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Excellent uniaxial alignment of poly(9,9-dioctylfluorenyl-2,7-diyl) induced by photoaligned polyimide films

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We have investigated the alignment of poly (9,9-dioctylfluorenyl-2,7-diyl) (PFO) induced by photoaligned polyimide films. To induce anisotropic orientation of polyimide backbone structures by optical treatment, we used a specially designed polyimide (Azo-PI), which contains azobenzene in the backbone structure. The 30-nm-thick PFO layer, spincoated onto a photoaligned Azo-PI film, was heated to the liquid crystalline phase of PFO, and then cooled down to room temperature at −0.1 °C/min. The thermally treated PFO layer showed a polarization ratio of approximately 30 in photoluminescence. This high polarization ratio has not previously been reported in PFO films formed by other alignment techniques. This result indicates that the photoaligned Azo-PI film has an excellent ability to align liquid crystalline polymers. © *2005 American Institute of Physics*.

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Alignment control of conjugated polymers is of great importance for the fabrication of polymer-based electronic devices with high performance. The charge carrier mobility of conjugated polymer films can be significantly enhanced by aligning the polymer backbone structures along a certain direction.[1] This enhancement improves the switching frequency of polymer-based thin-film transistors (TFTs). Polarized light-emitting diodes (LEDs) can be realized by uniaxially aligning light-emitting polymers. Uniaxial alignment of conjugated polymers is achieved by various techniques, such as stretching,[2] direct rubbing,[3] the Langmuir–Blodgett technique,[4] and a friction transfer method.[5]

An attractive way to realize uniaxial alignment is to use the liquid-crystalline nature of polymers, e.g., polyfluorene (PF) derivatives,[6,7] which have rigid backbone structures with flexible side chains. By depositing liquid-crystalline polymers onto a proper alignment layer and subsequently performing a suitable thermal treatment, uniaxial alignment of the polymer can be obtained. Rubbed films of polyimide[1,7–9] and poly (p-phenylenevinylene) (PPV) (Ref. 10) are often used as the alignment layer. However, mechanical rubbing produces dust and scratches, and its uniformity is poor.[11] These drawbacks are expected to severely affect the alignment of conjugated polymers, especially in thin films. Thus, the development of a noncontact alignment technique is of crucial importance for improvements in the device performance.

Photoalignment is a promising noncontact alternative to the mechanical rubbing technique. Various photoalignment methods[12–15] have been proposed for low-molecular-weight liquid-crystal molecules. Recently, azobenzene side chain polymers have been used as photoalignment layer materials to induce uniaxial alignment of PF.[16] However, the photoinduced alignment of the azobenzene side chains is not permanent and can be reoriented by subsequent irradiation of light.[17] Unexpected reorientation of the azobenzene side chain might cause the deterioration of the alignment of conjugated polymers in the overlying layer. Stable photoalignment layers are required for practical applications.

We are focusing on a method using the photoisomerization reaction of a polyamic acid containing azobenzene in the backbone structure (Azo-PAA).[14,18] As described below, the alignment layer obtained by this method is polyimide, which is chemically and thermally stable.[19] The photoinduced alignment of the Azo-PAA backbone structure is stabilized by thermal imidization.[14,20] Thus, this photoalignment method provides optically, chemically, and thermally stable alignment layers. In this letter, we have shown that the photoalignment layer has an excellent ability to align PF, which is an attractive material for polymer-based LEDs and TFTs.

The molecular structure of Azo-PAA used in this study is shown in Fig. 1(a). The Azo-PAA films were spincoated onto quartz substrates, and then irradiated with linearly polarized light (LP-L) at normal incidence. A 500 W deep ultraviolet (UV) lamp (Ushio Inc. UXM-501MD) was used as the light source, and the wavelength was selected with a band-pass filter of transmission wavelength 340–500 nm (Asahi Spec-

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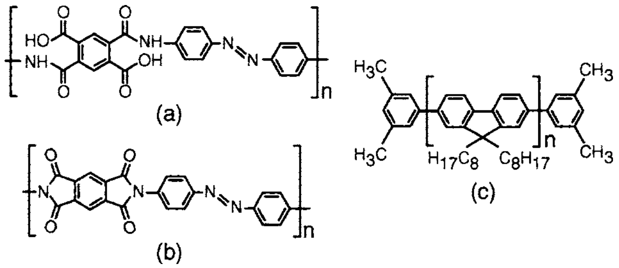

FIG. 1. The molecular structure of (a) Azo-PAA, (b) Azo-PI, and (c) PFO used in this study.

tra Co., Ltd.). To produce linear polarization, a Glan-Taylor prism polarizer was used. The LP-L exposure was varied up to 155 J/cm^2 to induce different surface anisotropies. After the photoalignment treatment, the Azo-PAA films were converted into the corresponding polyimide (Azo-PI) films by thermal imidization at 250 °C for 2 h in a nitrogen atmosphere. The molecular structure of Azo-PI is shown in Fig. 1(b). The thickness of the Azo-PI films was ~12 nm. The molecular orientation was determined by measuring the polarized UV-visible (UV-VIS) absorption spectra at normal incidence.

