Control of Linearly and Circularly Polarized Fluorescences on Photoresponsive Liquid Crystalline and Chiral Conjugated Polymer

Hiroyuki Hayasaka¹, Kazuya Tamura², Kazuo Akagi¹*

¹Department of Polymer Chemistry, Kyoto University, Katsura Nishikyou-ku, Kyoto 615-8510, Japan Fax: 81-75-383-2599, e-mail: akagi@star.polym.kyoto-u.ac.jp ²Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

Fax: 81-29-855-7440

A photoresponsive chiral substituent consisting of dithienylethene moiety and chiral center was introduced into the side chain of bithienylene-phenylene copolymer. Reversible photoisomerization of the dithienylethene moiety was observed in both in CHCl₃ solution and in cast film. Fluorescence of the polymer was quenched when the photochromic moiety changed from an open form to a closed one upon an irradiation of ultraviolet light. The quenched fluorescence was recovered through the reverse photoisomerization using visible light. Polarizing optical microscope demonstrated that the polymer has a main chain type liquid crystallinity. The polymer aligned by a rubbing technique exhibited a linearly polarized fluorescence (LPF). The cast film of the polymer showed Cotton effects in the region of $\pi - \pi^*$ transition of main chain in both circularly dichroism (CD) and circularly polarized fluorescence (CPF) spectra. The anisotropic fluorescence was controlled by the photochemical switching.

Key words: conjugated polymer, liquid crystallinity, photoswitching, linearly polarized fluorescence, circularly polarized fluorescence

1. INTRODUCTION

 π -Conjugated aromatic polymers, represented by polythiophene, poly(p-phenylene) and poly(p-phenylenevinylene), are promising candidates for optical and electrical materials. Main chain or side chain type liquid crystalline (LC) conjugated polymers are attracting current interests. This is because they are easily macroscopically aligned by external perturbation in LC phase, giving anisotropic optical and electrical properties, such as linearly polarized absorption and fluorescence and anisotropic transport phenomena [1-5]. Besides, chiral or helical conjugated polymers are of recent interest since they afford circularly polarized fluorescence (CPF) as well as circularly dichroic absorption [6, 7]. On the other hand, it is known that the dithienylethene derivatives are one of the most feasible photochromic materials, because of their outstanding fatigue resistance, thermal stability and reversibility in photoisomerization [8]. If the above-mentioned functions, namely the liquid crystallinity, chirality, and photochromic nature, could be built into one conjugated polymer, so-called advanced multifunctional conjugated polymer would be generated.

In this study, we synthesized novel photoresponsive LC conjugated polymer, where the dithienylethene moiety linked with optical active alkyl group was introduced into the side chain of bithienylene-phenylene copolymer. It is expected that the polymer might exhibit not only main chain type liquid crystallinity to give a linear dichroism, but also a chirality responsible for a circular dichroism (CD), as well as a photochemical reversible isomerization. Therefore, the polymer would have linearly and circularly polarized dichroisms in absorption and fluorescence. These optical intensities can be changed by switchable photochemical

isomerization between the open and closed forms of the dithienylethene moiety in the side chain.

2. Synthesis

The synthetic route of the polymer is shown in Scheme 1. The dithienylethene derivative 3 and 5,5'-bis-trimethylstannyl-2,2'-bithiophene were synthesized according to literature procedures [9-11]. Methyl-[(R)-1-methyloctoxy]benzene 1 was synthesized coupling methyl *p*-hydroxybenzoate by with (S)-2-nonanol via Mitsunobu reaction in THF [12]. The hydrolysis of 1 with NaOH in a solution of methanol and water gave 4-[(R)-1-methyloctoxy] benzoic acid 2. The dithienylethene derivative 3 was reacted with 2,5-dibromobenzene to give 4. The esterification and between 2 4 in the presence of dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) gave monomer 5. Finally, the polymerization of monomer 5 and 5,5'-bis-trimethylstannyl-2,2'-bithiophene in the presence of palladium(0) as a catalyst were carried out through Still polycondensation reaction, giving photoresponsive and chiral substituted polymer, P1, P1 was fusible and soluble in organic solvents such as THF, toluene and CHCl₃. GPC measurement using THF as an eluent gave a number-average molecular weight (Mn) of 1.6×10^4 , a weight-average molecular weights (*Mw*) of 6.2×10^4 , and a dispersion ratio (*Mw* / *M*n) of 5.5. ¹H NMR measurement in CDCl₃ showed that the dithienylethene moiety has all open form. Irradiation of ultraviolet (UV) light (λ = 254 nm) resulted in photocyclization to the closed form with а photostationary state (PSS; [closed form] / ([open form] + [closed form]) × 100) of 30 % [13, 14]. Subsequent irradiation of visible (Vis.) light ($\lambda > 400$ nm) gave all



