

Crystals grown from the gaseous phase of nylon-6

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Three types of crystals (whiskers, rhombic and twinned crystals) are obtained by vacuum extraction at 160°C from the gaseous phase of nylon-6 that has not been previously subjected to water extraction. The crystals are characterized by differential scanning calorimetry (d.s.c.), gel permeation chromatography (g.p.c.) and infra-red (i.r.) spectroscopy. The rhombic crystals are additionally studied by reflection high-energy electron diffraction (r.h.e.e.d.). On the basis of d.s.c., g.p.c. and i.r. spectral data the conclusion is drawn that crystals formed from the volatile substances contained in nylon-6 consist of ϵ -caprolactam. R.h.e.e.d. pattern interpretation leads to a rhomboidal unit cell with parameters $a = 4.37 \text{ \AA}$ and $\alpha = 80^\circ$, giving an ideal crystal density $\rho_c^{\text{id}} = 1.16 \text{ g cm}^{-3}$.

(Keywords: ϵ -caprolactam; nylon-6; vacuum extraction; gaseous phase; reflection high-energy electron diffraction; crystal structure)

INTRODUCTION

It is well known that nylon-6 obtained by polymerization of ϵ -caprolactam contains a portion of unreacted lactam and oligomers, amounting to roughly 10%. The latter can be removed from the polymer by extraction with a suitable solvent, such as water or methanol. The soluble fraction from technical polyamides is found to consist of caprolactam (about two-thirds of its dry weight) and crystallizable low-molecular-weight compounds. The substances extracted, after being freed of caprolactam by sublimation in vacuum at 110°C, do not contain free amino or carboxy groups, as shown by potentiometric end-group titration¹. Earlier investigations recognized these products as being cyclic oligomers (dimer and trimer) of caprolactam².

Two stereoisomeric forms of the cyclic dimer and cyclic trimer are isolated from the hot-water extract of caprolactam polymerizates with an average degree of polymerization of ~ 150 . None of these compounds contains free COOH or NH₂ groups, and their elemental composition is identical to that of caprolactam¹. The isolation of the individual substances from the mixture in a pure form has been found to be a tedious task and it is achieved by repeated fractional crystallization from water or dilute alcohol¹.

The study of the extractable low-molecular-weight products coexisting with nylon-6 is important for understanding the theory of the polymerization reactions. On the other hand, the isolation and structural characterization of caprolactam oligomers can also be useful for a better understanding of the crystal structure and polymorphism of nylon-6.

The present study deals with obtaining and characterizing crystals grown from the gaseous phase of nylon-6 by vacuum extraction.

EXPERIMENTAL

Three types of single crystals grown from the gaseous

phase of nylon-6 by vacuum extraction were obtained in the following way. Commercial nylon-6 bristles, $\sim 15 \text{ cm}$ long, containing about 10% low-molecular-weight compounds, were placed in a flask connected with a vacuum distilling adapter and a vacuum pump (2–5 Torr). The flask was dipped into an oil bath (160°C). Thus the volatile compounds evaporated and crystallized from the gaseous phase, forming single crystals. Depending on the crystallization conditions in the different parts of the vacuum distillation equipment, three types of crystals were observed:

- (i) thin needles (whiskers), $\sim 1 \text{ cm}$ long;
- (ii) thin rhombic platelets (side of $\sim 0.2\text{--}0.5 \text{ cm}$); and
- (iii) thin leaf-like twinned plates, $\sim 0.5\text{--}1 \text{ cm}$ long.

In addition to these three types of crystals, a thick white polycrystalline deposit was observed near the connection with the liquid-nitrogen trap.

