

Synthesis of Novel Photochromic Spiropyran Dyes Containing Quaternary Ammonium Salt or Cinnamoyl Moiety and Their Properties as Photoinitiators

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ABSTRACT: Three novel spiropyran (SP) dyes containing quaternary ammonium salt or cinnamoyl moiety were synthesized and their photosensitive properties as photoinitiator were characterized by UV-vis spectroscopy. The intramolecular electron transfer of SP dyes containing quaternary ammonium salt was much faster and can initiate the photopolymerization under UV irradiation though the photochromic properties than those of SPs containing cinnamoyl group. A photoinitiation system containing SPs and the hexarylbisimidazoles was studied, and the initiation properties

were tested by monitoring the conversion rate of double bond at 810 and 1640 cm^{-1} with time infrared spectroscopy. It was found that the system containing our SP derivatives exhibited much higher initiating efficiency than ever reported SP dyes in the photopolymerization of 2-phenoxyethylacrylate/*N*-vinylcarbazole. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: spiropyran; photopolymerization; photochromism

INTRODUCTION

Spiropyran (SP) has potential applications in rewritable data storage, optical switches, and chemical sensors. Typically, it undergoes a photoisomerization from its electrically neutral SP form to the zwitterionic merocyanine (MR) form under UV irradiation, and reverses back to the SP form under either visible light or heat.^{1–3} However, the SP produces too few radicals to initiate the photopolymerization during its excitation process by UV irradiation. Much effort has been devoted to the development of UV-sensitive organic materials because of increasing demand on miniaturization and better electronic production⁴ in recent years.

Photoinitiative radical polymerization can be initiated by both E-cleavage (Type I) and H-abstraction (Type II) initiators.⁵ Type I photoinitiators undergo E-cleavage to give two radical species. Type II photoinitiators, along with hydrogen donors, produce the initiating radicals based on a bimolecular reaction. Examples of Type II initiators include benzophenone and its derivatives, thioxanthenes, benzil, quionones, as well as organic dyes, while alcohols,

ethers, amines and thiols could also serve as coinitiator.^{6–8} Type II photoinitiators generally have better optical absorption properties than Type I initiators near UV region; however, their induced photopolymerization process would be relatively slower due to relative slower bimolecular initiation reaction.

To overcome the existing shortcomings of the Type II photoinitiators, a lot of research has been exploited to modify their structures and amine coinitiators. Some improved photoinitiators showed significant advantages over traditional low-molecular weight photoinitiators, such as less odor, less toxicity, and possessing polymeric effect etc. Moreover, *N*-methyl, *N*-ethyl aliphatic, or aromatic amines were also reported as coinitiators.^{9–13}

The aim of this study is to evaluate the performance of novel SP dyes as UV radical initiator and show their potential application in polymerization system. Three novel SP derivatives (compound 4, 5, and 7) containing quaternary ammonium salt or cinnamoyl moiety were prepared, and their photochromic properties were characterized by UV-Vis spectroscopy. Under UV irradiation, the photoinduced electron-transfer reaction takes place within the dyes and amine, and the electron-transfer process was monitored by UV-Vis. SP derivatives containing quaternary ammonium salt were more efficient in its quenching process, and the rate of electron transfer increased intramolecularly.

Photopolymerization was tested. The compositions of photoinitiating system included SP containing

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quaternary ammonium salt as photosensitive dye, 2-phenoxyethylacrylate (POEA 40% wt)/*N*-vinylcarbazole (NVC 40% wt) as functional monomer, triethanolamine (TEA) as coinitiator agent, hexaaryl-bisimidazoles (HABI) as radical source, which has stronger absorption at 255–275 nm and weaker absorption above 300 nm, and cellulose acetate as binder polymer.^{14–16} The efficiency of this system was evaluated by monitoring the conversion of the double bonds at 810 and 1640 cm^{-1} using real-time infrared spectroscopy (RTIR). The conversion rate achieved was as high as 60–75%, indicating that the novel SPs were good photoinitiators under UV irradiation.

EXPERIMENTAL

General

All reagents were of analytical grade and used without further purification unless otherwise mentioned. *N,N*-dimethylformamide (DMF), ethyl acetate, and chloroform were purified by standard distillation and used as solvents. ¹H-NMR was recorded in deuterated chloroform and DMSO on a Varian INO spectrometer. Mass data was analyzed by HP1100 LC/MSD (Agilent). UV-Vis spectra were recorded on a HP8453 spectrometer using a cuvette of 1 cm path length.

The measurement of the conversion of double bond was as follows: (1) a mixture of monomers POEA (40% wt)/NVC (40% wt), photosensitive dye SP (1% wt), initiator HABI (3% wt), coinitiators agent TEA (3% wt), and cellulose acetate (CA) were dissolved in solvent (methanol : chloroform = 1 : 9, v/v), and then the mixture was made either as cast films on KBr discs or KBr pellets. (2) the discs or pellets were irradiated with a UV spot light source (EFOS Lite, Canada, 50 W miniature arc lamp, with 5 mm crystal optical fiber) at room temperature. The light intensity on the surface of the samples was 15 mW/cm^2 detected by radiometry (Honle UV meter, Germany). RTIR spectra were obtained using a Nicolet 5700 instrument (Nicolet Instrument Corp., Thermo Scientific, Waltham, MA). The conversion of double bond was monitored by the changes of double bond absorption peaks, respectively, using OMINIC 7.0 software. A series of RTIR programs were used to determine the conversion of double bond. Each sample was measured three times.

