Influence of annealing and casting solvent on the morphology of poly(ethylene oxide)-b-polystyrene-b-poly(ethylene oxide) triblock copolymer: compatibility effects

C. Tsitsilianis, G. Staikos and A. Dondos
Department of Chemical Engineering, University of Patras, 26110 Patras, Greece

and P. Lutz and P. Rempp
Institut Charles Sadron (CNRS-ULP), 6, rue Boussingault, 67083 Strasbourg Cedex, France
(Received 10 December 1990; revised 8 July 1991; accepted 24 July 1991)

The influence of annealing on the morphology of solvent-cast films of poly(ethylene oxide)-b-polystyrene-b-poly(ethylene oxide) (PEO-b-PS-b-PEO) triblock copolymer was studied. The annealing temperature was chosen between the melting temperature of PEO and the glass transition temperature of PS. If the casting solvent is selective for PEO, microphase separation occurs and the crystallinity of the PEO is not affected by annealing. On the other hand, if the casting solvent is a good solvent for both blocks, a dramatic decrease in crystallinity of PEO is observed. This phenomenon is due to compatibility effects. The T_g region of the PS-rich phase is shifted towards lower values. This behaviour was elucidated using differential scanning calorimetry combined with enthalpy relaxation experiments.

(Keywords: poly(ethylene oxide)-b-polystyrene-b-poly(ethylene oxide); casting solvent; annealing; compatibility effects; crystallinity; enthalpy relaxation method)

INTRODUCTION

The phase behaviour of block copolymers in the bulk has been the subject of extensive research since the mid-1960s[1,2]. One of the main categories of block copolymers comprises those constituted of amorphous and crystallizable blocks. Typical representatives of these polymeric species are the block copolymers of polystyrene (PS, amorphous) and poly(ethylene oxide) (PEO, crystallizable). It is well known that these two polymers are incompatible, leading to microphase-separated structures. Morphological studies on diblock, triblock and multiblock PS–PEO copolymers have shown that crystallization occurs in the PEO domain. Unique structures are formed, depending on the relative composition, casting solvent, rate of evaporation and molecular weights of the individual segments[1,3–6]. Optical and scanning electron microscopy reveal that PEO forms spherulites which are characterized by fibrillar radial growth from a nucleation centre[4].

In this communication, new findings are reported concerning the phase behaviour of a PEO–PS–PEO triblock copolymer in the bulk. More precisely, films cast from various solvents were submitted to annealing at a temperature T_a between the melting temperature T_m of PEO and the glass transition temperature T_g of PS. The samples were then left to crystallize isothermally at a temperature T_c lower than T_m.

As will be reported, the crystallization process is strongly affected by the nature of the casting solvent and the annealing conditions. Furthermore, it is well known that the amorphous PS phase undergoes relaxation upon sub-T_g annealing[7–9]. A distinct endothermic peak in the glass transition region is evidenced. These peaks can reveal very useful information concerning the phase behaviour of the system. This method has already been used to investigate miscibility in polymer blends[10–12] and phase behaviour in block copolymers[13].

EXPERIMENTAL

The block copolymer sample was made by sequential anionic polymerization of styrene and ethylene oxide, using a bifunctional initiator, in tetrahydrofuran. The synthesis was carried out in a sealed reactor, under a slight overpressure of argon after the monomers and solvents had been dried carefully according to standard procedures.

A known amount of the potassium naphthalene initiator solution was introduced into the reactor containing the dry solvent. The temperature was lowered to $-30°C$ and the chosen amount of styrene was added dropwise at that temperature. A fraction of the reaction medium was then sampled and deactivated protonically, for characterization of the PS block.

To the rest of the active polystyrene solution was immediately added the chosen quantity of pure ethylene oxide (EO) and the temperature was slowly increased to $\approx 25–30°C$. The time required for the EO polymerization

0032-3861/92/163369-06

to be completed at that temperature amounted to ≈24 h. The active alkoxide sites were then deactivated protonically and the raw triblock copolymer was recovered by precipitation into excess heptane. It was then redissolved in benzene, filtered and freeze-dried.

The block copolymer exhibited a rather sharp unimodal molecular weight distribution, indicating the absence of accidental deactivation during the process. Molecular weights were determined by light scattering on both the PS block (sampled) and the triblock copolymer. The polystyrene content of the latter was determined from elemental analysis and by differential refractometry.

