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Effects of Mixing Tetracontane on the Melting and Crystallization of Polyethylene under High Pressure

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ABSTRACT: The effects of mixing tetracontane (TC) on melting and crystallization processes of polyethylene (PE) were studied at elevated pressures up to 500 MPa, by high pressure differential thermal analysis (DTA). The high pressure phase of PE shifts to higher pressures and temperatures with TC content in the mixture. However, the high pressure phase disappears when the weight fraction of PE is less than 0.7 at 500 MPa. Extended chain crystal is not formed in the mixture of the weight fraction of PE below 0.5. In the weight fraction between 1.0 and 0.5, T_m of thick PE crystal decreases with TC content. The decreasing rate of melting and crystallization temperatures of the binary mixture of PE and TC remained unchanged with pressure up to 350 MPa.

KEY WORDS Polyethylene / Tetracontane / Binary Mixture / High Pressure / Melting / Crystallization / Differential Thermal Analysis / Phase Diagram / Extended Chain Crystal /

It is well known that the crystallization of polyethylene (PE) from the melt under high pressure above 350 MPa yields so-called "extended chain crystal" (ECC),[1] and a high pressure phase appears between the orthorhombic phase and the liquid phase. The high pressure phase is hexagonal[2–4] and a conformational disorder of the PE chains in this phase has been reported.[5] According to ultrasonic shear wave measurement under high pressure, the phase is like a liquid-crystal.[6]

The high pressure phase of PE is not always stable. On γ-ray irradiation, the range where the high pressure phase appears shifts to the low pressure side, even to atmospheric pressure.[7,8] The effects of mixing with high melting temperature diluents on the high pressure phase was studied recently by Nakafuku.[9,10] On blending 1,2,4,5-tetrachlorobenzene or 1,3,5-tribromobenzene with PE, the high pressure phase disappeared in the DTA curve measured at high pressure. In addition, the formation of ECC of PE under high pressure was also inhibited by blending the diluents.

The effect of paraffin diluents on the melting temperature (T_m) of PE at atmospheric pressure has been studied.[11,12] Deperession in T_m of PE occurs in the mixtures with normal paraffins, such as hexatriacontane (C_{36}) and octadecane (C_{18}).

In this paper, the melting and crystallization processes of PE mixed with tetracontane (C_{40}) (TC) is studied under high pressures up to 500 MPa.

EXPERIMENTAL

A powder sample of PE (Hizex 2200 JP, molecular weight: 67000 supplied by Mitsui Petrochemical Industries Co.) was used. TC was purchased from Tokyo Chemical Industry Co., Ltd. A pwowder sample of TC was prepared by crushing it in an agate mortar. In order to make binary mixtures of PE and TC, a mixed powder with the desired weight fraction of PE (W_{PE}) put in a glass tube (1.8 mm in inside diameter and 10 mm in length) was melted at 180°C at atmospheric pressure and then cooled to room temperature at a rate of about $1.2\,\mathrm{K\,min^{-1}}$.

High pressure DTA was measured by apparatus described elsewhere.[9] The rod-like sample of the size described above was cut into rods of 1.8 mm in length and wrapped with aluminum foil (thickness 0.01 mm) and attached to a thermocouple junction of the DTA cell.

DTA curves of melting and crystallization were obtained by the following way. At a desired pressure, the sample was heated at a rate of $6\,\mathrm{K\,min^{-1}}$ (run 1) and then crystallized at a cooling rate of about $5\,\mathrm{K\,min^{-1}}$ (run 2). Run 3 was the melting process of the sample crystallized through run 2 at the same heating rate as run 1.

High pressure crystallizations were performed by cooling the sample at the same cooling rate as in run 2 of DTA after it was heated to a temperature higher by about 20°C.

DSC measurements were performed at atmospheric pressure on the PE samples crystallized at atmospheric pressure and high pressure with a Rigaku Denki low temperature thermal analyser at a heating rate of $5\,\mathrm{K\,min^{-1}}$.

