

Effect of pressure on the melting and crystallization of pseudo binary mixtures of polyethylene and high melting temperature diluents

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The melting and crystallization behaviour of pseudo binary mixtures of polyethylene (PE)/1,3,5-tribromobenzene and PE/hexamethylbenzene were studied at elevated pressures up to 500 MPa by differential thermal analysis (d.t.a.). The phase diagram of these binary mixtures under high pressure was determined and compared with that of a PE/1,2,4,5-tetrachlorobenzene binary mixture. The pressure dependence of the eutectic temperature T_e of the PE/1,3,5-tribromobenzene mixture at 1 atm was $0.33^\circ\text{C}/\text{MPa}$ and for PE/hexamethylbenzene $0.31^\circ\text{C}/\text{MPa}$. The eutectic composition does not move at elevated pressure. In both mixtures, the area between the liquidus curve of the diluents and the eutectic line of the hypoeutectic region in the phase diagram increases with pressure but the area between the liquidus curve for PE and the eutectic line in the hypereutectic region decreases with pressure. In the PE/1,3,5-tribromobenzene system, the phase transition from the orthorhombic phase to the hexagonal phase of PE does not occur under high pressure but the transition did occur in the PE/hexamethylbenzene system. The d.t.a. study at 1 atm showed that the formation of an extended chain crystal of PE was largely impeded in the mixture with 1,3,5-tribromobenzene and 1,2,4,5-tetrachlorobenzene.

(Keywords: high pressure; differential thermal analysis; binary mixture; polyethylene; 1,3,5-tribromobenzene; hexamethylbenzene; melting; crystallization)

INTRODUCTION

In recent years, many studies have been performed on the melting and crystallization behaviour of eutectic binary mixtures of polymers and low molecular weight high melting temperature diluents¹⁻⁵. Smith and Pennings^{1,2} have shown that polyethylene (PE) forms a simple eutectic with 1,2,4,5-tetrachlorobenzene and hexamethylbenzene at atmospheric pressure. Hodge *et al.*⁵ also reported that eutectic solidification occurs in a PE/1,3,5-tribromobenzene pseudo binary mixture at atmospheric pressure.

The pressure change of the phase diagram of the PE/1,2,4,5-tetrachlorobenzene mixture was recently studied⁶ where the phase diagram changes with increasing pressure, i.e., in the hypereutectic region with respect to PE in the phase diagram, the difference between the melting temperature T_m of PE and the eutectic temperature T_e decreases with pressure. On the contrary, however, the temperature difference between T_m for 1,2,4,5-tetrachlorobenzene and T_e increases with pressure in the hypoeutectic region.

During the melting process of pure PE under high pressure above 350 MPa, a phase transition from the orthorhombic to the hexagonal phase occurs, but in the binary mixture with 1,2,4,5-tetrachlorobenzene, PE showed no evidence of such a transition in the differential thermal analysis (d.t.a.) melting curve. Furthermore, the d.t.a. melting curve at atmospheric pressure for the PE/1,2,4,5-tetrachlorobenzene binary mixture crystallized under high pressure indicates that an extended chain crystal (ECC) of PE is quite rarely formed in such a

diluent, although in pure PE, it is easily formed by melt crystallization under high pressure.

It is the purpose of this paper to determine the phase diagram of the PE/1,3,5-tribromobenzene and PE/hexamethylbenzene pseudo binary mixtures under high pressure. The eutectic composition and the eutectic temperature in the phase diagrams of these binary mixtures at atmospheric pressure are different from those of PE/1,2,4,5-tetrachlorobenzene binary mixtures, so that a different phase diagram is expected under high pressure. High pressure d.t.a. was performed up to 500 MPa and the phase diagram of the binary mixture was determined up to 400 MPa. The effect of 1,3,5-tribromobenzene and hexamethylbenzene on the phase transition of PE under high pressure was also studied. The high pressure crystallized binary mixture was studied by d.t.a. at atmospheric pressure to elucidate the effect of these high melting temperature diluents on the ECC formation of PE.

EXPERIMENTAL

The PE sample pellet (Hizex 2200 J supplied by Mitsui Petrochemical Ind., Ltd.) was dissolved in xylene at 130°C and recrystallized by slow cooling. The PE powder obtained by evaporation of the solvent was used for the mixture sample. The 1,3,5-tribromobenzene, purchased from Wako Pure Chemical Ind., Ltd., and hexamethylbenzene (Aldrich Chemical Co. Inc.), were used as obtained.

The sample for the d.t.a. was prepared by the following method⁶. The mixed powder of PE and the high melting temperature diluent (20 mg) was sealed in a glass tube (inner diameter 1.6 mm) and heated in an oil bath. The temperature of the bath was kept at 190°C and the sample was homogenized for 25 min in the bath. After cooling to room temperature in air, the sample was removed from the glass tube and cut into a rod 1.5 mm in length. In the d.t.a. measurement, the sample was wrapped in aluminium foil (thickness 0.01 mm) and covered with epoxy resin and adhered to the thermocouple junction. The high pressure d.t.a. apparatus has been described elsewhere⁷. The phase diagrams were determined by the peak melting temperature in the d.t.a. curve with a heating rate of 6°C/min. Crystallization of the mixture at 1 atm under high pressure was effected by cooling the high pressure d.t.a. cell with an electric fan after the endothermic peak of melting was observed in the d.t.a. curve. The cooling rate in each run was about 5°C/min. The maximum temperature attained in each d.t.a. run was ~20°C higher than the peak temperature of melting under pressure. All the d.t.a. measurements on the melting of the binary mixture were performed for the samples crystallized with the cooling rate described above.

