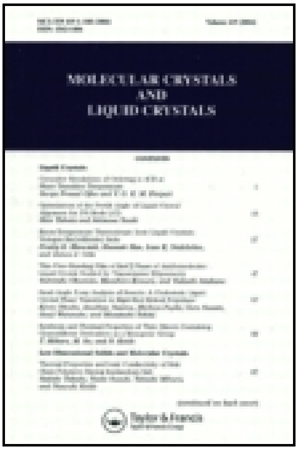

Molecular Crystals and Liquid Crystals

Effect of Photocrosslinking on Photochromism of Chalcone-based Polymeric Materials bearing Spiropyran Dye

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Effect of Photocrosslinking on Photochromism of Chalcone-Based Polymeric Materials Bearing Spiropyran Dye

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The epoxy oligomer was prepared to contain spiropyran in the side chain successfully. The rate of ring closure reaction of photochromic dye tethered in the side chain of the epoxy oligomer was controlled by virtue of [$2\pi + 2\pi$] photocycloaddition between the double bonds in the chalcone units and photopolymerization of epoxy group placed in the chain ends, which is expected to control the free volume surrounding photochromic moiety. The kinetic measurement was conducted to prove the improved photostability of the merocyanine chromophore that is colored species of spiropyran. In short, the cationic photopolymerization and photocrosslinking reaction were accompanied under illumination of the identical wavelength UV light.

Keywords: cationic photopolymerization; chalcone; interpenetrating network; photochromic behavior; photocrosslink; spiropyran

INTRODUCTION

Photoresponsive polymeric materials have recently attained much interest owing to their high responsivity, reversibility, broad-band sensitivity etc. Among many kinds of photoresponsive materials,

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photochromic compounds have attracted much attention because of their potential ability for various photoactive devices such as optical memory system, display device, optoelectronic devices [1–4]. Despite many advantages of photochromic materials, the reason of lacking practical applications, particularly organic functional compounds has poor stability of photochromism [5]. Although the extensive study on improving the durability for photochromic property in many dyes was performed, the stable compound still remains rather limited for real devices.

In this report, we suggest that photochromism of spiropyran dye can be affected by controlling the free volume around spiropyran units using the newly synthesized spiropyran-epoxy oligomer (SPEO) and chalcone-epoxy oligomer (CCEO). Spiropyran-epoxy oligonmer with a trace amount of triarylsulfonium hexafluoroantimonate (0.04%wt) undergoes cationic photopolymerization through the epoxy end groups [6,7]. Additionally, the photocycloaddition reaction of chalcone groups was also employed to control the free volume in the polymer blend matrix. Thus, the intermolecular photochemical reactions of photopolymerization and photocrosslinking control the rate of photochromism and retard the decolorization process.

EXPERIMENTAL

Synthesis of Spiropyran Precursor

Protective and deprotective reaction of 4,4-bis(hydroxyphenyl)valeric acid was performed according to the method in the literature [8]. The hydroxyl group was protected with 3,4-dihydro-*2H*-pyran in the presence of pyridium p-toluenesulfonate. (Compound 1, Yield, 65%) To a solution of compound 1 and N-ethoxyl-3′3′-dimethylspiro(2H-3-nitro-1-benzopyran-2,2′-indoline) in dry CH_2Cl_2 were added 4-(N,N-dimethylamino)pyridine and dicyclohexylcarbodiimide at 0°C under argon atmosphere. Compound 2 was separated with the silica-gel column chromatography (THF/hexane = 1/3) in 43% yield. The deprotection of pyran moieties was performed in the presence of *p*-toluenesulfonic acid monohydrate [8]. To an ethanol solution of pyran protected valeric acid-spiropyran compound in CH_2Cl_2 was added *p*-toluenesulfonic acid monohydrate at room temperature. The crude product was purified by silica-gel column chromatography (THF/hexane = 1/2) to afford 4,4-bis(hydroxyphenyl)valeric acid-spiropyran precursor (compound 3). Yield, 80%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 8.01 ~ 7.97 (m, 2H), 7.18 (dt, 1H, $J_1 = 8.0$Hz, $J_2 = 1.6$Hz), 7.09 (d, 1H, J = 7.2Hz), 6.99 ~ 6.97 (m, 4H), 6.89 (t, 1H, J = 7.2Hz), 6.83 (d, 1H, J = 10.4), 6.77 ~ 6.70 (m, 5H), 6.64 (d, 1H, J = 7.6Hz), 5.82 (d, 1H, J = 10Hz), 5.14 (br, 2H), 4.25 ~ 4.19 (m, 1H), 4.15 ~ 4.06 (m, 1H), 3.48 ~ 3.41 (m, 1H), 3.39 ~ 3.32 (m, 1H), 2.30 (m, 2H), 2.03(m, 2H), 1.50 (s, 3H), 1.26 (s, 3H), 1.14 (s, 3H).