RESULTS AND DISCUSSION

Phase Diagram of PE and TC Binary Mixture

Figure 1 shows DSC curves at atmospheric pressure on the melting process of the binary mixtures of PE and TC. Two endothermic peaks of PE and TC are cklearly observed at about 120—140°C and about 80°C, respectively. Both peak intensity and position of melting of PE decrease with decreasing PE

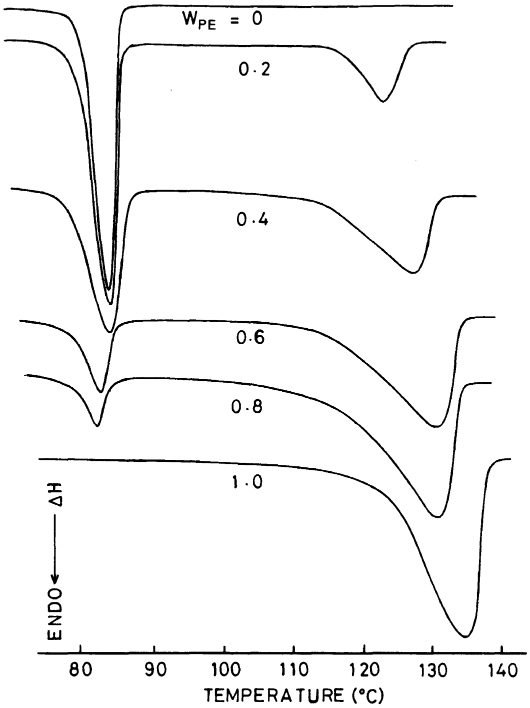


Figure 1. DSC curve of melting of PE and TC binary mixtures measured at atmospheric pressure. Samples were crystallized from the melt at atmospheric pressure (cooling rate $8\,\mathrm{K\,min^{-1}}$).

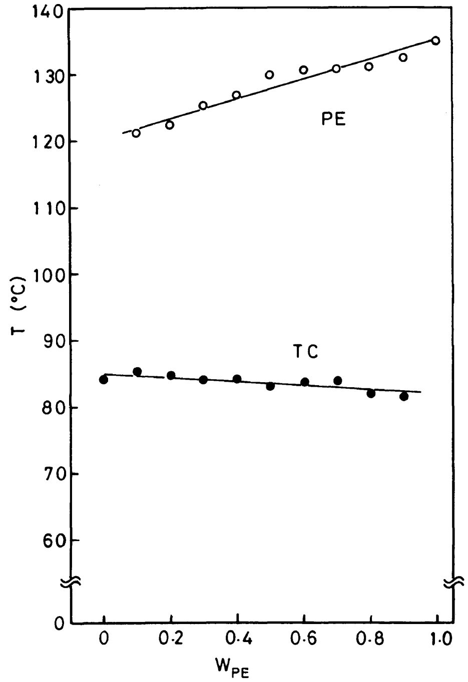
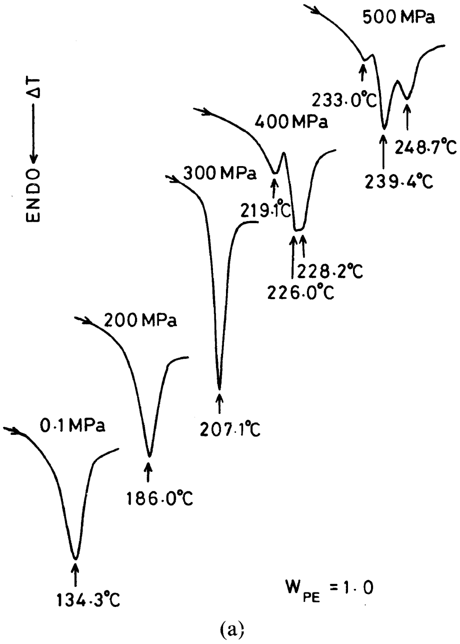


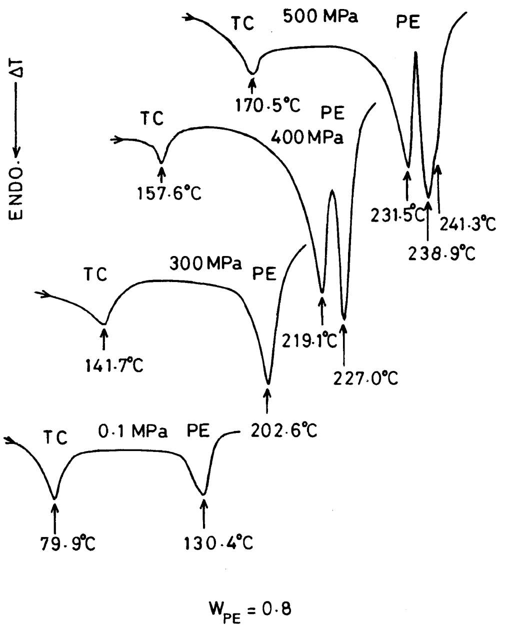
Figure 2. Phase diagram of the binary mixture of PE and TC. ○, melting of PE; ●, melting of TC.

