Crystallization of polyamides under elevated pressure: 4. Annealing of nylon-6 (polycapramide) under pressure

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A study has been made on the annealing of nylon-6 under elevated pressure. Heat treatment of melt-crystallized nylon-6 at 6.5 kbar and 20°C below the beginning of melting for a period of 120 h yielded an increase in the heat of fusion from 14.2 to 41.2 cal/g and an increase in atmospheric melting temperature from 222° to 256°C (1 kbar = 100 MN/m^2; 1 cal/g = 4.187 kJ/kg). Stepwise annealing by exposing nylon-6 to progressively higher temperatures at 6.5 kbar led to a heat fusion of 40.8 cal/g and a melting temperature of 269°C. Annealing was found to be particularly effective in improving the crystalline structure at pressures exceeding 4 kbar. The rate of annealing at 6.5 kbar increased with temperature in the range between 260° and 280°C. Electron microscopy of fracture surfaces disclosed that annealing could give rise to a marked increase in lamellar thickness. Wide-angle X-ray diffraction showed that crystal growth also occurred in the lateral direction and that the alpha-crystalline modification was preserved during annealing. From a comparison between the melting characteristics of nylon-6 obtained by pressure-induced crystallization from the melt and by annealing under pressure of folded-chain material, it is inferred that the folded-chain lamellar state may be an essential intermediate stage of the chain extension in polyamides under pressure.

INTRODUCTION

Annealing[1,2,32,33] of melt-crystallized as well as of solution-grown polymer crystals at ambient pressure and temperatures sufficiently close to the melting range enhances the melting temperature of the crystals as a result of a decrease in lattice imperfections[3] and an increase in crystallite dimensions in lateral[4–6] and chain direction[4,7]. Bassett *et al.*[8,9,30,31] have shown that pressures of 5 kbar have a profound effect on the annealing of polyethylene crystals near the melting point (1 kbar = 100 MN/m^2). These authors as well as Gruner, Wunderlich and Bopp[10] were able to convert folded-chain polyethylene into chain-extended crystals with maintenance of molecular orientation and texture. Since pressures exceeding 4 kbar could also induce chain-extended crystallization[11,12] in nylon-6 it was considered of prime interest to find out whether similar crystals could be produced by annealing folded-chain material under pressure far from the melting range.

The main purpose of the present paper is to describe the effect of pressure, temperature and annealing time on the heat treatment of nylon-6. Structural and morphological changes were investigated using differential scanning calorimetry, electron microscopy and X-ray diffraction techniques. It will be demonstrated that annealing of melt-crystallized nylon-6 at a pressure of 6.5 kbar and temperatures far below the melting range can give rise to a marked increase in crystallinity in lamellar thickness and in melting temperature from 220° to 269°C

EXPERIMENTAL

Materials

The nylon-6 used in the present study was sample C described in detail previously[11,12]. This sample, after purification and extruding under vacuum, was free from caprolactam and oligomers and had a viscosity-average molecular weight of 95 x 10^3 and a polydispersity ratio $\bar{M}_w/\bar{M}_n = 3.5$.

Determination of melting temperature under pressure

Melting temperature of the nylon-6 under pressure was determined from dependence of the piston height on temperature at different pressures. Samples with cylindrical shape and dimensions of 8 x 14 mm were pressurized in the cell to the desired value, and the temperature was increased in steps of 5°C. After the equilibrium conditions were reached, the piston was moved three times to reduce the pressure loss by friction and the height of the piston was measured. Each step was carried out in about 25 min.

