

# Thermal Properties of Solution Flow-Induced PVA Crystals

LIXING DAI,<sup>1</sup> KUMIKO IDE,<sup>2</sup> KAZUO YAMAURA<sup>2</sup>

<sup>1</sup> Department of Polymer Materials and Textile Chemistry, Suzhou Institute of Silk Textile Technology, Suzhou, Jiangsu 215005, People's Republic of China

<sup>2</sup> Faculty of Textile Science and Technology, Shinshu University, Tokida 3-15-1, Ueda-city, Nagano-prefecture 386, Japan

Received 27 June 1996; accepted 6 October 1996.

**ABSTRACT:** Poly(vinyl alcohol) was crystallized from its aqueous solution under a steady-state flow with different conditions. Using a differential scanning calorimeter (DSC), the thermal properties of PVA precipitates obtained by the flow-induced crystallization were measured, showing a single melting peak in the DSC curve. The melting temperature of PVA crystallized depended on the rate of stirring, crystallization temperature, concentration of PVA, yield of precipitates, and morphology of the crystals. Particularly, there was a closer relationship between the melting temperature and the yield of precipitates, i.e., it was through the effect on the yield of precipitates that crystallization conditions influenced the melting temperature. Generally, with certain conditions, the higher the yield of precipitates, the lower the melting temperature. Moreover, using electron microscopy, it was observed that there were some structural differences between the inner and outer sides of a PVA crystal mat round stirrer and between film-shaped and block-shaped crystals, leading to different melting temperatures. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1337–1344, 1997

## INTRODUCTION

Polyethylene (PE), as a typical crystallizable polymer, was first paid attention to by researchers in respect to its crystallization in a stirred solution. Pennings and Kiel<sup>1</sup> demonstrated that a linear PE can crystallize through stirring its dilute solution and give rise to a shish-kebab structure which contains both an extended-chain central backbone and chain-folded lamellae epitaxially overgrown on it. This extraordinary structure results in a double peak in the DSC curves, i.e., there are two melting temperatures, one of which locates at a higher temperature representing that of central backbone and the other at lower temperature belonging to that of lamellae.<sup>2</sup>

Because of its structure similar to PE, poly(vinyl alcohol) (PVA) can also be crystallized

through stirring its dilute solution, resulting in fibrillar crystals.<sup>3,4</sup> Compared with PVA<sub>VAc</sub> obtained from poly(vinyl acetate), PVA<sub>VTFA</sub> from poly(vinyl trifluoroacetate), which has a higher syndiotacticity, is easier to be crystallized in a stirred solution.<sup>5</sup> Moreover, Monobe et al.<sup>6</sup> reported that unlike PE PVA had no shish-kebab structure in its crystals formed from PVA<sub>VAc</sub> aqueous solutions under a shearing force. So far, very limited work has been done on the thermal properties of the PVA crystals obtained from flow-induced crystallization. Monobe et al.<sup>6</sup> reported that there was only one single melting peak in a DSC curve of PVA crystals. Kitajima et al.<sup>7</sup> compared a DSC curve of the PVA crystals formed from a stirred solution with that of those obtained through isothermal crystallization and discovered that the melting temperature of the former was higher than that of the latter. Yamaura et al.<sup>8</sup> carried out fractionation during flow-induced crystallization of PVA and reported that the melting point decreased in the order of fractionation; the difference between the initial and the last

Correspondence to: K. Yamaura.

This article is Mechanical Denaturation of High Polymers in Solutions XXXX.

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/071337-08

fraction was about 10°C. In addition, it was reported in a previous article<sup>9</sup> that the occurrence of crystallization changed with polymer concentration, molecular weight, and temperature of a solution. However, a systematic study about the effects of crystallization conditions of PVA in a stirred solution and other factors on thermal properties of the crystals has still not been done.

In this experiment, crystallization of PVA<sub>VTF</sub>A made by ourselves was carried out in a dilute aqueous solution under a steady-state flow with different conditions. The thermal properties of the samples crystallized were measured by DSC and the morphology of the crystals was observed by electron microphotography. The relations between thermal properties and some factors, including conditions of crystallization, morphology of crystals, and yield of precipitates, are discussed in detail.