The data were self-consistent and compatible with the value of the molecular weight expected from the molar ratio of monomers and initiator used, account being taken of the low polydispersity of the sample. The values found were: $M_{wPS} = 68\,000$; $M_{wCOP} = 133\,000$; PS content 53 wt%.

Films of this PEO-b-PS-b-PEO triblock copolymer were cast from the various solvents: THF and benzene, which are good solvents for both blocks, and acetone and a 52:48 (v/v) benzene–methanol mixture, which are preferential solvents for the PEO blocks. A glass vessel device was used to control the rate of evaporation. The films obtained were dried under vacuum at 30°C for several days to remove the last traces of solvent, and stored in a desiccator over P_2O_5. The films were heated to 130°C for 15 min to erase any thermal history, annealed for various times at 83°C and quenched immediately to 25°C. At that temperature the films were left for 5 days until complete crystallization of the PEO had occurred. The annealing experiments were performed in a thermal cabinet at a temperature kept constant within ±0.2°C.

Differential scanning calorimetry (d.s.c.) measurements were carried out using a Du Pont 910 calorimeter equipped with a 99 Thermal Analyzer. The heating rate was 10 K min^{-1}.

A Zeiss Photomi II optical microscope, fitted with crossed nicols, was used to visualize the crystallization of the PEO domains.

RESULTS AND DISCUSSION

Two main features were examined as a function of the nature of the casting solvent: the crystallinity of the PEO domains and the glassy state of the amorphous PS domains. The degree of crystallinity of the PEO phase is given by

$$X_c = \frac{\Delta H_f}{\Delta H_f^\circ} \qquad (1)$$

where ΔH_f is the enthalpy of fusion per unit mass of the PEO in the copolymer, and ΔH_f° is the enthalpy of fusion of 100% crystalline PEO ($\Delta H_f^\circ = 205$ J g^{-1})[14].

Three parameters characterizing the glassy state of PS are considered: the onset of glass transition region, $T_{g,ons}$, defined as the intersection of the extrapolated baseline below T_g and the line drawn through the inflection step of the C_p change; T_g itself at half the step change in C_p; and ΔT_g, the width of the glass transition region, which is the difference in temperature between the points where the tangent to the inflection intersects the extrapolated baselines above and below T_g.

Table 1 Crystallinity, melting temperature of PEO-rich phase, and glass transition of PS-rich phase of PEO–PS–PEO block copolymer, for various casting solvents

Casting	PEO-rich phase		PS-rich phase		
solvent	T_m (°C)	X_c (%)	$T_{g,ons}$	T_g	ΔT_g (°C)
Acetone	58	66.5	91	97	13
Benzene–methanol	59	70.5	89	96	15
Benzene	59	64.5	91	97	13
THF	59	60.8	90	96	12
PS homopolymer	–	–	104	107	6

All the above-mentioned parameters arising from d.s.c. experiments are reported as a function of the nature of the casting solvent in *Table 1*. The following remarks can be made. The melting temperature T_m is independent of the nature of the casting solvent, whereas the degree of crystallinity is slightly higher when the casting solvent is selective for the crystallizable block. The glassy state of the PS-rich phase seems to be independent of the nature of the solvent. On the other hand, significant differences are evident in all parameters describing the glassy state – i.e. $T_{g,ons}$, T_g and ΔT_g – between the PS phase in the triblock copolymer and PS homopolymer. This can be attributed to the block structure of the copolymer, as the PS segments are linked at both ends with PEO blocks, rather than to solvent traces that could have remained on the films after drying.

The overall crystallinity of the PEO-rich phase as indicated by d.s.c. measurements is approximately the same, regardless of the nature of the casting solvent, but the morphology of the crystalline phase differs significantly as revealed by polarized-light microscopy. *Figure 1* shows micrographs of thin films obtained as described above. A general observation is that the whole space is filled with spherulites, with no dark amorphous domains of PS, although the PS content is 53%, in agreement with previous studies[1,15]. The same behaviour has been observed in miscible PEO–PMMA[16] and PEO–PVAc[17] blends, showing that the amorphous material is incorporated into the interlamellar regions of PEO spherulites.