content in the mixture. A phase diagram of the binary mixtures at atmospheric pressure was obtained by plotting the peak melting temperature against W_{PE} as shown in Figure 2. Depression of T_m of PE occurs with decreasing weight fraction of PE in the binary mixture. T_m of TC decreases slightly with decreasing TC content in the mixture. This is also observed in the data from DTA experiments under high pressure in this study. In the mixture with ultra-high molecular weight PE (molecular weight: 1900000), decreasing T_m of TC des not occur.[13] Therefore, this phenomenon may occur due to an interaction of TC and low molecular weight component of the PE sample used in this study. Further experiments are needed on the mixture of TC and low molecular weight PE.

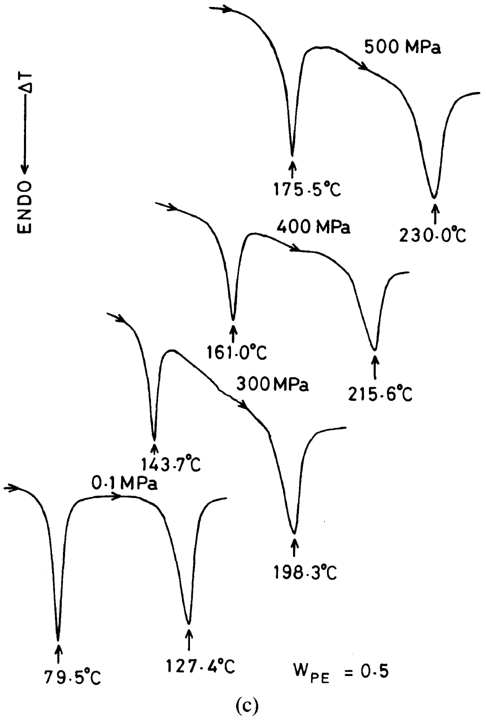
In the high pressure DTA of pure PE ($W_{PE} = 1.0$) crystallized at atmospheric pressure, the endothermic melting peak shifts to the high temperature side at elevated pressure and three peaks appear above 350 MPa.[14] Figures 3(a), (b), and (c) show the DTA curves on the melting process of the binary mixtures



(a)



(b)



(c)

Figure 3. Pressure dependence of the DTA curve of melting of the binary mixtures crystallized at atmospheric pressure. (a), $W_{PE} = 1.0$; (b), $W_{PE} = 0.8$; (c), $W_{PE} = 0.5$.

crystallized at atmospheric pressure for the samples with $W_{PE}=1.0$, 0.8, and 0.5, respectively, at elevated pressures. The melting temperatures of PE and TC in the mixtures shift to the high temperature side with increase in pressure. Above 400 MPa, three peaks appear in the melting range of pure PE. The assignment of these peaks has already been given.[14,15] The lowest peak is due to the melting of the folded chain crystal (FCC) and the medium one to the phase transition from the orthorhombic to the high pressure phase. The highest peak is due to the melting of the high pressure phase. The DTA curve measured at the pressure above 350 MPa for the mixtures changes with W_{PE}. The intensity of the lowest temperature melting peak of PE around 232°C at 500 MPa increases with increasing TC content, and only this peak appears in the case of $W_{PE}=0.5$.

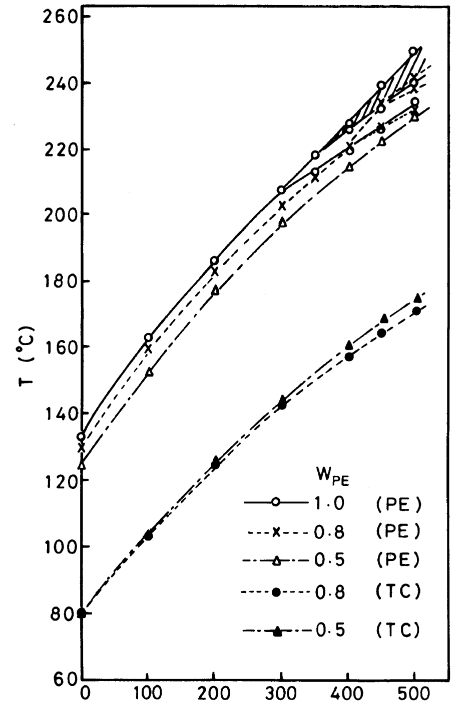


Figure 4. Pressure dependence of melting temperatures of PE and TC in the binary mixtures at $W_{PE}=1.0$, 0.8 and 0.5. ○, pure PE; ×, PE in $W_{PE}=0.8$; △, PE in $W_{PE}=0.5$; ●, TC in $W_{PE}=0.8$; ▲, TC in $W_{PE}=0.5$. The hatched area indicates the high pressure phase region of PE.

