Compatibility of poly(*p*-fluorostyrene-co-*o*-fluorostyrene) with poly(2,6-dimethyl-1,4-phenylene oxide) and polystyrene

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The compatibility of blends prepared from random copolymers of *p*-fluorostyrene and *o*-fluorostyrene with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and blends of the copolymers with polystyrene (PS) has been examined using differential scanning calorimetry. It was found that compatibility in these systems depends on copolymer composition: copolymers containing from 10 to 38% of *p*-fluorostyrene are miscible with PPO in all proportions. The thermally induced phase separation in these systems was also studied and the existence of lower critical solution temperatures (LCST) was established for all compatible blends. The copolymers were found to be incompatible with PS regardless of composition.

Keywords Polymer compatibility; PPO blends; PS blends; thermogravimetry; differential scanning calorimetry

INTRODUCTION

In previous publications, the compatibility and phase separation behaviour of blends of polystyrene, chloro- and fluoro-substituted styrenes and PPO were investigated[1,2]. In these studies it was shown that PS and PPO are compatible on the segmental level[1]. Miscibility of copolymers of styrene and *p*-chlorostyrene with PPO depends on copolymer compositions as well as on the position of the substituent chlorine. Poly(*p*-chlorostyrene) (P*p*ClS) and poly(*o*-chlorostyrene) (P*o*ClS) are both immiscible with PPO[1]. At the same time P*o*ClS is compatible with PS in certain molecular weight ranges[3]; recently it was found that homopolymers of *p*-fluorostyrene (P*p*FS) and *o*-fluorostyrene (P*o*FS) are incompatible with PPO and PS. However, it was found that copolymers of styrene and *p*-fluorostyrene and copolymers of styrene and *o*-fluorostyrene containing approximately equal molar fractions of the respective monomers were compatible with PPO[4]. The compatibility of copolymers of *p*-chlorostyrene and *o*-chlorostyrene with PPO and PS has also been studied[1,2,5]. Copolymers of *p*- and *o*-chlorostyrene, containing from 23 to 64% of the *para* monomer, are miscible with PPO in all proportions. All compatible blends studied exhibit phase separation upon annealing at elevated temperatures, indicating that a lower critical solution temperature (LCST) must exist[6]. Such behaviour has been observed for several miscible polymer blend systems[7-13]. This paper describes the preparation of copolymers of *p*- and *o*-fluorostyrene and the results of a study of their compatibility with PPO and PS and of the thermally induced phase separation in these systems.

EXPERIMENTAL

Materials

The free radical polymerization of *ortho* and *para*-fluorostyrene was carried out at 60° ± 1°C in toluene solution, using azobisisobutyronitrile (AIBN) as initiator. The respective monomers (Columbia Chemical Co.) were purified prior to polymerization in the usual manner[4]. The initiator and toluene concentrations were chosen so that $\bar{M}_w$ of the samples would be greater than 100 000. The reactions were stopped at 50–60% conversion in order to limit copolymer composition drift. The polymers obtained were purified by precipitation from toluene solution into a large excess of methanol, and then dried at 80°C *in vacuo*. P*p*FS and P*o*FS were prepared using the same procedure. Copolymer compositions were determined by quantitative infra-red analysis of CCl_4 solutions on a Perkin-Elmer Model 283 Infrared Spectrophotometer using selected absorbance peaks. The copolymers will hereafter be designated by the abbreviation PO *n*, where *n* is the measured mole fraction of *p*-fluorostryene in the structure. Copolymer compositions as a function of monomer feed ratio are shown in *Figure 1*. The results indicate approximately random copolymerization with a small drift toward alternating behaviour. Reactivity ratios were determined using the Fineman–Ross equation[14]. For the copolymer pairs, *p*-fluorostyrene (r_1) and *o*-fluorostyrene (r_2), the values $r_1 = 0.55$, and $r_2 = 0.80$, were obtained. Molecular weights and molecular weight distributions for the copolymers were determined by g.p.c. at 25°C in tetrahydrofuran. Characterization of the synthesized polymers and copolymers is presented in *Table 1*.

