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Isomerization of spirobenzopyrans bearing electron-donating and electron-withdrawing groups in acidic aqueous solutions

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Spirobenzopyrans, which are well known as photochromic compounds, exist as thermodynamically stable protonated ring-opened isomers (protonated merocyanine form, McH) in an acidic aqueous solution in the dark. In the present study, we investigated effects of substitution of the spirobenzopyrans on a ring-opening behavior in an aqueous system. We prepared five polymerizable spirobenzopyrans that are substituted with a methoxy group or a nitro group at the 6′- or 8′-positions and without a substituent. These monomers were copolymerized with *N*,*N*-dimethylacrylamide to evaluate the spirobenzopyrans in aqueous solution. Correlation between ring-opening rates and the kind and position of the substitution can be summarized as follows: the substitution of an electron-donating methoxy group and the substitution at the 8′-position increased the ring-opening rate, whereas the substitution of an electron-withdrawing nitro group decreased the rate. The effects of the substitution can be explained by changes in the electron density of the oxygen atom of the spirobenzopyrans.

1. Introduction

Photochromic compounds undergo a reversible isomerization by light-irradiation.[1] This unique nature has attracted considerable attention both for their fundamental characteristics and potential applications in photonic devices. Spirobenzopyrans that are typical of the photochromic compounds have been intensively studied over the past few decades.[2] Almost all studies on characteristics of the spirobenzopyrans have been performed in organic solvents or their binary mixtures with water because of insolubility of those in water. A dominant isomer of the spirobenzopyrans in organic solvents is a colorless ring-closed form (spiro form; Sp) in general. An isomerization of the Sp to a colored ring-opened form (merocyanine form; Mc) is induced by UV-light irradiation and the reverse isomerization undergoes by visible-light irradiation (Fig. 1). The isomerization also occurs thermally in the dark. Moreover, a substitution,[3–6] a solvent polarity,[6,7] and the presence of proton[8–10] affect the isomerization behavior.

Recently, photoresponse of the spirobenzopyrans in aqueous solutions has been investigated by conjugation to water-soluble polymers[11,12] or peptides.[13–15] We have demonstrated a reversible volume phase transition of spirobenzopyran-bearing hydrogels in response to light-irradiation[11] and have examined their applications to a light-controllable valve and actuator to control microfluidic systems.[16] The volume changes in the hydrogels include stages of visible-light-induced shrinking and spontaneous re-swelling. The isomerization of a spirobenzopyran is essential in the volume changes. The present problem is a slow swelling of the hydrogels, which is likely due to a slow ring opening of an unsubstituted spirobenzopyran.

Isomerization behaviors of the spirobenzopyrans in water,[15] as well as that in organic solvents, are significantly affected by substitutions. Therefore, a suitable choice of substituents is

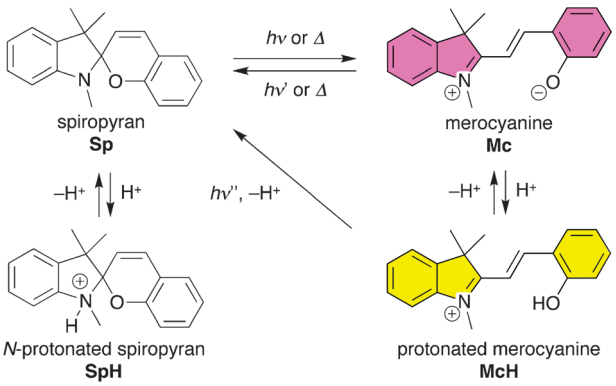

Fig. 1 Chemical structures of spiropyran (Sp), merocyanine (Mc), protonated Mc (McH), and N-protonated Sp (SpH) and their equilibria. A bridge region of the Mc and the McH allows conformational changes in them.

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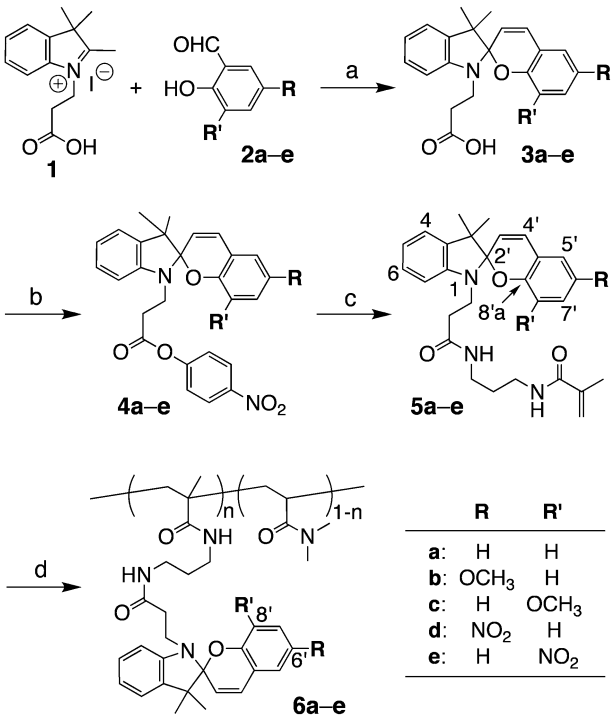

Scheme 1 Synthetic route to spirobenzopyran-bearing polymers **6a–e**. (a) Piperidine, 2-butanone, reflux, 3 h. (b) 4-Nitrophenol, DCC, DMAP, THF, rt, 4 h. (c) *N*-(3-Aminopropyl)methacrylamide hydrochloride, triethylamine, DMF, rt, 4 h. (d) DMAAm, AIBN, dry THF, 65 °C, 20 h.

necessary to achieve desired characteristics of spirobenzopyrans in aqueous solutions. Effects of substitutions on the isomerization have been extensively investigated in organic solvents,[3–6] whereas little is known about those in water.[15] Thus, it is important to obtain a clear relationship between the kind and position of a substituent and the isomerization behavior of a substituted spirobenzopyran in water.

In this study, we investigated effects of substitution on the spontaneous ring opening of spirobenzopyrans in water. We prepared water-soluble polymers with pendant spirobenzopyran derivatives in which an electron-donating group and an electron-withdrawing group were substituted at the 6′- or 8′-position (Scheme 1). The spontaneous isomerization behavior of the substituted spirobenzopyrans from the Sp to the McH in water was evaluated by using the polymers with pendant spirobenzopyrans.

