# Crystallization of polyamides under elevated pressure: 3.The morphology and structure of pressure-crystallized nylon-6 (polycapramide)

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The morphology and structure of nylon-6, crystallized from the melt under elevated pressure, has been investigated. Scanning and transmission electron microscopy on replicas of the fracture surfaces reveal that crystallization under pressures exceeding 4 kbar (1 kbar = 100 MN/m$^2$) results in rough lamellar structures with some step heights corresponding to the contour lengths of the chains. Infra-red spectroscopy on the pressure-crystallized nylon-6 shows a considerable improvement of crystalline order, a closer packing of the polymer chains within the crystal, and the presence of a large proportion of free N–H groups. An absorption band at 1170 cm$^{-1}$ was assigned to the presence of folds in the nylon-6 crystals. Wide-angle X-ray measurements indicate that the crystal modification of the pressure-crystallized nylon-6 is predominantly the alpha phase. Pressure gives rise to an increase in crystallite dimensions as well as to a decrease of the distance between the crystal planes bonded by the hydrogen bonds and by the Van der Waals forces.

## INTRODUCTION

In preceding papers on this topic it was demonstrated[1,2] that the melt of nylon-6 may be transformed into a solid of high crystallinity, if the crystallization is induced by pressure exceeding 4 kbar (1 kbar = 100 MN/m$^2$), the polymer is purified, and thermal decomposition is minimized by heating the polymer under pressure. The highest melting temperature and heat of melting found for pressure-crystallized samples were 256°C and 37 cal/g, respectively.

This article deals with the morphology and structure of the pressure-crystallized nylon-6. Scanning electron microscopy was employed to obtain an overall view of the nylon fracture surface. Detailed observation of the polymer structure was conducted on two-stage replicas using transmission electron microscopy. Transmission infra-red spectroscopy was applied to provide information on the effect of pressure on hydrogen bonding, crystalline and amorphous bands, and bands that may be associated with the folds. The wide-angle X-ray diffraction technique was employed for the comparative study of the crystal modification, unit cell, crystalline order and lateral crystal dimension of the nylon-6 samples crystallized under various conditions.

## EXPERIMENTAL

### Materials and techniques

The nylon-6 sample used as a starting material throughout these investigations did not contain additives and was extruded under high vacuum in order to remove the free caprolactam and to reduce the void content. Details of this procedure were described in part 2 in which this nylon-6 was referred to as sample C. The viscosity-average molecular weight of the extruded nylon-6 was 95 x 10$^3$.

### Crystallization under pressure

The samples were pressurized to 8 kbar in a high pressure cell and heated to the desired crystallization temperatures. The pressure was reduced to 100 bar, in order to melt the polymer for 15 min, and crystallization was induced by applying a proper crystallization pressure for a certain period of time. At the end of the crystallization run, the cell was cooled to room temperature and the pressure was released.

### Electron microscopy

A Jeol scanning electron microscope was used (25 kV, 10$^{-9}$ A, and diaphragm 200 μm) to examine the fracture surfaces, which were shadowed with gold. Two-stage surface replicas of the fractured samples were made using cellulose acetate film (Bioden) swollen in methyl acetate according to the method described by Wunderlich[7].

After replication, the dried cellulose acetate films were shadowed with platinum at an angle of 45° and backed during rotation with carbon. To check whether the methyl acetate used for replication had any effect on the surface morphology of the nylon-6 samples, one-stage replicas were also prepared. Small pieces of the shadowed polymer sample were placed on the grids, and the polymer was dissolved with the vapour from boiling formic acid. No differences in the surface morphology were found as a result of the replication technique used. A Philips EM 200 electron microscope was used for examining the replicas.

### Infra-red spectroscopy

A Perkin–Elmer Model 421 grating spectrophotometer

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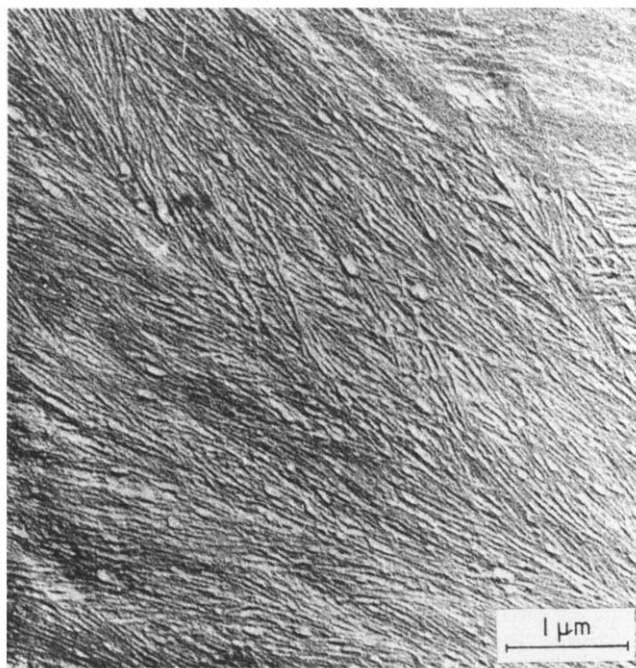
*Figure 1* Transmission electron micrograph of a replica of the fracture surface of a nylon-6 sample crystallized isothermally from the melt at 215°C for 48 h under atmospheric pressure. Magnification 15 000 X.

