Crystallization of polyamides under elevated pressure: 6. Pressure-induced crystallization from the melt and annealing of folded-chain crystals of nylon-12, polylaurolactam under pressure

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The influence of pressure on the crystallization and annealing of polylaurolactam, nylon-12, has been investigated. The increase of the final melting temperature of this polyamide with pressure amounted to 20°C per kbar as determined by high pressure dilatometry. Crystallization as well as annealing under pressure led to a partial transformation of the pseudo-hexagonal or monoclinic crystal structure to an alpha modification. Samples crystallized at a pressure of 4.9 kbar (1 kbar = 100 MN/m^2) displayed multiple melting behaviour, whereas annealing under pressure gave rise to one melting peak in the d.s.c. thermograms. The heat of fusion could be enhanced from 16 to 32 cal/g and the melting peak temperature could be increased from 179° to 209°C by annealing under 4.9 kbar and 260°C for 336 h. Small-angle X-ray scattering curves reveal that annealing brings about considerable broadening of the distribution of the crystal dimensions. The pressure treated nylon-12, consisting of well developed spherulites, could be fractured very easily along inter-spherulitic and trans-spherulitic planes. The striations in the fracture surfaces as observed in the electron microscope were arranged perpendicular to the radial arms of the spherulites. Annealing at 320°C and 10 kbar for 48 h caused efficient cross-linking of the polylaurolactam.

INTRODUCTION

Previous papers in this series[1–5] reported the effect of pressure on the crystallization and annealing of nylon-6 and nylon-11. The thermal properties, as well as the morphology of these polyamides, appeared to be remarkably changed after pressure-induced crystallization or annealing under pressure at pressures exceeding 3–4 kbar (1 kbar = 100 MN/m^2). The atmospheric melting temperature of nylon-6 could be increased from 225° to 256°C by pressure-induced crystallization. Stepwise annealing of this polymer gave rise to an increase in melting temperature of more than 40°C and the heat of fusion reached 40 cal/g. In the case of nylon-11, increases in melting temperature and heat of fusion of 36°C and 21 cal/g respectively were found after pressure-induced crystallization.

The aim of this study was to explore whether a polyamide such as polylaurolactam, commonly referred to as nylon-12, would be more susceptible to the effect of high pressure than nylon-6 and nylon-11, since nylon-12 occurs in the γ-form, a pseudo-hexagonal crystal structure that is less dense than the α-modification of nylon-6 and nylon-11. It is conceivable that the pseudo-hexagonal modification of nylon-12 has the same favourable effect on the chain extension as the hexagonal high pressure phase in polyethylene as discovered by Bassett[6,7]. The crystalline density of nylon-12 calculated from the unit cell dimensions amounts[8] to 1.034 g/cm^3. This is considerably less than the density of the α modification of nylon-11, 1.15 g/cm^3 [9], and of the α and γ modifications of nylon-6, which are[10,11] 1.235 g/cm^3 and 1.163 g/cm^3 respectively. Furthermore, as for nylon-11 the thermal stability of nylon-12 is better than that of nylon-6, and possible interference due to thermal degradation would be less effective at elevated pressure and temperature.

This paper gives an account of the effect of high pressures, temperature and time on the crystallization and annealing of nylon-12. The melting process was assessed by high pressure dilatometry. The polyamide specimens were characterized by wide-angle X-ray diffraction analysis, small-angle X-ray scattering, and differential scanning calorimetry. Fracture surfaces were examined by scanning electron microscopy and by means of two-stage replicas in the transmission electron microscope.

EXPERIMENTAL

Materials

Polylaurolactam (Vestamid L 1600) was used throughout this study as purchased from Chemische Werke Hüls AG. The polymer was prepared by homopolymerization of laurolactam and did not contain any nucleating agent or stabilizer. The weight-averaged molecular weight (M_w) amounted to 35 x 10^3 according to the specification of the manufacturer. The relative viscosity of a 0.5% solution (by weight) of the polyamide in concentrated sulphuric acid (98%) was found to be 1.57. The granulated polymer was compression

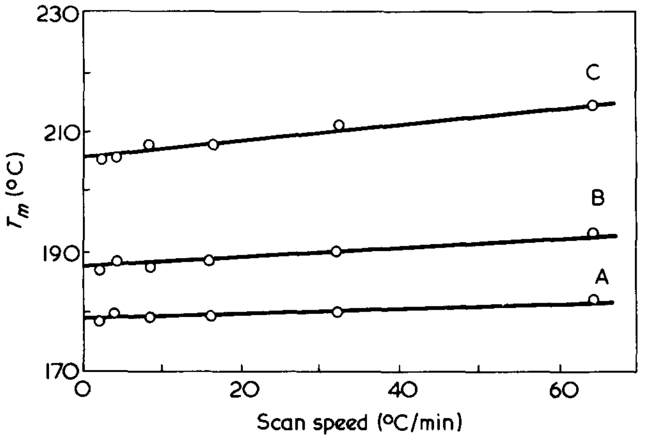

Figure 1 Effect of the scan speed of the d.s.c. on the melting peak temperature for various nylon-12 samples. A, original sample; B, sample annealed at 260°C and 4.9 kbar for 4½ h; C, sample annealed at 260°C and 4.9 kbar for 336 h

moulded at 220°C to form a sheet of 3 mm thickness. After melting and compression the mould was quickly cooled down to room temperature in order to produce a rather poorly crystalline material. Pellets with a diameter of 14 mm were punched out of the sheet, just fitting in the inner hole of the high pressure cylinder.

High pressure technique

The high pressure experiments were performed using the high pressure apparatus described in a previous paper of this series[2]. Volume changes during experiments were recorded by measurement of the piston displacement with a d.c.–d.c. linear voltage displacement transmitter (LVDT). Three pellets of the original material were compressed at 10 kbar and 100°C for two hours to remove air from the small clearance between sealing rings, sample and cylinder. Melting, crystallization and annealing experiments were carried out in essentially the same manner as reported in the previous papers[2–5].

