Macromolecules **2008**, *41*, 2341−2346

Dynamic Switching of Linearly Polarized Emission in Liquid-Crystallinity-Embedded Photoresponsive Conjugated Polymers

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Received January 19, 2008; Revised Manuscript Received January 29, 2008

ABSTRACT: Multifunctional conjugated polymers bearing fluorescent, liquid crystalline, and photoresponsive functions were synthesized by introducing the dithienylethene moieties into side chains of poly(*p*-phenylene−vinylene) [**P1**] and poly(bithienylene−phenylene) [**P2**]. Observation of polarizing optical microscope showed that the polymers have main-chain-type liquid crystallinity. Reversible photoisomerization of the dithienylethene moiety was observed in both solution and cast film. Drastic quenching of fluorescence occurred when the photoresponsive moiety changed from an open form to a closed one upon irradiation of ultraviolet light. The quenched fluorescence was recovered through a photoisomerization from the closed form to the open one. Macroscopically aligned **P2** film, prepared by a rubbing in liquid crystalline phase, exhibited a linearly polarized fluorescence with significant anisotropy. Reversible quenching and emitting behavior in anisotropic fluorescence was well controlled by the photochemical switching.

1. Introduction

π-Conjugated aromatic polymers represented by poly(*p*-phenylene), poly(*p*-phenylene−vinylene), and polythiophene and their copolymers are promising candidates for advanced functional materials and devices, such as polymer light-emitting diodes,[1] photodiodes,[2] and photovoltaic cells.[3] Liquid crystalline (LC) conjugated polymers are attracting current interests since they are spontaneously oriented and furthermore macroscopically aligned by an external force such as shear stress, electric field, and magnetic force field, giving rise to electrical and optical anisotropies and even a linearly polarized luminescence. Thus, LC conjugated polymers can be regarded as advanced materials with anisotropic optical properties as well as anisotropic electrical conductivity. The LC conjugated polymers are prepared by introducing mesogenic moieties into backbones of main chains or into side chains.[4,5] However, the linearly polarized fluorescence itself cannot be controlled in intensity or interchanged between emitting and nonemitting (quenching) modes, which should be required for dynamic control of luminescence and optical read−write memory functions.[6]

Meanwhile, dithienylethene derivatives are the most feasible photochromic materials among various photoresponsive compounds because of their outstanding fatigue resistance, thermal stability, and reversible properties.[7] Addition of the photoresponsive moiety into the aromatic conjugated polymer is attractive for dynamical control of luminescence through photoisomerization driven switching.[8–11]

If the substituent of main-chain-type LC conjugated polymer is a photoresponsive moiety, the polymer should be not only macroscopically aligned by application of an external force but also photochemically switched by an irradiation of an external light. Particularly, the linearly polarized fluorescence (LPF) of the macroscopically aligned LC conjugated polymer can be dynamically controlled by virtue of the reversible photoswitching of the photoresponsive moiety upon irradiations of ultraviolet (UV) and visible (vis) light.

Here, with an aim to develop multifunctional polymers having fluorescence, liquid crystallinity, and photoswitching ability, we designed and synthesized novel photoresponsive LC conjugated copolymers, LC poly(*p*-phenylene−vinylene) [**P1**] and LC poly(bithienylene−phenylene) [**P2**]. As described in Scheme 1, the polymers are composed of both LC main chain, where the π-conjugated aromatic units are fluorescent moieties (enclosed by green frames) and also behave as mesogenic cores (blue frames) and the side chains of photoresponsive dithienylethene moieties (red frames) linked with secondary long alkyl groups. The linearly polarized fluorescence in the aligned **P2** film, which was prepared by a rubbing in LC phase, showed reversible quenching and emitting behaviors owing to the photochemical isomerization upon irradiations of ultraviolet and visible light. The present article is the first report for realizing a reversible quenching and emitting behaviors in linearly polarized fluorescence by using liquid crystallinity and photoresponsive ability.

2. Experimental Section

2.1. Measurements. ^{1}H NMR spectra were measured in $CDCl_3$ using a JEOL EX-270 spectrometer. Chemical shifts were represented in parts per million downfield from TMS as an internal standard. IR spectra were measured with JASCO FT-IR 550 spectrometer using the KBr method. Optical absorption spectra were measured using a Hitachi U-3500 spectrometer, and optical fluorescence spectra were measured using a JASCO FP-750 spectrometer with quartz cell. Phase transition texture observations were made using a Nicon ECLIPSE E600 POL polarizing microscope equipped with a Linkam TH-600PM heating and cooling stage. The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Shodex A-80 M column and a JASCO HPLC 870-UV detector with THF used as solvent during measurements, with the instrument calibrated by polystyrene standard.