Figure 4 shows the pressure dependence of the melting and crystallization temperatures of the binary mixtures with $W_{PE}=1.0$, 0.8, and 0.5 in the pressure range up to 500 MPa. The hatched triangular region for $W_{PE}=1.0$ corresponds to the high pressure phase of PE. This phase appears above 350 MPa for $W_{PE}=1.0$ (triple point), but above 450 MPa for $W_{PE}=0.8$ as indicated (×). In $W_{PE}=0.8$, a shoulder due to the melting of the high pressure phase appears clearly on the high temperature side of the high temperature peak of melting at 500 MPa as shown in Figure 3(b). For $W_{PE}=0.7$, the high pressure phase of PE does not appear even at 500 MPa.

Pressure dependence of the melting temperature of PE or TC for all the mixtures fits the quadratic equation, $T_m=A+BP-CP^2$, and coefficients A, B, and C are determined by the least squares method using the data up to 500 MPa. Above 350 MPa, the pressure dependence of the melting temperature of PE is

Table I. Values of A, B, and C in the quadratic equation,

$$T_m=A+BP-CP^2$$

for the melting temperature of PE in the mixture with a different weight fraction ($W_{PE}=0.1$—0.6) in run 1 in DTA up to 500 MPa. For $W_{PE}=0.7$—1.0, the values are determined by the data of T_m up to 350 MPa and that of low temperature peak above 400 MPa

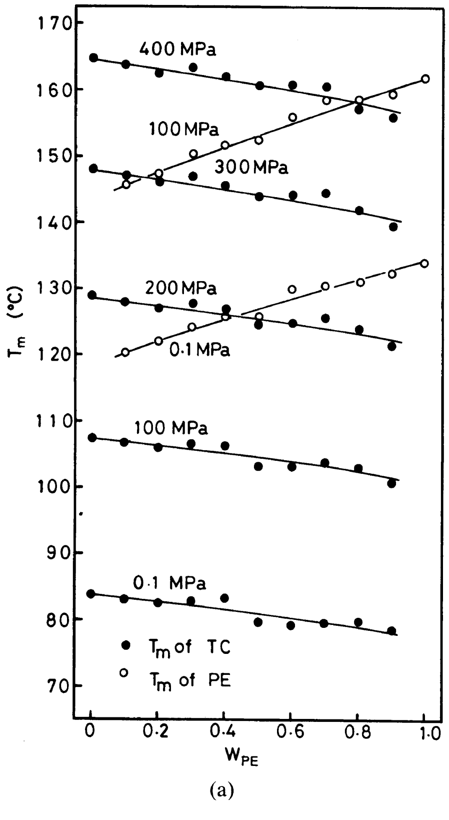
W_{PE}	A °C	B K MPa^{-1}	C K MPa^{-2}
1.0	134.5	0.30	2.09×10^{-4}
0.9	132.6	0.29	1.81×10^{-4}
0.8	130.9	0.30	1.98×10^{-4}
0.7	130.7	0.30	1.87×10^{-4}
0.6	129.2	0.28	1.48×10^{-4}
0.5	127.4	0.28	1.52×10^{-4}
0.4	126.3	0.27	1.27×10^{-4}
0.3	124.7	0.27	1.28×10^{-4}
0.2	122.4	0.26	1.22×10^{-4}
0.1	120.6	0.26	1.13×10^{-4}

Table II. Values of A, B, and C in the quadratic equation,

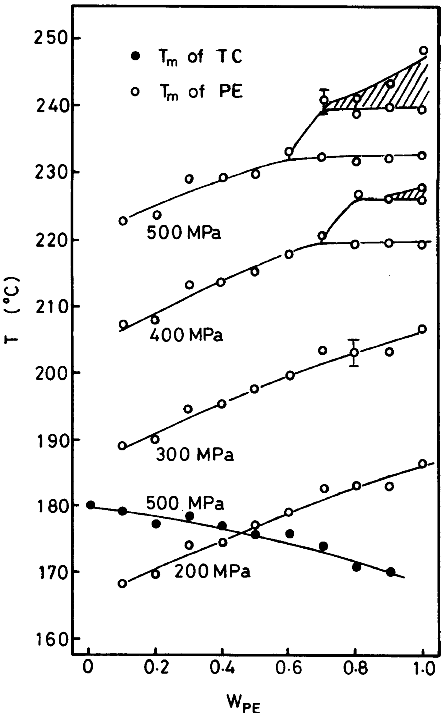
$$T_m = A + BP - CP^2$$

for the melting temperature of TC in the mixture with a different weight fraction in run 1 of DTA up to 500 MPa

