

Novel UV-sensitive bis-chalcone derivatives: synthesis and photocrosslinking properties in solution and solid PMMA film

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Abstract A series of chalcone derivatives in which two chalcone groups are attached by alkyldioxy chains were synthesized and characterized by ^1H NMR, UV–Vis, and Fourier transform infrared (FTIR) spectral analysis. Upon the irradiation of 365-nm UV light, the chalcone groups in the molecules underwent $[2\pi + 2\pi]$ photodimerization. The photocrosslinking properties were investigated both in solution and in polymethyl methacrylate (PMMA) solid films on quartz plate. It has been found that the photocrosslinking rates of the compounds depended on the different flexibility of the functional groups, which was determined by the length of the spacer chain between the two chalcone moieties. The longest soft chain containing derivatives has a faster photocrosslinking rate both in solution and in solid film. Irradiated by polarized ultraviolet light (PUV), all of the films doped with bis-chalcone derivatives showed an anisotropic absorption property, which may give a promising application as LC-alignment materials.

Keywords Chalcone · UV irradiation · Photocrosslinking · Photodimerization

Introduction

Photosensitive materials have attracted considerable attention in the past several decades, since the photochemical reactions in organic materials may induce many changes in the properties, such as solubility, optical behavior, photomechanical effect, refractive index, and dielectric constant [1–6]. Among the photosensitive materials, the UV-sensitive polymers have been highlighted because of their excellent properties and wide applications in many fields. The technological

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applications of these photoactive materials are in the fields of lithography [7–10], liquid crystals [11–14], nonlinear optical materials [15–18], optical anisotropy [19–21], and UV curing process [22–24].

Photocrosslinking is one of the most attractive photochemical reactions. The polymers containing α , β -unsaturated carbonyl groups, such as cinnamoyl and chalcone groups, are very sensitive to UV light and undergo crosslinking reaction upon UV light irradiation [25–28]. These polymers would have the properties of high photosensitivity, good solubility, ability to form films, good resistance towards solvents, and thermal stability after $[2\pi + 2\pi]$ photodimerization reaction, which are very important for the practical applications. As the chalcone groups possess very high absorption coefficients of around 300–365 nm, its photocrosslinking reaction rate is relatively faster compared to that of cinnamoyl groups under the irradiation of UV light [15]. This will enable chalcone derivatives to have more interesting properties, including better thermal stability and resistance capacity than cinnamoyl groups. However, most research work has focused on compounds with chalcone groups embedded in the main chain or pended as side chains [29–36]. As the chalcone groups of the dichalcone functionalized monomer can be dimerized under UV light irradiation, it is theoretically possible to obtain linear polymers if the reaction takes place intermolecularly [19, 37, 38]. Nevertheless, to the best of our knowledge, few research works have been reported on the photocrosslinking properties of molecules containing double chalcone moieties.

Herein, we, for the first time, report the synthesis and characterization of a series of new photosensitive bis-chalcone derivatives with a structure of two chalcone units connected by different alkylidioxy spacer chains. Upon irradiation of 365-nm UV light, the chalcone units crosslinked each other and the photocrosslinking properties were studied both in solution and in solid film, as well as the effect of the spacer chain on the rate of crosslinking. The research would be seen as preceding exploration to evaluate the applications of these materials.

Experimental

Materials

4-Hydroxybenzaldehyde, acetophenone, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, and 1,6-dibromohexane (CP) were purchased from Sinopharm Chemical Reagent Co., Ltd and used as received. Polymethyl methacrylate (PMMA) was kindly provided by the Shanghai Zhibi Chemical Factory. *N,N*-dimethylformamide was dried by 4A molecular sieves. Anhydrous potassium carbonate and potassium iodide (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. Ethanol, chloroform, and other solvents were used without further purification.

