# Thermally Induced Phase Separation in Homogeneous Blends of Poly(2,6-Dimethyl-1,4-Phenylene Oxide) with Poly(*o*-Fluorostyrene-co-*p*-Chlorostyrene) and with Poly(*o*-Fluorostyrene-co-*o*-Chlorostyrene)

R. VUKOVIĆ, V. KUREŠEVIĆ, *INA—Research and Development Institute, Zagreb, Yugoslavia,* and F. E. KARASZ and W. J. MacKNIGHT, *Department of Polymer Science and Engineering, Material Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003*

## Synopsis

The phase separation behavior of initially compatible blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with poly(*o*-fluorostyrene-co-*p*-chlorostyrene) [poly(oFS-co-pClS)] and with poly(*o*-fluorostyrene-co-*o*-chlorostyrene) [poly(oFS-co-oClS)] was studied by DSC. It was found that copolymers of poly(oFS-co-pClS) containing between 15 and 62 mol % pClS have shown no phase separation after annealing at temperatures up to 320°C. It was also observed that blends containing this copolymer with 74 mol % pClS show phase separation at 250°C, which depended on blend composition. Additionally, all PPO/poly(oFS-co-oClS) blends exhibit phase separation after annealing to a temperature of 230°C. Thermal degradation of the polymer blends was not observed at the temperatures studied.

## INTRODUCTION

As is well known, compatible polymer–polymer blends undergo phase separation upon heating to elevated temperatures indicative of the existence of a lower critical solution temperature (LCST). This behavior has been theoretically predicted[1–4] and is shown experimentally in several systems.[5–19] For example, such behavior is shown in polymer blends containing styrene–acrylonitrile copolymers and poly(methyl methacrylate),[9] poly(vinyl chloride) and ethylene–vinylacetate copolymers,[10] and poly(vinylidene fluoride) in blends with various acrylate polymers and with poly(vinyl methyl ketone).[11,12] Polystyrene in blends with poly(vinyl methyl ether)[6–8] and polycarbonate[13] also shows such behavior. Recently, it was found here that systems containing poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and several copolymers of halogen substituted styrene show LCSTs at high temperatures.[14–19] It has been previously found that homogeneous blends of PPO with copolymers of *o*-chlorostyrene and *p*-chlorostyrene copolymers show phase separation that is dependent on copolymer composition and annealing temperature.[14,15] Similar behavior was discovered for the corresponding fluorinated copolymers in blends with PPO.[16,19] Thermally induced phase separation has also been observed in blends of PPO with the copolymers

of styrene with *ortho*- and *para*-fluorostyrene as well as with *ortho*- and *para*-chlorostyrene.[15,17,18]

Phase separation in these systems was reversible on cooling to lower temperatures. This reversibility depends upon the cooling rate, the annealing time and temperature, the thermal history of the sample, and the polymer–polymer system.

Recently it was found that copolymers of poly(oFS-co-pClS) and poly(oFS-co-oClS) were compatible with PPO in certain copolymer composition ranges.[20,21] To further investigate the behavior of these blends, samples were annealed at high temperatures, and phase separation behavior was examined by the DSC method, and thermal stability by thermogravimetric analysis.

## EXPERIMENTAL

### Materials

Copolymers of poly(oFS-co-pClS) and poly(oFS-co-oClS) were prepared by free radical polymerization with azobisisobutyronitrile initiator in toluene solution. Conversion was kept to less than 50%. Copolymer compositions were determined by infrared and elemental chlorine analysis. Copolymer molecular weights were determined by light scattering and osmometry. These results indicated that the syntheses produced high molecular weight materials with a polydispersity index below 2. The details of the synthesis and characterization of the copolymers listed in this study are described elsewhere.[20,21]

The PPO used was supplied by General Electric Co. and was purified by precipitation in methanol from toluene solution.[18,20]

Blends were prepared by coprecipitation of PPO and copolymers from toluene solution in methanol as a nonsolvent. Films for DSC measurements were compression-molded from the vacuum-dried powders at temperatures and pressures which were sample-dependent.[20,21]

### Calorimetric Measurements

Differential scanning calorimetry experiments were performed using a Perkin-Elmer Model DSC-2. Sample sizes of approximately 20 mg were used and a heating rate of 20°C/min was employed. Glass transitions ($T_g$) were determined as the temperature at which the heat capacity achieved one-half the total step change associated with the transition.

