Microwave-assisted synthesis of novel spirooxazines and their photochromic behaviors in polymer matrices

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A series of 1,3,3-trimethylspiro[2H]-indol-2,3′-[3H]-naphtho[2,1-b][1,4]oxazine derivatives (spirooxazine) were synthesized using the microwave method. Their photochromic behaviors in styrene-butadiene-styrene copolymer (SBS), polycarbonate (PC), and polymethylmethacrylate (PMMA) were investigated. Results show that the colored form of spirooxazine is more stable in polar PMMA and cause a blue shift in the absorption spectrum of merocyanine. Furthermore, a broad thermal relaxation time range was obtained, from 129 s to 1724s (in PMMA, at 20 °C) through a structural modification of 6′-heterocycle and 9′-acyloxy. These results present a new strategy for designing photochromic molecules that feature different and acceptable relaxation times.

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1. Introduction

Since the first report by Hirshberg in 1956 [1], photochromic materials have attracted considerable attention because of their applications in memory devices, optical switches, displays, chemical sensors, and ophthalmic plastic lenses [2-8]. For practical applications, thermal decoloration rates determine the specific application fields [9]. For example, if the fading process is sufficiently fast, 1,3,3-trimethylspiro[2H]-indol-2,3′-[3H]-naphtho[2,1-b][1,4]oxazine derivatives (spirooxazine) can be used in optical switches. By contrast, spirooxazine can be used in sunglasses when the fading time is moderate. However, when colored form is too stable to finish the thermal decoloration at room temperature, the photochromic system can be used for optical storage. Although spirooxazines have been used in several applications, they usually exhibit an unacceptable thermal decoloration process of the colored photomerocyanine species. Thus, the development of a novel photochromic molecule, which features an acceptable decoloration process, and further studies on structure-property relationships present an interesting challenge.

Compared with other known organic photochromic compounds, indolinespironaphthooxazine compounds have attracted great interest because of their excellent photochromic properties [10-12]. These compounds are obtained by traditional thermal synthesis methods, long reaction time, and low yield, which are inefficient. Thus, another method is required for a more efficient production. Furthermore, considering several applications of photochromic compounds should be in film form, the effect of the polymeric medium on photochromism is also an important issue in product development [13-14].

In the present work, a series of novel spirooxazines (**1b–1c** and **2a–2f**) were synthesized by microwave irradiation. Compound **1a** was synthesized as a reference compound in a previous study [15]. Photochromic behaviors and thermal stability in styrene-butadiene-styrene copolymer (SBS), polycarbonate (PC), and polymethylmethacrylate (PMMA) films were investigated to understand the structure-photochromic property relationships and develop potential photochromic materials.

2. Experimental

Materials and instrumentation

All reagents were purchased from commercial sources and used without further purification unless otherwise noted. 1-Nitroso-2,7-dihydroxynaphthalene was synthesized according to previously described methods [5]. SBS was obtained from Philips, USA. PMMA was obtained from ICI, UK. PC was purchased from Aldrich, USA.

Microwave reaction was carried out in an MAS-I Microwave Synthesis Instrument (Shanghai Microwave Chemistry Technology Corp., China). Melting points were measured on an X-4 microscope electrothermal apparatus and remained uncorrected (Taike, China). ^{1}H NMR and ^{13}C NMR spectra were obtained in DMSO-d_6 or $CDCl_3$ using a Bruker AV-500 spectrometer at 500 MHz or a Bruker AV-300 spectrometer at 300 MHz (Rheinstetten, Germany). Chemical shifts were reported in δ (ppm) relative to tetramethylsilane, which was used as the internal standard. Fourier transformation infrared (FTIR) spectra were recorded in KBr pellets using an FTIR

spectrometer (Nicolet iS10, Thermo Nicolet). Elemental analyses were carried out on a Vario EL III elemental analyzer (Hanau, Germany). Optical absorption spectra were recorded using a CARY 1101 UV-Vis spectrophotometer (Varian, USA).

General procedure for the synthesis of compounds 1a–1c

1-Nitroso-2,7-dihydroxynaphthalene (3.78 g, 20 mmol) and methanol (200 mL) were placed in a flask (250 mL), heated to reflux under nitrogen, and then treated with R_1H solution (40 mmol) in methanol (10 mL). Thereafter, the flask was placed in the microwave reactor (600 W microwave irradiation) to react for 5 min at 64 °C. The reactions were stopped, and the solution was cooled to room temperature. Within 5 min, the resulting solution was mixed with 1,3,3-trimethyl-2-methyleneindoline solution (3.46 g, 20 mmol) in methanol (10 mL) and subjected to microwave irradiation (600 W) for 20 min at 64 °C. After irradiation, a brown solid was produced and separated by filtering. The residue was purified by column chromatography (silica, petroleum ether/ethyl acetate, 1/3, v/v).

