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

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Abstract

It was found that alkylating amino-nitropyridine was able to crystallize epitaxially in a matrix of polyethylene, as laid its alkyl chain along the extended chain axis of polyethylene even in case of such short alkyl chain as carbon numbers of 12. From the X-ray diffraction patterns, the infrared dichroism and the optical second harmonic generation of the drawn mixture, one of the possible models on its epitaxy structure has been deduced. The triclinic unit cell and the molecular packing having a center of symmetry were proposed for DANP and OANP crystals in a matrix of highly oriented polyethylene. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Alkylating amino-nitropyridine; Polyethylene; Epitaxial growth

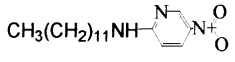
1. Introduction

It is known that the single crystal [1] and the LB membrane [2] of alkylating amino-nitropyridines have an optical second harmonic generation (OSHG). The present study was carried out for realizing the similar structure in a polyethylene (PE) matrix as that of the above single crystal or LB membrane with an expectation of producing a polymer material with OSHG. The possibility of this was examined by ultra-drawing of the mixture of alkylating amino-nitropyridine and ultra-high-molecular weight PE.

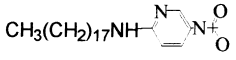
2. Experimental

2.1. Materials

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



DANP



OANP

The confirmation of both materials was carried out with mainly FT-IR spectrum. The peak temperatures of the melting curves of the DANP and OANP powders were 70.0 and 80.4°C, respectively. Ultra-high-molecular-weight polyethylene ($M_w = 2 \times 10^6$, HIZEX 240M) was used as a matrix of mixtures.

2.2. Preparation and drawing of mixtures

The gel-casting mixtures of PE and DANP (or OANP) were prepared by cooling the decalin solution at 160°C of 2.0 wt% concentration of PE, adding the fixed amount of DANP (or OANP) to it. The ratios of DANP/PE and OANP/PE in the dacalin solutions were, respectively, 50/50 and 37.5/62.5. The mixtures of PE 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 reduced pressure at room temperature to remove the decalin. The thickness of the thus-obtained films was 0.8–1.0 mm.

The obtained mixtures of DANP/PE and OANP/PE were drawn at 100°C under the deformation rate of 50% min^{-1}. The contents of DANP and OANP in the drawn mixture

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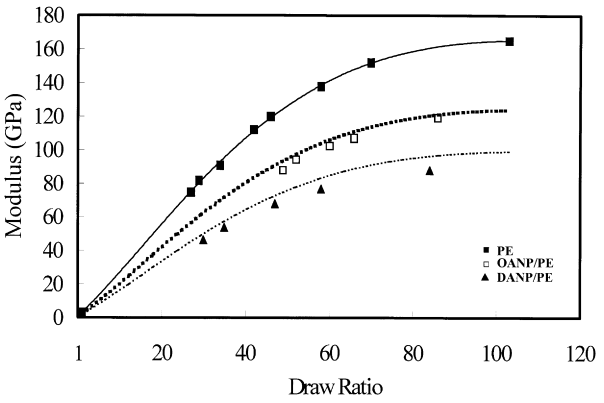

Fig. 1. Relation between tensile modulus and draw ratio of DANP/PE (▲) and OANP/PE (□) in comparison with that of gel casting film of PE (■). The broken lines are corresponding to the line of 75 and 60% for the solid line of PE, respectively.

were respectively, about 40 and 25 wt%, which were determined by extraction method using benzene solvent.

3. Results and discussion

3.1. Drawing behavior of mixtures

Stress–strain curves of both the mixtures showed the typical neck deformation during the 1st step drawing at 100°C. Their natural draw ratios were six for DANP/PE and eight for OANP/PE. The stress at necking was 0.0022 GPa for DANP/PE and 0.0031 GPa for OANP/PE. These values were lower than that of the gel-casting film prepared from 2 wt% decalin solution of PE [3], the decreasing ratios of which were 40% in DANP/PE and 25% in OANP/PE, corresponding to the contents of DANP and OANP in both mixtures. The relation between tensile modulus and draw ratio of both mixtures is shown in Fig. 1. The tensile modulus at a certain draw ratio of the mixtures was lower than that of the gel-casting film of PE [3], the decreasing ratios of which well agreed with the contents of DANP and OANP. The maximum draw ratio was about 92 in DANP/PE and about 108 in OANP/PE.

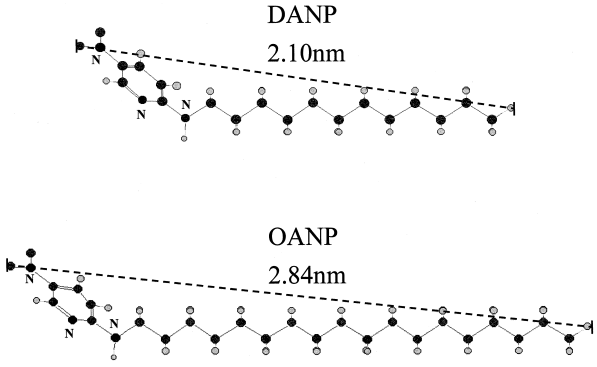

Fig. 2. Molecular length of DANP and OANP.

