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Analysis of growth habits of polar organic crystal N-4-nitrophenyl-(L)-prolinol (NPP) based on the incorporation of growth units

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Abstract

The growth habits of the polar organic crystal N-4-nitrophenyl-(L)-prolinol (NPP) in organic solvents have been studied from the standpoint of the incorporation of growth units. Qualitative explanations of the observed growth forms are based on (1) the interaction between the solvent molecules and the growth units, and (2) the influence of the solvent molecules on growth interfaces, particularly on two polar faces of the polar organic crystal. Since the incorporation rates of the growth units are different on positive and negative polar faces, a variety of growth habits appear. The surface structures of the grown crystal have been investigated through ex-situ observations of atomic force microscopy (AFM).

1. Introduction

The polar organic molecular crystal N-4-nitrophenyl-(L)-prolinol (NPP) displays very large quadratic nonlinear optical efficiencies in the visible and near infrared spectral range [1] and is open to various applications in nonlinear optical field [2–5]. Some methods of growing NPP crystals have been reported [6–8]. The large perfect single crystals have been obtained successfully by improving the solution techniques [10]. The nonlinear optical mechanism of the crystal has been widely studied from the standpoint of “molecular engineering”. However, the growth habits and morphology of the crystals are seldom concerned. In this paper, the growth habits of the crystals have been investigated, their formation

mechanism will be discussed, and relations between the morphology of the crystal and the incorporation of the growth units have been suggested.

2. Growth and morphology of NPP crystals

2.1. Crystal growth

Although growth of NPP crystals either by solution methods or by melt techniques has been reported, it has been difficult to grow high quality large sized NPP crystals. After investigating the crystal habits in various organic solvents and improving the solution growth techniques, we have been successful in growing large perfect NPP crystals attaining up to $21 \times 12 \times 3 \text{ mm}^3$ in size from acetone and tetrahydrofuran (THF) solutions by a

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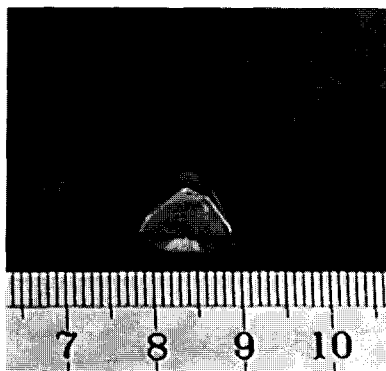


Fig. 1. Photograph of an as-grown single crystal.

solution-cooling or solvent-evaporation technique [9]. The crystal shown in Fig. 1 is an example of successfully grown crystals. For the solution-cooling method, the cooling rate was kept at $0.05^{\circ}\text{C}/\text{day}$ under control with a temperature fluctuation of less than 0.01°C . Controlling a proper supersaturation and selecting a good seed were the most important factors in both cases.

2.2. Morphology of NPP crystals

All possible faces of the organic crystals fully appeared when the crystals were grown from solution. However, the relative growth rates of faces changed depending on solvents, supersaturation degree of the solution, or other physico-chemical factors. Normally, faces appearing on NPP crystals grown from acetone or THF solutions are $(0\bar{1}0)$, (001) and (011) , and the grown crystal takes a cone-shaped form and has arch-shaped faces except for the $(0\bar{1}0)$ face [7,9], as shown in Fig. 1. Although the growth rates of these faces are influenced by the seed orientation and the degree of supersaturation, $(0\bar{1}0)$, (011) faces are commonly observed. It clearly represents the growth characteristics of polar crystals [11–14] in that the positive polar face grows faster than the negative polar face. For the NPP crystal, the polar axis of the crystal coincides with the binary axis, the positive polar direction is the b -axis positive direction. Therefore, the negative polar face $(0\bar{1}0)$ commonly appears, whereas the positive polar face grows so fast that it disappears (Fig. 2a).

However, the growth shape of the crystal grown from the mixture of dimethylsulfoxide (DMSO) and

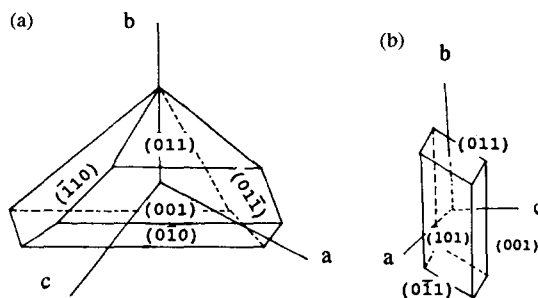


Fig. 2. Growth habits of NPP crystals in different solvents (a) in acetone, and (b) in DMSO + H_2O .

water (volume 2:1) [15] or from the toluene solution [10] takes an elongated rhombic form, bounded by (101) , (001) and (011) (Fig. 2b). The morphology of NPP crystals varies depending on the growth solvents.