2. Materials and methods

2.1 General

N,*N*-Dimethylacrylamide (DMAAm) (Tokyo Kasei Co., Tokyo, Japan) was distilled before use. All other reagents and solvents were used as received from commercial sources. ^{1}H NMR, ^{13}C NMR, ^{1}H–^{1}H COSY, and ^{1}H–^{13}C HMQC spectra were measured on a JEOL JNM-LA 600 FT-NMR system (JEOL, Tokyo, Japan) operating at 600 MHz and 150 MHz for ^{1}H NMR and ^{13}C NMR, respectively, except for using a JEOL JNM-ECX 400 system (JEOL) operating at 400 MHz for ^{1}H NMR. All NMR spectra were recorded in $CDCl_3$ at 25 °C. Tetramethylsilane or residual solvent was used as internal reference. Multiplicities on the ^{1}H NMR spectra are represented as s, singlet; d, doublet; dd, double doublet; ddd, double double doublet; and m, multiplet. High-resolution mass spectra (HRMS) were recorded with a JEOL JMS-700T Tandem MStation mass spectrometer (JEOL) in the positive ion electron impact mode (EI^+). Gel permeation chromatography (GPC) was performed by using a HLC-8121GPC/HT GPC system (Tosoh Co., Tokyo, Japan) equipped with two serial-coupled Shodex LF-804 columns (Showa Denko K.K., Tokyo, Japan) and a differential refractometer under the following conditions: mobile phase, THF; temperature, 50 °C; and flow rate, 0.5 mL min^{-1}. Polystyrene standards (Tosoh Co.) were used as calibration standards. UV–visible spectroscopy was performed on a V-560 UV/VIS spectrophotometer (Jasco Co., Tokyo, Japan). Light-irradiation was carried out by using a Lightningcure LC6 light generator (Hamamatsu Photonics K.K., Hamamatsu, Japan) with blue-light peaked at 436 nm with a total intensity of 80 mW.

2.2 Syntheses of poly(*N*,*N*-dimethylacrylamide) with pendant spirobenzopyrans

2.2.1 1-(2-Carboxyethyl)-3,3-dimethylspiro(2′*H*-1′-benzopyran-2,2′-indoline) derivatives (3a–e). A mixture solution of 1-(2-carboxyethyl)-2,3,3-trimethyl-3*H*-indolenium iodide **1** (2.00 g, 5.57 mmol), salicylaldehyde **2a** (0.59 mL, 5.65 mmol), and piperidine (0.56 mL, 5.66 mmol) in 2-butanone (16.7 mL) was refluxed for 3 h. The reaction products were extracted with CH_2Cl_2 and then the desired product was isolated by silica gel column chromatography with a step gradient from ethyl acetate/hexane in 3 : 1 (v/v) to methanol/ethyl acetate in 1 : 1 (v/v). After drying under reduced pressure, the purified product **3a** was obtained as a reddish brown powder in a yield of 74% (1.37 g, 4.10 mmol). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.12 (3H, s, C3–*CH*$_3$), 1.27 (3H, s, C3–*CH*$_3$), 2.60 (1H, m, CO–*CH*$_2$–), 2.67 (1H, m, CO–*CH*$_2$–), 3.52 (1H, m, N1–*CH*$_2$–), 3.64 (1H, m, N1–*CH*$_2$–), 5.64 (1H, d, J = 10 Hz, H3′), 6.56 (1H, d, J = 8 Hz, H7), 6.65 (1H, d, J = 8 Hz, H8′), 6.79 (1H, ddd, J = 1 Hz, 7 Hz, and 8 Hz, H6′), 6.82 (1H, d, J = 10 Hz, H4′), 6.84 (1H, ddd, J = 1 Hz, 7 Hz, and 7 Hz, H5), 7.01 (1H, dd, J = 1 Hz and 8 Hz, H5′), 7.05 (1H, ddd, J = 1 Hz, 7 Hz and 8 Hz, H7′), 7.07 (1H, dd, J = 1 Hz and 7 Hz, H4), 7.16 (1H, ddd, J = 1 Hz, 8 Hz and 8 Hz, H6).

Other derivatives **3b–e** were prepared by a similar method to that of **3a**. In synthesis of **3e**, a crystalline crude product was formed at room temperature (rt) after the reflux. The purified product was isolated by filtration and washing with acetone.

Compound **3b**. Yield of 69%, a reddish brown powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.11 (3H, s, C3–*CH*$_3$), 1.27 (3H, s, C3–*CH*$_3$), 2.61 (1H, m, CO–*CH*$_2$–), 2.68 (1H, m, CO–*CH*$_2$–), 3.51 (1H, m, N1–*CH*$_2$–), 3.64 (1H, m, N1–*CH*$_2$–), 3.74 (3H, s, O*CH*$_3$), 5.67 (1H, d, J = 10 Hz, H3′), 6.56 (1H, d, J = 8 Hz, H7), 6.59 (1H, d, J = 3 Hz, H5′), 6.59 (1H, d, J = 8 Hz, H8′), 6.65 (1H, dd, J = 3 Hz and 8 Hz, H7′), 6.78 (1H, d, J = 10 Hz, H4′), 6.84 (1H, dd, J = 7 Hz and 7 Hz, H5), 7.06 (1H, dd, J = 1 Hz and 7 Hz, H4), 7.16 (1H, ddd, J = 1 Hz, 8 Hz and 8 Hz, H6).

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Compound **3c**. Yield of 91%, a yellow powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.12 (3H, s, C3–CH_3), 1.28 (3H, s, C3–CH_3), 2.60 (1H, m, CO–CH_2–), 2.71 (1H, m, CO–CH_2–), 3.54 (1H, m, N1–CH_2–), 3.66 (3H, s, OCH_3), 3.69 (1H, m, N1–CH_2–), 5.64 (1H, d, J = 10 Hz, H3′), 6.55 (1H, d, J = 8 Hz, H7), 6.67 (1H, dd, J = 2 Hz and 7 Hz, H7′), 6.72–6.75 (2H, m, H5′ and H6′), 6.80 (1H, d, J = 10 Hz, H4′), 6.82 (1H, dd, J = 7 Hz and 7 Hz, H5), 7.06 (1H, d, J = 7 Hz, H4), 7.14 (1H, ddd, J = 1 Hz, 7 Hz and 7 Hz, H7).

Compound **3d**. Yield of 61%, a brown powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.14 (3H, s, C3–CH_3), 1.26 (3H, s, C3–CH_3), 2.61 (1H, m, CO–CH_2–), 2.67 (1H, m, CO–CH_2–), 3.54 (1H, m, N1–CH_2–), 3.63 (1H, m, N1–CH_2–), 5.84 (1H, d, J = 11 Hz, H3′), 6.60 (1H, d, J = 8 Hz, H7), 6.72 (1H, d, J = 8 Hz, H8′), 6.90 (1H, ddd, J = 1 Hz, 7 Hz, and 8 Hz, H5), 6.91 (1H, d, J = 11 Hz, H4′), 7.09 (1H, dd, J = 1 Hz and 8 Hz, H4), 7.20 (1H, ddd, J = 1 Hz, 8 Hz and 8 Hz, H6), 7.99–8.01 (2H, m, H5′ and H7′).

