

# A Study on single Crystals of Nylon 12

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Single crystals of two crystalline forms,  $\alpha$  and  $\gamma$ , in nylon 12 were obtained from dilute solutions. The single crystals of  $\gamma$ -form from diols solutions are ribbon like lamellae in shape, and that of  $\alpha$ -form obtained from solution in water-formic acid are parallelogramic. Electron diffraction study shows that chain packings in single crystals of two crystalline forms are very similar to those of nylon 6, respectively.

## § 1. Introduction

It is well known that the crystalline state in bulk polymers plays an important role to the physical properties of the matter. The crystalline structures of nylons have been investigated by several workers<sup>1-4)</sup> because of their commercial importance and varieties of crystalline structures.

The usual  $\alpha$ - and  $\beta$ -forms<sup>1)</sup> of nylon 6 are easily converted to a new crystalline form when treated with iodine<sup>2,3)</sup>. This new crystalline form was called the  $\gamma$ -form by Kinoshita<sup>4)</sup>. He reported also that in the series of nylons from  $\omega$ -amino acids with even numbers of carbon, nylons 4 and 6 usually contain the  $\alpha$ - and  $\beta$ -forms, but nylons 8 and 10 appear in the  $\gamma$ -form. The usual  $\gamma$ -form of nylons 8 and 10 can be converted into the  $\alpha$ -form by phenol treatment. Thus, it is easy to obtain the  $\alpha$  ( $\beta$ ) and  $\gamma$ -crystalline forms in fibers of nylons 6, 8 and 10.

Geil<sup>5)</sup> obtained at first lozenge single crystals of the  $\gamma$ -form of nylon 6 from dilute solution in glycerine, and Nagai et al.<sup>6,7)</sup> obtained parallelogramic single crystals of the  $\alpha$ -form from dilute solution in water.

The present authors studied on the fibers of nylon 12 by x-ray method and recognized that the x-ray fiber diagrams showed the characteristics of the  $\gamma$ -form and the  $\alpha$ -form could not be easily converted to the  $\alpha$ -form by phenol treatment.

During the investigation of single crystals of nylon 12, we are interested in following points; (a) whether the single crystal of nylon 12 of  $\alpha$ -form can be obtained or not, (b) what are the factors to control the growth of these two crystalline forms. This paper deals with the results of

our study on nylon 12 single crystals by electron microscopy and electron diffraction method.

## § 2. Materials and Experimental Techniques

The material used in this study was unfractionated nylon 12 and the solvents used were triethylene glycol, water and water-formic acid.

Single crystals were prepared by the following two methods.

(a) A small amount of nylon 12 was dissolved in triethylene glycol at 180°C at concentration ranging from 0.01 to 0.001% and was precipitated in the form of single crystal by cooling slowly or by maintaining the solution at suitable crystallization temperature (170–150°C).

(b) A small amount of the polymer was sealed into a glass tube with water or water-formic acid. The tube was heated in a electric furnace at 250°C until the polymer was dissolved in hot solvents and was cooled slowly.

Drops of resulting crystal suspension were placed on carbon-coated grids and the solvent was evaporated *in vacuo* at 80–120°C. The specimens were shadowed with Pt-Pd and examined by direct transmission in JEM-6A electron microscope. Selected area electron diffraction works were carried out with the same instrument. Calibration of the diffraction spots was made with the aid of a thin layer of aluminium on the same specimen.

## § 3. Results

### (1) Morphology

It was found that the crystal habit is very strongly dependent upon the nature of solvents. A lamellar crystal obtained from solution in triethylene glycol and its selected area electron diffraction pattern are shown in Fig. 1. The

lamellar thickness deduced from shadow angle is about 80A. The overgrowth depending upon the screw dislocation is observed on both sides of lamella. Both of mother crystal and daughter crystal show linear long edge and short zigzag, which have an obtuse angle in larger crystal. At higher concentration, single crystals show the remarkable difference of the growth rate between long edge and short one. Thus they grow as ribbons.