was used for infra-red studies of the nylon-6 samples in the wavenumber range from 4000 to 250 cm$^{-1}$. The infra-red spectra of the folded-chain material were recorded using a polymer film of 0.1 to 0.25 mm thickness cast from formic acid on a KBr block. Samples in powdered form were precipitated from formic acid using acetone—water mixture (1:1 by volume). Cast films, as well as the precipitated samples, were washed with water and acetone. The pressure-crystallized material was powdered with a ball-mill. All the samples used for the i.r. measurements were dried under a vacuum of 10$^{-6}$ mm Hg and stored in a desiccator over phosphoric pentoxide for at least 24 h before experimentation. Samples in powdered form were mixed with KBr (5 mg of polymer with 400 mg of KBr), and tablets were formed by applying standard techniques.

*X-ray diffraction*

The X-ray diffraction patterns were recorded at room temperature over the range of diffraction angles ($2\theta$) from 7° to 45° with nickel-filtered CuK$\alpha$ radiation using a Philips generator equipped with a diffractometer and scintillation counter. The conditions of the X-ray scattering were as follows: the voltage was 42 kV, a current of 18 mA was used, time constant was 2, window 250 x 1 and the scan speed 1°/min. The positions of two principal diffraction peaks at ($2\theta$) 19.9° (alpha$_1$) and 23.75° (alpha$_2$), which correspond to the spacing $d\ \alpha_1 = 4.4$ Å and $d\ \alpha_2 = 3.8$ Å respectively, were observed in order to obtain information on the structural modification, unit cell, crystalline order and crystal dimension of the nylon-6 samples crystallized under various conditions.

RESULTS AND DISCUSSION

*Electron microscopy*

Most of the high pressure-crystallized samples fractured

during removal of the nylon from the cell. In some cases portions of the nylon were also quenched in liquid nitrogen and subsequently fractured using a hammer but the morphological features of the surfaces obtained by both procedures were the same.

Nylon-6 crystallized at ambient pressure could only be fractured after quenching in liquid nitrogen. *Figure 1* shows a transmission electron micrograph of a replica of a fracture surface of nylon-6 crystallized isothermally from the melt at 215°C and atmospheric pressure for 48 h. The melting temperature of this sample was 225°C and the heat of melting was 21 cal/g as determined by the d.s.c. method. The thickness of the radially arranged, thin lamellae appears to be 70 Å as estimated from this micrograph. This is in agreement with values determined by small-angle X-ray scattering.

When a pressure of 1.5 kbar is applied and nylon-6 crystallizes at a temperature of 230°C for 36 h, the spherulitic structure becomes coarser as revealed by the scanning electron micrograph of a fracture surface in *Figures 2* and *3*.
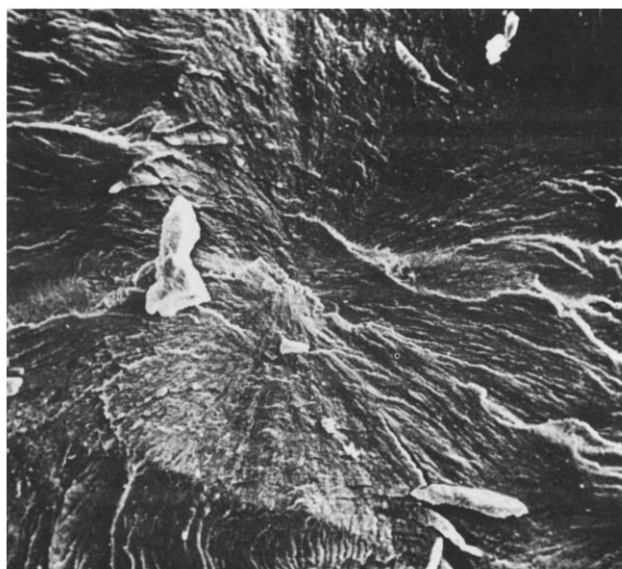