Synthesis

Synthesis of 1-(3-chloro-2-hydroxypropyl)-2,3,3-trimethyl-3H-indolium (1)

2,3,3-trimethyl-3H-indole (6 g, 0.038 mol) was added dropwise into a 20 mL epichlorohydrin (14.06 g, 0.152 mol) ethanol solution at 45°C and the reaction was kept at 45°C for 24 h. After cooling to room

temperature, the solution was evaporated under reduced pressure. The oily residue was recrystallized three times from methanol, and 8.74 g (91% yield) compound 1 was obtained as white crystal. ¹H-NMR (400 MHz, CDCl_3): δ (ppm) 7.15 (m, $J = 7.1$ Hz, 1H), 7.08 (d, $J = 7.2$ Hz, 1H), 6.91 (m, $J = 7.5$ Hz, 1H), 6.79 (m, $J = 7.8$ Hz, 1H), 4.20 (m, 0.5H), 3.93 (m, 0.5H), 3.75 (m, 2H), 3.50 (m, 0.5H), 3.38 (m, 0.5H), 3.14 (m, 0.5H), 2.69 (m, 0.5H), 1.45 (d, 6H), 1.15 (d, 3H). API-ES Positive-Mass: m/z 252 ($[\text{M} + \text{H}]^+$, 100%).

Synthesis of 1-(2-hydroxy-*N,N,N*-trimethylpropan-1-aminium)-2,3,3-trimethyl-3H-indolium (2)

Compound 1 (4 g, 0.0158 mol) was dissolved in ethanol 20 mL, to which aqueous solution of the trimethylamine (33% wt) was added dropwise within 2 h under vigorous stirring. The mixture was stirred for another 48 h at 35°C to complete the reaction. After evaporating the solvent, the crude product was purified by column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 5, v/v) to remove trace amount of starting material 1. The residue was recrystallized three times from acetone, and 2.73 g of white crystal (compound 2) was obtained, the yield was 62.7%. ¹H-NMR (400 MHz, CDCl_3): δ (ppm) 7.12 (m, $J = 7.2$ Hz, 1H), 7.00 (d, $J = 7.2$ Hz, 1H), 6.9 (m, $J = 7.6$ Hz, 1H), 6.72–6.84 (m, $J = 7.8$ Hz, 1H), 4.10, 4.68 (m, 1H), 3.94, 4.40 (m, 2H), 3.20–3.61 (m, 11H, $-\text{CH}_2\text{N}^+\text{Me}_3$), 1.35–1.46 (m, 6H), 1.14–1.15 (m, 3H). API-ES Positive-Mass: m/z 276 ($[\text{M} + \text{H}]^+$, 100%).

Synthesis of 1-(2-hydroxy-*N,N,N*-dimethyl-*N*-octadecylpropan-1-aminium)-2,3,3-trimethyl-3H-indolium (3)

Compound 1 (4 g, 0.0158 mol) was dissolved in 20 mL ethanol and several drops of aqueous Na_2CO_3 solution (10% wt) was added to adjust the pH value of the mixture to 8–9. *N*-Octadecyldimethylamine (4.46 g, 0.015 mol) was added dropwise to the mixture under vigorous stirring for half an hour, and then the mixture was refluxed while stirring for another 24 h. After evaporating the solvent, the crude product was purified by column chromatography on silica gel (methanol : chloroform = 1 : 19, v/v), the product was recrystallized three times from acetone to give 3.66 g (yield 45%) of compound 3 as white powder. API-ES Positive-Mass: C_{16} m/z 485 ($[\text{M} + \text{H}]^+$, 100%), C_{18} m/z 513 ($[\text{M} + \text{H}]^+$, 100%).

Synthesis of 1-(2-hydroxy-*N,N,N*-trimethylpropan-1-aminium)-3',3'-dimethylspiro (2H-5-nitrobenzopyran-2, 2'-indoline) (4)

Compound 2 (1 g, 0.036 mol), 5-nitrosalicylaldehyde (0.67 g, 0.04 mol), 15 mL ethanol and several drops

of piperidine were placed in a 50 mL round-bottomed flask with a mechanical stirrer and a reflux condenser. The mixture was refluxed for 8 h to complete the reaction. After evaporating the solvent, the crude product was purified by column chromatography on silica gel (acetone : water = 20 : 1, v/v) to give 0.78 g (yield 49%) of compound 4 as yellow solid. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.01 (m, $J = 6.0$ Hz, 1H), 7.77 (m, $J = 8.0$ Hz, 1H), 7.14 (m, $J = 7.4$ Hz, 2H), 6.85–6.99 (m, $J = 7.7$ Hz, 2H), 6.02 (t, $J = 7.5$ Hz, 1H), 6.60 (d, $J = 16.1$ Hz, 0.5H), 5.33 (d, $J = 16.1$ Hz, 0.5H), 6.91 (d, $J = 15.9$ Hz, 0.5 Hz), 6.33 (d, $J = 15.9$ Hz, 0.5H), 4.42, 3.61 (m, 2H), 4.1 (m, 1H), 2.77–3.44 (m, 11H, $-\text{CH}_2\text{N}^+\text{Me}_3$), 1.37 (m, 3H), 1.05 (m, 3H). API-ES Positive-Mass: 424 ($[\text{M} + \text{H}]^+$, 100%).

