

Alignment of Liquid Crystalline Polyfluorene Films by an Optically Aligned Polymer Layer

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An optically aligned polymer with linearly polarized light is used to align uniaxially a liquid crystalline fluorescent polymer, poly(9,9-dioctylfluorene) (PFO). The optically aligned polymer has negligible absorption for visible light regime and is stable at relatively high temperature in air. The aligned PFO film shows the significant dichroic ratios in absorption and photoluminescence. The photoconductivity is sensitive to the polarization of the excitation light.

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Uniaxial alignment of conjugated polymers is an important goal. With aligned polymer films, the intrinsic properties such as optical and electronic properties can be investigated. Also, chain alignment is useful for linearly polarized organic light emitting devices (OLEDs),¹⁾ liquid crystal devices,^{2,3)} and flexible devices.⁴⁾ Recent technological developments enable us to control the local alignment in nanometer scales.^{5–7)}

Liquid crystalline fluorescent polymers are obvious candidates for chain alignment because the liquid crystalline moieties can be aligned by uniaxial surface morphology. One of the most studied blue-emitting polymer, polyfluorene (PF), has liquid crystalline properties.⁸⁾ Hence PFs are promising as polymers for linearly polarized OLEDs.

Polarized emission has been reported for fluorene oligomers.⁹⁾ For PFs, the most common alignment technique used is heating the polymer film above the liquid crystal transition temperature on a mechanically rubbed polymer substrate, followed by cooling to room temperature.⁸⁾ However, mechanical rubbing of the polymer is disadvantageous because the polymer has to be mechanically hard and because the removal of dust after the rubbing is necessary. On the other hand, photoreactive polymers such as side-chain azo polymers and crosslinkable side-chain polymers are useful to prepare aligned substrates: that function as optical alignment layers after exposure to linearly polarized light.¹⁰⁾ This method is relatively fast with low cost experimental facility, and the noncontact process eliminates the above disadvantages. In addition, various alignments can be patterned easily with high resolution.¹¹⁾ In order to obtain higher polarization ratios and good fluorescence performance for liquid crystalline fluorescent polymers, the optically aligned polymer (OAP) must have a high degree of optical alignment, and must exhibit chemical stability both at high temperatures and in the processing atmosphere.

Polarized luminescence from PFs on OAPs has been recently reported.^{11–13)} Linearly polarized UV or visible light was used for the optical alignment. The dichroic ratios in absorption and photoluminescence with magnitudes greater

than 10 were achieved. Here, we report an alignment for poly(9,9-dioctylfluorene) (PFO) by using a new class of OAP, that is stable at relatively high temperature $\sim 200^\circ\text{C}$. The absorption and photoluminescence perpendicular to the alignment direction are significantly suppressed. Dichroic ratios in photoluminescence over 20 are obtained. In addition, the intrachain photoconductivity shows strong anisotropy when the films are exposed to polarized light.

Molecular structure of the OAP is shown in Fig. 1(a).¹⁴⁾ The OAP is comprised substantially of covalently bonded two polymers (polyimide A and polymethacrylate B) forming a branched comb-like structure, linked by units of connector C, which incorporates both polyimide and polyolefin repeat units. The polyimide gives good mechanical, electrical, wetting, and adhesion properties, whereas the polymethacrylate provides a high density of chromophores

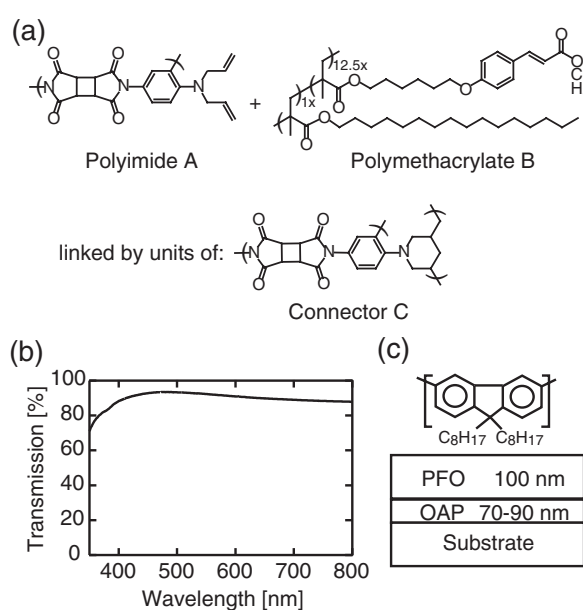


Fig. 1. (a) Molecular structures of the OAP hybrid polymer. (b) Transmission spectrum for OAP layer without UV light exposure. (c) Cross section of aligned PFO film. The inset shows the molecular structure of PFO.

