

## Highly Uniaxial Orientation in Oligo(*p*-phenylenevinylene) Films Induced During Wet-Coating Process

Takeshi Nishizawa,<sup>†</sup> Hady Kesuma Lim,<sup>†</sup> Keisuke Tajima,<sup>\*,†</sup> and Kazuhito Hashimoto<sup>\*,†,‡</sup>

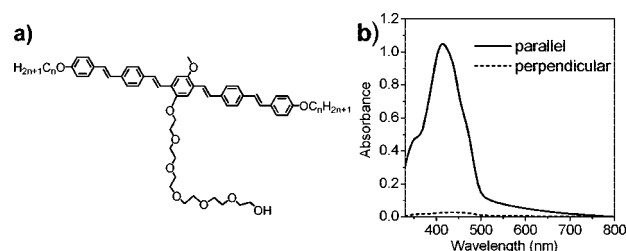
Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, and HASHIMOTO Light Energy Conversion Project, Exploratory Research for Advanced Technology (ERATO), Japan Science Technology Agency (JST)

Received December 29, 2008; E-mail: k-tajima@light.t.u-tokyo.ac.jp; hashimoto@light.t.u-tokyo.ac.jp

The molecular orientation of  $\pi$ -conjugated polymers and oligomers in thin solid films is of great importance for achieving high performance in organic electronic devices such as field effect transistors,<sup>1</sup> light emitting diodes,<sup>2</sup> and photovoltaic devices,<sup>3</sup> given that the molecular shapes and the electronic properties of the organic materials are highly anisotropic. Various techniques have been used to align molecules in films including rubbing,<sup>4</sup> zone-casting,<sup>5</sup> friction transfer,<sup>6</sup> solution shearing,<sup>7</sup> and irradiation with polarized light.<sup>8</sup> Among them, a rubbing method is one of the most widely used techniques for achieving uniaxial alignment of molecules. In this method, polymer thin films such as polyimides are mechanically rubbed and used as alignment layers. The molecules in contact with the alignment layers interact with the surface to orient their easy axes along the rubbing direction, and the alignment is transferred throughout the films. In conventional rubbing method, however, the driving force to transfer the alignment induced at the interface is self-organization of thermotropic liquid crystals (LCs)<sup>9</sup> or the van der Waals interactions of the crystalline molecules during vacuum evaporations.<sup>10</sup> Thus, induction of the LC phase transition by thermal annealing or compatibility with a dry deposition technique is a prerequisite for this alignment method, which could limit molecular designs and device applications. If weak intermolecular interactions in solution such as  $\pi$ - $\pi$  or polar/nonpolar interactions can be utilized in dynamic situations such as a spin-coating process to transfer the molecular orientation induced at the interface, it would be a useful approach for controlling the alignment of molecules in thin solid films. Moreover, such spontaneous alignment of molecules without any special treatment such as induction of thermotropic LC phases would be easily applicable to the organic optoelectronic devices.

In this study, we report the synthesis of novel oligo(*p*-phenylenevinylene)s (OPVs) and their highly uniaxial alignment in the as-cast films spin-coated from solution onto rubbed polymer alignment layers such as poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonic acid) (PEDOT:PSS) film. The chemical structures of the OPVs are shown in Figure 1a. By changing the alkyl side chain lengths, the  $\pi$ - $\pi$  interactions between the oligo(*p*-phenylenevinylene) groups and the polar/nonpolar interactions of the molecules are tuned to realize the alignment of the molecules during the spin-coating process. The anisotropic structures of the OPVs in the thin films were investigated by measuring polarized absorption spectra and in-plane X-ray diffractions (XRD). Application to an electronic device was also demonstrated.

OPVs **1**–**3** were synthesized by following the procedures in Supporting Information (SI). The thin films of OPVs were prepared by spin-coating the chloroform solutions on a rubbed PEDOT:PSS



**Figure 1.** (a) Molecular structures of oligo(*p*-phenylenevinylene)s, **1** ( $n = 6$ ), **2** ( $n = 12$ ), and **3** ( $n = 1$ ). (b) Absorption spectra of the as-cast film of **1** ( $n = 6$ ) on a rubbed PEDOT:PSS layer with polarized incident light parallel (solid line) or perpendicular (dashed line) to the rubbing direction.

