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Photochromic behavior of spiropyran in the photoreactive polymer containing chalcone moieties

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Abstract

The rate control of decolorization of photochromic chalcone containing polymer with spiropyran dye was achieved successfully by virtue of [2π + 2π] photo-cycloaddition between the chalcone units. The kinetic measurement was conducted to prove the photostability of the merocyanine chromophore that is colored species of spiropyran. The chalcone–epoxy polymer system that contains chalcone group in the repeating unit was proved to retard the decaying behavior of photochromism most effectively resulting from the steric hindrance after UV irradiation.

Keywords: Photochromic behavior; Spiropyran; Chalcone; Photocrosslink; Photopolyemrization; Photostability

1. Introduction

Photochemical reactions in organic materials can induce much change in physical properties such as solubility, optical property, dielectric constant, and refractive index, [1–4]. Therefore, it can be used in various photoactive devices, such as optical memory system, optoelectronic circuit, display devices, optic, and electro-optic component. Among many kinds of photoreactive materials, especially, organic photochromic compounds have attracted much attention because of their potential ability for many technological applications in molecular electronics to implement molecular optical switches and optical memory devices [5–9].

Although we can employ the photochromic materials to many applications, they usually show the poor stability of colored species. While the extensive study on improving the durability of photochromic property in many dyes was performed, the stable compound still remains rather limited in practical applications [10]. In this report, we suggested that the photochromic property of spiropyran dye could be controlled by the change of molecular structure surrounding the dye in the guest–host system.

On the other hand, the photoreaction property of chalcone containing polymers was studied much by our group, which revealed the [2π + 2π] photo-cycloaddition occurred in the film state, effectively [11–13]. Thus, the intermolecular

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cycloaddition between chalcone units in polymers can reduce the excluded volume surrounding spiropyran and merocyanine molecule, which lowers the rate of photochromic process, significantly, compared with that in a photochemically inert medium.

We have tried to control the rate of decolorization process of spiropyran with various ways changing the molecular environment of photochromic moiety [14]. When the spiropyran moiety should change their chemical structure (ring opening and *cis–trans* isomerization) to merocynine chromophore, a certain extent of free volume should be necessary to change their molecular structure and its shape. We believe that the photocrosslink of chalcone moiety can induce steric hindrance during the photochromism and it can also retard the rate of photochromic decolorization process, effectively. It was proved that the photocycloaddition of the chalcone groups in main chain polymer affects the decolorization of photochromic dye effectively than that in side chain polymer.

2. Experimental

2.1. Synthesis

We followed the literature methods for syntheses of compounds, spiropyran [*N*-ethoxyl-3′,3′-dimethylspiro(2H-3-nitro-5-methoxy-1-benzopyran-2,2′-indoline)], the side-chain chalcone polymer, and the main-chain chalcone polymer [15]

2.2. Film fabrication

For preparing the thin film on quartz plate, we prepared four different solutions bearing photochromic dye and polymers. (1) 10 wt.% of spiropyran dye was mixed into polymethylmethacrylate (SP–PMMA). (2) 50 wt.% of spiropyran dye was mixed into methacrylate homopolymer containing a chalcone in the side chain (SP–MCP). (3) 50 wt.% of spiropyran dye was mixed into chalcone epoxy polymer (SP–CEP). (4) 50 wt.% of spiropyran dye was mixed into chalcone epoxy polymer in the presence of 4 wt.% of triarylsulfonium hexafluoroantimonate as photoinitiator for epoxy ring (SP–CEPI). The solution (10 wt.%) of each mixture dissolved in tetrahydrofuran was filtered through acrodisc syringe filter (Millipore 0.2 μm) and then spin-coated on the quartz plate. The film was dried overnight at 80 °C under vacuum and it was quite helpful for removing a trace of color completely.

2.3. Instruments

UV–Vis absorption spectroscopic study was performed on a Hewlett Packard 8453 spectrophotometer (PDA type, $\lambda = 190$–1100 nm). For observing the photochromism of each sample, all the films on quartz plates were irradiated with a 1 kW high pressure mercury lamp equipped with a liquid optical cable and a bandpass filter (UG11, Oriel Co.). Intensity of the UV light on the exposed surface was 1.15 mW/cm^2 ($\lambda = 280$–390 nm), which was measured with a broadband power/energy meter model 13PEM001 (MELLES GRIOT). For observing the decolorization process, we irradiated the white light ($I = 1.0$ mW/cm^2) on the film sample. The experimental setup was built for investigating the colorization and decolorization (Fig. 1).