PPO used was supplied by the General Electric Co., and had $\bar{M}_w = 35\,000$ and $\bar{M}_n = 17\,000$. Before use,

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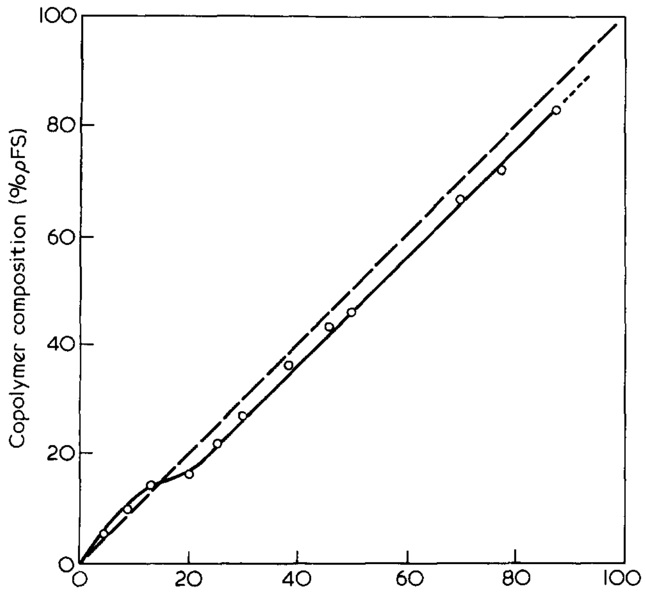

Figure 1 Copolymer composition *versus* feed composition

Table 1

Sample*	T_g (°C)	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
PO 5		120	63	1.89
PO 10		131	64	2.03
PO 14		112	57	1.95
PO 16	96	168	91	1.84
PO 23	96	161	85	1.89
PO 29	97	167	90	1.80
PO 38	98	160	80	1.99
PO 43	99	162	82	1.96
PO 46	99	164	88	1.87
PO 56	101	161	85	1.62
PO 66	103	151	77	1.97
PO 71	103	134	70	1.91
PO 81	104	137	73	1.86
PpFS	106	127	66	1.90
PoFS	96	121	62	1.93
PS	101	–	200	–
PPO	218	35	17	2.06

* Numbers indicate mole fraction *p*-fluorostyrene in the respective copolymers

the polymer was purified by precipitating with methanol from a toluene solution and was then dried at 80°C *in vacuo*.

Atactic polystyrene (Monsanto Co.), $\bar{M}_n = 200\,000$, was purified in the same manner as PPO.

Film preparation

Polymer blends were prepared by dissolving appropriate quantities of the pure components in toluene and precipitating the solution into a large excess of methanol. Blends were dried at 80°C *in vacuo* for ~60 h. Films were obtained by compression moulding of the dried blends. All pure components except PPO were moulded at 180°C; PPO was moulded at 270°C. The moulding temperature for the blends with PPO was 215°C, while the blends with PS were moulded at 180°C. The film thickness (~0.3 mm) was regulated by using steel plates with spacers. Pre-heating time was one minute and subsequently a pressure of 20000 psi was applied for different lengths of time depending on blend composition. With the given thermal histories, it was found that the results reported below are unchanged by longer equilibration times.

Measurements

Differential scanning calorimetry was used to determine blend compatibility. It was found that for the comparatively high molecular weight polymers used in this study there was a good correlation between the d.s.c. results and film clarity. All differential scanning calorimetry (Perkin-Elmer DSC-2) was done using a heating rate of 20°C min^{-1} with sample sizes of 15–20 mg. The glass transition(s) was (were) the only distinctive feature(s) of the d.s.c. thermograms.