Synthesis of 1-(2-hydroxy-*N,N*-dimethyl-*N*-octadecylpropan-1-aminium)-3',3'-dimethylspiro(2H-5-nitro-1-benzopyran-2, 2'-indoline) (5)

Compound 3 (1.711 g, 0.033 mol), 5-nitrosalicylaldehyde (0.61 g, 0.036 mol), 15 mL ethanol and several drops of piperidine were placed in a 50 mL round-bottomed flask with a mechanical stirrer and a reflux condenser. The mixture was refluxed for 10 h to complete the reaction. After evaporating the solvent, the crude product was purified by column chromatography on silica gel (methanol : chloroform = 1 : 19, v/v) to give a red solid (compound 5) 0.76 g (yield 35%). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.01 (m, $J = 7.7$ Hz, 2H), 7.20 (m, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 7.2$ Hz, 1H), 6.75 (m, $J = 7.6$ Hz, 2H), 6.73 (m, $J = 6.6$ Hz, 1H), 7.00 (d, $J = 10.4$ Hz, 1H), 5.95 (d, $J = 10.4$ Hz, 1H), 3.57–4.66 (m, 2H), 3.48 (m, 1H), 2.78–3.44 (m, 10H, $-\text{CH}_2\text{N}^+\text{CH}_2(\text{Me})_2$), 1.18 (m, 38H), 0.89 (t, 3H, $-\text{CH}_2\text{CH}_3$). Positive-mass: C_{16} m/z 634 ($[\text{M} + \text{H}]^+$, 100%), C_{18} m/z 662 ($[\text{M} + \text{H}]^+$, 100%).

Synthesis of *N*-ethoxyl-3',3'-dimethylspiro (2H-5-nitro-1-benzopyran-2,2'- indoline) (6)

A solution of 2,3,3-trimethyl-3H-indole (6.0 g, 0.038 mol) and 2-bromoethanol (7.4 g, 0.046 mol) in ether (100 mL) was refluxed and stirred for 4 h. Then, the reaction mixture was stirred for 1 h at room temperature and the precipitated solid (8.2 g) was collected by filtration. After washing the crude solid with acetone, the clean solid (1.82 g, 0.0055 mol) was dissolved in aqueous NaOH solution (2M, 8 mL) and then the resultant *N*-ethoxyl-substituted indoline was extracted with chloroform 3 mL. The organic chloroform layer was dried with anhydrous Na_2SO_4 and the solvent was evaporated. The obtained residue and 2-hydroxy-5-nitrobenzaldehyde (0.874 g, 5.2 mmol) were dissolved in 50 mL DMF again, and the mixture was stirred at 60°C for 4 h and then was poured into 200 mL of distilled water. After the

resultant solid was collected and recrystallized from acetone, a red-brown crystal (compound 6, 1.92 g) was obtained with a yield of 75%. m.p. 163°C. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.00 (d, $J = 7.5$ Hz, 1H), 7.99 (s, 1H), 7.18 (t, $J = 7.5$ Hz, 1H), 7.10 (d, $J = 7.2$ Hz, 1H), 6.88–6.94 (m, 2H), 6.77 (d, $J = 7.8$ Hz, 1H), 6.68 (d, $J = 7.2$ Hz, 1H), 5.89 (d, $J = 7.2$ Hz, 1H), 3.80–3.85 (m, 1H), 3.71–3.76 (m, 1H), 3.42–3.49 (m, 1H), 3.30–3.36 (m, 1H), 1.28 (s, 3H), 1.17 (s, 3H).

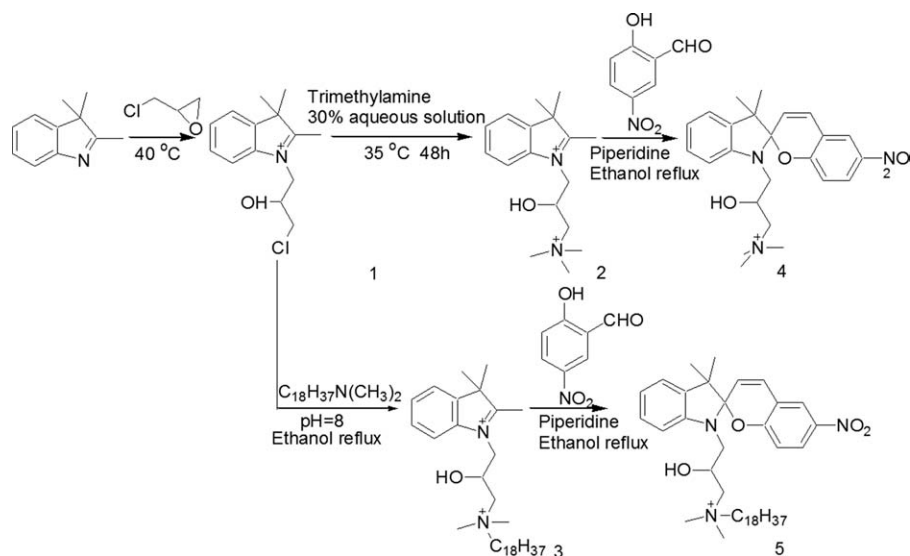
Synthesis of *N*-ethoxy cinnamate-3',3'-dimethylspiro (2H-5-nitro-1-benzopyran-2, 2'-indoline) (7)