Synthesis of 4-hydroxyphenyl styryl ketone (4-hydroxychalcone)

In a three-necked flask equipped with a magnetic stirrer and dropping funnel, a solution of 2.0 g (50 mmol) NaOH in 3 mL deionized water was added to 2.40 g

(20 mmol) acetophenone in 60 mL of ethanol. The mixture was cooled to room temperature. A solution of 2.45 g (20 mmol) 4-hydroxybenzaldehyde in 40 mL ethanol was then added dropwise with constant stirring and the temperature was not allowed to exceed 25 °C. After stirring for 24 h, the mixture was poured into 500 mL water. The pH of the solution was adjusted to about 6 by adding 1 mol/L HCl and the solution was set aside for more than 12 h. The precipitated product was filtered, washed several times with ice-cold water, and purified by recrystallization from 95% ethanol into a yellow crystalline product. Yield: 57.8%, mp 186–187 °C. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.94 (s, 1H, $-\text{OH}$), 8.02–8.00 (d, 2H, Ar-H), 7.80–7.76 (d, 1H, $=\text{CH}-\text{CO}-$), 7.58–7.55 (m, 3H, Ar-H), 7.52–7.48 (t, 2H, Ar-H), 7.43–7.39 (d, 1H, $=\text{CH}-\text{Ar}$), 6.91–6.88 (d, 2H, Ar-H). Elemental analysis (%): Calculated: C 80.34, H 5.39; Found: C 81.37, H 5.36. FTIR (KBr, cm^{-1}): 3216 ($-\text{OH}$), 3020 (Ar-H), 1650 ($>\text{C}=\text{O}$), 1599 (s, $-\text{C}=\text{C}-$ olefinic), 1557, 1512 (s, $-\text{C}=\text{C}-\text{Ar}$), 834, 725, 690 ($-\text{C}-\text{H}$).

General procedure for the synthesis of dichalcone derivatives

In a dry two-necked flask fitted with a dropping funnel and condenser closed with a calcium chloride tube, 5 mmol of the corresponding dibrominated alkane was added dropwise with stirring to a solution of 2.47 g (11 mmol) 4-hydroxychalcone dissolved in 20 mL DMF in the presence of 3.04 g (22 mmol) anhydrous potassium carbonate and a small amount of potassium iodide. The mixture was reacted at 80 °C with stirring for 24 h and was then poured into 300 mL deionized water. The solution was set aside overnight. The product was collected by filtration and purified by recrystallization from a mixture of ethanol and chloroform.

1,2-Di (2'-benzoyl-4-styryloxy) ethane (BSOE)

Yield: 32.5%, mp 189–191 °C. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.02–8.00 (d, 4H, Ar-H), 7.81–7.77 (d, 2H, $=\text{CH}-\text{CO}-$), 7.63–7.61 (d, 4H, Ar-H), 7.58–7.56 (d, 2H, Ar-H), 7.52–7.48 (t, 4H, Ar-H), 7.45–7.41 (d, 2H, $=\text{CH}-\text{Ar}$), 7.01–6.98 (d, 4H, Ar-H), 4.40 (s, 4H, $-\text{O}-\text{CH}_2-$). LC-MS: m/z 474.0 (M^+). Elemental analysis (%): Calculated: C 80.99, H 5.52; Found: C 81.01, H 5.48. FTIR (KBr, cm^{-1}): 3066 (Ar-H), 2941, 2879 ($-\text{C}-\text{H}$), 1654 ($>\text{C}=\text{O}$), 1599 (s, $-\text{C}=\text{C}-$ olefinic), 1589, 1570, 1511, 1426 ($-\text{C}=\text{C}-$ aromatic), 1175, 1033 (s, $-\text{C}-\text{O}-\text{C}-$), 834, 724, 696 ($-\text{C}-\text{H}$).

