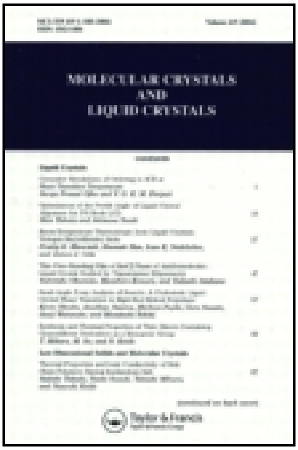

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EFFECT OF PHOTOPOLYMERIZATION AND PHOTOCROSSLINK ON THE PHOTOCHROMIC BEHAVIOR OF A HYBRID SYSTEM COMPOSED OF CHALCONE-EPOXY COMPOUND

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EFFECT OF PHOTOPOLYMERIZATION AND PHOTOCROSSLINK ON THE PHOTOCHROMIC BEHAVIOR OF A HYBRID SYSTEM COMPOSED OF CHALCONE-EPOXY COMPOUND

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The rate control of ring closure reaction of photochromic chalcone-epoxy doped with spiropyran dye was achieved successfully by virtue of [$2\pi + 2\pi$] photocycloaddition between the chalcone units of host polymer and photopolymerization of epoxy group at 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. The chalcone-epoxy polymer system that contains chalcone group in the repeating unit of the main chain was proved to retard ring closure reaction of merocyanine significantly by the effective steric hindrance after UV irradiation than that of methacrylate polymer containing chalcone in the side chain.

Keywords: chalcone; photochromic behavior; photocrosslink; photostability

INTRODUCTION

Polymeric materials have recently attained much interest as photoreactive materials. Among many kinds of photoreactive materials, photochromic compounds have attracted much attention because of their potential ability for various photoactive devices, such as optical memory system, display device, optic, and electro-optic component [1]. Despite many advantages of photochromic materials, the reason of lacking industrial applications of the

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*Corresponding author. E-mail: dhchoi@khu.ac.kr photochromic materials, particularly organic photochromic compounds is their poor stability of photochromism [2]. Although the extensive study on improving the durability for photochromic property in many dyes was performed, the stable compound still remains rather limited in practical applications.

Spiropyrans and spirooxazines are well-known photochromic compounds, which undergo ring opening and E/Z-transformation from the spiropyran form to their corresponding merocyanine form by irradiation of UV light and vice versa by visible light or heat [3]. Since the merocyanine form is much different from the pristine spiropyran moiety in their polarity and chemical structures, the colorization, and decolorization process would be affected with micro-environmental condition. There were extensive efforts to control the photochromic process that can be regulated by many factors such as solvent polarity, viscosity, ionic strength, steric effect of side groups and complex formation with cyclodextrins.

In this work, we suggested that photochromism of spiropyran dye could be affected by the control of the free volume around spiropyran units using the chalcone containing polymers. The photocycloaddition reaction of chalcone groups was employed to control the free volume in the polymer matrix. The photoreaction property of chalcone containing polymers was studied by our group which revealed the $[2\pi + 2\pi]$ photocycloaddition in the film state [4,5]. Thus, the intermolecular photochemical reactions in chalcone-epoxy compound can reduce the free volume surrounding merocyanine more effectively, which lowers the rate of photochromic process. The UV-Vis absorption spectral analysis and dynamic analysis of photoreaction kinetics were carried out to evaluate the effect of photoreaction in chalcone containing polymers on the stability of photochromism of spiropyran.

EXPERIMENTAL

Film Fabrication

For preparing the thin film on quartz plate, we prepared three different solution of photochromic polymer. 1 wt% of N-methyl spiropyran was mixed into PMMA(SP-PMMA). 50 wt% of N-methyl spiropyran was mixed into methacrylate homopolymer containing chalcone in the side chain(SP-MCP). The sample of spiropyran (50 wt%) doped chalcone-epoxy contains 4 wt% of triarylsulfonium hexafluoroantimonate(SP-CEP). The solutions were filtered through acrodisc syringe filter (Millipore 0.2 μm) and then cast on the quartz plate. The films were dried overnight at 75°C under vacuum and it was quite helpful for removing a trace of color completely.