Synthesis of Compound 4 (SPEO)

A solution of 4,4-bis(hydroxyphenyl)valeric acid-spiropyran precursor (2.48 g, 0.004 mol) and epichlorohydrin (3.70 g, 0.04 mol) in 30 mL of THF was stirred in room temperature. The 20 mL of aq. solution of NaOH (1 M) was added dropwise into the mixture and then refluxed for 24 hr under vigorous stirring. The reaction mixture was quenched in H_2O and extracted with CH_2Cl_2. The organic layer was washed with water and dried under Na_2SO_4. The crude product was purified by the precipitation with THF and hexane mixture. Yield, 54%. ^{1}H-NMR (400 MHz,$CDCl_3$): δ (ppm) 8.01 ~ 7.95 (m, 2H), 7.18 (t, 1H, J = 7.6Hz), 7.6Hz), 7.09 ~ 7.07 (m, 5H), 6.89 (t, 1H, J = 7.2Hz), 6.83 (d, 1H, J = 10.8Hz), 6.74 ~ 6.70 (m, 5H), 6.62 (d, 1H, J = 6.8Hz), 5.82 (d, 1H, J = 10Hz), 5.29 (br, 1H), 4.30 ~ 4.18 (m, 1H), 4.15 ~ 4.03 (m, 1H), 4.01 ~ 4.20 (m, 4H), 3.96 ~ 3.91 (m, 1H), 3.48 ~ 3.41 (m, 1H), 3.41 ~ 3.39 (m, 1H), 2.91 (t, 1H, J = 4.8Hz), 2.76 (dd, 1H, J_1 = 4.8Hz, J_2 = 3.2Hz), 2.32 ~ 2.28 (m, 2H), 2.05 ~ 2.01 (m, 2H), 1.67 (s, 3H), 1.26 (s, 3H), 1.14 (s, 3H).

Film Fabrication

For preparing the thin film on quartz plate, we prepared three different solutions using the photosensitive oligomers. SPEO (0.05 g) was dissolved in 1 mL of THF and the film was cast on the quartz plate (**Sample I**). SPEO (0.1 g) and CCEO (0.1 g) were mixed in THF (4 mL) and the film was cast on the quartz plate (**Sample II**). The **Sample III** was prepared using the solution of the sample II after adding a trace amount of triarylsulfonium hexafluoroantimonate (0.01 wt%). The prepared solutions were all filtered through acrodisc syringe filter (Millipore 0.2 μm) before casting the film. The films were dried at 70°C under vacuum for 12 hrs.

Instruments

Proton NMR was recorded with JEOL 300 NMR spectrometer. Deuterated chloroform ($CDCl_3$) was used as a solvent for recording the spectra. UV-Vis absorption spectroscopic study was performed on a Hewlett Packard 8453 spectrophotometer (PDA type, λ = 190–1100 nm).

All the films on quartz plates were irradiated with a 1 kW high pressure mercury lamp equipped with a liquid optical cable. Intensity of the UV light on the exposed surface was 29.2 mW/cm^2 ($\lambda = 250$–390 nm), which was measured with a broadband power/energy meter model 13PEM001 (MELLES GRIOT).