1,3-Di (2'-benzoyl-4-styryloxy) propane (BSOP)

Yield: 46.2%, mp 184–185 °C. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.02–7.99 (d, 4H, Ar-H), 7.80–7.76 (d, 2H, $=\text{CH}-\text{CO}-$), 7.61–7.59 (d, 4H, Ar-H), 7.57–7.56 (m, 2H, Ar-H), 7.51–7.48 (t, 4H, Ar-H), 7.44–7.40 (d, 2H, $=\text{CH}-\text{Ar}$), 6.96–6.94 (d, 4H, Ar-H), 4.24–4.21 (t, 4H, $-\text{O}-\text{CH}_2-$), 2.34–2.28 (m, 2H, $-\text{C}-\text{CH}_2-\text{C}-$). LC-MS: m/z 488.3 (M^+). Elemental analysis (%): Calculated: C 81.12, H 5.78; Found: C 81.14, H 5.75. FTIR (KBr, cm^{-1}): 3055 (Ar-H), 2941, 2880 ($-\text{C}-\text{H}$), 1661 ($>\text{C}=\text{O}$), 1600 ($-\text{CH}=\text{CH}-$ olefinic), 1572, 1511, 1422 ($-\text{C}=\text{C}-$ aromatic), 1176, 1018 ($-\text{C}-\text{O}-\text{C}-$), 826, 720, 686 ($-\text{C}-\text{H}$).

1,4-Di (2'-benzoyl-4-styryloxy) butane (BSOB)

Yield: 84.6%, mp 156–158 °C. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.02–8.00 (d, 4H, Ar-H), 7.81–7.77 (d, 2H, =CH-CO-), 7.61–7.59 (d, 4H, Ar-H), 7.58–7.56 (d, 2H, Ar-H), 7.52–7.48 (t, 4H, Ar-H), 7.44–7.40 (d, 2H, =CH-Ar), 6.94–6.92 (d, 4H, Ar-H), 4.10–4.08 (t, 4H, -O-CH₂-), 2.03–2.01 (m, 4H, -O-C-CH₂-). LC-MS: m/z 502.4 (M^+). Elemental analysis (%): Calculated: C 81.25, H 6.02; Found: C 81.28, H 5.99. FTIR (KBr, cm^{-1}): 3059 (Ar-H), 2929, 2870 (-C-H), 1654 (>C=O), 1598 (-CH=CH- olefinic), 1589, 1569, 1512, 1473 (-C=C- aromatic), 1174, 1018 (-C-O-C-), 831, 724, 696 (-C-H).

1,6-Di (2'-benzoyl-4-styryloxy) hexane (BSOH)

Yield: 85.2%, mp 166–168 °C. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.02–8.00 (d, 4H, Ar-H), 7.81–7.77 (d, 2H, =CH-CO-), 7.61–7.58 (d, 4H, Ar-H), 7.57–7.55 (d, 2H, Ar-H), 7.51–7.48 (t, 4H, Ar-H), 7.43–7.39 (d, 2H, =CH-Ar), 6.93–6.91 (d, 4H, Ar-H), 4.02 (t, 4H, -O-CH₂-), 1.85 (m, 4H, -O-C-CH₂-), 1.58 (m, 4H, -O-C-C-CH₂-). LC-MS: m/z 530.1 (M^+). Elemental analysis (%): Calculated: C 81.48, H 6.46; Found: C 81.50, H 6.44. FTIR (KBr, cm^{-1}): 3056 (Ar-H), 2943, 2899, 2868, 2851 (-C-H), 1653 (>C=O), 1599 (-CH=CH- olefinic), 1589, 1567, 1511, 1473(-C=C- aromatic), 1173, 1038 (-C-O-C-), 833, 725, 696 (-C-H).

Measurements

^1H -NMR spectra of the dichalcone compounds were obtained on a Mercury Plus 400 (400 MHz for proton) spectrometer with TMS as the internal standard reference in CDCl_3 solution. Fourier transform infrared (FTIR) spectra were recorded using a Perkin Elmer Paragon 1000 spectrophotometer by incorporating dichalcone compounds in the potassium bromide tablets. Elemental analysis was performed with a Vario EL II analyzer. Mass spectra were recorded on an Agilent 1100LC/MSD system. The UV-Vis spectra of the spin-coated films on quartz plate were determined on a Beijing Purkinje TU-1901 spectrophotometer. The melting points were taken from an X-4 digital apparatus without correction. The intensity of the UV light was detected with a broadband UV light radiometer (365 nm, Photoelectric Instrument Factory of Beijing Normal University, China).