Compound 6 (1.85 g, 0.5 mmol) and triethylamine (2.02 g, 2 mmol) were dissolved in THF (50 mL) and cooled in an ice bath. A solution of cinnamoyl chloride (1.63 g, 1 mmol) in 5 mL THF was added dropwise into the mixture under vigorous stirring. Then the mixture was continually stirred for 6 h at room temperature to complete the reaction. After the reaction was finished, the mixture was poured into water and extracted with CHCl_3 3 mL. The organic layer was washed with water repeatedly until neutral and dried with anhydrous Na_2SO_4 . The crude product was purified by column chromatography on silica gel (chloroform/hexane = 6 : 1, v/v) and 1.63 g of light-yellow solid (compound 7) was obtained with a yield of 65%, m.p. 136°C. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.00 (d, $J = 7.5$ Hz, 1H), 7.99 (s, 1H), 7.64 (d, $J = 15.9$ Hz, 1H), 7.36–7.50 (m, 5H), 7.23 (t, $J = 7.5$, 1H), 7.10 (d, $J = 7.2$ Hz, 1H), 6.88–6.93 (m, 2H), 6.76 (d, $J = 8.4$ Hz, 1H), 6.73 (d, $J = 7.2$ Hz, 1H), 6.30 (d, $J = 15.9$ Hz, 1H), 5.89 (d, $J = 10.2$ Hz, 1H), 4.35 (t, 2H), 3.54–3.64 (m, 1H), 3.46–3.54 (m, 1H), 1.28 (s, 3H), 1.17 (s, 3H).

RESULTS AND DISCUSSION

Synthesis and characterization of SP containing quaternary ammonium salt

The synthesis of SP containing quaternary ammonium salt was carried out according to Scheme 1. The objective compounds 4 and 5 were synthesized via the intermediate compound 1, which was obtained by reacting 2,3,3-trimethyl-3H-indole with epichlorohydrin in ethanol. By using excess epichlorohydrin and controlling the appropriate reaction time, the formation of bi-alkylation products and color by-products were avoided. Compound 1 and the aqueous solution of the trimethylamine (33% wt) were stirred for 48 h to get compound 2. 5-Nitro salicylaldehyde was then condensed with compound 2 to obtain compound 4 in 49% yield. For preparing compound 5, intermediate compound 3 was prepared first by using aqueous Na_2CO_3 (10% wt) to adjust the pH of reaction mixture to 8–9, and



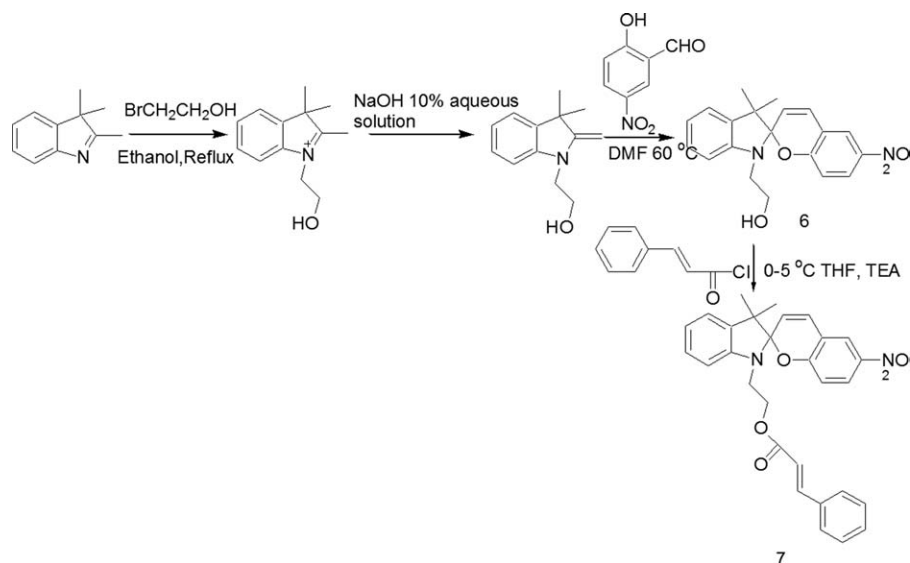
Scheme 1 Synthetic procedure for photochromic spirobenzopyrans containing quaternary ammonium salt.

compound 3 was then condensed with 5-nitrosalicylaldehyde to get compound 5 in 35% yield. Strong adsorption with the silica gel during purification by column chromatography resulted in low-yields of compound 4 and 5.

The structures of two objective compounds were confirmed by API-MS and $^1\text{H-NMR}$. The chemical shifts of the ethylenic protons ($-\text{CH}=\text{CH}-$) in compound 4 were observed at 6.34 (0.5H, d, $J = 16.1$ Hz), 7.09 (0.5H, d, $J = 16.1$ Hz), 6.60 (0.5H, d, $J = 15.9$ Hz), and 6.91 ppm (0.5H, d, $J = 15.9$ Hz), indicating two *trans*-conformation configurations of compound 4. For compound 5, the chemical shift of the ethylenic protons ($-\text{CH}=\text{CH}-$) appeared at 5.95 (1H, d, $J = 10.1$ Hz) and 7.00 ppm (1H, d, $J = 10.1$ Hz), indicating its *cis*-conformation.

Synthesis and characterization of SP containing cinnamoyl moiety

SP containing cinnamoyl moiety was synthesized as illustrated in Scheme 2. *N*-Ethoxyl-3',3'-dimethylspiro-(2H-5-nitro-1-benzopyran-2,2'-indoline) (compound 6) was prepared by reacting *N*-ethoxyl-2,3,3-trimethyl-3-indole with 2-hydroxy-5-nitro-benzaldehyde in DMF. The cinnamoyl group was attached afterwards to compound 6 by esterification with cinnamoyl chloride and compound 7 was obtained in 65% yield. The structure of compound 7 was confirmed by $^1\text{H-NMR}$ spectroscopic analysis. The chemical shifts of the ethylenic protons ($-\text{CH}=\text{CH}-$) in compound 7 were observed at 6.30 (1H, d, $J = 15.9$ Hz) and 7.64 ppm (1H, d, $J = 15.9$ Hz), indicating its *trans*-conformation.