1,3,3-Trimethyl-9′-hydroxy-spiro[indoline-2,3′(3H) naphtho[2,1-b][1,4]oxazine] (1a): gray solid, yield: 71.2%, m.p. 167-170℃ (lit. : mp:167-168℃) [17]. IR (KBr, cm^{-1}): 3330, 2970, 1625, 1480, 1450, 1360, 1235, 1090, 1190, 980, 897, 835, 844, 744. Anal. calcd. for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N 8.13. Found: C,77.02; H, 5.82; N, 8.16%.

1,3,3-Trimethyl-6′-morpholino-9′-hydroxy-spiro[indoline-2,3′(3H)naphtho[2,1-b][1,4]oxazine] (1b): blue solid, yield: 47.8%, m.p. 246-248℃. IR (KBr, cm^{-1}): 3400, 2960, 1620, 1460, 1360, 1230, 1110, 1150, 982, 825, 742. ^{1}H NMR (DMSO, 500 MHz): δ 9.79 (1H, s, OH), 7.86 (1H, d, J = 8.9 Hz, ArH), 7.73 (1H, s, 2′-H), 7.66 (1H, s, ArH), 7.16–7.12 (2H, m, ArH), 6.93 (1H, d, J = 8.2 Hz, ArH), 6.82 (1H, t, J = 7.3 Hz, ArH), 6.63 (1H, d, J = 7.6 Hz, ArH), 6.41 (1H, s, ArH), 3.80 (4H, t, J = 4.3 Hz, $2CH_2$), 2.95 (4H, t, J = 4.3 Hz, $2CH_2$), 2.67 (3H, s, CH_3), 1.26 (6H, s, CH_3). Anal. calcd. for $C_{26}H_{27}N_3O_3$: C, 72.71; H, 6.34; N 9.78. Found: C, 72.59; H, 6.32; N, 9.81%. MS (ESI): calcd. for $[M + H]^+$ 430.21; found 430.5.

1,3,3-Trimethyl-6′-indolino-9′-hydroxy-spiro[indoline-2,3′(3H)naphtho[2,1-b][1,4]oxazine] (1c): grey-green solid, yield: 49.7%, m.p. 124-126℃. IR (KBr, cm^{-1}): 3420, 2960, 1620, 1480, 1460, 1260, 1030, 1160, 982, 748. ^{1}H NMR (DMSO, 500 MHz): δ 9.90 (1H, s, OH), 7.79 (1H, d, J=2.5 Hz, ArH), 7.72 (1H, s, 2′-H), 7.65 (1H, s, ArH), 7.13–7.10 (4H, m, ArH), 6.90 (1H, t, J=2.6 Hz, ArH), 6.81–6.64 (3H, m, ArH), 6.61 (1H, d, J=7.7 Hz, ArH), 6.08 (1H, d, J=7.8 Hz, ArH), 3.86 (2H, t, J=8.5 Hz, CH_2), 3.08 (2H, t, J=8.5 Hz, CH_2), 2.67 (3H, s, CH_3), 1.27 (3H, s, CH_3), 1.26 (3H, s, CH_3). Anal. calcd. for $C_{30}H_{27}N_3O_2$: C, 78.07; H, 5.90; N, 9.10. Found C, 77.94; H, 5.88; N, 9.13%.

General procedure for the synthesis of compounds 2a–2f

Compounds **1a–1c** (2 mmol) and 1,4-dioxane (20 mL) were placed in a 250 mL flask. Benzene (140 mL) was added until the substances were completely dissolved. R_2COCl (20 mmol in benzene, 10 mL) was added dropwise over a period of 20 min at 5 °C. Thereafter, the flask was placed in the microwave reactor and subjected to microwave irradiation at 600 W for 9 min at room temperature. After irradiation, the contents were cooled to room temperature. A small amount of insoluble matter was filtered out and the solution was removed in vacuo. The obtained residue was recrystallized in hot methyl alcohol to yield compounds **2a–2f** as pure products.

1,3,3-Trimethyl-9′-methacryloyloxy-spiro[indoline-2,3′(3H)naphtho[2,1-b]

[1,4]oxazine](2a): gray solid, yield: 98.6%, m.p. 151-153℃. IR (KBr, cm^{-1}): 3047, 2971, 1730, 1630, 1480, 1440, 1360, 1256, 1080, 1170, 1120, 978, 903, 823, 748. ^{1}H NMR($CDCl_3$, 500 MHz): δ 8.27 (1H, d, J=2.3Hz, ArH), 7.76 (1H, d, J=8.9 Hz, ArH), 7.71 (1H, s , 2′-H), 7.65 (1H, d, J=8.9 Hz, ArH), 7.23–7.17 (2H, m, ArH), 7.08 (1H, d, J=7.1 Hz, ArH), 6.99 (1H, d, J=8.9 Hz, ArH), 6.90 (1H, t, J=7.4 Hz, ArH), 6.58 (1H, d, J=7.7 Hz, ArH), 6.41 (1H, s, CH), 5.78 (1H, s, CH), 2.76 (3H, s, CH_3), 2.11 (3H, s, CH_3), 1.35 (6H, s, CH_3). ^{13}C NMR (DMSO, 300 MHz): d 18.0, 20.4, 25.1, 29.2, 51.5, 98.4, 107.1, 1123, 116.5, 119.5, 119.6, 121.5, 122.2, 126.8, 127.8, 127.8, 129.7, 130.2, 130.9, 135.3, 135.4, 144.4, 147.2, 149.6, 151.6, 165.4. Anal. calcd. for $C_{26}H_{24}N_2O_3$: C, 75.71; H, 5.86; N, 6.79. Found C, 75.57; H, 5.84; N, 6.81%.