The crystals were characterized by ebullioscopic determination of the molecular weight (Knauer apparatus, using benzene solutions) and by gel permeation chromatography (Waters g.p.c. system, toluene solvent, Ultrastyrigel column, 1 ml min^{-1} at 25°C). Their melting temperature was determined on a Mettler TA-3000 differential scanning calorimeter. The rhombic monocrystals were additionally characterized by i.r. spectroscopy in CCl₄ solution and KBr pellets. Their structure was investigated by reflection high-energy electron diffraction (r.h.e.e.d.) using an EF-4 electron microscope (Carl Zeiss-Jena, GDR) provided with facilities for precise r.h.e.e.d. The instrument constant λL_1 was determined using thallium chloride evaporated on a thin formvar film as a standard. The interplanar distances as well as parameters of the rhombic crystals were calculated from different r.h.e.e.d. patterns with an accuracy of 1.1%, which is within the range of error typical of this technique³.

All measurements were performed immediately after obtaining the crystals, because of their low stability under normal conditions.

RESULTS AND DISCUSSION

To the best of our knowledge, this technique of directly obtaining crystals of low-molecular-weight substances by sublimation from polymer that has never been subjected to water extraction has not previously been reported in the literature. The crystals grown from the gaseous phase are well shaped but they break easily upon detachment. A broken single crystal (of type (ii)) is shown in *Figure 1* taken in an optical microscope.

The symmetry of the single crystals suggests that they are of the rhombohedral class. This crystal symmetry is supported also by the interpretation of the electron diffraction patterns. By means of a contact goniometer the angles of the single crystals are measured and $\alpha = 80^\circ$ is established.

A typical r.h.e.e.d. pattern representing the (021) reciprocal-lattice projection is shown in *Figure 2*. One can see the large number of very sharp reflections usually observed with solution-grown polymer single crystals. Some extra reflections are also seen in the r.h.e.e.d. pattern. In an X-ray investigation of the crystal structure of caprolactam cyclic dimer⁴ such extra reflections have also been observed.

After indexing of the point diffraction pattern, the parameters a and α of the rhombohedral unit cell are calculated from the Miller indices and interplanar spacings, and $\alpha = 80^\circ$ and $a = 4.37 \text{ \AA}$ are obtained. These values are obtained from patterns taken from several samples.

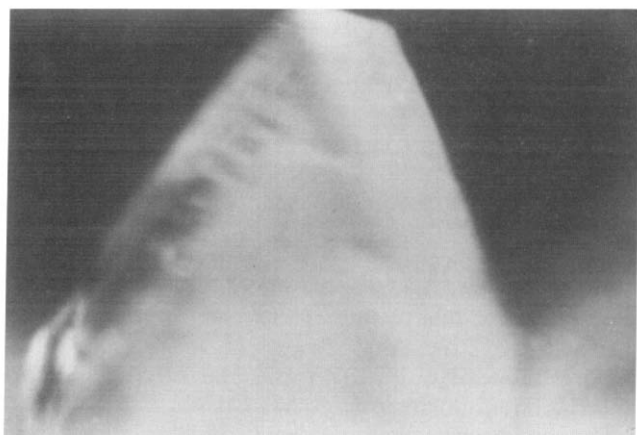


Figure 1 Optical microscope photograph of a rhombic single crystal grown from the gaseous phase by vacuum extraction of nylon-6 (20 \times)

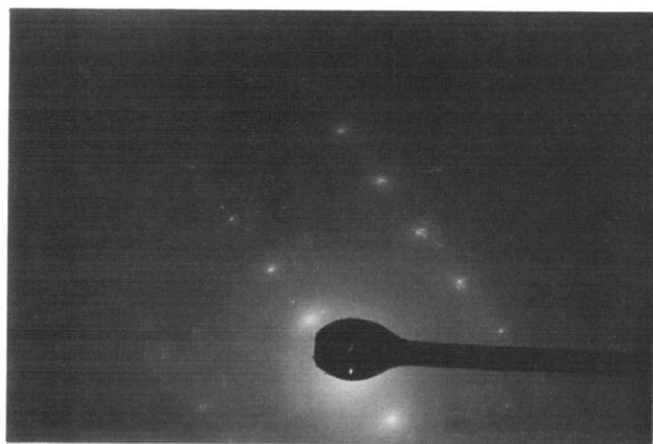


Figure 2 R.h.e.e.d. pattern of the rhombic single crystal shown in *Figure 1*; (021) projection of the reciprocal lattice

