

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

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## Synopsis

The effect of pressure on miscibility and phase separation in blends of random copolymers of *ortho*- and *para*-fluorostyrene, P(*o*-FS-co-*p*-FS) and poly(2,6-dimethyl-1,4-phenylene oxide), PPO, has been studied by differential thermal analysis (DTA) at pressures up to 300 MPa. At 200 MPa the copolymers containing from 10 to 38 mol% *p*-FS are miscible with PPO below 230°C using the customary criterion of a single calorimetric glass transition temperature ( $T_g$ ). Each blend undergoes phase separation upon annealing at higher temperatures at both atmospheric and elevated pressures indicating the presence of a lower critical solution temperature (LCST). When the phase behaviors of the 50/50 wt% blends are examined as a function of temperature and copolymer composition, a symmetric miscibility "window" can be observed in the resulting temperature-composition diagram with a maximum at about 22 mol% *p*-FS. In a complementary set of experiments, the pressure dependence of the phase boundary for the blend of PPO and P(*o*-FS-co-*p*-FS) in which the copolymer contained 29 mol% *p*-FS was studied. The temperature minimum of the phase boundary is at about 50 wt% PPO and is independent of pressure. The consolute temperature,  $T_c$ , increases at about 0.1°C/MPa up to 200 MPa and then becomes independent of pressure to reach an asymptotic value at around 270°C. Similar behavior is also observed for blends in which the copolymer composition contains either 16 or 23 mol% *p*-FS. In these blends the decrease of  $dT_c/dP$  at higher pressures may indicate that the negative volume of mixing approaches zero above 200 MPa. This study shows therefore, that pressure no longer plays a role in increasing the miscibility above 200 MPa.

## INTRODUCTION

In a previous publication<sup>1</sup> the effect of pressure on the miscibility and phase separation of polymer blends of random copolymers of styrene and *p*-FS, P(S-co-*p*-FS), with PPO was investigated. All the miscible blends can be separated into two phases at elevated temperatures, indicating that this behavior is of the LCST type.<sup>2</sup> The pressure dependence of the phase boundary for the blends of PPO/P(S-co-*p*-FS) in which the copolymer contains 46 mol% *p*-FS (here designated as P(S-co-46*p*-FS)) indicated that the critical composition at about 50 wt% PPO for these blends is independent of pressure while the consolute temperature,  $T_c$ , increases monotonically at a rate of

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$dT_c/dP = 0.35^\circ\text{C}/\text{MPa}$  with increasing pressure up to 200 MPa. In these blends, a very slight increase in the *p*-FS content of the copolymer resulted in a shift from miscibility to immiscibility and because PPO and pure polystyrene are compatible the miscibility/immiscibility boundary in the temperature-composition diagram, i.e., the plot of phase state as a function of temperature and copolymer composition (increasing mole fraction *p*-FS) is approximately a straight line of negative slope. In addition, it was shown that increasing pressure displaced this boundary to higher temperatures.

In another study,<sup>3</sup> the miscibility behaviors of mixtures of PPO and P(*o*-FS-co-*p*-FS) were investigated. The behaviors of the 50/50 wt% blends with different copolymer compositions displayed a characteristic miscibility window in that the blends of the respective homopolymers with PPO were immiscible while the blends were homogeneous with random copolymers of a given composition range. The range and hence the phase separation temperatures were dependent on copolymer composition. Similar results were found for blends of the corresponding chlorinated copolymers with PPO.<sup>4</sup> The P(*o*-FS-co-*p*-FS) copolymers containing from 10 to 38 mol% *p*-FS were miscible with PPO in all proportions<sup>3</sup> while the P(*o*-ClS-co-*p*-ClS) copolymers containing from 23 to 64 mol% *p*-ClS were miscible at atmospheric pressure.<sup>4</sup> The phase behaviors in these blends were also of the LCST type and symmetric miscibility windows were obtained in the temperature-composition diagrams. Similar behavior has been reported for other polymer blends.<sup>5-7</sup>

In this paper, the study of the effect of pressure on the miscibility and phase separation of blends of PPO/P(*o*-FS-co-*p*-FS) has been extended by using the high pressure differential thermal analysis technique (HPDTA) described previously.<sup>1</sup>

## EXPERIMENTAL

### Materials

The copolymer samples prepared by Vuković et al.<sup>3</sup> were used in this study and details are given in Table I. The molecular weights of the purified PPO (General Electric Co.) used were  $\bar{M}_w = 35,000$  and  $\bar{M}_n = 17,000$ , determined by gel permeation chromatography. The copolymers were blended with PPO by coprecipitation from a dilute toluene solution (3–4 wt%) into a large quantity of methanol. The precipitates were dried under vacuum at 80°C for 60 h. Films were made from the dried, precipitated blends by

TABLE I  
Copolymers Used

	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$T_g, ^\circ\text{C}$
P( <i>o</i> -FS-co-10 <i>p</i> -FS)	1.31	0.64	95
P( <i>o</i> -FS-co-16 <i>p</i> -FS)	1.68	0.91	96
P( <i>o</i> -FS-co-23 <i>p</i> -FS)	1.61	0.85	96
P( <i>o</i> -FS-co-29 <i>p</i> -FS)	1.67	0.90	97
P( <i>o</i> -FS-co-38 <i>p</i> -FS)	1.60	0.80	98

compression molding at 210°C. The criteria for miscibility used in this study were the presence of a single calorimetric glass transition temperature and film clarity.

The copolymer containing 29 mol% *p*-FS (i.e., P(*o*-FS-co-29*p*-FS)) was blended with PPO to obtain mixtures with weight fractions of 0.2, 0.4, 0.5, 0.6, and 0.8 in the study of the pressure dependence of the phase diagram for this blend.

### High Pressure Differential Thermal Analysis Measurements

The HPDTA apparatus, developed by Takamizawa and Karasz,<sup>8</sup> was used in this study. All the DTA experiments were performed similarly using heating rates of 20°C/min with a sample size of 10–15 mg. All blends were amorphous, and the only distinctive features of the DTA curves were glass transitions. The  $T_g$  was defined as the 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 DTA pressure vessel. An experiment consisted of heating a blend sample to a selected annealing temperature, and holding it at this temperature for a selected time, usually 15–20 min and at a predetermined pressure. Samples were then quenched to ambient temperature as rapidly as possible and were then reheated at 20°C/min to determine whether one or two phases were present, as indicated by the number of glass transitions.

Differential scanning calorimetry (DSC) was used to determine the miscibility of these blends under atmospheric pressure. All differential scanning calorimetry (Perkin-Elmer DSC-2) was done under a nitrogen atmosphere using heating rates of 20°C/min.

