Crystallization of copolyamides under elevated pressure*

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The effect of pressure up to 10 kbar and temperature up to 320°C on melting and crystallization behaviour of various random copolyamides has been investigated. Samples used for the studies were obtained by condensation of caprolactam and respectively: piperazine adipate, piperazine terephthalate or hexamethylene terephthalate in various molar proportions. Samples were free from additives. Under comparable conditions of the thermal treatment, the melting temperature and the heat of melting of the crystals grown under pressure increased with increase in temperature and time of crystallization and decreased with increase in the comonomer content. The long periodicity of copolyamides crystallized under pressure increased from 50 to 600–900 Å, the melting temperature and the heat of melting increased from 208°C and 9 cal/g to 228°C and 24 cal/g respectively.

INTRODUCTION

Pressure in the range of 3 kbar enhanced a growth of the chain-extended crystals in polyethylene[1]. Formation of these crystals proceeds via an intermediate high-pressure phase of hexagonal packing[2,3]. It has recently been found that for some polyamides like nylon-6 or nylon-11[4–6] the chain-extended crystals can be grown when a pressure exceeding 5 kbar is applied to the polymer melt, or when the folded-chain crystals are annealed under pressure. It was also suggested that in polyamides under drastic conditions of temperature and pressure, the transamidation reaction occurs between the –CO–NH– groups of the broken folds of adjacent lamellae, which may lead to the chain extension[7], concurrently with an isothermal thickening or mutual rearrangement within the folded-chain molecule[8,9]. A suggestion on the transamidation mechanism of growth of the chain-extended crystals in polyamides[7] is in line with recent finding of Ruscher and co-workers[10] that an initial step of crystallization of nylon-6 under pressure is associated with a decrease in the lamellar thickness.

This work was undertaken to examine whether random copolyamides are able to form chain-extended crystals during crystallization under elevated pressure. It was expected that if the transamidation is of importance in the chain extension in polyamides under pressure, then disturbed regularity of the chain and irregular placement of the polar groups in the random copolyamides, will restrict such an extension in the random copolyamides.

The present paper deals with crystallization from the melt and annealing of the folded-chain crystals of nylon 6-piperazine adipate, nylon 6-piperazine terephthalate and nylon-6-hexamethylene terephthalate random copolyamides under elevated pressure.

The crystalline properties of these copolamides were not practically investigated. Except for some data dealing with spherulitic crystallization kinetics from the melt at low supercooling[11,12] and the effects of comonomer contents on the kinetics of crystallization from the melt[13], there are no published data on the crystalline structure of the polymers.

High-pressure dilatometry, differential scanning calorimetry, electron microscopy and X-ray diffraction were used as the investigative techniques.

EXPERIMENTAL

Materials

All the experiments were performed on copolyamides obtained by condensation of caprolactam and respectively: piperazine adipate, piperazine terephthalate or hexamethylene terephthalate in various molar proportions. Samples were free from additives. Original samples in the form of pellets were extracted with water, acetone and ethanol, dried to a constant weight and extruded from the melt under vacuum of 2×10^{-6}mm Hg[14].

Extruded samples had a cylindrical shape and diameter only slightly smaller than the inner diameter of the high-pressure cell and were free from cavities. The extruded samples were placed into glass ampoules and evacuated under a vacuum of 2×10^{-6} mm Hg at 80°C for 5 h. The ampoules were then heat-sealed and kept at $\Delta T = 10°C$ for 40 h in a thermostatically controlled bath. Annealed material when viewed under a polarizing microscope showed a fine-grain spherulitic structure. The intrinsic viscosity of the samples were measured in 98% sulphuric acid at 25°C, using polymer solutions with concentration in the range 0.35–0.117 g/100 ml. The characterization of the samples is given in *Table 1*.

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Table 1 Copolyamides used in the experiments

Sample	Comonomer content mol %	Sample symbol	Intrinsic viscosity dl/g	T_m (°C)	ΔH_m (cal/g)
Nylon 6-piperazine adipate	3	N6-PPA3	1.06	217	11.6
Nylon 6-piperazine adipate	4	N6-PPA4	1.08	209	11.2
Nylon 6-piperazine adipate	6	N6-PPA6	1.07	202	10.4
Nylon 6-piperazine terephthalate	3	N6-PPT3	1.13	209	11.3
Nylon 6-piperazine terephthalate	6	N6-PPT6	1.05	199	10.6
Nylon 6-piperazine terephthalate	8	N6-PPT8	1.08	191	10.2
Nylon 6-hexamethylene terephthalate	1	N6-HMT1	1.19	216	11.0
Nylon 6-hexamethylene terephthalate	2	N6-HMT2	1.18	212	10.5
Nylon 6-hexamethylene terephthalate	3	N6-HMT3	1.17	211	10.0
Nylon 6-hexamethylene terephthalate	5	N6-HMT5	1.18	208	9.0
Nylon 6-hexamethylene terephthalate	7	N6-HMT7	1.16	205	8.5
Nylon 6	0	N6	1.20	223	15.5

High-pressure cell. Crystallization and annealing of the polymer under pressure were carried out using a modified high-pressure dilatometer of the type developed by Pennings[15].