## EXPERIMENTAL

### Sample Preparation of PVA<sub>VTF</sub>A and Determination of Its Properties

Poly(vinyl trifluoroacetate) was obtained through bulk polymerization for 480 min at 60°C employing benzoyl peroxide and then converted to PVA<sub>VTF</sub>A by dissolving it in diethylenetriamine. The degree of polymerization (DP) of PVA<sub>VTF</sub>A was determined according to Nakajima's formula<sup>10</sup>  $[\eta] = 5.63 \times 10^{-4} M^{0.62}$ , where  $M$  is the molecular weight, and  $[\eta]$ , the intrinsic viscosity of PVA<sub>VTF</sub>A [poly(vinyl acetate)] converted from PVA<sub>VTF</sub>A. The viscosity was measured by means of a Ubbelohde viscometer at 30°C and with benzene as a solvent. The content of syndiotactic diads [*s*-(diad) %] was estimated by Murahashi's formula<sup>11</sup>  $s\text{-(diad)\%} = 72.4 \times (D_{916}/D_{849})^{0.43}$ , where  $D_{916}$  and  $D_{849}$  are the absorbance at 916 and 849  $\text{cm}^{-1}$  measured by an FT-infrared 7000 spectrometer. The DP and *s*-(diad) % of the PVA<sub>VTF</sub>A were 2990 and 54.7, respectively.

### Flow-induced Crystallization

PVA<sub>VTF</sub>A aqueous solutions of different concentrations were prepared by dissolving a given amount of the PVA in 20 mL water in a sealed tube at about 120°C; then, they were transferred into a test tube 23 mm in diameter through a glass filter. Flow-induced crystallization was carried out at the stirring rate of 2070, 1220, 810, and 420 rpm, respectively, using a stainless-steel cylindrical stirrer 15 mm in diameter (Chemystirrer B-100

made by Tokyo Rikakikai Co.). With the solution stirred for a given time, precipitates in the form of a fibrillar crystal mat around the stirrer were formed. The stirring time was determined according to the yield of precipitates during the time. Generally, to obtain certain precipitates, a longer time for a low rate of stirring was needed than for a high rate of stirring.<sup>12</sup> Then, the mat was separated from the residual solutions, weighed, dried by freeze-drying, and weighed again. The yield of precipitates was calculated in terms of the weight of dried crystals and polymers in the residual solution as follows:

Yield of precipitates (%) =

$$\frac{\text{weight of dried crystals}}{\text{weight of dried crystals} + \text{polymers in the residual solution}} \times 100$$

Table I shows the conditions and subsequences of the crystallization.

### DSC Measurement

The thermal properties of the precipitates were tested at a heating rate of 20°C/min using a differential scanning calorimeter (DSC) made by MAC Science Co., Japan. As the same crystal sample formed in different places and shapes during the crystallization might lead to different thermal properties, at first, a general measurement including every representative part of a crystal sample was made for every sample, and then the sample was tested again in sections in detail; for example, the same crystal mat was divided into inner and outer sides or film-shaped and block-shaped crystals. The degree of crystallinity was calculated as the experimental heat of fusion divided by the heat of fusion of an ideal PVA crystal, which is taken to be 37.28 cal/g.<sup>13</sup> For comparison, the PVA<sub>VTF</sub>A sample prepared was dissolved in water at 120°C and the solution was cast to yield film at room temperature. The cast film obtained, which had no elongation, was used for the DSC measurement.

### Electron Microscopy

By use of a scanning electron microscope, Superscope JEM 50 made by the Japan Electron Optics Laboratory Co., the observation of the crystals was made in a replica method, by which replicas were obtained by chromium-carbon vapor shadowing of the acetyl cellulose film that was shaped

**Table I Conditions of Flow-induced Crystallization and Yield of Precipitates**

Sample No.	Rate of Stirring (%)	Time (min)	Temperature (°C)	Concentration (%)	Yield of Precipitates (%)
1	2070	30	30	0.5	20.7
2	2070	30	30	0.75	94.8
3	2070	60	50	1.0	82.0
4	2070	60	60	1.0	13.4
5	1220	120	30	0.5	27.5
6	1220	120	30	1.0	13.8
7	1220	120	30	1.25	8.2
8	810	400	30	0.5	88.7
9	810	360	30	1.25	12.7
10	420	720	30	1	91.3

to the surface structure of the crystals under the vapor of methyl acetate.