Compound **3e**. Yield of 99%, a dark grey powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.14 (3H, s, C3–CH_3), 1.31 (3H, s, C3–CH_3), 2.64 (1H, m, CO–CH_2–), 2.75 (1H, m, CO–CH_2–), 3.55 (1H, m, N1–CH_2–), 3.65 (1H, m, N1–CH_2–), 5.81 (1H, d, J = 10 Hz, H3′), 6.56 (1H, d, J = 8 Hz, H7), 6.85–6.88 (2H, m, H-5 and H-6′), 6.89 (1H, d, J = 10 Hz, H4′), 7.06 (1H, d, J = 7 Hz, H4), 7.16 (1H, ddd, J = 1 Hz, 8 Hz and 8 Hz, H6), 7.35 (1H, dd, J = 2 Hz and 8 Hz, H5′), 7.65 (1H, dd, J = 2 Hz and 8 Hz, H7′).

2.2.2 1-[2-(4-Nitrophenyl)oxycarbonylethyl]-3,3-dimethylspiro(2′*H*-1′-benzopyran-2,2′-indoline) derivatives (4a–e). A mixture solution of 4-nitrophenol (0.608 g, 4.37 mmol), *N*,*N*′-dicyclohexylcarbodiimide (DCC) (0.902 g, 4.37 mmol), and 4-dimethylaminopyridine (DMAP) (0.050 g, 0.41 mmol) in THF (16 mL) was added dropwise to a solution of **3a** (1.33 g, 3.97 mmol) in THF (24 mL) with stirring. After the stirring of the reaction mixture for 4 h at rt, the formed precipitates were removed by filtration. The reaction products were extracted with ethyl acetate and then the desired product was isolated by silica gel column chromatography with a step gradient from ethyl acetate/hexane in 1 : 4 to 1 : 1 (v/v). After drying under reduced pressure, the purified product **4a** was obtained in a yield of 66% (1.20 g, 2.63 mmol).

Other derivatives **4b–e** were prepared by a similar method to that of **4a**. The yields of compounds **4b**, **4c**, **4d**, and **4e** were 44%, 60%, 59%, and 57%, respectively.

2.2.3 *N*-[3-[2-[3,3-Dimethylspiro(2′*H*-1′-benzopyran-2,2′-indolin)-1-yl]ethylcarbonylamino]propyl]methacrylamide derivatives (5a–e). A solution of **4a** (0.518 g, 2.90 mmol) in DMF (6.0 mL) was added dropwise to a mixture solution of *N*-(3-aminopropyl)methacrylamide hydrochloride (1.20 g, 2.63 mmol) and triethylamine (0.41 mL, 2.94 mmol) in DMF (4.5 mL) with stirring. After the stirring for 4 h at rt, the reaction products were extracted with ethyl acetate and then the desired product was isolated by silica gel column chromatography with a step gradient from ethyl acetate/hexane in 3 : 1 (v/v) to ethyl acetate. After drying under reduced pressure, the purified product **5a** was obtained as a pale green powder in a yield of 92% (1.11 g, 2.43 mmol). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.12 (3H, s, C3–CH_3), 1.29 (3H, s, C3–CH_3), 1.53 (2H, m, CH_2–CH_2–CH_2), 1.98 (3H, s, vinyl-CH_3), 2.36 (2H, m, CO–CH_2–), 2.57 (2H, m, CO–CH_2–), 3.13 (2H, m, NH–CH_2–), 3.20 (2H, m, NH–CH_2–), 3.47 (1H, m, N1–CH_2–), 3.73 (1H, m, N1–CH_2–), 5.33 (1H, m, vinyl CH_2), 5.65 (1H, d, J = 10 Hz, H3′), 5.75 (1H, m, vinyl CH_2), 6.62 (1H, d, J = 8 Hz, H7), 6.67 (1H, d, J = 8 Hz, H8′), 6.83 (1H, dd, J = 7 Hz and 7 Hz, H6′), 6.83 (1H, dd, J = 7 Hz and 7 Hz, H5), 6.84 (1H, d, J = 10 Hz, H4′), 7.06 (1H, d, J = 7 Hz, H5′), 7.06 (1H, d, J = 7 Hz, H4), 7.10 (1H, dd, J = 7 Hz and 8 Hz, H7′), 7.14 (1H, dd, J = 7 Hz and 8 Hz, H6). HRMS (EI$^+$): m/z calcd for $C_{28}H_{33}N_3O_3$ 459.2522, found 459.2519.

Other derivatives **5b–e** were prepared by similar methods to that of **5a**.

Compound **5b**. Yield of 90%, a pale grey powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.12 (3H, s, C3–CH_3), 1.28 (3H, s, C3–CH_3), 1.53 (2H, m, CH_2–CH_2–CH_2), 1.98 (3H, s, vinyl-CH_3), 2.36 (2H, m, CO–CH_2–), 2.56 (2H, m, CO–CH_2–), 3.17 (4H, m, NH–CH_2–), 3.45 (1H, m, N1–CH_2–), 3.72 (1H, m, N1–CH_2–), 3.75 (3H, s, OCH_3), 5.34 (1H, m, vinyl CH_2), 5.68 (1H, d, J = 10 Hz, H3′), 5.75 (1H, m, vinyl CH_2), 6.61 (1H, d, J = 8 Hz, H8′), 6.61 (1H, s, H5′), 6.61 (1H, d, J = 8 Hz, H7), 6.67 (1H, d, J = 8 Hz, H7′), 6.80 (1H, d, J = 10 Hz, H4′), 6.81 (1H, dd, J = 7 Hz and 8 Hz, H5), 7.14 (1H, dd, J = 8 Hz and 8 Hz, H6), 7.14 (1H, d, J = 7 Hz, H4). HRMS (EI$^+$): m/z calcd for $C_{29}H_{35}N_3O_4$ 489.2628, found 489.2631.