Scheme 1. Synthetic routes of the polymer. a) (S)-2-nonanol, DIAD, PPh₃, THF; b) NaOH, H₂O, MeOH; c) 2,5-dibromobenzoic acid, DIAD, PPh₃, THF; d) DCC, DMAP, CH_2Cl_2 ; e) 5,5'-bis-trimethylstannyl-2,2'-bithiophene, $Pd_2(dba)_3$, tri-2-furylphosphine, THF.

DIAD = diisopropyl azodicarboxylate, dba = dibenzylidenacetone, R* = chiral center-containing alkyl group

signals of the open form. These results imply that a reversible photoisomerization of the dithienylethene moiety occurs upon the irradiations of UV and Vis. lights.

3. Result and Discussion

Phase transition behavior of P1(open form) was examined through POM and DSC measurements. Figure 1(a) shows polarizing optical micrograph of P1(open form). Schlieren texture observed is characteristic of nematic LC phase. The polymer showed liquid crystallinity in both hearting and cooling process in wide range of temperature, indicating an enantiotropic nature. This suggests that the polymer might be macroscopically aligned to form a monodomain structure in the LC temperature. Phase transition temperatures of P1(open form) are as follows.

glassy
$$\frac{76 \text{ °C}}{60 \text{ °C}}$$
 nematic $\frac{250 \text{ °C}}{220 \text{ °C}}$ isotropic

No sharp peak associated with the phase transition was observed in DSC measurement. This may be due to high viscosity of the polymer [15].

P1(open form) dissolved in CHCl₃ showed an absorption band at 435 nm corresponding to $\pi - \pi^*$ transition of the polymer main chain, as shown in Figure 2(a). The band at 255 nm due to the open form of the dithienylethene moiety decreased in intensity upon an irradiation of UV light. At the same time, the shoulder band around 550 nm due to the closed form gradually increased in intensity. Subsequent irradiation of Vis. light after that of UV light caused an increase in intensity for the band at 255 nm, and a decrease for the shoulder band around 550 nm. Similar change in absorption intensity was observed in the cast film, as shown in Figure 2(b).

P1(open form) in $CHCl_3$ showed a green color fluorescence at 530 nm under the excitation light at 350 nm. The fluorescence of the polymer main chain decreased in intensity upon the irradiation of UV light at 254 nm. The fluorescence of P1(open form) was reproduced by the Vis. light irradiation. The ratio of fluorescence intensity (I_{open} / I_{closed}) between P1(open form) and P1(closed form) was 40. The quenching of the fluorescence should be due to a Förester type energy transfer [16], where the photon emitting from the excited polymer main chain is reabsorbed 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 case of the closed form.



Figure 1. Polarizing optical micrographs of the cast film (a) and the aligned films (b, c) of P1(open form). The polarizer is set to have an angle of 45° (b) and 0° (c) with respect to the rubbing direction indicated by the arrow.

The quenching mechanism is well understood by the fact that the fluorescence band of the polymer main chain around 530 nm is very close to the absorption band for the dithienylethene moiety in the closed form. Similar quenching in fluorescence was observed in the cast film. The ratio, I_{open} / I_{closed} in the cast film was 100 (see, Figure 4(a)). The value is two times higher than that in CHCl₃ solution. It is worthy of remark that both interchain energy transfer from the exited polymer main chain to the closed form of the dithienylethene moiety in the side chain and intrachain energy transfer of the polymer might have occurred simultaneously in the cast film.