RESULTS AND DISCUSSIONS

Differential scanning calorimetry

The usual criterion of polymer compatibility employed was the detection of one or two glass transition regions using the d.s.c. technique. In a previous publication incompatibility of PpFS and PoFS with PPO and with PS had been reported[4]. Independent of blend compositions, two glass transitions were found, each closely corresponding to those of pure constituents. In this study, it was found that d.s.c. thermograms of 50/50 wt% blends of PPO and poly(*p*-fluorostyrene-co-*o*-fluorostyrene) containing from 10 to 38% *p*FS in the copolymer show one T_g, see *Figure 2*. Blends of PPO with all other copolymers (PO 5, PO 43, PO 46, PO 56, PO 66, PO 71, PO 81) exhibited two glass transitions, see *Figure 3*. However, some intermediate behaviour is also observed. Thus, although the PPO blends with PO 10 and PO 38 exhibit only one resolvable T_g, the temperature of the latter is low compared to the value anticipated in a truly compatible blend. This would imply that for the particular thermal histories imparted to the system,

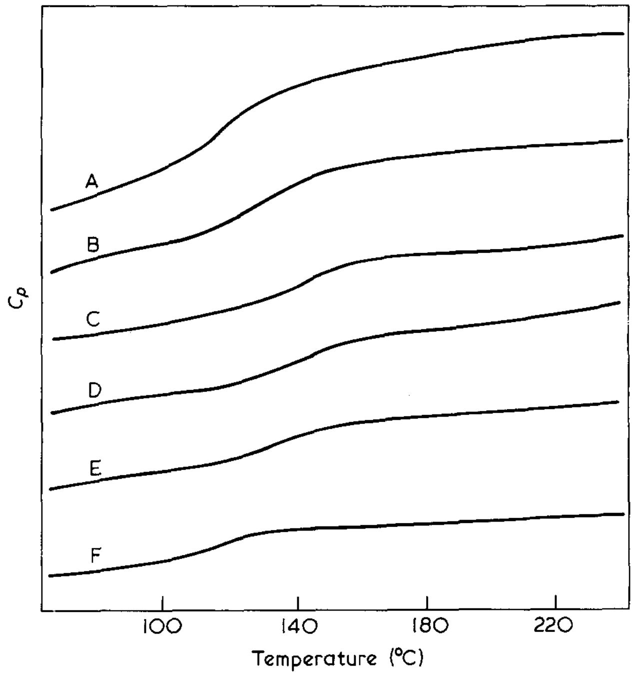

Figure 2 D.s.c. thermograms of PO–PPO compatible blends. (A) PO 10; (B) PO 14; (C) PO 16; (D) PO 23; (E) PO 29; (F) PO 38

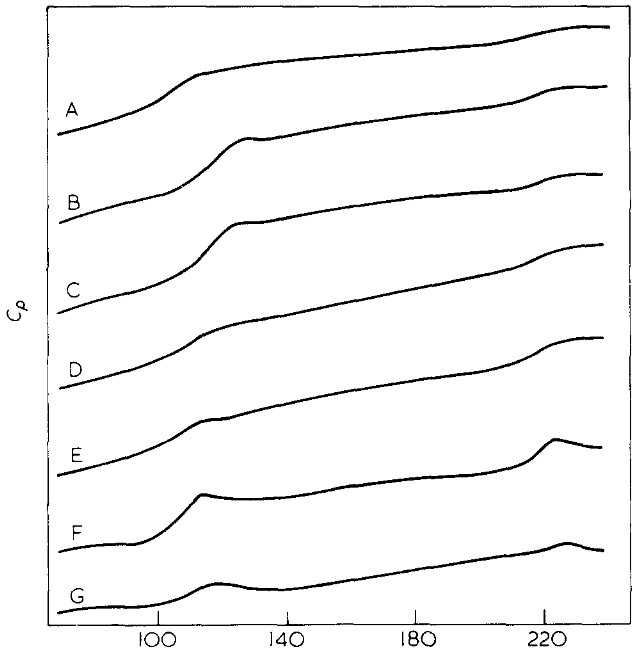

Figure 3 D.s.c. thermograms of PO–PPO incompatible blends. (A) PO 5; (B) PO 43; (C) PO 46; (D) PO 56; (E) PO 66; (F) PO 71; (G) PO 81