3. Growth habits and growth units of NPP crystals

3.1. Structural units of NPP crystals

Because the chirality and hydrogen bonding are present in the molecule, NPP crystal is a successful example of “molecular engineering”, which has an optimal molecular structure and crystal structure [6], as shown in Fig. 3a and 3b. NPP belongs to the monoclinic system with space group $P2_1$, and crystal cell parameters $a = 0.5260 \text{ nm}$, $b = 1.4906 \text{ nm}$, $c = 0.7183 \text{ nm}$ and $\beta = 105.217^{\circ}$.

The crystal structure reveals that the lattice is built up of dimers due to hydrogen bridges between the two molecules. We consider monomers or dimers

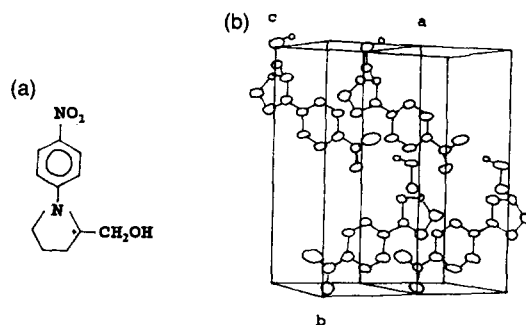


Fig. 3. Molecular (a) and crystal structures (b) of NPP.

of NPP molecules as growth units in organic solvents from the analyses of the solution structure [15–17]. In the former case, hydroxyl of monomer NPP molecule may be linked to oxygen of carbonyl of acetone molecule in the acetone solution or to the oxygen of the THF molecule when using THF as a solvent through hydrogen bonding. The solvent molecules will be desorbed when the growth units incorporate on the growing interface. In the second case, two NPP molecules are connected by intermolecular hydrogen bridges between the alcohol of one molecule and the nitro-group of the next. The probability of forming dimers in the solution is considered to have two cases: one is when the concentration of the solute increases as increasing supersaturation; the other is when the solute–solvent interaction in the growth solution is weak, for example, when the crystal grows from the mixture of DMSO and water or from the toluene solution. Two structural forms of growth units are shown in Fig. 4. The two kinds of growth units (monomers or dimers) show features of polaron; the ends of the nitro-group of the growth units possess negative charge, the other end of the alcohol of the growth units has positive charge. The growth unit of the dimers is equal to the size of a unit cell.

3.2. Incorporation of growth units on crystal faces

The incorporation rates of growth units on molecular crystal faces in organic solution depend on the polarity of growth interfaces, orientation of the inter-

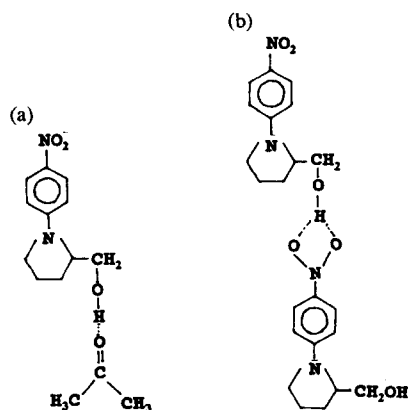


Fig. 4. Structural forms of the growth unit of the NPP crystal.

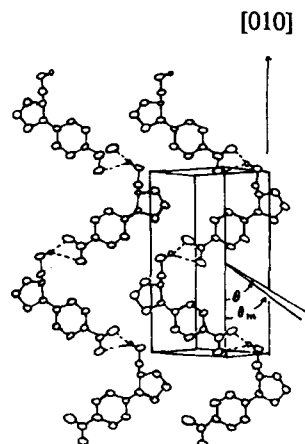


Fig. 5. The distribution of structural units along the [010] direction in the NPP crystal.

molecular hydrogen bonds and the structural forms of the growth units. When the growing interface of the crystal has no polarity, the incorporation of the growth units will follow principally the direction of stronger bonding, as described by the PBC theory.

3.2.1. Incorporation of growth units along [010] and $[0\bar{1}0]$ direction

Fig. 5 shows the orientation of structural units along the [010] direction in the NPP crystal. The *b*-axis is polar, and the distribution of structural units along the polar axis of the crystal is asymmetrical, one end of the crystal being nitro-rich and the other hydroxyl-rich. The negative end of the polar growth units favors to link the end of hydroxyl-rich of the growing crystal, whereas the end of the nitro-group of the growing crystal hinders incorporation of growth units due to the strong solute–solvent interaction when the crystal grows from acetone or THF solutions [18–20]. Therefore, the positive polar face of the crystal grows faster than that of the negative polar face, revealing the persistent appearance of the negative polar face (010) while the positive polar face usually disappears. The shape of the crystal appears as cone-shaped. This is a common character observed in growth habits of polar crystals [11,12]. In fact, this is in accord also with the growth behaviour identified by our experiments [9]. In addition, it is interesting to note that the effect of supersaturation upon the growth habits should be consid-

