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# Effect of Pressure on Phase Behavior in Polymer Blends of Poly(2,6-Dimethyl-1,4-Phenylene Oxide) and Poly(Styrene-co-*p*-Fluorostyrene) Copolymers

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## Synopsis

The effect of pressure on the miscibility of blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with a random copolymer of styrene and *para*-fluorostyrene, P(S-co-*p*-FS), has been studied by high pressure differential thermal analysis (HPDTA). P(S-co-*p*-FS) copolymers less than 36 mole % *p*-FS are miscible with PPO in all proportions irrespective of pressure up to 200 MPa, using the customary criterion of a single calorimetric glass relaxation. P(S-co-*p*-FS) copolymers containing 40 to 50 mole % *p*-FS undergo phase separation upon annealing at elevated temperatures, indicating the existence of a lower critical solution temperature (LCST). In these blends, pressure displaces the phase boundary associated with the LCST to higher temperatures causing an apparent increase in polymer miscibility. The phase diagram for the blend of PPO and P(S-co-*p*-FS) containing 46 mole % *p*-FS, shows that the critical composition at about 50 wt % PPO does not change with pressure, but the consolute temperature  $T_c$  increases with increasing pressure. The pressure dependence of the LCST ( $dT_c/dP$ ) of this system is about 0.35°C/MPa.

## INTRODUCTION

Although several hundred polymer blends have been studied,<sup>1</sup> the blend system of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is one of the few polymer blends which can be classified as miscible. The system PS/PPO meets all criteria for miscibility over the entire composition range<sup>2-10</sup> and exhibits a single, compositionally dependent glass transition when examined by a variety of techniques, including differential scanning calorimetry, thermomechanical, dynamic mechanical, and thermal optical analysis, and dielectric methods. Furthermore, there is direct calorimetric evidence for the expected negative heat of mixing  $\Delta H_m$  across the entire range of composition.<sup>11</sup>

However, relatively small changes in the chemical structure of the PS component are sufficient to render the resulting system entirely immiscible.<sup>6,7,10,12,13</sup> A recent study has shown that homopolymers of *o*-chlorostyrene P(*o*-ClS) or *p*-chlorostyrene P(*p*-ClS) are immiscible with PPO.<sup>10</sup>

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Random copolymers of styrene and *o*-ClS or *p*-ClS, however, form homogeneous blends with PPO if styrene is the predominant monomer. Shultz and Beach,<sup>12</sup> as well as Fried,<sup>10</sup> reported that a slight increase in the *p*-ClS content of P(S-co-*p*-ClS) (from 65.3 to 68 mole %) results in a shift from miscibility to immiscibility with PPO. In addition, random copolymers of *o*-ClS and *p*-ClS formed homogeneous blends with PPO at compositions between 23 and 64 mole % *p*-ClS.<sup>13,14</sup>

The miscibility behavior of fluorostyrene copolymer/PPO blends is similar to that of blends of the corresponding chlorinated copolymers with PPO.<sup>15-17</sup> Both the homopolymers poly(*p*-fluorostyrene), P(*p*-FS), and poly(*o*-fluorostyrene), P(*o*-FS), are immiscible with PPO while the miscibility of blends of P(S-co-*p*-FS), P(S-co-*o*-FS), P(*p*-FS-co-*o*-FS), and PPO depends on the copolymer composition. In these systems, miscibility occurs for a certain range of copolymer compositions; in a given system, phase separation occurs above a certain temperature. The phase behavior in these quasibinary mixtures is, therefore, of the lower critical solution temperature (LCST) type.<sup>13</sup> In the diagram of temperature versus copolymer composition, the boundary between domains of miscibility and immiscibility delineate the loci of the LCST's. More recently, ten Brinke *et al.*<sup>18</sup> have applied the mean-field theory of phase behavior to blends of random copolymers with homopolymers and explained the occurrence for example of a miscibility window in the temperature-copolymer composition diagram; furthermore, they were able to calculate the respective segmental interaction parameters ( $\chi_{ij}$ ) for these blends.

The miscibility behavior of these copolymer blends has been extensively studied under atmospheric pressure; however, the effect of pressure on miscibility remains unknown. In this article, the effect of pressure on the miscibility of blends of PPO and P(S-co-*p*-FS) was investigated by high-pressure differential thermal analysis (HPDTA) which allows the direct study of the glass transition phenomenon of polymer blends under elevated pressures.

## EXPERIMENTAL

### Materials

Blends using the copolymers prepared by Vuković *et al.*<sup>15</sup> were used in this study and details are given in Table I. The molecular weights of purified PPO (General Electric Co.) were  $\bar{M}_n = 17\,000$  and  $\bar{M}_w = 35\,000$ , as determined by size-exclusion chromatography. The copolymers were blended with PPO by coprecipitation from dilute toluene solution (3-4wt%) into a large quantity of methanol. The precipitates were dried under vacuum at 80°C for 60 hs. The

TABLE I  
The polystyrene-equivalent molecular weights are shown for the *p*-fluorostyrene copolymers.

