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# Structures of vinylidene fluoride oligomer thin films on alkali halide substrate

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Structures and crystal transformation of the newly synthesized vinylidene fluoride (VDF) oligomer with large electric dipoles evaporated on KCl (001) at various substrate temperatures have been investigated by an energy dispersive–grazing incidence x-ray diffraction system, Fourier transform infrared spectroscopy, and atomic force microscope (AFM). It was revealed that the molecules grow epitaxially and are influenced greatly by forces of the crystal surface field in terms of van der Waals or electrostatic potentials, and found that the phase transformation from form II ( $\alpha$  phase) to form I ( $\beta$  phase) is induced by raising the temperature of the substrate from 50 to 80 °C, accompanying the alternation in the crystal axes on the substrate from the  $a$  axis of form II to the polar  $b$  axis of the form I crystal. This fact suggests that the molecular chain of VDF oligomers aligns their  $c$  axes along the  $\langle 110 \rangle$  row of  $K^+$  or  $Cl^-$  with the aid of electrostatic interaction under enough thermal movement. Moreover, in the transformation process, a pair of “rod-like” crystals, suggesting ferroelectric activity, were observed by AFM. © 1999 American Institute of Physics.

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## I. INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is well known as a polar polymer with a large electric dipole moment at vinylidene fluoride ( $CH_2CF_2$ ; VDF) units, and it shows several crystal phases with different unit cells and molecular conformations, namely, form I ( $\beta$  phase,  $a=8.58$  Å,  $b=4.91$  Å,  $c=2.56$  Å; all *trans*), form II ( $\alpha$  phase,  $a=4.96$  Å,  $b=9.64$  Å,  $c=4.62$  Å; TGTG'), and form III ( $\gamma$  phase,  $a=4.96$  Å,  $b=9.56$  Å,  $c=9.23$  Å;  $T_3GT_3G'$ ).<sup>1</sup> In the case of form I, the large electric dipoles perpendicular to the molecular chain ( $c$  axis) are arranged in specific directions because the molecular chains have zigzag planar structures with all-*trans* conformation, differing from other crystal forms. Thus PVDF in the crystal phase of form I has large spontaneous polarizations, and is able to be applied as piezo- and pyroelectric films. Moreover, it has been recognized that poly(vinylidene fluoride-trifluoroethylene) [P(VDF/TrFE)] at proper molar percents reveals much clearer Curie temperatures,<sup>2,3</sup> which is characteristic of ferroelectric materials. To realize ferroelectric applications in PVDF and P(VDF/TrFE),<sup>4–11</sup> it is necessary to control their crystal structures, and these ferroelectric polymeric films can be prepared by means of thermal, mechanical, and polar treatments. Although these methods are effective for bulky films thicker than 1  $\mu$ m, they cannot be used for the preparation of ultrathin films with ferroelectric properties.

In order to fabricate organic ferroelectric thin films, it is essential to control the molecular structure as well as the

orientation, because their physical properties are greatly influenced by structural characteristics such as the crystalline structure, molecular orientation, conformation, thickness, and so on.

Vacuum evaporation is one possible method to prepare organic ultrathin films. In vacuum evaporation for polymeric films, however, it is difficult to fabricate highly crystalline films because of thermal decomposition of the molecular chain during the evaporation process.

In this study, we chose a newly synthesized vinylidene fluoride oligomer (VDF oligomer)<sup>12–14</sup> with low molecular weight as the evaporation material. The VDF oligomer, which consists of a finite number of VDF units with electric dipole moments, has the possibility for fabrication of thin films without pyrolysis and for control of the crystalline phase and molecular orientation by selecting a variety of substrates with differing temperatures during evaporation. Therefore we attempted to make epitaxially grown ferroelectric ultrathin films by vacuum evaporation.