Sample characterization

The polyamide specimens were characterized by differential scanning calorimetry (d.s.c.), X-ray diffraction and electron microscopy. Details of the techniques used have been given previously[2–5]. The superheatability of the materials is illustrated in *Figure 1*, in which the melting peak temperature is plotted against the scan speed of the d.s.c. The effect of superheating of the polyamide annealed at 4.9 kbar and 260°C for 336 h was only slightly different from that of the original material. A scan speed of 8°C/min was applied throughout all further d.s.c. measurements. Small-angle X-ray scattering measurements were performed on the bulk polymers using a Philips–Kratky small-angle X-ray diffraction unit. The intensity curves obtained were de-smeared using a computer program developed by Dr G. Vonk (DSC-Geleen, Holland).

RESULTS

Effect of pressure on the melting temperature

At first some volume–temperature curves were determined at various pressures in order to find the appropriate conditions of temperature and pressure for the crystallization and annealing experiments. In *Figure 2* the change in piston height is plotted against temperature for nylon-12 at pressures of 4.9, 6.5 and 8.2 kbar. There is no abrupt change in volume; the polymer seems to melt over a broad temperature range. This may be accounted for by the fact that the polymer was quenched from the melt giving rise to an abundance of crystal imperfection. Nevertheless the end of the melting process can easily be discerned since there is a sharp turn due to the constant value of the thermal expansion of the true melt.

The effect of pressure on the melting temperature is illustrated in *Figure 3*, where the final melting point of the folded-chain crystals of nylon-12 is plotted as a function of pressure. In the pressure range up to 3 kbar the increase in melting temperature is approximately 20°C per kbar. This is comparable with the dependence of the melting temperature of

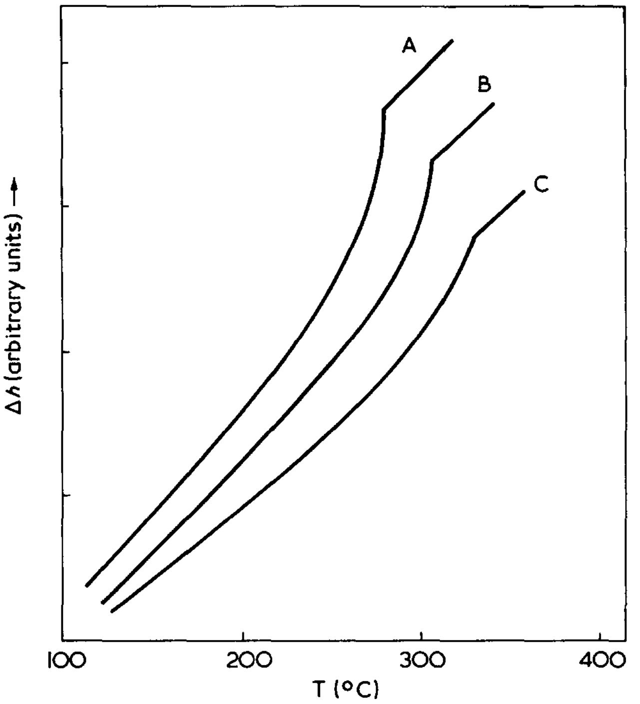

Figure 2 Change in piston height (Δ*h*) with temperature for nylon-12 at various pressures. A, nylon-12 at a pressure of 4.9 kbar; B, nylon-12 at a pressure of 6.5 kbar; C, nylon-12 at a pressure of 8.2 kbar

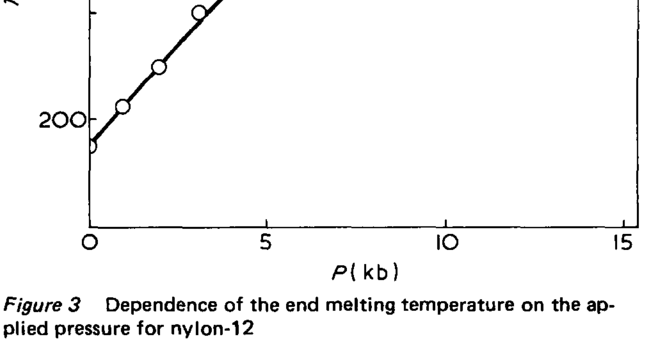

Figure 3 Dependence of the end melting temperature on the applied pressure for nylon-12