The thermally induced phase separation was examined by heating a sample to the selected temperature and holding for 15 min. No further changes were observed in any system at longer annealing times. The samples were then cooled to room temperature and rescanned in the DSC.[18] The appearance of a single $T_g$ in the DSC measurements was used as the criterion for compatibility.

Thermogravimetric analysis experiments were carried out using a Perkin-Elmer Model TGS-2 at a heating rate of 10°C/min in a nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Thermal Stability of Polymer Blends

Since this work was conducted at temperatures between 230 and 320°C, it was necessary to evaluate the thermal stability of the blends under these conditions by using thermogravimetric analysis. This investigation consisted of two separate experiments. First, PPO/copolymer blends were heated from 50 to 320°C, and the sample weight loss was determined from the thermograms. It was found that the observed weight loss was slightly dependent on the type of copolymer and its composition. In both systems no weight loss was observed at 250°C; at 320°C, both PPO/copolymer blends were found to experience a loss of less than 0.4%. In a second experiment, in which the blends were annealed at 250, 280, and 320°C for 15 min, similar behavior was observed. The weight loss data are given in Table I. It can be seen that the weight loss for both PPO/copolymer systems was less than 0.2% at 250°C, less than 0.35% at 280°C, and between 0.5% and 0.6% at 320°C.

Recently it was shown that poly(*ortho*-chlorostyrene) exhibited a decrease in molecular weight without any observed weight loss during thermogravimetric analysis experiments.[22] In the present study we observed negligible differences in intrinsic viscosities measured before and after annealing. It

TABLE I
Thermal Stability of PPO/Poly(oFS-co-pClS) and PPO/Poly(oFS-co-oClS) Blends

| Sample[a] | % Weight loss, annealed 15 min at | | |
|---|---|---|---|
| | 250°C | 280°C | 320°C |
| PPO/poly(oFS-co-pClS)[b] | | | |
| 0.15 pClS | 0.15 | 0.25 | 0.53 |
| 0.25 pClS | 0.15 | 0.27 | 0.55 |
| 0.35 pClS | 0.17 | 0.27 | 0.52 |
| 0.40 pClS | 0.17 | 0.26 | 0.57 |
| 0.55 pClS | 0.16 | 0.29 | 0.55 |
| 0.62 pClS | 0.20 | 0.29 | 0.60 |
| 0.74 pClS | 0.19 | 0.32 | 0.58 |
| 0.82 pClS | 0.18 | 0.32 | 0.57 |
| 0.90 pClS | 0.20 | 0.32 | 0.59 |
| PPO/poly(oFS-co-oClS)[b] | | | |
| 0.15 oClS | 0.13 | 0.20 | 0.45 |
| 0.27 oClS | 0.14 | 0.22 | 0.47 |
| 0.36 oClS | 0.13 | 0.20 | 0.47 |
| 0.45 oClS | 0.15 | 0.23 | 0.48 |
| 0.56 oClS | 0.15 | 0.25 | 0.49 |
| 0.61 oClS | 0.15 | 0.25 | 0.50 |
| 0.67 oClS | 0.17 | 0.27 | 0.51 |
| 0.79 oClS | 0.18 | 0.28 | 0.49 |
| 0.86 oClS | 0.18 | 0.28 | 0.50 |

[a] In all cases, blends contain equal weight fractions of the respective components.
[b] Numbers indicate mole fraction of *para*-chlorostyrene or *ortho*-chlorostyrene in the copolymer.

was thus concluded that thermal degradation was not an important factor in this study.

### Thermally Induced Phase Separation

Blends of PPO/poly(oFS-co-pClS) and PPO/poly(oFS-co-oClS) were found to be compatible or incompatible depending on the copolymer composition and the molding temperature.[20,21] As discussed earlier, compatible blends are susceptible to phase separation at elevated temperatures indicating the existence of a lower critical solution temperature. Among other systems, it has been found that chlorinated and fluorinated styrene copolymers blended with PPO display such behavior in given copolymer composition ranges.[14-19] From this point of view it is of interest to further analyze the behavior of poly(oFS-co-pClS)/PPO and poly(oFS-co-oClS)/PPO systems, which were found to be compatible at the molding temperature of 210°C, as a function of copolymer composition, blend composition, and annealing temperature. These studies were carried out directly in the DSC following the procedure we have used previously.[18]

