Lamellar thickening behaviour of nylon-6,6 crystal by annealing

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Nylon-6,6 – a typical polyamide – was annealed in the swollen state in glycerol to promote the partial melting of the polymer crystal. The recrystallization or lamellar thickening of nylon-6,6 crystal following partial melting was easily induced by this annealing, and the lamellar thickness of the crystal increased stepwise by ½ monomer unit length with increasing annealing temperature or annealing time. In addition, another distinct layer-thickening mechanism was observed which led to approximately doubling (and frequently quadrupling) the straight stem length of the lamellar crystal for all samples annealed under adequate conditions. New melting endotherms corresponding to these layer thicknesses (range of long spacings 140–180 Å) were obtained by differential scanning calorimetry (d.s.c.) at temperatures ranging from 270° to 282°C. The mechanism of lamellar thickening is discussed with reference to the experimental results.

INTRODUCTION

It has been reported[1–6] that the lamellar thickness of solution-grown crystals of several polyamides is not affected by crystallization temperatures and solvents, and that the layer thickness corresponds closely to 4 monomer units. Dreyfuss *et al.*[1,7], however, have observed that under critical conditions the layer thickness doubled in a discontinuous jump on annealing. They attributed these characteristics of lamellar thickening to hydrogen bonding between the amide groups of molecular chains, and they proposed a new mechanism of lamellar thickening for crystals of polyamides different from that for crystalline polymers such as polyethylene.

In the previous paper[8], nylon-6,6 was annealed for 24 h at various temperatures and examined by differential scanning calorimetry (d.s.c.) and small-angle X-ray scattering (SAXS). It was concluded that the layer thickness of the crystal increases stepwise by ½ monomer unit length; another layer thickness (approximately doubled) which was found by Dreyfuss *et al.* was also observed under adequate annealing conditions. In the present paper, to discuss the mechanism of lamellar thickening more precisely, the influence of a small quantity of glycerol on the d.s.c. thermogram of the unannealed sample has been examined and the effective range of annealing temperature determined.

We have also found an annealing time of 4 h to be more suitable for detecting the typical stepwise lamellar thickening. By carefully examining the layer thicknesses of the unannealed sample and combining all the experimental results, we may discuss the mechanism for the lamellar thickening of the nylon-6,6 crystal.

EXPERIMENTAL

The raw nylon-6,6 material used was in the form of moulded pellets (Catalogue no. CM3001N) supplied by Toyo Rayon Co. Ltd. It was purified by the same procedure as described in the preceding paper[8]. A 3% solution of the nylon in 60% aqueous formic acid was prepared at 95°C. On cooling to room temperature, purified nylon-6,6 was precipitated. The precipitate was isolated, washed, dried and subjected to a pressure of 100 kg/cm^2 at 160°C to form a disc-like sheet (which we call the unannealed sample).

The thin disc-like sample, wrapped in perforated aluminium foil, was immersed in glycerol in a glass tube, which was incubated in a silicone oil bath at selected temperatures, kept constant to within ±0.1°C. At the start of annealing, the pressure in the glass tube was reduced and the equipment flushed with nitrogen gas. The same procedure was repeated many times. By this method, the sample could be brought into good contact with glycerol and prevented from undergoing oxidation during annealing. After annealing, the sample was quenched in methanol at room temperature and then immersed in fresh water for a few weeks to remove the solvent completely. The sample was again dried and pressed.

The melting behaviour of 3 mg sample was studied in a Perkin–Elmer DSC-1B differential scanning calorimeter (d.s.c.) at a heating rate of 8°C/min under a nitrogen atmosphere. The temperature scale was calibrated with tin (231.8°C) and bismuth (271°C). Small-angle X-ray scattering (SAXS) patterns were recorded photographically using nickel-filtered CuKα radiation from a Jeol Rotex JRX-12 (or sometimes from a Rigaku Denki RU-3) rotating anode