Structural and orientational evaluation of VDF oligomer thin films was conducted by an energy-dispersive grazing incidence x-ray diffraction (ED-GIXD) system, developed in our laboratory.<sup>15,16</sup> In addition, an atomic force microscope (AFM) was utilized for observing the surface morphology. The conformation of molecules in evaporated films was measured by Fourier transform infrared (FTIR) spectroscopy. Through these measurements, we will discuss the factors governing the structures in ultrathin films on substrates as well as the most suitable conditions for fabricating ferroelectric ultrathin films.

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## II. SAMPLE AND EXPERIMENT

The VDF oligomer  $[\text{CF}_3-(\text{CH}_2\text{CF}_2)_n-\text{I}]$  ( $n=17$ ) used here as the evaporation source was newly synthesized by the telomerization method at Daikin Kogyo Co., Ltd. The VDF oligomer thin films were fabricated by vacuum evaporation on air cleaved KCl (001). The substrate was preheated at 200 °C for 2 h to obtain a clean surface, and then maintained at different substrate temperatures ( $T_s$ ), room temperature (RT), 50, 60, 70, 80, and 90 °C, under a vacuum of  $10^{-4}$  Pa during evaporation. The evaporation rate and average thickness were controlled to be 3–4 Å/min and 300 Å, respectively, by monitoring them with a quartz oscillator. After the deposition process, the substrate was slowly cooled to RT in vacuum, and then the fabricated thin films were investigated by AFM, FTIR, and ED-GIXD under an atmosphere.

A commercial AFM (Seiko Instruments SPA 300) was used in contact mode to obtain topographic images. IR spectra of the films were measured by a JEOL JIR7500EM. The crystal structure and orientation were investigated by ED-GIXD and by conventional  $\theta$ – $2\theta$  method with a Mac Science MXP<sup>3</sup>. Since the ED-GIXD system has been described in detail elsewhere,<sup>15,16</sup> a brief explanation of the ED-GIXD technique is as follows.

The ED-GIXD system is capable of analyzing the crystal structure as well as the molecular orientation. Especially, the epitaxial growth can be evaluated by the variation in relative intensities of the diffraction peaks observed at different azimuthal angles  $\omega$ .

White x rays at a very shallow glancing angle (about 0.1°) were used as incident x rays. These x rays are totally reflected at the interface between the film and the substrate. Then the diffracted x rays from the film can be efficiently observed without any scattering x rays from the substrate. In our measuring system, the rotating anode x-ray generator of the Mo target was used. A solid state x-ray detector [SSD, Si(Li)] can be moved in both the horizontal and vertical directions on  $\theta$ – $\theta$  goniometer arms. So the diffracted x rays from the films with arbitrary orientations can be detected at certain fixed scattering angle ( $2\theta$ ), determined by the horizontal ( $\theta_H$ ) and vertical ( $\theta_V$ ) scanning angles, as shown in Fig. 1.

The energies of the diffraction peaks in the ED-GIXD profiles,  $E(hkl)$ , are represented by

$$E(hkl) = \frac{6.1995}{d(hkl)\sin\theta} \quad (1)$$

where  $d(hkl)$  is the lattice spacing and  $\theta$  is the Bragg angle.

In this study we characterized evaporated thin films of VDF oligomer with reference data obtained from some papers on PVDF,<sup>1,17,18</sup> because no reliable data on the VDF oligomer exist.

## III. RESULTS AND DISCUSSION

Figure 2 shows AFM images of VDF oligomer films evaporated on KCl (001) at various  $T_s$ . In the films evaporated at  $T_s$  higher than 50 °C, “rod-like” crystals were observed. Moreover, it was revealed that the crystals grow in specific directions on KCl (001). These results imply the

