# Melting of Binary Mixtures of Nylon 6 and Nylon 66. A Study by Pressure–Volume–Temperature Measurements

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ABSTRACT: Pressure–volume–temperature (*PVT*) measurements on binary mixtures of nylon 6 and nylon 66 were performed for melt-spun monofilament samples. During heating in the isobaric modes (form 20 to 180 MPa), two definite volume changes corresponding to the melting of nylon 6 and nylon 66 in mixtures were observed in the composition range where nylon 6 is the major part. From observed volume change at the melting, the heat of fusion $\Delta H_m$ was estimated using the Clausius–Clapeyron equation. Thus, the amounts of coexisting two crystalline phases of both nylon components at a given composition can be estimated. A series of estimated $\Delta H_m$ is self-consistent and reasonable. However, $\Delta H_m$, obtained from the estimated values at finite pressures by extrapolating as $P \to 0$, are 33 and 28 (cal g$^{-1}$) for nylon 6 and nylon 66, and smaller than the literature data of 45 (cal g$^{-1}$). The cause for this difference is discussed.

KEY WORDS    Binary Mixtures / Clausius–Clapeyron Equation / Degree of Crystallinity / Finite Size Crystal / Heat of Fusion / Melting / Nylon 6 / Nylon 66 / Polymer Blend / Pressure–Volume–Temperature /

Investigation using pressure–volume–temperature (*PVT*) measurements has been done over broad areas of polymer science and engineering, probably due to the fact that the volume–temperature coefficient at constant pressure: $\alpha$ and the volume–pressure coefficient at constant temperature: $\beta$ can be obtained from the measurement. From a practical viewpoint, information obtained from *PVT* measurements are essential for application to polymer processing, and from the more academic viewpoint, data of $\alpha$ and $\beta$ are needed for the analysis of entropy change on the phase transition of melting, as made early for ordinary synthetic polymers by many researchers[1-4] and recently for dimer liquid crystals by Abe and *et al.*[5]

Apart from these main-stream subjects, our *PVT* study is confined to melting of binary mixture systems of two crystalline polymers where both components are missible and crystallize separately. We believe that the required conditions above are satisfied in binary mixtures of nylon 6 and nylon 66, we have undertaken the present work, on the melting of nylon 6/nylon 66 mixtures. The experimental results are discussed from various aspects, especially, attention is directed to examine the applicability of the Clausius–Clapeyron equation to such binary systems.

## EXPERIMENTAL

Pellets of nylon 6 ($M_w = 16000$) and nylon 66 ($M_w = 22000$) were blended in an extruder at various ratios of both nylons, namely, nylon 6/nylon 66: 100/0, 80/20, 70/30, 60/40, 50/50, (40/60), (30/70) and 0/100, and melt-spun blend samples of monofilament with diameter of *ca.* 1.0 mm were obtained. The blend samples of (40/60) and (30/70) were used only in a preliminary study of the measurement.

As *PVT* apparatus, Shimadzu model PVT200 tester was used. The apparatus consists of a cell containing several grams of sample and Wood's metal as confining fluid. Each melt-spun monofilament sample was cut in pieces (each with length *ca.* 5 mm), and *ca.* 1 g of these pieces collected and 10 g (*ca.* 1 cm$^3$) of Wood's metal (mp 58°C) were confined in the cell. Measurements were made to determine changes in specific volume as a function of temperature under a constant pressure ranging from 20 to 180 MPa at a fixed interval (40 MPa). As the heating rate, 1°C min$^{-1}$ was employed.

## RESULTS AND DISCUSSION

As a preliminary study, we performed *PVT* measurements for two mixture samples of nylon 6 (N6) and nylon 66 (N66), (N6/N66): (40/60) and (30/70), and in volume–temperature diagram for both mixture samples, we could not find any definite change in volume at the melting temperature of nylon 6. This shows that in the composition range where the content of nylon 6 is small (less than 50%), the existence of nylon 6-crystalline phase is not appreciable in contrast to the predominance of nylon 66-crystalline phase. Thus, in this work, we used nylon 6/nylon 66 mixtures in the composition range where the content of nylon 6 is 50% or more, in addition to the pure nylon 6 and nylon 66 as control.