1,3,3-Trimethyl-9′-benzoyloxy-spiro[indoline-2,3′(3H)naphtho[2,1-b][1,4]

oxazine](2b): gray solid, yield: 98.6%, m.p. 214-216℃. IR (KBr, cm^{-1}): 3047, 2960, 1630, 1480, 1370, 1250, 1060, 1114, 971, 829, 741. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.38 (1H, d, J=1.9 Hz, ArH), 8.27 (2H, d, J=7.3Hz, ArH), 7.81 (1H, d, J=8.8 Hz, ArH), 7.71 (1H, s , 2′-H), 7.68 (2H, m, ArH), 7.54 (2H, t, J=7.6 Hz, ArH), 7.28 (1H, d, J=2.2 Hz, ArH), 7.22 (1H, t, J=7.7 Hz, ArH), 7.08 (1H, d, J=7.2 Hz, ArH), 7.01 (1H, d, J=8.8 Hz, ArH), 6.90 (1H, t, J=7.4 Hz, ArH), 6.58 (1H, d, J=7.7 Hz, ArH), 2.77 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.35 (3H, s, CH_3). Anal. calcd. for $C_{29}H_{24}N_2O_3$: C, 77.66; H, 5.39; N, 6.25. Found C, 77.53; H, 5.38; N, 6.27%.

1,3,3-Trimethyl-9′-(p-chlorobenzoyloxy)-spiro[indoline-2,3′(3H)naphtho[2,1-b]

[1,4]oxazine](2c): gray solid, yield: 98.9%, m.p. 234-235℃. IR (KBr, cm^{-1}): 3048, 2961, 1624, 1465, 1362, 1263, 1067, 1116, 975, 848, 753, 680. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.37 (1H, d, J=1.7 Hz, ArH), 8.20 (2H, d, J=8.4 Hz, ArH), 7.78 (1H, d, J=8.8 Hz, ArH), 7.71 (1H, s , 2′-H), 7.68 (1H, d, J=8.9 Hz, ArH), 7.51 (2H, d, J=8.4 Hz, ArH), 7.26 (1H, m, ArH), 7.22 (1H, t, J=7.6 Hz, ArH), 7.09 (1H, d, J=7.2 Hz, ArH), 7.01 (1H, d, J=8.9 Hz, ArH), 6.90 (1H, t, J=7.4 Hz, ArH), 6.58 (1H, d, J=7.7 Hz, ArH), 2.76 (3H, s, CH_3), 1.36 (3, s, CH_3), 1.35 (3, s, CH_3). ^{13}C NMR (DMSO, 300 MHz): d 20.4, 25.1, 29.2, 51.5, 98.5, 107.1, 112.4, 116.6, 119.4, 119.6, 121.4, 122.3, 126.9, 127.8, 127.8, 129.1, 129.7, 130.2, 130.9, 131.7, 135.4,

138.99, 144.4, 147.2, 149.5, 151.7, 163.9. Anal. calcd. for $C_{29}H_{23}ClN_2O_3$: C, 72.12; H, 4.80; N, 5.80. Found C, 71.98; H, 4.78; N, 5.82%.

1,3,3-Trimethyl-9′-methacryloyloxy-6′-morpholino-spiro[indoline-2,3'(3H)naphtho[2,1-b][1,4]oxazine](2d): gray solid, yield: 93.4%, m.p. 193-195℃. IR (KBr, cm^{-1}): 3050, 2960, 1730, 1620, 1490, 1260, 1030, 1135, 978, 742. ^{1}H NMR (DMSO, 500 MHz): δ 8.16 (1H, d, J=2.4 Hz, ArH), 8.08 (1H, d, J=9.1 Hz, ArH), 7.73 (1H, s, 2′-H), 7.24 (1H, d, J=2.4 Hz, ArH), 7.17–7.10 (2H, m, ArH), 6.84 (1H, t, J=7.5 Hz, ArH), 6.69 (1H, s, ArH), 6.65 (1H, d, J=7.6 Hz, ArH), 6.35 (1H, s, CH), 5.94 (1H, s, CH), 3.82 (4H, t, J=4.4 Hz, $2CH_2$), 3.01 (4H, t, J=4.4 Hz, $2CH_2$), 2.70 (3H, s, CH_3), 2.06 (3H, s, CH_3), 1.28 (6H, s, $2CH_3$). ^{13}C NMR (DMSO, 300 MHz): d 18.0, 20.3, 25.2, 29.2, 51.3, 52.9, 66.3, 98.6, 105.2, 107.1, 112.8, 118.6, 118.7, 119.5, 121.5, 125.5, 127.8, 132.2, 135.3, 135.50, 144.9, 147.2, 149.1, 149.6, 151.5, 165.3. Anal. calcd. for $C_{30}H_{31}N_3O_4$: C, 72.41; H, 6.28; N, 8.44. Found C, 72.29; H, 6.26; N, 8.46%.