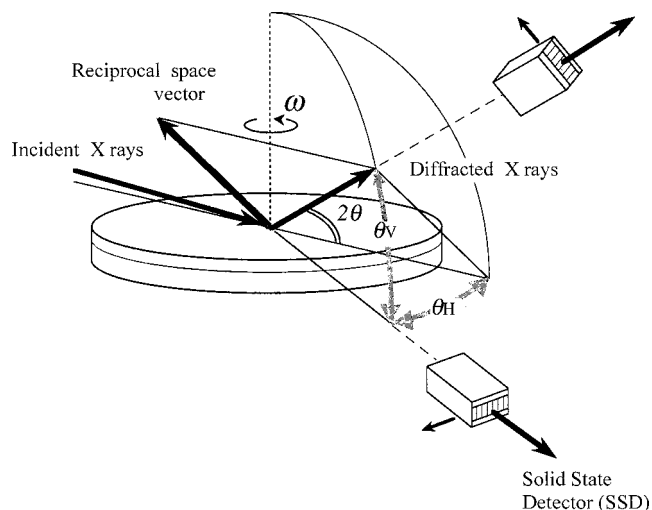


FIG. 1. Schematic diagram of the x-ray diffraction geometry with Ewald's construction in all reciprocal lattice spaces.

possibility of epitaxial growth of the crystal resulting from the interaction between the molecules and the KCl substrate. At  $T_s=60$  °C, several pairs of two rod-like crystals were observed. The reason for this phenomenon may be as follows.

First, ferroelectric single domains of VDF oligomers with electric dipole moments crystallize into a rod-like shape. With a rise of  $T_s$ , these ferroelectric domains grow larger and then neighboring ferroelectric domains with oppo-

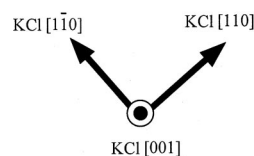
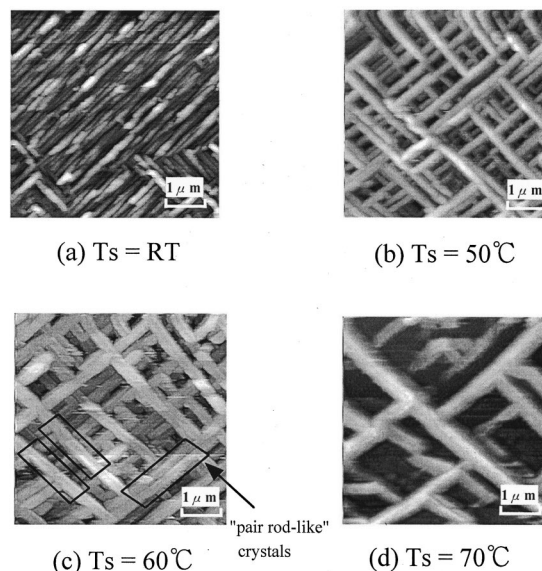


FIG. 2. AFM images of VDF oligomer thin films evaporated on KCl substrates.

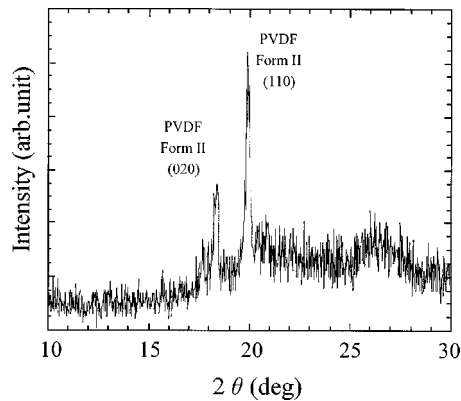


FIG. 3. Conventional  $\theta$ - $2\theta$  x-ray diffraction profile of a powder sample of a VDF oligomer.

site polarity combine to compensate for their electric potentials and form energetically stabler films.

According to this consideration, it was expected that the *b* axis (polar axis in a form I crystal) and the *c* axis (molecular chain axis) are parallel to the KCl substrate. So detailed structural and orientational analyses of the thin films were conducted to ascertain this possibility.

A powder sample of a VDF oligomer was measured by conventional x-ray diffraction. As shown in Fig. 3, peaks corresponding to (020) and (110) reflections of the form II crystal of PVDF were detected. From this result, it is judged that the form II crystal is significant in the powder sample of a VDF oligomer.