## RESULTS AND DISCUSSION

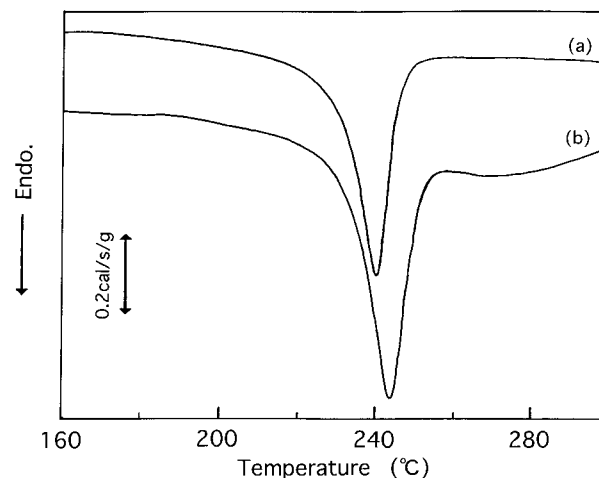
### Thermal Behavior

The samples of flow-induced crystallization and the PVA<sub>VTFA</sub> cast film were heated at a rate of 20°C/min from room temperature to above 300°C in the differential scanning calorimeter, and a single endothermic peak, the temperature of which was regarded as the melting temperature, appeared between about 240 and 247°C in the DSC curves; so, the temperature range that we focused on was from 160 to 300°C. Table II shows the results of the DSC measurement of the samples crystallized and the cast film. It is obvious from Table II that differences of melting temperatures between samples crystallized and the cast film

and among the samples crystallized are significant, and so are those of the degree of crystallinity. The melting temperature of the cast film is only 240.2°C, about 4–6°C lower than that of all the samples crystallized, and the degree of crystallinity of the former is about 3–28% lower than that of the latter, which indicates that through crystallization the thermal properties are greatly changed. As the cast film had no elongation, namely, no orientation, the growth of its crystalline nuclei was considered not to be favored. On the contrary, during flow-induced crystallization, all polymer molecular chains had good conditions to extend, favoring the formation of crystalline nuclei and the growth of crystals and leading to high degree of crystallinity and high melting temperature. In contrast, Figure 1 shows the DSC curves of the cast film and one of the sample crys-

**Table II Melting Temperature and Degree of Crystallinity of PVA<sub>VTFA</sub> Cast Film and Its Crystals from Flow-Induced Crystallization**

Sample No.	Melting Temperature (°C)	Degree of Crystallinity (%)
Cast film	240.2	53.6
1	244.3	59.9
2	243.9	59.2
3	244.7	66.0
4	246.0	56.3
5	244.5	81.9
6	244.8	67.1
7	245.4	60.2
8	243.9	64.6
9	244.5	65.1
10	244.1	60.1



**Figure 1** DSC curves of original PVA<sub>VTFA</sub> sample and of one of the samples crystallized: (a) PVA<sub>VTFA</sub>; (b) sample crystallized at 420 rpm, 720 min, and 30°C in 1% aqueous solution.

tallized. Obviously, the peak of the latter moves toward the direction of high temperature. Among the samples crystallized, because of different conditions of crystallization, the melting temperature and the degree of crystallinity are also considerably different, the largest difference of the former between two samples being about 2°C and that of the latter being about 25% as shown in Table II.

### Crystallization Conditions Affecting Thermal Properties

#### Temperature

It is well known that the melting point of polymer crystals formed in an ordinary way is closely related to its temperature during crystallization. Many researchers have studied the relations between the melting point and the temperature of flow-induced crystallization of polyethylene and other related polymers. The results showed that a higher melting point corresponded to a higher crystallization temperature,<sup>2,14</sup> and in particular for PE, when the temperature reached a certain value, a double peak appeared in the DSC curves. However, it was still unknown what effect the crystallization temperature had on the melting points of PVA precipitates. Matsuzawa et al.<sup>15</sup> studied the relationship between the crystallization temperature and the yield of precipitates of PVA<sub>VTFA</sub> and showed that the temperature should be below about 65°C, above which it was difficult for PVA<sub>VTFA</sub> to be crystallized. In this experiment, two different temperatures, 50 and 60°C, were set for crystallization under the same conditions to determine the effect of the temperature on the thermal properties. From the results of Samples 3 and 4 shown in Table I, it can be seen that lower temperature leads to a higher yield of precipitates, while higher temperature does the contrary. Although the difference of crystallization temperature between the two samples is only 10°C, the difference of the yield of precipitates is surprisingly up to about 70%, indicating the great effect of the temperature on precipitates. It was considered that at lower temperature almost all PVA<sub>VTFA</sub> molecules with lower and higher crystallizability could crystallize with a lot of bubbles, but at higher temperature, the crystallization became difficult as the elongation and orientation of polymer chains were prevented by the thermal motion with increasing temperature and only those with higher crystallizability could crystallize, which agreed with the results reported in a previous article.<sup>15</sup> Therefore, it was reasonable