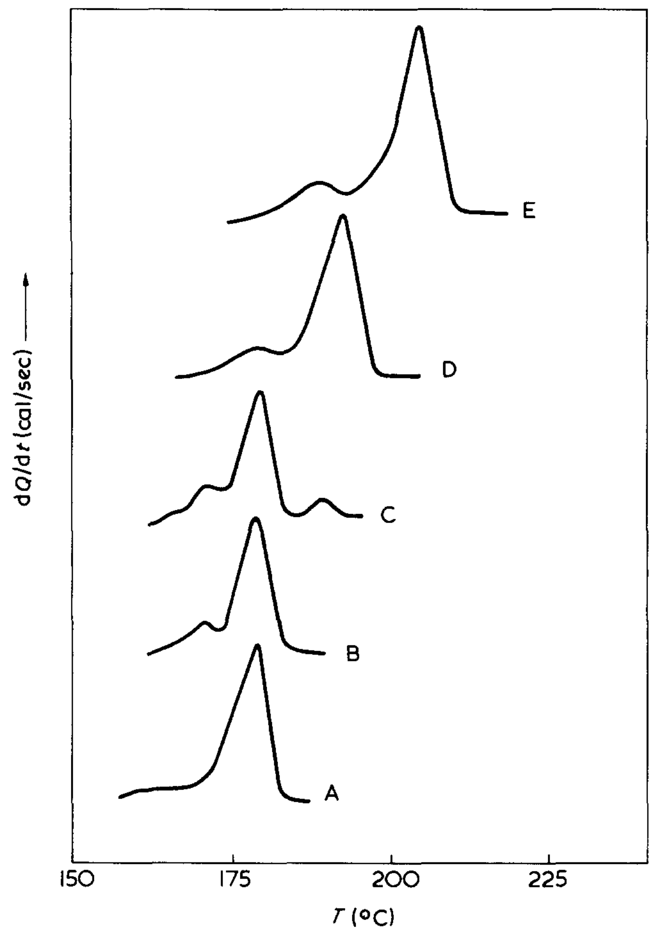

Figure 4 D.s.c. melting thermograms for various nylon-12 samples. A, original sample; B, sample crystallized at 260°C and 4.9 kbar for 16 h; C, sample crystallized at 250°C and 4.9 kbar for 16 h; D, sample crystallized at 240°C and 4.9 kbar for 16 h; E, sample crystallized at 240°C and 4.9 kbar for 48 h

polyethylene on pressure as reported by several authors[12,13] and that for nylon-6. The dependence of the final melting temperature on pressure levels off at higher pressure to a value of 12°C per kbar at a pressure of 8 kbar.

Crystallization under elevated pressure

Crystallization of nylon-12 under a pressure of 4.9 kbar was found to begin at a temperature of 240°C as judged from the decrease in volume upon lowering of the temperature. For the applied pressure this crystallization temperature is about 40°C below the final melting temperature of the folded-chain crystals. Similar values for the apparent supercooling were found for nylon-6 and nylon-11. The nylon-12 was allowed to crystallize isothermally for 16 h and was subsequently cooled down to room temperature in 1.5 h. The thermogram of this specimen (*Figure 4*) exhibits two melting peaks. The small peak is located at a temperature that corresponds to the melting peak temperature of the original sample. The large melting peak is found at 12°C above that of the small one. Extension of the crystallization time from 16 to 48 h resulted only in a shift of both peaks to higher temperatures. Crystallization from the melt under a pressure of 4.9 kbar at 260°C for 16 h, followed by cooling to room temperature in 1.5 h, did also result in multiple melting behaviour of the material (*Figure 4*), but no increase in melting peak temperature occurred. After crystallization at 250°C at this pressure the first higher melting crystals could be observed.

The occurrence of multiple melting peaks has been in some cases associated with the presence of low molecular weight polymer, for instance due to thermal degradation. This does not seem to be so for nylon-12 since the relative viscosity of the polymer, after pressure-induced crystallization, was 1.66 – slightly higher than that of the original material (1.57). The multiple melting-peak phenomenon here may be attributed to the presence of two crystalline modifications, the γ-form and the α-form, as indicated by the wide-angle X-ray diffraction data. The shift towards higher melting temperatures of the two peaks upon extension of the crystallization time might be due to an improvement of both crystalline structures.

Annealing under elevated pressure

Since the melting range of nylon-12 under pressure was rather broad, preliminary experiments were carried out to find the appropriate temperature for annealing. It was found that, at an annealing temperature of 240°C and a pressure of 4.9 kbar, the melting peak temperature at ambient pressure of the polyamide increased by 12°C when the annealing experiment was extended for a period of 16 h. Annealing at 260°C for the same pressure and period of time led to an increase in melting temperature of 16°C. That we are dealing here with annealing and not with melting may be inferred from the facts that the annealing temperature is still 20°C below the end melting temperature, and that the three discs

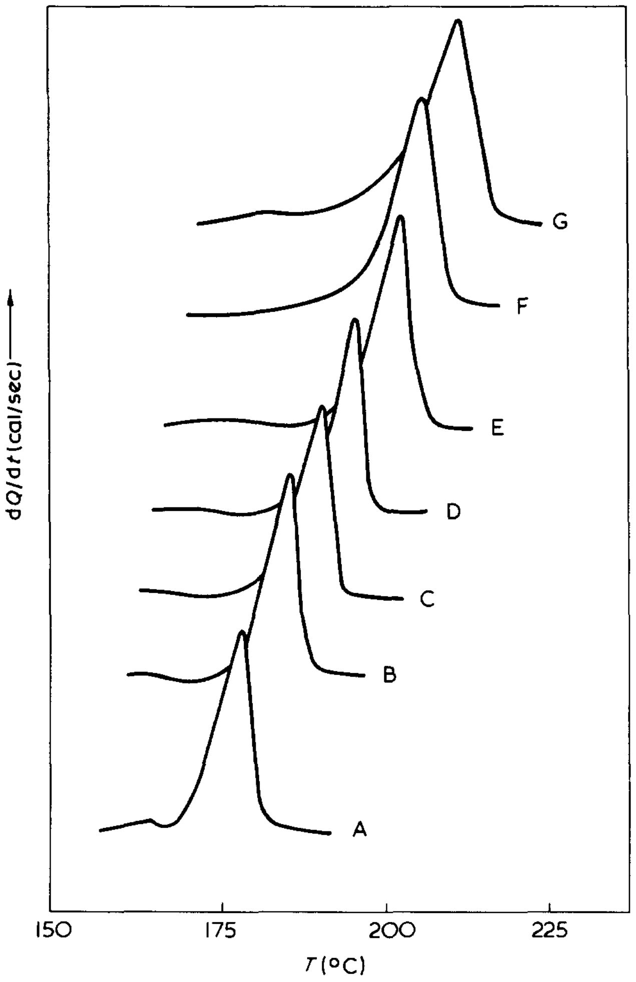

Figure 5 D.s.c. melting thermograms for various nylon-12 samples after annealing under various pressures for 48 h. A, original sample; B, sample annealed at 200°C and 2.0 kbar; C, sample annealed at 220°C and 2.9 kbar; D, sample annealed at 241°C and 3.9 kbar; E, sample annealed at 260°C and 4.9 kbar; F, sample annealed at 287°C and 7.2 kbar; G, sample annealed at 320°C and 9.8 kbar

