

## Melting and Crystallization of Poly(vinylidene fluoride) in the Blend with Poly(methyl methacrylate) under High Pressure

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**ABSTRACT:** Melting and crystallization of poly(vinylidene fluoride) (PVF<sub>2</sub>) in the blend with poly(methyl methacrylate) (PMMA) was studied by differential thermal analysis (DTA) under high pressures up to 350 MPa. Characterization of the pressure-crystallized blend sample with different weight fractions of PVF<sub>2</sub> between 1.0 and 0.5 was performed at atmospheric pressure by DTA, differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD) measurements. Pressure dependence of the melting temperature of form II of PVF<sub>2</sub> in the blend between 1.0 and 0.6 of the weight fraction was almost the same (about 0.34 K MPa<sup>-1</sup>). The WAXD patterns and thermal analysis of the blend show that form I of PVF<sub>2</sub> crystallizes at lower pressure with increasing PMMA content in the sample. DTA and DSC at atmospheric pressure show that the high pressure crystallization of PVF<sub>2</sub> in the blend with PMMA results in the formation of form I which melts at lower temperature than form II.

**KEY WORDS** Poly(vinylidene fluoride) / Poly(methyl methacrylate) / Blend / Phase Diagram / High Pressure / Crystallization / Compatibility / WAXD / DSC / DTA /

It is well known that in poly(vinylidene fluoride) (PVF<sub>2</sub>), two different crystalline forms (form I and form II) are obtained according to the crystallization conditions. Form I is obtained by melt-crystallization under high pressure above 350 MPa<sup>1-7</sup> or drawing the form II film. The crystal structure of form I is orthorhombic and the molecular conformation is the TT type. Form I crystal melts at about 190°C at atmospheric pressure. Form II is obtained usually by melt-crystallization at atmospheric pressure. The crystal structure of form II is monoclinic<sup>8</sup> and the molecular conformation is the TGTG' type.<sup>9</sup> The melting temperature  $T_m$  of form II at atmospheric pressure is about 170°C and it changes with the content of head-to-tail linkage.

Several investigators have reported that

PVF<sub>2</sub> and poly(methyl methacrylate) (PMMA) form a compatible mixture in the melt.<sup>10-13</sup> The melting temperature of PVF<sub>2</sub> decreases with decreasing PVF<sub>2</sub> content in the blend. Nishi and Wang<sup>10</sup> studied the melting and crystallization behavior of the blend and showed that the melting and crystallization temperatures strongly depend on both the composition and cooling rate. It is assumed that under high pressure, the compatibility of these two polymers increases in the melt and the increasing effect of PMMA molecule on the crystallization of PVF<sub>2</sub> is expected.

In the present investigation, differential thermal analysis (DTA) of PVF<sub>2</sub> and PMMA blends was performed under high pressures up to 350 MPa. The effect of pressure on the melting and crystallization of PVF<sub>2</sub> in the blend was studied. In addition, character-

ization of the pressure-crystallized blend sample was carried out by DTA, differential scanning calorimetry (DSC) and the wide angle X-ray diffraction (WAXD).

## EXPERIMENTAL

The samples used in this study were as follows. A PVF<sub>2</sub> sample was a fine powder of Forafon 1000 V.L.D.<sup>®</sup> (product of Puck Co. in France) supplied by Showa Denko Co. The number-average molecular weight  $\bar{M}_n$  is  $1.09 \times 10^5$  and the weight-average one  $\bar{M}_w$  is  $2.90 \times 10^5$  (supplier's data). The fluorine content of this sample is 59% in the catalog. PMMA with a molecular weight  $9.33 \times 10^4$  was purchased from Scientific Polymer Products Inc. The mixed powder of 3g of PVF<sub>2</sub> and PMMA with the desired weight fraction was dissolved in *N,N*-dimethylformamide (100 cm<sup>3</sup>) at 30°C in a laboratory dish. The solvent was completely evaporated in a vacuum vessel after exposure to flowing air for 5 days in a glass box. By this procedure, a semitransparent film was obtained. To make the rod-like sample, the semitransparent film was stuffed in a glass tube and melt-crystallized in an oil bath at atmospheric pressure. Finally, a rod-like sample which is 1.8 mm in diameter and 11 mm in length was obtained.

