

## The Melting of 66 Nylon: Observations by Differential Thermal Analysis

F. J. HYBART and J. D. PLATT, *Chemistry Department, The University of Aston in Birmingham, Gosta Green, Birmingham 4, England*

### Synopsis

Differential thermal analyses of many 66 nylon samples have shown two endotherms in the melting range. This effect occurs with drawn nylon yarn, as previously observed by White, and also with annealed and precipitated nylon samples. Methods for the preparation of these samples are reported. At 242°C. the development from the melt of crystalline material which gives two melting peaks is associated with annealing rather than with the primary crystallization process. Previous observations of multiple melting peaks with other polymers are discussed.

### INTRODUCTION

White<sup>1</sup> has reported his differential thermal analysis (DTA) observations on the melting of drawn and undrawn 66 nylon yarns. He showed that with drawn 66 nylon yarn, two endothermic peaks could be resolved in the melting range, whereas only one peak was observed with undrawn yarn. When the drawn yarn was heated just to the temperature between the two peaks, disorientation had occurred, i.e., the yarn had shrunk, no longer showed orientation birefringence, and did not give the usual x-ray reflections. White attributed the first peak to the disorientation of the drawn yarn. Melting of the crystalline regions caused the second peak.

Some years ago, one of us<sup>2</sup> observed that two peaks could be obtained with 66 and 6 nylon polymers precipitated from solution in formic acid with methanol. It appeared that this effect was not restricted to oriented samples. In this paper we show that two endothermic melting peaks can be observed with many 66 nylon samples.

### EXPERIMENTAL

#### Apparatus

An instrument showing good resolution was needed to observe the double peak in the melting range. This was obtained with the DuPont 900 Thermoanalyzer<sup>3</sup> when using small samples (3 mg.) and a heating rate of 5°C./min. above 200°C. The sample was usually heated at 30°C./min. up to 200°C. After being purged several times with vacuum, samples were heated with nitrogen flowing over them (1.5 ft.<sup>3</sup>/hr.). The temperature

difference  $\Delta T$  between the two cells was plotted directly against the temperature of the sample cell. The melting point of the sample was taken to be the tip of the melting peak.<sup>3</sup> Glass beads were used in the reference cell.

### Materials

One sample of yarn and one sample of polymer were used for these experiments and both were supplied by I.C.I. Fibres Ltd., Pontypool, Mon. 30-den. (10 filaments) production yarn was used with the following properties:  $\text{TiO}_2$  content 0.3%, average tenacity 4.5 g./den., relative viscosity (the solution viscosity ratio for 8.4% by weight 66 nylon in 90% formic acid) 35. The 66 nylon polymer contained no  $\text{TiO}_2$  or other additives and had a relative viscosity of 35 with 44 and 58  $\mu\text{eq./g.}$  of amine and carboxyl end groups, respectively. 0.5 mole-% of acetic acid was incorporated in the 66 nylon during polymerization to control the molecular weight.

