

# High-Pressure Differential Thermal Analysis of Polymers

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**ABSTRACT:** Melting behavior under high pressure of nylon 6, nylon 6-clay hybrid (NCH) and poly(butylene terephthalate) was investigated by high-pressure differential thermal analysis (DTA). It was found that the melting temperature and the pressure dependency of the melting temperature of NCH were low compared with those of nylon 6. Using the melting temperature, the pressure dependency of the melting temperature, and the heat of fusion (the enthalpy of fusion), the Clausius-Clapeyron equation was used to determine the volume changes on melting of the polymers at atmospheric pressure  $\Delta V_{m0}$ (DTA).  $\Delta V_{m0}$ (DTA) of NCH was lower than that of the nylon 6  $\alpha$ -form. The smaller  $\Delta V_{m0}$ (DTA) of NCH was attributed to the presence of nylon 6  $\gamma$ -form in NCH. The values of  $\Delta V_{m0}$ (DTA) for nylon 6 and poly(butylene terephthalate) were similar to those obtained from pressure-volume-temperature relationships  $\Delta V_{m0}$ (PVT) of those polymers. The entropies of fusion were constant and independent of pressures up to 100 MPa. The volume changes on melting ( $\Delta V_m$  in  $\text{cm}^3/\text{g}$ ) under high pressure can be approximately described by the following equation:  $\Delta V_m = 0.165T_m V_w (dT_m/dP)/(dT_{m0}/dP)/298$ , where  $T_m$  and  $T_{m0}$  are the melting temperatures (in K) under high pressure and atmospheric pressure, respectively and  $V_w$  is the van der Waals volume of the polymer ( $\text{cm}^3/\text{g}$ ). © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1046–1051, 2001

**Key words:** high pressure thermal analysis; nylon 6; nylon 6-clay hybrid; poly(butylene terephthalate)

## INTRODUCTION

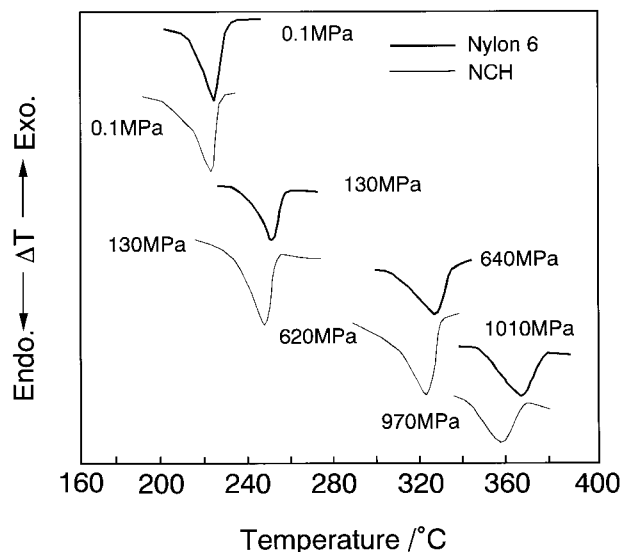
The melting of crystalline polymers under high pressure has been studied by many investigators.<sup>1–14</sup> Nelson et al.<sup>1</sup> studied the melting behavior of *n*-paraffins at high pressure. Melting measurement up to 60 MPa was performed for polytetrafluoroethylene.<sup>2</sup> Melting measurements of polymers such as polyethylene, polypropylene, poly(ethylene oxide) and poly-1-butene under high pressure have also been reported.<sup>3–8</sup> In the study of the melting of the polymer under high pressure, volume changes of polymers caused by melting were obtained by the pressure-volume-

temperature (PVT) method.<sup>1–8</sup> Based on a concept of Simha and Boyer,<sup>15</sup> Van Krevelen and Hoftyzer<sup>16</sup> showed that the volume changes on melting at atmospheric pressure ( $\Delta V_{m0}$ ) of polymers could be expressed according to the relationship,  $\Delta V_{m0} = 0.165T_m V_w/298$ , where  $T_m$  is the melting temperature and  $V_w$  is the van der Waals volume of the polymer.