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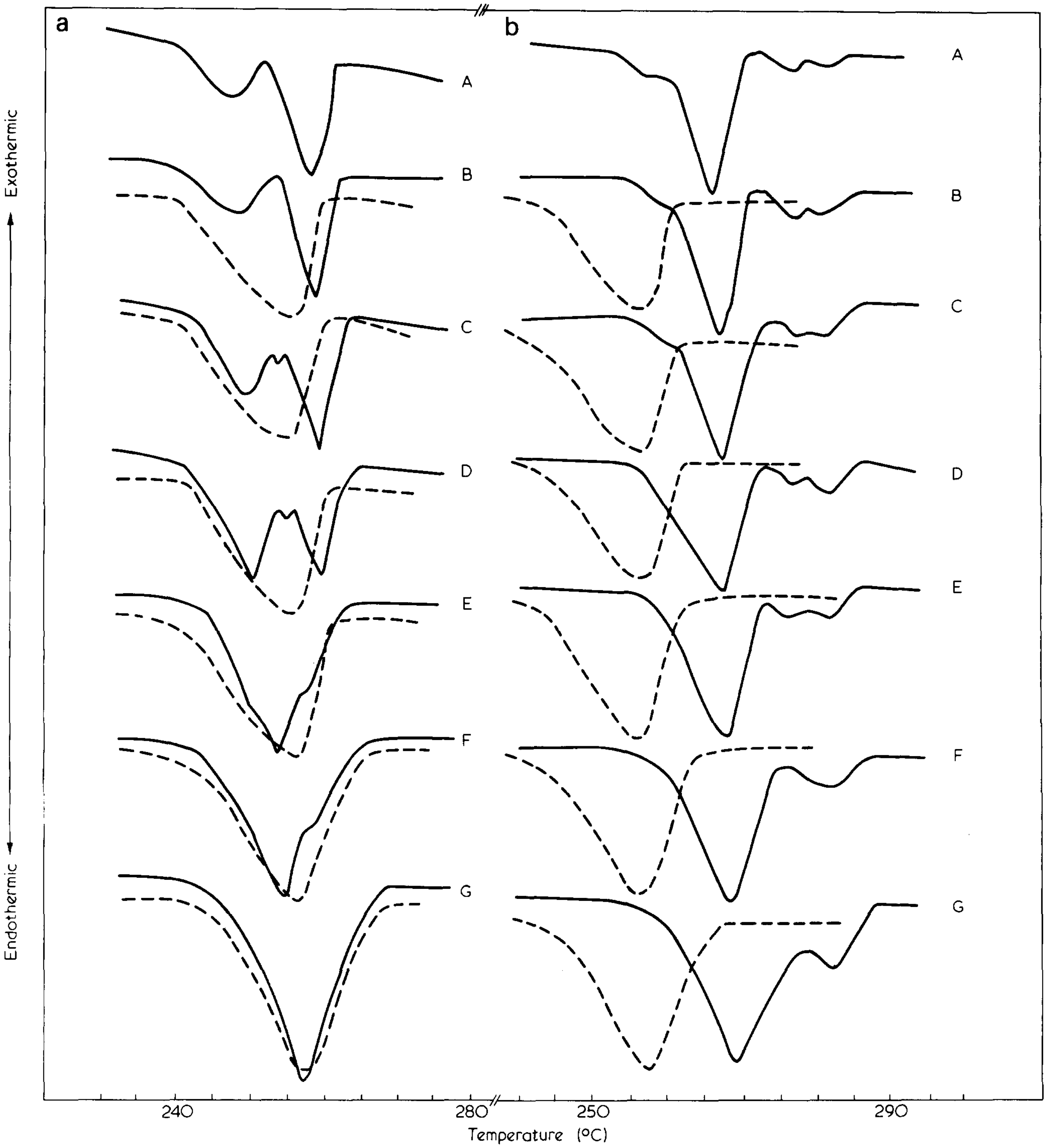

Figure 1 Effect of heating rate on heating curves: (a) for the unannealed sample and (b) for the typical sample annealed in glycerol at 196° C for 17 h. Broken lines show the remelting thermograms (2nd run). Heating rates: A, 1°C/min; B, 2°C/min; C, 4°C/min; D, 8°C/min; E, 16°C/min; F, 32°C/min; G, 64°C/min

with pinhole collimation system (0.5 and 0.3 mm diameter) and a specimen-to-film distance of 350 mm. The long spacing was determined from the microdensitometer trace along the pressing direction of the sample.

RESULTS AND DISCUSSION

Effect of heating rate on the d.s.c. thermograms of the unannealed and the annealed samples

The effect of heating rate on the d.s.c. thermograms of the unannealed sample is shown in *Figure 1a*. This material shows typical double endothermic peaks which have been discussed by many workers[9,10]. As the heating rate increases, the temperature of the high temperature peak rises at first, then is slightly lowered and its peak area becomes smaller. On the other hand, the temperature of the low temperature peak rises and its area increases. The low temperature peak can be interpreted as being due to the melting of the original crystals of the unannealed sample, whereas the high temperature peak is supposed to be caused mainly by the 'reorganized' material forming during the heating process[11].

