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Synthesis of novel chalcone derivatives and their stabilization effect of spiropyran in PMMA films

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Abstract

Three novel bis-chalcone derivatives with different alkyldioxy spacers were synthesized and dispersed into polymethyl methacrylate (PMMA) chloroform solution with 6-nitro-1'-ethyl-3',3'-dimethylspiro-2*H*-1-benzopyran-2,2'-indoline (ESP) to prepare photochromic PMMA films in a facile way. After irradiation with 365 nm UV light, the photocrosslinking reaction between chalcone units was proved to retard the decolorization of merocyanine form of the photochromic spiropyran effectively, as results of the steric hindrance produced by photocycloaddition of chalcone groups. It has been found that the bis-chalcone molecule with the shortest spacer has the most effective stabilizing effect on retardation of decoloration of spiropyran. © 2011 Yan Gang Liu. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Photochromism; Chalcone; Spiropyran; Photocycloaddition; Stabilization effect

Spiropyran derivatives, as one of the most well known class of organic photochromic compounds, have attracted much attention for several decades due to their potential application in fields of optical switch, rewritable data storage and biological labeling [1-3]. Nevertheless, the poor stability of the colored merocyanine form of spiropyran usually restricts its practical applications [4]. Extensive study has been carried out to improve the durability of photochromic property. For example, Oda [5] examined the protecting effect of spiropyran by amphoteric counter-ionic complexes against the decolorization reaction on cellulose. Lin [6] and Tork *et al.* [7] studied the photo-chromic characters of spiropyran in different polymer matrices. However, spiropyran derivatives still remain on the way to be practical devices.

It is known that, photocrosslinking reaction between α , β -unsaturated carbonyl groups (named chalcone or cinnamoyl units) obeys the $[2\pi + 2\pi]$ mechanism [8]. Choi [4,9] found that after the introduction of photocrosslinkable moieties into photochromic polymers in the main chain and the side chain, the photocycloaddition can control the free volume surrounding merocyanine moiety and then retard the relaxation. While such work involved a much more complicated synthesis and polymerization process, which therefore limited its application.

Herein, we report the synthesis of three novel chalcone derivatives of 1,2-di(2'-benzoyl-4-styryloxy)ethane (BSOE), 1,4-di(2'-benzoyl-4-styryloxy)butane (BSOB), 1,6-di(2'-benzoyl-4-styryloxy)hexane (BSOH) with the

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n= 2, BSOE; 4, BSOB; 6, BSOH

Scheme 1. Synthesis procedure of bis-chalcone derivatives.



Scheme 2. Photocycloaddition reaction of bis-chalcone derivatives during 365 nm UV light irradiation.

structure of two chalcone moieties connected by different alkyldioxy spacer chains. We also prepared photochromic films in a facile way by dispersing ESP with the bis-chalcone derivatives into PMMA/CHCl₃ solution, then studied the photochromic properties of the films after being irradiated with 365 nm UV light. The novel chalcone derivatives would retard the transformation of merocyanine to the form of spiropyran and improved the stability *via* photocrosslinking of chalcone groups.

ESP was synthesized as the similar method described in Ref. [10]. 4-Hydroxychalcone was prepared according to the method of Rehab [11]. The general preparation of BSOE, BSOB and BSOH was illustrated in Scheme 1. The structures of the compounds were confirmed with ¹H NMR, MS and elemental analysis [12]. Photoreactive films were prepared by spin-coating the dissolved chalcone derivatives, ESP and PMMA in chloroform according to the proportion of 0.05 mmol/0.05 mmol/0.1 g onto quartz plates.

The photoreactions in solid PMMA films were monitored by UV-vis spectra at the relevant characteristic absorption wavelength as shown in Fig. 1(a). The maximum absorbance at 339 nm attributed to chalcone groups successively decreased with the exposure to UV light, as the result of the $[2\pi + 2\pi]$ photocycloaddition of the double bonds of chalcone groups. While the colored merocyanine form of spiropyran showed maximum absorbance at 581 nm and the absorption intensity of the chromophore increased gradually with the irradiation time increasing. Therefore, it is obvious that the photocrosslinking reaction between chalcone units (Scheme 2) and photochromic transformation of spiropyran in the films proceeded coincidently with the irradiation of 365 nm UV light.

FTIR spectra and ¹H NMR were also helpful to observe the photoreaction of chalcone groups. The FTIR spectra were recorded with the samples before and after UV irradiation. As shown in Fig. 1(b), significant changes in the



Fig. 1. Spectral changes of BSOB/ESP/PMMA film irradiated with UV light: (a) UV-vis spectra and (b) infrared spectra.



Fig. 2. ¹H NMR of BSOB/PMMA film in CDCl₃ after irradiation with 365 nm UV light.