Annealing under pressure

Procedure 1. The extruded polymer in the form of a rod with dimensions 40 x 14 mm was machined into pieces of 4 x 14 mm. Five pieces of the polymer were placed simultaneously into the cell. For some sets of experiments each piece of polymer sample was separated with an aluminium disc of 1 x 14 mm. After closing the cell, the pressure was increased to the required value, and the sample heated at a rate of 50°C/h under pressure to the annealing temperature. After a specified time, the sample was cooled to room temperature, the pressure released and the first piece of the

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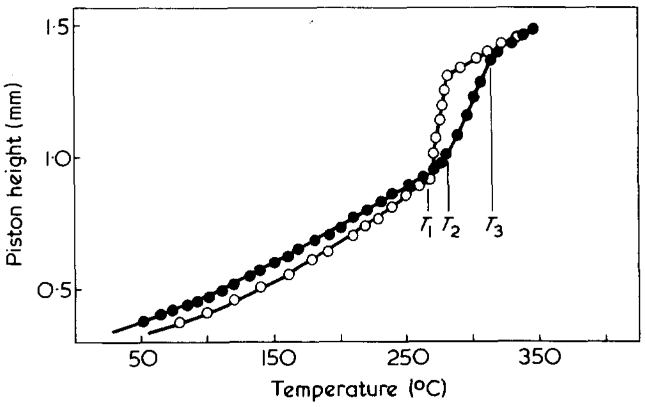

Figure 1 Dependence of the piston height on temperature measured for sample C under pressure of 6 kbar: ○, heating run; ●, cooling run

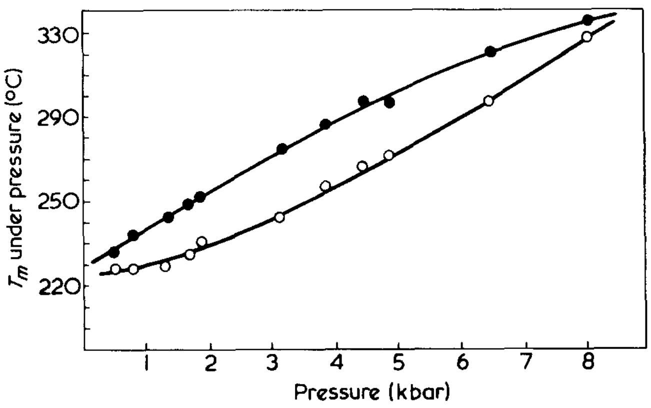

Figure 2 Dependence of the melting temperature on the pressure applied for nylon-6: ●, the end of the melting range (temperature T_3); ○, the beginning of the melting range (temperature T_2)

polymer was removed from the cell. The procedure was then repeated, and at each of five steps, one piece of the cut sample was removed and analysed.

Procedure 2. The sample was annealed for 90 h after pressurization up to 6.5 kbar and raising the temperature to 280°C. Subsequently the temperature was raised stepwise to 285°, 290° and 295°C and the sample was kept at each of these temperatures for 10 h. The entire annealing period lasted 120 h.

Characterization of the samples

Differential scanning calorimetry, infra-red spectroscopy, electron microscopy, and X-ray scattering methods were used for characterization of the samples. Details of the techniques applied and their utility for analysis of the chain-extended crystals of nylon-6 have been given previously[11–13].

RESULTS AND DISCUSSION

Effect of pressure on the melting temperature

In *Figure 1* a typical dependence of the piston height on temperature is presented, measured for the nylon-6 sample under a pressure of 6 kbar.

Measurements were carried out for the heating run (●) and for the cooling run (○) as well. The data obtained on the melting temperature under pressure are in good agreement with those reported in earlier papers of this series[11,12].

The effect of pressure on the initial and final melting temperatures (T_2 and T_3) is shown in *Figure 2*. It is evident that for higher pressures close to 8 kbar, the melting range of the polymer becomes more narrow, suggesting the presence of more uniform crystals. It was found that for the range of pressures investigated, the melting temperature increases by 16°C/kbar, the slope decreasing slightly for the highest pressure, in accordance with previous results[11,12] on nylon-6.

The dependence of the melting temperature on pressure served to determine the proper temperature range within which samples could be annealed without melting. Temperatures of 20°C below the initial melting temperature (T_2), or 40°C below the final melting temperature (T_3), were selected for annealing experiments. After annealing at these temperatures, the grooves on the sample surface caused by machining were still present, and the aluminium discs separating the cutting were not flooded with the polymer. At these temperatures, however, it was still possible to produce samples with a very high melting temperature and heat of melting. Based on these observations, all annealing experiments under pressure were carried out in this range of temperature if not stated otherwise.