Scheme 2 Synthetic procedure for photochromic spirobenzopyran containing cinnamoyl moiety.

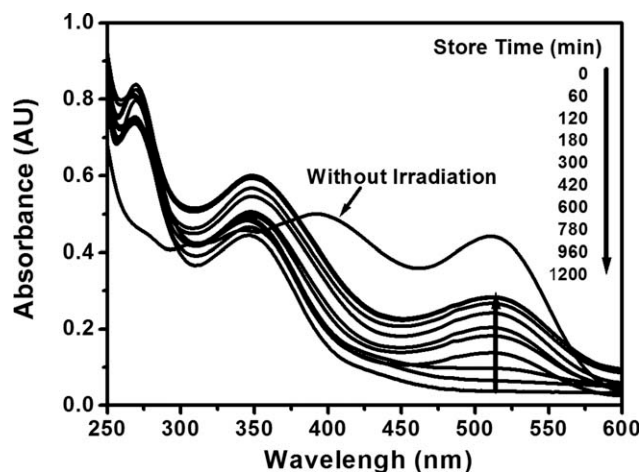


Figure 1 Absorption spectra of compound 4 before (dashed line) and after (solid line) irradiation of visible light. The aqueous solution (5.0×10^{-5} mol/L) was irradiated under visible light for 3 min, and then the solution was stored in the dark to check the spectra change.

Photochromic properties

To character the photochromic properties of SP containing quaternary ammonium salt (compound 4), the UV-Vis absorption spectra were measured in aqueous solution both before and after visible light irradiation. Figure 1 shows the UV-Vis absorption spectra of compound 4 at the concentration of 5×10^{-5} mol/L, in which a characteristic peak was clearly shown around 510 nm before visible light irradiation. The peak then disappeared as a result of visible light irradiation for 5 min, indicating the photoisomerization from MC form to SP form. This phenomenon was called “negative-photochromism” by Nippon et al.¹⁷ and the zwitterionic MC form in aqueous solution was more stable than the nonionic SP form. The colorless solution after visible light irradiation was stored in dark for 5 min and the

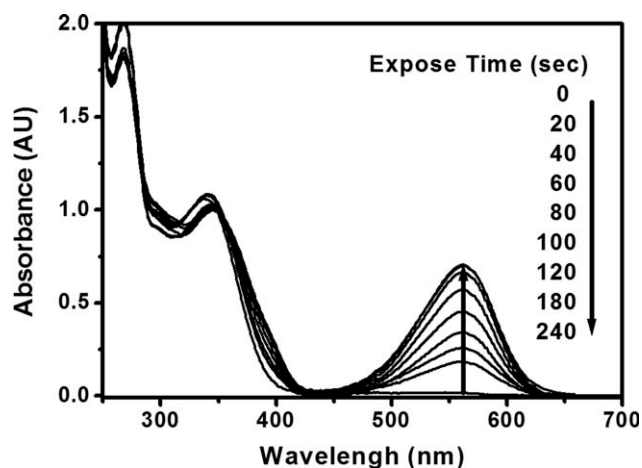


Figure 2 The UV-Vis spectra of compound 5 in CH_2Cl_2 . The solution (5.0×10^{-5} mol/L) was irradiated under visible light to check the spectra change.

adsorption spectra were measured as a function of time concurrently. The peak at 510 nm gradually recovered as time increased. However, the intensity of the peak was not completely regained to original level even after equilibration of 1200 min.

Figure 2 showed the UV-Vis absorption spectra of compound 5 in CH_2Cl_2 . Because of long-chain octadecylpropan amine, compound 5 was characterized the photoisomerization from MC form to SP form with irradiation of UV light. Result indicates that SP containing octadecylpropan amine only exhibited normal photochromic properties during the irradiation process of UV light.

Compound 7 is distinct from spirobenzopyrans for its cinnamoyl moiety, and it was expected to display different photosensitive properties besides photochromism, because of its photocrosslinking reaction ability. Figure 3 shows the absorption spectra of the compound 7 in solution under irradiation of UV light at 365 or 275 nm, respectively. In this case, colorization in chloroform was observed during irradiation with UV light at 365 nm [Fig. 1(a)] and photocrosslinking reaction was observed during irradiation at

