Partial miscibility in the system poly(*para*-chlorostyrene-co-*ortho*-chlorostyrene)/poly(2,6-dimethyl-1,4-phenylene oxide)

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The compatibility of random copolymers of *para*-chlorostyrene and *ortho*-chlorostyrene (PO copolymers) with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has been studied by differential scanning calorimetry (d.s.c.). Blends prepared by compression moulding of coprecipitated powders display either one or two glass transitions, dependent on the composition of the copolymer component of the blend. PO copolymers of *para*-chlorostyrene content from 23 to 64% are miscible with PPO in all proportions, using the customary criteria of a single calorimetric glass relaxation and optical clarity. Both homopolymers poly(*para*-chlorostyrene) (P*p*ClS) and poly(*ortho*-chlorostyrene) (P*o*ClS) are found to be incompatible with PPO; such blends exhibit two glass transitions at temperatures characteristic of the pure component phases. All compatible PO–PPO blends undergo phase separation upon annealing at elevated temperatures, indicating that a lower critical solution temperature (*LCST*) must exist. The phase separation is found to be reversible by annealing below the *LCST*, at temperatures which are still above the glass transitions of both blend components.

INTRODUCTION

Chemically dissimilar polymer pairs are generally found to be incompatible. That is, binary blends contain two distinct macroscopic phases. Even fairly dilute solutions of such pairs in solvents which dissolve both components are heterogeneous. However, a number of compatible pairs are known[1,2]; of these, blends of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) have been subjected to especially close scrutiny[3–11]. The system PS–PPO exhibits a single compositionally dependent glass transition when examined by a variety of techniques, including differential scanning calorimetry[3–7], dynamic mechanical relaxation[4,8,9], and measurement of dielectric properties[9–11]. In such studies PS and PPO are found to be miscible in all proportions, and the composite of all available evidence indicates that the pair is compatible at the segmental level[3].

With the PS–PPO pair as a starting point, similar, although 'less' compatible blends have been studied by using derivatives of PS. Specifically, the miscibility behaviour of random copolymers of styrene and *para*-chlorostyrene with PPO has been reported[3,9,12]. Homopolymers of *para*-chlorostyrene and its copolymers with low mole fractions of styrene are incompatible with PPO. However, similar copolymers mix with PPO if styrene is present in larger proportions. Furthemore, Fried has reported an abrupt shift from miscibility to immiscibility with PPO when the *para*-chlorostyrene content of such copolymers is raised from 67.1 to 67.7 mol %; this assertion being based on visual observation of the clarity of films, and on glass transition, density and ultimate tensile property studies[3]. Shultz and Beach similarly concluded that such copolymers exhibited a compatibility–incompatibility transition with PPO at compositions between 65.3 and 68 mol % *para*-chlorostyrene comonomer; their conclusion being based on thermo-optical analysis, dynamic mechanical analysis and d.s.c. studies[12]. Tkacik has further confirmed the compatibility or incompatibility of these blends in observations of their dielectric relaxation properties[9].

Complete substitution with chlorine at the *para* position in PS thus leads to a polymer incompatible with PPO. The same has been found to be true with *ortho* substitution, i.e. poly(*ortho*-chlorostyrene) (P*o*ClS) is immiscible with PPO[3]. The observation that random copolymers (PO copolymers) of these two chlorinated styrenes form homogeneous blends with PPO and provides a unique opportunity for extended studies of factors relating to polymer–polymer miscibility. This system displays two compatibility–incompatibility transitions: PO copolymers of low *p*ClS content are insoluble in PPO, those with *p*ClS content between 23 and 64% form homogeneous blends, and finally those with high *p*ClS content are again incompatible with PPO. This miscibility range is temperature dependent. In fact, homogeneous PO–PPO blends become heterogeneous when annealed at elevated temperatures. Such phase separation can be studied, since it may be 'quenched in' by rapid cooling to temperatures below the glass transitions of both blend components. This behaviour indicates the existence of a lower critical solution temperature (*LCST*) for these mixtures, a phenomenon which is theoretically predicted[13,14] and has been observed experimentally in other systems[15–17]. This paper describes the compatibility behaviour of PO–PPO mixtures, and the thermally induced phase separation of homogeneous blends.