Analysis of the thermal properties

Figure 3 presents the dependence of melting temperature on scan speed for original nylon-6, and for the samples annealed under pressure, one annealed at 6.5 kbar and 280°C for 48 h, and the other at the same temperature and pressure for 120 h.

In both cases a superheability of about 25°C was found, as measured for a scan speed of 8 and 64°C/min, while the samples crystallized from the melt under the same conditions showed a superheatability fo 20°C. This demonstrates that, when the samples are kept under pressure for the same period of time, annealing of the folded-chain crystals of nylon-6 produces even better crystals than pressure-induced crystallization from the melt.

Figure 4 shows the dependence of piston height on annealing time for the sample annealed under a pressure of 6.5 kbar at 280°C for 120 h. For a better illustration of the effect of pressure on crystal perfection of the annealed samples, the standardized melting endotherms have also been included in *Figure 4*.

It can be seen from *Figure 4* that improvement of the crystalline order under pressure, as estimated from the thermograms, is a time-dependent process. With prolongation of annealing time, the melting endotherms become narrow, their height increases and they shift towards a higher tem-

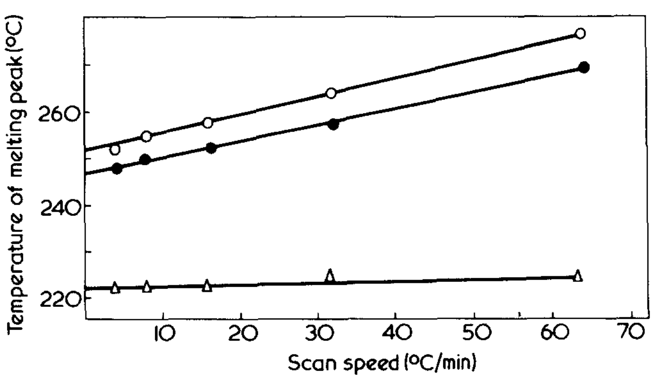

Figure 3 Dependence of the atmospheric melting peak temperature on the scan speed: △, sample C; ●, sample annealed at 280°C and 6.5 kbar for 48 h; ○, sample annealed at 280°C and 6.5 kbar for 120 h

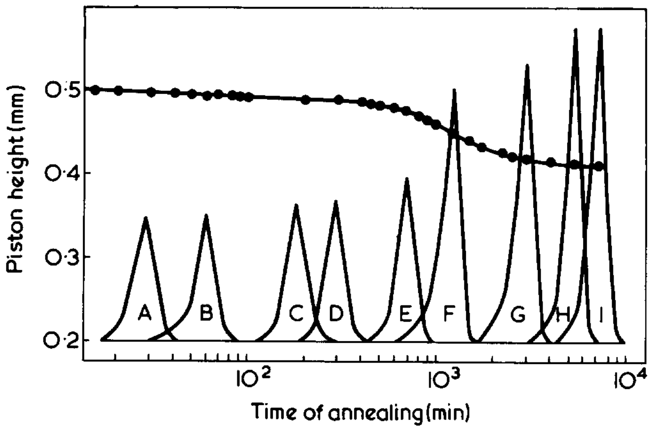

Figure 4 Changes of piston height on the annealing time for the sample annealed at 280°C and 6.5 kbar for 120 h: A, T_m = 220°C, ΔH_m = 13.7; B, T_m = 222°C, ΔH_m = 13.7; C, T_m = 225°C, ΔH_m = 14.2; D, T_m = 228°C, ΔH_m = 15.2; E, T_m = 241°C, ΔH_m = 28.9; F, T_m = 246°C, ΔH_m = 30.2; G, T_m = 253°C, ΔH_m = 38.0; H, T_m = 255°C, ΔH_m = 40.3; I, T_m = 256°C, ΔH_m = 41.2 cal/g

