Single crystals of poly(*m*-xylylene adipamide)

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Single crystals of poly(*m*-xylylene adipamide) can be formed by slow cooling of a dilute glycerine solution. The morphology and structure of the obtained crystals are discussed on the basis of the crystal structure of this polymer. The following conclusions are deduced from the electron microscopic results. (1) Single crystals are composed of folded-chain molecules. (2) The molecular axis is perpendicular to the lamellar surface. (3) The growth rate of this crystal is highest in the hydrogen-bonding direction.

(Keywords: single crystals; morphology; poly(*m*-xylylene adipamide); electron diffraction; structure model; hydrogen-bonded sheet)

INTRODUCTION

There are many studies on single crystals of aliphatic polyamides[1–3]. However, no study on solution-grown crystals of aromatic polyamides including an aromatic ring as a chemical unit has yet been reported. It is very important to know whether one such polymer, poly(*m*-xylylene adipamide), crystallizes with chain molecules folded or not, for better understanding of the influence of polymer rigidity on chain folding. In this paper the morphology and structure of a single crystal of poly(*m*-xylylene adipamide) have been discussed, based on its crystal structure[4].

EXPERIMENTAL

Poly(*m*-xylylene adipamide) having a number-average molecular weight of 21 000 was polymerized by a well known method[5] and supplied by Toyobo Co. Ltd Research Center.

A dilute polymer solution of 0.02% was prepared by dissolving the above polymer in glycerine or various diols at 200°C. This solution was transferred to an oven kept at 170°C and slowly cooled at rates of 0.2–0.3°C h^{-1}. The solution became turbid at 167°C due to precipitation of crystallites. A tiny drop of the suspension was put on a carbon thin film spread on a mesh for electron microscopy. To evaporate the solvent, the mesh was dried at 150°C under a vacuum of 10^{-3} mmHg. The electron microscopic observations of the deposit remaining on the mesh was carried out using an electron microscope (Hitachi HU-11B), which was operated at an accelerating voltage of 100 kV. Electron diffraction patterns were taken under the same accelerating voltage after being shadowed with Pt–Pd.

RESULTS AND DISCUSSION

The selection of solvent and crystallization conditions was important to prepare polymer single crystals. When poly(*m*-xylylene adipamide) was precipitated from diols such as 1,3-butanediol, 2,3-butanediol, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol and poly(ethylene glycol), fibrillar crystals grew as shown in *Figure 1*. They very often extended in ribbons to a length of several tens of micrometres. On the other hand, when crystals were grown from glycerine solution, they showed a lamellar morphology, which is common to solution-grown crystals of most of the linear polymers[1]. The influence of crystallization temperature and rate of cooling on the crystallization behaviour of this polymer from glycerine solution was summarized as follows.

(1) During isothermal crystallization at temperatures below 165°C or crystallization by rapid cooling at rates of 0.1–1.0°C min^{-1}, an aggregate of lamellae, exhibiting the morphology of a spherulite at an early stage, was obtained as shown in *Figure 2*.

(2) At temperatures above 170°C, no crystals were observed as turbid deposits even after several days.

(3) By cooling a dilute solution of 170°C at slow cooling rates of 0.2–0.3°C h^{-1}, lamellar crystals were grown as shown in *Figure 3*.

The lamella-like crystals in *Figure 3* showed the piling up of several lamellae, the edge of which was mutually parallel to their long direction. At their growth fronts, the lamellae are bounded by planes that meet at a constant angle of about 60°. This angle coincides well with the angles of 65° between the (100) and (010) planes of this polymer crystal, or 64° between the (100) and (110) planes[4]. This coincidence means that the *c* axis (molecular axis) is perpendicular to the lamellar surface, and hence suggests that this lamella is composed of

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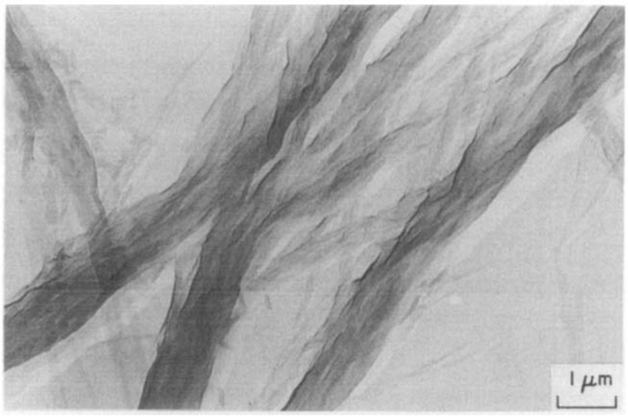