Table 1

Sample*	[η] (dl/g)	$\bar{M}_v$
P*p*ClS	0.28	140 000
P*o*ClS	0.27	134 000
PO8	0.41	260 000
P017	0.38	230 000
PO23	0.37	220 000
PO27	0.40	250 000
PO31	0.36	210 000
PO36	0.39	240 000
PO40	0.39	240 000
PO43	0.41	260 000
PO47	0.37	220 000
PO57	0.39	240 000
PO64	0.36	210 000
PO38 †	0.81	730 000

* Numbers indicate mole fraction *para*-chlorostyrene in the respective copolymers. † Dow copolymer

EXPERIMENTAL

Materials

PPO powder was supplied by the General Electric Co., through the courtesy of Dr A. Katchman, and was purified by dissolution in toluene and reprecipitation into a 12:1 excess of methanol. Characterization of this material gives the values: $\bar{M}_w \sim 35\,000$ and $\bar{M}_n \sim 17\,000$. Strong, clear films with a yellowish tint result from moulding the reprecipitated fluffy powders.

The PO copolymers were prepared in these laboratories, as were P*p*ClS and P*o*ClS homopolymers. The respective monomers (Aldrich Chemical Company) were purified by distillation. Solution polymerizations were carried out in toluene at 60°C, using azobisisobutyronitrile as a free radical initiator. The resulting homopolymers and copolymers were purified by precipitation from toluene solutions into a 12:1 excess of methanol. 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. Conversion was held to approximately 50 to 60%, in order to minimize copolymer composition drift. Molecular weights were obtained by measuring intrinsic viscosities in toluene at 30°C. In addition, a PO copolymer of higher molecular weight was obtained from the Dow Chemical Company, courtesy of Dr R. F. Boyer. *Table 1* lists characterization information for these materials. The numeral in the sample identification represents the percentage *p*ClS in the copolymer. Copolymer $\bar{M}_v$ values were estimated from the Mark–Houwink empirical relation, using *K*, *a* values, which were an arithmetic average of the respective literature values for P*p*ClS and P*o*ClS[18].

Figure 1 shows copolymer composition as a function of monomer feed ratio. Such a curve is indicative of a nearly ideal random copolymerization, with slight alternating tendency[19]. Reactivity ratios calculated using the Fineman–Ross equation[20] are $r_1 = 0.55$ and $r_2 = 0.71$; monomer 1 is *p*ClS.

Measurements

Blends were prepared by dissolving appropriate quantities of the pure components in toluene, followed by coprecipitation into a 12:1 excess of methanol. The resulting powders were dried *in vacuo* at 80°C for 4 days. Films ~0.03 cm thick were compression moulded at temperatures that are discussed in a later section. Moulding conditions were such that samples were in the press approximately 1.5 min, and were quenched in air upon removal. Small discs were punched out for calorimetric analysis. All differential scanning calorimetry was carried out on a Perkin–Elmer model DSC-2 using heating rates of 20°C/min with sample sizes of 15 to 20 mg. All materials were amorphous, and the only distinctive features of the d.s.c. thermograms were glass transitions. The T_g was taken as the temperature at which one half of the ΔC_p of the transition was achieved.

Densities of pure PO copolymers and P*p*ClS and P*o*ClS homopolymers were measured using calibrated sodium nitrate–water density gradient columns.

RESULTS

Pure components

Films of unblended PPO were compression moulded at 270°C; they were transparent and of yellowish tint. The T_g was found to be 218°C. Films of chlorostyrene homopolymers and copolymers were compression moulded at 200°C; they were clear and colourless. T_g for all was found to be approximately 128°C.

Homopolymer blends

Blends with compositions of 20, 40, 60 and 80% by wt were prepared with PPO and the respective homopolymers and copolymers. P*p*ClS–PPO and P*o*ClS–PPO blends were compression moulded at 250°C. The resulting films were opaque, with a yellow tint whose intensity depended on the weight fraction PPO in the blend. *Figure 2* shows representative d.s.c. thermograms of P*o*ClS–PPO blends. Two glass transitions are present in all blends, each closely corresponding to the T_g of either PPO or P*o*ClS. P*p*ClS–PPO traces were identical. The homopolymers P*p*ClS and P*o*ClS are thus concluded to be incompatible with PPO.

