

A possible mechanism of chain extension in nylon-6 during crystallization under pressure

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(Received 16 March 1976; revised 9 August 1976)

The effect of pressure on crystallization from the melt and annealing of nylon-6 fractions has been investigated. Pressures exceeding 5 kbar and temperatures 40°C below the final melting temperature of the fractions under pressure, were sufficient to produce the extended-chain crystals by an isothermal crystallization from the melt as well as by annealing of the chain-folded material. Crystalline structure and the thermal characteristics of the extended-chain crystals formed from the fractionated nylon-6, were identical to those of unfractionated polymer. G.p.c. analysis of the extended-chain material formed from the fractions of narrow molecular weight distribution showed that this material most probably had a wide molecular weight distribution, similar to that of unfractionated nylon-6. Based on a change in the molecular weight distribution and decrease in the molecular weight, concurrent with the extended-chain crystallization it is suggested that on the thermal treatment of polyamides under pressure a transamidation reaction occurs between the $-\text{CO}-\text{NH}-$ groups of the broken folds of adjacent lamellae, which may lead to the chain extension.

INTRODUCTION

Polyamides crystallized from solution form lamellar crystals with thickness of 50–100 Å¹⁻⁴. Crystallization from the melt leads to growth of lamellar spherulites of comparable long-spacing¹. The general feature of these two types of crystallization processes is a chain-folding. In some cases, however, when the kinetic hindrances were overcome, it was possible to crystallize the polyamides in an extended-chain conformation. Zone-polymerization of caprolactam led to growth of spherulites with a lamellar thickness equal to the contour length of the molecules⁵. Pressure induced crystallization from the melt as well as annealing of the folded-chain crystals under pressure, produced the extended-chain crystals of nylon-6⁶⁻⁹, nylon-11¹⁰, and nylon-12¹¹. The most striking feature found in the investigated polyamides was their ability to form the extended-chain crystals by annealing under pressure the chain-folded ones, at temperatures far from the melting range of the polymer under appropriate pressure. The extended-chain crystals of polyamides displayed some peculiar features, e.g. in the region of the infra-red spectra which is assigned to the unbonded NH groups, a significant absorption was found^{8,10}, and additionally for nylon-11 and nylon-12^{10,11} no distinct boundaries between the extended-chain lamellae were observed. These facts have suggested that because of the $-\text{CO}-\text{NH}-$ groups present in the polymer chain, the mechanism of the extended-chain crystallization in polyamides may differ from that proposed for polyethylene.

It has been suggested for polyethylene that growth of the extended-chain crystals proceeds in two stages. The first stage is the nucleation step leading to the folded-chain nuclei, and the second, the chain extension process which is an isothermal thickening¹². It was also proposed that initially grown thin lamellae, thicken under pressure with time into the extended-chain lamellae¹³, or that the extended-chain crystals are formed under pressure directly in the melt¹⁴.

It is currently considered¹⁵ that the extended-chain crystals in polyethylene are formed from the melt via an intermediate phase, not 'directly in the melt'. On the other hand for selenium the chemical reaction between the open folds of the lamellae, was an essential step of the chain extension¹⁶.

This work was undertaken in order to obtain a better understanding of the mechanism of the extended-chain crystallization in polyamides. The results to be described deal with the annealing under pressure and pressure induced crystallization from the melt of the fractionated nylon-6. It will be shown that the extended-chain crystallization of polyamides is accompanied by a chemical reaction which changes the molecular weight and the molecular weight distribution of the fractions. One of the possible mechanisms of the chain extension in polyamides under pressure is proposed. It is suggested that the extended-chain crystals are formed from the folded-chain ones, and that under drastic conditions of pressure and temperature, the transamidation occurs between the $-\text{CO}-\text{NH}-$ groups of the broken folds, which may play an important role in the chain extension.