## RESULTS AND DISCUSSION

### Effect of Pressure on $T_g$

Figure 1 shows the pressure dependence of  $T_g$ 's for PPO, the pure copolymer, P(*o*-FS-co-23*p*-FS), and for three 50/50 wt% blends of PPO/P(*o*-FS-co-*p*-FS) containing 23, 29, and 38 mol% *p*-FS, respectively. The results show that the  $T_g$  of PPO increases initially at ca. 0.5°C/MPa with pressure as reported in the previous paper,<sup>1</sup> while the initial pressure dependence of the glass transition temperature of the copolymer is somewhat lower at ca. 0.2–0.3°C/MPa. For the blends containing copolymers with different mol% *p*-FS, a single, compositionally dependent  $T_g$  is observed for each blend with all three  $dT_g/dP$ 's approximately equal. As anticipated, the  $T_g$ 's of these copolymer blends lie between the  $T_g$ 's of the pure PPO and that of the copolymer.

Figure 2 shows the effect of copolymer composition on the  $T_g$  of a 50/50 wt% blend of PPO/P(*o*-FS-co-*p*-FS) at elevated pressures. A set of symmetrical curves with almost equal slopes of  $\pm 1^\circ\text{C}/\text{mol}\%$  *p*-FS is obtained indicating maximum  $T_g$ 's for all pressures at about 22 mol% *p*-FS.

Figure 3 shows  $T_g$  as a function of blend composition for the PPO/P(*o*-FS-co-29*p*-FS) blends at elevated pressures. The value of  $dT_g/dP$  for the 20/80

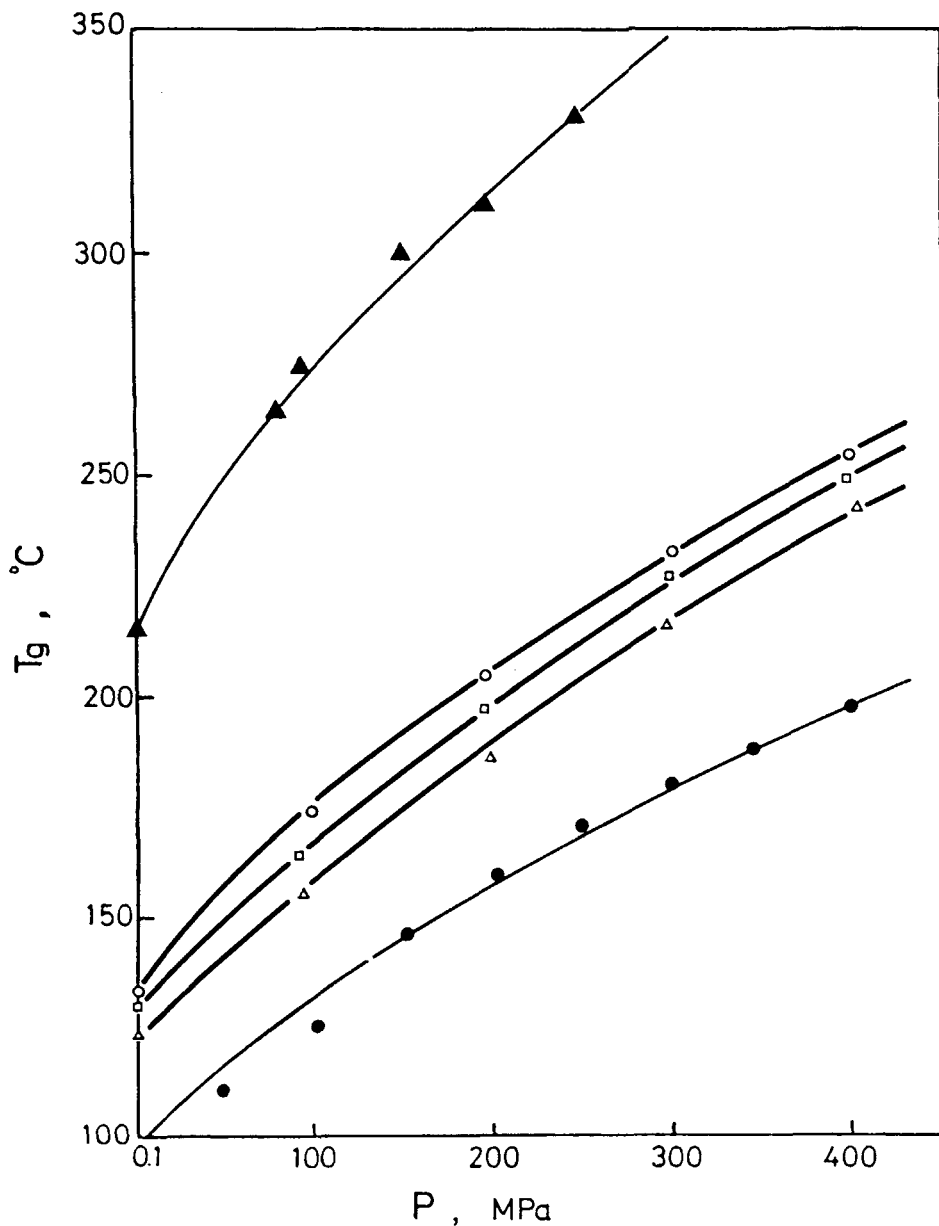


Fig. 1. Effect of pressure on the  $T_g$  for PPO (▲), P(*o*-FS-co-23*p*-FS) (●), and three blends of PPO/P(*o*-FS-co-*p*-FS) containing 23 (○), 29 (□), and 38 (△) mol% *p*-FS, respectively.

wt% PPO/P(*o*-FS-co-29*p*-FS) blend changes from 0.2<sub>0</sub> to 0.3<sub>2</sub>°C/MPa, while that for the 80/20 wt% blend changes from 0.3<sub>0</sub> to 0.4<sub>0</sub>°C/MPa up to 300 MPa. The blend  $T_g$  can be predicted approximately from the Wood equation<sup>9</sup> in which the empirical constant  $k$  is independent of pressure with  $k \cong 0.45$ –0.50.