In this work, the melting temperature and pressure dependence of the melting temperature of nylon 6, nylon 6-clay hybrid (NCH), and poly(butylene terephthalate) (PBT) were obtained by high-pressure differential thermal analysis (DTA). Using these results and the heat of fusion, the volume changes on melting of the polymers were determined with the Clausius-Clapeyron equation and were compared with the values obtained from PVT data. We also investigated the

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**Figure 1** High-pressure DTA thermograms of nylon 6.

relationships among the volume change on melting under high pressure, melting temperature, van der Waals volume of the polymer, and the pressure dependence of the melting temperature.

## EXPERIMENTAL

NCH, commercial pellets of nylon 6 (1013B; Ube Industries, Ltd., Tokyo, Japan) and PBT (101G X54 GF20%; Toray Industries, Inc., Tokyo, Japan) were used in this work. NCH is a molecular composite of nylon 6 in which silicate monolayers of montmorillonite, 1 nm in thickness and 100 nm in width, are uniformly dispersed. NCH with a montmorillonite content of 1.6 wt % was synthesized by the same method described in previous articles.<sup>17-19</sup> Residual Caprolactam was removed by washing at 80°C for 1 h.

Thermal properties were investigated with differential scanning calorimetry and a thermal controller SSC/580 from Seiko Instruments & Electronics, at a heating rate of 5°C/min. The endothermic peaks of the differential scanning calorimetry thermograms were assigned as the melting temperatures.

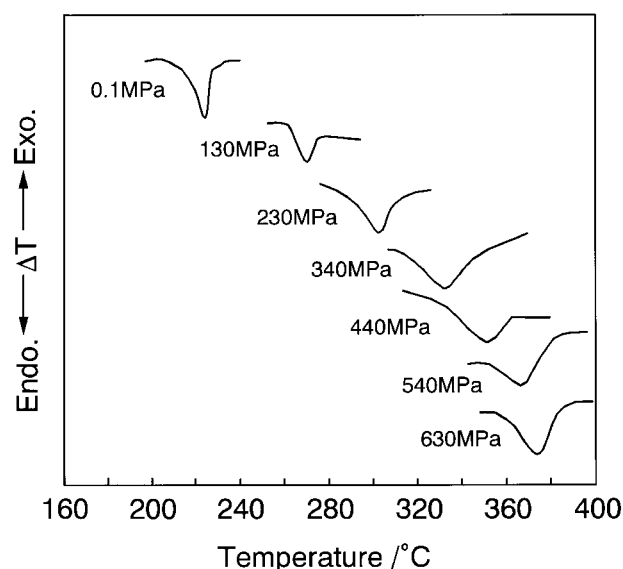
Crystalline structures were investigated by wide-angle X-ray diffraction. The X-ray diffraction patterns were recorded at room temperature by using a Rigaku Denki Rad-B over a range of diffraction angle ( $2\theta$ ) from 10 to 40° with  $\text{CoK}\alpha$  radiation (30 kV, 30 mA) filtered by a monochromator.

High-pressure DTA thermograms of the polymers were obtained by using a Rigaku-Denki high-pressure DTA apparatus from room temperature to 400°C and at pressures up to 1000 MPa.<sup>20</sup> Pressure measurements were performed using a Bourdon gauge (Heise gauge) and a manganin coil gauge. Low viscosity silicone oil (KF-96-10CS or KF-96L-2CS; Shinetsu Chemical) was used as the pressure transmitting fluid.

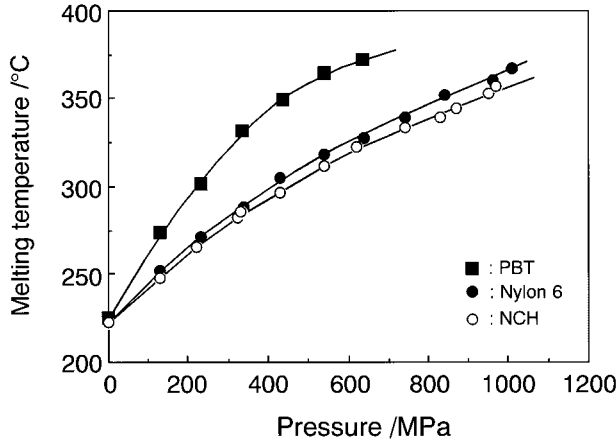
The specially designed apparatus used for obtaining PVT relationships has been described in detail.<sup>21</sup> It consists of a specimen cell containing the sample and mercury as a confining liquid. A piston closes one end of the cell. The linear displacements of the piston resulting from pressure and temperature changes were measured with a linear variable differential transformer, and used to calculate the specific volumes of samples with respect to a standard state at which the specific volume was known. Measurements were performed between 30 and 300°C and at pressures from atmospheric pressure to 100 MPa.