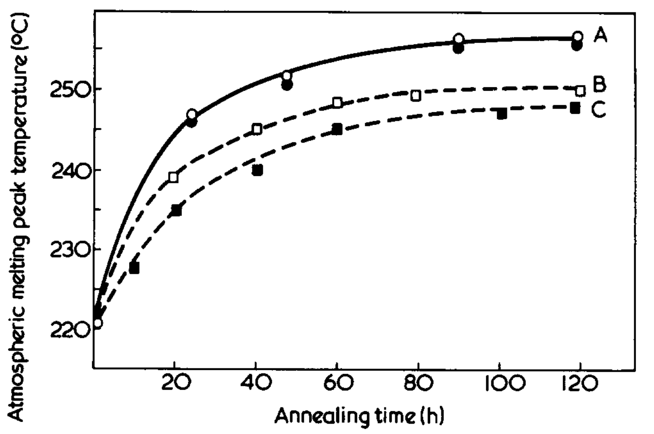

Figure 5 Dependence of the atmospheric melting peak temperature on the annealing time under pressure indicated: A, annealing experiments: ●, 6.5 kbar, 280°C; ○, 6.5 kbar, 290°C. B, C, pressure-induced crystallization from the melt: □, 6.5 kbar, 290°C; ■, 6.5 kbar, 280°C

perature, pointing at an improvement of the crystalline structure. No additional melting peak was found for any heating rate applied. This indicates that only one type of crystal may be present in the pressure-annealed material.

Figure 5 illustrates the dependence of atmospheric melting peak temperature on the annealing time at a pressure of 6.5 kbar and a supercooling of 30° and 40°C (curve A). For comparison, data for the samples crystallized from the melt at identical conditions of pressure and temperature have also been included in *Figure 5* (curves B and C). It can be seen that for both cases, after about 80 h of annealing or crystallization under pressure, there is no significant further increase in the melting temperature. It seems that, after that time, the chain extension and lateral growth are completed. At comparable conditions of pressure, temperature and time, much higher values of melting temperature, i.e. better crystals, are generated by annealing of the folded-chain crystals under pressure, than by the pressure-induced crystallization from the melt. The highest value of T_m found for the nylon-6 samples annealed under pressure according to procedure[1] was 256°C, while for the samples crystallized from the melt at the same conditions of temperature, pressure and time, the value of T_m was 247°C. Stepwise annealing (procedure 2) gave even higher values of T_m, up to 269°C. The dependence of atmospheric melting temperature on the annealing temperature under pressure is presented in *Figure 6*. The samples were annealed at 6.5 kbar for 48 h. The melting temperature increases sharply for temperatures in the range between 260° and 280°C, indicating that the rate of annealing increases with temperature, and stays almost constant for the temperature in the range from 280° to 290°C. At a temperature close to 300°C the melting temperature decreases slightly. This may result from partial melting of the polymer. Thus in this case there are probably two processes occurring simultaneously; annealing of the folded-chain material under pressure, and pressure-induced crystallization from the melt of poorer material, occurring probably during the cooling run of the sample. Further evidence for partial melting is provided by the observations that the grooves in the surface of the specimen were distorted and pieces of the polymer separated with the aluminium discs slightly stuck together, when the samples were annealed at this temperature. It is also possible that, because of a high temperature, some degradation of the polymer could have occurred.

Figure 7 shows the dependence of the atmospheric melt-

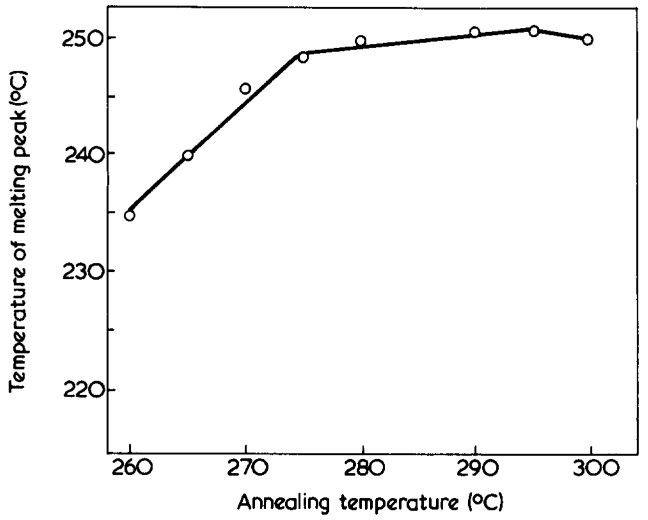

Figure 6 Dependence of the atmospheric melting peak temperature on the annealing temperature under pressure for samples annealed at 6.5 kbar for 48 h