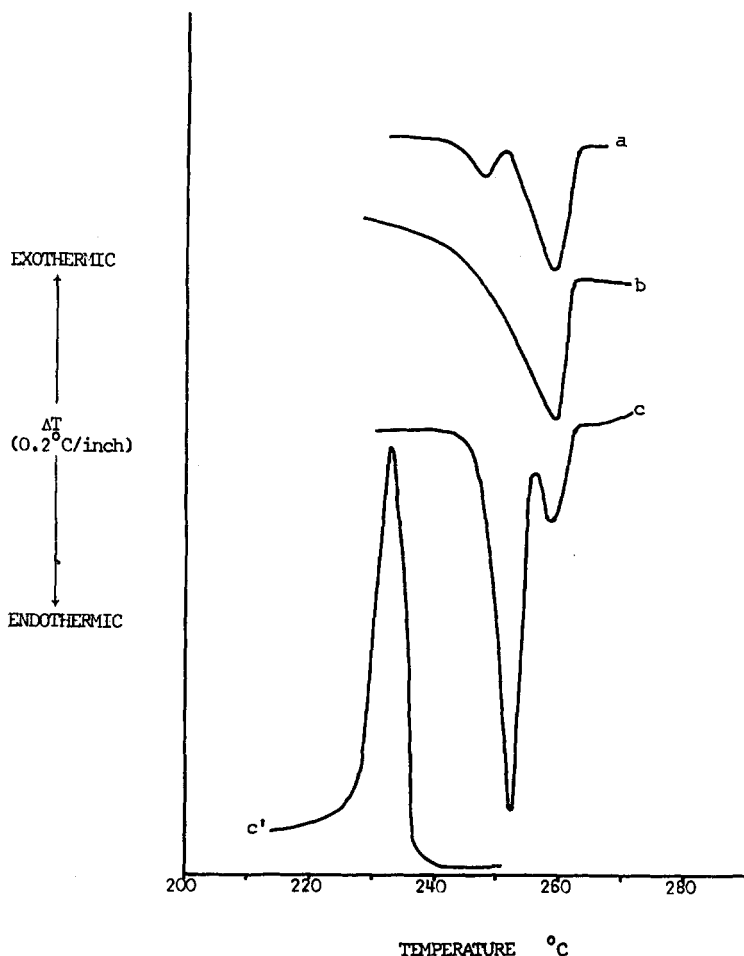


Fig. 1. DTA traces for the melting and crystallization of 66 nylon samples.

## RESULTS

## DTA Traces on 66 Nylon Yarn and 66 Polymer

Traces, at a heating rate of  $5^{\circ}\text{C./min.}$  obtained from the yarn and from a ground sample of the polymer are shown (Fig. 1). These agree with the results of White, the yarn (Fig. 1c) showing two peaks in the melting range, whereas the polymer (Fig. 1b) only shows one peak. After melting, the samples were heated at  $270^{\circ}\text{C.}$  for 10 min. Unprogrammed cooling of the instrument ( $11\text{--}12^{\circ}\text{C./min.}$ ) resulted in trace 1c' which shows a crystallization exotherm in the range  $227\text{--}237^{\circ}\text{C.}$  Remelting a 66 nylon sample crystallized in this way always resulted in a small endotherm at about  $247^{\circ}\text{C.}$  followed by a very much larger endotherm usually at  $258 \pm 1^{\circ}\text{C.}$  (Fig. 1a). Ten minutes heating at  $270^{\circ}\text{C.}$  always resulted in the same subsequent cooling and remelting peaks irrespective of the previous thermal his-

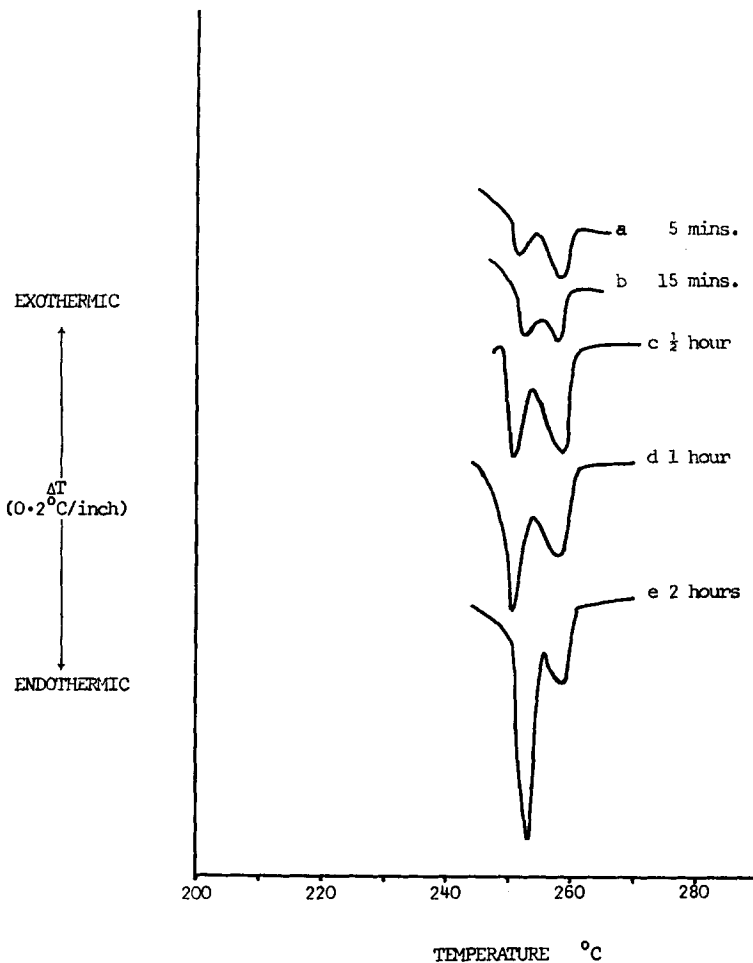


Fig. 2. DTA melting traces for 66 nylon samples crystallized for different times at  $242^{\circ}\text{C.}$