	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$T_g(^{\circ}\text{C})$
P(S-co-36p-FS)	0.96	0.49	103
P(S-co-46p-FS)	0.99	0.52	103
P(S-co-49p-FS)	0.95	0.51	103
P(S-co-56p-FS)	0.99	0.49	103

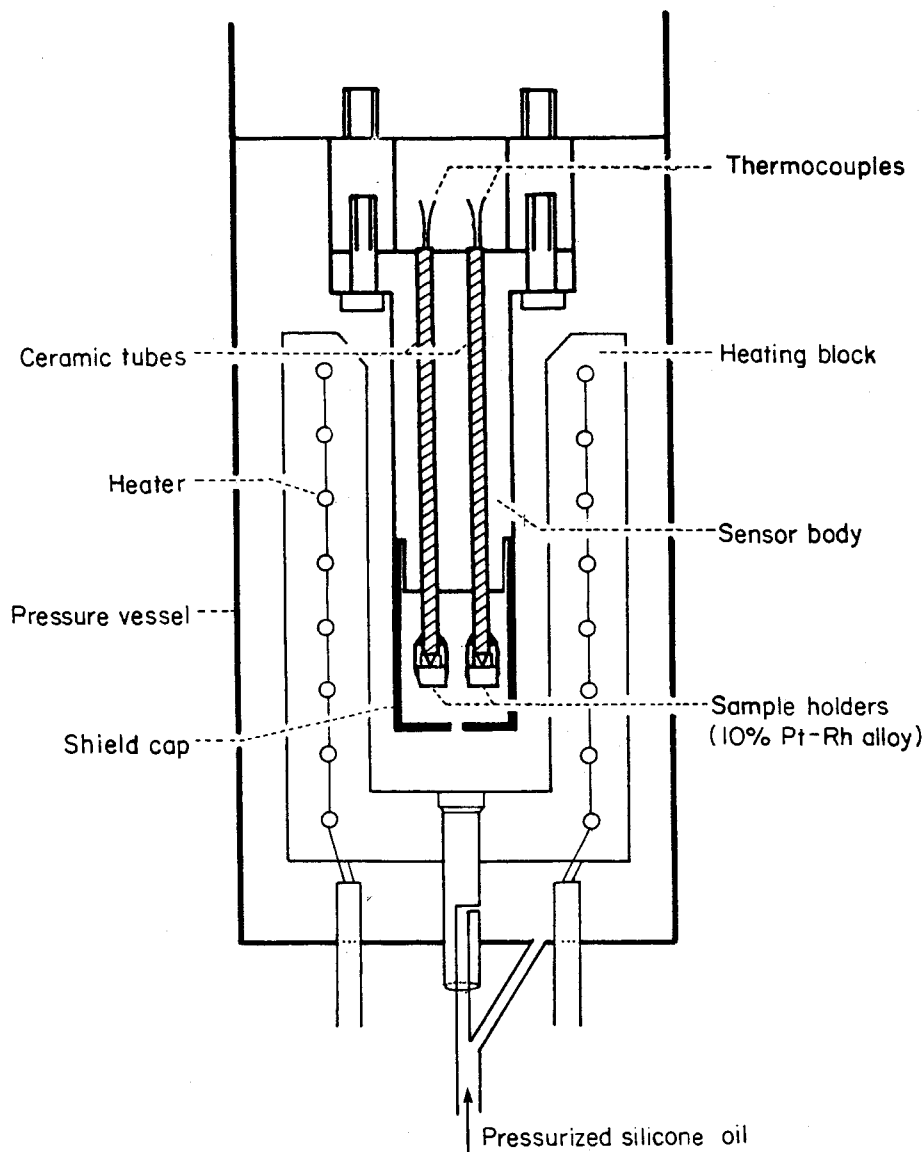


Fig. 1. Schematic diagram of modified high-pressure DTA sensor.

dried blends were then compression molded into films at 210°C. The miscibility of the P(S-co-p-FS) copolymers with PPO was judged according to the usual criteria of a single calorimetric glass transition and film clarity.

#### High Pressure Differential Thermal Analysis

The high-pressure DTA apparatus, developed by Takamizawa and Karasz<sup>19</sup> was used in this study. Figure 1 shows a simplified schematic diagram of the HPDTA sensor. Because the heating block is located inside the pressure vessel, measurements can be carried out at rapid rates of heating and cooling. The DTA sensor was modified in order to obtain the sensitivity needed for

detecting the  $T_g$ 's of the polymer blends at higher temperatures by doubling the size of the sample holders so that they can hold up to 16 mg of polymer sample and developing a heat-resistant DTA sensor for use at temperatures up to 400°C.

Pressure was monitored with an accuracy of  $\pm 1$  MPa by a manganin gauge which had been calibrated using a Heise gauge. Temperature was measured, with an accuracy of  $\pm 0.1^\circ\text{C}$ , by chromel-alumel thermocouples (Omega Engineering, Inc., CHAL-005) located beneath the sample holders the thermocouples had been calibrated using the melting points of In, Sn, and Pb.

The DTA studies were performed using a heating rate of  $20^\circ\text{C}/\text{min}$  with a sample size of 10–15 mg. All blends were amorphous; the only distinctive features of the DTA curves were glass transitions. The  $T_g$  was determined as that temperature at which the heat capacity achieved one-half of the entire change observed  $\Delta C_p$ . Annealing experiments were also carried out in the pressure vessel of the HPDTA. These experiments consisted of heating a sample of a miscible blend to a selected annealing temperature, and holding it at this temperature for 15–20 min. This time was selected as a compromise between avoiding degradation and allowing enough time for equilibrium to be established. Samples were then quenched to ambient temperatures as rapidly as possible in the instrument. The samples were then reheated at  $20^\circ\text{C}/\text{min}$  to determine whether one or two phases were present, as indicated by the number of observed  $C_p$  discontinuities, i.e., glass transitions.

The copolymer containing 46 mol% p-FS, designated as P(S-co-46p-FS) was investigated in greater detail than the others and consequently blends containing a PPO weight fraction of 0.2, 0.4, 0.5, 0.6, and 0.8 were prepared.