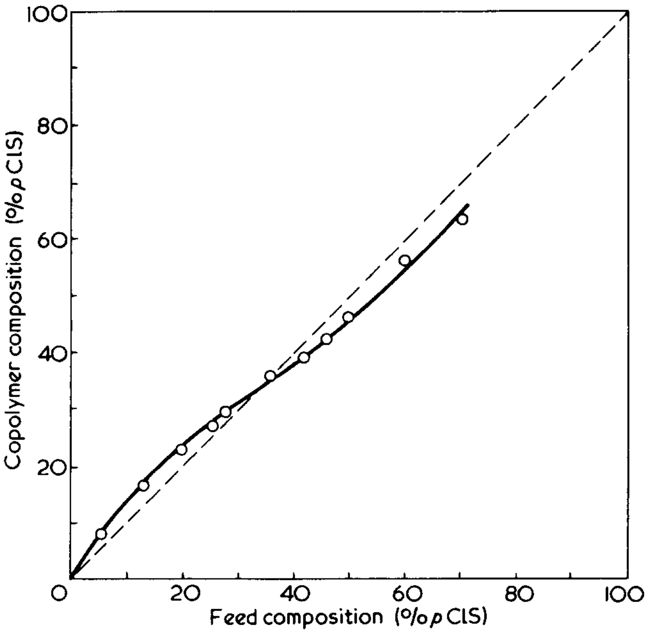

Figure 1 Copolymer composition *versus* feed composition

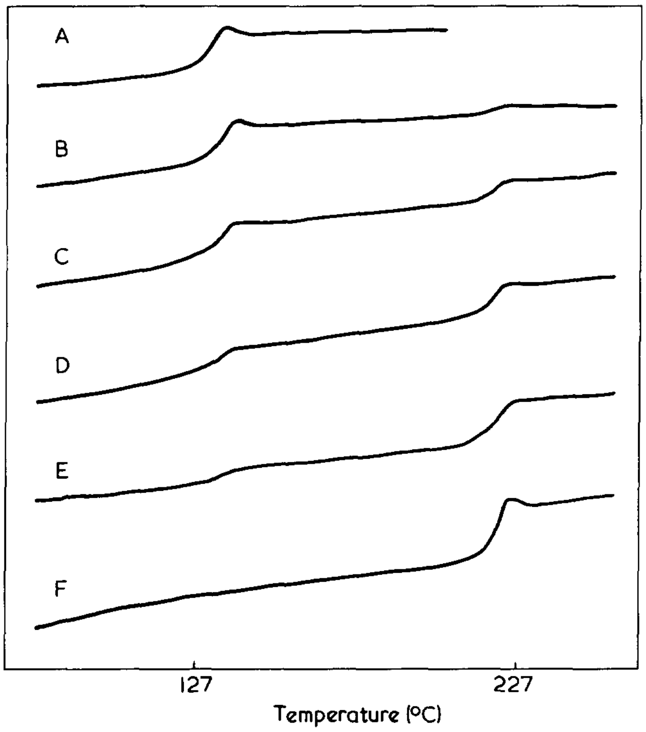

Figure 2 D.s.c. thermograms of PoClS, PPO, and blends: A, PoClS; B, 20% PPO; C, 40% PPO; D, 60% PPO; E, 80% PPO; F, PPO