The temperature of the dilatometer was controlled to within an accuracy of ±0.5°C using a feed-back type temperature regulator connected into the system with a chromel–alumel thermocouple and a chart recorder. Displacement of the piston during experiments was read to within an accuracy of 0.001 mm with a dial micrometer and additionally recorded with a displacement transducer-chart recorder system.

Determination of the melting temperature under pressure. The melting temperatures of copolyamides under specified pressure were estimated from the dependence of piston height measured as a function of temperature.

Examination of the effect of thermal treatment under pressure on the viscosity of the samples. To find the optimum crystallization conditions which would produce the highest crystalline order and to allow for the avoidance of thermal degradation of copolyamides, the intrinsic viscosities of the samples were measured as a function of temperature and the time the polymer was kept under pressure.

Conditions for pressure-induced crystallization from the melt and annealing under pressure. Crystallization and annealing of the copolyamides under pressure were carried out under the conditions which, as shown previously[5,6], led to the growth of the chain-extended crystals in nylon-6.

The procedure applied was corrected with regard to the thermal stability of copolyamides under pressure. For pressure-induced crystallization from the melt, the samples in the high-pressure dilatometer were pressurized at room temperature to 8 kbar and heated to the desired crystallization temperature in the range 240°–250°C. After the temperature of the dilatometer reached an equilibrium, the pressure was reduced to 0.5 kbar, the samples were melted for 15 min and a crystallization pressure in the range of 5–7 kbar was applied to the polymer melt. The samples were maintained at these conditions for various times ranging from 1 to 70 h. At the end of the crystallization run the samples were cooled down at 0.5°C min^{-1} to room temperature and the pressure was released.

For the annealing experiments, samples in the dilatometer were pressurized to the required annealing pressure within the range of 5–7 kbar and heated to annealing temperature in the range of 240–250°C. These temperatures were 50–70°C lower than the melting temperature of the copolyamide under pressure ~5–7 kbar. The samples were annealed under these conditions for 1 to 70 h, then cooled down at 0.5°C min^{-1} to room temperature and the pressure was released. All the samples from the high-pressure experiments showed brittle fracture at room temperature.

Analysis of the samples

Melting temperatures and the heats of melting of the samples were determined with a Perkin-Elmer DSC-1B instrument with a scan speed of 8° min^{-1} according to the standard procedure.

Electron microscopy studies were performed on two-stage replicas of fracture surfaces. The Philips EM 201 electron microscope was used to obtain the electron micrographs. Wide-angle X-ray diffraction patterns were recorded at room temperature over the range of diffraction angles (2θ) from 2° to 45° with Ni filtered CuKα radiation using a Philips diffractometer. Long-period measurements by the small-angle X-ray diffraction were obtained on the Rigaku–Denki unit. The details concerning the techniques applied were given previously[6].

RESULTS AND DISCUSSION

Melting temperature of copolyamides under pressure

Figure 1 shows the dependence of the melting temperature as measured under pressure on the pressure applied. Upper line was drawn for nylon-6 and lower one for N6-HMT3, N6-PPA3, N6-PPT3 copolyamides.

It can be seen that as usual consequence of random copolymerization the resulted copolymers have lower melting temperature than that of nylon-6. The melting point depression of copolyamides containing a small percentage of the second component seems to be a feature of copolyamides prepared by melt-polycondensation, and may be due to the inability to fit a repeating unit of different size into the lattice of the first component without producing considerable disturbences[16–18]. Disturbing the regularity of amide groups reduces hydrogen bonding and thereby reduces the heat of melting affecting the melting temperature of the copolyamide.

