Stability of Photochromism in New Bifunctional Copolymers Containing Spiropyran and Chalcone Moiety in the Side Chain

Dong Hoon Choi,* **Si Young Ban, and Jae Hong Kim**

College of Environment and Applied Chemistry, Institute of Natural Sciences, Kyung Hee University, Suwon 449-701, Korea
Received August 13, 2002

We synthesized three copolymers bearing photochromic spiropyran dye and chalcone moiety in the side chain for studying the dynamic properties of their photochromism. They contain methacrylate-spiropyran (MA-spiropyran) and methacrylate-chalcone (MA-chalcone) with the different concentration. The photosensitivity of the newly synthesized copolymers was investigated by using UV-Vis absorption spectroscopy. We observed photodimerization and photochromic behavior under UV irradiation at the same time. The effect of photocrosslink on the rate and stability of photochromism in three copolymers was considered in this study. This study might be helpful to design photochromic materials for irreversible optical memory by virtue of photocrosslinking reaction.

Key Words : Photochromic, Chalcone, Spiropyran, Copolymer, Photocrosslink

Introduction

Polymeric materials have recently received much interest as photoreactive materials.[1-4] Among many kinds of photoreactive materials, especially, 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] Despite many advantages of photochromic materials, one of the prime reasons lacking industrial applications of the photochromic materials, particularly organic photochromic compounds, is their poor stability of photochromism.[10] Although 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.

On the other hand, 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.[11] 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.[12,13]

In order to improve the stability of photochromism in the polymer with spiropyran, photocrosslink can be induced under irradiation of the same UV light source that is usually utilized for photochromism. In this work, we report that the kinetics of colorization and decolorization of the photochromic spiropyran dye could be affected by the concentration of the methacrylate-chalcone (MA-chalcone) in the copolymer. The photoreaction property of chalcone-containing polymers was well-studied which revealed $[2\pi + 2\pi]$ photocycloaddition in the film state.[14,15] Thus, the intermolecular photocycloaddition of chalcone units in their copolymers can reduce the free volume surrounding spiropyran and merocyanine, which lower the rate of the photochromic process.

We have synthesized the photochemically bifunctional copolymers (BFCP-1, 2, 3) that contain 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 could be sensitive photochemically and behaves as a separated functional moiety at the similar wavelength region. The UV-Vis absorption spectral analysis and dynamic analysis of photoreaction kinetics were carried out to evaluate the effect of the density of photodimerized chalcone moieties on the stability of photochromism in the copolymers.

Experimental Section

Synthesis. We followed the literature methods for synthesis of the compounds for the copolymers.[16,17] The synthetic procedure of one copolymer was described herein as an example.

Synthesis of copolymer (BFCP-1) with MA-spiropyran, 1 and MA-chalcone, 2. The MA-spiropyran (3 g, 7.2 mmole) and MA-chalcone (0.702 g, 2.4 mmole) were dissolved in dried DMF (17 mL) in the presence of AIBN (0.0084 g, 0.048 mmole). The solution was kept at 70 °C for 48 hr under argon atmosphere. Copolymer was collected and purified by reprecipitation from DMF/methanol. The solid was reprecipitated twice from tetrahydrofuran/methanol until there was no monomer left and dried under vacuum at 90 °C for 48 hr. Yield, 79%. T_g ~150 °C.

^{1}H-NMR (CDCl$_3$) δ (ppm) 1.10 (4H, 2x-$^\beta$CH$_2$-), 1.40-1.55 (6H, 2x-CH$_3$ in spiropyran unit), 2.25 (6H, 2x -$^\alpha$CH$_3$), 3.45 (2H, -CH$_2$-), 4.05 (2H, -CH$_2$-), 5.72 (1H, -CH=), 6.25-8.05 (6H, H in aromatic ring).

The other two copolymers (BFCP-2, BFCP-3) were prepared,

*To whom correspondence should be addressed: E-mail: dhchoi @khu.ac.kr

following the same method above besides changing the feeding ratio of the monomer.

