

Single-Crystal-like Structure of Poly(9,9-dioctylfluorene) Thin Films Evaluated by Synchrotron-Sourced Grazing-Incidence X-ray Diffraction

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(Received June 4, 2007; Accepted September 23, 2007; Published November 2, 2007)

ABSTRACT: Detailed structures of friction-transferred poly(9,9-dioctylfluorene) (PFO) thin films have been studied using synchrotron-sourced grazing-incidence X-ray diffraction (GIXD). The results of in-plane GIXD were in full agreement with those of electron diffraction in our previous study. We also revealed the structures of liquid-crystalline (LC) and crystalline films that were prepared by rapid and slow cooling from the LC melted state of the friction-transferred films, respectively. For the crystalline films, the results of in-plane GIXD were not in full agreement with those of electron diffraction; additional weak peaks of the odd 00l reflections were observed only in the GIXD profiles. This implies that the twofold screw symmetry along the c-axis of PFO is broken. The rocking profiles for each reflection gave the order parameter of almost one for the crystalline films and 0.67 for the LC films. These results suggest the ability of friction transfer for obtaining single-crystal-like thin films and the importance of carefully designed annealing process for the applications of the films to various optoelectronic devices. [doi:10.1295/polymj.PJ2007063]

KEY WORDS Polyfluorene / Friction Transfer / Oriented Films / Synchrotron Radiation /
Grazing Incidence X-ray Diffraction / Polymer Light-emitting Diodes / Polarized Emission /

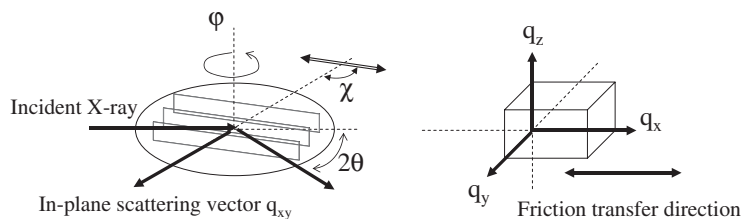
Polyfluorenes (PFs) have emerged as a very attractive class of conjugated polymer, especially for display applications, owing to their efficient blue electroluminescence, high charge-carrier mobility and easy processability.^{1–3} An important property of PFs is their thermotropic liquid crystallinity as first reported by Grell *et al.*⁴ They demonstrated that well-aligned films of PFs can be prepared on rubbed polyimide layers. The films with controlled molecular orientations are expected to exhibit anisotropic properties because the intrinsic characteristic of PFs originates from the π electrons delocalized along the polymer backbone (main-chain). For instance, oriented films result in emission of linearly polarized light when used in light-emitting diodes (LEDs),^{5–8} and in enhanced charge mobility when used in field-effect transistors (FETs).^{9–11} Thus, there are various benefits of using oriented films in optoelectronic devices.

One of useful methods for preparing such oriented films is the friction-transfer technique.^{12–19} Formation of highly oriented poly(tetrafluoroethylene) (PTFE) films demonstrated by Tabor *et al.* has been well known since 1964.¹² Wittmann and Smith reported

that the friction-transferred PTFE films induce the orientation of a variety of crystalline and liquid-crystalline (LC) materials, including polymers, monomers and small organic and inorganic molecules.^{13–18} We have applied the friction-transfer technique to the preparation of oriented films of various conjugated polymers such as polysilane, poly(p-phenylene), poly(p-phenylenevinylene), poly(alkylthiophene), and their derivatives.^{19–24} Recently, highly oriented thin films of poly(9,9-dioctylfluorene) (PFO) was found to be formed by this technique.²⁵ Furthermore, we have succeeded in fabrication of polarized polymer LEDs (polarized PLEDs) utilizing the oriented PFO films.²⁶

Evaluation of film structure is important for the application of oriented films to optoelectronic devices. In our previous study,²⁵ we investigated the structure of friction-transferred PFO films by using transmission electron microscope (TEM) and found that subsequent thermal treatments were specifically effective for improvement of molecular orientation. In this study, we have quantitatively investigated the distribution of molecular orientation by using synchro-

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Scheme 1. Geometry of in-plane GIXD measurements and definition of the scattering vectors, q_x , q_y and q_z , with respect to the friction transfer direction.

tron-sourced grazing-incidence X-ray diffraction (GIXD). In-plane diffraction and rocking profiles clearly showed the effects of subsequent thermal treatments on the molecular orientations. We demonstrate the ability of friction transfer for obtaining single-crystal-like films and the importance of carefully designed annealing process for applications of the films to various optoelectronic devices.