W_{PE} (W_{TC})	A	B	C
	°C	KMPa^{-1}	KMPa^{-2}
1.0 (0)	—	—	—
0.9 (0.1)	78.9	0.24	1.04×10^{-4}
0.8 (0.2)	80.2	0.25	1.29×10^{-4}
0.7 (0.3)	79.6	0.26	1.46×10^{-4}
0.6 (0.4)	79.4	0.25	1.13×10^{-4}
0.5 (0.5)	80.1	0.25	1.24×10^{-4}
0.4 (0.6)	84.2	0.24	0.99×10^{-4}
0.3 (0.7)	83.3	0.24	1.09×10^{-4}
0.2 (0.8)	82.4	0.25	1.11×10^{-4}
0.1 (0.9)	83.2	0.25	1.13×10^{-4}
0 (1.0)	84.2	0.25	1.11×10^{-4}



(a)



(b)

Figure 5. Phase diagram of PE and TC in the binary mixture at intervals of 100 MPa. The hatched area on T_m of PE indicates the high pressure phase.

complicated and two or three endothermic peaks appear for the sample of $W_{PE} = 1.0$—0.7. Therefore, in this range of W_{PE}, curve fitting was performed using the melting point of low temperature peak above 350 MPa. Table I lists the values of A, B, and C in the quadratic equation for PE. The values of A and B decrease with decreasing PE content in the mixture within experimental error. Table II lists the values of A, B, and C for TC. The value of A slightly decreases with decreasing TC content in the mixture but the value of B does not change with TC within experimental error.

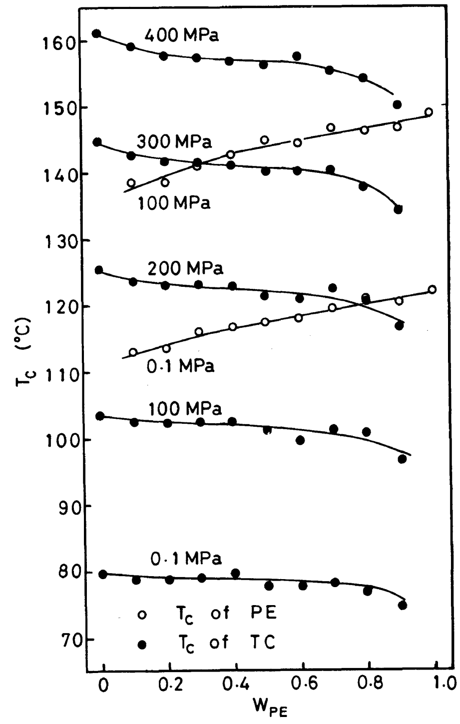
The phase diagram of the binary mixtures at a desired pressure can be obtained by plotting the values of T_m and T_c (the peak temperature of the exothermic peak of crystallization) calculated from the quadratic equation using the values in Tables I and II. Figures 5(a) and (b) show the composition dependence of the melting points of PE and TC in the binary mixtures. The melting point depression of PE and

Table III. Values of A', B', and C' in the quadratic equation,

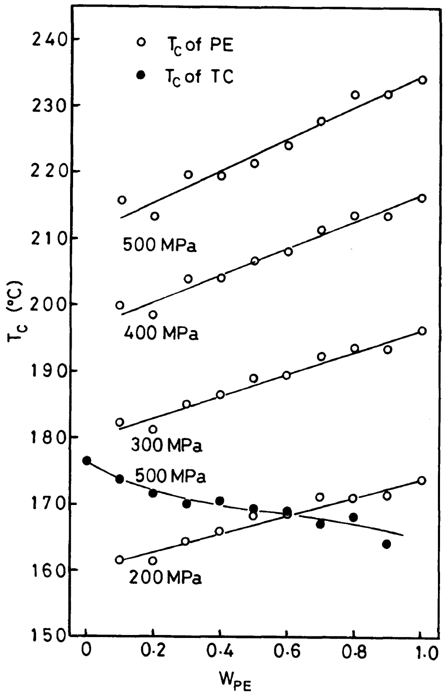
$$T_c = A' + B'P - C'P^2$$

for the crystallization temperature of PE in the mixtures with a different weight fraction in run 1 of DTA up to 500 MPa