Compound **5c**. Yield of 88%, a blue grey powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.09 (3H, s, C3–CH_3), 1.29 (3H, s, C3–CH_3), 1.34 (2H, m, CH_2–CH_2–CH_2), 2.00 (3H, s, vinyl-CH_3), 2.21 (2H, m, CO–CH_2–), 2.49 (2H, m, CO–CH_2–), 2.96 (2H, m, NH–CH_2–), 3.05 (2H, m, NH–CH_2–), 3.55 (1H, m, N1–CH_2–), 3.75 (3H, s, OCH_3), 3.98 (1H, m, N1–CH_2–), 5.34 (1H, m, vinyl CH_2), 5.61 (1H, d, J = 10 Hz, H3′), 5.75 (1H, m, vinyl CH_2), 6.65 (1H, d, J = 7 Hz, H7), 6.73 (1H, d, J = 7 Hz, H7′), 6.75 (1H, dd, J = 7 Hz and 8 Hz, H5), 6.79 (1H, d, J = 8 Hz, H5′), 6.81 (1H, dd, J = 7 Hz and 8 Hz, H6′), 6.83 (1H, d, J = 10 Hz, H4′), 7.01 (1H, d, J = 8 Hz, H4), 7.10 (1H, dd, J = 7 Hz and 7 Hz, H6). HRMS (EI$^+$): m/z calcd for $C_{29}H_{35}N_3O_4$ 489.2628, found 489.2638.

Compound **5d**. Yield of 78%, a pale yellow powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.14 (3H, s, C3–CH_3), 1.26 (3H, s, C3–CH_3), 1.57 (2H, m, CH_2–CH_2–CH_2), 1.97 (3H, s, vinyl-CH_3), 2.43 (2H, m, CO–CH_2–), 2.56 (2H, m, CO–CH_2–), 3.20 (4H, m, NH–CH_2–), 3.50 (1H, m, N1–CH_2–), 3.68 (1H, m, N1–CH_2–), 5.35 (1H, m, vinyl CH_2), 5.73 (1H, m, vinyl CH_2), 5.86 (1H, d, J = 11 Hz, H3′), 6.67 (1H, d, J = 8 Hz, H7), 6.75 (1H, d, J = 8 Hz, H8′), 6.87 (1H, dd, J = 7 Hz and 7 Hz, H5), 6.91 (1H, d, J = 11 Hz, H4′), 7.07 (1H, d, J = 7 Hz, H4), 7.18 (1H, dd, J = 7 Hz and 8 Hz, H6), 7.98 (1H, s, H5′), 8.00 (1H, d, J = 8 Hz, H7′). HRMS (EI$^+$): m/z calcd for $C_{28}H_{32}N_4O_5$ 504.2373, found 504.2370.

Compound **5e**. Yield of 76%, a dark blue grey powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.11 (3H, s, C3–CH_3), 1.28

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Table 1 The ^{13}C NMR chemical shift assignments of the monomeric spirobenzopyrans **5a–e**[a]

Position	5a	5b	5c	5d	5e
Indoline ring					
C2,2′	104.6	104.3	105.0	106.8	107.9
C3	52.2	52.2	53.0	52.8	53.5
C3–*CH*$_3$	25.8	25.8	26.0	25.8	25.9
	20.1	20.2	20.0	19.8	20.2
C3a	136.4	136.4	135.3	135.9	135.0
C4	121.8	121.8	121.7	121.8	121.7
C5	119.1	119.0	118.4	119.7	119.6
C6	127.6	127.6	127.6	127.8	127.8
C7	106.6	106.6	106.5	106.9	106.8
C7a	146.6	146.6	146.7	146.4	145.8
Benzopyran ring					
C3′	119.5	120.5	120.2	121.9	122.4
C4′	129.5	129.4	129.5	128.3	128.6
C4′a	118.7[b]	119.0[b]	119.5[b]	118.7[b]	121.9[b]
C5′	126.9	111.7	119.3[b]	122.8	131.7[b]
C6′	120.4	153.4[b]	120.2	141.1	119.7
C7′	129.8	115.3	112.7[b]	125.9	125.4[b]
C8′	114.9	115.5	146.8[b]	115.5	137.2[b]
C8′a	153.8[b]	147.9[b]	142.3[b]	159.4[b]	148.1[b]
OCH_3	—	55.8	56.0	—	—
Linker chain					
C=O	172.5	172.6	173.1	171.6	172.7
	168.6	168.6	168.3	169.0	168.4
N1–*CH*$_2$	39.9	40.0	39.6	40.0	39.7
CO–*CH*$_2$	36.2	36.3	37.5	36.0	36.7
NH–*CH*$_2$	35.9	35.9	36.5	35.7	36.1
	35.6	35.6	36.0	35.7	35.6
CH_2–*CH*$_2$–CH_2	29.5	29.5	28.9	29.6	29.1
Vinyl-*C*	139.9	139.9	140.2	139.7	140.0
Vinyl-*CH*$_2$	119.7	119.7	119.5	119.9	119.5
Vinyl-*CH*$_3$	18.6	18.6	18.7	18.6	18.6

[a] The NMR spectra were recorded in $CDCl_3$ at 25 °C and the chemical shifts are reported in ppm units. [b] The denoted signals were assigned by the calculation based on an additivity rule.

(3H, s, C3–*CH*$_3$), 1.51 (2H, m, CH_2–*CH*$_2$–CH_2), 1.98 (3H, s, vinyl-*CH*$_3$), 2.36 (2H, m, CO–*CH*$_2$–), 2.59 (2H, m, CO–*CH*$_2$–), 2.98 (2H, m, NH–*CH*$_2$–), 3.18 (2H, m, NH–*CH*$_2$–), 3.60 (1H, m, N1–*CH*$_2$–), 3.88 (1H, m, N1–*CH*$_2$–), 5.33 (1H, m, vinyl *CH*$_2$), 5.77 (1H, m, vinyl *CH*$_2$), 5.80 (1H, d, J = 11 Hz, H3′), 6.63 (1H, d, J = 8 Hz, H7), 6.81 (1H, dd, J = 7 Hz and 8 Hz, H5), 6.91 (1H, d, J = 11 Hz, H4′), 6.92 (1H, dd, J = 7 Hz and 8 Hz, H6′), 7.01 (1H, d, J = 7 Hz, H4), 7.13 (1H, dd, J = 8 Hz and 8 Hz, H6), 7.30 (1H, d, J = 7 Hz, H5′), 7.70 (1H, d, J = 8 Hz, H7′). HRMS (EI^+): m/z calcd for $C_{28}H_{32}N_4O_5$ 504.2373, found 504.2382.

^{13}C NMR assignments of compounds **5a–e** are listed in Table 1.

