

Compatibility of Some Fluorosubstituted Styrene Polymers and Copolymers in Blends with Poly(2,6-Dimethyl-1,4-Phenylene Oxide) and with Polystyrene

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Synopsis

Blends of poly(*p*-fluorostyrene) (PpFS), poly(*o*-fluorostyrene) (PoFS), poly(styrene-co-*p*-fluorostyrene) (SP46), poly(styrene-co-*o*-fluorostyrene) (SO49), with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and with polystyrene (PS), have been prepared by compression molding of coprecipitated polymers. Compatibility of these systems has been studied by differential scanning calorimetry. Detection of one or two glass transition regions was used to classify the blends as compatible or incompatible. Homopolymers of pFS and oFS were found to be incompatible with PPO and PS. The SP46 copolymer and SO49 copolymer were compatible with PPO in all proportions.

INTRODUCTION

The compatibility of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polystyrene (PS) has been the subject of many investigations. Using a variety of techniques, it was found that PS and PPO are miscible at all blend compositions.¹⁻⁸ Further, compatibility studies of chlorinated polystyrene derivatives with PPO and PS have also been reported.^{5,8-10} It was found that miscibility depends on the copolymer compositions, molecular weight, and the position of the substituent chlorine. Shultz and Beach,⁹ as well as Fried,⁵ have found that styrene-*p*-chlorostyrene random copolymer with a relatively high content of *p*-chlorostyrene itself is incompatible with PPO and PS. Recently it was found in these laboratories that poly(*o*-chlorostyrene) is compatible with PS.¹⁰ Consequently, it is of interest to investigate the behavior of the corresponding fluorinated compounds. This paper describes the preparation and analysis of *p*-fluoro- and *o*-fluorostyrene homopolymers and poly(styrene-co-*p*-fluorostyrene) containing 46 mol % of pFS (SP46) and poly(styrene-co-*o*-fluorostyrene) with 49 mol % of oFS (SO49) and the compatibility of these systems with PPO and with PS.

EXPERIMENTAL

Materials

PPO was obtained from the General Electric Co. and was purified by filtration of a dilute solution in toluene prior to precipitation with a large excess of meth-

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anol (15:1). It had \overline{M}_w of 35,000 and \overline{M}_n of 17,000. Polystyrene (Monsanto Co.), \overline{M}_v of 200,000, was purified in the same manner as PPO. Monomers for polymerization were styrene (Eastman Co.), and *p*-fluorostyrene and *o*-fluorostyrene (Columbia Chemical Co.). These were purified prior to polymerization by washing with 10% aqueous solution of sodium hydroxide and after that were distilled under vacuum.

The initiator 2,2'-azobisisobutyronitrile (AIBN) (Polysciences) was purified by crystallization from methanol. Spectral grade toluene (Eastman Co.) was used as solvent in a free radical polymerization without further purification.

All homopolymers and random copolymers were prepared by free radical polymerization at 60°C in toluene solution with AIBN as the initiator. Polymers were purified by dissolution in toluene and precipitation in methanol. Samples were then dried in vacuum at 80°C to constant weight. Conversion was held to approximately 60%. Molecular weights were obtained by GPC in THF at 25°C. Data on the synthesized polymers are presented in Table I. Copolymer compositions were obtained by fluorine analysis.

Polmer blends were prepared by dissolving the respective components in toluene and precipitating into a large excess of methanol. The resulting precipitates were filtered and dried at 80°C under vacuum to constant weight (60 h).

Measurements

Films of both pure components and blends were prepared by compression molding of the precipitated powders between aluminum foil in a hydraulic press. Samples were in the press approximately 1 min at selected temperatures without pressure and about 30 s under a pressure of 20,000 psi. Samples were subsequently cooled under nitrogen to ambient temperatures. The molding temperatures were in the range from 180°C to 210°C depending on the homopolymer and blend compositions. Thickness of the films was approximately 0.3 mm. DSC measurements were made on a Perkin-Elmer Differential Scanning Calorimeter, Model DSC-2, at a heating rate of 20°C/min. Samples weighed between 15 and 20 mg. The glass transition temperature T_g was taken as the temperature at which the measured C_p was halfway between the C_p of the glass and liquid states.

TABLE I

Sample	T_g (°C)	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
PpFS	106	127	66	1.90
PoFS	96	121	62	1.93
PoFS	96	265	129	2.00
SP46 ^a	103	99	57	1.93
SO49 ^a	98	114	593	1.92
PS	101			
PPO	218			

^a Numbers indicate mole fraction of *p*-fluorostyrene or *o*-fluorostyrene in the corresponding copolymer.

