Crystallization of polyamides under elevated pressure: 5. Pressure-induced crystallization from the melt and annealing of folded-chain crystals of nylon-11, poly(aminoundecaneamide) under pressure

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High pressure dilatometry, differential scanning calorimetry, electron microscopy, X-ray diffraction, and infra-red spectroscopy to study how the crystallization of nylon-11 from the melt, as well as annealing of the folded-chain crystals, are affected by pressure in the range from 1 to 10 kbar (1 kbar = 100 MN/m^2) and temperature in the range from 200° to 320°C. Pressures exceeding 3 kbar and temperatures higher than 230°C are sufficient for growth of the chain-extended crystals of nylon-11 either by pressure-induced crystallization from the melt or by annealing of the folded-chain crystals. Crystallization from the melt or annealing at 320°C or higher, and 10 kbar, resulted in crosslinking of the polymer. The highest melting temperature and heat of melting found for the chain-extended crystals of nylon-11 were 226°C and 35 cal/g respectively, as compared to 190°C and 13.6 cal/g for the folded-chain material. The texture of the chain-extended crystals of nylon-11 was found to be spherulitic with well developed striations forming circle patterns, and polymer chains passing through several lamellae. No sharp boundaries were found between the chain-extended lamellae. The alpha-crystalline modification, found for the folded-chain crystals of nylon-11, was preserved in the high pressure crystallization and annealing experiments. Infra-red absorption bands at 1420 and 1225 cm^{-1} seem to be associated with the presence of folds in the nylon-11 crystals. It is suggested that, during the initial stage of crystallization under pressure, folded-chain crystals are formed, with a crystalline order and long spacing larger than that of the starting nylon-11.

INTRODUCTION

It has been shown in recent papers that elevated pressure can enhance the rate of growth of the chain-extended crystals in nylon-6.

The chain-extended crystals were grown either by pressure-induced crystallization from the melt[1–3], or by annealing of the folded-chain crystals under pressure[4]. Based on the melting characteristics, as well as the surface morphology and X-ray scattering patterns of these crystals grown by two different methods, the conclusion was drawn that the chain-extended crystals of polyamides do not grow directly from the melt under pressure; folded-chain crystals form first, followed by an increase in lamellar thickness up to a size equal to the molecular length[4]. Chain-extension may proceed by isothermal thickening and mutual rearrangement within a folded-chain molecule[5]; also, interchange reactions involving the –CO–NH– groups may play a role[6].

This paper deals with crystallization from the melt, and annealing of the folded-chain crystals of nylon-11 under elevated pressure in the range between 1 and 10 kbar (1 kbar = 100 MN/m^2). Nylon-11 was chosen as an intermediate between nylon-6 and polyethylene, for which extensive studies have been reported in the literature and were recently reviewed by Bassett[32].

Only a few papers are concerned with the crystalline properties of nylon-11[7–21], and the data pertinent to the present study can be summarized as follows. Nylon-11 can crystallize in two polymorphic forms, alpha and gamma[10–13]. The zig-zag chains of the polymer are fully extended in the unit cell, and can be arranged parallel or antiparallel within the hydrogen bonded sheets depending on the polymorphic form. The distance between the CO–NH groups of the adjacent chains within the sheet ranges[9] from 2.85 to 4.77 Å. The distance between the sheets[20] is in the range of 4.2 Å. Depending on the crystalline modification the amide groups are aligned perpendicular to, or tilted from, the plane of the chain axis[9–11]. Nylon-11 quenched from the melt[10] or cast from a trifluoroacetic acid[16] forms the gamma hexagonal, or smectic, modification, while isothermal crystallization from the melt[10] or casting from a phenol/formic acid mixture[17] gives an alpha-triclinic modification. In contrast to the gamma form obtained by quenching the melt, the gamma form grown from trifluoroacetic acid solution is stable against heat treatment, and can only be converted to the alpha form by stretching or melting and subsequently crystallization[16]. The most stable alpha form is triclinic or monoclinic[7–13]; the unit cell dimensions have been estimated by various authors[7–14] as follows: a = 4.78 to 9.6 Å, b = 4.13 to 5.4 Å, c = 13.1 to 15.0 Å, and alpha = 49° to 81°7′, beta = 75°20′ to 90°, gamma = 63°5′ to 65°7′. The unit cell contains one[11] or two[13] monomer units. The density of the crystalline phase of nylon-11, as calculated from the unit cell parameters, is[7,11,13] 1.12, 1.153, or 1.195 g/cm^3, and the density of the amorphous phase[7,14,15] is 1.01 g/cm^3. The melting temperature of the crystalline phase is

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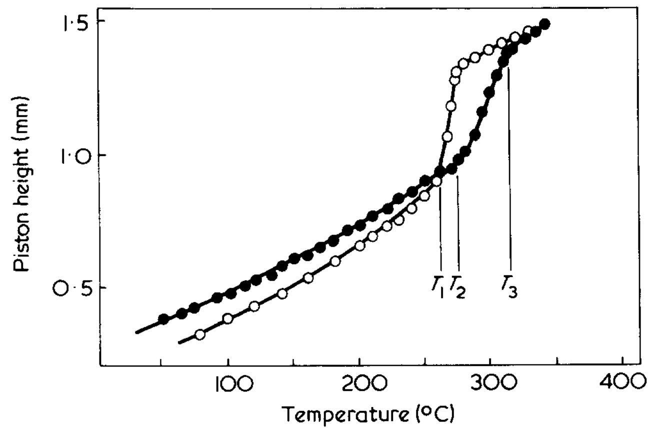

