1983

Compatibility of Poly(2,6-Dimethyl-1,4-Phenylene Oxide)/Poly(fluorostyrene-Co-chlorostyrene) Blends

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Synopsis

The compatibility of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with random copolymers of *ortho*- and *para*-fluorostyrene as well as with *ortho*- and *para*-chlorostyrene of various copolymer compositions was examined. The compatibility was studied by DSC and visual observation of film clarity. It was found that copolymers of *ortho*-fluorostyrene with *para*-chlorostyrene containing 15–74 mol % *p*-ClS are compatible with PPO in all proportions. Compatibility of the PPO/poly(*ortho*-fluorostyrene-co-*ortho*-chlorostyrene) system was observed for copolymers containing between 15 and 36 mol % *ortho*-chlorostyrene. Copolymers of *para*-fluorostyrene with *para*-chlorostyrene, as well as copolymers of *para*-fluorostyrene with *ortho*-chlorostyrene appear to be incompatible with PPO at 210°C.

INTRODUCTION

Previous publications have shown that the compatibility of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blends with random copolymers of styrene and *ortho*-chlorostyrene (*o*-ClS) or *para*-chlorostyrene (*p*-ClS), depends on the copolymer composition as well as the position of the substitution on the aromatic ring.^{1–4} Similar results were found for the corresponding fluorinated copolymers in blends with PPO.^{5–8} It was also found that the compatibility of copolymers of *o*-ClS-co-*p*-ClS blended with PPO,⁹ as well as the compatibility of *ortho*-fluorostyrene-co-*para*-fluorostyrene (*o*-FS-co-*p*-FS) in blends with PPO^{8,10} depends on the copolymer composition. Additionally all homopolymers of chlorinated and fluorinated styrene were found to be incompatible with PPO in all proportions.^{2–6} To further analyze the behavior of blends which are compatible at the molding temperature (usually 210°C), these samples were annealed at temperatures up to 320°C.^{9–11} In these experiments, it was found that phase separation depended on the copolymer composition, the position of the substituted halogen, and the annealing temperature.

The compatibility of poly(*o*-ClS-co-*p*-ClS)/PPO and poly(*o*-FS-co-*p*-FS)/PPO seems rather unusual in light of the incompatibility of the corresponding

* Presented at the Macromolecular Symposium of the International Union of Pure and Applied Chemistry, July 12–16, 1982, Amherst, MA.

Fig. 1. Copolymer composition vs. feed composition for *o*-FS-co-*p*-ClS.

homopolymers in blends with PPO. However, similar behavior has been found for other polymer-polymer blends.¹²⁻¹⁴

Because of these observations we have extended our studies by preparing new copolymers of fluoro- and chlorostyrene with various copolymer compositions. In this paper we shall report the syntheses and behavior of the copolymers of *ortho*- and *para*-fluorostyrene with *ortho*- and *para*-chlorostyrene in blends with PPO. The compatibility has been studied by differential scanning calorimetry and by visual observations of film clarity. Thermal stability of the pure copolymers and blends was studied by thermogravimetric analysis.

EXPERIMENTAL

Polymerizations and Polymer Characterization

The procedure for the preparation of these new copolymers was identical with the methods employed in our previous publications.^{2,6,8} All copolymer samples were prepared by the solution polymerization of corresponding monomers in toluene at 60°C, using azobisisobutyronitrile (AIBN) as the free radical initiator. The resulting copolymers were purified by precipitation from toluene solution into a large excess of methanol. To avoid the variation of copolymer structure with conversion, all polymerizations were stopped at conversions less than 50%. To evaluate experimental drift of copolymer composition with conversion in the system *o*-FS-co-*p*-ClS, for example, samples were removed at various times from a batch containing from 10 mol % to 90% *o*-FS. At each conversion the composition of the copolymer was determined. By plotting copolymer composition as a function of conversion, a drift of 1.5% was found for conversion below 50%.

Fig. 2. Copolymer composition vs. feed composition for *o*-FS-co-*o*-ClS.

All other copolymer systems were evaluated in the same manner, and similar results were observed.