Figure 4 shows conventional x-ray diffraction profiles observed for the VDF oligomer films evaporated at various substrate temperatures. In this profile, the sharp peaks of 4.78 and 4.32 Å correspond to (020) reflection of form II and (200) reflection of form I, respectively. From the x-ray diffraction (XRD) pattern shown in Fig. 4, it was suggested that the structure of the evaporated oligomer film is predominantly the one of form II mixed with that of form I, and it transfers to that of form I with increasing KCl substrate tem-

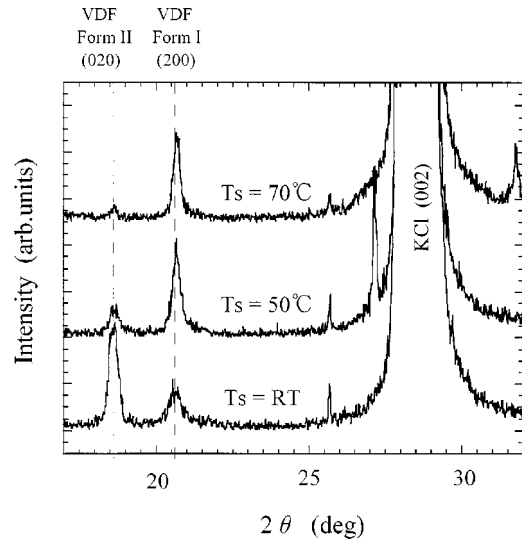


FIG. 4. Conventional  $\theta$ - $2\theta$  x-ray diffraction patterns of VDF oligomer thin films evaporated on KCl at various temperatures.

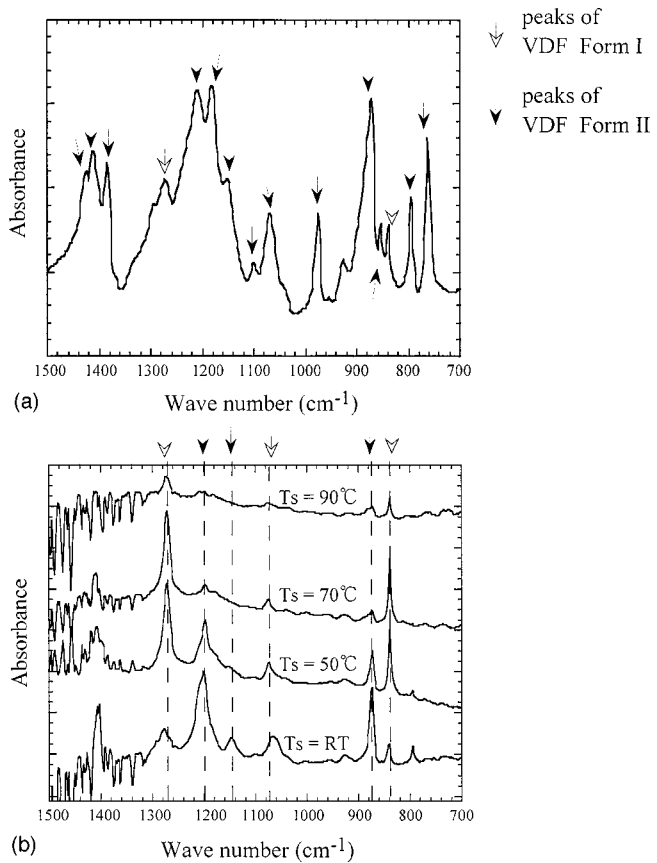


FIG. 5. Transmission FTIR spectra of (a) powder and (b) evaporated films of a VDF oligomer.

perature. It was also considered that the long chain axes (*c* axes) of VDF oligomer molecules are parallel to the substrate.

