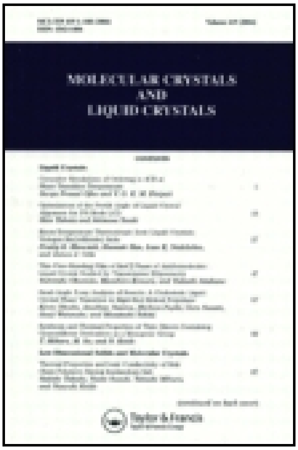

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Photocurrent Generation of Diarylethene Polymers

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Photocurrent Generation of Diarylethene Polymers

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The combination of photochromism and electrical properties in diarylethene (DA) polymers were investigated. Photoswitching function could be introduced into a polymer by incorporating 2,3-bis(2-methylbenzo[b]thiophene-3-yl)hexafluorocyclopentene (BTF) unit plus p*-phenylene vinylene (PPV) unit alternatively. The photochromic film of BTF-PPV polymer become dark colored upon exposure to a UV light because π-conjugation delocalizes between the π-conjugative groups and the new absorption band centered at 570 nm was observed from the colored film. In dark the photochromic electrode coated with BTF-PPV copolymer did not show current generation. Upon exposure to UV, large incident photon-to-current generation was observed with the quinone/hydroquinone carrier couple under a bias potential of 165 mV (vs. Ag/AgCl). By optical modulation, a reversible photocurrent generation was observed from the photochromic electrode. On the otherhands, DA polymers derived from 2,3-bis(2-methyl-3-thienyl)hexafluorocyclopentene (TF) and PPV showed no photocurrent generation, indicating photodecomposition of the closed isomer.*

Keywords: diarylethene; electrochemical properties; modulation; photochromic; photocurrent; photoswitching

INTRODUCTION

Photochromism has gained increasing interest as a tool to optically control various phenomena such as refractive index, fluorescence,

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and electrical conduction [1]. In particular reversible change in electrical conduction accompanied by the changes in color has became one of the important method for the development of organic electronic devices [2]. Such a function can be introduced into a molecule by incorporating a photochromic unit plus electrically active group such as polyene [3]. In our previous study we report DA polymers alternatively connected with a PPV [4]. Since PPV is a conjugative bridge, reversible modulation of the electrical properties could be achieved by reversibly interrupting the conjugation into a PPV unit through photochromic control of DA unit by irradiation at selected wavelength. Here in we report reversible modulation of photocurrent generation using DA main chain polymers, in which DA molecules are alternatively attached to a π-conjugative PPV unit.

EXPERIMENTAL

Materials

Two types of diarylethene polymers, BTF-PPV was synthesized from benzothiophene in three to four steps as reported previously [4]. Similarly, 2,3-bis(5-formyl, 2-methyl-3-thienyl)hexafluorocyclopentene was polycondensated with a Wittig salt of PPV to give TF-PPV (Mn = 6527, Mn/Mw = 1.61).

Preparation of Photochromic Polymer Electrode

To a mixture containing DA polymers (10 wt%) and polystyrene (PS) or PMMA (90 wt%) was added and stirred well to give a transparent and homogeneous solution. The solution was filtered using membranes of 0.45 μm pore size attached to a Teflon syringe, and the resultant solution was casted on an ITO glass. The polymer coated ITO glass was dried at 80°C for 12 h in a vacuum oven, to afford transparent and homogeneous film coated on the ITO glass, with typical coating thickness of 2 μm.

Instruments

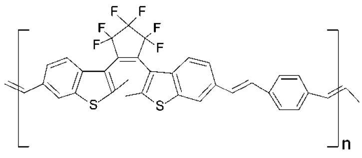
The photoelectrochemical experiments was carried out using a potentiostat-galvanostat (EG & G Princeton Applied Research PAR-273A) and a Xe lamp (Oriel) equipped with a monochromator. The working electrode was an ITO of area 1 cm^2. Platinum wire was the counter electrode, and Ag/AgCl (BAS) was used as the reference electrode. Electrolyte solution was consisted of aqueous solution of hydroquinone

(5 mM) and potassium hydrogen phthalate (0.2 M) buffer solution (pH 4.0). UV absorption spectra were recorded with a UV-2550 (Shimadzu Co.). The light sources for the photochromic conversion were UV lamp (365 nm, Spectronics Corp.) as a UV source, and 532 nm laser as a visible light source.

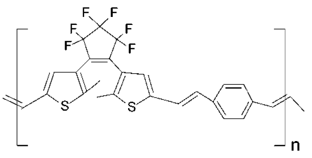
RESULT AND DISCUSSIONS

Photochromic Properties of Diarylethene-PPV Polymers

Wittig polycondensation of diformyl substituted BTF and TF, respectively, with a phosphosnium salt of PPV derivative gave DA main chain polymers, BTF-PPV and TF-PPV, respectively, in which DA units are alternatively connected by the PPV unit, as shown below:



BTF-PPV



TF-PPV

The polymers were soluble and showed photochromic conversion as shown in Figure 1. A new visible band centered at 570 nm and 690 nm, characteristic of a closed isomer were appeared for BTF-PPV and TF-PPV, respectively, upon excitation with a UV light. The color and band at in visible region of BTF-PPV were disappeared as the solution was irradiated by a visible light. However, the reverse reaction for TF-PPV was too slow to detect any change in color nor the absorption spectra even after extended excitation with a visible light.

