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Photochromic behavior of new bifunctional copolymer containing spiropyran and chalcone moiety in the side chain

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Abstract

We synthesized two copolymers bearing photochromic spiropyran dye in the side chain for studying the dynamic properties of their photochromism. The dynamic processes of colorization and decolorization under an excitation light were investigated using the two copolymers. One of the copolymers contains methylmethacrylate (MMA) and methacrylate-spiropyran (MA-spiropyran). The other one contains methacrylate-spiropyran (MA-spiropyran) and methacrylate-chalcone (MA-chalcone) as a comonomer. Investigation of the photosensitivity of the newly synthesized copolymers was carried out by using UV–vis absorption spectroscopy. We observed the photodimerization and photochromic behavior under UV irradiation simultaneously. The effect of photocrosslink on the stability of photochromism was considered from this study.

Keywords: Photochromism; Chalcone; Spiropyran; Photocrosslink; UV irradiation

1. Introduction

Polymeric materials have recently attained remarkable interests as optical, electro-optical, and photoreactive materials [1–4]. Photochemical reactions in organic materials can induce much change in physical properties such as solubility, optical transparency, dielectric constant, and refractive index. 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 [5–9]. One of prime reasons lacking industrial applications of the photochromic materials, particularly organic photochromic compounds, is their poor durability of colorization [10]. Although the extensive study on improving the durability for photochromic property was performed, the stable compound still remains rather limited in practical applications.

On the other hand, spiropyrans and spiroxazines are well-known photochromic compounds, which undergo colorization from the spiropyran form to their corresponding merocyanine form by irradiation of UV light and vice versa by visible light or heat [11]. Since the colorized form of

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spiropyran is much different from the pristine spiropyran moiety in their polarity and chemical structure, the colorization and decolorization process would be affected with micro-environmental condition [12]. 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 [13].

In order to increase the density of the polymer matrix and provide some geometrical hindrance to the isomerization behavior of merocyanine moiety, photocrosslink can be induced under irradiation of the same light source that is usually utilized for including photochromism. Polymers containing unsaturated aromatic acid or ester units, especially the cinnamic acid and its ester derivatives were studied for phototransformation phenomena, which occurred during the irradiation with UV light ($\lambda = 250$–300 nm). Among many promising photosensitive groups, a chalcone group has been well studied and can be used in photocrosslinkable side chain polymers because it affords high sensitivity to UV radiation ($\lambda = 300$–350 nm).

In this report, we suggested that the photochromic property of spiropyran dye could be affected by the control of the free volume around spiropyran units. The photoreaction property of chalcone containing polymers was studied by our group which revealed the $[2\pi + 2\pi]$ photocycloaddition in the film state [14–16]. The intra- and intermolecular photocycloaddition of chalcone units in their copolymers can reduce the free volume surrounding spiropyran and merocyanine, which lowers the rate of photochromic process. Thus, we have synthesized a new bifunctional copolymer (BFCP) which contains spiropyran and chalcone moieties as photochromic and photocrosslinkable unit in the side chain, respectively. This design is based on the premise that each functional moiety should be sensitive photochemically and behaves as a separated functional moiety at the same wavelength region. The UV–vis absorption spectral analysis and dynamic analysis of photoreaction kinetics were carried out to evaluate the effect of photodimerized chalcone moieties on the stability of photochromism in the copolymer.

2. Experimental

2.1. Synthesis

We followed the literature methods for synthesis of the compounds for the copolymers [17,18]. The synthetic procedures of two copolymers were described as follows.