Film preparation and UV light irradiation

For fabricating the thin films, the synthesized chalcone derivatives and PMMA (ratio: 1:10 wt) were dissolved in CHCl_3 to give solutions with a concentration of 0.04 g/mL. The solutions were filtered through membranes with the pore size of 0.2 μm and were then spin-coated onto quartz plates (20 $\times$ 20 mm). The spin-coating rate was controlled to be 600 rpm for 9 s and then 1,500 rpm for 30 s to obtain films with similar thickness. The films were then dried at 60 °C under a vacuum condition overnight to remove the residual solvent completely.

A high-pressure mercury lamp equipped with a band pass filter to obtain an emission of wavelengths mainly between 300 and 380 nm was used for the irradiation of derivatives in solution and film on quartz plate. The intensity of the UV light on the exposed surface was 3.44 mW/cm^2 at 365 nm. The polarized ultraviolet light (PUV) was achieved by the addition of a polarizer in the light route, the intensity of which was 0.52 mW/cm^2 at 365 nm. After each exposure interval, the UV spectrum of the sample was recorded immediately. The rate of disappearance of the UV-reactive chalcone group was monitored according to the following equation:

$$\text{Extent of conversion (\%)} = (A_0 - A_T)/A_0 \times 100 \quad (1)$$

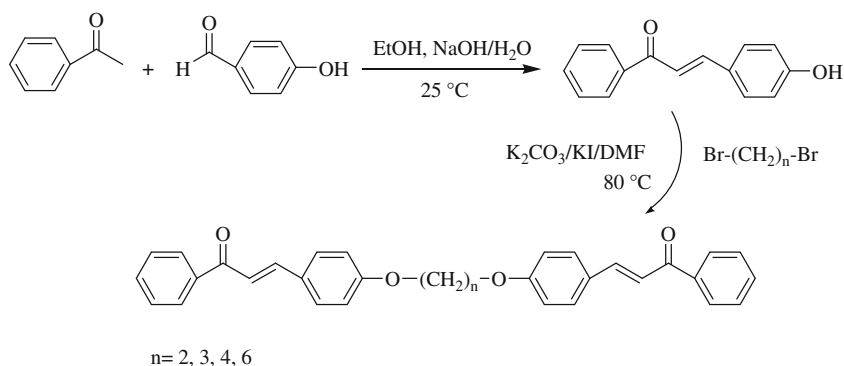
where A_0 and A_T are the absorption intensities due to $>\text{C}=\text{C}<$ after irradiation times $t = 0$ and $t = T$, respectively.

Results and discussion

Synthesis

A series of UV-sensitive compounds with a structure of two chalcone moieties connected by alkylidioxo soft spacer chains were synthesized as illustrated in Scheme 1. The 4-hydroxychalcone was prepared by reacting 4-hydroxybenzaldehyde with acetophenone in ethanol/water solution in the presence of sodium hydroxide as the base [27]. The reaction of 4-hydroxychalcone with the corresponding alkyl dihalide, such as 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, and 1,6-dibromohexane, through Williamson reaction in the presence of anhydrous K_2CO_3 and KI led to the target bis-chalcone compounds. The solubility of the prepared chalcone derivatives in various solvents was tested since it is one of the most important factors for practical applications of these compound; all of the derivatives are easily soluble in polar aprotic solvents and chlorinated solvents such as chloroform, dichloromethane, *N,N*-dimethylformamide, *N*-methyl-2-pyrrolidone, and dimethyl sulfoxide.