2.2. 1-{5-(2,5-Dibromobenzoyloxymethylene)-2-methylthien-3′-yl}-2-(5-methylhydroxy-2-methylthien-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (2). To a mixture of compound **1** (1.50 g, 3.30 mmol), triphenylphosphine (734 mg, 2.80 mmol), and 2,5-dibromobenzoic acid (784 mg, 2.80 mmol) in THF (50 mL), a solution of DIAD (1.45 g, 40 wt % in toluene, 2.80 mmol) in THF (20 mL) was very slowly added via a pressure-equalized dropping funnel. The reaction mixture was stirred at 0 °C overnight under an Ar atmosphere. The resulting precipitate was extracted with $CHCl_3$, thoroughly washed with saturated NaCl solution, and dried over

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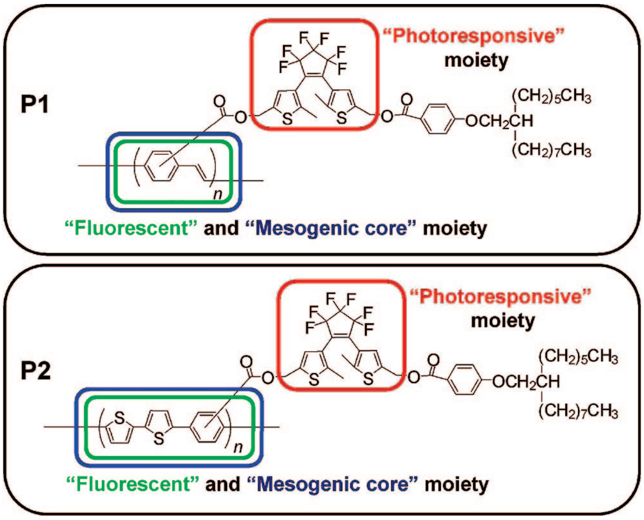
10.1021/ma800132v CCC: $40.75

Scheme 1. Structures of Multifunctional Conjugated Polymers



anhydrous sodium sulfate. The precipitate was removed by filtration, and filtrate was evaporated under reduced pressure. The residue was purified with column chromatography (silica gel; CH_2Cl_2) to give 1.28 g (66%) of **2** as yellow oil. Anal. Calcd for $C_{24}H_{16}O_3F_6Br_2S_2$: C 41.76, H 2.34. Found: C 41.66, H 2.33. IR (KBr): 3380, 2922, 1734, 1557, 1443, 1338, 1277, 1111, 1047, 986, 735 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 1.84−1.93 (m, 6H, thiophenyl−CH_3), 4.75 (s, 2H, $-\mathit{CH}_2$OH), 5.41 (s, 2H, $-COOCH_2-$), 6.95 (s, 1H, thiophenyl−H), 7.12 (s, 1H, thiophenyl−H), 7.41 (m, 4H, phenyl−H), 7.88 (s, 1H, phenyl−H).

2.3. Methyl 4-(2-Hexyldecyloxy)benzoate (3). Methyl 4-hydroxybenzoate (5.06 g, 33.3 mmol), 1-bromo-2-hexyldecane (12.2 g, 39.9 mmol), K_2CO_3 (5.52 g, 39.9 mmol), a catalytic amount of 18-crown-6-ether and 80 mL of acetone were refluxed at 60 °C for 12 h. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over anhydrous sodium sulfate. The precipitate was removed by filtration, and filtrate was evaporated under reduced pressure. The residue was purified with column chromatography (silica gel; chloroform/hexane = 1/1) to give 6.03 g (48%) of **3** as colorless oil. Anal. Calcd for $C_{24}H_{40}O_3$: C 76.55, H 10.71. Found: C 76.25, H 10.88. IR (KBr): 2925, 2855, 1722, 1606, 1511, 1435, 1254, 1104, 1205, 846, 770 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 0.87 (t, 6H, J = 6.6 Hz, $-CH_3$), 1.27−1.57 (m, 24H, $-OCH_2CH(\mathit{CH}_2)_5CH_3$ and $-OCH_2CH(\mathit{CH}_2)_7CH_3$), 1.79 (m, 1H, $-OCH_2\mathit{CH}(CH_2)_6C_8H_{17}$), 3.88 (s, 3H, $-COOCH_3$), 3.87 (d, 2H, J = 4.6 Hz, $-O\mathit{CH}_2CH-$), 6.90 (d, 2H, J = 8.7 Hz, *ortho* to $-OCH_2CH(CH_2)_6C_8H_{17}$), 7.97 (d, 2H, J = 8.7 Hz, *meta* to $-OCH_2CH(CH_2)_6C_8H_{17}$).

2.4. 4-(2-Hexyldecyloxy)benzoic Acid (4). Compound **3** (5.54 g, 14.7 mmol) was hydrolyzed by KOH (3.00 g, 75.0 mmol) in 40 mL of water and 250 mL of MeOH at 50 °C for 12 h. Then solvent was evaporated, and it was dissolved in water. The mixture was acidified to pH = 2 by hydrochloric acid solution. The resulting precipitate was extracted with CH_2Cl_2, thoroughly washed with saturated NaCl solution, and dried over anhydrous sodium sulfate. The precipitate was removed by filtration, and filtrate was evaporated under reduced pressure to yield 4.09 mg (77%) of colorless oil. Anal. Calcd for $C_{23}H_{38}O_3$: C 76.20, H 10.56. Found: C 76.10, H 10.24. IR (KBr): 2925, 2856, 2667, 2552, 1686, 1605, 1426, 1255, 1168, 1024, 848, 774 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 0.85−0.90 (m, 6H, $-CH_3$), 1.26−1.41 (m, 24H, $-OCH_2CH(\mathit{CH}_2)_5CH_3$ and $-OCH_2CH(\mathit{CH}_2)_7CH_3$), 1.76 (m, 1H, $-OCH_2\mathit{CH}(CH_2)_6C_8H_{17}$), 3.89 (d, 2H, J = 5.6 Hz, $-O\mathit{CH}_2CH-$), 6.93 (d, 2H, J = 8.9 Hz, *ortho* to $-OCH_2CH_2(\mathit{CH}_2)_9CH_3$), 8.05 (d, 2H, J = 8.9 Hz, *meta* to $-OCH_2CH_2(\mathit{CH}_2)_9CH_3$).