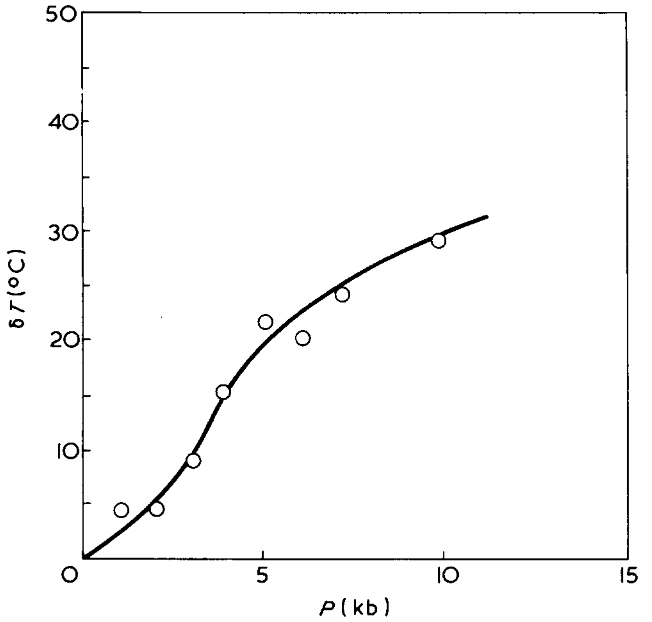

Figure 6 Dependence of the increase in atmospheric melting peak temperature (δT) on the annealing pressure. The annealing time was 48 h and the temperature 20° C below the end melting temperature for all pressures

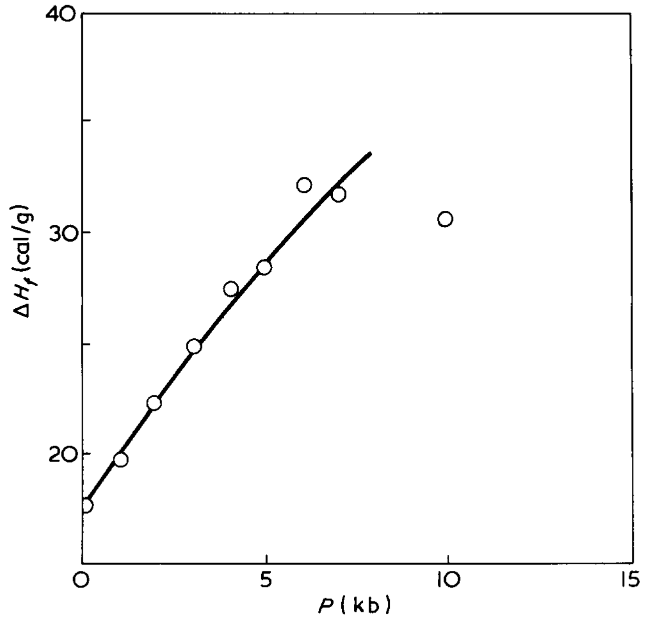

Figure 7 Dependence of the heat of fusion (ΔH_f) on the annealing pressure. The annealing time was 48 h and the temperature 20° C below the end melting temperature for all pressures

of nylon-12 that were put in the high-pressure cell did not stick together after annealing but could be easily separated. This was in sharp contrast to the experiments in which the three nylon-12 discs were heated under pressure above the end melting temperature. In the latter case the three discs became moulded together and fracturing did not occur along the original edges of the discs but somewhere across the three pieces.

The effect of pressure on the annealing process was examined in the following manner. The specimens were heated to temperatures 20°C below the end melting temperature of the folded-chain material under the corresponding pressure and the annealing period amounted to 48 h. The effect of pressure on the melting thermograms, on the increase in melting peak temperature (δT), and on the heat of fusion (ΔH_f) is given in *Figures 5–7*. It should be noted that the endotherms display one peak instead of two as in the case of pressure-induced crystallization. The heat of fusion increases from 16 cal/g to 32 cal/g and the maximum increase of the melting temperature is 30°C. The specimen annealed at 9.8 kbar and 320°C had an unexpectedly low heat fusion of 26 cal/g, while the increase in melting temperature for this specimen is still on the curve in *Figure 6*. The samples were subjected to further investigations in order to find out whether chemical modification might have taken place. It was found that all samples could be dissolved in concentrated sulphuric acid and that the relative viscosity of the sample annealed at 6.0 kbar and 270°C was 1.58, the same as that of the original polymer. The sample annealed at 9.8 kbar and 320°C did not dissolve but remained swollen to a degree of swelling of about 3. So the lower enthalpy of fusion of this 9.8 kbar sample originates from a rather effective manner of chemical crosslinking.