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.

Instruments: 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 1.15 mW/cm^2 (λ = 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 (λ = 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 Figure 1.

The molecular weight was 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 Erlmer DSC7.
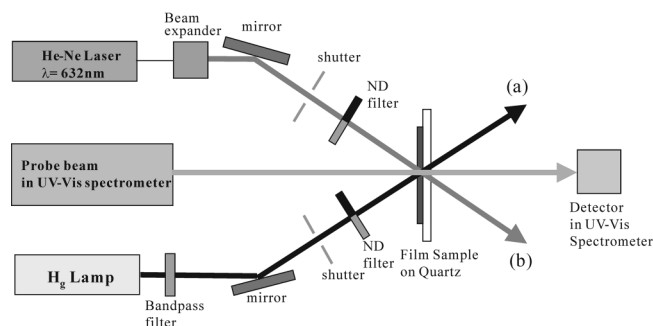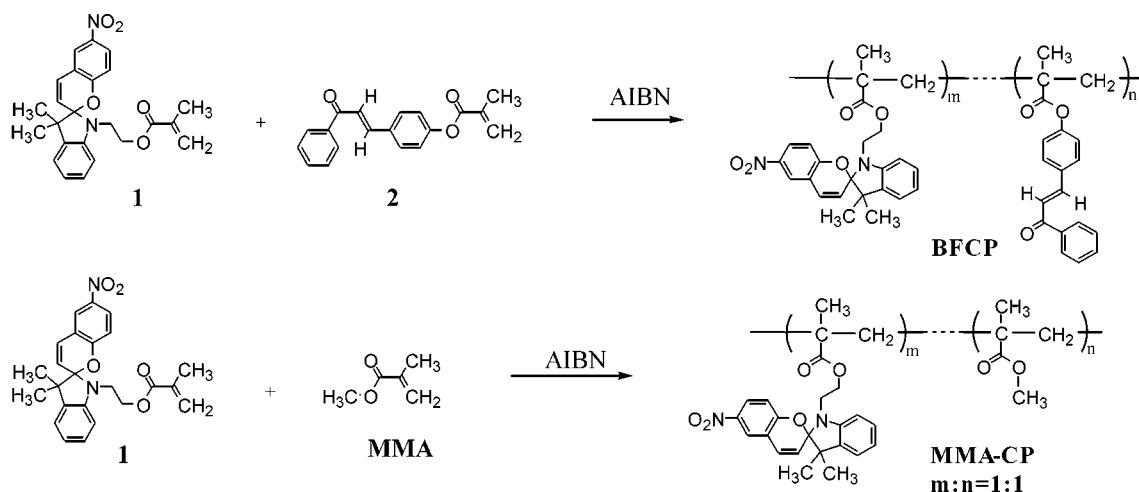

Figure 1. Optical setup for investigating the photochromism of the copolymers.

Results and Discussion

Polymerization and properties. Bifunctional copolymers (BFCP) were synthesized by the radical polymerization of MA-spiropyran, **1** with MA-chalcone, **2** that can act as a photochromic unit and a photocrosslinkable one, respectively. The yields of polymerizations were relatively high around 79-85%. Additionally, we also synthesized copolymer (MMA-CP) with MA-spiropyran and methylmethacrylate (MMA) to compare the photochromic properties of bifunctional copolymers.

The mole ratio of each component in copolymers was determined with ^{1}H-NMR spectroscopy and elemental analysis. The monomer feeding ratios of MA-spiropyran and MA-chalcone were selected to be 3 : 1, 1 : 1, and 1 : 3 for BFCP-1, BFCP-2, and BFCP-3. The composition ratio of each monomer in the copolymers was quite similar to the monomer feeding ratio as is shown in Table 1. The weight average molecular weight (M_w) and glass transition temperature (T_g) were measured by the GPC and DSC, respectively. The molecular weights of three copolymers were in the range of 12300-21100. The glass transition temperatures of BFCP-1, BFCP-2, and BFCP-3 were 150, 134, and 125 °C, respectively. As the concentration of MA-spiropyran increases, the higher glass transition temperature was observed due to the bulkiness of the spiropyran dye. Physical properties of the synthesized copolymers were shown in Table 1.