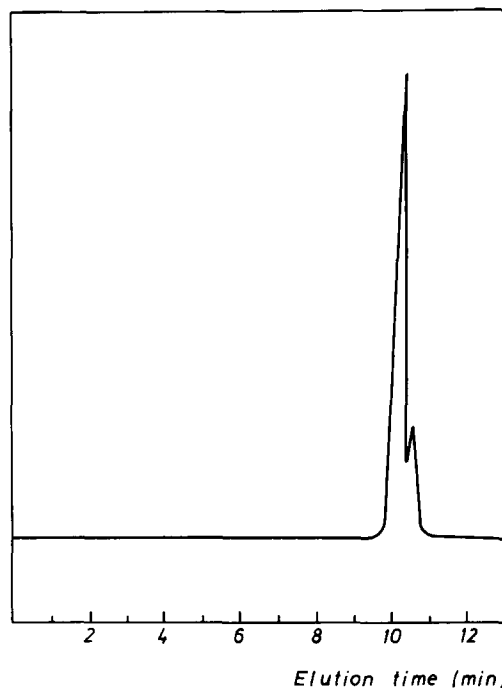


Figure 3 G.p.c. curve of crystals grown from the gaseous phase by vacuum extraction of nylon-6; whiskers, rhombic and twinned crystals have identical g.p.c. curves

The ideal crystal density derived from these unit-cell dimensions is $\rho_c^{\text{id}} = 1.16 \text{ g cm}^{-3}$. Owing to the very high solubility of the single crystals in both polar and non-polar liquids, experimental density measurement proves impossible.

The structure of the studied single crystals grown from gaseous low-molecular-weight substances derived from nylon-6 differs from the reported structure of the caprolactam cyclic dimer obtained from a solution in acetonitrile and dimethylformamide⁴. A triclinic unit cell with parameters $a = 15.469 \text{ \AA}$, $b = 8.985 \text{ \AA}$, $c = 8.918 \text{ \AA}$, $\alpha = 89^\circ 23'$, $\beta = 88^\circ 32'$ and $\gamma = 91^\circ 55'$ has been reported⁴. The molecules are linked together by $\text{N-H} \cdots \text{O}=\text{C}$ hydrogen bonds into sheets parallel to the (100) plane⁴. Furthermore, the unit-cell parameters obtained in the present study differ also from those of the crystalline monomer (ϵ -caprolactam)⁵: $a = 19.290 \text{ \AA}$, $b = 7.787 \text{ \AA}$, $c = 9.560 \text{ \AA}$ and $\beta = 112^\circ 35'$.

During crystal growth, conditions are suitable for the evaporation of different low-molecular-weight substances coexisting in nylon-6. Therefore, a question arises concerning the type of molecules building up the crystals studied.

The ebullioscopic determination of the molecular weight of the rhombohedral crystals in benzene solution reveals the value of 160. The latter corresponds neither to the monomer nor to the dimer. It can be attributed to a composition of 58% caprolactam and 42% dimer but it seems quite improbable that such a mixture could build up perfect single crystals.

