

Side-Chain Effects on Friction-Transferred Polymer Orientation

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ABSTRACT: Effects of substituted side-chains of poly(2,5-dialkoxy-1,4-phenylenevinylene) derivatives (PPV) on polymer orientation have been studied using polarized optical spectroscopy and synchrotron-sourced grazing incidence X-ray diffraction (GIXD) analysis. The results of polarized optical spectroscopy indicate that the symmetrically substituted PPV is suitable for homogeneous oriented film preparation by friction-transfer technique. The formed film of poly(2,5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (BEHPPV) exhibited large light emission dichroism of up to 42.0. The results of synchrotron-sourced GIXD for BEHPPV film indicated that the BEHPPV molecules crystallized in not a different manner from that of other PPV. [doi:10.1295/polymj.PJ2007062]

KEY WORDS Polymer Alignment / Friction-Transfer / Poly(1,4-phenylenevinylene) / Polarized Spectroscopy / Grazing Incidence X-ray Diffraction Analysis / Synchrotron Radiation /

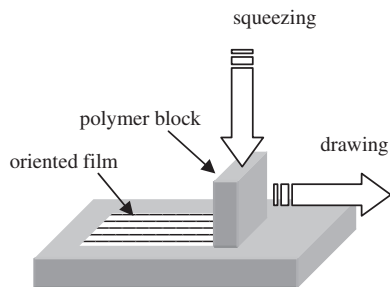
Conjugated polymers are extensively studied for organic light-emitting diodes (OLED), organic thin film transistors (OTFT) and organic photovoltaic cells (OPVC), due to their excellent optoelectronic properties, chemical stability and ease of processability.^{1–3} Since the intrinsic characteristics of conjugated polymers originate from the π -electrons delocalized along polymer backbone, conjugated polymers are expected to exhibit anisotropic properties such as polarized luminescence. Therefore, the alignment of polymer backbones can affect their physical properties in films. However, polymer films prepared without using a polymer backbone alignment technique exhibit isotropic properties.^{1–3} Various methods have been applied to align polymers, such as the stretching method, the mechanical rubbing method, Langmuir-Blodgett method and the utilization liquid-crystallinity of polymers.^{4–17}

One of the simple methods to align the polymer backbone is the friction-transfer technique proposed by Wittmann and Smith in 1991.¹⁸ When the solid block of polymer, such as poly(tetrafluoroethylene) (PTFE), is squeezed and drawn against a clean surface of metal or glass substrate, a very thin film of the polymer remains at the substrate surface. (see Scheme 1) The polymer backbones in the formed film were found to be highly aligned along the drawing direction of the friction-transfer by transmission electron microscopy (TEM) and X-ray diffraction (XRD)

analysis. The friction-transfer technique is useful for the preparation of thin films of insoluble solid-state polymers and for the polymer backbone alignment. By the friction-transfer, polymers were aligned without using any secondary processing such as the mechanical rubbing or the thermal treatment for the liquid-crystals. We have applied this method to both of insoluble and soluble π -conjugated semiconducting polymers, such as poly(*p*-phenylene) (PPP), poly(*p*-phenylenevinylene) (PPV), polythiophene (PT), polyfluorene (PF) and their derivatives.^{19–30} Recently, we have succeeded in preparation of single-crystal-like films of poly(9,9-dioctylfluorene) (PF8) by the friction-transfer, and found that the friction-transferred polymer films were very satisfactory to analysis of crystal structure of polymer because that polymer molecules were arranged three-dimensionally.^{22,24–26}

However, some kinds of conjugated polymers did not form to the uniform film by the friction-transfer. Here, we present the substituted side-chain structure effects on the π -conjugated polymer oriented film preparation using the friction-transfer. We have selected the 2,5-alkoxy-substituted poly(1,4-phenylenevinylene) (PPV) as a model π -conjugated polymer, because the PPV are most popular light emissive conjugated polymer and a large number of their derivatives, such as poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEHPPV) for OLED and poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenyl-

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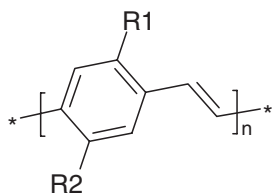


Scheme 1. Schematic image of the friction-transfer technique.

enevinylene) (MDMOPPV) for OPVC, are commercially available. We obtained the results that the friction-transferred film qualities strongly depend on the side-chain structure and substitution. The asymmetrically substituted PPV such as MEHPPV and MDMOPPV do not form a film by the friction-transfer. The symmetrically substituted PPV, on the other hand, form a homogeneous oriented thin film by the friction-transfer. In addition, the side-chain structure, normal or branched, strongly affects the polymer backbone alignments in the friction-transferred film.