The copolymer compositions were determined by an empirical procedure using the ratios of infrared peak heights,^{5,9} using a Perkin-Elmer Model 580B Infrared Spectrophotometer. Since copolymer composition is an important factor in the investigation of blend compatibility, a potentiometric titration of fluorine was used as a second independent method. Good correlation with differences of less than 2% between the two methods was found.

The reactivity ratios were determined using the Fineman-Ross form of the instantaneous copolymerization equation.¹⁵ Figure 1 shows copolymer composition as a function of monomer feed ratio for the copolymers of *o*-FS with *p*-ClS, while Figure 2 is for the poly(*o*-FS-co-*o*-ClS) system. Similar curves were found for the poly(*p*-FS-co-*o*-ClS) and poly(*p*-FS-co-*p*-ClS) systems. Such curves are indicative of a nearly random copolymerization with slight alternating tendency which is somewhat higher in the poly(*p*-FS-co-*o*-ClS) and poly(*p*-FS-co-*p*-ClS) systems. The reactivity ratios listed in Table I show this tendency.

Molecular weights of the synthesized copolymers were determined by osmometry and light scattering methods. Number average molecular weights were determined by using a Knauer membrane osmometer, at 37°C, in toluene using Sartorius 11539 membranes. Weight average molecular weights were determined using a Chromatix KMX-6 laser photometer, at room temperature, with a field stop of 0.2 and an annulus of 6–7°. THF was used as the solvent. A Brice-Phoenix differential refractometer was used to determine dn/dc values in the same solvent, at 25°C. A summary of the molecular weight data for the copolymers of various compositions is listed in Tables II and III.

TABLE I
 Copolymerization Reactivity Ratios

Copolymer	m_1	m_2	r_1	r_2
Poly(<i>o</i> -FS-co- <i>p</i> -ClS)	<i>o</i> -FS	<i>p</i> -ClS	0.72	1.08
Poly(<i>o</i> -FS-co- <i>o</i> -ClS)	<i>o</i> -FS	<i>o</i> -ClS	0.58	0.70
Poly(<i>p</i> -FS-co- <i>o</i> -ClS)	<i>p</i> -FS	<i>o</i> -ClS	0.22	0.78
Poly(<i>p</i> -FS-co- <i>p</i> -ClS)	<i>p</i> -FS	<i>p</i> -ClS	0.44	0.70

Glass transition temperatures (T_g) for the pure component were measured on compression molded films using a Perkin-Elmer DSC-2, at heating rates of 20°C/min, with a sample size of ca. 20 mg. T_g was taken as the temperature at which the heat capacity reached one half of the entire step change as observed on the thermogram. Table IV lists the T_g values.

The pure copolymer and blend stabilities were also investigated by thermogravimetric analysis, using a Perkin-Elmer TGS-2 at a heating rate of 10°C/min under a nitrogen atmosphere.

The PPO used in this study was obtained from the General Electric Co. It was purified by dissolution in toluene and precipitation from an excess of methanol. Measurements of molecular weights by GPC at 25°C in THF gave values of $\overline{M}_w = 35,000$ and $\overline{M}_n = 17,000$.

Preparation of Blends and Films

All blends discussed in this work were prepared by coprecipitation from toluene solution. The desired quantities of the materials to be blended were dis-

 TABLE II
 Copolymer Compositions and Molecular Weight Values in Poly(*o*-FS-co-*p*-ClS) and Poly(*o*-FS-co-*o*-ClS) Systems