2.2. Synthesis of copolymer (MFCP)

Copolymer of MA-spiropyran and MMA was prepared by radical polymerization. The MA-spiropyran (1 g, 2.4 mmol) and MMA (0.238 g, 2.4 mmol) were dissolved in dried dimethylformamide (DMF, 13 ml) in the presence of AIBN (0.0084 g, 0.048 mmol). The solution was kept at 70 °C for 48 h under argon atmosphere. Copolymer was collected and purified by reprecipitation from DMF/methanol until there is no monomer left and dried in vacuum at 90 °C for 48 h. Yield, 85%. ^{1}H-NMR ($CDCl_3$) δ (ppm) 0.79 (6H), 1.17, 1.28 (3H, 3H–CH_3 in spiropyran unit), 1.76 (4H), 3.49 (2H, –CH_2–), 3.59 (3H, –O–CH_3), 4.05 (2H, –CH_2–), 5.87 (1H, –CH=), 6.71–7.26 (6H, H in aromatic ring), 8.00 (2H, H in aromatic ring).

2.3. Synthesis of copolymer BFCP

The MA-spiropyran (1 g, 2.4 mmol) and MA-chalcone (0.702 g, 2.4 mmol) were dissolved in dried DMF (17 ml) in the presence of AIBN (0.0084 g, 0.048 mmol). The solution was kept at 70 °C for 48 h under argon atmosphere. Copolymer was collected and purified by reprecipitation from DMF/methanol. The solid was repricipitated twice from tetrahydrofuran/methanol until there is no monomer left and dried in vacuum at 90 °C for 48 h. Yield, 79%. ^{1}H-NMR ($CDCl_3$) δ (ppm) 0.8–1.35 (12H, 6H in –CH_3 and 6H in –CH_3 in spiropyran unit), 2.19 (4H), 3.76 (2H), 4.04 (2H), 5.74 (1H, –CH=), 6.64–7.06 (9H), 7.47–7.95 (11H).

2.3.1. Film fabrication

For preparing the thin film, the solution (10 wt.%) of each copolymer in tetrahydrofuran was filtered through acrodisc syringe filter (Millipore

0.2 μm) and then cast 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.

2.3.2. Instruments

UV–vis absorption spectroscopic study was performed on a Hewlett Packard 8453 spectrophotometer (PDA type, $\lambda = 190$–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 1.15 mW/cm^2 ($\lambda = 250$–390 nm), which was measured with a broadband power/energy meter model 13PEM001(MELLES GRIOT). For irradiation of visible light, we utilized He–Ne laser ($\lambda = 633$ nm, 6.88 mW/cm^2) for observing the decolorization behavior. For investigating the above two processes precisely, we setup the optical equipments as is shown in Fig. 1.

The molecular weights of two copolymers were measured with gel permeation chromatography (GPC, Waters M616LC) using polystyrene standard. The elemental analysis was performed with HP5890 GC chromatography. The thermal behaviors of the copolymers were investigated by differential scanning calorimetry (DSC) using a Perkin Elmer DSC7. The heating rate was 10 °C/min in all cases.

3. Results and discussion

3.1. Physical properties of photochromic copolymers

The synthetic approach for the functional copolymer was explored by the radical polymerization with addition of AIBN as an initiator [19]. Bifunctional copolymer (BFCP) was synthesized by the polymerization of MA-spiropyran, **1** with MA-chalcone, **3** which can act as a photochromic and a photocrosslinkable unit, respectively. Monofunctional copolymer (MFCP) containing MA-spiropyran, **1** and MMA, **2** was also synthesized for the comparison of the photochromic behavior (Scheme 1).

Resultant mole ratio of each component in two copolymers was determined with ^{1}H-NMR spectroscopy and elemental analysis which was shown in Table 1. And the weight average molecular weight (M_w) and glass transition temperature (T_g) were determined with the GPC and DSC, respectively (see experimental section). The molecular weights of two copolymers are in the range of 12,348–15,416. The glass transition temperatures of MFCP and BFCP are 140 and 134 °C, respectively, which are relatively high and close each other. The properties of the synthesized copolymers were shown in Table 1.