RESULTS AND DISCUSSION

Phase diagram of the pseudo binary mixtures at elevated pressure

The d.t.a. curves of melting for a PE/1,3,5-tribromobenzene pseudo binary mixture at atmospheric pressure are shown in Figure 1. Double endothermic peaks are observed in the d.t.a. melting curve except for the samples with weight fractions of PE (W_{PE}) = 0 and 0.3.

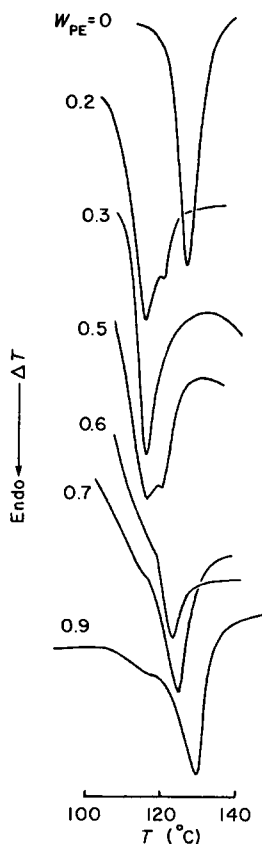


Figure 1 D.t.a. melting curve, at 1 atm, of PE/1,3,5-tribromobenzene binary mixture for various weight fractions of PE (W_{PE})

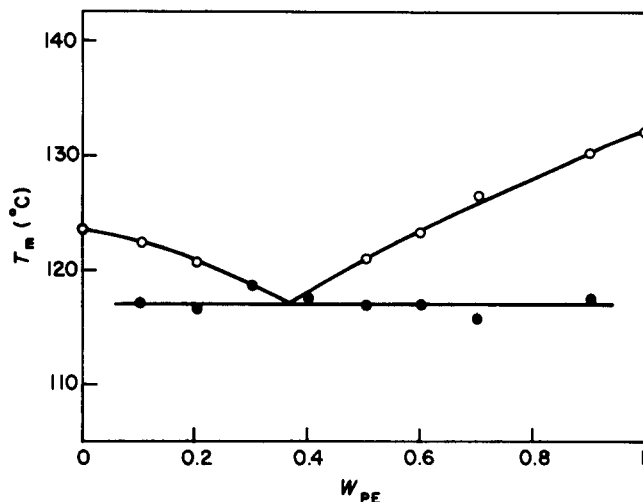


Figure 2 Phase diagram of PE/1,3,5-tribromobenzene pseudo binary mixture at 1 atm

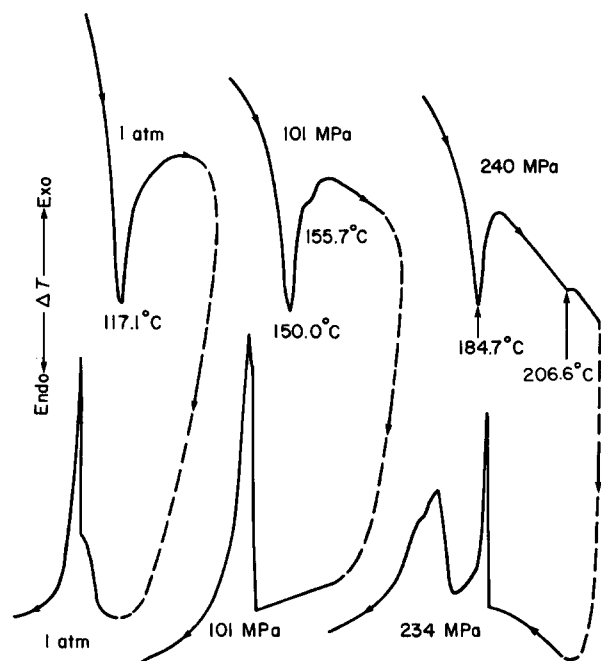


Figure 3 D.t.a. melting curve, at 1 atm, and under high pressure of PE/1,3,5-tribromobenzene binary mixture with W_{PE} = 0.3

The high temperature peak of the curve for W_{PE} = 0.2 is ascribed to the melting of 1,3,5-tribromobenzene and the low temperature peak, which locates at about 117°C for all compositions, is ascribed to the eutectic melting⁵.

Figure 2 shows the phase diagram of the PE/1,3,5-tribromobenzene mixture at atmospheric pressure obtained by plotting the temperature of the endothermic peak in the d.t.a. curve in Figure 1 against the weight fraction of PE. The phase diagram of the mixture reported by Hodge *et al.*⁵ was obtained by plotting the melting temperatures reduced to zero scan speed during differential scanning calorimetry (d.s.c.); however, in our study the peak melting temperature was plotted because of the restricted scan speed of the d.t.a. apparatus (6°C/min): The slight variation in the eutectic temperature in the phase diagram may be due to this difference. The eutectic temperature in this Figure is about 117°C and the eutectic composition is ~0.4 for W_{PE} .