Next, the structures were examined from the point of view of vibrational spectra. Figure 5 shows the FTIR transmission spectra of powder as well as of evaporated films of a VDF oligomer. The powder was measured as KBr pellets, prepared by pressing a mixture of KBr and VDF oligomer powders. The peaks observed in the IR spectra were assigned as listed in Table I. The arrows in Fig. 5 indicate the remarkable absorption peaks. The characteristic peaks assigned to form I (840 and 1270  $\text{cm}^{-1}$ ) and to form II (790, 875, 1180,

TABLE I. Assignments of vibrational modes of the VDF oligomer observed in IR spectra.

Wave number ( $\text{cm}^{-1}$ )	Form	Vibrational mode
790	II	$\nu_s(\text{CF}_2) + \delta(\text{CF}_2)$
840	I	$\nu_s(\text{CF}_2) + \nu_s(\text{CC})$
875	II	$\nu_a(\text{CF}_2) + r(\text{CH}_2)$
1070	I	$\nu_a(\text{CC})$
1160	II	$\nu_s(\text{CF}_2) + \nu_a(\text{CC}) + w(\text{CH}_2)$
1180	II	$\nu_a(\text{CF}_2) + t(\text{CH}_2)$
1210	II	$\nu_s(\text{CF}_2) + w(\text{CH}_2)$
1270	I	$\nu_s(\text{CF}_2) + \nu_s(\text{CC}) + \delta(\text{CCC})$
1400	II	$w(\text{CH}_2)$



and  $1210\text{ cm}^{-1}$ ) were observed in the spectrum of the powder sample.

The results suggested that form II crystals are dominant in the powder sample, although it consisted of a mixture of form I and II crystals. In the case of thin films evaporated on KCl at various  $T_s$ , the peaks for form II appeared at  $T_s = \text{RT}$ , but became weaker with a rise in the substrate temperature. On the other hand, the characteristic peaks for form I became much more intense with an increase in  $T_s$ . Thus it was suggested that the molecular conformation in the evaporated VDF oligomer films changes from that of form II to form I with increasing  $T_s$ . These facts support the results obtained by the x-ray diffraction measurements.

Furthermore, it is worth noting that the peaks at  $840$  and  $1270\text{ cm}^{-1}$ , assigned to  $\nu_s(\text{CF}_2)$  of form I, grow greatly with increasing of  $T_s$ . Since the transition moments of the  $\nu_s(\text{CF}_2)$  mode are parallel to the  $b$  axis of form I and the incident infrared ray in the IR measurement setup employed reacts preferentially to the transition moments parallel to the substrate, it was suggested that the  $b$  axis of the form I crystal is oriented parallel to the substrate at high substrate temperatures. On the other hand, the peak at  $1200\text{ cm}^{-1}$ , which probably arose from the shift of the peaks of form II at  $1180$  or  $1210\text{ cm}^{-1}$  gradually decreased and then disappeared at  $T_s > 70^\circ\text{C}$ . This shift in the peaks might be caused by the epitaxial growth of form II crystals in the films.

From the results of the conventional XRD and FTIR measurements, it was suggested that form I and II crystals of VDF oligomer films evaporated on a KCl substrate can be represented schematically like in Fig. 6, where the structure of form I crystals at substrate temperatures in the range of  $50^\circ\text{C} < T_s < 80^\circ\text{C}$ , is pseudo hexagonal and the reciprocal space vector of (110) reflection of form I is inclined towards the KCl substrate by about  $30^\circ$ , while the reciprocal space vector of (110) reflection of form II is inclined towards the substrate by about  $27^\circ$ . In order to analyze the spatial distribution of the relative intensities of form I (110) and form II (110) reflections in the evaporated films, the ED-GIXD measuring system was utilized. An x-ray detector (the SSD) was mounted at a fixed Bragg angle, determined by the horizontal ( $\theta_H = 9.80^\circ$ ) and vertical ( $\theta_V = 5.80^\circ$ ) scanning angles. These parameters were calculated by formulas that were explained elsewhere.<sup>15</sup> Here, the azimuthal rotation angle  $\omega = 0^\circ$  was defined conventionally as the  $[100]$  direction of the KCl substrate. Then integral reflection intensities of the diffraction peaks from the thin films were analyzed at various  $\omega$  to characterize the molecular orientation of the evaporated films.