tory of the sample. After a DTA melting run, samples were always heated at 270°C. for 10 min. if any further observations were to be made on that sample.

### DTA Traces on 66 Nylon Crystallized Isothermally at 242°C.

The 66 nylon yarn was heated at 270°C. for 10 min. and then cooled to 242°C. in the DuPont instrument. (Cooling to 242°C. took 2.5 min. but little crystallization was observed in this time). The sample was then held at 242°C. for various times and then reheated. Figure 2 shows the remelting DTA traces for samples that had been crystallized for 5, 15, 30, 60, and 120 min., respectively. With increasing time of crystallization, endotherm 1 increases and endotherm 2 decreases. The increase in the size of the first peak continues for periods greater than 15 min., although ac-

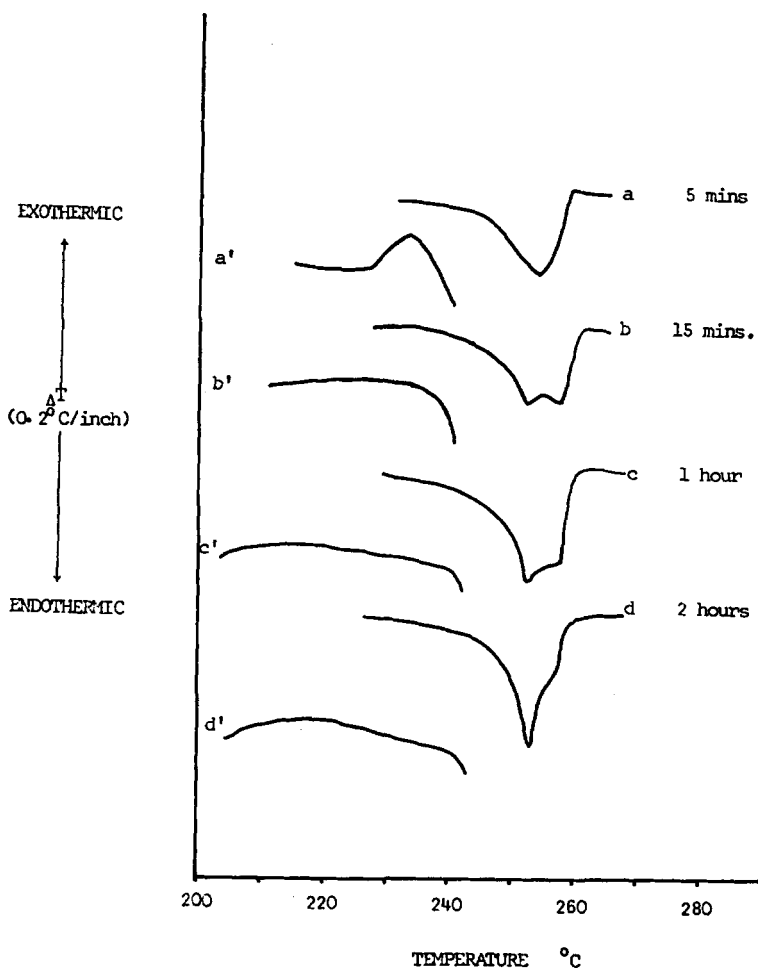


Fig. 3. DTA crystallization and subsequent melting traces for molten 66 nylon samples held at 242°C., cooled to 200°C., and then remelted.

ording to the work of Magill,<sup>4</sup> crystallization should have finished within 5 min. at 242°C.

Crystallizations at 242°C. were repeated but after the crystallization period the instrument was allowed to cool to about 200°C. Any polymer not crystallized at 242°C. then showed a crystallization exotherm. Figure 3a' shows some crystallization at 234–238°C. after allowing only 5 min. at 242°C.