Absorption spectral analysis of photochromic copolymers. Functional copolymers containing spiropyran moieties shows the photochromic properties both in their solution and in the film state. Figure 2 shows the absorption properties of the solution before and after irradiation of UV light. In Figure 2(A), solution spectra of three copolymers were illustrated before UV irradiation. The solutions having the same molar concentration of the polymer were taken for recording the absorption spectra. As the concentration of chalcone is higher, the absorbance at 313 nm is higher as we expected. However, if the absorbance at 313 nm is superimposed with the absorbance band of spiropyran dye in the similar

Scheme 1. Syntheses and structures of copolymers used in this study.

Table 1. Measured physical parameters of the copolymers

		BFCP-1		BFCP-2		BFCP-3		MMA-CP	
T_g (°C)		150		134		125		140	
M_w		18096		12348		21145		15416	
Mole Ratio[a]		76.1:23.9		44.4:55.6		24.0:76.0		48.7:51.2[b]	
		Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
Elemental Analysis	C	70.35	68.32	72.46	67.67	74.98	74.78	66.9	64.72
	H	5.71	5.94	5.66	6.52	5.59	5.51	6.20	6.27
	N	5.41	4.43	3.93	1.62	2.16	1.44	5.38	5.43

[a]MA-spiropyran: MA-chalcone. [b]MA-spiropyran: MMA.

absorption wavelength region, it will be difficult to expect the photochemical reaction of chalcone unit effectively. After UV irradiation, the spectral change is shown in Figure 2(B). This is quite reasonable in the copolymer containing higher concentration of the photochromic dye. Figure 3 shows the absorption spectral changes of **BFCP-1**, **2**, and **3** films during the UV irradiation at 250-390 nm. The colorized form of spiropyran in the film state shows the absorption maximum at 586 nm in the beginning stage, which proves *trans*-conformation of merocyanine chromophore (see Scheme 2).

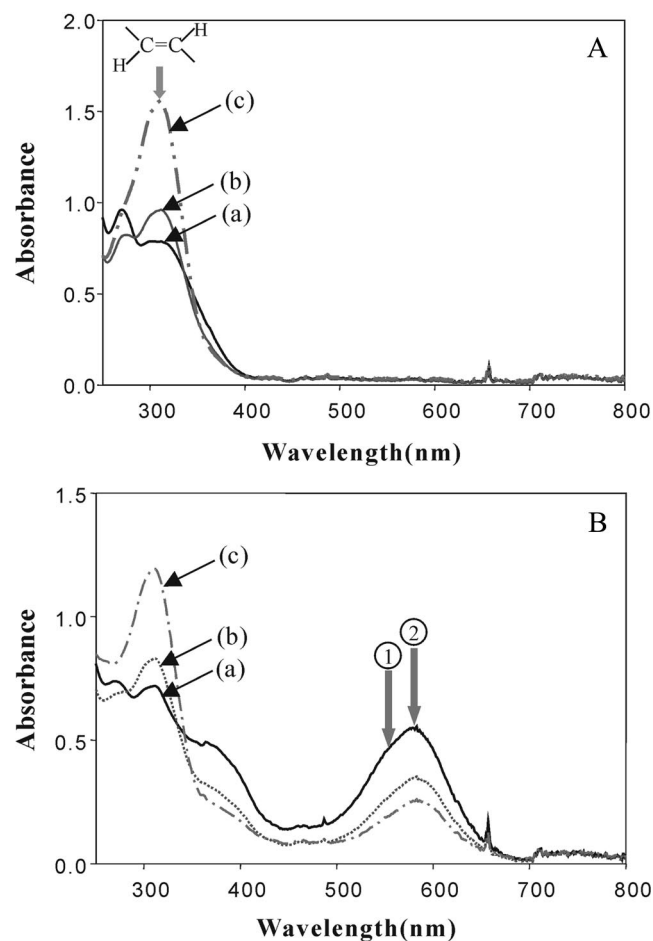The $\pi \rightarrow \pi*$ absorption band of merocyanine chromophore