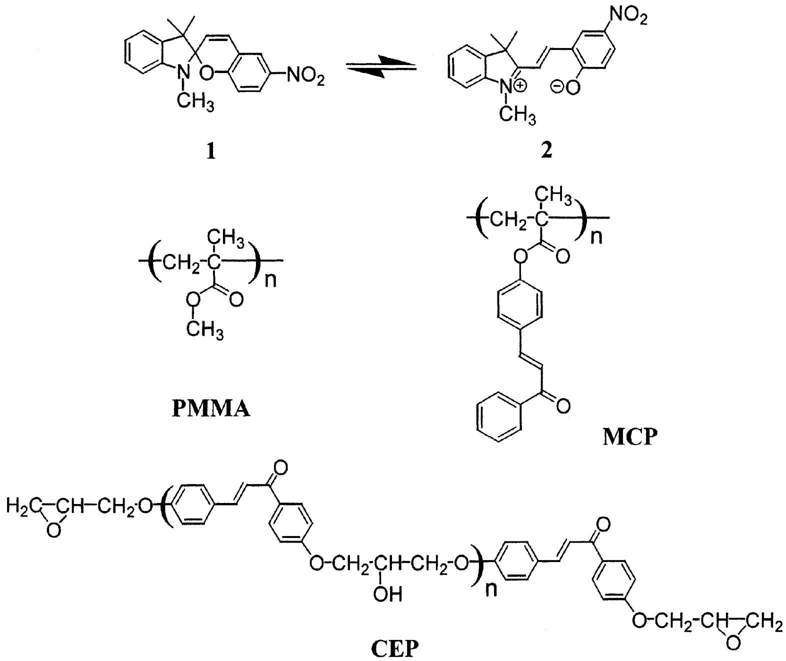
Instruments

UV-Vis absorption spectroscopic study was performed on a Hewlett Packard 8453 spectrophotometer (PDA type, $\lambda = 190$–$100\,\mathrm{nm}$). 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 $1.15\,\mathrm{mW/cm^2}$ ($\lambda = 250$–$390\,\mathrm{nm}$), which was measured with a broadband power/energy meter model 13PEM001(MELLES GRIOT). For irradiation of visible light, we used He-Ne laser ($\lambda = 633\,\mathrm{nm}$, $6.88\,\mathrm{mW/cm^2}$) in order to observe the ring closing behavior.

RESULTS AND DISCUSSION

Absorption Spectral Analysis of Photochromic Polymer Hybrid System

N-methyl spiropyran 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 (see Scheme 1).



SCHEME 1 The photochromic behavior of spiropyran molecule and the compounds used in this study.

To improve stability of photochromism in the merocyanine dye, we prepared the host polymers that contains chalcone moiety in the side chain (methacrylate-chalcone-polymer, **MCP**) and in the repeating unit of the main chain (chalcone-epoxy-polymer, **CEP**).

Figure 1 shows the absorption spectral change of **CEP-1** polymer hybrid system containing **CEP** and **1** 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 555 nm, which proves *trans*-conformation of merocyanine chromophore (see Scheme 1). The $\pi \rightarrow \pi^*$ absorption band of merocyanine chromophore at 555 nm increased gradually with the UV irradiation time. Simultaneously, the absorption band of the chalcone moiety (λ_{max} : 340 nm) decreased which means the breakage of double bond in chalcone group during colorization under UV irradiation. From the UV-Vis spectral analysis, we could expect 35–40% of maximum degree of crosslink that can be calculated from the variation of the absorbance at 340 nm approximately. Photoreaction of the chalcone chromophores was studied significantly by our group in the field of nonlinear optics, liquid crystal display, diffraction grating etc. which revealed that the chalcone moiety can be dimerized easily in their films and resulted in forming the