RESULTS AND DISCUSSION

Synthesis and Characterization

We synthesized the diepoxy oligomer containing the spiropyran dye in the side chain following the procedure as depicted in Figure 1. Pyran protected 4,4-bis-(4-hydroxy-phenyl)-pentanoic acid was reacted with hydroxy spiropyran compound. Then using p-toluenesulfonic acid, we removed the pyran group from the hydroxyl-protected compound. After deprotection of two pyran groups, we obtained compound 2 with a high yield (80%). Then, using the sodium hydroxide, we condensed the compound 2 with epichlorohydrin. The composition of the reaction mixture of 4,4′-dihydroxychalcone and epichlorohydrin was selected to be 1:10 in the presence of aqueous NaOH (40 wt%) solution. They are well soluble in many common organic solvents such as tetrahydrofuran, chloroform, ethylacetate, DMF, acetone, and methanol.

In order to determine the degree of polymerization, (n), we used the integration area of the chemical shifts of $-CH_2-$ in epoxy group and $-CH_3$ in the repeating group. The average value of n was ranged from 1.3–1.5 that indicates the two or three repeating group existed in the polymer main chain. For preparing the **sample II** and **III**, we employed the chalcone-epoxy oligomer (Figure 1) that was synthesized following the literature method [9].

Absorption Spectral Analysis of Photochromic Materials System

Spiropyran in the side chain of compound 3 (SPEO) undergoes ring opening and E/Z-transformation from the spiropyran form to their corresponding merocyanine by irradiation of UV light and *vice versa* by visible light or heat. Figure 2(A) shows the absorption spectral change of **SPEO** oligomer film (Sample I) during the UV irradiation ($\lambda = 250$–390 nm) in the film state. The colorized form of spiropyran in the film state shows the absorption maximum at 560 nm, which proves *trans*-conformation of merocyanine chromophore. The $\pi \rightarrow \pi^*$ absorption intensity of merocyanine chromophore at 560 nm increased gradually with the UV irradiation time.