The main conclusion from *Figure 1* is that the nature of the casting solvent significantly affects the morphology of the films. It is suggested that selective solvent casting leads to better-separated crystallizable microdomains (from PEO blocks: *Figure 1a,b*), whereas with a common solvent (*Figure 1c,d*), microdomain separation is imperfect, leading to a higher degree of dispersion of the crystallizable component and hence, owing to the high viscosity of the amorphous material (PS) surrounding the PEO components, yielding ill-defined spherulites.

The main aim of this work was to investigate the possible effects of annealing on the phase behaviour of the crystallizable and the amorphous domains in such solvent-cast films. The annealing temperature, T_a, was chosen to lie between T_m of the crystallizable component and T_g of the amorphous component (i.e. $T_{mPEO} < T_a < T_{gPS}$). At that temperature PEO is melted, while PS is in a non-equilibrium glassy state, and it is well known that structural changes occur until the material approaches equilibrium.

Figures 2 and *3* show d.s.c. thermograms of samples cast from acetone and THF respectively, annealed at 83°C for various times. The thermograms are presented in two parts, concerning (a) the melting endotherm of

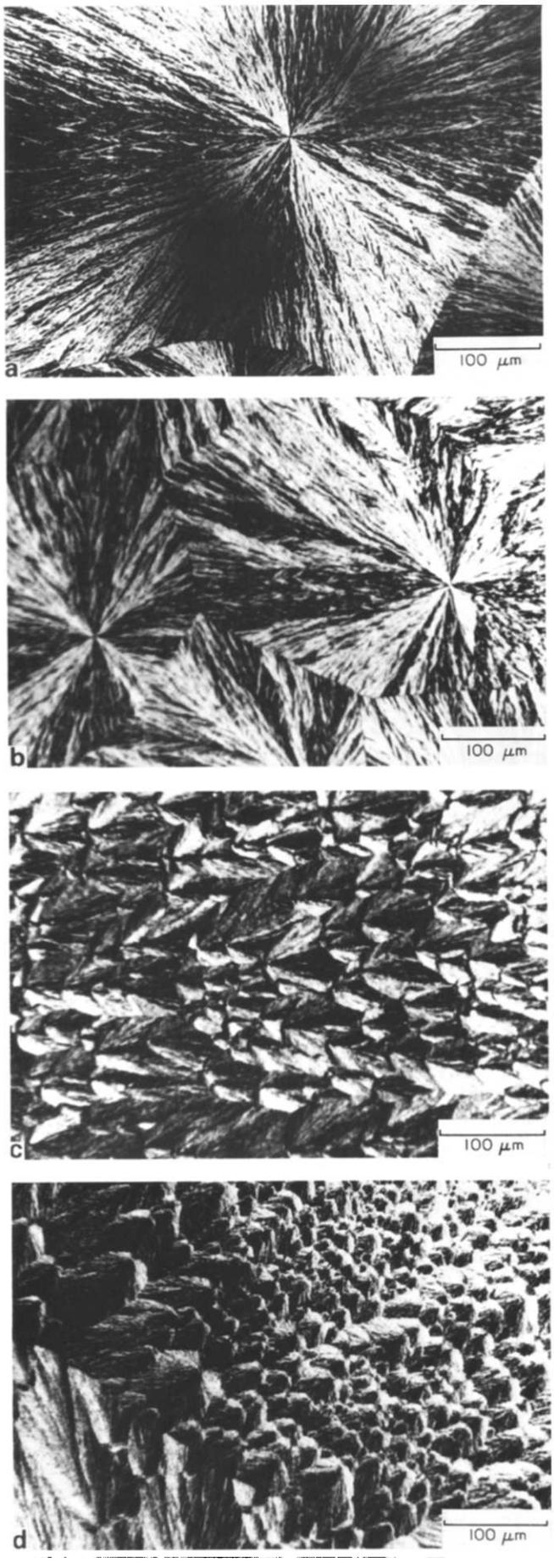

Figure 1 Optical micrographs of thin films of PEO-b-PS-b-PEO triblock copolymer cast from various solvents: (a) acetone; (b) benzene–methanol; (c) benzene; (d) THF