From the work on the annealing of nylon-6 and nylon-11 it was known that the solid state transformation under pressure was strongly time dependent. This effect for nylon-12 was examined by recording the displacement of the upper piston as a function of time during annealing at 4.9 kbar and 260°C. The change in piston height (Δh) is plotted against the logarithm of time in *Figure 8a*. This curve shows that the annealing process is rather slow for the first 30 min but then proceeds more rapidly and starts to level off after about 50 h. The increase in atmospheric melting peak temperature (δT) measured on new samples that were annealed at progressively longer times is a function of the logarithm of time

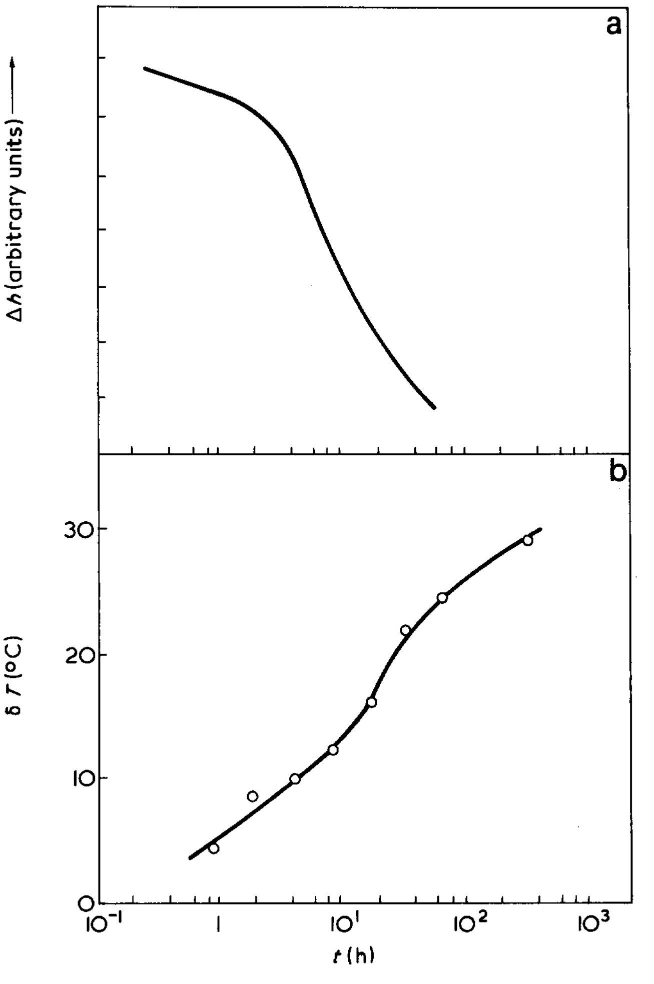

Figure 8 (b) Increase in atmospheric melting peak temperature (δT) after annealing at 260° C and 4.9 kbar for various times; (a) change in piston height (Δh) during annealing at 260° C and 4.9 kbar

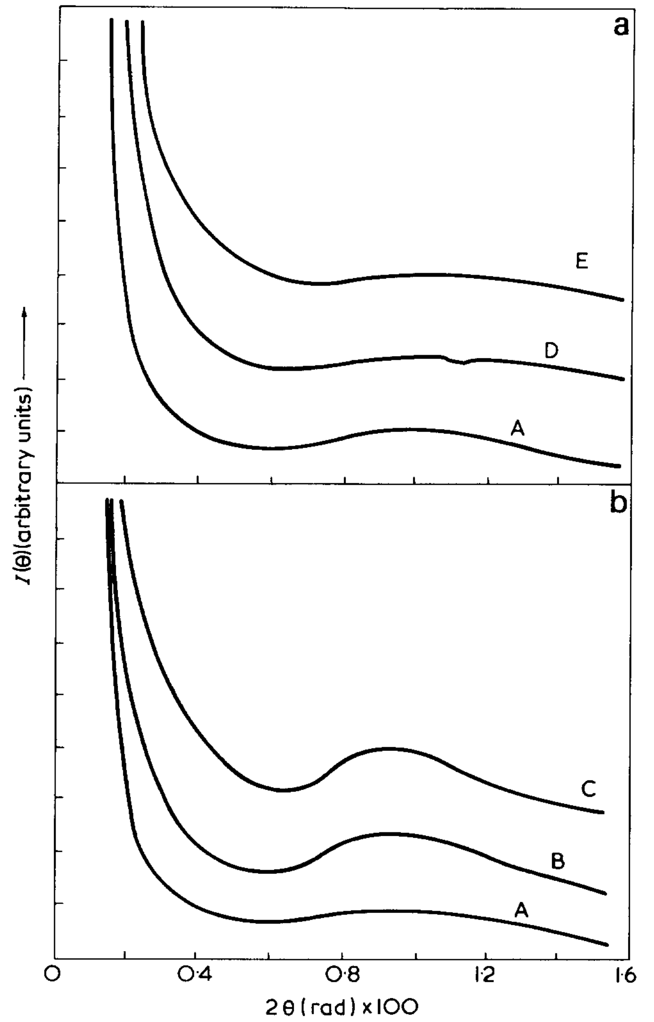

Figure 9 (b) Small-angle X-ray intensity curves for nylon-12 annealed at 165°C and ambient pressure for various times: A, original material; B, sample annealed for 20 h; C, sample annealed for 300 h. (a) Small-angle X-ray intensity curves for nylon-12 annealed at 260°C and 4.9 kbar for various times: A, original sample; B, sample annealed for 4½ h; C, sample annealed for 36 h

with a weakly sigmoidal shape as indicated in *Figure 8b*. The increase of melting temperature after 336 h was 30°C.

In order to gain a better insight into the annealing process some small-angle X-ray scattering experiments were performed. Samples annealed at ambient pressure and 165°C (20°C below the end melting temperature) display a weak maximum in the small-angle X-ray scattering curve (*Figure 9b*) corresponding to a long period of 150 Å. Upon annealing this maximum becomes more pronounced and shifts only slightly to a smaller angle. One may infer from these curves that the average long period increases somewhat upon annealing under the above conditions and the amount of crystalline material contributing to the Bragg reflection increases with time. *Figure 9a* shows the X-ray scattering curves for samples annealed at 4.9 kbar and 260°C for various times. The curves for longer annealing times up to 36 h display only a very faint maximum that has broadened substantially. Annealing leading to an increase in melting temperature of 30°C and a doubling of the crystallinity is therefore not due to a process whereby all lamellar crystals have a uniform long period but the distribution of the crystal dimensions has broadened substantially.