2.5. 1-{5-(2,5-Dibromobenzoyloxymethylene)-2-methylthien-3′-yl}-2-[5-{4-(2-hexyldecyloxybenzoyloxymethylene)}-2-methylthien-3-yl]-3,3,4,4,5,5-hexafluorocyclopentene (5). A solution of **2** (596 mg, 0.82 mmol), **4** (359 mg, 0.99 mmol), DCC (255 mg, 1.2 mmol), and DMAP (151 mg, 1.2 mmol) in CH_2Cl_2 (10 mL) was stirred for 12 h at room temperature. The crude product was extracted with CH_2Cl_2. The organic layer was washed with saturated NaCl solution and dried over anhydrous sodium sulfate. The precipitate was removed by filtration, and filtrate was evaporated under reduced pressure. The residue was purified with column chromatography (silica gel; CH_2Cl_2) to give 343 mg (40%) of **5** as yellow oil. Anal. Calcd for $C_{47}H_{52}Br_2F_6O_5S_2$: C 54.55, H 5.06. Found: C 54.55, H 5.00. IR (KBr): 2925, 2854, 1716, 1606, 1510, 1458, 1337, 1275, 1112, 1047, 985, 848, 770 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 0.87 (m, 6H, $-CH_3$), 0.90−1.40 (m, 24H, $-OCH_2CH(\mathit{CH}_2)_5CH_3$ and $-OCH_2CH(\mathit{CH}_2)_7CH_3$), 1.79 (m, 1H, $-OCH_2\mathit{CH}(CH_2)_6C_8H_{17}$), 1.88 (s, 6H, thiophenyl−CH_3), 3.87 (d, 2H, J = 5.6 Hz, $-O\mathit{CH}_2CH-$), 5.36 (s, 2H, $-COOCH_2-$), 5.40 (s, 2H, $-COOCH_2-$), 6.90 (d, 2H, J = 9.0 Hz, *ortho* to $-OCH_2CH(CH_2)_6C_8H_{17}$), 7.08 (s, 1H, thiophenyl−H), 7.13 (s, 1H, thiophenyl−H), 7.45 (dd, 1H, J = 2.3 and 8.6 Hz, phenyl−H), 7.52 (d, 1H, J = 8.6 Hz, phenyl−H), 7.88 (d, 1H, J = 2.3 Hz, phenyl−H), 7.97 (d, 2H, J = 9.0 Hz, *meta* to $-OCH_2\mathit{CH}(CH_2)_6C_8H_{17}$).

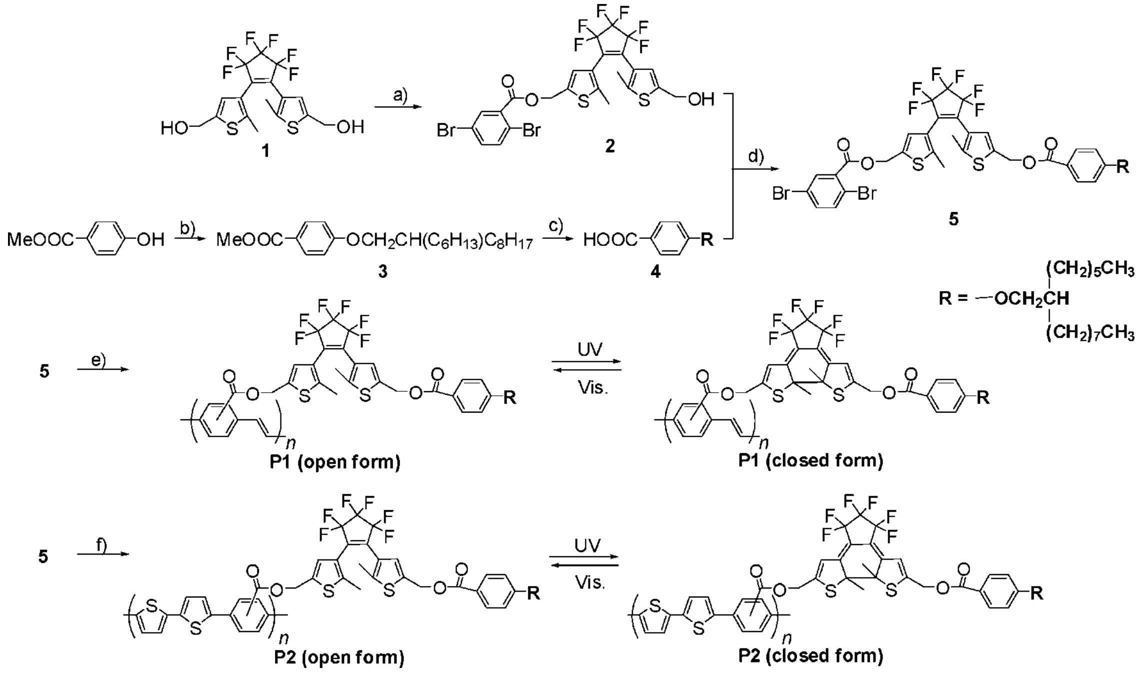
2.6. LC Poly(*p*-phenylene−vinylene) (P1). A solution of **5** (152 mg, 0.15 mmol), 1,2-bis(tributylstannyl)ethylene (89.0 mg, 0.15 mmol), $Pd_2(DBA)_3$ (1.35 mg, 1.47 μmol), and (2-furyl)$_3$P (1.36 mg, 5.88 μmol) in 1 mL of *N*,*N*-dimethylformamid (DMF) was stirred under Ar at 80 °C for 5 days. The reaction mixture was poured into a large amount of methanol (300 mL) containing HCl and vigorously stirred for 3 h. The resulting precipitate was collected by filtration and dissolved in minimum amount of THF (3 mL) and stirred in methanol (300 mL) for 24 h. After filtration, the product was dried under vacuum to give 78 mg (74%) as brown powder. ^1H NMR (270 MHz, $CDCl_3$, δ): 0.86 (br, $-CH_3$), 1.25 (br, $-OCH_2CH(\mathit{C_5H_{10}}CH_3)$ $\mathit{C_7H_{17}}CH_3$), 1.63 (br, $-OCH_2\mathit{CH}(C_6H_{13})C_8H_{17}-$), 1.85 (br, thiophenyl−$CH_3$), 3.85 (br, $-O\mathit{CH}_2CH-$), 5.33 (br, $-COOCH_2-$), 5.44 (br, $-COOCH_2-$), 6.87 (br, *ortho* to $-O(CH_2)_{11}CH_3$), 7.07 (br, thiophenyl−H in dithienylethene), 7.17 (br, thiophenyl−H in dithienylethene), 7.72 (br, phenyl−H and vinyl−H), 7.96 (br, *meta* to $-OCH_2\mathit{CH}(C_6H_{13})C_8H_{17}-$).