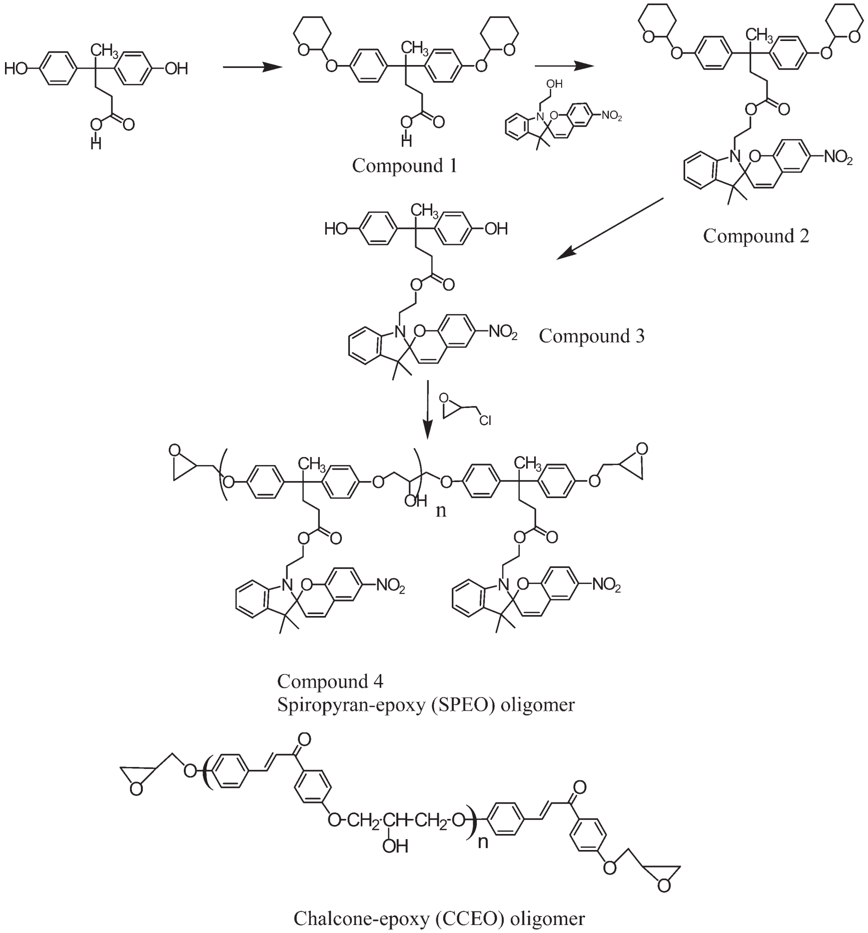

FIGURE 1 Synthetic procedure of spiropyran-epoxy oligomer (SPEO) and the structure of calcone-epoxy oligomer (CCEO).

Under illumination of UV light in **sample II** that contains SPEO and CCEO oligomer with an equimolar concentration (1:1), we could observe the photochromism in this film and also decrease of the absorption in the range of 345 nm which brought about the photocycloaddition of chalcone moieties in CCEO (Fig. 2(B)). The epoxy terminal end groups are photochemically inert even under long-term illumination of 365 and 560 nm light.

To improve the stability of photochromism in the merocyanine dye, we induced photopolymerization with cationic triarylsulfonium initiator through epoxy end groups in addition to photocrosslinking

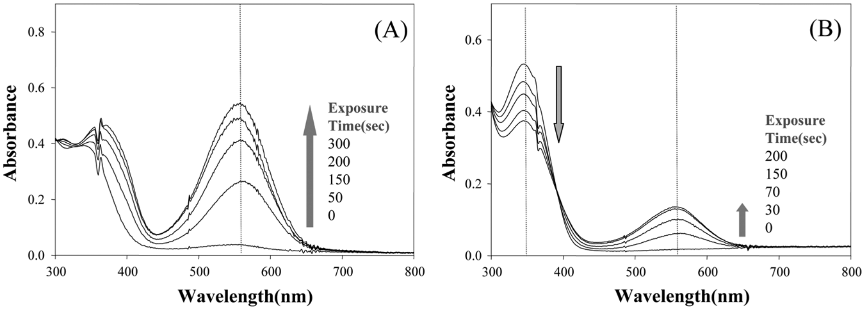

FIGURE 2 UV-Vis absorption spectral change of SPEO sample (A), and blend sample of SPEO and CCEO (B) during UV light irradiation ($\lambda = 365\,\text{nm}$).

reaction. Using this film sample (**sample III**), we irradiated the sample wavelength of UV light ($\lambda = 250$–$390\,\text{nm}$) to observe the photochemical reactions. First of all, the absorbance at 560 nm increases to imply the ring opening and E/Z transformation. Simultaneously, the absorption band of the chalcone moiety (λ_{max}: 345 nm) decreased which means the breakage of double bond in chalcone group during colorization under UV irradiation. Thus, the free volume surrounding the spiropyran unit needed for the ring closure process is expected to decrease significantly by $[2\pi + 2\pi]$ photocycloaddition of chalcone moieties that can reduce the distance between polymer chains. The kinetic study of photochromism was conducted to evaluate the effect of photoreaction on the ring closure process.

Stability of Photochromism in Three Different Samples After UV Light Exposure

The kinetic evaluation for photo-accelerated ring closure reaction of three samples (**sample I**, **sample II**, and **sample III**) were carried out by measuring the absorbance changes at λ_{max} during irradiation of the visible light ($\lambda = 632\,\text{nm}$) in the film state as shown in Figure 3.

The decaying curve of absorbance in **sample I** in Figure 3 shows the fastest ring closure reaction of spiropyran dye. In the case of **sample II** composed of the spiropyran-epoxy oligomer with chalcone-epoxy oligomer (CCEO), the rate of ring closure was much smaller than that in **sample I**. When we add cationic initiator into the **sample II** solution and cured it under 365 nm UV irradiation, the decaying rate in **sample III** was affected significantly by the photocrosslink of chalcone units and the cationic photopolymerization of epoxy group at both chain ends.