## RESULTS AND DISCUSSION

Figures 1 and 2 show high-pressure DTA thermograms of nylon 6, NCH, and PBT. Only one endotherm was obtained in each DTA thermogram for those samples. The endotherms are due to melting of the crystalline domains. We define the peak temperature of the endotherms as the melting temperature. Figure 3 shows the pressure depen-



**Figure 2** High-pressure DTA thermograms of PBT.



**Figure 3** Influence of pressure on melting temperatures of nylon 6, NCH, and PBT.

dence of the melting temperatures of nylon 6 and PBT, together with NCH. The melting temperature increases with increasing pressure and the pressure dependence of the melting temperature decreases with pressure. A least squares fit to each plot of melting temperature  $T_m$  (K) of nylon 6, NCH, and PBT versus pressure  $P$  (Pa) gave the following values:

$$T_m = 499.5 + 2.057 \times 10^{-7}P - 6.76 \times 10^{-17}P^2 \quad (R^2 = 0.999, \text{Nylon 6}) \quad (1)$$

$$T_m = 497.3 + 1.994 \times 10^{-7}P - 6.71 \times 10^{-17}P^2 \quad (R^2 = 0.999, \text{NCH}) \quad (2)$$

$$T_m = 498.0 + 4.051 \times 10^{-7}P - 2.717 \times 10^{-16}P^2 \quad (R^2 = 0.999, \text{PBT}) \quad (3)$$

NCH has lower melting temperatures than nylon 6 in the pressure range from 0.1 to 1000 MPa. Figure 4 gives X-ray diffraction patterns of NCH and nylon 6. The unit cell of the  $\alpha$ -form is monoclinic in shape with  $a = 0.956$  nm,  $b = 1.724$  nm (chain axis),  $c = 0.801$  nm, and  $\beta = 67.5^\circ$ , crystal density =  $1.24$  g/cm<sup>3</sup><sup>22</sup> whereas that of the  $\gamma$ -form is orthorhombic with  $a = 0.382$  nm,  $b = 0.782$  nm, and  $c = 1.67$  nm (chain axis), crystal density =  $1.19$  g/cm<sup>3</sup>.<sup>23</sup> The diffraction peaks of NCH at  $2\theta$  of  $23.2^\circ$  and  $27.8^\circ$  are from 200 and 002 planes, plus the 202 planes of the  $\alpha$ -form, and the diffraction peaks at  $2\theta$  of  $12.2^\circ$  and  $25.0^\circ$  are from the 002 and 110 plus 020 planes of the  $\gamma$ -form, respectively. Thus, NCH has the  $\alpha$ - and  $\gamma$ -form crystalline forms as shown in Figure 4. The lower melt-

ing temperature and the lower  $dT_m/dP$  of NCH are assumed to be due to the presence of the  $\gamma$ -form crystalline domains.

At the melting temperature under high pressure, the following equation is satisfied:

$$G_{c(P,T_m)} = G_{a(P,T_m)} \quad (4)$$

where,  $G_c$  and  $G_a$  are the free energies of the crystalline and amorphous phases, respectively, and are functions of pressure and temperature. Because equilibrium is maintained for an infinitesimal change in the system, the differential equation is:

$$dG_{c(P,T_m)} = dG_{a(P,T_m)} \quad (5)$$

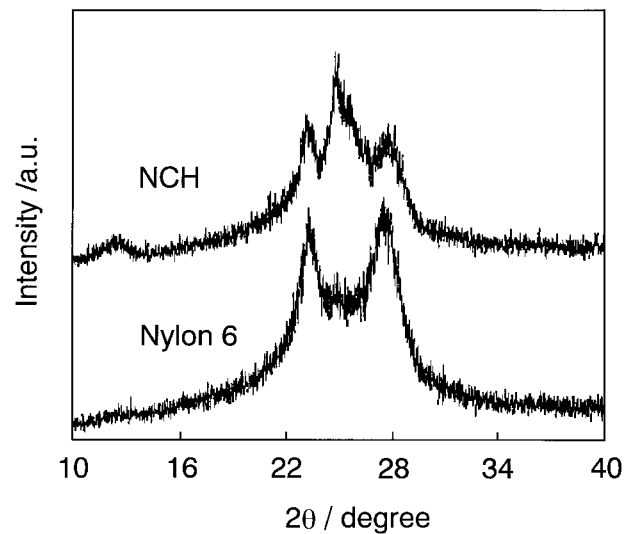
where  $dG$  is related to the molar volume  $V$  and entropy  $S$  according to:

$$dG_c = V_c dP - S_c dT_m \quad (6)$$

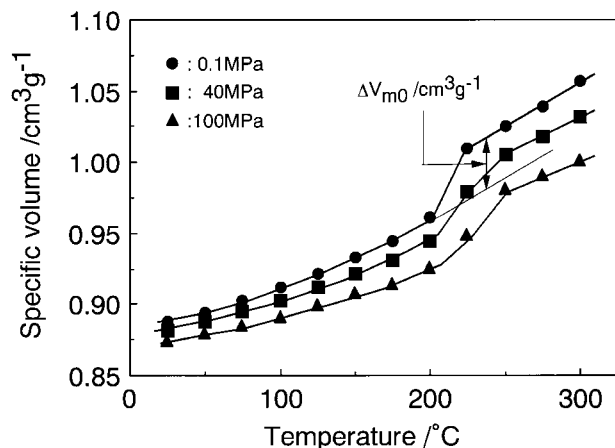
$$dG_a = V_a dP - S_a dT_m \quad (7)$$

Here, suffixes  $c$  and  $a$  indicate the crystalline and amorphous phases, respectively. Substituting eqs. (6) and (7) into (5), the following Clausius-Clapeyron equation is obtained:

$$\Delta V_m = (dT_m/dP)(1/T_m)\Delta H \quad (8)$$



**Figure 4** Wide-angle X-ray diffraction intensity curves of NCH and nylon 6.



**Figure 5** Specific volume versus temperature at various pressures for nylon 6.

where  $\Delta V_m$  and  $\Delta H$  are the volume change on melting and the heat of fusion (the enthalpy of fusion), respectively.  $\Delta H$  of the nylon 6  $\alpha$ -form and  $\gamma$ -form, and of PBT, are 250 J/g,<sup>24</sup> 213 J/g,<sup>25</sup> and 142 J/g,<sup>24</sup> respectively. The pressure dependencies of the melting temperature  $dT_m/dP$  at atmospheric pressure ( $dT_{m0}/dP$ ) were obtained by eqs. (1)–(3), as follows:  $dT_{m0}/dP$  of nylon 6  $2.057 \times 10^{-7} \text{ KPa}^{-1}$ ,  $dT_{m0}/dP$  of NCH  $1.994 \times 10^{-7} \text{ KPa}^{-1}$ , and  $dT_{m0}/dP$  of PBT  $4.051 \times 10^{-7} \text{ KPa}^{-1}$ . These values plus the enthalpy of fusion, the melting temperature at atmospheric pressure and eq. (8) were used to calculate the volume changes on melting at atmospheric pressure,  $\Delta V_{m0}(\text{DTA})$ . The values of  $\Delta V_{m0}(\text{DTA})$  for nylon 6 and PBT are 0.103 and 0.116  $\text{cm}^3/\text{g}$ , respectively. The values of  $\Delta V_{m0}(\text{DTA})$  of the polymers are distributed around 0.1  $\text{cm}^3/\text{g}$ .