EXPERIMENTAL

Material

PFO was used as purchased (American Dye Source, Inc.). The number- and weight-average molecular weights, as determined by gel permeation chromatography (GPC, Shimadzu LC-10Vp HPLC System) with a TOSOH G5000HHR GPC column calibrated using a polystyrene standard, are $M_n = 25000$ and $M_w = 55000$ (polydispersity = 2.2), respectively. The differential scanning calorimetry (DSC, Perkin Elmer Instruments) scans showed a crystallization peak at approximately 80–90 °C and a melting endothermal peak at approximately 160 °C at a heating and cooling rate of 20 °C/min. Above this temperature, PFO shows birefringent LC melt and becomes isotropic at approximately 270–280 °C.

Film Preparation

PFO films were prepared on silicon substrates by the friction-transfer technique. Then, the friction-transferred films were thermally annealed with two different procedures as described below. In one case, the films were heated at 200 °C for one hour and rapidly cooled to room temperature. In the other case, the films were heated at 200 °C and slowly cooled to room temperature at a rate of 0.2 °C/min.

Evaluation

In-plane GIXD measurements were performed at a BL13XU beam line of SPring-8 (Japan Synchrotron Radiation Research Institute (JASRI), Hyogo, Japan) equipped with an ATX-GSOR, one of the ATX series of Rigaku Co.²⁷ The wavelength, λ , was 0.128 nm, and the beam size at incident slits was 0.1 mm ×

0.1 mm square. The grazing angle of incidence, ω , was fixed at 0.14° which is the critical angle for total reflection against the silicon substrate. A soller slit with a divergence angle of 0.41° was placed before the detector. The scattering vector, q ($= 4\pi \sin \theta / \lambda$), was decomposed into the in-plane scattering vector q_{xy} and the out-of-plane scattering vector q_z . The angle between the q_{xy} and the friction transfer direction, χ , was fixed during the in-plane diffraction scans. We defined the in-plane scattering vectors, q_x and q_y , for fixed χ of 0° and 90°, as shown in scheme 1. The scanning speed was 2°/min, and the angular interval between steps was 0.01° for the in-plane diffraction. We also monitored the changes of scattered intensities at a locked q_{xy} with a sample rotating angle, ϕ , which is called rocking scans or ϕ scans. The rocking profiles correspond to a distribution of orientation for a diffracted lattice plane. The scanning speed was 10°/min, and the angular interval between steps was 0.1° for the rocking scans. The samples were placed into a special holder covered with a Kapton hemisphere dome of 200 mm in diameter and purged with helium gas during all the measurements. Replacing by helium gas leads to the reduction of background scattering and as well prevents the samples from oxidation.

Assignment

The profiles were analyzed using the putative unit cell parameters of PFO (orthorhombic, $a = 2.56$ nm, $b = 2.34$ nm, $c = 3.32$ nm, eight chains, with space group $P2_12_12_1$) reported by Chen *et al.*²⁸

RESULTS AND DISCUSSION

As-deposited Films

The results of in-plane GIXD for the as-deposited films are shown in Figure 1. In-plane diffraction profiles plotted as a function of q_x (Figure 1(a)) shows a series of long period peaks at $q_x = 3.8, 11.4, 15.1, 19.1, 22.6$ and 26.5 nm^{-1} that corresponds to the 001 ($l = 2, 6, 8, 10, 12, 14$) reflections. This indicates that the main-chains of PFO (c -axis) are oriented parallel to the friction direction. On the other hand, in-