Figures 3b', c' and d' show no crystallization exotherm after 0.25, 1, and 2 hr., respectively, at 242°C. Figures 3a, b, c, d show the remelting traces after 3a', b', c', d', respectively.

#### Annealing of Ground 66 Nylon at 242°C.

The DTA melting traces of samples of ground 66 polymer were determined after the sample was held at 242°C. in the instrument for 0.5, 1, 2, 4, and 8 hr. before melting. A normal melting trace on ground 66 nylon shows only one melting peak (Fig. 1b). Annealing at 242°C. results in two endothermic peaks with the initial peak growing with increasing time of annealment at 242°C. (Fig. 4).

#### Isothermal Crystallization of Molten 66 Nylon at Other Temperatures

The 66 nylon yarn was melted at 270°C. for 10 min. and then crystallized isothermally at known temperatures for various times. After the samples were cooled to about 200°C., so that any residual molten polymer would crystallize, the DTA melting traces were determined. Figure 5 shows the results that were obtained at 245°C. using crystallization times of 5, 15, 30, 60, and 120 min. Crystallization at 245°C. is complete between 30 and 60 min. since curve 5d' shows no sign of a crystallization exotherm. The subsequent melting traces 5a, b, c, d, e show very little resolution into two peaks but some sharpening of the peak has occurred. Isothermal crystallization for 2 hr. at 245°C. resulted in a very sharp melting endotherm with a peak temperature (254°C.) lower than that obtained for samples crystallized for shorter times.

The melting traces for samples crystallized at 250°C. were also obtained (Fig. 6). This temperature is higher than that at which the start of the first peak is normally observed. Crystallization is not complete within 1 hr. at 250°C. since a significant exotherm is observed on cooling further. Crystallization seems to be almost complete after 2 hr. at 250°C. The melting trace of this sample (Fig. 6b) shows a sharp peak with its tip at 259°C.

#### DTA Traces from Precipitated 66 Nylon Polymers

**From 98% Aqueous Formic Acid into Methanol.** 66 Nylon was precipitated by pouring a 10% solution of the nylon in 98% formic acid (10 ml.) into excess methanol (100 ml.). The product was isolated and dried in a vacuum oven at 40–50°C. to remove methanol and formic acid. The DTA trace showed a single melting peak (Fig. 7a). To a