2.2.4 Poly(*N*,*N*-dimethylacrylamide) with pendant spirobenzopyran derivatives (6a–e). A mixture solution of the monomeric spirobenzopyran **5a** (0.501 mg, 1.09 mmol), DMAAm (0.973 mg, 9.81 mmol), and 2,2′-azoisobutyronitrile (AIBN) (0.018 mg, 0.11 mmol) in dry THF (6.0 mL) (the molar ratio of **5a**/DMAAm/AIBN was 10 : 90 : 1) was subjected to freeze–pump–thaw cycles to remove oxygen. Nitrogen was filled to the degassed reaction equipments and the mixture solution was stirred for 20 h at 65 °C. After cooling to rt, the reaction mixture was poured into ether (200 mL). The resulting precipitates were collected by filtration and were dried under reduced pressure. The product **6a** was obtained as a pale grey powder in a yield of 88% (w/w). The content of the spirobenzopyran in the obtained polymers was estimated to be 11 mol% by ^1H NMR spectroscopy. Weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the polymers were determined to be 2400 and 1.7, respectively, by GPC. ^1H NMR (400 MHz, $CDCl_3$): 0.8–2.0 (54H, br, C3–*CH*$_3$, CH_2–*CH*$_2$–CH_2, vinyl-*CH*$_3$, DMAAm *CH*$_2$, and DMAAm *CH*), 2.3–3.4 (64H, br, CO–*CH*$_2$–, DMAAm *CH*$_3$, and NH–*CH*$_2$–), 3.4–3.5 (1H, br, N1–*CH*$_2$–), 3.6–3.8 (1H, br, N1–*CH*$_2$–), 5.6–5.7 (1H, br, H3′), 6.5–6.7 (2H, br, H7 and H8′), 6.7–6.9 (3H, br, H5, H6′, and H4′), 7.0–7.2 (4H, br, H5′, H4, H7′, and H6).

Other polymers **6b–e** were prepared by a similar method to that of **6a**.

Polymer **6b**. The molar ratio of **5b**/DMAAm/AIBN was 10 : 90 : 1, a yield of 87%, the spirobenzopyran content of 11 mol%, a pale green powder, M_w 1700, M_w/M_n 1.1. ^1H NMR (600 MHz, $CDCl_3$): 0.8–2.0 (71H, br, C3–*CH*$_3$, CH_2–*CH*$_2$–CH_2, vinyl-*CH*$_3$, and DMAAm *CH*$_2$), 2.3–3.3 (28H, br, DMAAm *CH*, CO–*CH*$_2$–, DMAAm *CH*$_3$, and NH–*CH*$_2$–), 3.4–3.5 (1H, br, N1–*CH*$_2$–), 3.6–3.8 (4H, br, N1–*CH*$_2$– and O*CH*$_3$), 5.6–5.7 (1H, br, H3′), 6.5–6.7 (4H, br, H8′, H7, H5′, and H7′), 6.7–6.8 (2H, br, H4′ and H5), 7.0–7.1 (1H, br, H4), 7.1–7.2 (1H, br, H6).

Polymer **6c**. The molar ratio of **5c**/DMAAm/AIBN was 10 : 90 : 1, a yield of 82%, the spirobenzopyran content of 11 mol%, a blue-grey powder, M_w 2200, M_w/M_n 1.2. ^1H NMR (600 MHz, $CDCl_3$): 0.8–2.0 (29H, br, C3–*CH*$_3$, CH_2–*CH*$_2$–CH_2, vinyl-*CH*$_3$, and DMAAm *CH*$_2$), 2.2–3.2 (72H, br, DMAAm CH, CO–*CH*$_2$–, DMAAm *CH*$_3$, and NH–*CH*$_2$–), 3.5–3.6 (1H, br, N1–*CH*$_2$–), 3.6–3.9 (4H, br, O*CH*$_3$, N1–*CH*$_2$–), 5.6–5.7 (1H, br, H3′), 6.5–6.6 (1H, br, H7), 6.7–6.9 (5H, br, H7′, H5, H5′, H4′, and H6′), 7.0–7.1 (1H, br, H4), 7.1–7.2 (1H, br, H6).

Polymer **6d**. The molar ratio of **5d**/DMAAm/AIBN was 5 : 95 : 1, a yield of 72%, the spirobenzopyran content of 5 mol%, a reddish purple powder, M_w 4100, M_w/M_n 1.4. ^1H NMR (600 MHz, $CDCl_3$): 0.8–1.9 (47H, br, C3–*CH*$_3$, CH_2–*CH*$_2$–CH_2, vinyl-*CH*$_3$, and DMAAm *CH*$_2$), 2.3–3.4 (140H, br, DMAAm *CH*, CO–*CH*$_2$–, DMAAm *CH*$_3$, and NH–*CH*$_2$–), 3.4–3.5 (1H, br, N1–*CH*$_2$–), 3.6–3.7 (1H, br, N1–*CH*$_2$–), 5.8–5.9 (1H, br, H3′), 6.6–6.7 (1H, br, H7), 6.7–6.8 (1H, br, H8′), 6.8–6.9 (1H, br, H5), 6.9–7.0 (1H, br, H4′), 7.0–7.1 (1H, br, H4), 7.1–7.2 (1H, br, H6), 7.9–8.0 (2H, br, H5′ and H7′).

Polymer **6e**. The molar ratio of **5e**/DMAAm/AIBN was 5 : 95 : 5, a yield of 45%, the spirobenzopyran content of 3 mol%, a grey powder, M_w 2700, M_w/M_n 1.3. ^1H NMR (600 MHz, $CDCl_3$): 0.8–1.9 (84H, br, C3–*CH*$_3$, CH_2–*CH*$_2$–CH_2, vinyl-*CH*$_3$, and DMAAm *CH*$_2$), 2.3–3.4 (246H, br, DMAAm *CH*, CO–*CH*$_2$–, DMAAm *CH*$_3$, and NH–*CH*$_2$–), 3.5–3.6 (1H, br, N1–*CH*$_2$–), 3.7–3.8 (1H, br, N1–*CH*$_2$–), 5.8–5.9 (1H, br, H3′), 6.5–6.6 (1H, br, H7), 6.7–6.8 (1H, br, H5), 6.8–7.0 (2H, br, H4′ and H6′), 7.0–7.1 (1H, br, H4), 7.1–7.2 (1H, br, H6), 7.2–7.3 (1H, br, H5′), 7.6–7.7 (1H, br, H7′).

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2.3 UV–visible spectroscopy of the spirobenzopyrans in aqueous solutions

UV–visible spectra of polymers **6a–e** were recorded both in 10 mM HCl and in neutral aqueous solution containing 10 mM triethylamine hydrochloride at 0.5 °C with stirring. The neutral conditions were set up immediately before the measurements by an addition of triethylamine to the solutions of polymers **6a–e** in 10 mM HCl. After the measurements in the neutral conditions, the solution was acidified again with 1 M HCl to evaluate reversibility in the acid–base changes.

UV–visible spectra were also recorded before and after light-irradiation in 2 mM HCl at 0.5 °C.