## RESULTS AND DISCUSSION

### Effect of Pressure on $T_g$

Figure 2 shows the pressure dependence of  $T_g$ 's for PPO, P(S-co-46p-FS), several blends (50/50 wt%) of PPO, and P(S-co-p-FS) containing from 36 to 56 mole % p-FS. The  $T_g$  of PPO increases rapidly with increasing pressure with  $dT_g/dP$  attaining a maximum value of  $0.5^\circ\text{C}/\text{MPa}$ , while the  $T_g$  of the P(S-co-46p-FS) copolymer increases almost linearly with pressure at a rate  $dT_g/dP = 0.28^\circ\text{C}/\text{MPa}$ . For the miscible blends of PPO and P(S-co-p-FS) the pressure dependence of the  $T_g$ 's shows a concave downward trend and the  $dT_g/dP$  values vary from 0.48 to  $0.20^\circ\text{C}/\text{MPa}$ .

The dependence of  $T_g$  on the weight fraction of PPO for the blend system PPO/P(S-co-46p-FS) is plotted at various pressures in Figure 3. At all pressures, the blend  $T_g$  can be described by the Wood equation,<sup>20</sup> represented by the solid curves in Figure 3. This equation is given by

$$W_1(T_g - T_{g_1}) + kW_2(T_g - T_{g_2}) = 0 \quad (1)$$

where  $W_1$ ,  $W_2$ , and  $T_{g_1}$ ,  $T_{g_2}$  are the weight fractions and  $T_g$ 's of components 1 and 2, respectively. In eq. (1)  $T_g$  is the glass transition for the blend and  $k$  is an empirical constant whose value was found from least squares fitting to be 0.59 at 1 atm, 0.54 at 100 MPa, and 0.47 at 200 MPa. However, the  $T_g$ 's of

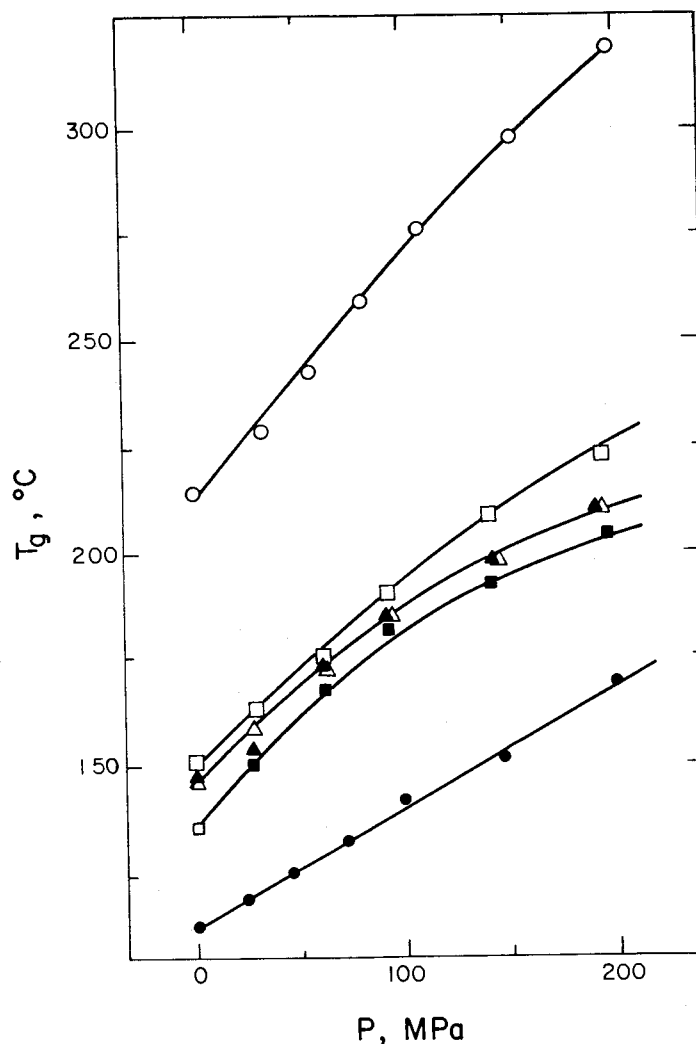


Fig. 2. Effect of pressure on the  $T_g$ 's of PPO ( $\circ$ ), P(S-co-46p-FS) ( $\bullet$ ), and four 50/50 weight % blends of PPO/P(S-co-p-FS) containing p-FS of 36 ( $\square$ ), 46 ( $\blacktriangle$ ), 49 ( $\triangle$ ) and 56 ( $\blacksquare$ ) mole %.

these blends at each pressure are depressed from those predicted by the Fox equation:<sup>21</sup>

$$1/T_g = W_1/T_{g_1} + W_2/T_{g_2}. \quad (2)$$

This is illustrated by the broken lines in Figure 3. The depression of  $T_g$  becomes larger with increasing pressure. It has been reported<sup>14</sup> that the  $T_g$ 's of the PPO and P(S-co-o-ClS) blend system can be empirically fitted by the Wood equation with  $k = 0.69$ , but these  $T_g$ 's were observed to depart from the Fox equation under atmospheric pressure.