EXPERIMENTAL

Materials

For the present study the nylon-6 (polycapramide) fractions used were obtained by fractionation of polymer prepared by hydrolytic polycondensation of caprolactam. The fractionation was carried out by the method of distribution between two liquid phases¹⁷.

All powdered samples were dried and extruded under vacuum using a technique described previously¹⁸. Extruded samples as well as the samples from the high pressure experiments were characterized by gel permeation chroma-

tography (g.p.c.), according to the method reported recently for nylon-6¹⁹. The characterization of the samples used throughout the present study is given in Table 1.

High pressure system

All experiments under pressure were carried out using a system which was a modified version of the system developed by Pennings²⁰. Use of a double-walled high pressure cylinder and additional heating device, ensured a high stability of temperature of the system. Pressure changes in the dilatometer during experiments, were measured with a calibrated pressure transducer.

Measurements of melting temperature under pressure

The sample in the dilatometer was pressurized to the desired value, and the temperature increased in steps of 5°C. After the temperature reached equilibrium, the piston was moved in order to reduce the pressure loss resulting from friction, and the piston height was then measured. After the temperature exceeded the melting range, the sample was cooled down in the same way and the height of the piston was again determined. Melting temperature of the polymer under pressure was obtained from a volume/temperature plot.

Pressure induced crystallization from the melt

The sample under a pressure of 10 kbar was heated to the defined crystallization temperature in the range of 260°–290°C. The pressure was then reduced to 100 bar, and the sample was melted for 15 min. After the melting was completed, crystallization was induced applying a pressure of 6.5 kbar. At the end of the crystallization run, the sample was cooled down gradually to room temperature, and pressure released.

Annealing under pressure

The sample was pressurized to 6.5 kbar and then heated under pressure to the temperature in the range of 260°–290°C. After an appropriate time of annealing, the temperature was decreased to 25°C and pressure released. All details concerning the technique used for the annealing and crystallization under pressure has been given previously^{6,7,9,10,21}.

Characterization of the samples

Samples from the high-pressure experiments were analysed using a differential scanning calorimeter (d.s.c.) with a scan speed of 8°C/min (unless stated otherwise), electron microscopy and gel permeation chromatography.

Table 1 Materials used for experiments

Sample	\bar{M}_v	\bar{M}_w/\bar{M}_n	T_m (°C)	ΔH_m (cal/g)
Original	35 000	2.21	220	14.1
A	20 500	1.23	218.7	13.9
B	31 100	1.27	220	14.0
Fractions C	40 500	1.27	220	14.2
D	49 600	1.31	221	14.2
E	75 000	1.29	223	14.1

RESULTS AND DISCUSSION

Effect of pressure on the melting temperature

The effect of pressure on the melting temperatures was determined from the dependence of the specific volume of the sample on temperature under appropriate pressure. For polyethylene this dependence had a two-stage character^{15,22}. It was postulated that this character of the curve reflects the existence of a high pressure phase of polyethylene, intermediate in properties between the orthorhombic solid and melt¹⁵, or presence of two kinds of extended-chain crystals differing in crystalline order²², especially pronounced for the fractions with a narrow molecular weight distribution²³.

For the nylon-6 crystals under pressure, no effect of the molecular weight distribution on character of the dependence of V on T was observed. This fact seems to indicate that in polyamides under pressure only one type of the extended-chain crystals is formed, or that concurrent with the crystallization, an additional process takes place, which changes the molecular weight distribution of the polymer.

Figure 1 shows the dependence of the melting temperature under pressure on the pressure applied, for three fractions of nylon-6 and the whole polymer. For the investigated pressure range the melting temperature of the fractions as well as unfractionated polymer increased by about 16°C/kbar, in accordance with data for other nylon-6 samples of various molecular weight⁷. The same slope of dT/dP for both the fractionated and unfractionated polymer, even with a high polydispersity ratio ($M_w/M_n = 3.5$ for the nylon-6 under for previous study⁷) shows, that the melting temperature under pressure does not depend either on the molecular weight or the molecular weight distribution of the polymer.

