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Oriented crystallization of alkylating amino-nitropyridine in a matrix of polypropylene

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Abstract

It was found that alkylating amino-nitropyridine was able to crystallize epitaxially in a matrix of the oriented polypropylene (PP) as its longest spacing crossed the periodical spacing between the oriented PP chains, that is, as its alkyl chain crossed the oriented PP chains. The degree of crystalline orientation of alkylating amino-nitropyridine in a drawn matrix of PP was somewhat lower than that of PP over all ranges of draw ratio, supporting the suggestion that its epitaxial growth progresses according to the degree of crystalline orientation of a drawn PP matrix. One of the possible models of this epitaxy structure, which matched its X-ray diffraction patterns well, has been deduced by using the crystal structure proposed in a previous paper. © 2000 Published by Elsevier Science Ltd.

Keywords: Alkylating amino-nitropyridine; Polypropylene; Epitaxial growth

1. Introduction

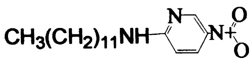
In a previous paper [1], we reported that alkylating amino-nitropyridine was able to crystallize epitaxially in a matrix of polyethylene (PE), as it laid its alkyl chain upon the highly oriented chain of PE. From X-ray diffraction photographs, results of crystalline orientation, and infrared dichroism of drawn mixtures, a possible model of its epitaxy structure has been deduced. Furthermore, for the crystal of alkylating amino-nitropyridine in a matrix of highly oriented PE, a triclinic unit cell and a molecular packing having a center of symmetry were proposed. This study was carried out to prove that the structure of a PE matrix is similar to that of a single crystal [2] or that the LB membrane [3] of alkylating amino-nitropyridine generates an optical second harmonic.

Subsequently, the realization of the above structure in a matrix of polymers other than PE attracted our interest. In this paper, this is examined by drawing the mixture of alkylating amino-nitropyridine and ultra-high molecular weight polypropylene (PP).

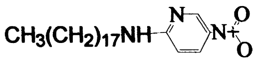
2. Experimental

2.1. Materials

Two kinds of alkylating amino-nitropyridine, 2-dodecylamino-5-nitropyridine (DANP) and 2-octadecylamino-5-nitropyridine (OANP), were synthesized, based on EP 0 329 613 A2. The chemical formulae of both materials are as follows.



DANP



OANP

The confirmation of the structure of both materials was carried out primarily with FT-IR spectra. The peak temperatures of the melting curve of DANP and OANP powders were 70.0 and 80.4°C, respectively. Ultra-high molecular weight PP ($M_{\mathrm{w}} \fallingdotseq 1.8 \times 10^6$, supplied by Tokuyama Co. Ltd) was used as a matrix of mixtures.

2.2. Preparation and drawing of mixtures

The gel-casting mixtures of PP and DANP (or OANP) were prepared by cooling a decalin solution of 6.0 wt% concentration of PP at 160°C, adding the fixed amount of DANP (or OANP) to it. The ratios of DANP/PP and

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OANP/PP in the decalin solutions were, respectively, 37.5/62.5 and 30/70. The mixtures of PP and DANP (or OANP) were prepared by compressing the gel-casting mixture under a pressure of 50 kg cm^{-2} at room temperature, and subsequently drying the compressed material under the reduced pressure at room temperature to remove the decalin. The thickness of the mixtures obtained was 0.3–0.7 mm.

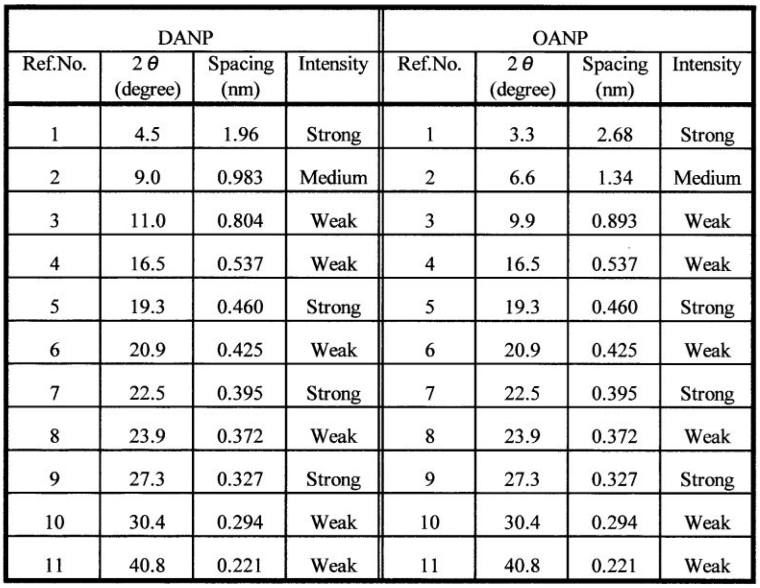
The mixtures of DANP/PP and OANP/PP obtained were drawn by the two-step hot drawing of 120 and 130°C under the deformation rate of 50%/min. The first-step drawn mixture of draw ratio = 10 was used for the second-step drawing. The contents of DANP and OANP in the first-step drawn mixture were, respectively, about 28 and 22 wt%, determined by the extraction method using benzene as solvent. Stress vs. strain curves of both mixtures during first-step drawing at 120°C did not show the neck deformation, and the maximum draw ratios were 39.0 for DANP and 24.0 for OANP.