1,3,3-Trimethyl-9′-(p-chlorobenzoyloxy)-6′-morpholino-spiro[indoline-2,3′(3H)naphtho[2,1-b][1,4]oxazine](2e): gray solid, yield: 90.7%, m.p. 177-178℃. IR (KBr, cm^{-1}): 3049, 2961, 1624, 1467, 1360, 1251, 1117, 1162, 977, 847, 754, 745. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.36 (1H, d, J = 2.1 Hz, ArH), 8.21 (2H, d, J=8.5 Hz, ArH), 8.12 (1H, d, J = 9.0 Hz, ArH), 7.61 (1H, s, 2′-H), 7.52 (2H, d, J = 8.5 Hz, ArH), 7.25–7.21 (2H, m, ArH), 7.09 (1H, d, J = 7.1 Hz, ArH), 6.89 (1H, t, J = 7.4 Hz, ArH), 6.61 (1H, s, ArH), 6.58 (1H, d, J = 7.7 Hz, ArH), 3.95 (4H, t, J = 4.4 Hz, CH_2), 3.07 (4H, t, J = 4.4 Hz, CH_2), 2.76 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.34 (3H, s, CH_3). ^{13}C NMR (DMSO, 300 MHz): d 20.3, 25.2, 29.2, 51.3, 52.9, 66.3, 98.7, 105.4, 107.1, 112.9, 118.6, 119.5, 121.5, 121.6, 125.6, 127.8, 127.8, 129.1, 131.7, 132.2, 135.5, 138.9, 145.0, 147.2, 149.2, 149.5, 151.6, 163.9. Anal. calcd. for $C_{33}H_{30}ClN_3O_4$: C, 69.77; H, 5.32; N, 7.40. Found C, 69.64; H, 5.31; N, 7.42%.

1,3,3-Trimethyl-6′-indolino-9′-methacryloyloxy-spiro[indoline-2,3′(3H)naphtho[2,1-b][1,4]oxazine] (2f): green crystal, yield: 91.3%, m.p. 206-209℃. IR (KBr, cm^{-1}): 3050, 2957, 2920, 1730, 1630, 1480, 1460, 1385, 1256, 1099, 1180, 1125, 977, 830, 744. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.27 (1H, d, J=2.1 Hz, ArH), 7.97 (1H, d, J=9.0 Hz, ArH), 7.64 (1H, s , 2′-H), 7.21-7.18 (2H, m, ArH), 7.10 (1H, t, J=2.3 Hz, ArH), 7.06 (1H, d, J=3.6 Hz, ArH), 6.92 (1H, d, J=7.7 Hz, ArH), 6.89–6.86 (2H, m, ArH), 6.75 (1H, t, J=7.3 Hz, ArH), 6.56 (1H, d, J=7.7 Hz, ArH), 6.41 (1H, s, ArH), 6.31 (1H, d, J=7.9 Hz, ArH), 5.78 (1H, s, ArH), 3.90 (2H, t, J=8.5 Hz, CH_2), 3.17 (2H, t, J=8.5 Hz, CH_2), 2.76 (3H, s, CH_3), 2.11 (3H, s, CH_3), 1.34 (6H, s, CH_3). Anal. calcd. for $C_{34}H_{31}N_3O_3$: C, 77.10; H, 5.90; N, 7.93. Found C, 76.98; H, 5.88; N, 7.95%.

Preparation of thin polymer films

Polymer (0.40 g) was dissolved in 20 mL CH_2Cl_2 and stirred to ensure complete dissolution. A specified amount (5 wt% of the polymer) of spirooxazine was added to the polymer solution and stirred thoroughly. The resulting solution (approximately 0.3 mL) was then spread over a glass plate and left covered overnight in the dark [16]. After the solvent completely evaporated, the film was peeled off from the dish. The resulting films were approximately 20 μm to 30 μm thick and kept in a dark room.

Photochromism and fatigue resistance measurements

Photochromism was characterized by monitoring the absorption spectra of the film at different time of illumination. A 40 W UV lamp (UV40A, 365nm, Beijing CBIO Bioscience & Technologies CO., Ltd. China) was used as the irradiation source. The absorption spectra were recorded on CARY 1101 UV-Vis spectrophotometer. The films were maintained at 20 °C during illumination, and the temperature was controlled by a DC heater supply. Fatigue resistance was determined by monitoring the absorbance at λ_{max} after every irradiation cycle of UV and visible light. In every cycle, the nearly colorless spiro-isomer was transformed into colored photomerocyanine (UV) when reverting back to the spiro-isomer form (visible light). This color transformation was termed "switch on" (UV) and "switch off" (visible light).