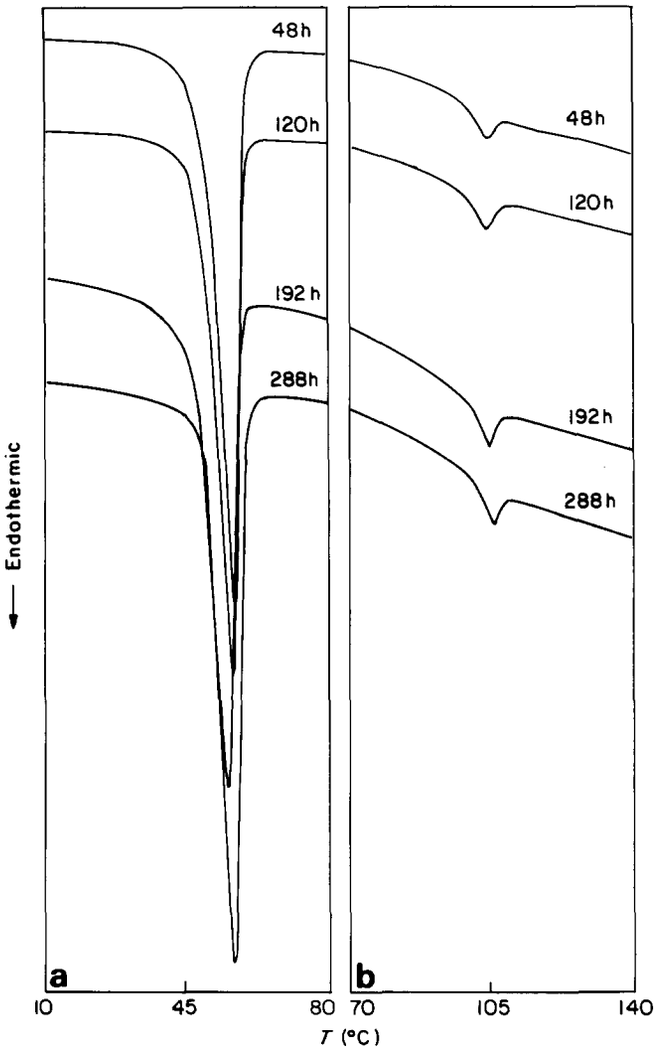

Figure 2 D.s.c. thermograms of PEO-b-PS-b-PEO triblock copolymer films cast from acetone and annealed at 83°C for the times indicated; (a), (b), see text. *Y*-axis sensitivity (mV cm^{-1}): (a) 5; (b) 2

crystalline domains, and (b) the enthalpy relaxation of the amorphous PS phase. These phenomena will be examined separately.

Considerable differences are observed in the crystallinity behaviour between the samples cast from different solvents. With acetone, a selective solvent for PEO, the sharp endothermic peak related to the melting of PEO spherulites remains unaffected by the annealing time (*Figure 2a*). The melting temperature T_m also remains approximately constant. Similar results are observed when the casting solvent is benzene–methanol mixture (*Table 2*). On the other hand, when a good solvent for both blocks (THF, benzene) is used, there are dramatic changes in the crystallinity behaviour of the PEO component as a function of annealing time. The shape, the position and the magnitude of the endothermic peak at the melting point of the crystalline component change significantly with annealing time. In *Figure 3a*, the variation of the endothermic peak as a function of t_a for the films cast from THF is shown. At a relatively long annealing time (t_a = 288 h), the peak vanishes completely. The diminution of the peak is even faster for the films cast from benzene (the time needed for complete disappearance is 192 h).

