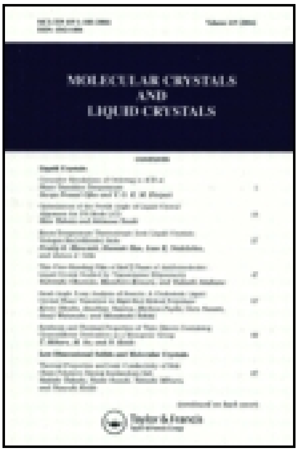

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Photochromic Polymer Films Prepared by Photocuring of Fluoroalkyldiacrylate and diarylethene derivatives

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Preparation of photochromic polymer films by photocuring methods was investigated using a solution of 2,2,3,3-tetrafluoro-1,4-butyldiacrylate (TFBDA) and diarylethenes (DA) in the presence of a photo initiator. The photopolymerization rate of DA mixture was highly dependent on the diarylethene structure. The rate was much faster in the mixture containing radical curable DA monomers than those without reactive group. Quantum yield for the photochromic cyclization was higher in the polymer film in which DA were chemically bound to the polymer network, than in the DA doped polymer films. Rewritable recording was attempted by using two light sources of UV and visible light.

Keywords photochromic; diarylethene ; quantum yield; photopolymerization; photocylization; erasable recording

INTRODUCTION

The idea of a photochromic switch to photochemically control various phenomena has gained recent interest due to its all-optical controllability. Such photochromic control is based on reversible structural changes of molecules on irradiation with suitable light. Among the photochromic molecules, diarylethene derivatives have attracted interest for their high photochromic efficiency and thermal stability[1]. The photochromic electrocyclic reaction of diarylethene represented below (eq 1) obeys to the Woodward-Hoffmann rules applied to the molecular orbital symmetries of cyclohexadiene (closed isomer) and hexatriene (open isomer).

(1)

Such photochromic reactions occur in solution as well as in solid phase. Since solid state polymer films containing photochromophores are a demanding media for device applications, the studies on the photochromic reactions of various types of photochromic dyes in the polymer matrices are of great importance from the view points of practical applications. In this paper we present simple preparation of photochromic polymer films by photocuring methods.

EXPERIMENTAL

Materials

Four types of diarylethene molecules were synthesized from benzothiophene in three to four steps as reported previously [2]. TFBDA was synthesized from 2,2,3,3-tetrafluoro-1,4-butanediol and acryloylchloride in the presence of triethylamine. Other chemicals and solvents were purchased from either Aldrich or Tokyo Kasei and purified according to the literature.

PREPARATION OF POLYMER FILMS

To a mixture containing TFBDA (88 wt%) and photoinitiator (2 wt%), DA (10 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 solution was casted on a substrate (silicon wafer, fused silica, or slide glass). The film was polymerized by exposure to UV light (365 nm) in 5-20 min. The coated films were dried at 80 °C for 12h in a vacuum oven to give transparent and homogeneous films.

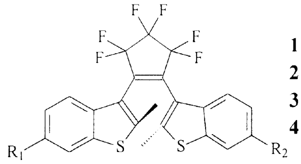
INSTRUMENTS

Photopolymerization rates for formulations with DA were determined by photo-DSC. The photopolymerization kinetics of the TFBDA containing each diarylethene derivative was monitored by a differential photocalorimeter (DuPont Instruments) equipped with a 365 nm monochromatic light source. The light source for the characterization of the photochromic property of polymer films was a Xe lamp (Oriel) equipped with a monochromator. The light sources for the photochromic recording were UV lamp (365 nm, Spectronics Corp.) or He-Cd laser (325 nm) as a UV source, and 532 nm laser as a visible light source.