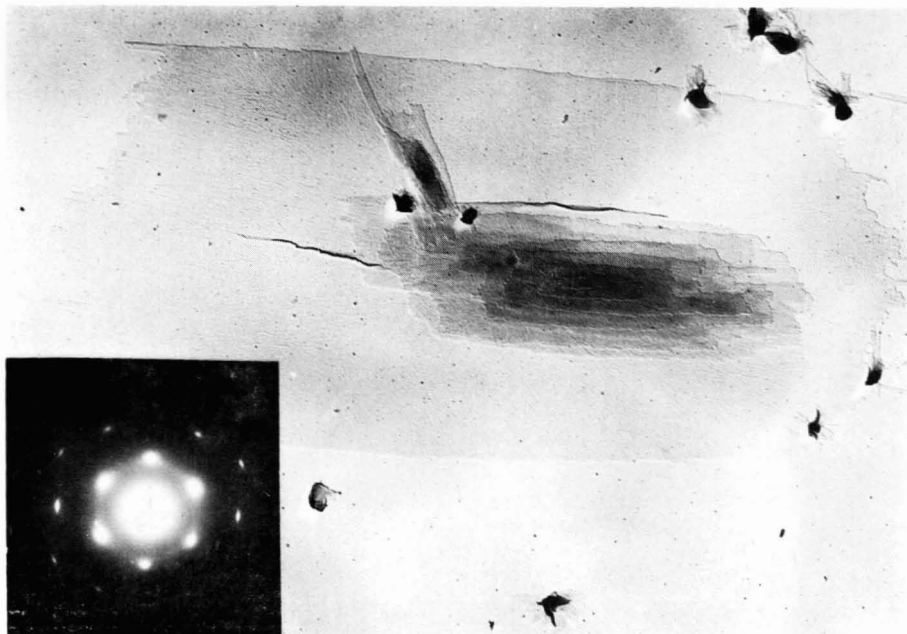
Two types of single crystals, which are different in morphology and structure, were obtained from water and water-formic acid solution. The first type shown in Fig. 2 is lozenge-like parallelogram and is similar to the  $\gamma$ -form single crystals of nylon 6 reported by Geil<sup>5)</sup> and Nagai et al.<sup>6)</sup> The lamellar thickness is about 300A, and the another electron micrographs show that these lamellae are stacks of thinner lamellae.

Fig. 3 shows another type of single crystal from water-formic acid solution and its selected area electron diffraction pattern. The single crystal is very thin lamella and no dislocation was observed on the lamella. The longer edges of parallelogram are linear and have some grains, but shorter ones are zigzag.

