Uniaxially Aligned Poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-bithiophene] Thin Films Characterized by the X-ray Diffraction Pole Figure Technique

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ABSTRACT: Aligned thin films of the liquid-crystalline polymer poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-bithiophene] were prepared, and the correlation between the optical anisotropy and the structural properties was shown. A series of samples with different thicknesses were prepared via a spin-casting process on rubbed polyimide surfaces. The alignment of the polymer chains was obtained by a temperature treatment just below the clearing temperature. The degree of alignment was investigated with ultraviolet–visible absorption spectroscopy and in-plane X-ray diffraction. Independently, each technique revealed Hermans orientation functions in the range of 0.75–0.8. Surprisingly, a layer-thickness dependence was not observed. In addition, the X-ray diffraction pole figure technique revealed that the polymer chains were uniaxially aligned along the rubbing direction. The aligned films were in the nematic state, with the director elongated along the rubbing direction. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1817–1821, 2008

Key words: block copolymers; conjugated polymers; thin films; uniaxial; X-ray

INTRODUCTION

Conjugated polymers with liquid-crystalline behavior are of great interest for optical and electronic applications. The liquid-crystalline polymer poly[(9,9-dioctyl-fluorenyl-2,7-diyl)-*co*-bithiophene] (F8T2) is a promising material for transistor applications as well as optical applications (e.g., solar cells and photodiodes) because it shows high field-effect mobility together with good stability.[1–3] The use of uniaxially treated surfaces such as rubbed polyimide presents an opportunity to introduce alignment to the F8T2 backbones with respect to the rubbing direction.[3,4] This leads directly to anisotropy of the optical and electrical properties of the films.[5,6]

Different approaches are described in the literature to verify the alignment of F8T2 backbones. Polarized ultraviolet–visible (UV–vis) spectroscopy in transmission is performed to quantify the anisotropic absorption behavior.[7] Angular-resolved near-edge X-ray absorption fine structure (NEXAFS) measurements are performed to get additional information about the surface properties of films.[8]

A detailed correlation between the structural properties and optical properties of aligned F8T2 films is still missing. This study reveals the orientation and packing of the F8T2 polymer chains within thin films. This is of great interest for basic optoelectronic research and for its technological applications because the packing of the backbones together with the preferred orientation of the same influences the field-effect mobility and the optical absorption directly.[5,6]

EXPERIMENTAL

Materials

Polyimide was produced from a poly(amic acid) precursor purchased from Merck Chemicals (Vienna, Austria) (Liquicoat PI ZLI-2650). F8T2 was delivered from American Dye Source (Quebec, Canada) (weight-average molecular weight = 19,000 g/mol) and was dissolved in xylene in different concentrations.

TABLE I
Parameters of the Film Preparation and Results for the Aligned F8T2 Thin Films on Rubbed Polyimide

No.	c (wt %)	d (nm)	D	f	State
1	0.5	26	10.2	0.75	Aligned
2	1.0	48	13.4	0.80	Aligned
3	1.5	138	10.6	0.76	Aligned
4	2.0	161	10.0	0.75	Aligned
5a	3.3	453	—	—	As prepared
5b	3.3	453	—	—	Aligned

c = concentration of F8T2 in xylene; d = layer thickness; D = dichroic ratio; f = Hermans orientation function (calculated from optical data and the state of the film); no. = notation of the sample.

Film preparation and precharacterization

The poly(amic acid) precursor was spin-cast from a 3 wt % solution in cyclopentanone. After imidization at a temperature of 573 K, the films were rubbed with a velvet cloth. The layer thicknesses were about 60 nm, as determined by X-ray reflectivity (XRR).

Homogeneous films of F8T2 on rubbed polyimide substrates were achieved via spin casting; the spin speeds and times were first 1500 rpm for 30 s and then 3000 rpm for 5 s. The variations of the layer thickness, determined by XRR, due to different concentrations are listed in Table I.

Phase-transition temperatures were determined with a PerkinElmer (Waltham, MA) DSC-4 differential scanning calorimeter under inert gas conditions with a slope of 10 K/min. In addition, temperature-dependent X-ray diffraction (XRD) measurements were performed. The clearing temperature of F8T2 was determined at 560 K, and additional phase transitions were observed at 370 (glass transition) and 500 K (crystal–mesophase transition). All phase transitions were obtained with increasing temperature.

On the basis of the knowledge of the phase behavior, the alignment procedure of F8T2 films was performed by the annealing of the samples at 553 K. The hold time was 15 min, with subsequent quenching to room temperature.