Figure 1 Dependence of the piston height on temperature for nylon-11 sample under pressure of 6.5 kbar: ●, heating run; ○, cooling run. T_3, T_2, and T_1 denote the end of melting, the beginning of melting, and the end of crystallization respectively

assumed[7,10,18,12] to be 189°C, 193°C or 194°C; the glass transition temperature[18] is 43°C, and the heat of melting[19] is 54.1 cal/g. Crystallization from the melt leads to the growth of spherulites[21]. Commercial material[22] has a crystallinity in the range of 10–30%.

The aim of the present work was to find whether: (a) nylon-11 can crystallize in the chain-extended conformation by annealing under pressure of the folded-chain crystals, or by pressure-induced crystallization from the melt; (b) a smaller number of hydrogen bonds and longer methylene chain, as compared with those for nylon-6, have any effect on the crystallization behaviour under pressure and morphology of the crystals; (c) pressure influences the crystal modification of the folded material.

It was hoped that the data obtained might throw some light on the mechanism of chain extension in polyamides under pressure. Differential scanning calorimetry, electron microscopy and X-ray scattering were used to study the thermal characteristics, surface morphology and crystal modification. Infra-red spectrometry was applied in order to find whether any absorption band might be associated with the presence of folds in the conformation of the chain of nylon-11.

EXPERIMENTAL

Materials

The sample[23] used for the high pressure experiments was commercial nylon-11 (Rilsan) made by the Societé Organico, France, with weight-average molecular weight of 24 x 10^3, number-average molecular weight 13 x 10^3, and heterogeneity ratio 1.8. The samples used for the experiments were prepared from the original pellitized material by means of extruding under high vacuum[24].

Apparatus

Crystallization and annealing under pressure were carried out in a high pressure dilatometer, consisting of two pistons and a thick-walled, heated cylinder. Pressure was generated by a hydraulic press[25].

Determination of the melting temperature under pressure. In order to find the proper crystallization conditions, the melting temperature of nylon-11 under pressure was determined by measuring the dependence of the piston height on temperature under different pressures with the sample in the high pressure cell at the required pressure, the temperature was increased in steps of 5°C. When the temperature was constant, the piston was moved three times in order to minimize the pressure loss by friction, and the piston height was measured with an accuracy of the order of ±0.001 mm. Each temperature step was carried out in about 25 min.

Crystallization conditions under pressure

The sample in the dilatometer was pressurized to 12 kbar and heated to a temperature in the range of 200°–320°C. These temperatures were much lower than the melting temperature of the polymer under a pressure of 12 kbar. Then the pressure was decreased to 100 bar and the sample was melted during 15 min (the shortest time necessary to obtain a homogeneous melt). Next the crystallization pressure between 1 and 10 kbar was applied to the polymer melt. After an appropriate time of crystallization, the sample was cooled at 50°C/h to room temperature, and the pressure was released.

Annealing conditions under pressure

A folded-chain sample was pressurized to the required annealing pressure in the range 1–10 kbar. Subsequently the temperature was increased to the selected annealing temperature in the range 40°–60°C below the end melting temperature T_3. After an appropriate annealing time, the sample was cooled to room temperature and the pressure was released.

Characterization of samples from high pressure experiments

Melting temperature and heat of melting were determined by means of differential scanning calorimetry, using a Perkin–Elmer DSC-1B instrument, with a scan speed of 8°C/min. Electron microscopy investigations were carried out on two-stage replicas of fracture surfaces. X-ray wide-angle diffraction patterns were recorded with a Philips X-ray diffractometer system coupled with a scintillating counter. Infra-red spectra were obtained with a Perkin–Elmer grating spectrophotometer over the wavenumber region from 250 to 4000 cm^{-1}. Details of the techniques used have been given previously[3].

RESULTS AND DISCUSSION

Melting temperature under pressure

Figure 1 shows an example of the dependence of the piston height on temperature measured for nylon-11 under a pressure of 6.5 kbar. It was found that the rate of heating and cooling in the range between 5 and 50°C/h had no effect on the shape of the recorded curves. The character of the heating and cooling curves indicates that the pressure losses resulting from internal stress and friction are minimal. *Figure 2* represents the dependence of the final melting temperature T_3, as measured under pressure, on the pressure applied. A broken line was drawn for the sample C of nylon-6[4], and a full line for the nylon-11 samples used throughout this investigation. It can be seen that the melting temperature of nylon-11 under pressure increases with pressure. This is especially true for the lower values of pressure. This dependence is very similar to that observed for polyethylene[26,27], and differs from that of nylon-6[3,4], for which an almost rectilinear dependence of $T_m(p)$ on P was found for the same range of pressures investigated. For the linear part of