RESULT AND DISCUSSIONS

Photocuring of diarylethene containing acrylic mixture

Diarylethene conataining polymeric films were prepared from a mixture of diarylethene, a fluoroalkylacrylate and a photoinitiator by irradiation with a UV light. As a fluoroalkylacrylate monomer 2,2,3,3-tetrafluoro-1,4-butyldiacrylate (TFBDA) was used due to its fast reactivity under radical polymerization condition plus optical clarity of the resultant polymer film. Chemical structure of diarylethene derivatives for photocuring solution are summarized below:



1; R_1: $-COCH_3$, R_2: $-H$
2; R_1: $-COCH_3$, R_2: $-COCH_3$
3; R_1: $-C(=O)OCH_2CH_2\,OC(=O)C(CH_3)=CH_2$, R_2: $-H$
4; R_1: $-COC_6\,H_4\,CH=CH_2$, R_2: $-H$

Transparent red colored films were obtained upon exposure to a UV light but bleached to a colorless when the film was left under room light or exposed to a visible light. The photopolymerization of TFBDA in the presence of diarylethene derivatives differs significantly depending on the structure of diarylethene. Figure 1 shows photopolymerizaton rate determined by a photo DSC [3].

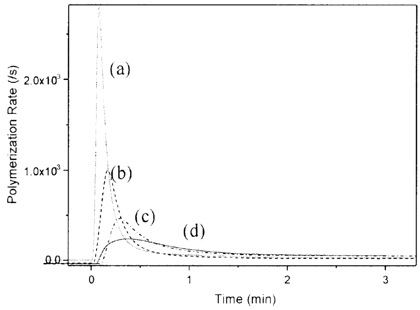


FIGURE 1. Polymerization rate of TFBDA solution (a) without diarylethene, with (b) **3**, (c) **1**, and (d) **2** by a UV light (365 nm).

The rate for TFBDA without diarylethene was faster than those with compounds **1-3**. This result indicates that photocyclization of diarylethene is much faster than the photo crosslinking of TFBDA. Interestingly, the rate for TFBDA with **3** was faster than the TFBDA solution containing **1** or **2**. The methacrylic unit in compound **3** could participate the crosslinking reaction of TFBDA, resulting in the increase in the polymerization rate. Since the polymerization rate of vinylic reaction has been known to be much faster than acrylic or methacrylic monomers under radical polymerization condition, the rate of polymerization for TFBDA containing **4** would be much faster than the TFBDA solution of **3** or TFBDA only. Indeed the rate of polymerization for the TFBDA solution of **4** was too fast to determine by photo DSC. Thus by changing the side chain structure of diarylethene, the photocuring reaction rate could be controlled.

Quantum yieild for photocyclization of diarylethene polymer films

The photochromic spectral changes in the UV-Vis absorption spectra of the photocured films are shown in Figure 2. Within a few minutes of irradiation, the film changed its color to red, which was bleached completely to an original colorless state upon irradiation with a visible light. Coloration by UV exposure was followed by absorbance increase at ~540 nm as shown in Figure 3. Quantum yields of the photochromic ring-cyclization ($\mathbf{\Phi_{pc}}$) can be determined from the changes of absorption bands due to ring-cyclization reactions, by calculating the degrees of conversion and the number of absorbed photons at the given radiation power and absorbance of the samples. $\mathbf{\Phi_{pc}}$ was determined from the linear region of the plot in Figure 3, using the equation (2-4).

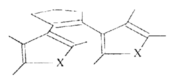
$$\Phi_{pc} = n / N \qquad (2)$$

$$n = n_0 f = n_0 (C_0 - C_\tau)/ C_0 \qquad (3)$$

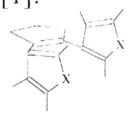
$$N = [I_0 (1\text{-}10^{-A})\ \tau\ \lambda]/(hc) \qquad (4)$$

where n is the number of the converted chromophoric unit for time τ, N the number of photons absorbed, I_0 the irradiation power, f the fraction of the converted chromophoric unit, A the absorbance at irradiation wavelength λ. [4]. The photocured film, in which diarylethens are doped, showed much lower quantum yield (0.0043 and 0.0050 for the film containing **1** and **2**, respectively) than that of the bound system (0.11 and 0.095 for the film containing **3** and **4**, respectively).