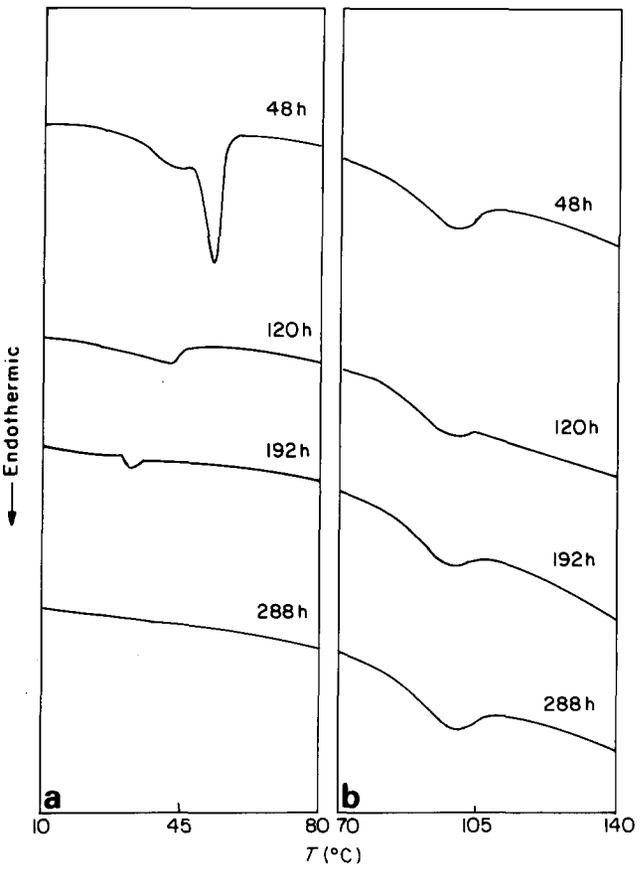

Figure 3 As in *Figure 2* for films cast from THF

Moreover, an abrupt melting point depression is observed with both THF and benzene (*Table 2*). T_m depression is usually associated with morphological changes and/or crystal reduction[18]. This has been observed in miscible semicrystalline–amorphous blends where specific interactions are present[19]. In the present instance however, it should be attributed to crystal size reduction, since a similar T_m depression was not observed in selective-solvent cast films; see *Table 1* and *Figures 2a* and *3a*.

Figure 4 shows the variation with t_a of the degree of crystallinity as calculated from equation (1). When casting is performed from a selective solvent for PEO, the degree of crystallinity hardly varies with t_a, whereas with a good solvent for both blocks, a dramatic decrease towards zero can be observed.

In order to confirm the above results, optical micrographs were obtained from thin films which had been annealed at 83°C for 144 h and allowed to crystallize at 25°C for 100 h (*Figure 5*). Again, the samples cast from a selective solvent for PEO (acetone, benzene–methanol) exhibit a filled spherulitic structure which resembles the micrograph of the unannealed samples (*Figure 1*). In contrast, the micrographs of the annealed samples cast from a good solvent for both components are quite different from those for unannealed films. Large dark domains corresponding to the amorphous phase can be observed (*Figure 5c,d*), with some very small crystalline domains still remaining, in agreement with d.s.c. results.

Next the enthalpy relaxation of the amorphous PS-rich phase is examined. *Figures 2b* and *3b* are thermograms of films cast from acetone and THF respectively and annealed at 83°C for various times. The observed endotherms show considerable differences, depending upon the casting solvent. The shape and the position of the enthalpy relaxation peaks seem to depend on the nature of the solvent. The peaks for the films cast from THF (good solvent for both blocks) are broadened and shifted towards lower temperatures, relative to those cast from acetone (selective solvent for PEO). T_{max} is defined as the temperature corresponding to the peak of the thermogram, and T_{ons} as the temperature corresponding to the intersection point between the extrapolated baseline below T_g and the tangent drawn on the low-temperature side of the endothermic peak. In *Figure 6* these characteristics are plotted *versus* log t_a for samples cast from various solvents. In the case of the films cast from a selective solvent for PEO (acetone, benzene–methanol), T_{ons} and T_{max} increase linearly with log t_a. This behaviour is characteristic of a purely glassy polymer not very close to thermodynamic equilibrium. The experimental points corresponding to acetone and to benzene–methanol coincide, providing good reproducibility of the results. On the other hand, if the

Table 2 Melting temperature T_m (°C) for PEO in PEO–PS–PEO block copolymer as a function of annealing time t_a

Casting	t_a (°C)				
solvent	0	48	120	192	288
Acetone	58	57	56	55	56
Benzene–methanol	59	57	57	56	57
Benzene	59	44/35[a]	35	–	–
THF	59	53/45[a]	43	32	–

