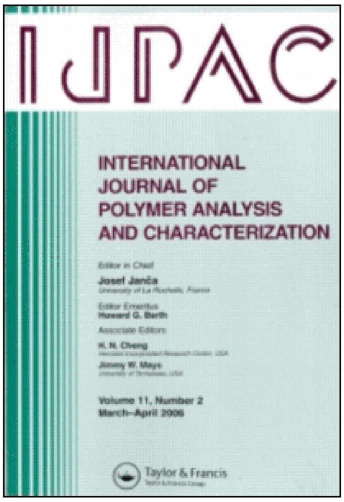

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Physical Aging in Block Copolymers by Thermal Analysis

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The enthalpy relaxation behavior of physically aged diblock copolymers was studied using differential scanning calorimetry. For polystyrene-*b*-poly(*t*-butyl acrylate), where the T_g values of the components are different, it was demonstrated that the higher T_g component (i.e., polystyrene) relaxes in a similar manner with the corresponding homopolymer. For polystyrene-*b*-poly(*t*-butyl methacrylate) and polystyrene-*b*-poly(methyl methacrylate), the T_g regions of the components overlapped. Therefore these systems were used as models to demonstrate that the enthalpy relaxation method proposed for the investigation of miscibility in polymer blends can be applied to the investigation of phase behavior in block copolymers.

KEY WORDS Block copolymers, differential scanning calorimetry, polystyrene-*b*-poly(*t*-butyl acrylate) polystyrene-*b*-poly (*t*-butyl methacrylate.)

INTRODUCTION

The physical aging of glassy polymers is an important phenomenon affecting significantly the physical properties of these materials [1]. A convenient property to monitor the aging phenomena is the enthalpy, as it can be measured easily and accurately by using thermal analysis. It is well established that polymer glasses are in a non-equilibrium thermodynamic state in which excess enthalpy is present. When the polymer is annealed at a temperature lower than its glass transition temperature T_g, the enthalpy decays approaching the equilibrium state.

The aim of this communication is to study the physical aging of diblock copolymers consisting of amorphous components using differential scanning calorimetry (DSC). In a DSC thermogram of a physically aged sample, an endothermic peak at the T_g region reveals the enthalpy relaxation phenomenon. The position and the magnitude of this peak depends upon the thermal history of the sample, as well as the structural characteristic of the polymeric glass itself.

The first part of this study was devoted to the copolymer polystyrene-*b*-poly (*t*-butyl acrylate) (PS-*b*-PtBA). This copolymer consists of components in which the their T_g values are different. The second advantage of studying this copolymer is that the T_g values of the components coincide with those of the parent homopoly-

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mers. Therefore, the method and the polymeric species chosen here allow the study of the relaxation behavior of the individual blocks in the microphase separation state, as well as the comparison of this behavior to that of the parent homopolymers.

The second part of this study deals with block copolymers in which the T_g values of the components are close to each other. In this case, conventional thermal analysis cannot be used successfully to study the phase behavior of the system. We attempt to show, however, that DSC combined with the enthalpy relaxation phenomenon occurring when the polymer samples are subjected to annealing at temperatures below their T_g, remains a useful experimental technique for the investigation of the phase behavior of block copolymers.

This method has been proposed first for the investigation of miscibility in polymer blends and relies on the position of the peak maximum, T_{max}, and the onset, T_{ons}, of the enthalpy relaxation peak of the blend relative to the pure components [2-4]. In blends that are miscible on the molecular level, a single endothermic peak appears at an intermediate position between the peaks of the pure components; whereas, in a two-phase separated blend, it is possible to generate two peaks which approach those of the pure components. Whether the two peaks will appear or not depends upon the enthalpy relaxation kinetics and the difference between the T_g values of the pure components. The enthalpy, relaxation method has been applied to the investigation of the phase behavior of several block copolymers [5–10].

In the second part of this study two diblock copolymers, that is, polystyrene-*b*-poly(*t*-butyl methacrylate) (PS-b-PtBMA) and polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA), in which T_g values differ by less than 20° C, are examined.