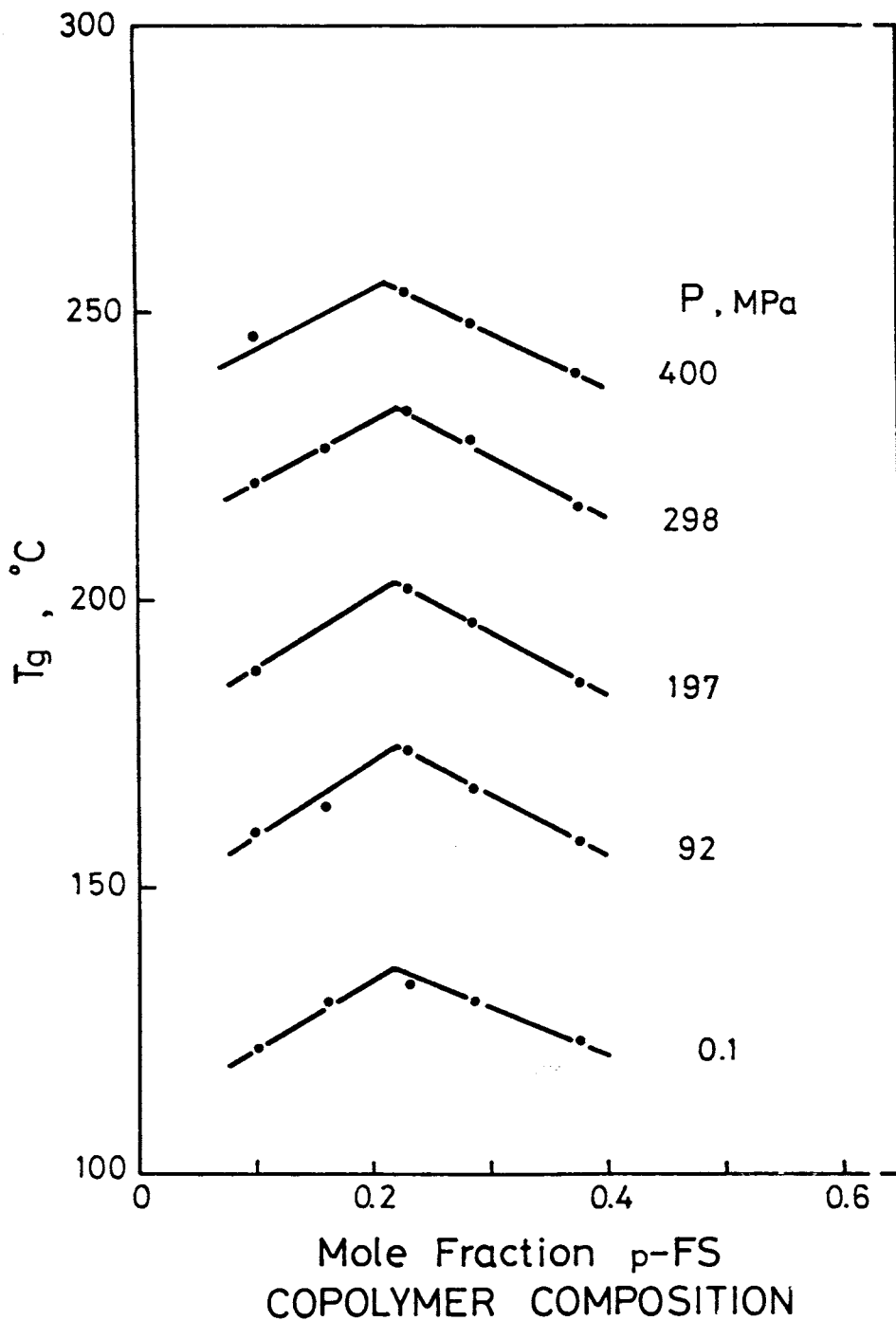


Fig. 2.  $T_g$  vs. copolymer composition for the 50/50 wt% blends of PPO/P(*o*-FS-co-*p*-FS) as a function of pressure.

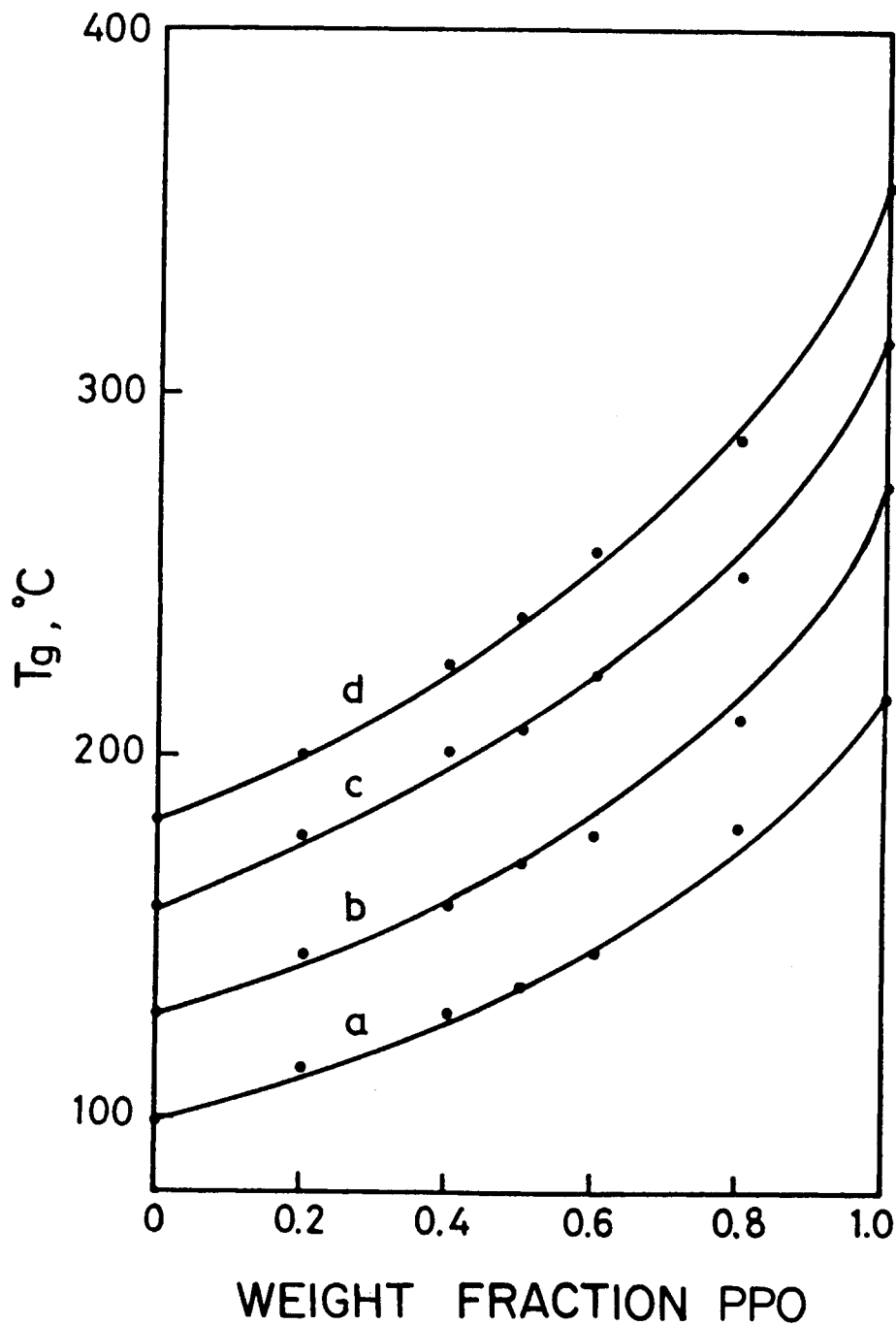


Fig. 3.  $T_g$  vs. blend composition for the blend of PPO/P(*o*-FS-co-29*p*-FS) at 0.1 MPa(a), 92 MPa(b), 197 MPa(c), and 298 MPa(d).

