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Photophysical Switching Properties of Spironaphthoxazine-poly(styrene-sulfonic acid) Polyion Complex

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This research focuses on the preparation of polyion complex having spironaphthoxazine and their photochromic behaviors including absorbance and fluorescence switching. The polyion complex was prepared by the ion complex formation between spironaphthoxazine 3 (cationic monomer) and poly(styrene-sulfonic acid) (anionic polymer). Spironaphthoxazine group showed reversible photoisomerization in this polyion complex upon UV irradiation. It reversibly changed the fluorescent intensity by alternative irradiation with ultraviolet and visible light. The photoinduced ionic conductivity in polyion complex solution gradually increased upon UV irradiation and subsequently decreased in the dark.

Keywords Fluorescence; photochromism; photoisomerization; polyion complex; spironaphthoxazine; switching

1. Introduction

Photochromic materials have gained much attention recently because of their tremendous importance in biological phenomena as well as their potential application in the area of linear and nonlinear optics [1]. Structurally, spironaphthoxazines consist of two pi systems linked by a tetrahedral spirocarbon. Upon UV irradiation, the C-O bond of the colorless spironaphthoxazine is cleaved and the colored merocyanine form is obtained. Thus, the interconversion of the spiro (SP)-merocyanine (MC) system has been extensively investigated due to its potential application in molecular devices and in biotechnology [2–4]. We have previously reported the synthesis, photochromic property, and photoviscosity effect of ionic polymers having spironaphthoxazine moiety [5–8]. We have also reported that switching properties of photochromic carbazole-spironaphthoxazine copolymer [9,10]. The study of cation and polyanion association and interaction is important to the understanding

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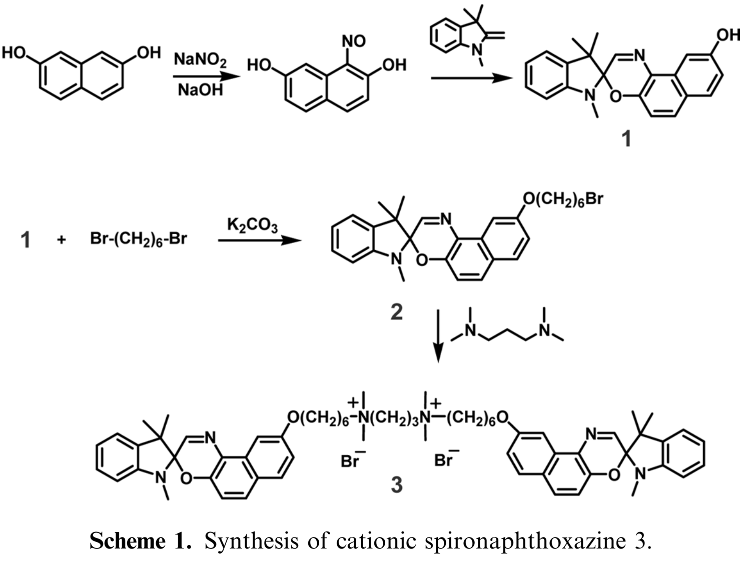
of various physicochemical behaviors in environmental research and biological science. Such an association also has many direct technological application. We have previously reported the synthesis and electrostatic layer-by-layer, self-assembly of bolarform spironaphthoxazine [11]. This paper concerned with the preparation, photochromism and fluorescence switching of spironaphthoxazine-poly(styrene-sulfonic acid) polyion complex. The photoinduced ionic conductivity response of polyion complex was also studied.