Figure 2. Changes of UV-Vis. absorption spectra of P1 upon photoisomerizations in $CHCl_3$ (a) and in the cast film (b). CD spectra of P1 in the cast film (c).

We carried out the macroscopic alignment of P1(open form) by the rubbing technique: The polymer was heated to the LC temperature region on the quartz substrate, and then it was rubbed with a glass rod. The polymer was further cooled to room temperature to yield an aligned film. The polarized optical microscopy of the aligned film showed that the LC texture was maintained even in the glassy state, and the multidomain of nematic LC phase was uniaxially aligned along the rubbing direction, as shown in Figure 1(b) and (c).

In linearly polarized fluorescence (LPF) measurements, the polarizer was placed parallel and perpendicular to the rubbing direction of the sample. The LPF intensity at 570 nm on the parallel direction to the rubbing direction $(I_{ll, open})$ was larger than that in the perpendicular one $(I_{L, open})$, as shown in Figure 3. The dichloic ratio (*R*) and order parameter (*S*) of Pl(open form) were evaluated to be 11 and 0.83, respectively, where *R* and *S* are defined

as follows,

$$R = I_{H, \text{ open}} / I_{\underline{1}, \text{ opens}}$$
$$S = (R-1) / (R+1)$$

It is clear that the aligned polymer has a high anisotropy in LPF.



Figure 3. Changes of linearly polarized fluorescence (LPF) spectra of the aligned film of P1

The parallel intensity at 570 nm for the open form $(I_{H_{,open}})$ (the excitation light of 380 nm) was quenched in the photoisomerized closed form, and it was well recovered by the reverse photoisomerization. The ratio of LPF intensity between P1(open form) and P1(closed form) in the parallel direction, $(I_{H,open} / I_{H,closed})$, was 70, as shown in Figure 3. Similar linear dichroism was observed in the perpendicular intensities between the open form $(I_{1,open})$ and closed one $(I_{1,closed})$. It follows that LPF of the aligned film is photochemically switched with the irradiations of external UV and Vis. lights.

When the polymer was dissolved in CHCl₃ or THF, no circularly dichroism (CD) signal was observed. However, the cast film showed an exciton-coupled CD signal with positive Cotton effect in the region of $\pi - \pi^*$ transition of the main chain. After an irradiation of UV light, however, the CD signal showed no change in the closed form, as shown in Figure 2(c). This result suggests that the neighboring polymer main chains in the cast film have stable helical structures [17], which can be preserved even after the irradiations of UV and Vis. lights.

It is of keen interest that the CPF spectrum of the cast film also showed a positive Cotton effect around 570 nm corresponding to $\pi^* - \pi$ emission of the main chain. The positive sign of Cotton effect indicated that the fluorescence has a left-handed polarization. The intensity in CPF was also controlled through the photoisomerization of the dithienylethene moiety in the side chain, as shown in Figure 4(b). The degree of circular polarization in fluorescence was next evaluated by using a dissymmetry factor, g_{em} , which is defined by the following equation,

$g_{\rm em} = (I_{\rm L} - I_{\rm R}) / [(I_{\rm L} + I_{\rm R}) / 2] = \Delta I / I = V_{\rm AC} / V_{\rm DC}$

where I denotes the fluorescence intensity, R and L denote the right- and left-handed components, respectively, and V_{DC} and V_{AC} are intensities of fluorescence and CPF, respectively. As shown in Figure 4(c), the $g_{\rm em}$ values were estimated to be 5.4×10^{-2} and 3.7×10^{-3} at 570 nm in the open and closed forms of the dithienylethene moiety, respectively. It is also found from Figure 4(b) and (c) that CPF as well as the g_{em} drastically changed in accompany with the photoisomerization between the open and closed forms.



Figure 4. Changes of fluorescence (a) and CPF (b) spectra, and g_{em} factors (c) in the cast film of P1.

photoresponsive In conclusion. the novel LC-bithienylene-phenylene copolymer has been synthesized by introducing the chiral photoresponsive substituent into the side chain. The emission and quenching are reversibly switched through the photoisomerization of the dithienylethene moiety. The macroscopically aligned film and the cast film of the polymer exhibited LPF and CPF, respectively, as well as the photoresponsive switching behavior.

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5. References

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