Figure 1 Fibrillar crystals grown from 2,3-butanediol solution

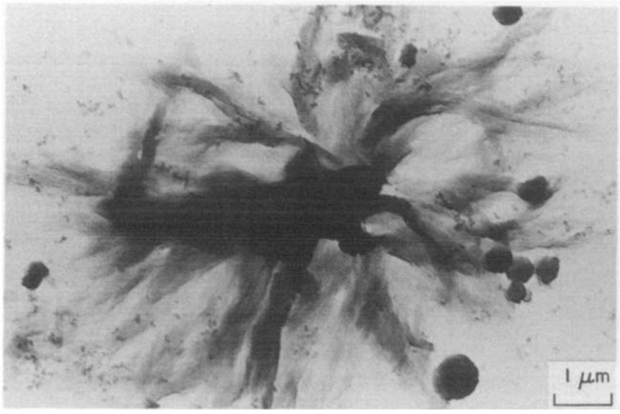

Figure 2 An aggregate of lamella-like crystals from glycerine solution

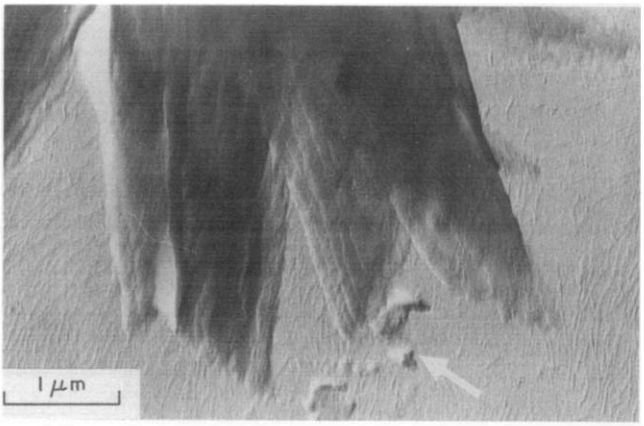

Figure 3 Lamella-like crystal from glycerine solution. The shadowing direction is shown by an arrow

folded-chain molecules. A lamella formed from glycerine solution and its electron diffraction pattern are shown in *Figure 4*, in which incident electron beams are perpendicular to the lamellar surface. In order to elucidate the relation between crystal structure and lamellar morphology, a long thin lamella as can be seen in the right-hand side of *Figure 3* was selected for electron diffraction, because it was difficult to obtain sharp diffraction spots in a lamella-like crystal as shown in the central part of *Figure 3*. Six strong diffraction spots and four weak diffraction spots are observed and can be indexed on the basis of the reciprocal lattice of a poly(*m*-xylylene adipamide) crystal[4], as depicted in *Figure 5*. The indices and spacings are given in *Table 1*. The six strong spots labelled I, II and III are indexed as 1 0 0, 0 1 0 and 1 1 0 diffractions, respectively. The four weak spots labelled IV and V are indexed as $1\,0\,\bar{1}$, 2 0 2 and 2 1 2 diffractions, respectively. In all diffractions except 1 1 0, the observed lattice spacings agree well with the calculated ones. Only the observed spacing of 1 1 0 is somewhat larger than the calculated one. This fact is thought to be due to the anisotropy of thermal expansion by heating during the electron diffraction experiment. The $1\,0\,\bar{1}$, 2 0 2 and 2 1 2 reciprocal lattice vectors are respectively inclined to the plane containing the a^* and b^* axes at small angles of about 9°, 19° and 18°; the fibre period is as large as 2.98 nm, so that the separation between reciprocal lattice planes is small. If the incident electron beam was rigorously parallel to the molecular axes, these diffraction spots could not be observed as shown in *Figure 4b*. When lamellae are inclined with

Table 1 Observed and calculated interplanar spacings of each electron diffraction spot and their indices

Diffractions	Observed spacings (Å)	Calculated spacings (Å)	Index of crystal plane
I	4.73	4.72	(1 0 0)
II	4.19	4.20	(0 1 0)
III	4.29	4.17	(1 1 0)
IV	3.49	3.49	$(1\,0\,\bar{1})$
		3.47	(2 0 2)
V	3.74	3.72	(2 1 2)