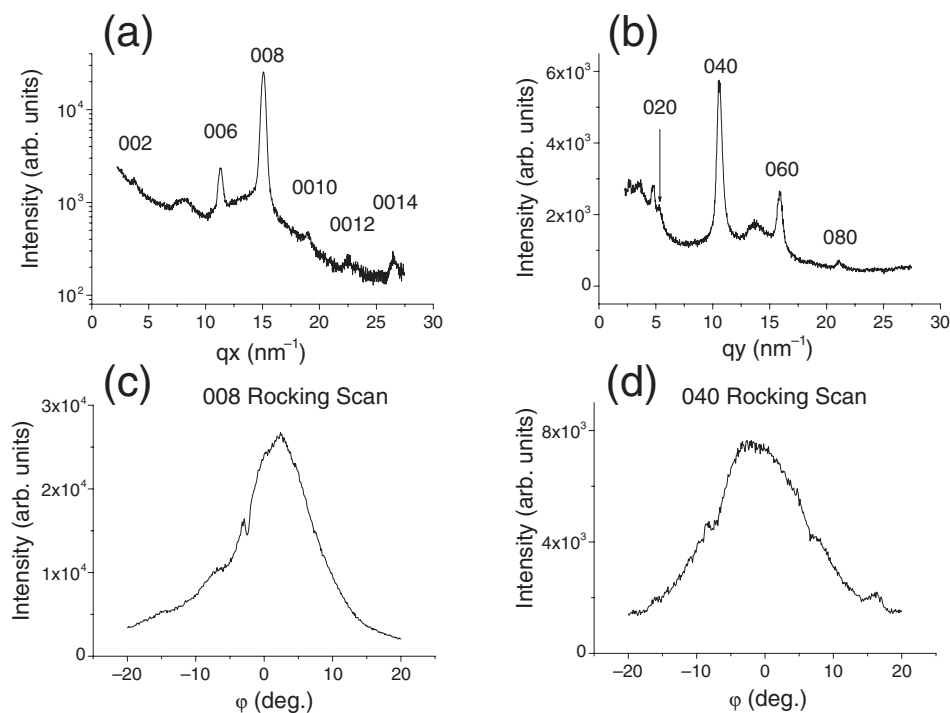


Figure 1. In-plane GIXD results of the as-deposited films: in-plane diffraction profiles plotted as a function of the q_x (a) and q_y (b), and rocking profiles for the 008 (c) and 040 (d) reflection.

plane diffraction profiles plotted as a function of q_y (Figure 1(b)) shows no 00l reflections. This finding implies again that the c-axis is parallel to the friction direction. Instead of the 00l reflections, we observed a series of long period peaks at $q_y = 5.3, 10.6, 15.9$ and 21.1 nm^{-1} that corresponds to the $0k0$ ($k = 2, 4, 6, 8$) reflections. This indicates that the alkyl side chains (b-axis) are oriented orthogonal to the friction direction. All of the results of in-plane GIXD are in full agreement with those of electron diffraction;²⁵ the q_x and q_y scans in GIXD correspond to the meridian and equator in electron diffraction, respectively.

An advantage of GIXD as compared with electron diffraction is feasibility of yielding more quantitative profiles for a distribution of orientation. Figure 1(c) and 1(d) show the rocking profiles for the 008 and 040 reflection of as-deposited films, respectively. The intensities for both reflections clearly decreased to the background level with the rotating angles of approximately $\pm 20^\circ$. The full width at half maximum (FWHM) by the Gaussian distribution were estimated to be about 10° and 13° for 008 and 040 reflection, respectively. Compared with “standard” values reported for PFO oriented films with other molecular orientation methods,^{4–6,29} these values appear to be quite small. For example, in a pioneer study for PFO oriented films on the rubbed polyimide by Kawana *et al.*, the FWHM for the 008 reflection was estimated to be approximately 70° .²⁹ Thus, poly-

mer chains arranged by the friction-transfer technique are found to be well-ordered to the friction transfer direction.

Crystalline Films Obtained by Slow Cooling

The results of in-plane GIXD for the films obtained by slow cooling are shown in Figure 2. As in the case of the as-deposited films, Figure 2(a) and 2(b) show only a series of 00l and $0k0$ reflections for q_x and q_y scans, respectively. But, it is clearly seen that each reflection of the films is much stronger than that of as-deposited films. Surprisingly, long-range order, the 00l reflections up to the 14th and the $0k0$ reflections up to the tenth, were observed in the range of the measurements ($2 \text{ nm}^{-1} < q_{xy} < 27 \text{ nm}^{-1}$). It is well known that simple one-dimensional molecules such as polyethylene exhibit high degree of order in thin films,³⁰ while more complicated molecules such as π conjugated polymers used in organic devices usually exhibit low degree of order in thin films. This is the first report of higher order reflections from π conjugated polymer films.