The high pressure DTA apparatus used in this study was described previously.<sup>14</sup> The rod like sample was cut 1.8 mm in length and drilled to make a hole (0.8 mm  $\phi$   $\times$  0.9 mm l) in the center of the rod. The junction of a thermocouple was inserted in the hole and both the sample and the thermocouple were covered by epoxy resin according to the conventional method.<sup>14</sup> The heating rate of the high pressure DTA was 6 K min<sup>-1</sup> and the cooling rate was about 5 K min<sup>-1</sup>.

To make a pressure-crystallized blend sample, the rod of 11 mm in length was wrapped by aluminum foil and covered by epoxy resin. Its high pressure crystallization was performed

in a high pressure vessel with sheathed heater on the outside. The sample was heated up to a temperature higher than its melting temperature by about 10 K at a desired pressure and then cooled at the same pressure. The heating and cooling rates in the crystallization process under high pressure of the sample were the same as that of the high pressure DTA.

WAXD measurements were performed on the rod like sample by a transmission method using a diffractometer. Nickel filtered Cu-K<sub>α</sub> radiation was used as an incident X-ray beam. DSC measurements were performed with a Rigaku Denki low temperature thermal analyser. The heating rate of DSC was 5 K min<sup>-1</sup> for all measurements.

## RESULTS AND DISCUSSION

Figure 1 shows DSC melting traces of PVF<sub>2</sub>-PMMA blends with different weight fractions of PVF<sub>2</sub> at atmospheric pressure. All the samples were melt-crystallized at atmospheric pressure before the melting experiments. The endothermic peaks are due to the melting of form II of PVF<sub>2</sub>. The melting peak becomes broader and the peak temperature decreases with decreasing PVF<sub>2</sub> content. Peak temperatures of the DSC and DTA melting

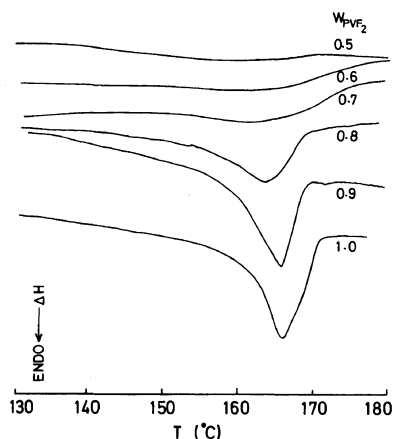
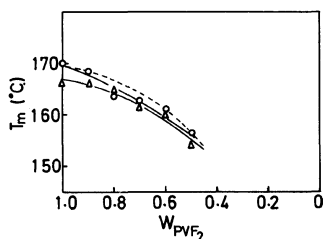


Figure 1. DSC traces of melting of blend samples crystallized at atmospheric pressure.  $W_{\text{PVF}_2}$  means the weight fraction of PVF<sub>2</sub>.

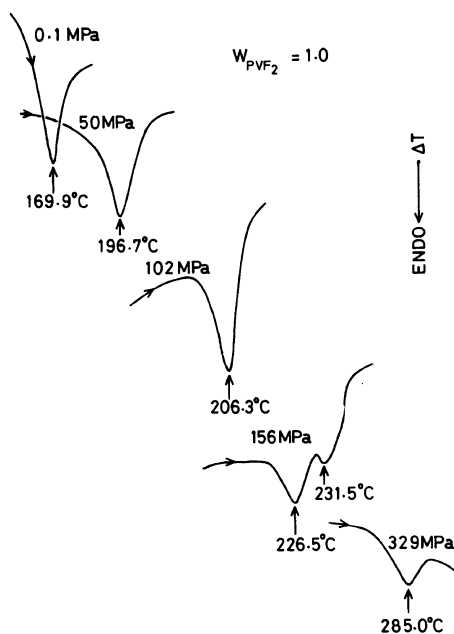


**Figure 2.** Change of melting temperature of PVF<sub>2</sub> as a function of  $W_{\text{PVF}_2}$  by DTA (—○—) and DSC (—△—) in this work. ----, Nishi and Wang.<sup>10</sup>