Melting characteristics of pressure treated samples

Figure 2 illustrates the effect of the scan speed on the melting peak temperature for various nylon-6 samples. For clarity only data for the fractions with the lowest (A), medium (C), and the highest molecular weight (E) were included in Figure 2 but for the other fractions the same results were obtained. Curve 1 was drawn for the fractions A, C, and E annealed under pressure of 6.5 kbar and 285°C for 50 h, and curve 2 for the same fractions crystallized isothermally from the melt under identical conditions of pressure, temperature and time. It can be seen that the points split into two regions of temperature. The samples annealed under pressure showed higher values of the melt-

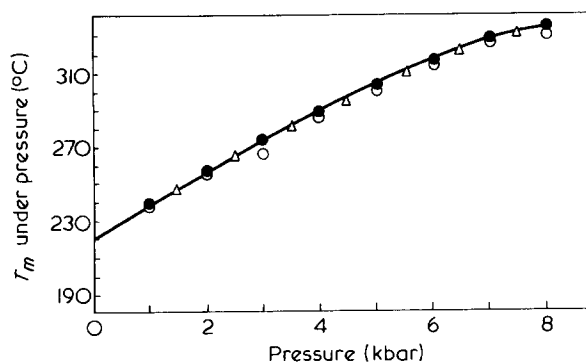


Figure 1 Dependence of the final melting temperature under pressure on the pressure applied. ○, Sample A ($\bar{M}_v = 20.5 \times 10^3$); △, sample C ($\bar{M}_v = 40.5 \times 10^3$); ●, sample E ($\bar{M}_v = 75.0 \times 10^3$)

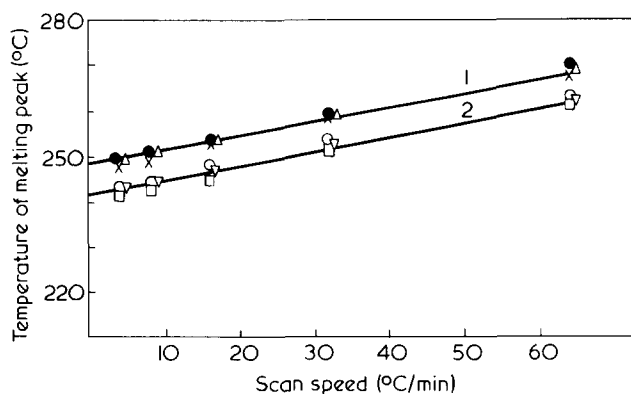


Figure 2 Effect of the scan speed on the melting temperature for various samples of nylon-6. Curve 1: ●, sample E; △, sample C; X, sample A annealed at 285°C and 6.5 kbar for 50 h. Curve 2: ○, sample E; ▽, sample C; □, sample A crystallized from the melt at 285°C and 6.5 kbar for 50 h

ing temperature than the samples crystallized under pressure from the melt. In both regions however the superheatability of the pressure treated fractions as measured between the zero heating rate and the rate of 64°C/min was ~24°C, which agrees with the value found for unfractionated nylon-6^{7,9}.

It has frequently been reported for the extended-chain crystals of polyethylene, that there exist multiple melting peaks in the d.s.c. thermograms^{22,25-27}. The additional melting peaks for a lower temperature range were related to multistage crystallization resulting in 'ordinary' and 'highly' extended-chain crystals²², presence of the folded-chain crystals²⁵ or preferential segregation of the low molecular weight portion of polyethylene fractions into a limited number of mixed crystals, each including a narrow molecular weight distribution²⁶. No fraction of nylon-6 crystallized or annealed under pressure showed the multiple melting peaks for any heating rate. The unfractionated polymer showed the same feature^{7,9}. Thus it seems that all folded-chain crystals are probably transformed into better i.e. extended-chain crystals, or that as a result of the chemical reaction, the shorter molecules may be incorporated into the extended-chain lamellae.

