

MULTIPLE MELTING IN NYLON 1010

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ABSTRACT

Multiple melting behavior of nylon 1010 has been investigated by using DSC instrument. Effects of partial scanning, partial scanning and annealing, heating rate, cooling rate and stepwise annealing on the melting curve were studied. Experimental results indicate that the sample undergoes a process of continuous melting and recrystallization during DSC scanning. Nylon 1010 contains a distribution of crystallites of different degrees of perfection which is strongly dependent on its previous thermal history. From the structural reorganization point of view, the origin of double and multiple peaks of the melting curve is explained.

Semicrystalline polymers, obtained by slow cooling from their melts, or rapid cooling from their melts but annealed at definite temperatures, show double melting peaks in their DSC curves. There are two explanations for this phenomenon. Bell and Murayama^[1] attributed the high temperature peak to the melting of folded chain crystals and the low temperature one to the melting of extended chain crystals. Roberts^[2], Holdsworth and Turner-Jones^[3] and Ikada^[4], however, had renounced the above viewpoint, and claimed that the low temperature peak is due to the melting of the crystallites originally formed when the material is cooled from its melt, or is due to the melting of the crystallites formed at thermal treatment, while the high temperature peak is due to the melting of the crystallites formed from recrystallization of the material melted at the low temperatures during the scanning process. These two controversial viewpoints existed concurrently for many years and became the main subject for investigation in this field.

Double melting behavior of several semi-crystalline polymers such as nylon 66^[1], PET^[2, 3, 5, 6], isopolystyrene^[7], polyethylene^[8] and polypropylene^[9, 10] has been extensively studied in the past decade. To the author's knowledge, no investigation on nylon 1010 has been made. By means of studying the multiple melting behavior of nylon 1010, this paper is to demonstrate the structural reorganization point of view of Roberts and Holdsworth.

EXPERIMENTAL

Starting material was nylon 1010 bristles. It was heated to 230°C in a Shimadzu DSC-20 instrument, kept at this temperature for 10 minutes and then allowed to crystallize at a cooling rate of 5°C/min. Thus, the previous thermal history of starting material was erased.

The weight of sample used was 8 mg. All the experiments were carried out in nitrogen.

Melting behavior of samples was examined at a scanning rate of 10°C/min unless otherwise indicated. The relative peak areas were obtained, a base line drawn and the double peaks resolved in the manner as shown in Fig. 1. Peak area was determined by the cut-and-weigh method.

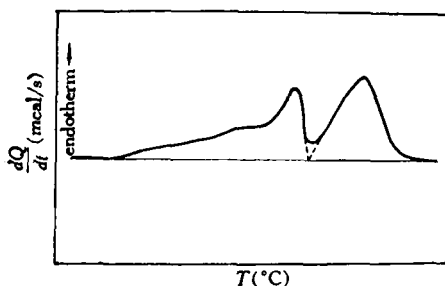


Fig. 1 Method of endothermic peak resolution

RESULTS AND DISCUSSION

1. Melting behavior after partial scanning

Nylon 1010 sample was heated to 230°C, kept at this temperature for 10 minutes and then allowed to crystallize at a cooling rate of 5°C/min in the DSC instrument. The sample was then scanned at a heating rate of 10°C/min. The result was shown in Fig. 2(a). Two melting endothermic peaks (I and II) were observed. The same sample was scanned to a temperature just beyond that of peak II as shown in Fig. 2(b). It was taken out and quenched in ice-water. Upon rescanning of the quenched sample, only one peak (H) was observed as shown in Fig. 2(c). The peak temperature of the peak H is the same as that of peak I, while the area of the peak H almost equals to the sum of the areas of peaks I and II, as listed in Table 1. This implies that crystallites (HM, IM) symbolized by peaks H and I are much the same in degree of perfection, crystallites (II) symbolized by peak II become very imperfect after melting and quenching; they continuously melt and recrystallize to high melting crystals during the rescanning process as suggested by Holdsworth and Turner-Jones^[3]. Therefore, peak II did not appear and the amount of high melting crystals increased. On the contrary, if peaks I and II were originated from the melting of two morphologically different crystallites, one would expect the areas of peaks I and H to be equal^[7].