*Figure 2* Scanning electron micrograph of a fracture surface of nylon-6 crystallized under a pressure of 1.5 kbar, at temperature 230°C for 36 h. Magnification 800 X
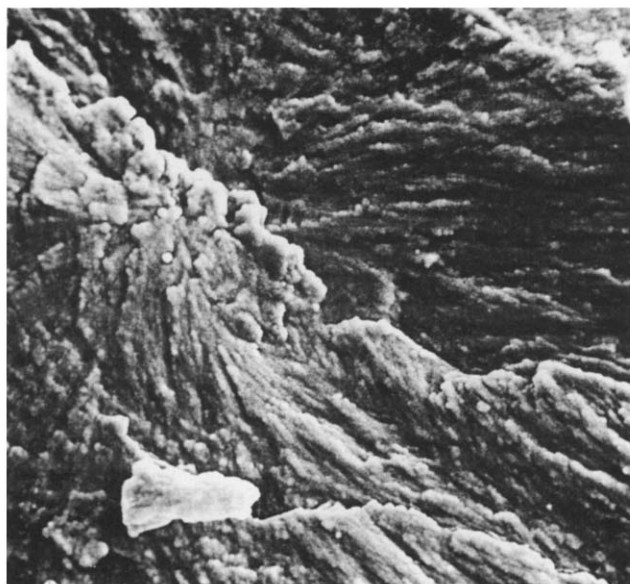


*Figure 3* Scanning electron micrograph of a fracture surface of the nylon-6 sample shown in *Figure 2*. Magnification 4000 X
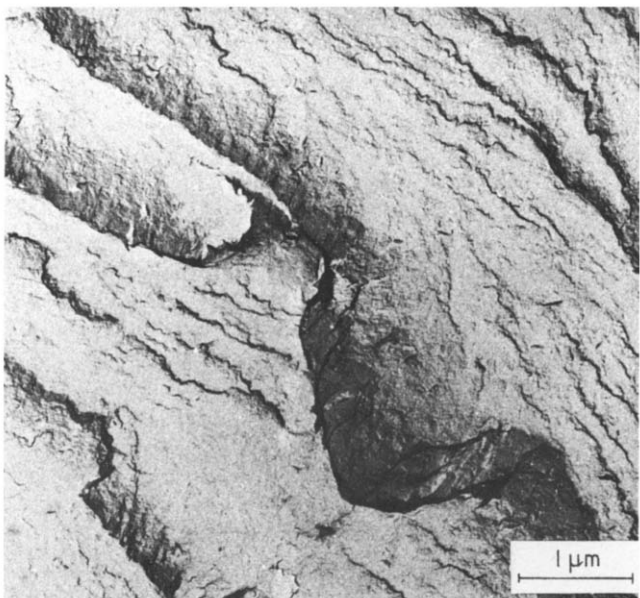
*Figure 4* Electron micrograph of a replica of a fracture surface of nylon-6 crystallized under pressure 3.5 kbar at 235°C for 36 h. Magnification 15 000 X
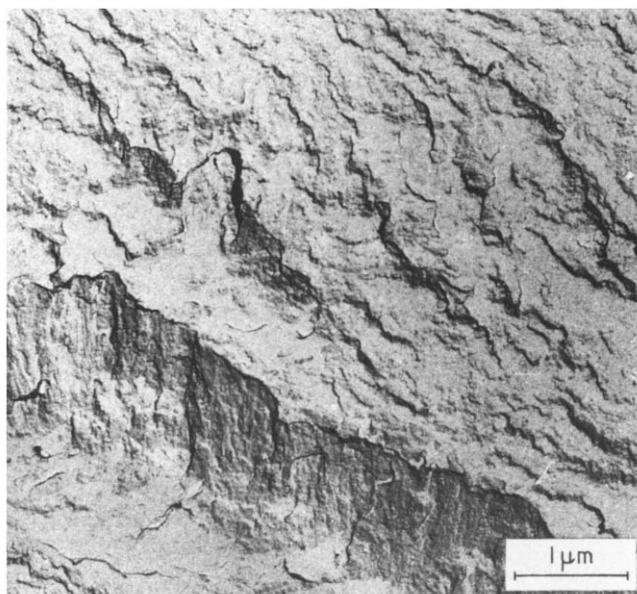


*Figure 5* Electron micrograph of a replica of a fracture surface of nylon-6 crystallized at 3.5 kbar and 245°C for 72 h. Magnification 15 000 X

Small-angle X-ray scattering shows that the long period is increased to 190 Å but the melting temperature is 225°C, the same as that of the nylon-6 sample with a lamellar thickness of 70 Å, and the heat of fusion (15.5 cal/g) is even less than that of the 70 Å specimen.