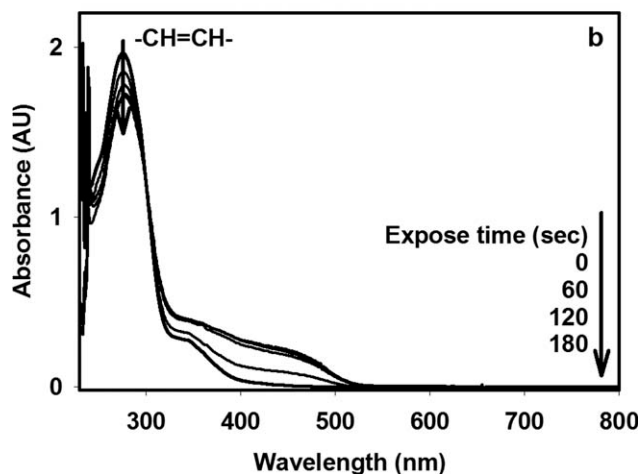
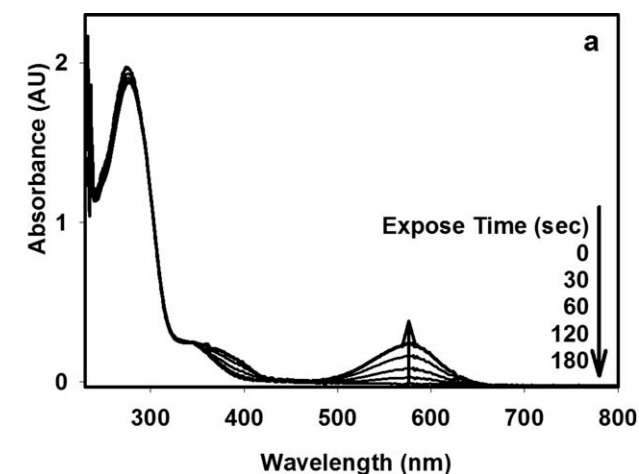
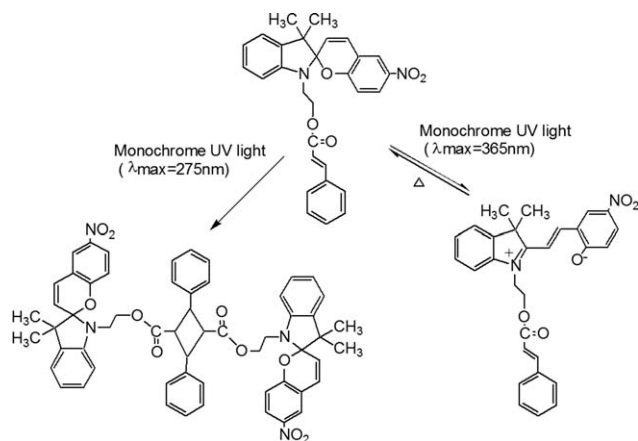


Figure 3 Absorption spectra of compound 7 in chloroform (5.515×10^{-5} mol/L) during irradiation by different UV lights at room temperature (a) 365 nm and (b) 275 nm.



Scheme 3 The expected photochromism and photocrosslinking reaction of spirobenzopyran containing cinnamoyl moiety during irradiation of different UV lights (275/365 nm).

275 nm [Fig. 1(b)]. Spectra indicate that the absorption band of cinnamoyl moiety was quite inert photochemically under UV 365 nm irradiation irrespective of a small decrease of absorbance in Figure 1(a).

The maximum absorption at 580 nm of compound 7 during irradiation at 365 nm proves *trans*-conformation of MR chromophore. If the wavelength of UV light switched from 365 to 275 nm, the absorption of the cinnamoyl moiety decreased distinctly, which means the break of double bond of cinnamoyl group in the bifunctional dye during irradiation at 275 nm (see Scheme 3).

Therefore, in the aspect of photoinduced electron-transfer reaction and electron transfer process there was big difference between SPs containing cinnamoyl moiety and those quaternary ammonium salts.

Photoinitiating properties

RTIR spectroscopy is one of the most important techniques to measure the kinetics data of photopolymerization. The conversion data can be collected by monitoring the decay of double bond peak around 1640 cm^{-1} . Upon irradiation, the accurate decrease of the absorption peak area reflects the extent of polymerization and is directly proportional to the number of double bonds that have polymerized. The degree of conversion (DC) of the function groups can be calculated by measuring the peak area at each time of the reaction and determined by the following equation¹⁸:

$$\text{DC}(\%) = (A_0 - A_t)A_0 * 100 \quad (1)$$

where DC is the conversion at time t , and A_0 and A_t are the peak area of the double bond before irradiation and at time t respectively. The rate of polymerization (R_p) can be determined by the differentials of the curve of the conversion versus irradiation time and expressed by the following equation¹⁸:

$$R_p = \frac{-\delta[M]}{\delta t} = \frac{k_p}{k_t^{1/2}} [M] (\Phi_i \epsilon I_0 [PI_0])^{1/2}$$

where k_p and k_t are the propagation and termination rate constants, respectively; $[M]$ the molar concentration of the double bond group; Φ_i the photoinitiation quantum yield; ϵ the molar extinction coefficient of initiator; I_0 the incident light intensity, and $[PI_0]$ is the concentration of photoinitiator.

Figure 4 shows initial and final FTIR spectra of the polymerizations of POEA, NVC, TEA, a HABI in the presence of compound 4. It can be seen that the intensity of the double bond peak around 1640 cm^{-1} tended to be weaker and weaker with UV irradiation during a period of 15 min. This phenomenon indicates that the free radical photopolymerization processes had happened.

The photopolymerization observed via real-time infrared analysis is shown in Figure 5. An interesting feature is that the effect of amine is highly synergistic with SP containing quaternary ammonium salt (Fig. 5). In the absence of amine, photoconversion of SPs was very low; see conversion rate in Figure 5(a) and R_p s in Figure 5(b). Changes between the initial and the final RTIR spectra were small for POEA/NVC mixtures without any SPs or TEA coinitiator, since the CH=CH₂ vinyl group band (1640 cm^{-1}) was stable. Once compound 4 or 5 as well as TEA coinitiator were added into the system, the polymerization of monomer was accelerated and its final conversion was greatly increased. In addition, the conversion of the double bond calculated reached about 62% for compound 4 and 75% for compound 5 (Fig. 5), respectively, much higher than the system without the photosensitive dye.