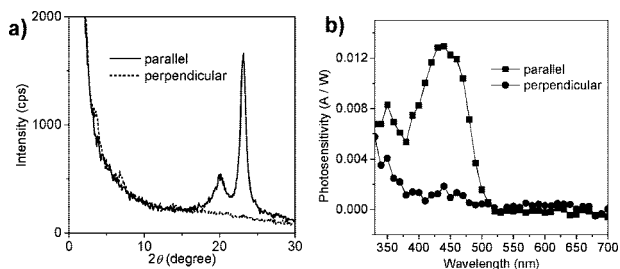
layer (alignment layer) (see SI). The film thicknesses as measured by a profilometer (Dektak 6M, ULVAC) were about 96, 75, and 60 nm for **1**, **2**, and **3**, respectively. Note that the films were completely dried after the spin-coating and no thermal treatment or induction of any LC phases was conducted on the OPV films.

Figure 1b shows the absorption spectra of the as-cast film of **1** on a rubbed PEDOT:PSS film with the incident light linearly polarized parallel or perpendicular to the rubbing direction. Strong absorption was observed when the light was parallel, while much weaker absorption was observed when it was perpendicular, resulting in a high dichroic ratio ( $A_{\parallel}/A_{\perp}$ ) of 41.0 at the maximum absorption of 414 nm. The order parameter defined by  $S = (A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp})$  was calculated as 0.93, which is among the highest values reported for uniaxially aligned films with conventional conjugated LC molecules.<sup>11</sup> We confirmed that there was no anisotropic absorption without the rubbing procedure on the PEDOT:PSS films. These results indicate that **1** is highly uniaxially aligned with the long axis of the molecule parallel to the rubbing direction. Considering the fact that the sample is simply an as-cast film spin-coated from a dilute solution, this highly anisotropic absorption or alignment of the molecules throughout the film with the thickness of approximately 100 nm is quite surprising.

To further investigate the uniaxial alignment of the molecules, in-plane XRD measurement of the film was conducted. Figure 2a shows the XRD patterns of the as-cast film of **1** with the incident X-ray beam parallel or perpendicular to the rubbing direction. When the incident X-ray beam was parallel, two peaks were observed at  $2\theta$  of 19.8° and 23.4° ( $d$ -spacings of 4.5 and 3.8 Å, respectively), which could be assigned to the  $\pi$ - $\pi$  stacking of the oligo(*p*-phenylenevinylene) groups.<sup>12</sup> In contrast, when the incident X-ray beam was perpendicular to the rubbing direction, no diffraction peak was observed in this region. These results indicate that the long axis of the molecules is uniaxially aligned parallel to the rubbing direction, which coincides with the results observed in the polarized absorption spectra. The presence of the diffraction peak from the  $\pi$ - $\pi$  stacking

<sup>†</sup> The University of Tokyo.

<sup>‡</sup> Japan Science Technology Agency.



**Figure 2.** (a) In-plane XRD patterns of the as-cast film of **1** ( $n = 6$ ) on a rubbed PEDOT:PSS layer with polarized incident light parallel (solid line) or perpendicular (dashed line) to the rubbing direction. (b) Photosensitivity of photovoltaic device with **1** ( $n = 6$ ) under the irradiation of monochromatic polarized light parallel (squares) or perpendicular (circles) to the rubbing direction.

distance in the in-plane XRD measurement also indicates that the orientation of the conjugated plane of **1** is not parallel to the substrate (face-on) but is perpendicular to the substrate (edge-on) or tilted.

The dispersion of the alignment axes was also evaluated by rotating the substrate horizontally and monitoring the diffraction intensities at  $23.4^\circ$ . The rotation angle was set as  $0^\circ$  when the incident light was perpendicular to the rubbing direction. As a result (see SI), two diffraction peaks were observed at approximately  $90^\circ$  and  $270^\circ$ . The half-width-half-maximum value of the peak was estimated to be around  $7^\circ$ , which indicates a narrow distribution of the alignment axis in the film.