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Table I. Treatment conditions for optically aligned polymers (OAPs) and PFOs.

Polymer	Group	Condition
OAP	A	polarized UV light exposure
	B	heating at 180°C → polarized UV light exposure
	C	polarized UV light exposure → heating at 180°C
PFO		r.t. → 200°C → 170°C → r.t.
		~20°C/min -1°C/min quench

needed for low energy density of UV exposure and sufficient cross-linking densities for the thermal and optical stability.

The γ -butyrolactone solution (4.5 wt %) of the OAP was spin-cast onto passivated glass substrate with an indium–tin-oxide (ITO) pad at 2500 rpm for 1 min. The resulting film thickness was 70–90 nm as measured by a commercial profilometer. Three groups of the OAP layers were prepared; their respective process conditions are summarized in Table I. Heating was performed for one hour in air. All UV exposures to align the OAP unidirectionally were performed (Elsicon E3-UV-600-A UV lamp exposure system), where 280–365 nm p-polarized light was irradiated with an angle of incidence of 45 deg. Figure 1(b) shows transmission spectrum for the OAP layer without UV light exposure. The transmission through the OAP layer is about 90% for wavelengths below ~400 nm. The transmission spectrum of the OAP layer after the optical alignment and/or the heat treatment was approximately the same.

After processing the OAP layers as described in Table I, toluene solution (2 wt %) of PFO was spin-cast on the OAP layer with thickness of 100 nm as illustrated in Fig. 1(c). Following the previous report,⁸⁾ the PFO film was heated to 200°C at a rate of ~20°C/min (into the liquid crystalline phase), then cooled to 170°C at a rate of -1°C/min. Finally, the film was quenched to room temperature (Table I).

All procedures, including the absorption and photoluminescence measurements, were performed in dry nitrogen atmosphere. Polarized absorption measurements were performed using a sheet polarizer between sample and detector, and polarized photoluminescence measurements by using two sheet polarizers between sample and excitation light source and between sample and detector. Photoconductivity was measured in top-contact configuration in vacuum. Two gold electrodes separated by a gap of 20 μ m were used to measure the steady-state photocurrent with the conventional modulation technique using a lock-in amplifier; the data were normalized to constant incident photon flux. The incident light on the sample was dispersed by a monochromator and polarized by a Glan–Taylor polarizer.

Figure 2 shows polarized absorption and photoluminescence spectra for aligned PFO film on OAP layer (group C). Significant suppression of both absorption and photoluminescence perpendicular to the alignment direction can be seen for the PFO film, indicative of a relatively high degree of alignment of the PFO chains. The absorption and photoluminescence spectra for groups A–C represent similar spectral shape (not shown). Table II shows the summarized dichroic ratios in polarized absorption and photoluminescence for aligned PFOs on OAP layers with different exposure energy density of UV light. The dichroic ratio in

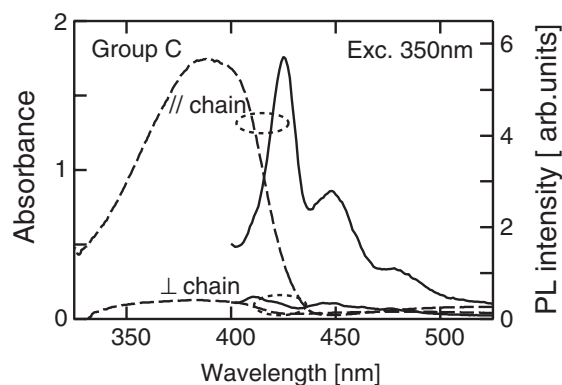


Fig. 2. Polarized absorption (dashed line) and photoluminescence spectra (solid line) for an aligned PFO film on group C OAP layer (with 2.5 J/cm² UV exposure) with the light polarized parallel and perpendicular to the PFO chains. The excitation wavelength of photoluminescence is 350 nm.

