

Photovoltaic effect of a thiophene substituted diarylethene polymer film

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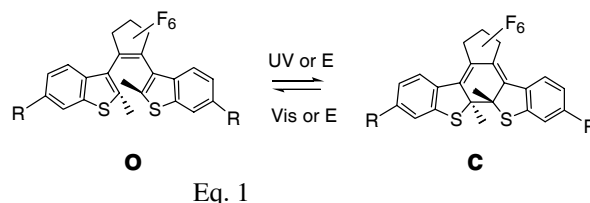
Abstract

Diarylethenes having thiophene unit show low oxidation potential to afford polymer film by electrochemical polymerization. The thickness of the polymer deposit on the electrode was conveniently controlled by the number of the potential cycles. The polymeric films showed reversible photocurrent generation property, by the alternative irradiation with a light. The photo-electrode prepared from a mixture of diarylethene and an electroactive monomer or nanoparticles showed much increased photocurrent generation with faster response. An all solid type photocell structure was prepared to show high open circuit voltage (Voc) of 0.79 V under a simulated sunlight (100mW/cm²).

Keywords: Photochromic, electrochemical polymerization, photocell, photovoltaic, photocurrent generation,.

Introduction

Photochromic molecules such as diarylethene have attracted much interest as a switching material as well as photoelectric materials.¹⁻⁷ Conversion from the central ring open to a closed structure by irradiation with UV light, it is possible to switch their properties not only in electronic absorption but also for various physical and chemical properties,⁷⁻¹⁰ which are important for electronic and photonic applications.¹¹ In particular, upon UV excitation, the π -system of two aryl rings are connected throughout the molecule in a closed-ring isomer (c), whereas they are separated in an open-ring isomer (o)¹²⁻¹³:



Thus, the oxidation potential of the **c** isomer is lower than that of the open-form (**o**) isomer,¹⁴ and there is a high possibility of oxidative coupling in the **c** isomer to lead anodic polymerization, which can offer a convenient method for the preparation of a photochromic diarylethene film.¹⁵ Furthermore, the resultant ring closed polymer showed lower oxidation potential, indicating that the ionization potential of the polymer become low. Thus photocurrent generation and voltaic properties of these diarylethene polymer could be explored. This paper reports on the film preparation and photovoltaic effect of redox active diarylethene polymers

Experimental Section

Instruments. The surface roughness of a polymer film was measured on an α step (TENCOR instrument, α step). The UV-Vis spectra were recorded for chloroform solutions with a AvaSpec (AvaSpec-2048, light source: AvaLight-DHS). The electrochemical and photoelectrochemical properties were studied using an electrochemical analyzer (CH Instruments Inc, CHI624B).

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The light source for the photovoltaic experiment and photocurrent generation were a UV light (PowerArc UV100, 100 mW/cm²).

Preparation of diarylethene polymer film

Diarylethene polymer films could be deposited on a conductive substrate such as ITO glass and ITO film by direct electro-deposition using an electrolyte solution containing diarylethene monomer substituted with thiophenes, additives (co-monomer or nanoparticles), and electrolyte. Dark purple film was deposited on the ITO glass and the film color was intensified as the potential cycles were continued as reported before. This indicates that polymer is deposited on the ITO glass (working electrode) by the electropolymerization of redox active diarylethene, as reported before.¹⁵ Figure 1 (a) shows the thickness growth of the polymer films. The growth is linearly dependent on the potential cycles indicating that the thickness of the film could be conveniently controlled by the number of the potential cycles. The thickness of the polymer film was 170 nm after 10 cycles, as determined by an alpha step.

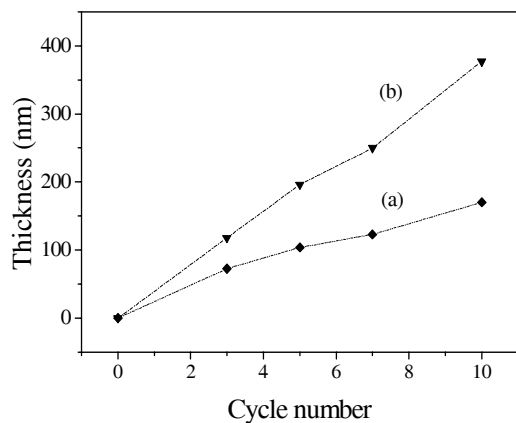


Figure 1. Growth of the polymer films by the potential cycles. After 10cycles, each film thickness reached to (a) 170nm (■) and (b) 377nm(▼) in the presence of additional monomer.

Interestingly in the presence of an electrochemically active monomer, the film thickness was much more increased than that of the homo polymer. This indicates the formation of copolymers in the presence of the additional monomer. Similarly diarylethene polymer film growth was observed when metal oxide nanoparticles were present in the

electrolyte solution. Thus the electro-polymerization of an electrochemically active diarylethene afforded convenient method for the preparation of diarylethene containing photo electrode.

Photo-current generation of the electrodeposited diarylethene polymer film

Photo-electrochemical measurements were performed in a buffer solution containing a quinone/hydroquinone (Q/H₂Q) redox couple by using the polymer deposited ITO electrode as a working electrode, Ag/AgCl as a reference, and a platinum wire as a counter electrode. In acidic electrolytes, quinones undergo a reversible multistage reduction-oxidation reaction.¹⁶ Figure 2 show a typical photocurrent response of the diarylethene polymer film under irradiation with a UV light.