The mechanism of the high molecular alignment during the spin-coating is not clear at this point. When the concentration of OPV increases in the solution during the solvent evaporation in the coating process, OPVs might start to crystallize from the surface and the orientation could be transferred to the whole organic film as the film is dried.<sup>13</sup> We can expect that the interfacial interactions between OPV in solution and the alignment layer first induce the orientation and that the intermolecular interactions between OPV molecules then induce the alignment throughout the film. Thus, these two interactions during the spin-coating process are of high importance for achieving such high alignment of the molecules in the films.

To investigate this notion, OPVs with different alkyl chain lengths (**2** and **3** in Figure 1) were compared. The thin films of the two also showed anisotropic absorptions with dichroic ratios of 18.8 ( $S = 0.86$ ) at 415 nm for **2** and 3.76 ( $S = 0.48$ ) at 442 nm for **3** (see SI). These values are lower than those of **1**, indicating that the molecular alignment is less ordered in the films of **2** and **3**. This might be attributed to differences in the crystallization behavior in solution during the spin-coating process. The longer alkyl chains of OPV **2** could provide better solubility than **1** and therefore the crystallization of **2** could occur at a higher concentration in the liquid films. This might make the crystallization faster and thus lower the order of the packing of **2** in the films. In the case of OPV **3**, lower solubility and stronger intermolecular interactions could cause crystallization in solution with little influence from the interface at the alignment layer during the spin-coating, which hinders the transfer of the alignment from the substrate and thus lowers the order.

To investigate the effect of the alignment layer on the molecular orientation, OPV **1** film was also prepared on other alignment layers in the same manner. Interestingly, uniaxial alignment was also observed in the as-cast films of **1** on the rubbed surfaces of

polyimide and poly(vinyl alcohol) with dichroic ratios of 21.7 ( $S = 0.87$ ) and 40.5 ( $S = 0.93$ ), respectively. The difference in the order parameters between the materials might suggest different interaction strengths between the surfaces and the OPVs, possibly due to polar interaction with the hexa(ethylene glycol) chains. Further investigation is necessary to elucidate the mechanism of the alignment.

The molecular alignment is simply achieved by spin-coating without any further treatment, and thus can be easily applicable to thin film electronic devices. To demonstrate this, photovoltaic devices were fabricated by successively depositing fullerene (1 nm), bathocuproine (10 nm), and aluminum (40 nm) in vacuo onto the layer of OPV **1** which was prepared in the same manner as the films for the absorption spectra (see SI). Figure 2b shows the photosensitivity of the device under the irradiation of polarized monochromatic light. Photocurrent generation was observed when the incident light was parallel to the rubbing direction while it was almost silent when the polarization was perpendicular, resulting in a high anisotropic photosensitivity at 440 nm.<sup>14</sup> This result shows the compatibility of this molecular alignment method to the organic thin film electronic devices.

In summary, highly uniaxial alignment of oligo(*p*-phenylenevinylene)s was demonstrated in films during the spin-coating process by using polymer alignment layers. This simple and easy approach can be applied to various organic electronic/optoelectronic devices to control the carrier flow thereby improving the device performance.

**Acknowledgment.** This work was financially supported in part by the Global COE Program "Chemistry Innovation through Cooperation of Science and Engineering", MEXT, Japan. We thank Rigaku Co., Ltd. for XRD measurements. T.N. thanks JSPS for financial support.

**Supporting Information Available:** Synthesis, absorption spectra, XRD patterns, preparation of the thin films and devices. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The in-plane XRD pattern of the thermally annealed film at  $150^\circ\text{C}$  showed only a single peak at  $23.1^\circ$  (not shown), suggesting that the peak at  $19.8^\circ$  is derived from the metastable packing of the molecules formed during spin-coating.
- Optical microscope observation under crossed nicols showed no lyotropic LC property of the molecules in concentrated  $\text{CHCl}_3$  solution at room temperature (see SI).
- The small response around 350 nm in the spectrum under perpendicular light irradiation can be attributed to the contribution from the absorption of the fullerene layer.

JA810123B