An interesting aspect of the crystalline structure shown in Figure 2(a) is the appearance of odd 00l reflections ($l = 3, 5, 7, 9, 11, 13$), which can not be accounted for by the unit cell of PFO (orthorhombic with space group $P2_12_12_1$) proposed by Chen *et al.*,²⁸ if taking into account of their unit cell, the odd 00l reflections are forbidden. In other words, the appearance of odd 00l reflections implies the twofold

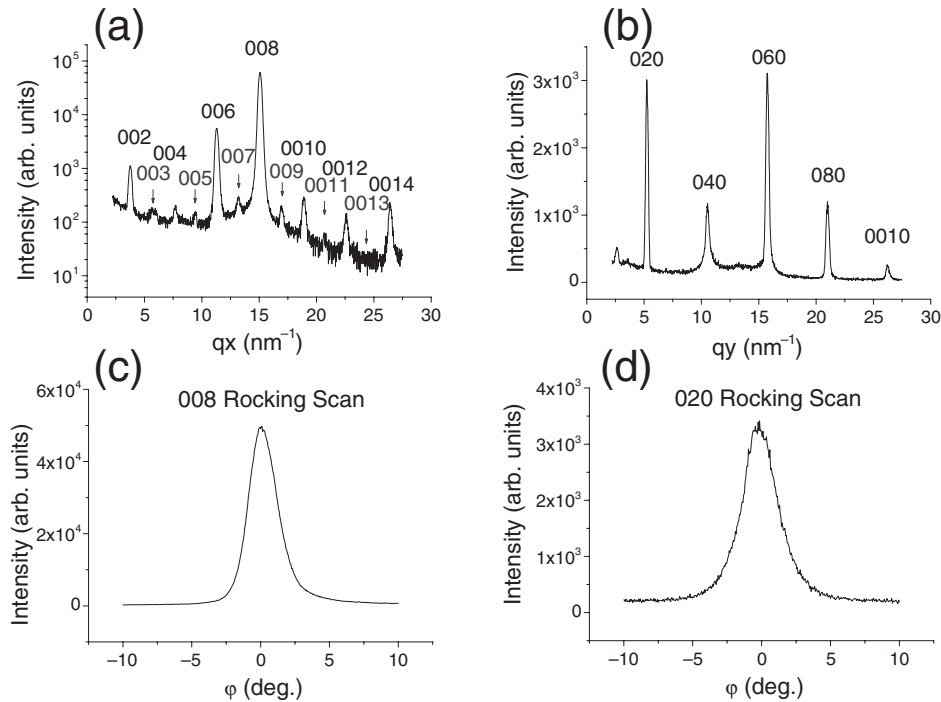


Figure 2. In-plane GIXD results of the films obtained by slow cooling: in-plane diffraction profiles plotted as a function of the q_x (a) and q_y (b), and rocking profiles for the 008 (c) and 020 (d) reflection.

screw symmetry along c -axis of PFO is broken. We assume that the odd $00l$ reflections were not observed by electron diffraction simply because those peaks are too weak to discriminate from the background. Further study of X-ray scattering simulation is currently under way to clear up the speculations described above.

Rocking scans clearly show the effect of subsequent thermal treatments on the molecular orientation. Figure 2(c) and 2(d) show the rocking profiles for the 008 and 020 reflections of the films, respectively. The intensities decreased to the background level with the rotating angles of approximately ± 3 – 5° . The peaks are indeed narrow with the FWHM of about 2° for the 008 reflection and 3° for the 020 reflection. To the best of our knowledge, such narrow FWHM has not been reported for thin films of π conjugated polymers used in organic devices. Here, we introduce the order parameter, f_{20} , to estimate the degree of molecular ordering.³¹ The f_{20} is given by;

$$f_{20} = (3\langle \cos^2 \varphi \rangle - 1)/2, \quad (1)$$

where

$$\langle \cos^2 \varphi \rangle = \frac{\left(\int I(\varphi) \cos^2 \varphi \sin \varphi \, d\varphi \right)}{\left(\int I(\varphi) \sin \varphi \, d\varphi \right)}, \quad (2)$$