The chemical structures of the four chalcone derivatives were confirmed by elemental analysis, ^1H NMR, and FTIR spectra; the details have been given in the experimental part. The typical ^1H NMR spectra will be presented here for further discussion as a sample. Figure 1a shows the ^1H NMR spectrum of 4-hydroxychalcone. The chemical shifts and the integral areas are clearly consistent with the proposed structure. After reaction with dibrominated alkanes, resonance at 8.94, which belongs to the proton on the hydroxyl, disappeared completely and new resonances at the high field of 4.40 in BSOE, 4.22 in BSOP, 4.10 in BSOB, and 4.02 in BSOH indicate the formation of aralkyl ether bond. The spectral variations of 2.31 (Fig. 1c), 2.02 (Fig. 1d), 1.85, and 1.58 (Fig. 1e) can be assigned to the other methylene protons of spacer chains. By comparing the proton peaks and integral area, which are all very consistent with the chemical structure of bis-chalcone molecules, it can be concluded that the new chalcone derivatives were obtained.



Scheme 1 Synthetic procedure of dichalcone moieties containing molecules BSOE, BSOP, BSOB, and BSOH. ChemDraw Ultra 9.0 was used to create the artwork

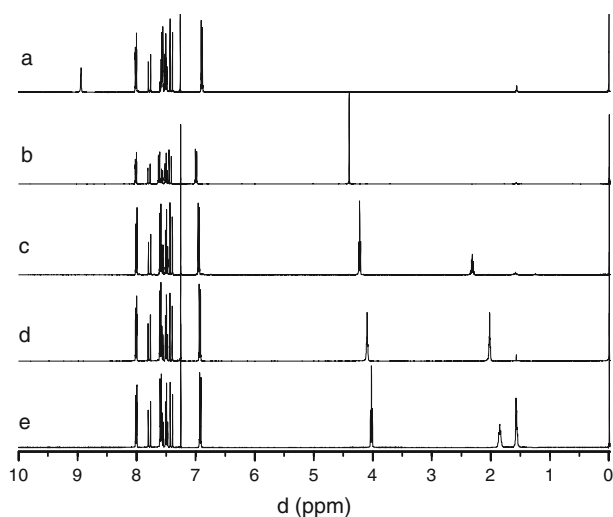
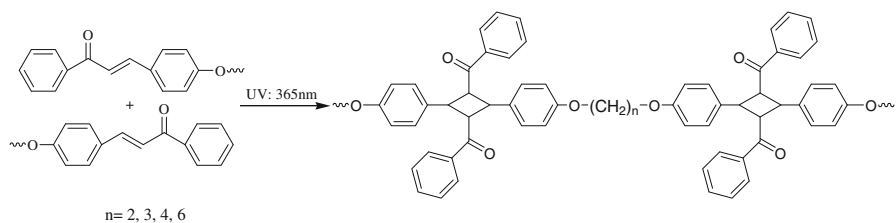


Fig. 1 ^1H NMR spectra of (a) 4-hydroxychalcone, (b) BSOE, (c) BSOP, (d) BSOB, (e) BSOH. MestReNova (version: 5.3.1) and OriginPro 7.5 were used to create the artwork

Photocrosslinking behavior in solution

The photosensitivity of the chalcone derivatives toward UV light was investigated by measuring the UV absorption of the chalcone moieties in the molecules. The bis-chalcone compounds undergo crosslinking reaction by dimerization between the double bonds in chalcone groups (Scheme 2). The UV–Vis absorption spectra of BSOP in CHCl_3 solution were recorded for different time intervals during UV irradiation (Fig. 2). The UV absorption spectroscopy of BSOP showed a maximum absorption at 341 nm, corresponding to the $\pi\text{--}\pi^*$ transition of the chalcone moiety. Under irradiation, the decrease of the absorption at 341 nm was evident, which can



Scheme 2 Structural change of bis-chalcone derivatives during UV light irradiation. ChemDraw Ultra 9.0 was used to create the artwork