2. Melting behavior after partial scanning and isothermal annealing

The same sample used in Experiment I was scanned to 192°C (just beyond peak II) and then kept isothermally at this temperature for 3.5 minutes. A broad exothermic peak (Rec) was observed. Continued scanning showed the final endothermic peak H. The whole process is shown in Fig. 3. The temperature and area of the peaks are given in Table 2. It is seen that the area of peak Rec is approximately equal to that of peak II. This again proves that crystallites symbolized by peak II converted to crystallites symbolized by peak H; this conversion took place by melting and recrystallization^[2]. If peaks I and II were originated

from the melting of two morphologically different crystallites, one would expect no exothermic peak^[11] and the areas of peaks I and H be equal^[7].

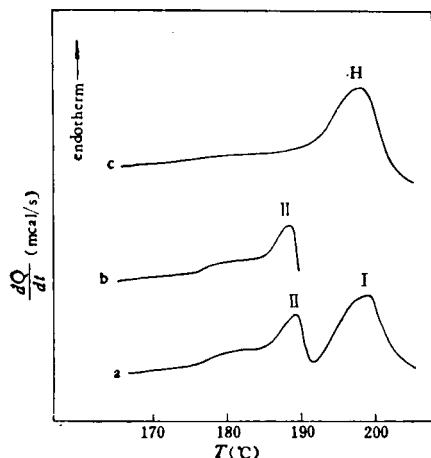


Fig. 2 Effect of partial scanning on melting behavior (a) continuous scanning; (b) sample scanned just beyond the peak II; (c) rescanning of sample (b) after quenched in ice-water.

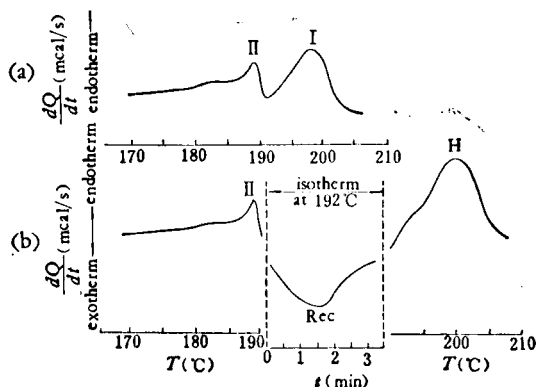


Fig. 3 Effect of partial scanning then keeping isothermally on melting behavior (a) continuously scanned at 10°C/min to 210°C; (b) scanned at 10°C/min to 192°C, kept 3.5 min at 192°C, scanning continued at 10°C/min to 210°C.

Table 1

Scanned mode	Continuous scanning		Rescanning after partial scanning
Peak area (cm ²)	A_{II} 3.00	A_I 2.51	A_{II} 5.40
Peak temperature (°C)	T_{IIM} 187	T_{IM} 199	T_{IIM} 199

Table 2

Scanned mode	Continuous scanning		Keeping isothermally	Continuing scanning after keeping isothermally
Peak area (cm ²)	A_{II} 3.00	A_I 2.51	A_{Rec} 3.06	A_{II} 5.26
Peak temperature (°C)	T_{IIM} 187	T_{IM} 199	T_{Rec} 192	T_{IIM} 199

3. Effect of heating rate on melting behavior

The same sample used in Experiment I was scanned at various heating rates. Results are shown in Fig. 4 and listed in Table 3. It is seen that as the heating rate increased, both the temperature and area of peak I decreased while those of peak II increased; the sum of areas of peaks I and II, however, remained approximately constant.