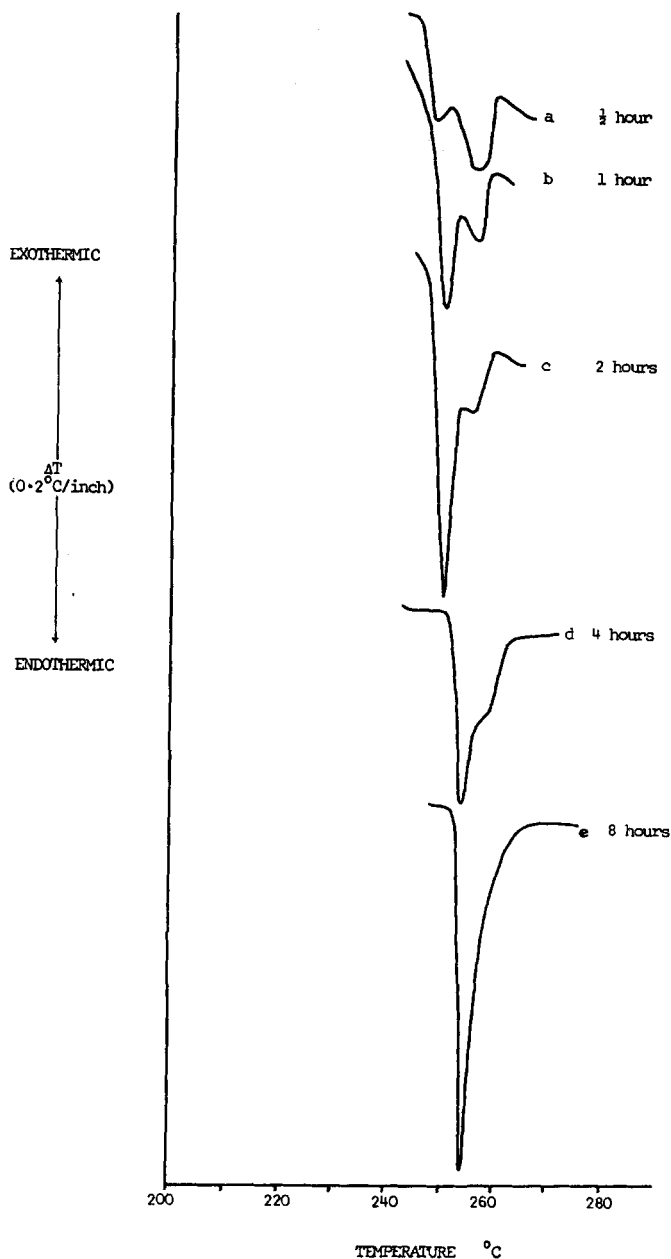


Fig. 4. DTA melting traces for samples of ground 66 nylon polymers annealed at 242°C. for various times.

second portion (10 ml.) of the nylon solution, methanol was added until the precipitate just began to form (7.5 ml. were required). On standing at room temperature the 66 nylon precipitated. The sample was isolated and dried as just described. A DTA trace was obtained and showed two

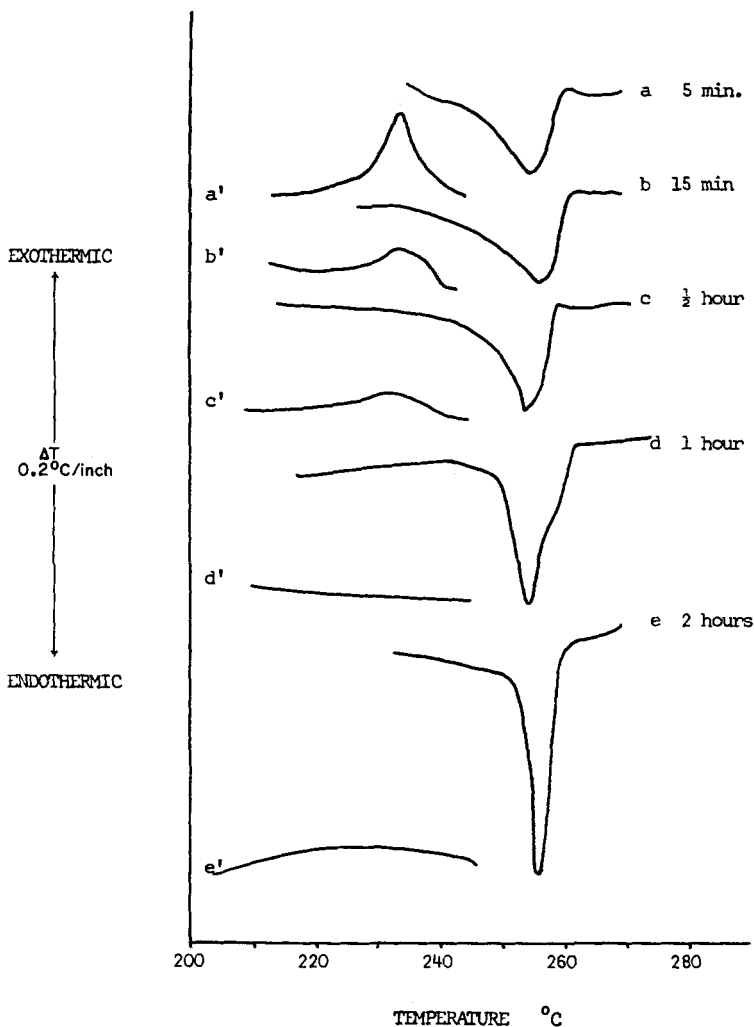


Fig. 5. DTA crystallization and subsequent melting traces for molten 66 nylon held at 242°C., cooled to 200°C., and then remelted.

peaks (Fig. 7*b*). Similar DTA results were obtained when the 66 nylon was precipitated in the same way at 25 and at 40°C., and when using smaller concentrations of methanol.