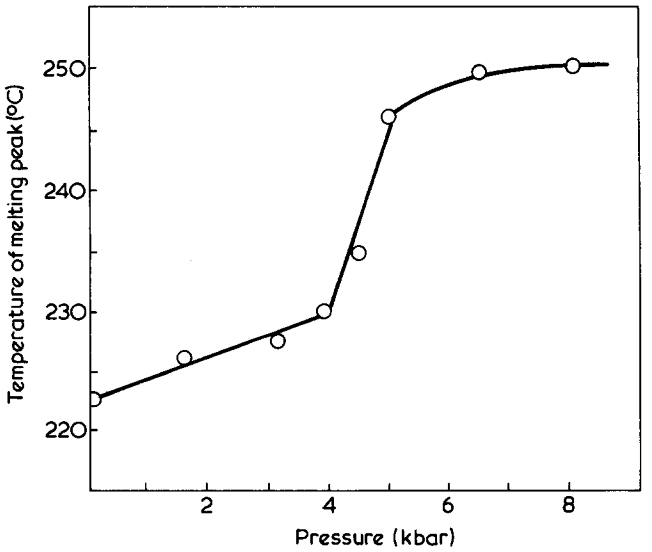

Figure 7 Dependence of the atmospheric melting peak temperature on the annealing pressure for samples annealed at 280°C for 48 h

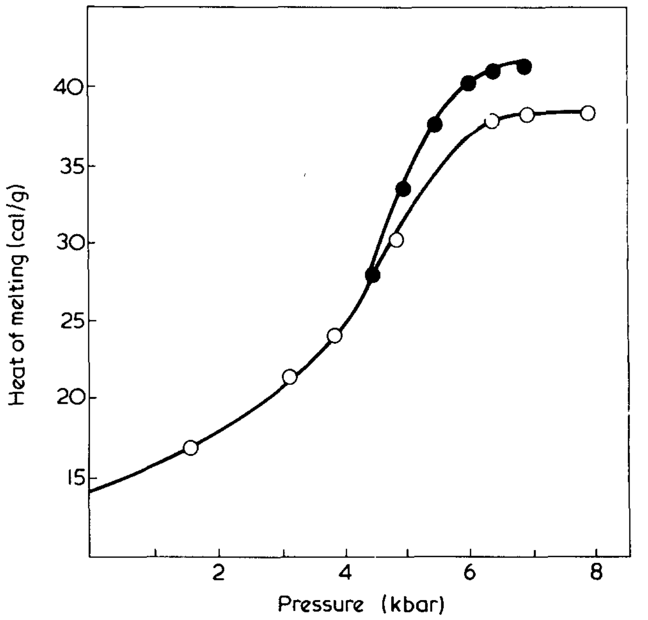

Figure 8 Dependence of the heat of melting on the annealed pressure for samples annealed at 280°C. ○, 48 h; ●, 120 h

Table 1 Melting temperature and heat of melting of various nylon-6 samples
(a) Ultimate values as reported in literature

T_m (°C)	ΔH_m (cal/g)	Reference
232	45.0	15
260	55.0–64.0	23
225	45.0	14
–	38.2	16
226–228	38.0	17
–	45.6	18
232	33.0	19
250 ± 2	–	20
245	–	21, 22
270–306	–	21, 22