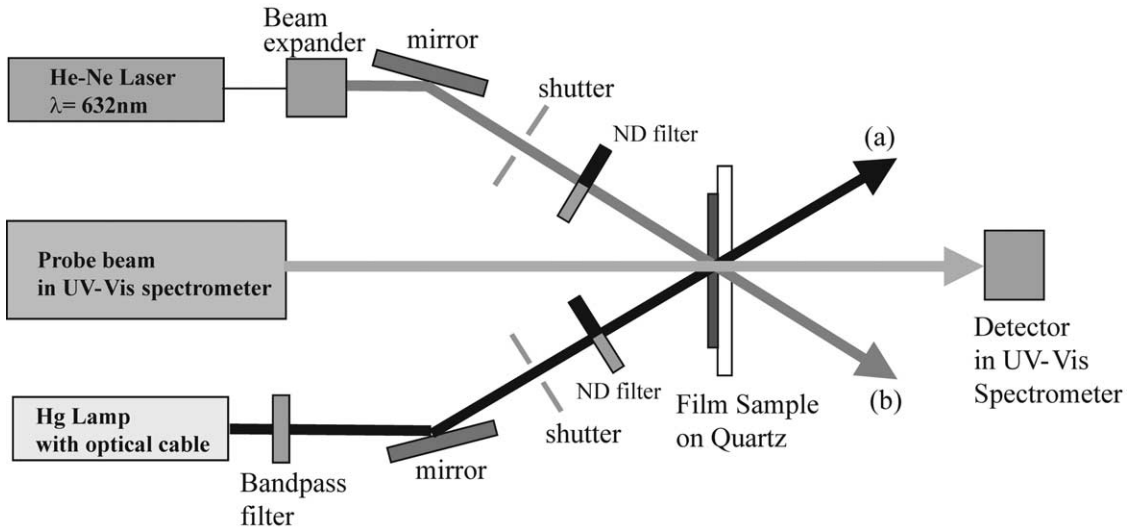
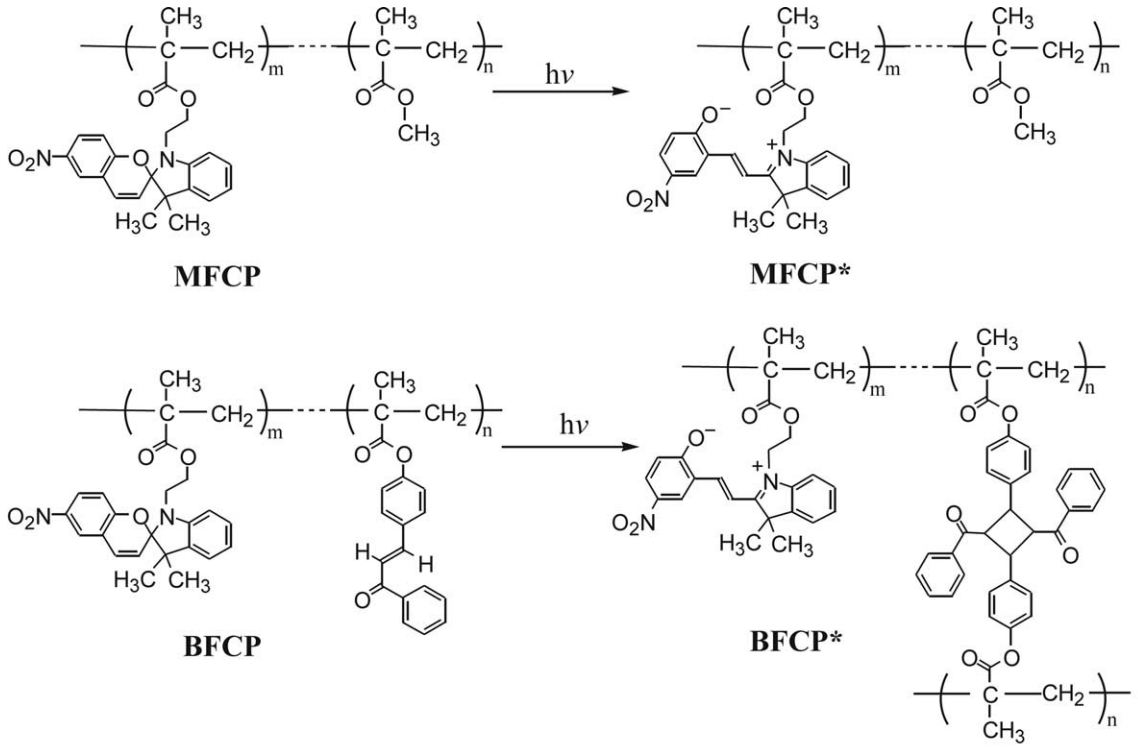


Fig. 1. Optical setup for investigating the photochromism of the copolymers.