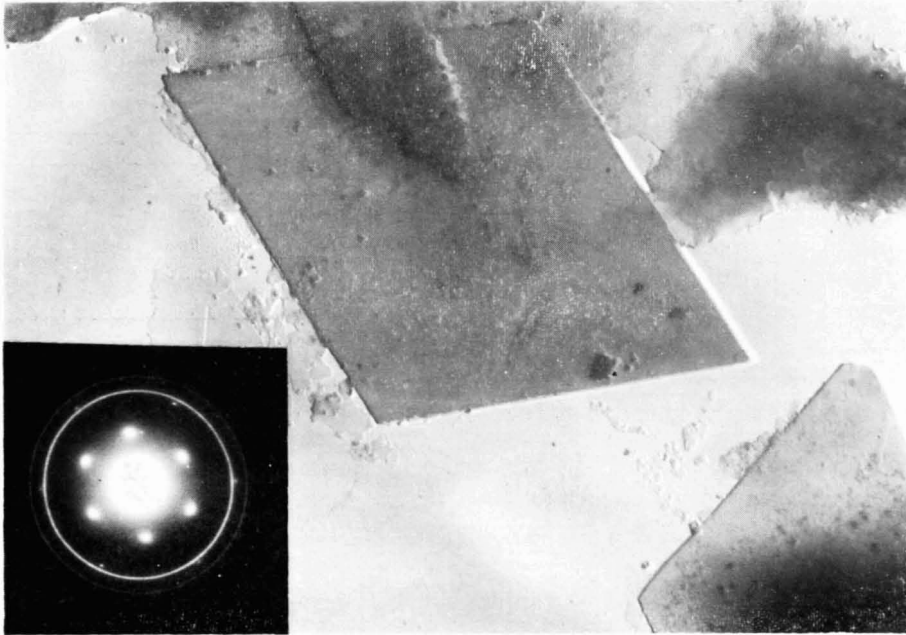
## (2) Electron Diffraction

Selected area electron diffraction pattern shown in Figs. 1 and 2 are fully interpreted, when the same structure of the  $\gamma$ -form as in nylon 6 is adopted. That is, the four of the six innermost spots with spacing 4.1A, and the two with spacing 4.0A will be assigned to reflections of the plane of [(001) and (20 $\bar{1}$ )] and (200) respectively, and remaining ones are other equatorials.

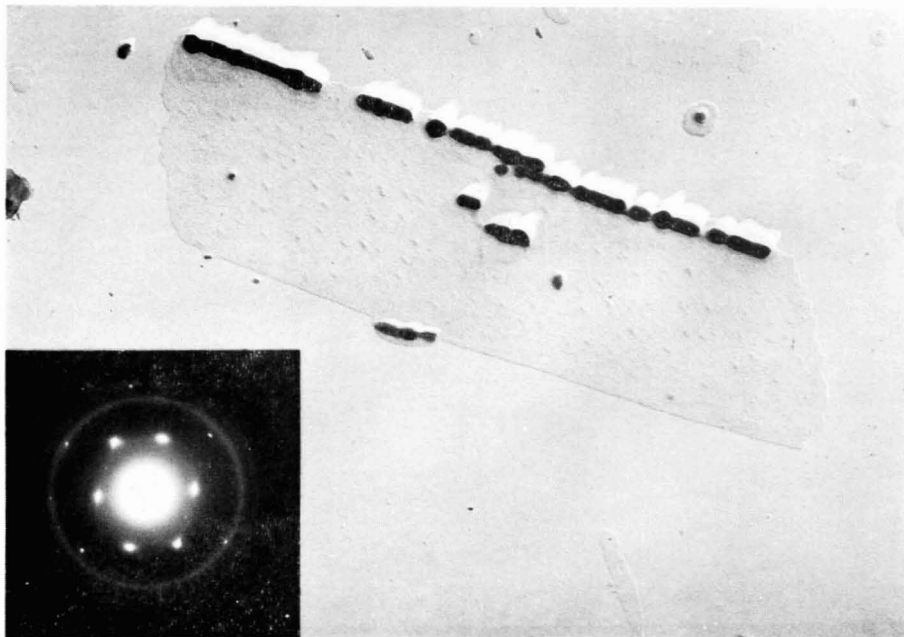
Fig. 4 shows a schematic representation of the diffraction patterns with respect to the single crystals.  $a(a^*)$  and  $c(c^*)$  are the real (reciprocal) axis based on a model<sup>8)</sup>. This diagram shows that the long edge of ribbon-like lamellae from triethylene glycol solution corresponds to (200) plane, and the hydrogen bonded planes are parallel to this direction. In the  $\gamma$ -form crystal it should be noticed that hydrogen bonds are formed between parallel segments, and that the folding of segments are permitted in (001) and (20 $\bar{1}$ ) planes. Thus the shorter zigzag edge of the ribbon corresponded to (001) plane can be the growing face, but the longer linear edge assigned to (200) planes can not be the fold planes. The growth of longer edge will be assumed to depend upon either alternate folding in (001) and (20 $\bar{1}$ )



**Fig. 1** Electron micrograph of a single crystal of nylon 12 ( $\gamma$ -form) crystallized from dilute solution in triethylene glycol and its corresponding electron diffraction pattern. Remarkable spiral growth centered on screw dislocations.  $\times 7,500$ .