Figure 3 shows the d.t.a. melting curve and crystallization of the binary mixture of PE/1,3,5-tribromobenzene with W_{PE} = 0.3 under various pressures.

At atmospheric pressure, only a single peak is apparent in the d.t.a. melting curve, but under high pressure a small peak appears on the high temperature side of the large peak which is due to the eutectic melting. This small peak is ascribed to the melting of excess 1,3,5-tribromobenzene in the mixture and appears under high pressure due to the difference in the pressure dependence between the melting temperatures of the eutectic and 1,3,5-tribromobenzene. The somewhat broad single peak at atmospheric pressure becomes separated into two peaks under high pressure, so that the high pressure d.t.a. is useful in precisely determining the eutectic composition of the pseudo binary mixture. On cooling, two exothermic peaks due to the crystallization of excess 1,3,5-tribromobenzene (sharp peak) and the eutectic crystallization appear.

Figure 4 shows the d.t.a. melting curve at atmospheric pressure and under high pressure for the sample with $W_{PE}=0.9$. The high and low temperature peaks are due to the melting of excess PE and the eutectic melting in this weight fraction, respectively. Both peaks shift to the high temperature side with increasing pressure and the temperature dependence of both peaks decreases with pressure. At 500 MPa, a single peak appears.

Figure 5 shows the pressure change of the high and low temperature peaks for the samples with $W_{PE}=0$, 0.7 and 0.9 in the PE/1,3,5-tribromobenzene mixtures. The temperature of melting of 1,3,5-tribromobenzene (high temperature peak) in the mixture in the hypoeutectic region shifts to the low temperature side with increasing 1,3,5-tribromobenzene content as observed in the case of the PE/1,2,4,5-tetrachlorobenzene system. The T_m of PE with $W_{PE}=0.7$ in the PE/1,3,5-tribromobenzene mixture coincides with the eutectic melting temperature at about 350 MPa, but with $W_{PE}=0.9$, the coincidence of the two peaks occurs at 500 MPa in contrast with the PE/1,2,4,5-

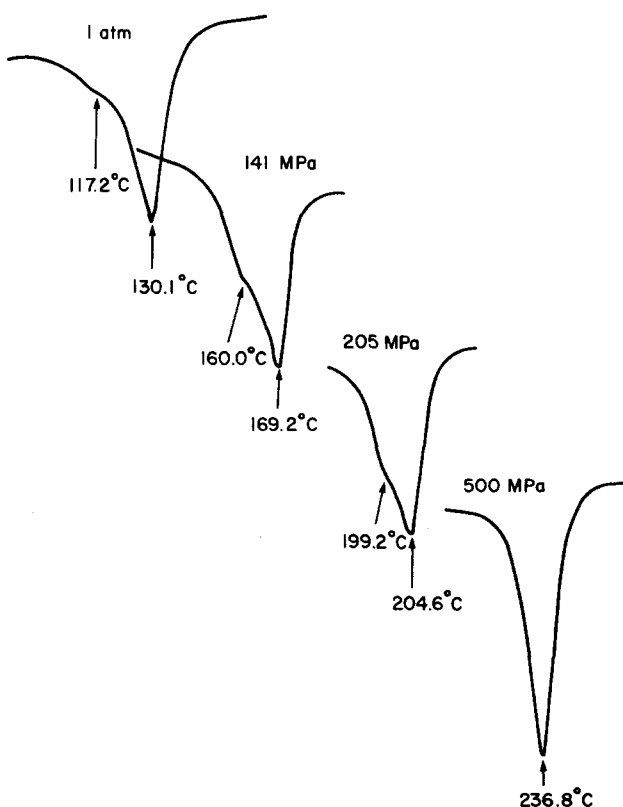


Figure 4 D.t.a. curve of melting, at 1 atm and under high pressure, of PE/1,3,5-tribromobenzene binary mixture with $W_{PE}=0.9$

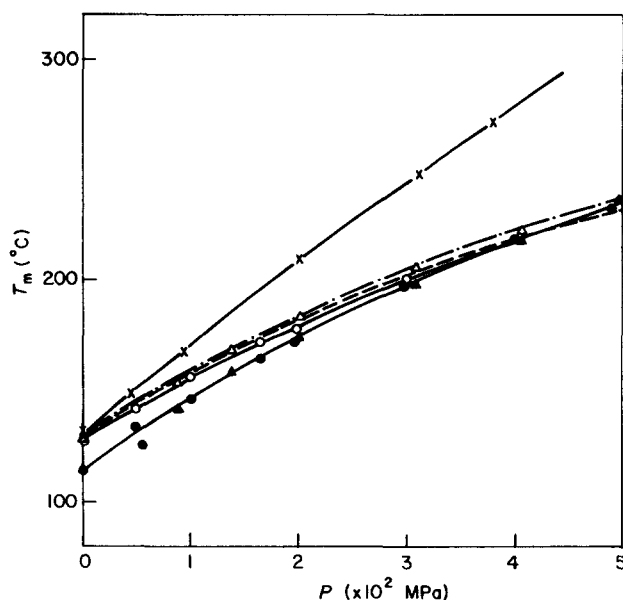


Figure 5 Pressure dependence of peak melting temperatures in the d.t.a. curve for the FCC or PE (—), pure 1,3,5-tribromobenzene (—x—), PE in the mixture with $W_{PE}=0.7$ (—o—) and 0.9 (—△—) (high temperature peak) and the eutectic melting temperature (low temperature peak) with $W_{PE}=0.7$ (—●—) and 0.9 (—▲—) of PE/1,3,5-tribromobenzene

tetrachlorobenzene system which showed the 2 peaks coinciding at 300 MPa and 201°C when $W_{PE}=0.9$.