Crystallization under higher pressures leads to larger step heights in the fracture surfaces. *Figure 4* shows the transmission electron micrograph of a typical example. The nylon-6 was crystallized at 245°C and 3.5 kbar for 36 h. The atmospheric melting temperature and heat of melting for this sample were 229°C and 21 cal/g respectively. Extension of the crystallization time to 72 h, with the other conditions remaining the same, leads to more pronounced step heights in the fracture surface (*Figure 5*) (some lamellae are 1000 Å thick) and an increase in the melting tempe-

rature from 229° to 234°C and heat of melting from 21 to 22.5 cal/g.

Electron micrographs of fracture surfaces of nylon-6 crystallized at 295°C and 6.5 kbar for 48 h are shown in *Figures 6–8*. This sample had a melting temperature of 250°C, a heat of melting of 37 cal/g and a density of 1.205 g/cm$^3$ pointing to a high crystallinity[29], of the order of 90%. *Figure 6* shows the middle part of a spherulite and the radial



*Figure 6* Electron micrograph of a replica of a fracture surface of nylon-6 crystallized at 295°C for 48 h, under pressure 6.5 kbar. The arrow shows the growth direction. Magnification 15 000 X



*Figure 7* Transmission electron micrograph of a replica of another part of the fracture surface of the sample shown in *Figure 6*. Magnification 15 000 X
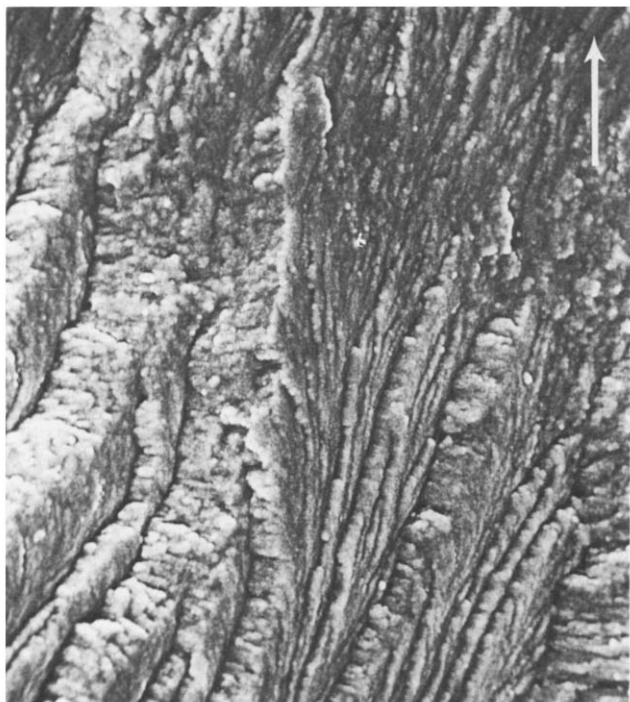
*Figure 8* Scanning electron micrograph of a fracture surface of nylon-6 crystallized at 295°C for 48 h, under pressure 6.5 kbar. Magnification 4000 X

arrangement of a stack of lamellae. The thickness of the lamellae may correspond to the bright strips running radially from the spherulite centre, and ranges up to 7000 Å. The thickness of these lamellae corresponds roughly to the contour length of nylon-6 with a molecular weight of $90 \times 10^3$. The fracture surface also exhibits lamellae of larger dimensions, with a thickness of about twice the chain length, as well as lamellae with a thickness of 0.1 µm and some of about 400 Å. The variations in size of the step heights in the fracture surfaces may be due to fractionation accompanying the crystallization under pressure. The results presented here are in close agreement with data by Wunderlich on nylon-6 produced by zone-polymerization of caprolactam[28]. He found that step heights in the fracture surfaces corresponded to the extended-chain length of the nylon molecules while the melting temperature was 226°C and the heat of fusion 24.8 cal/g.

The general impression of the fracture surfaces of nylon-6 is that they are considerably rougher than those of pressure-crystallized polyethylene. For the latter polymer one frequently finds striated lamellar surfaces resulting from breaking along the polymer chains. To explain the surface morphology of pressure-crystallized nylon-6, it should be borne in mind that, during mechanical loading, cracks are likely to propagate through many critical flow regions which contain less ordered or tie molecules and other defects[3–6]. The marked increase in brittleness resulting from crystallization under elevated pressure may be attributed primarily to a lowering of the density of interlamellar links and tie molecules as a result of chain extension. Furthermore, it should be noted that the spherulites of nylon-6 are positive, implying that the hydrogen bonds are parallel to the radial arms of the spherulites[30] and the remaining folds are located in the tangential planes. Consequently, the cracks may preferentially proceed along the (010) planes containing the chain ends as well as impurities rejected from

the crystal growth front and along the (002) hydrogen bonded sheets.