(b) Experimental values found for chain extended nylon-6

T_m (°C)	ΔH_m (cal/g)	Reference
225.6	24.8	Zone polymerization[15]
248	37.0	Crystallization from the melt[11,12], 6.5 kbar, 290°C, 120 h
256	37.0	Crystallization from the melt[11,12], 8 kbar, 315°C, 320 h
256	41.2	Annealing of folded-chain crystals, 6.5 kbar, 290°C, 120 h (this work)
269	40.8	Stepwise annealing of folded-chain crystals, 6.5 kbar, 290°C, 120 h (this work)

temperature on the applied pressure, found for the samples annealed at 40°C below the final melting temperature T_3 for 48 hours. This temperature strongly increases with the applied pressure, in particular for pressures in the range 4–6 kbar. Above 6.5 kbar there was only a slight additional effect of pressure on the melting temperature. The dependence of the heat of melting on the applied pressure is shown in *Figure 8*. The heat of melting increases from 14.2 cal/g under a pressure of 1 bar to 38.2 cal/g for a pressure of 6.5 kbar, and remains practically constant above this pressure range (1 cal/g = 4.187 kJ/kg). It was found that, although stepwise annealing leads to higher values of T_m as compared with the standard annealing procedure, it produces crystals with the same value of ΔH_m. The highest value of a heat of melting found for the nylon-6 samples annealed under pressure was 41.2 cal/g, while the ultimate value of a heat of melting for crystalline nylon-6 is 45 cal/g as calculated by Dole and Wunderlich[14].

Table 1 compares the highest values of the melting temperature and heat of melting found for the chain-extended crystals of nylon-6 grown by annealing of the folded-chain material under pressure, or pressure-induced crystallization from the melt, with the ultimate values for nylon-6 reported in the literature[14–23]. It can be seen that the melting temperature of the chain-extended nylon-6 is in the range, or close to the ultimate values calculated by various authors as an equilibrium melting temperature of the alpha- form of nylon-6. The heat of melting of the chain-extended nylon-6, except for the value given by Illers and Haberkorn[23], is only slightly lower than the values for 100% crystallinity. This shows that a very high level of crystalline perfection was reached in the nylon-6 heat-treated under pressure, although deviation from the ultimate values of melting temperature and heat of melting, as well as the morphology and infra-red data presented elsewhere[13] suggest the existence of defects in the crystalline lattice of the polymer. It is evident that the melting temperature and heat of melting of the chain-extended crystals of nylon-6 produced by annealing of the folded-chain crystals under pressure are much higher than those of the nylon-6 grown by pressure-induced crystallization from the melt. This shows that the effect of pressure on the crystalline order developed in polyamides is more efficient in the case when the folded-chain crystals are already present in the polymer.

From the presented observations the conclusion can be drawn that the chain-extended crystals of polyamides may not necessarily grow directly in the melt under pressure, but that the formation of imperfect crystals of the folded-chain type might be an intermediate step of the chain extension.

Finally some remarks should be made about the morphology and the structure formed during annealing of the folded chain material under pressure. *Figure 9* shows an electron micrograph of a fracture surface of a nylon-6 sample an-

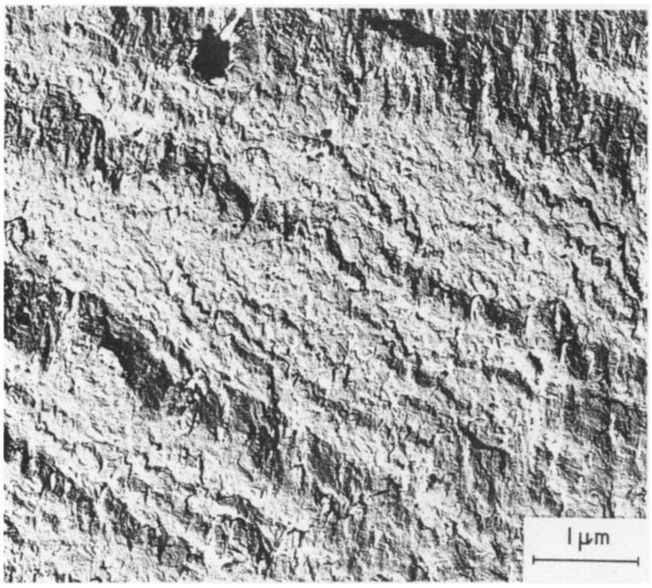

Figure 9 Electron micrograph of replica of a fracture surface of nylon-6 sample annealed at 280°C and 6.5 kbar for 48 h