3. Results and discussion

3.1. Molecular length and WAXD patterns of DANP and OANP

Since the crystal structure of DANP and OANP is not yet clear, their molecular lengths have been speculated using CS Chem 3D Pro (Molecular Modeling and Analysis). As shown in a previous paper [1], their lengths are 2.10 and 2.84 nm, respectively.

WAXD patterns of DANP and OANP powder are shown in Fig. 1. The spacing of reflections 1 and 2 for DANP, and



DANP				OANP			
Ref.No.	2θ (degree)	Spacing (nm)	Intensity	Ref.No.	2θ (degree)	Spacing (nm)	Intensity
1	4.5	1.96	Strong	1	3.3	2.68	Strong
2	9.0	0.983	Medium	2	6.6	1.34	Medium
3	11.0	0.804	Weak	3	9.9	0.893	Weak
4	16.5	0.537	Weak	4	16.5	0.537	Weak
5	19.3	0.460	Strong	5	19.3	0.460	Strong
6	20.9	0.425	Weak	6	20.9	0.425	Weak
7	22.5	0.395	Strong	7	22.5	0.395	Strong
8	23.9	0.372	Weak	8	23.9	0.372	Weak
9	27.3	0.327	Strong	9	27.3	0.327	Strong
10	30.4	0.294	Weak	10	30.4	0.294	Weak
11	40.8	0.221	Weak	11	40.8	0.221	Weak

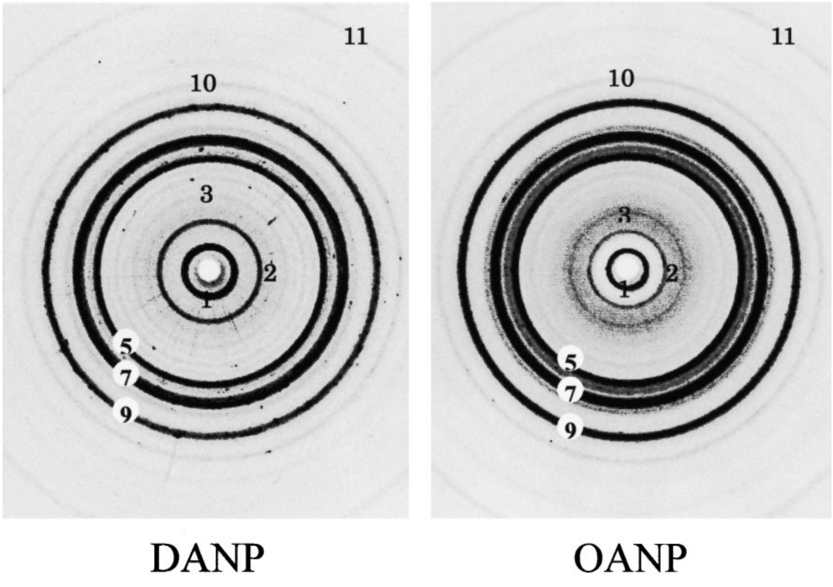


Fig. 1. WAXD patterns of DANP and OANP powder.

1, 2 and 3 for OANP, changed depending on the alkyl-chain length. The spacing of reflections 4–11 was common to both materials, in which three strong reflections, 5, 7 and 9, were used for discussion in this paper. Further, the relative intensity of each reflection (1, 2 and 4–11) was also very similar in both materials. From this, the crystal structures of both materials are considered to be similar for the molecular packing mode in the unit cell.