[a]Double peak

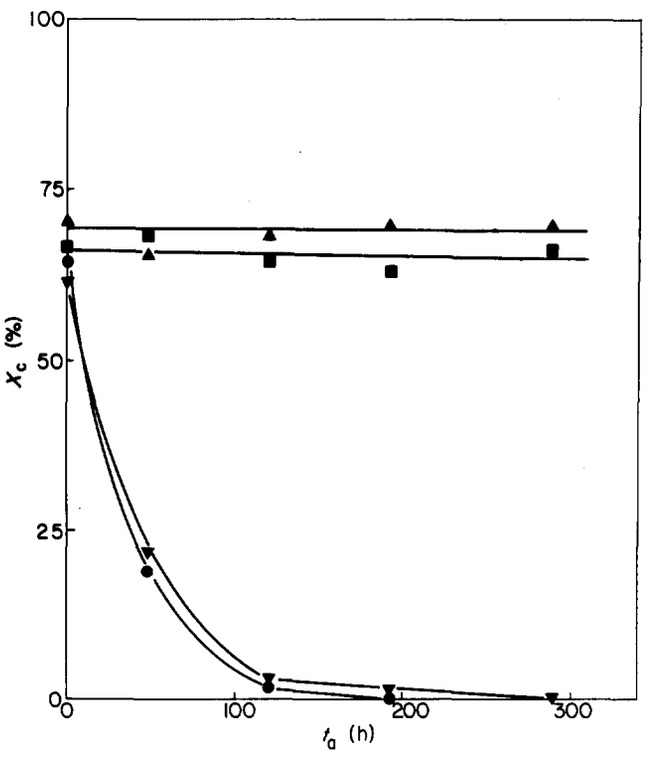

Figure 4 Degree of crystallinity X_c *versus* annealing time t_A for the PEO-rich phase of PEO-b-PS-b-PEO triblock copolymer cast from various solvents: (▲), acetone; (■), benzene–methanol; (●), benzene; (▼), THF

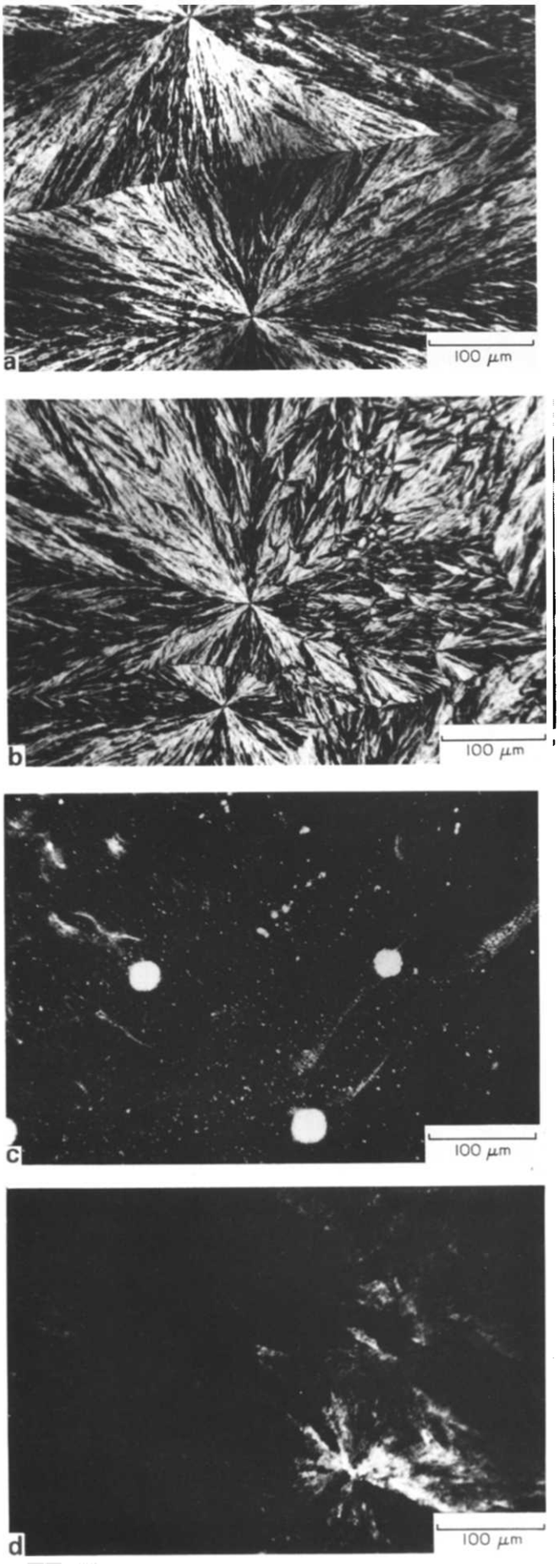

Figure 5 As in *Figure 1* but with annealing at 83°C for 144 h: (a) acetone; (b) benzene–methanol; (c) benzene; (d) THF