3. Results and discussion

3.1. Photoreactive polymer containing chalcone moieties

Photo-functional polymers containing chalcone moiety in the side chain (methacrylate chalcone polymer, MCP) or in main chain (chalcone epoxy polymer, CEP) behave as a negative photoresist resulting from the photocycloaddition, as is well known. Those polymers were synthesized following the known method. (Scheme 1).

When we synthesized CEP for casting the solid film, the composition of dihydroxychalcone and epichlorohydrin was carefully adjusted to get a high molecular weight. (e.g. dihydroxychalcone: epichlorohydrin = 1:20) Cycloaddition of chalcone was confirmed by the infrared spectral change during UV irradiation at 280–390 nm as shown is

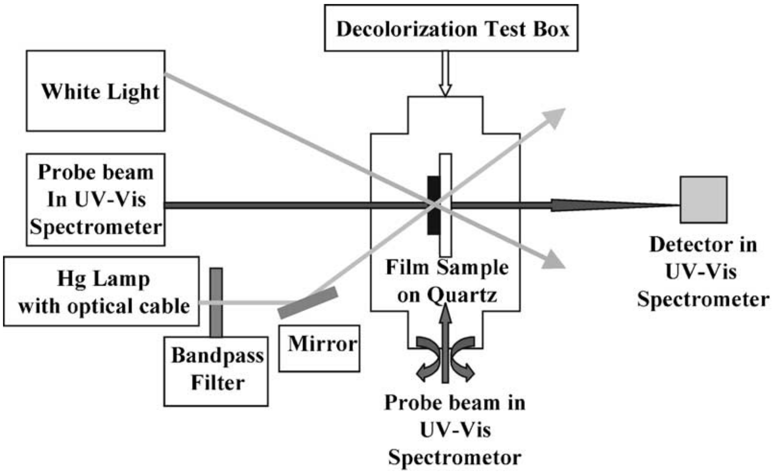
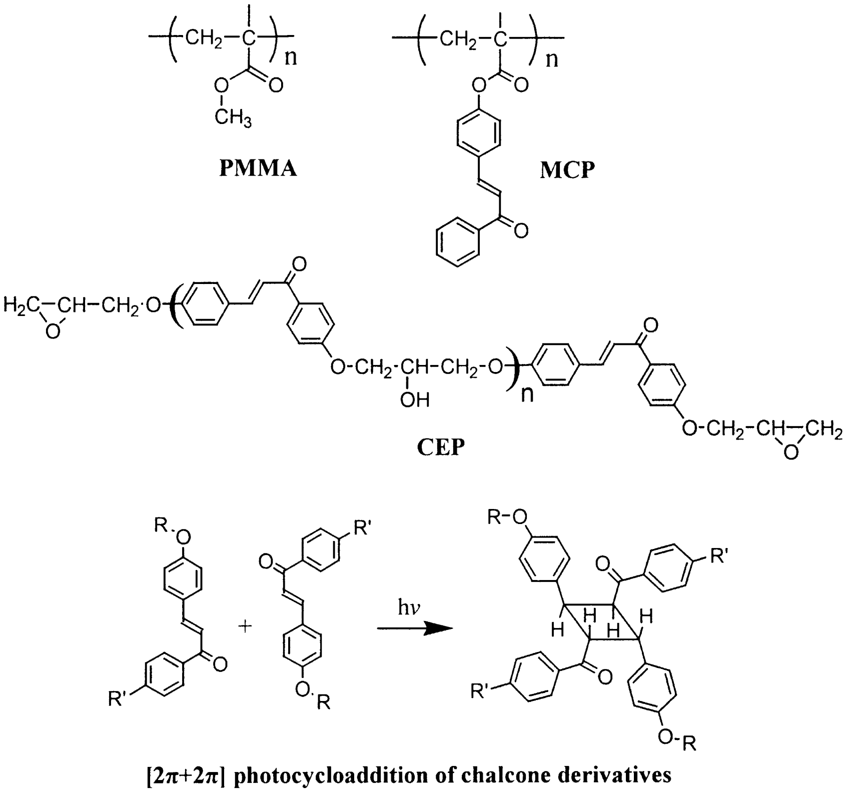


Fig. 1. Optical setup for investigating the photochromism spiropyran in the film state.