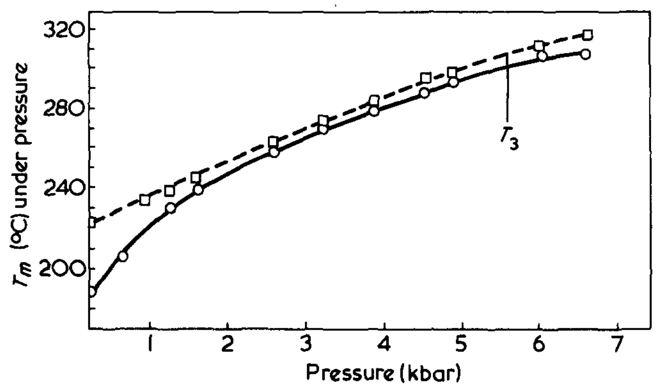

Figure 2 Dependence of the end melting temperature on pressure applied for: □, nylon-6; ○, nylon-11

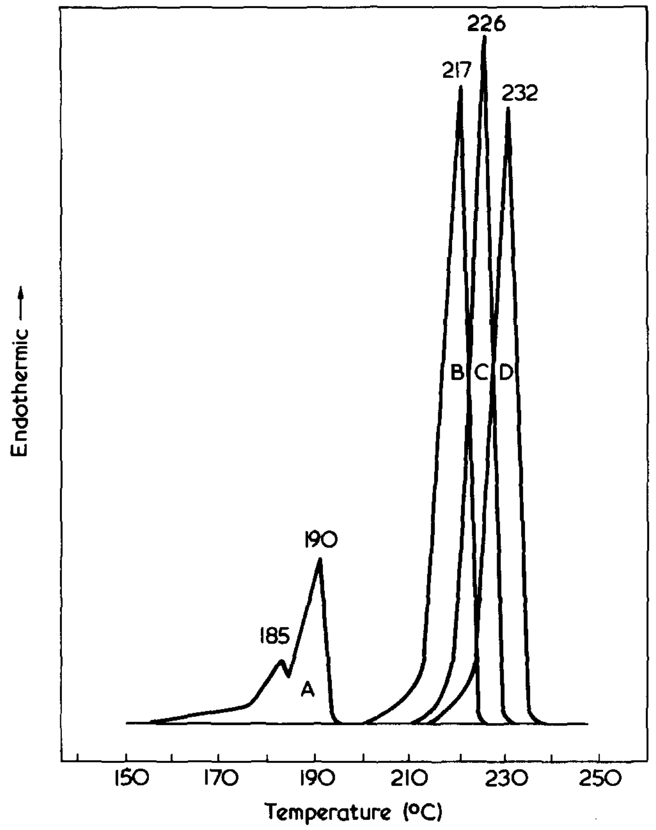

Figure 3 Melting thermograms for various nylon-11 samples: A, original sample; B, sample annealed at 260°C and 6.5 kbar for 48 h; C, sample crystallized from the melt at 260°C and 6.5 kbar for 48 h; D, sample annealed at 320°C and 10 kbar for 48 h

the curve the increase in melting temperature with pressure for nylon-11 is about 16°C/kbar, the same value as found[2,4] for nylon-6.

Melting characteristics of the samples from high pressure experiments

Figure 3 shows the melting thermograms of the original sample (A), a sample annealed at 260°C and 6.5 kbar for 48 h (B), a sample crystallized from the melt at 260°C and 6.5 kbar for 48 h (C), and a sample annealed at 320°C and 10 kbar for 48 h. The original sample displayed the second melting peak at 185°C; this changed only slightly with heating rate. Thus it seems that this peak can be related to the impurity contents resulting from the 'production history', and to the presence of an amorphous material in the sample, rather than to reorganization of metastable crystals, to the presence of crystals with a different degree of crystalline order, or to the phase transformation[28].

The melting thermograms of nylon-11 samples heat-treated under pressure show an increase in melting temperature, and display only one high and narrow melting peak. This suggests a high crystalline order in these samples. *Figure 4* illustrates the effect of the scan speed on the melting peak temperature of the samples crystallized or annealed under pressure. All the samples in these experiments exhibited a superheating effect of about 10°C. This confirms the presence of large, chain-extended crystals[29]. It was found that the sample annealed at 320°C and 10 kbar for 48 h was completely insoluble in any solvent suitable for nylon-11, indicating that, under very high temperature and pressure, crosslinking of the polymer took place. *Figure 5* shows the dependence of the atmospheric melting peak temperature on crystallization pressure for the samples of nylon-11 crystallized from the melt at temperatures 40°C lower than the final melting temperature T_3 for 14 and 24 h. It shows that the crystalline order formed in the nylon-11 under pressure, as estimated from the melting temperature,

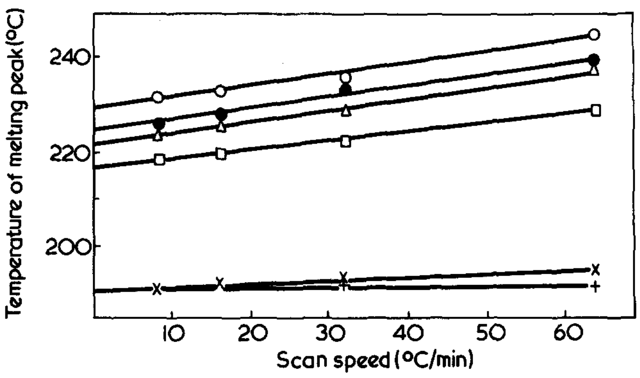

Figure 4 Effect of scan speed on melting peak temperature for various nylon-11 samples: +, original sample; X, sample extruded under vacuum; □, sample annealed at 260°C and 6.5 kbar for 48 h; △ and ●, samples crystallized from the melt at 260°C and 6.5 kbar for 24 and 48 h respectively; ○, sample annealed at 320°C and 10 kbar for 48 h