### Thermally Induced Phase Separation

The PPO/P(*o*-FS-co-*p*-FS) blends undergo phase separation at elevated temperatures, indicating the existence of an LCST.<sup>2</sup> As an example, Figure 4 shows the DTA curves for the blend of 50/50 wt% of PPO/P(*o*-FS-co-23*p*-FS) at 200 MPa. The sample molded at 210°C, shows a single, broad glass transition at 204°C. Samples annealed at 270 and 280°C show broader transitions at essentially identical temperatures. However, a sample annealed at 290°C shows two well resolved glass transitions at 198 and 251°C while one annealed at 300°C also exhibited two  $T_g$ 's with further slight changes to 197 and 261°C. As expected, the  $T_g$  values for the homogeneous blends (I, II, and III in Fig. 4) lie between those of the pure homopolymers, i.e., 157 and 319°C at 200 MPa for P(*o*-FS-co-23*p*-FS) and PPO, respectively. Other miscible blends were analyzed using the same procedures. Phase separation was exhibited in all the blends but the lowest annealing temperature at which separation depended as expected on the copolymer composition as shown in Figure 5. A symmetric miscibility window is observed with a maximum at about 22 mol% *p*-FS. Figure 6 shows the effect of pressure on the miscibility windows for the 50/50 wt% blends of PPO/P(*o*-FS-co-*p*-FS) up to 300 MPa. The copolymer composition showing a maximum miscibility is about 22 mol% *p*-FS and is independent of pressure. The phase separation temperatures of all the copolymer blends increase approximately at 0.1°C/MPa with pressures up to 200 MPa. This increase with pressure is lower than the value of 0.35°C/MPa found for PPO/P(S-co-*p*-FS)<sup>1</sup> and the value of 0.3°C/MPa found for blend systems of PS/poly(vinylmethylether)<sup>10</sup> and

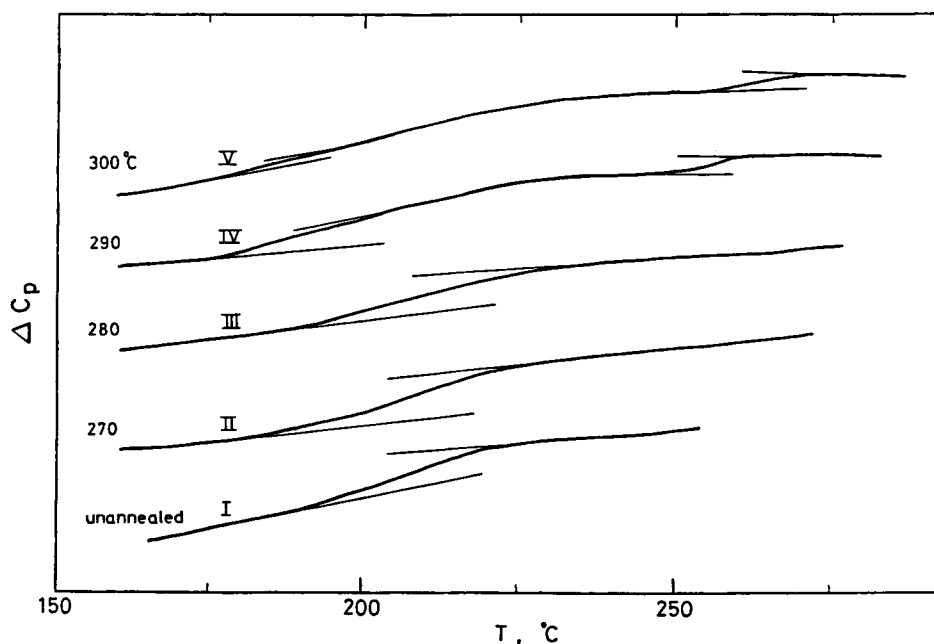


Fig. 4. DTA curves of 50/50 wt% blends of PPO/P(*o*-FS-co-29*p*-FS) at 200 MPa. (I), as molded at 210°C; (II), annealed at 270°C for 24 min; (III), annealed at 280°C for 20 min; (IV), annealed at 290°C for 20 min; (V), annealed at 300°C for 15 min.

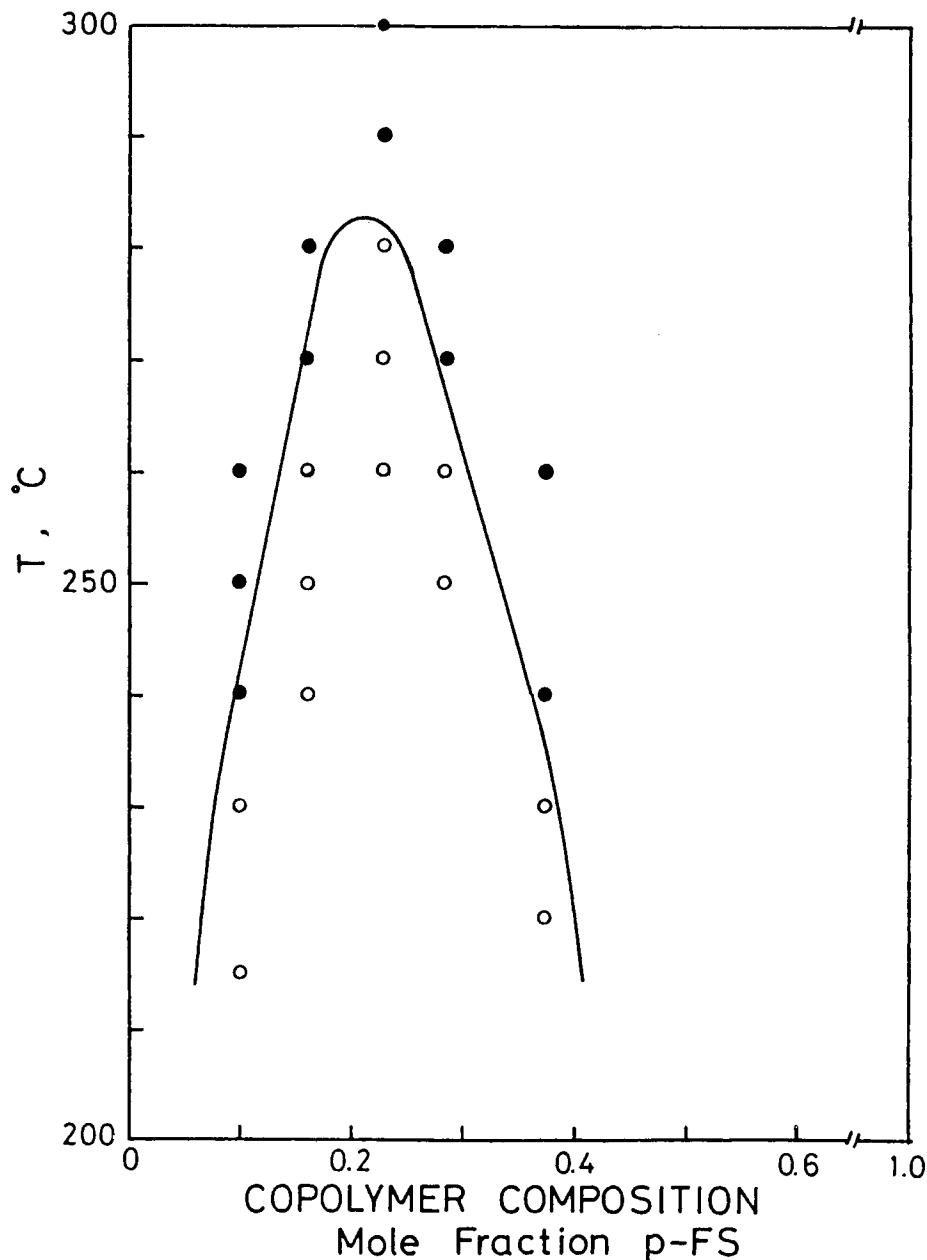


Fig. 5. Temperature-composition diagram of 50/50 wt% blends of PPO/P(*o*-FS-co-*p*-FS) at 200 MPa. ○: one phase; ●: two phases.