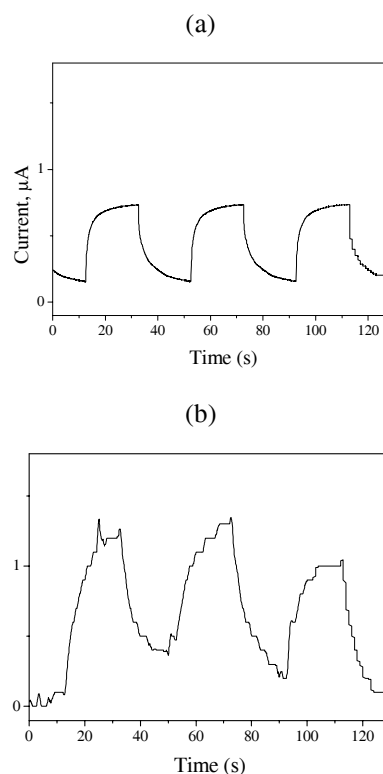


Figure 2. Photocurrent generation of the photo-electrode, immersed in a buffer solution containing hydroquinone, at a bias potential of +0.6 V under an alternative irradiation of a UV light.. The photo-electrode was prepared on an ITO glass from (a) diarylethene by electro-polymerization and (b) nanoparticles by spin coating of a nanoparticles dispersed solution.

The photo switching response was reversible by the alternative switching of the UV light on and off. The photo response time of the diarylethene polymer film was faster than that of a photo electrode prepared from nanoparticles as compared in Figure 2 (b).

Interestingly, the photo-electrode prepared from a mixture of monomer of diarylethene and an electroactive monomer showed much increased photocurrent generation with faster response (Figure 3 (a)) compared to that of homo polymer. Furthermore, the photo current generation was further increased when the electrode was prepared from a mixture of diarylethene and nanoparticles (Figure 3 (b)). This result indicates that the photoactivity of the diarylethene polymer film could be optimized by the film composition for the electro-polymerization.

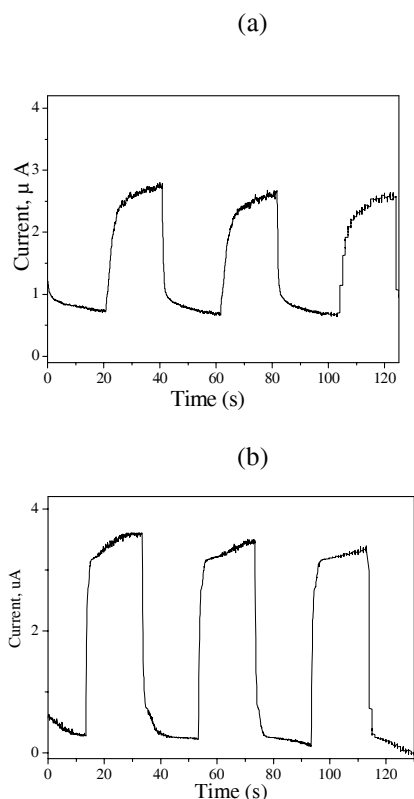


Figure 3. Photocurrent generation of the diarylethene polymer thin film, immersed in a buffer solution containing hydroquinone, at a bias potential of +0.6 V under an alternative irradiation of a UV light. The electrodes were prepared from (a) a mixture of diarylethene and a co-monomer by electro-polymerization and (b) a mixture of diarylethene and nanoparticles by electro-polymerization.

Photocells structured as counter electrode/polymer film/ITO glass and counter electrode/SPE/polymer film/ITO glass were prepared to examine photovoltaic effect of the diarylethene polymer film. A photocell structured as counter electrode/polymer film/ITO glass show high open circuit voltage (V_{oc}) of 0.79 V under a simulated sunlight ($100\text{mW}/\text{cm}^2$). The diarylethene polymer films prepared from different compositions showed enhanced photovoltaic properties. Optimization and mechanism of the photo activation in diarylethene polymer film deposited on ITO glass will be discussed

Conclusion

We prepared photoactive organic nano-thin films from electro-deposition of an electroactive diarylethene. The polymer film showed reversible photocurrent photo switching by UV light irradiation. The current generation from the polymer film was higher when the polymer was grown in the presence of additional electroactive monomer or nanoparticles, compared to the homo polymer film. The response time for the photocurrent switching was also a function of the additives, indicating the importance of film composition in photoactive films.

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Biography

Eunkyoung Kim received her BS degree in chemistry from Yonsei University in Seoul (Korea) in 1982, a master's degree in chemistry from Seoul National University in Seoul (Korea) in 1984, and PhD in chemistry from University of Houston in 1990. She worked for Korea Research Institute of Chemical Technology in Daejeon (KRICT) from 1992 to 2004. Since 2004, she has been a professor of chemical engineering at Yonsei University, Seoul, Korea. Her work has primarily focused on the development of functional polymers, including chromogenic polymers, photopolymers, and charge transport issues in polymeric media. She is an editorial committee (Macromolecular Research), committee member (Korea Polymer Society), and general manager (Korean Society for Imaging Science and Technology).