Figure 7 shows GIXD profiles observed for VDF oligomer thin films evaporated on KCl (001) at  $\omega = 45^\circ$ . A peak corresponding to (110) reflection of PVDF form I was observed in this profile, however, it was not at  $\omega = 0^\circ$ . In Fig. 7, the characteristic x rays of the Mo element used as the x-ray target were also detected.

In the case of  $T_s = \text{RT}$ , a peak corresponding to (110) reflection of VDF oligomer form II was observed with a small shoulder peak corresponding to the (110) reflection of form I. The detection of form II crystals might suggest that form II crystals with any wide molecular distribution exist in

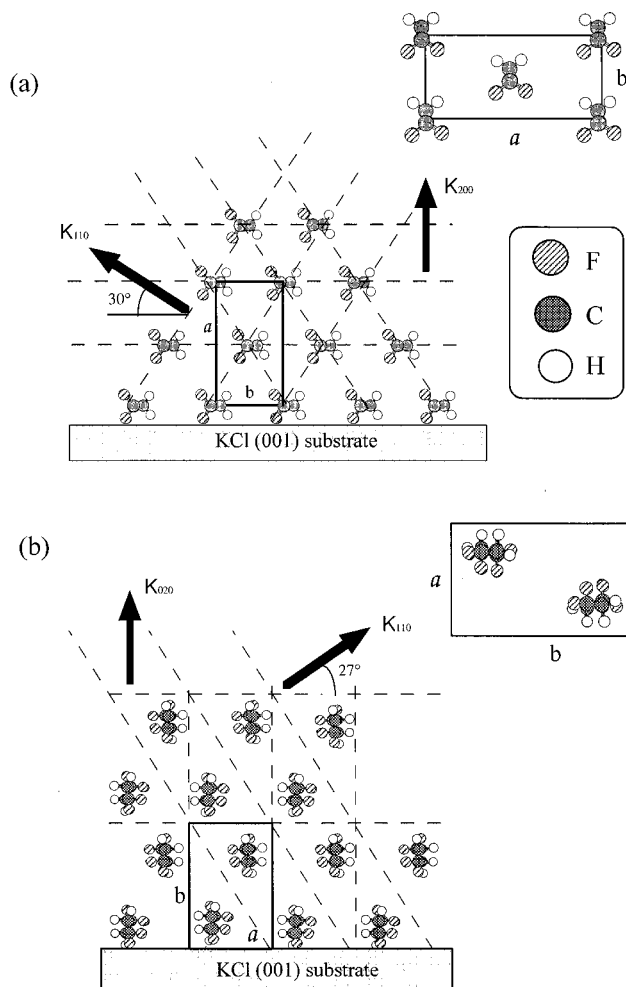


FIG. 6. Schematic models of a VDF oligomer: (a) form I and (b) form II crystals on a KCl substrate.

the films. Thus, the VDF oligomer crystal evaporated on KCl (001) tends to be formed with form II of PVDF at  $T_s = \text{RT}$  and with form I at  $50^\circ\text{C} < T_s < 80^\circ\text{C}$ .

Figure 8 shows the  $\omega$  variations of the (110) reflection intensities of form I in VDF oligomer thin film at  $T_s = 70^\circ\text{C}$  and the (110) reflection intensities of form II at  $T_s = \text{RT}$ . In Figs. 8(a) and 8(b), the (110) reflection intensities showed a

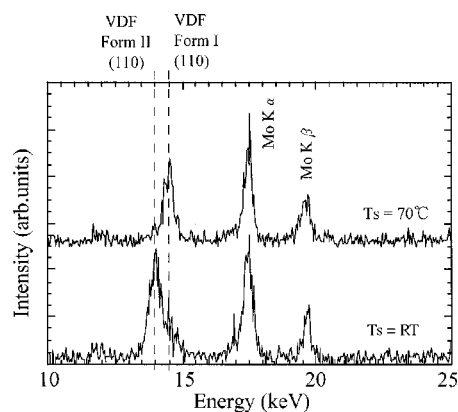


FIG. 7. GIXD profiles of VDF oligomer thin films evaporated on KCl at various temperatures at  $\omega = 45^\circ$ .