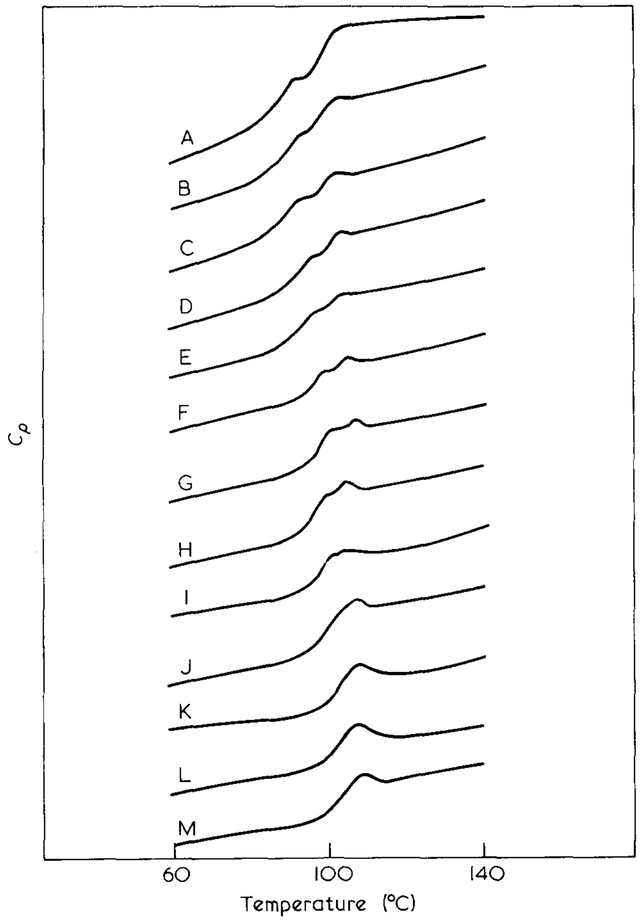

Figure 4 D.s.c. thermograms of 50/50 wt.% PO–PS blends. (A) PO 5–PS; (B) PO 10–PS; (C) PO 14–PS; (D) PO 16–PS; (E) PO 23–PS; (F) PO 29–PS; (G) PO 38–PS; (H) PO 43–PS; (I) PO 46–PS; (J) PO 56–PS; (K) PO 66–PS; (L) PO 71–PS; (M) PO 81–PS

compatibility is barely achieved. Similarly, (*Figure 3*), the blends containing PO 43 and PO 46 show a slight elevation of the lower T_g compared to the values expected for strict incompatibility. These results demonstrate that the single T_g criterion is insufficient for an absolute designation of compatibility in border-line cases.

Blends of PO copolymers and PS show either one or two T_g's. This data is shown in *Figure 4*. The almost linear upward trend in the T_g's of the pure copolymers containing from 5 to 46 mole per cent *p*FS is clearly indicated. Thermograms of blends of PS with PO copolymers containing the higher contents of *p*FS copolymers (PO 56, PO 66, PO 71 and PO 81) show one T_g, possibly because the T_g's of the pure copolymers and polystyrene are very close. It will be necessary to examine these results using other techniques. It is important to note that all the copolymers used in this study have nearly equal molecular weights (*Table 1*). This implies that the present results reflect true copolymer composition dependent effects.

In general, comparing the results of d.s.c. measurements and visual observations of film clarity showed a good correlation. Blends exhibiting one T_g were transparent; blends with two T_g's had a waxy or opaque appearance.

Thermally induced phase separation

Blends of PO copolymers and PPO contain one or two phases depending on the copolymer composition. Current theories predict that polymer–polymer blends which are miscible at lower temperatures are likely to exhibit phase separation at higher temperatures[15–17]. From this point of view it was interesting to analyse the behaviour of compatible PO–PPO blends as a function of temperature. The experiments were carried out in the d.s.c. using samples with initially identical thermal histories. In these experiments, samples were heated at 320°C min^{-1} to a selected annealing temperature. Samples were then annealed for 15 min. Experiments showed equilibrium had been substantially achieved with these times. (For sample PO29, phase separation was also tried at a shorter annealing time of 5 min with identical results.) After annealing, the films were cooled to ambient temperature at 320°C min^{-1}. The annealed blends were then analysed for T_g's at a 20°C min^{-1} heating rate. The influence of annealing temperature on 50/50 wt% PO 16–PPO blends is shown in *Figure 5*. The reference sample showing a single T_g (134°C), prepared at 210°C, is also indicated. Samples annealed at 255°C showed a broadened T_g transition at a slightly reduced value, ~127°C. Samples annealed at 280°C exhibited two well resolved glass transitions at 117° and 200°C. Samples annealed at 305°C showed two glass transitions with further slight changes to 109° and 192°C. However, T_g values observed for the annealed blend samples did not correspond precisely to those of the pure polymers, 96° and 218°C, respectively. Other compatible blends were analysed using the same procedure. Phase separation was exhibited in all these blends but the lowest annealing temperature at which the phase separation appears depends on the copolymer composition. This data is shown in *Figure 6*. The effect of the blend composition at the phase separation during the annealing was analysed in the PO 29–PPO system shown in *Figure 7*. For the blends containing 80% of either component, it was difficult to observe the individual transition temperatures. This data