Because of the larger pressure dependence of T_e in comparison with that of T_m for the FCC of pure PE, the inversion of T_m of the folded chain crystal (FCC) in pure PE and T_e in the mixture occurs at 420 MPa. This feature is conspicuous for the higher weight fraction sample of PE, i.e. the inversion of T_m of the FCC for pure PE and T_e occurs at 380 MPa. At 500 MPa, the eutectic melting temperature is 5–6°C higher than the T_m of the FCC in pure PE. This feature is also observed in the PE/1,2,4,5-tetrachlorobenzene mixture with $W_{PE}=0.7\sim 0.9$. In the isotactic polypropylene/1,2,4,5-tetrachlorobenzene pseudo binary mixture, this inversion does not occur⁸, so that this phenomenon is assumed to be a characteristic of PE under high pressure.

Figure 6 shows the d.t.a. curves of melting for the PE/hexamethylbenzene pseudo binary mixture with $W_{PE}=0.4$ at elevated pressure. A small peak at 114.2°C in the d.t.a. curve at atmospheric pressure is due to the solid–solid phase transition of hexamethylbenzene and the peak at 156.6°C is due to the melting of excess hexamethylbenzene in the eutectic mixture. The eutectic melting temperature at atmospheric pressure is 123.9°C with this composition. The difference between the eutectic temperature T_e and T_m of hexamethylbenzene increases with pressure. The solid–solid transition temperature of hexamethylbenzene increases with pressure more rapidly than the eutectic melting temperature.

Figure 7 shows the d.t.a. melting curves at elevated pressures for the sample with $W_{PE}=0.9$ in the PE/hexamethylbenzene mixture. The temperature difference at atmospheric pressure between the melting peak of PE (126.8°C) and the eutectic melting is 6.3°C, and both peaks rapidly approach each other with pressure as compared with the other two pseudo binary mixtures. The single peak begins to appear above 100 MPa in the

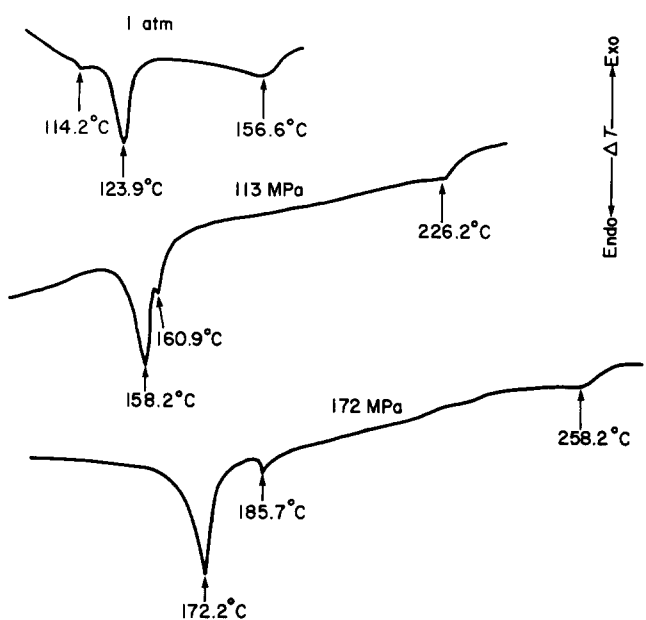


Figure 6 D.t.a. melting curve, at 1 atm and under high pressure, of PE/hexamethylbenzene binary mixture with $W_{PE}=0.4$

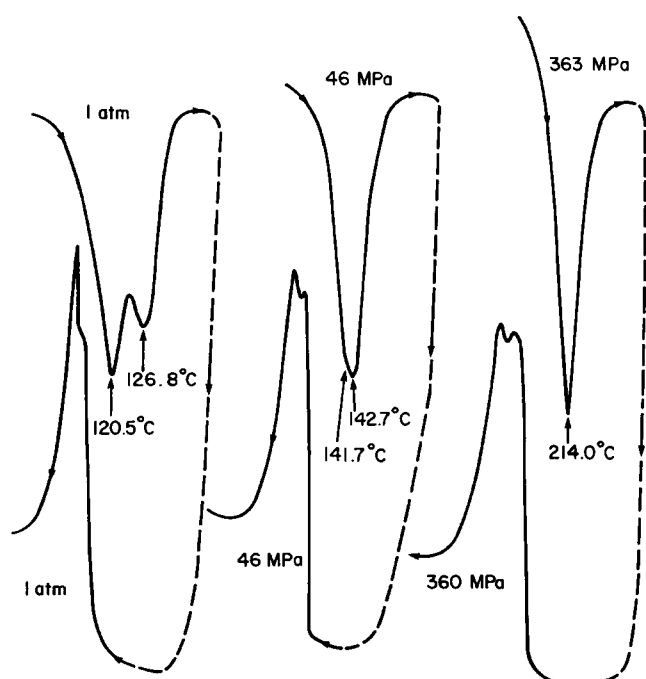


Figure 7 D.t.a. melting curve at 1 atm and under high pressure of PE/hexamethylbenzene binary mixture with $W_{PE}=0.9$

sample with $W_{PE}=0.9$ in the PE/hexamethylbenzene system.