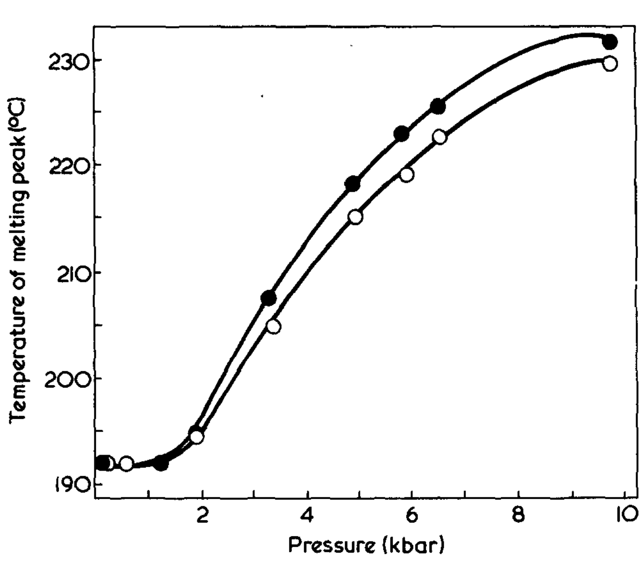

Figure 5 Dependence of atmospheric melting peak temperature on crystallization pressure applied for various nylon-11 samples crystallized at temperatures 40°C lower from the end melting temperature under respective pressure: ○, 14 h; ●, 24 h

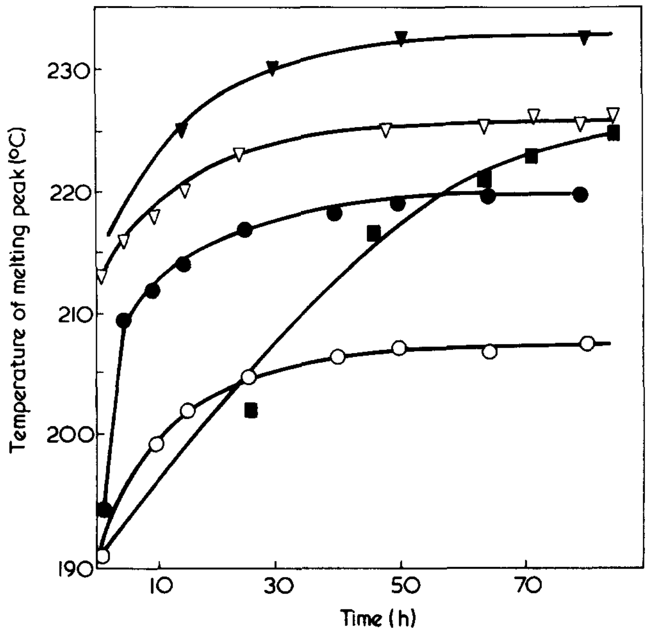

Figure 6 Dependence of atmospheric melting peak temperature on crystallization time: ○, 230°C and 4 kbar; ■, samples annealed without melting at 260°C and 6.5 kbar; ○, 255°C and 5.5 kbar; ▽, 260°C and 6.5 kbar; ▼, 320°C and 10 kbar

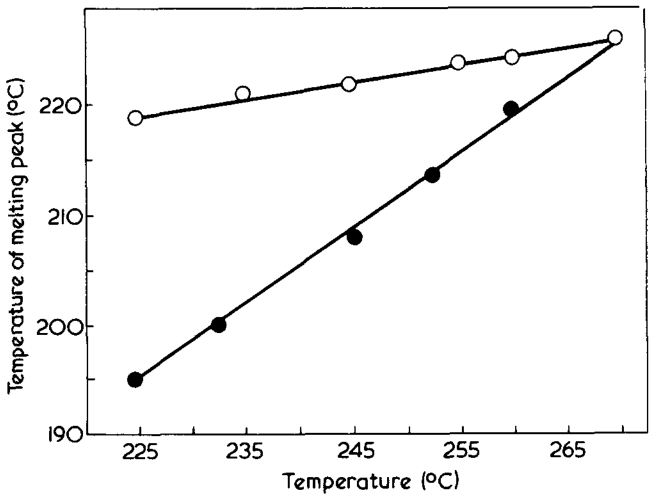

Figure 7 Dependence of atmospheric melting peak temperature on crystallization or annealing temperature for nylon-11 samples: ○, sample crystallized from the melt at 6.5 kbar for 48 h; ●, sample annealed without melting at 6.5 kbar for 48 h

increases with pressure. The effect of pressure becomes significant beyond 3 kbar.