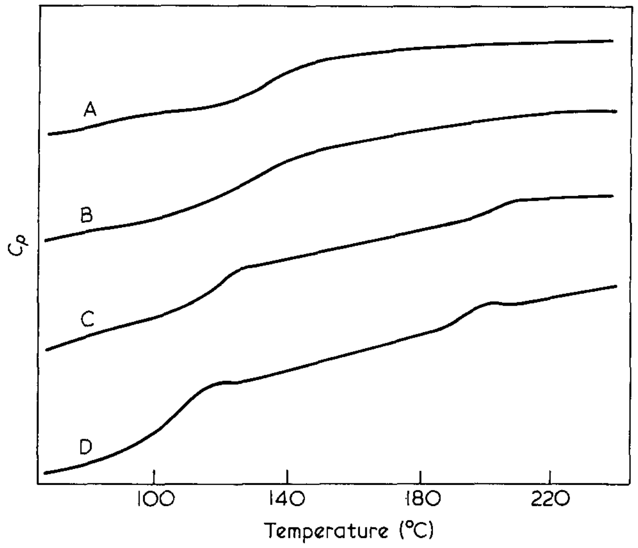

Figure 5 D.s.c. thermograms illustrating phase separation. 50/50 PO 16–PPO blends. (A) As moulded, 210°C; (B) annealed 15 min, 255°C; (C) annealed 15 min, 280°C; (D) annealed 15 min, 305°C

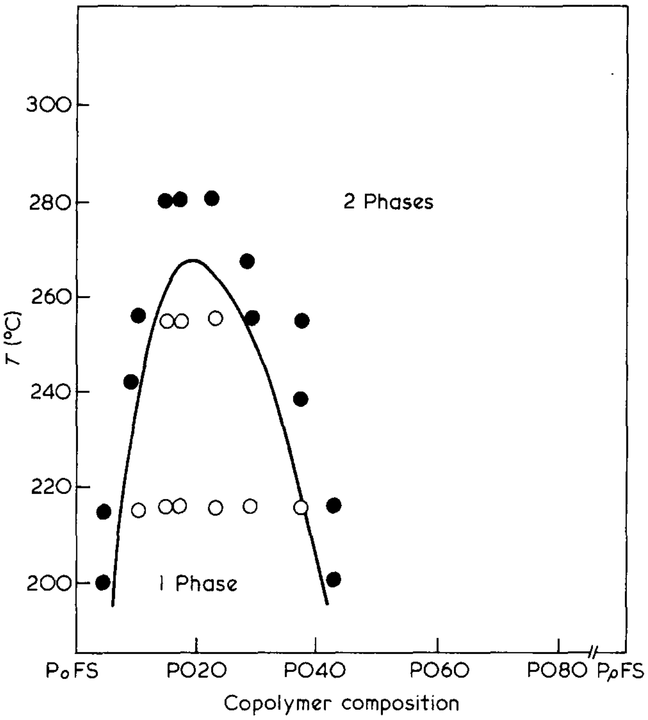

Figure 6 Compatibility–incompatibility transition for 50/50 wt.% PO–PPO blends as a function of copolymer composition

permitted the construction of the phase diagram for the system as shown in *Figure 7*. It is thus clear that the curve representing the boundary of the compatibility–incompatibility regimes in *Figure 6* also corresponds approximately to the locus of the lower critical solution temperatures (LCSTs) for the systems indicated.