Figure 8 shows the pressure dependence of T_m of hexamethylbenzene and the eutectic melting temperature with $W_{PE}=0.4$. The pressure dependence of T_m of pure hexamethylbenzene is greater than that for pure 1,2,4,5-tetrachlorobenzene and 1,3,5-tribromobenzene, but the pressure dependence of the eutectic melting temperature of the PE/hexamethylbenzene mixture is almost the same as that of T_e in the PE/1,2,4,5-tetrachlorobenzene and PE/1,3,5-tribromobenzene mixtures. The data for the melting temperature *versus* pressure were fitted to the quadratic equation,

$$T_m = A + BP - CP^2 \quad (1)$$

where the coefficients A , B and C were determined by the least squares method. Tables 1 and 2 list all the values of A , B and C for various compositions of the PE/1,3,5-tribromobenzene and PE/hexamethylbenzene systems, respectively. The value B exhibits the pressure dependence (dT_m/dP) at atmospheric pressure of the high melting temperature diluents, PE and the eutectics. The average value of B for 1,3,5-tribromobenzene is $0.43^\circ\text{C}/\text{MPa}$ which is nearly the same value as that for 1,2,4,5-tetrachlorobenzene ($0.42^\circ\text{C}/\text{MPa}$). On the con-

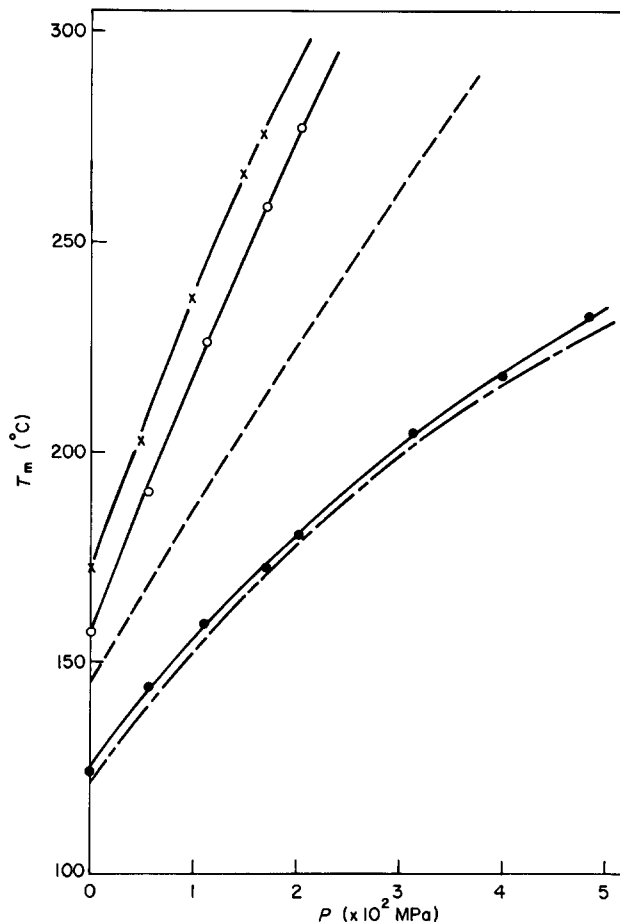


Figure 8 Pressure dependence of melting temperatures of hexamethylbenzene ($-x-$), pure 1,2,4,5-tetrachlorobenzene ($---$), hexamethylbenzene in the mixture with $W_{PE}=0.4$ ($-O-$), eutectic melting temperature of PE/hexamethylbenzene with $W_{PE}=0.4$ ($-●-$) and the eutectic melting of the PE/1,2,4,5-tetrachlorobenzene mixture ($-●-●-$)

Table 1 A , B and C in quadratic equation (1) for peak melting temperatures of the high temperature peak (T_m of PE and 1,3,5-tribromobenzene) and the low temperature peak (T_e) in the d.t.a. melting curve for PE/1,3,5-tribromobenzene mixture

| W_{PE} | T_m | | | T_e | | |
|----------|--------------------------|-----------------------------------|-----------------------------------|--------------------------|-----------------------------------|-----------------------------------|
| | A ($^\circ\text{C}$) | B ($^\circ\text{C MPa}^{-1}$) | C ($^\circ\text{C MPa}^{-2}$) | A ($^\circ\text{C}$) | B ($^\circ\text{C MPa}^{-1}$) | C ($^\circ\text{C MPa}^{-2}$) |
| 0 | 123.5 | 0.42 | 1.09×10^{-4} | - | - | - |
| 0.1 | 122.0 | 0.44 | 1.46×10^{-4} | 118.3 | 0.33 | 2.09×10^{-4} |
| 0.2 | 119.7 | 0.45 | 1.78×10^{-4} | 115.8 | 0.33 | 2.10×10^{-4} |
| 0.3 | 115.5 | 0.40 | 0.81×10^{-4} | 118.0 | 0.33 | 1.93×10^{-4} |
| 0.4 | - | - | - | 117.8 | 0.34 | 2.19×10^{-4} |
| 0.5 | - | - | - | 118.8 | 0.34 | 2.35×10^{-4} |
| 0.6 | 123.4 | 0.30 | 1.83×10^{-4} | 118.1 | 0.34 | 2.28×10^{-4} |
| 0.7 | 126.8 | 0.31 | 2.23×10^{-4} | 116.2 | 0.33 | 2.00×10^{-4} |
| 0.9 | 131.0 | 0.29 | 1.63×10^{-4} | 117.2 | 0.32 | 1.59×10^{-4} |
| 1.0 | 132.4 | 0.28 | 1.65×10^{-4} | - | - | - |