3.2. Fine structure of undrawn mixtures

WAXD patterns of both undrawn mixtures are shown in Fig. 2. The terms "through" and "edge" are used in this paper to indicate where the X-ray incident beam is perpendicular and parallel, respectively, to the surface of mixtures. In the edge-pattern, the thickness direction of mixtures is parallel to the meridian direction. In the through-pattern, four reflection rings from (110), (040), (130) and (111) planes of the α-form crystal of PP and five reflection rings from DANP or OANP (1, 2, 5, 7 and 9) were observed. Each spacing of DANP and OANP, respectively, agreed well with that of both powder patterns in Fig. 1. In both mixtures, moreover, a weak reflection of 0.343 nm in through- and edge-patterns (shown by the arrow) was observed, which was not observed in the DANP or OANP powder patterns shown in Fig. 1. So the crystal structure of DANP or OANP in the undrawn mixture was considered to be somewhat different from that of the powder, because this reflection could be indexed to the $(1\bar{1}0)$ plane of the triclinic unit cell determined for the OANP crystal in the matrix of drawn PE in our previous paper [1].

In the edge-pattern, the shape of the above reflections was arc-like. The arc-like (040) reflection of PP was clearly observed in the direction parallel (or equatorial) to the surface of both undrawn mixtures. This indicates that the molecular axis in the lamellae of PP is oriented perpendicular to the surface of undrawn mixtures and uniaxially dispersed around the axis normal to the above surface.

On the other hand, two reflections of 1.96 and 0.980 nm from DANP (1 and 2) and two reflections of 2.68 and 1.34 nm from OANP (1 and 2) were observed in the thickness (or meridian) direction of both undrawn mixtures. These reflections of DANP or OANP, respectively, held the relation of first- and second-order reflection. The direction of three reflections of 0.460, 0.395 and 0.327 nm from DANP or OANP (5, 7 and 9) was not clear in the edge-pattern, but they seemed to be inclined to the equatorial direction.

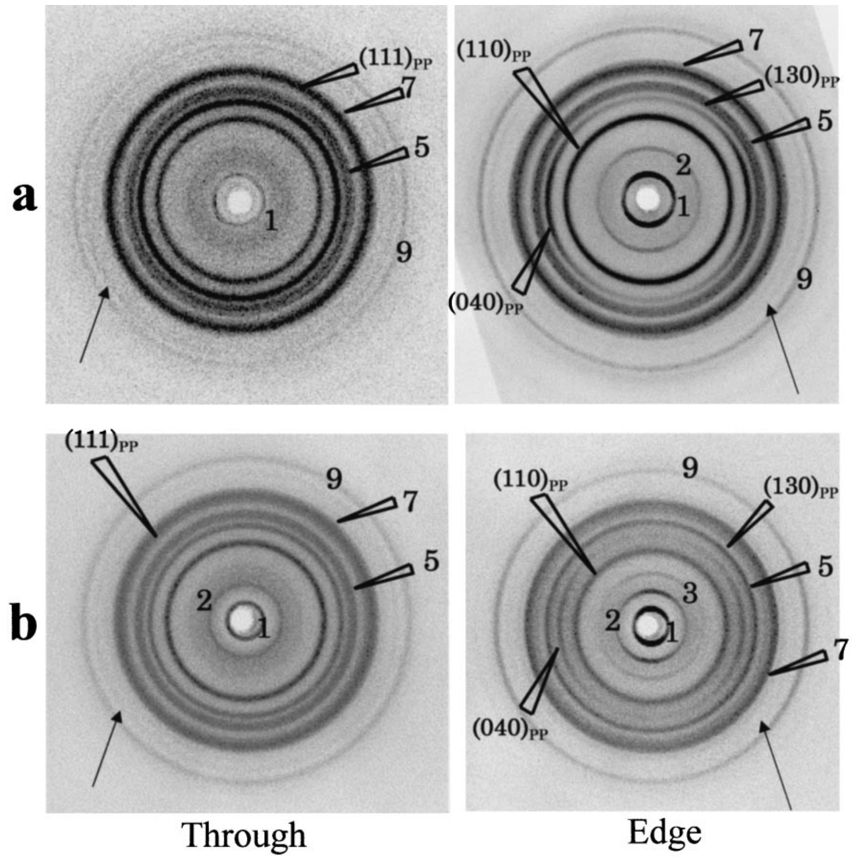


Fig. 2. Through- and edge-WAXD patterns of both undrawn mixtures, the thickness direction of which is parallel to the meridian direction in edge-patterns: (a) DANP/PP, and (b) OANP/PP.

As described in the previous paper [1], by considering that the reflections from the longest spacing of 1.96 nm for DANP or 2.68 nm for OANP arise from the periodicity corresponding to the molecular length of 2.10 nm for DANP or 2.84 nm for OANP and that three reflections 5, 7 and 9 arise from the periodical spacing between alkyl chains of DANP or OANP, the above results on the WAXD patterns indicate that the alkyl chain of DANP or OANP crosses the oriented PP chains in both undrawn mixtures. Thus the crystalline orientation of DANP or OANP in the undrawn mixtures is similar to that in the drawn mixtures as described in Section 3.3. However, it was deduced that the former could not be formed with the epitaxial crystallization upon the crystal of PP, because of the preceding crystallization of small molecules in each solution of both mixtures.