that lower and higher temperature led to a higher and lower yield of precipitates, respectively. It was also worth noting that the former led to a lower melting point, whereas the latter led to a higher melting point as shown in Table II. The melting point at 60°C (Sample 4) is 1.3°C higher than that at 50°C (Sample 3). It follows that a higher crystallization temperature corresponds to a lower yield of precipitates and a higher melting point, while a lower crystallization temperature corresponds to a higher yield of precipitates and a lower melting point. As described above, because almost all the PVA<sub>VTFA</sub> molecules crystallized at a lower temperature, the crystals formed were of various sizes, which led to a broader distribution of melting temperatures, showing a broader peak in the DSC curve. However, at higher temperature, it was difficult for common polymers to crystallize, leading to a limited number of nuclei, each of which can grow to a large and perfect crystal before encountering interference from other growing nuclei, which reflects that a sharper peak in the higher temperature covered a narrow range of temperature in the DSC curves.

#### Concentration and Rate of Stirring

As mentioned above, the crystallization was carried out in a stirred dilute aqueous solution. There were some previous articles about the effect of the concentration and rate of stirring on crystallization, but no articles with a systematic discussion about the effect on thermal properties of the crystals. In this study, the influence of concentration and rate of stirring on the thermal properties was discussed in detail. From Table I, the relations between concentration and yield of precipitates of three samples, 5, 6, and 7, with concentrations of 0.5, 1, 1.25%, respectively, under the same conditions (1220 rpm, 120 min, and 30°C) are shown clearly. With increase of the concentration, the yield of precipitates decreases. It was likely that at 1220 rpm, i.e., at a lower rate of stirring, with decrease of the concentration, the viscosity of the solution decreased, leading to more effective stirring, which favors chain elongation and orientation of the molecules with various crystallizability. Moreover, with increase of the concentration, the depression of the yield of precipitates slows down. For instance, although the difference of concentration between Samples 5 and 6 is twice as much as that between Samples 6 and 7, the difference of the yield of precipitates between the former is 2.5 times as much as that between the latter. Another more obvious example is that of

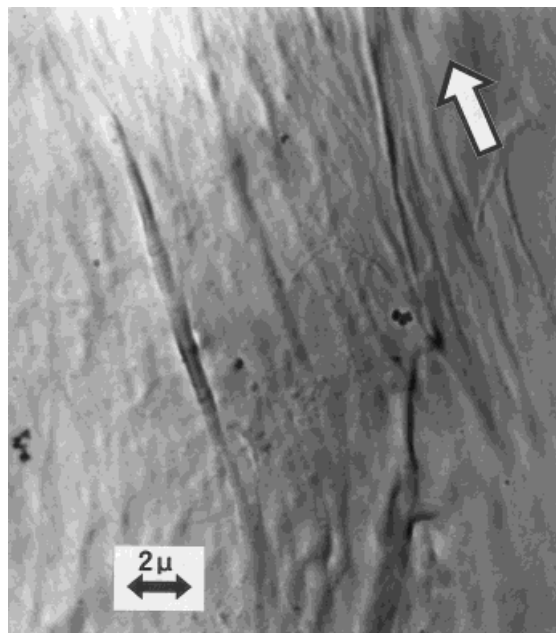
Samples 8 and 9 shown in Table I in spite of a small difference of stirring time. As for the melting temperature, it is clear that with increase of the concentration the melting points move forward in the direction of high temperature and the peaks in the DSC curves seem a little bit sharper at a higher concentration than at a lower concentration. At lower concentration, the precipitates contain smaller crystals of various sizes, whereas at higher concentration, they contain bigger ones and the distribution of crystal size covers a narrow range. In addition, the higher the concentration, the more rapidly the increase of the melting temperature. The melting temperature difference between Samples 5 and 6 is only  $0.3^{\circ}\text{C}$ , while that between Samples 6 and 7 is  $0.6^{\circ}\text{C}$  as shown in Table II. Unlike melting temperature, the degree of crystallinity increases rapidly with decrease of the concentration also as shown in Table II.