Thermal decoloration of the colored merocyanine form of 1a–1c and 2a–2f in polymer matrices

Spirooxazine compound film in appropriate polymer matrices (5 wt% loading) was exposed to UV light (40 W UV lamp) until the color was fully developed. Trial and error experiments were performed to determine the optimum exposure time for the maximum build-up of the photomerocyanine concentration. Thermal decoloration was then recorded on a spectrophotometer after photoequilibrium was obtained by closing the shutter (zero time). The discoloration dynamic at maximum absorption wavelength (λ_{max}) was fitted according to the following equation [14]:

$$\ln\left(\frac{A_t - A_\infty}{A_0 - A_\infty}\right) = -k \cdot t$$

where A_0, A_t, and A_∞ are the absorbances at zero, times, and infinity, respectively.

Photodegradation of 1a–1c and 2a–2f in colored merocyanine form in PMMA matrix

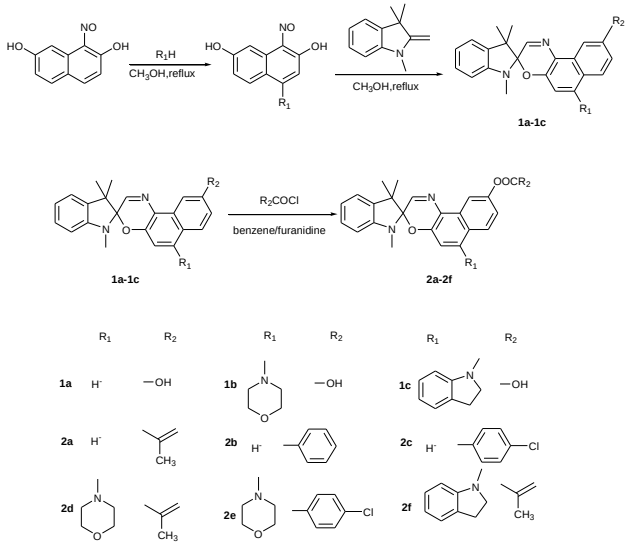
Twenty slices of spirooxazine (5 wt% loading) PMMA films were prepared. All films were irradiated at the same time under a 40 W UV lamp. The absorbances at λ_{max} of a given film at different irradiation times were recorded on a spectrophotometer immediately after irradiation.

3. Results and discussion

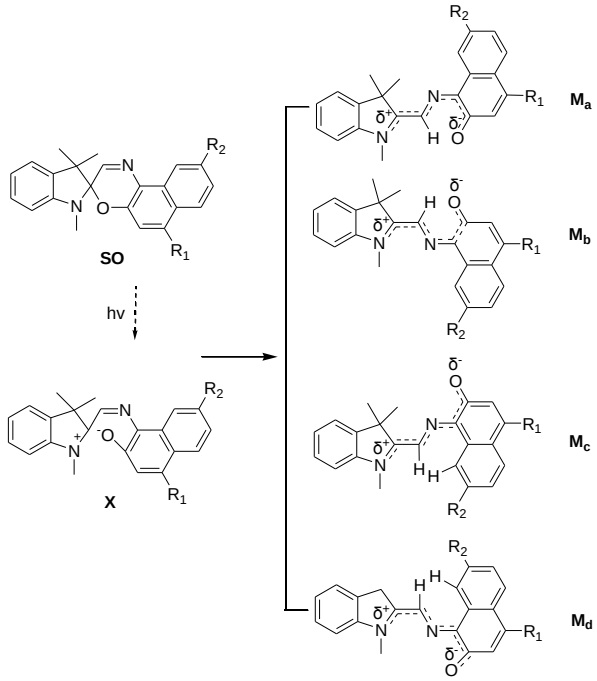
In this study, the reactions of spirooxazines **1a–1c** and **2a–2f** (Scheme 1) were subjected to microwave irradiation, which were completed within a few minutes, and produced good yields compared with those of traditional methods

[11-12]. All the compounds were confirmed by FTIR, ^{1}H NMR, and ^{13}C NMR spectra, as well as by elemental analyses.

The ground state of spirooxazine exhibits a light color. Upon exposure to UV for several minutes, spirooxazine changes to a colored merocyanine (Scheme 2). After illumination, intermediate X was initially produced. The geometrically perpendicular naphthalene and indoline groups rotated to a planar structure, which might result in the *cis* and *trans* forms of merocyanine (M_a–M_d). The trans structure exists in isomers depending on the rotation [18].



Scheme 1. Synthesis of spirooxazines (1a–1c and 2a–2f)



Scheme 2. Coloring mechanism of spirooxazines (1a–1c and 2a–2f)

Table 1. Maximum absorption wavelength[a] of 1a–1c and 2a–2f.