From the above facts, it was concluded that the fine structure of both undrawn mixtures was composed of the accumulated structure of PP lamellae including the oriented crystals of DANP or OANP, whose longest spacing was parallel to the thickness direction of mixtures. Thus the orientation of the longest spacing of DANP or OANP was considered to be due to the crystalline morphology as a plate-like crystal, because this crystalline orientation was caused by compression while preparing the undrawn mixtures.

3.3. Oriented crystallization of DANP or OANP in drawn mixtures

The through- and edge-WAXD patterns of DANP/PP and OANP/PP as a function of draw ratio (DR), respectively, are shown in Figs. 3 and 4, where the draw direction is in the meridian direction. In edge-patterns, the thickness direction of mixtures is in the equatorial direction. The reflections other than (110), (040), (130), (060), (200), (220), $(\bar{1}31)$, (111) and (022) reflections of the α-form crystal of PP are from the DANP or OANP crystal. Five reflection spots (1, 2, 5, 7 and 9) from DANP or OANP can be clearly observed. Such a high degree of crystalline orientation of DANP or OANP from the molten state at the second-step drawing temperature of 130°C was considered to be subject to the crystalline orientation of the drawn PP matrix. Hence the epitaxial growth of DANP or OANP along the periodicity of the oriented α-form crystal of PP would be deduced.

It was found that the through-patterns of both mixtures were almost the same as the corresponding edge-patterns at the high draw ratio, though the relative intensities reflections 1, 2, and 5 between both patterns were considerably different at the low draw ratio. The end-patterns of both mixtures are shown in Fig. 5, whose draw ratios are 13 for the former and 16 for the latter. The term "end" in this paper indicates that the X-ray incident beam is parallel to the draw