Figure 3 illustrates the dependence of the atmospheric melting peak temperature on the temperature at which the samples were crystallized from the melt (broken lines) or annealed (full lines) under pressure of 6.5 kbar for 50 h. It shows that atmospheric melting temperature increases with increase in the crystallization or annealing temperature, and to some extent with the molecular weight of the sample, which agrees with the data for polyethylene²⁶. It can be seen from Figure 3 that the character of the dependence of melting temperature on temperature for the samples crystallized under pressure from the melt, is different from that of samples annealed under pressure. While for the melt crystallized samples a rectilinear dependence of melting temperature on crystallization temperature was found, for the latter a T_m/T_a plot had an inflection point at $T_a = 280^\circ\text{C}$.

The heat of fusion/temperature plot for pressure crystallized or pressure annealed fractions showed a similar change in slope. The same shape of the dependences described above, was also observed for an unfractionated nylon-6^{7,9}; Possible explanation of different behaviour of the crystallized and annealed samples has been given previously⁹. Figure 4 presents the effect of the time the samples were

crystallized or annealed under pressure of 6.5 kbar and 285°C, on the atmospheric melting peak temperature.

As it has already been found for whole polymer^{7,9} the crystalline order which is produced in the nylon-6 fractions under pressure as estimated from the values of melting temperature, depends on time—up to 70 h annealing. After that time no significant increase in the melting temperature was observed.

To explain this behaviour of nylon-6 it was suggested⁹, that after about 70–80 h of thermal treatment of the polyamide under pressure the chain extension process is already completed, or that under applied conditions the rearrangement within the crystal which could lead to a higher melting temperature, may be associated with a thermal degradation which effectively decreases the melting temperature.

Figure 5 shows the dependence of the heat of melting on the pressure at which the fractions were crystallized or annealed. The dependence reveals the same S-shape character as reported for unfractionated polyamide^{7,9}, and transformation to higher values of ΔH_m appears in the

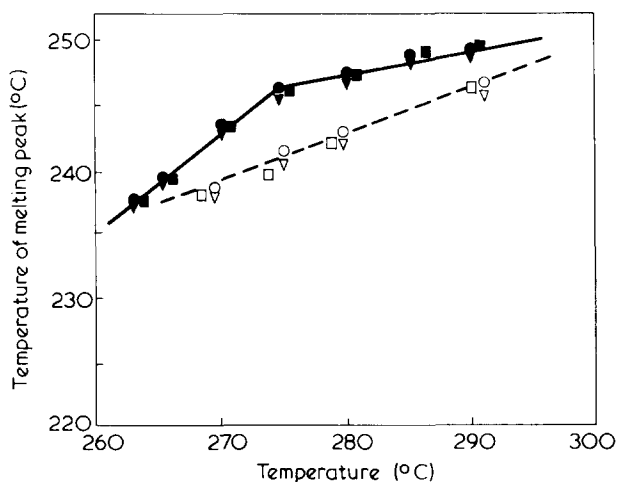


Figure 3 Dependence of the atmospheric melting peak temperature on the annealing or crystallization temperature. ●, Sample E; ■, sample C; ▼, sample A annealed at 285°C and 6.5 kbar for 50 h; ○, sample E; □, sample C; ▽, sample A crystallized from the melt at 285°C and 6.5 kbar for 50 h