2. Experimental

2.1. *Materials and Instruments*

A functional alkyl bromide of spironaphthoxazine **2** was prepared by the reaction of compound **1** and 1,6-dibromohexane as described in Scheme 1. Then compound **2** was reacted in 2-methoxyethanol with *N,N,N′,N′*-tetramethyl-1,3-propanediamine to yield bisquaternized compound **3** [11]. Poly(styrene-sulfonic acid) was purchased from Aldrich. Absorption spectra were measured with an Agilent 8453 spectrophotometer. Fluorescence spectra were measured on a Shimadzu RF-5310PC fluorescence spectrophotometer. IR spectra were measured with a Spectrum GX & Auto Image IR spectrometer. A high pressure mercury lamp (Ushio, SP3-250D) was used as the UV radiation source and calibrated with a monochrometor at 366 nm. For the measurement of photoinduced ionic conductivity, the device comprised with two ITO glass (3 × 3 cm) separated by a 0.1 mm thickness spacer of polyethyleneterephthalate(PET) film was prepared and placed so as to face each other on the inside of the cell, and the edges of the cell were sealed with insulating epoxide resin. Prior to the final sealing, the space between the electrodes was filled with 0.1% polyion complex in Milli-Q water and 1 mmol of tetra-n-butylammonium perchlorate, $[CH_3(CH_2)_3]_4NClO_4$, as electrolyte (Fig. 1).



Scheme 1. Synthesis of cationic spironaphthoxazine 3.

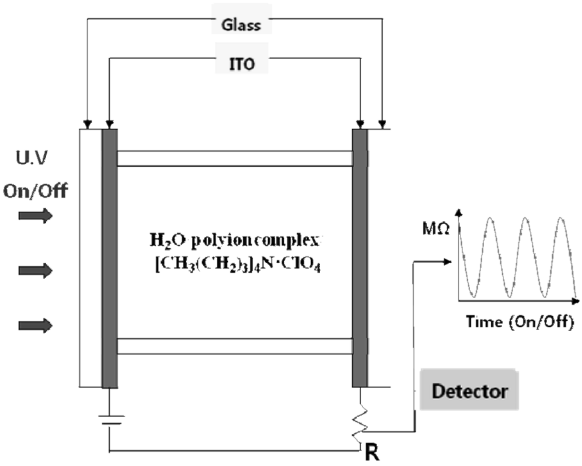


Figure 1. Measurement cell of photoinduced conductivity changes.

2.2. *Preparation of Polyion Complex*

Poly(styrene-sulfonic acid) (2 g) was dissolved in 50 ml of deionized water. (0.8 g, 0.7 mmol) of compound 3 dissolved in Milli-Q water (30 ml) was added to the aqueous solution of poly(styrene-sulfonic acid). And the mixture solution was stirred 2 h. Following this, the solution was filtered, washed with water and dried under vacuum.

3. Results and Discussion

Water insoluble polyion complex was obtained through just mixing two aqueous solution of cationic spironapthoxazine **3** and poly(styrene-sulfonic acid). FTIR spectra of the polyion complex are shown in Figure 2. The FTIR spectrum shows the C=N stretching band at 1625 cm^{-1}. The bands at 2935 and 2865 cm^{-1} correspond to CH_2 asymmetric and symmetric stretching of spironaphthoxazine hydrocarbon chain.

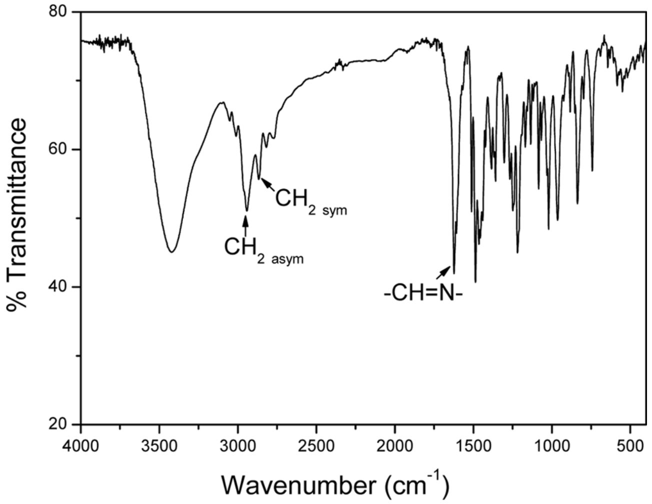


Figure 2. IR spectra of polyion complex.

The photochromic reaction is caused by the reversible heterolytic cleavage of the C(spiro)-O bond under UV irradiation, yielding the colored form that can return to the colorless form by ring closure under visible light irradiation or in the dark. Electronic absorption spectra changes of polyion complex upon UV irradiation in DMF are depicted in Figure 3.