Table II. Dichroic ratios in polarized absorption and photoluminescence, D_{abs} and D_{PL} respectively, for aligned PFOs on OAP layers with different exposure energy density of UV light.

	Energy density (J/cm ²)	D_{abs} (at 390 nm)	D_{PL} (at 427 nm)
PFO/OAP (Group A)	1.0	14	9
	2.5	18	24
PFO/OAP (Group B)	1.0	12	15
	2.5	11	21
PFO/OAP (Group C)	1.0	14	21
	2.5	14	20

photoluminescence at the strongest 0–0 emission peak is over 20 for most of the samples with exposures of 2.5 J/cm². The dichroic properties in absorption are weakly dependent on the heating conditions indicating that the surface morphology of OAP layer formed by UV light exposure is stable under the heat treatment at high temperatures. Because of the stable alignment of the OAP layer at high temperatures, it is useful for liquid crystalline polymers having high liquid crystal transition temperatures.

The high degree of alignment of the PFO chains is also observed in electronic transport. Figure 3 shows photoconductivity spectra for transport parallel to the PFO chains under linearly polarized light parallel and perpendicular to PFO chains. The applied electric field between electrodes is 1.5×10^5 V/cm. Photocurrent with perpendicularly polarized light is relatively larger considering the small absorption with perpendicularly polarized light (Fig. 2) into account. This is most likely caused by the larger absorption depth for perpendicularly polarized light and thereby longer carrier lifetime, leading to the larger photocurrent. The onset of photocurrent with perpendicularly polarized light is 426 nm and that with parallel polarized light is 440 nm, where the photocurrent with perpendicularly polarized light is almost completely suppressed for wavelengths in the range from 426–440 nm. These onsets of the photocurrents with perpendicularly and parallel polarized lights coincide with those in the absorption spectra, respectively. Photoconductivity spectra for aligned poly(9,9-diethylhexylfluor-

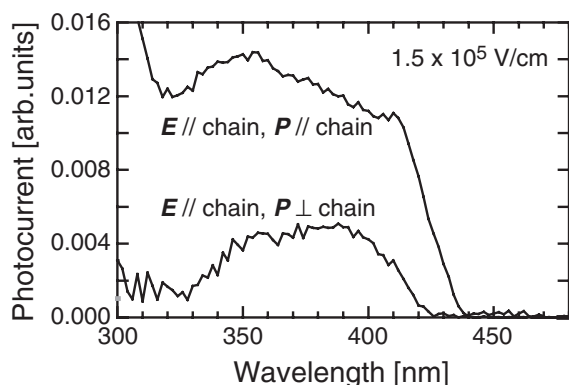


Fig. 3. Photoconductivity spectra with transport along the PFO chain for an aligned PFO film on a group B OAP layer (with 2.5 J/cm^2 UV exposure) with the light polarized parallel and perpendicular to the PFO chains. The applied electric field is $1.5 \times 10^5 \text{ V/cm}$.

ene) with 10% allyl end group (PF2/6B10) in a sandwich configuration has been reported.¹⁵ The suppressed range of wavelength for photocurrent under perpendicularly polarized light is narrow in comparison with that reported here.

Although the photoconductivity spectra has no sharp shoulder near the absorption edge as was observed in poly(phenylene vinylene),¹⁶ the low energy onset of the photoconductivity in response to parallel polarized light could be caused by exciton dissociation by electric field ionization. With this interpretation, the exciton binding energy is estimated to be $\sim 0.1 \text{ eV}$ from the energy difference of the parallel and perpendicular onsets. Alternatively, the low energy response to parallel polarized light could simply be the result of the anisotropic $\pi-\pi^*$ interband transition (i.e., intra- and inter-PFO chains). In this energy range, the photocarriers are excited only by parallel polarized light.

In conclusion, highly aligned PFO films are obtained by using a new class of optically aligned polymer. Significant dichroic ratios over 20 were observed in photoluminescence. The photoconductivity is sensitive to the polarization of the excitation light: Under polarized light, the photocurrent parallel to the PFO chains is enhanced while the photocurrent perpendicular to the chains is suppressed near absorption edge. The high transparency for visible light

and the stability at high temperature are suitable for alignment of broad range of liquid crystalline fluorescent polymers. The high degree of alignment is useful for investigating the intrinsic optical and electronic properties of liquid crystalline conjugated polymers.

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