ered further since the dimensions of the growth unit increase with an increase of the supersaturation degree of the solution. As increasing the supersaturation degree of solution, the possibility of forming larger growth units consisted of two or three NPP molecules is expected to increase; therefore, the positive polar direction of the crystal will grow faster, because the polarity of larger growth units is stronger than that of the smaller growth unit, e.g. NPP monomers. As a matter of fact, it became difficult to control the growth of the crystal in the acetone solution in our solvent-evaporation growth experiment at a later stage, where the supersaturation degree increases ($\Delta T \approx 1^\circ\text{C}$). Under such a condition, the mother liquid inclusions are easily trapped and the crystal tends to take a dendritic form along the $[010]$ direction. At the same time, the negative polar face ($0\bar{1}0$) appears as a smooth face, as shown in Fig. 1, indicating that the growth rate of $[0\bar{1}0]$ becomes much smaller.

On the other hand, the growth of the crystal, for example, from the toluene solution is different; because, in our opinion, the interaction of solute–solvent at this time is small, and the influence of the solvent on the growth interface tends to be suppressed. The NPP molecules are expected to link to form the growth units of the long chain, and these growth units can incorporate either on the positive face (010) or on the negative face $(0\bar{1}0)$. Therefore, under such a condition, it becomes easier for the crystal to take an elongated rhombic form.

3.2.2. Incorporation of growth units on (101) , (001) and (011) faces

As can be seen from the molecular structure, the NPP molecule consists of a phenyl ring and a pyrrolidine ring. The end of nitro-phenyl shows the negative charge, the other shows the positive charge. The structure is characterized by infinite hydrogen-bonded zig-zag chains along $[010]$. However, the (101) face has a layered structure, indicating that the face may grow layer by layer, as shown in Fig. 6, and that there is an effect of hydrogen bonding along the $[101]$ direction in addition to the Van der Waals force, when the incorporation of growth units takes place along the $[101]$ direction. Therefore, the (101) face is expected to grow with a rather large growth rate and will disappear from the habit although it is

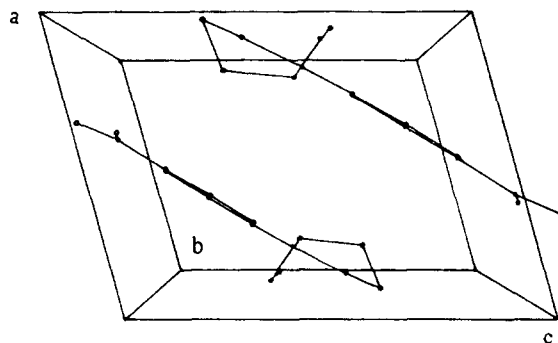


Fig. 6. The structure projected along the $[010]$ direction.

the cleavage face. In addition, the (101) face will tend to disappear with the development of the (011) face. The incorporation of growth units on the (001) and (011) faces is not vertical but slanted, so the relative face areas of (011) and (001) gradually diminish as the crystal grows larger. This leads to the development of arch-shaped faces.

The appearance of the crystal grown from acetone or THF solutions is in disagreement with BFDH analysis (the order of morphological importance is $(101) > (110) > (011) > (001) > (010)$). In contrast, the crystal grown from the mixture of DMSO and water can develop along both polar directions because there is little effect of the solvent on the growth interfaces at this time. The crystal takes a form bounded by the (101) , (001) and (011) faces, which is in agreement with BFDH analysis. The difference between the two cases can be attributed to the interaction of solute–solvent. We consider that the big interaction of solute–solvent is expected to strongly affect the crystal morphology; in other words, the less the interaction of solute–solvent, the more the crystal tends to take the ideal form. Further studies on the solute–solvent interaction are in progress.

4. Surface structures of the crystal

The atomic force microscope (AFM) has been applied so far to investigate the structures of organic molecular crystals with a resolution of an atomic scale in real space. It is also powerful to investigate concurrently the surface structures and the surface