poly(ethyl acrylate)/poly(vinylidene fluoride).<sup>11</sup> For pressures higher than 200 MPa, it is observed that the lowest phase separation temperatures for the blends of PPO and copolymers containing 16, 23, and 29 mol% of *p*-FS become independent of pressure. Figure 7 shows this point in the depicted pressure dependence of the phase separation temperature,  $T_c$ , for blends containing 23 and 29 mol% *p*-FS. For the blends of 10, 16, and 38 mol% *p*-



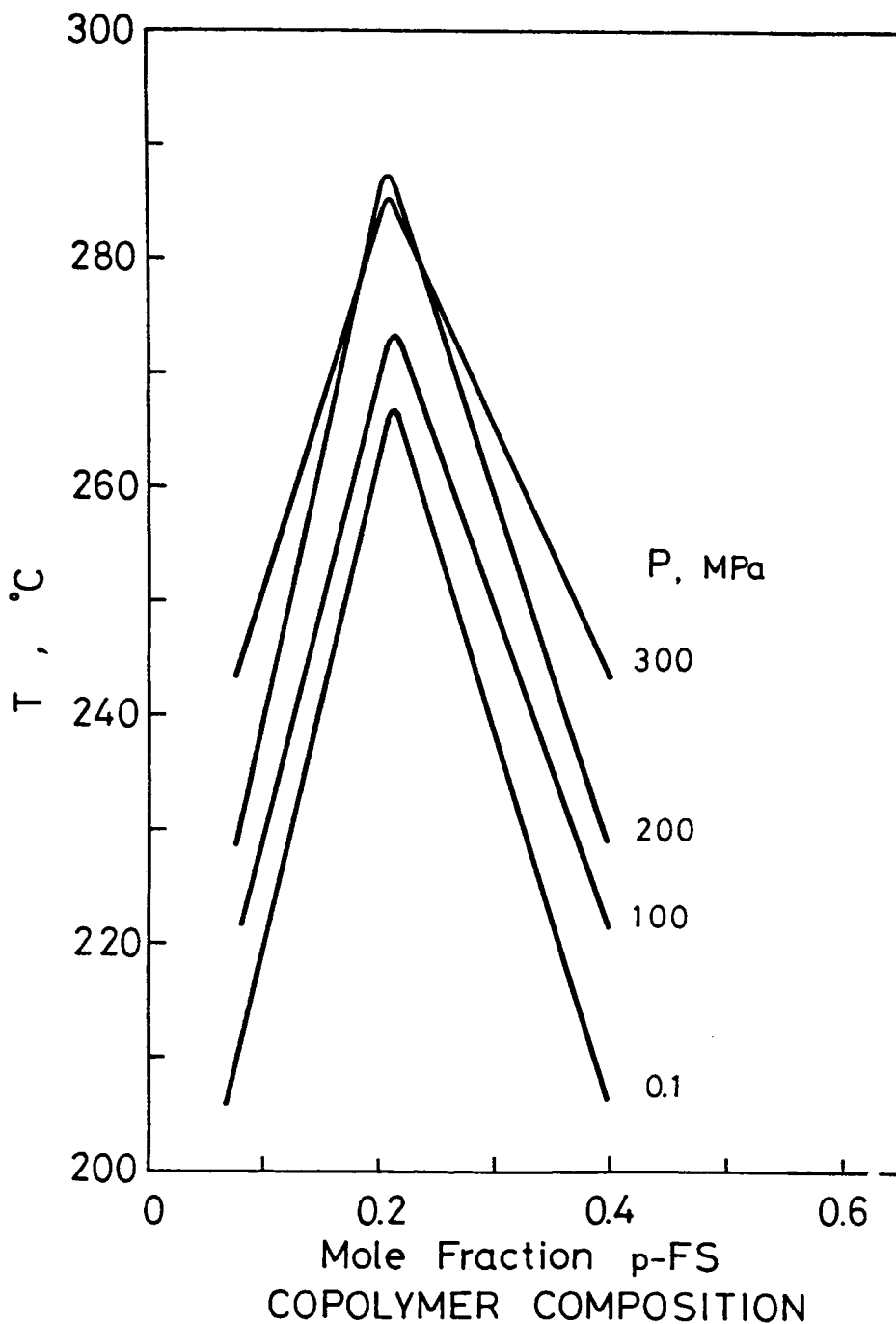


Fig. 6. Effect of pressure on the miscibility window of the 50/50 wt% blends of PPO/P(o-FS-co-p-FS). Pressures as indicated.