The new band is ascribable to the generation of the open merocyanine form from the closed spiro form. Spectra measured after UV irradiating are at any time proportional to each other in the visible region, indicating that only one species is formed. The original spectrum pattern was reversibly recovered within 5 s. This allowed the absorption to be monitored at λ_{max} (600 nm) as a function of time to obtain thermal color fading rate (k). The kinetic equation approach to the open merocyanine to closed spiro form via first-order reaction [Eq. (1)]:

$$\mathrm{In}(A_t - A_\infty/A_i) = kt \tag{1}$$

In the present case, where A_i is the absorbance at 600 nm, and A_t is the absorbance at 600 nm at any time t after UV irradiation. A_∞ and k refer to absorbance at 600 nm after 1 h and first-order color changing rate constant, respectively. In the thermal color changing process, the kinetic analysis predicts the logarithm of the difference between A_∞ and A_t at time t to be linear with time, the slope giving the discoloration rate constant, k. First-order plots according to Eq. (1) for polyion complex is shown in Figure 3 inset. The color changing rate constant $k = 10.4 \times 10^{-2}\,s^{-1}$ was obtained from the slope.

Figure 4 shows the absorption spectral changes of polyion complex in a DMF solution by light, proton and base stimuli. Like other spironaphthoxazine molecule, the polyion complex undergoes reversible photochromic reaction. Irradiation of a DMF solution of polyion complex with UV light leads to the appearance of a new absorption band at around 600 nm and colorless solution of polyion complex

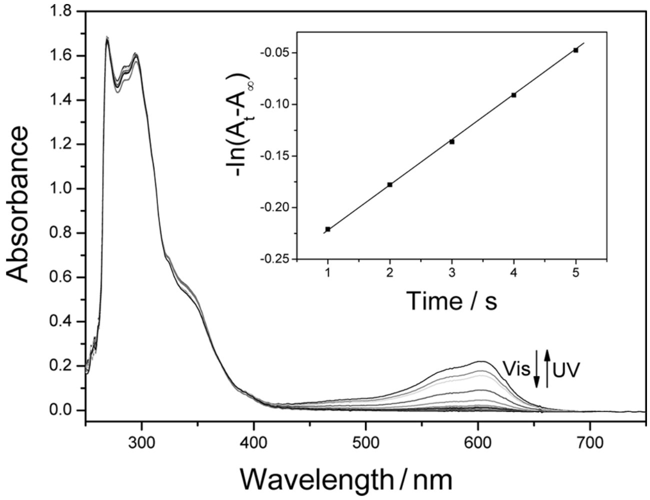


Figure 3. UV-Vis absorption spectra change of polyion complex in DMF solution (1 g/L) upon irradiation with UV and Visible light. The inset shows the first order decoloration kinetic plot of photoisomerization reaction of polyion complex.

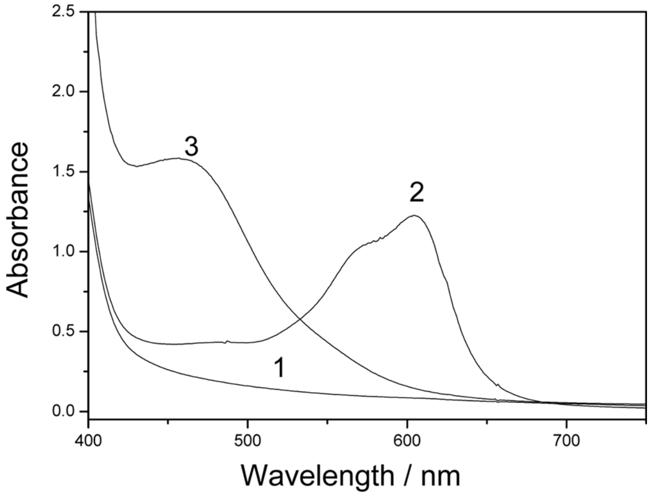


Figure 4. (1) Absorption spectra of the closed form of SPO polyion complex in DMF solution; (2) Absorption spectra of the photostationary state of SPO polyion complex upon irradiation with 365 nm light at room temperature in DMF solution; (3) Absorption spectra of the closed form of SPO polyion complex titration with proton in DMF solution.

turned blue (shown in Figure 4: line 1 and 2), this result is attributed to the UV-induced dissociation of the spiro C-O bond, from the oxazine ring to form a planar structure in Figure 5(ME). And after visible light irradiation the original absorption spectrum was converted back to the initial closed-ring isomer of SPO.