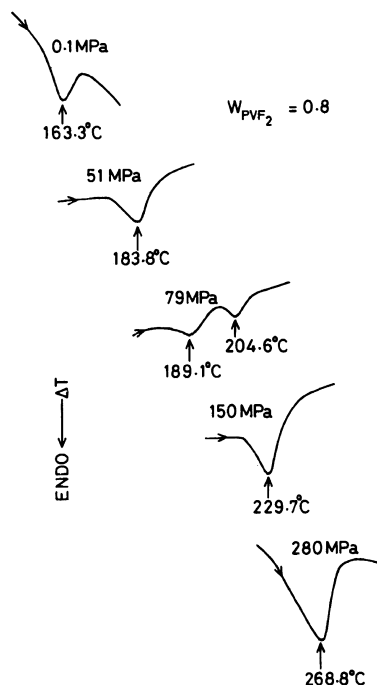
trace were plotted against the weight fraction of PVF<sub>2</sub> as shown in Figure 2. The data in this study agree with the data reported by Nishi and Wang<sup>10</sup> though the sample of PVF<sub>2</sub> used in this study is different from their sample (Kynar of Pennwalt Co.).

Melting and crystallization processes of pure PVF<sub>2</sub> (KF polymer of Kureha Chemical Industry Co., Ltd.) under high pressure were studied in detail by Matsushige and Takemura.<sup>6</sup> They determined the pressure dependence of  $T_m$  of folded chain crystals (FCC) of forms I and II and extended chain crystal (ECC) of form I obtained by high pressure crystallization above 350 MPa. They have shown that FCC of form II transformed to FCC of form I upon heating at pressures above 350 MPa and to ECC of form I above 400 MPa.

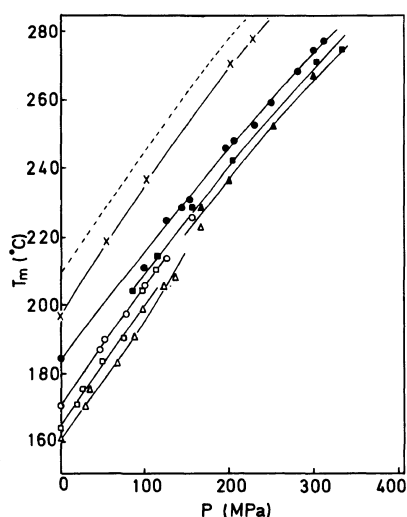
High pressure DTA measurements were performed for the blend samples with the weight fraction of PVF<sub>2</sub> ( $W_{\text{PVF}_2}$ ) between 1.0 and 0.5. Figures 3(a) and (b) show the DTA melting traces at high pressure for pure PVF<sub>2</sub> and the blend sample of  $W_{\text{PVF}_2}=0.8$ . The melting peak shifts to the higher temperature with increasing pressure for both samples. At 156 MPa for pure PVF<sub>2</sub>, two peaks appear in the melting trace. It is supposed that transformation from form II to form I during heating process occurs at a heating rate as slow as 6 K min<sup>-1</sup> in comparison with 10 K min<sup>-1</sup> by Matsushige and Takemura under this pressure, and that the high temperature peak is