The data obtained on the melting behaviour of N6-PPA, N6-PPT and N6-HMT copolyamides under atmospheric and elevated pressure seem to show that for these polymers, the chance of isomorphous replacement is not

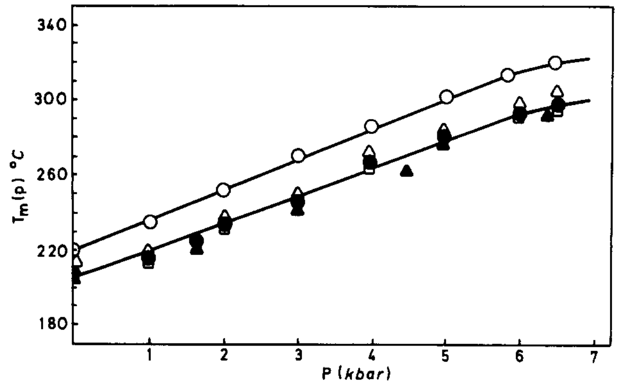

Figure 1 Dependence of the melting temperature under pressure $T_m(p)$ on the pressure applied for various copolyamides. ○, nylon 6; ●, N6-HMT3; △, N6-PPA3; □, N6-PPT3

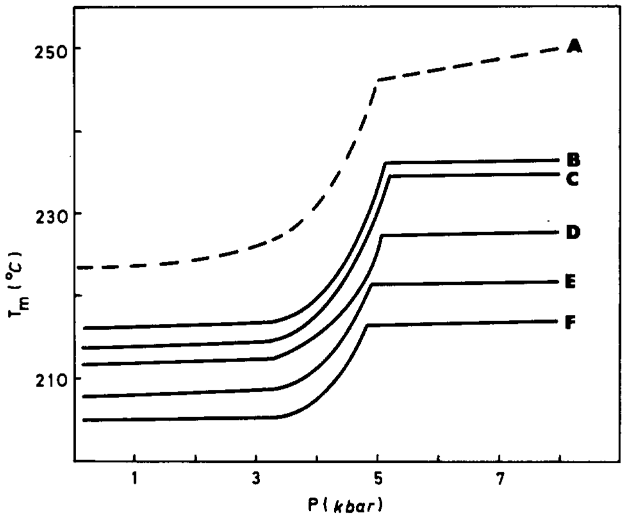

Figure 2 Dependence of the atmospheric melting peak temperature for copolyamides crystallized for 40 h at temperatures of 40° C below the final melting temperature on pressure applied. A, N6; B, N6-HMT1; C, N6-HMT2; D, N6-HMT3; E, N6-HMT5; F, N6-HMT7

probable which is in contrast with nylon 6T and nylon 66-6T copolyamides, which exhibited an isomorphism[16,18].

The melting temperature of investigated copolyamides under pressure, $T_m(p)$, increases on pressure of about 14°C/kbar, which is of 2°C lower than the similar value found for nylon-6[5].

Melting characteristics of copolyamide crystals

It was found that in all the copolyamide samples subjected to high-pressure experiments the soft material was present in amounts of ~1–2% by weight of whole sample. This white-opaque material was located at the top of cylindrical samples and formed a regular cone. Its melting temperature was in the range of values found for an original copolyamide as obtained by polycondensation. It seems that this material originated probably from non-transformed copolyamide and comonomer which did not completely react during polycondensation, and was effectively repealed from the polymer melt under pressure.

To avoid the effect of this material on the results of polymer analysis, the top part of each sample was cut off and rejected. All the results presented in this paper were obtained for the solid part of the samples crystallized from the melt or annealed under elevated pressure.

Figures 2–6 show the data for the melting characteristics for N6-HMT copolyamide. *Figure 2* illustrates the dependence of the atmospheric melting peak temperature on the pressure applied (crystallization temperatures were in the range of 40°C below the end of melting under pressure; crystallization time 40 h). The dependence reveals the same S-shape character as reported for nylon-6[4–6]. A similar shape of curve was found for the dependence of the heat of melting of the copolyamide crystals grown under pressure on the pressure applied. It can be seen that measured values of T_m and ΔH_m of the copolyamide crystals grown under pressure decrease with increase in the comonomer content. It suggests that the crystalline lattice of the copolyamide is distorted and less stable than that of the homopolymer by the presence of noncrystallizable units. It can happen not only in the case when the B units enter the crystalline lattice, but also when they are present at the fold surface which brings about a certain strain to the lattice.

Figure 3 presents the typical d.s.c. thermograms of N6-HMT5 copolyamide. Curve 1 was recorded for the original polymer which was extracted and dried before analysis. The broadened main melting peak is followed by a long low-temperature tail which starts at temperature 100°C lower than the position of main peak. Similar character of d.s.c. curves was also observed for the copolyamide cast or precipitated from formic acid and seems to be typical for other copolyamides[16] of various degrees of substitution. The low-temperature tail in the d.s.c. thermograms may be due to the poor material of a low crystalline order present in the copolyamide.