As a contrary example, if the rate of stirring was changed to 2070 rpm, the situation was completely different from the fact described above. Also, as Table I shows, for Samples 1 and 2, the concentration of the former is 0.25% lower than that of the latter, but the yield of the precipitates of the former is 74% higher than that of the latter, which indicates that at a higher rate of stirring a small increase of concentration can result in a significant increase of yield of the precipitates. Obviously, this result is not consistent with that mentioned above. It seems possible that when the rate of stirring increases to a certain extent, such a small increase of concentration is not enough to affect the flow of the solution. Instead, because at a high rate of stirring chain extension and orientation become easier, a small increase of concentration will lead to a great increase of chances for precipitating. However, the trend of the melting points is still that the higher the yield of precipitates the lower the melting temperature.

It is possible to conclude that at a lower rate of stirring a higher concentration corresponds to a lower yield of precipitates and higher melting temperature; at a higher rate of stirring, the relation between the first two is completely the contrary, but that between the yield of the precipitates and the melting temperature is still the same as described above.

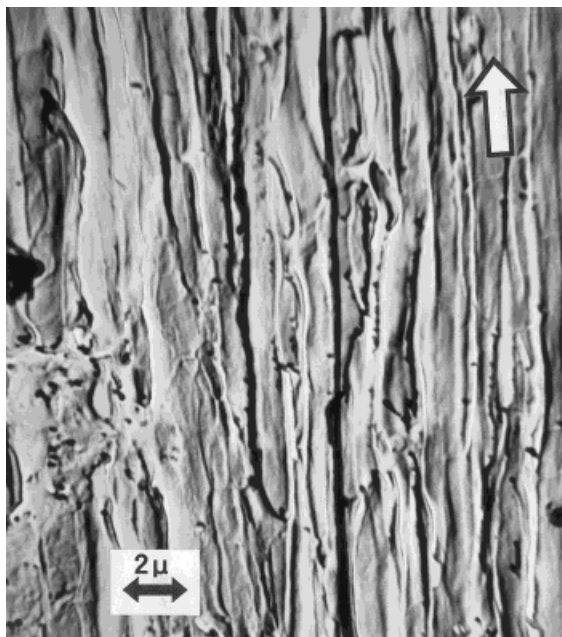
### Effect of Morphology

In the process of flow-induced crystallization of  $\text{PVA}_{\text{VTFA}}$ , the crystal film consisting of fibrillar crystals was gradually wound on the stirrer, causing a thick mat with a layer structure which led



**Figure 2** Electron micrograph of  $\text{PVA}_{\text{VTFA}}$  precipitates obtained by flow-induced crystallization at 1220 rpm, 120 min, and  $30^{\circ}\text{C}$  in 0.5% aqueous solution (replica, inner side). Arrow shows shear direction.