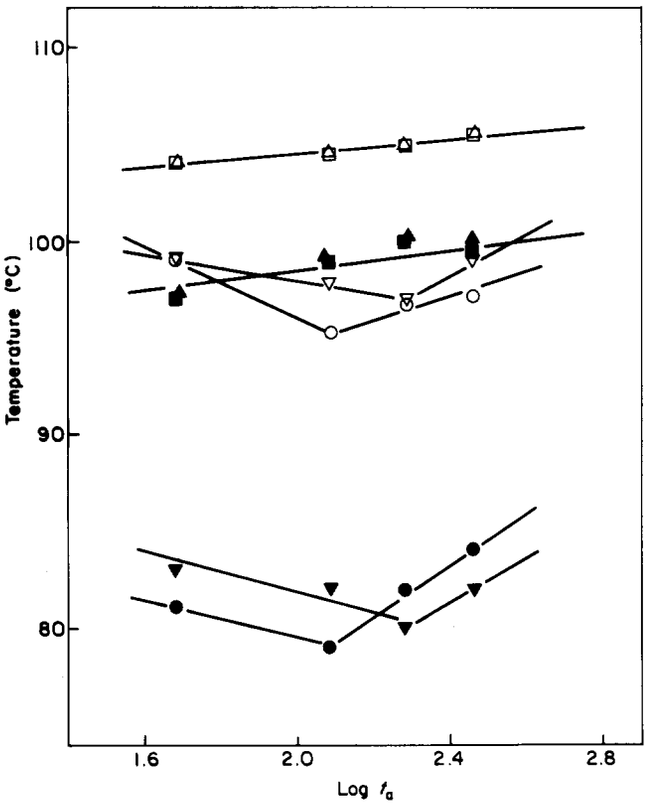

Figure 6 T_{max} (open symbols) and T_{ons} (solid symbols) *versus* log t_a for the PS-rich phase of PEO-b-PS-b-PEO triblock copolymer films cast from various solvents: (□, ■), benzene–methanol; (△, ▲), acetone; (○, ●), benzene; (▽, ▼), THF

casting solvent is a good solvent for both components (benzene, THF), T_{ons} and T_{max} exhibit a minimum, and moreover are about 16°C and 8°C lower, respectively, than the values obtained with a selective casting solvent. Another observation is that the difference $T_{max} - T_{ons}$, which may be taken as a measure of the width of the enthalpy relaxation peak, is about 6°C for a selective solvent and 16°C for a good solvent.

The above results (i.e. the shift of T_{ons} and T_{max} towards lower values and the broadening of the enthalpy relaxation peak) suggest that the glass transition region of the PS-rich phase has been shifted towards lower temperatures and broadened. The existence of a minimum in T_{ons} or T_{max} vs. log t_a suggests that as T_g of the PS-rich phase decreases, T_{ons} and T_{max} also decrease. After a specified period of time this process ceases, and T_{ons} and T_{max} again increase with annealing time. These minima appear at shorter annealing times for benzene than for THF. The same order was found for the degree of crystallinity (see *Figure 4*). This supports the idea that both phenomena are closely related.

The samples that had been annealed for 288 h and allowed to crystallize at 25°C for 100 h were reheated to 140°C and immediately quenched at 25°C. After storage for 450 h at that temperature, d.s.c. measurements were performed, yielding the thermograms in *Figure 7* and the data in *Table 3*. Again when the casting solvent is selective for PEO, a sharp endothermic peak, attributed to the melting of the crystalline domains (PEO), can be observed. If the casting solvent is a good solvent for both components, no endotherms are evident (*Figure 7a*). The observed shift towards lower temperatures and broadening of the glass transition of the PS-rich phase