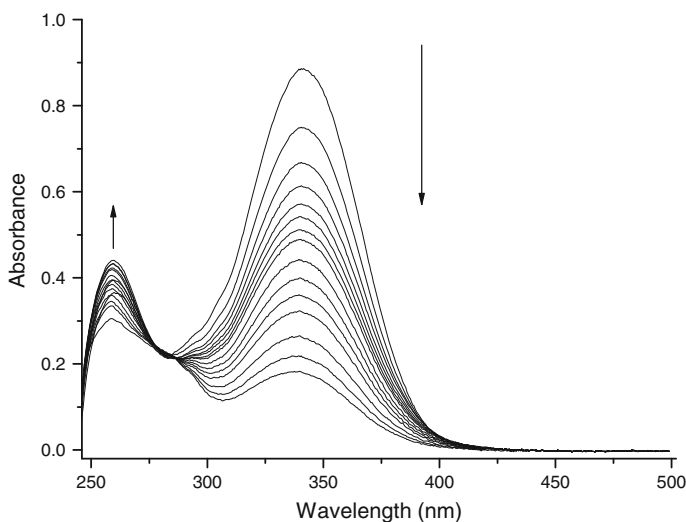


Fig. 2 Absorbance spectral change of BSOP in CHCl_3 solution irradiated with 365-nm UV light. Top to bottom: $t = 0, 5, 10, 20, 40, 60, 90, 120, 180, 240, 300, 390, 480, 600$, and 900 s

be attributed to the decrease in the conjugated system and a concomitant increase in the absorbance at a shorter wavelength of 259 nm due to the formation of cyclobutane rings through $[2\pi + 2\pi]$ cycloaddition of the double bond in the chalcone unit. The maximum absorbance at 341 nm of the double bond decreased drastically upon UV irradiation. Therefore, the bis-chalcone compounds react photochemically according to a mechanism that is well studied for cinnamic acid and its derivatives in which cyclobutane structures are formed [39].

The photocrosslinking rate of the chalcone derivatives was studied in solutions in terms of the disappearance of photoactive double bond in the chalcone unit. BSOH has the fastest and highest rate, while BSOE has the lowest compared with the other samples. This result may be attributed to the fact that the spacer units between the two chalcone moieties could determine the free movements of the photosensitive groups. The long and soft alkoxy chain gives more flexibility of chalcone units to

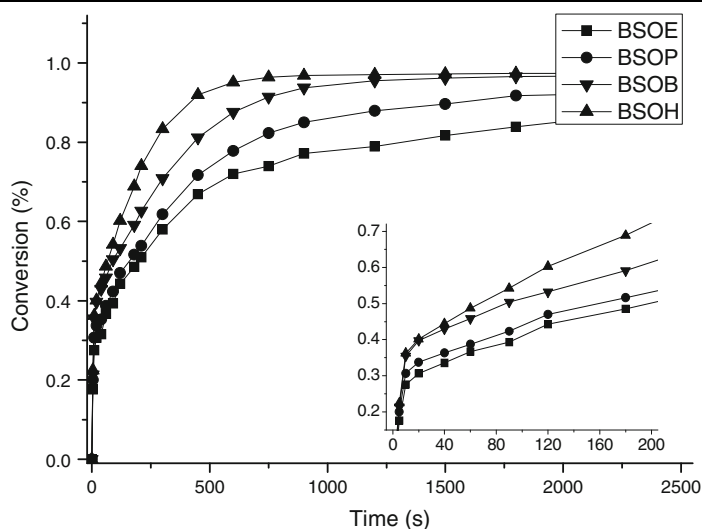


Fig. 3 Photocrosslinking rate of the chalcone units of BSOE, BSOP, BSOB, and BSOH with UV irradiation in CHCl_3 solutions

increase the rate of crosslinking, which is similar to the results described in the literature [27–29]. Thus, the photocrosslinking rate of the chalcone derivatives is $\text{BSOH} > \text{BSOB} > \text{BSOP} > \text{BSOE}$, as shown in Fig. 3.