The SPO polyion complex showed interesting acid-chromic reaction like photochromic spiropyran [11,12]. Upon the addition of proton to the SPO solution, the

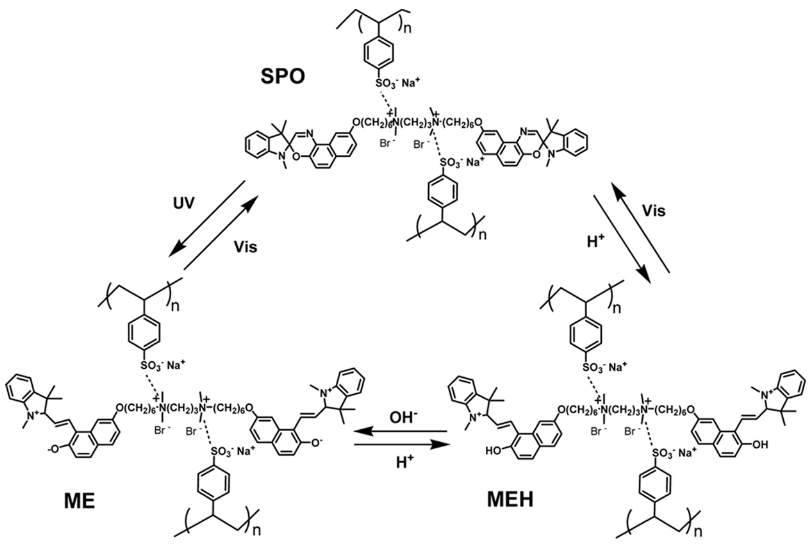


Figure 5. Schematic presentation of the polyion complex formation between poly(styrene sulfonic acid) and spironaphthoxazine 3. The structure of photochromic polyion complex associated with three state SPO, ME and MEH.

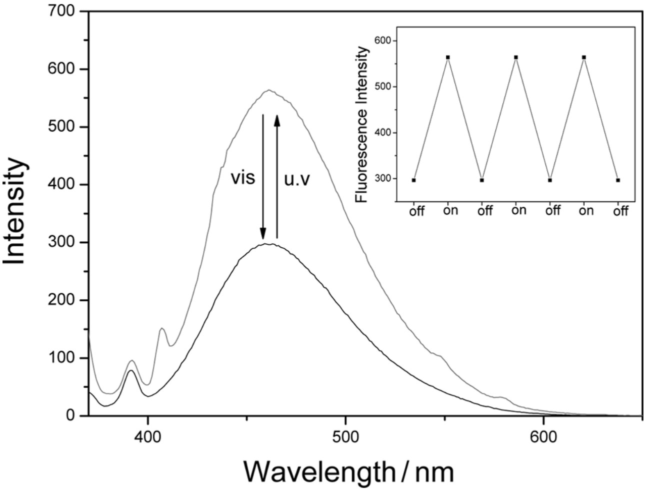


Figure 6. Fluorescence emission spectra change of polyion complex in DMF solution upon irradiation with UV light at room temperature. The inset figure shows the fluorescence monitoring of on and off (by alternative irradiation with UV and visible light) photoconversion of polyion complex in DMF solution (Excited at 350 nm, $\lambda_{em} = 460$ nm).

colorless solution of SPO became pink red. In Figure 4, line 3 shows the titration spectra of SPO with proton. Addition of H^+ to the SPO, the band with a peak at around 480 nm appeared and produced the protonated merocyanine MEH form. And after visible light irradiation to the MEH, the original spectral pattern is reversibly recovered. Interestingly, upon addition of equivalent OH^- in the MEH solution titrated with proton, the pink solution became blue in color and then colorless. Because of the life time of the blue colored merocyanine ME is too short it is difficult to scan the absorption spectrum of the merocyanine intermediate.