The photochromic conversion was also effective in polymeric film, which was consist of 10 wt% of the DA polymers and 90% of PMMA

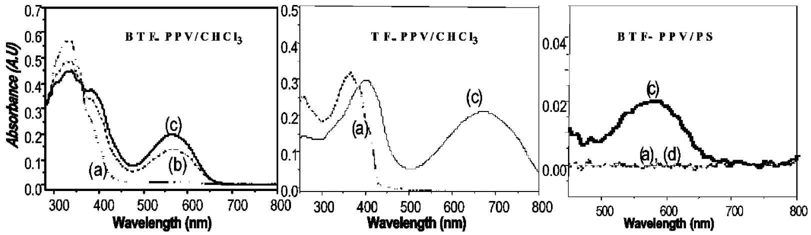


FIGURE 1 UV spectral change of DA polymers: (a) before, (b) after 3 min, (c) after 5 min of UV excitation at room temperature. (d) After visible excitation to (c). (DA polymer concentration in $CHCl_3$: $= 10^{-6}$ M; in PS $= 10$ wt%).

or PS. The photochromic film become dark colored upon exposure to a UV light with new band at visible region, as shown in Figure 1 for the film of BTF-PPV dispersed in PS.

The photo modulation of current generation was examined using Q/H_2Q redox couple by a photo-chronoamppherometry. In acidic electrolytes, quinones undergo a reversible multistage reduction-oxidation reaction according to the overall equation (1) [5]:

$$\mathrm{Q} + 2\mathrm{e}^- + 2\mathrm{H}^+ \rightarrow \mathrm{H_2Q} \tag{1}$$

Thus Q/H_2Q couples have been used as acceptors of electrons or holes (supersensitizer) from photoexcited dyes in dye-sensitized semiconductor photoelectrochemical cells [6]. In our study, DA polymers are mediators for the charge transfer from the electrode to the redox species in electrolyte. In the presence of reduced (oxidized) species in the electrolyte, which are able to accept a hole (electron) from the DA polymer, the photocurrents caused by redox processes of the Q/H_2Q couple should increase. The acceptors of holes (electrons) can be H_2Q (Q) molecules dissolved in the electrolyte.

The ITO glass electrode coated with BTF-PPV/PS polymer film was immersed in a liquid electrolyte containing Q/H_2Q redox couples. In dark the electrode did not show any current generation because the π-conjugative groups in the open-ring isomer, in which PPV unit are electronically separated from each other and there is no appreciable interaction between them.

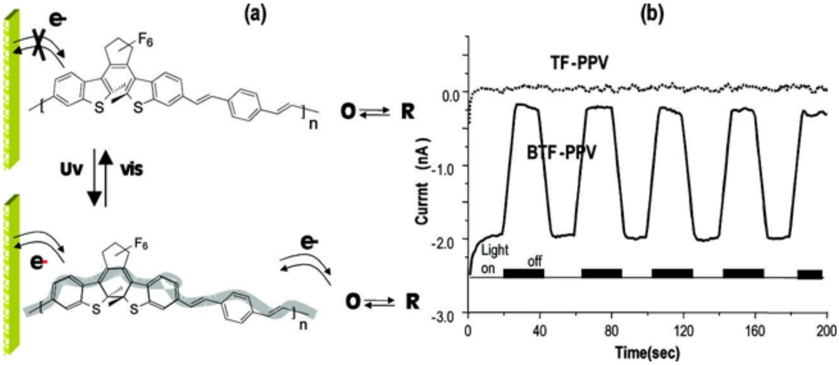


FIGURE 2 (a) Scheme of photocurrent generation from DA polymers in the presence of a redox couple (O/R = Q/H_2Q). (b) Photocurrent generation from BTF-PPV coated ITO glass electrode in Q/H_2Q solution.

However, upon UV exposure the ring of DA could be closed to extend π-conjugation as drawn in Figure 2 (a). Since holes (electrons) conduction became possible in the closed ring isomer, holes (electrons) could be transferred through DA polymers to the redox couple, to induce electrochemical reaction to generate photocurrent.

Indeed photocurrent of 1.7 nA/cm^2 was observed from the BTF-PPV (10 wt%)/PMMA electrode upon exposure to UV, under the bias potential of 165 mV (vs. Ag/AgCl) (Fig. 2b). The current generation was dropped completely when the light was off. The current generation was switched reversibly by switching light on and off, to allow optical modulation of current generation. On the other hands, an analogous DA polymer of TF-PPV (10 wt%)/PMMA electrode did not show such photocurrent modulation under the same condition. Since most thiophene derivatives without substituents at 4-position undergo decomposition reaction, the closed form of DA in the TF-PPV could undergo further reaction toward decomposed product [7]. Further characterization and optimization of photocurrent generation from DA polymers are in progress.

In conclusion, photo current switching was achieved by a photochromic main chain polymer, in which BTF units are connected to PPV units alternatively. By optical modulation, a reversible photocurrent generation was observed from BTF-PPV doped polymer electrode, indicating that the diarylethene-redox structure is a viable model for a photochromic electrochemical switch, to produce a reversible photocurrent generation in polymeric media.

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