The g.p.c. curves of all three types of crystals observed are identical and have the shape shown in *Figure 3*. It is seen that the peak is bimodal, which is unexpected for crystals consisting of one substance. The main peak has an elution time corresponding to molecular weight of 222 (calculated using an internal standard). This value, calculated with an accuracy of 2%, is twice that of caprolactam (113). The lower peak in *Figure 3* yields a

molecular weight of 205. This magnitude is not a multiple of $C_6H_{11}ON$ but it is exactly the sum of the molecular weights of caprolactam and toluene. In fact, it can be assumed that in toluene solutions π -complexes of caprolactam with the benzene ring of toluene could be formed⁶. On the other hand, it is well known that caprolactam forms a stable hydrogen-bound dimer, which dissociates to monomer molecules only at very low concentrations of the solution⁷. Thus it could be assumed that the crystals studied consist of caprolactam. In the solutions prepared for ebullioscopic and g.p.c. studies, caprolactam exists in both forms—as dimer and monomer. For this reason the ebullioscopically determined molecular weight value is between those of the monomer and the dimer. The g.p.c. curves (Figure 3) show a peak for the dimer and another one for the monomer (probably a π -complex with toluene).

In order to check this assumption, d.s.c. and i.r. spectroscopic studies have been carried out with the three types of crystals. The melting points obtained are given in Table 1; they suggest that all crystals are built up by caprolactam since the dimer and trimer have much higher melting temperatures (241°C, cyclic trimer; 247°C, β -cyclic dimer; and 347°C, α -cyclic dimer¹).

This assumption is also confirmed by i.r. spectroscopy data. The i.r. spectra in the region from 3800 to 800 cm^{-1} of the rhombic crystals are presented in Figure 4. It is seen that the spectrum in KBr (curve (a)) differs substantially from that in CCl_4 (curve (b)). This difference could be explained by taking into account the above-mentioned dimerization of caprolactam. It is found⁷ that in caprolactam solutions non-hydrogen-bound NH groups exist, and they are related to the peak absorbance of the monomer band at 3430 cm^{-1} . The spectrum of solid caprolactam lacks this band, i.e. no monomer is present in the solid⁷. It is seen in Figure 4 that an absorption maximum exists at 3430 cm^{-1} in CCl_4 solution of the crystals studied (curve (b)); however, the spectrum taken in the solid state (curve (a)) lacks this maximum. The cyclic oligomer band⁸ at 1550 cm^{-1} is absent in both spectra. Once again, this is an indication that the crystals consist of caprolactam.

On the basis of melting temperature and molecular-weight determinations as well as infra-red spectroscopy data, a conclusion can be drawn that crystals grown from the gaseous phase of volatile substances derived from nylon-6 consist of caprolactam. Crystals with a similar habit have been described earlier as being formed

Table 1 Melting temperatures (d.s.c.) of the crystals formed

Crystal type	t (°C)
Whiskers	69.0
Rhombic	70.5
Twins	70.5

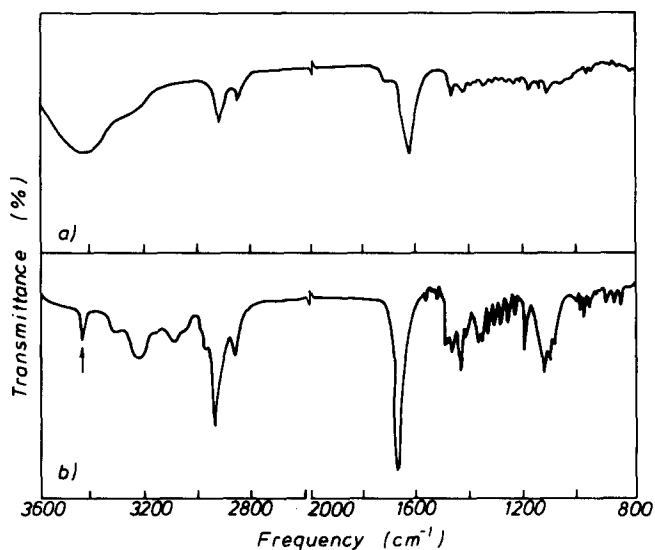


Figure 4 Infra-red spectra of rhombic crystals: (a) in KBr pellet; (b) in CCl_4 solution

by cyclic dimers and trimers¹. More precise X-ray studies of the crystal structure of the three types of crystals observed are in progress.

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