2.7. LC Poly(bithienylene−phenylene) (P2). A solution of **5** (191 mg, 0.19 mmol), $Pd_2(DBA)_3$ (1.72 mg, 1.85 μmol), and (2-furyl)$_3$P (1.71 mg, 7.38 μmol) in 0.5 mL of THF was stirred under Ar at 60 °C for 30 min. To the mixture was then added 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (91 mg, 0.19 mmol). After stirring at 60 °C overnight, the reaction mixture was poured into a large amount of methanol (800 mL) containing HCl and vigorously stirred for 3 h. The resulting precipitate was collected by filtration and dissolved in minimum amount of THF (3 mL) and stirred in methanol (800 mL) for 24 h. After filtration, the product was dried under vacuum to give 158 mg (82%) as orange powder. ^1H NMR (270 MHz, $CDCl_3$, δ): 0.86 (br, $-CH_3$), 1.25 (br, $-OCH_2CH(\mathit{CH}_2)_5CH_3$ and $-OCH_2CH(\mathit{CH}_2)_7CH_3$), 1.63 (br, $-OCH_2\mathit{CH}(C_6H_{13})C_8H_{17}$), 1.79 (br, thiophenyl−$CH_3$), 1.84 (br, thiophenyl−$CH_3$), 3.86 (br, $-O\mathit{CH}_2CH-$), 5.30 (br, $-COOCH_2-$), 5.34 (br, $-COOCH_2-$), 6.89 (br, *ortho* to $-OCH_2CH(C_6H_{13})C_8H_{17}$), 7.05 (br, thiophenyl−H in dithienylethene), 7.14 (br, thiophenyl−H in dithienylethene), 7.50 (br, thiophenyl−H in main chain), 7.71 (br, phenyl−H in main chain), 7.94 (br, *meta* to $-OCH_2\mathit{CH}(C_6H_{13})C_8H_{17}$).

3. Results and Discussion

3.1. Synthesis and Characterization of Polymers. Synthetic routes of **P1** and **P2** are shown in Scheme 2. The dithienylethene derivative **1**[12,13] was coupled with 2,5-dibromobenzene via Mitsunobu reaction in THF to give **2**.[14] Methyl-4-(2-hexyldecyloxy)benzoate (**3**) was synthesized by alkaline-mediated coupling of methyl *p*-hydroxybenzoate with 1-bromo-2-hexyldecane in acetone. The hydrolysis of **3** with NaOH in a mixed solvent of MeOH and water gave 4-(2-hexyldecyloxy)benzoic acid (**4**). The esterification between **2** and **4** in the presence of dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyri-

Scheme 2. Synthetic Routes and Photoisomerization of the Polymers[a]



[a] Conditions: (a) 2,5-dibromobenzoic acid, DIAD, PPh_3, THF; (b) 1-bromo-2-hexyldecane, K_2CO_3, 18-crown-6, acetone; (c) NaOH, H_2O, MeOH; (d) DCC, DMAP, CH_2Cl_2; (e) 1,2-bis(tributylstannyl)ethylene, $Pd_2(DBA)_3$, $(2\text{-furyl})_3P$, DMF; (f) 5,5′-bis(trimethylstannyl)-2,2′-bithiophene, $Pd_2(DBA)_3$, $(2\text{-furyl})_3P$, THF. DIAD = diisopropyl azodicarboxylate, DBA = dibenzilideneacetone.