3.2. Molecular length and WAXD pattern of DANP and OANP

Since the crystal structures of DANP and OANP have not yet been clarified, their molecular lengths have been speculated using the CS Chem 3 D Pro (Molecular Modeling and Analysis). As shown in Fig. 2, their lengths are 2.10 nm for DANP and 2.84 nm for OANP.

WAXD patterns of DANP and OANP powder are shown in Fig. 3. The spacing of reflections of no. 1 and 2 in DANP and no. 1, 2 and 3 in OANP changed depending on the alkyl-chain length. The spacing of reflections no. 4–11 was well common to both materials, in which three strong reflections of no. 5, 7 and 9 were used for discussion in this paper. Furthermore, the relative intensity of each reflection (no. 1, 2 and 4–11) was also very similar in both materials. From this, the crystal structures of these two materials are considered to be similar for the molecular packing mode in the unit cell.

3.3. Fine structure of undrawn mixtures

WAXD and SAXS patterns of the gel-casting mixtures are shown in Fig. 4, whose surfaces in edge pattern are parallel to the horizontal plane. The terms of “through” and “edge” in this paper indicate the X-ray incident beam is, respectively, perpendicular and parallel to the surface of mixtures. Two reflection rings from the (110) and (200) planes of PE crystal, five reflection rings from DANP crystal (Ref. No. 1, 2, 5, 7 and 9 in Fig. 3) and six reflection rings from OANP crystal (Ref. No. 1, 2, 3, 5, 7 and 9 in Fig. 3) were observed in the through pattern. In edge pattern of WAXD, the shape of the above reflections was arc-like. The reflections from the (110) and (200) planes of PE were observed in the horizontal direction. This indicates that the lamellar surface of PE is oriented parallel to the surface of the undrawn mixtures but uniaxially distributed around the normal axis to the above surface. In edge pattern of SAXS, the interference from long period structure of 9.8 nm of PE was observed in the vertical direction, which nearly corresponds to the lamellar thickness. This indicates that a multilayer structure accumulating PE lamellae is formed in the undrawn mixture of DANP/PE or OANP/PE, like in the gel casting film of PE [4].

On the other hand, two reflections from the DANP crystal (1.96, 0.980 nm) or three reflections from OANP crystals (2.68, 1.34 and 0.893 nm) seemed to be observed in the vertical (or diagonal) direction. The former held the relation of the 1st- and 2nd-order and the latter held the 1st-, 2nd- and 3rd-order relation. The three reflections (no. 5, 7 and 9) from the spacing of DANP or OANP crystal (0.460, 0.395, and 0.327 nm) seemed to be observed in the horizontal (or diagonal) direction. From these facts, its was considered that the reflections with the longest spacing 1.96 nm of DANP or 2.68 nm of OANP arise from the periodical spacing corresponding to the molecular length of 2.10 nm of DANP or

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

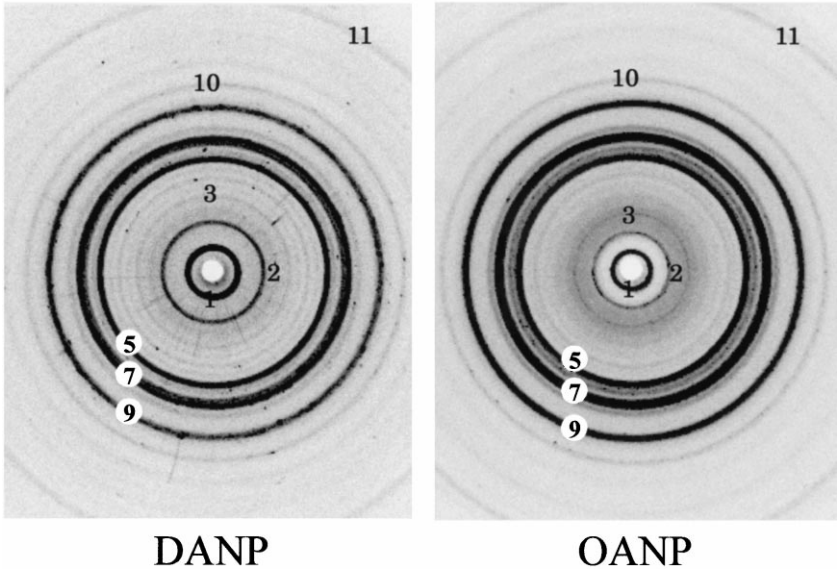

Fig. 3. WAXD patterns and the observed reflections of DANP and OANP powders. The numbers show the reflections fixed in the order of small reflection angle.