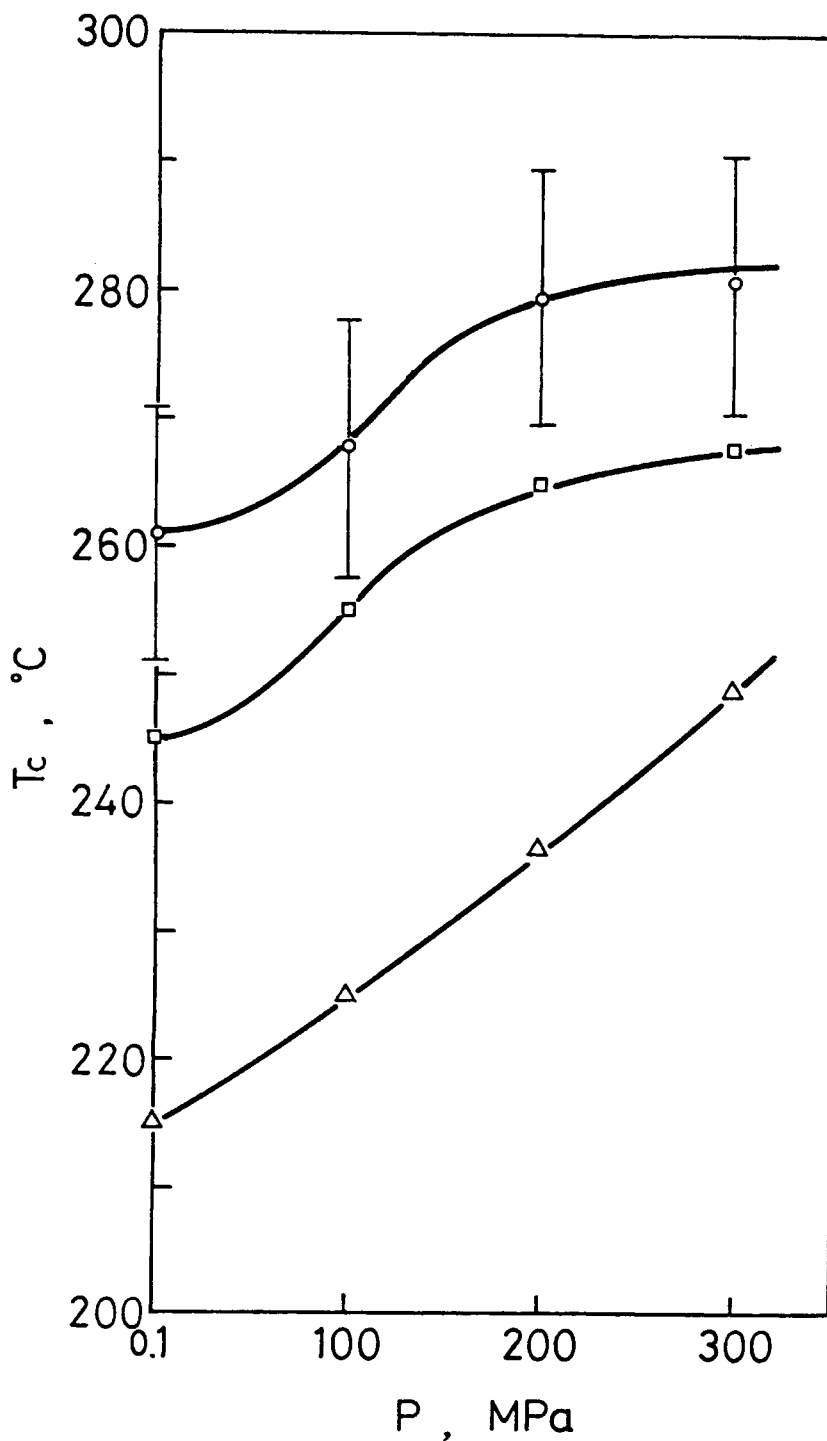


Fig. 7. Effect of pressure on  $T_c$  of PPO/P(*o*-FS-co-*p*-FS) containing 23 (○), 29 (□), and 38 (△) mol% *p*-FS in the copolymer.

FS, the  $T_c$ 's increase monotonically with increasing pressure showing  $dT_c/dP$ 's of ca.  $0.1^\circ\text{C}/\text{MPa}$ .

The phase diagram for the blend of a particular copolymer, P(*o*-FS-co-29*p*-FS) and PPO was also obtained as a function of pressure. Figure 8 shows the relevant phase boundary at 200 MPa. As at atmospheric pressure, the

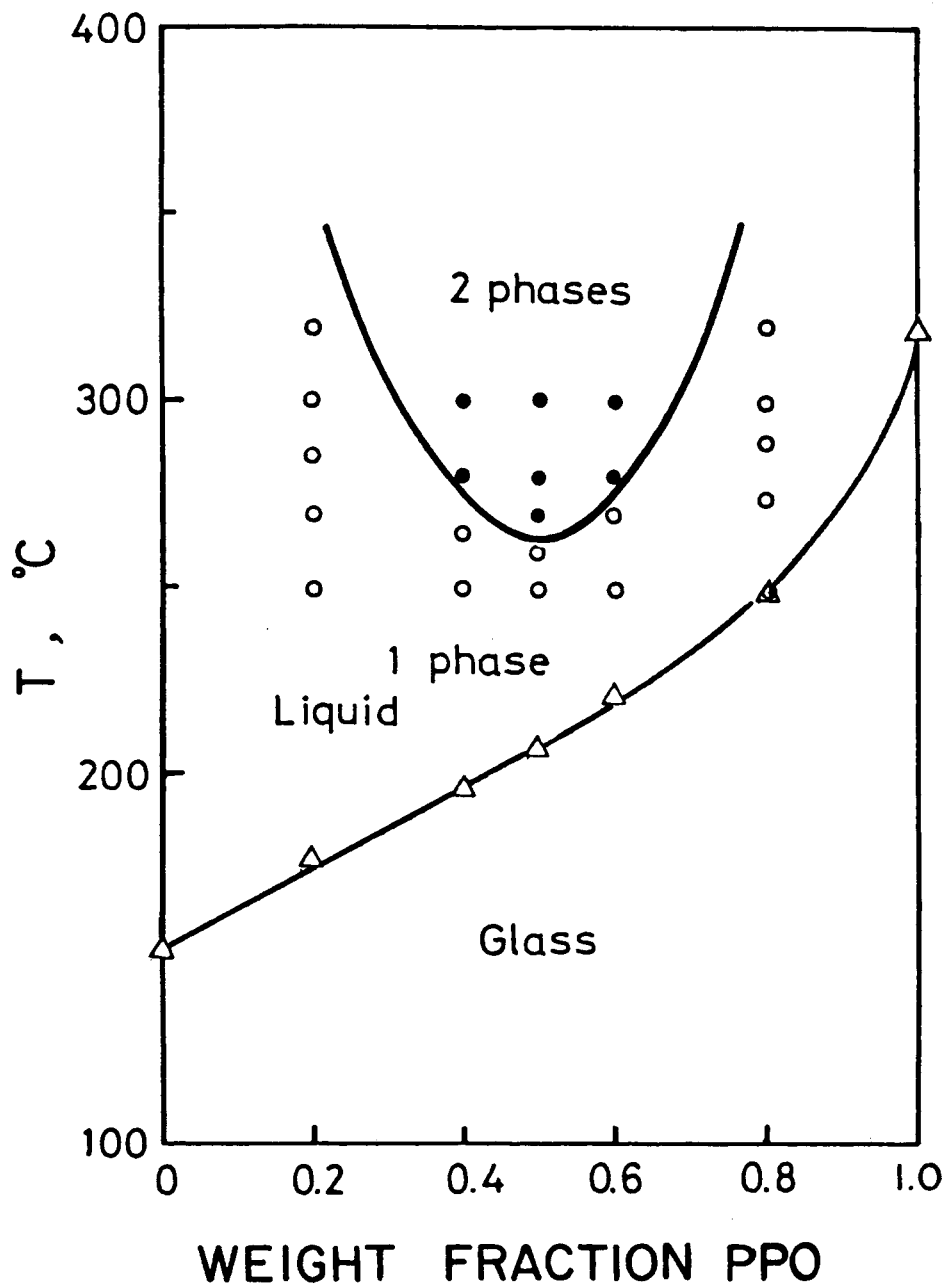


Fig. 8. Phase diagram for PPO/P(*o*-FS-co-29*p*-FS) at 200 MPa.  $\circ$ : one phase,  $\bullet$ : two phases. The lower curve in the figure indicates the dependence of  $T_g$  on blend composition.