Photocrosslinking behavior in PMMA film

The photocrosslinking reactions of the chalcone derivatives were also carried out in PMMA films (Fig. 4). It is notable that the photoreactivity order of the four chalcone derivatives in PMMA films is similar to that observed in solutions, while the difference in photocrosslinking rates between each sample is not so obvious. It may be explained by the fact that the PMMA chains restrict the movement of chalcone groups, thus, leaving very little free volume for crosslinking and the influence of the soft spacer chain is not as significant as that in solution. The geometrical hindrance also leads to the photocrosslinking rates being much slower in solid films than those in solutions and the relevant photocrosslinking degree is smaller than that in solution also (Fig. 5). It is reasonable to consider that the bis-chalcone derivatives could move freely and the *cis-trans* configuration of chalcone moieties may transform easily in solution, which leads to increased rate of crosslinking. As the exposure time was prolonged, the unreacted chalcone molecules could move closely to crosslink, which results in a much higher crosslinking extent. However, the chalcone groups in solid PMMA film would be restricted by the polymer chains and the photocrosslinking reaction could only occur between the adjacent chalcone units. So, the procedure of photoreaction in film is much slower and the reaction conversion is lower than that in solution.

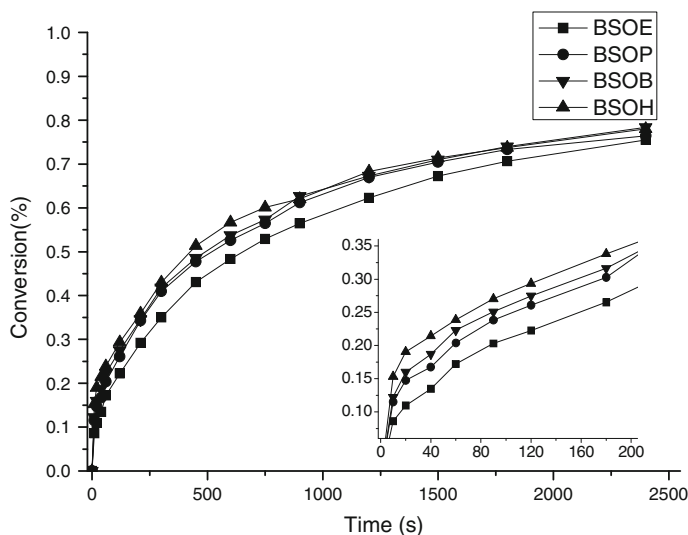


Fig. 4 Photocrosslinking rate of chalcone units of BSOE, BSOP, BSOB, and BSOH with UV irradiation in PMMA films

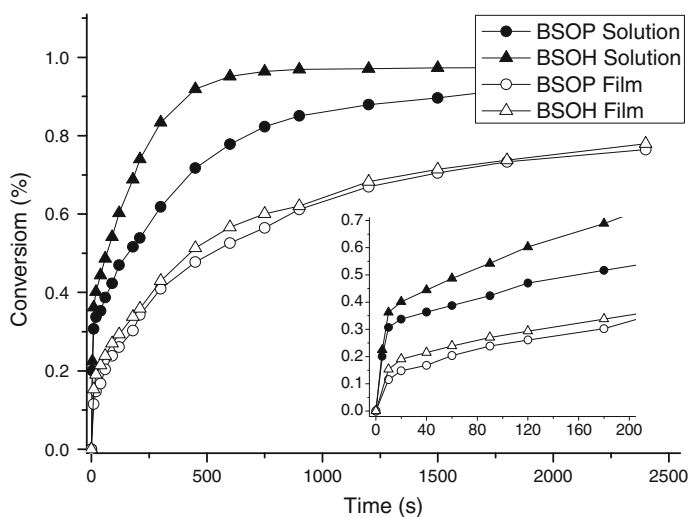


Fig. 5 Photocrosslinking rate of BSOP and BSOH in CHCl_3 solution and in PMMA films

Anisotropic behavior after PUV irradiation

In order to investigate the UV-induced optical properties of the chalcone derivatives, the prepared PMMA films were also exposed to PUV for a certain amount of time and then shown anisotropic spectra absorption by monitoring the maximum absorbance. In Fig. 6, the differences of absorption spectra between the