$I(\varphi)$ is the intensity in rocking scans. The rocking profile for the 008 reflection of the films (Figure 2(c))

gives $f_{20} = 0.999$, which implies that the degree of alignment for the c -axis is indeed close to the perfect orientation. Furthermore, the rocking profile for the 020 reflection of the films (Figure 2(d)) also shows that the degree of alignment for the b -axis is also close to the perfect orientation. We therefore conclude that the films obtained by slow cooling exhibit a single-crystal-like structure. The fact that the almost ultimate alignment is accomplished in the films is very surprising taking into account of simple processes of friction-transfer and annealing without the need for any aligning layer such as polyimide. We assume the mechanism of above-mentioned perfect orientation as follows.²⁵ First, polymer chains close to the substrate are probably highly oriented and firmly fixed to the substrate by the friction-transfer technique. Second, the orientation of the immobilized polymer chains at the interface induces the homogeneous bulk alignment above the LC transition temperature. Finally, the rearrangement of whole polymer chains in the film is achieved during the slow cooling to room temperature, resulting in perfect orientation of the bulk polymer chains along the friction direction. Further studies by “*in situ*” GIXD experiments are being planned to reveal the mechanism in detail.

Liquid-crystalline Films Obtained by Rapid Cooling

For the films obtained by rapid cooling, diffused scattering (halo), which are typical of an LC state, were observed in electron diffraction.²⁵ The scatter-