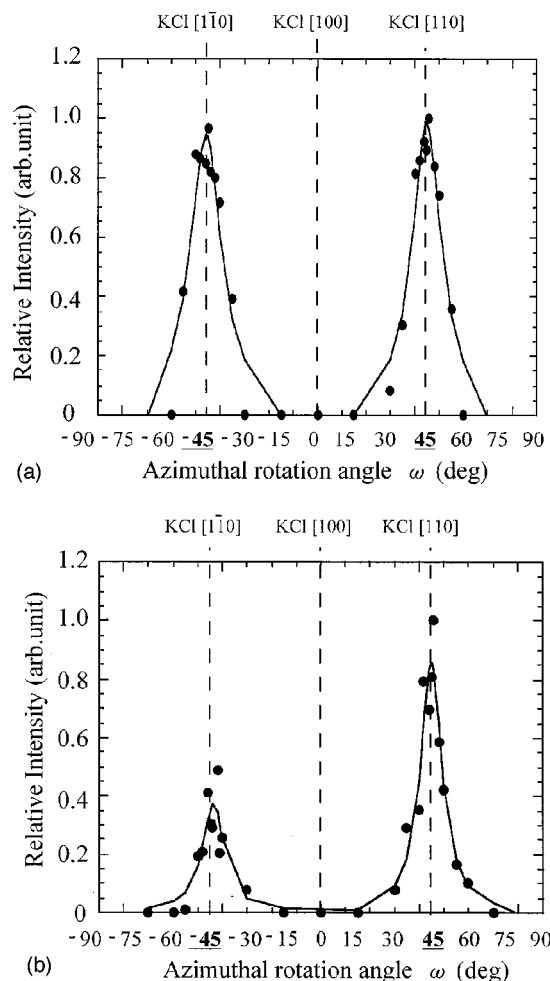


FIG. 8. Angular variations of (110) reflection intensities and lattice spacings observed for the films on KCl substrates. (a)  $T_s = 70^\circ\text{C}$  (form I) and (b)  $T_s = \text{RT}$  (form II).

maximum value at  $\omega = \pm 45^\circ$  and symmetric dependence on the  $\omega$  rotation. Supposing the molecular orientational distribution is a Lorentian curve; the distribution is almost  $15^\circ$ , regardless of whether it is a form I or II crystal. Since the intensity of x-ray diffraction is attributed to a number of crystalline grains, it was concluded that VDF oligomer molecules arrange their  $c$  axes along the  $\text{KCl}\langle 110 \rangle$  directions, with a fluctuation of about  $15^\circ$ . Thus, VDF oligomer crystals in thin films are epitaxially crystallized on KCl (001). The orientation model of an epitaxially grown VDF oligomer crystal is illustrated in Fig. 9. A model of the form I crystal is shown in Fig. 9(a) and that of form II in Fig. 9(b). Judging from Figs. 6 and 9, the dipole moments of the VDF oligomer in form I crystals are aligned along specific directions with fourfold symmetry. In the crystallization of  $\beta$  (form I) PVDF from the melt at atmospheric pressure, epitaxial growth with fourfold symmetry on KBr (001) was observed by Lovinger.<sup>19</sup>

A crystal surface field formed by the atomic arrangement of the KCl surface caused interaction between VDF oligomer molecules and the substrate. And when molecules are absorbed on the substrate, they obtain thermal energy from the substrate. It might be suggested that the interaction and ther-