Step heights corresponding to the contour length of the chain may preferentially be formed by fracturing (200) planes along the hydrogen bonded sheets if, locally, chain folds are absent. This will occasionally occur when spherulite radii are oriented parallel to a crack already formed interspherulitically. The roughness of the fracture surface could then arise if the hydrogen bonded sheets were somewhere connected by some folds or hydrogen bonds in the (200) plane due to disclinations of chains.

Cracks then propagate through the defects in the hydrogen bonded sheets and proceed along other (002) planes as depicted in the model in *Figure 9*. This interpretation is in essence borne out by observations of a substantial portion of non-hydrogen bond N–H group as disclosed by infra-red spectroscopy.

### Infra-red spectroscopy

*Figure 10* shows typical infra-red spectra of nylon-6. Spectrum A was recorded for folded-chain nylon-6 crystallized at atmospheric pressure, and spectrum B for pressure-crystallized nylon-6. The most interesting differences between the spectra of these two nylon samples were observed for the frequency range from 4000 to 2500 cm$^{-1}$ and from 1600 to 800 cm$^{-1}$, and hence only these parts are presented in *Figure 10*. Information about the hydrogen bonding can be acquired by examining the N–H stretching vibration at 3290 cm$^{-1}$ [9–18]. It was found that the band at 3290 cm$^{-1}$ for pressure-crystallized nylon-6 shifted in the direction of lower frequencies. This indicates that the N–C bond length is shortened, i.e. a closer packing of the polymer chains as a result of a stronger attraction between H and C. At the same time a shift of about 10 cm$^{-1}$ toward higher frequencies was observed for the bonds at 2920 and 2845 cm$^{-1}$. Since these bonds are assigned to the asymmetric and symmetric vibrations of the CH$_2$ groups[9–18], the shift toward higher frequencies means that pressure crystallization gives
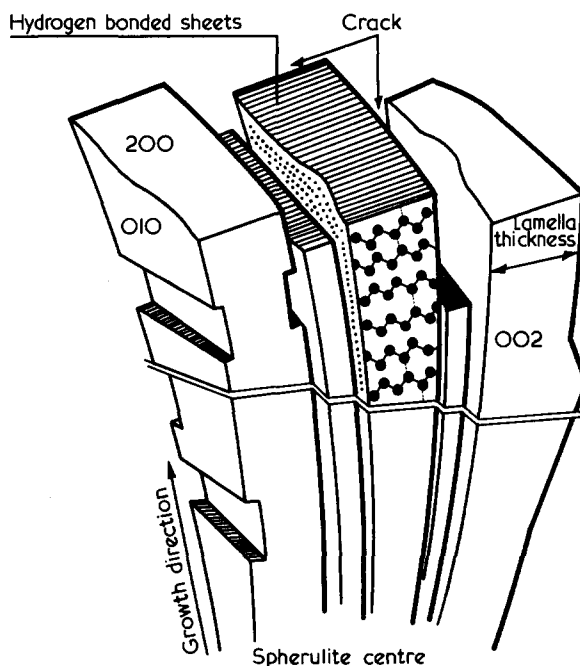