3.2. Absorption spectral analysis of photochromic copolymers

Functional copolymers containing spiropyran moiety shows the photochromic properties both in the solution and in the film state. Fig. 2 shows the absorption spectral change of MFCP film during the UV irradiation at 280–390 nm.

The colored form of spiropyran in the film state shows the absorption maximum at 586 nm which proves *trans*-conformation of merocyanine chromophore (see Scheme 1). The $\pi \rightarrow \pi^*$ absorption band of merocyanine chromophore at 586 nm increased gradually with the UV irradiation time. In the case of BFCP, the absorption band of the chalcone moiety (λ_{max}: 310 nm) decreased



Scheme 1. Chemical structures of photochromic copolymers.

Table 1
Measured physical parameters of two copolymers

	Mole ratio[a]	Yield[b]	T_g[c]	M_w[d]	Elemental analysis Obs. (calcd)		
MFCP	44.4/55.6[f]	85%	140	15416 (2.774932)[e]	C: 67.84 (66.92)	H: 7.32 (6.15)	N: 5.29 (5.38)
BFCP	48.7/51.2[g]	79%	134	12348 (2.646648)[e]	C: 73.20 (72.47)	H: 5.94 (5.61)	N: 4.58 (3.93)

[a] Mole ratio was determined with ^{1}H-NMR spectroscopy.
[b] Separation yield.
[c] (°C) Determined with DSC.
[d] Determined with GPC.
[e] Polydispersity (M_w/M_n).
[f] (MA-spiropyran/MMA).
[g] (MA-spiropyran/MA-chalcone).

simultaneously accompanying with increase of the absorption intensity resulting from increase of the concentration of merocyanine dye. That means the breakage of double bond in chalcone group during colorization. The 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 corresponding cyclobutane derivatives [14–16]. Thus, by the $[2\pi+2\pi]$ photocycloaddition of chalcone moieties, the distance between polymer chains reduced. The free volume surrounding the spiropyran unit needed for the decolorization process is expected to decrease significantly although the quantum efficiency of photochromism was relatively lower than that of MFCP due to two UV absorbing moieties. The kinetic study of photochromism was conducted to evaluate the effect of photocrosslink on the decolorization process.

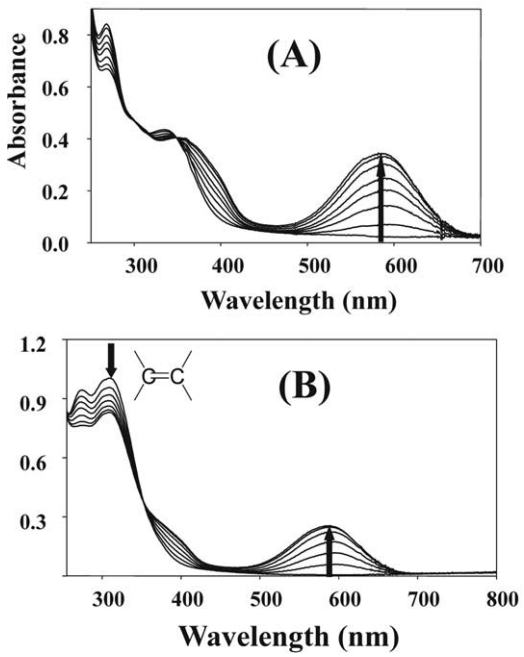


Fig. 2. UV–vis absorption spectral analysis of MFCP (A) and BFCP (B) during UV irradiation.

3.3. Kinetics of photochromism

The kinetic evaluation of photochromic process of MFCP and BFCP was carried out by the measurement of absorption change during irradiation under He–Ne laser ($\lambda = 632$ nm) for the photo-decolorization in the film state.

