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Oriented crystallization of alkylating amino-nitropyridine in a matrix of polyvinyl alcohol

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Abstract

It was found that alkylating amino-nitropyridine was able to crystallize epitaxially in a matrix of polyvinyl alcohol (PVA). Its longest spacing lay upon the periodical spacing between highly oriented PVA chains, i.e. its alkyl chains were across PVA chains. The degree of crystalline orientation of alkylating amino-nitropyridine in a drawn matrix of PVA was markedly higher than that of PVA at the low draw ratio below 6, which suggested that its epitaxial growth progressed with selecting the micro-fibrils composed of the highly oriented PVA. One of possible models of this epitaxy structure has been deduced with using its crystal structure proposed in a previous paper, which well matches its X-ray diffraction patterns. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Alkylating amino-nitropyridine; Polyvinyl alcohol; Epitaxial growth

1. Introduction

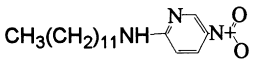
In our previous paper [1], we presented that the alkylating amino-nitropyridine was able to crystallize epitaxially in a matrix of polyethylene (PE), where its alkyl chain lay upon the highly oriented chain of PE. From the X-ray diffraction photographs, the results of crystalline orientation and the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

From the above, the realization of the above structure in a polymer matrix other than PE attracted our interest. In this paper, it was examined by drawing of the mixture of alkylating amino-nitropyridine and polyvinyl alcohol (PVA).

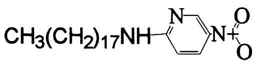
2. Experimental

2.1. Materials

Two kinds of alkylating amino-nitropyridine of 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 both materials was primarily carried out by FT-IR spectral measurements. The peak temperatures of melting curve on the powders of DANP and OANP were 70.0 and 80.4°C, respectively. PVA having a degree of polymerization of 1750 (supplied by Kuraray Co. Ltd.) was used as a matrix for the mixtures.

2.2. Preparation and drawing of mixtures

The gel-casting mixtures of PVA and DANP (or OANP) were prepared by cooling a dimethyl sulfoxide (DMSO) solution at 90°C of 10.0 wt% PVA and adding the fixed amount of DANP (or OANP) to it. The ratio of DANP/PVA and OANP/PVA in DMSO solution was 37.5/62.5. The mixtures of PVA

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and DANP (or OANP) were prepared by drying the gel-casting mixture under reduced pressure at 50°C to remove DMSO and subsequently compressing it under a pressure of 50 kg cm^{-2} at 50°C. The thickness of the obtained mixtures was 0.3–0.7 mm.

The obtained mixtures of DANP/PVA and OANP/PVA were drawn at 110°C under a deformation rate of 50%/min. The contents of DANP and OANP in the drawn mixture were, respectively, about 29 and 30 wt%, which were determined by extraction method using benzene solvent. Stress versus strain curves of both mixtures during drawing at 110°C did not show the neck deformation and their maximum draw ratios were: 14.0 for DANP/PVA and 10.0 for OANP/PVA.

3. Results and discussion

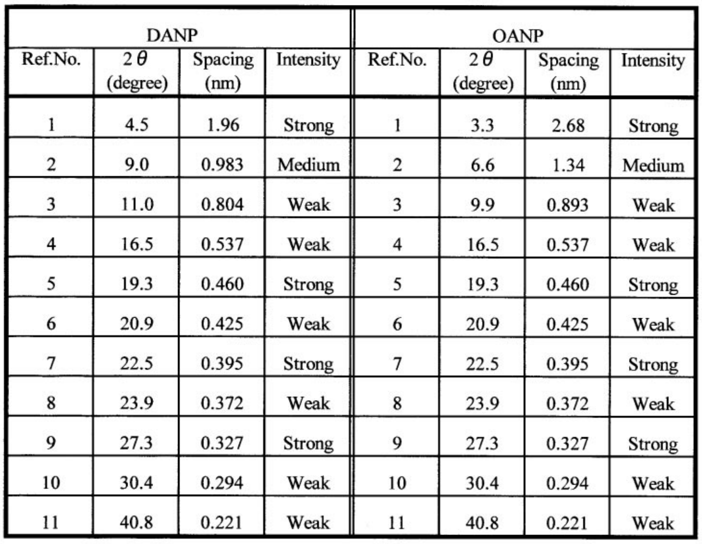
3.1. Molecular length and WAXD patterns of DANP and OANP

Since the crystal structures of DANP and OANP are not yet clarified, their molecular lengths have been speculated by using CS Chem 3D Pro (Molecular Modeling and Analysis). As shown in our previous paper [1], their lengths are: 2.10 nm for DANP and 2.84 nm for OANP.