W_{PE}	A' °C	B' KMPa^{-1}	C' KMPa^{-2}
1.0	122.4	0.28	1.13×10^{-4}
0.9	120.8	0.27	0.99×10^{-4}
0.8	121.3	0.27	0.89×10^{-7}
0.3	120.0	0.28	1.52×10^{-4}
0.6	117.9	0.28	1.36×10^{-4}
0.5	117.9	0.28	1.53×10^{-4}
0.4	116.6	0.27	1.38×10^{-4}
0.3	115.7	0.27	1.17×10^{-4}
0.2	113.3	0.26	1.29×10^{-4}
0.1	113.4	0.27	1.21×10^{-4}
0	—	—	—



(a)



(b)

Figure 6. Phase diagram of PE and TC in the binary mixture at intervals of 100 MPa.

Table IV. Values of A', B', and C' in the equation,

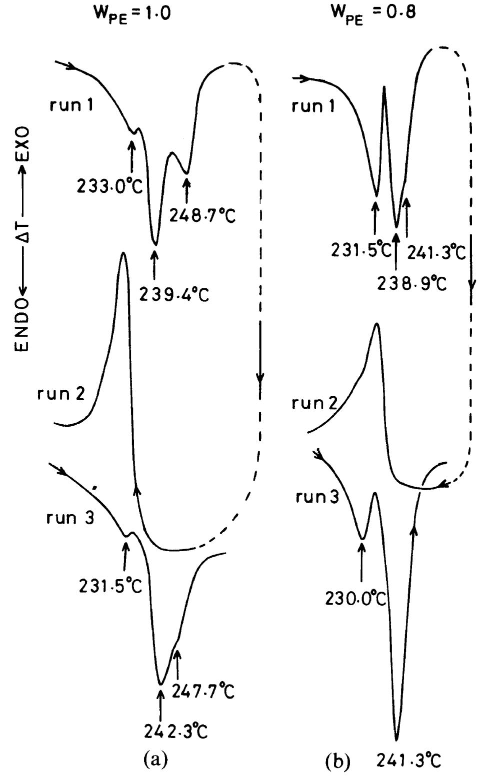
$$T_c = A' + B'P - C'P^2$$

for the crystallization temperature of TC in the mixture with a different weight fraction in run 1 of DTA up to 500 MPa

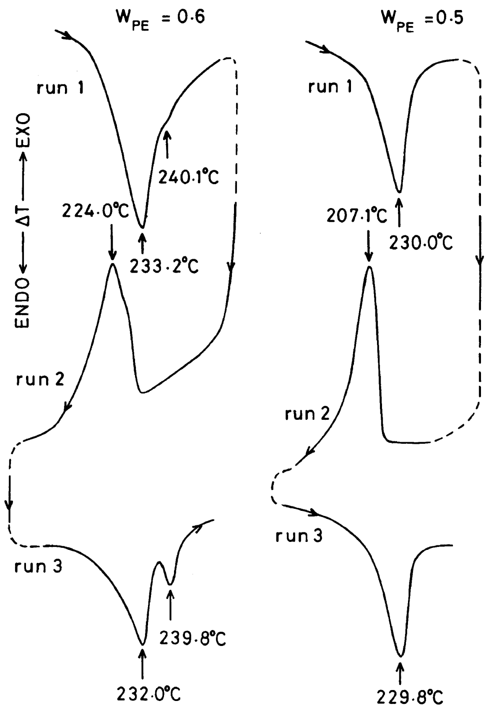
W_{PE} (W_{TC})	A' °C	B' KMPa^{-1}	C' KMPa^{-2}
1.0 (0)	—	—	—
0.9 (0.1)	74.6	0.23	1.05×10^{-4}
0.8 (0.2)	76.7	0.25	1.26×10^{-4}
0.7 (0.3)	77.1	0.26	1.61×10^{-4}
0.6 (0.4)	76.5	0.25	1.33×10^{-4}
0.5 (0.5)	77.7	0.25	1.25×10^{-4}
0.4 (0.6)	80.0	0.24	1.14×10^{-4}
0.3 (0.7)	79.1	0.25	1.33×10^{-4}
0.2 (0.8)	78.8	0.24	1.19×10^{-4}
0.1 (0.9)	78.9	0.25	1.15×10^{-4}
0 (1.0)	79.5	0.25	1.19×10^{-4}

TC does not change with pressures up to 350 MPa. This suggests that the interaction between PE and TC does not change with pressures up to 350 MPa. The hatched area between 400 and 500 MPa shows the range where the high pressure phase of PE exists. It is observed that the shifting of the triple point of the higher pressure phase occurs, *i.e.*, from 500 MPa for $W_{\mathrm{PE}}=0.7$ to 400 MPa for $W_{\mathrm{PE}}=0.9$.