RESULTS AND DISCUSSION

Films of unblended PS, as well as of PoFS, SP46, and SO49 molded at 180°C were clear and colorless. Films of unblended PPO prepared at 270°C were somewhat yellowish and transparent. T_g values for all are listed in Table I. Substitution of fluorine atoms in the ortho position in polystyrene reduced the T_g , while parasubstitution raised T_g . In the case of PpFS, our data are consistent with the literature.^{11,12} For PoFS we found that the data in the literature vary.^{13,14} A sample of PoFS with higher molecular weight ($\overline{M}_w = 2.6 \times 10^5$; $\overline{M}_n = 1.3 \times 10^5$) had an identical value for T_g (see Table I). Other workers have found that T_g for poly(*m*-chlorostyrene) is lower than that of the parent polystyrene.¹¹

Blends with compositions of 20%, 40%, 50%, 60%, and 80% by weight were prepared with PPO and the respective homopolymers and copolymers by molding the coprecipitated powders at 215°C. The films of PPO-PpFS and of PPO-PoFS were opaque with a yellowish tint. In these blends two glass transitions are present, each corresponding to the constituent homopolymers. Figure 1 shows DSC thermograms of PoFs-PPO blends. From this data it is apparent that complete substitution with fluorine at the ortho position in polystyrene yields a polymer incompatible with PPO. The same was found for blends of PpFS and PPO. The same behavior is reported for the corresponding chlorinated compounds⁵ at high molecular weights.

The blends of PPO and the copolymer SP46, and of PPO and SO49 prepared at the same conditions, were transparent and yellowish. A single glass transition temperature for each copolymer-PPO blend is noted with the transition temperature increasing monotonically with increasing PPO content. In Figure 2

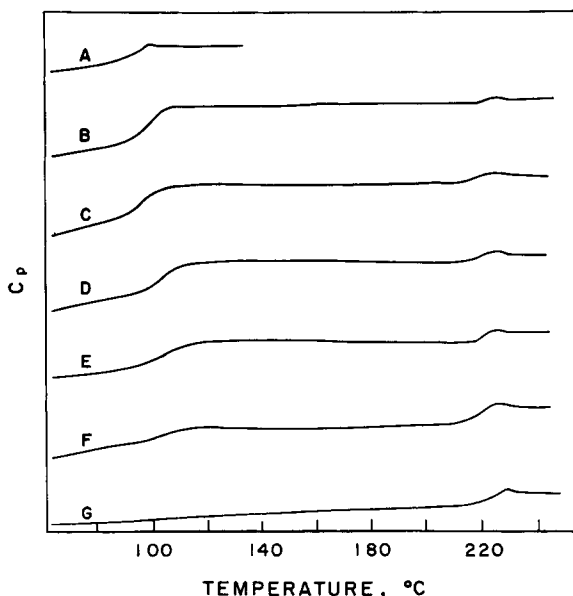


Fig. 1. DSC thermograms of PoFS, PPO, and blends: (A) PoFS; (B) 20% PPO; (C) 40% PPO; (D) 50% PPO; (E) 60% PPO; (F) 80% PPO; (G) PPO.

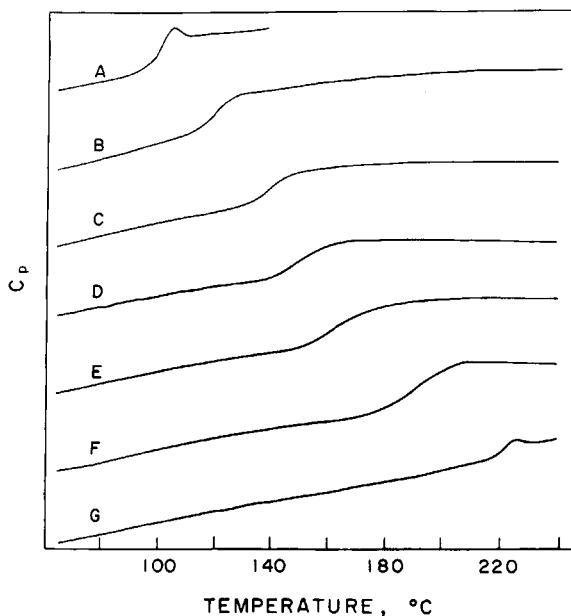


Fig. 2. DSC thermograms of SO49, PPO, and blends: (A) SO49; (B) 20% PPO; (C) 40% PPO; (D) 50% PPO; (E) 60% PPO; (F) 80% PPO; (G) PPO.

are shown DSC thermograms of SO49-PPO blends. Blends of SP46-PPO show similar behavior. The influence of blend composition on T_g for both SP and SO copolymers with PPO are shown. T_g of these blends is plotted in Figure 3. It is noteworthy that both copolymers cause almost an identical change of T_g when blended with PPO.