2.4 Spontaneous ring-opening rates of the spirobenzopyrans in aqueous solutions

Solutions of polymers **6a–e** in 2 mM HCl were irradiated with blue-light at 25 °C. After stopping the irradiation, the solutions were stored in the dark. Time-course of absorbance of the McH was monitored during the light-irradiation and the subsequent storage period.

3. Results and discussion

3.1 Syntheses

A series of spirobenzopyran-bearing polymers **6a–e** were synthesized according to the previous studies[17–20] or with some modifications of them (Scheme 1). First, a Fisher's base **1** was reacted with unsubstituted and appropriately substituted salicylaldehydes **2a–e** to give 1-(2-carboxyethyl)spirobenzopyrans **3a–e**.[17] Second, compounds **3a–e** and 4-nitrophenol were condensed in the presence of DCC to yield the corresponding 4-nitrophenyl ester derivatives **4a–e**.[18] Third, monomeric spirobenzopyrans **5a–e** were obtained by reaction of compounds **4a–e** with *N*-(3-aminopropyl)methacrylamide hydrochloride in the presence of triethylamine.[19] HRMS of compounds **5a–e** supported their formula weights. Detailed chemical structures of compounds **5a–e** were resolved by ^{1}H NMR, ^{1}H–^{1}H COSY, ^{13}C NMR, and ^{1}H–^{13}C HMQC spectroscopies. Finally, polymers **6a–e** were prepared by a free radical random polymerization of the monomeric spirobenzopyrans **5a–e** and *N*,*N*-dimethylacrylamide (DMAAm) initiated by AIBN at 65 °C.[20] The fed monomeric spirobenzopyrans **5a–e** were 10 mol% for **6a–c** and 5 mol% for **6d** and **6e**. The amounts of the spirobenzopyrans introduced in the polymers were 11, 11, 11, 5, and 3 mol% in the order from **6a** to **6e**, which were determined by comparison of the integrated intensities between the peak assigned to spirobenzopyran's H3′ proton and that assigned to DMAAm's methyl groups on the ^{1}H NMR spectra. The M_w of the polymers was determined to be in the range of 1700 to 4100 with a polydispersity between 1.1 and 1.7. Polymers **6a–e** were completely soluble in aqueous solutions at any pH.

The ^{13}C NMR chemical shift assignments of the monomeric spirobenzopyrans **5a–e** in $CDCl_3$ are listed in Table 1. The isomerization between Sp and Mc forms of the monomeric spirobenzopyrans **5a–e** highly favored the Sp form in the $CDCl_3$, in which the chemical structures of **5a–e** seem the same as those in a photoinduced ring-closed form. The assignments were carried out by a conventional method. Since the chemical shifts of the carbon atoms in the benzopyran aromatic ring were significantly affected by the substitutions, a part of the signal was difficult to directly assign by the NMR measurements in this study. However, the chemical shifts of the unassigned peaks were separated enough from each other ($\geq$ 4.5 ppm for the unassigned quaternary carbons). Therefore, simple calculations based on an additivity rule were valid to assign the signals. We used NMR data of benzene, methoxybenzene (anisole), and nitrobenzene in $CDCl_3$[21] in the following calculation: at first, changes in chemical shifts of benzene caused by methoxy and nitro substitutions were calculated for each carbon at *ortho*-, *meta*-, and *para*-positions of the substituents. Second, the chemical shifts of compounds **5b–e** were estimated based on those of unsubstituted **5a** and the additivity of the substitution effects. The differences between the calculated and the found values were within $\pm$1.7 ppm, $\pm$2.9 ppm, $\pm$1.1 ppm, and $\pm$2.4 ppm in compounds **5b**, **5c**, **5d**, and **5e**, respectively, for the six carbons in the benzopyran aromatic ring. The calculated values for signals of the C4′a and C8′a agreed with the found ones when the signal at around 120 ppm was assigned to the C4′a. These assignments for compound **5b** were coincident with the literatures.[22,23]

3.2 UV–visible spectroscopy

3.2.1 Isomerization by acid–base changes. Fig. 2 shows UV–visible spectra of the aqueous solutions of spirobenzopyran-bearing polymers **6a–e** acidified with 10 mM HCl and stored in the dark. Each solution was yellowish due to the strong absorbance band with peaks at around 400–470 nm. Since the protonated Mc (McH) was a major and stable ring-opened isomer under acidic and dark conditions, the spectra were attributed to McH.[24–26] Meanwhile, by neutralizing the acidic solutions with the triethylamine, the color of solutions which had been yellowish under acidic conditions turned reddish or purple in no time, and returned to the former color in a moment of the acidification by adding excess HCl. Considering also that the both spectra exhibited strong absorbance bands in the visible range suggesting the extendedly conjugated systems, these spectral changes were strongly suggested to be in the deprotonation and re-protonation of McH, and the spectra observed just after the neutralization were attributed to Mc (Fig. 2).

After neutralizing the acidic solutions with triethylamine, the absorbance attributed to Mc gradually decreased in each solution (Fig. 2, indicated by filled arrows). This decolorization suggests the isomerization from the Mc to the Sp. UV–visible spectroscopy recorded in organic solvents indicates that the remaining absorption band at a wavelength shorter than 400 nm can be attributed to the Sp. In polymers **6d** and **6e**, the band attributed to the Mc remained to some extent in the neutral solutions. Furthermore, another absorption band was observed at 400–500 nm, which seems similar to that of 6-nitro-8-bromo-substituted spirobenzopyran in a basic methanol solution.[27]

UV–visible spectra recorded after re-acidification (Fig. 2, indicated by open arrows) were the same as those in the

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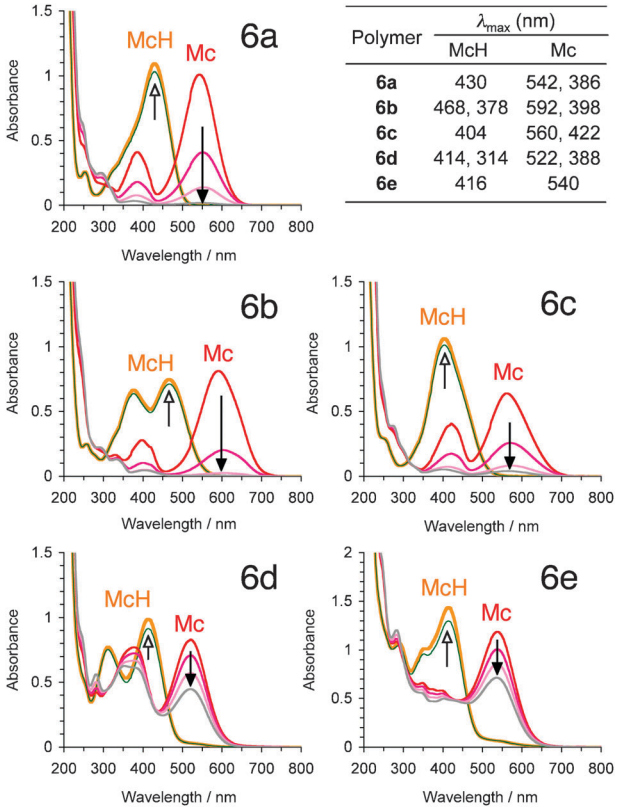