**From Benzyl Alcohol.** A 2% solution of 66 nylon was prepared in hot benzyl alcohol (180°C.). On cooling, a precipitate formed. All traces of benzyl alcohol were extracted with acetone and ether. The vacuum dried sample was then examined by DTA. Two peaks, of approximately equal size were observed (Fig. 7*c*). Crystallization at 100 or at 120°C. resulted in samples which gave similar DTA traces. However, a sample which was prepared by crystallization from benzyl alcohol at 130°C. gave only one melting peak.

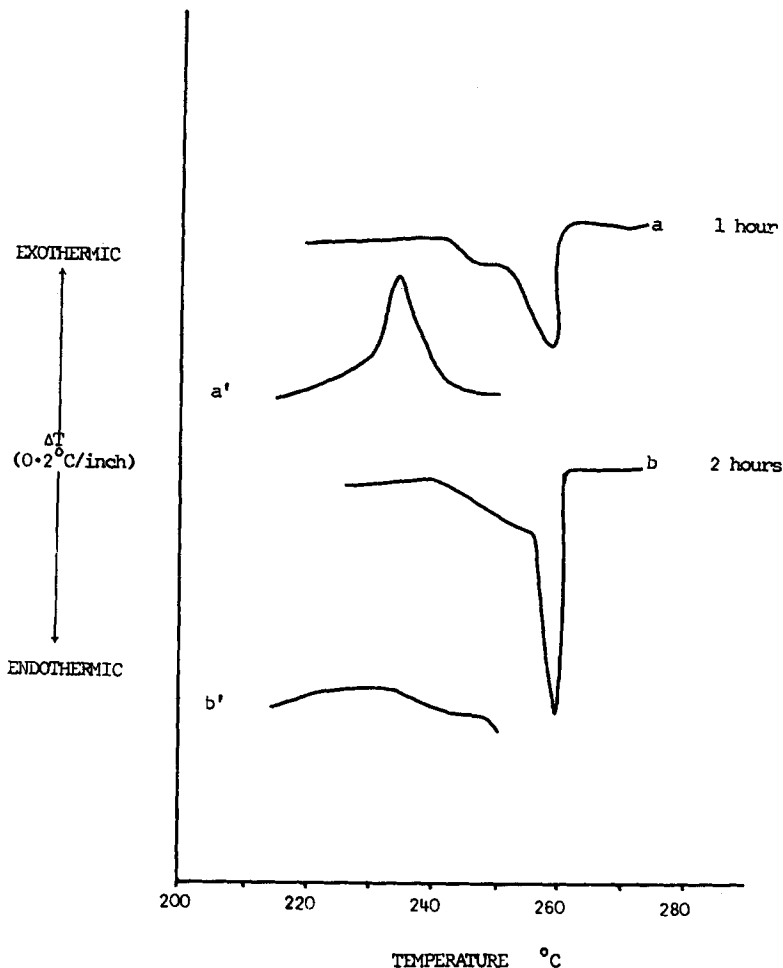


Fig. 6. DTA crystallization and subsequent melting traces for molten 66 nylon held at 250°C., cooled to 200°C., and then remelted.

## DISCUSSION

### Suitable Apparatus for the Detection of Two Melting Endotherms with 66 Nylon

Our first attempts to obtain two melting peaks for drawn 66 nylon yarn were unsuccessful. We were using large samples (0.5 g.) in an apparatus similar to that of Keavney and Eberlin.<sup>6</sup> One thermocouple was completely surrounded by nylon and air so that the conduction of heat to it from outside the cell was poor. After the first peak, the temperature of the thermocouple in the sample cell did not quickly reattain that of the thermocouple in the reference cell. Hence poor resolution of the two peaks was obtained.