Tables III and IV list the values of coefficients of the quadratic equations for the pressure dependence of T_c. Figures 6(a) and (b) show the phase diagram deduced from crystallization temperature of the binary mixtures. The depression rate in T_c of PE with the weight fraction of TC becomes remarkable at high pressure. A cause for the difference of the depression behavior of T_m and T_c at elevated pressure is considered as follows. The crystallization behavior of PE is affected by TC through nucleation and crystal growth, while melting behavior is affected through the heat of fusion.



(a) (b)



(c) (d)

Figure 7. DTA curve of melting and crystallization of PE in the four binary mixtures at 500 MPa. The endothermic peak of melting of TC which appeared at a lower temperature than the peak of PE in the mixture is not drawn to avoid complexity. (a), $W_{\mathrm{PE}}=1.0$; (b), $W_{\mathrm{PE}}=0.8$; (c), $W_{\mathrm{PE}}=0.6$; (d), $W_{\mathrm{PE}}=0.5$.

High Pressure Phase Transition and ECC Formation of PE in the Mixture with TC

The melting and crystallization processes of PE above 350 MPa are complicated because of the occurrence of the phase transition between orthorhombic and high pressure phases. Figures 7(a), (b), (c), and (d) show the DTA curves of melting and crystallization of PE for the four binary mixtures ($W_{\mathrm{PE}}=1.0$, 0.8, 0.6, and 0.5, respectively) measured at 500 MPa. In run 1 of pure PE ($W_{\mathrm{PE}}=1.0$), the phase transition from the orthorhombic phase to the high pressure phase exhibits an endothermic peak at 239.4°C and the resultant high pressure phase melts at 248.7°C. A small additional peak appears at around 232°C in both run 1 (233.0°C peak) and run 3 (231.5°C peak) for pure PE. In the mixture of $W_{PE}=0.8$, the endothermic peak around 232°C (231.5°C peak in this experiment) is sharp and the temperature gap between the two higher temperature peaks at 238.9°C and 241.3°C becomes very small. In run 3 of this mixture, the high temperature peaks overlap each other in a single peak. This means that the high pressure phase of PE does not appear under 500 MPa in the mixture of $W_{PE}=0.8$ crystallized at 500 MPa. That is, the high temperature peak (the 241.3°C peak in run 3) is due to the melting of ECC. The intensity of this peak decreases with increasing TC content as shown in (c) for $W_{PE}=0.6$ and at $W_{PE}=0.5$ (d), and only low temperature peak of PE appears. In the case of $W_{PE}=0.7$, a very small peak due to the melting of ECC and a large peak due to the melting of FCC were observed, so that the high pressure phase of PE disappears for $W_{PE}=0.7$ at 500 MPa. The high pressure phase of PE disappears also in binary mixtures of PE and diluent with high melting temperature such as 1,2,4,5-tetrachlorobenzene[9] or 1,3,5-tribromobenzene[10] for $W_{PE}=0.8$. In the mixture with TC, the high pressure phase of PE survives to a slightly lower W_{PE}. The above experimental facts indicate that the orthorhombic PE dissolves even at 500 MPa in the heating process. As for the mechanism of the formation of the high pressure phase of PE, Nagata *et al.*[6] gave the following interpretation, that cross-linkages are induced at the crossing points between PE chains by the reduction of free volume under high pressure, and they are fastened so strongly that they remain even in the high temperature region above the true melting temperature of the orthorhombic phase. Further, according to van Aerle and Lemstra,[16] the hexagonal phase of PE is related to some strong restrictions, for example, effective entanglements or reduction of free volume under high hydrostatic pressures. In the binary mixture of PE and TC, the liquid TC behaves like a lubricant and impedes the formation of entanglements or pressure induced cross-linkages of PE molecules. Therefore, high pressure phase of PE disappears in the binary mixture of the weight fracton below $W_{PE}=0.7$.