Curve 2 is an exemplary thermogram of the sample extruded under vacuum and subsequently annealed at 198°C for 40 h. The thermogram shows slight increase of the melting temperature, presence of two melting peaks and shortening of the low-temperature part of the melting curve.

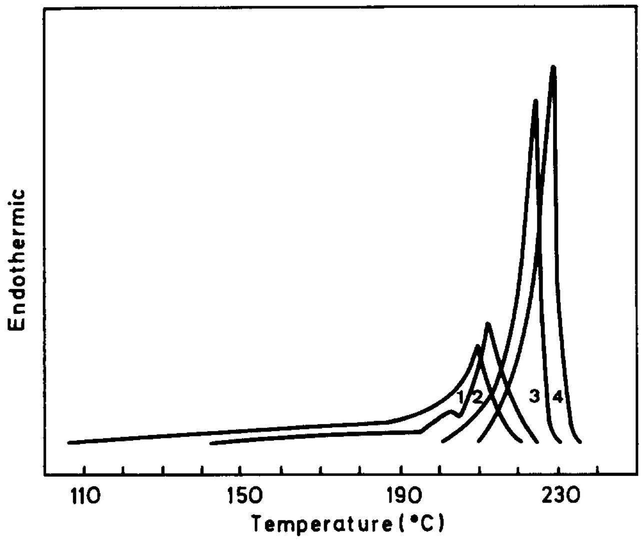

Figure 3 Melting thermograms for various samples of N6-HMT5 copolyamide. 1. Original polymer (T_m = 208°C, ΔH_m = 10.1 cal/g); 2. Sample extruded under vacuum and annealed at 198° C under atmospheric pressure for 40 h (T_m = 210° C, ΔH_m = 10.2 cal/g); 3. Sample annealed at 240°C and 6.5 kbar for 40 h (T_m = 221° C, ΔH_m = 21 cal/g); 4. Sample crystallized from the melt at 240° C and 6.5 kbar for 40 h (T_m = 228°C, ΔH_m = 24 cal/g)

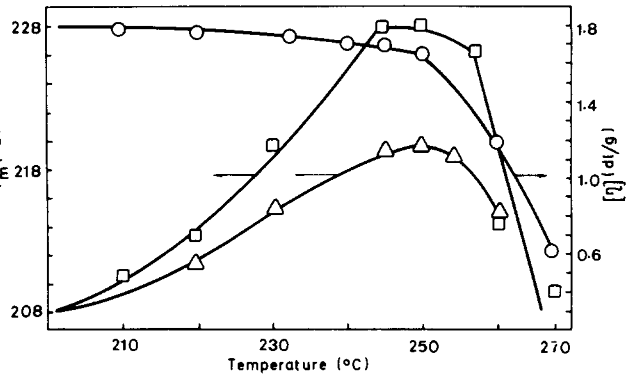

Figure 4 Dependence of the atmospheric melting peak temperature and the intrinsic viscosity on the crystallization or annealing temperature. □, melting temperature and ○, intrinsic viscosity of N6-HMT5 copolyamide crystallized from the melt at 240°C and kbar for 40 h; △, melting temperature and ○, intrinsic viscosity of N6-HMT5 copolyamide annealed without melting at 240°C and 6.5 kbar for 40 h

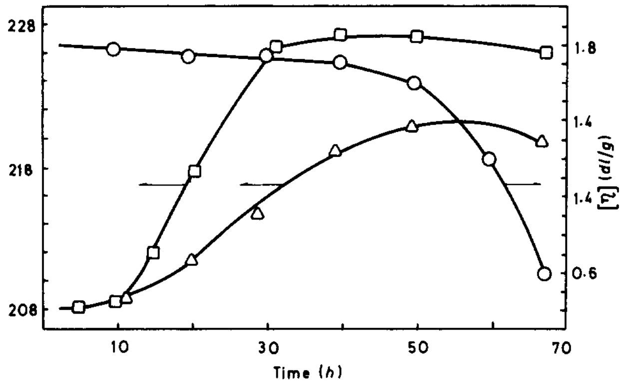

Figure 5 Dependence of the atmospheric melting peak temperature and intrinsic viscosity of N6-HMT5 copolyamide on the crystallization or annealing time. □, melting temperature and ○, intrinsic viscosity of the samples crystallized from the melt at 240°C and 6.5 kbar; △, melting temperature and ○, intrinsic viscosity of the samples annealed at 240°C and 6.5 kbar

The second melting peak for the lower temperature range probably results from the partial melting and subsequent recrystallization of the components in the amorphous state[19] which was associated with simultaneous decreasing of the gamma (γ) maximum in the X-ray diffraction pattern of these samples. Curves 3 and 4 are the thermograms of copolyamide annealed or crystallized from the melt at 240°C and 6.5 kbar for 40 h. The melting endotherms become narrow and high and at the same time they shift to higher temperatures which show an increase in the crystalline order in the pressure-treated copolyamides. The low-temperature tail practically disappeared but as a consequence of copolymerization, the low-temperature side of the thermograms is still much more pronounced than that of the homopolymer crystallized or annealed under similar conditions of pressure and temperature[5,6].