Figure 6 shows the dependence of the atmospheric melting peak temperature on crystallization time. It can be seen that the melting temperature of the samples crystallized from the melt under pressure increased with time during the first 30–40 h of the crystallization process. After that time, no significant increase of the melting temperature was observed. For annealing of the folded-chain crystals at the same temperature and pressure, the melting temperature increased continuously over about 70–80 h and reached a value which was still lower than that of the melt-crystallized samples. This shows that for nylon-11, in contrast[2,4] to nylon-6, pressure is more effective in this case, when crystallization proceeds from the molten state.

Figure 7 presents the dependence of the atmospheric melting temperature on both the crystallization and annealing temperatures. The samples were annealed at 6.5 kbar for 48 h, and crystallized from the melt under a pressure of 6.5 kbar for 48 h. It is evident that the increase in crystalline order in nylon-11 under pressure increases with temperature, and this effect is especially pronounced for the folded-chain crystals annealed under pressure. At temperatures close to 270°C, the effect of temperature seems to be the same for annealing as well as for pressure-induced crystallization from the melt.

Figure 8 shows the effect of pressure on the heat of melting of nylon-11 samples crystallized from the melt at 40°C below the final melting temperature for 24 h, and for the samples annealed under the same conditions. The Figure shows that not only the atmospheric melting temperature, as described above, but also the heat of melting is lower for the chain-extended crystals of nylon-11 grown by annealing of the folded-chain material under pressure, than for those grown by pressure-induced crystallization from the melt.

It was found that the melting temperature increased by about 4°–6°C, and the heat of melting by 2–3 cal/g, when the nylon-11 samples were heated under pressure above the melting range and then cooled quickly down to room temperature. The increase of the melting temperature and heat of melting probably results from increased crystalline order and lamellar thickness of the folded-chain crystals, which are formed in the melt during the initial stage of crystallization under pressure.

A comparison of the melting characteristics of the chain-extended crystals of nylon-11 grown by pressure-induced crystallization and by annealing of folded-chain material under pressure suggests that, in the initial stage of the pressure-induced crystallization from the melt, crystals are formed with a relatively large fold length and a higher degree

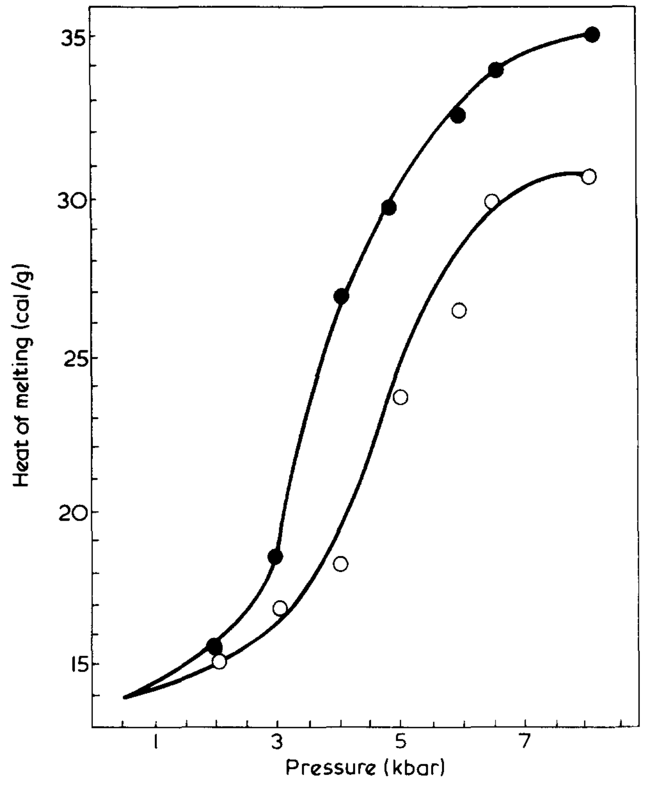

Figure 8 Dependence of heat of melting on applied pressure: ○, samples annealed at 40°C below end melting temperature for 24 h; ●, sample crystallized from the melt at 40°C below end melting temperature for 24 h

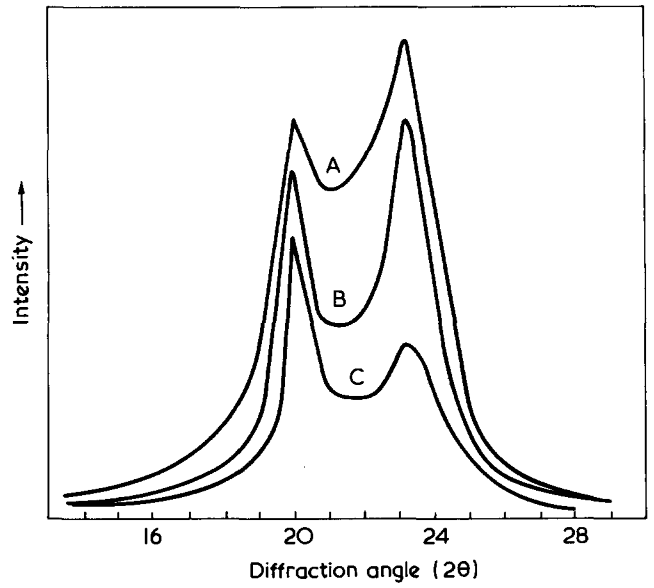

Figure 9 X-ray diffraction spectra of various samples of nylon-11: A, sample annealed at 260°C and 6.5 kbar for 48 h; B, sample crystallized from the melt at 260°C and 6.5 kbar for 48 h; C, sample crystallized isothermally from the melt at 180°C and atmospheric pressure for 48 h