WAXD patterns of DANP and OANP powders are shown in Fig. 1. The spacing of reflections of Nos.1, 2 in DANP and Nos.1–3 in OANP changed, depending on the alkyl-chain length. The spacing of reflections of Nos. 4–11 was common to both materials, in which three strong reflections of Nos. 5, 7 and 9 were used for discussion in this paper. Furthermore, the relative intensity of each reflection (Nos.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” used in this paper



DANP				OANP			
Ref.No.	2 θ (degree)	Spacing (nm)	Intensity	Ref.No.	2 θ (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

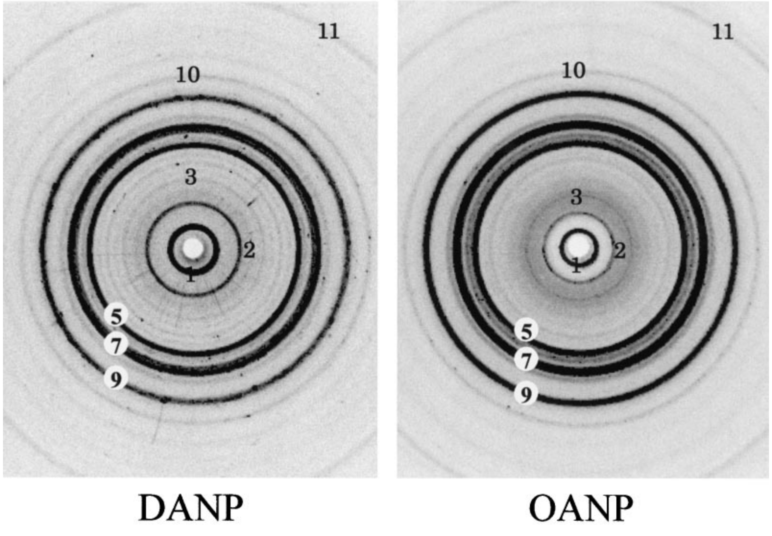


Fig. 1. WAXD patterns of DANP and OANP powders.

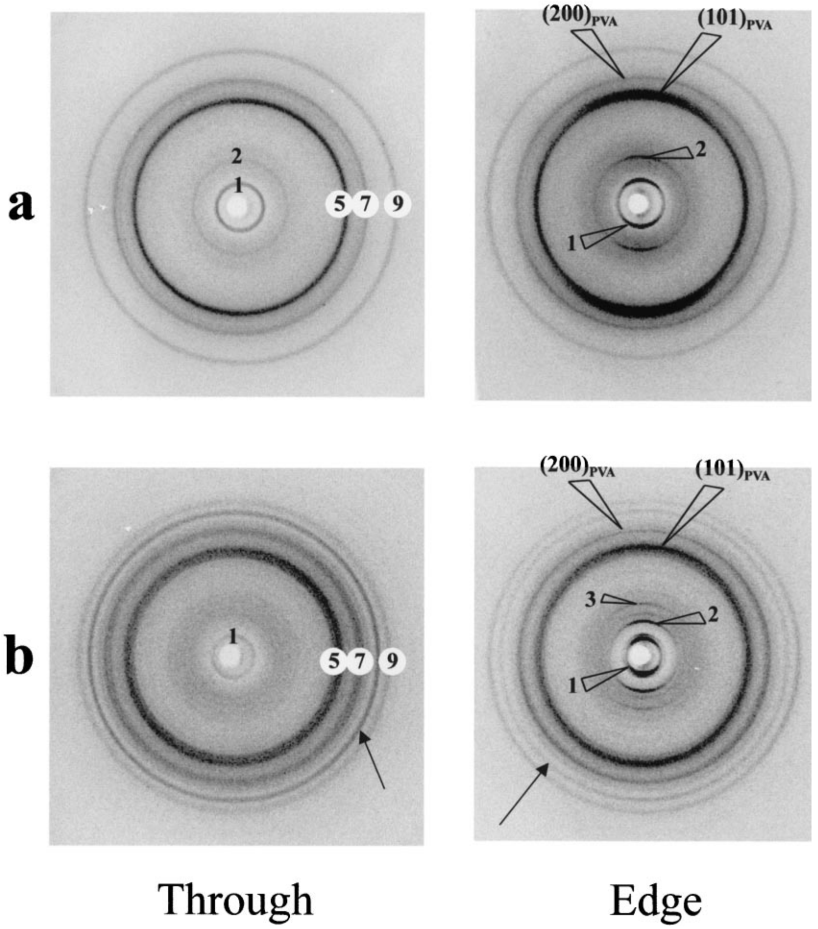


Fig. 2. Through- and edge-WAXD patterns of undrawn mixtures, whose thickness direction in the edge-pattern is in the meridian direction. (a) DANP/PVA; (b) OANP/PVA.