The rate of decolorization was measured in the film state by following the decrease of the absorption band at λ_{max} with the single exponential decay function (1) (see Fig. 3 (A) for MFCP and (B) for BFCP) [20]

$$A(t)/A(0) = A_0 \quad \exp(-kt) + A_r \tag{1}$$

In the photo-accelerated decolorization process, the kinetic results were shown in Table 2 which show the rate (k) of BFCP is much smaller than that of MFCP. It means that during the irradiation of UV light, photodimerization between the chalcone moieties would reduce the distance between polymer chains and give smaller free volume needed for transforming from *trans*-merocyanine dye into spiropyran. Since in the condensed system of UV-irradiated sample, the molecular motion of the side chain is significantly limited to compare with that of MFCP. It could be saying that the decolorization reaction in BFCP film after UV irradiation is much retarded by increasing steric hindrances resulted from intermolecular photocycloaddition of chalcone units. Thus, residual concentration of the colored form after long-term decay of photochromism in BFCP is also much larger than that in MFCP. This residual form of merocyanine in the film should be surrounded and entrapped by cyclobutane derivatives so that it could not have enough free volume for backward reaction to the pristine spiropyran dye.

Table 2
Calculated parameters from the dynamic behavior of photochromism in two copolymers

	k[a]	E_a (kJ mol^{-1})[b]
MFCP	0.01844	7.94
BFCP	0.01295	8.75

[a] Photo-induced decolorization rate constant.
[b] Thermal back transfer activation energy.

Most importantly, we could control the rate of decolorization behavior of spiropyran in the film state by introducing the chalcone moiety in the copolymer so that it improved thermal stability of colored species.

It should be noted that the annealing of the copolymers leads to the backward conversions from the merocyanine form to the spiropyran forming the film state, in other words, the isomeric transition between spiropyran and merocyanine forms are thermally reversible. To perform kinetic evaluation for this thermal back conversion more precisely, we calculated the decaying rate constants (k) at different temperatures and the activation energy for the ring closure reaction was also calculated using the *Arrhenius* relationship between ln k and the reciprocal absolute temperature (Fig. 4). It is meaningful that we can exclude the effect of molecular weight and the glass transition temperature on the dynamic behavior of photochromism since those properties are very similar in two copolymers (see Table 1). For two copolymers in the film state, analysis of the dependences of optical density on annealing time shows some deviation from the usual first order kinetics. This deviation is likely to be associated with the possible formation of dimer and aggregates of the merocyanine form [19]. Nevertheless, we can estimate the rate constants k of the thermal back reactions using the dynamic curves with the following Eq. (2) for first order kinetics in integral form,

$$\ln[(A(\infty) - A(t))/(A(\infty) - A(0))] = -kt \qquad (2)$$

The kinetic parameters for copolymers were shown in Table 2. The activation energy for the ring closure reaction of BFCP is larger than that of MFCP. We believe that this difference is attributed to the higher steric effect in BFCP resulting from photocrosslink between chalcone units. The residual form in the BFCP film should be surrounded with the photo-crosslinked species that could not have enough free volume for the backward reaction. It means that changing micro-environmental conditions surrounding the photochromic moieties in copolymer, BFCP, can control the stability of colored species. The photocycloaddition of chalcone occurred by the irradiation at similar UV wavelength region for the ring opening reaction in the photochromic process can reduce the free volume surrounding merocyanine dye, effectively.