EXPERIMENTAL

Poly(2,5-dioctyloxy-1,4-phenylenevinylene) (DOPPV), poly(2,5-bis(3,7-dimethyloctyloxy)-1,4-phenylenevinylene) (BDMOPPV), MDMOPPV and MEHPPV were purchased from Aldrich Chem. Co. and used without further purification. Poly(2-methoxy-5-octyloxy-1,4-phenylenevinylene) (MOPPV) and poly(2,5-bis(2-ethylhexyloxy)-1,4-phenylenevinylene) (BEHPPV) were synthesized in our laboratory according to the literature³¹ (see Scheme 2). The PPV films were prepared on quartz glass and silicon substrates by the friction-transfer. For friction-transfer process, each of the PPV powders was compressed into pellets with an applied load of 1250 kilogram-force (kgf)/cm² under vacuum. The condition of friction-transfer process was carried out by squeezing and drawing a PPV pellet with a contact area of 0.1 cm²



| | |
|---------|--|
| DOPPV | :R ₁ =R ₂ =octyloxy |
| BDMOPPV | :R ₁ =R ₂ =3,7-dimethyloctyloxy |
| BEHPPV | :R ₁ =R ₂ =2-ethylhexyloxy |
| MOPPV | :R ₁ =methoxy, R ₂ =octyloxy |
| MDMOPPV | :R ₁ =methoxy, R ₂ =3,7-dimethyloctyloxy |
| MEHPPV | :R ₁ =methoxy, R ₂ =2-ethylhexyloxy |

Scheme 2. Molecular structure of PPV derivatives.

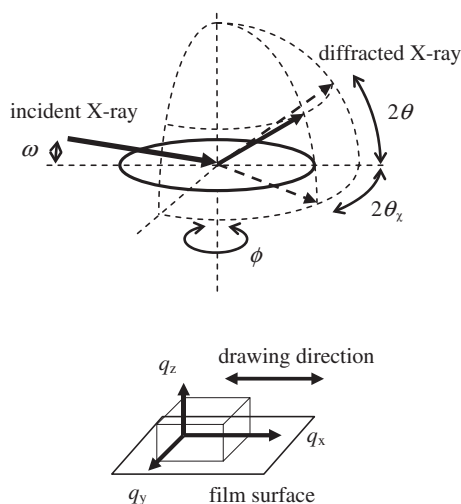
on the heated substrate at a temperature between 80 and 100 °C, and the applied load for squeezing was 30 kgf/cm², and the drawing speed was 1 m/min.

The films friction-transferred on quartz glass substrates were investigated by polarized ultraviolet-visible (UV-vis) absorption spectroscopy (Shimadzu MPS2000) and polarized photoluminescence (PL) spectroscopy (JASCO FP777) with a Glan-Thompson polarized prism. The dichroic ratio of absorption is defined as $D_{\text{abs}} = A_{\parallel}/A_{\perp}$, where A_{\parallel} and A_{\perp} are the absorption intensities for the lights polarized parallel and orthogonal to the drawing direction of friction-transfer, respectively. The dichroic ratio describes the anisotropy of the absorption process. The transition probability is maximized when the transition moment of the molecule lies parallel to the electric vector of the light. Also, dichroic ratio of photoluminescence intensities is defined as $D_{\text{PL}} = I_{\parallel}/I_{\perp}$, where I_{\parallel} and I_{\perp} are the emission intensities for the lights emitting polarized parallel and orthogonal to the drawing direction of friction-transfer, respectively. The excitation light is non-polarized and is fixed at a wavelength of $\lambda_{\text{ex}} = 480$ nm.

The both of the out-of-plane and the in-plane structure of the films friction-transferred on silicon wafers were studied by the synchrotron-sourced grazing incidence X-ray diffraction (GIXD).^{25,32–38} In general, scattering from a polymer thin film is relatively weak in intensity. Therefore, utilizing the high brilliance and highly parallel synchrotron X-rays as the incident beams is effective in detecting from polymer thin film, and the GIXD method is a powerful tool for evaluating nano-scale structures of polymer ultra-thin film because of the long lateral correlation length according to the total reflection by the grazing incidence.