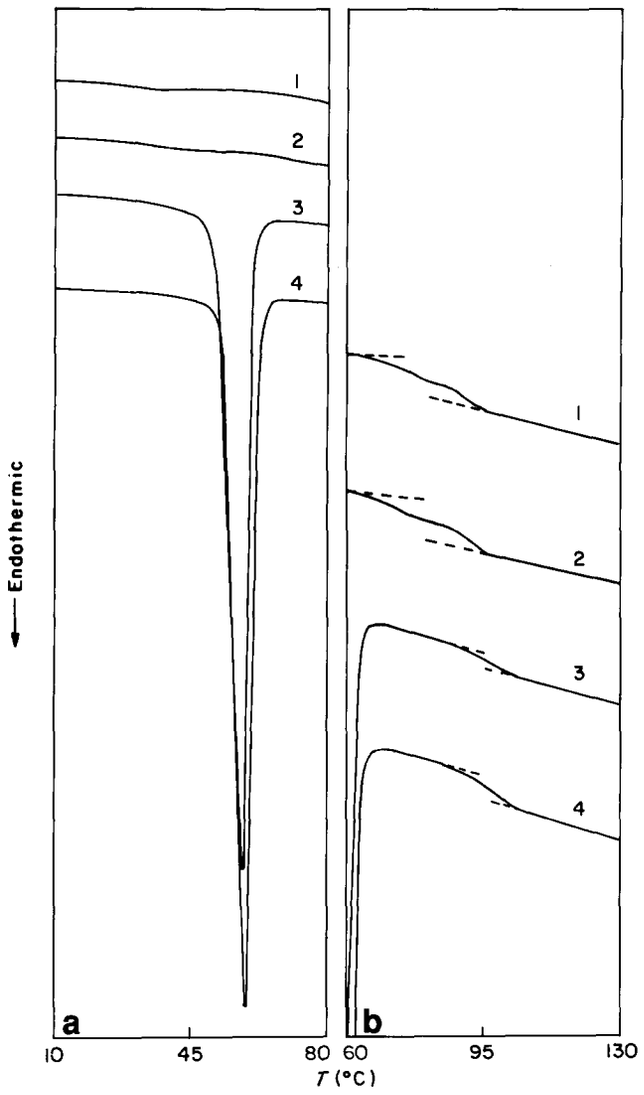

Figure 7 D.s.c. thermograms of PEO-b-PS-b-PEO triblock copolymer films cast from various solvents: (1) THF; (2) benzene; (3) acetone; (4) benzene–methanol. Thermal history as in *Table 3*; (a), (b) as in *Figure 2*

Table 3 Characteristics as in *Table 1* but with different thermal history[a]

Casting	PEO-rich phase		PS-rich phase		
solvent	T_m (°C)	X_c (%)	$T_{g,ons}$	T_g	ΔT_g (°C)
Acetone	58	68.2	91	98	13
Benzene–methanol	59	71.0	90	96	13
Benzene	–	–	65	84	30
THF	–	–	64	80	29

[a] 135°C (15 min) → 83°C (288 h) → 25°C (100 h) → 140°C → 25°C (450 h)

(*Figure 7b*) is in satisfactory agreement with the conclusion from the investigation of the relaxation parameters (i.e. T_{ons}, T_{max}, $T_{max} - T_{ons}$). Comparison of *Tables 1* and *3* shows that $T_{g,ons}$ has been shifted by about 36°C, while ΔT_g, a measure of the width of the T_g region, is now 17°C broader than for the untreated samples.

The following interpretation may be proposed to account for the strong reduction of the degree of crystallinity in the PEO-rich phase and the lowering of the T_g region of the PS-rich phase. During annealing at a temperature T_a higher than T_m of PEO and near T_g of PS, the molten crystalline component diffuses into the PS domains, leading to partial mixing at their interface. This is supported by the reduction and broadening of T_g of the PS-rich phase (see *Table 3*). This diffusion is probably enhanced by the fact that the PS-rich phase is in a non-equilibrium state providing higher free volume. Annealing at temperatures higher than T_g of PS must be carried out to confirm this assumption. This phenomenon occurs only when the casting is performed from a good solvent for both components. In this case, better intermingling of microdomains occurs, leading to favourable conditions for partial mixing upon annealing. An interesting consequence of this effect is that after prolonged annealing, crystallization of the PEO component is entirely inhibited.

It may be objected against these interpretations that chemical modifications may occur in the PEO during annealing. However, this hypothesis cannot be valid, since the same phenomena should occur regardless of the casting solvent.

Finally it seems that further work is needed to elucidate fully the origin of this behaviour, i.e. crystallinity elimination, since analogous phenomena have not been observed in the case of miscible polymer blends of PEO with other glassy polymers, e.g. PMMA[16].

ACKNOWLEDGEMENTS

This research project was carried out within the frame of the 'SCIENCE' programme sponsored by the European Community (ST2J-0035). The authors are greatly indebted to Prof. N. Kalfoglou for useful discussions and to Mrs Sabine Graff for technical assistance and development of the optical micrographs.

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