Polymer matrix	**1a**	**1b**	**1c**	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**
SBS	625.0	635.0	644.9	635.1	635.0	635.0	620.0	614.9	635.0
PC	595.0	600.0	625.0	600.1	600.0	599.9	590.0	585.0	605.0
PMMA	575.0	585.0	590.0	595.0	595.0	595.1	585.0	580.0	595.0

[a]Measured in PMMA (5 wt% loading) after irradiation at 365 nm with a 40 W ultraviolet lamp. All measurements at 20 °C.

Absorption spectra of spirooxazines in the polymer matrix before and after UV irradiation

The λ_{max} of these open-colored forms measured in SBS, PMMA, and PC films are listed in Table 1. We observed that the λ_{max} of spirooxazines **1a–1c** and **2a–2f** in PC films are shorter than that in SBS films, which is known as blue shift, because merocyanine is an amphoteric ion that can interact with a polar polymer matrix [19-20]. The polarity of PMMA is higher than that of PC; thus, spirooxazines highly interact with PMMA, which occurs toward a blue shift. We also observed that, the group linked as a pendant affected the λ_{max}. Compared with unsubstituted **1a**, 6′-heterocycle-substituted **1b** and **1c** showed an evident red-shift, and the λ_{max} were ranked in the order of **1c** > **1b** > **1a**, this was assigned to the electron-donating ability of 6′- substitutent on the naphthoxazine ring moiety [21]. Thus, it presumably indicated that the electron-donating power of indolino > morpholino which resulted in bathochromic effects. Spirooxazine **2a, 2b,** and **2c** exhibited approximately equal absorption in the same polymer matrix. For instance, the λ_{max} of PMMA was 595.0, 595.0, and 595.1 respectively, indicating that the alkyl group on the 9′-acyloxy had little effect on the π-electrons of the photomerocyanine part and heteroaromatic part. Fig. 1 shows the absorption spectra of compound **2d** in PMMA. Upon excitation at 365 nm,

compound **2d** exhibited photochromism with an increase in band intensity at 585 nm.

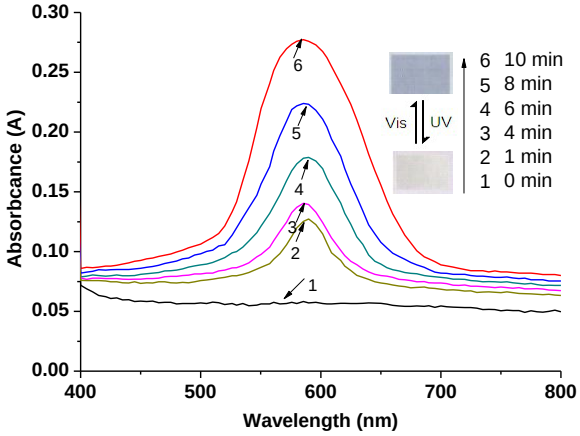


Fig. 1. Absorption spectra of 5% (wt% loading) 2d in PMMA film; successive spectra taken after (1) 0 min; (2) 1 min; (3) 4 min; (4) 6 min; (5) 8 min; (6) 10 min of irradiation at 365 nm with a 40 W ultraviolet lamp.

Thermal decoloration of the colored merocyanine form of 1a–1c and 2a–2f in polymer matrices

The thermal decoloration of the colored merocyanine form of **1a**–**1c** and **2a**–**2f** in polymer matrices (5 wt% loading) were investigated by analyzing the absorption spectra. The thermal decoloration of the compounds followed the first order kinetics since the $[\ln(A_t-A_\infty)/(A_0-A_\infty)]$ plots are linear. The kinetic runs of **1a**–**1c** and **2a**–**2f** in PMMA films are shown in Figs. 2 and 3, respectively. The relaxation time of the photomerocyanines (τ) was obtained from the first order rate constant using the expression $\tau = 1/k$, where k and τ are given in Table 2. We observed that the group linked as a pendant affected the thermal relaxation time. For 6′-substituted-9′-hydroxyl spirooxazine, the thermal relaxation time prolonged with the increase of the electron-donating ability of the 6′-heterocycle substituent. For example, the τ_{MC-SO} values of the photomerocyanines in compounds **1b** and **1c** are 6 and 13 times higher than those in unsubstituted compound **1a**, respectively. For 6′-H-9′-hydroxyl spirooxazine, the thermal relaxation time prolonged because of π-electron delocalization caused by acyloxy moiety after esterification was completed. For example, the τ_{MC-SO} value of photomerocyanines derived from the esterified 2a–2c compounds varied from 196 s to 232 s, which indicates a twofold increase compared with that of the unesterified **1a**. By contrast, the thermal relaxation time of 6′-substituted-9′-acyl oxygen spirooxazine evidently decreased compared with that of 6′-substituted-9′-hydroxyl spirooxazine, which may be attributed to the steric hindrance effect caused by the 6′ and 9′ structure-modified groups. A broad range of relaxation time (129 s to 1724 s) was obtained by tuning the structure modification groups on the 6′ and 9′ positions. Thus, the compounds with different τ_{MC-SO} can presumably be designed and synthesized using this method to allow their successful use in various applications. For example, the moderate τ of **2d**–**2f** compounds can be applied in sunglasses.