The remelting thermograms (2nd run) of unannealed samples which had been melted and then cooled down rapidly

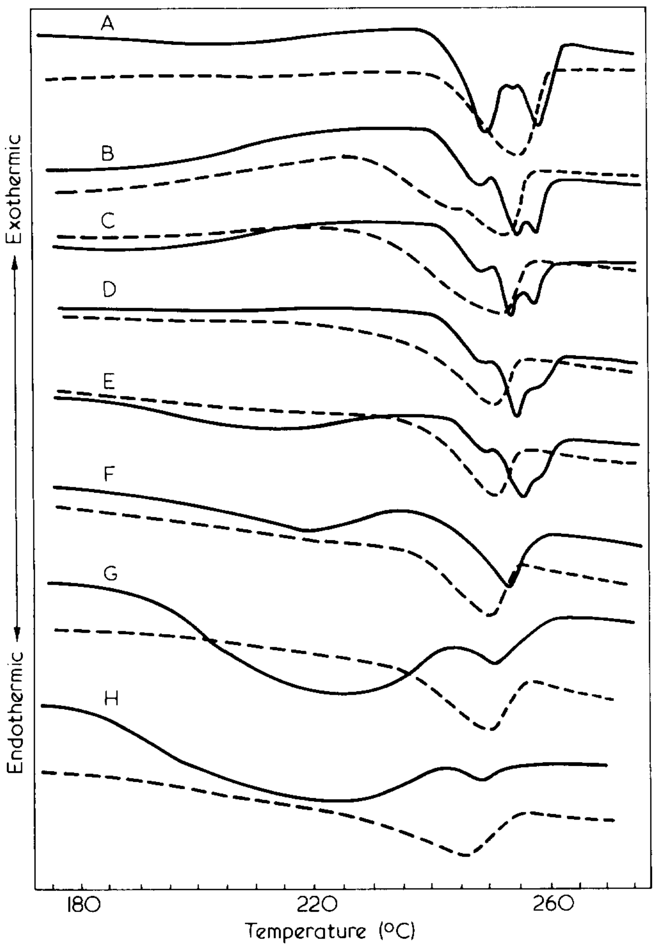

Figure 2 Heating curves of the unannealed samples with various glycerol contents. Glycerol content (%). A, 0; B, 1; C, 1; D, 4; E, 8; F, 15; G, 20; H, 30

to room temperature are shown in *Figure 1a* (broken lines), where the double peaks are seen to overlap each other.

The effect of heating rate on the d.s.c. thermograms of a typical sample annealed in glycerol at 196°C for 17 h is shown in *Figure 1b*. There are two series of melting endotherms which will be discussed. As the heating rate increases, the peaks at lower temperatures (ranging from 257° to 273°C) rise to higher temperatures, while the peaks at higher temperatures (ranging from 275° to 282°C) seem hardly to shift towards higher temperatures. The areas of the two series of melting peaks scarcely change. In the remelting thermograms of the annealed sample (broken lines in *Figure 1b*) there is a broad melting peak which appears at slightly lower temperatures than that of the unannealed sample; this is caused by the thermal degradation of the sample which occurs during annealing. These facts imply that two kinds of crystal modification, corresponding to the two series of melting endotherms, are formed during annealing.

Diluent effect of a small quantity of glycerol on the d.s.c. thermogram of the unannealed sample

Figure 2 shows the d.s.c. thermograms of the unannealed samples (about 60% amorphous content) with various contents of glycerol. When the glycerol content is less than 8%, the melting endotherms hardly change (in the heating curves), but these endotherms shift slightly to lower temperatures as the glycerol content increases. In contrast, in the case of glycerol content above 8%, the area and peak temperature of the endotherm clearly decreases. In addition, at 8% glycerol content, another broad endotherm appears at the lower temperature range (180°–240°C) and increases in area as the glycerol content increases. This new endotherm is considered to correspond to the real melting endotherm of nylon-6,6 crystal, swollen with a large quantity of glycerol.

In this study, to anneal the sample, the amount of glycerol used was about 100 times the sample quantity. The typical annealing effect is expected at temperatures above 180°C. From a high temperature wide-angle X-ray study[12], it was observed that the crystal lattice of nylon-6,6 began to dilate considerably at temperatures above 150°C, and simultaneously, it began to transform from the triclinic to the cylindrical hexagonal from in a similar manner to nylon-6[13,14]. In the wide-angle X-ray patterns at high temperatures[12], there were no significant differences in lattice constant between the samples containing no glycerol and those with a small quantity of glycerol.

The increase in long spacing of the samples containing glycerol was observed by small-angle X-ray scattering at room temperature. The long spacing of the sample containing 30% glycerol is estimated to increase by about 7%. If the sample contains the equivalent weight of glycerol (i.e. 100% glycerol), the long spacing is estimated to increase by about 25%. The intensity of the diffraction decreases rapidly as the glycerol content increases. From these results, we can presume that the glycerol molecule does not enter into the crystal lattice at lower temperatures but remains in the noncrystalline regions. At temperatures higher than 150°C (preferably above 180°C), the glycerol molecule can easily enter into the crystal lattice and the crystal begins to melt partially.