2.84 nm of OANP. Furthermore, three reflections with the spacing of 0.460, 0.395 and 0.327 nm are considered to arise from the periodical spacing between the alkyl chain stems of DANP or OANP.

From the above consideration, the following fine structure would be deduced for the undrawn mixtures of DANP/PE or OANP/PE, that is, a multilayer structure composed of the stacked lamellae of PE, including an oriented crystallite of DANP or OANP.

3.4. Oriented crystallization of DANP and OANP in drawn mixtures

Through-WAXD patterns of the drawn mixtures of DANP/PE and OANP/PE are shown in Fig. 5, the draw direction of which is parallel to the meridian direction. All of the detected reflection spots except the (200) and (110) reflections of PE are from the DANP or OANP crystal. In the patterns of DANP/PE mixture at the higher draw ratio, many reflection spots can be clearly observed. But, in the patterns of OANP/PE mixture at the higher draw ratio, it was difficult to detect the reflections on the layer line. This indicates the oriented crystallization of DANP or OANP arises from the molten state at 100°C in a drawn mixture. That is, the epitaxial growth of DANP or OANP chains upon the highly oriented PE chains might be deduced. Three reflection spots (no. 5, 7, and 9) from DANP or OANP crystal were observed in the equatorial direction. The 1st- and 2nd-order reflection spots (no. 1 and 2) from the longest spacing of 1.96 nm in DANP crystal were observed in the

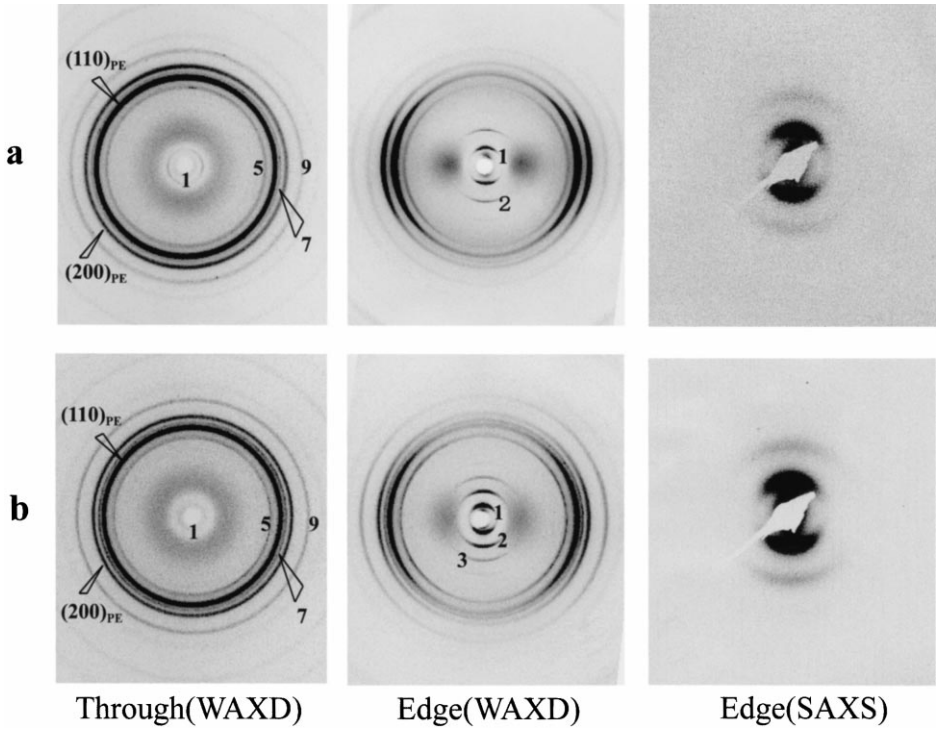

Fig. 4. WAXD and SAXS patterns of undrawn mixtures: (a) DANP/PE; (b) OANP/PE.

diagonal direction crossing at the angle of 56° from the equatorial direction. The 1st-, 2nd-, and 3rd-order reflection spots (no. 1, 2 and 3) from the longest spacing of 2.68 nm in OANP crystal were observed in the diagonal direction crossing at the angle of 57.5° from the equatorial direction.

The through-, edge- and end-WAXD patterns of the drawn mixtures of DANP/PE and OANP/PE are shown in