*Figure 9* Model proposed for fracturing behaviour and surface morphology of the chain-extended crystals of nylon-6
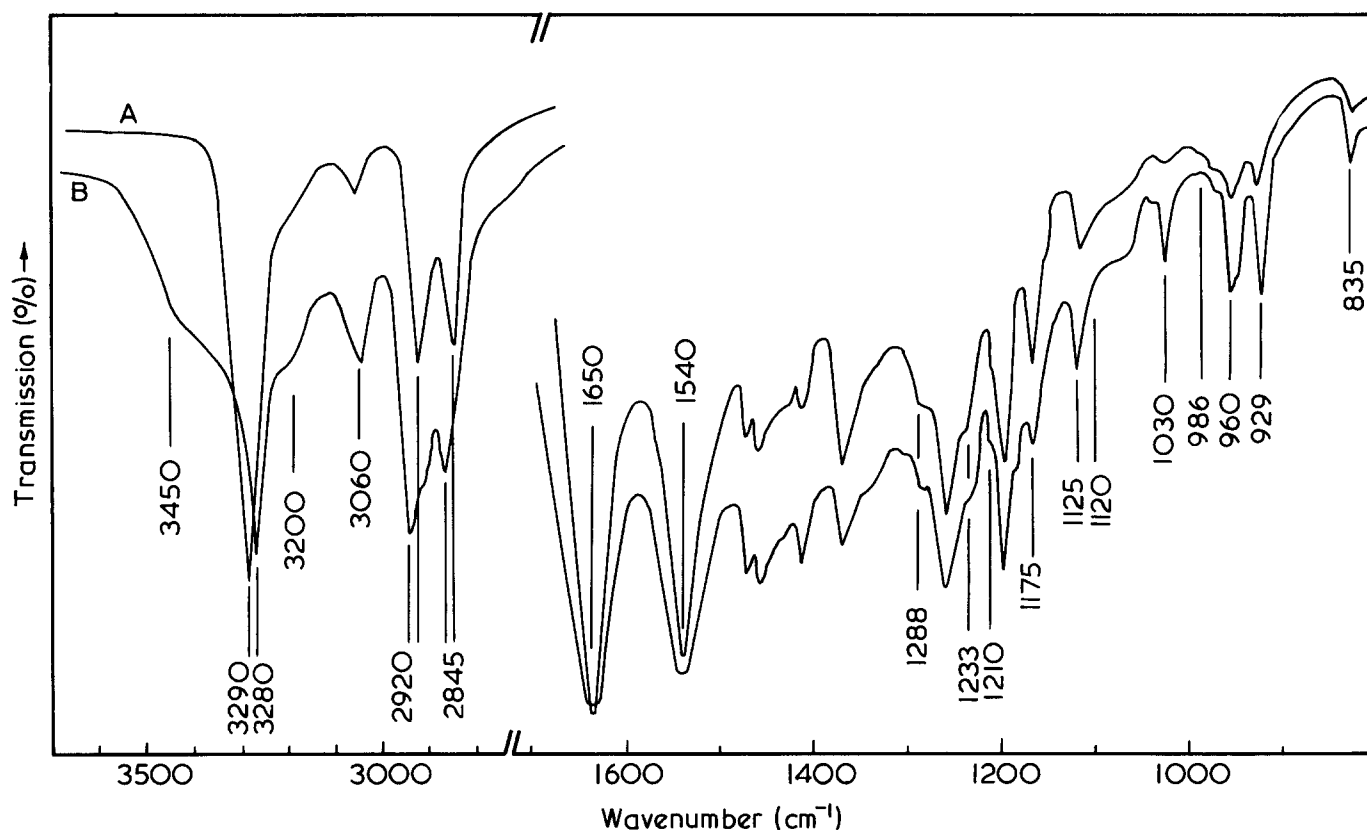
*Figure 10* Infra-red spectra of nylon-6 samples crystallized under various conditions: A, sample crystallized isothermally from the melt at 215°C for 48 h under atmospheric pressure, folded-chain crystals; B, sample crystallized at 295°C for 48 h under pressure 6.5 kbar, chain-extended crystals

rise to a closer packing of neighbouring chains, a decrease in the mean C—H bond length and an increase in the H—C—H angle. This inference is also corroborated by the diminution of the symmetric $CH_2$ stretching bond for the pressure-crystallized nylon-6 whereas the asymmetric bond decreased only a little. These observations are in accordance with the data by Reynolds and Sternstein on the effect of pressure on the infra-red spectra of some hydrogen bonded polymers[31]. There are also other peculiar differences between the spectra of the pressure-crystallized and the ordinary nylon-6. Thus in the range between 3400 and 3500 cm$^{-1}$, where unbonded N—H groups absorb[9,13,15,16,32,33], there is a significant absorption in the spectrum for the pressure-crystallized nylon-6. Polyamides crystallized at ambient pressure show less than 1% of unbonded N—H groups, as is known from the work by Trifan[32] and Bessler[33]. A broad absorption bond in the 3400 –3500 cm$^{-1}$ region may also arise from the presence of water in nylon[34–36] but this interpretation cannot be applied to the pressure-crystallized nylon-6 since we have taken measures to keep the samples dry. Also, the results of the X-ray diffraction patterns prove the absence of water in our nylon-6 specimen. Campbell[37] showed that water in nylon gives rise to an increase in the height of the alpha$_1$ peak in the X-ray diffraction pattern at 20° ($2\theta$), and a decrease in the height of the alpha$_2$ peak at 23.5°. The alpha$_2$ peak for the pressure-crystallized nylon-6 is about twice as high as the alpha$_1$ peak, as is illustrated in *Figure 11*. This strongly supports the assumption that the samples investigated did not contain water.