Crystalline structure

Wide-angle X-ray diffractograms for various samples of nylon-12 are shown in *Figure 10*. The diffraction pattern of the original material displays only one reflection at an angle corresponding to a periodicity of 4.25 Å. This reflection stems from the pseudo-hexagonal or monoclinic γ phase which is normally formed on crystallization of nylon-12 at one atmosphere[8,14]. The sample solidified by the pressure-induced crystallization method at 4.9 kbar and 240°C over a period of 16 h exhibits additional reflections at 3.90 and 4.55 Å indicating that a partial transformation into a crystalline α-modification has taken place. This kind of polymorphism has also been reported by Northolt *et al.*[15], for nylon-12 that was stretched just below the melting temperature. In the diffraction pattern of the sample annealed at 4.9 kbar and 240°C for the same period of 16 h the intensity of the peak at 3.90 Å originating from the α structure exceeds that of the γ peak.

In general, for samples annealed under pressure, the γ peak is less than that for the pressure-induced crystallized nylon-12. It may therefore well be that the second melting peak in the thermograms of these samples is due to the remains of the γ modification.

Morphology

The morphology of fracture surfaces of the crystallized and annealed nylon-12 was examined in order to achieve a better understanding of the crystallization and annealing process under elevated pressure. *Figure 11* shows a scanning electron micrograph of the original quenched polymer. This material was rather tough and could only be broken after being cooled down to liquid nitrogen temperature. *Figure 11* does not reveal any distinct spherulitic structure. A fracture surface of the polyamide crystallized at 4.9 kbar and 240°C

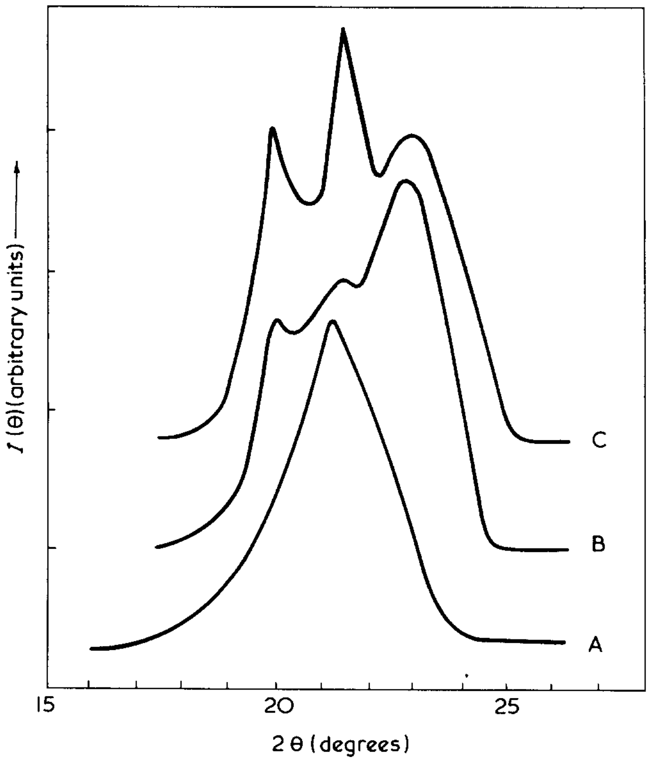

Figure 10 Wide-angle X-ray diffraction patterns of various nylon-12 samples: A, original sample; B, sample annealed at 240°C and 4.9 kbar for 16 h; C, sample crystallized at 240°C and 4.9 kbar for 16 h

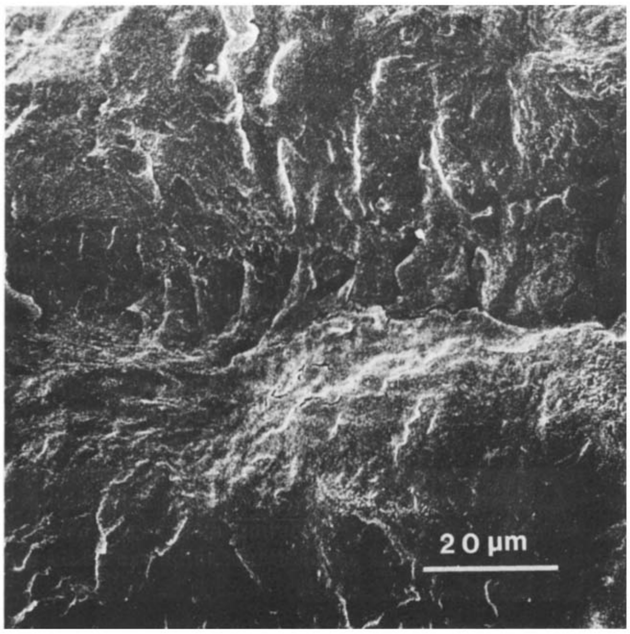

Figure 11 Scanning electron micrograph of a fracture surface of the original quenched polymer