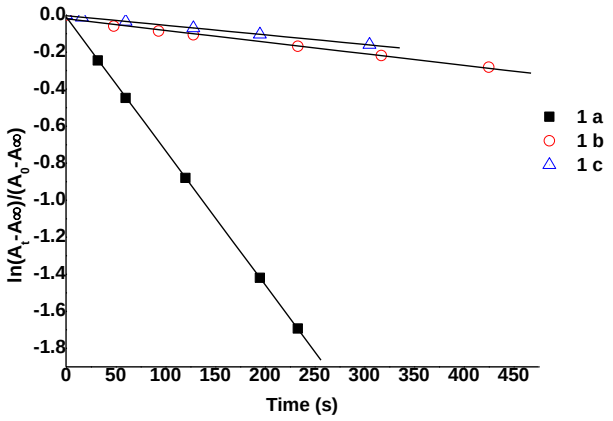


Fig. 2. Thermal relaxation of compounds 1a-1c in PMMA.

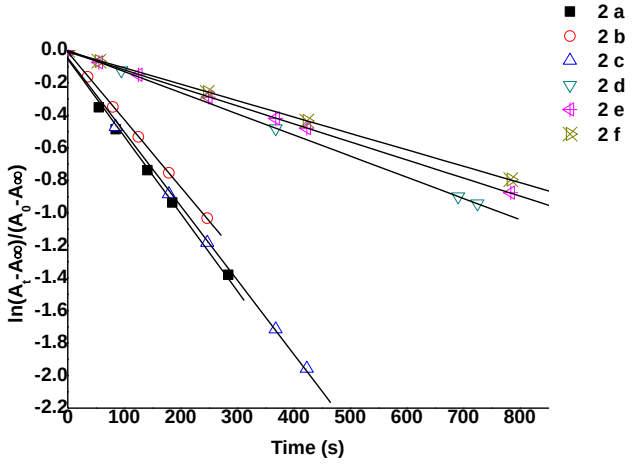


Fig. 3. Thermal relaxation of compounds 2a–2f in PMMA.

Table 2. Rate constants k (s^{-1}) of thermal ring closure of photomerocyanines derived from compounds 1a–1c and 2a–2f and their lifetimes (s)[a].

SO compound	Rate constants k ($\times10^{-3}s^{-1}$)	Lifetimes (s)
1a	7.7	129
1b	1.2	833
1c	0.58	1724
2a	5.2	196
2b	4.3	232
2c	4.7	212
2d	1.3	769
2e	1.2	909
2f	1.0	1000

[a]Measured in PMMA (5 wt% loading) after irradiation at 365 nm with a 40 W ultraviolet lamp. All measurements at 20 °C.

The effect of polymer matrices to the thermal decoloration of spirooxazine was also investigated. The kinetic runs of compound **2d** in SBS, PC, and PMMA films are shown in Fig. 4, and the k and τ values are listed in Table 3. These values indicate that the polarity of polymer matrices affects the thermal decoloration rates. The relaxation time was ranked in the order of PMMA > PC > SBS. Merocyanine, the colored form of spirooxazine, is an amphoteric ion. Therefore, merocyanine is more stable in polar PMMA and PC, hence, the relaxation time is longer. However, when spirooxazine is dispersed in non-polar SBS, the thermal stability decreases, and the relaxation time is shorter [22].

Table 3. Rate constants k (s^{-1}) of thermal ring closure of photomerocyanine derived from 2d and its lifetime (s)[a].

Films	Rate constants k ($\times 10^{-3} s^{-1}$)	Lifetimes (s)
SBS	3.6	277
PC	2.7	369
PMMA	1.3	769

[a]Measured in the films of PMMA, PC, and SBS (5 wt% loading) after irradiation at 365 nm with a 40 W ultraviolet lamp. All measurements at 20 °C.

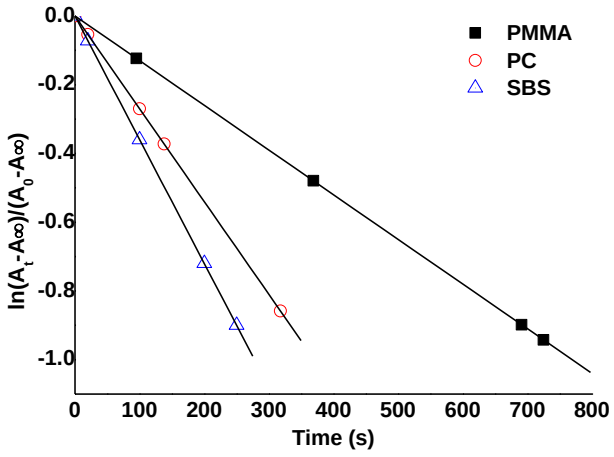


Fig. 4. Thermal relaxation of 2d in the films of PMMA, PC, and SBS (5 wt% loading) after irradiation at 365 nm with a 40 W ultraviolet lamp.