In combination with Type II photoinitiators, amines act as coinitiators and produce the initiating radicals (see Scheme 4).^{19–22} The addition of amines

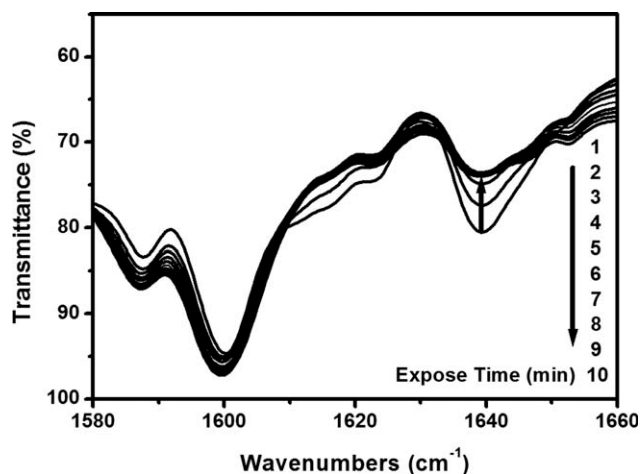


Figure 4 The decrease of adsorption double bond at 1640 cm^{-1} of the HIBA/compound 4/triethanolamine system during 15 min UV irradiation.

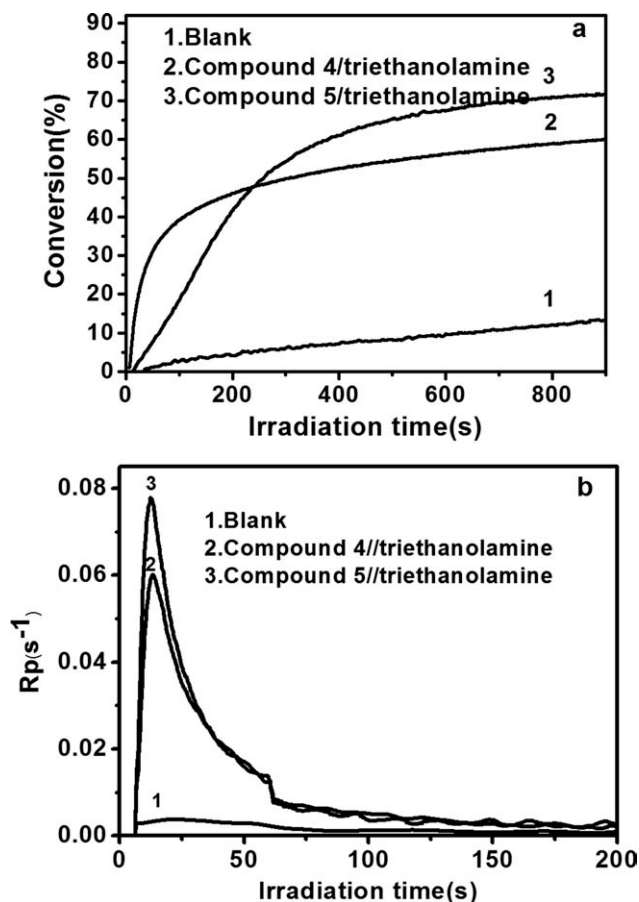
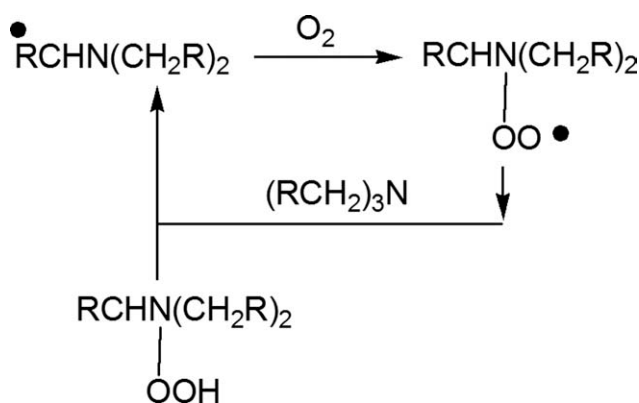


Figure 5 (a) Plots of relative double bond conversion vs. irradiation time for (1) HIBA only, (2) HIBA/compound 4 and triethanolamine, (3) HIBA/compound 5 and triethanolamine, (b) the rate of photopolymerization as a function of irradiation time.

to some photoinitiators is an effective way to reduce oxygen inhibition and the aminoalkyl radical produced in the initiation process, as noted by name of Davidson et al.²² Upon polymerization of POEA/NVC, SP containing quaternary ammonium salt (compound 4 and 5) acting as photoinitiators, showed a very slow initiating process without any TEA, possibly because of quenching of SP by oxygen.



Scheme 4 Oxygen quenching by amines.

A comparative study of Figure 5(a,b) showed that the double bond conversion of the system with compound 4 was lower than that with compound 5 as photoinitiator, but the rate of photopolymerization was higher in the system with compound 4. This might be due to the difference of the quaternary ammonium group presented. When compared with a methyl group in compound 4, the 18 carbon long chain in compound 5 could likely weakened the positive charge at nitrogen atom and the intramolecular electron transfer might be changed.