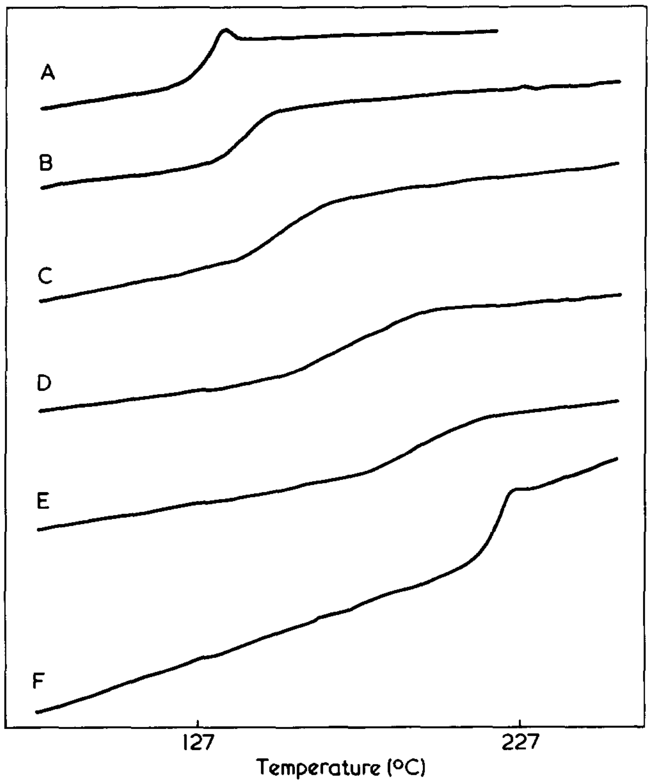

Figure 3 D.s.c. thermograms of P036, PPO, and blends. A, P036; B, 20% PPO; C, 40% PPO; D, 60% PPO; E, 80% PPO; F, PPO

Copolymer blends

Depending on moulding temperatures, films of blends of PO copolymers with PPO were either cloudy or transparent. Blends of copolymers P031, P036, P040, P043 and P047 were moulded at 250°C. The resulting films were transparent, and yellowish depending on PPO content. Similar results were obtained by moulding blends of P023, P027, P057 and P064 with PPO at 210°C. Transparent films of P08, P017 (or PpClS and PoClS) blends were not obtainable with any moulding conditions. Blends of P017, P023, P057 and P064 moulded at 280°C yielded cloudy films; d.s.c. scans confirmed the presence of two T_g in these samples.

Figure 3 shows d.s.c. thermograms of P036–PPO blends. A single, compositionally dependent glass transition is observed. T_g of these blends is plotted as a function of weight fraction PPO in *Figure 4*. All clear films discussed above yielded similar traces, and the respective T_g closely adhered to the curve in *Figure 4*.

Thermally induced phase separation

Blends of the copolymers were found to contain either one or two phases depending on moulding temperature. To further elucidate this effect, annealing at elevated temperatures was carried out in the DSC-2. An experiment consisted of heating a sample known to be homogeneous at the fastest available rate (320°C/min) to a selected annealing temperature, and holding it at the latter for an arbitrary time period, usually 15 min. Samples were then quenched to ambient temperatures as rapidly as possible in the instrument. The samples were then reheated at 20°C/min to determine whether one or two phases were present, as indicated by the number of observed C_p discontinuities, i.e. glass transitions. *Figure 5* shows d.s.c. thermograms from such experiments on 40/60 P036–PPO blends. Annealing at 305°C for 15 min is seen to greatly broaden the single T_g; as if 'partial' separation has occurred. Annealing of another sample 15 min at 327°C is seen to produce two glass transitions. A third sample held for 15 min at 285°C produced a d.s.c. trace identical to that obtained from the as-moulded sample.

The annealing period of 15 min was arbitrarily selected. It was found, however, that annealing a 40/60 P038–PO blend for 2 min at 327°C was sufficient to phase separate the sample as fully as was observed with 45 min at this temperature.