Lamellar thickening by annealing in hot glycerol

Typical d.s.c. thermograms of nylon-6,6 samples annealed in glycerol for 4 h at various temperatures are shown in *Figure 3*. The endothermic melting curve of the sample annealed below 180°C has two peaks (main peak or peak 1 in the Figure) and it is similar to that of the unannealed sample. As the annealing temperature increases, the main endothermic peak shifts discontinuously to a high temperature and this peak increases in area at the expense of the low temperature peak (150°–180°C). At the next higher temperature (184°C), the latter peak disappears and the former peak, which remains at the same temperature, appears as a slightly broadened peak, with a shoulder on its higher temperature side. Successively, at the next higher temperature (192°C), this shoulder grows in area at the expense of the broadened peak. A similar process is repeated at a higher temperature. At the same time, distinct secondary endothermic peaks (peak 2) appear at temperatures ~10°C higher than the main peak temperature for samples annealed at temperatures above 180°C. These melting peaks also shift discontinuously, parallel to the main peak, as the annealing temperature increases. Both peaks (peaks 1 and 2) may be due to new crystal modifications formed during the annealing. If the sample is annealed for a longer period of time[8], both melting peak temperatures also increase stepwise as the annealing time increases in a manner similar to that seen in *Figure 3*. Under more severe annealing conditions, the weight loss of the sample increases. (For example, that of the sample annealed at 200°C for 4 h is estimated to be about 10% and that of the sample annealed at 209°C for 4 h rises above 90%.) The area of the main peak decreases gradually whereas that of the peak 2 increases in proportion and both peaks become broader. The sample is rapidly dissolved in glycerol at temperatures above 210°C.

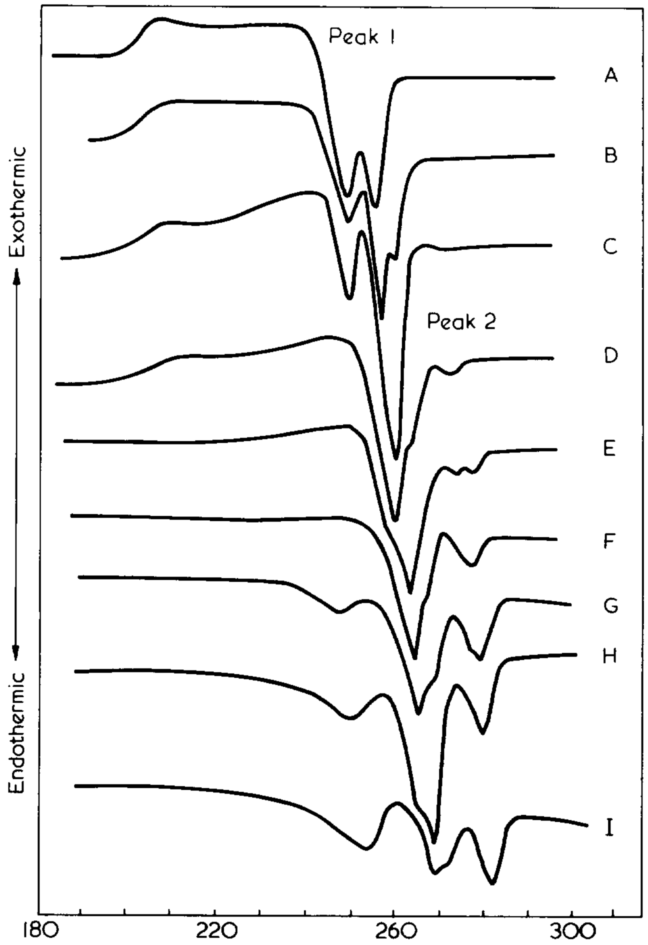

Figure 3 Heating curves of nylon-6,6 samples annealed for 4 h at various temperatures as indicated. A, 150°C; B, 170°C; C, 180°C; D, 184°C; E, 192°C; F, 196°C; G, 201°C; H, 204°C; I, 206°C

The typical change in SAXS patterns of samples annealed for 4 h at various temperatures is shown in *Figure 4*. As the annealing temperature increases, SAXS spots (or arcs) are clearly observed to shift stepwise. In addition, in every SAXS pattern of the annealed samples, diffuse inner arcs (arc 2) appear inside the outer main arcs (arc 1), and they seem to increase in their intensities as the annealing temperature increases. A typical SAXS pattern of the sample annealed at 190°C for 24 h and the schematic drawing of it are shown for comparison in *Figures 4g* and *4h*. In the case of the sample annealed for 24 h, we can easily observe arc 1 and arc 2[8], although we can hardly see the inside of arc 1 for the sample annealed for 4 h, because the annealing effect is incomplete. However, above the optimum annealing temperature (or time), the intensity of arc 2 decreases and finally can hardly be detected for samples annealed at a temperature above 206°C (or for longer times[8]). This observation, combined with the results of thermal analyses, leads us to conclude that the distribution of layer thickness becomes broader. The growth of formed microvoids is enhanced by the more severe annealing condition (the sample becomes very porous and stiff to press) and may be considered to be another reason for the disappearance of arc 2. If this porous sample is swollen with glycerol, arc 2 can easily be detected.