Fig. 3. Change of absorbance at 581 nm during dark decolorization and the decay rate constant. ESP: ESP/PMMA film k (s⁻¹): 2.01 × 10⁻⁴; BSOH: BSOH/ESP/PMMA film, k (s⁻¹): 1.35 × 10⁻⁴; BSOB: BSOB/ESP/PMMA film, k (s⁻¹): 1.04 × 10⁻⁴; BSOE: BSOE/ESP/PMMA film, k (s⁻¹): 9.24 × 10⁻⁵.

spectra occurred indeed. The intensities of stretching vibration of the double bond at 1598 cm⁻¹ and the unsaturated ketone carbonyl at 1659 cm⁻¹ in chalcone moiety decreased significantly with UV irradiation. In ¹H NMR spectra of BSOB/PMMA film (Fig. 2), new chemical shifts of 6.78, 6.58, 4.80, 4.50 and 4.31 [13], which were due to the hydrogen atoms in oxyalkyl substituted benzene and cyclobutane, appeared after UV irradiation and were all consistent with the literature [14] Thus, the occurrence of the $[2\pi + 2\pi]$ photocrosslinking between chalcone moieties could be confirmed by ¹H NMR, UV-vis and FTIR spectral analysis.

The stabilization effect of the chalcone derivatives on merocyanine ring closure reaction was carried out by monitoring the absorption change at λ_{max} during dark decolorization of the colored merocyanine in PMMA films which were irradiated with the 365 nm UV light for 15 min. The results in Fig. 3 showed that the film's decolorized rates doped with chalcone derivatives were much slower than that of sample ESP after UV irradiation. It could be explained that photocrosslinking between chalcone moieties could reduce the distance between PMMA polymer chains and confine the transformation from the colored *trans*-merocyanine to spiropyran, then stabilize the merocyanine structure in solid films effectively.

It should be noted that the films contained three chalcone derivatives exhibited different decay rates (Fig. 3). Sample BSOE had the lowest decolorized rate while sample BSOH had the fastest one which was induced by the length of spacer chains between chalcone units. After UV irradiation the photocrosslinked polymer of BSOE with shortest spacer was most rigid which results in the smallest free volume between polymer chains. While the photoproduct of BSOH, containing a six CH_2 soft chain between the chalcone moieties, might be looser than the

photoproduct of BSOE and the photochromic reaction could occur easily. Sample BSOB had a moderate soft spacer and decay rate compared to the other samples, which confirmed that the photocrosslinking between chalcone moieties reduced free volume surrounding merocyanine and then stabilized the colored structure.

In conclusion, three novel bis-chalcone derivatives had been synthesized. Photochromic PMMA films doped with ESP and bis-chalcone derivatives were prepared *via* a facile method and the photochemical reactions were investigated under irradiation of UV light. It had been found that photocrosslinking between chalcone units stabilized the decolorization behavior of merocyanine effectively resulting from the steric hindrance produced by photocycloaddition, while the shortest soft chain containing bis-chalcone BSOE was the most effective one among the three derivatives. These facilely prepared photochromic films might be used in low cost data storage.

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- [12] BSOE: ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, 4H, J = 6.8 Hz), 7.79 (d, 2H, J = 15.6 Hz), 7.62 (d, 4H, J = 8.8 Hz), 7.58 (t, 2H, J = 7.2 Hz), 7.50 (t, 4H, J = 7.2 Hz), 7.43 (d, 2H, J = 15.6 Hz); 7.00 (d, 4H, J = 8.8 Hz), 4.40 (s, 4H); LC–MS: m/z 474.0 ([M⁺]). Anal. Calcd. for C₃₂H₂₆O₄: C, 80.99; H, 5.52. Found: C, 81.01; H, 5.48. BSOB: ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, 4H, J = 7.2 Hz), 7.79 (d, 2H, J = 15.6 Hz), 7.60 (d, 4H, J = 8.8 Hz), 7.56 (t, 2H, J = 7.6 Hz), 7.50 (t, 4H, J = 7.6 Hz), 7.56 (t, 2H, J = 7.6 Hz), 7.50 (t, 4H, J = 7.6 Hz), 7.42 (d, 2H, J = 15.6 Hz), 6.93 (d, 4H, J = 8.8 Hz), 4.09 (t, 4H, J = 5.6 Hz), 2.02 (m, 4H, J = 2.8 Hz); LC-MS: m/z 502.2 ([M⁺]). Anal. Calcd. for C₃₄H₃₀O₄: C, 81.25; H, 6.02. Found: C, 81.28; H, 6.00. BSOH: ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, 4H, J = 7.2 Hz), 7.79 (d, 2H, J = 7.6 Hz), 7.50 (t, 4H, J = 7.6 Hz), 7.60 (d, 4H, J = 8.8 Hz), 7.57 (t, 2H, J = 7.6 Hz), 7.50 (t, 4H, J = 7.6 Hz), 7.60 (d, 4H, J = 8.8 Hz), 1.58 (m, 4H, J = 3.6 Hz), 1.58 (m, 4H, J = 3.6 Hz); LC-MS: m/z 530.1 ([M⁺]). Anal. Calcd. for C₃₆H₃₄O₄: C, 81.48; H, 6.46. Found: C, 81.51; H 6.42.
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