Scheme 1. Chemical structures of chalcone containing polymers (MCP, CEP) and their [2π + 2π] photo-cycloaddition.

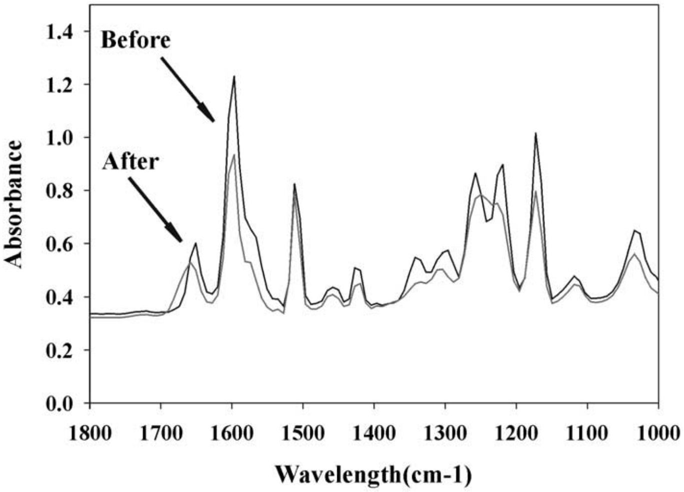


Fig. 2. Infrared spectral change of chalcone containing polymer in film state before and after irradiation.

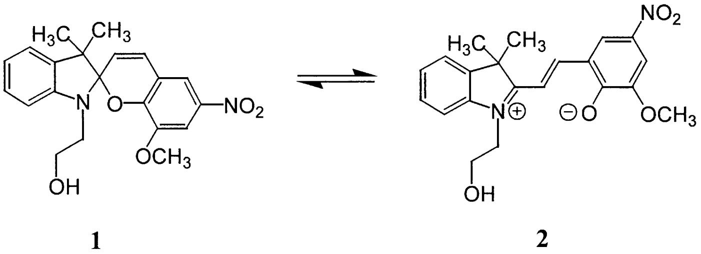
Fig. 2. Thus, the irradiation of UV light on polymer composite film can induce the colorization of photochromic compound and cycloaddition of chalcone, simultaneously. Two photochemical behaviors are all sensitive to the wavelength ranging from 290 to 390 nm. We suggest that the cycloaddition of chalcone moieties can reduce intermolecular distance between polymer chains effectively in film state, which could retard or quench the decolorization of photochromism. Furthermore in the CEP with cationic initiator, the end groups of epoxy ring also could be polymerized cationically because the photoinitiator can be photolyzed under irradiation of the same wavelength region for inducing above behaviors. The effect of photocycloaddition, photoinduced colorization, and photopolymerization of CEP, spiropyran, and epoxy ring can be considered on the photochromism and its stability.

In IR spectral analysis, we could observe the shift of the absorbance band at 1655 cm^{-1} that can be assigned to the unsaturated carbonyl stretching band. Additionally, the absorbance at 1600 cm^{-1} of the double bond stretching in the chalcone group decreased after UV irradiation. Therefore, we could confirm the occurrence of the cycloadded photoproduct between the chalcone moieties.

3.2. Absorption spectral analysis of photochromism

The spiropyran dye undergoes ring opening and E/Z transformation to be merocyanine dye form as is well known (Scheme 2). The colored form (merocyanine) of spiropyran has a typical zwitterion structure. The synthesized spiropyran dye shows the photochromic properties both in the solution and in the film state. Fig. 3 shows the absorption spectrum of spiropyran after irradiation at 280–390 nm in various solvents and PMMA.

In general, merocyanine dye shows solvatochromic property with the solvent polarity. As the solvent is more polar, $\lambda_{\max}$ of absorption band shifts to the short wavelength region because of the stabilization of the ground state than that of excited state. Solvent effects on the physico-chemical properties of spiropyran derivatives had been investigated on the basis of theoretical method which showed an inverted solvatochromism: ΔE increases when going from the gas phase to solutions of increasing polarity, [16,17]. Thus, as shown in Fig. 3, the more polar medium, the absorption band of the colored form appears in shorter wavelength region. In the film of the dye doped PMMA, the $\lambda_{\max}$ of merocyanine



Scheme 2. Structural change of spiropyran molecule during photochromism.