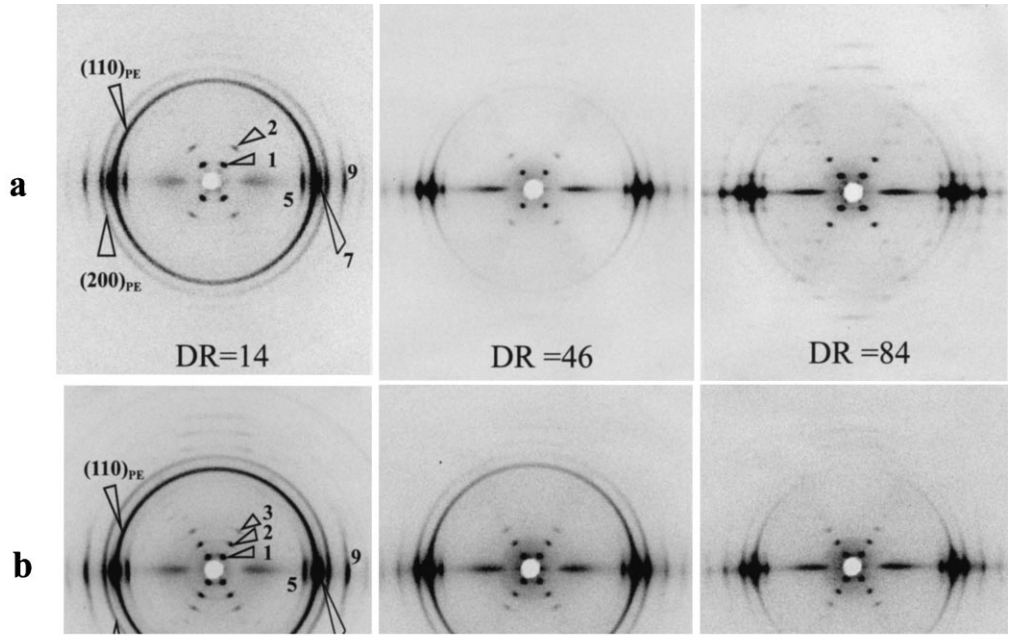

Fig. 5. Through-WAXD patterns of drawn mixtures as a function of draw ratio (DR), whose draw direction is vertical: (a) DANP/PE; (b) OANP/PE.

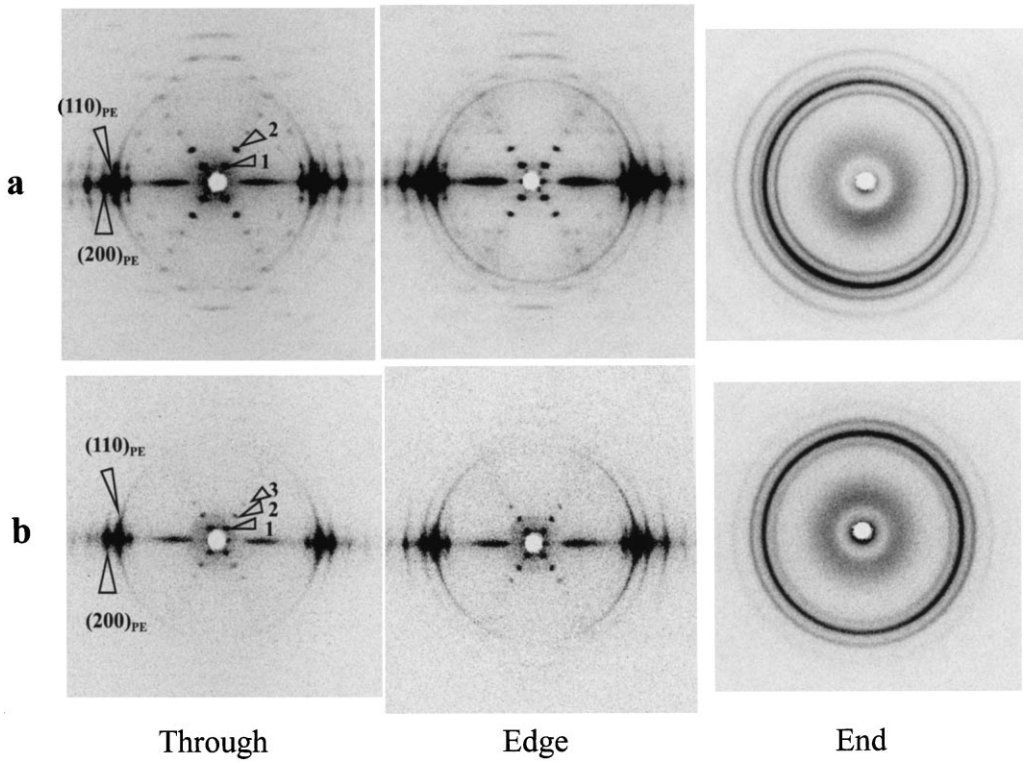

Fig. 6. Through-, edge- and end-WAXD patterns of drawn mixtures, at draw ratios of which are: (a) 77 for DANP; and (b) 65 for OANP.

Fig. 6, in which the term of "end" indicates the X-ray incident beam is parallel to the draw direction and the surface of mixtures. The draw direction is parallel to the meridian direction in the through- and edge-patterns. The through-pattern of DANP or OANP was nearly in agreement with the edge-pattern of them. Moreover, in the end-pattern of both mixtures, the (200) and (110) reflections of PE and the reflection no. 5 (0.460 nm) of DANP or OANP were found to take the ring shape, indicating that the crystalline orientation of DANP and OANP is also uniaxial, as in the case of PE.