indicate that the X-ray incident beam is, respectively, perpendicular and parallel to the surface of mixtures. In the edge pattern, the thickness direction of mixtures is parallel to the meridian direction. In the through pattern, two reflection rings from the (101), $(10\hat{1})$ and (200) planes of PVA, five reflection rings from DANP (Nos.1, 2, 5, 7 and 9) and three reflection rings from OANP (Nos.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 the OANP/PVA mixture, moreover, a medium reflection of 0.343 nm in the through- and edge-patterns (shown by the arrow) was observed, but not observed in the OANP powder pattern shown in Fig. 1. So it was considered that the crystal structure of OANP in the undrawn mixture was somewhat different from that of its powder, because this reflection could be indexed to the $(1\hat{1}0)$ plane of the triclinic unit cell determined for 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 (101) reflection of PVA was observed in the thickness (or meridian) direction of both undrawn mixtures. The shape of the (200) reflection of PVA was not clear, because its spacing nearly overlapped with that of reflection No. 7 (0.395 nm) of DANP or OANP, but its intensity peak seemed to be in the same direction as that of the (101) reflection. This indicates that the molecular axis in the lamellae of PVA is oriented parallel to the surface of undrawn mixtures and uniaxially dispersed around the normal axis to the above surface.

On the other hand, two reflections of 1.96 and 0.980 nm from DANP (Nos. 1 and 2) and three reflections of 2.68, 1.34 and 0.893 nm from OANP (Nos. 1–3) were observed in the thickness (or meridian) direction of both undrawn mixtures. These reflections of DANP or OANP, respectively, held the relation of first-, second and third-order reflection. The direction of three reflections of 0.460, 0.395 and 0.327 nm from DANP or OANP (Nos. 5, 7 and 9) was not clear in the edge-pattern, but they seemed to be in the direction inclined to the horizontal axis.

As described in our previous paper [1], by considering that the reflections from the longest spacing of 1.96 nm of DANP (or 2.68 nm of OANP) would arise from the periodicity corresponding to the molecular length of 2.10 nm of DANP (or 2.84 nm of OANP) and that three reflections of Nos. 5, 7 and 9 would 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) cross the oriented PVA chains in both undrawn mixtures. Thus, crystalline orientation of DANP or OANP in the undrawn mixtures is similar to that in the drawn mixtures as described in the next section. However, it was deduced that the former could not be formed with the epitaxial crystallization upon the PVA crystal, because of the preceding crystallization of small molecule 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 PVA lamellae including the oriented crystalline 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 a plate-like crystalline morphology, because this crystalline orientation was caused by compression during the preparation of the undrawn mixtures.

3.3. Oriented crystallization of DANP or OANP in drawn mixtures

The edge-WAXD patterns as a function of the draw ratio in the drawn mixtures of DANP/PVA and OANP/PVA are shown in Fig. 3, whose draw direction is parallel to the meridian direction. All reflections except (100), (001), (101), (10$\hat{1}$) and (200) of PVA are from DANP or OANP crystal. Many reflection spots from DANP or OANP crystal can be clearly observed for both mixtures of the high draw ratio. Such high degree of crystalline orientation of DANP or OANP from their molten state at the drawing temperature of 110°C was considered to be subjected to the crystalline orientation of a drawn PVA matrix. Therefore, the epitaxial growth of DANP or OANP along the periodicity between the oriented PVA chains would be deduced.

Through-, edge- and end-WAXD patterns of the drawn mixtures of DANP/PVA and OANP/PVA are shown in Fig. 4, the draw ratios of which are 11 for the former and 5 for the latter. The term “end” in this paper indicates that the X-ray incident beam is parallel to the draw direction. The draw direction in through- and edge-pattern is parallel to the meridian direction. The thickness direction of mixtures in the edge- and end-pattern is in the equatorial direction. It was found from these patterns that the crystallites of PVA uniaxially oriented around the draw direction of the drawn mixtures, in which the molecular axis (*b*-axis) of PVA was oriented parallel to the draw direction.