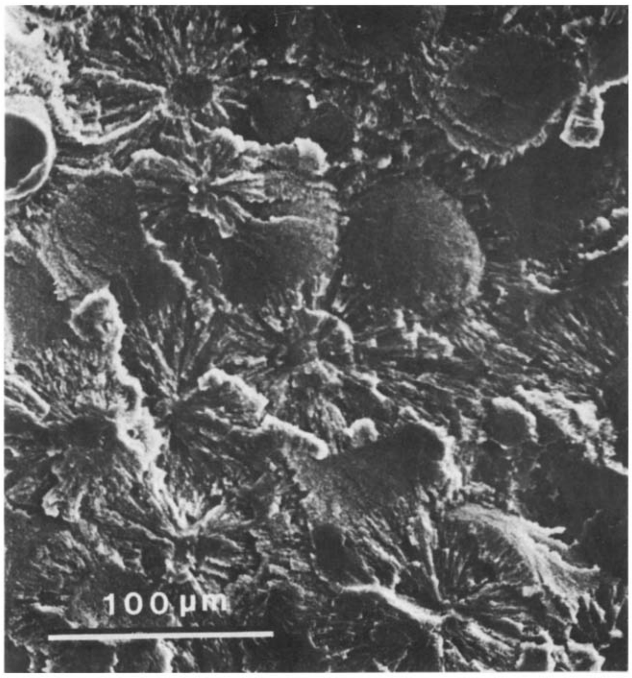

Figure 12 Scanning electron micrograph of a fracture surface of nylon-12 crystallized at 240°C and 4.9 kbar for 48 h

for 48 h is illustrated in *Figure 12*. This scanning electron micrograph reveals that crystallization has brought about a clear delineation of the spherulites of almost 100 μm in diameter. Another interesting feature is that one can distinguish convex and concave surface areas that are smooth, in addition to radially striated spherical portions. The latter originate from trans-spherulitic fracture, the former from inter-spherulitic fracture. The well-annealed or crystallized material fractured at room temperature remarkably easily, suggesting that also the trans-spherulitic fracture path is unlikely to come across many tie molecules or hydrogen bonds. *Figure 13* shows a spherulite in more detail and *Figure 14* gives a scanning electron micrograph of the centre of the spherulites which is frequently noticed to be a hole. It might be that this hole was occupied by an impurity of cylindrical shape that served as a foreign nucleus.

Finally some second-stage replicas were viewed in the transmission electron microscope and some characteristic pictures are illustrated in *Figures 15–17*. *Figure 15* presents a transmission electron micrograph of a replica of the fracture surface of the starting material. The variations in the height on this micrograph are of the order of 150 Å corresponding to the long period measured by small-angle X-ray scattering. Electron micrographs of replicas of the fracture surfaces of well-annealed or crystallized specimens are illustrated in *Figures 16* and *17*. *Figure 16* shows that the surfaces are rather rough and some terraces may be discerned. This electron micrograph exhibits a surface topology very

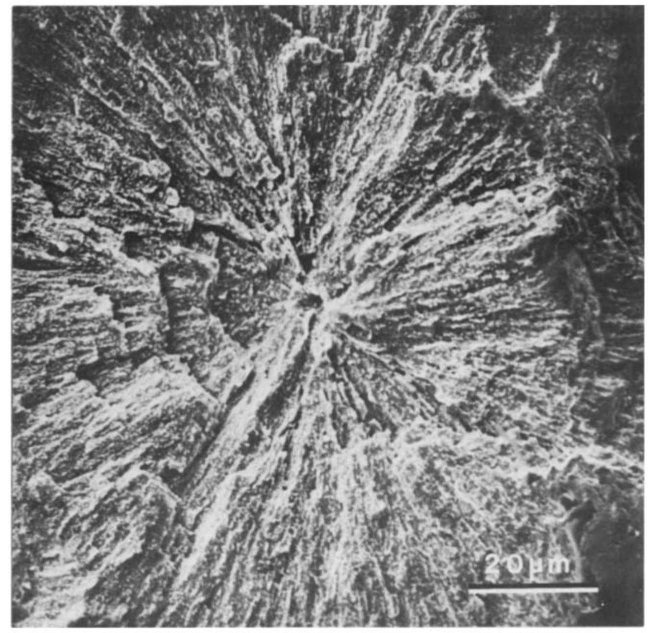

Figure 13 Scanning electron micrograph of a fracture surface of nylon-12 annealed at 287°C and 7.2 kbar for 48 h

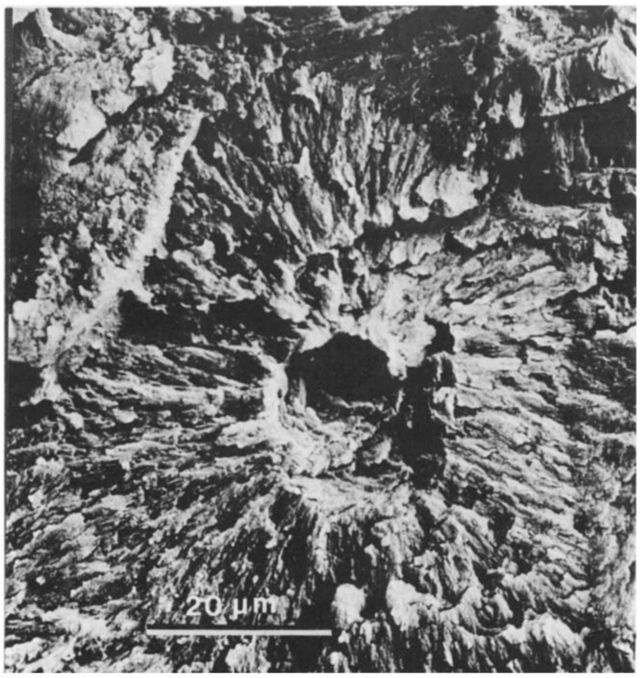

Figure 14 Scanning electron micrograph of a fracture surface of nylon-12 annealed at 260°C and 4.9 kbar for 8½ h