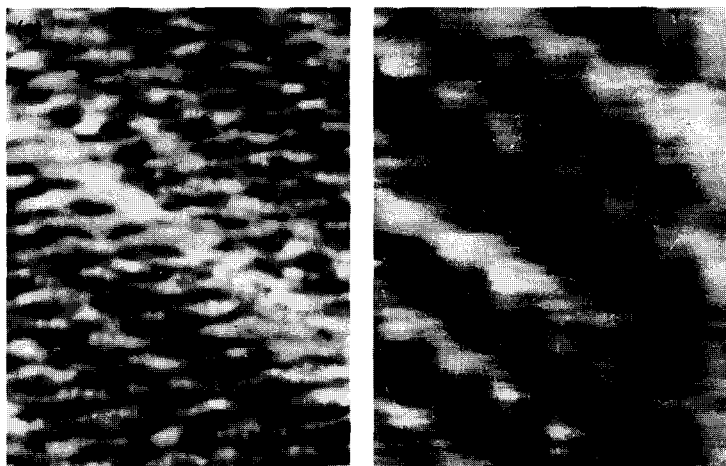


Fig. 7. Surface structures of (a) (001) and (b) (101) of the NPP crystal under AFM. (a) Tunneling current of 0.94 nA, bias voltage of 8 mV, and scanning area of 4.5 nm \times 5.7 nm. (b) Tunneling current of 0.88 nA, bias voltage of 19 mV, and scanning area of 4.6 nm \times 5.3 nm.

microtopography through ex-situ and even in-situ observations. As-grown surface microtopography after the cessation of growth and after the crystal has been taken out from the growth solution represent the final stage of the crystal growth and provide molecular information relating to such growth processes [13], provided that the post-growth artifact can be entirely eliminated. The surface structures of the (001) natural face and the (101) cleaved plane of the grown crystal have been investigated [21]. The typical AFM images of the (001) face and the (101) plane are shown in Fig. 7a and 7b. The force sensor was made of tungsten. A piece of foil was electrochemically etched in a solution of NaOH, resulting in a tongue-shaped cantilever, the deflection of the cantilever was detected by tunneling to its back. The AFM image of highly oriented pyrolytic graphite (HOPG) was used for calibrating the observed AFM image of NPP.

The AFM image of the NPP (001) face indicated the existence of periodical structure. This structure consists of an elongated protrusion arranged in a parallelogram with a long line of 1.4 nm and a short line of 0.4 nm. The observed length of the elongated protrusion is approximately the same as the theoretical molecular length of NPP. Two small protrusion structures of the elongated protrusion are coincident with the molecular structure of NPP, which contains

a phenyl ring and a pyrrolidine ring. So it is considered that the observed elongated protrusion shows a NPP molecule. In fact, based on the analysis of the incorporation of the growth units on the (001) face, as discussed above, the molecular arrangements should be a parallelogram.

From the image of the (101) cleaved plane, the zig-zag chain is seen running from bottom-right to top-left. This corresponds to the arrangement of growth units on the (101) face, which parallels the binary axis of the crystal, shown in Fig. 5.

NPP crystal displays a very large nonlinear efficiency ($d_{21} = 56.5$ pm/v) [3] due to an optimum nonlinear value of θ angle between the molecular charge-transfer axis and the binary axis ($\theta = 58.6^\circ$) closing to the optimal angle ($\theta_{\text{opt}} = 54.74^\circ$). We obtained the angle θ to be 56° by AFM, which is very close to the result obtained by X-ray measurement ($\theta = 58.6^\circ$).

5. Discussion

The growth rate of various faces on a crystal is related to the incorporation rate of growth units on respective faces, which determine the final morphology of the crystal. The sizes and structural forms of growth units may vary with various physico-chem-

ical conditions, such as the growth solvents, the supersaturation degree, etc. The incorporation of growth units will be different depending on both the nature of growth interfaces and the forms of growth units; particularly, the incorporation of the growth units for polar organic crystals depends on the polarity of the growth interface [22] as well as the direction of hydrogen bonding and the molecular structure. In general, the positive polar face grows faster than the negative, and often disappears, whereas the negative polar face develops large. Maybe the absorption of the solvent molecules on the negative face is so big that hinders the incorporation of growth units on it, as discussed above. It is necessary to note that the polarity of a face is determined by the atoms which are exposed normal to the face. Normally, for a polar organic crystal the end at which the electron-acceptor groups appear is the negative polar face, the opposite is the positive face.

The relations between the structure and the morphology for many organic crystals can be explained well simply based on the PBC theory of Hartman-Perdok [23]. However, we analyzed in this paper the growth habits of NPP crystals assuming the incorporation of growth units on various faces, and demonstrated that the analysis can offer a satisfactory explanation for the difference in the growth rates between the positive and negative polar faces, and the influence of solvents on crystal habits. In order to understand the habits of polar organic crystals, the present analysis assuming the incorporation of the growth units appears to be useful to account for the diversity of the morphology of organic crystals such as in bulk, platelet or fibre forms under different growth conditions, particularly in different solvents [24,25].

In summary, the growth habits of polar organic crystal N-4-nitrophenyl-(L)-prolinol (NPP) have been investigated, and the relations between the crystal morphology and its growth units have been discussed. The morphological characteristics and their changes depending on solvents and supersaturation are analyzed based on the incorporation of growth units. This was supported by the observations of micro-radicals and the surface structures of the grown crystal by using atomic force microscopy (AFM).

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