Considering all the experimental data described in the above sections, the following facts were deduced:

1. the reflection spots in the diagonal direction arise from the periodicity corresponding to the molecular length of DANP or OANP;
2. three equatorial reflections of no. 5, 7 and 9 arise from the periodicity of the parallel packing of the alkyl chains of DANP or OANP.

Therefore, it was concluded that DANP or OANP crystallized epitaxially as it laid its alkyl chain upon the *c*-axis of PE. Such epitaxy of DANP or OANP was considered to be formed on the surface of micro-fibrils of PE, instantaneously in the cooling process after hot drawing of both mixtures at 100°C which was higher than the melting points of DANP and OANP.

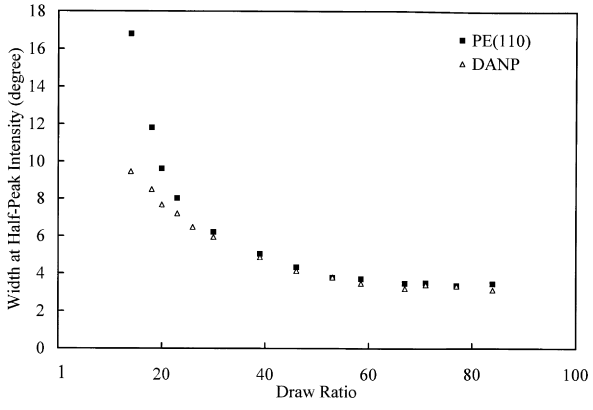

Fig. 7. Width at half-peak intensity of the reflection no. 5 (0.460 nm) of DANP (△) and the (110) reflection of PE (■), as a function of draw ratio.

3.5. Crystalline orientation of DANP or OANP in a drawn mixture

The degree of crystalline orientation of DANP or OANP in a PE matrix is expected to be affected by the degree of crystalline orientation of PE. 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 equatorial reflection with the d-spacing 0.460 nm of DANP/PE and OANP/PE mixture was compared with that of (110) reflection of PE, as shown in Figs. 7 and 8. In here, the direction of

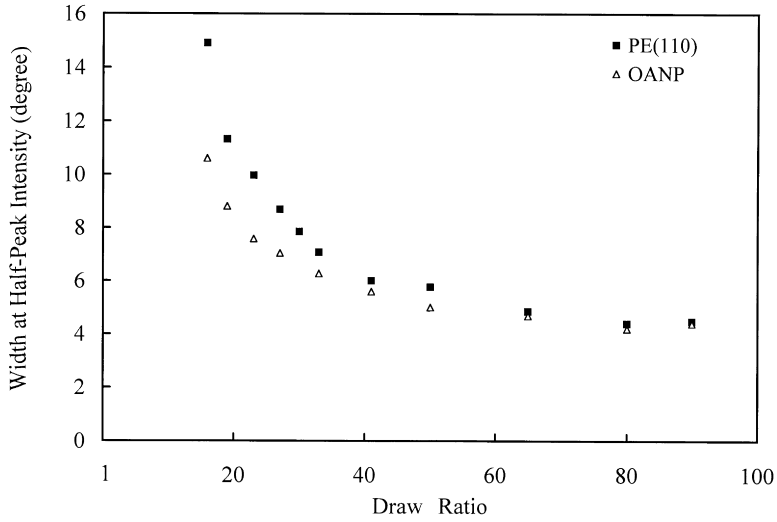

Fig. 8. Width at half-peak intensity of the reflection no. 5 (0.460 nm) of OANP (△) and the (110) reflection of PE (■), as a function of draw ratio.

incident X-ray beam was vertical to the draw direction and the surface of mixture (through pattern). In both mixtures of draw ratio below 30, the peak width of DANP or OANP was found to be narrower than that of PE, suggesting the high degree of orientation of the DANP or OANP crystal than that of PE crystal. Therefore, it might be considered that the epitaxial growth of DANP or OANP progresses with laying its alkyl chain upon the surface of micro-fibril composed of the extended chains of PE.

3.6. Infra-red dichroism of nitropyridine group in a drawn mixture

The degree of orientation of nitropyridine group in the drawn mixture was investigated using the infrared dichroism ($I_{\parallel}/I_{\perp}$) of 1345 cm^{-1} assigned to the symmetric stretching vibration of nitro group [5], in which the direction of polarized infrared incident beam was vertical to the surface of the drawn mixture. $I_{\parallel}$ and $I_{\perp}$ mean, respectively, the absorption intensity under the polarized direction of the incident beam being parallel and vertical to the draw direction.