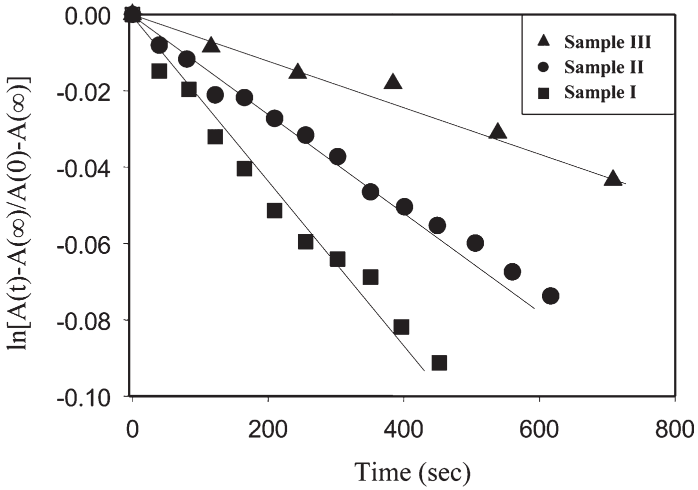

FIGURE 3 Change of absorbance at 560 nm during irradiation of He–Ne laser ($\lambda = 633$nm). *Sample I: SPEO only, Sample II: SPEO/CCEO, Sample III: SPEO/CCEO with triarylsulfonium hexafluoroantimonate (in propylene carbonate).

The rate of ring closure was measured in the film state by following the decrease of the absorbance at $\lambda_{\max}$ by way of the following single exponential decay function (1).

$$\ln[A(t) - A(\infty)/A(0) - A(\infty)] = -k\,t \tag{1}$$

where A(∞) is the residual absorbance after long term exposure and k is the rate constant. The calculated parameters were tabulated in Table 1.

In the photo-accelerated ring closure process, the rate constant, k of **sample III** is determined to be 0.0000574/sec that is the smallest

TABLE 1 Calculated Parameters for Ring Closure Reaction in Three Photochromic Polymer Systems. *Sample I: SPEO only, Sample II: SPEO/CCEO, Sample III: SPEO/CCEO with Triarylsulfonium Hexafluoroantimonate (in Propylene Carbonate)

	k/sec
Sample I	0.0002064
Sample II	0.0001209
Sample III	0.0000574

value compared to those of **sample II**(0.0001209/sec) and **sample I** (0.0002064/sec). This indicates that during illumination of UV light, photocrosslink between the chalcone moieties and photopolymerization through epoxy groups can be thought to reduce the distance between polymer chains further although the quantum efficiency of photochromism was relatively smaller than that of **sample I** due to two UV absorbing moieties. The ring closure reaction in **sample III** after UV irradiation becomes much more retarded comparing with that in **sample II** and **sample I** by virtue of increasing geometric hindrances owing to formation of intermolecular photoproduct of chalcone units and 3-dimensional network through epoxy groups. This residual merocyanine moiety in **sample III** the film would be surrounded and entrapped more densely by cyclobutane derivatives and polymer network so that it could not have enough free volume for backward reaction to the pristine spiropyran dye.

CONCLUSION

The inherent stability of photochromism in spiropyran dye is well known, which is relatively poor. Overcoming the disadvantage, we prepared new polymer hybrid system including photochromic spiropyran and photocrosslinkable moieties. The rate control of ring closure reaction of spiropyran dye was successfully achieved by virtue of $[2\pi + 2\pi]$ photocycloaddition and photopolymerization that are expected to control the free volume surrounding photochromic moiety. Spiropyran-epoxy and chalcone-epoxy oligomeric system showed effective retardation of ring closure reaction significantly by virtue of photocrosslink and photopolymerization.

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