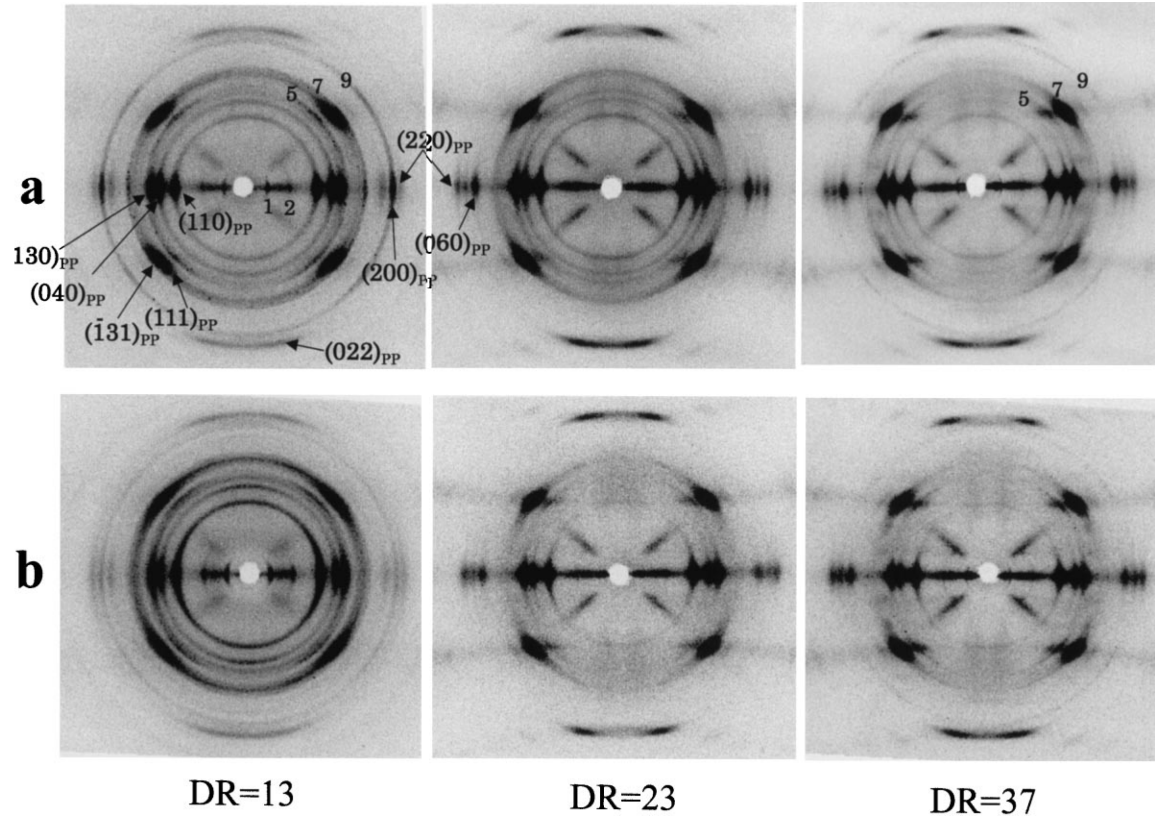


Fig. 3. Through- and edge-WAXD patterns of DANP/PP as a function of draw ratio (DR), whose draw direction is in the meridian direction. (a) Through-pattern. (b) Edge-pattern (thickness direction of mixtures is the equatorial direction).

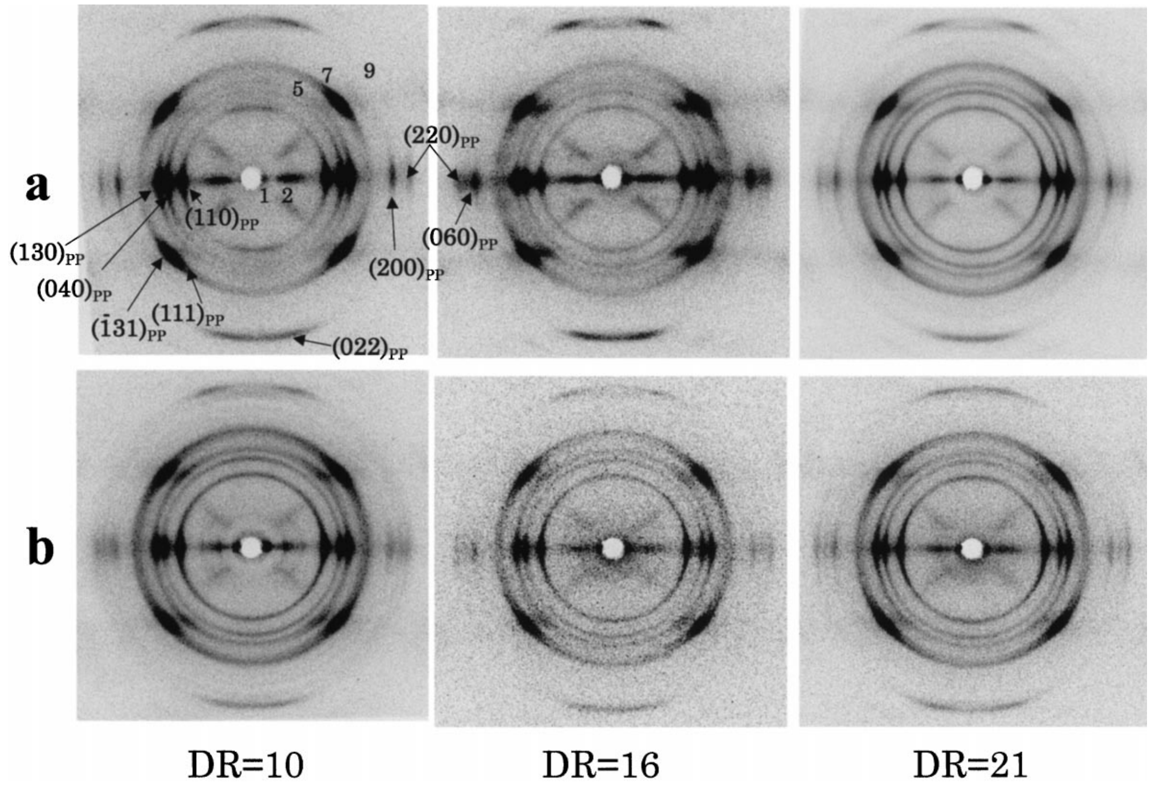


Fig. 4. Through- and edge-WAXD patterns of OANP/PP as a function of draw ratio (DR), whose draw direction is in the meridian direction. (a) Through-pattern. (b) Edge-pattern (thickness direction of mixtures is the equatorial direction).

direction. The thickness direction of mixtures in Fig. 5 is the equatorial direction. The reflections from DANP (or OANP) and PP were ring-like even at the low draw ratio. It was concluded from these facts that the crystals of PP and DANP (or OANP) were uniaxially oriented around the draw direction of both highly drawn mixtures, in which the molecular (*b*-) axis of PP and the longest spacing of the DANP (or OANP) crystal were oriented, respectively, parallel and normal to the draw direction.