Photodegradation of 1a–1c and 2a–2f in the colored merocyanine form in the PMMA matrix

Within minutes of the initial exposure to UV radiation, absorbance of all the spirooxazines rapidly increased to maximum, which then decreased slowly after a period of continuous irradiation, this might be the photodegradation caused by long time UV irradiating [23]. A plot of absorbance against irradiation time is shown in Fig. 5 for **2d** and **2f**. For the series of spirooxazines **1a**–**1c** and **2a**–**2f**, photodegradation was determined by following the decrease in the absorbance at the λ_{max} of their respective colored merocyanine forms. The stability of the spirooxazines to UV light might be represented by the parameters $t_{A0/2}$, which is defined as the time (min) required to decrease the A_0 at the λ_{max} of the merocyanine form to the half value ($A_{0/2}$) (Table 4). The results showed that spirooxazines **1a**–**1c** and **2a**–**2f** exhibited high fatigue resistance to continuous UV irradiation under a UV lamp (40 W) in air [11].

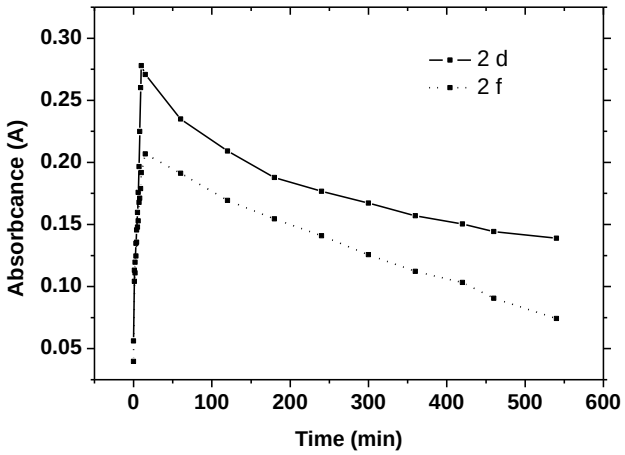


Fig. 5. Change in absorbance at λ_{max} of 2d (λ_{max} = 585 nm, 5 wt% loading) and 2f (λ_{max} = 595 nm, 5 wt% loading) in PMMA film under continuous UV irradiation.

Table 4. Parameters ($t_{A0/2}$) of 1a–1c and 2a–2f in PMMA film.

SO compound	$t_{A0/2}$[a] (min)
1a	460
1b	570
1c	640
2a	550
2b	490
2c	530
2d	540
2e	550
2f	420

[a] $t_{A0/2}$ is the time (min) required to decrease the A_0 at the λ_{max} of the merocyanine form to the half value ($A_{0/2}$).

Evaluation of the fatigue resistance of 1a–1c and 2a–2f in the PMMA matrix

Fatigue resistance was determined by examining the absorbance at λ_{max} after every irradiation cycle of UV and

visible light. Compounds **1a**–**1c** and **2a**–**2f** in PMMA film exhibited excellent fatigue resistance after repeated photocoloration. The fatigue resistance of compound **2d** in PMMA is shown in Fig. 6. After 170-cycle irradiation, the absorbance was kept at 99.5%. As it was analogized, the absorbance of the 1200-cycle would be kept at 96.6% [$A = A_0(1–X)^n$, where X is the variational absorbance, and n is the number of cycles]. Thus, these spirooxazines exhibit excellent stability.

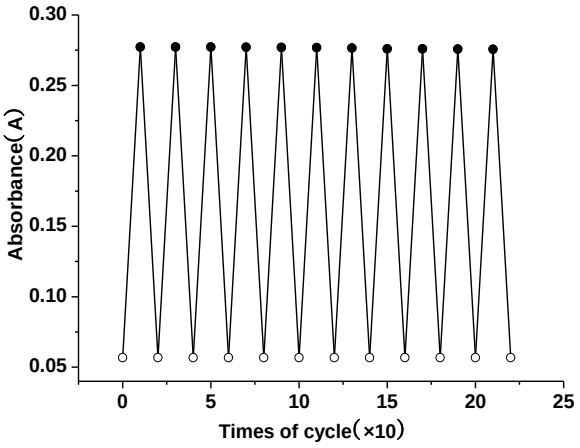


Fig. 6. Photoinduced absorption changes for 2d in PMMA film; photoirradiation started at each point of ○ for visible light and then finished at the point of ● for UV light.

4. Conclusions

The microwave method was used to synthesize a series of novel spirooxazines. All the compounds exhibited excellent photochromic properties upon UV irradiation in the SBS, PMMA, and PC films. The relaxation times obtained ranged broadly from 129 s to 1724 s. Further studies are necessary to produce more spirooxazines at different relaxation time. Their photochromic behaviors and applications should also be investigated.

Acknowledgments

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