EXPERIMENTAL

All the samples investigated have been synthesized by anionic polymerization and their polydispersity, determined by gel permeation chromatography, was found to be less than 1.15. The synthetic procedure for the diblock copolymer samples relies on sequential addition of monomers. From each synthesis, part of the PS precursor was collected. These PS samples were used as the PS parent homopolymers. The molecular characteristics of all the samples are shown in Table I.

TABLE I

Molecular characteristics and T_g values of block copolymers and their parent homopolymers

Sample	M_W(LS)	Sty, %[a]	T_{g1}(° C)	T_{g2}(° C)
PS-b-PtBA	146000	51	110	49
PS	80000		110	
PtBA	51000			48
PS-b-PtBMA	85000	50		
PS	42500		109	
PtBMA	50000			120
PS-b-PMMA	83000	67		
PS	55000		109	
PMMA	29000			127

[a] By differential refractometer.

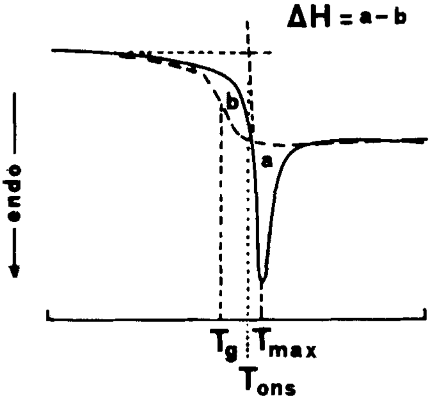

FIGURE 1 Schematic representation of thermograms of aged (—) and quenced (--) samples showing definitions of T_g, ΔH, T_{ons}, and T_{max}.

The PS-b-PtBA samples were used in powder form while for the other two copolymers the samples were prepared as a film, formed by solvent casting. The PS-b-PtBMA samples were cast from 10% acetone solutions and the PS-b-PMMA from 8% benzene solutions.

All the samples were dried under vacuum for several days at gradually increasing temperature up to 100° C to ensure removal of the solvent.

DSC measurements were carried out using a Du Pont model 910 calorimeter equipped with a model 99 thermal analyzer. The samples' weights were about 10 mg for the homopolymers and about 20 mg for the copolymers. The heating rate was always 20° C/min.

Definitions for T_g and for the enthalpy relaxation parameters, that is, temperature at the heat capacity maximum, T_{max}, temperature at the onset of the relaxation peak, T_{ons}, and enthalpy relaxation ΔH, are given schematically in Figure 1. T_g values, obtained at half the step change in c_p, of all the samples are summarized in Table I.

The annealing experiments at high temperatures were performed in a thermal oven, while at low temperatures in a thermoregulated water bath. For PS-b-PtBA, the pans were enclosed in vials under argon to prevent decomposition of the PtBA.

RESULTS AND DISCUSSION

Polystyrene-b-poly(t-butyl acrylate) Block Copolymer

Samples of PS-b-PtBA and the corresponding homopolymers were heated at 140° C for 10 min and then were quenched at the annealing temperature $T_a = T_g - 16°\mathrm{C}$ (see definition of T_g in Figure 1) for various annealing times. Accordingly, they were quenched to 0° C and then reheated at a rate of 20° C/min.

The enthalpy relaxation data were analyzed according to the following empirical equation proposed by Cowie and Ferguson [11].