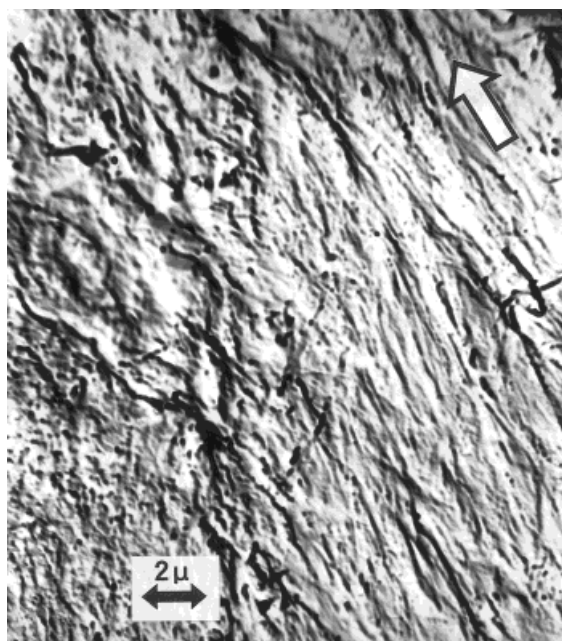
to differences in thermal properties, especially at the inner and outer sides of the mat. As described above, flow-induced crystallization was done in a test tube with a small diameter, but there were still large velocity gradients of flow in the direction of the diameter, which seriously affected the properties of the precipitates. The maximum velocity gradients at 420, 810, 1220, and 2070 rpm were  $150$ ,  $260$ ,  $350$  and  $750\text{ s}^{-1}$ , respectively. It is observed from Figures 2 and 3 that the fibrillar crystals on the inner side were aligned in the direction of the shearing force, indicating the crystals with good orientation. On the other hand, from Figure 4, showing the crystals on the outer side, it can be seen clearly that the fibrillar crystals are considerably disordered over the entire film, besides which on the left-half of the photograph there are some block-shaped crystals. It was believed that with increase of the thickness of a crystal mat round stirrer, the interval which the solution occupied decreased, which made stirring more effective and favored chain extension of molecules with various crystallizability. On the other hand, the strong stirring made the solution tend to be a turbulent flow. Therefore, it was understandable that on the outer side of the film during crystallization the yield of precipitates increased and the fibrillar crystals aligned disorderly. Figure 5 shows the middle layer of a crystal



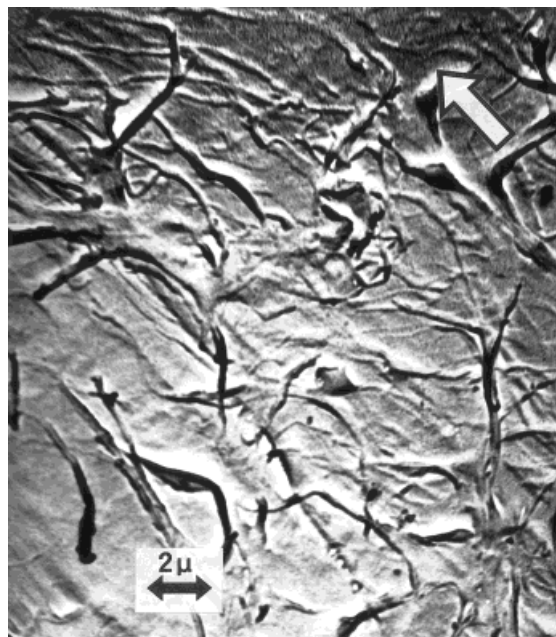
**Figure 3** Electron micrograph of the precipitates obtained by stirring a 0.5% aqueous solution of PVA at 2070 rpm, 30 min, and 30°C (replica, inner side). Arrow shows the shear direction.

mat with a disordered arrangement of fibrillar crystals because of being separated by force.

DSC results of the inner and outer sides of of



**Figure 4** Electron micrograph of PVA<sub>VTFA</sub> precipitates obtained by stirring a 1.0% aqueous solution at 420 rpm, 720 min, and 30°C (outer side, replica). Arrow shows shear direction.

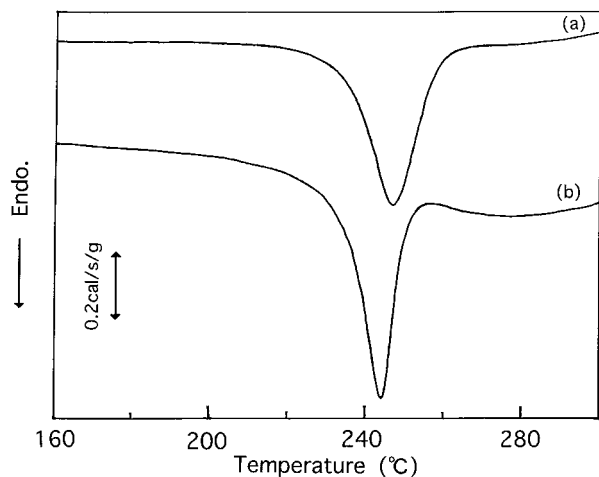


**Figure 5** Electron micrograph of middle layer of PVA<sub>VTFA</sub> precipitates obtained from stirring a 0.5% aqueous solution at 1220 rpm, 120 min, and 30°C (replica, middle part). Arrow shows shear direction.