In the edge-patterns, the first-, second and third-order reflection spots from the longest spacing of 1.96 nm in DANP crystal or 2.68 nm in OANP crystal were clearly observed in the equatorial direction, namely, the thickness

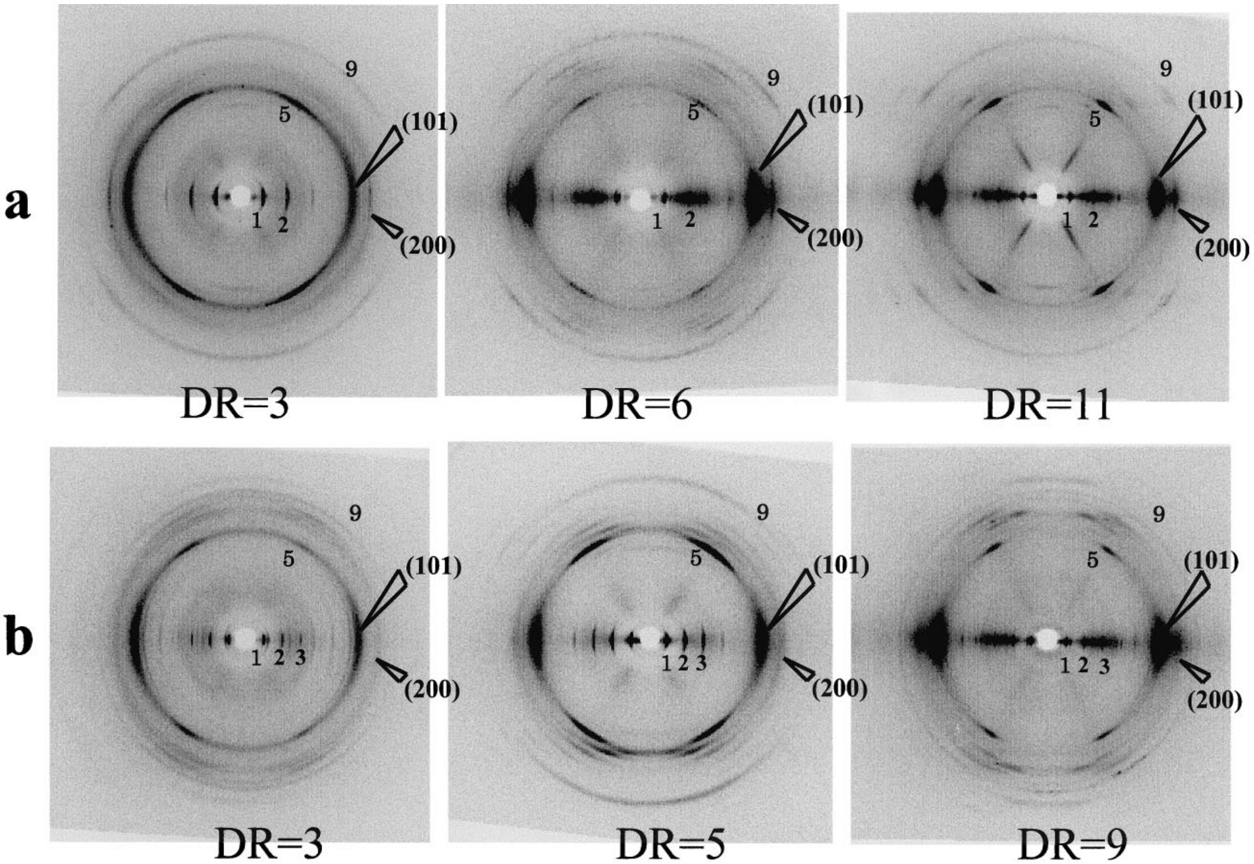


Fig. 3. Edge-WAXD patterns of drawn mixtures as a function of the draw ratio (DR). (a) DANP/PVA; (b) OANP/PVA.