The effect of composition on glass-transition temperature in miscible polymer blends has also been discussed by Couchman and Karasz.<sup>22</sup> Furthermore, Couchman<sup>23</sup> derived a relation from the mixed-system entropy in terms of the

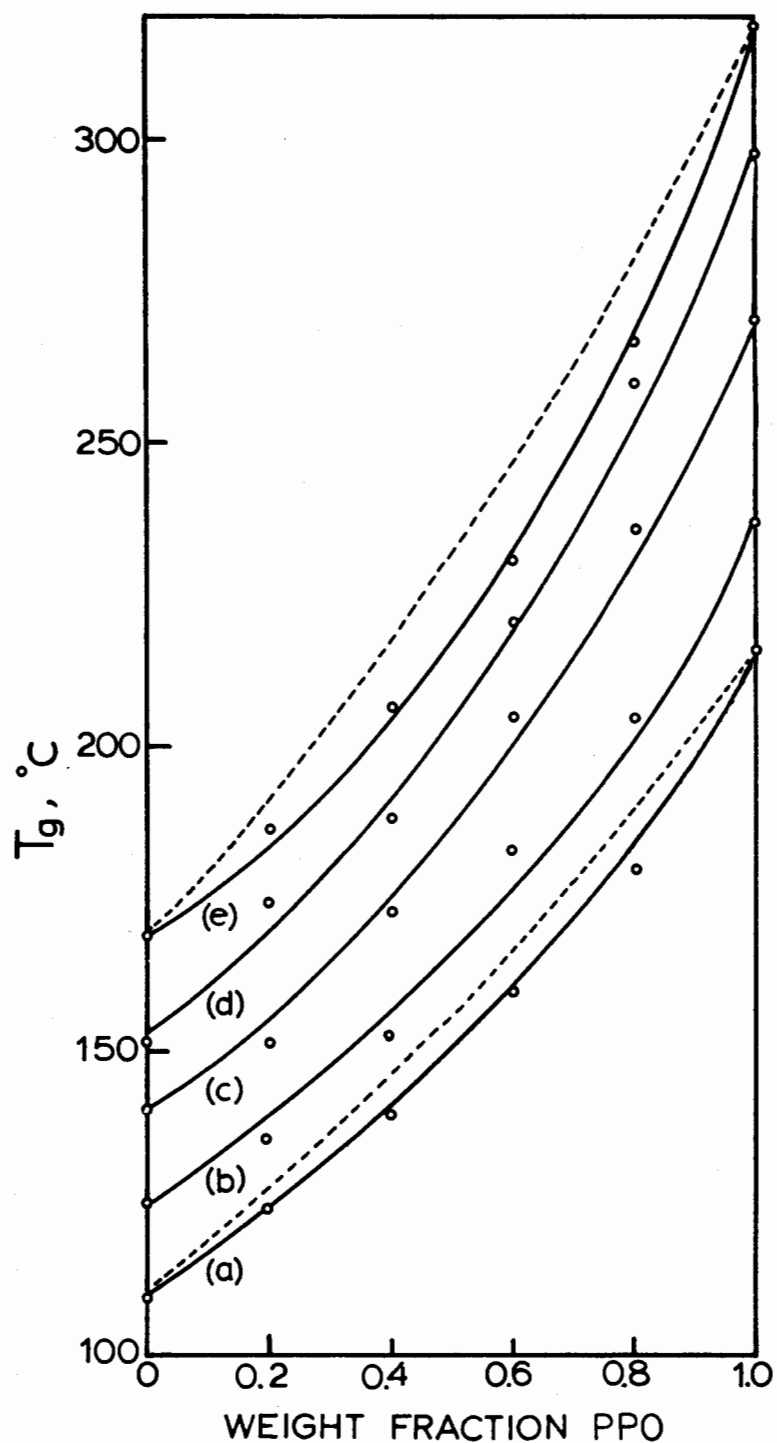


Fig. 3. Dependence of  $T_g$ 's on the weight fraction of PPO for the PPO/P(S-co-46p-FS) system at indicated pressures: (a) 0.1 MPa, (b) 50 MPa, (c) 100 MPa, (d) 150 MPa, and (e) 200 MPa. Solid lines represent the Wood equation, and broken lines represent the Fox equation.

pure component heat capacity increment  $\Delta C_{p_i}$  ( $i = 1, 2$ ) and glass transition temperature  $T_{g_i}$  ( $i = 1, 2$ ):

$$\ln T_g = \frac{W_1 \Delta C_{p_1} \ln T_{g_1} + W_2 \Delta C_{p_2} \ln T_{g_2}}{W_1 \Delta C_{p_1} + W_2 \Delta C_{p_2}} \quad (3)$$

It was shown that eq. (3) gives a satisfactory prediction of the observed effect of composition on  $T_g$  for the two polymer blends PPO/PS and PPO/P(S-co-p-ClS). Both the Wood and Fox equations are obtained as special cases of this equation.

The  $dT_g/dP$  values for the system in Figure 3 are estimated to be  $0.28^\circ\text{C}/\text{MPa}$ , which is similar to the value found for the pure P(S-co-46p-FS) copolymer. Another important feature of the DTA curves is the breadth of the glass transition. The glass transition for the single-phase blends is broader than that of the unblended pure materials which probably can be explained on the basis of phase inhomogeneity, which implies that localized compositional fluctuations may be present in the system. These may arise from failure to attain equilibrium and/or from preferential solubilization arising from molecular weight distribution.