As shown in Scheme 3, the film was examined in three principal directions of scattering vector, which is defined as the difference between the incident and scattered X-ray wave vector, chosen to relate with the drawing direction of friction-transfer. From these three settings, one can obtain a partial crystal structure of PPV.⁸

The synchrotron-sourced GIXD measurements were performed at a BL13XU beamline of SPring-8 (Japan Synchrotron Radiation Research Institute (JASRI), Hyogo, Japan) equipped with ATX-GSOR, one of the ATX series of Rigaku Co.^{25,38} The wavelength, λ , of monochromatized incident X-ray used in this study was 0.128 nm. The beam was focused on the sample, and the resulting beam size in the experimental hutch was 0.1 × 0.1 mm square. The grazing angle of the incidence, ω , in this study is fixed at 0.14°, which is the critical angle for total reflection against the silicon substrate. A soller slit with an acceptance angle of 0.41° was placed before the detec-



Scheme 3. Geometry of the GIXD measurements and definition of the scattering vectors, q_x , q_y and q_z , with respect to the drawing direction of friction-transfer.

tor. The out-of-plane X-ray scattering vector q_z and the in-plane X-ray scattering vector q_{xy} are positioned normal and parallel to the film surface, respectively. The components of the in-plane and out-of-plane X-ray scattering vectors were defined as $q_{xy} = (4\pi/\lambda) \sin \theta_\chi$ and $q_z = (2\pi/\lambda)(\sin(\omega) + \sin(2\theta))$, respectively. The angle, χ , between the in-plane scattering vector and the drawing direction of friction-transfer was fixed during the in-plane ϕ - $2\theta_\chi$ scan. We defined the χ related scattering vectors, q_x and q_y , for fixed- χ -angles of 0° and 90° , respectively.

For both of the out-of-plane 2θ scan and the in-plane ϕ - $2\theta_\chi$ scan, the scanning speed was $2^\circ/\text{min}$, and the angular interval between steps was 0.02° . The molecular orientation distribution is determined by the rocking-curve scan. Changes in scattered intensity at a locked q correspond to the distribution of orientation of the diffracted lattice plane. For rocking-curve scan, the scanning speed was $10^\circ/\text{min}$, and the angular interval between steps was 0.1° . The sample was placed into a special holder covered with a Kapton hemisphere dome of 200 mm in diameter and purged with helium gas during the all GIXD measurement. Background intensity was reduced by replacing the air inside by helium gas. The helium gas purged Kapton-dome also plays a role to prevent thin films from oxidation.

RESULTS AND DISCUSSIONS

Since the transition moment of the lowest singlet exciton associated with the π - π^* band gap is almost parallel to the backbone in π -conjugated polymers, one can use polarized light to probe the structural anisotropy in the films. The typical polarized absorption

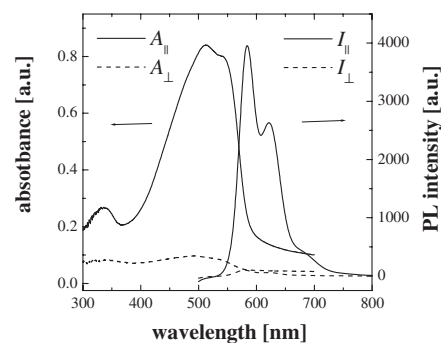


Figure 1. Polarized absorption and PL spectra of friction-transferred BEHPPV.

and PL spectra of the friction-transferred PPV derivative are shown in Figure 1 as the case of BEHPPV. Both of the optical spectra show different profiles much depending on the type of polarization. A significantly large absorption ascribed to the transition was observed for the incident light polarized parallel to the drawing direction. A dichroic ratio of absorption, D_{abs} , at a maximum of parallel polarization of 512 nm was estimated to be 9.1. This implies that the PPV backbones were aligned parallel to the drawing direction. Also, the PL spectra show large anisotropy, the light emission with parallel polarization being much larger than that of the orthogonal polarization. A dichroic ratio of PL, D_{PL} , at a maximum of parallel light emission of 584 nm was estimated to be 42.0. The higher dichroism in PL than that in absorption might be consistent with the migration of excitons to the most highly oriented segments of the polymer before emission. These large dichroic ratios, D_{abs} and D_{PL} , imply that the PPV backbones in friction-transferred film were highly aligned along the parallel to the drawing direction of friction-transfer.