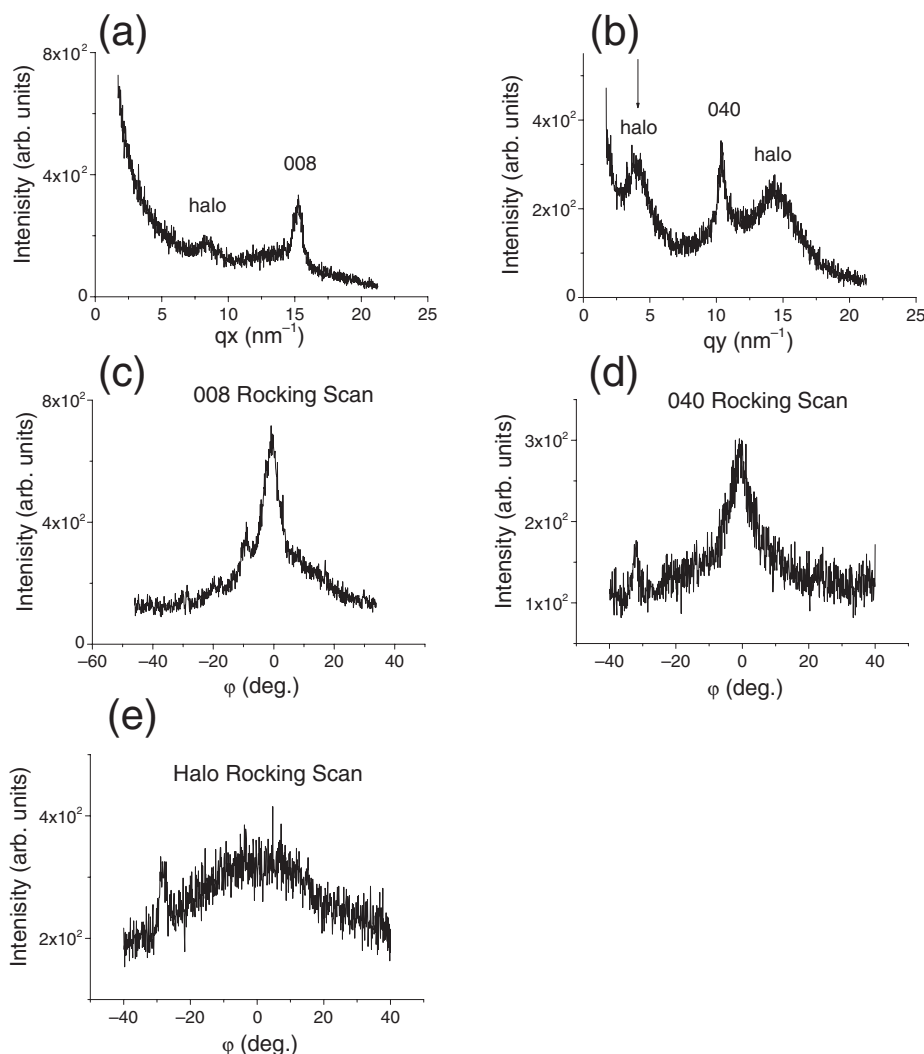


Figure 3. In-plane GIXD results of the films obtained by rapid cooling: in-plane diffraction profiles plotted as a function of the q_x (a) and q_y (b), and rocking profiles for the 008 (c), 040 (d) reflection and diffused scattering (e).

ing, however, could not be detected by a laboratory system of GIXD.³² We therefore applied synchrotron sourced GIXD to the films.

The results of in-plane GIXD for the films obtained by rapid cooling are shown in Figure 3. Two different types of diffractions were observed both in Figure 3(a) and 3(b); one is sharp diffractions assigned to the 080 and 040 reflections, and the other is diffused scattering around $q_x = 8 \text{ nm}^{-1}$ and $q_y = 4, 14 \text{ nm}^{-1}$ (indicated as “halo”).

We carried out the rocking scans for each type of diffractions. Figure 3(c) and 3(d) show the rocking profiles for the sharp diffractions (the 008 and 040 reflections). The peaks are narrow, with FWHM of 12° for the 008 reflection and 10° for the 040 reflection. The FWHM are found to be roughly the same values as those of the as-deposited film. This finding is interpreted as the existence of unmelted portion of the friction-transferred film in spite of the annealing at high temperature of 200°C . On the other hand, Figure 3(e)

shows the rocking profile for the diffused scattering around $q_y = 4 \text{ nm}^{-1}$ (indicated by an arrow in Figure 3(b)). The peak is very broad as compared with Figure 3(c) and 3(d), with a FWHM of about 40° . The equations (1) and (2) give $f_{20} = 0.68$, which is almost equal to a typical order of nematic LC.⁴ This value corresponds to our previous result ($f_{\text{opt}} = \sim 0.7$) judged by the optical (UV-vis) anisotropy.²⁵ The above results show that synchrotron-sourced GIXD is effective to quantitatively detect the signals of the LC state in thin films.

CONCLUSION

By means of synchrotron-sourced GIXD, we have studied the structure of friction-transferred PFO thin films. For the as-deposited films, the results of in-plane GIXD were in full agreement with those of electron diffraction. For the crystalline films (obtained by slow cooling), additional weak peaks of odd 00l re-

flections were seen only in the GIXD profiles. This implies that the twofold screw symmetry along the c-axis of PFO is broken. For the LC films (obtained by rapid cooling), diffused scattering, which could not be detected by a laboratory system of GIXD, were successfully observed. The above results show that synchrotron-sourced GIXD is effective to probe the detailed structures of polymer thin films. The rocking scans clearly showed the structural differences between these films. The rocking profiles of crystalline films gave the order parameters of almost one, which indicates that the films show a single-crystal-like structure. On the other hand, the rocking profiles of LC films gave the order parameter of 0.67, which indicates that the films are composed of the nematic LC glass. In general, high crystallinity achieved by slow cooling is advantageous for the application of thin film transistors (TFTs).³³ Meanwhile, the LC glass state achieved by rapid cooling is advantageous for the application of LEDs.²⁶ Therefore, it is very important to carefully design the annealing process, especially cooling rate, for the applications of the films of LC polymers to various optoelectronic devices.

Acknowledgment. The authors are grateful to Dr. Hirokawa, Dr. Koganezawa, Dr. Sakata (JASRI), Dr. Omote (Rigaku Co.) and Prof. Yoshimoto (Iwate Univ.) for GIXD measurements and helpful discussions. We also acknowledge Dr. Honda (AIST) for his helpful discussion on data analyses.

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