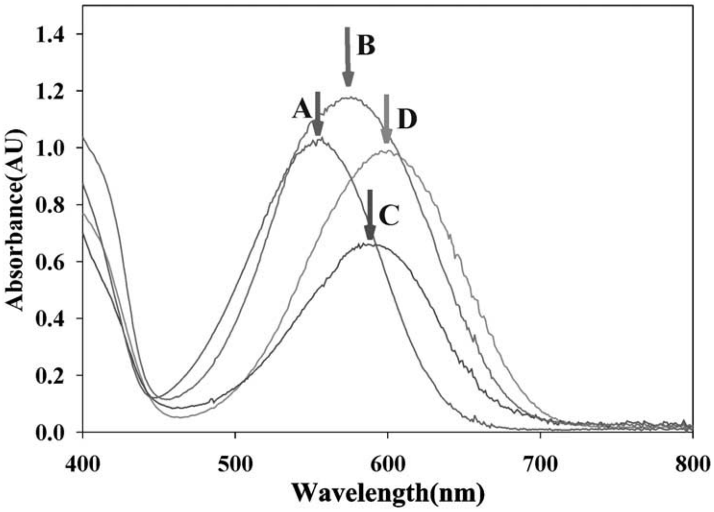


Fig. 3. UV–vis absorption spectra of merocyanine dye generated by irradiation of UV light in various solvents and in PMMA film. (A: methanol; 555 nm, B: PMMA; 578 nm, C: dichloromethane; 584 nm, D: benzene; 601 nm).

chromophore was 578 nm which is similar with in dichloromethane ($\lambda_{\max}$ = 584nm).

Thus, under the irradiation of UV light, the cycloaddition and photocolorization of chalcone and spiropyran occurred concomitantly which was shown in Fig. 4. The π→π* absorption band of merocyanine chromophore at 580 nm increased gradually with the UV irradiation time. The absorption band of the chalcone moiety ($\lambda_{\max}$: 312 nm) decreased which means the breakage of double bond in chalcone group during colorization under UV irradiation. 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 photodimerized easily in their films and resulted in forming the corresponding cyclobutane derivatives [12].

3.3. Stability of photochromism

The kinetic evaluation of photochromic process of PMMA, MCP, CEP, and CEP containing photoinitiator in film state was carried out by the measurement of absorption change during white light irradiation for the photo-decolorization in the film state. The results were illustrated in Fig. 5.

The rate constant of decolorization process was measured by following the decrease of the absorption bond at $\lambda_{\max}$ with the single exponential decay function (1).

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

where $A_{(t)}$ is the absorbance at time t, k, the rate constant and A_r is the residual absorbance at $t = \infty$. Kinetic results for the photo-accelerated

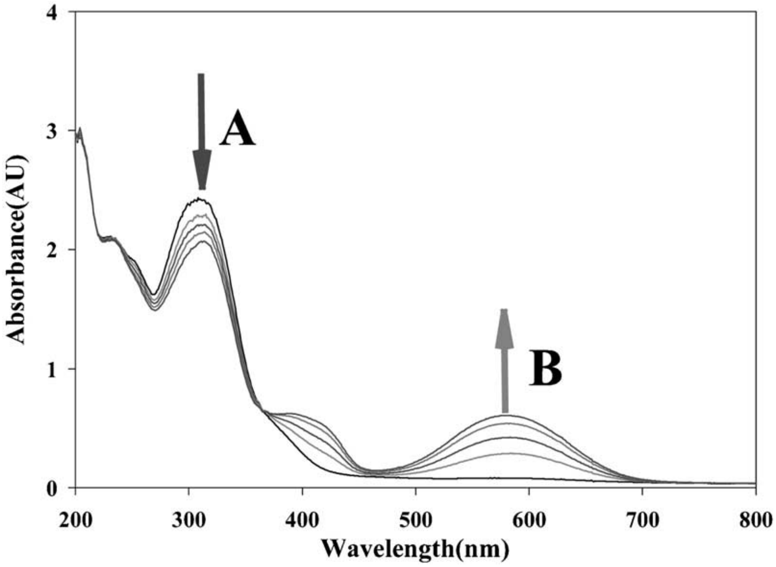


Fig. 4. UV–vis absorption spectral change of the film sample containing spiropyran and side chain chalcone polymer(MCP) film during UV light irradiation, A: π–π* transition band of chalcone moiety (312 nm), B: absorption band of merocyanine (588 nm).