Sample ^a	Mol wt $\times 10^{-5}$		
	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
Poly(<i>o</i> -FS-0.90 <i>p</i> -ClS)	2.49	1.49	1.67
Poly(<i>o</i> -FS-0.82 <i>p</i> -ClS)	2.44	1.26	1.94
Poly(<i>o</i> -FS-0.74 <i>p</i> -ClS)	2.30	1.55	1.48
Poly(<i>o</i> -FS-0.62 <i>p</i> -ClS)	1.94	1.14	1.70
Poly(<i>o</i> -FS-0.55 <i>p</i> -ClS)	2.30	1.60	1.43
Poly(<i>o</i> -FS-0.40 <i>p</i> -ClS)	1.85	1.44	1.28
Poly(<i>o</i> -FS-0.35 <i>p</i> -ClS)	1.71	1.09	1.56
Poly(<i>o</i> -FS-0.25 <i>p</i> -ClS)	1.63	1.04	1.56
Poly(<i>o</i> -FS-0.15 <i>p</i> -ClS)	1.53	0.95	1.61
Poly(<i>o</i> -FS-0.86 <i>o</i> -ClS)	3.51	1.69	1.86
Poly(<i>o</i> -FS-0.79 <i>o</i> -ClS)	2.72	1.61	1.69
Poly(<i>o</i> -FS-0.67 <i>o</i> -ClS)	2.82	1.36	2.07
Poly(<i>o</i> -FS-0.61 <i>o</i> -ClS)	2.35	1.73	1.36
Poly(<i>o</i> -FS-0.56 <i>o</i> -ClS)	3.15	1.65	1.91
Poly(<i>o</i> -FS-0.45 <i>o</i> -ClS)	1.87	1.03	1.87
Poly(<i>o</i> -FS-0.36 <i>o</i> -ClS)	1.79	0.97	1.84
Poly(<i>o</i> -FS-0.27 <i>o</i> -ClS)	1.60	0.95	1.68
Poly(<i>o</i> -FS-0.15 <i>o</i> -ClS)	1.36	0.84	1.62

^a Numbers indicate mole fraction of *para*-chloro or *ortho*-chlorostyrene in the copolymer.

TABLE III
Copolymer Compositions and Molecular Weight Values in the Poly(*o*-FS-co-*p*-ClS) and Poly(*p*-FS-co-*o*-ClS) Systems

Sample ^a	Mol wt $\times 10^{-5}$		
	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
Poly(<i>o</i> -FS-0.89 <i>p</i> -ClS)	1.77	1.18	1.50
Poly(<i>o</i> -FS-0.74 <i>p</i> -ClS)	1.47	1.89	1.65
Poly(<i>o</i> -FS-0.66 <i>p</i> -ClS)	1.46	0.81	1.80
Poly(<i>o</i> -FS-0.64 <i>p</i> -ClS)	1.17	0.78	1.50
Poly(<i>o</i> -FS-0.58 <i>p</i> -ClS)	1.46	0.85	1.71
Poly(<i>o</i> -FS-0.53 <i>p</i> -ClS)	1.13	0.65	1.74
Poly(<i>o</i> -FS-0.41 <i>p</i> -ClS)	1.14	0.60	1.90
Poly(<i>o</i> -FS-0.30 <i>p</i> -ClS)	0.93	0.60	1.55
Poly(<i>o</i> -FS-0.18 <i>p</i> -ClS)	0.95	0.66	1.44
Poly(<i>o</i> -FS-0.84 <i>o</i> -ClS)	3.32	1.39	2.39
Poly(<i>o</i> -FS-0.78 <i>o</i> -ClS)	3.51	1.43	2.45
Poly(<i>o</i> -FS-0.71 <i>o</i> -ClS)	2.67	1.71	1.56
Poly(<i>o</i> -FS-0.65 <i>o</i> -ClS)	2.14	1.50	1.43
Poly(<i>o</i> -FS-0.55 <i>o</i> -ClS)	1.90	1.03	1.84
Poly(<i>o</i> -FS-0.47 <i>o</i> -ClS)	1.73	0.98	1.75
Poly(<i>o</i> -FS-0.38 <i>o</i> -ClS)	1.32	0.89	1.49
Poly(<i>o</i> -FS-0.28 <i>o</i> -ClS)	1.24	0.79	1.57
Poly(<i>o</i> -FS-0.19 <i>o</i> -ClS)	0.95	0.79	1.20

^a Numbers indicate mole fraction of *para*-chloro or *ortho*-chlorostyrene in the copolymer.

solved in toluene and precipitated with methanol. Films were prepared from the dried samples by compression molding at pressure between 10,000 and 20,000 psi for 45 s at temperatures ranging between 180°C and 230°C, depending upon blend composition. All pure components were compression molded at 180°C, while all blends were prepared at 210°C.

RESULTS AND DISCUSSION

The compatibility of these blends was determined by the observation of film clarity and the appearance of a single glass transition in the DSC measurements. All pure copolymers showed a single T_g that varied linearly with the copolymer composition as shown in Table IV. The T_g was the only distinctive feature of the thermograms. According to the data in Tables II and III, it is evident that all copolymers have similar molecular weights and relatively narrow molecular weight distributions.