The aligned films showed clear anisotropic behavior observed by polarized optical microscopy, which gave evidence that the F8T2 chains were aligned. For the quantification of the alignment, the polarized UV–vis absorption intensity was measured in two directions, that is, parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the rubbing direction. Dichroic ratio (D) values were calculated as follows: $D = A_{\parallel}/A_{\perp}$. Values in the range of 10–13 were obtained (cf. Table I), and they are in good agreement with literature data.[6] Because of the high optical density of sample 5, D could not be precisely determined. Additionally, the macroscopic Hermans orientation function (f) values were calculated and gave a quantity for the chain

alignment with respect to a preferential alignment axis, which was in this case the rubbing direction. f is connected to D via $f = \frac{D-1}{D+2}$ (cf. Table I). f values are in the range of 0–1, where 1 is for perfect alignment and 0 is for random orientation.[9]

XRD

Specular X-ray diffraction (sXRD) and X-ray diffraction pole figure (XRD–PF) measurements were performed with a Bruker (Karlsruhe, Germany) D8 Discover diffractometer equipped with an Eulerian cradle. The system was set up in a Bragg–Brentano configuration with Cu radiation and a secondary side graphite monochromator.

sXRD measurements were performed to investigate intermolecular distances with an orientation perpendicular to the surface. The surface normal scattering vector (q_z) values varied from 0.2 to 2.1 Å^{-1}. The corresponding intermolecular distances (d) were calculated via Bragg's equation: $|q| = \frac{2\pi}{d}$.

The XRD–PF technique was applied to map the whole orientation space for a defined intermolecular distance. For the mapping procedure, scattering vector $|\mathbf{q}|$ is fixed (the incident angle and exit angle are equal and fixed) while the sample is rotated around its surface normal (ϕ scan) and stepwise tilted around the rotation axis (ψ). ψ is directed perpendicularly to the ϕ-scan axis and in the coplanar direction of the primary beam. The ϕ scan gives information about the alignment of the intermolecular distances with respect to the rubbing direction. The variation of the ψ value gives information about the orientation with respect to the surface normal, that is, if the polymer confinement stacking with respect to the substrate is perpendicular (normal), parallel (in plane), or somewhere between (out of plane).[10,11]

Data collection for the XRD–PF measurements was performed via ϕ scans from 0 to 360° with stepwise tilting in the ψ direction from 0 to 90° with a step width of 6°. The integration time for each ϕ/ψ pair was 70 s. The data are depicted in polar contour plots with ϕ as the polar angle, ψ as the polar radius, and the intensity as the height. Corrections to the data were not applied. The strong decrease in the intensity at high ψ values is a geometrical effect due to defocusing.[12]

Additional experiments for thinner films (samples 1–4) were performed at beam line G2 of the Cornell High Energy Synchrotron Source. A four-circle goniometer in κ geometry was used in combination with a one-dimensional position-sensitive detector. The detector was mounted coplanar to the primary beam, covering an exit angle of 5°. The detector was set in an integrating mode because only resolution in the ϕ direction was required. The wavelength was 1.32 Å.
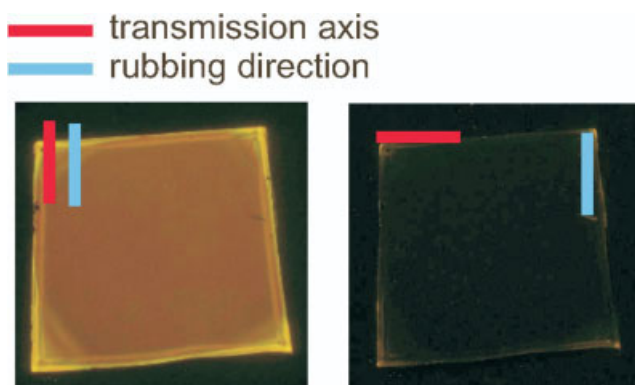
Figure 1 Linearly polarized photographs of the F8T2 film (sample 5b) in the aligned state illuminated with isotropic UV light. The rubbing direction coincides with the transmission axis of the polarizer (left), and the rubbing direction is perpendicular to the transmission axis of the polarizer (right). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

A micrograph from sample 5a in the as-prepared state does not show a significant feature and appears optically isotropic. The aligned film (sample 5b) shows clear optical anisotropy (Fig. 1).