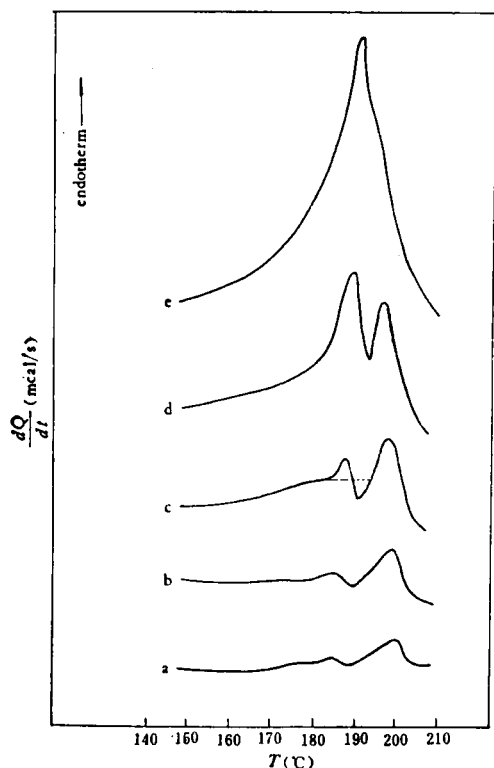


Fig. 4 Effect of heating rate on melting behavior
(a) 2.5; (b) 5; (c) 10; (d) 20; (e) 40°C/min (The areas under the curves are not directly comparable since different chart speeds were used. But in comparing the areas, the same chart speed was used).

Table 3

Heating rate (°C/min)	Peak II		Peak I		Peak II+Peak I
	(T_{IIM} (°C))	$A_{II}(\text{cm}^2)$	T_{IM} (°C)	$A_I(\text{cm}^2)$	$A_{II} + A_I (\text{cm}^2)$
2.5	186	—	201	—	—
5	186	2.10	200	3.03	5.13
10	187	3.00	199	2.51	5.51
20	189	3.57	197	1.97	5.54
40	191	5.23	195	0.33	5.56

These results may also be explained on the basis of melting and recrystallization during scanning process. High heating rate suppresses recrystallization, decreases the area of peak I; low heating rate facilitates recrystallization, increases the area of peak I^[8]. As heating rate is increased, recrystallization is suppressed, the degree of perfection of crystallites IM decreases, so the peak temperature of peak I decreases. The peak temperature of peak II

remains fairly constant at lower heating rates because it is the melting temperature of the original crystallites. However, it increases 5°C at higher heating rate. This increase is in the order of magnitude to be expected for lamellar-type crystals^[12]. If peaks I and II were originated from two morphologically different crystallites, then heating rate should not affect their relative positions^[8]. One may also observe that at lower heating rates, the valley between the two endothermic peaks I and II lies below the dotted line and appears as an exothermic peak as shown in curve c of Fig. 4. This exothermic peak is a proof of recrystallization^[7].

4. Effect of cooling rate on melting behavior

In order to understand more clearly the nature of recrystallization process during DSC scanning, the effect of cooling rate on melting behavior was studied, since cooling rate determines the condition of crystallization from the melt. Nylon 1010 bristles were melted completely in DSC and allowed to crystallize at different cooling rates. Different samples thus obtained were scanned at a heating rate of 10°C/min. Results are shown in Fig. 5. It is seen that both the temperature and area of peak II decrease with increasing cooling rate, while the area of peak I increases, its temperature is essentially unaffected. The quenched sample shows only one endothermic peak. All the samples obtained with a cooling rate from 1°C/min to 40°C/min show exothermic peaks between peaks I and II. The ratio of the area of the exothermic peak to that of peak II above the dotted line increases with increased cooling rate.

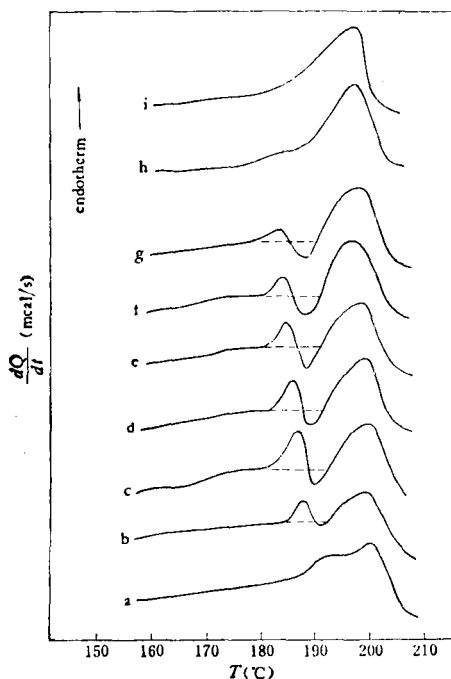


Fig. 5 Effect of cooling rate on melting behavior

The sample was rescanned at 10°C/min after each different cooling rate. (a) 0.5; (b) 1; (c) 2.5; (d) 5; (e) 10; (f) 20; (g) 40°C/min; (h) The molten sample was quickly cooled to room temperature; (i) The molten sample was quenched in ice-water.

