Novel Photochromic Conducting Polymer Having Diarylethene Derivative in the Main Chain

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A conducting polymer having photochromic diarylethene units in the main chain was synthesized. Reversible photochromism was observed in solid film, and photoluminescence and electrical conductivity were found to change along with the photoisomerization.

Recently, conducting polymers which have extended π-conjugation in the main chain have attracted considerable interests from view points of both fundamental aspects of low-dimensional electron systems and also practical applications to organic electroluminescence (EL) devices and sensors.[1,2] The properties of conducting polymers depend on the π-conjugation length. It is, thus, of interest to introduce photochromic units which reversibly change the π-conjugation length by photoirradiation, in the main chain of conducting polymers.

In the present study, a novel π-conjugated polymer which has photochromic diarylethene units in the main chain, as shown in Figure 1, was synthesized and its photo-responsive behavior was studied. Among a number of photochromic dyes so far developed, diarylethene derivatives such as BFCP (1,2-bis(2-methyl-benzo[b]thiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene) (Figure 1 b) have notable features.[3] They undergo thermally irreversible and fatigue resist photochromic reactions. In the open-ring form, π-electrons are localized in the two benzo[b]thiophene units, while in the closed-ring form π-electrons delocalize throughout the molecule.

The photochromic units was copolymerized with fluorene units. Since poly(9,9-dialkylfluorene) is known as a conducting polymer which exhibits clear blue EL.[4] The alkyl groups at the fluorene moiety help the polymer to be soluble in common solvents. Polymer **1** was synthesized similarly to the previous paper.[5] The polymer was purified carefully by Shoxlet extraction with methanol, and by reprecipitation from chloroform/methanol for three times. Polymer **1** was soluble in chloroform, tetrahydrofuran, and other conventional organic solvents, and gave pale yellow color. The molecular weight of polymer **1** was Mn = 4600 and Mw = 6500 (based on the polystyrene standard in tetrahydrofuran). The sample films were prepared by spin-coating the sample solution on a glass or a quartz plates.

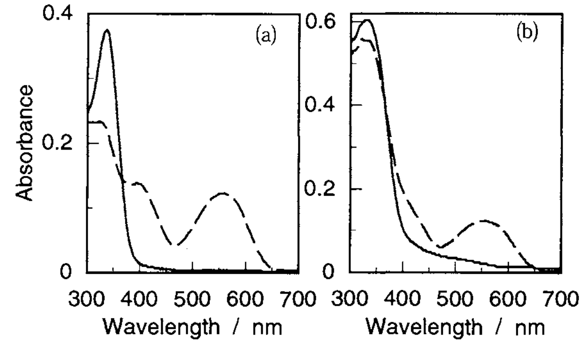

Figure 2. UV-vis absorption spectra of (a) polymer 1 in THF solution and (b) spin coated film of polymer 1 . solid line: in the original state, where all of the diarylethene units are in the open-ring form, broken line: at the photostationary state under irradiation with 313 nm.

UV/visible absorption spectra and photoluminescence spectra were measured with a spectrophotometer, Hitachi 3500 and a photoluminescence spectrometer, Hitachi F-3010, respectively. Electrochemical properties were measured in a conventional glass cell using silver and platinum wires as the reference and the counter electrodes, respectively. Acetonitrile and lithium tetrafluoroborate ($LiBF_4$) were used as the electrolyte solvent and salt, respectively. These reagents were purified before use and the electrochemical cells were prepared in an argon filled grove box.

Figure 2 shows absorption spectra of polymer **1** in (a) THF solution and of (b) spin-coating film. Before photoirradiation the absorption peak was observed at 340 nm in both phases and its threshold wavelength was around 400 nm. Upon irradiation with UV light (Hg lamp, 313 nm), the pale yellow film turned to dark red and an absorption band appeared at 560 nm. The closed-ring form of corresponding diarylethene molecule (BFCP) is known to give an absorption band at 520 nm.[3] Therefore, the absorption band at 560 nm is assigned to the closed-ring forms in the polymer main chain. It should be noted that broken lines in

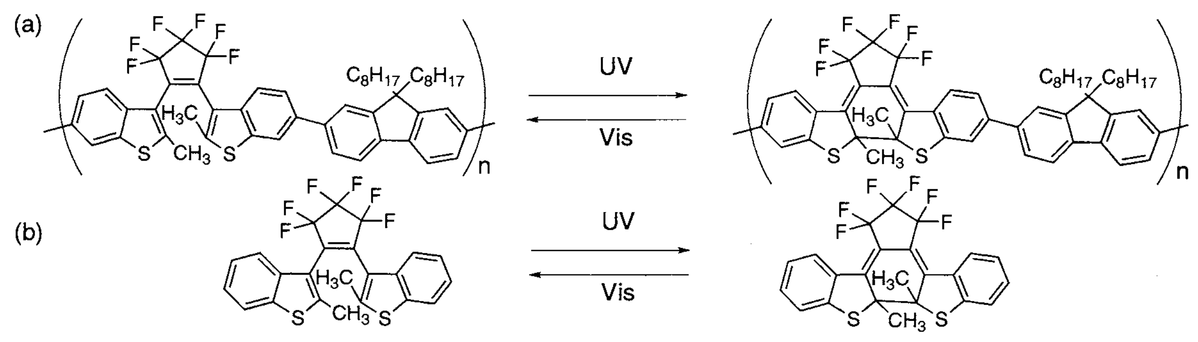

Figure 1. Photochromis of (a) polymer **1** and (b) BFCP.