Figure 2. UV-Vis absorption spectral analysis of BFCPs during UV irradiation. (a) BFCP-1, (b) BFCP-2, (c) BFCP-3.
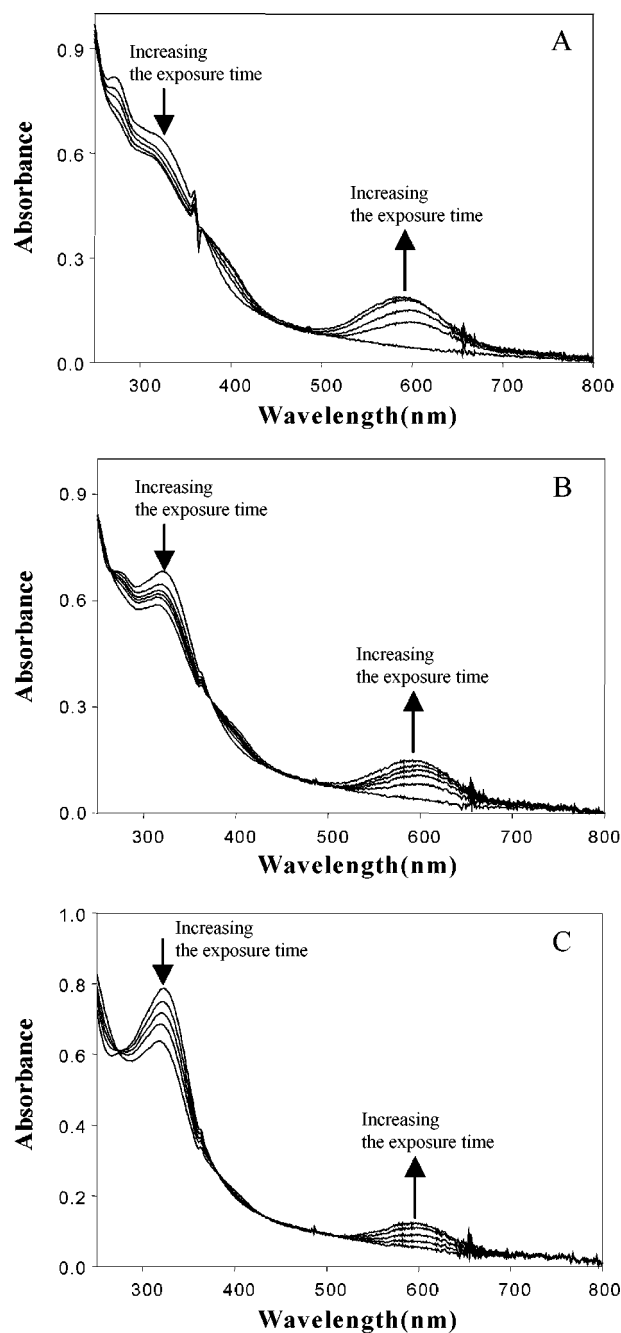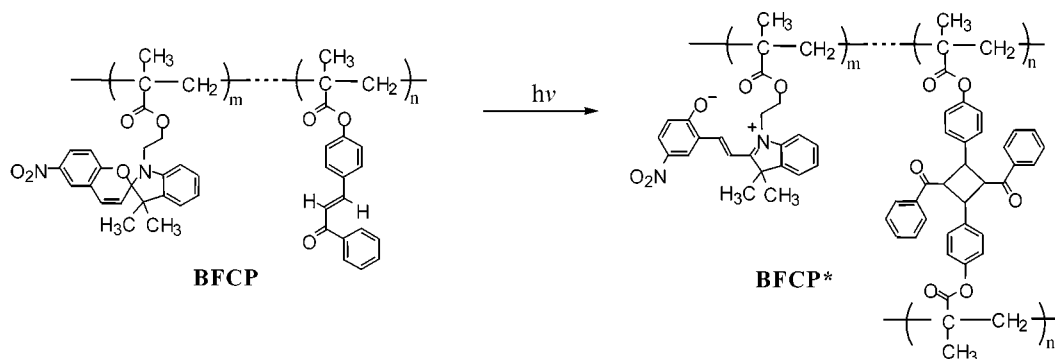
Figure 3. Change of absorption spectrum during irradiation of UV and visible light. (A) BFCP-1, (B) BFCP-2 (C) BFCP-3 film.