**Figure 3(a).** DTA traces of melting of pure PVF<sub>2</sub> under high pressure.



**Figure 3(b).** DTA traces of melting in a blend sample of  $W_{\text{PVF}_2}=0.8$  under high pressure.



**Figure 4.** Pressure dependence of melting temperature of PVF<sub>2</sub> in blend of melting temperature of PVF<sub>2</sub> in blend samples. ×,  $W_{\text{PVF}_2}=1.0$  (form I, ECC); ●,  $W_{\text{PVF}_2}=1.0$  (form I, FCC); ○,  $W_{\text{PVF}_2}=1.0$  (form II); ■,  $W_{\text{PVF}_2}=0.8$  (form I); □,  $W_{\text{PVF}_2}=0.8$  (form II); ▲,  $W_{\text{PVF}_2}=0.6$  (form I); △,  $W_{\text{PVF}_2}=0.6$  (form II); ---, ECC of KF polymer.<sup>6</sup>

due to the melting of form I. To confirm this fact, high pressure DTA was carried out at a heating rate of 6 K min<sup>-1</sup> for KF polymer. The double peak also appeared in the DTA melting trace at 50 MPa in the KF polymer in the heating rate of 6 K min<sup>-1</sup>, and the high temperature peak agreed with the melting point of form I at 50 MPa.

The transformation also occurs in the blend sample during heating under high pressure above about 70 MPa in the heating rate of 6 K min<sup>-1</sup> as shown in Figure 3(b); two peaks appeared between about 70 and 140 MPa. Above this critical pressure range for transformation at the same heating rate, only a high temperature peak due to the melting of form I appeared in the DTA trace. In the cooling, a single endothermic peak of crystallization was observed up to the maximum pressure range studied.

Figure 4 shows the pressure dependence of  $T_m$  of PVF<sub>2</sub> in the blend sample. The transformation occurs between 90 and 150 MPa at a

**Table I.** Comparison of the melting temperature  $T_m$  of Foraflon by DSC and DTA and that of KF polymer<sup>6</sup>

Polymer	Form I,	Form II,	Form I,
	FCC	FCC	ECC
	$T/^\circ\text{C}$	$T/^\circ\text{C}$	$T/^\circ\text{C}$
KF polymer <sup>6</sup>	190	175	207
Foraflon (DSC)	182.8	166.0	193.2
	(178)		
Foraflon (DTA)	176.0	169.9	196.7

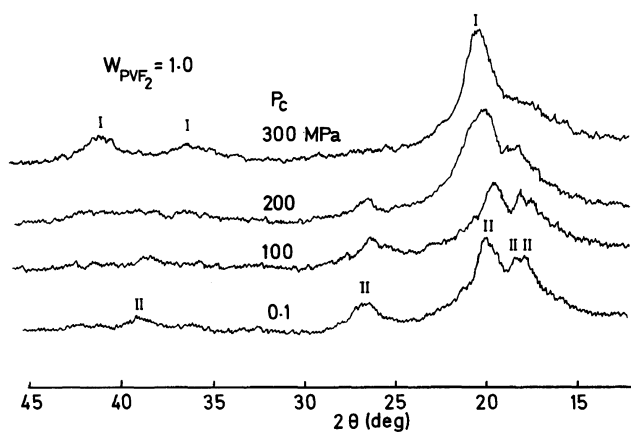
**Table II.** Melting temperature ( $T_m$ ) and pressure dependence ( $dT_m/dP$ ) at 0.1 MPa of ECC of form I and form II in the blend by DTA

$W_{\text{PVF}_2}$	$T_m/^\circ\text{C}$	$dT_m/dP$
		K MPa <sup>-1</sup>
1.0 (form I—ECC)	196.7	0.41
1.0 (form II)	169.9	0.34
0.9	168.5	0.33
0.8	163.3	0.34
0.7	162.6	0.35
0.6	161.5	0.33
0.5	155.8	—