The copolyamide samples from the high pressure experiments showed a superheatibility of about 7°C. This value is however much lower than the value of 25°C obtained for pure nylon-6 which crystallized under elevated pressure in the chain-extended conformation[5,6]. It suggests that the chain extension and enlargement of lateral dimensions of the crystals under pressure, occurs for the copolyamides to a lesser degree than those for the homopolymer.

Figure 4 shows the dependence of the atmospheric melting peak temperature and the viscosity on the temperature, the N6-HMT5 copolyamide was crystallized or annealed at 6.5 kbar for 40 h. Within the limited temperature range, the atmospheric melting peak temperature of the copolyamide crystals formed under pressure increases with crystallization or annealing temperature. Above that range the melting temperature drops as a result of thermal degradation. It has to be emphasized that the crystallization of copolyamides under atmospheric pressure did not affect their melting temperatures, the heats of melting as well as the intrinsic viscosities and the long-period, even for prolonged annealing times.

Figures 5 and *6* show the dependence of the atmospheric melting peak temperature, the heat of melting and the intrinsic viscosity of the N6-HMT5 copolyamide on the crystallization or annealing time. T_m and ΔH_m of the copolyamide crystallized or annealed under pressure increased for the 40 h thermal treatment from 208°C and 10 cal/g to 228°C and 24 cal/g respectively. The intrinsic viscosity of pressure-treated copolyamide decreases gradually with time and drops abruptly after ~50 h crystallization or annealing under pressure. It should be noted that while the viscosity of pressure-treated copolyamides drops to one-third of the initial value, the melting temperature and the heat of melting of the polymers are still high. It seems that two concurrent processes might at least give occasion to the observed changes of the melting temperature, the heat of melting and the molecular weight of the copolyamides under pressure, i.e. thermal degradation and transamidation. The thermal degradation, because of a decrease in the molecular weight, causes decrease in T_m and ΔH_m exclusively. The transamidation on the surfaces of the lamellae containing the broken folds decreases to some extent the molecular weight, but at the same time may increase T_m and ΔH_m as a result of the increase in the lamellar thickness and strength of the intermolecular forces. For relatively short times of crystallization or annealing under pressure the transamidation may play a predominant role. For prolonged thermal treatment of the copolyamides under pressure the thermal

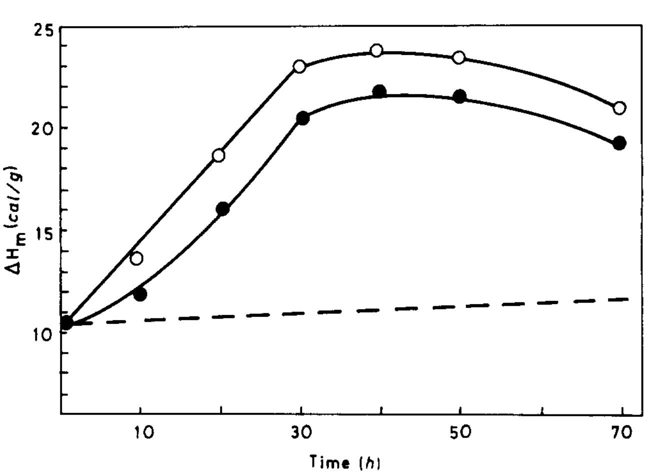

Figure 6 Dependence of the heat of melting of N6-HMT5 copolyamide on the crystallization or annealing time. (— — — —), samples crystallized from the melt at 198°C under ambient pressure; ○, samples crystallized from the melt at 240°C and 6.5 kbar; ●, samples annealed without melting at 240°C and 6.5 kbar

Figure 7 Transmission electron micrograph of a replica of fracture surface of copolyamide crystallized from the melt at 198°C for 40 h under ambient pressure. Scale bar represents 1 μm

Figure 8 Transmission electron micrograph of a replica of fracture surface of copolyamide annealed at 240°C and 6.5 kbar for 40 h. Scale bar represents 1 μm

degradation appears more effective. It was found that for copolyamides kept under identical temperature and pressure for the same length of time, the samples crystallized under pressure from the melt exhibited much higher values of the melting temperature and the heat of melting, i.e. higher crystalline order than those annealed under pressure without melting. This may result from the fact that stiff chains of copolyamides have higher mobility in the melt which facilitates their fitting in the crystalline lattice.