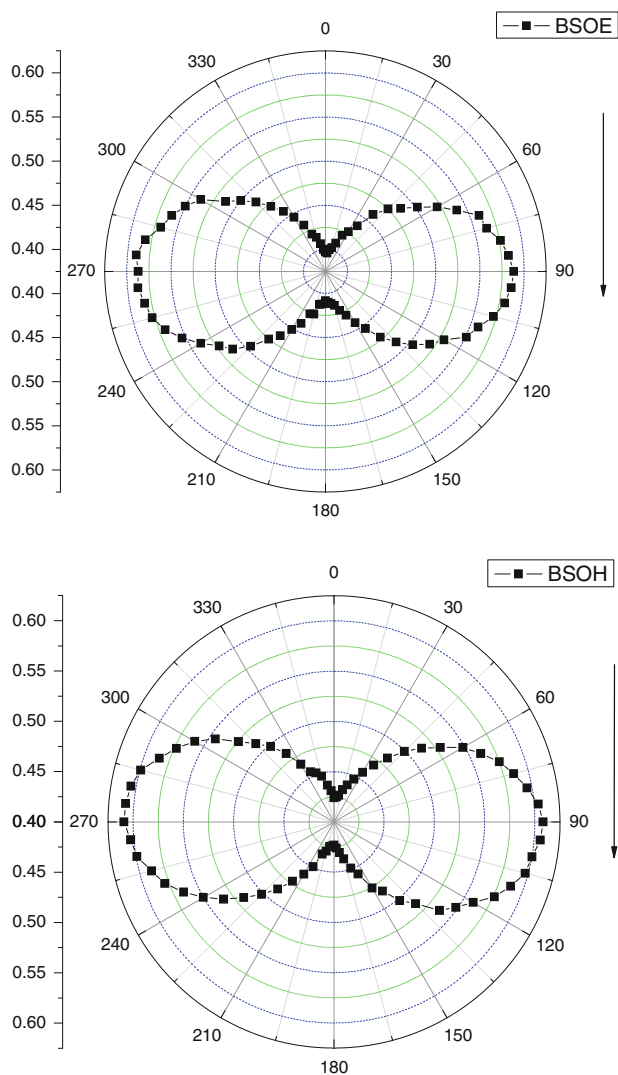


Fig. 6 Circular diagrams of the absorbance of chalcone units in BSOE and BSOH after irradiation with PUV in PMMA films. OriginPro 7.5 was used to create the artwork

perpendicular and parallel polarization direction of the PUV were illustrated by samples of BSOE and BSOH. The parallel absorbance was observed to be smaller than the perpendicular absorbance in the whole range of the irradiation, which may attributed to the directional selectivity of photocrosslinking of the double bond in chalcone groups. It can be assumed that the anisotropically UV-dimerized cyclobutane rings of the C=C in chalcone moieties and the rearrangement of the groups attaching to them will induce the directional orientation of liquid crystal, although further studies are necessary in order to measure the parameters of the

PUV-exposed films. Thus, these molecules could give a potential application as LC-alignment materials.

Conclusion

Four chalcone derivatives with a structure of two chalcone moieties connected by different alkylidioxy chains have been synthesized and characterized by ^1H -NMR, UV-Vis, and Fourier transform infrared (FTIR) spectra. Upon irradiation of the 365-nm UV light, the molecules, which have an absorption maximum at about 340 nm, undergo $[2 + 2]$ photodimerization reaction. The photocrosslinking properties were studied both in solutions and polymethyl methacrylate (PMMA) films on quartz plate. It is found that the photocrosslinking rates of the bis-chalcone compounds in the PMMA films were much slower than those in the solutions, and the derivatives containing the longest spacer chain had a faster photocrosslinking rate. Irradiated with polarized ultraviolet light (PUV), films doped with the chalcone derivatives showed an anisotropic absorption property. It is reasonable to assume that the chalcone derivatives doped into commercially available polymer matrix would give promising applications as photoresist and photoalignment materials.

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