An sXRD pattern of sample 5a (as prepared) is shown in Figure 2 (full squares). The pattern shows two halos with maxima at 0.38 and 1.42 Å^{-1}. The corresponding intermolecular distances are 16.3 and 4.3 Å. Generally, it has been established that 16.3 Å halos are typical for backbone–backbone distances as they have been observed for alkyl-substituted polyfluorenes.[13,14] The second halo belongs to close packing of the polymer backbones without side-chain separation or is due to the arrangement of the side chains.[6,15,16]
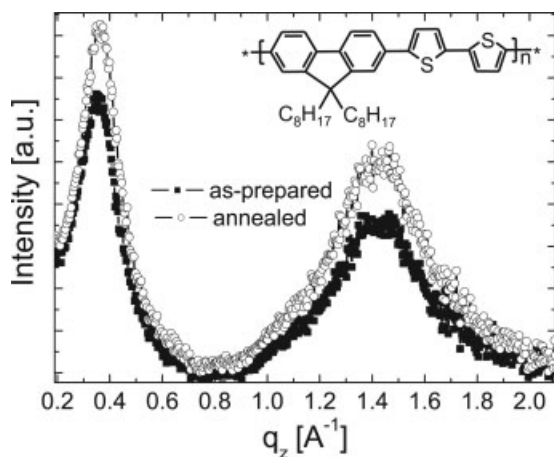

Figure 2 sXRD pattern of (■) the as-prepared film and (○) the aligned film. The inset shows the chemical structure of F8T2.
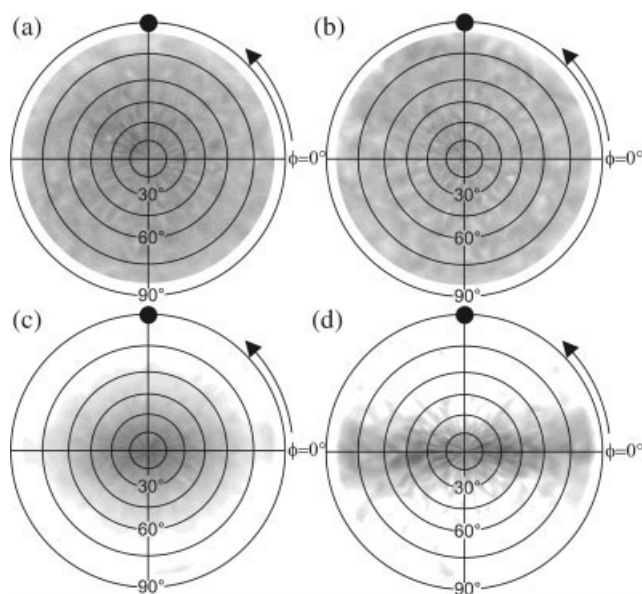

Figure 3 XRD–PFs of (a,b) sample 5a in the as-prepared state and (c,d) sample 5b in the aligned state. The pole figures were taken at (a,c) $|\mathbf{q}| = 0.38 \text{ Å}^{-1}$ and (b,d) $|\mathbf{q}| = 1.42 \text{ Å}^{-1}$. The full dots denote the rubbing direction.

The sXRD pattern for sample 5b (aligned film; Fig. 2, open circles) reveals the same two halos, but they are more pronounced. It is known that spin casting leaves the system in a nonequilibrium state; annealing of the sample brings the film to a more defined state with closer packing, which results in more pronounced halos.[17]

A set of XRD–PFs was measured on as-prepared sample 5a. The $|\mathbf{q}|$ value was varied from 0.2 to 2.1 Å^{-1}. No texture can be observed for the as-prepared film. The pole figures at $|\mathbf{q}| = 0.38 \text{ Å}^{-1}$ and $|\mathbf{q}| = 1.42 \text{ Å}^{-1}$ are depicted in Figure 3(a,b). This gives evidence that the polymer chains in the as-prepared film are randomly distributed within the complete orientation space. There is only a decrease in the intensity at higher ψ values, and this appears due to defocusing of the primary beam.

The same set of pole figures was measured for aligned sample 5b. The results are depicted in Figure 3(c,d). The results are different from those of the as-prepared film. A strong texture can be observed. Streaks at 0 and 180° in the ϕ direction occur. These streaks go from the center of the pole figure up to high ψ values. The set of pole figures shows that the texture is present in two $|\mathbf{q}|$ ranges, that is, from 0.21 to 0.48 Å^{-1} and from 0.95 to 1.9 Å^{-1}. These are the same ranges that belong to the two halos in the specular scan.