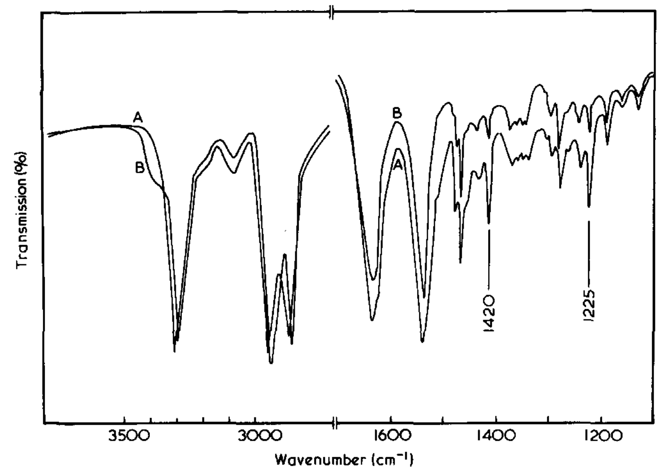

Figure 10 Infra-red spectra of various nylon-11 samples: A, folded-chain crystals – sample cast from formic acid and then annealed at 180°C and atmospheric pressure for 48 h; B, chain-extended crystals – sample crystallized from the melt at 260°C and 6.5 kbar for 48 h

of crystalline order than present in the original material. *Figure 9* presents the X-ray diffraction spectra of various nylon-11 samples. Sample 1 was annealed at 260°C and 6.5 kbar for 48 h, sample 2 crystallized from the melt at 260°C and 6.5 kbar for 48 h, and sample 3 crystallized from the melt at 180°C and atmospheric pressure for 48 h. It can be seen that all the samples of nylon-11 investigated, i.e. folded-chain as well as chain-extended, crystallized in the alpha modification[7–13]. The intensity of the alpha$_1$ peak with spacing $d = 4.4$ Å remains almost unchanged for all investigated samples, while the intensity of the alpha$_2$ peak with spacing $d = 3.8$ Å increases considerably. The decrease of width of the alpha$_2$ peak suggests an increase of the crystal size and perfection. The position of the alpha$_1$ peaks did not change, within the limit of experimental error. The separation of the peaks is largest for the sample crystallized from the melt under pressure. This shows that the degree of order and perfection of hydrogen bonds is much higher for the chain-extended crystals of nylon-11 formed by pressure-induced crystallization from the melt, than for the folded-chain material annealed under pressure. This is in accordance with the thermal characteristics of the corresponding nylon-11 solids discussed above.

Additional information on the crystalline structure of nylon-11 can be obtained from infra-red analysis. *Figure 10* shows the infra-red spectra of two samples of nylon-11. Sample 1 was a folded-chain material precipitated from boiling formic acid with a water–acetone mixture, and subsequently annealed at 180°C under atmospheric pressure for 48 h. Sample 2 was nylon-11 crystallized from the melt at 6.5 kbar and 260°C for 48 h.

Detailed discussion of the infra-red bands of polyamide and the effects of pressure on some absorption bands were reported in part 3 of this series[3]. The shoulder on the high frequency side of the CO–NH stretching vibration band, related to unbonded NH groups, is much less[3] for nylon-11 than for nylon-6. Thus it seems that, because the total number of CO–NH groups able to form hydrogen bonds per comparable chain length in nylon-11 is half that in nylon-6, the number of unbonded NH groups is also lower. It may be that, as already suggested[3] for the chain-extended crystals of nylon-6, some chains within the sheets in the alpha modification are arranged parallel, which does not permit complete hydrogen bonding. It was found that the intensity of bands at 1225 cm^{-1} related to the vibration of Amide III with gamma$_w$ (CH_2) and gamma$_t$ (CH_2), and at 1420 cm^{-1} related to the vibration of delta (CH_2), CO vic[30], was greatly diminished for the chain-extended nylon-11, compared with the folded-chain one. Therefore it seems that these bands may be associated with presence of folds in the nylon-11 crystals.

Finally some morphological features as observed in the electron microscope will be described. *Figure 11* is an electron micrograph of a replica of a fracture surface of nylon-11 crystallized isothermally from the melt at 180°C under atmospheric pressure for 24 h, and shows part of a typical, lamellar folded-chain spherulite. *Figure 12* is an electron micrograph of a replica of a fracture surface of nylon-11 crystallized from the melt at 260°C and 6.5 kbar for 12 h.