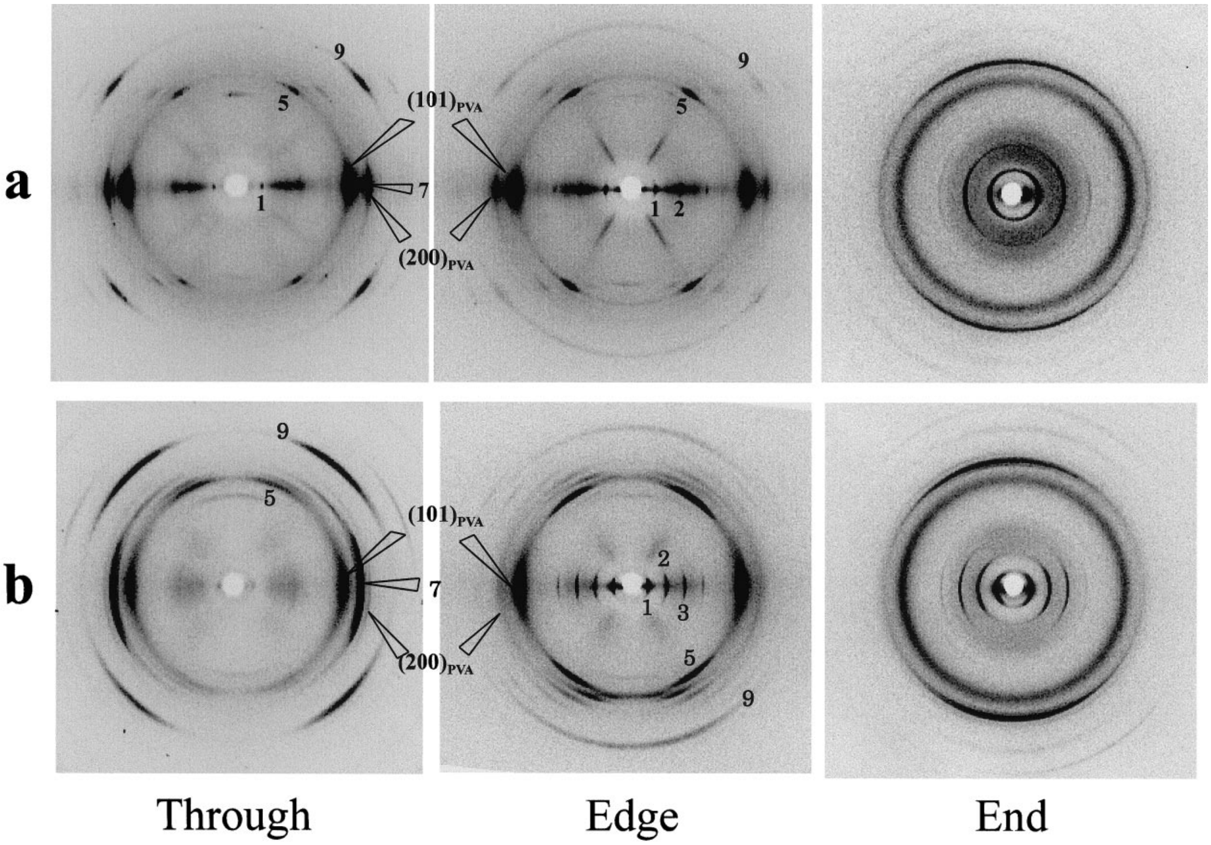


Fig. 4. Through-, edge- and end-WAXD patterns of drawn mixtures. (a) DANP/PVA drawn mixture of DR = 11; (b) OANP/PVA drawn mixture of DR = 5.

direction of each mixture. In the through- and edge-patterns, the two reflections of 0.460 and 0.327 nm (Nos.5 and 9) and the weak reflection of 0.395 nm (No. 7) were, respectively, observed in the diagonal and the equatorial direction. In the through-pattern, the strong reflection of 0.395 nm (No. 7) was observed in the equatorial direction, nearly overlapping with the (200) reflection of PVA. From these facts, it was found that the mode of crystalline orientation of DANP or OANP was biaxial, the longest spacing of which was oriented parallel to the thickness direction of mixtures. This difference from the uniaxial crystalline orientation of PVA matrix could be considered to originate from the temperature gradient, arising in the thickness direction of drawn mixtures during a cooling process from the melt of DANP or OANP, because there was no other reason based on the processing conditions of drawn mixtures.