dine (DMAP) in CH_2Cl_2 gave the monomer **5**. Finally, the copolymerizations between the monomer **5** and 1,2-bis(tributylstannyl)ethylene in DMF, and that between **5** and 5,5′-bis(trimethylstannyl)-2,2′-bithiophene in THF, in the presence of palladium as a catalyst, were carried out through Still polycondensation reaction,[15] giving the polymers, **P1** and **P2**, respectively. Both the polymers were fusible and soluble in organic solvents such as THF, toluene, and $CHCl_3$. GPC measurements using THF as an eluent showed that **P1** has a number-average molecular weight (M_n) of 1.3×10^4, a weight-average molecular weight (M_w) of 3.6×10^4, a dispersion ratio (M_w/M_n) of 2.7, and a degree of the polymerization (DP) of 14. On the other hand, **P2** has M_n of 1.4×10^4, M_w of 3.6×10^4, M_w/M_n of 1.3, and DP of 14.

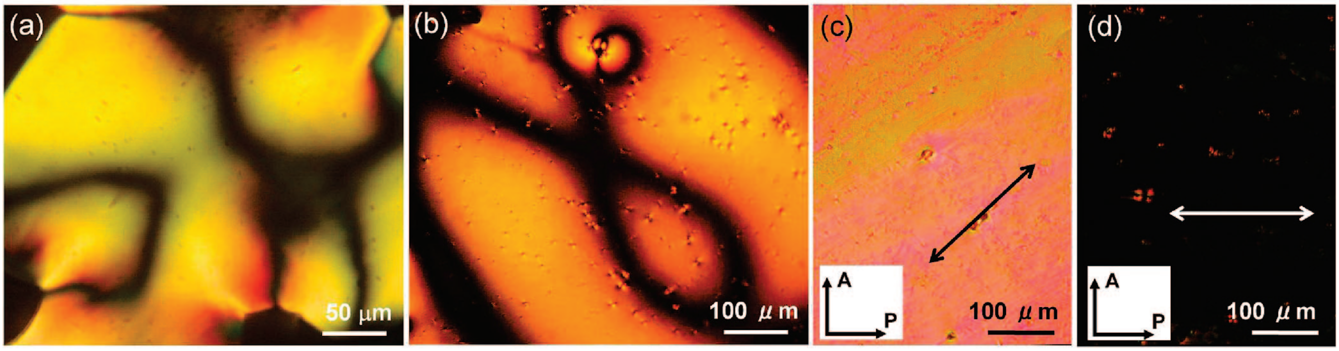
The photoisomerization of the dithienylethene moiety upon irradiations of UV and vis light was examined by ^1H NMR measurement in $CDCl_3$. Two broad signals observed at 5.30 and 5.34 ppm were assigned to the methylene protons neighboring to the dithienylethene moiety with open form. Irradiation of UV light ($\lambda = 254$ nm, 16 W) caused the photoisomerization, giving new broad signals at 5.05 and 5.08 ppm corresponding to the methylene protons neighboring to the dithienylethene moiety with closed form. The integrated intensities of the proton signals indicated the open forms of 47% and 42% were converted into the closed forms in the photostationary states (PSS) of **P1** and **P2**, respectively. Therein, the PSS is defined as {[closed form]/([open form] + [closed form])} × 100[7a,16] (see Supporting Information). In other words, the dithienylethene moieties of 53 and 58% remained unchanged in the open forms of **P1** and **P2**, respectively, even by UV light irradiation. After the subsequent irradiation of vis light ($\lambda > 400$ nm, 100 W), all signals of the open forms reappeared. The values of conversion in the PSS were similar to that in the monomer **5**. Note that since the closed form is not completely formed even after UV light irradiation, the expression of the PSS will be used hereafter instead of the closed form.

3.2. Liquid Crystallinity of Polymers.

Phase transition behaviors of **P1** (open form) and **P2** (open form) were elucidated through polarizing optical microscope (POM). Parts a and b of Figure 1 show POM photographs of **P1** (open from) and **P2** (open form), respectively. Schlieren textures observed are characteristic of nematic LC phase. The liquid crystallinity of the polymers was observed in both hearting and cooling processes, indicating an enantiotropic nature. This suggests that the polymers have a main-chain-type liquid crystallinity and might be macroscopically aligned to form a monodomain structure in the LC temperature. Phase transition temperatures of **P1** (open form) and **P2** (open form) were G 95 °C (85) N over 200 °C (over 200 °C) Iso, and those of **P2** (open form) were G 65 °C (60) N over 200 °C (over 200 °C) Iso (G = glassy, N = nematic, Iso = isotropic; parentheses denote the transition temperatures in the cooling process). No sharp peak associated with the phase transition was observed in differential scanning calorimetry (DSC) measurement, which may be due to high viscosity of the polymers.[17]

3.3. Absorption and Fluorescence Changes of Polymers.

P1 and **P2** dissolved in $CHCl_3$ showed absorption bands at 423 and 426 nm, respectively, corresponding to $\pi-\pi^*$ transitions of the polymer main chains. The band at 256 nm in the open form of the dithienylethene moiety decreased in intensity upon the irradiation of UV light for 1 min. At the same time, the shoulder band around 350 and 550 nm due to the closed form of the dithienylethene moiety gradually increased in intensity. Subsequent irradiation of vis light for 5 min after that of UV light caused an increase in intensity for the band at 256 nm and a decrease for the shoulder around 550 nm, as shown in Figure 2a,c. On the other hand, the cast films of **P1** and **P2** had the absorption bands due to conjugated main chains at 430 and 458 nm, respectively, as shown in Figure 3a,d. It is worthy noting that **P2** showed a large red shift by 32 nm in the absorption band of the main chain after the formation of the cast film form the solution, though **P1** had a very small red shift by 7 nm. This may be due to the fact that the interchain π-stacking to enhance the