composition at the temperature minimum,  $T_c$ , is about 50 wt% PPO.  $T_g$  is also shown for this blend at 200 MPa. By comparison, Figures 9 and 10 show the phase diagrams at atmospheric pressure and 300 MPa, respectively. It is notable that the critical composition at  $T_c$  is independent of pressure. Since the  $T_g$ 's of these blends increase more rapidly with increasing

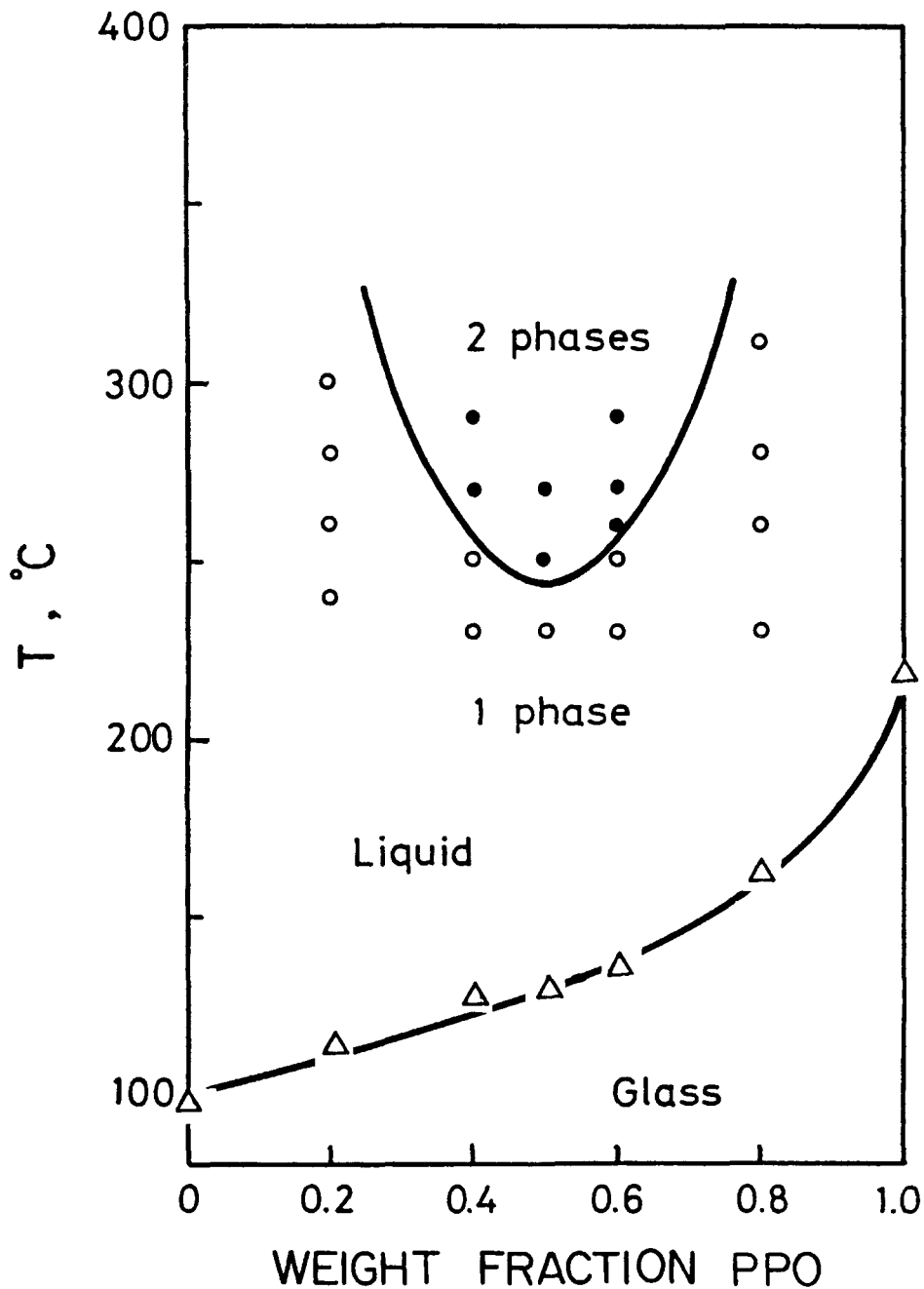


Fig. 9. Phase diagram for PPO/P(*o*-FS-co-29*p*-FS) at atmospheric pressure. See legend for Fig. 8.