#### Thermally Induced Phase Separation

It is known<sup>15</sup> that blends of the copolymers containing 36–56 mole % p-FS undergo phase separation upon annealing at elevated temperatures at atmospheric pressure, indicating the existence of an LCST. To analyze the effect of pressure on the miscibility behavior of the copolymer/PPO blends, the sam-

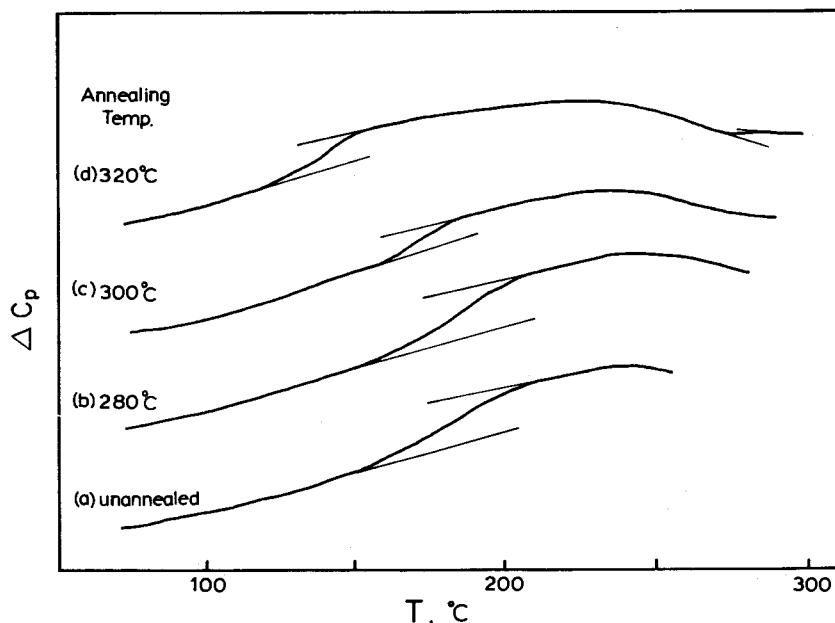


Fig. 4. DTA curves of the 50/50 weight % blend of PPO/P(S-co-46p-FS) at 100 MPa: (a) molded at  $210^\circ\text{C}$ , (b) annealed at  $280^\circ\text{C}$  for 15 minutes, (c) annealed at  $300^\circ\text{C}$  for 20 minutes, and (d) annealed at  $320^\circ\text{C}$  for 20 min.



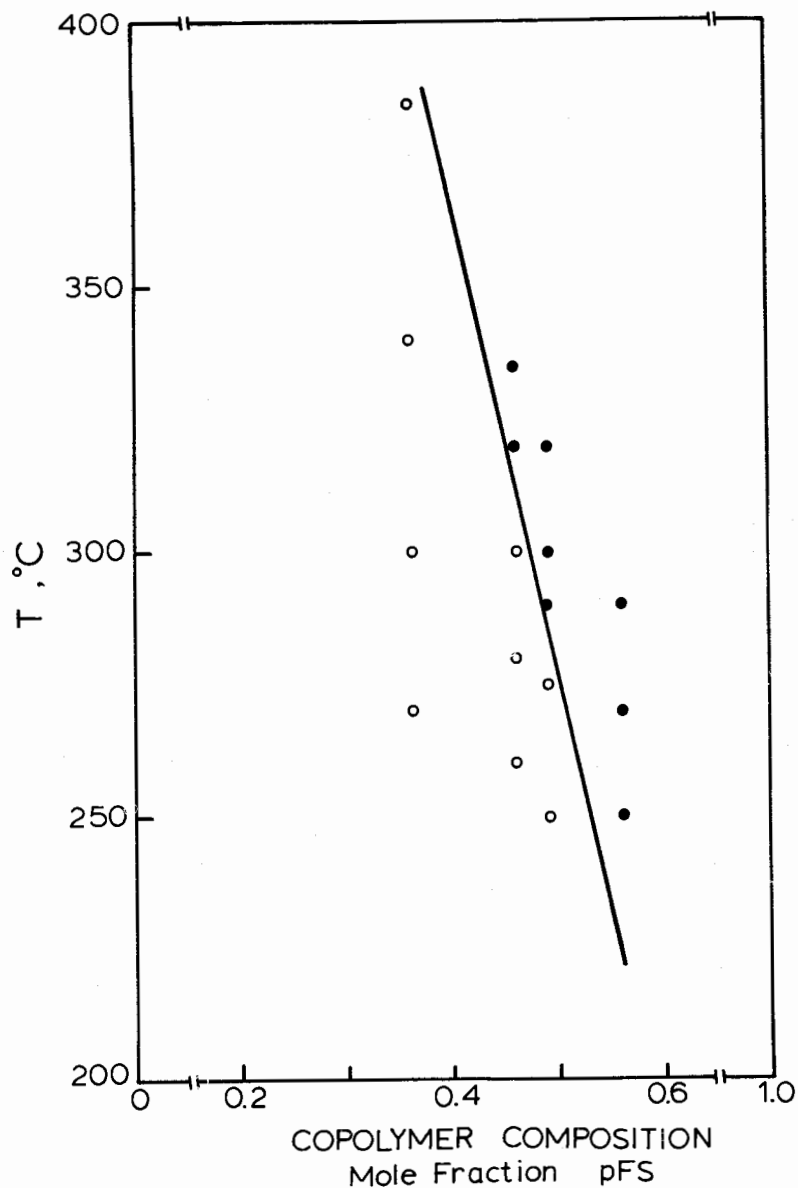


Fig. 5. Phase-separation temperature as a function of copolymer composition for the 50/50 weight % blends of PPO/P(S-co-p-FS) at 100 MPa: ○; one phase, ●; two phases.

ples were annealed at elevated temperatures for 20 min at specific pressures. Figure 4 shows the DTA curves of the 50/50 wt% blends of PPO and P(S-co-46p-FS) at 100 MPa. The unannealed sample, molded at 210°C, shows one  $T_g$ . The sample annealed at 320°C exhibits two  $T_g$ 's indicating phase separation. This behavior suggests the existence of an LCST for this mixture even at high pressure. Other samples were annealed at the same pressure; the phase-separation temperatures are shown in Figure 5. It is evident that miscibility strongly depends on copolymer composition as first reported by Vuković *et al.*<sup>15</sup> Samples with a higher styrene content in the copolymer are