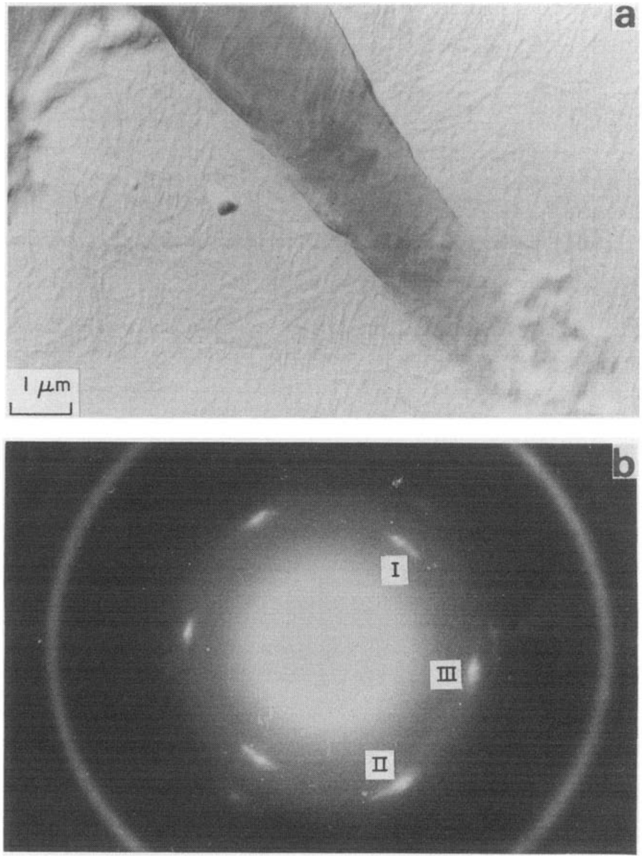

Figure 4 (a) A lamella from glycerine solution and (b) corresponding electron diffraction pattern taken after being shadowed with Pt–Pd

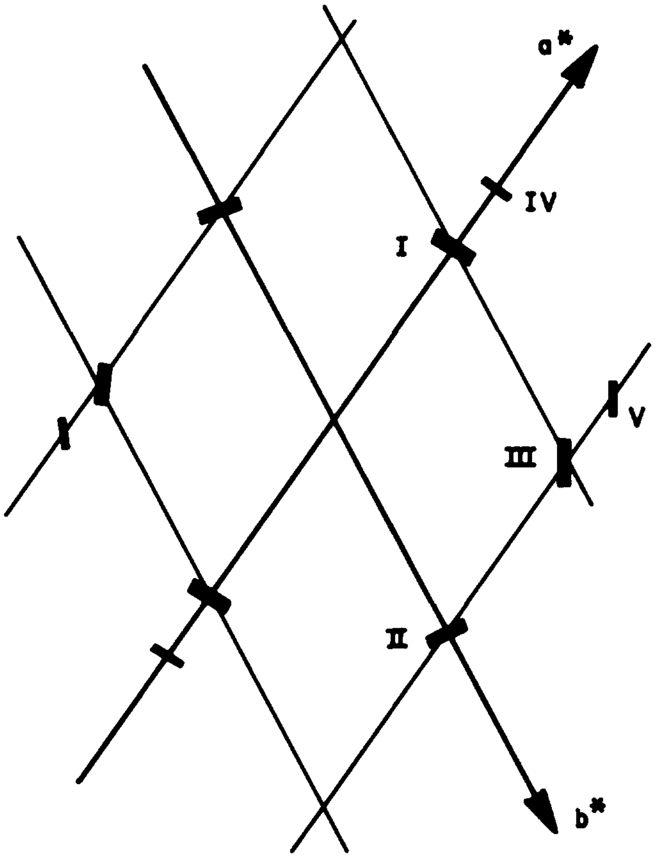

Figure 5 Schematic representation between electron diffraction pattern in *Figure 4b* and reciprocal lattice of poly(*m*-xylylene adipamide) crystal[4]

respect to the incident electron beams, or when molecular chains are not normal to the lamellar surface, the reflection condition of these spots is fulfilled by considering the extension of a reciprocal lattice point due to a thin lamellar sheet. The weak IV and V diffractions can be observed owing to a small deviation from parallelism between electron beams and molecular chain axes. It is thus concluded that the lamella in *Figure 4* is a single crystal and molecular axes are almost perpendicular to the lamellar surface. From the shadow direction and shadowing angle of 30°, the maximum lamellar thickness was estimated at about 145 Å (*Figure 3*). Therefore, we conclude that a lamellar single crystal of this polymer is composed of folded-chain molecules, taking account of the molecular weight of 21 000, corresponding to a molecular length of 1366 Å.

The orientational relation between lamellar morphology and the electron diffraction pattern in *Figure 5* shows that the long axis of the lamella is nearly parallel to the (1 0 0) plane, namely, the hydrogen-bonded sheet. The same orientational relation was also observed in the fibrillar crystals grown from diol solutions. These observations indicate that crystals of this polymer grow at the highest rate in the hydrogen-bonding direction. We propose two types of single crystal, depending on which type of crystallographic plane becomes the growth front. One has the (0 1 0) growth front and the other has (1 1 0).

CONCLUSIONS

From the above results the following information is obtained. (1) A single crystal of poly(*m*-xylylene adipamide) is formed by slow cooling a dilute glycerine solution from 170°C. (2) The molecular axis is almost perpendicular to the lamellar surface. (3) Single crystals of this polymer comprise folded-chain molecules. (4) The growth rate of the single crystals is highest in the hydrogen-bonding direction. (5) Two types of single crystal are put forward. One has the growth front of the (0 1 0) plane and the other has that of the (1 1 0) plane.

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