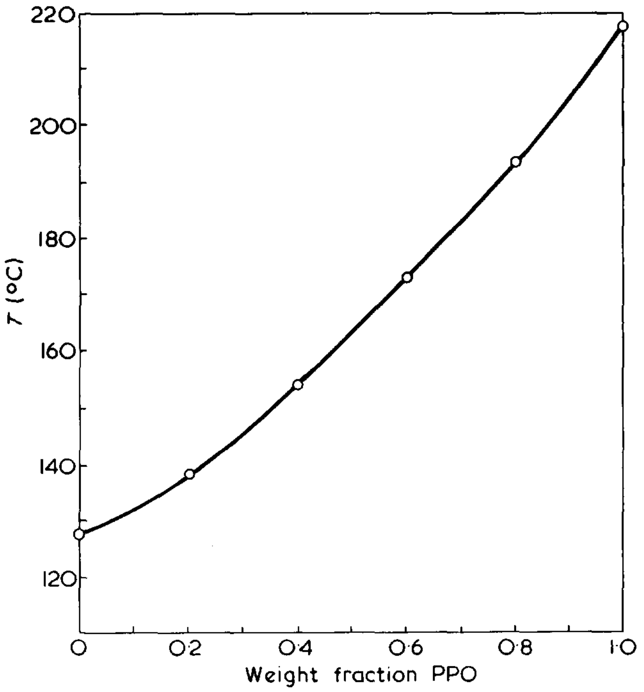

Figure 4 T_g of P036 – PPO blends

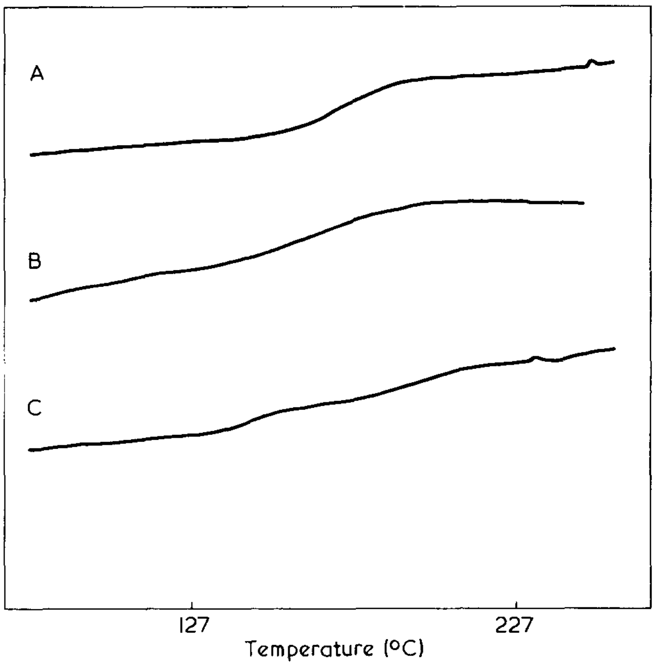

Figure 5 D.s.c. thermograms illustrating phase separation. 40/60 PO36–PPO blends. A, as moulded, 250°C; B, annealed 15 min, 350°C; C, annealed 15 min, 327°C

The described annealing, quenching and reheating cycles were performed for all 40/60 and 60/40 PO–PPO blends to determine the respective regions of phase stability. This procedure bracketed the lower critical solution temperature within limits, assuming that the 15 min annealing regime permits the attainment of 'equilibrium'. In all cases the two T_g values observed did not correspond to those of the pure components as observed in P*o*ClS–PPO and P*p*ClS–PPO blends, indicating rather a separation into mixed phases. Demonstrating the separation of 80/20 and 20/80 blends was difficult. Although in some cases two T_g values were observable, the small quantity of material in the minor phase generally lowered the detectability of the glass transition below instrumental resolution.

Blends that had been separated by annealing could also be made homogeneous again by annealing at lower temperatures. For example, 1 h at temperatures 20°C below the determined *LCST* values was sufficient to again solubilize 40/60 blends of P027, P031, P043 and P057 with PPO. Overnight annealing homogenized blends of P057 and P023 that had been moulded at 280°C. Phase separation found in these systems appears to be completely reversible.

DISCUSSION

Figure 6 shows the curve of *LCST versus* copolymer composition for 40/60 PO–PPO blends. Each data point represents the results of 15 min annealing; ●, indicate resulting phase separation; ○, represent blends that remained as a single phase. The greatest compatibility with PPO occurs at copolymer compositions of approximately 36 to 40% *p*ClS (P036 or P040). Within the framework of this study, the *LCST versus* copolymer composition plot for 60/40; PO–PPO blends is indistinguishable from that for the 40/60 blends. Extrapolation of the curve to copolymer compositions outside the P023 to P064 range rapidly intersects the T_g values of the blend components. Preparing single phase blends of such copolymers is probably thus limited by the restriction of long range diffusional motions in the glassy state.