Polymer	λ_{max} (nm)	
	McH	Mc
6a	430	542, 386
6b	468, 378	592, 398
6c	404	560, 422
6d	414, 314	522, 388
6e	416	540

Fig. 2 UV–visible spectra of polymers **6a–e** in 10 mM HCl and neutral solutions at 0.5 °C. The McH isomers in the HCl solutions were converted into the Mc isomers by neutralization. Absorption bands attributed to the Mc gradually decreased in the 5 neutral solutions (indicated by filled arrows; storage for 0, 3, 10, and 30 min). The McH was regenerated by re-acidification (open arrows, 3 h after the re-acidification). Each absorbance was normalized at 50 μM of the spirobenzopyran concentration. The table in the figure lists wavelengths of absorption maxima.

original acidic solutions, indicating that the isomerization caused by the acid–base changes was reversible.

3.2.2 Isomerization by light-irradiation. Previous studies have demonstrated that the McH irradiated with visible-light usually underwent the ring closure and proton dissociation to give the corresponding Sp.[28–30] Fig. 3 represents UV–visible spectra of polymers **6a–e** recorded before and after blue-light-irradiation in 2 mM HCl at 0.5 °C. The light-irradiation time needed to reach photostationary states (PSS) was approximately 20, 210, 120, 60, and 60 s in the order from **6a** to **6e**. The absorbance of the McH was significantly decreased by the light-irradiation, suggesting the light-induced ring closure. The decreases in the absorbance associated with the isomerization from the McH to the Sp were 98, 82, 77, 97, and 86% in the order from **6a** to **6e** at the PSS. The values were determined from changes in the absorbance in the range of 400–500 nm, where the absorption is only attributed to the McH in the acidic solutions. The incomplete ring closure observed in polymers **6b**, **6c**, and **6e** was due to concurrent ring opening that occurred even under the light-irradiation in the experiments.

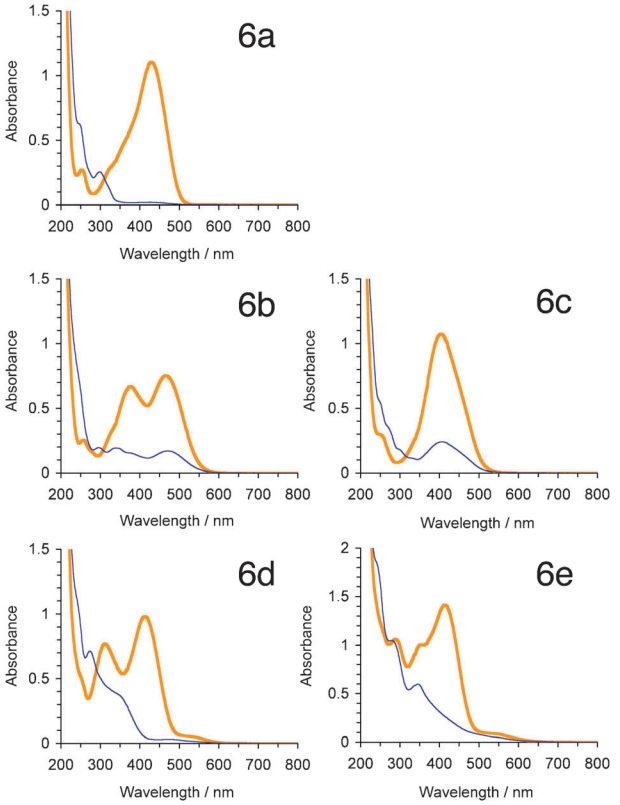

Fig. 3 UV–visible spectra of polymers **6a–e** before and after blue-light-irradiation (thick line and thin line, respectively) in 2 mM HCl at 0.5 °C. Each absorbance was normalized at 50 μM of the spirobenzopyran concentration.

The spectra of polymers **6a–e** after the light-irradiation showed an absorption band at a wavelength shorter than 400 nm. We obtained difference spectra by subtracting contribution of the McH from the spectra recorded after the irradiation (data not shown). The spectra at a wavelength shorter than 400 nm were likely to be similar to those observed in the neutral solutions and can be attributed to the Sp and possibly N-protonated Sp (SpH).

3.3 Effects of the substitution on the ring-opening rates

The solutions of polymers **6a–e** were irradiated with blue-light until they reached PSS in 2 mM HCl at 25 °C. The absorbance of the McH gradually increased after stopping the light-irradiation, suggesting the spontaneous ring opening of the Sp. We monitored time courses of absorbance of the McH in polymers **6a–e** under and after the light-irradiation (Fig. 4). The ring-opening rates were estimated from the changes in the absorbance.

Compared with the unsubstituted derivative (**6a**), the methoxy-substitution (**6b** and **6c**) significantly increased the ring-opening rates, whereas a slight change and a decrease in the rates were observed in the nitro-substitution (**6d** and **6e**). Table 2 lists the ring-opening rate constants ($k_{Sp\rightarrow McH}$) calculated by fitting the experimental data to a single exponential. The methoxy-substitution at the 8′- and the 6′-positions (**6b** and **6c**) accelerated the $k_{Sp\rightarrow McH}$ up to 19.8 and 3.2 times, respectively, as compared to the unsubstituted

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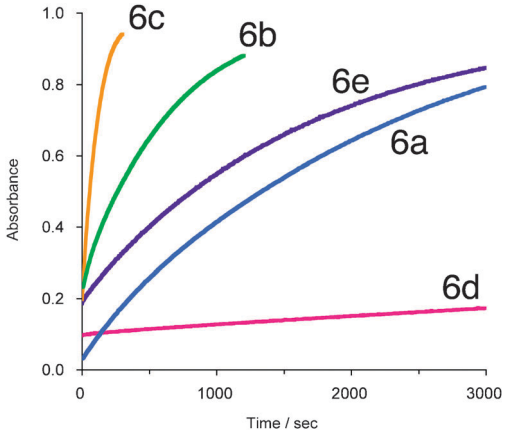

Fig. 4 Time-course of the absorbance of the McH in polymers **6a–e** after stopping the light-irradiation. The measurements were performed in 2 mM HCl at 25 °C. The values of the absorbance before the light-irradiation were normalized to be 1.0 for comparison.