For the sample annealed at a temperature higher than 200°C, a broad endothermic peak appears at a low temperature (*Figure 3*) and the new outside arc at a larger angle (*Figure 4*). They are presumed to be connected with the crystal modification formed by quenching after annealing.

Correspondence of the melting peak temperatures to the long spacings of annealed samples

In *Figure 5*, the melting peak temperatures and the long spacings of samples annealed at various temperatures for 4 h

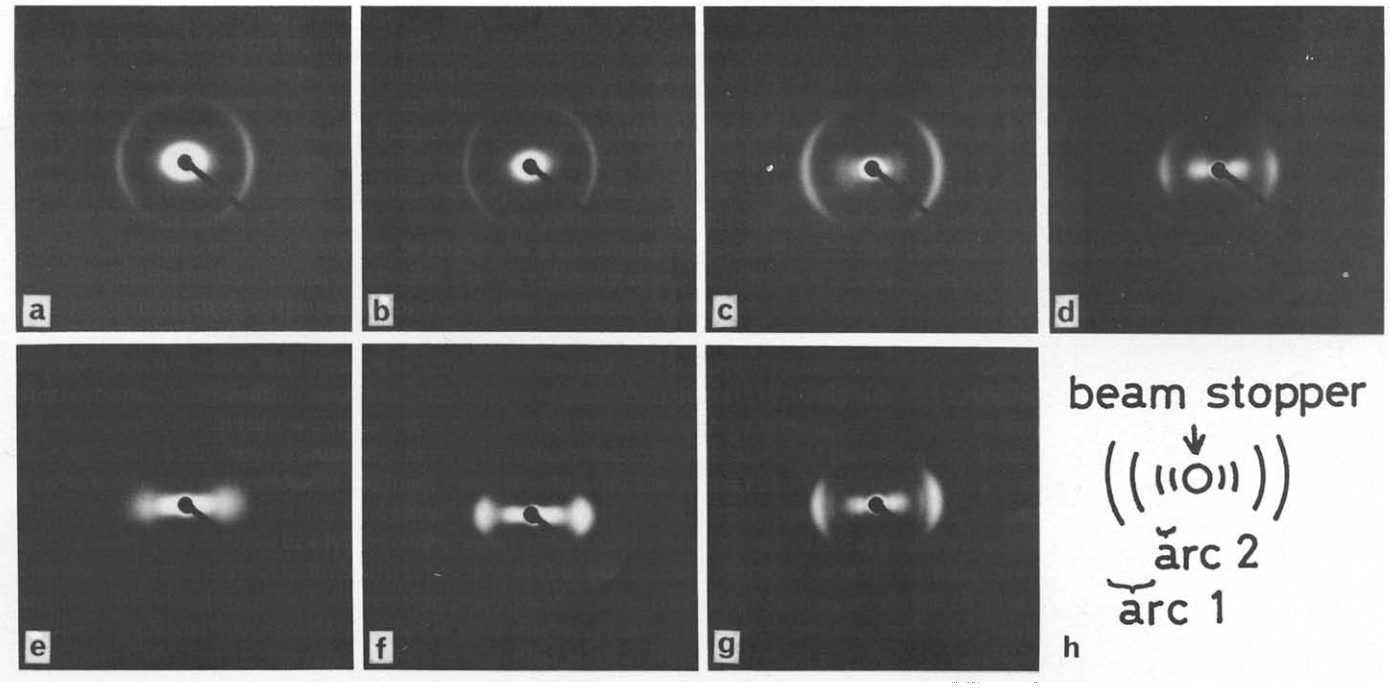

Figure 4 Typical SAXS photographs of nylon-6,6 samples annealed for 4 h at various temperatures: (a) 150°C; (b) 160°C; (c) 180°C, (d) 195°C; (e) 201°C; (f) 204°C. Typical SAXS photograph (g) and the schematic drawing (h) of the sample annealed for 24 h at 190°C are shown for comparison