**Fig. 2** Electron micrograph of a lozenge single crystal of nylon 12 ( $\gamma$ -form) crystallized from dilute solution in water and its corresponding electron diffraction. Rings in the electron diffraction patterns are the reflections from thin evaporated layer of Al used for references. Calculated spacings agree with those of single crystals from the solution in triethylene glycol.  $\times 7,500$ .



**Fig. 3** Electron micrograph of a parallelogramic single crystal of nylon 12 ( $\alpha$ -form) crystallized from dilute solution in water-formic acid and its corresponding electron diffraction pattern.  $\times 13,000$ .

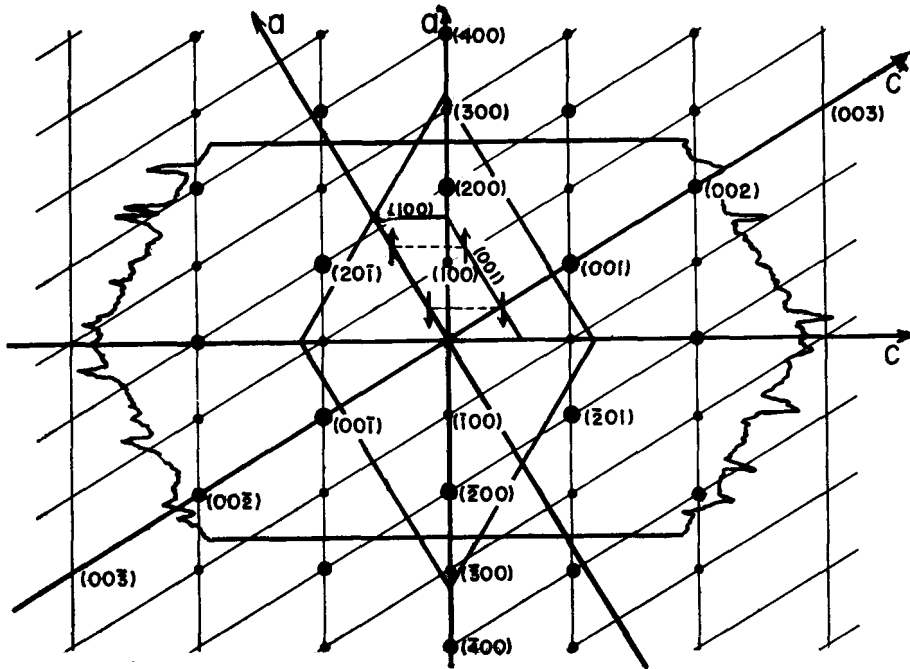


Fig. 4 Schematic representation of two morphologically different single crystals of 7-form and their reciprocal lattice. Dots show observed reflections in the electron diffraction patterns.

planes or the stacks of (001) fold planes.

On the other hand, in the case of crystals from water and water-formic acid solutions, the minor axis of the lozenge corresponds to  $c$  axis and is parallel to the hydrogen bonded plane (200). The four edges are assigned to (001) and (201) planes. Two pairs of edges of this crystal have not equal length. This fact suggests that they are not same crystallographic plane, and that the growth rates are different between these two planes.

We shall consider that the shape of  $\gamma$ -form single crystals of nylon 12 depends on the growth rates in (001) and (201) planes. In the case of lozenge type crystals, these two growth rates are nearly equal, while in the ribbon like crystals the growth rate of (001) plane is larger than that of (201) plane. These differences depend on the nature of solvents and other crystallization conditions.

A selected area electron diffraction pattern from a parallelogramic crystal obtained from water-formic acid solution is shown in Fig. 3. The spacings of the strong six reflections are 4.5 Å, 3.7 Å and 3.5 Å, which agree with the spacings of (200), (002) and (202) planes of  $\alpha$  (or  $\beta$ ) form of nylon 6 proposed by Bunn<sup>1</sup>, respectively. The correlation between the mor-

phology and selected area electron diffraction pattern in Fig. 5 shows that the long and short edges of parallelogram correspond to (002) and (200) planes, respectively. These relations agree with those of nylon 6 by us<sup>9</sup>. As the chain folding is possible in (002) and (202) planes in the  $\alpha$ -form, the similar questions to the  $\gamma$ -form arise. The long edge can be the fold plane. On the other hand, the short edge cannot be the fold plane as in the case of (200) plane in the  $\gamma$ -form. The growth of this face, therefore, depends upon either alternate folding in (002) and (202) planes or stacks of (002) fold planes only.