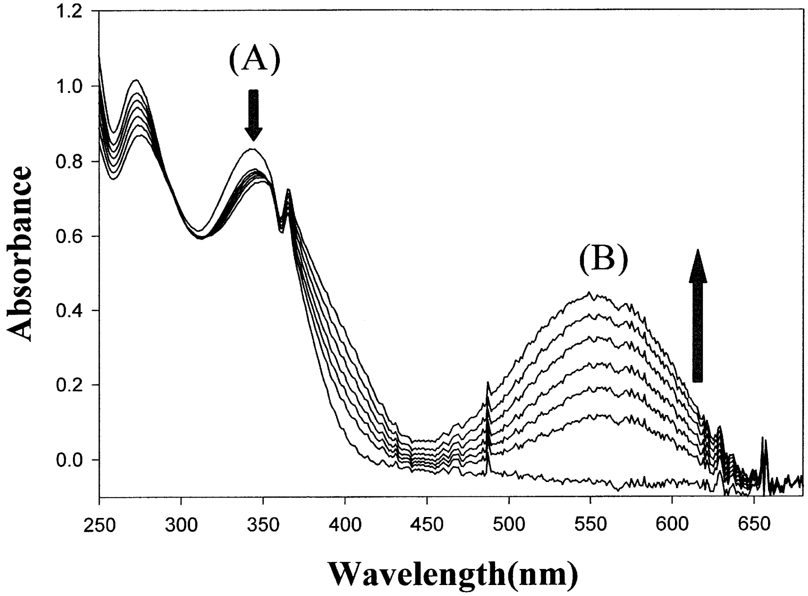


FIGURE 1 UV-Vis absorption spectral change of **SP-CEP** film during UV light irradiation. A : $\pi \rightarrow \pi^*$ transition band of chalcone group B: Absorption band of merocyanine.

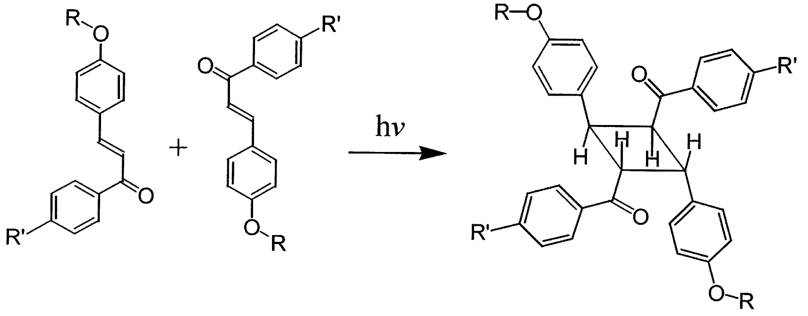
corresponding cyclobutane derivatives [4–6]. Thus, the free volume surrounding the spiropyran unit needed for the ring closure process is expected to decrease significantly by $[2\pi + 2\pi]$ photocycloaddition of chalcone moieties which can reduce the distance between polymer chains (see Scheme 2). This phenomenon could also be confirmed by way of the infrared spectral analysis in terms of the change and shift of the absorption band at $1655\,\mathrm{cm}^{-1}$ that is assigned to the unsaturated carbonyl stretching band in the chalcone group. The kinetic study of photochromism was conducted to evaluate the effect of photoreaction on the ring closure process.

Kinetics of Ring Closure Reaction

The kinetic evaluation of accelerated ring closure reaction of polymer hybrid system (**SP-PMMA**, **SP-MCP**, and **SP-CEP**) was carried out by the measurement of absorption $\lambda_{\max}$ changes at $\lambda_{\max}$ during irradiation of He-Ne laser ($\lambda = 632\,\mathrm{nm}$) in the film state as shown in Figure 2.

The decaying curve of absorbance at $\lambda_{\max}$ in **SP-PMMA** polymer system in Figure 2 shows the fastest ring closure reaction of spiropyran dye. In the case of **SP-MCP** composed of the chalcone-methacrylate polymer with chalcone group in the side chain, the rate of ring closure was smaller than that in **SP-PMMA**. On the other hand, the rate in **SP-CEP** system was affected significantly by the photocrosslink of chalcone units and the cationic photopolymerization of epoxy group at both chain ends. Two photochemical reactions in CEP were confirmed in our previous study [5].

The rate of ring closure was measured in the film state by following the decrease of the absorption band at $\lambda_{\max}$ with an aid of the following single exponential decay function (1) where A_r is the residual absorbance after long term exposure and k is the rate constant.