P1 (open form) **P2** (open form) Aligned **P2** (open form)

Figure 1. Polarized optical micrographs of the cast film of **P1** (open form) at 70 °C in heating process (a) and that of **P2** (open form) at 86 °C in cooling process (b). The aligned films of **P2** (open form) at room temperature. The polarizer is set to have an angle of 45° (c) and 0° (d) with respect to the rubbing direction indicated by the arrow.

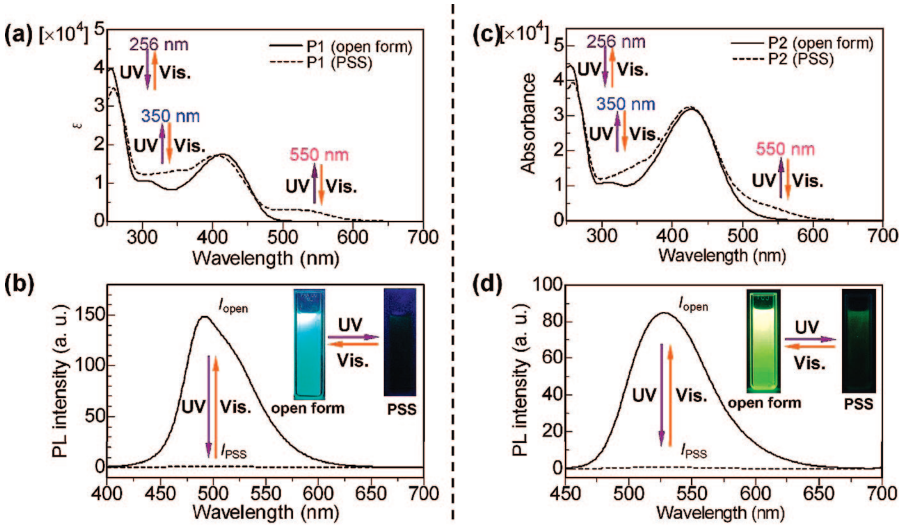


Figure 2. UV–vis absorption spectra of **P1** (a) and **P2** (c) and fluorescence spectra (excitation light of $\lambda = 350$ nm, 100 W) of **P1** (b) and **P2** (d) in $CHCl_3$ (4.0×10^{-5} M). Inset shows photographs of emitting and quenching between open form and PSS in solution (excitation light of $\lambda = 330-390$ nm, 16 W, handy lamp).

coplanarity of the main chain is more effectively formed in the cast film of **P2** than **P1**. Nevertheless, the photoisomerization between the open and closed forms was observed in both the films of **P1** and **P2**, similar to the cases of the solution.

The fluorescence band at 492 nm of **P1** (open form) and that at 524 nm of **P2** (open form) in $CHCl_3$ drastically decreased in intensity upon the irradiation of UV light for 1 min, leading to a phenomenon of quenching in fluorescence. However, the quenched fluorescence of the open forms was well regenerated by the irradiation of vis light for 5 min, as shown in Figure 2b,d. The ratio of fluorescence intensity (I_{open}/I_{PSS}) of between the open form and PSS was 123 for **P1** and 94 for **P2**. Fluorescence quantum yields of the open form and PSS, evaluated by using quinine sulfate in 1.0 M sulfuric acid as a standard compound, were 0.24 and 0.002, respectively, for **P1**, and those were 0.23 and 0.002 for **P2**. The quenching of the fluorescence might be due to an energy transfer through reabsorption, where the photon emitting from the excited main chain is absorbed by the dithienylethene moiety of the closed form. The excited dithienylethene moiety, however, releases the photon through nonradiative transition. This causes the apparent disappearance of the fluorescence in the closed form. The above argument can be supported by the fact that the fluorescence band of the main chain at 492 nm (**P1**) or 524 nm (**P2**) is very close to the absorption band around 550 nm of the dithienylethene moiety in the closed form. A similar quenching in fluorescence was also observed even in the cast film, as seen in Figure 3b,e. The demonstrative photographs of emitting and quenching in fluorescence of **P1** film upon irradiations UV and vis light are given in Figure 4 (see also movies 1 and 2 in the Supporting Information). The ratio of fluorescence intensity (I_{open}/I_{PSS}) at 539 nm between the open form and PSS in **P1** film was 261, and the corresponding value at 575 nm in **P2** film was 323. The values of I_{open}/I_{PSS}, i.e., the degree of the quenching, were 2 times (**P1**) or 3 times (**P2**) larger in the cast films than those in solutions. The reversible changes between the quenching and emission were repeated with more than 20 cycles in both films of **P1** and **P2**, as shown in Figure 3c,f. The fluorescence bands and the ratios of fluorescence intensities (I_{open}/I_{PSS}) of **P1** and **P2** are summarized in Table 1.