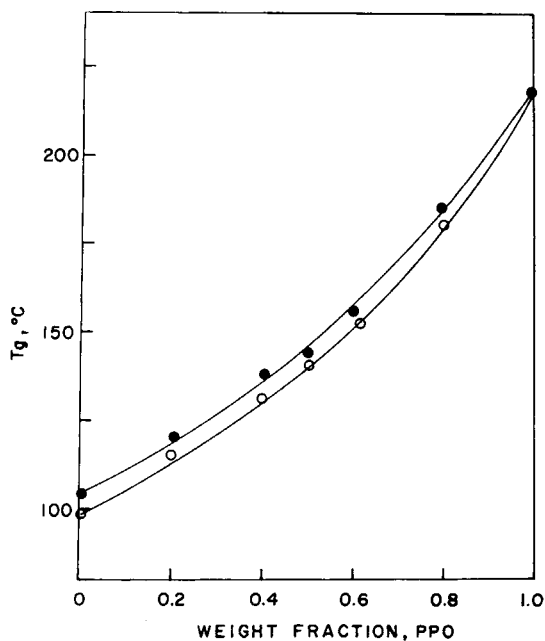


Fig. 3. T_g of SP46 and SO49 and PPO blends: (●) SP46-PPO blends; (○) SO49-PPO blends.

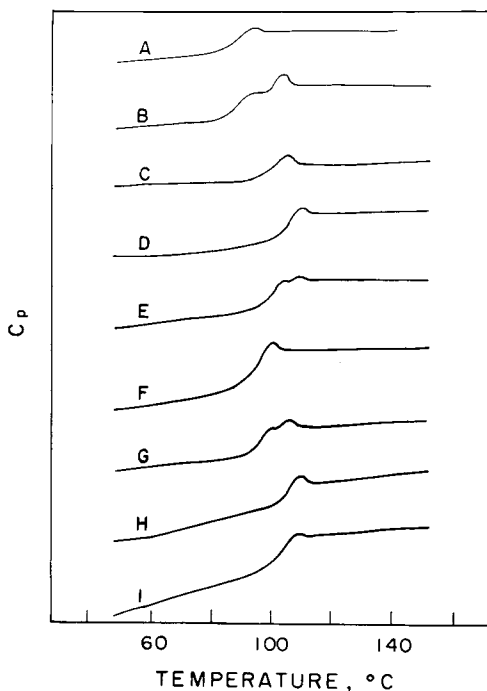


Fig. 4. DSC thermograms of PoFS, PpFS, SP46, SO49, PS, and blends, see text: (A) PoFS; (B) PoFS-PS; (C) PS; (D) PpFS; (E) PpPS-PS; (F) SO49; (G) SO49-PS; (H) SP46; (I) SP46-PS.

Blends of PS and PpFS, and of PS with PoFS, 50:50 wt %, were prepared by compression molding at 185°C. The resulting films were cloudy, and exhibited two glass transitions as is shown in Figure 4. A 50:50 wt % blend of SO49 and of SP46 with PS was prepared using the standard methods and a molding temperature of 185°C. The former system also exhibited two T_g 's (Fig. 4). Thermograms of PS and SP46 blends show one glass transition temperature. This single glass transition temperature may or may not be indicative of compatibility; the ambiguity is due to the very close T_g 's of the respective components. It is necessary to use additional analysis in order to draw definitive conclusions regarding the behavior of these systems.

Since our analysis made on 50:50 wt % blends of polystyrene or PPO with either homopolymer or approximately 50:50 random copolymers containing fluorine-substituted styrene show an interesting behavior, we consider it useful to make the analysis of blends containing different compositions and different contents of PPO and PS, respectively. Since already reported results show that PoFS and PpFS are incompatible with PPO and PS, we may expect to find a specific copolymer composition being the limit for the compatibility, as was found in the case of poly(styrene-co-*p*-chlorostyrene) blends with PPO.^{4,5}

CONCLUSIONS

- (1) Poly(*p*-fluorostyrene) and poly(*o*-fluorostyrene) are both incompatible with PPO and with PS.
- (2) The copolymer of styrene-*p*-fluorostyrene with 46% *p*-fluorostyrene content, and the copolymer of styrene and *o*-fluorostyrene with 49% *o*-fluo-

rostyrene content, are compatible with PPO in all proportions, as observed using the DSC method.

(3) Copolymers of styrene-*o*-fluorostyrene are incompatible with PS.

(4) Copolymers of styrene-*p*-fluorostyrene show one T_g , but additional proof is necessary to show that this is a compatible blend.

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