It could be deduced from this fact that DANP or OANP crystallized epitaxially as it laid its longest spacing upon the periodical spacing between the oriented PP chains. As factors promoting this epitaxial crystallization, the following were considered. The longest spacing of DANP (1.96 nm) and OANP (2.68 nm), respectively, coincides well with three and four times the spacing of the (100) plane of PP (0.656 nm). So, it was deduced that an epitaxy was formed in a drawn matrix of PP as the longest spacing was laid upon the spacing of the (100) plane of the oriented PP. Another factor promoting the above

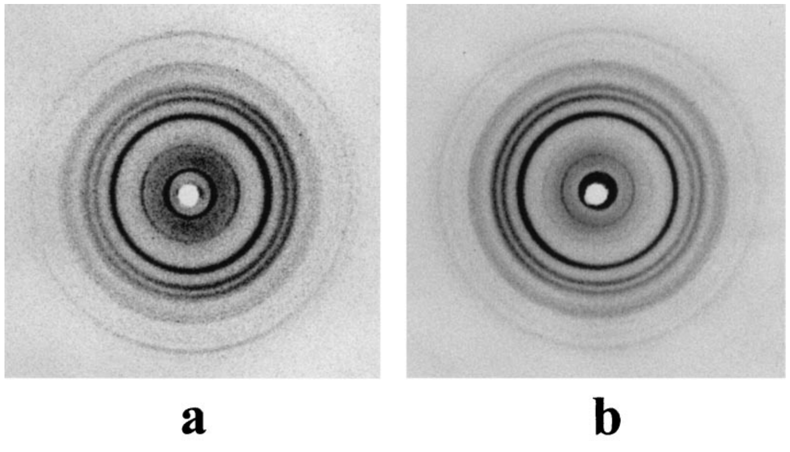


Fig. 5. End-WAXD patterns of drawn mixtures. (a) DANP/PP drawn mixture of DR = 13. (b) OANP/PP drawn mixture of DR = 16.

epitaxial crystallization of DANP or OANP would be the good coincidence between the spacing of reflection 9 (0.327 nm) and the spacing of the (200) reflection of PP (0.328 nm). Such an epitaxy of DANP or OANP was thought to be formed during a cooling process after drawing of both mixtures, because the melting points of DANP (70.0°C) and OANP (80.4°C) were considerably lower than the drawing temperature of 130°C.

3.4. Crystalline orientation of DANP or OANP in drawn mixtures

The degree of crystalline orientation of DANP or OANP in a PP matrix should be affected by the degree of crystalline orientation of PP. As a measure of the degree of crystalline orientation, the width at half-peak intensity along the Debye–Scherrer ring of a reflection was used.

The width of reflection 5 (0.460 nm) from DANP or OANP in the edge-pattern at half-peak intensity was compared with that of the (130) reflection of PP, and consequently, it was found that the degree of crystalline orientation of the former was somewhat lower than that of PP over all the ranges of draw ratio, as shown in Fig. 6, which is in contrast to the results of the drawn DANP (or OANP)/PE [1] or DANP (or OANP)/PVA mixtures [4]. This fact suggests that the epitaxial growth of DANP or OANP progresses according to the degree of crystalline orientation of PP. This is in contrast to the phenomenon that the epitaxial growth of DANP or OANP in the drawn PE [1] or PVA [4] matrix progresses with selection of the highly oriented PE or PVA chains.

3.5. Optical second-harmonic generation of drawn mixtures

Since the drawn mixtures of DANP/PP or OANP/PP were expected to show an optical second-harmonic generation from the above results, it was measured using a *Q*-switched Nd–YAG laser (power 573 mJ, repetition rate 10 Hz, pulse width 6–9 ns). The drawn mixtures were irradiated with the laser beam of 3.0 mm diameter. The second-harmonic signal ($\lambda = 532$ nm) was detected with a photo-multiplier (PS-310 of SRS, HV: 1000 V) within the range of an incident angle of ±70°, which was changed by rotating the irradiated surface of the specimens.

Contrary to the above expectation, however, the harmonic signals from all of the drawn mixtures were too weak to detect, the relative intensities of which were two orders lower than that of the Y-cut quartz single crystal at each incident angle. Further, a similar behavior was observed for the harmonic signals from the undrawn mixtures and even from the raw materials of DANP or OANP. From these results, it was deduced that almost no optical second-harmonic generation could be observed and therefore the crystal structure of DANP or OANP in a matrix of PP must have a center of symmetry, as in a matrix of PE [1].

