

A photoswitch from conjugative aromatic polymers

Taechang Kwon, Yong Jung Kim, Yuna Kim, Hyojin Lee,
Krishnamurthy Rameshbabu, Bhimrao D. Sarwade and Eunhyoung Kim*

Department of Chemical Engineering,
Yonsei University, 134 Shinchon-dong, Seodaemun-gu,
Seoul, 120-749, South Korea

Introduction

Polymers containing aromatic units have potential photo-electrical or electro-optical switching properties.^{1,5} The physical properties such as fluorescence, refractive index, and electrical properties of these polymers are changed in response to an optical or electrochemical stimuli and attract much interest as core materials for sensor and information processing devices. In our lab, many efforts have been made to design polymers containing two different functionality such as photochromism and emission, by covalently connecting different monomers having different functionality. For examples, photochromic fluorescent or photo-electroactive polymers containing π -electron systems have been synthesized for an organic switches.^{6,9} The polymers show multifunctional switching properties and provide the means to unveil how two different functionality of molecules interact in polymeric systems, leading emergence of adaptive and/or collective responses to external stimuli.

We present here the synthesis and photoswitching properties of aromatic polymers by condensing two different functional monomers.

Results and Discussion

Aromatic polymers having average Mw less than 10,000 were prepared by condensing two different functional monomers through Wittig polycondensation reaction. As synthesized polymers were soluble in an organic solvent showed significantly enhanced optical properties compared to its monomer. Variation in the monomer composition afforded polymers having multifunctionality such as photochromic-fluorescent polymers.

Conjugated- conjugated spacer-type polymers of diarylethene and *p*-phenylene vinylene (PPV) was synthesized to achieve photo-induced fluorescence and electrical change in a solid medium. The photo-isomerization of the polymer was induced by incorporating a 2,3-bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (BTF) unit, while trimethylsilyl-substituted *p*-phenylene vinylene (TPV) units directly connected to BTF allowed the extension of π -electron delocalization. The polymers were soluble in organic solvent and miscible with transparent binder such as polymethylmethacrylate (PMMA), polyvinylcarbazole (PVK) and polystyrene (PS), to allow solution processing using a spin coater for the film fabrication.

The polymer showed photochromism in solution as well as in solid media. New visible bands centered at 440 nm and 580 nm, characteristic of the closed isomer for BTF unit were appeared, upon excitation with a UV light. The visible bands were disappeared as the film was irradiated with a visible light. Such a coloration and bleaching were reversible and originated from the photoisomerization of BTF unit to a closed form by UV and ring opening reaction to an open form by a visible light, as reported before.

The polymers of BTF-TPV showed strong fluorescence in the open form, however, it decreased much in the closed form. The fluorescence switching of the film by a light was reversibly achieved by using two light source of UV and visible.

The conductivity of BTF-TPV was significantly increased when the BTF unit was converted to a closed form (colored) using UV light. The conductivity switching was reversible by using UV and visible-light sources.

As the coloured form of the polymer is more conductive than the colourless, the mobility switching is possible to generate new technological concept such as opto-tunable transistor. In addition, the electrode composed of the mainchain polymer could be utilized as a

photoswitch, a photoelectrode for a photo-induced electrochemistry and biology, or a photodiode that can switch photocurrent direction. Figure 1 shows photocurrent generation observed when the polymer coated ITO electrode was immersed in a solution containing quinine (Q)/hydroquinone(H₂Q) redox couple.

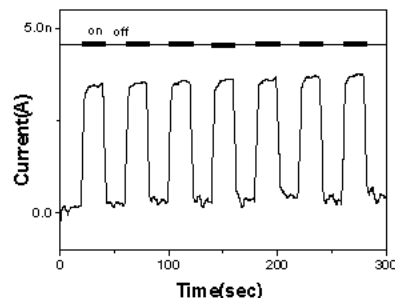


Fig. 1. Photocurrent generation from BTF-TPV coated ITO glass electrode in Q/H₂Q solution with a Hg/Xe lamp under switching time of 20 s.

Structural variation and the characterization of these photo switchable polymers are in progress, to understand the mechanism and optimize the switching efficiency.

ACKNOWLEDGMENTS

This work was conducted through a financial grant from the Ministry of Science and Technology (MOST) of Korea.

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