$$\Delta H(t_a, T_a) = \Delta H_\infty(T_a)[1 - \phi(t_a)] \tag{1}$$

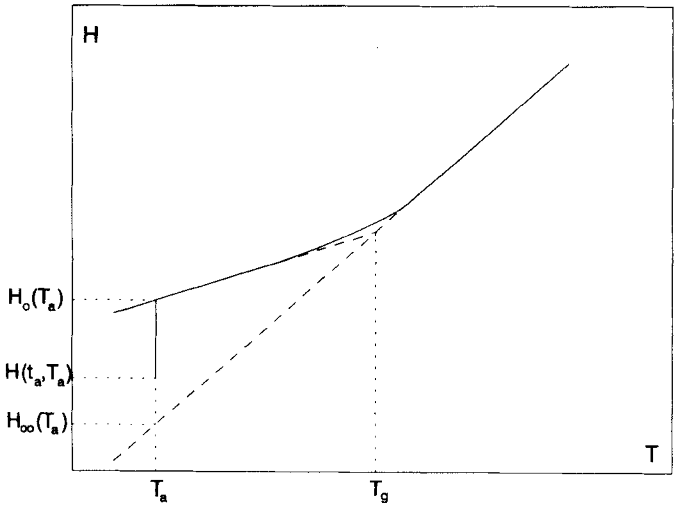

FIGURE 2 Temperature–enthalpy curve for a polymer sample showing the enthalpy relaxation phenomenon.

where $\phi(t_a)$ is the Williams-Watts relaxation function

$$\phi(t_a) = \exp\left[-(t/t_c)^\beta\right] \tag{2}$$

$\Delta H(t_a, T_a)$ and $\Delta H_\infty(T_a)$ are the enthalpy lost after an annealing time t_a and after the samples have attained their thermodynamic equilibrium, respectively (see definition in Figure 2); t_c is a characteristic time, and β is a measure of the width of the relaxation time spectrum.

Some characteristic DSC thermograms of samples annealed at 16° C below the T_g of the PtBA and/or PS are illustrated in Figure 3. The thermograms indicate that the system is apparently phase separated. In fact, when T_a is between the T_g values of the components, the thermogram exhibits a heat capacity jump corresponding to the PtBA-rich phase and an enthalpy recovery peak corresponding to the aged PS-rich phase. The inverse behavior is evidenced when T_a is below the T_g of PtBA. At that temperature, the relaxation of the PS-rich phase is very slow and therefore no enthalpy relaxation peak is observed.

In Figure 4, $\Delta H(t_a, T_a)$ is plotted as a function of ln t_a for the PS and PtBA rich phases of the copolymer and the corresponding parent homopolymers. The parameters ΔH_∞, t_c and β of the *C-F* model are listed in Table II and call for some comments. The exponent β is the same for the PS-rich phase and the PS homopolymer, whereas this is not the case for the PtBA-rich phase. Taking into account that the t_c values are almost the same, we could conclude that the pure PS-rich phase relaxes in a similar manner as the parent homopolymer, while remarkable differences are observed for the PtBA-rich phase. Further experimental results and a more detailed analysis will be given in a forthcoming paper. An interesting point that arises from Table II is that the values of $\Delta H_\infty(T_a)$ for the

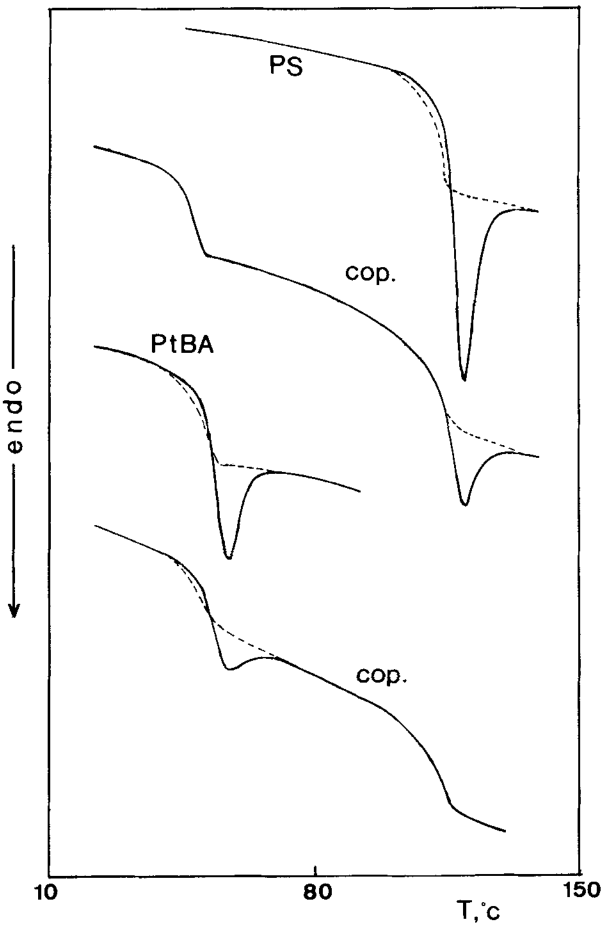

FIGURE 3 Characteristics DSC thermograms of PS-b-PtBA, PS and PtBA annealed at $T_a = Tg - 16°C$.

copolymer phases are lower than those of the parent homopolymers. This should be attributed to the fact that part of the PS and/or PtBA phase is located at the interphase.