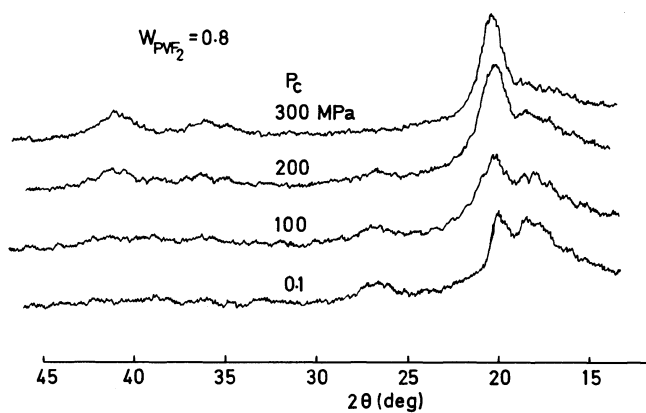
heating rate of 6 K min<sup>-1</sup>; the curve is not continuous in this critical pressure range. The curve shifts to the low temperature side with decreasing PVF<sub>2</sub> content in the blend for both pressure range below 90 MPa (form II melting) and above 150 MPa (form I melting). The melting curve was obtained for all samples with different weight fractions between 1.0 and 0.5 of PVF<sub>2</sub> in the blend.

In the DTA trace of melting at atmospheric pressure of pure PVF<sub>2</sub> crystallized at 300 MPa, two peaks appeared, a sharp peak at 196.7°C, and a broad peak around 176.0°C. The peak temperature at the high temperature side in pure PVF<sub>2</sub> crystallized at 300 MPa is also shown as (×) in Figure 4. From the comparison of the pressure dependence of  $T_m$  of the sample crystallized at 300 MPa with that of ECC of KF polymer obtained by Matsushige and Takemura, it is assumed that the high temperature peak that appeared in the DTA trace of the sample crystallized at 300 MPa is

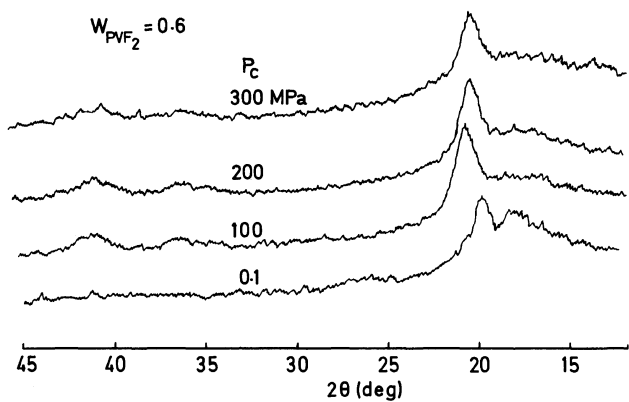
Melting and Crystallization of PVF<sub>2</sub> and PMMA



(a)



(b)



(c)

**Figure 5.** Wide angle X-ray diffraction patterns of high pressure crystallized PVF<sub>2</sub> in the blend. I and II indicate the diffraction peak from forms I and II. (a)  $W_{PVF_2} = 1.0$ . (b)  $W_{PVF_2} = 0.8$ . (c)  $W_{PVF_2} = 0.6$ .

due to the melting of ECC. The  $T_m$  of FCC of form II and form I in Forafilon at atmospheric pressure is lower than that of form II and form I in KF polymer as shown in Table I. Therefore, it is reasonable to assume that  $T_m$  of ECC of form I in Forafilon is also lower than that of ECC of form I in KF polymer. The pressure dependence of  $T_m$  at atmospheric pressure ( $dT_m/dP$ ) for form II in the blend with different composition ratios was determined from the data below 90 MPa using the least squares method. Table II lists the values of  $T_m$  and  $dT_m/dP$  at atmospheric pressure determined by DTA for pure PVF<sub>2</sub> and the blend. The value of  $dT_m/dP$  is almost constant, although  $T_m$  decreases with decreasing PVF<sub>2</sub> content. In the case of  $W_{\text{PVF}_2}=0.5$ , the melting peak in high pressure DTA was very broad and the value of  $dT_m/dP$  was not determined.