Under UV irradiation, the open isomer undergoes a ring-closure to yield colored isomer. The open isomer is predicted to exist in two different conformations of antiparallel (*ap*) and parallel (*p*) conformations having local symmetry of C_2 and Cs, respectively [1]:



antiparallel (*ap*)



parallel (*p*)

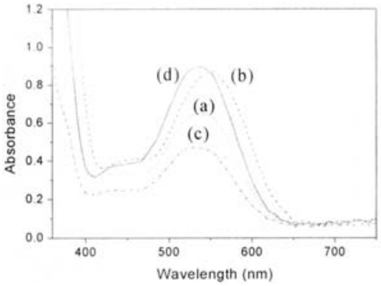


FIGURE 2. UV-Vis spectra of the film prepared from the solution of TFBDA and (a) **1**, (b) **2**, (c) **3**, and (d) **4**, under UV irradiation.

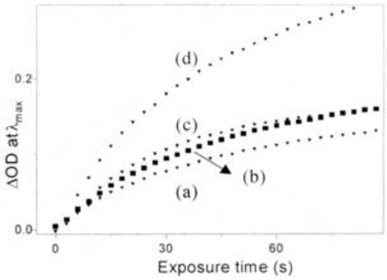


FIGURE 3. Absorbance increase at λ_{max} (~540 nm) of the film prepared from the solution of TFBDA and (a) **1**, (b) **3**, (c) **2**, and (d) **4**, under UV irradiation.

The *ap* conformation undergoes ring-closure reaction, while the conrotatory rotation in the *p* conformation is sterically hindered for the conrotatory ring closure. In the doped films (films prepared from the solution of TFBDA and **1** or **2**), diarylethenes are free of chemical bonding to TFBDA network and thus have higher chance to transform to the *p* form. However, in the bound system (film prepared from the solution of TFBDA and **3** and **4**), diarylethenes are covalently bound to TFBDA network and thus transformation from *ap* to *p* would be less favorable. Therefore in the bound system the population of open *ap* form would be higher as compared to the doped system, resulting in higher quantum yields.

Rewritable recording

Photochromic films prepared by photocuring methods were applied in an erasable photon-mode recording. Recording was possible with either a UV light source using a photocured colorless film or a visible light using a UV exposed film (colored). Figure 4 shows a photograph of a mask image transferred on a photocured colored film by writing with a 532 nm laser, indicating possible photon mode writing with a resolution of ~2 μm. The image was completely erased by irradiating with a UV light. New image was also recorded on the erased film. Recording cyclability was determined by analyzing optical response of the photocured film by switching with a UV (365 nm) and visible (532 nm laser) light sources. The initial optical contrast was not decreased even after 1000 cycles (Figure 5), from which we assume that the cyclability of diarylethene bound polymer film is over 10,000cycles. The recorded image was analyzed by a near IR light (> 700 nm) without destruction

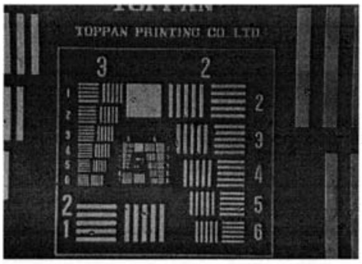


FIGURE 4. Photographs of photochromic recording with a 532 nm laser on a colored film containing **4**.

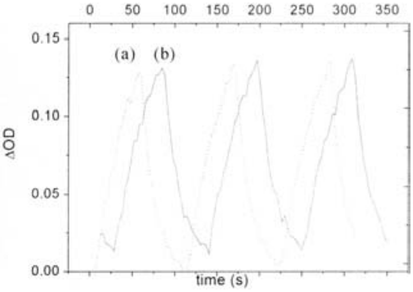


FIGURE 5. Reversible photochromic response of the film in Figure 4 on the UV and visible light: (a) initial 3 cycles and (b) after 1000 cycles.

of the original image.

In conclusion photopolymerization of a solution of TFBDA and DA in the presence of a photo initiator afforded photochromic films. Content of open *ap* isomers of DA was higher in a DA bound system as compared to a doped system, of which quantum yield was lower than the bound system. The photochormic films were applied in an erasable photon mode recording.

ACKNOWLEDGEMENTS

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