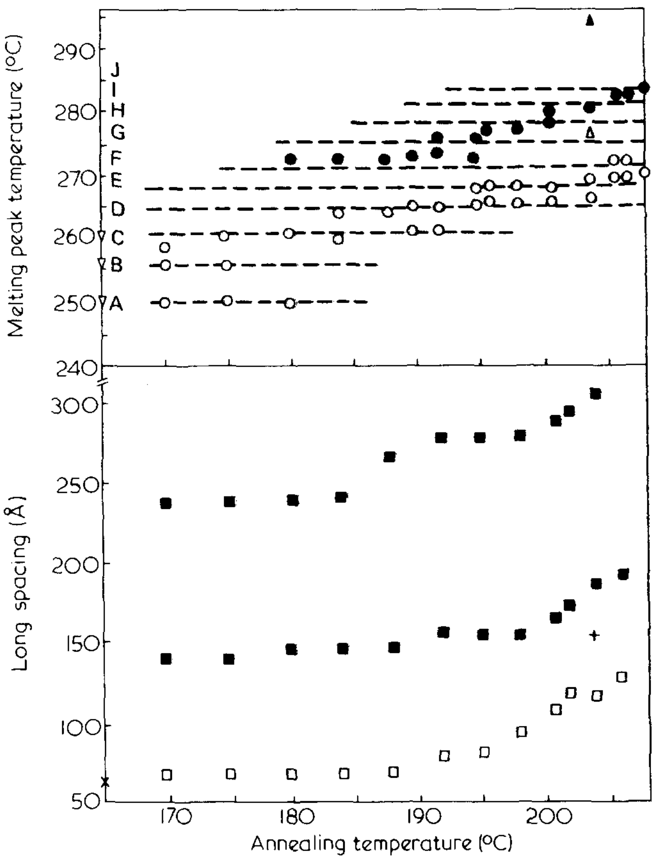

Figure 5 Plots of melting peak temperature and long spacing against annealing temperature. Plots of melting peak temperatures of peak 1 (○) and peak 2 (●), and long spacings obtained from arc 1 (□) and arc 2 (■) for samples annealed for 4 h at various temperatures. (▽,X), Plots of melting peak temperatures (peak 1) and long spacing (arc 1) of the unannealed sample. (△,▲,+), plots of melting peak temperatures of peak 1 and peak 2, and long spacing (arc 1), respectively, for the sample annealed at 204°C for 75 h. Monomer units/crystal thickness: A, 3.5; B, 4; C, 4.5; D, 5; E, 5.5; F, 6; G, 7; H, 8; I, 9; J, 10;

in glycerol are plotted against the annealing temperatures. The stepwise increase of melting peak temperature is seen to occur in a manner similar to the stepwise increase of long spacings. The sample annealed at 204°C for 75 h (also shown in *Figure 5*) has a main long spacing of ~155 Å which is almost the same as the long spacing corresponding to the outside arc of arc 2 for the sample annealed at 196°C (or 198°C) for 4 h. The main endothermic peak temperature taken from differential scanning calorimetry of the former sample is also identical to the lower peak temperature of peak 2 of the latter sample. This shows that peak 1 corresponds to arc 1 of the SAXS photographs, and peak 2 corresponds to the outside arc of arc 2.

The melting point and the long spacing of the unannealed sample are assumed to be 250°C and 58 Å, respectively, as indicated in *Figure 5*. If we assume that the crystal thickness (or the stem length of the lamellar crystal[1]) of the unannealed sample consists of 3.5 monomer units as proposed by Dreyfuss *et al.*[1,5], and the equilibrium melting point, T_m^0, is approximately 300°C[14], we can estimate the melting point, T_m, corresponding to the crystal thickness l_c for the annealed sample by using the equation[15]:

$$T_m = T_m^0(1 - 2\sigma_e/\Delta h_f l_c) \qquad (1)$$

where σ_e is the end surface free energy and Δh_f the heat of fusion of the crystals. The calculated T_m corresponding to the crystal thickness (or number of monomer units/stem of lamellar crystal) is shown as the broken line in *Figure 5*. Close agreement is obtained between the calculated and observed values. Peaks 1 and 2 correspond to long spacings in the range of 60–130 Å (arc 1) and 140–180 Å (the outside arc of arc 2), respectively. However, we can scarcely detect peak 2 series corresponding to the inside arc of arc 2.

Figure 6 shows SAXS photographs of the unannealed sample (a) and single crystal mats crystallized for 24 h from a 0.01% solution of the nylon in 60% aqueous formic acid at room temperature (the temperature was lowered slowly from 95°C to room temperature) (b) and from a 0.04% solution in 1,4-butanediol cooled down from 200°C to isothermal crystallization temperature, 140°C, (c). We can observe both arc 1 and the very diffuse arc 2 for all the samples (although the unannealed sample barely shows arc 2). On the contrary, we can scarcely detect peak 2 (corresponding to the arc 2) in the d.s.c. thermograms of these samples as shown in *Figures 7a–7c*. However, if the samples are treated adequately, we can easily detect peak 2[16]. For example, the sample treated at 100°C for 24 h in 42% aqueous formic acid clearly exhibits both arc 2 in the SAXS photograph and peak 2 in the d.s.c. thermogram as shown in *Figures 6d* and *7d*, respectively.

In *Figure 6*, SAXS photographs of the single crystal mat (e) and the film cold drawn to 200% (f) which were annealed at 201°C for 24 h in glycerol are also shown. The corresponding d.s.c. thermograms are shown in *Figures 7e* and *7f*. These annealed samples show almost the same endotherms for peak 1 and peak 2 as those in *Figure 3* and similar SAXS patterns to those in *Figure 4*. We can conclude that the characteristics of lamellar thickening are essentially independent of sample preparation.