The pressure-crystallized blend sample was studied by WAXD to check the pressure effect on the formation of form I and form II crystal. Figures 5(a), (b), and (c) shows WAXD patterns of the blend crystallized under pressure. In the figure, the diffraction peaks around 18°, 20°, 26°, and 38° are due to form II and the peaks around 21°, 36°, and 41° are due to form I. It is clear that the intensity of the diffraction peaks from form I increases and that of the peaks from form II decreases with increasing pressure. The WAXD pattern of the sample crystallized at 300 MPa shows that most of the crystals in the sample is form I. In the blend with  $W_{\text{PVF}_2}=0.8$ , the diffraction peaks from form I begin to appear at 200 MPa. In the blend of the lower PVF<sub>2</sub> content, the diffraction peaks from form I appear at the lower crystallization pressure  $P_c$ . The WAXD pattern of the sample crystallized at 100 MPa on  $W_{\text{PVF}_2}=0.6$  shows that only form I crystallized.

The change in the content of form I and form II with pressure and the weight fraction of PVF<sub>2</sub> obtained from WAXD measurement is summarized in Table III. It is clear from the table that form I of PVF<sub>2</sub> crystallizes at lower

**Table III.** Dominant crystal form of PVF<sub>2</sub> determined from the X-ray diffraction pattern in pressure-crystallized blend. Crystalline form at the left is dominant

$W_{\text{PVF}_2}$	$P_c$			
	300/MPa	200/MPa	100/MPa	0.1/MPa
1.0	I	II, I	II	II
0.9	I	I, II	II	II
0.8	I	I, II	II, I	II
0.7	I	I	II, I	II
0.6	I	I	I	II
0.5	I	I	I	II (I)

pressure with increasing PMMA content in the blend. In  $W_{\text{PVF}_2}=0.5$ , form I appears even in the crystallization at atmospheric pressure. Leonard *et al.*<sup>15</sup> studied the formation of form I of PVF<sub>2</sub> in the blend with PMMA at atmospheric pressure using infrared (IR) absorption method. They reported that the content of form I of PVF<sub>2</sub> increases in blends, if the blend is quenched from the melt and then annealed in the temperature range between 330 and 390 K.

Figure 6 shows the change in DSC melting traces at atmospheric pressure on the blend sample crystallized at 300 MPa. X-Ray diffraction for all the samples in this figure shows diffraction peaks from form I and no peaks from form II. In pure PVF<sub>2</sub>, three endothermic peaks appear in the trace. The peak at 193.2°C is ascribed to the melting of ECC of form I, and the other two peaks at 182.8 and 176.8°C are assigned to the melting of FCC of form I. The reason why two melting peaks of FCC form I appears is not clear. The melting peak for the pressure-crystallized blend sample is broad especially at lower content of PVF<sub>2</sub> and the peak temperature is very low; in  $W_{\text{PVF}_2}=0.9$ , a single peak appears at 162°C and in  $W_{\text{PVF}_2}=0.8$ , the peak temperature is 159°C. It should be noted that the crystallization of PVF<sub>2</sub> in the blend with PMMA under high pressure produces form I with lower melting temperature than form II obtained by melt-

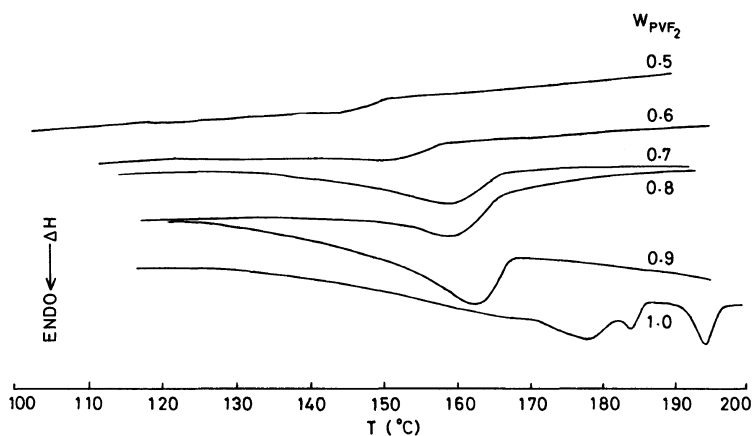


Figure 6. DSC traces of melting of PVF<sub>2</sub> in blend crystallized under 300 MPa.