Table 2 *A*, *B* and *C* in quadratic equation (1) for peak melting temperatures of the high temperature peak (T_m of PE and hexamethylbenzene) and the low temperature peak (T_e) in the d.t.a. melting curve of PE/hexamethylbenzene mixture

| W_{PE} | T_m | | | T_e | | |
|----------|---------------|----------------------------------|----------------------------------|---------------|----------------------------------|----------------------------------|
| | <i>A</i> (°C) | <i>B</i> (°C MPa ⁻¹) | <i>C</i> (°C MPa ⁻²) | <i>A</i> (°C) | <i>B</i> (°C MPa ⁻¹) | <i>C</i> (°C MPa ⁻²) |
| 0 | 171.0 | 0.68 | 3.37×10^{-4} | — | — | — |
| 0.2 | 116.2 | 0.64 | 1.28×10^{-4} | 125.5 | 0.31 | 1.92×10^{-4} |
| 0.4 | 156.0 | 0.69 | 9.89×10^{-6} | 125.3 | 0.31 | 1.77×10^{-4} |
| 0.6 | — | — | — | 125.1 | 0.31 | 1.34×10^{-4} |
| 0.8 | — | — | — | 125.8 | 0.31 | 1.80×10^{-4} |
| 0.9 | — | — | — | 124.1 | 0.33 | 2.05×10^{-4} |
| 1 | 132.4 | 0.28 | 1.65×10^{-4} | — | — | — |

trary, however, the value of *B* in pure hexamethylbenzene is 0.68°C/MPa which is ~40% larger than the value for pure 1,3,5-tribromobenzene while the pressure dependence of the eutectic melting temperature in the PE/hexamethylbenzene mixture shows nearly the same value as that for the other two binary mixtures. From these facts, it is considered that the pressure dependence of the eutectic temperature is dominated by the pressure dependence of the melting temperature of PE and not of the high melting temperature diluents.

To draw the experimentally determined phase diagram of the eutectic mixture under high pressure, T_m and T_e values under high pressure were calculated at intervals of 100 MPa using the values of *A*, *B* and *C* in Tables 1 and 2. Figure 9 shows the phase diagram of the PE/1,3,5-tribromobenzene mixture under high pressure. The eutectic composition W_{PE}^e does not seem to move along the W_{PE} axis with increasing pressure as in the case of PE/1,2,4,5-tetrachlorobenzene mixture. With $W_{PE} = 0.4$, a single peak appears in the d.t.a. melting curve at atmospheric pressure and under high pressure. In the pressure change of the phase diagram of the PE/1,3,5-tribromobenzene mixture, the following trends: (i) that the temperature difference between T_m of the diluent and T_e increases in the hypoeutectic region and (ii) the difference between T_m of PE and T_e decreases in the hypereutectic region with increasing pressure; correspond to those trends in the case of the PE/1,2,4,5-tetrachlorobenzene system. These trends seem to be common for PE and high melting temperature diluent mixtures, as the phase diagram of PE/hexamethylbenzene eutectic mixture under high pressure shows the same features as shown in Figure 10. The separated liquidus line for PE disappears at 200 MPa in the hypereutectic region in the phase diagram. The values of T_e , eutectic composition W_{PE}^e , and pressure dependence of T_e and T_m at atmospheric pressure for each constituent of the three binary mixtures are summarized in Table 3. The mole fraction at the eutectic composition N_{PE}^e with respect to the repeat unit (—CH₂—CH₂—) is also listed. The mixture with the higher temperature of the eutectic melting shows the higher values of mole fraction of PE as the eutectic composition (N_{PE}^e).

Effect of high melting temperature diluents on the melting and crystallization of PE under high pressure

In the melting process of pure PE crystallized from the melt at atmospheric pressure, three endothermic peaks appear in the d.t.a. curve above 350 MPa. These peaks are

ascribed to the melting of the FCC, phase transition from the orthorhombic to the hexagonal phase and the melting of the phase, respectively, on increasing the temperature. In the d.t.a. melting curve, under high pressure, for the PE/1,2,4,5-tetrachlorobenzene mixture, a single peak appeared between 350 and 500 MPa, and it was concluded that the phase transition of PE did not occur. If the crystallization of pure PE is performed under high pressure, an ECC is formed. The melting temperature of the ECC at atmospheric pressure is about 142°C which is 9°C higher than the T_m of the FCC and the electron micrograph of the fracture surface of the high pressure crystallized PE sample shows many striation bands.