All of the results of the polarized optical properties of friction-transferred PPV derivatives found in this study are listed in Table I. These results show interesting difference between the symmetrically ($R_1 = R_2$) and asymmetrically ($R_1 \neq R_2$) substituted PPV. The friction-transferred symmetric PPV derivatives showed large anisotropic optical properties, and satisfy the homogeneous oriented film quality. The symmetric PPV derivatives formed quite uniform thin films by the friction-transfer. On the other hand, the friction-transferred asymmetric PPV derivatives showed weak optical intensities and low dichroism, and dissatisfy the film formation. The asymmetric PPV derivatives did not form the films by the friction-transfer. A large number of grooves, which are the uncovered area, existed in the friction-transferred asymmetric PPV derivatives. The quality of the formed film by the friction-transfer method strongly depended on the kinds of the side-chain substitution.

Table I. Summary of the optical dichroism of friction-transferred PPV derivatives

| | Compounds | A_{\parallel} maximum [a.u.] | D_{abs} | I_{\parallel} maximum [a.u.] | D_{PL} | quality |
|---------------------------------|-----------|-----------------------------------|------------------|-----------------------------------|-----------------|--------------|
| symmetry ($R_1 = R_2$) | DOPPV | 0.46 | 8.2 | 2500 | 19.9 | uniform film |
| | BDMOPPV | 2.05 | 3.7 | 4500 | 13.2 | uniform film |
| | BEHPPV | 0.84 | 9.1 | 4000 | 42.0 | uniform film |
| asymmetry ($R_1 \neq R_2$) | MOPPV | 0.13 | 1.9 | 320 | 2.5 | — |
| | MDMOPPV | 0.28 | 2.6 | 550 | 5.0 | — |
| | MEHPPV | 0.08 | 1.8 | 290 | 4.7 | — |

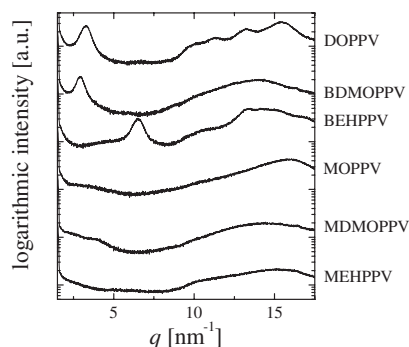
**Figure 2.** Powder diffraction profiles of PPV derivatives.

Figure 2 shows the powder diffraction profiles from the each of PPV pellets investigated by XRD analysis which was carried out on a Rigaku RU-300 using θ - 2θ scan method with focused Cu $K\alpha$ radiation. In the XRD results of the symmetric PPV (upper three profiles), several peaks were observed. On the other hand, in XRD results of the asymmetric PPV (lower three profiles), no peaks were observed. These results indicate that the PPV crystallinity strongly depends on the kinds of the side-chain substitution. The symmetric PPV, which formed the homogeneous oriented film by the friction-transfer, are highly crystallized, while the asymmetric PPV, which did not form the thin film, are almost amorphous. We consider that the symmetric PPV molecules are easily extracted from pellet by their well-ordered structure, and that the asymmetric PPV molecules are hardly extracted from pellet by their disordered structure and possibly the polymers tangle.

The asymmetric PPV derivatives show higher solubility in common organic solvents than the symmetric PPV derivatives because of the loose molecular packing from the asymmetric side-chain substitution. One can consider that the extraction from the solid state of the asymmetric PPV derivatives is easier than that of the symmetric PPV derivatives. However our results and consideration of the case of the friction-transfer are opposite to the case of the dissolution. Note that the distinctiveness of the friction-transfer method is the solid-to-solid-formation, which is ordering process, while the dissolution into the solvent is the solid-

to-liquid-formation, which is disordering process. The latter is not the present case. We conceive that the order-to-order transition, which is the case of the symmetric PPV derivatives, was organized easier than the disorder-to-order transition, which is the case of asymmetric PPV derivatives, because of the large entropy of the disorder-to-order transition. We believe that the crystallinity of polymer is an important factor for providing the homogeneous oriented film by the friction-transfer process.

In the results of polarized optical properties in symmetric PPV, note that the dichroism of BEHPPV is much higher than that of the other two symmetric PPV, DOPPV and BDMOPPV. From our previous experiment (including the case of BDMOPPV), the homogeneous highly oriented films by friction-transfer can not be obtained from the branched side-chain substituted conjugated polymers. However, the homogeneous highly oriented film was obtained from the BEHPPV although a branched side-chain is substituted. Note that the first intense peaks corresponding to the side-chain length, $d = 1.89$ nm for DOPPV and $d = 2.18$ nm for BDMOPPV show the d -spacing value increase, which might be arise from the substitution of the branched side-chain. On the other hand, BEHPPV shows the d -spacing value decrease compared with that of poly(2,5-hexyloxy-1,4-phenylenevinylene) (DHPPV), $d = 0.98$ nm for BEHPPV and $d = 1.53$ nm for DHPPV (data is not shown). This finding suggests that BEHPPV might be crystallized in a different manner from that of other PPV derivatives, monoclinic system.^{6-12,25}