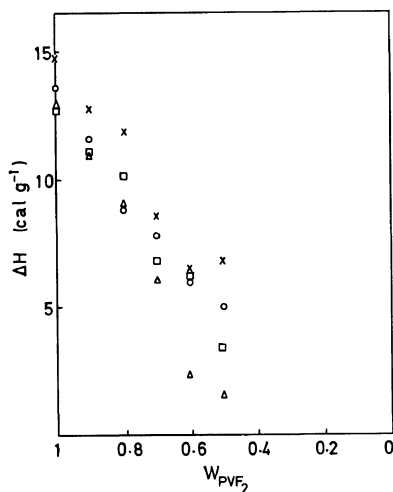


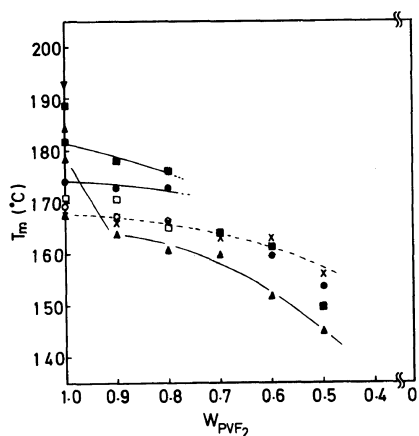
Figure 7. Weight fraction ( $W_{\text{PVF}_2}$ ) dependence of heat of fusion ( $\Delta H$ ) of PVF<sub>2</sub> in blend at various crystallization pressures ( $P_c$ ).  $\circ$ ,  $P_c=0.1$  MPa;  $\times$ , 100 MPa;  $\square$ , 200 MPa;  $\triangle$ , 300 MPa.

crystallization at atmospheric pressure on pure PVF<sub>2</sub>.

Heat of fusion ( $\Delta H$ ) for the pressure-crystallized pure PVF<sub>2</sub> and the blend was determined by DSC. Figure 7 shows the weight fraction dependence of the heat of fusion of the blend crystallized under high pressure.  $\Delta H$  decreases with decreasing weight fraction of PVF<sub>2</sub> and the decreasing rate is larger in the pressure-crystallized blend. At a crystallization

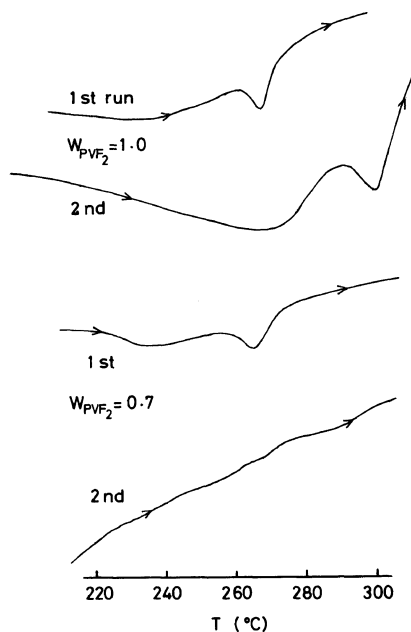
pressure of 300 MPa,  $\Delta H$  decreased to 1.6 cal g<sup>-1</sup> for the blend of  $W_{\text{PVF}_2}=0.5$  from 13 cal g<sup>-1</sup> for  $W_{\text{PVF}_2}=1.0$ . According to Nishi and Wang,<sup>10</sup> the endothermic area in the DSC melting trace of PVF<sub>2</sub> in the PVF<sub>2</sub>/PMMA blend decreases with decreasing PVF<sub>2</sub> content more rapidly than the decreasing rate determined by assuming no interaction between the component. The two polymers form a compatible mixture in the melt. The drastic decrease of  $\Delta H$  with decreasing PVF<sub>2</sub> content in the high pressure crystallized blend in comparison with the blend crystallized at atmospheric pressure suggests that the high pressure crystallization increases the compatibility of PVF<sub>2</sub>/PMMA during crystallization, although the crystallization curve of DTA was not compared because the cooling rate changed slightly in the crystallization process. Crystallinity of PVF<sub>2</sub> in the blend does not seem to drop by high pressure crystallization considering that the intensity of the diffraction peak of PVF<sub>2</sub> in the WAXD of Figure 5 does not decrease so much in the pressure-crystallized blend.