The d.t.a. melting curve, under high pressure, for the PE/1,3,5-tribromobenzene mixture with $W_{PE} = 0.7$ shows a single peak at 231.5°C as shown in Figure 11a where the single peak appears between 350 and 500 MPa. It is assumed that the high pressure phase transition of PE does not occur in the PE/1,3,5-tribromobenzene mixture either. The d.t.a. melting curve, at atmospheric pressure, for the sample crystallized at 484 MPa shows two peaks at 112.4°C and 130.7°C and a shoulder which is assumed to be due to the melting of a small amount of the ECC which is formed during cooling under high pressure. The PE/1,3,5-tribromobenzene mixture shows nearly the same melting and crystallization behaviour under high pressure as that for the PE/1,2,4,5-tetrachlorobenzene mixture, although the eutectic composition and the eutectic temperature at atmospheric pressure are

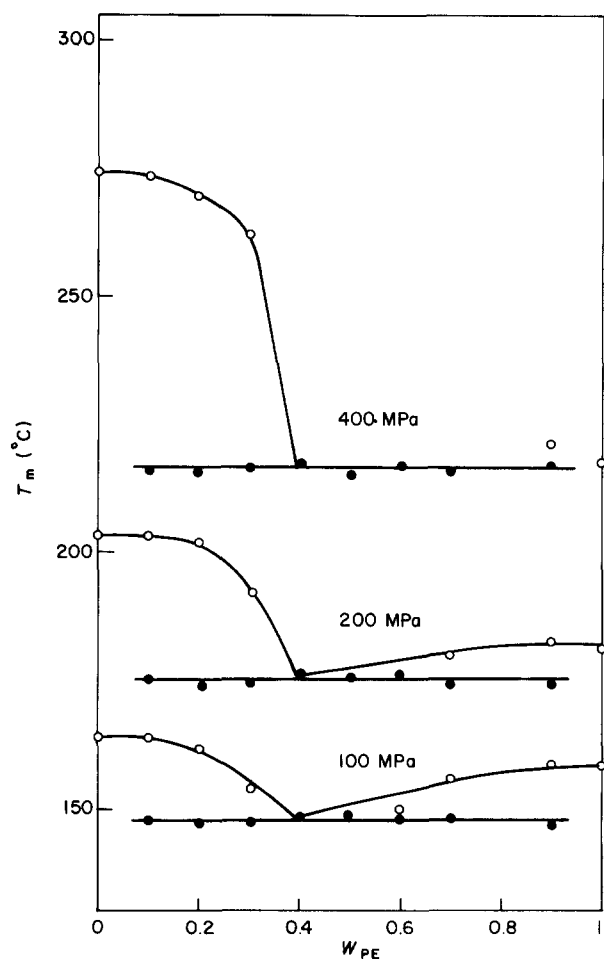


Figure 9 Pressure change of the phase diagram of PE/1,3,5-tribromobenzene binary mixture. (●) eutectic melting; (○) high temperature peak

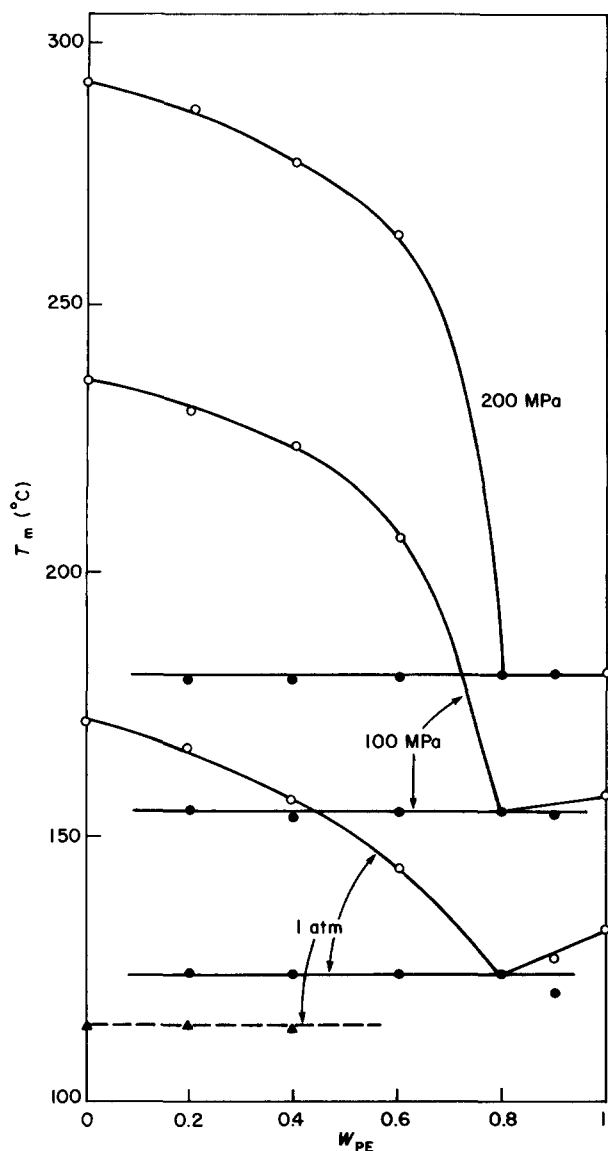


Figure 10 Pressure change of the phase diagram of PE/hexamethylbenzene binary mixture: (●) eutectic melting; (○) high temperature peak; (▲) phase transition of hexamethylbenzene at 1 atm