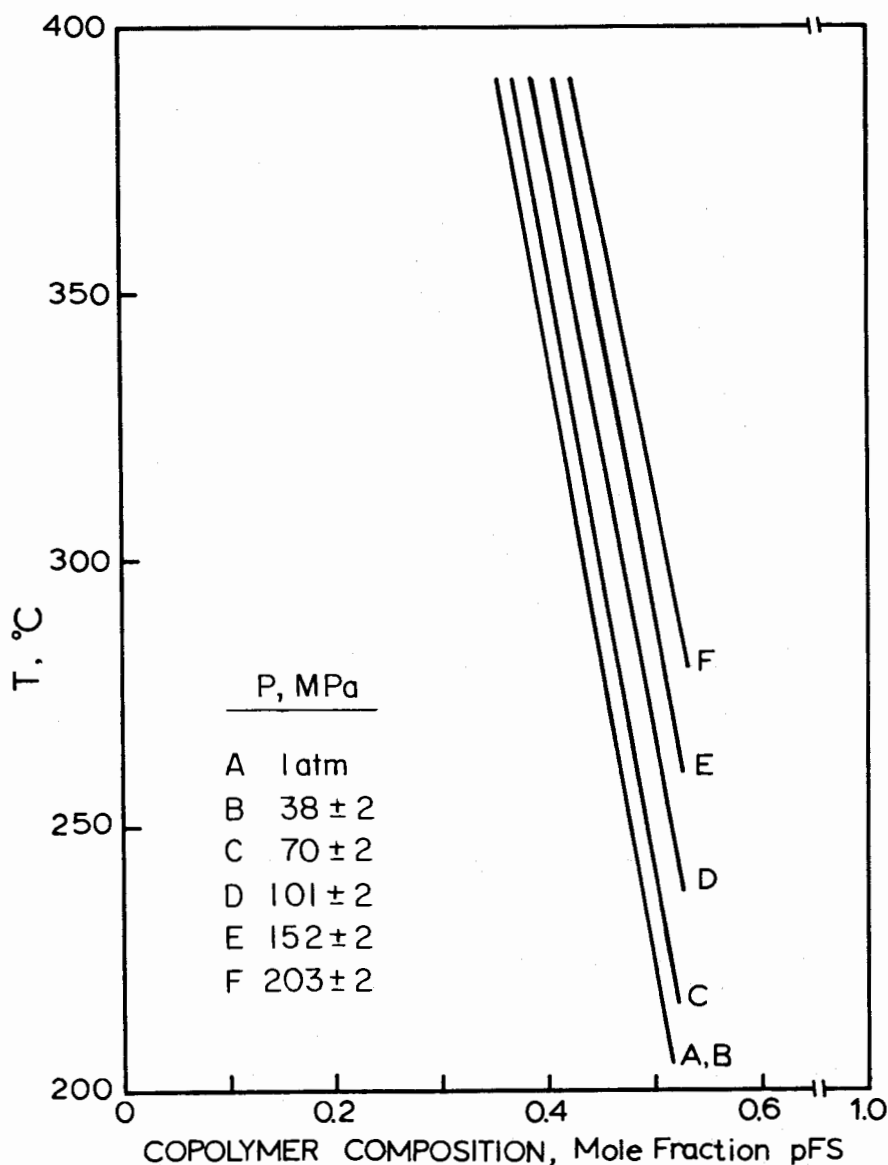


Fig. 6. Effect of pressure on the miscibility of the PPO/P(S-co-p-FS) system. Miscibility occurs on the left side of these curves.

miscible with PPO; these results are consistent with the results obtained at atmospheric pressure and with the finding that polystyrene is miscible with PPO.<sup>10</sup> Figure 6 shows the effect of pressure on the phase-separation temperature for the 50/50 wt% blends of PPO/P(S-co-p-FS) at pressures up to 200 MPa. These curves are essentially parallel indicating that the pressure dependence of the consolute temperatures for the four PPO/P(S-co-p-FS) blends (36, 46, 49, and 56 mole% p-FS) are the same within experimental error. It is clear that the curves representing the boundary of the miscibility-immiscibility regimes in Figures 5 and 6 in fact define the loci of the LCST's for these systems. Figure 7 shows the pressure dependence of the phase separation