The glass transition temperatures of the separated phases can be determined by the 1/2 ΔC_p technique as has been discussed. Assuming that the composition of these phases can be determined by using the known T_g *versus* blend composition curve for the homogeneous blends allows construction of a phase diagram. *Figure 7* shows such a diagram for P047–PPO blends. Again, ●, represent points of 15 min annealing leading to phase separation, ○, show annealing regimes leading to no phase transition. Tie lines were constructed via the T_g vs. composition curve shown in the lower portion of the diagram. This line separates a one phase glass from a one phase liquid. Two phase glasses can be produced only by rapid cooling from above the *LCST* curve. This presumably is not an equilibrium situation.

The effect of increased molecular weight of copolymer can be seen in the case of P038. A 40/60 P038–PPO blend separated at 285°C, whereas P036 and P040 blends with PPO were stable at this temperature.

Density measurements of the pure copolymers and P*p*ClS and P*o*ClS were also performed, partly to determine whether this property displayed an extremum at copolymer composition in the 36 to 40% *p*ClS range. Using a sodium nitrate–water gradient column, measured densities at 25°C were 1.245 and 1.226 g/cm^3 for P*o*ClS and P*p*ClS, respectively; copolymers fell approximately linearly between these limits. Thus, within the expected error of such measurements, about ± 0.01 g/cm^3, the results are inconclusive with regard to the above question.

The compatibility of PO copolymers with PPO seems rather unusual in light of the incompatibility of both P*p*ClS