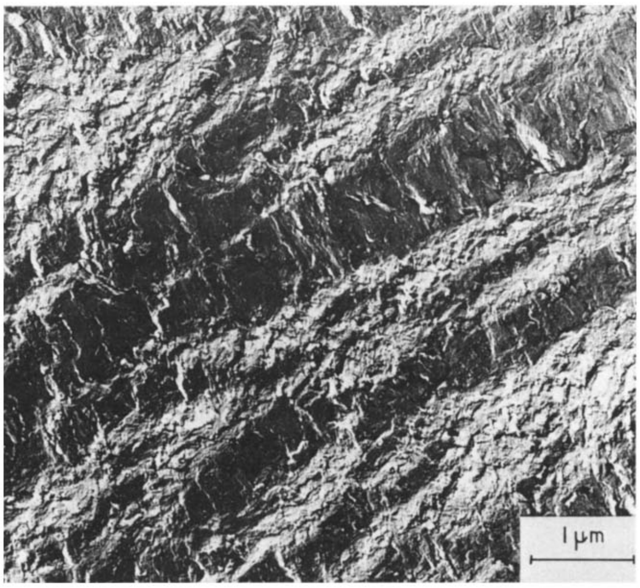

Figure 10 Electron micrograph of replica of a fracture surface of nylon-6 sample annealed at 280°C and 6.5 kbar for 90 h

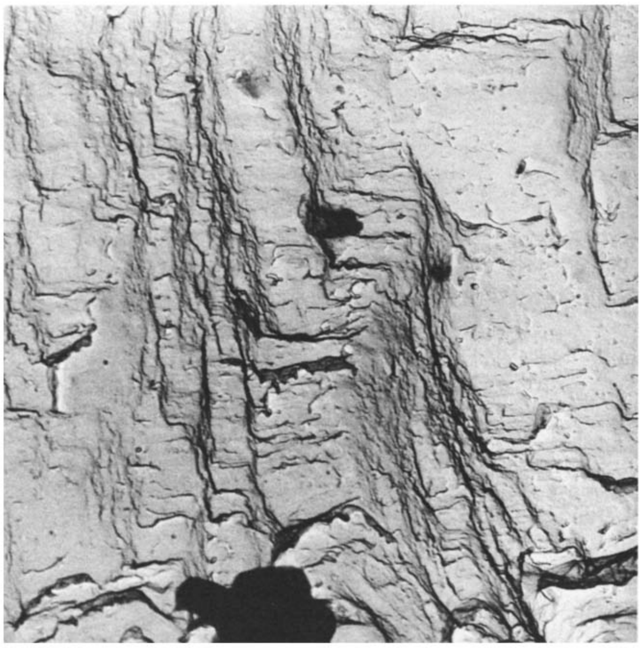

Figure 11 Electron micrograph of replica of a fracture surface of nylon-6 sample annealed at 280°C and 6.5 kbar for 200 h

nealed at 280°C and 6.5 kbar for 48 h. The chain-extended lamellae with thickness ranging from 2 to 5 μm as estimated from the fracture surface can be seen in the picture.

Figure 10 presents an electron micrograph of a nylon-6 sample annealed at 6.5 kbar and 280°C for 90 h. It shows that the lamellar thickness, which equals the dark strips of the surface structure in the electron micrograph, increased with time of annealing under pressure. The thickest lamellae are in the range of 10 μm, probably resulting from fractionation process occurring during annealing. The lighter areas may correspond to the (010) planes of the crystal and often reveal the thinner lamellae. *Figure 11* is an electron micrograph of a fracture surface of the sample annealed for 200 h under a pressure of 6.5 kbar and 280°C. It can be seen that the steps of the lamellae are much more pronounced, indicating a better arrangement of the chains in the crystal. This is consistent with the observation that the sample annealed for 200 h was much more brittle than the samples shown in *Figure 9* and *10*. The morphology of the chain-extended crystals of nylon-6 formed during annealing of the folded-chain material under pressure is identical with that found for the pressure-crystallized nylon-6 from the melt and was discussed in detail in the previous paper of this series[13]. In *Figure 12* the X-ray diffraction spectra of different nylon-6 samples are presented and show the typical alpha-structure. Curve A was recorded for a folded-chain material annealed under atmospheric pressure at 210°C for 64 h. Curves B and C represent the nylon-6 samples crystallized from the melt and annealed for 64 h under a pressure of 6.5 kbar at 280°C, and at atmospheric pressure of 210°C, respectively. It can be seen that for the chain-extended material, the separation of the alpha$_1$ and alpha$_2$ peaks is much better than for the folded-chain crystals. The height of these peaks increases, and their width decreases. The position of the alpha$_1$ and alpha$_2$ peaks shifts to the higher values of 2θ. All presented data show that, as a result of high pressure crystallization from the melt or annealing under pressure, the crystal thickness greatly increased, the packing of chains in the crystal lattice is improved, and the strength of the hydrogen bonding as well as van der Waals' forces between the hydrogen bonded sheets increased. The infra-red spectra of the annealed nylon-6 were the same as those of the samples crystallized under pressure from the melt[13] and the viscosity-average molecular weight decreased upon annealing from 95×10^3 to 85×10^3.