From Figure 2 we have

$$\Delta H_\infty(T_a) = \Delta C_p(T_g - T_a) \tag{3}$$

Taking the ratio of the $\Delta H_\infty(T_a)$ for the copolymer PS-rich phase and the corresponding parent homopolymer and provided that T_g-T_a is the same for both, we obtain

$$\frac{\Delta H_\infty(T_a)}{\Delta H'_\infty(T_a)} = \frac{\Delta C_p}{\Delta C'_p} \tag{4}$$

where the primed quantities are related to the homopolymer. The above equation

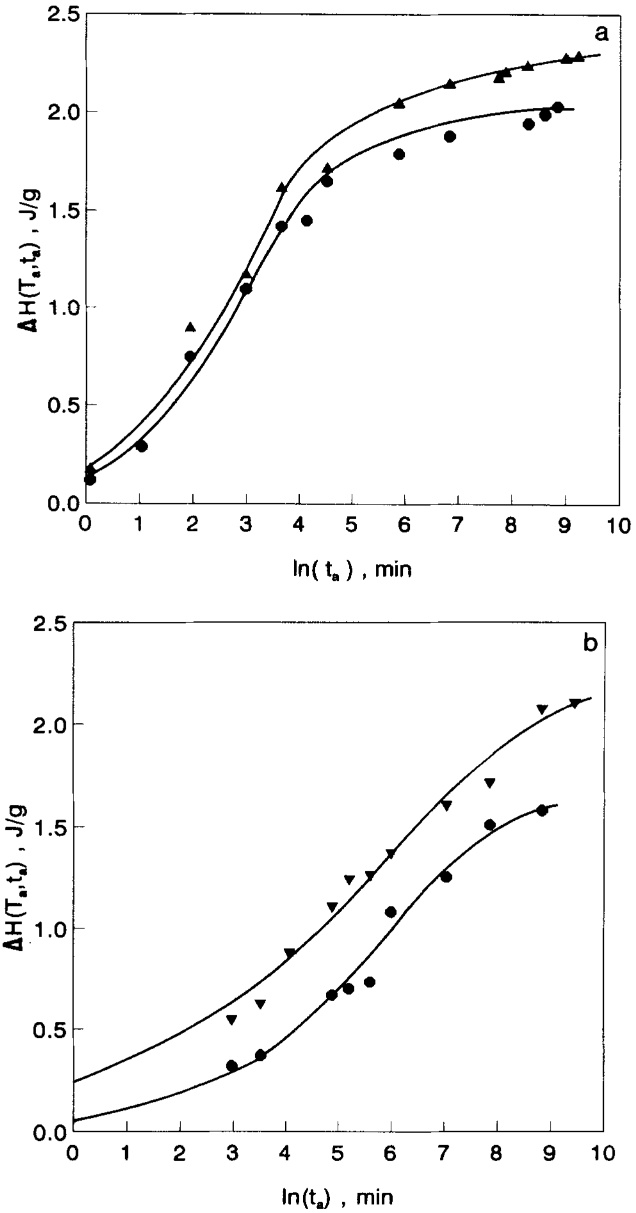

FIGURE 4 $\Delta H(t_a, T_a)$ as a function of $\ln t_a$ for a) PS_{cop} (●), PS_{hom} (▲), b)$PtBA_{cop}$ (●), $PtBA_{hom}$ (▼). Solid lines are fits to the *C-F* model.