It could be deduced from these facts that DANP or OANP crystallized epitaxially and its longest spacing lay upon the periodical spacing between the oriented PVA chains. As the factors promoting this epitaxial crystallization, the following facts were considered. In the case of DANP/PVA, the longest spacing of 1.96 nm was coincident with five times the spacing of the (200) plane of PVA (0.390 nm). So, it was deduced that an epitaxy where its longest spacing lay upon the spacing of the (200) plane of the oriented PVA was formed in a matrix of drawn PVA. In the case of OANP/PVA, the longest spacing of 2.68 nm corresponded to six times the spacing of the (101) plane of PVA (0.443 nm). So, it was deduced that an epitaxy where its longest spacing lay upon the spacing of the (101) plane of the oriented PVA was formed in a matrix of drawn PVA. Furthermore, as the other factor promoting the above epitaxial crystallization of DANP or OANP, it could be considered that the spacing of reflection of No. 7 (0.395 nm) was coincident with the spacing of the (200) reflection of PVA (0.390 nm).

Such epitaxy of DANP or OANP was considered 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 110°C.

3.4. Crystalline orientation of DANP or OANP in drawn mixtures

The degree of crystalline orientation of DANP or OANP in a PVA matrix must be affected by the degree of crystalline orientation of PVA. 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 at half-peak intensity of the reflection No.5 (0.460 nm) from DANP or OANP in the edge pattern was compared with that of (101) reflection of PVA, and

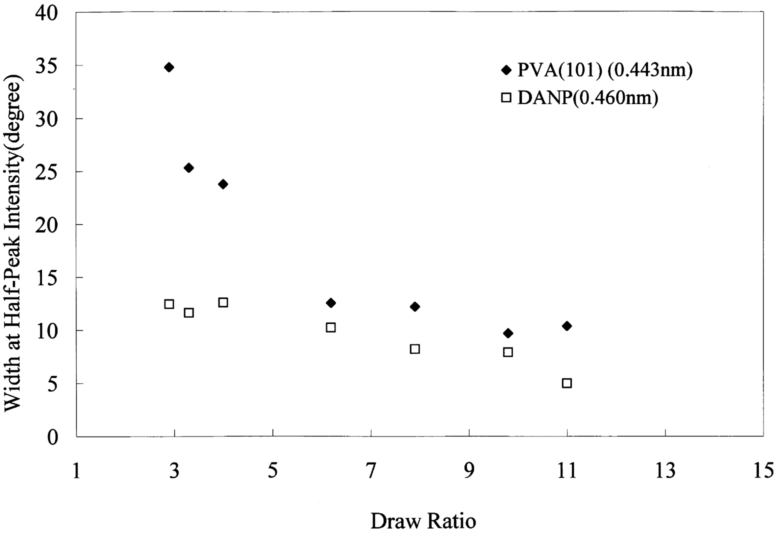


Fig. 5. Width at half-peak intensity along the Debye–Scherrer ring of the No. 5 reflection (0.460 nm) of DANP (□) and (101) reflection of PVA (◆) as a function of the draw ratio.

consequently it was found that the degree of crystalline orientation of the former was higher than that of PVA over all ranges of draw ratio, as shown in Figs. 5 and 6. Especially, in both mixtures of the low draw ratio below 6, the above width of the former was found to be markedly narrower than that of PVA. This fact suggests that the epitaxial growth of DANP or OANP progresses by selecting the micro-fibrils composed of highly oriented PVA chains.

3.5. Optical second harmonic generation of drawn mixtures

Since the drawn mixtures of DANP/PVA or OANP/PVA were expected to show an optical second harmonic generation from the above results, it was measured by 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 a 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) under the range of incident angle of ±70°, the angle of which was changed by rotating the irradiated surface of specimens.

Contrary to the above expectation, however, the harmonic signals from all of the drawn mixtures were too weak to be detectable, the relative intensities of which were two orders lower than that of the Y-cut quartz single crystal at each incident angle. Furthermore, similar behavior was observed for the harmonic signals from the undrawn