This change in molecular weight of the polymer may be due to any of the thermally activated degradation processes[27], in particular hydrolysis if some trace of water is still present in the sample. Additionally, interchange reactions may occur, and it has been shown that these processes proceed quite rapidly, even at temperatures below the melting point of the polyamide[24,25]. The change in molecular weight distribution as a result of the polyamidation equilibrium in the solid phase has been accounted for by assuming that the chain ends are excluded from the crystalline

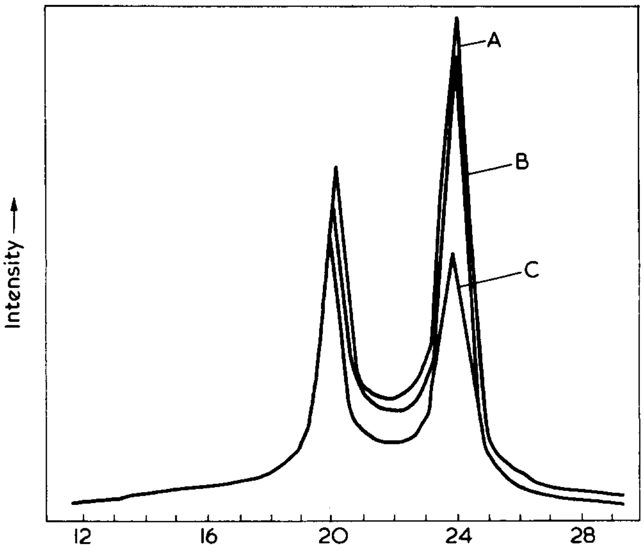

Figure 12 X-ray diffraction spectra of various nylon-6 samples:
A, Sample annealed at 280°C and 6.5 kbar for 64 h.
B, Sample crystallized from the melt at 280°C and 6.5 kbar for 64 h.
C, Sample annealed under atmospheric pressure at 210°C for 64 h

core and can interchange with amide groups occurring in the folds[25,26]. Furthermore, reactions of one amide group with another leading to 'amide interchange' seem to be possible[27], although it has been reported[28,29] that this 'transamidation' does not take place in the absence of water at 250°C. It is conceivable that the interchange reactions play a role in the rearrangement of polymer chains during annealing of polyamides under pressure. A more detailed investigation of this problem will be the subject of a subsequent paper[34].

In summary, for comparable conditions of pressure, temperature and time, the better crystals as estimated from the X-ray scattering curves and melting points were formed during annealing of melt-crystallized nylon-6 under pressure rather than during pressure-induced crystallization from the melt. Results of the X-ray analysis are in accordance with the melting characteristics of the chain-extended crystals of nylon-6 and the morphological observations of fracture surfaces and confirm the suggestion that the chain-extended crystals of polyamides with a lamellar thickness exceeding 2000 Å can be formed under pressure from the folded-chain ones which are grown from the melt during the early stage of crystallization under pressure.

Stepwise annealing by exposing nylon-6 to progressively higher temperatures at 6.5 kbar yielded a melting temperature of 269°C. The rate of annealing at 6.5 kbar was found to increase with temperature in the range between 260° and 280°C

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