The occurrence of free N—H groups in the pressure-crystallized nylon-6 may be attributed to the fact that re-arrangement of adjacent chains takes place in this mode of crystallization so that not all the chains are antiparallel, and
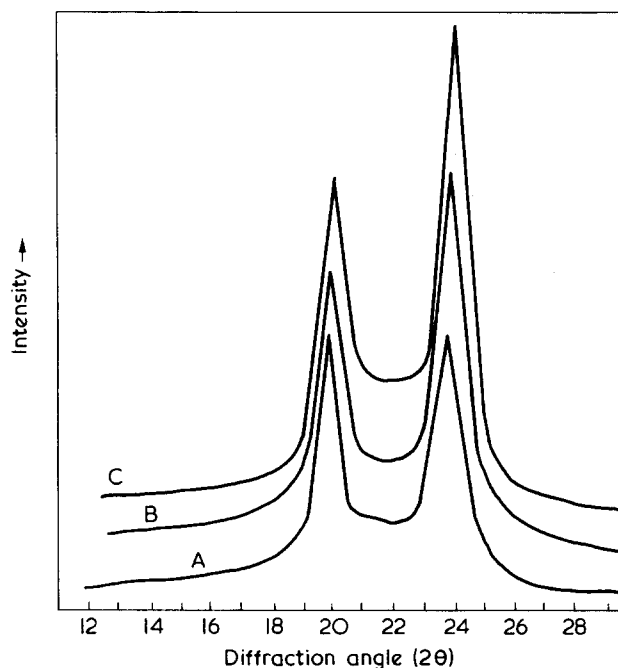


*Figure 11* Wide-angle-X-ray scattering curves of nylon-6 samples crystallized under various conditons: A, sample precipitated from formic acid and dried at 180°C for 48 h under vacuum 10$^{-6}$ mmHg; B, sample crystallized from the melt at 280°C and 6.5 kbar for 48 h; C, sample crystallized from the melt at 280°C and 6.5 kbar for 64 h

some will be arranged in a parallel manner. Parallel chains in flat zig-zag conformation can only form half of the total number of possible hydrogen bonds. The presence of free N—H groups could also account for the fact that the heat of fusion is relatively low, whereas the morphology of the

fracture surfaces suggests that the chains might have reached a high degree of extension.

The isolated maximum at 3060 cm$^{-1}$ resulting from a combination of vibrations of NH groups, and a shoulder at 3200 cm$^{-1}$ assigned to *cis–trans* isomerism of amide group[33] or Fermi resonance of Amide I + Amide II with $v$ (NH) group, also displays an increase in intensity. This increase in intensity observed for bands related to the intramolecular hydrogen bonded NH groups[9] suggests that, during crystallization under pressure, some twisting of polymer chains can occur, resulting in incomplete hydrogen bonding within the sheets. An increase of the intensity at 3200 cm$^{-1}$, accompanied by more intense bands at 1641 and 1545 cm$^{-1}$ assigned to Amide I and Amide II respectively, seems to support the suggestion made above. The bands at 1210 and 1233 cm$^{-1}$ assigned to *gauche* vibration of the HN–CH$_2$ group in the unique conformation in tightly folded chains with adjacent re-entry, and a band at 1288 cm$^{-1}$ assigned to *gauche* vibration of CO–CH$_2$ in the fold, may be related to the presence of folds in the alpha-form of nylon-6[19].

It was found that the intensity of these bands, in the infra-red spectra of the pressure-crystallized nylon-6, was within the limit of experimental error equal to that recorded for the folded-chain samples. Thus it seems that the presence or absence of these bands in the infra-red spectra of the pressure-crystallized nylon-6 may not necessarily be a measure of the chain extension. This suggestion agrees also with Koenig's finding[19] that, although annealing of nylon-6 increased the long period of the crystals, no decreasing of the infra-red 'fold bands' was observed.

From comparison of the infra-red spectra of the folded-chain samples and of those crystallized under pressure exceeding 5 kbar, it is evident that the intensity of the crystalline bands[19–26] increases and the intensity of the amorphous bands decreases for the pressure-crystallized samples. The presence of a weak absorption in the amorphous region of the infra-red spectra shows, however, that some amount of less ordered amorphous material is still left in the pressure-crystallized nylon-6, in accordance with the crystallinity derived from density measurements. It was found that the intensity of the band at 1175 cm$^{-1}$ related to $\gamma_t$ (CH$_2$) or $v$ (C$_\alpha$N) vibration[13] decreased as the extension of chains in the pressure-crystallized samples increased. It seems that, to some approximation, the absorption band in this frequency range may be a measure of the chain extension in nylon-6. This suggestion can be supported by results of Sibilia[24] who has found, for drawn nylon-6 films, that the band at 1175 cm$^{-1}$ characteristic for twisted or pleated-chain conformation[23] decreased with increasing of the draw ratio, and at the same time increased the intensity of the bands at 835 and 930 cm$^{-1}$ characteristic for the extended-chain conformation that exists in the alpha-crystalline state. The absence in the infra-red spectra of pressure-crystallized nylon-6 of bands at 805, 890–900, 980–990 and 1100 cm$^{-1}$ related to the presence of monomer[27] shows that, during high pressure crystallization, no depolymerization took place.