DSC traces for the PPO/poly(*o*-FS-co-*p*-ClS) system of 50/50 wt % mixtures are shown in Figure 3. It can be seen that the copolymer containing between 15 and 74 mol % *p*-ClS show only a single T_g , thus indicating blend compatibility. Copolymers containing 82 and 90 mol % *p*-ClS are incompatible with PPO, as shown by the two T_g 's which have values close to that of the two pure components. Pure poly(*p*-ClS)² and poly(*o*-FS)⁷ are also incompatible with PPO.

Copolymers of *o*-FS and *o*-ClS exhibited quite different behavior in their 50/50 wt % blends with PPO. DSC thermograms for this system (not shown) showed a single T_g only for copolymers containing between 15 and 36 mol % *o*-ClS. Because this compatibility was only found over a relatively narrow copolymer

TABLE IV
 T_g Values of Unblended Copolymers

Sample ^a	T_g (°C)	Sample ^a	T_g (°C)
Poly(<i>o</i> -FS-co- <i>p</i> -ClS)		Poly(<i>p</i> -FS-co- <i>o</i> -ClS)	
0.90 <i>p</i> -ClS	132	0.84 <i>o</i> -ClS	131
0.82 <i>p</i> -ClS	127	0.78 <i>o</i> -ClS	129
0.74 <i>p</i> -ClS	124	0.71 <i>o</i> -ClS	125
0.62 <i>p</i> -ClS	121	0.65 <i>o</i> -ClS	124
0.55 <i>p</i> -ClS	119	0.55 <i>o</i> -ClS	122
0.40 <i>p</i> -ClS	115	0.47 <i>o</i> -ClS	120
0.35 <i>p</i> -ClS	110	0.38 <i>o</i> -ClS	117
0.25 <i>p</i> -ClS	107	0.28 <i>o</i> -ClS	114
0.15 <i>p</i> -ClS	104	0.19 <i>o</i> -ClS	112
Poly(<i>o</i> -FS-co- <i>o</i> -ClS)		Poly(<i>p</i> -FS-co- <i>p</i> -ClS)	
0.86 <i>o</i> -ClS	132	0.89 <i>p</i> -ClS	132
0.79 <i>o</i> -ClS	128	0.74 <i>p</i> -ClS	132
0.61 <i>o</i> -ClS	124	0.66 <i>p</i> -ClS	129
0.56 <i>o</i> -ClS	118	0.54 <i>p</i> -ClS	129
0.45 <i>o</i> -ClS	114	0.52 <i>p</i> -ClS	125
0.36 <i>o</i> -ClS	110	0.48 <i>p</i> -ClS	122
0.27 <i>o</i> -ClS	104	0.41 <i>p</i> -ClS	122
0.15 <i>o</i> -ClS	100	0.30 <i>p</i> -ClS	120
		0.18 <i>p</i> -ClS	114

^a Numbers indicate mole fraction of *para*-chlorostyrene or *ortho*-chlorostyrene in the respective copolymers.

composition interval, the effect of lower molding temperature and pressure was investigated. Additional blends were prepared at molding temperatures of 180°C, 190°C, and 200°C at a pressure of 20,000 psi, and at a lower pressure of 10,000 psi at 190°C. Under these conditions, compatibility was found over the same narrow copolymer composition interval.

In view of the above results it was unexpected that copolymers of *p*-FS with *p*-ClS containing between 19 and 89 mol % of *p*-ClS were found to exhibit two T_g 's in their 50/50 blends with PPO. Yet, since the pure homopolymers are also incompatible, it is reasonable to suppose that at 210°C, no copolymers of *p*-FS and *p*-ClS are compatible with PPO.

Two T_g 's were also found in all blends of PPO and poly(*p*-FS-co-*o*-ClS) containing between 19 and 84 mol % *o*-ClS content.

For all the polymer blends studied, the DSC observations correlated perfectly with visual observations of film clarity.

In addition, the compatibility and the transition widths of the PPO/poly(*o*-FS-co-*p*-ClS) and PPO/poly(*o*-FS-co-*o*-ClS) systems were studied as a function of blend composition. Figure 4 shows T_g values of the copolymers of poly(*o*-FS-co-*p*-ClS) containing 40 mol % *p*-ClS as a function of weight fraction of PPO. Other compatible copolymer-PPO blends yielded similar traces, and the respective T_g values closely followed the curves shown in Figure 4.