SCHEME 2 $[2\pi + 2\pi]$ photocycloaddition of chalcone derivatives.

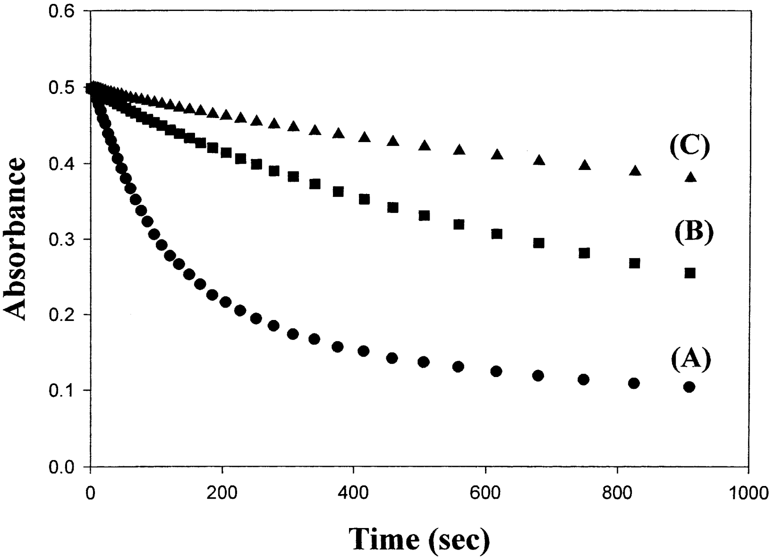


FIGURE 2 Change of absorbance at 555 nm during irradiation of He-Ne laser ($\lambda = 633\,\text{nm}$). (A) SP-PMMA; (B) SP-MCP; (C) SP-CEP

$$A(t)/A(0) = A_0 \exp(-kt) + A_r \qquad (1)$$

The calculated parameters were tabulated in Table 1. In the photo-accelerated ring closure process, the rate constant, k of **SP-CEP** is determined to be 0.00100/sec that is the smallest value compared to those of **SP-MCP**(0.00137/sec) and **SP-PMMA** (0.00711/sec). This indicates that during the irradiation of UV light, photoreaction between the chalcone moieties and photopolymerization through epoxy groups in **SP-CEP** reduced the distance between polymer chains further although the quantum efficiency of photochromism was relatively smaller than that of SP-PMMA due to two UV absorbing moieties. Thus, it reduces free volume

TABLE 1 Calculated Parameters for Ring Closure Reaction in Three Photochromic Polymer Systems.

	Decaying curve		
	A_0	k	A_r
SP-PMMA	0.7392	0.0071	0.2456
SP-MCP	0.6689	0.0013	0.3258
SP-CEP	0.3736	0.0010	0.6237

needed for transforming from *trans*-merocyanine into spiropyran dye. It could be saying that the ring closure reaction in **SP-CEP** after UV irradiation is much retarded compare with that in **SP-MCP** and **SP-PMMA** by increasing steric hindrances resulted from intermolecular photoproduct of chalcone units and photopolymerization through epoxy groups. Thus, residual concentration of the colored form after long-term decay of photochromism in **SP-CEP** is also much larger than that in **SP-MCP** and **SP-PMMA**. This residual merocyanine moiety in **SP-CEP** the film should be surrounded and entrapped more densely by cyclobutane derivatives so that it could not have enough free volume for backward reaction to the pristine spiropyran dye.

CONCLUSION

The inherent stability of photochromic property in spiropyran dye itself is well known, which is very relatively poor. Overcoming the disadvantage, we prepared new polymer hybrid system including photochromic spiropyran and photoreactive moieties. The rate control of ring closure reaction of spiropyran dye was successfully achieved by virtue of $[2\pi + 2\pi]$ photocycloaddition between the chalcone units, which is expected to control the free volume surrounding photochromic moiety. Chalcone-epoxy system (**SP-CEP**) that contains chalcone and epoxy in the main chain showed effective retardation of ring closure reaction significantly by virtue of photocrosslink and photopolymerization.

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