Scheme 2. The transformed structure of the copolymer after UV irradiation.

from spiropyran moiety at 586 nm increased gradually with the UV irradiation time. In the case of BFCPs film, the absorption band of the chalcone moiety (λ_{max}: 310 nm) decreased simultaneously with increase in the absorption intensity resulting from increase of the concentration of merocyanine dye. This means the disruption of double bond in chalcone group during colorization. The BFCP-3 (Figure 3C) showed higher absorbance at 310 nm due to higher concentration (76%) of chalcone unit. By the $[2\pi + 2\pi]$ photocycloaddition of chalcone moieties that can reduce the distance between polymer chains, the free volume surrounding the spiropyran unit, which is necessary for the photo-colorization and decolorization process is expected to decrease significantly. The kinetic study of photochromism was conducted to evaluate the effect of photocrosslink on colorization and decolorization process, It depends on the concentration of chalcone moiety in the copolymer.

Kinetics of photochromism. The kinetic evaluation of photochromic process of BFCPs was carried out by the measurement of absorption change during irradiation under UV light (λ = 250-390 nm) for the ring opening and E/Z transformation and under He-Ne laser (λ = 632 nm) for the ring closure reactions in the film state.

Rates of colorization of BFCPs were measured from change of the absorbance at λ_{max}, which were shown in Figure 4A. The intensity of irradiated UV light was 1.15 mW/cm^2 and rate constant was calculated by following the double exponential equation (1) shown below.[18]

$$A(t)/A(0) = A_1[1-\exp(-k_1t)]+A_2[1-\exp(-k_2t)] \qquad (1)$$

The rate of decolorization was also measured in the film state by following the decrease of the absorption band at λ_{max} and can be calculated using double exponential decay function (2) (see Figure 4B).[18]

$$A(t)/A(0) = A_3 + A_4\exp(-k_3t) + A_5\exp(-k_4t) \qquad (2)$$

In the colorization process, the BFCP-1 showed smaller rate constant, k_1 than BFCP-2 and BFCP-3 does.(See Table 2) This is likely to be affected by the higher concentration of the spiropyran unit and higher glass transition temperature of the BFCP-1. (T_g of BFCP-1: 150 °C) As the concentration of the spiropyran dye increases, the E/Z transformation will be much more difficult to perform. In a later stage of colorization, we can also expect the effect of electrostatic interaction between the dyes. If the concentration of the merocyanine dye became larger, there would be a high degree of aggregation between the dyes themselves. Sometimes, the closed form of spiropyran dyes will be caged inside the aggregation. Additionally, we can confirm that the photocycloaddition between the chalcone groups may affect the dynamic behavior of photochromism in part since MMA-CP has the highest rate constant, k_1. But it is not so significant to compare with the effect on decolorization process.