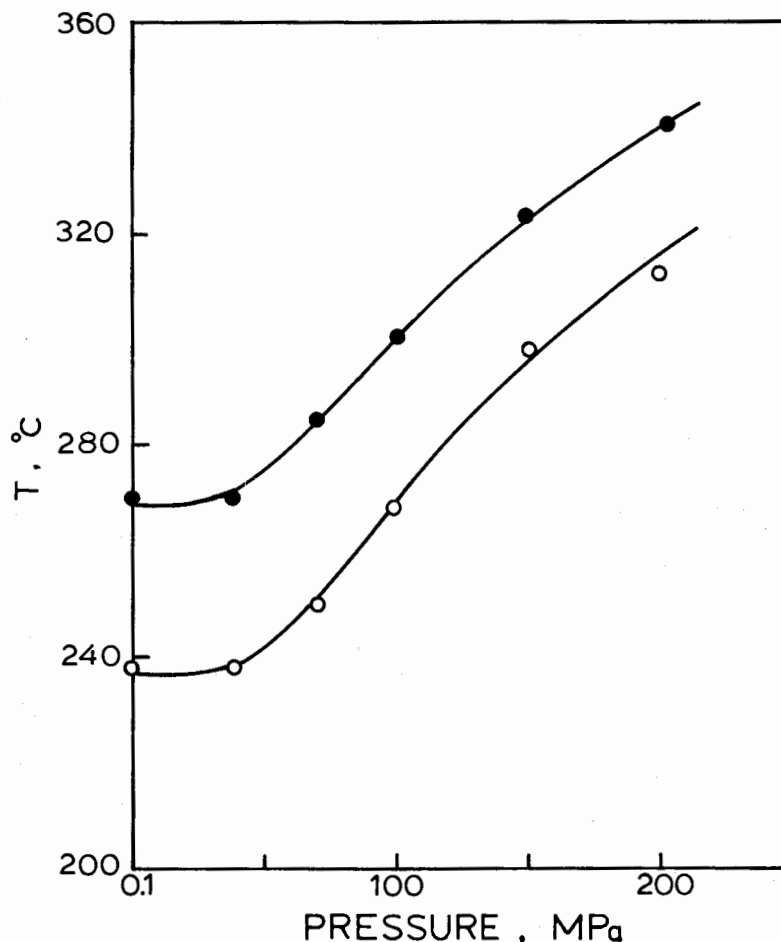


Fig. 7. Effect of pressure on the phase-separation temperatures of two 50/50 wt % blends; PPO/P(S-co-46p-FS), (●) and PPO/P(S-co-49p-FS), (○).

temperatures for the two blends (50/50 wt %) PPO/P(S-co-46p-FS) and PPO/P(S-co-49p-FS). These temperatures at first increase gradually and then more rapidly at an average value of  $(dT_c/dP) = 0.35 \pm 0.05^\circ\text{C}/\text{MPa}$ .

In a phase-separated system the glass transition temperatures of the two phases can be determined from the HPDTA results. A phase diagram can then be constructed by assuming that the composition of these phases can be determined by using the  $T_g$  versus blend composition curve for the homogeneous blends. Figure 8 shows such a diagram for the blend of PPO with P(S-co-46p-FS) at 100 MPa. The phase boundary is symmetrical with respect to composition at all pressures; no phase separation of blends containing 80 wt% PPO was detected at temperatures up to  $380^\circ\text{C}$  though experimental considerations may be responsible for this absence. At higher temperatures, the annealing time was reduced to 10 min to prevent sample degradation. In the lower portion of the diagram, the  $T_g$  versus composition curve is shown for the compatible blend. Two-phase glasses can be produced by rapid cooling from above the LCST for appropriate compositions.

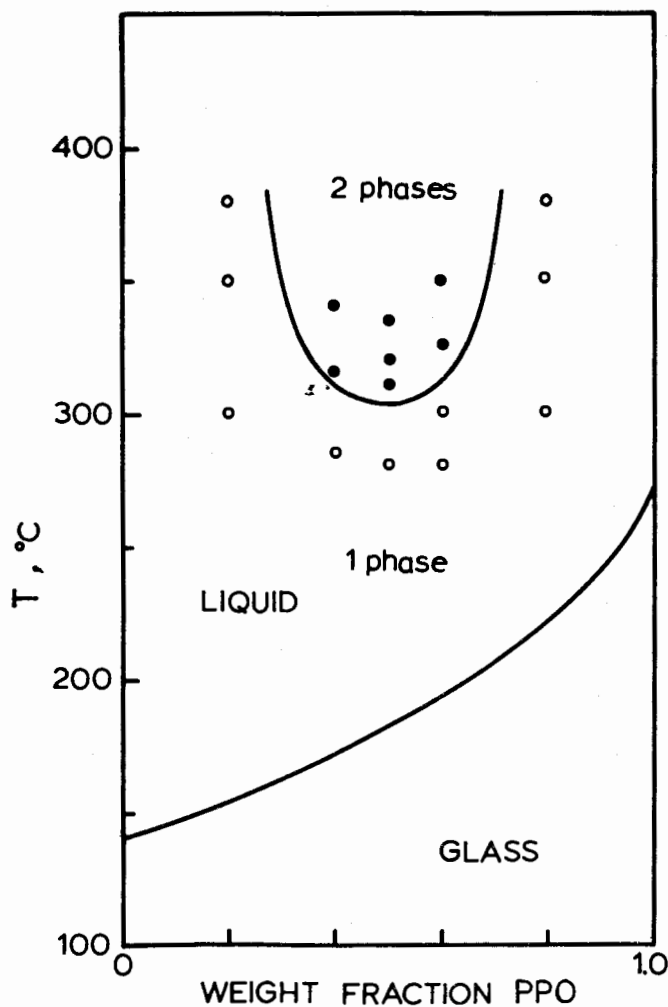


Fig. 8. Phase diagram of PPO/P(S-co-46p-FS) at 100 MPa: ○; one phase, ●; two phases.

Figure 9 shows the phase diagram of PPO/P(S-co-46p-FS) with respect to pressure  $P$ , temperature  $T$ , and weight fraction PPO. It should be noted that the critical composition of the LCST curve is constant at 50 wt % PPO, independent of the applied pressure, while the LCST's themselves increase with increasing pressure at a rate  $dT_c/dP \approx 0.35^\circ\text{C}/\text{MPa}$ .

The effects of pressure on phase-separation behavior in nonpolymeric mixtures have been reviewed by Schneider.<sup>24</sup> He classified 14 categories of phase diagram for binary liquid-liquid mixtures with respect to pressure, temperature, and composition. The change in pattern of the phase diagram with pressure for the PPO/P(S-co-46p-FS) system is of the type "m" (see Figure 5, ref. 24), i.e., the LCST increases with increasing pressure.