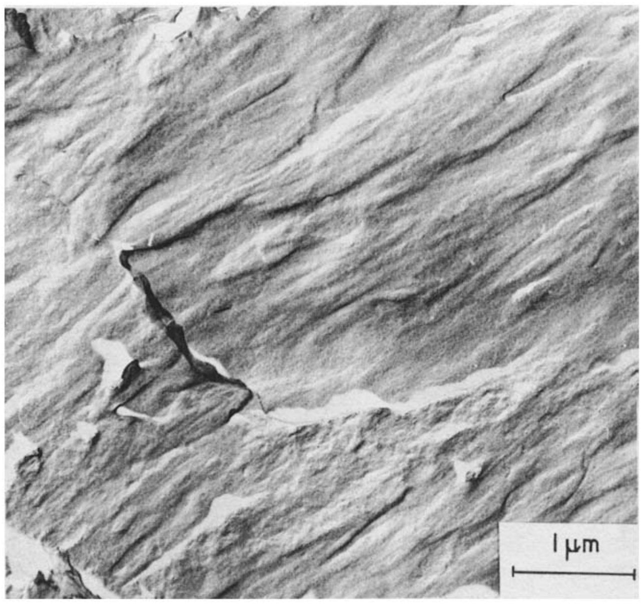

Figure 11 Electron micrograph of a fracture surface of nylon-11 crystallized isothermally from the melt at 180°C under atmospheric pressure for 24 h

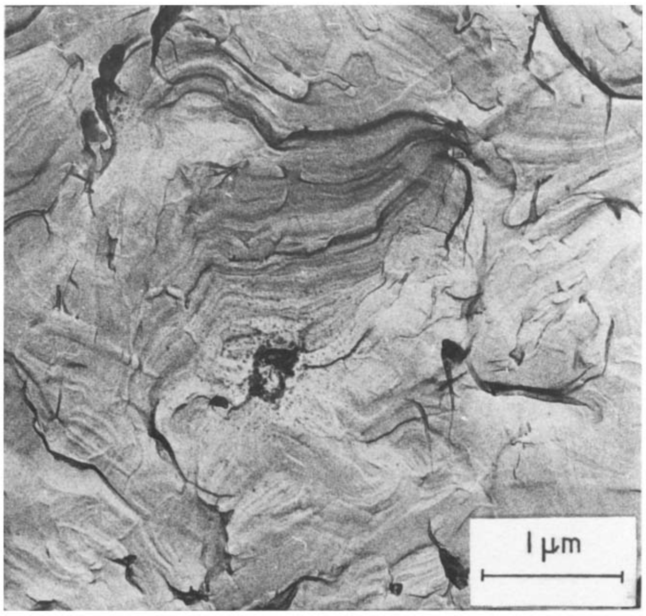

Figure 12 Electron micrograph of a fracture surface of nylon-11 crystallized at 260°C and 6.5 kbar for 12 h

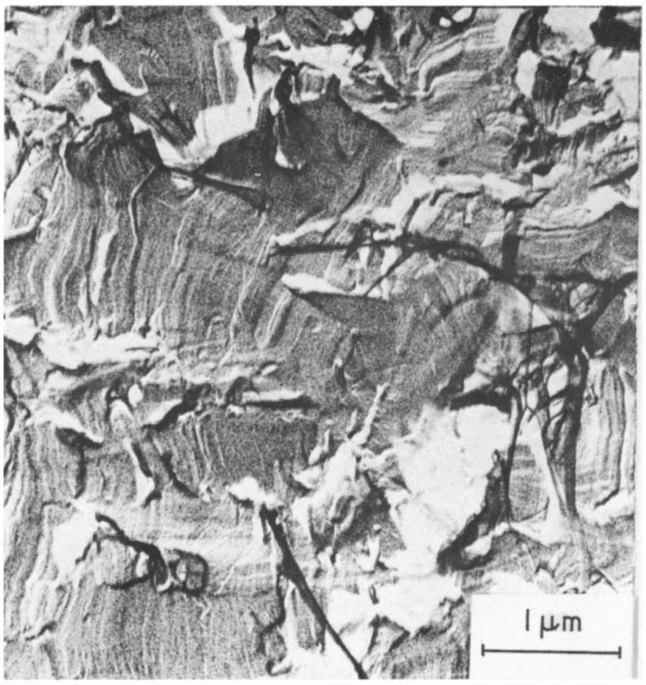

Figure 13 Electron micrograph of a fracture surface of nylon-11 crystallized at 260°C and 6.5 kbar for 24 h

The surface morphology differs from that shown in *Figure 11* in that the randomly distributed chain-extended lamellae exhibit some striations. *Figures 13* and *14* illustrate the effect of time under pressure on the surface morphology. Samples were crystallized from the melt at 260°C and 6.5 kbar for 24 and 80 h. It can be seen that, together with prolongation of the time the samples were crystallized under pressure, the surface morphology and striations become more pronounced. In *Figure 14* part of the chain-extended spherulite is presented and shows no boundaries between the chain-extended lamellae. Chains are aligned parallel to the striation and pass in continuous manner from one lamella into another, forming curved patterns. In some parts of the crystal kink bands can be discerned. The morphology of the fracture surface of the chain-extended crystals of nylon-11 appears to be very similar to that found in the extended-chain crystals of selenium[31]. *Figure 15* shows the surface morphology of the chain-extended crystals of nylon-11 grown by annealing of the folded-chain material at 6.5 kbar and 260°C for 50 h. Note that the length of the striation is considerably shorter than those of the pressure-crystallized nylon-11. Furthermore, the crystalline domains in the annealed samples seem to be much smaller and are randomly oriented.