Figure 1 shows volume–temperature diagram in the isobaric modes ($P = 20$, 60, 100, 140, 180 MPa) for nylon 6 / nylon 66 mixtures, namely (N6/N66): (100/0), (80/20), (70/30), (60/40), (50/50) and (0/100). We examined the experimental data shown in Figure 1, using the thermodynamic relationship of phase transition. In the classical thermodynamics, the Clausius–Clapeyron equation for the solid–liquid phase transition is,

$$T_m \frac{dP}{dT_m} = \frac{\Delta H_m}{\Delta V_m} \qquad (1)$$

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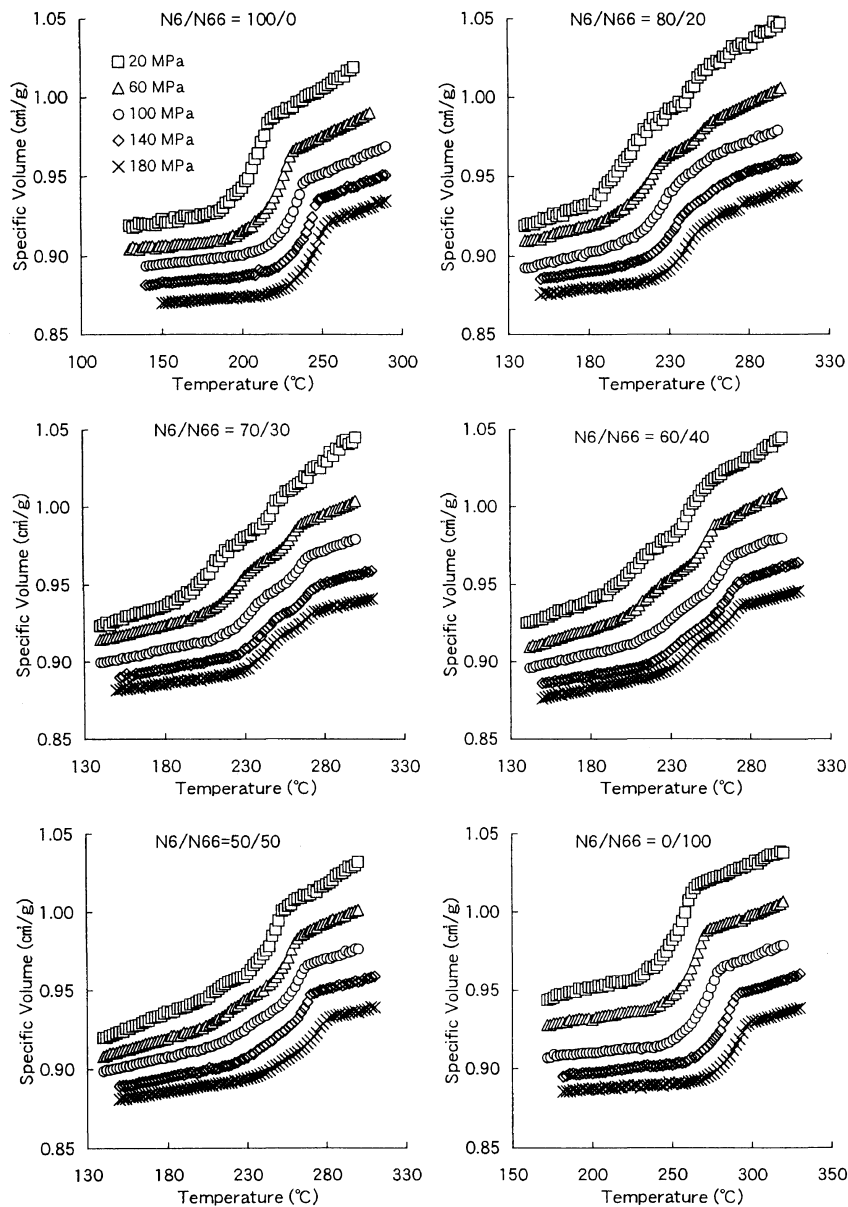
**Figure 1.** Volume *vs.* temperature in the isobaric modes ($P = 20$—180 MPa) for nylon 6 (N6), nylon 66 (N66) and mixtures : N6/N66 = (a) 100/0, (b) 80/20, (c) 70/30, (d) 60/40, (e) 50/50, and (f) 0/100.

where $T_m$ is the melting temperature ($K$), and $\Delta V_m$ and $\Delta H_m$ are changes of volume and enthalpy accompanying melting of the crystalline phase. In eq 1, it is assumed implicitly that the solid phase is wholly-crystalline such as metals and organic substances of low molecular weight. When the relationship is applied to semicrystalline polymer systems, $\Delta V_m$ and $\Delta H_m$ should be replaced by $\Delta V_m'$ and $\Delta H_m'$, respectively, which are defined by,

$$\Delta V_m' = \Delta V_m / Y \quad \text{and} \quad \Delta H_m' = \Delta H_m / Y \qquad (2)$$