In the photo-accelerated decolorization process, the rate constant k_3 of BFCP-3 was slightly smaller than those of BFCP-1 and BFCP-2. (See Table 2) MMA-CP showed the
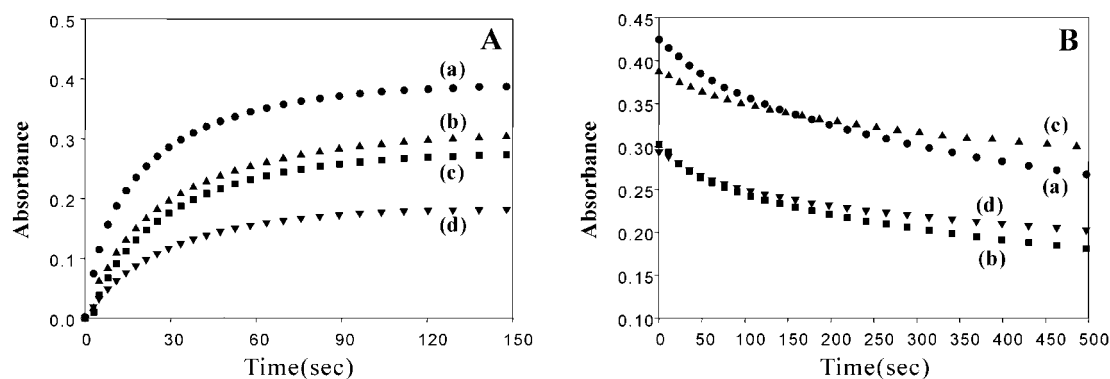

Figure 4. Dynamic behavior of photochromism in colorization and decolorization as a function of time. A: Rising curves, B: Decaying curves. (a) MMA-CP, (b) BFCP-1, (c) BFCP-2, (d) BFCP-3.

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

	Rising Curve				Decaying Curve				
	A1	k_1	A_2	k_2	A_3	k_3	A_4	k_4	*R*
BFCP-1	0.1447	0.0501	0.1703	0.0166	0.0490	0.0115	0.1422	0.0012	0.1026
BFCP-2	0.2226	0.0515	0.0603	0.0157	0.0371	0.0109	0.1387	0.0009	0.1909
BFCP-3	0.0321	0.0949	0.1523	0.0285	0.0449	0.0107	0.0944	0.0011	0.1516
MMA-CP	0.1447	0.1593	0.2456	0.0291	0.0650	0.0120	0.2098	0.0017	0.1477

Rise: $A(t) = A_1(1-\exp(-k_1 t)) + A_2(1-\exp(-k_2 t))$. Decay: $A(t) = A_3\exp(-k_3 t) + A_4\exp(-k_4 t) + R$.

highest decaying constant compared to the chalcone-containing copolymers. It means that during the UV irradiation, photo-dimerization between the chalcone moieties reduced the distance between polymer chains and gave smaller free volume necessary for transforming from *trans*-merocyanine dye to the spiropyran dye.

Although the concentration of the chalcone monomer in BFCP-3 is three fold of that of BFCP-1, the rate constants did not show significant difference. This can be explained as follows; In case of BFCP-1, we can think about the attractive electrostatic interaction between merocyanine dyes due to higher concentration of the spiropyran dye. However, in BFCP-3, the merocyanine dyes were not subject to strong electrostatic interaction because of the low concentration of the spiropyran dye. Therefore, we can consider the compen-sated effect between the electrostatic interaction and the geometrical hindrance. Shortly, it can be concluded that the effect of steric hindrance is dominant over the electrostatic interaction in this case.

Since in the condensed system of UV-irradiated sample, the molecular motion of the side chain is significantly limited to compare with that of guest-host system or thermoplastic copolymer. It could be saying that the ring closure reaction in BFCP film after UV irradiation is much retarded by increasing steric hindrances resulted from intermolecular photocycloaddition of chalcone units. 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 Z/E transformation to the pristine form of spiropyran dye.

We could control the rate of photochromic behavior of spiropyran in the film state by introducing the chalcone moiety in the copolymer somewhat so that it improved thermal stability of colored species.