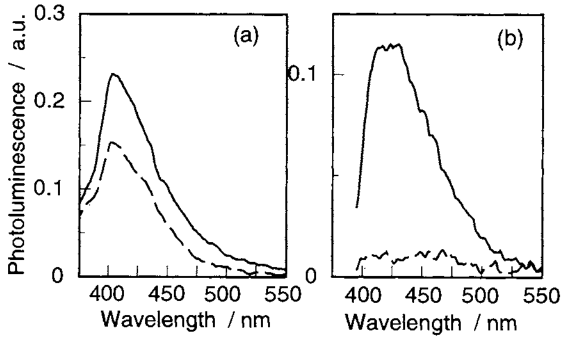

Figure 3. Photoluminescence spectra of (a) polymer **1** in THF solution and (b) in spin coated film of polymer **1**. solid line: in the original state, where all of the diarylethene units are in the open-ring form, broken line: at the photostationary state under irradiation with 313 nm. Excitation wavelength = 365 nm.

Figure 2 (a) and (b) are in the photostationary states under illumination with 313 nm light. The red-shift of the absorption maximum in the polymer **1** is attributed to slightly larger conjugation in the polymer. Upon visible light irradiation, the characteristic band at 560 nm disappeared and original absorption spectrum was recovered. The photochemical coloration-bleaching cycle could be repeated at least 20 cycles. The maximum conversion from the open- to the closed-ring forms in the film is about 11-14 % and that in solution is about 35-40 % on the basis of Figure 2 and also NMR spectra.

The polymer **1** exhibited clear photoluminescence at around 410 nm both in THF solution and in spin-coating film, as shown in Figure 3, where the samples were excited at 365 nm, isosbestic point in Figure 2. The blue emission was suppressed at the photostationary state upon irradiation with 313 nm light as illustrated with the broken lines in both phases. The closed-ring form has the second absorption band at 400 nm. The overlapping of the emission and the absorption bands suggests efficient energy transfer to the closed-ring form, resulting in quenching of the photoluminescence.[6] The original photoluminescence was restored by irradiation with $\lambda > 500$ nm light. The decrease in the photoluminescence intensity upon the photoisomerization was much remarkable in the polymer film than that in THF solution. The remarkable suppress in the polymer film indicates that the excited state migrates in the polymer film, and is efficiently quenched by the closed-ring form. Both intra- and and inter-chain energy migrations are considered to take place in the film.

The polymer film was formed on a quartz plate coated with ITO (indium-tin oxide) and electrochemical doping was carried out. The polymer having open-ring form diarylethene units showed anodic current wave at about 1.5 V vs. Ag and corresponding cathodic wave at about 1.4 V as shown in Figure 4 inset. The threshold potential of the anodic wave, which roughly corresponds to the top of the valence band in the case of conducting polymer, was about 1.35 V vs. Ag. Poly(9,9-dialkylfluorene) is known to show doping-undoping current waves at about 1.2 V vs. Ag, the observed current waves can be attributed to doping and undoping reaction of the fluorene units. Accompanying with the doping current wave the color of the polymer film clearly changes to red. A new absorption appeared at 510 nm and the absorption at 310 nm slightly decreased as shown in Figure 4. Photochromism was not observed in the doped state .

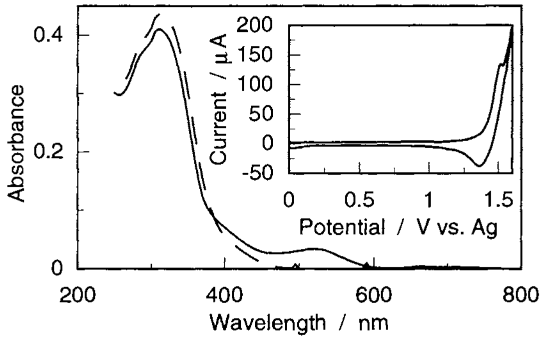

Figure 4. Absorption spectra of spin coated film of polymer **1** on a ITO-coated quartz plate. broken line: at potential 0 - 1.3 V vs. Ag solid line: at potential 1.35 V Vs. Ag (inset: cyclic voltammogram of polymer **1** coated electrode) Electrolyte: LiBF$_4$ (0.1M) - acetonitrile. Counter electrode: Pt wire , Reference electrode: Ag wire QRE (Eo = -0.2 V vs Ag/AgCl).

Effect of iodine doping on the electrical conductivity was also investigated. In this experiment, change in the resistance of the sample film was measured upon exposure of iodine vapor at room temperature. In the neutral state, the conductivity was originally 5.3×10^{-13} S cm^{-1} , while it increased up to 1.4×10^{-8} S cm^{-1} upon doping. The remarkable increase in the conductivity is attributed to generation of charge carriers in the polymer. It should be noted that the open-ring form diarylethene unit in the polymer dose not allow formation of polaronic quasi-particles in the main chain because π-conjugation is disconnected at 3-position of the thiophene rings. The transport mechanism of the polymer should not be based on polaronic charge carriers. Hopping of positive charges formed on the substituted fluorene units is considered to take place in the conduction mechanism.

The electrical conductivity of the polymer film having closed-ring unit was observed to be about 1.2×10^{-12} S cm^{-1} in the undoped state. In this measurement, the polymer solution was irradiated with 313 nm until the photostationary state (conversion was about 35%). Then the solvent (THF) was removed under dark condition. The twice larger conductivity in comparison with that in the open-ring form indicates that the closed-ring form allow π-conjugation in the polymer main chain.

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