3.6. Structure model on an epitaxy of DANP and OANP

In our previous paper [1], the triclinic unit cell and the molecular packing having a center of symmetry were proposed for a DANP or OANP crystal in a matrix of highly oriented PE. Using the above crystal structure of DANP or OANP, the structure model of an epitaxy of DANP or OANP in a matrix of PP was analyzed, because the spacing of all reflections from a DANP or OANP crystal in a matrix of PP is in good agreement with that in a matrix of PE. From this triclinic unit cell, the main reflections, 1, 2, 5, 7 and 9 in Figs. 3 and 4, were, respectively, indexed to the (001), (002), (020), (100) and (120) planes of the DANP or OANP crystal.

The obtained structure model of an epitaxy of DANP

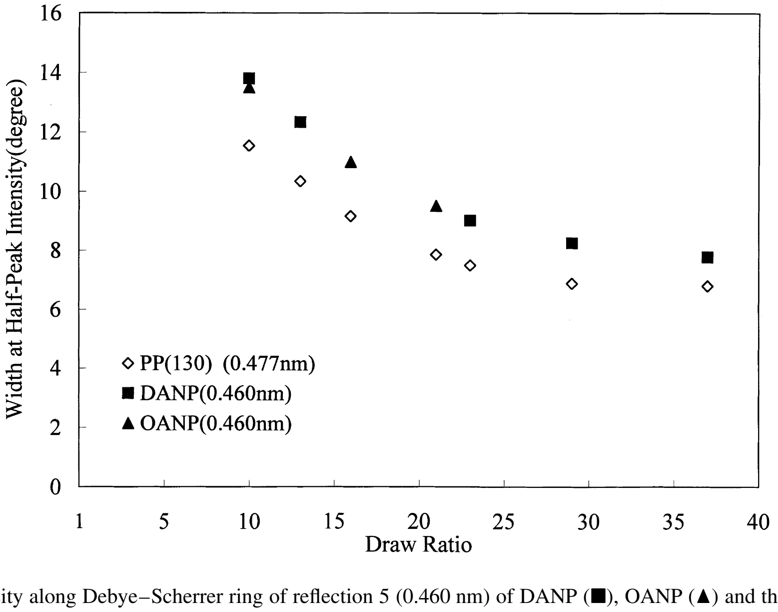


Fig. 6. Width at half-peak intensity along Debye–Scherrer ring of reflection 5 (0.460 nm) of DANP (■), OANP (▲) and the (130) reflection of PP (◇) as a function of draw ratio.

in a matrix of PP is shown in Fig. 7a and b as a representation of DANP and OANP, because the difference between the epitaxy structure of DANP and OANP is considered to be only in the longest periodicity, originating from the difference in the alkyl-chain length. Fig. 7a is the projection of the epitaxy model of DANP on the plane parallel to the draw direction, corresponding to the WAXD through- and edge-patterns. That is, the a–c''-axis plane made the a–c'-axis plane of the triclinic unit cell [1] rotate with an angle of 5.8° around the a-axis in the a–c'-axis plane, in which the c''-axis is the projection of the c-axis having an angle of 2.4°. The planar zigzag plane of the alkyl chain of DANP (or OANP) is coincident with the a–c'-axis plane [1]. The (001) plane of DANP (or OANP) is perpendicular to the a–c''-axis plane. The direction of the longest spacing (1.96 nm for DANP) is perpendicular (or somewhat inclined) to the draw direction (the oriented direction of PP chains), that is to say, the alkyl-chain axis of DANP (or OANP) inclines to the oriented direction of the PP chains. By uniaxially rotating this epitaxy model around the draw axis, WAXD patterns of DANP (or OANP)/PP mixtures shown in Fig. 3 (or Fig. 4) can be explained well.

Fig. 7b is the projection along the draw direction (the oriented direction of the PP chain), the plane of which is vertical to the a–c''-axis plane of Fig. 7a, corresponding to the WAXD end-pattern. This is the b'–c'''-axis plane of the triclinic unit cell [1], in which the b'-axis is the projection of the b-axis having an angle of 9.0°. The (001) plane of DANP (or OANP) is perpendicular to the b'–c'''-axis plane. In the direction of the b'-axis, two molecules having a center of symmetry are packed in a unit cell. By uniaxially rotating this epitaxy model around the draw axis, the WAXD patterns of DANP (or OANP)/PP mixtures shown in Fig. 5 can be explained well.

From the above facts, it was concluded that DANP (or OANP) in a matrix of PP crystallized epitaxially as it laid its longest spacing of 1.96 nm (or 2.68 nm) upon the periodical spacing between the oriented PP chains, that is, as its alkyl chain crossed the oriented PP chains. Finally, it was considered that such an epitaxy of DANP (or OANP) in a matrix of the oriented PP was formed in a space between the micro-fibrils composed of the oriented PP chains.