TABLE II

C-F model parameters for PS-b-PtBA, PS and PtBA

	PS_{cop}	PS_{hom}	$PtBA_{cop}$	$PtBA_{hom}$
T_a(° C)	94	94	33	32
$\Delta H_\infty(J/g)$	1.95	2.201	1.917	2.154
$T_c(h)$	0.72	0.53	7.203	6.955
β	0.59	0.59	0.577	0.357

TABLE III

DPM (%) of PS-b-PtBA block copolymer

t_a (min)	$\Delta H(t_aT_a)/\Delta H'(t_a,T_a)$	DPM
7	0.830	17
20	0.930	7
39	0.876	12.4
4000	0.830	17

implies that ΔH_∞ could be used in order to estimate the degree of phase mixing (DPM) in a manner analogous to that in which the heat capacity jump ΔC_p has been used [12, 13].

$$\mathrm{DPM} = \left[1 - (\Delta C_p/\Delta C_p')\right] \times 100\% \tag{5}$$

In fact, the values of the ratio $\Delta C_p/\Delta C_p'$ and $\Delta H_\infty(T_a)/\Delta H_\infty'(T_a)$ for the *PS*-rich phase are 0.864 and 0.885, respectively, which confirms the validity of Equation (4). Therefore, Equation (5) can be written:

$$\mathrm{DPM} = \left[1 - (\Delta H_\infty(T_a)/\Delta H_\infty'(T_a)\right] \times 100\% \tag{6}$$

From Equations (1) and (3) we can obtain:

$$\Delta H(t_aT_a) = \Delta C_p(T_g - T_a)[1 - \phi(t)] \tag{7}$$

Equation (7) demonstrates that one can use also the quantity $\Delta H(t_a, T_a)$ provided that the constants of the Williams Watts functions, $\phi(t)$, for the copolymer constituent and the parent homopolymer are the same. As shown, this is the case for the PS phase (Table III). DPM values have been calculated using ΔH at different annealing times and are listed in Table III. The mean value of DPM is 15.8% in very good agreement with that obtained using ΔC_p (i.e., 13, 6%).

The possibility of DPM estimation using enthalpy relaxation data may prove useful in the case where the percentage of the one component is very low and/or the T_g regions of the components overlap [8].

Polystyrene-b-Poly(t-butyl-methacrylate) Block Copolymer

Samples of PS-b-PtBMA cast from acetone, which is a selective solvent for PtBMA, and the corresponding homopolymers were heated up to 160° C for 15 min to erase any previous thermal history, and then were annealed at 90° C for various annealing times.

The thermograms of the copolymer reveal two distinct relaxation peaks, the T_{max} and T_{ons} of which are depicted as functions of the logarithm of t_a in Figure 5. In this figure, the data concerning the parent homopolymers are also incorporated. As is apparent, T_{max} and T_{ons} varies linearly with $\ln t_a$ also for the copolymer constituents. This behavior has been established for the homopolymers provided that the aged glass is far from the equilibrium.