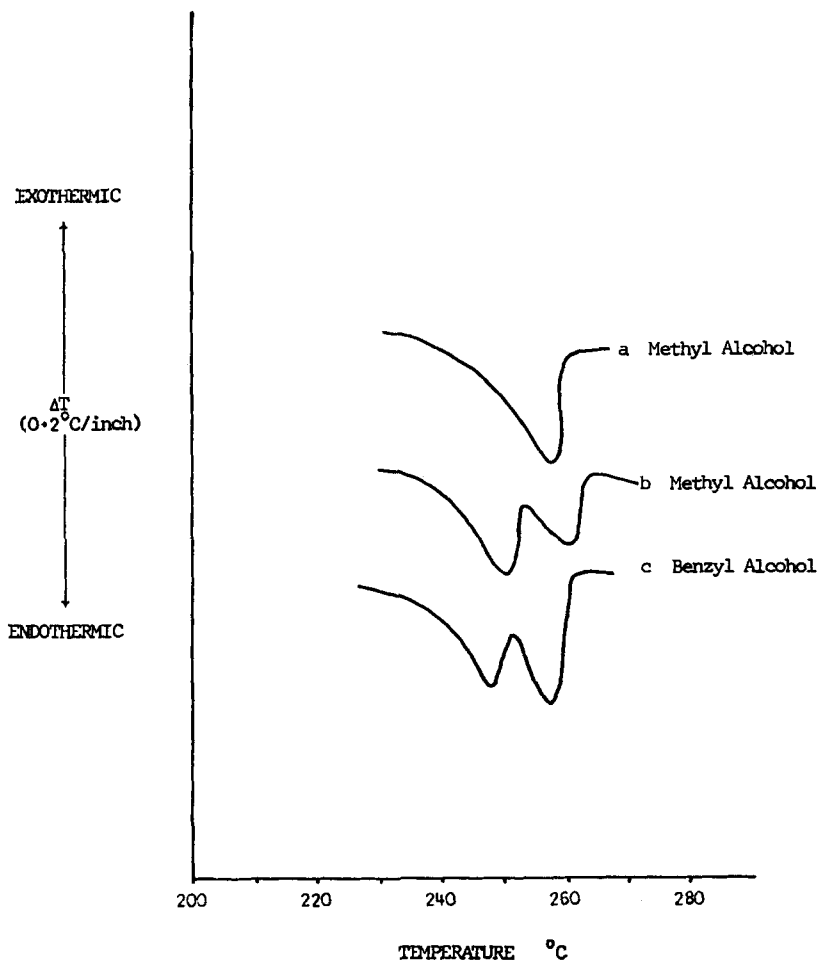


Fig. 7. DTA melting traces for precipitated 66 nylon samples.

Much better resolution was obtained when the sample and reference in the cells were immersed in silicone oil resulting in better conduction of heat to the thermocouples.

Satisfactory resolution was also observed when using the DuPont 900 Differential Thermoanalyzer with a small sample (3 mg.). However, with the DuPont Calorimeter, which needs larger samples and in which the cells are more isolated from the remainder of the apparatus, poorer resolution of the two peaks occurred. Lower heating rates ( $2^{\circ}\text{C./min.}$ ) had to be used to obtain similar resolution as with the Thermoanalyzer.

White<sup>1</sup> probably obtained good resolution in his work because although he used large samples (0.5 g.) in air, his thermocouples were placed in metal pockets inside the cells. Yarn samples were usually wound around these metal pockets. Hence heat could be conducted along the metal of the pocket to the thermocouples.

### The Melting of 66 Nylon and other Polymers

The differential thermal analyses have shown that samples of 66 nylon showing two distinct endotherms in the melting range occur more widely than is suggested by White. Undoubtedly they are associated with drawn yarn as White states but they also occur with annealed and precipitated samples, i.e., with samples which are not oriented. In other work we have observed similar effects with unoriented samples of 11 nylon, 6 nylon, and from copolymers of 6 and 11 nylon. Other workers<sup>7</sup> have obtained a double melting peak with 66 nylon yarn but only obtained single peaks with 66 nylon polymers.

Our results show that the material which gives the first melting peak is formed during a secondary crystallization or an annealing process rather than during the primary crystallization. We found no evidence of two exotherms on crystallization as reported for 6 nylon by Inoue.<sup>8</sup> Many authors<sup>9-12</sup> have reported the formation from 66 nylon of positive and negative spherulites with different melting points but these were formed during the primary rather than the secondary crystallization process. Negative spherulites melted at higher temperatures than positive spherulites. Work is in progress to determine the differential thermal analyses of nylon samples crystallized to provide positive and negative spherulites.