where ($Y \times 100$) is the degree of crystallinity %. After substitution of eq 2 into eq 1, in the right-hand side of eq 1, $Y$ in numerator and in denominator cancel each other, and the relationship is reduced to the same expression of eq 1. Then, for a semicrystalline polymer system, experimental data can be analyzed using eq 1. There still remains a question concerning the applicability of eq 1 to the present binary system. The following analysis assumes that eq 1 is applicable to each component of both nylons in mixtures, and total enthalpy
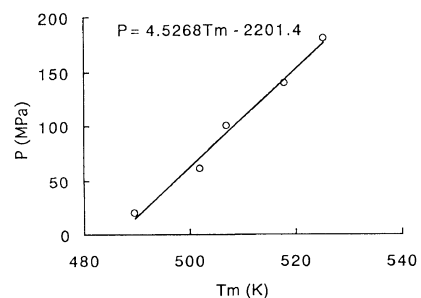


**Figure 2.** Plots of pressure *vs.* melting temperature of nylon 6 for the mixture of (N6/N66) = (70/30).

of melting of the mixture can thus be obtained as the sum of contributions from each component.

At given $T_m$, by substituting the observed values of $(dP/dT_m)$ and $\Delta V_m$ into eq 1, $\Delta H_m$ was estimated. In Figure 2, the plot of $P$ *vs.* $T_m$ of nylon 6 in the mixture of (N6/N66):(70/30) is shown as an example and the good linearity of the plot can be seen. The evaluation

**Table I.** $\Delta H_m$ for nylon 6, nylon 66, and their mixtures

| N6/N66 | | 100/0 | 80/20 | 70/30 | 60/40 | 50/50 | 0/100 |
|---|---|---|---|---|---|---|---|
| $\dfrac{\Delta H_m^{PVT\,a}}{\text{cal g}^{-1}}$ | N6 | 32.7 (100%) | 21.2 (67%) | 17.5 (57%) | 10.8 (37%) | 6.2 (21.%) | — |
| | N66 | — | 10.4 (33%) | 13.0 (43%) | 18.1 (63%) | 22.8 (79%) | 28.1 (100%) |
| | Sum | 32.7 | 31.6 | 30.5 | 28.9 | 29.0 | 28.1 |
| $\dfrac{\Delta H_m^{*\,b}}{\text{cal g}^{-1}}$ | N6 | 45 (100%) | 29.2 (64%) | 24.1 (54%) | 14.9 (33%) | 8.5 (19%) | — |
| | N66 | — | 16.6 (36%) | 20.8 (46%) | 29.0 (66%) | 36.5 (81%) | 45.0 (100%) |
| | Sum | 45.0 | 45.8 | 44.9 | 43.9 | 45.0 | 45.0 |

[a] Estimated from experimental data of $PVT$ measurements. [b] Converted to adjust $\Delta H_m^{PVT}$ of N6 and N66 to literature data.
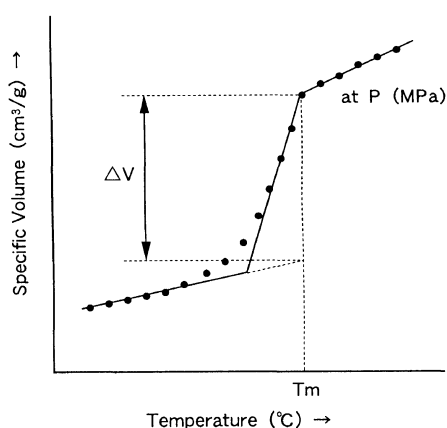


**Figure 3.** Evaluation procedure of $T_m$ and $\Delta V_m$ from volume–temperature curve in the isobaric mode.

procedure of $T_m$ and $\Delta V_m$ from the volume–temperature curve in diagram is illustrated in Figure 3. $\Delta H_m$ obtained from the estimated values at finite pressures by extrapolating as $P \to 0$ are shown in Table I. For convenience, $\Delta H_m$ estimated from $PVT$ measurements and $\Delta H_m$ of literature data are designated as $\Delta H_m^{PVT}$ and $\Delta H_m^*$, respectively, and quantities related to nylon 6 and nylon 66 indicated by the suffix 1 and 2. As can be seen in Table I, enthalpy changes accompanying the melting of crystalline phases of the pure nylon 6 and nylon 66 are $\Delta H_{m1}^{PVT} = 33$ (cal g$^{-1}$) and $\Delta H_{m2}^{PVT} = 28$ (cal g$^{-1}$), which are smaller than the literature data[6] $\Delta H_{m1}^* = \Delta H_{m2}^* = 45$ (cal g$^{-1}$). We introduce a parameter $f$, i.e., the conversion coefficient which adjusts the value of $\Delta H_m^{PVT}$ to the literature data $\Delta H_m^*$ by the relation,