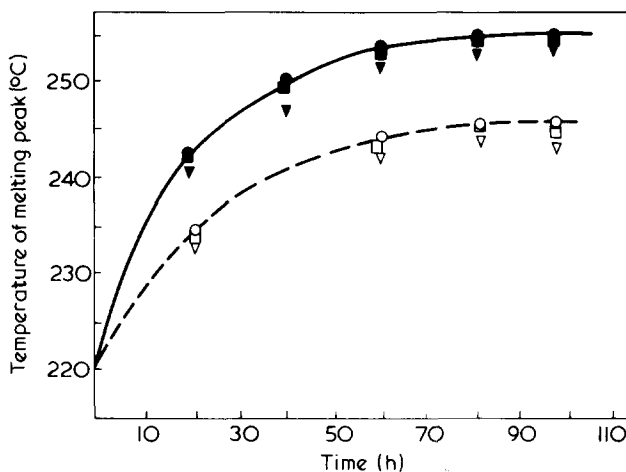


Figure 4 Dependence of the atmospheric melting peak temperature on the annealing or crystallization time. ●, Sample E; ■, sample C; ▼, sample A annealed at 285°C and 6.5 kbar; ○, sample E; □, sample C; ▽, sample A crystallized from the melt at 285°C and 6.5 kbar

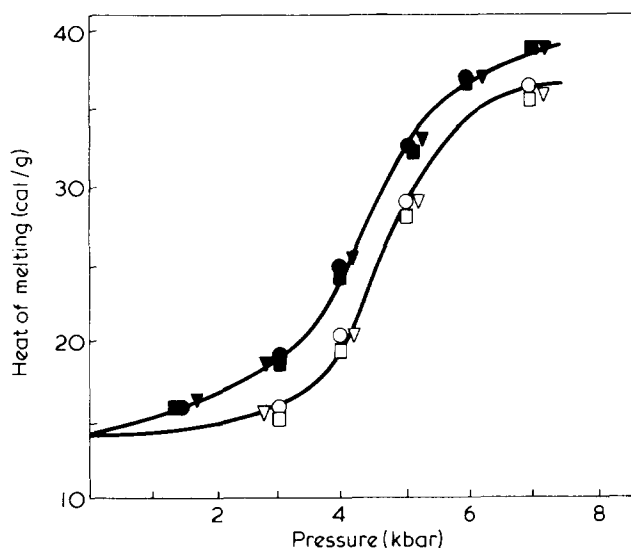


Figure 5 Dependence of the heat of melting on the pressure applied (temperatures of 40°C below the final melting temperature, time 50 h). ●, Sample E; ■, sample C; ▼, sample A annealing experiments; ○, sample E; □, sample C; ▽, sample A, pressure induced crystallization from the melt

same pressure range. From the data on the melting behaviour of the nylon-6 fractions presented here it is evident, that as it has already been found for whole polymer⁹, annealing of folded-chain crystals under comparable conditions of pressure, temperature and time, produces more perfect crystals with higher melting temperature and a heat of melting, than does pressure induced crystallization from the melt.

One might expect that better crystals of more uniform dimensions should be formed from the material of narrow molecular weight distribution, as has been observed for polyethylene²⁴. Comparison of the data of the melting characteristics of nylon-6 fractions with those of unfractionated nylon-6^{7,9} leads to the conclusion that there is no difference in the crystalline order and perfection of the crystals formed under pressure in the fractionated and unfractionated nylon-6. That is to say that during thermal treatment of polyamides under pressure, crystallization is accompanied by another process which changes the molecular weight distribution of the fractions.

It has been postulated⁹ that formation of the folded-chain crystals is a preceding, necessary stage of the extended-chain crystallization in polyamides under pressure. It was considered that the next stage of crystallization is the chain extension, which proceeds after the folded-chain crystals formation is terminated.

This suggestion was based among others on the following facts: at identical conditions of pressure and temperature, annealing of the folded-chain crystals produced high values of melting temperature and heat of melting, i.e. more perfect crystals after shorter time, than pressure induced crystallization from the melt. Extended-chain crystals with a lamellar thickness equal to the contour length of the molecule were grown by annealing of the folded-chain ones far from the melting range under pressure. The results presented here are consistent with this suggestion.