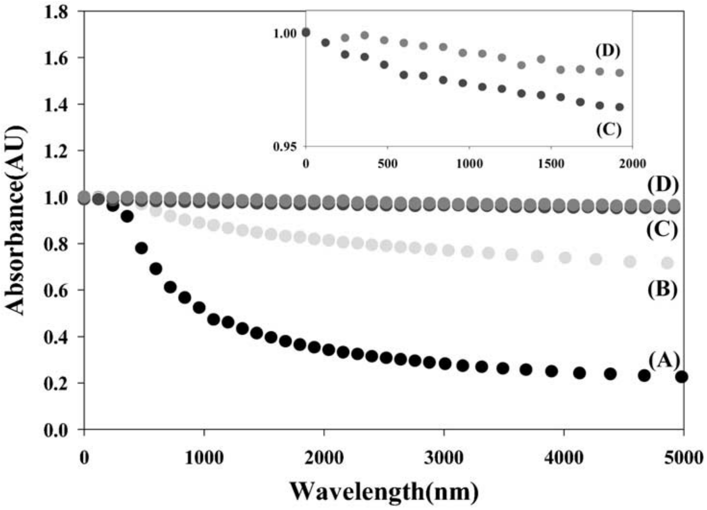


Fig. 5. Change of absorbance of photochromic film at 574 nm during irradiation of the white light. (A) in PMMA, (B) in MCP, (C) in CEP, (D) in CEP with photoinitiator.

decolorization process were shown in Table 1. It was shown that the decolorization became much slower in the MCP ($K=9.05\times10^{-4}$ s^{-1}) and CEP ($K=4.33\times10^{-4}$ s^{-1}) compared with that in PMMA (1.73×10^{-3}). That is attributable to the photocrosslink between chalcone units, resulting in steric hindrence around merocyanine dye.

It is interesting that the rate constant in CEP was two times slower than that in MCP. It can be explained that photo-cycloaddition of chalcone in main chain can reduce the distance between polymer chains more effectively which can induce strong steric hindrance for the decolorization process of spiropyran dye. The geometric restriction

Table 1
Observed kinetic parameters for decolorization of spiropyran in three polymer system

	K (s^{-1})	R	A_0
PMMA	1.73×10^{-3}	3.40×10^{-1}	6.41×10^{-4}
MCP	9.05×10^{-4}	7.87×10^{-1}	2.06×10^{-4}
CEP	4.33×10^{-4}	9.67×10^{-1}	3.27×10^{-4}
CEPI	3.70×10^{-4}	9.61×10^{-1}	3.83×10^{-4}

can retard the Z/E transformation. Then, it is more difficult to perform the ring closure reaction to the spiropyran dye. The residual concentration of the colored form after long-term decay of photochromism in CEP is also much larger than that in MCP. The residual merocyanine dye molecules in the film were entrapped by the network structure from cyclobutane ring structure so that it could not have enough free volume for backward reaction to the pristine spiropyran. Consequently, the activation energy for the decolorization process increases by steric effect of cyclobutanes. Although the difference of the rate constant is relatively small, in CEPI system that contain main chain chalcone and cationic photoinitiator (triarylsulfonium hexafluoroantimonate) for photopolymerization of epoxy ring, [12], the rate constant was decreased to 3.70×10^{-4} s^{-1}. Two photochemical reactions also affect the rate retardation of decolorization of spiropyran.

Unfortunately, in this system, the colorization process of spiropyran was also retarded by the competition of single photon absorption with chalcone moiety and the decrease of the free volume resulted from the photocycloaddition of chalcone. We believe that the above-mentioned problem could be solved with the control of wavelength of the excitation light for differentiating the colorization and the photo-cycloaddition.

4. Conclusion

The stability of photochromic property in spiropyran dye itself is well known to be relatively poor. We elaborated new polymer hybrid systems including photochromic spiropyran and photoreactive moieties for improve their stability. The rate control of decolorization was successfully achieved by virtue of photo-cycloaddition between the chalcone units, which is expected to control the free volume surrounding photochromic moiety. Z/E tranformation was very much limited due to quenching the excluded volume around the merocyanine dye. Chalcone–epoxy system (SP–CEP) and that with cationic photoinitiator (SP–CEPI) showed quite effective retardation of decolorization significantly by virtue of photocrosslink and photopolymerization.

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