$$\Delta H_m^{PVT} = f \Delta H_m^* \qquad (3)$$

Apparently in this case, we have $f_1 = 0.73$ and $f_2 = 0.62$. The adjustment was similarly applied to coexisting two crystalline phases of both nylons in mixtures. Letting $W_1$ represent the fraction of nylon 6, the values of $W_1 \Delta H_{m1}^{PVT}/f_1$, $(1 - W_1)\Delta H_{m2}^{PVT}/f_2$ and their sum, i.e.,

$$\Delta H_m^* = W_1 \Delta H_{m1}^{PVT}/f_1 + (1 - W_1)\Delta H_{m2}^{PVT}/f_2 \qquad (4)$$

are included in Table I. For all samples, converted $\Delta H_m^{PVT}$, that is $\Delta H_m^*$, represented by eq 4 lie in the same level, ca. 45 (cal g$^{-1}$). This means that a series of estimated $\Delta H_m$ is self-consistent and reasonable. This supports the validity of the assumption that eq 1 is applicable to.

each component of both nylons in mixtures as well as pure nylon 6 and nylon 66. The amounts of coexiting two crystalline phases of nylon 6 and nylon 66 at a given composition can thus be obtained. This is advantageous for application of $PVT$ measurements to binary mixture systems where both components crystallize separately.

Finally, the physical meaning of the conversion coefficient $f$ is discussed. The definition was made so that $f = 1$ corresponds to the crystalline state of nylon 6 and nylon 66 which gives the heat of fusion $\Delta H_m^* = 45$ (cal g$^{-1}$) cited in reference 6, while $f = 0$ refers to disappearance of the crystalline phase as the standard state. Literature data[6] of $\Delta H_m^* = 45$ (cal g$^{-1}$) were estimated from both calorimetric measurments[7–9] and melting temperature depression by monomeric diluents.[10–12] In the former method, the heat of fusion of the wholly-crystalline state is estimated in a limiting case as the degree of crystallinity $\to 100\%$. In the latter method, the melting temperature is determined by the final diappearance of crystallinity which corresponds to the highest ordered portion of the sample and longest crystallite should distribution of crystalline sequence exists. Although data of $\Delta H_m^*$ reported by many researchers[7–12] scatter in the range of 40—45 (cal g$^{-1}$), here $\Delta H_m^* = 45$ (cal g$^{-1}$) as cited in reference 6 was used.

$\Delta H_m^{PVT}$ expresses the enthalpy change accompanying melting of the crystalline phase as a whole, which includes the surface of a finite size crystal and imperfection in bulk such as defects and less-ordered portions. Further, nylon molecules synthesized by condensation polymerization have an approximately most probable distribution of chain length, and some short molecular chains yields small size crystals which contribute to the lowering the enthalpy of fusion. The cause for the difference between $\Delta H_m^*$ and $\Delta H_m^{PVT}$ is attributed to factors mentioned above.

Summarizing the results, the conversion coefficient $f$ may be regarded as a parameter which represents the degree of perfection of crystalline phase. The estimate of $\Delta H_m^{PVT}$ can be made independent of the degree of crystallinity. The usefulness of estimated $\Delta H_m^{PVT}$ along with the relation of eq 4 as shown in this work is applicable to other semicrystalline polymer systems, for pure polymers and polymer mixtures.

## CONCLUSIONS

*PVT* measurements on binary mixtures of nylon 6 and nylon 66 for melt-spun monofilament samples were performed and the following conclusions were obtained.

(1) From volume–temperature diagram made in the isobaric modes (from 20 to 180 MPa) for nylon 6, nylon 66 and mixtures (content of nylon 6 is 50—80%), definite volume changes corresponding to the melting of nylon 6 and nylon 66 were observed.

(2) The Clausius–Clapeyron equation was applied to the two nylons in mixtures as well as pure nylon 6 and nylon 66, and from the observed volume change the enthalpy change $\Delta H_m^{PVT}$ accompanying melting of crystalline phase was estimated. Amounts of coexisting two crystalline phases of both nylon components at a given composition in their mixtures were determined.

(3) $\Delta H_m^{PVT}$ obtained from the estimated values at finite pressures by extrapolating as $P \to 0$, are 33 and 28 ($\mathrm{cal\,g^{-1}}$) for nylon 6 and nylon 66 which are smaller than the literature data of $\Delta H_m^* = 45$ ($\mathrm{cal\,g^{-1}}$) estimated from calorimetric measurements and melting temperature depression by diluents. The factor $f = (\Delta H_m^{PVT} / \Delta H_m^*)$ may be regarded as a parameter representing the degree of perfection of crystalline phase.

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