**PPO/Poly(oFS-co-pClS) Blends.** Annealing the compatible blends at elevated temperatures led to phase separation at 250°C only for the blend containing 74 mol % pClS, as evidenced by the observation of two glass transitions. Other copolymers containing between 15 and 62 mol % pClS did not phase separate even after annealing up to 320°C. These results are shown in Figure 1 and represent measurements of 50/50 wt % blends. The boundary separating the one and two phase regimes represents the locus of a series of LCSTs for mixtures of PPO with the respective copolymers.
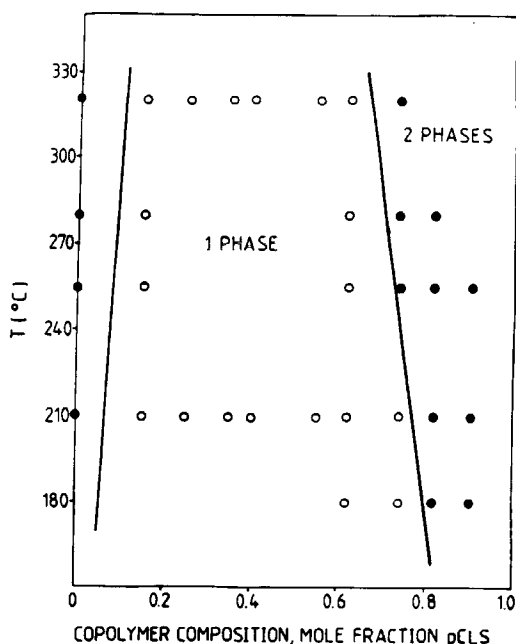


Fig. 1.   Compatibility of 50/50 wt % blends of PPO with copolymers of oFS and pClS: (○) one phase; (●) two phase.
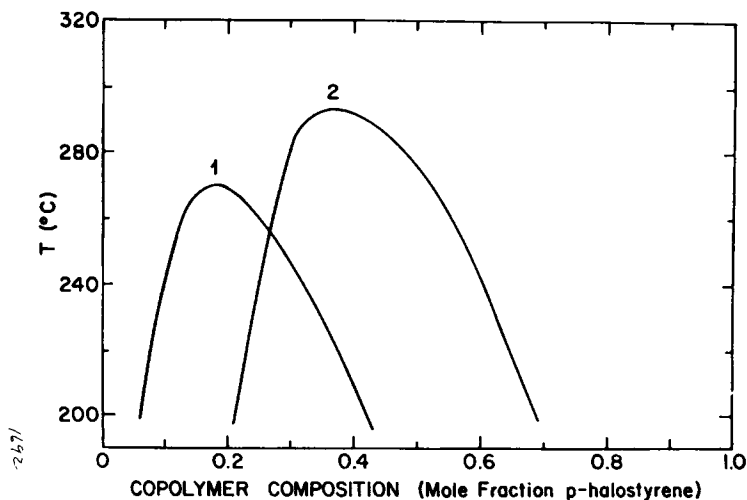
Fig. 2. Phase separation behavior of 50/50 wt % blends of PPO with poly(oFS-co-pFS) (curve 1) and poly(oClS-co-pClS) (curve 2).

We can also infer, of course, that a second phase boundary must be present for compositions between 0 and 15% pClS, though even at its highest attainable temperature no phase separation was observed for the 15% composition. This is interesting behavior in light of the incompatibility found for chlorinated and fluorinated homopolymers with PPO and also in comparison with the results obtained for poly(oFS-co-pFS) and poly(oClS-co-pClS) systems in blends with PPO (Fig. 2).[14-19] From this figure it can be seen that a compatibility window exists for the chlorinated copolymers over a wider range of compositions than for the fluorinated system.[14,19] In the
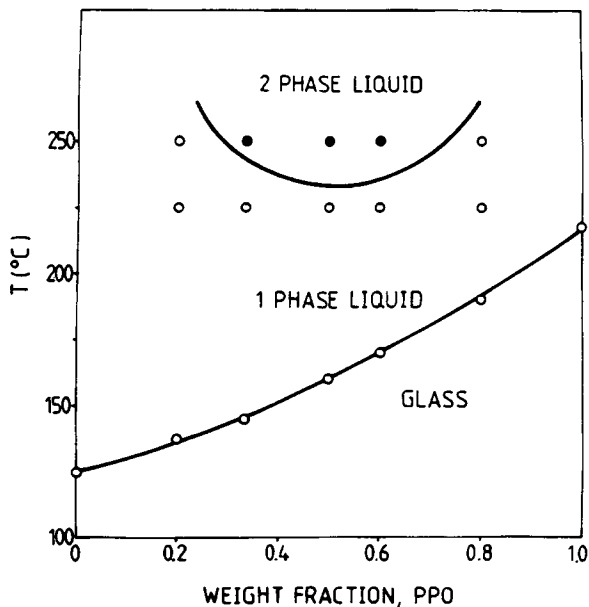