The infrared dichroism ($I_{\parallel}/I_{\perp}$) at 1345 cm^{-1} of DANP/PE and OANP/PE is shown in Fig. 9. The high degree of parallel dichroism of 3.9–6.9 was observed for DANP/PE at the range of draw ratio of 20–84. Similarly, the high degree of parallel dichroism of 4.0–8.2 was observed for OANP/PE at the range of draw ratio of 23–90. The maximum values of 6.9 and 8.2 correspond to the calculated value of 6.0 for the perfect orientation of the alkyl chain axis of DANP and

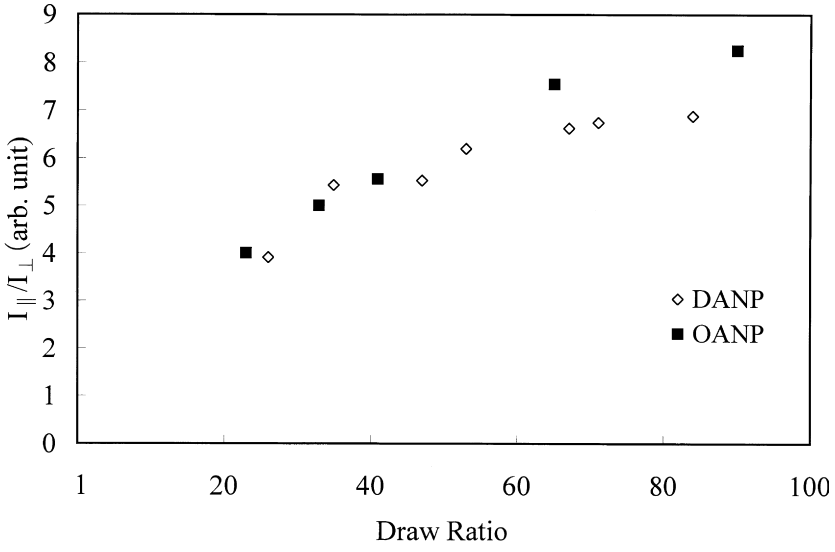

Fig. 9. Infrared dichroism of 1345 cm^{-1} of drawn DANP/PE (◇) and OANP/PE (■) as a function of draw ratio, which is assigned to the symmetric stretching vibration of nitro group [5].

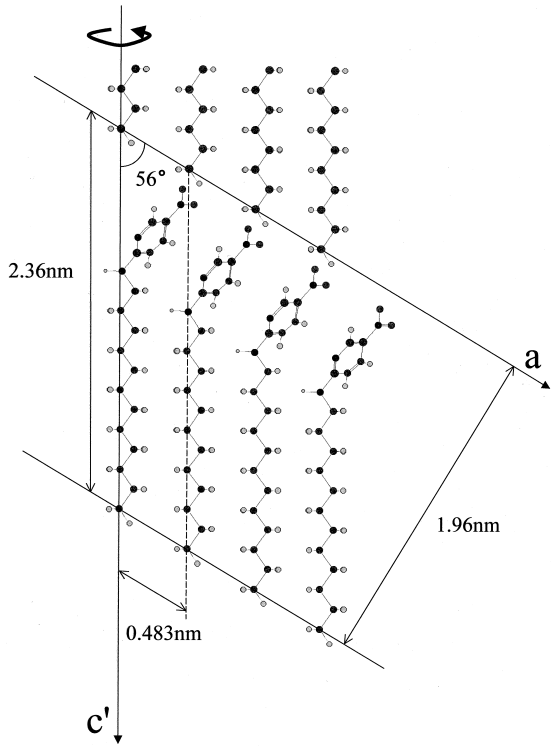

Fig. 10. One of possible models on an epitaxy structure of drawn DANP/PE, shown as a representative of drawn DANP and OANP/PE, whose draw direction is vertical. The planar plane of alkyl carbon chain is parallel to the a–c'-axis plane, where c'-axis is projection the c-axis having the angle of 3.4°.

OANP to the draw direction, which was calculated with using the following equation [6,7]:

$$I_{\parallel}/I_{\perp} = \frac{\frac{1}{2\pi}\int_0^{2\pi} |\mu|^2|\mathrm{Eo}|^2 \cos^2\phi \,\mathrm{d}\theta}{\frac{1}{2\pi}\int_0^{2\pi} |\mu|^2|\mathrm{Eo}|^2 \sin^2\phi \sin^2\theta \,\mathrm{d}\theta} = 2\cot^2\phi$$

where Eo is the electric vector of the incident infrared beam and the angle θ indicates the lateral directions perpendicular to the draw axis or the alkyl chain axis. The angle (ϕ) between the alkyl chain axis and the direction of the transition moment (μ) for the symmetric stretching vibration of nitro group was assumed to be 30°.

3.7. Optical second harmonic generation of a drawn mixture

Since the drawn mixtures of DANP/PE or OANP/PE 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 photomultiplier (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 detect, the relative intensities of which were two order lower than that of the Y-cut quartz single crystal at each incident angle. Furthermore, the 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 must have a center of symmetry.

3.8. Possible model on an epitaxy structure of DANP and OANP

From the above results, one of the possible models on an epitaxy structure of DANP is shown in Fig. 10, as a representative of DANP and OANP. The c'-axis (vertical axis) indicates the drawing direction. The difference on an epitaxy structure of DANP and OANP was considered to be only in its periodicity along the draw direction, originating from the difference in the alkyl chain length. In the following discussion, the numerical values in a bracket are for OANP.