The rubbing direction given in all pole figures is at $\phi = \psi = 90°$. It follows that intermolecular distances belonging to the observed streaks are elongated perpendicularly to the rubbing direction.
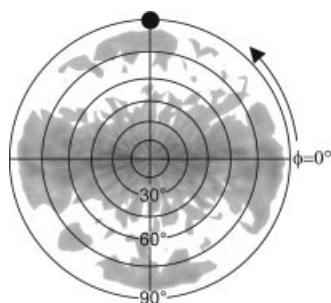
Figure 4 XRD–PF of film sample 5 at $|\mathbf{q}| = 1.25$ Å^{-1}.

Combining the UV–vis results with XRD reveals that the absorption in polarized UV–vis measurements is maximal along the rubbing direction. It is well established that the absorption of molecules is preferential along the long polymer axis.[18] The anisotropy of the absorption and the pole figures reveal that the polymer backbones are aligned along the rubbing direction and that the intermolecular distances with maxima at $|\mathbf{q}| = 0.38$ Å^{-1} and $|\mathbf{q}| = 1.42$ Å^{-1} are perpendicular to the polymer chains.

The ψ spreading of the streaks from the normal direction to the in-plane direction shows that there is not a preferred order with respect to the surface normal for the two halos observed in the specular scan. The polymer chains or blocks within the chain are randomly rotated along the chain axis.

The streaks at $|\mathbf{q}| = 0.38$ Å^{-1} are less pronounced; in addition, the streaks become narrower at higher ψ values. For quantification, the Hermans orientation function for several azimuthal scans (f_ϕ) was calculated[19]:

$$f_\phi = \frac{1}{2}\left(3\langle\cos^2\phi\rangle - 1\right)$$

with

$$\langle\cos^2\phi\rangle = \frac{\int\limits_0^{2\pi} I(\phi)\cdot\cos^2\phi\cdot d\phi}{\int\limits_0^{2\pi} I(\phi)\cdot d\phi}$$

where $I(\phi)$ is the intensity of angle ϕ.

The obtained f_ϕ values are similar for $|\mathbf{q}| = 0.38$ Å^{-1} and $|\mathbf{q}| = 1.42$ Å^{-1}. The f_ϕ values obtained for $|\mathbf{q}| = 0.38$ Å^{-1} range from 0.25 at small ψ values to 0.68 at higher ψ values. The results for $|\mathbf{q}| = 1.42$ Å^{-1} show that $f_\phi = 0.36$ at $\psi = 12°$. A continuous increase in f_ϕ with increasing ψ values can be observed up to 0.71 at $\psi = 85°$. The f_ϕ values show that the directional order is more defined in the in-plane direction.

In addition, distinct enhanced pole densities occur in the pole figures measured at $|\mathbf{q}| = 1.25$ Å^{-1} (Fig. 4). The corresponding intermolecular distance is

5 Å. The poles are located at 90 and 270° in ϕ and range from 75 to 90° in ψ. This is close to the in-plane direction, representing a defined in-plane order along the rubbing direction, and is along the polymer backbone.

Because a fully solved crystal structure is still missing for poly(9,9′-n-dioctylfluorence) (F8) and F8T2, only a qualitative explanation can be given for this diffraction feature. From this study on F8T2 and from a grazing incident diffraction experiment on F8, it is known that the polymer chains are elongated parallel to the surface.[13] Therefore, it can be concluded that the 5 Å poles occur from interfering atoms along the backbone because 5 Å is a frequent distance along the fluorene–thiophene subunits.

The observed intermolecular distances and their location in the orientation space reveal that the film can be classified as uniaxially aligned.[19] Furthermore, because the intermolecular distances are weakly defined and the micrographs of the aligned film show clear anisotropy, it is deduced that the aligned film is in a thermotropic nematic state stabilized by quenching. The director of the nematic state coincides with the rubbing direction.