The weight fraction of  $\gamma$ -form in NCH was determined using the X-ray diffraction. The weight fraction of  $\gamma$ -form in NCH was calculated as 70% using a calibrating curve which was obtained from relative intensities of X-ray diffraction for standard samples.<sup>26</sup> As the enthalpy of fusion  $\Delta H$  of the mixtures of  $\alpha$ -form and  $\gamma$ -form in NCH was obtained to be 224 J/g, the value  $\Delta V_{m0}(\text{DTA})$  of the nylon 6 crystallites in NCH is estimated to be 0.090  $\text{cm}^3/\text{g}$ . The smaller value of  $\Delta V_{m0}(\text{DTA})$  of NCH compared with that of  $\alpha$ -form nylon 6 is due to the presence of the  $\gamma$ -form in NCH, which has a lower crystal density.

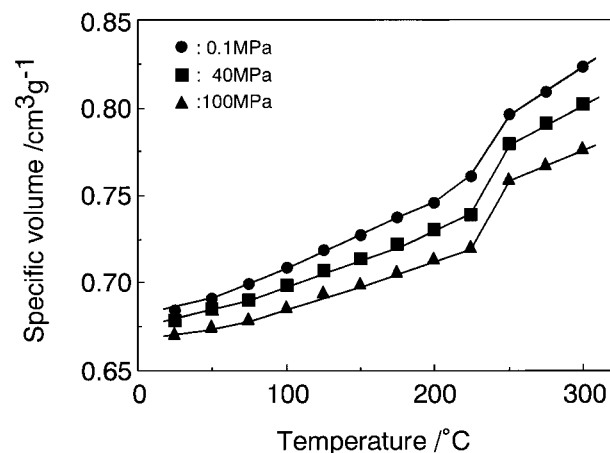
The volume changes on melting at atmospheric pressure of nylon 6 and PBT were also obtained by PVT relationships. The melting expansions  $\Delta V_{m0}(\text{PVT})$  were determined by measuring the difference between the volume at  $T_m$  and the vol-

ume where the curves began to deviate from the normal thermal expansion behavior of the solid polymers, as shown in Figures 5 and 6. The values of  $\Delta V_{m0}(\text{PVT})$  of nylon 6 and PBT were 0.0949 and 0.128  $\text{cm}^3/\text{g}$ , respectively. Nakafuku<sup>12</sup> indicated that  $T_m$  and  $dT_m/dP$  of polypropylene were 437.1 K and  $3.66 \times 10^{-7} \text{ KPa}^{-1}$ , respectively, whereas the enthalpy of fusion was 234 J/g.<sup>16</sup>  $\Delta V_{m0}(\text{DTA})$  for polypropylene is calculated to be 0.196  $\text{cm}^3/\text{g}$ , which is similar to the value obtained from PVT data (0.21  $\text{cm}^3/\text{g}$ ).<sup>4</sup> We found that  $\Delta V_{m0}(\text{DTA})$  and  $\Delta V_{m0}(\text{PVT})$  generally agree well.

The simplified model to visualize thermal expansion phenomena is based on a concept of Simha and Boyer.<sup>15</sup> When a polymer liquid is cooled below its crystalline melting temperature, it either crystallizes or becomes a supercooled liquid. Undercooling of the liquid occurs down to the glass transition temperature. It is assumed that the specific volumes of the supercooled liquid and the crystalline solid at 0 K are equal. On the basis of the concept of Simha and Boyer,<sup>16</sup> the melting expansion  $\Delta V_{m0}$  of polymers at atmospheric pressure is expressed as:

$$\Delta V_{m0} = 0.165 T_{m0} V_w / 298 \quad (9)$$

where  $T_{m0}$  is the melting temperature of the polymer at atmospheric pressure (K), and  $V_w$  is the van der Waals volume of the polymer ( $\text{cm}^3/\text{g}$ ).<sup>16</sup> Experimental values of  $\Delta V_{m0}(\text{DTA})$  and  $\Delta V_{m0}(\text{PVT})$  for nylon 6, PBT, and polypropylene, along with the values calculated according to eq. (9), are shown in Table I. The calculated values of