The PF used in this study was poly (9,9-dioctylfluorenyl-2,7-diyl) endcapped with 3,5-dimethylphenyl (PFO), which was used as received from American Dye Source, Inc. Its molecular structure is shown in Fig. 1(c). Approximately 30 nm thick PFO layers were deposited on the Azo-PI films by spincoating a filtered toluene solution of PFO (1 wt %) at 3000 rpm for 60 s. To align the PFO, the samples were annealed at 220 °C (liquid-crystalline phase of PFO)[21] for 2 h, and then cooled down to room temperature at −0.1 °C/min, which formed crystalline PFO layers.[21] The thermal treatment was performed in a nitrogen atmosphere to prevent thermal oxidation. The molecular orientation of the PFO layers was determined by measuring the polarized photoluminescence (PL) spectra with a fluorescence spectrometer (JASCO FP777). Unpolarized light of wavelength 390 nm was used as the excitation light, which impinged onto the PFO layer at 45° from the surface normal. The light emitted from the PFO layer was collected along the surface normal through a Glan-Thompson prism polarizer.

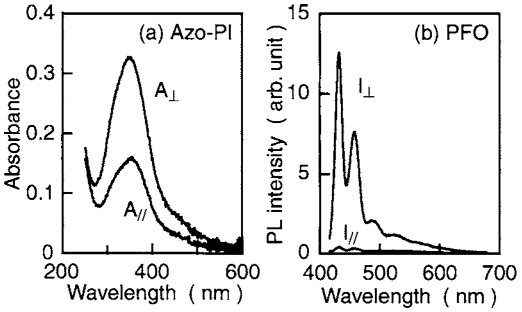

FIG. 2. (a) Polarized UV-VIS absorption spectra of the Azo-PI film that was obtained by thermally imidizing an Azo-PAA film exposed to LP-L of 39 J/cm^2. $A_\perp$ and $A_\parallel$ are the spectra for the light polarized perpendicular and parallel, respectively, to the polarization direction of the LP-L. (b) Polarized PL spectra of the crystalline PFO layer formed on the same Azo-PI film. $I_\perp$ and $I_\parallel$ are the perpendicular and parallel component spectra with respect to the polarization direction of the LP-L.

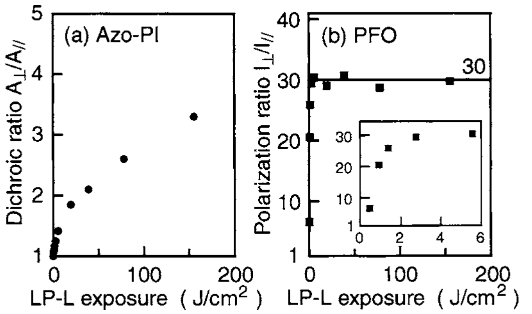

FIG. 3. LP-L exposure dependence of (a) the dichroic ratio ($A_\perp/A_\parallel$ at 351 nm) of the Azo-PI films and (b) the PL polarization ratio ($I_\perp/I_\parallel$ at 432 nm) of the crystalline PFO layer. The horizontal straight line shows the polarization ratio of 30. The inset in (b) shows the LP-L dependence of $I_\perp/I_\parallel$ in the low LP-L exposure region.

Figure 2(a) shows the polarized UV-VIS absorption spectra of the Azo-PI film that was obtained by thermal imidization of the Azo-PAA film exposed to LP-L of 39 J/cm^2. Here, $A_\perp$ and $A_\parallel$ are absorbance for the light polarized perpendicular and parallel, respectively, to the polarization direction of the LP-L. A well-defined peak was observed at 351 nm, which is assigned to the π-π^* transition of azobenzene in the Azo-PI backbone structure.[22] The dichroic ratio defined by $A_\perp/A_\parallel$ was 2.1. Since the transition dipole lies parallel to the backbone structure, the dichroic ratio reflects the anisotropic orientation of the Azo-PI backbone structure. Thus, we see that the Azo-PI backbone structures align on average perpendicular to the polarization direction of the LP-L.