3.4. Macroscopic Alignment of Polymers. Next, we carried out the macroscopic alignment of **P1** (open form) and **P2** (open form) films by the rubbing technique.[18] The polymers on the quartz substrates were heated to the LC temperature region, and they were rubbed with a glass rod. Then the polymers were cooled to room temperature. It turned out that **P1** (open form) gives no macroscopic alignment in spite of having the liquid crystallinity. On the other hand, **P2** (open form) was well aligned parallel to the rubbing direction to give a monodomain structure, as shown in Figure 1c,d. The optical texture of the aligned **P2** film was preserved even in the glassy state. It is understood

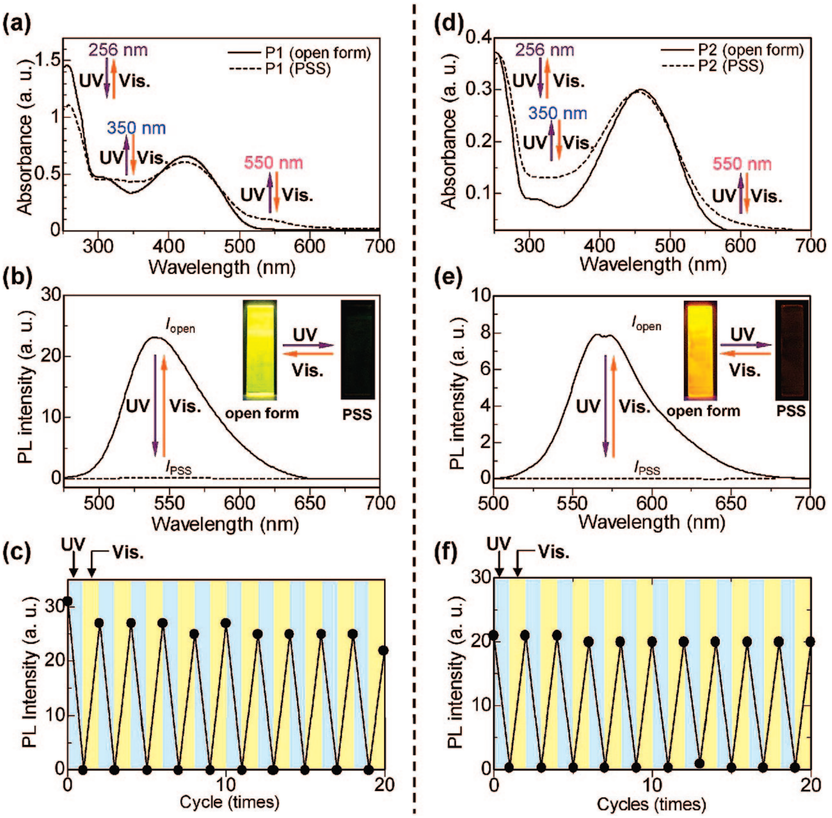


Figure 3. UV–vis absorption spectra of **P1** (a) and **P2** (d) in cast film. Fluorescence spectra of **P1** (b) and **P2** (e) in cast films. Insets show photographs of emitting and quenched films in open form and PSS (excitation light of $\lambda = 330-390$ nm, 16 W, handy lamp). Reversible changes of fluorescence intensities of **P1** at 539 nm (c) and those of **P2** at 575 nm (f) in cast films upon alternative irradiations of UV (blue area) and vis (yellow area) light.

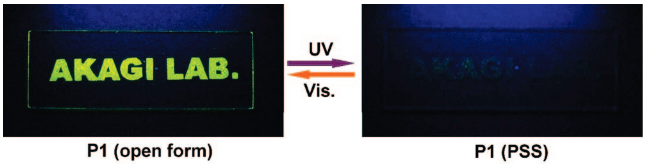


Figure 4. Photographs of emitting (left) and quenching (right) in fluorescence (excitation light of $\lambda = 330-390$ nm, 16 W, handy lamp) of **P1** film upon irradiations of UV and vis light. The polymer has been cast in the area of "AKAGI LAB" of the glass substrate by masking other area (see also movies 1 and 2 in the Supporting Information).

Table 1. Optical Fluorescence and the Ratios of Fluorescence Intensities between Open and PSS of the Dithienylethene Moiety in $CHCl_3$ and Film of the Polymers (P1 and P2)

	in $CHCl_3$		film	
polymer	E_m (nm)[a]	I_{open}/I_{PSS}	E_m (nm)[b]	I_{open}/I_{PSS}
P1	492	123	539	261
P2	524	94	575	323
∥ (parallel)			575	310[c]
⊥ (perpendicular)			575	480[c]

[a] Excitation at 350 nm. [b] Excitation at 380 nm. [c] The ratios of linearly polarized fluorescence intensities between open form and PSS in the parallel ($I_{\parallel,open}/I_{\parallel,PSS}$) and perpendicular ($I_{\perp,open}/I_{\perp,PSS}$) components of the aligned **P2** film.

that the main chain of **P2** consists of bithienylene−phenylene unit which can be regarded as a mesogenic moiety, and hence it is aligned parallel to the rubbing direction.

3.5. Linearly Polarized Fluorescence Change of P2. Since only **P2** showed macroscopic alignment, we will hereafter focus on the aligned film of **P2** as the material with a linear dichroism. Figure 5 shows linearly polarized fluorescence (LPF) of the aligned film of **P2** (open form), in which the polarizer was placed parallel or perpendicular to the rubbing direction.