Theoretical investigations of miscible polymeric mixtures have been performed by McMaster<sup>25</sup> and by Sanchez and Lacombe.<sup>26</sup> The results of the present study are consistent with their prediction that LCST behavior is common in polymer-polymer mixtures. McMaster predicted that the LCST

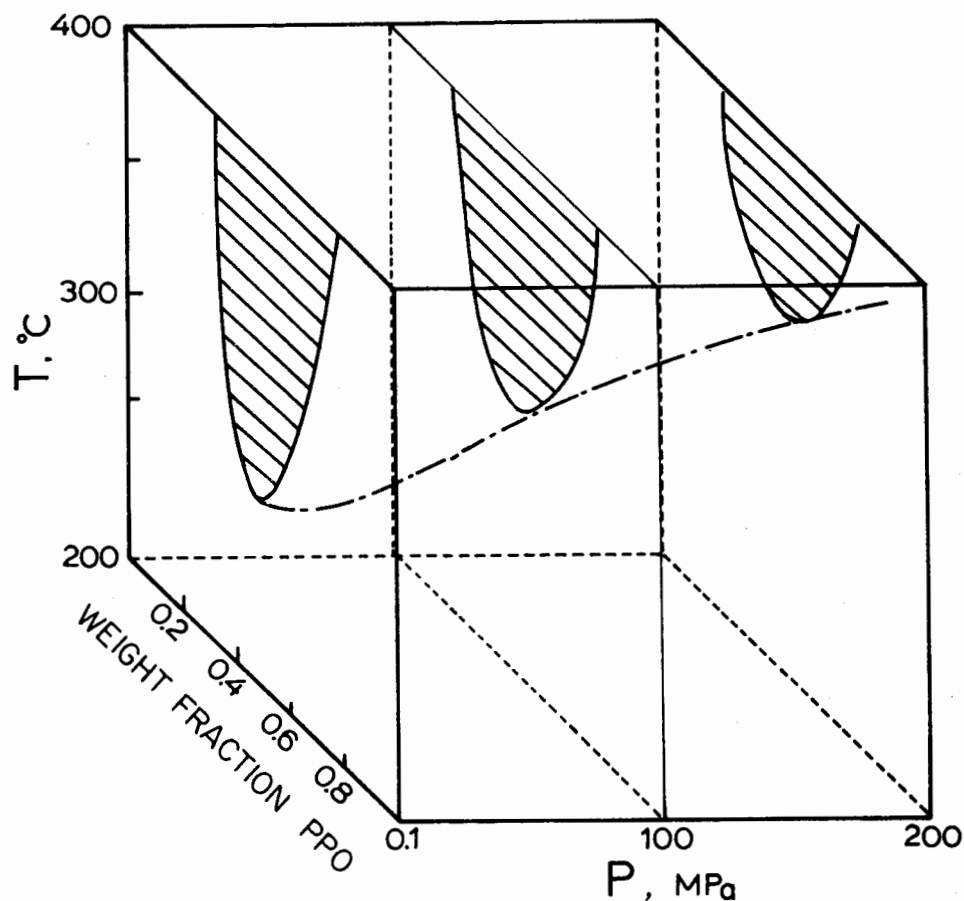


Fig. 9. Combined phase diagram of PPO/P(S-co-46p-FS).

should either increase monotonically or have a relative minimum with increasing pressure depending on the magnitudes of the thermal pressure coefficients. The present PPO/P(S-co-p-FS) system shows a monotonic increase in LCST with pressure; the latter type of phase diagram, however, has yet to be observed.

Patterson and Robard<sup>27</sup> estimated the pressure-dependence of the LCST and UCST, based on the Prigogine-Flory theory in which the  $\chi$  parameter (i.e., the segmental interaction parameter) is expected to be a function of temperature and pressure. Their calculated values for the LCST pressure dependence for the PS/poly(vinyl methyl ether) and poly(vinyl chloride)/poly( $\epsilon$ -caprolactone) blends are 1.3 and 2.0°C/MPa, respectively. The experimental value of  $dT_c/dP$  for the PPO/P(S-co-46p-FS) blend reported here is about 0.35°C/MPa. Recently, two studies of the pressure dependence of phase diagrams for the poly(ethyl acrylate)/poly(vinylidene fluoride)<sup>28</sup> and PS/poly(vinyl methyl ether) blends,<sup>29</sup> using cloudpoint measurements have been reported and a  $dT_c/dP$  value of 0.3°C/MPa was given which is comparable to our value. Thus there appears to be a discrepancy in the order of magnitude of the calculated values for the few systems so far investigated.

## CONCLUSIONS

The dependence of  $T_g$  on pressure was determined for the PPO/P(S-co-p-FS) blend system in which the p-FS content of the copolymer varied from 36 to 56 mole %. A single compositionally dependent  $T_g$  could be observed, indicating miscibility for the blends which were annealed below the phase-separation temperature. In addition, the dependence of  $T_g$  on weight fraction PPO for the PPO/P(S-co-46p-FS) blend system was determined at various pressures. At each pressure, the Wood equation provided a satisfactory representation of the experimental data. The temperature-pressure composition-phase diagram for the particular blend PPO/P(S-co-46p-FS), was constructed by annealing each mixture at a fixed temperature and pressure in the high-pressure DTA apparatus. The LCST for this system increased with pressure at an average rate  $dT_c/dP = 0.35^\circ\text{C}/\text{MPa}$ .

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