Figure 2(b) shows the polarized PL spectra of the crystalline PFO layer formed on the Azo-PI film (LP-L exposure: 39 J/cm^2). $I_\perp$ and $I_\parallel$ are the perpendicular and parallel components of the PL intensity with respect to the polarization direction of the LP-L. The sharp peaks at 432, 458, 491, and 525 nm are assigned to the excitonic emission and its vibronic progression from noninteracting single chains.[6,21] Although for crystalline PFO layers the broad fluorescence assigned to emission from excimers or aggregates was often observed in the longer-wavelength region beyond 480 nm,[5,6,21] it was strongly suppressed for our samples. We observed highly polarized emission from the PFO layer, whose polarization ratio defined by $I_\perp/I_\parallel$ was 30 at 432 nm. This polarization ratio corresponds to the uniaxial molecular order parameter of $0.91[=(I_\perp - I_\parallel)/(I_\perp + 2I_\parallel)]$. To our knowledge, the highest polarization ratio in PL reported previously was 25, which was observed for the crystalline PFO layer prepared by a friction-transfer method followed by a slow-cooling thermal treatment.[5] The highly polarized PL observed in this study indicates that the photoaligned Azo-PI film is an excellent alignment layer for PFO.

Figures 3(a) and 3(b) show the LP-L exposure dependence of the dichroic ratio $A_\perp/A_\parallel$ of the Azo-PI films and the polarization ratio $I_\perp/I_\parallel$ of the crystalline PFO layers, respectively. The dichroic ratio of the Azo-PI film increases monotonically with the LP-L exposure, although the rate of increase decreases as the LP-L exposure increases. It reaches 3.3 at 155 J/cm^2. On the other hand, the polarization ratio of the PFO layer increases rapidly up to ~30, and beyond 2.8 J/cm^2 it becomes constant. This result shows that 2.8 J/cm^2 is enough LP-L exposure to realize the highly oriented PFO layer.

Before we proceed to further discussion, we would like to mention the relationship between the in-plane anisotropies of the Azo-PI *film* and its *surface*. In this study, we used 12 nm thick Azo-PI films as photoalignment layers. For such very thin films, we can assume that the photoaligned Azo-PI film has a uniform in-plane molecular orientation over the entire film thickness.[18] Thus, the dichroic ratio shown in Fig. 3(a) reflects not only the in-plane anisotropy of the Azo-PI *film* but also that of its *surface*. Indeed, we have recently reported that the in-plane anisotropy of a 15 nm thick photoaligned Azo-PI film is transferred to the 4-*n*-octyl-4′-cyanobiphenyl *monolayer* in contact with it.[23] This experimental result strongly supports the above assumption. Therefore, we believe that $A_\perp/A_\parallel$ shown in Fig. 3(a) can be considered as the in-plane anisotropy of the Azo-PI film *surface*.

Now we can discuss the relationship between the in-plane anisotropy of the Azo-PI film surface $(A_\perp/A_\parallel)$ and the molecular order of the crystalline PFO layer $(I_\perp/I_\parallel)$. From Fig. 3, we see that the molecular order of the PFO layer is much higher than the in-plane anisotropy of the Azo-PI film surface. This result suggests that the molecular order of the crystalline PFO layer is determined by the bulk nature of PFO, rather than the interaction between the Azo-PI and PFO molecules. Here, the bulk nature of PFO means the self-organization of PFO in the liquid-crystalline phase and in the crystallization process from the liquid-crystalline phase. This is supported by the fact that for $A_\perp/A_\parallel \geqslant 1.25$, the PL polarization ratio of the PFO layer is ~30, independent of $A_\perp/A_\parallel$. The in-plane anisotropy of the Azo-PI film surface does not affect the molecular order of the crystalline PFO layer when the in-plane anisotropy is sufficiently large $(A_\perp/A_\parallel \geqslant 1.25)$. The main role of the Azo-PI film is to determine the preferential alignment direction of PFO.

The formation of highly oriented PFO layers can be explained as follows. When the PFO layer is heated to the liquid-crystalline phase, the PFO molecules self-align along the preferential alignment direction determined by the underlying Azo-PI film. At this stage, the PL polarization ratio increases up to ~10.[10,24] The subsequent crystallization of the PFO layer from the liquid-crystalline phase further enhances the orientational molecular order, and the PL polarization ratio reaches ~30.

When the in-plane anisotropy of the Azo-PI film surface is small $(A_\perp/A_\parallel < 1.25)$, the small in-plane anisotropy causes lowering of the molecular order of the PFO layer as seen in Fig. 3. This is due to the insufficient surface anchoring strength of the Azo-PI film along the preferential alignment direction. Thus the photoaligned Azo-PI film with $A_\perp/A_\parallel \geqslant 1.25$ must be used to obtain a highly oriented crystalline PFO layer.

To conclude, we have investigated the molecular orientation of the crystalline PFO layers induced by photoaligned Azo-PI films, which are thermally, chemically, and optically stable. We succeeded in forming highly oriented PFO layers that showed a polarization ratio of approximately 30 in PL. This polarization ratio corresponds to a uniaxial molecular order parameter of 0.91. To our knowledge, the polarization ratio of ~30 has not previously been reported in PFO films formed by other alignment techniques. This means that the photoaligned Azo-PI film is an excellent alignment layer for PFO derivatives and probably for other liquid-crystalline polymers. We believe that the excellent alignment ability is attributed to the uniformity and the sufficiently large in-plane anisotropy of the photoaligned film surface.

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