Effect of thermal treatment under pressure on the molecular weight and the molecular weight distribution of nylon-6 fractions

The results of measurements of molecular weight and

polydispersity ratio M_w/M_n as well as the melting characteristics of the nylon-6 fractions crystallized from the melt or annealed under pressure of 6.5 kbar and 285°C for 50 h are presented in Tables 2 and 3. It can be seen that the molecular weight of the fractions decreased, and polydispersity ratio increased reaching the values close to M_w/M_n of the unfractionated nylon-6. Figure 6 shows the g.p.c. chromatograms of the investigated samples. Curves were drawn for the material as obtained from fractionation, for the fractions annealed under pressure, and for the unfractionated nylon-6. The fractions crystallized under pressure from the melt, showed the same character of the chromatograms as the samples annealed under pressure. At least two processes might cause the observed changes in the molecular weight and molecular weight distribution, e.g. the transamidation reaction causing the chain scission, or the action of oxygen and heat, resulting in the cleavage and crosslinking of the molecules. As the samples from the high pressure experiments were completely soluble and no caprolactam was found in the infra-red spectra of these samples, the latter process seems to be negligible. Presented data lead to the conclusion that during the thermal treatment of polyamides under pressure, a chemical reaction occurs which changes the narrow molecular weight distribution of the fractions, to wider, the most probable one.

On the grounds of changes in the molecular weight and the molecular weight distribution observed for the nylon-6 fractions crystallized or annealed under pressure, the following mechanism of formation of the extended-chain crystals in polyamides is implied. Under drastic conditions of pressure and temperature, the chain-folds of the polyamide crystals formed in the melt at the early stage of crystallization under pressure are broken. Then transamidation proceeds between the $-\text{CO}-\text{NH}-$ groups of the open folds in adjacent lamellae, which may lead to the chain extension.

It has to be emphasized however that the other processes leading to increase in the lamellar thickness, such as isothermal thickening with a longitudinal displacement of the chain segments²⁸, or mutual rearrangements within the folded-chain molecule²⁹ can occur concurrently to the transamidation process. The suggestion of a transamidation reaction occurring in polyamides under pressure can

Table 2 Materials from pressure induced crystallization from the melt (6.5 kbar, 285°C, 50 h)

Sample	\bar{M}_v	\bar{M}_w/\bar{M}_n	T_m (°C)	ΔH_m (cal/g)
Original	30 000	2.20	246	37.1
Fractions A	15 800	1.89	241.2	37.2
B	25 750	1.90	243.2	36.9
C	32 620	1.96	243.4	36.8
D	41 100	1.88	244.9	37.0
E	64 100	1.98	247	37.0

Table 3 Materials from annealing under pressure (6.5 kbar, 285°C, 50 h)

Sample	\bar{M}_v	\bar{M}_w/\bar{M}_n	T_m (°C)	ΔH_m (cal/g)
Original	30 600	2.20	251	38.1
Fractions A	16 200	1.99	250.2	39.0
B	26 800	2.00	251.0	38.6
C	33 500	1.98	252.3	39.0
D	41 630	2.01	253.6	38.8
E	66 050	2.10	255.2	38.6