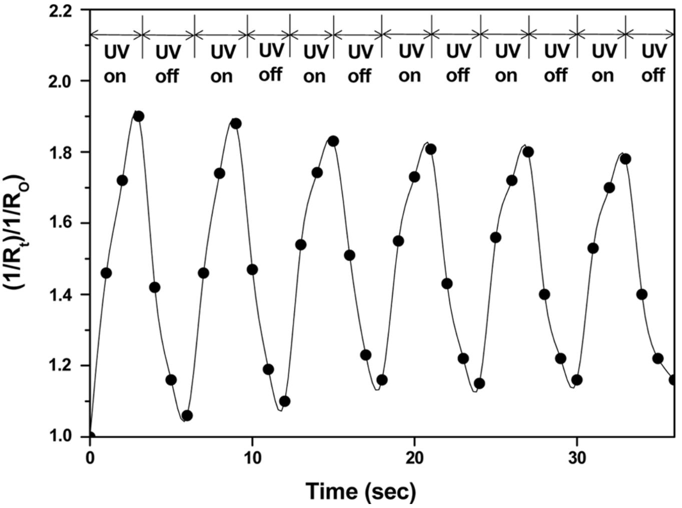


Figure 7. Photoinduced ionic conductivity response for polyion complex at 15°C.

Figure 6 shows the fluorescence spectra change of polyion complex in DMF solution with excitation wavelength at 350 nm. The fluorescence intensity change was regulated by the photochromic reaction. Before irradiation with UV light, it showed a broad emission in the range of 400–600 nm with λ_{em} round 460 nm. Upon irradiation with UV light, the fluorescent intensity of polyion complex gradually increased.

Photoinduced ionic conductivity response was analyzed at 15°C and is shown in Figure 7. The photoinduced ionic conductivity can be estimated from the expression $(1/R_t)/(1/R_o)$ where R_o and R_t are the resistance before and after UV irradiation. The ionic conductivity increased upon UV irradiation, which brought about the generation of zwitterion form, and subsequently decreased in dark, which in turn brought about the generation of closed spiro form. Sufficient reversibility was found in this polyion complex and this response was completely synchronized with that in the absorbance changes.

4. Conclusions

In conclusion, we investigated the preparation of polyion complex between cationic spironaphthoxazine and poly(styrene-sulfonic acid) and their photophysical properties. Upon UV irradiation, a broad absorption band appeared at around 600 nm. When the sample was left in the dark at room temperature after irradiation, the absorbance at 600 nm decreased rapidly. The fluorescence of polyion complex is effectively regulated by toggling between the two isomers of spironaphthoxazine. Measurement of the photoinduced ionic conductivity response at showed that sufficient reversibility was obtained.

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References

[1] Durr, H. & Bouas-Laurent, H. (1990). *Photochromism: Molecules and System*, Amsterdam: Elsevier.
[2] Berkovic, G., Krongauz, V., & Weiss, V. (2000). *Chem. Rev.*, *100*, 1741.
[3] Kawata, S. & Kawata, Y. (2000). *Chem. Rev*, *100*, 1777.
[4] Collins, G. E., Choi, L. S., Edwig, K. J., Michelet, V., Bowen, C. M., & Winkler, J. D. (1999). *Chem. Commun*, 321.
[5] Kim, S. H., Park, S. Y., Yoon, N. S., Keum, S. R., & Koh, K. N. (2005). *Dyes and Pigments*, *66*, 155.
[6] Kim, S. H., Lee, S. J., Park, S. Y., Suh, H. J., Jin, S. H., & Gal, Y. S. (2006). *Dyes and Pigments*, *68*, 61.
[7] Kim, S. H., Park, S. Y., Shin, C. J., & Yoon, N. S. (2007). *Dyes and Pigments*, *72*, 299.
[8] Kim, S. H., Yu, C., Shin, C. J., & Choi, M. S. (2007). *Dyes and Pigments*, *75*, 250.
[9] Wang, S., Yu, C., Choi, M. S., & Kim, S. H. (2007). *Journal of Photochemistry and Photobiology A: Chemistry*, *192*, 17.
[10] Wang, S., Yu, C., Choi, M. S., & Kim, S. H. (2008). *Dyes and Pigments*, *77*, 245.
[11] Kim, S. H., Shin, C. J., Choi, M. S., & Wang, S. (2008). *Dyes and Pigments*, *77*, 70.
[12] Wang, S., Chio, M. S., & Kim, S. H. (2008). *Dyes and Pigments*, *78*, 8.