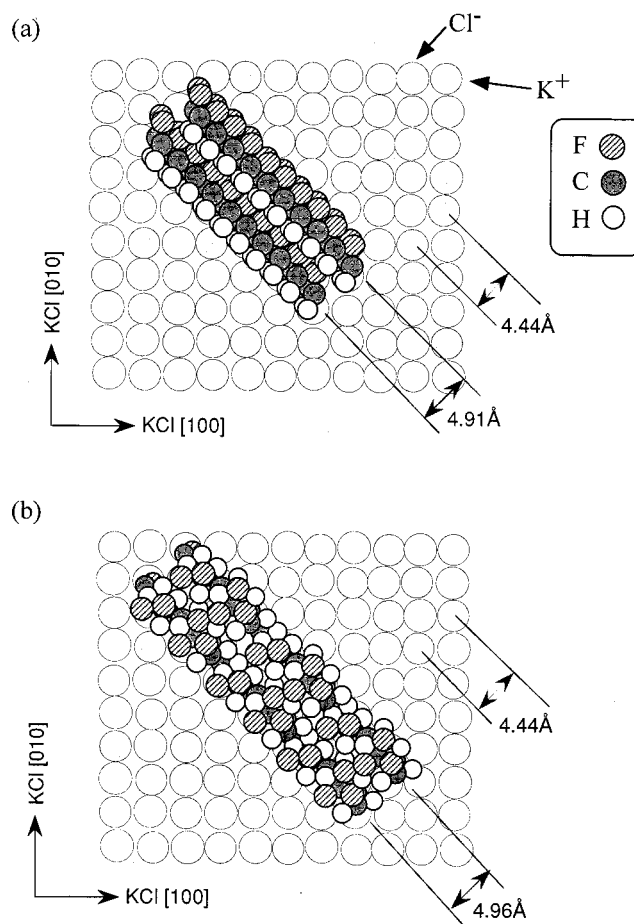


FIG. 9. Epitaxial growth model of VDF oligomer thin films on a KCl substrate: (a) form I crystal and (b) form II crystal.

mal energy contribute to characteristics of the crystalline phase in VDF oligomer thin films.

As is shown in Fig. 9, F atoms of VDF oligomer molecules in form I crystals are located on  $\text{K}^+$  and H atoms on  $\text{Cl}^-$  along the  $\text{KCl}\langle 110 \rangle$  directions. In form II, H and F atoms are located alternately on  $\text{K}^+$  or  $\text{Cl}^-$  rows of the substrate. It was expected that there are at least two stable states in terms of van der Waals or electrostatic potentials, and that thermal energy supplies from the substrate to the molecules caused the transition between these states.

Thus, it was considered that this epitaxial growth and the difference in the molecular orientation by the substrate temperature are influenced by the potential, that depended on a crystalline field of the KCl substrate, and thermal energy given to molecules.

#### IV. CONCLUSIONS

The crystal structure and molecular orientations in VDF oligomer thin films evaporated on KCl (001) were evaluated. The VDF oligomer formed a rod-like crystal in specific directions with fourfold symmetry. And a pair of rod-like crystals grew up next to each other, suggesting the existence of directly opposed ferroelectric domains in the films evaporated at  $T_s > 60^\circ\text{C}$ . In the films, long chain axes of VDF oligomer molecules were parallel to the substrate and exhib-

ited epitaxial growth behavior along the KCl  $\langle 110 \rangle$  directions. Moreover, the VDF oligomer was prone to crystallize with form II at  $T_s = RT$  and with form I at  $50^\circ C < T_s < 80^\circ C$ . Furthermore, the  $b$  axis of form I crystals is thought to be parallel to the KCl substrate. That is to say, the direction of the electric dipole moments is parallel to the substrate and oriented in a specific direction. It is thought that both the crystalline field of the KCl substrate and the thermal interaction between molecules and KCl have a great influence on the characteristics of the crystalline phase and epitaxial growth in VDF oligomer thin films.

## ACKNOWLEDGMENTS

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