If this ratio is taken as an expression for the driving force of recrystallization, it is apparent that the driving force increases with increased cooling rate. This is understandable because at higher cooling rate the crystallites formed are less perfect; their melting point is lower than that of more perfect crystallites. Their melt could be visualized as a supercooled liquid of perfect crystallites, and has a tendency to recrystallize. The higher the cooling rate, the higher is the degree of supercooling and the greater is the amount of recrystallization^[11]. It is also apparent that crystallites formed at a higher cooling rate have lower melting point and also smaller heat of fusion. This explains the decreasing of area and temperature of peak II with increased cooling rate. Thus, in the range of cooling rate between 1°C/min to 40°C/min the scanning reveals the process of melting and recrystallization. At very high cooling rate, the crystallites formed are very imperfect, under the same scanning rate, the process of melting and recrystallization are overcasted in the overall melting curve^[5]. As a result, only the final endothermic peak is observed, which characterizes the melting of those crystallites formed by continuous melting and recrystallization. At a very slow cooling rate, crystallites formed from the melt are highly perfect. Their melting points become close to that of the crystallites formed by recrystallization therefore peak II and peak I almost coincide and no exothermic peak, which is the characteristic of recrystallization, could be seen.

5. Multiple melting behavior after annealing at stepwise lowering temperature

The same sample used in Experiment I was heated to a temperature below that of peak II and annealed at that temperature for 1.5 hrs. The sample was taken out and quenched in ice-water. The quenched sample was reheated to a second temperature below that of the first annealing temperature and annealed for another 1.5 hrs and again quenched in ice-water. It was again reheated to a third temperature below that of the second annealing temperature and annealed for another 1.5 hrs and quenched into ice-water. The final sample was scanned at a heating rate of 10°C/min. Three additional peaks III, IV, V were observed as shown in Fig. 6. The temperatures of these peaks are all a few degrees higher than their respective annealing temperatures and their height and area increase with increased annealing temperature. This result may be interpreted as follows.

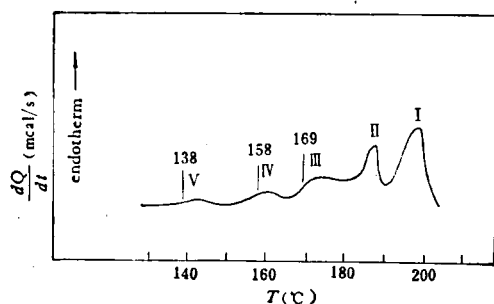


Fig. 6 A proof of stabilizing crystallites by annealing

Nylon 1010 crystallized from the melt contains an assembly of crystallites with different degrees of perfection, which depends strongly on the previous thermal history. The crystal-

lites of different degrees of perfection, of course, have different melting points. The higher the perfect degree, the higher is the melting point. When a sample is annealed at a certain temperature, crystallite, whose degree of perfection corresponds to that annealing temperature is stabilized^[8]. Upon scanning, the melting curve will show an endothermic peak due to the melting of the crystallites stabilized at the annealing temperature. Since, during scanning, the crystallites melt partially and recrystallize into more perfect crystallites, therefore the melting endothermic peak occurs at a temperature somewhat higher than the annealing temperature. If annealing treatments were carried out at several temperatures from high to low successively, several types of crystallites with different degrees of perfection will be stabilized. Upon scanning, they will melt at temperatures somewhat higher than their respective stabilizing temperatures. Therefore several endothermic peaks are observed. As the degree of perfection of stabilized crystallites decreases with decreased annealing temperatures, so is the size of the additional endothermic peak^[13]. This result may also be interpreted as follows. When we subjected the sample to stepwise annealing, in initial step, the sample was kept isothermally at higher temperature for 1.5 hrs, it did not reach equilibrium crystallinity, there were still uncrystallized parts. As annealing temperature went down stepwise, the sample would continue to crystallize, but in this case, the crystalline rate became slow. A few incomplete crystallites were formed. Therefore, the additional melting endothermic peak would be small and the melting point be low.

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