Under comparable crystallization or annealing conditions and for the same comonomer content, N6-PPA copolyamide showed the highest crystal perfectness, and the N6-PPT copolyamides lowest crystal perfectness. This may be due to the differences in the chemical structure of the chain. The chain of N6-PPT having a greater volume due to side groups is more rigid than that of N6-PPA of N6-HMT which brings about an additional restriction in the proper packing of the chains within the lattice. In all the cases however, perfectness of the crystals grown under pressure was much lower for the copolyamides than for nylon-6.

Electron microscopy

Figure 7 is an electron micrograph of a fracture surface of N6-HMT5 copolyamide crystallized under ambient pressure and shows a lamellar chain folded spherulite. The micrograph reveals a radial arrangement of thin lamellae. In contrast to the surface morphology of chain folded crystals of nylon-6 crystallized under comparable conditions[6], the fine detail of the copolyamide crystals are somewhat indistinct.

Figure 8 shows an electron micrograph of a replica of the fracture surface of copolyamide annealed at 240°C and 6.5 kbar for 40 h, and shows a selected part of a spherulite. Roughness of the surface is considerably increased, the interlamellar boundaries are obscure, although it seems probable that the thickness of the lamellae may correspond to the radially arranged black strips visible on the micrograph. On the fracture surface of the spherulite, structureless areas are frequently observed, whose origin is probably from the amorphous material effectively rejected by the crystalline growth front and deposited on the 010 plane of the crystal.

Figure 9 is an electron micrograph of a replica of the fracture surface of a copolyamide crystallized from the melt at 240°C and 6.5 kbar for 40 h. The micrograph shows a central part of the spherulite with a texture typical for copolyamides crystallized under pressure from the

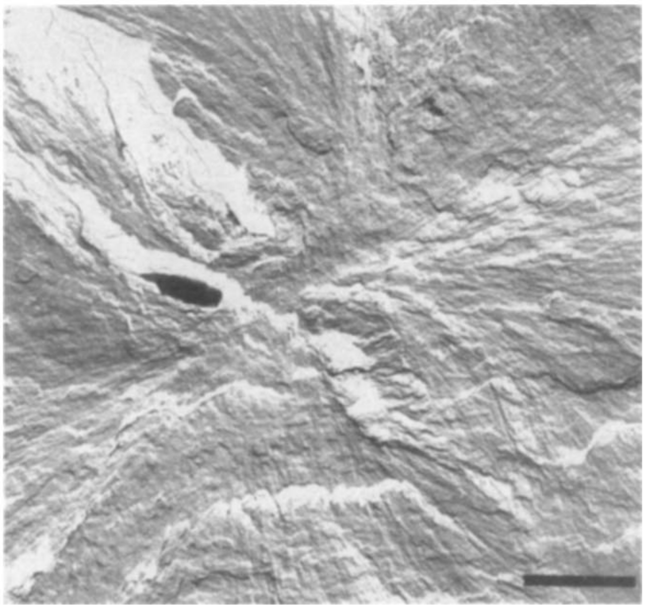

Figure 9 Transmission electron micrograph of a replica of fracture surface of copolyamide crystallized from the melt at 240°C and 6.5 kbar for 40 h. Scale bar represents 1 μm