Fig. 3. Phase diagram for PPO/poly(oFS-co-pClS) blends containing 74 mol % pClS with different PPO weight percentages: (○) one phase; (●) two phase.
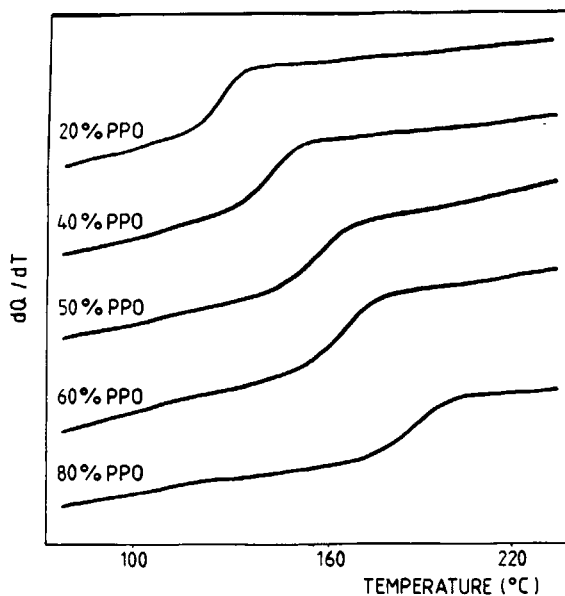
Fig. 4.   DSC thermograms of PPO/poly(oFS-co-pClS) with different PPO weight percentages, annealed 15 min at 320°C.

PPO/poly(oFS-co-pClS) system, the compatibility window is much wider.

Further insight into the thermal behavior of PPO/poly(oFS-co-pClS) blends can be gained by an examination of Figure 3 which shows the phase diagram for the blend containing the copolymer of 74 mol % pClS as a function of PPO content. Blends with the compositions 50/50, 40/60, and 60/40 wt % of either component exhibit phase separation after annealing
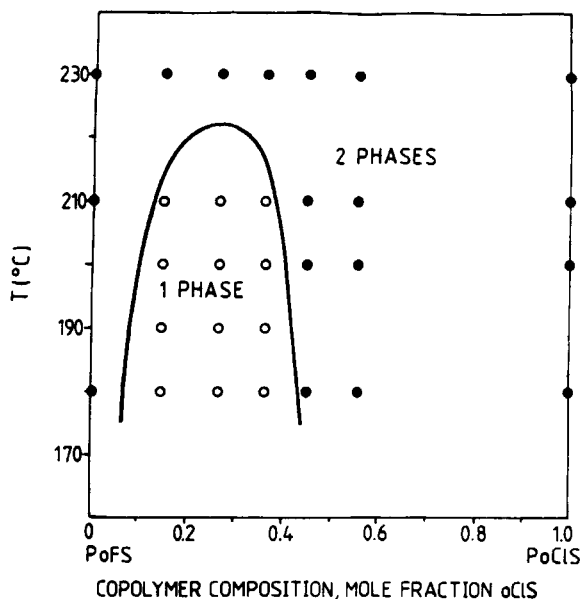


Fig. 5.   Compatibility of 50/50 wt % blends of PPO with copolymers of oFS and oClS: (○) one phase; (●) two phase.

at 250°C. Blends containing 80% of either component exhibited only one $T_g$ value. DSC traces of PPO/poly(oFS-co-pClS) blends containing 40 mol % pClS at various blend compositions, annealed at 320°C, are shown in Figure 4. From these thermograms it can be seen that no changes in compatibility were observed, as evidenced by a single $T_g$. Moreover, the glass transition widths have not changed, indicating an intimate level of mixing in such blends.

**PPO/Poly(oFS-co-oClS) Blends.** Annealing studies of this system showed somewhat different behavior in comparison to the above-discussed blends. The compatibility range for this system was found for copolymers containing between 15 and 36 mol % oClS in blends with PPO.[20,21] By annealing these samples at temperatures of 210°C and 230°C it was observed that all the blends show the same behavior and exhibit phase separation at 230°C as shown in Figure 5. Blends of PPO/poly(oFS-co-oClS) containing 27 mol % oClS showed phase separation at 230°C for all blend compositions studied. It was found that blends that had been phase-separated by annealing could be made homogeneous again by annealing at lower temperatures for an adequate period of time.