Fig. 10 is an epitaxy structure of DANP (or OANP), grown as it laid its alkyl chain upon the extend chain (c-axis) of PE which is highly oriented to the drawn direction. The planar plane of alkyl carbon chain is parallel to the projection plane. The periodicity of 2.36 nm (3.18 nm) in the direction of alkyl chain axis is calculated from the azimuth angle of 56.0° (57.5°) evaluated from the reflections with the longest spacing of 1.96 nm for DANP (2.68 nm for OANP). The spacing between alkyl chain axis is 0.400 nm, which agrees well with the value 0.395 nm of the reflection no. 7. The adjustment of molecular packing in the direction of alkyl chain axis was required, because the closest spacing between the oxygen atom of the nitro group and the hydrogen atom of the neighbor molecular ends was 0.123 nm. This is adjustable by a gap of nearly 0.14 nm at the molecular ends in the vertical direction to the projection plane.

This structure model is supported, furthermore, from the maximum value of infrared dichroism as described in the above section, if the angle of about 30° is assumed between the symmetric axis of nitro group and the alkyl chain axis.

3.9. Unit-cell dimension and molecular packing in DANP or OANP crystal

A unit cell dimension and the molecular packing mode of OANP crystal could be induced by the same method as that of DANP described below. In this section, the numerical values in brackets are for OANP crystal.

From the experimental data described in the above sections, the lattice constants of $a = 0.483$ nm, $c = 2.37$ nm and $\beta = 56°$ ($a = 0.468$ nm, $c = 3.18$ nm and $\beta = 57.5°$)

Table 1
Index of (*h*,*k*,*l*) crystal plane to observed reflection of DANP

No.	Observed reflections			Calculated	Index
	Layer	Intensity[a]	Spacing (nm)	Spacing (nm)	(*h*,*k*,*l*)
1	Equatorial	Very strong	0.460	0.461	(0,2,0)
2		Very strong	0.395	0.398	(1,0,0)
3		Very strong	0.327	0.319	(1,2,0)
4		Medium	0.297	0.307	(0,3,0)
				0.287	($\bar{1}$,2,0)
5	1st	Very strong	1.96	1.963	(0,0,1)
6		Very weak	0.835	0.848	(0,1,1)
				0.821	(0,$\bar{1}$,1)
7		Strong	0.455	0.453	(0,2,1)
8		Very strong	0.413	0.418	(1,1,1)
9		Medium	0.329	0.321	($\bar{1}$,1,1)
10		Medium	0.294	0.293	($\bar{1}$,$\bar{2}$,1)
				0.300	(1,$\bar{2}$,1)
11	2nd	Very strong	0.982	0.981	(0,0,2)
12		Very weak	0.425	0.424	(0,2,2)
13		Medium	0.325	0.314	($\bar{1}$,0,2)
14	3rd	Medium	0.656	0.654	(0,0,3)
15		Medium	0.448	0.453	(1,1,3)
16		Weak	0.313	0.308	(1,$\bar{2}$,3)
17	4th	Medium	0.493	0.491	(0,0,4)
18		Very weak	0.425	0.426	(0,$\bar{1}$,4)
19		Weak	0.325	0.329	(0,$\bar{2}$,4)
20	5th	Medium	0.413	0.417	(1,0,5)
21	6th	Medium	0.375	0.373	(1,0,6)
22	7th	Medium	0.338	0.330	(1,0,7)
23		Weak	0.291	0.298	(1,$\bar{1}$,7)
24		Weak	0.270	0.271	(0,1,7)
25	8th	Medium	0.298	0.293	(1,0,8)
26	9th	Medium	0.221	0.221	(2,1,9)
				0.217	(1,$\bar{2}$,9)
				0.219	(2,0,9)

[a] By eye measurement.

were assumed for DANP (OANP), in which the directions of the *a*-axis and the c'-axis were fixed as shown in Fig. 10. The plane of alkyl zigzag chain is parallel to the ac$'$ plane, where the c'-axis is the projection of the *c*-axis and the angle between the c'- and the *c*-axis is 3.4 (2.5)°, as calculated from the ratio 0.14 nm/2.36 nm (0.14 nm/3.18 nm). The other lattice constants of $b = 0.934$ nm, $\alpha = 83°$ and $\gamma = 81°$ ($b = 0.934$ nm, $\alpha = 85°$ and $\gamma = 81°$) were determined by assuming that the four strong reflections of no. 1, 5, 7 and 9 were indexed to the (0,0,1), (0,2,0), (1,0,0) and (1,2,0) crystal planes of DANP (OANP), respectively. Two molecules of DANP (OANP) were considered to be included in the above triclinic unit cell. The calculated density of DANP (OANP) crystal is 1.165 g/cm^3 (1.121 g/cm^3), which is rational in comparison with the observed one of 1.135 g/cm^3 (1.090 g/cm^3), measured at 25°C by floating or sinking method using an aqueous solution of sodium chloride.