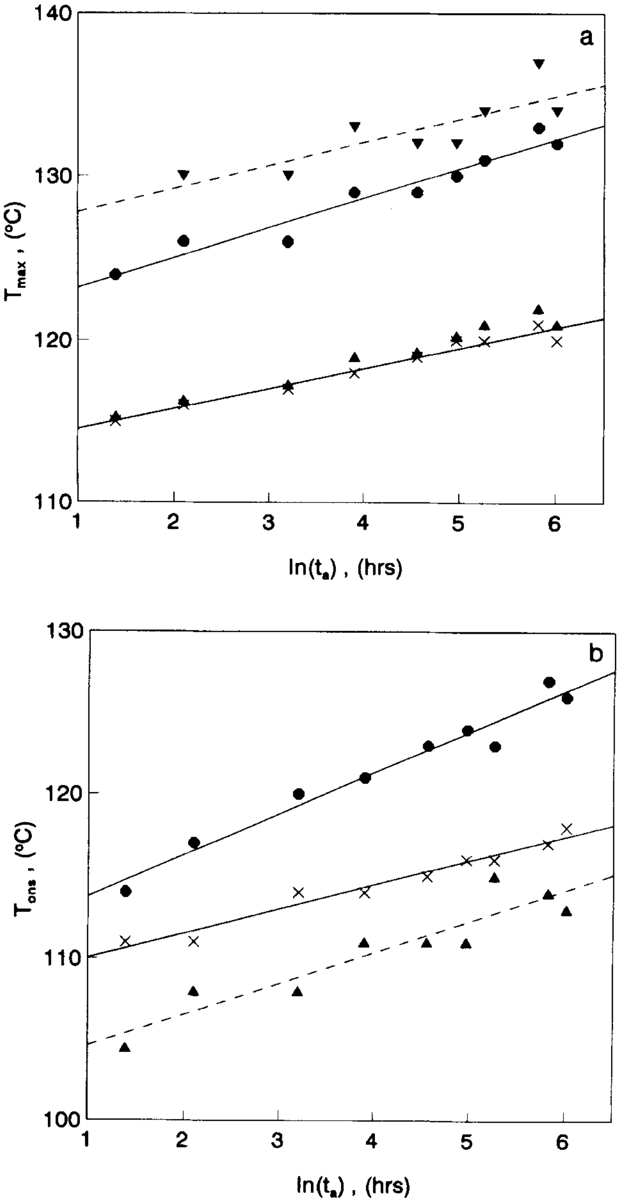

FIGURE 5 T_{max} (a) and T_{ons} (b) as a function of for samples annealed at 90° C: PS_{cop} (▲) PS_{hom} (x), $PtBMA_{cop}$ (▼) $PtBMA_{hom}$ (●).

Figure 5 also shows that the block copolymer exhibits unambiguously a two-phase morphology, as the points concerning the t_{max} of the copolymer constituents lie out of the intermediated positions between the respective T_{max} of the parent homopolymers. The T_{max} of the second peak (PtBMA) appears at higher temperatures than those of the homopolymer. This peculiar behavior has also been reported by Ellis [14] in aromatic polyamide blends. Moreover, the T_{ons} of the first peak (PS) appear in lower temperatures than those of the homopolymer.

A plausible explanation could be the following: The T_{ons} lowering of the PS-rich phase could be attributed to some mixing of PtBMA chain ends into the PS matrix giving rise to an excess free volume and therefore a t_g broadening toward lower temperatures. The respective loss of these chain ends in the PtBMA-rich phase, however, could cause T_g broadening towards higher temperatures.

Polystyrene-b-poly(methyl-methacrylate) block Copolymer

Samples of PS-b-PMMA cast from benzene were subjected to annealing at 98° C for various annealing times up to 310 *h*. The same thermal treatment was carried out also with the parent homopolymers. DSC thermograms show one endothermic peak for the copolymer, the T_{max} of which lies at an intermediate position between those of the homopolymers (Figure 6). This may demonstrate that the system exhibits a one-phase structure. However, this is not implied by the Leibler theory [15] as the $X_{AB}N$ value is 34.8, much higher than the critical value which is 14 at $f = N_A/(N_A + N_B) = 0.66$. N is the degree of polymerization of the copolymer and X_{AB} is the Flory-Huggins interaction parameter taken as 0.041 [16].

In order to elucidate the above discrepancy, another procedure has been undertaken. Keeping the annealing time constant at 24 *h*, we have annealed the samples at various temperatures approaching the T_g of PMMA. At temperatures higher than 103° C, a second peak is generated lying at the position of the peak of the PMMA homopolymer, whereas the first peak has now been eliminated.

In Figure 7 the T_{max} of the relaxation peaks for the copolymer and the respective homopolymers are plotted as a function of T_a. As is shown, the T_{max} of the first peak at low T_a lies between those of the homopolymers while the T_{max} of the second peak, appearing at high T_a, lies on the line corresponding to PMMA