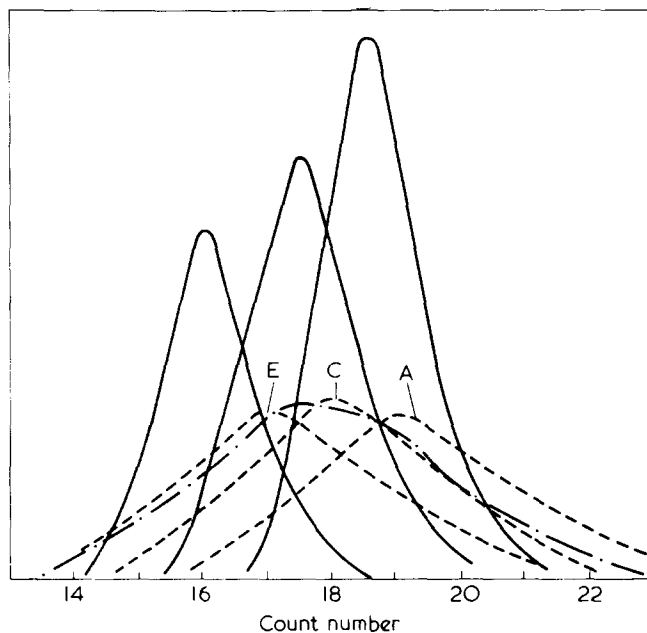


Figure 6 G.p.c. chromatograms of the nylon-6 samples used. —, Fractions E, C and A after extruding under high vacuum; --- fractions E, C and A annealed under pressure of 6.5 kbar and 285°C for 50 h; - · - · - unfractionated polymer

be supported by the results of electron microscopy investigations, which are discussed in detail elsewhere^{8,9}. In the present paper only two micrographs are shown to illustrate the surface morphology.

Figure 7 is an electron micrograph of the fracture surface of the fraction E crystallized isothermally from the melt at 210°C for 50 h under atmospheric pressure, and reveals typical folded-chain morphology.

Figure 8 is an electron micrograph of the fracture surface of the fraction E crystallized at 285°C and 6.5 kbar for 50 h. The micrograph reveals the same morphology as an unfractionated nylon-6^{8,9} crystallized under similar conditions. The other fractions crystallized or annealed under pressure showed a morphology similar to that shown in Figure 8. It should be noted, that the surface morphology of other polyamides which have formed the extended-chain crystals seems also to confirm the chemical character of the chain extension process in polyamides.

Extended-chain lamellae of nylon-11¹⁰ and nylon-12¹¹ with molecular chains passing through several lamellae, did not reveal the interlamellar boundaries. This morphology appeared to be very similar to that reported for the extended-chain crystals of selenium, for which it was found that the folds opening and reformation of bonds, was the third step of the chain extension¹⁶.

In Figure 9 the model of formation of the extended-chain crystals in polyamides under pressure is proposed, based on the data presented.

(A) The strained folds of the lamellar crystals are broken, and as a result of transamidation of new $-\text{CO}-\text{NH}-$ bonds are formed between the cut chains of the adjacent lamellae, that may lead to the chain extension.

(B) When the folds in the adjacent lamellae are displaced to each other, the kink bands may be formed.

(C) If the distance between the CO and NH groups of the exposed folds of adjacent lamellae is too large to reform a proper $-\text{CO}-\text{NH}-$ bond, they will stay unbonded after breaking, and may result in the point defects included

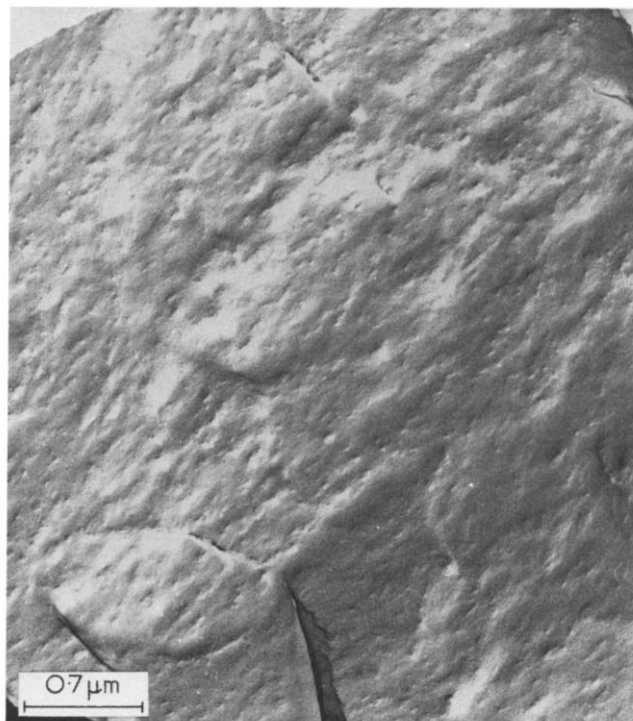


Figure 7 Electron micrograph of a fracture surface of fraction E crystallized from the melt at 210°C under atmospheric pressure for 50 h