The behavior of the blends in this study demonstrates again the effect of relatively small structural changes on miscibility in polymers. The data provided by these experiments together with results from blend studies of other halogenated styrene systems has been combined to provide individual segmental interaction parameters. This calculation is based on a first-order mean field theory recently developed here.[23] The $\chi$ parameters describing the interaction of PPO with fluorinated and chlorinated styrene polymers are shown to be sensitive to the isomeric placement of the halogen substituent, particularly in the case of the fluorinated systems. (At 200°C, $\chi_{PO,oFS}$ = 0.013, $\chi_{PO,pFS}$ = 0.09, where the subscripts of the interaction parameter define the segment pairs involved.) This asymmetry, while difficult to explain from *a priori* structural considerations, can, however, quantitatively account for the existence of the miscibility window studied here. The greater asymmetry of the window with respect to copolymer composition of the fluorinated as compared to the chlorinated system (Fig. 2) is also accounted for by the $\chi$ parameters. One may also predict from the observed and calculated near miscibility of PPO and PoFS at 200°C that this system would become miscible at this temperature if PoFS of lower molecular weight (ca. 30,000) were employed.

## References

1. P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507, 3515 (1964).
2. P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1833 (1965).
3. R. H. Lacombe and I. C. Sanchez, *J. Phys. Chem.*, **80**, 2568 (1976).
4. R. L. Scott and P. H. van Konynenburg, *Discuss. Faraday Soc.*, **49**, 87 (1970).
5. L. P. McMaster, *Macromolecules*, **6**, 760 (1973).
6. T. K. Kwei, T. Nishi, and R. F. Roberts, *Macromolecules*, **7**, 667 (1974).
7. T. Nishi and T. K. Kwei, *Polymer*, **16**, 285 (1975).
8. M. Bank, J. Leffingwell, and C. Thies, *Macromolecules*, **4**, 43 (1971).
9. L. P. McMaster, *Adv. Chem. Ser.*, **142**, 43 (1975).

10. E. Nollery, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.,* **23**, 623 (1979).

11. D. R. Paul, J. W. Barlow, R. E. Bernstein, and D. C. Wahmund, *Polym. Eng. Sci.,* **16**, 593 (1976).

12. R. E. Bernstein, C. A. Cruz, D. R. Paul, and J. W. Barlow, *Macromolecules,* **10**, 681 (1977).

13. G. Humme, R. Rohr, and V. Serini, *Angew. Makromol. Chem.,* **58/59**, 85 (1977).

14. P. Alexandrovich, F. E. Karasz, and W. J. MacKnight, *Polymer,* **18**, 1022 (1977).

15. P. Alexandrovich, Ph.D. dissertation, University of Massachusetts, 1978.

16. R. Vuković, V. Kurešević, F. E. Karasz, and W. J. MacKnight, *27th Int. Symp. Macromolecules,* Strasbourg, July 1981, Vol. 2, p. 1231.

17. R. Vuković, V. Kuresević, F. E. Karasz, and W. J. MacKnight, *Proceedings of the Second European Symposium on Thermal Analysis,* D. Dollimore, Ed., Heyden, London, 1981, p. 273.

18. R. Vuković, V. Kuresević, F. E. Karasz, and W. J. MacKnight, *Thermochim. Acta,* **59**, 349 (1982).

19. R. Vuković, F. E. Karasz, and W. J. MacKnight, *Polymer,* **24**, 529 (1983).

20. R. Vuković, V. Kuresević, N. Segudović, F. E. Karasz, and W. J. MacKnight, *Proceedings IUPAC Macro 1982,* Amherst, Mass., July 1982, p. 707.

21. R. Vuković, V. Kuresević, N. Segudović, F. E. Karasz, and W. J. MacKnight, *J. Appl. Polym. Sci.,* **28**, 1379 (1983).

22. M. B. Djordjevic and R. S. Porter, *Proceedings IUPAC Macro 82,* Amherst, Mass., July 1982, p. 319.

23. G. ten Brinke, F. E. Karasz, and W. J. MacKnight, *Macromolecules,* **16**, 1827 (1983).