From the experimental results it is inferred that, on annealing in glycerol, the straight stem length of nylon-6,6 crystals increases stepwise by ½ monomer unit length (or the hydrogen bond period) with increasing annealing temperature, or annealing time. This lamellar thickening process, which can hardly be detected by annealing without a swelling agent at temperatures near to the melting point, can be explained by the well-known mechanism which has been applied to many crystalline polymers such as polyethylene. Furthermore, another layer thickness which approximately doubles, and frequently quadruples, the straight stem length of the lamellar crystal can be detected for all samples annealed under adequate conditons. This double layer thickness also increases stepwise (maybe by 1 monomer unit length). The mechanism for the refolding of the polymer proposed by Dreyfuss and Keller[1,2] may be applicable to this thickening process. We can observe these layer thickening mechanisms more easily by annealing in glycerol for 4 h at suitable temperatures than by the annealing for 24 h as described in the previous paper[8].

The two layer thicknesses could also be observed in completely unannealed samples. Under the annealing conditions, these two layer thicknesses in the unannealed sample play the role of crystal nuclei and promote the growth of large crystallites. Consequently, we can easily detect these two types of crystal modification by SAXS and d.s.c. methods for samples annealed at a temperature above 180°C. By annealing at a temperature higher than 180°C, the layer thickness (corresponding to arc 1) increases stepwise by ½ monomer unit length as the annealing temperature increases. Simultaneously, a layer thickness about twice the original seems to increase stepwise with increase in the severity of annealing conditions. Moreover, a layer thickness about four

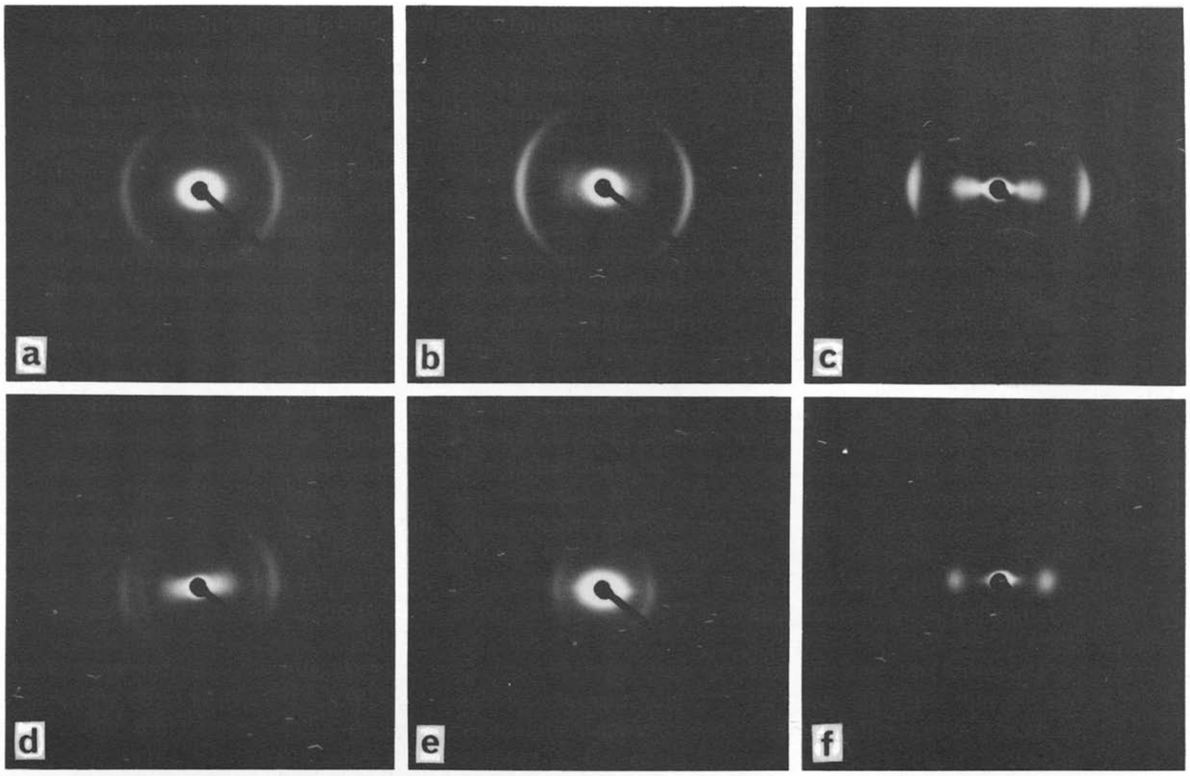

Figure 6 SAXS photographs: (a) unannealed sample; (b) the single crystal mats crystallized for 24 h from a 0.01% solution of the nylon in 60% aqueous formic acid at room temperature and (c) from a 0.04% in 1,4-butanediol at isothermal crystallization temperature 140°C; (d) SAXS photograph of the unannealed sample treated in 42% aqueous formic acid at 100°C for 24 h; (e) SAXS photographs of the single crystal mat and (f) the film (melt crystallized) cold drawn to 200% which were annealed at 201°C for 24 h in glycerol