Table 3 Values of eutectic temperature T_e , mole fraction N_{PE}^e at the eutectic composition (W_{PE}^e), and pressure dependence of T_e and T_m of the diluents and PE in the three pseudo binary mixtures

| Mixture | T_e (°C) | N_{PE}^e | (W_{PE}^e) | dT_e/dP (°C MPa ⁻¹) | dT_m/dP (°C MPa ⁻¹) |
|-------------------------------|-------------------|------------|----------------|-----------------------------------|-----------------------------------|
| PE/1,3,5-tribromobenzene | 117.0 | 0.87 | (0.38) | 0.33 | 0.42 |
| PE/1,2,4,5-tetrachlorobenzene | 120.5 | 0.91 | (0.58) | 0.33 | 0.42 |
| PE/hexamethylbenzene | 125.0 | 0.96 | (0.80) | 0.31 | 0.68 |
| pure PE | ($T_m = 132$ °C) | | | | 0.28 |

different. The d.t.a. melting curve, under high pressure, for the sample with $W_{PE} = 0.8$ in the PE/hexamethylbenzene mixture shows two peaks as shown in Figure 11b. The low temperature peak is ascribed to the eutectic melting. The peak temperature of the high temperature peak is 9°C higher than the T_m of the FCC of PE and it is close to the T_m of the high pressure phase of PE at the same pressure. The high pressure phase transition of PE is supposed to

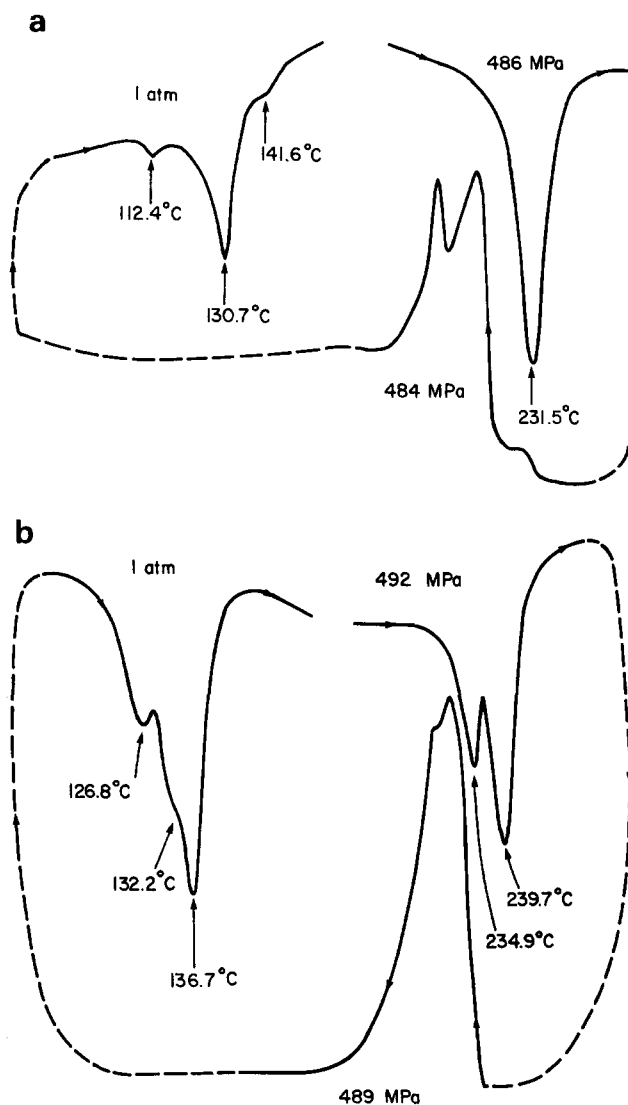


Figure 11 (a) D.t.a. melting curve and crystallization under high pressure followed by melting at 1 atm for PE/1,3,5-tribromobenzene mixture with $W_{PE} = 0.7$. (b) D.t.a. melting curve and crystallization under high pressure followed by melting at 1 atm for PE/hexamethylbenzene mixture with $W_{PE} = 0.8$

occur in this mixture. The d.t.a. melting curve, at 406 MPa, for the same sample shows a single peak, so that the triple point for the curves of the melting of the orthorhombic phase, the hexagonal phase and the ortho-hexagonal transition of PE lies between 400 and 500 MPa in this mixture. To confirm the appearance of the high pressure phase, high pressure X-ray diffraction measurements are necessary⁹. In the d.t.a. melting curve, at atmospheric pressure, for the same sample crystallized at 489 MPa, three endothermic peaks are observed. Two peaks at 126.8°C and 132.2°C are ascribed to the eutectic melting and the melting of the FCC of PE, respectively. The peak temperature (136.7°C) of the high temperature peak is lower than the melting temperature of the ECC of PE but much higher than the melting temperature of the FCC of pure PE. It seems that the high pressure crystallization of the PE/hexamethylbenzene mixture predominantly produces the crystals with thickness between the FCC and the ECC. These different melting and crystallization behaviours of PE in the PE/hexamethylbenzene mixture compared with the other mixtures may be related to the eutectic nature at

atmospheric pressure, i.e. the highest eutectic temperature and the highest composition ratio of PE being exhibited in this mixture among the three binary mixtures.

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