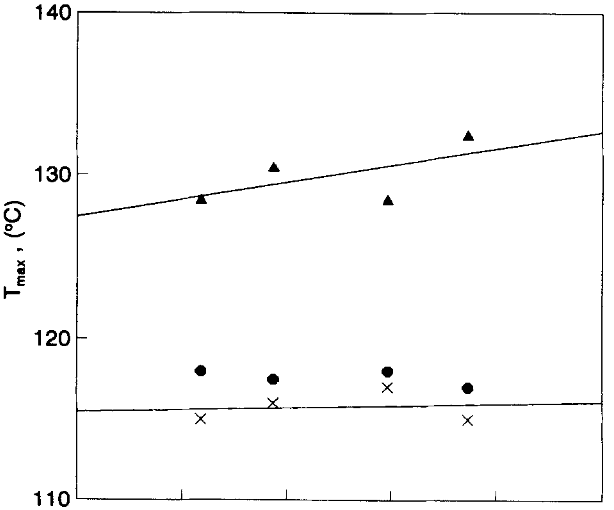

FIGURE 6 T_{max} as function of ln t_a for PS-b-PMMA copolymer and PS, PMMA parent homopolymers annealed at 98° C: PS_{hom} (x) $PMMA_{hom}$ (▲), PS-b-PMMA (●).

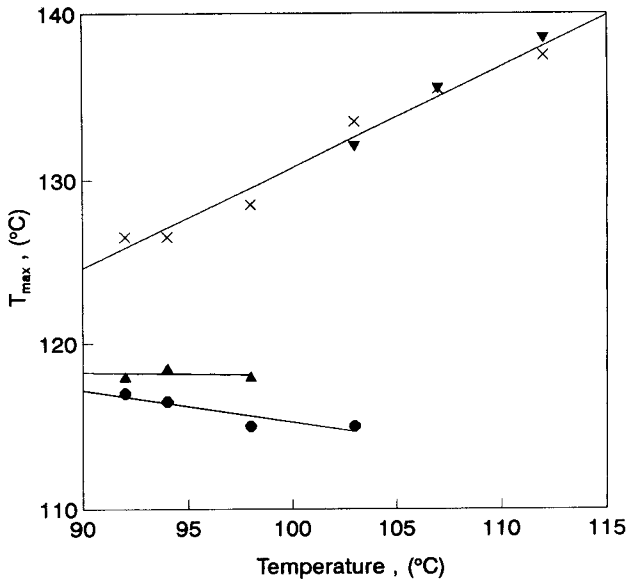

FIGURE 7 T_{max} as a function of annealing temperature for PS-b.PMMA copolymer and PS, PMMA parent homopolymers annealed for 24h: PS_{hom} (●), PS_{cop} (▲) $PMMA_{(hom)}$ (x), $PMMA_{cop}$ (▼).

homopolymer. This implies eventually that the system exhibits two-phase morphology: one PMMA pure phase and the PS-rich phase. Since the T_{max} of the phase has been shifted toward intermediate positions between those of the parent homopolymers, this reveals that part of PMMA has been dissolved into the PS phase. This partial miscibility could be attributed to solvent effects. Analogous results have been reported elsewhere [8].

CONCLUSIONS

The physical aging of three diblock copolymers was investigated by monitoring their enthalpy relaxation behavior using DSC. The block copolymer PS-b-PtBA, having a high glass-transition temperature difference of the two homopolymers ($tg_{PS} - Tg_{PtPtBA} = 62°$ C), allows us to study the relaxation kinetics of the individual blocks. Our preliminary results have shown that the higher T_g component (PS) relaxes in a similar manner with the corresponding homopolymer. Furthermore, the enthalpy relaxation data can be used to estimate the degree of phase mixing (DPM) in an analogous manner to that in which ΔC_p has been already used [12, 13].

In the block copolymers PS-b-PtBMA and PS-b-PMMA studied, the T_g regions of the components overlap. These copolymers were used as models to demonstrate that in such cases the phase behavior can be investigated using DSC combined with enthalpy relaxation experiments. Two different procedures were followed depending upon the identity of the polymeric system. For PS-b-PtBMA, the annealing temperature T_a was kept constant and the enthalpy relaxation was studied as a function of the annealing time t_a. For PS-b-PMMA, t_a was kept constant and T_a was varied approaching the higher T_g value. For PS-b-PMMA, the second method proved critical, because it was possible to detect the PMMA phase. In both cases the data concerning the copolymer were compared with those of the parent homopolymers subjected to the same thermal history. It was shown that both copolymers exhibit a two-phase morphology.

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