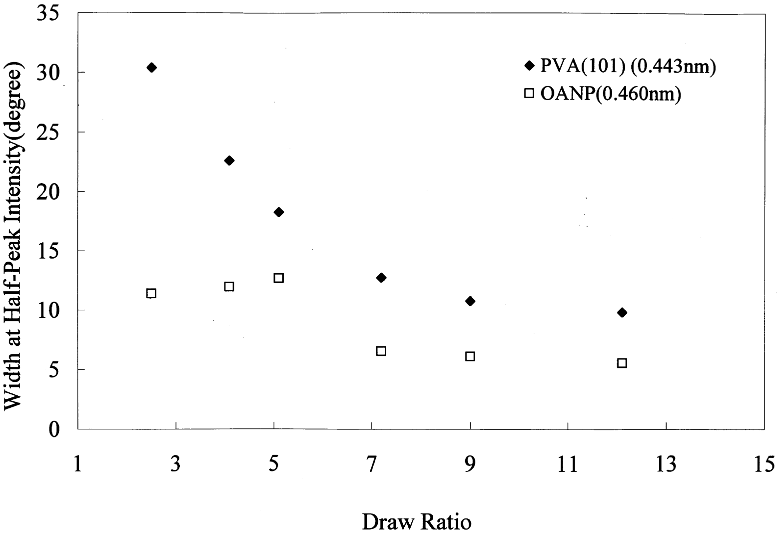


Fig. 6. Width at half-peak intensity along the Debye–Scherrer ring of No. 5 reflection (0.460 nm) of OANP (□) and (101) reflection of PVA (◆) as a function of the draw ratio.

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 PVA must have a center of symmetry, like in a matrix of PE.

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 DANP or OANP crystal in a matrix of highly oriented PE. By using the above crystal structure of DANP or OANP, the structure model on an epitaxy of DANP or OANP in a matrix of PVA was searched, because the spacings of all the reflections from DANP or OANP crystal in a matrix of PVA were in good agreement with those in a PE matrix. From this triclinic unit cell, the main reflections of Nos. 1, 2, 5, 7 and 9 in Fig. 4 were, respectively, indexed to the (001), (002), (020), (100) and (120) planes of DANP or OANP crystal.

The obtained structure model on an epitaxy of DANP in a PVA matrix is shown in Fig. 7(a) and (b) as a representative of DANP and OANP, because the difference on an epitaxy structure of DANP and OANP is considered to be only in its longest periodicity, originating from the difference in the alkyl chain length. Fig. 7(a) is the projection along the draw direction, namely, along the oriented chain axis of PVA, in which the thickness direction of DANP/PVA mixture is in the horizontal axis. This is the a–c''-axis plane obtained from the a–c'-axis plane of the triclinic unit cell [1] upon rotation by an angle of 5.8° around the a-axis in the a–c'-axis plane, in which c''-axis is the projection of the c-axis having an angle of 2.4°. The planar zig-zag plane of the alkyl chain of DANP (or OANP) is coincident with the a–c'-axis plane, as shown in our previous paper [1]. The direction of the longest spacing (1.96 nm for DANP) is perpendicular (or somewhat inclined) to the surface of mixtures, that is to say, the alkyl chain axis of DANP (or OANP) considerably incline towards the surface of the mixtures.

Fig. 7(b) is the projection along the a-axis in Fig. 7(a), which corresponds to the WAXD edge-pattern of Fig. 4. This is the b'–c'''-axis plane of the above triclinic unit cell [1], in which the b'-axis is the projection of b-axis having an angle of 9.0°. The thickness direction of mixture and the draw direction (the oriented direction of PVA chains), respectively, are in the horizontal and vertical direction. The b'-axis is parallel (or somewhat inclined) to the draw direction. In the direction of the b′-axis, two molecules