some crystal films are given in Table III. It is noted that the differences of melting points of the inner and outer sides of the samples are between 0.2 and 0.9°C. Every temperature here is an average value which was measured three to five times. In spite of the small temperature differences, the trend that the melting points of the inner sides are higher than those of outer sides is basically certain. From these results, it is obvious that on the inner sides the precipitates are due mainly to the chain extension of molecules which have high crystallizability and the crystal nuclei can grow to large sizes, causing high melting points. Furthermore, it seems likely that polymers with a high molecular weight have good crystallizability. As pointed out in previous articles,<sup>4,8</sup> the syndiotactic sequence of PVA plays an important role in solu-

**Table III** Melting Temperature of Inner and Outer Sides of Some Crystal Mats

Sample No.	Melting Temperature (°C)	
	Inner	Outer
5	244.7	244.5
7	245.0	244.5
8	244.1	243.2
10	244.4	244.0



**Figure 6** DSC curves of film-shaped and block-shaped crystals of the same sample crystallized in a 1.0% aqueous solution at 2070 rpm, 60 min, and 50°C: (a) film-shaped crystal,  $T_m = 247^\circ\text{C}$ ; (b) block-shaped crystal,  $T_m = 244.1^\circ\text{C}$ .

tion flow-induced crystallization, and with increasing molecular weight, the sequence length of the syndiotactic part and the number of the sequence in a molecule increase statistically. Therefore, the higher the molecular weight is, the easier the crystallization occurs. Apparently, on the other side, various polymers with different molecular weight were involved during the crystallization because of a stronger stirring effect, leading to different sizes of crystals and showing a broader melting peak and a lower melting point in the DSC curves.

Besides the differences between the inner and outer sides discussed above, there is a difference between film-shaped and block-shaped crystals which also causes considerably different thermal properties. As mentioned above, the film-shaped crystal was made up of an oriented assembly of fibrous crystals collected, but with certain conditions, e.g., with a higher rate of precipitates in this experiment, block-shaped crystals appeared at the end of crystallization, which was suggested to be the consequence of a stronger stirring effect which hindered the growth of the crystals. Moreover, according to the observation, the block-shaped crystals can be divided into two categories: the crystals made up of very short fibrils and of a complete block form. Figure 6 shows the DSC scan of film-shaped and blocked-shaped crystals of the same sample. It can be seen from Figure 6 that the difference of the two curves is so distinct that it is hard to imagine that they are from the same sample crystallized. The difference of the

melting temperatures of them are nearly  $3^\circ\text{C}$ , which indicates that the shape of the crystals of flow-induced crystallization significantly affects its thermal properties, i.e., the film-shaped crystals have a much higher melting temperature than that of the block-shaped ones. The peak of the film-shaped crystals is much broader than that of the block-shaped crystals, indicating that the crystal sizes of the latter are more uniform than are those of the former.

### Relationship with Yield of Precipitates

Although this subject has been mentioned several times above, it is necessary to discuss it systematically because of the important role that it plays on the thermal properties of the precipitates. As pointed out above, the yield of precipitates has a great effect on thermal properties. Under certain conditions, if the yield of the precipitates is high, the melting temperature will be low, whereas if the former is low, the latter will be high, as shown in Tables I and II. In general, a high yield of precipitates is due to the conditions that favor chain extension and orientation of the molecules with low and high crystallizability, so the size distribution of the crystallites covers a wide range, giving rise to a broad melting peak and a lower melting temperature in the DSC curves. However, a low yield of precipitates is produced by the chain extension and orientation of the polymer molecules only with high crystallizability, resulting in large and uniform crystallites and reflecting a sharp melting peak and a high melting temperature in the DSC curves. On the other hand, under the first circumstance, because there are many growing centers of crystals, interferences between the neighbor centers is inevitable, resulting in a poorly ordered, perhaps even an amorphous, region, which is also a consequence of lower melting temperature. But under the second circumstance, only a limited number of growing centers exist; those interferences from neighbor centers can be omitted, leading to large, perfect, and uniform crystallites which cause a high melting temperature.