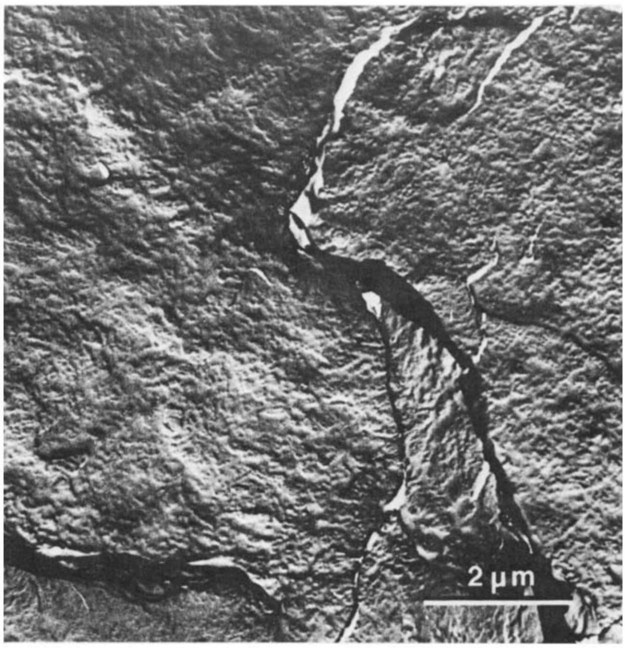

Figure 15 Transmission electron micrograph of a second-stage replica of a fracture surface of the original material

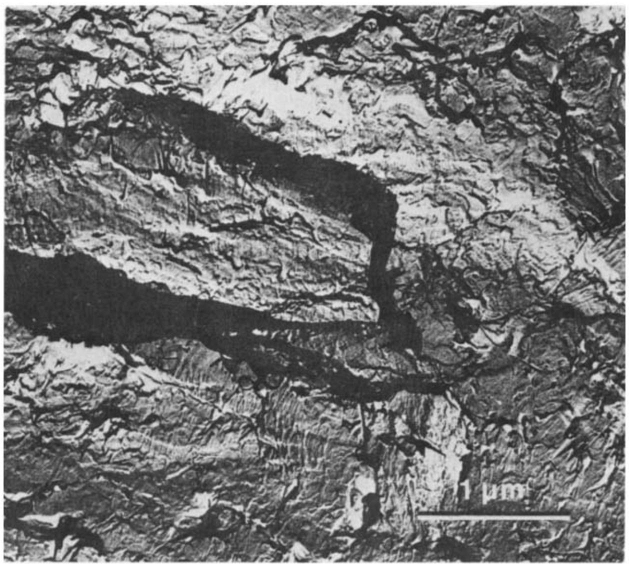

Figure 16 Transmission electron micrograph of a second-stage replica of a fracture surface of nylon-12 annealed at 260°C and 4.9 kbar for 70 h

similar to that found for pressure crystallized or annealed nylon-6 consisting of positively birefringent spherulites. Indeed, observation in the polarizing microscope of nylon-12 annealed at 260°C and 4.9 kbar for 36 h showed positive spherulites. In nylon-12 crystallized or annealed at a lower temperature two types of spherulites were observed. In addition to the negative spherulites found in this sample, spherulites were also seen which were not birefringent. *Figure 17* represents the striated structures frequently observed in these specimens comparable to that found for pressure-treated nylon-11. These striations run tangentially in the spherulites in very similar fashion to the striations in the chain-extended spherulites of polyethylene as found by Wunderlich *et al.*[16]. These observations suggest that the polyamide chains are oriented perpendicular to the radial arms of the spherulites. In contrast to the results on high pressure crystallized spherulites in polyethylene the edges of the lamellar crystals could not be detected and it seems that the polyamide chain-ends are not localized in certain planes.

DISCUSSION

The experimental observations described above demonstrate that high pressures also have a profound effect on the crystallization and annealing of nylon-12. The most conspicuous result might be the increase of the atmospheric melting temperature by as much as 30°C for well-annealed samples. But this finding does not differ appreciably from the increase in melting temperature of nylon-6 and nylon-11. This leads to the conclusion that, as far as this aspect is concerned, the pseudo-hexagonal structure of the starting material did not give rise to any specific phenomenon.

The crystallization process as induced by pressures of 4.9 kbar may proceed initially by the formation of folded chain crystals having the pseudo-hexagonal structure which partially transforms into the α modification during the annealing stage immediately following the primary crystallization. Such a mechanism would comply best with the double melting peak thermograms and the wide-angle X-ray diffraction patterns. The annealing process is actually characterized by a remarkable broadening of the distribution of lamellar dimensions as revealed by the small-angle X-ray scattering curves and by the polymorphism. That is to say the hydrogen bond network occurring in the γ modification has to be broken and new hydrogen bonds have to be formed that correspond to the α modification. It is not yet clear whether this lateral rearrangement of the chains is accompanied by a migration of straight stems through the lattice to achieve a larger fold length or whether the folds move giving rise to a discontinuous increase in fold length as proposed by Dreyfuss and Keller[17]. Furthermore it should be borne in mind that the marked increase in crystallinity, as reflected by a doubling of the heat of fusion, cannot originate only from a removal of the chain folds but also stems from a

Figure 17 Transmission electron micrograph of a second-stage replica of a fracture surface of nylon-12 crystallized at 230°C and 4.9 kbar for 40 h

transformation at the expense of the amorphous part which constitutes the major portion of the polyamides.

Finally, as we are dealing here with polyamides, possible equilibriation and redistribution reactions[18] in the amorphous regions of the polymer crystals may affect the disappearance of chain folds. These chemical processes are proposed to proceed very rapidly by catalysed reactions of amide bonds in the polymer chains and especially NH_2 end-groups, that are excluded from the crystalline core[19,20]. The relative viscosity of nylon-12, which appeared to be constant after several high-pressure treatments does not give conclusive evidence on this point. However, since the increase in melting peak temperature for annealing of nylon-6, 11 and 12 is more or less constant, this suggests that the improvement of the solid is not proportional to some function of the concentration of amide groups. Further systematic investigations have to be performed in order to disclose the actual nature of the intriguing process, resulting in more perfect crystalline materials, that occurs in polyamides at elevated pressure.

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