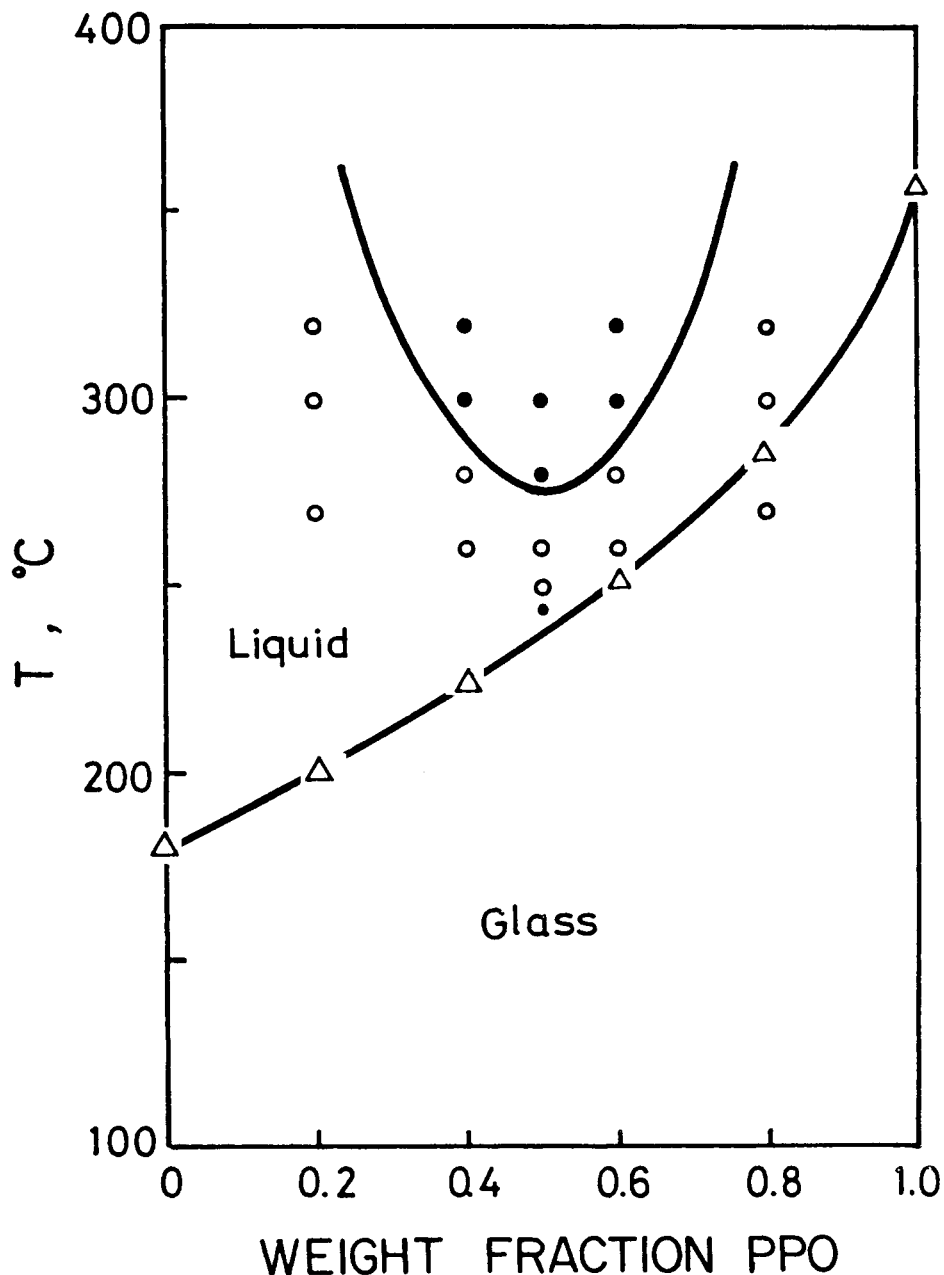


Fig. 10. Phase diagram for PPO/P(*o*-FS-co-29*p*-FS) at 300 MPa. See legend for Fig. 8.

pressure than the  $T_c$ 's the temperature interval in which miscibility may be obtained decreases markedly with increasing pressure.

Figure 11 shows the combined data of Figures 8–10 in a three-dimensional phase diagram of the PPO/P(*o*-FS-co-29*p*-FS) blend system with respect to pressure  $P$ , temperature  $T$ , weight fraction of PPO.

Morrison<sup>12</sup> recently discussed the implications of the stability criterion that in a binary mixture is given by  $(\partial^2 G / \partial x^2)_{T,P} \geq 0$ . He showed that in an LCST-type blend

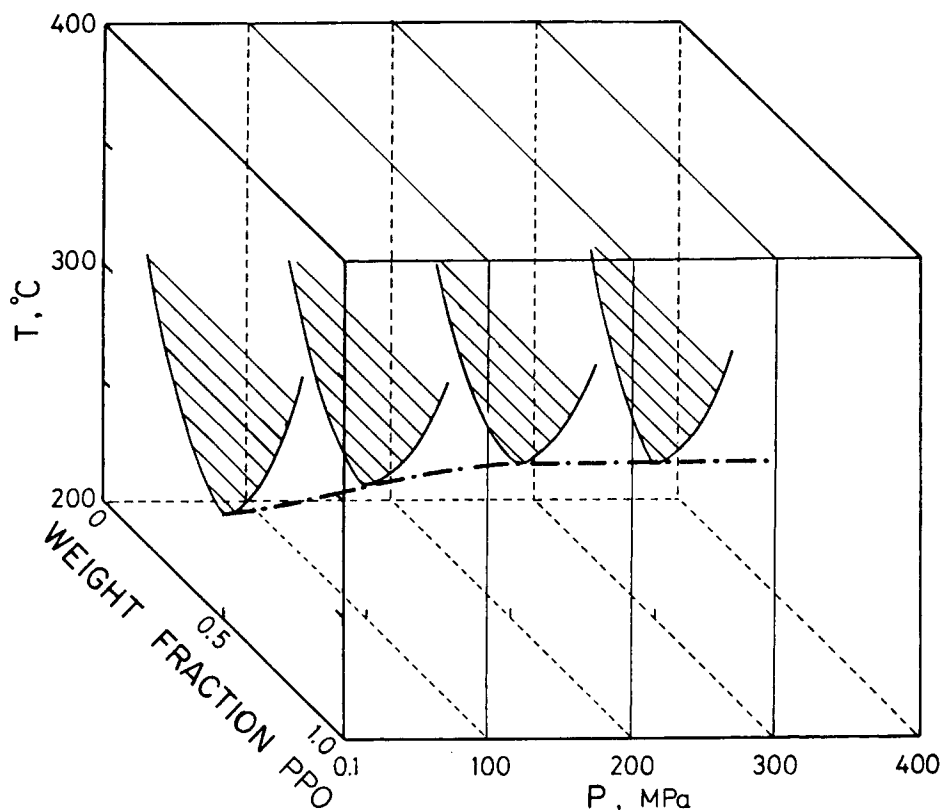


Fig. 11. Overall phase diagram of the PPO/P(o-FS-co-29p-FS) blend.

$$\left[ \frac{\partial}{\partial T} \left( \frac{\partial^2 G}{\partial x^2} \right) \right]_{P, x_c} = - \left( \frac{\partial^2 S}{\partial x^2} \right)_{T, P} \leq 0$$

where  $G$ ,  $S$ , and  $x$  are the Gibbs free energy of mixing, the entropy of mixing, and the concentration of the solute, respectively. Similar results were derived with respect to the volume and enthalpy derivatives:

$$\left[ \frac{\partial}{\partial P} \left( \frac{\partial^2 G}{\partial x^2} \right) \right]_{T, x_c} = \left( \frac{\partial^2 V}{\partial x^2} \right)_{T, P} = \left( \frac{\partial^2 V^e}{\partial x^2} \right)_{T, P} \begin{cases} \geq 0 & \text{for } dT_c/dP > 0 \\ \leq 0 & \text{for } dT_c/dP < 0 \end{cases}$$

and

$$\left[ \frac{\partial}{\partial T} \frac{1}{T} \left( \frac{\partial^2 G}{\partial x^2} \right) \right]_{T, P} = - \frac{1}{T^2} \left( \frac{\partial^2 H}{\partial x^2} \right)_{T, P} = - \frac{1}{T^2} \left( \frac{\partial^2 H^e}{\partial x^2} \right)_{T, P} \leq 0$$

where  $V^e$  and  $H^e$  are the respective excess quantities. By assuming that the sign of the curvature for the excess enthalpy or volume is the same for all compositions of the mixture, it can be shown further that

$$H^e < 0$$

and

$$V^e \quad \begin{cases} < 0 & \text{for } dT_c/dP > 0 \\ > 0 & \text{for } dT_c/dP < 0. \end{cases}$$

The above statements can be used to interpret the experimental results obtained in this study. Taking into consideration the  $dT_c/dP$  behaviors for the blends of PPO/P(*o*-FS-co-*p*-FS), the excess volume of mixing for all the copolymer blends is negative at pressures below 200 MPa. Furthermore, the fact that  $dT_c/dP$  decreases from small positive values to zero at higher pressures suggests that negative excess volume of mixing approaches zero for the blends containing from 16 to 29 mol% *p*-FS.

We have recently developed<sup>13</sup> a theory for blends of copolymers with homopolymers and showed that the phase behaviors in these systems are successfully explained by a simple Flory-Huggins type mean field theory. In the model miscibility windows occur as the result of a repulsive interaction between the differing monomer units in the copolymer. According to the interpretation of this theory in the present case, it is suggested that these repulsive interactions weaken at higher pressures.

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