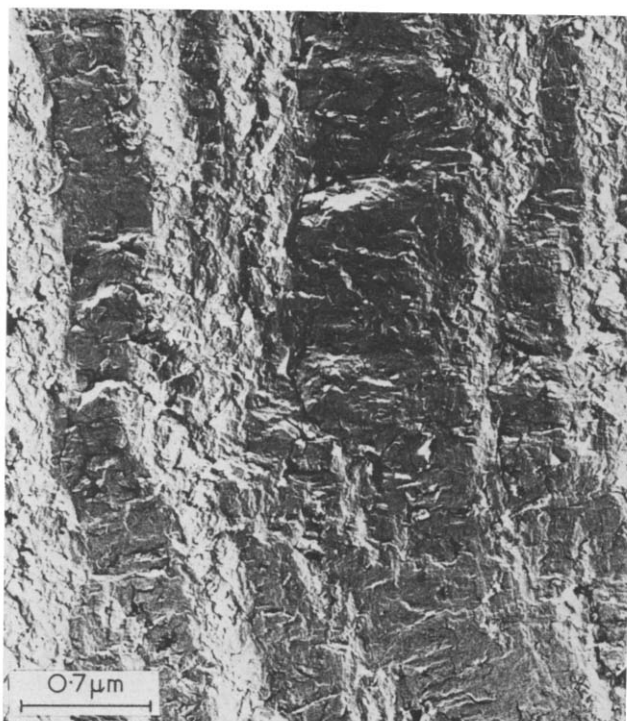


Figure 8 Electron micrograph of a fracture surface of fraction E crystallized from the melt at 285°C and 6.5 kbar for 50 h

in the crystal lattice. These unbonded NH groups as well as an irregular array of the zig-zag chain in some places of the crystal where the transamidation occurred, may be a reason for incomplete hydrogen bonding observed in the infra-red spectra of the pressure treated polyamides⁸⁻¹⁰. It has recently been suggested³⁰ that for polyesters of polyamides the transesterification or transamidation reaction may be a tool for an improvement of the crystal perfec-

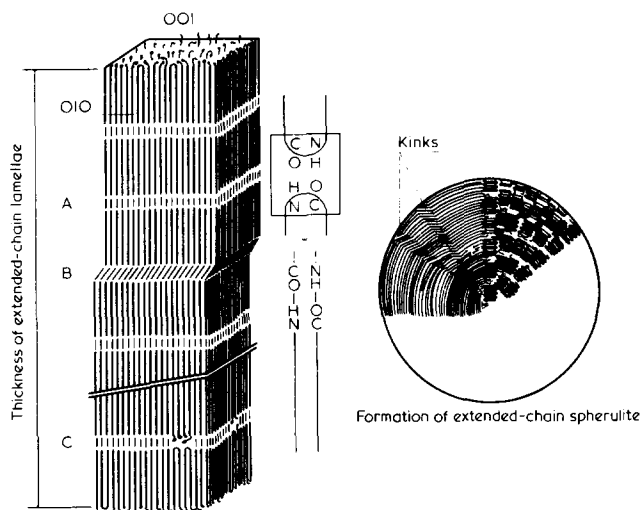


Figure 9 Model of the chain extension in polyamides under pressure

tion by tempering through the chain scission. It seems that the results presented here are in line with this suggestion.

ACKNOWLEDGEMENTS

The author is indebted to Dr A. J. Pennings Department of Polymer Chemistry, State University of Groningen, The Netherlands, who has initiated the author's interest in the field of high pressure crystallization of polymers. The author wishes to thank Professor E. Turska, Department of Polymers, Polish Academy of Sciences, and Doz. S. Polowinski, Institute of Synthetic Fibers, Technical University of Lodz, Poland, for valuable discussion.

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