Figure 16 is an electron micrograph of the nylon-11 sample annealed at 10 kbar and 320°C for 50 h. The surface morphology is different from that of the folded-chain crystals as well as the chain-extended ones. As this sample, which had the highest melting temperature, was completely crosslinked, one may expect that the morphology also reflects the changes occurring in the sample under high temperature and pressure. It was quite remarkable to find that this crosslinked nylon-11, insoluble in any solvent suitable for polyamides, could be processed by extruding and injection moulding.

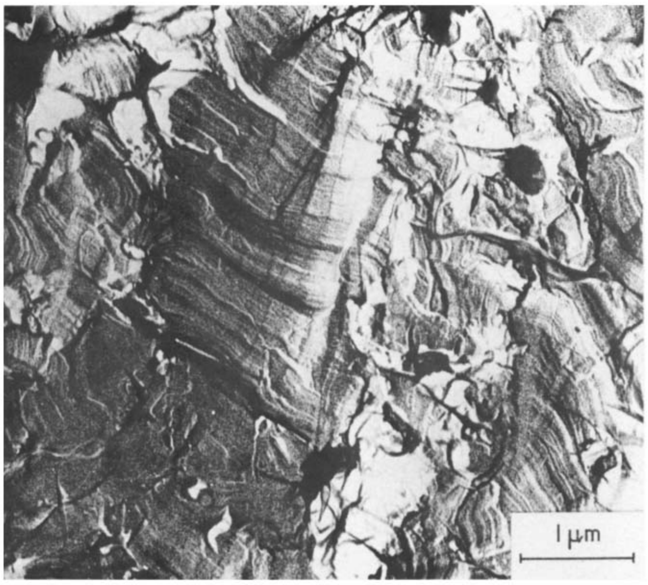

Figure 14 Electron micrograph of a fracture surface of nylon-11 crystallized at 260°C and 6.5 kbar for 80 h

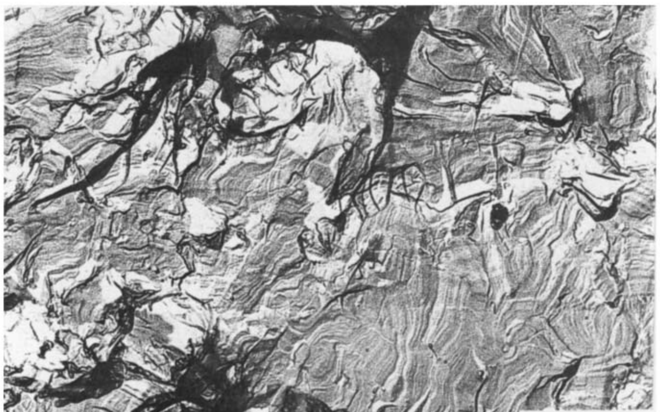

Figure 15 Electron micrograph of a fracture surface of nylon-11 annealed at 260°C and 6.5 kbar for 50 h

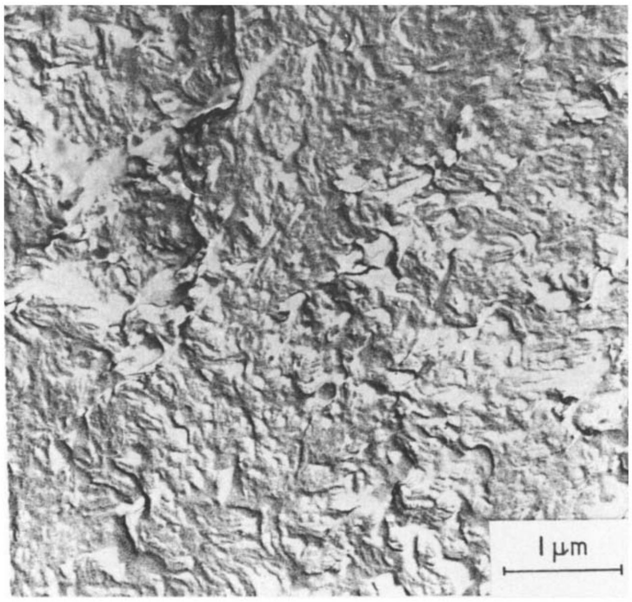

Figure 16 Electron micrograph of a fracture surface of nylon-11 annealed at 320°C and 10 kbar for 50 h

CONCLUSIONS

The results presented in this paper can be summarized as follows. Chain-extended crystals of nylon-11 are formed from folded-chain ones grown from the melt in the initial stage of crystallization under pressures exceeding 3 kbar. Transmission electron micrographs of replicas of fracture surfaces of the chain-extended nylon-11 display distinct striations likely to be due to parallel orientation of the chains. The lateral dimensions of these lamellae are rather small in comparison with those of high pressure crystallized polyethylene and no sharp boundaries of these nylon-11 crystals could be discerned. The heat of fusion as well as the melting temperature of nylon-11 are increased considerably by pressure-induced crystallization and by annealing under pressure. The atmospheric melting temperature depends on the annealing temperature and increases from 195° to 225°C by annealing at 6.5 kbar for 48 h in the temperature range 225°–270°C.

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