On the basis of the experimental results, the packing of the polymer chains can be suggested. A rough scheme is depicted in Figure 5. Because the features are very broad within the sXRD pattern and within the pole figures, several confinements are concluded. On the one hand, backbones are separated by side chains. Because the side chains are flexible, they are able to align along the backbone or can be fully stretched. On the other hand, a close packing of the backbones without side-chain separation is possible as well. Adjacent units along a backbone or two adjacent backbones are twisted and shifted to each other to fill the whole space. In addition, a zigzag confinement of the backbone units is possible that
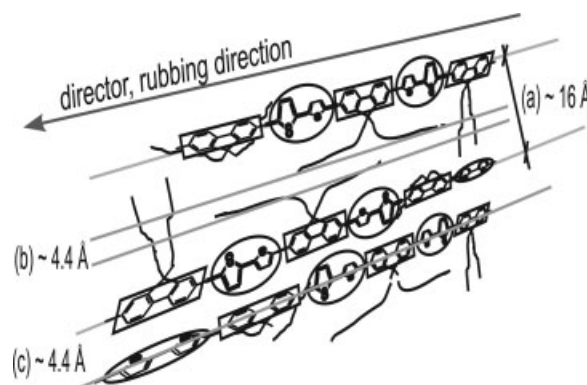

Figure 5 Rough scheme of the polymer chain alignment of F8T2 thin films within the nematic state. Characteristic distances are backbone–backbone packing separated by (a) alkyl chains, (b) side-chain arrangement, and (c) backbone–backbone packing without side-chain separation. The polymer chains are aligned along the rubbing direction.
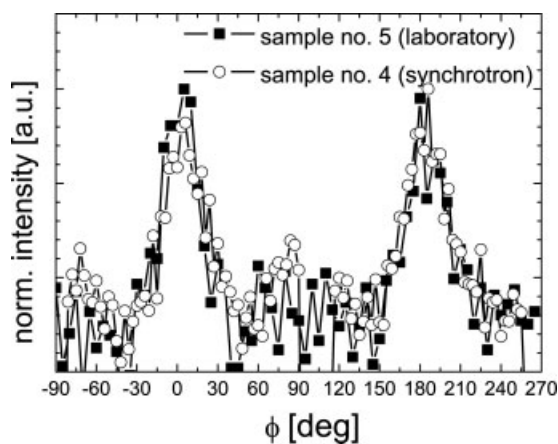
Figure 6 Two ϕ scans at $\psi = 85°$ and $|\mathbf{q}| = 1.46$ Å^{-1} for (■) sample 5b measured with a laboratory system and (○) sample 4 measured with synchrotron radiation.

introduces a smearing of the intermolecular distance perpendicular to the polymer chains too.

XRD–PF on aligned films of thinner samples (samples 1–4) shows the same texture in comparison with sample 5, but the peak-to-noise ratios are much worse. Therefore, synchrotron radiation was required to perform ϕ scans. The scan for $\psi = 85°$ is given in Figure 6 (open dots). The scan shows two clear peaks located around $\phi = 0°$ and $\phi = 180°$. For comparison, the data of a single ϕ scan taken at $\psi = 85°$ from the pole figure of Figure 3(d) are plotted. The full widths at half-maximum of both scans are in excellent agreement and are about 30°.

The calculated f_ϕ values for samples 4 and 5 are 0.74 and 0.71, respectively. This is in good agreement with the Hermans orientation functions calculated from the UV–vis measurements (cf. Table I). This is an indication of good reproducibility of the optical data together with the structural properties and is independent of layer-thickness variations.

It is remarkable that this work shows that the achieved information about alignment with respect to the rubbing direction is the same for UV–vis measurements and XRD ϕ scans close to the in-plane direction. This shows that the main contribution of the streaks comes from the backbone–backbone packing. The results show that the alignment is better pronounced parallel to the surface. This has not been shown before because specular scans together with UV–vis spectra do not give enough information on the out-of plane and in-plane orientations of the film and NEXAFS studies are only surface-sensitive.

CONCLUSIONS

Aligned films of F8T2 on rubbed polyimide surfaces have been prepared. D values measured by polarized absorption spectroscopy are in the range of 10–13,

showing good reproducibility of the processing. Variation of the degree of alignment due to different layer thicknesses ranging from 26 to 453 nm has not been observed.

With the XRD–PF technique, two perpendicular intermolecular distances (16.3 and 4.3 Å) and one parallel intramolecular distance (5 Å) with respect to the rubbing direction have been identified. Combining the results from sXRD, XRD–PF technique, and UV–vis measurements has lead to the conclusion that the backbones are aligned parallel to the rubbing direction. Hermans order parameters from XRD–PF measurements show small variations for different films. The in-plane order is in excellent agreement with UV–vis absorption measurements. Furthermore, uniaxial alignment has been deduced that is typical for films in a nematic state. The director of the nematic state is directed along the rubbing direction. The building blocks of the backbones are randomly oriented along the polymer chain. Two confinements of the side-chain arrangement are suggested, namely, bent and fully stretched.

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