The formation of ECC during the melt-crystallization of PE under high pressure is also affected by the coexisting TC. Figure 8 shows the DSC curves of melting measured at atmospheric pressure on PE in the binary mixture crystallized under 500 MPa. The melting behavior is similar to that reported by Wunderlich[17] and Sugioka *et al.*[18] A large high temperature peak of the melting of ECC is

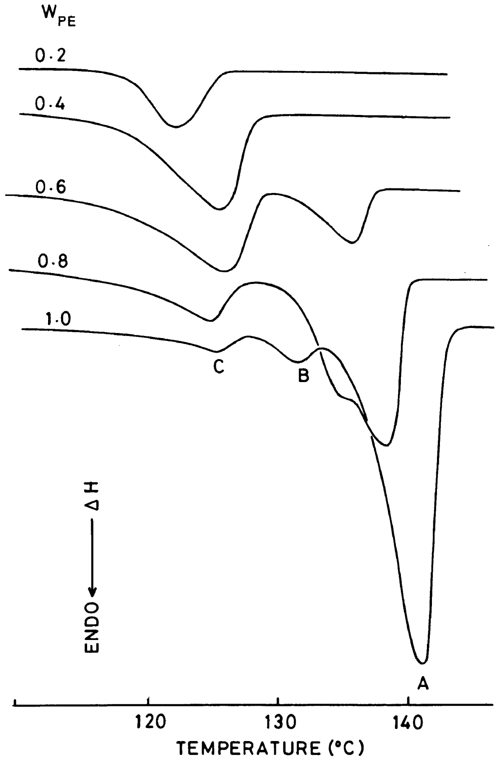


Figure 8. DSC curve at atmospheric pressure of melting of PE in the binary mixture crystallized under 500 MPa. Endothermic peak of melting of TC which appeared at a lower temperature is not drawn to avoid complexity.

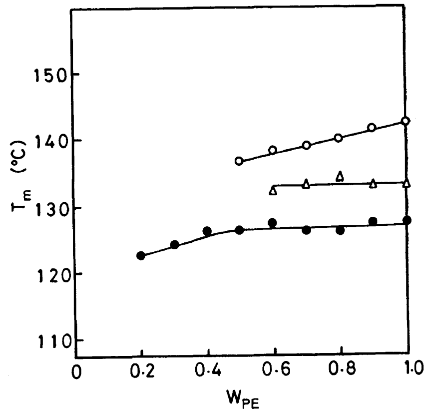


Figure 9. Change of the peak melting temperature in DSC curve of Figure 8, ○, peak A; △, peak B; ●, peak C.

observed at 141.5°C (peak A) and two small peaks appear at 127.0°C (peak C) and 132.8°C (peak B) in pure PE. With increasing TC content, the high temperature peak shifts to the low temperature side and peak intensity decreases. It is concluded that TC in the mixture impedes the formation of ECC of PE on crystallization at 500 MPa, taking into account the experimental fact that the melting peak of ECC decreases with TC content and the high temperature peak completely disappears at $W_{PE} = 0.4$. The intensity of the lowest temperature peak (peak C) increases with increasing TC content in correspondence with decrease of the peak intensity of melting of ECC.

The change in T_m of PE with W_{PE} is shown in Figure 9. The peak temperature of peak C is almost constant from $W_{PE} = 1.0$ to 0.4 and decreases with TC content below 0.4. The temperature of peak A due to the melting of ECC or thick crystals decreases with decreasing PE content from 1.0 to 0.4 and peak A disappears at $W_{PE} = 0.4$. It is considered that ECC of PE is formed with decreased molecular mobility by a application of high pressure. In this study, TC acts as diluent for PE and the mobility of PE at 500 MPa increases in the mixture, compared with the case of pure PE. That is, the increase of TC results in the formation of crystals whose chains are not fully extended. Therefore, depression of the melting temperature occurs for PE in the mixture crystallized under high pressure. Furthermore, in the mixture of $W_{PE} = 0.5$, ECC is not formed even at 500 MPa because of the increased mobility of PE chains as that of atmospheric pressure in pure PE.

CONCLUSIONS

(1) The phase diagram deduced from the melting of PE and TC in the binary system was determined up to 500 MPa. The high pressure phase transition of pure PE occurs above 350 MPa and the phase diagram of the binary system was complicated. Depression in the melting point of PE occurs with decreasing weight fraction of PE in the mixture but the decreasing rate does not change with pressure up to 350 MPa. The depression rate of crystallization temperature increases with pressure.

(2) The range where the high pressure phase of PE appears shifts to the high pressure side with increasing TC content. At 500 MPa, the high pressure phase is not found for the mixture of $W_{PE} < 0.7$.

(3) Formation of ECC of PE on the crystallization at 500 MPa is impeded by the presence of TC and at $W_{PE} < 0.4$, ECC is not formed. The role of TC as a lubricant is considered.

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