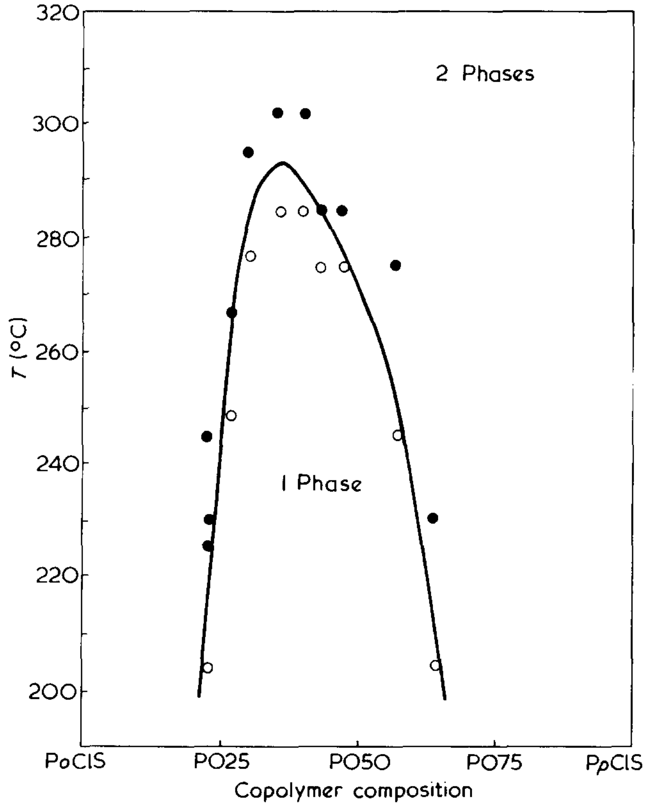

Figure 6 *LCST* of 40/60 PO–PPO blends *versus* copolymer composition

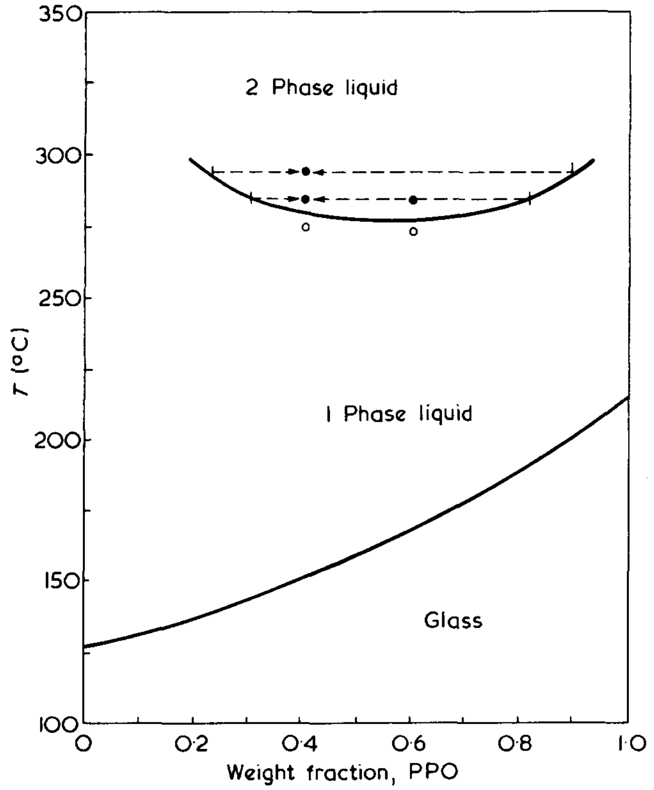

Figure 7 Phase diagram of P047–PPO blends

and PoClS with PPO. However, this situation is not unique. PVC has been shown to be compatible with both ethylene–vinyl acetate copolymers[21,22] and acrylonitrile–butadiene copolymers[23,24], whereas it is apparently not compatible with any of the four respective homopolymers[1].

CONCLUSIONS

(A) PO copolymers are compatible with PPO between compositions P023 and P064. Copolymers of other compositions and the two homopolymers, PpClS and PoClS are incompatible with PPO.

(B) All compatible PO copolymer–PPO pairs exhibit an *LCST*. The *LCST* attains a maximum at copolymer composition between P036 and P040.

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REFERENCES

1 Krause, S. *J. Macromol. Sci. (C)* 1972, 7, 251
2 Bohn, L. *Rubber Chem. Technol.* 1968, **41**, 495
3 Fried, J. R. *PhD Dissertation* University of Massachusetts (1976)
4 Stoelting, J., Karasz, F. E. and MacKnight, W. J. *Polym. Eng. Sci.* 1970, **10**, 133
5 Prest, W. M. Jr, and Porter, R. S. *J. Polym. Sci. (A-2)* 1972 **10**, 1639
6 Jacques, C. H. M. and Hopfenberg, H. B. *Polym. Eng. Sci.* 1974, **14**, 441
7 Shultz, A. R. and Gendron, B. M. *J. Appl. Polym. Sci.* 1972, **16**, 461
8 Yee, A. F. *Polym. Prepr.* 1976, **17**, 145
9 Tkacik, J. J. *PhD Dissertation* University of Massachusetts (1975)
10 MacKnight, W. J., Stoelting, J. and Karasz, F. E. *Adv. Chem. Ser.* 1971, **99**
11 Alexandrovich, P., Karasz, F. E. and MacKnight, W. J. *J. Appl. Phys.* 1976, **47**, 4251
12 Schultz, A. R. and Beach, B. M. *Macromolecules* 1974, **7**, 902
13 Lacombe, R. H. and Sanchez, I. C. *J. Phys. Chem.* 1976, **80**, 2568
14 McMaster, L. P., *Macromolecules* 1973, **6**, 760
15 Bank, M., Leffingwell, J. and Thies, C. *J. Polym. Sci. (A-2)* 1972, **10**, 1097
16 Nishi, T., Wang, T. T. and Kwei, T. K. *Macromolecules* 1975, **8**, 227
17 McMaster, L. P. *Adv. Chem. Ser.* 1975, **142**
18 'Polymer Handbook', (Eds J. Brandup and E. H. Immergut), Wiley–Interscience, New York, 1975
19 Odian, G. 'Principles of Polymerization', McGraw-Hill, New York, 1970
20 McCaffery, E. M. 'Laboratory Preparation for Macromolecular Chemistry', McGraw-Hill, New York, 1970
21 Hammer, C. F. *Macromolecules* 1971, **4**, 69
22 Shur, Y. J. and Rånby, B. *J. Appl. Polym. Sci.* 1975, **19**, 1337
23 Zakrzewski, G. A. *Polymer* 1973, **14**, 347
24 Shur, Y. J. and Rånby, B. *J. Appl. Polym. Sci.* 1975, **19**, 2143