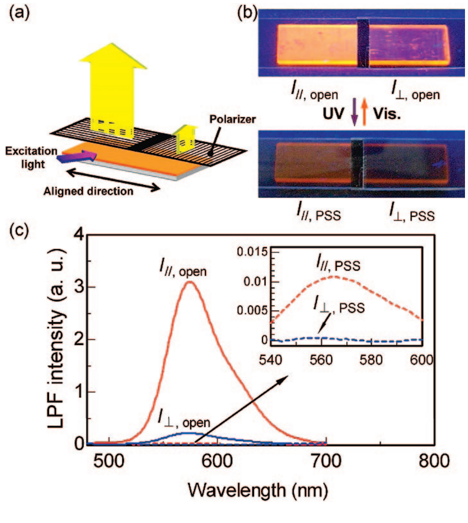


Figure 5. (a) Schematic illustration of linearly polarized fluorescence (LPF). The aligned **P2** film on the quartz substrate (size: 10 × 35 mm) shows LPF upon an irradiation of excitation light ($\lambda = 330-390$ nm, 16 W, handy lamp). Two polarizers are arranged parallel and perpendicular to the aligned direction of the film (right). (b) Both the parallel and perpendicular components of LPFs are reversibly switched in intensity between the open and PSS forms, by the irradiations of UV ($\lambda = 254$ nm, 16 W, handy lamp) and visible ($\lambda > 400$ nm, 100 W) light (left). (c) Spectroscopic changes of LPFs of the aligned **P2** film. Inset shows the expanded spectra of LPFs in the PSS form.

The LPF intensity at 575 nm under the nonpolarized excitation light ($\lambda = 380$ nm) in the parallel direction ($I_{\parallel,open}$) was larger than that in the perpendicular one ($I_{\perp,open}$). Dichroic ratio (R) and order

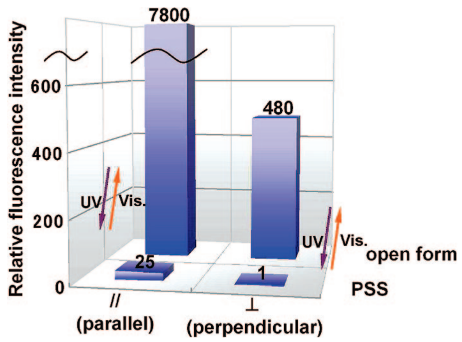


Figure 6. Relative intensities in fluorescence at 575 nm of the open form and PSS in terms of parallel and perpendicular components of aligned **P2** film.

parameter (S) of the aligned film (open form) were evaluated to be 16.0 and 0.83, respectively, where R and S are defined as $R = I_{\parallel,\text{open}}/I_{\perp,\text{open}}$ and $S = (R - 1)/(R + 2)$, respectively. It is evident that the aligned **P2** film has a high anisotropy in LPF and a high order parameter comparable to those of upper limits in nematic LC polymers. It is of keen interest that the parallel fluorescence of **P2** at 575 nm for the open form ($I_{\parallel,\text{open}}$) was quenched in the PSS and well recovered by vis light irradiation. The ratio of LPF intensity between the open form and PSS in the parallel direction, ($I_{\parallel,\text{open}}/I_{\parallel,\text{PSS}}$) was more than 310, which is comparable to that (323) of the nonoriented film. Similar emission and quenching phenomena were observed in the perpendicular intensities between the open form ($I_{\perp,\text{open}}$) and PSS ($I_{\perp,\text{PSS}}$), where the ratio was more than 480. The ratios of LPF intensities of the aligned **P2** film are also summarized in Table 1. It is found that LPF of the aligned **P2** film is photochemically switched by irradiations of UV and vis light. Taking account of LPF intensities in terms of the open form and PSS, and also the parallel and perpendicular components in the aligned film, the relative intensities at 575 nm of $I_{\parallel,\text{open}}$, $I_{\perp,\text{open}}$, $I_{\parallel,\text{PSS}}$, and $I_{\perp,\text{PSS}}$ were evaluated to be 7800, 480, 25, and 1, respectively, as schematically described in Figure 6. This implies that four kinds of fluorescence intensities are realized in a polymer and even controllable by using both LC-based macroscopic alignment and photochemical switching ability.

4. Conclusion

The novel photoresponsive LC poly(*p*-phenylene−vinylene) [**P1**] and LC poly(bithienylene−phenylene) [**P2**] have been synthesized by introducing the dithienylethene moieties into the side chains. The emission and quenching in fluorescence of the main chains were reversibly switched through the photoisomerization of the side chains in both polymers. The macroscopically aligned **P2** film further exhibited the linearly polarized fluorescence with a notable dichroic ratio and also the reversible photoswitching behavior between the open and closed forms. This is the first report for realizing a reversible quenching and emitting behaviors in linearly polarized fluorescence by using liquid crystallinity and photoresponsive ability. The present photoresponsive LC conjugated polymers, especially **P2** having anisotropic luminescence, may be applicable for advanced optical memory devices with multi-read−write functions.

Acknowledgment. This work was supported by a Grant-in-Aid for Science Research in a Priority Area “Super-Hierarchical Structures” (No. 446) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Details for synthetic procedures and spectral data of **P1** and **P2**; photoswitching movies of **P1**. This material is available free of change via the Internet at http://pubs.acs.org.

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MA800132V