Shown in Figure 3 are synchrotron-sourced GIXD profiles of friction-transferred BEHPPV film obtained by directing the scattering vector along three principal directions. In the case of DOPPV, each diffraction profile of such three directions, q_x , q_y and q_z , was observed having an obvious difference; the diffraction profile of the q_x , q_y and q_z directions shows only a series of periodic peaks corresponding to the $(00l)$, $(h00)$ and $(0k0)$ reflections, respectively.²⁵ In the present case, however, we found that the GIXD profiles of the q_z and q_y directions show almost equivalent diffractions, which might be corresponding to the $(hk0)$

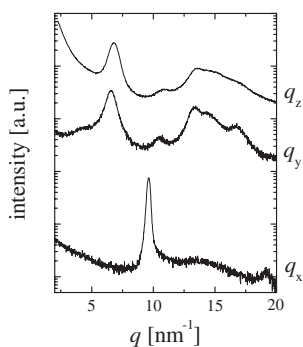


Figure 3. GIXD profiles of friction-transferred BEHPPV.

reflections. This finding possibly suggests that the BEHPPV assembled in a different manner from that of the other PPV derivatives. Two-dimensional (2D) GIXD study is currently under way to investigate the further crystal structure information of the friction-transferred PPV derivatives. The diffraction profile of the q_x direction shows a series of periodic peaks at $q_x = 9.65$ and 19.17 nm^{-1} corresponding to the $(00l)$ reflections and no other diffraction. The d -spacing value of 0.65 nm was estimated in this (001) diffraction by Bragg's equation. This value of the monomeric repeat is comparable to the values in previous reports.^{6–12,25}

The in-plane GIXD profiles with identical in-plane geometry strongly depended on the directions of scattering vector, q_x and q_y . Changes in scattered intensity at a locked q correspond to the distribution of the orientation of the diffracted lattice plane. Figure 4 shows the rocking curves of the first intense peaks of the friction-transferred BEHPPV film at the $q_y = 6.56 \text{ nm}^{-1}$ and $q_x = 9.65 \text{ nm}^{-1}$, respectively. The intensities for both reflections clearly decreased to the background level in $\pm 10^\circ$. The full width at half maximum by the Gaussian distribution were estimated to be about 9° for both reflections. Compared with the distribution values for other friction-transferred PPV, 13° – 20° , that of BEHPPV appear to be small. This finding shows that the BEHPPV backbones are highly aligned

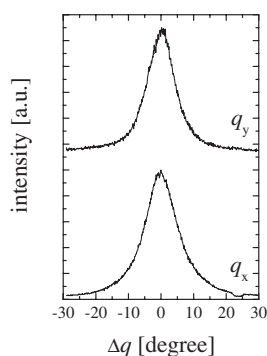


Figure 4. Rocking curves for the first intense peaks of friction-transferred BEHPPV.

along the drawing direction. Note that the distributions of (001) diffractions of BEHPPV and DOPPV show obvious difference. The distribution of (001) diffraction for BEHPPV exhibited single Gaussian distribution although that of DOPPV shows a set of two Gaussian distributions arising from the monoclinic system.²⁵ This suggests again that the BEHPPV crystallized in a different manner from that of other PPV derivatives, the monoclinic system.

SUMMARY

We have studied the effects of side groups on the friction-transfer PPV derivatives films investigated by polarized optical spectroscopy and synchrotron-sourced GIXD. The symmetric PPV derivatives, DOPPV, BDMOPPV and BEHPPV, formed homogeneous oriented films by this technique. On the other hand, the asymmetric PPV derivatives, MOPPV, BDMOPPV and MEHPPV, did not form the films. The polymer crystallinity is an important factor for providing the homogeneous oriented film using the friction-transfer process. The BEHPPV gave the best quality oriented film. The synchrotron-sourced GIXD results of BEHPPV exhibited absolute difference from that of DOPPV. The substituted side-chain structures, normal and branched chain, affect not the friction-transfer process but the crystal system of polymer. We suppose that the BEHPPV molecules crystallized in the suitable crystal system for the friction-transfer technique. Further structural studies by the synchrotron-sourced GIXD and 2D-GIXD experiments are being planned to reveal the crystal systems of the friction-transferred polymer thin films.

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