The change in melting temperature of PVF<sub>2</sub> at atmospheric pressure with the weight fraction is shown in Figure 8. Two or more peaks of melting are observed in pure PVF<sub>2</sub> crystallized under high pressure. The peak tempera-



**Figure 8.** Weight fraction ( $W_{PVF_2}$ ) dependence of peak melting temperature ( $T_m$ ) of PVF<sub>2</sub> in DSC curves at various crystallization pressures ( $P_c$ ). ---x---,  $P_c = 0.1$  MPa; ●,  $P_c = 100$  MPa (high temperature peak); ○,  $P_c = 100$  MPa (form II); ■,  $P_c = 200$  MPa (form I); □,  $P_c = 200$  MPa (form II); ▲,  $P_c = 300$  MPa (form I); ▼,  $P_c = 300$  MPa (form I, ECC); △,  $P_c = 300$  MPa (low temperature peak).

ture and the peak height of the high temperature peak appeared in the melting of pure and blend samples crystallized at 100 and 200 MPa decreases with decreasing PVF<sub>2</sub> content. The peak disappeared below a PVF<sub>2</sub> content of 0.7. Considering that the form II content decreases with decreasing weight fraction of PVF<sub>2</sub> in the blend sample crystallized at 100 and 200 MPa as shown in the WAXD pattern in Figure 5, the low temperature peak is the melting of form II and form I but the form II content decreased and the form I content increased continuously with the decreasing PVF<sub>2</sub> content.  $T_m$  of the PVF<sub>2</sub> sample crystallized at 300 MPa decreases drastically by blending only 10 wt% of PMMA. Furthermore, the decreasing rate of  $T_m$  with the weight fraction is the largest in the PVF<sub>2</sub> of the blend crystallized at 300 MPa. The decrease in  $T_m$  of the blend crystallized at 300 MPa also suggests the increased compatibility of the two polymers by high pressure crystallization. This is supported by the melting experiments under high pressure of the high pressure crystallized blend



**Figure 9.** DTA curves of melting at 300 MPa for samples of  $W_{PVF_2} = 1.0$  and  $0.7$ . The 2nd run was also performed after crystallization by cooling at 300 MPa.

sample. Figure 9 shows a comparison of the melting curve of DTA at 300 MPa for the sample crystallized from the melt at 300 MPa of  $W_{PVF_2} = 1.0$  and  $W_{PVF_2} = 0.7$ . The DTA curve of melting for  $W_{PVF_2} = 1.0$  is essentially the same as that of the DTA curve at atmospheric pressure. A broad low temperature peak and a high temperature peak which is due to the melting of ECC of form I is observed. However, the DTA curve in the melting process for  $W_{PVF_2} = 0.7$  shows no peaks up to 300°C at 300 MPa. This fact supports the idea that the compatibility of the two polymers increased under pressure, especially at 300 MPa.

All the PVF<sub>2</sub> samples crystallized at 300 MPa are form I as shown in Figure 5. Therefore, it is concluded that the high pressure crystallization of PVF<sub>2</sub> in the blend with PMMA results in the formation of form I crystals with much lower melting temperature than form II.



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