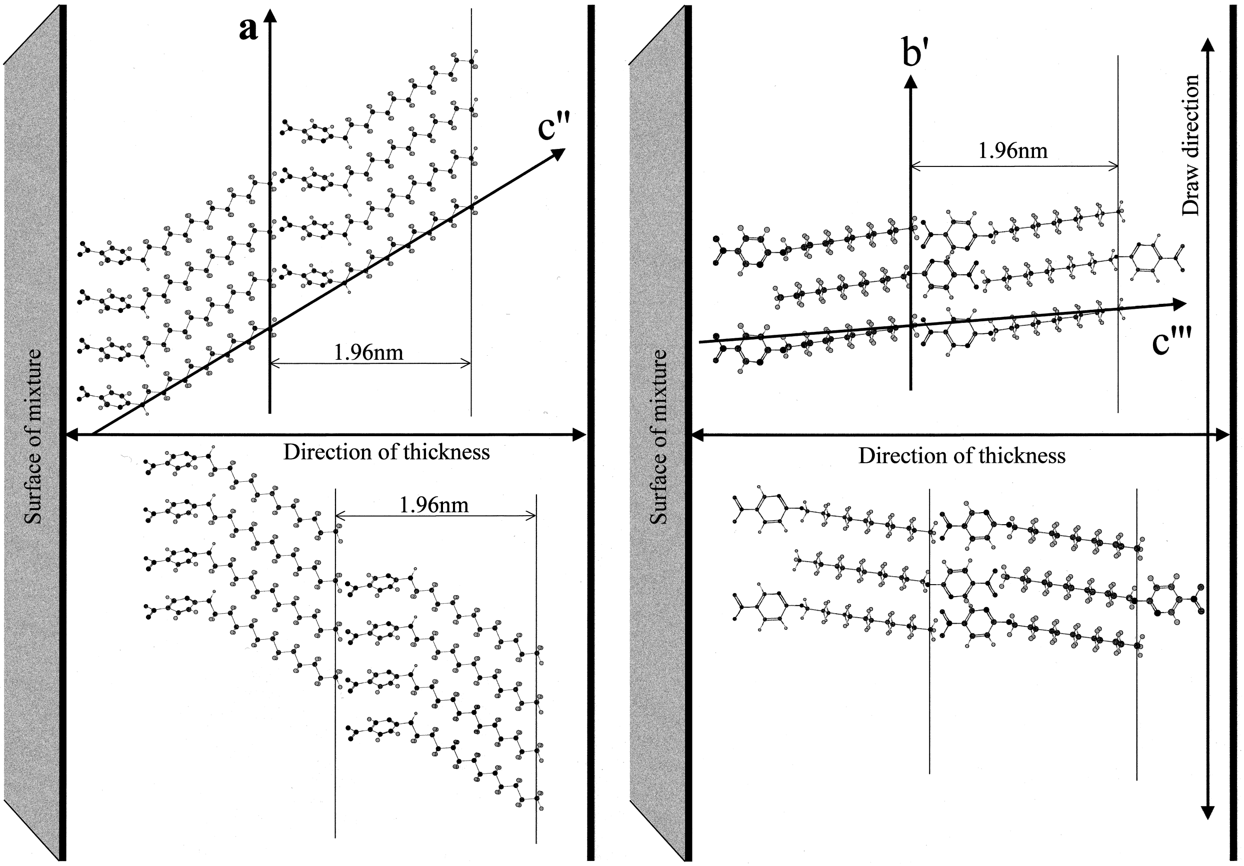


Fig. 7. Structure model on the epitaxy of DANP in a matrix of drawn PVA, as a representative of DANP and OANP. (a) Projection along the draw direction, corresponding to the end-WAXD pattern. (b) Projection along the a-axis in (a), corresponding to the edge-WAXD pattern.

having a center of symmetry are packed in a unit cell. It was found that the alkyl-chain axis of DANP is considerably inclined to the oriented chain axis of PVA (the draw direction), which could well explain the direction of each reflection from DANP and PVA in the WAXD edge-pattern of Fig. 4.

From the above facts, it was concluded that DANP (or OANP) in a matrix of PVA crystallized epitaxially with its longest spacing of 1.96 nm (or 2.68 nm) lying upon the periodical spacing between the highly oriented PVA chains, namely, its alkyl chain cross the PVA chains. It was considered that such epitaxy of DANP (or OANP) in a matrix of the drawn PVA was formed on the surface of the micro-fibrils composed of highly oriented PVA chains.

4. Conclusion remarks

It was found that alkylating amino-nitropyridine (DANP or OANP) was able to crystallize epitaxially in a matrix of PVA, and its longest spacing lay upon the periodical spacing between the highly oriented PVA chains, namely, its alkyl chain crossed the oriented PVA chains. As factors promoting such epitaxial crystallization, the following facts were considered. In the case of DANP/PVA, the longest spacing (1.96 nm) of DANP was coincident with five times the spacing of the (200) plane of PVA (0.390 nm). In the case of OANP/PVA, the longest spacing (2.68 nm) of OANP corresponded to six times the spacing of the (101) plane of PVA (0.443 nm). Furthermore, as the other factor promoting the above epitaxial crystallization of DANP or OANP, it was considered that the spacing of reflection No. 7 (0.395 nm) was well coincident with the spacing of the (200) reflection of PVA (0.390 nm). But, the further elucidation on this mechanism remains a subject for future research.

The degree of crystalline orientation of DANP or OANP in a matrix of drawn PVA was markedly higher than that of PVA at the low draw ratio below 6, as suggested by the fact that the epitaxial growth of DANP or OANP progressed by selecting the micro-fibrils composed of the highly oriented PVA chains.

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

One of the possible models on the epitaxy structure of DANP (or OANP) has been deduced by using the crystal structure of DANP (or OANP) proposed in our previous paper [1], which well matches the WAXD patterns of DANP (or OANP)/PVA mixtures.

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

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