#### § 4. Discussion

Two kinds of crystal modification in nylon 12,  $\alpha$ - and  $\gamma$ -forms, were obtained in the form of single crystals. Electron diffraction pattern shows that the side by side packing of molecular chains in these two single crystals closely resemble with those of nylon 6, respectively.

Although we did not succeed to obtain the  $\alpha$ -form crystals in nylon 12 by phenol treatment on fiber, we obtained them in the form of single crystals from dilute solution in water-formic acid. From various kinds of diol solvents, however, we obtained only the  $\gamma$ -form single

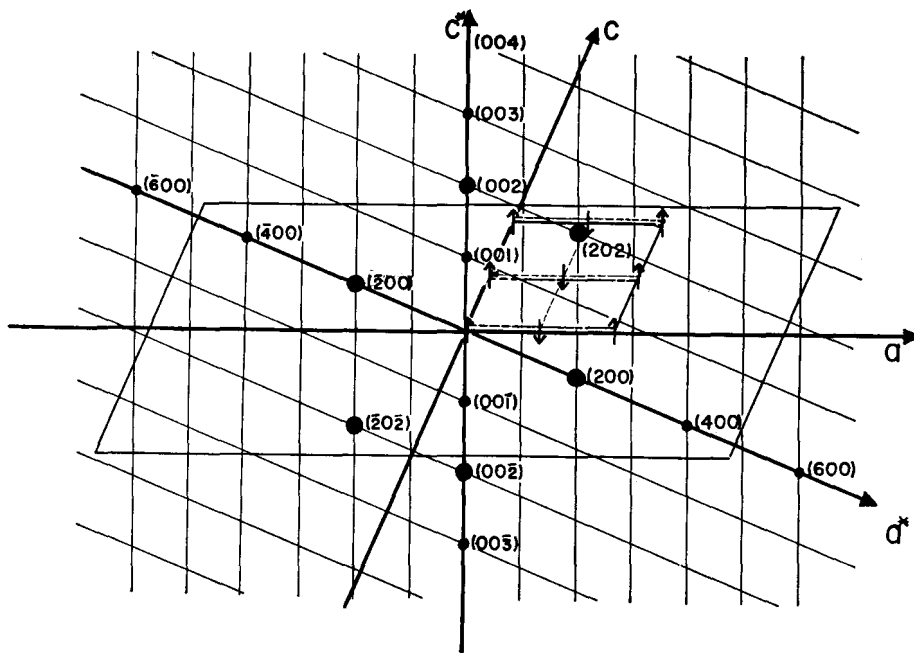


Fig. 5 Schematic representation of a parallelogramic single crystal of  $\alpha$ -form and its reciprocal lattice

crystals.

Nylon 12 has longer  $\text{CH}_2$  chains between amide groups than nylon 6. The stable crystalline form of nylon 12 is usually the  $\gamma$ -form, while the  $\alpha$ -form is more stable than the  $\gamma$ -form in nylon 6. The longer  $\text{CH}_2$  chains per the repeating unit in nylon homologue decrease the effect of the hydrogen bonding and increase the influence of the intermolecular van der Waals force. This seems to be the reason why the  $\gamma$ -form is stable in the even nylons which have longer  $\text{CH}_2$  chains in the repeating unit.

We used formic acid aqueous solutions as solvent for the  $\alpha$ -form single crystals of nylon 12. We shall suggest that polar solvent such as formic acid aqueous solution plays an important role to produce  $\alpha$ -crystalline form in nylon 12.

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