The results show that the maximum compatibility with PPO occurs with copolymers containing approximately 20% *p*FS. The maximum compatibility in the case of blends of chlorinated *para-ortho* copolymers with PPO was found in copolymer compositions of between 36 and 40% *p*-chlorostyrene. In both the chlorinated and fluorinated copolymers, compatibility with PPO is better when the content of *ortho* halogenated styrene in the copolymer is greater than 50%.

In the literature the evidence is shown that for several systems the thermally induced phase separation is easily reversed during the annealing of the blend below the respective LCST. From data shown in *Figure 8*, PO 16– and PO 23–PPO blends show this type of behaviour.

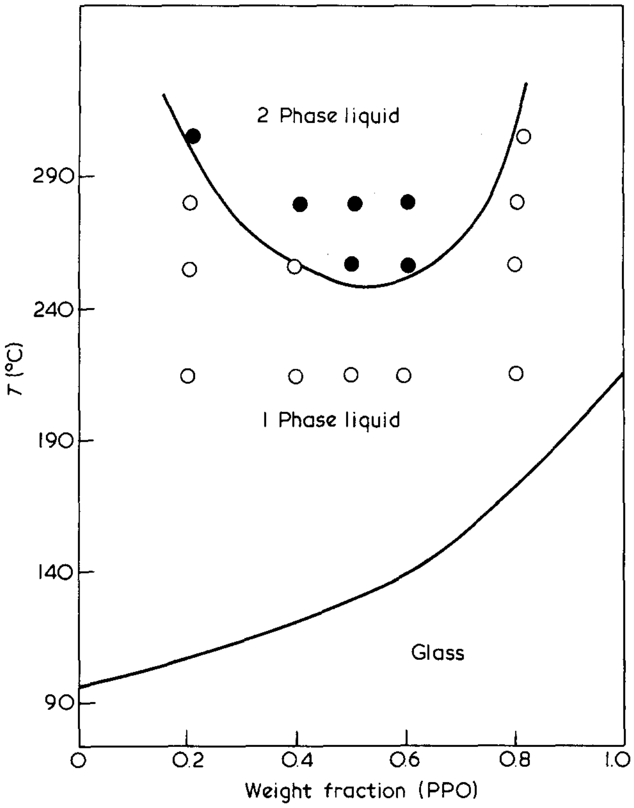

Figure 7 Phase diagram of PO 29–PPO blends

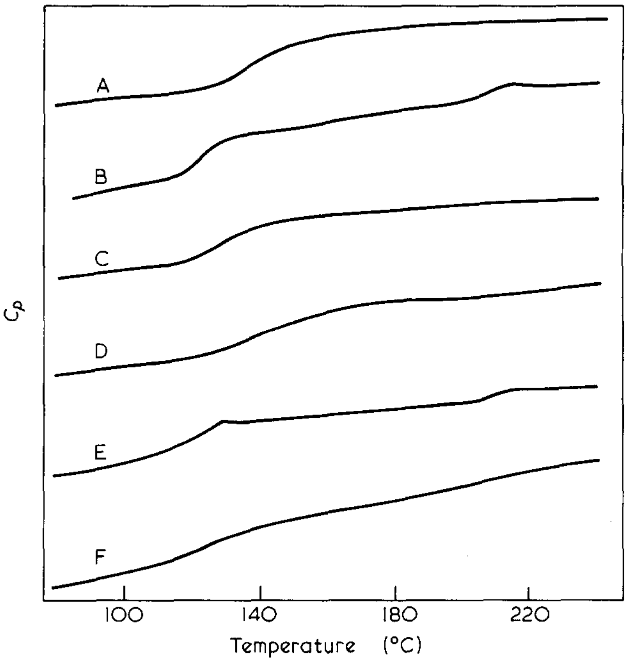

Figure 8 D.s.c. thermograms illustrating that phase separation on heating is reversed on cooling. 50/50, PO 16–PPO blends; (A) as moulded, 210°C; (B) annealed 15 min, 280°C; (C) sample B after cooling over night. 50/50 PO 23–PPO blends; (D) as moulded, 210°C; (E) annealed 15 min, 280°C; (F) sample E after cooling overnight

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