Unfortunately, in this system, the colorization process of spiropyran in copolymer was also

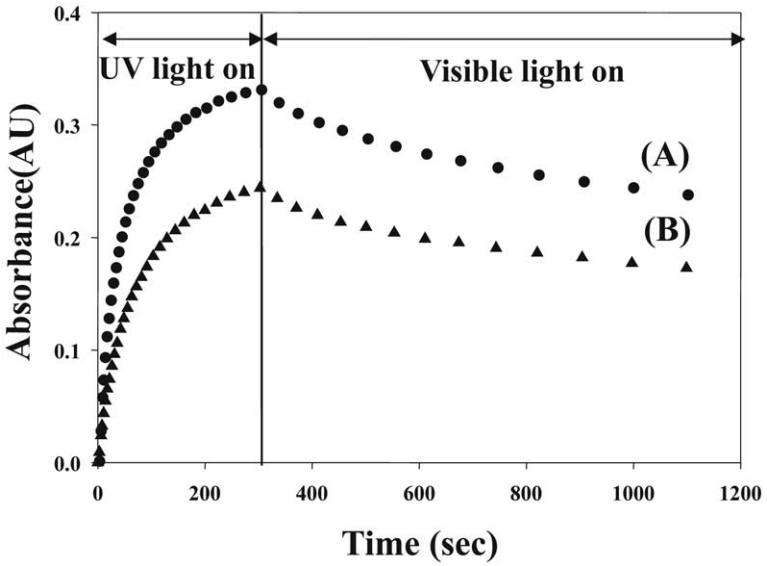


Fig. 3. Change of absorbance of copolymer film at 586 nm during irradiation of UV and visible light. (A) MFCP, (B) BFCP film.

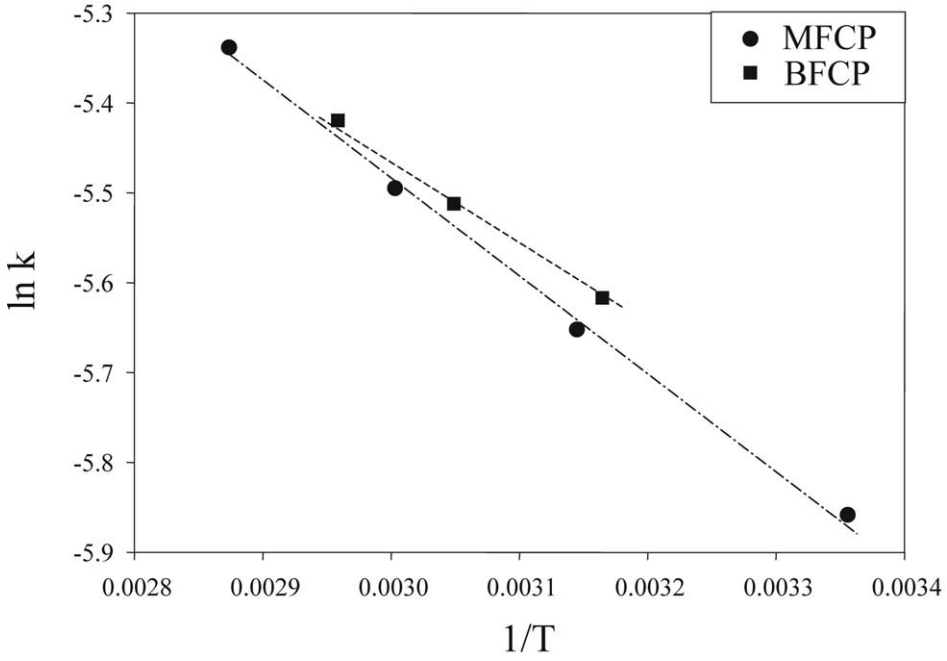


Fig. 4. *Arrhenius* plot of ln k versus $1/T$ for calculating the rate constant and the activation energy (E_a) for thermal backward reaction.

retarded by the competition of phonon absorption with chalcone moiety and the decrease of the free volume. We believe that the above-mentioned problem could be solved with the control of wavelength of the excitation light. Thus, control of the mole ratio of chalcone and spiropyran unit in copolymer and wavelength control of the irradiation light for the selective colorization process are now in progress.

4. Conclusion

To improve the stability of the colored species of photochromic spiropyran, we synthesized a new bifunctional copolymer (BFCP) including photochromic spiropyran and photo-crosslinkable chalcone moieties. The rate control of ring closure reactions of spiropyran dye in copolymer 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.

Acknowledgements

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