*X-ray diffraction*

No long spacing was found for the nylon-6 crystallized under pressure above 5 kbar. The wide-angle X-ray scattering curves consisting of the scattering intensity *versus* the diffraction angle ($2\theta$) are given in *Figure 11*. Curve A was recorded for a nylon-6 sample precipitated from formic acid and dried at 180°C and for 48 h under a vacuum of 10$^{-6}$ mmHg. Curve B was recorded for a sample crystallized from

the melt at 280°C and 6.5 kbar for 48 h, and curve C for a specimen crystallized at the same temperature and pressure, but for 64 h.

It is known that the width of the diffraction peak can be related to the size of crystallites[8]. The broadened peaks usually result from small crystallites, while the narrowed peaks may be due to large crystallites as well as to improvement of the crystal structure[38]. For nylon-6, additionally, the separation of alpha$_1$ and alpha$_2$ peaks can give a useful measure of the degree of order and degree of perfection of formation of hydrogen bonded sheets, the order being higher for a higher degree of separation[39]. Moving of the peaks to a lower angle, corresponding to larger spacing, means a decrease of the crystalline perfection.

It was found, in agreement with published data[40], that the folded-chain nylon-6 crystallized from formic acid and annealed, or crystallized isothermally from the melt at low supercooling, forms a monoclinic alpha-modification[41]. The heights of the alpha$_1$ and alpha$_2$ are practically the same, with the width of alpha$_2$ being slightly greater than that of alpha$_1$. The X-ray diffraction curves of the chain-extended nylon-6 also exhibit an alpha$_1$ and alpha$_2$ peak. The height of the alpha$_1$ $d$(200) peak for this material increases slightly, while the width of this peak remains almost unchanged, as compared with that for the folded-chain nylon-6. The height of the alpha$_2$ $d$(002 + 202) peak for the pressure-crystallized nylon is considerably increased to about twice the initial height, while the width of this peak is decreased as compared with the folded-chain crystals. At constant temperature and pressures exceeding 5 kbar, the height of alpha$_2$ peak increases with the time for which the sample was crystallized.

Together with the increase in intensity of the alpha$_1$ and alpha$_2$ peaks, the resolution of these peaks was also improved. At the same time a shifting of the peaks in the direction of higher angles and smaller spacing was observed. From these presented experimental facts one may infer that crystallization of nylon-6 under high pressure does not change the crystal modification of the polymer, i.e. the monoclinic alpha form is preserved. During high pressure crystallization of nylon-6, the size of crystals as well as the crystalline order increased considerably. Additionally, high pressure crystallization of nylon-6 leads to a decrease in the distance between the crystal planes (200) connected by the hydrogen bonds and those hold together by Van der Waals forces (002). This conclusion, that the nylon-6 chains are closer packed in the crystal lattice, is in agreement with the infra-red data and with the X-ray measurements by Prosvirin[42] on compressed nylon-6.

CONCLUSIONS

Pressure-crystallized nylon-6 fractures very easily, pointing to a considerable reduction of intercrystalline links and tie molecules. Fracture surfaces display rough structures as a result of fracturing interspherulitically, through (010) planes and, in an irregular way, through hydrogen bonded sheets. The step heights in the fracture surfaces correspond to the contour length of the nylon-6 chains. The long period, as measured by small-angle X-ray scattering, increased markedly already at low crystallization pressures and could not be detected for samples crystallized at pressures of 5 kbar; this also points to large size lamellae.

It may be inferred from the wide-angle X-ray diffraction curves that elevated pressure does not give rise to a change in the crystal modification, i.e. the monoclinic alpha form

is preserved. The lateral dimensions, as well as the crystal perfection, increase with pressure and crystallization time. The distance between the planes containing the hydrogen bonds (002) as well as between the (200) planes held together by Van der Waals bonds, decreases upon crystallization under elevated pressure. Infra-red spectroscopy of pressure-crystallized nylon-6 discloses that, in spite of an increase in crystallinity, the concentration of free N–H groups is considerably enhanced. This phenomenon may be attributed to the fact that, upon chain extension, the pairing of anti-parallel chains is disturbed and some parallel chain arrangements are incorporated in the crystal lattice which, in addition to some twisting of chains, reduced the possibilities for hydrogen bond formation. The lower intensity of the band at 1175 cm$^{-1}$ suggests that the number of chain folds in pressure-crystallized nylon-6 is considerably reduced.

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