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THERMALLY INDUCED PHASE SEPARATION IN POLY(STYRENE-CO-PARA(ORTHO)-BROMOSTYRENE)-PPO AND PS BLENDS

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ABSTRACT

Thermally induced phase separation in the initially compatible blends of poly(styrene-co-para-bromostyrene), poly(S-co-p-BrS), and poly(styrene-co-ortho-bromostyrene), poly(S-co-o-BrS), with PPO and with PS was studied by DSC. It was found that the blends of PPO with copolymers containing 47 mole % or less of o-BrS have shown no phase separation after annealing at temperatures up to 573 K. By annealing PPO blends with copolymers containing p-BrS, phase separation for the blends containing 54 mole % or more of p-BrS was observed. Initially compatible PS-poly(S-co-p-BrS) (18 mole % of p-BrS or less) and PS-poly(S-co-o-BrS) (36 mole % of o-BrS or less) have shown no phase separation after annealing at temperatures up to 573 K.

INTRODUCTION

In previous publications (ref. 1, 2) the phase separation behaviour of initially compatible blends of PPO with some fluoro and chloro substituted styrene derivatives, as well as the phase separation of PS-poly(o-ClS-co-p-ClS) was discussed (ref. 3). It was found that these systems show LCST's at higher temperatures. This behaviour has also been shown experimentally in other systems (ref. 4) and theoretically predicted (ref. 5, 6). One of the principal conclusions is the possibility of a miscibility "window" arising from a "repulsion effect" (ref. 5) and the fact that high temperature phase separation with concommitant LCST's arises as a result of a destabilizing effect of the compressibility in polymer-polymer systems (ref. 5, 6).

EXPERIMENTAL SECTION

Materials

All copolymers were prepared by free radical polymerization in toluene. A high molecular weight product of atactic structure was obtained. To

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prevent copolymer composition drift the polymerization was stopped at a conversion below 50%. The copolymer compositions were determined by bromine and IR analysis. Molecular weights were obtained by GPC at room temperature in THF.

PPO, General Electric Co. (Mw=35,000 and Mn=17,000) was purified before use by dissolution in toluene and precipitated from methanol before use.

PS, Monsanto Co. (Mw=280,000 and Mn=120,000) was purified before use in the same manner as PPO.

Polymer blends were prepared by coprecipitation of PPO or PS with copolymers from toluene solution in methanol as nonsolvent. Films for DSC measurements were compression molded from the vacuum dried powders at the temperature of 473 K and the pressure of $1,4\times10^{5}$ kPa.

METHODS

DSC experiments were conducted using a Perkin Elmer model DSC-2. Sample size was approximately 20 mg; a heating rate of 20K/min was employed.

TG data were performed using a Perkin Elmer model TGS-2. Sample size was about 4 mg;a heating rate of 10K/min was applied.

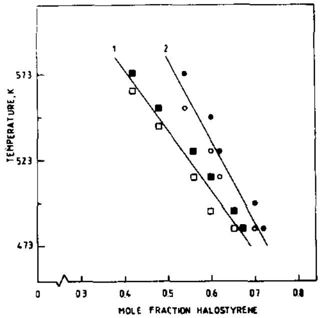
RESULTS AND DISCUSSION

PPO/Poly(S-co-p(o)-BrS) Blends

Annealing experiments were carried out directly in DSC (ref. 3) using samples having thermal histories that were essentially identical. Annealing the compatible blends of poly(S-co-o-BrS) with PPO at elevated temperatures led to phase separation at 528 K for the blend containing 47 mole % or more of o-BrS. Other blends of PPO with copolymers containing p-BrS showed a somewhat different behaviour. By annealing these samples at 528 K phase separation for the blends containing 54 mole % or more of p-BrS was observed (Fig. 2).

In both cases the samples with higher styrene content in the copolymer are compatible with PPO even at 573 K. This is expected in the light of the PS compatibility with PPO.

Further insight into the thermal behaviour of poly(S-co-o-BrS) blends can be gained by an examination of Fig. 2 which shows the phase diagram



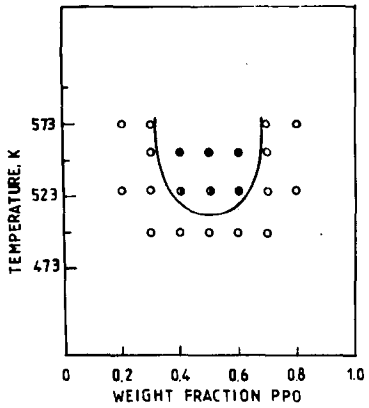


Fig. Diagram showing compatibility 50/50 weight % blends of PPO with poly(S-co-o-BrS) (curve 1) and with poly(S-co-p-BrS) (curve 2): ○ and □, one phase; ● and ■, two phase.

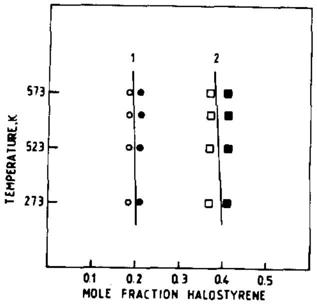
Fig. 2. Phase diagram form PPO/poly(S-co-o-BrS) blends containing 47 mole % o-BrS with different PPO weight %: ○ , one phase; ● , two phase; ◐, intermediate situation.

for the blend containing the copolymer of 47 mole % of o-BrS as a function of PPO content. Otherwise PPO/poly(S-co-p-BrS) blend of 47 mole % of p-BrS content is stable at a temperature of 573 K independent of blend composition.

From this data it is also clear that the curve representing the boundary of the compatibility-incompatibility region shown in the Fig. 1 also corresponds to, approximately, the locus of the LCST for the system indicated.

PS/poly(S-co-p(o)-BrS) Blends

It was found that the copolymer containing 18 mole % or less of p-BrS in the copolymers are compatible with PS. For the PS/poly(S-co-o-BrS) blends the compatibility was found in the mixture with 36 mole % or less of o-BrS in the copolymer. The results of the annealing experiments are shown in Fig. 3. Both systems are stable at the annealing temperatures up to 573 K. The influence of the blend composition on the compatibility in these system was also investigated at temperature up to 573 K. Independent on blend composition one phase was observed (Fig. 4).



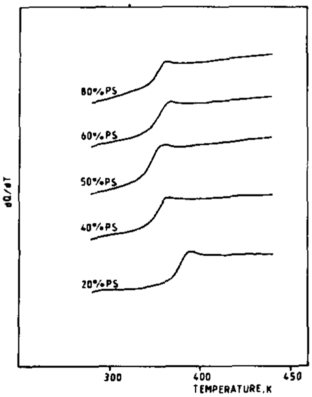


Fig. 3. Phase separation behaviour of 50/50 weight % blends of PS with poly(S-co-p-BrS) (curve 1) and poly(S-co-o-BrS) (curve 2): ○ and □, one phase; ● and ■, two phase.

Fig. 4. DSC thermograms of PS/poly(S-co-o-BrS) containing 36 mole % o-BrS with different PS weight %, annealed 15 min at 573 K.

From TG data and intrinsic viscosities measured it was concluded that the thermal degradation was not an important factor in this study.

The behaviour of the blends studied in the present work demonstrates again the effect of relatively small structure changes on miscibility in polymers. The obtained results concerning PPO blends are explained on the basis of first-order mean field theory (ref. 5).

PS/copolymer blend behaiour obtained in the present study shows that o-BrS and p-BrS in the copolymer with styrene exibit quite oposite behaviour in the blends with PS than in blends PPO/copolymer systems. The same theory (ref. 5) could also be applied to explain these results.

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