Based on the thus created triclinic unit cell of DANP crystal, the observed 26 reflections from the equatorial line to the ninth layer line could be indexed to the crystal plane as shown in Table 1. Only two weak reflections of 0.537 nm on 2nd layer line and 0.591 nm on 3rd layer line could not be indexed, which would be due to the other crystal modification. In the case of OANP, no reflections from the layer line were observed except the diagonal ones (the 1st to 4th order) with the longest spacing and the four equatorial ones having the same spacing as that of DANP. All the eight observed reflections could be indexed in consistency with the calculated spacing from the above triclinic cell.

As one of the possible models on packing of two molecules in a triclinic unit cell, a couple of anti-parallel molecules having a center of symmetry and the longest contact with neighbor alkyl chains was deduced. This structure model for DANP is shown in Fig. 11(a) and (b) as a representative of DANP and OANP, because both the molecular packings should be very similar. Fig. 11(a) is the projection on the b'–c' plane, perpendicular to the figure given in Fig. 10, where the b'-axis is the projection of the *b*-axis having the angle of 6.1°. Fig. 11(b) is the a'–b$''$ plane projection along the alkyl chain axis, where b''-axis is projection of the *b*-axis having the angle of 7.0° and a'-axis is the projection of *a*-axis having the angle of 34°. The spacing between the

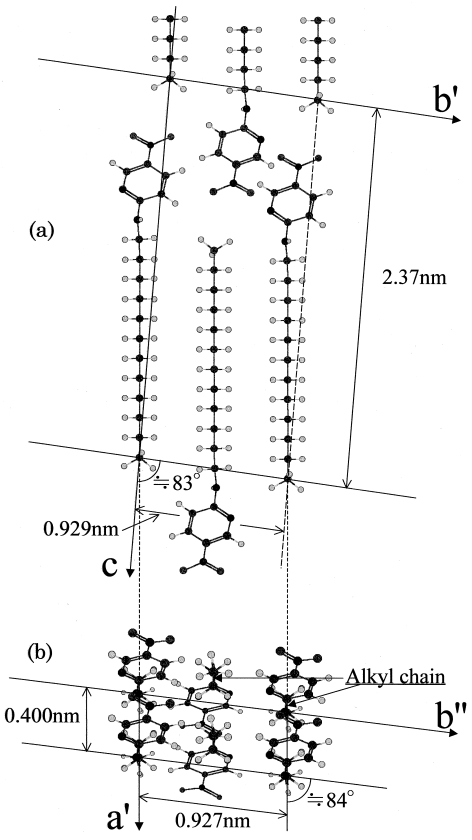

Fig. 11. One of the possible models on a molecular packing for DANP crystal. (a) b'–c projection, being vertical to the a–c' plane shown in Fig. 10, where b'-axis is projection of b-axis having the angle of 6.1°. (b) a'–b″ projection along the alkyl chain axis, where b''-axis is projection of b-axis having the angle of 7.0° and a'-axis is projection of a-axis having the angle of 34°.

neighboring alkyl chains is 0.461 nm, corresponding to the (0,2,0) reflection. The closest spacing is 0.298 nm between the hydrogen atoms of the neighbor alkyl chains, indicating the loose molecular packing.

Since the above molecular packing is comparatively loose, there will be other possibilities on the molecular packing having a center of symmetry by slipping between a couple of anti-parallel molecules along its alkyl chain axis. In order to check the suitability of the above model, we need to confirm the matching of the observed reflection intensities and the calculated ones on the drawn mixtures of DANP (or OANP)/PE. Furthermore, we need to carry out the structure analysis for the single crystal of the original DANP and OANP by taking into account the reflection intensities.

4. Concluding remarks

It was found that the alkylating amino-nitropyridine (DANP or OANP) was able to crystallize epitaxially in a matrix of PE, as laid its alkyl chain upon the extended chain of PE. From the results of crystalline orientation and infrared dichroism of the drawn mixtures, it was expected that they have a superior optical second harmonic generation, but no detection of the optical second harmonic signal from them was found. From this fact, it was deduced that the crystal structure of DANP and OANP should have a center of symmetry.

From the above information, the epitaxy structure of DANP and OANP in a matrix of highly oriented PE has been deduced. The triclinic unit cell and the molecular packing having a center of symmetry were proposed as one of possible crystal structure models. The details of crystal structure will be elucidated in a near future with using a single crystal of DANP (or OANP). The details of epitaxial growth of alkylating amino-nitropyridine on a micro-fibril composed of highly oriented PE will become clear.

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. By giving the external excitement to them, such as a polarizing treatment etc., however, the optical second harmonic signal from them might be observed because the above molecular packing might be changed to the one having no center of symmetry.

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

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