4. Concluding remarks

It was found that alkylating amino-nitropyridine (DANP or OANP) was able to crystallize epitaxially in a matrix of oriented PP, as it laid its longest spacing upon the periodical spacing between the oriented PP chains, that is, as its alkyl chain crossed the oriented PP chains. As factors promoting this epitaxial crystallization, the following were considered. The longest spacing of DANP (1.96 nm) and OANP (2.68 nm), respectively, is

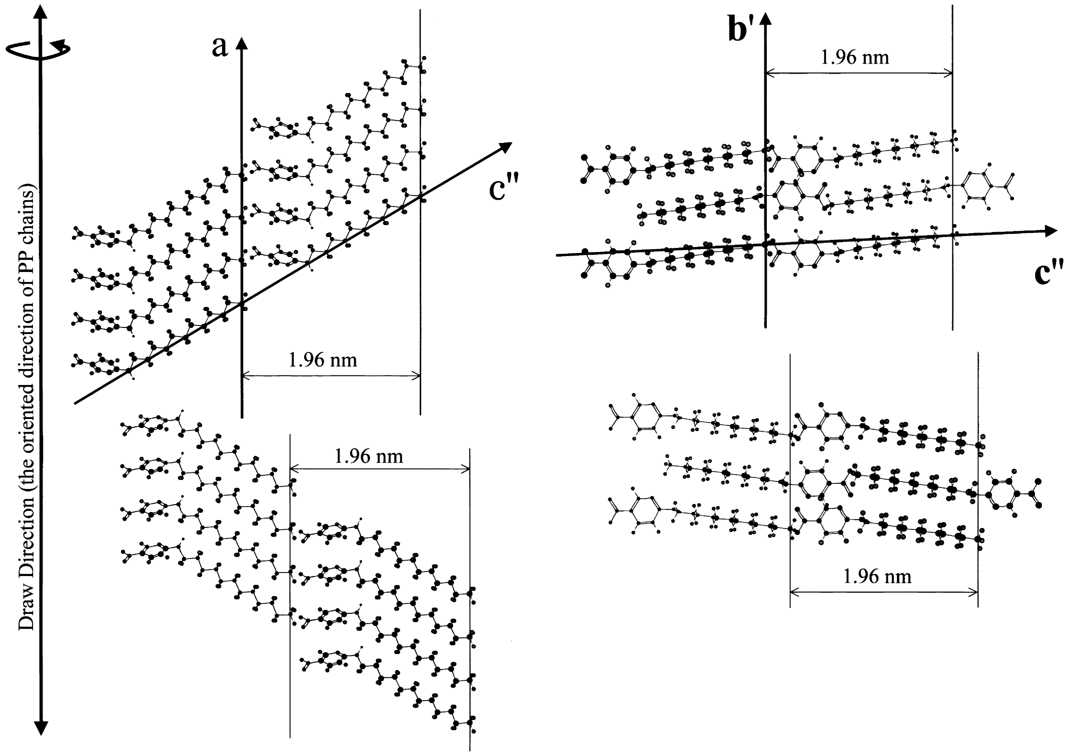


Fig. 7. Structure model of an epitaxy of DANP in a drawn matrix of PP as representative of DANP and OANP. (a) Projection to the plane parallel to the draw direction. (b) Projection along the draw direction.

well coincident with three and four times the spacing of the (100) plane of PP (0.656 nm). So, it was deduced that an epitaxy was formed in a drawn matrix of PP as it laid its longest spacing upon the spacing of the (100) plane of the oriented PP. Further, the other factor promoting the above epitaxial crystallization of DANP or OANP was considered to be the fact that the spacing of reflection 9 (0.327 nm) coincided well with the spacing of the (200) reflection of PP (0.328 nm). The details of this epitaxial crystallization, however, are not clear at present and remain as a future subject.

Contrary to our expectations, almost no optical second-harmonic generation could be observed for all of the drawn mixtures, undrawn mixtures and raw materials of DANP or OANP. By giving them external excitement, such as polarizing treatment, however, an optical second-harmonic signal from them might be observed because the above molecular packing might be changed to one having no center of symmetry.

Through this study, it was found that a functional small molecule having an alkyl chain crystallized epitaxially in a matrix of PP, even in a short alkyl chain of 12 carbons. This indicates that various functions of small molecules can be displayed more strongly in a drawn mixture. Further, the application of this phenomenon to other polymers and the possibility of epitaxy on a shorter alkyl chain has attracted our interest.

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