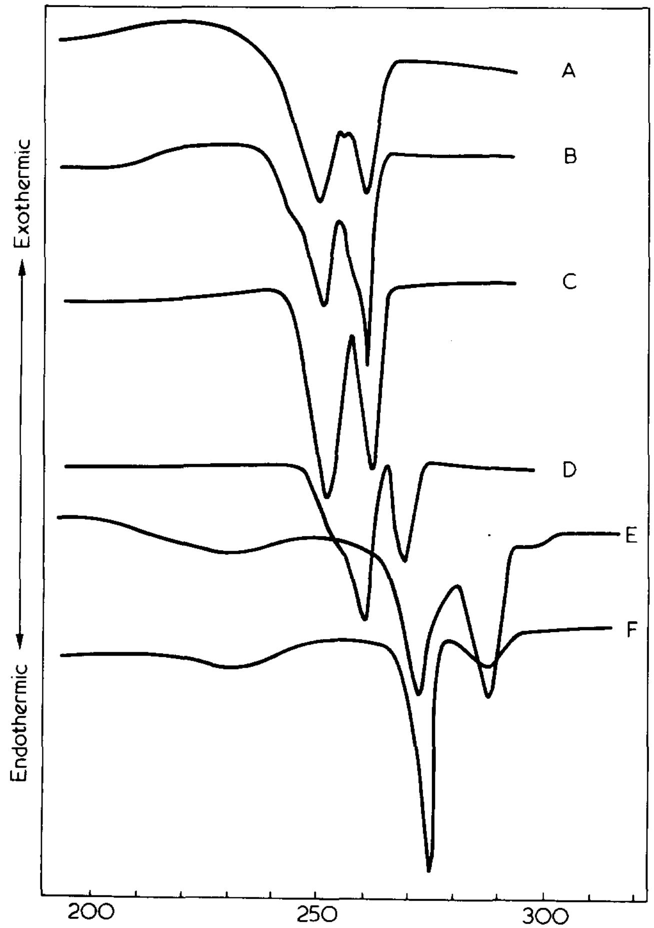

Figure 7 Heating curves for samples obtained by the same sample preparations (or treatment) as described in *Figure 6*

times the original can be observed in SAXS patterns (the inside arc of arc 2), and also increases stepwise, but the corresponding melting peak can hardly be detected in the d.s.c. thermogram. Further experimental results are needed to explain more precisely these mechanisms of lamellar thickening.

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REFERENCES

1 Dreyfuss, P. and Keller, A. *J. Macromol. Sci. (B)* 1970, **4**, 811
2 Dreyfuss, P. and Keller, A. *J. Polym. Sci. (B)* 1970, **8**, 253
3 Dreyfuss, P., Keller, A. and Willmouth, F. M. *J. Polym. Sci. (Polym. Phys. Edn)* 1972, **10**, 857
4 Atkins, E. D. T., Keller, A. and Sadler, D. M. *J. Polym. Sci. (Polym. Phys. Edn)* 1972, **10**, 863
5 Dreyfuss, P. and Keller, A. *J. Polym. Sci. (Polym. Phys. Edn)* 1973, **11**, 193
6 Dreyfuss, P. *J. Polym. Sci. (Polym. Phys. Edn)* 1973, **11**, 201
7 Burmester, A. F., Dreyfuss, P., Geil, P. and Keller, A. *J. Polym. Sci. (Polym. Lett.)* 1972, **10**, 769
8 Mitomo, H., Nakazato, K. and Kuriyama, I. *J. Polym. Sci. (Polym. Phys. Edn)* 1977, **15**, 915
9 Bell, J. P. and Murayama, T. *J. Polym. Sci. (A-2)* 1969, **7**, 1059
10 Sweet, G. E. and Bell, J. P. *J. Polym. Sci. (A-2)* 1972, **10**, 1273
11 Arakawa, T., Nagatoshi, F. and Arai, N. *J. Polym. Sci. (Polym. Lett.)* 1968, **6**, 513; *J. Polym. Sci. (Polym. Phys. Edn)* 1969, **7**, 1461
12 Mitomo, H., Nakazato, K. and Kuriyama, I. in press
13 Sandeman, I. and Keller, A. *J. Polym. Sci.* 1956, **19**, 401
14 Yasuda, T. *J. Soc. Fiber Sci. Technol. Jpn* 1968, **24**, 466
15 Takemori, H., Miyasaka, K. and Ishikawa, K. *J. Soc. Fiber Sci. Technol. Jpn.* 1970, **26**, 74
16 Hoffman, J. D. and Weeks, J. J. *J. Res. Nat. Bur. Stand. (A)* 1962, **66**, 13