**Figure 6** Specific volume versus temperature at various pressures for PBT.

**Table I** Calculated and Experimental Values of  $\Delta V_{m0}$ 

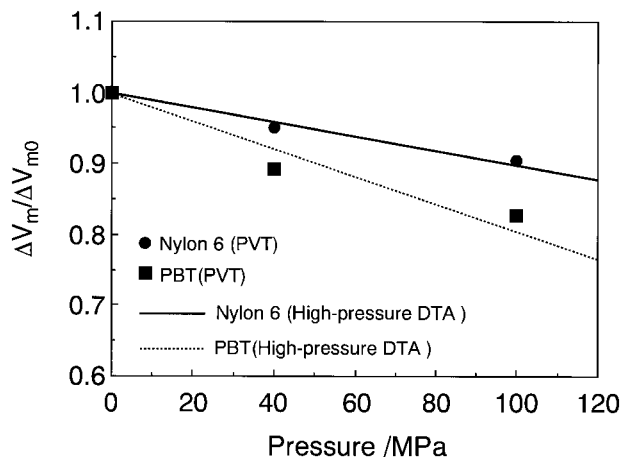
Polymer	$\Delta V_{m0}$ (DTA)/cm <sup>3</sup> g <sup>-1</sup> Experimental	$\Delta V_{m0}$ (PVT)/cm <sup>3</sup> g <sup>-1</sup> Experimental	$\Delta V_{m0}$ /cm <sup>3</sup> g <sup>-1</sup> Equation (9)
Nylon 6	0.103	0.0949	0.157
PBT	0.116	0.128	0.143
Polypropylene	0.196	0.210	0.183

$\Delta V_{m0}$  of the polymers are approximately similar to the experimental values of  $\Delta V_{m0}$ (DTA) and  $\Delta V_{m0}$ (PVT).

The relative volume changes on melting ( $\Delta V_m/\Delta V_{m0}$ ) for PBT and nylon 6 measured with the PVT method as a function of pressure correlated to 100% crystallinity, are shown in Figure 7. The relative volume change decreased with pressure. The effect of pressure on the entropy change of polyethylene at the melting temperature has been evaluated. Matsuoka<sup>5</sup> showed that the total entropy of fusion of polyethylene is independent of pressure, but Baer and Kardos<sup>4</sup> indicated that the entropy of fusion increased with pressure. Assuming that the entropy changes of PBT and nylon 6 at the melting temperature are constant and independent of pressure, the relative volume change on melting ( $\Delta V_m/\Delta V_{m0}$ ) is determined by:

$$\Delta V_m/\Delta V_{m0} = (dT_m/dP)/(dT_{m0}/dP) \quad (10)$$

Figure 7 shows a comparison of the relative volume changes on melting obtained by both the high-pressure DTA and the PVT method indicat-



**Figure 7** Pressure dependence of relative melting expansions  $\Delta V_m/\Delta V_{m0}$  obtained by high-pressure DTA and PVT method.

ing that they are similar. The results also indicate that the entropy changes of PBT and nylon 6 at the melting temperature are constant and independent of pressure up to 100 MPa. Substituting eq. (10) into eq. (9) results in:

$$\Delta V_m = 0.165T_{m0}V_w(dT_m/dP)/(dT_{m0}/dP)/298 \quad (11)$$

Equation (11) shows that the volume change on melting under high pressure can be calculated from the melting temperature at atmospheric pressure, the van der Waals volume of the polymer, and the pressure dependence of the melting temperature at both high pressure and atmospheric pressure.

## CONCLUSION

We found that the melting expansions at atmospheric pressure obtained by the high-pressure DTA and PVT methods agreed well. The entropies of melting of PBT and nylon 6 were independent of pressures up to 100 MPa, respectively. The volume changes on melting of the polymers under high pressure can be described by the equation:  $\Delta V_m = 0.165T_{m0}V_w(dT_m/dP)/(dT_{m0}/dP)/298$  (where  $T_{m0}$  is the melting temperature at atmospheric pressure,  $V_w$  is the van der Waals volume of polymer, and  $dT_m/dP$  and  $dT_{m0}/dP$  are the pressure dependencies of the melting temperature under high pressure and atmospheric pressure, respectively).

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