### CONCLUSIONS

1. In the DSC curves, it was observed that the melting peak of  $\text{PVA}_{\text{VTFA}}$  precipitates obtained from flow-induced crystallization was a single peak, which agreed with the results of Monobe's, and the melting peak

moved about 4–6°C toward the direction of high temperature as compared with the PVA<sub>VTFA</sub> cast film. In addition, through the crystallization, the degree of crystallinity of all samples was higher than that of the cast film.

2. Temperature is one of the important factors that affects the thermal properties of PVA<sub>VTFA</sub> precipitates obtained from flow-induced crystallization. Investigation showed that the higher the crystallization temperature, the lower the yield of precipitates and the higher the melting temperature. Moreover, higher crystallization temperature caused a sharper melting peak in the DSC curve, whereas lower crystallization temperature led to a broader peak, which was considered to be the consequence of different crystallites of various sizes.
3. Regarding the rate of stirring and concentration, it is more difficult to draw a conclusion than with temperature. At a lower rate of stirring, it was more likely to favor crystallization in lower concentration than in higher concentration, while at a higher rate of stirring, the results showed the contrary. However, under either situation, a higher yield of precipitates corresponded to a lower melting temperature, and a lower yield of precipitates, to a higher melting temperature.
4. The morphology of the precipitates is also an important factor. Both the inner and outer sides of a crystal mat wound around the stirrer had different morphology. The former consisted of fibrillar crystals with good orientation, and the latter, with the disturbed state, leading to the results that the inner side had a higher melting temperature than that of the outer side. At the same time, it was observed that apart from the film-shaped crystals consisting of fibrillar crystals there were some block-shaped crystals under certain conditions. The temperature difference between them was surprisingly great, indicating that the

fibrillar crystals were made up of uniform and perfect crystals.

5. The yield of precipitates played an important role in the effect on the thermal properties of the precipitates. Generally, with increase of the precipitates, the melting temperature decreased and the melting peak in the DSC curve became broader. It was suggested that a high yield of precipitates was due to conditions that favored chain extension and orientation of the molecules with various crystallizability, whereas a low yield of precipitates, to those that favored chain extension of the molecules only with high crystallizability. Moreover, the latter led to a higher melting temperature of the precipitates than did the former.

## REFERENCES

1. A. J. Pennings and A. M. Kiel, *Kolloid-Z. Z. Polym.*, **205**, 160 (1965).
2. A. G. Wijord and R. St. Jhon Manley, *J. Macromol. Sci. (Phys.) B*, **2**, 501 (1968).
3. T. Itoh, K. Noma, and I. Sakmada, *Kobunshi Kagaku*, **16**, 115 (1959).
4. Y. Go, S. Matsuzawa, Y. Kondoh, and K. Nakamura, *Kobunshi Kagaku*, **24**, 577 (1967).
5. Y. Go, S. Matsuzawa, Y. Kondoh, K. Nakamura, and T. Sakamoto, *Kobunshi Kagaku*, **25**, 55 (1968).
6. K. Monobe, Y. Fujiwara, and Y. Yamashita, *Kogyo Kagaku Zasshi*, **73**, 1420 (1970).
7. T. Kitajima, H. Nakagawa, K. Sugamiya, and T. Kawai, *Kobunshi Ronbunshu*, **34**, 597 (1977).
8. K. Yamaura, Y. Hoe, S. Matsuzawa, and Y. Go, *Kolloid-Z. Z. Polym.*, **243**, 7 (1971).
9. S. Matsuzawa, K. Yamaura, and H. Yanagisawa, *Kolloid-Z. Z. Polym.*, **250**, 20 (1972).
10. A. Nakajima, *Kobunshi Kagaku*, **6**, 451 (1949).
11. S. Murahashi, S. Nozakura, M. Sumi, H. Yuki, and K. Hatada, *J. Polym. Sci. B*, **4**, 65 (1966).
12. K. Yamaura, K. Ide, and S. Matsuzawa, *J. Macromol. Sci.-Phys. B*, **7**, 359 (1973).
13. R. K. Tubbs, *J. Polym. Sci. Part A*, **3**, 4181 (1965).
14. S. B. Clough, *J. Macromol. Sci. (Phys.) B*, **4**, 199 (1970).
15. S. Matsuzawa, K. Yamaura, and H. Yanagisawa, *Kolloid-Z. Z. Polym.*, **250**, 20 (1972).