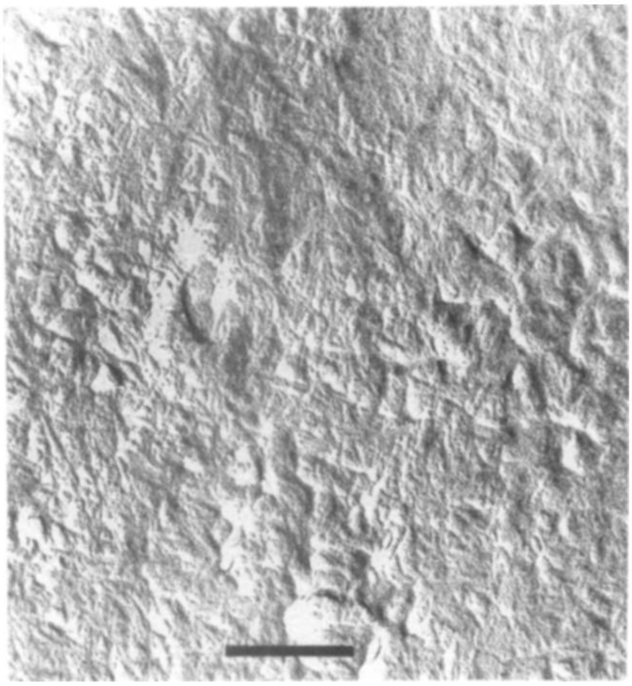

Figure 10 Transmission electron micrograph of a replica of fracture surface of copolyamide crystallized under pressure, showing the structureless areas mentioned in the text. Scale bar represents 2 μm

melt. The surface of copolyamide crystals grown under pressure from the melt reveals less of the amorphous, structureless material and higher crystalline order as compared with that of a copolyamide annealed under pressure. The lamellae are arranged in rows running radially from the spherulite centre, and the boundaries between them are relatively clear. The characteristics of the fracture surface of these crystals suggest, that in a similar fashion to nylon-6[6], the cracks within the copolyamide crystals, grown under pressure, propagate via inter- as well as intraspherulitic regions.

Figure 10 is a high magnification of the structureless areas observed on the fracture surface of copolyamides heat-treated under pressure, deposited probably on 010 planes of the crystals.

It is evident from *Figures 8–10* that the morphology of the copolyamide crystals formed under elevated pressure is different from that of nylon-6 crystallized under similar conditions[6]. It was found for nylon-6 that under pressure above 5 kbar the crystals with thickness in the range of 2000–10 000 Å were formed by pressure-induced crystallization from the melt as well as by annealing under pressure the chain-folded crystals. The surface morphology of nylon-6 crystals produced by these two different methods was the same[5,6]. The surface morphology of the copolyamide crystals grown under pressure from the melt were quite different from that of the crystals formed by annealing under pressure of the solid material. Thus it seems that disturbed regularity and stiffness of the copolyamide chain as well as a lower number of polar groups and a higher content of an amorphous material may be the reasons for the differences not only in the melting characteristics but also in the morphology for copolyamide and nylon-6 heat-treated under pressure.

X-ray diffraction

Small-angle X-ray scattering. The SAXS measurements of copolyamides crystallized from the melt or annealed at $\Delta T = 5^{\circ}$–10°C under atmospheric pressure showed that the long-periodicity of the crystals was in the range of 50–60 Å, and could not be increased even after 2000 h of annealing, although the crystalline order of the material was improved.

Annealing of copolyamides under a pressure of 6.5 kbar for 40 h increased the long-spacing from 50 to 400 Å. Pressure-induced crystallization of copolyamide from the melt at the same conditions of pressure, temperature and time increased the long-spacing to 900 Å and the highest value of the long-periodicity was found for pressure-treated copolyamides. However, this value is much lower than the value of 2000 Å which is the contour length of the copolyamide molecules.

Wide-angle X-ray scattering. Figure 11 shows the wide-angle X-ray diffraction patterns of copolyamide (N6-HMT) crystallized under various conditions. Curve 1 was recorded for the copolyamide crystallized from the melt at 198°C under atmospheric pressure for 40 h, curve 2 for the sample annealed at 6.5 kbar and 240°C for 40 h, and curve 3 for the sample crystallized from the melt at 6.5 kbar and 240°C for 40 h. As can be deduced from *Figure 11*, the alpha-crystalline modification prevails in the nylon 6-HMT copolyamide with the position of two principal peaks at (2θ) 20.0° (α_1) $d(100)$ and 23.5° (α_2) $d(001+101)$ which corresponds to the spacings of $d\alpha_1 = 4.4$ Å and $d\alpha_2 = 3.7$ Å. The values of d spacing found for the investigated copolyamides correspond exactly to those of nylon-6[6].

It was suggested by Tranter[21] that no change in the lattice spacings for some copolyamide systems may be a criterion for isomorphous replacement even in the case where the copolyamides had eutectic melting point curves. The same values od d spacing for the investigated