Table 2 The ring-opening rate constants ($k_{Sp\rightarrow McH}$) of the spirobenzopyrans in polymers **6a–e** and the ^{13}C NMR chemical shifts of the C8′a carbon of the monomeric spirobenzopyrans **5a–e**

Substituent	Polymer	$k_{Sp\rightarrow McH}$ / $s^{-1} \times 10^{3a}$	Monomer	Chemical shift[b] / ppm
None	**6a**	0.49	**5a**	153.8
6′-CH_3O	**6b**	1.57	**5b**	147.9
8′-CH_3O	**6c**	9.70	**5c**	142.3
6′-NO_2	**6d**	0.03	**5d**	159.4
8′-NO_2	**6e**	0.61	**5e**	148.1

[a] In 2 mM HCl at 298 K. [b] In $CDCl_3$ at 298 K.

spirobenzopyran **6a**. Furthermore, the 8′-nitro-substitution (**6e**) resulted in a slight increase in the $k_{Sp\rightarrow McH}$. In contrast, the 6′-nitro-substitution (**6d**) reduced the $k_{Sp\rightarrow McH}$ to 0.06 times of that of the unsubstitution (**6a**). The substitution at the 8′-position more accelerated the ring opening than that at the 6′-position in both methoxy and nitro groups. In summary, the effects of the substitution include the acceleration by a methoxy group, the deceleration by a nitro group, and the acceleration by the substitution at the 8′-position. The result of the 8′-nitro-substitution (**6d**) is probably due to combination of the latter two effects.

We suppose that the isomerization from the Sp to the McH proceeds *via* C–O cleavage of the Sp and the subsequent protonation of the resulting phenolate anion. It is reasonable to assume that the C–O cleavage is the rate-determining step because protonation occurs instantaneously in general in acidic aqueous systems. In fact, the absorption band attributed to the Mc was not observed in UV–visible spectra recorded after stopping the light-irradiation, suggesting rapid conversion of the Mc to the McH. The McH was expected to convert into a thermodynamically stable conformation by rotation of the C2,2′–C3′–C4′–C4′a bonds. UV–visible spectra of polymers **6a–e** in acidic aqueous solutions right after the recovery from light-induced ring closure coincided with those at 4 months after the last irradiation. This suggests that ring-opened isomers were converted into some stable conformation within the time scale of $1/k_{Sp\rightarrow McH}$.

The C–O cleavage of the spirobenzopyrans results in the conversion of the oxygen atom of the ether linkage into the phenolate anion. Thus, in this step, the Sp with higher electron density of the 1′O oxygen atom is likely to reduce the activation free energy ($\Delta G^{\ddagger}$). Therefore, changes in the electron density of the 1′O will strongly affect the ring-opening rates. We assume that these changes in the electron density are substantial in the effects of the substitution.

We paid attention to a ^{13}C NMR chemical shift of the C8′a carbon since a positive relationship was predicted between the electron densities of the 1′O and the adjacent C8′a. An increase in the electron density of the C8′a, which reflects in an upfield shift of its ^{13}C NMR signal, is likely to cause an increase in that of the 1′O. In fact, the ^{13}C NMR signal of the C8′a shifted to higher magnetic field with the increase in the $k_{Sp\rightarrow McH}$ values (Table 2). Therefore, the chemical shift of the C8′a can be regarded as a potential indicator to predict the $k_{Sp\rightarrow McH}$ values, although the relationship between the ^{13}C NMR signal of the C8′a and the $k_{Sp\rightarrow McH}$ value was qualitative but not quantitative trend.

Furthermore, the assumption presented above can account for the increase in the ring-opening rate by the 8′-nitro-substitution (**6e**). Although a nitro group is known as an electron-withdrawing group, the 8′-nitro-substitution led to an upfield shift of the ^{13}C NMR signal of the C8′a, suggesting the increase in the electron density of the C8′a carbon. This could contribute to the increase in the electron density of the adjacent 1′O oxygen which probably resulted in a decrease in $\Delta G^{\ddagger}$ for the ring opening of the Sp. The upfield shift of the ^{13}C NMR signal by a nitro-substitution at an adjacent position was observed not only in a spirobenzopyran, but also in aromatic compounds such as nitrobenzene, *o*-nitrophenol, and *o*-nitroanisole.[21]

3.4 Effects of N-protonation of the Sp on the ring-opening rates

Relating to the assumption described above, we note effects of the substitution on protonation at the N1 nitrogen of the Sp. An apparent rate of the ring opening from the Sp to the McH was reported to decrease with an increase in the proton concentration because of formation of N-protonated Sp (SpH) (Fig. 1).[8] If the N-protonation behavior had been affected by the substitution, the apparent ring-opening rate would have been changed. In this case we cannot explain the effects of the substitution on the order of the ring-opening rates solely in terms of the electron density of the 1′O oxygen.

In this study, however, the substitution is not considered to affect the N-protonation behavior of the Sp, because the indoline ring in the Sp is likely to have neither electronic coupling with the benzopyran ring nor steric interaction with the substituents. In fact, the ^{13}C NMR spectra of the monomeric spirobenzopyrans **5a–e** in the Sp form revealed that there were no significant differences in the chemical shifts of the indoline carbons in all of the derivatives (Table 1). This means that the electron density of the atoms constituting the indoline ring, including the N1 nitrogen, was not significantly affected by the substitution. Therefore, the N-protonation behavior of the Sp was likely to be similar in all of the

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polymers **6a–e** at a definite acid concentration. Consequently, we can discuss the effects of the substitution on the $k_{Sp\rightarrow McH}$ independently of those of the N-protonation.

4. Conclusions

We investigated the effects of substitution on the thermal ring-opening rate of the spirobenzopyrans in the acidic aqueous solution. An electron-donating methoxy group and an electron-withdrawing nitro group were introduced at the 6′- or 8′-position. The effects of the substitution on the ring-opening rate were summarized as follows: the $k_{Sp\rightarrow McH}$ values (1) were increased by the methoxy-substitution, (2) were basically decreased by the nitro-substitution, and (3) were increased by the substitution at the 8′-position itself. We consider that an essential effect of the substitution on the ring-opening rate was the changes in the electron density of the 1′O oxygen, because that is likely to affect $\Delta G^{\ddagger}$ values needed for the C–O cleavage of the Sp. The ^{13}C NMR of the Sp showed that the signal of the C8′a, which was bonded to the 1′O oxygen, shifted to higher magnetic field with the increase in the $k_{Sp\rightarrow McH}$ values. Thus, the chemical shift of C8′a is likely to be a potential indicator of the $k_{Sp\rightarrow McH}$ values.

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