If SP compound 7 (containing cinnamoyl moiety) was used as photoinitiator in the POEA/NVC system excluding TEA coinitiator (Fig. 6), it could be seen that conversion ratio of the double bond reached about 40% [Fig. 6(a)]. To our surprise, when TEA was added into this system, the conversion ratio of the double bond decreased to nearly 5% immediately, even lower than the system without the photoinitiator SP dyes. Because of the photofunctional cinnamoyl group, compound 7 could be changed after UV irradiation at 365 nm and free-radicals would be generated for initiating

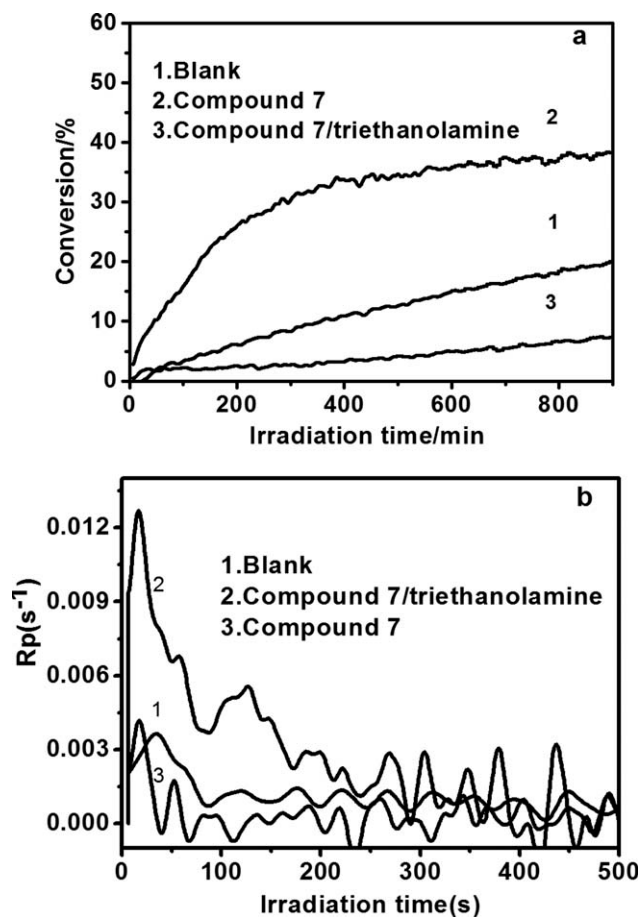


Figure 6 (a) Plots of relative double bond conversion vs. irradiation time for (1) HIBA only, (2) HIBA/compound 7, (3) HIBA/compound 7 and triethanolamine and (b) the rate of photopolymerization as a function of irradiation time.

photopolymerization. However, if TEA was added to the system, the photoinduced electron-transfer reaction and electron transfer process would move along in bimoleculars. Then, the free-radicals generated by compound 7 would be decreased, resulting in the decrease of the photopolymerization rate. This phenomenon was rather different from the systems mentioned above with cationic SPs.

In the course of studies on the photochromic properties of three molecules, some interesting features were also observed regarding their absorption spectra and excited states. Despite the close similarity in structure to SP, they nevertheless exhibited significant different absorption and emission properties. The first interesting feature of the spectroscopic properties of the SPs was seen that compound 4 was a kind of water-insoluble photochromic dye and shown a "negative-photochromism." Before visible-light irradiation, a characteristic peak appeared around 510 nm, and the peak disappeared when the system was exposed to the visible light, indicating the photoisomerization from MC form to SP form. Compound 5 was a weak photochromic compound when it was excited with UV irradiation.

A significant bathochromic shift was observed from SPs containing different quaternary ammonium salts by over 140 nm. Furthermore, SP containing cinnamoyl moiety exhibited a stronger photochromism and the maximum absorption wavelength appeared around 570 nm with an obvious bathochromic shift. This suggested that SPs with different quaternary ammonium salts had rigid planar molecular structures (aside from the long alkyl chain) with cationic contribution. On the other hand, fluorescence analysis provided further interesting proofs to support above conclusion. The two cationic derivatives exhibited very weak fluorescence emission while none could be detected and further the spectra were seen to be distinctly different for the two molecules 4 and 5. The weak fluorescence was associated with the dye's state transformation. The process was as follow: first, due to the rapid deactivation of the mentioned dye's lowest excited $^1\pi-\pi^*$ state, it translates to its second excited $^3n-\pi^*$ state through inter system crossing; then followed by internal conversion, the system converted to its lowest excited $^3\pi-\pi^*$ state, and finally, reverted to the ground-state by radiative emission.²² The fluorescence quantum yield of the SP with cinnamoyl group was higher than the other derivatives. This is associated with the electron withdrawing effect of the cinnamoyl group, which can weaken the $\pi-\pi^*$ character of the chromophore.

CONCLUSIONS

Three novel SPs containing either quaternary ammonium salt or cinnamoyl moiety were synthesized

successfully using epichlorohydrin as starting material. Compound 4 and 5 exhibited "photochromic" properties in bulk aqueous solution. The initiation functionality of SPs containing either quaternary ammonium salt or cinnamoyl moiety was shown to be efficient for initiating the polymerization of POEA/NVC system. The comparative studies of photopolymerization for both SPs photoinitiator containing quaternary ammonium salt and cinnamoyl moiety revealed that the photoinduced electron-transfer reaction and electron transfer process could be very important in the subsequent initiation reaction, which influences the resulting products and the kinetic process of polymerization. Meanwhile, the influence of TEA is strong on the photopolymerization of POEA/NVC system. As Type II photoinitiator, SPs containing quaternary ammonium group, and TEA are more efficient in initiative capability for UV-light irradiation system, but SPs containing cinnamoyl moiety should be used without amine.

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