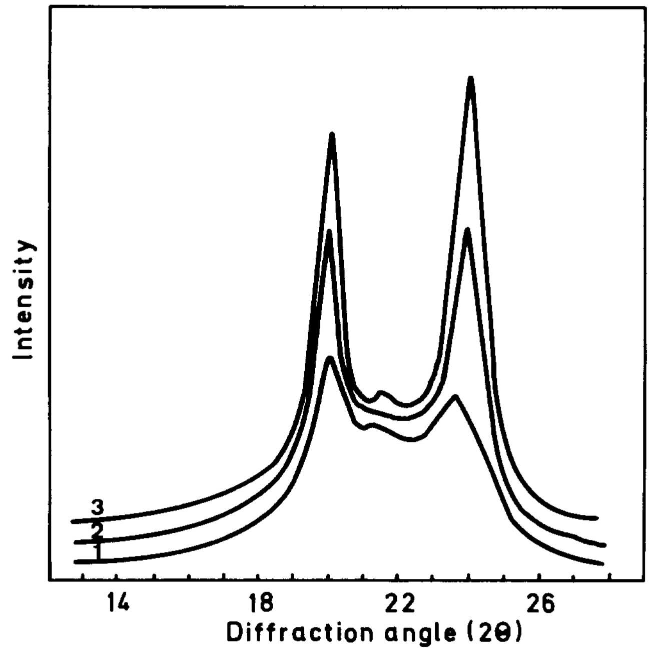

Figure 11 X-ray diffraction patterns of various copolyamide samples. 1. Sample crystallized from the melt at 198°C for 40 h under atmospheric pressure; 2. sample annealed at 240° C and 6.5 kbar for 40 h; 3. sample crystallized from the melt at 240°C and 6.5 kbar for 40 h

copolyamides and pure homopolymer would suggest isomorphous replacement, or at least partial isomorphism. The reduced crystallinity and type of morphology of copolyamide crystals differing from those of nylon-6, however, seem to contradict the above conclusion.

In contrast to the X-ray scattering patterns of nylon-6[6], curves 1 and 3 of the copolyamide shown in *Figure 11* reveal the third diffraction peak at (2θ) 21.3° (γ), which corresponds to a d spacing of 4.1 Å. Presence of the γ diffraction peak may be attributed to a poor-ordered material with pseudohexagonal packing between the chains which may exist in the random copolyamide.

No γ diffraction peak was found for the copolyamides annealed under elevated pressure without melting which shows that, as a result of breakage and reformation of the hydrogen bonds existing in the original metarial, the polymer forms the alpha (α) crystalline modification exclusively. Thus it seems that, although the crystalline order and the lamellar thickness are much higher in the samples crystallized under pressure from the melt than those of annealed under pressure without melting, the perfection of the hydrogen bonding is probably better in the latter samples. It can be seen in *Figure 11* that the relative intensities of the α_1 and α_2 peaks, as well as the separation of these peaks for the samples crystallized or annealed under pressure, increased. At the same time the width of these peaks decreased, that is to say that the dimensions of the crystals in the chain direction as well as perfection of the hydrogen bonds also increased. As was inferred from the shape of the diffraction peaks, pressure-induced crystallization from the melt produced thicker crystals of closer packing than those formed during annealing of solid copolyamide under pressure. This conclusion is in agreement with the data obtained from the SAXS measurements and electron microscopy observations.

For all the samples under investigation the positions of the α_1 and α_2 peaks are unchanged which means that although the crystalline order in pressure-treated copolyamides is evidently improved, the dimensions of the basal planes of the unit cell remain constant.

CONCLUSIONS

Crystallization of copolyamides from the melt and prolonged annealing at a low supercooling under atmospheric pressure do not increase the thickness of the lamellar crystals, their melting temperatures or their heats of melting.

Thermal treatment of copolyamides under pressure exceeding 5 kbar enhances lamellar thickening from 50 to about 900 Å and increases the melting temperature and the heat of melting of the crystals from 208°C and 10 cal/g to 228°C and 24 cal/g respectively, yet does not lead to the really chain-extended crystals, since the contour length of the molecules is in the range of 2000 Å.

Increased chain stiffness of the copolyamide chains resulted from *p*-phenylene linkages which seems to restrain the formation of the chain extended crystals by the long-range migration of the chain segments through the lattice, as well as by the mutual rearrangement within the chain folded molecule. Disturbed regularity of the copolyamide chain, irregular placement of the polar groups and presence of an amorphous material which stabilizes the folds and decreases accessibility of the –CO–NH– groups, may restrict the chain extension via transamidation.

The melting temperature of the random copolyamides under pressure increases on pressure of about 14°C/1 bar. The copolyamides under investigation, when heat treated under elevated pressure, form lamellar spherulites, predominantly of the α-crystalline modification, which are different from the chain extended spherulites of nylon-6 as well as from the spherulites grown in copolyamides under atmospheric pressure.

Crystalline order in pressure-treated copolyamides is much lower than that of the homopolymer crystallized under comparable conditions, which is a consequence of random copolymerization.

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