Other workers have reported multiple melting peaks observed by differential thermal analysis with other polymers. Gray and Casey<sup>13</sup> obtained a series of melting peaks from an annealed sample of an ethylene/butene copolymer containing 6% butene. They state they have obtained similar results with other polyethylenes. They observed that for this copolymer brief annealing times (1 min.) at various temperatures, followed by cooling, resulted in the observation of melting peaks by differential scanning calorimetry at the same temperatures. They attributed these melting peaks to the melting of regions recrystallized within a range of 5°C. of this temperature. They believe that similar annealing effects were responsible for the multiple peaks obtained with polyethylene by Holden<sup>14</sup> who suggested they were caused by different modes of crystallization. Clampitt<sup>15</sup> studied mixtures of high and low density polyethylene by differential thermal analysis. He obtained melting peaks corresponding to these materials but also a third peak which he thought was caused by the melting of a cocrystal formed from the two components. Kardos et al.<sup>16</sup> obtained four melting peaks when examining polyethylene samples which had been crystallized under high pressures. They show that two of these peaks can be explained by the melting of extended<sup>17</sup> and folded molecular lamellae. Tentatively they postulate that the additional peaks which precede their main peaks are caused by the onset of segmental motion within the crystals.

We have tried to determine whether these two peaks always occurred at the same temperatures. The start of melting varied between samples as would be expected for samples of varying crystalline perfection. We

found the peak of endotherm 1 occurred at  $250 \pm 2^\circ\text{C}$ . and of endotherm 2 at  $257 \pm 2^\circ\text{C}$ . for most samples. Some variation within these ranges occurred but we have established no trend. Further experiments are in progress. Melting was normally complete at  $260^\circ\text{C}$ . but in one sample (partially crystallized for 3 hr. at  $255^\circ\text{C}$ . and completed at  $240^\circ\text{C}$ .) a third peak at  $262^\circ\text{C}$ . was observed.

In our experiments with 66 nylon crystallized at  $242^\circ\text{C}$ ., it was shown that the primary crystallization did not result in a sample which showed two peaks on melting.

Heating for periods greater than 15 min. at  $242^\circ\text{C}$ . resulted in DTA melting traces showing better resolution of the two peaks. The first peak became sharper and increased in size as the annealment time was increased. The same effect was observed on annealing ground 66 polymer as well as on a nylon sample which had just been crystallized isothermally. All these results suggest a secondary crystallization process resulting in the formation of a more perfect crystalline lattice. However the melting temperature decreased rather than increased as one would have expected with a better crystalline lattice. An increase in the lamellae thickness would also be expected to result in an increase rather than a decrease in melting temperature.

More experimental work is in progress to determine the origin of these melting peaks. Precipitated samples which show two peaks have a higher density but give similar x-ray powder diagrams to samples with one peak. 66 nylon precipitated from benzyl alcohol at 130 and at  $100^\circ\text{C}$ . showed one and two peaks, respectively. This may have been caused by an annealing process at  $100^\circ\text{C}$ . after the primary crystallization. However, when 66 nylon was precipitated from formic acid with methanol at room temperature slow crystallization resulted in a sample showing two peaks whereas rapid crystallization resulted in one peak. These results suggest an annealing process is not essential for the formation of samples which show two endothermic melting peaks.

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### Résumé

Des analyses thermiques différentielles de nombreux échantillons de nylon-66 ont montré deux endothermes dans la zone de fusion. Cet effet se passe dans les films de nylon étiré comme observé précédemment par White mais aussi dans les échantillons des nylons recuits et précipités. Les méthodes pour la préparation de ces échantillons sont rapportées. A 242°C, le développement au départ de la masse fondue de matériaux cristallins qui donnaient deux pics de fusion, est associé au recuit plutôt qu'au processus de cristallisation primaire. Les observations préalables de nombreux pics de fusion pour d'autres polymères sont discutées.

### Zusammenfassung

Die Differentialthermoanalyse einer grossen Zahl von Nylon-66-Proben zeigte zwei endotherme Spitzen im Schmelzbereich. Dieser Effekt tritt, wie kürzlich White zeigte, bei gerecktem Nylongarn, aber auch bei getemperten und gefällten Nylonproben auf. Methoden zur Herstellung dieser Proben werden beschrieben. Bei 242°C hängt die Bildung von kristallinem Material mit zwei Schmelzmaxima aus der Schmelze mit der Temperung und nicht mit dem primären Kristallisationsprozess zusammen. Frühere Beobachtungen von mehrfachen Schmelzmaxima bei anderen Polymeren werden diskutiert.

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