Conclusion

The stability of photochromic property in spiropyran dye itself has been well known to be very poor. We synthesized new bifunctional copolymers (BFCPs) including photochromic spiropyran and photocrosslinkable chalcone moieties to improve the stability of chromism. The rate control of ring opening and ring closure reaction of spiropyran dye was successfully achieved by virtue of $[2\pi + 2\pi]$ photocyclo-addition between the chalcone units, which is expected to control the electrostatic interaction and steric hindrance surrounding photochromic moiety. As the concentration of chalcone moiety was higher in the copolymer, the stability of photochromism was found be somewhat better after UV irradiation although the difference is not significant.

References

1. Sun, S.-J.; Schwarz, G.; Kricheldorf, H. R.; Chang, T.-C. *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*(8), 1125.
2. Rehab, A.; Salahuddin, N. *Polymer* **1999**, *40*(9), 2197.
3. Kawatzuki, N.; Yamamoto, T.; Ono, H. *Appl. Phys. Lett.* **1999**, *74*(7), 935.
4. Gong, Y.-K.; Nakanishi, F. *Abe K. Mol. Cryst. Liq. Cryst.* **1999**, *327*, 123.
5. (a) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 7195. Also see (b) Matsuda, K.; Irie, M. *Polyhedron* **2001**, *20*, 1391. (c) Irie M. *Chem. Rev.* **2000**, *100*, 1685.
6. (a) Tamaoki, N.; Keuren, E. V.; Matsuda, H. *Appl. Phys. Lett.* **1996**, *69*(9), 1188. (b) Cullum, B. M.; Mobley, J.; Bogard, J. S.; Moscovitch, M.; Phillips, G. W.; Vo-Dinh, T. *Anal. Chem.* **2000**, *72*, 5612.
7. (a) Bobrovsky, A. Y.; Boiko, N. I.; Shibaev, V. P. *Liquid Crystals.* **2000**, *27*, 57. And also see (b) **2000**, *27*, 219. (c) Sasaki, K.; Nagamura, T. *Appl. Phys. Lett.* **1997**, *71*, 434.
8. Ock, K. S.; Jo, N. J.; Kim, J. H.; Kim, S. H.; Koh, K. N. *Synthetic Metal.* **2001**, *117*, 131.
9. (a) Jansson, R.; Zangooie, S.; Kugler, T.; Arwin, H. J. *Phys. Chem. of Solids* **2001**, *62*, 1219. (b) Ghailane, F.; Manivannan, G.; Lessard, R. A. *Optical Eng.* **1995**, *34*, 480.
10. Kim, S. H.; Lee, S. M.; Park, J. H.; Kim, J. H.; Koh, K. N.; Kang, S. W. *Dyes and Pigments* **2000**, *45*, 51.
11. Görner, H. *Chem. Physics* **1997**, *222*, 315.
12. Goldburt, E.; Shvartsman, F.; Fishmann, S.; Krongauz, V. *Macromolecules* **1984**, *17*, 1225.
13. (a) Zhou, J.; Sui, Q.; Huang, B. J. *Photochem. and Photobiol. A Chem.* **1998**, *117*, 129. (b) Zelichenok, A.; Buchholtz, F.; Yitzchaik, S.; Ratner, J.; Safro, M.; Krongauz, V. *Macromolecules* **1992**, *25*, 3175.
14. Choi, D. H.; Cha, Y. K. *Bull. Korean Chem. Soc.* **2002**, *23*, 4.
15. Choi, D. H.; Oh, S. J.; Cha, H. B.; Lee, J. Y. *European Polymer J.* **2001**, *37*, 1951.
16. Akelah, A.; Selim, A.; Salah El-Deen, N. *Polym. International* **1992**, *28*, 307.
17. Akelah, A.; Selim, A.; Salah El-Deen, N. *Polym. International* **1993**, *32*, 423.
18. (a) Allcock, H. R.; Kim, C. H. *Macromolecules* **1991**, *24*, 2846. (b) Biteau, J.; Chaput, F.; Boilot, J.-P. *J. Phys. Chem.* **1996**, *100*, 9024.