From the thermograms, systematic changes were also observed in the widths of the glass transitions for blends of increasing *p*-ClS content. Figure 5 shows the full-width results for a 50/50 blend of PPO with poly(*o*-FS-co-*p*-ClS) at various copolymer compositions. These transition widths (using the DSC traces

Fig. 3. DSC thermograms of 50/50 wt % mixtures of PPO/poly(*o*-FS-*co*-*p*-ClS) blends. Numbers indicate mole fraction of *p*-ClS in the copolymer.

of Fig. 3) were determined as the temperature interval over which the tangent to the slope of the dQ/dT curve intersected the extrapolation of the baseline before and after the T_g . The transition width increases with increasing *p*-ClS content up to phase separation. Above 74% *p*-ClS (and below 15%) in the copolymer composition, two phase blends are observed. The width of the two glass transitions for the incompatible blends decreases with increasing *p*-ClS copolymer composition. At the copolymer composition extremes, the two transitions of the incompatible poly(*p*-ClS) and poly(*o*-FS) with PPO blends have the same width as the unblended components. This observed transition width behavior may be explained on the basis of phase heterogeneity. In general the chemical composition of copolymer molecules is not uniform but varies during the course of the polymerization reaction. It is expected that changes in physical properties are more dependent upon the degree of heterogeneity than variations in molecular weight.^{16,17} Such broadening of T_g peaks has been attributed to fluctuations in the interaction of a chain segment with its nearest neighbor in excess of the normal thermal fluctuations.^{2,16,17} These changes in the phase transition width during compatibility investigations are a qualitative measure of the approach to phase separation.

Fig. 4. T_g values of PPO/poly(*o*-FS-co-0.40 *p*-ClS) blends.

The DSC thermograms of the incompatible blends exhibited T_g 's that were unchanged from those of the corresponding unblended components as indicated by the horizontal lines in Figure 6 for sample copolymer compositions of poly(*o*-FS-co-*o*-ClS) in blends with PPO.

Fig. 5. Glass transition widths of 50/50 wt % blends of poly(*o*-FS-co-*p*-ClS) and PPO as a function of copolymer composition (from Fig. 3). Width of the two phase blends (>74 mol % of *p*-ClS) are indicated for the poly(*o*-FS-co-*p*-ClS) component.

Fig. 6. T_g values of incompatible blends of PPO/poly(*o*-FS-co-*o*-ClS) vs. weight fraction of PPO.

Since poly(*o*-FS-co-*o*-ClS)/PPO blends show compatibility behavior in a very narrow copolymer composition range of 15–36 mol % *o*-ClS, we prepared additional films of these blends by molding at a higher temperature of 230°C. Cloudy films indicated phase separation had occurred. DSC measurements confirmed this observation. This behavior is indicative of a very small degree of blend compatibility.

The same experiment was carried out for all compatible PPO/poly(*o*-FS-co-*p*-ClS) blends. No changes in the film clarity and in the DSC traces were observed.

On the basis of thermogravimetric analysis, using the criterion of no observable weight loss, all copolymers and blends studied in this work were found to be thermally stable at temperatures up to 250°C.

The results reviewed here indicate that in the poly(*o*-FS-co-*p*-FS) and poly(*o*-FS-co-*o*-ClS) systems, there exists a high degree of influence of the copolymer structure on the compatibility with PPO. Furthermore, it was found that copolymers of *p*-FS with both *para*- and *ortho*-chlorostyrene form incompatible blends with PPO regardless of the copolymer composition. The range of compatibility and the degree of compatibility is much wider in the blends of PPO and copolymers of *o*-FS with *p*-ClS. This compatibility behavior is a striking indication of the effect of the location of the substituted phenyl halogen on the fine structure of the copolymer. The preparation of the copolymers of very narrow MW distribution by anionic polymerization can help in the further explanation of the above-mentioned behavior. Another possibility for further elucidation could be an investigation of certain critical physical properties, e.g., thermal expansion coefficient, solubility parameter, or critical temperature.

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Received September 8, 1982

Accepted November 15, 1982