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Bistable photoswitching in poly(*N*-isopropylacrylamide) with spironaphthoxazine hydrogel for optical data storage

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ABSTRACT

A bistable switching photochromic poly(*N*-isopropylacrylamide) with spironaphthoxazine hydrogel copolymer (PNIPA-SPO-BIS) has been designed and synthesized by radical polymerization. The PNIPA-SPO-BIS copolymer is identified by ^{1}H NMR spectroscopy, FIT-IR spectroscopy and gel permeation chromatography (GPC). The morphology of the internal microstructures of the PNIPA-SPO-BIS hydrogels was observed by scanning electron microscopy (SEM). The PNIPA-SPO-BIS copolymer showed excellent photochromic behavior in water solution and in gel state. In addition, erasable and rewritable (EARW) photoimaging on the PNIPA-SPO-BIS hydrogel was successfully demonstrated. A novel optical data storage materials based on photochromic hydrogel was developed. These developments are crucial for fundamental studies and eventual technical application for all-photo mode high-density optical data storage.

1. Introduction

Photonic devices that incorporate photochromic molecules represent the future of digital optical storage where the recording of information is an all photo-mode recording method that allows the read, write, and erase functions to be controlled by light energy [1,2]. In photo-mode recording, light characteristics such as wavelength, polarization, and phase can be multiplexed to enable data storage and potentially increases the memory density [3–5]. One promising approach is the development of photochromic materials. These materials can interconvert between two distinct isomeric states when stimulated by two different wavelengths of light, where each isomer of the photochromic materials can represent "0" and "1" of a digital mode. Molecules with this behavior are the best promising candidate optical storage materials as opposed to heat-mode recording employed with the optical media currently in use. Among various types of photochromic compounds, spirooxazines (SPO) [6,7] are well-known photochromic compounds that show their high fatigue resistance and excellent photostability, which have been attracting much interest from the viewpoint of fundamental elucidation of photochemical reactions and potential applications in optical memories. The photochromism of spirooxazines are attributable to the photochemical cleavage of the spiro-C–O bond (Scheme 1), which result in the extension of π-conjugation in the colored photomerocyanine conformer and thus shifts the absorption to the visible region.

In past decades, spirooxazines' application in memories has been severely restricted by the short lifetime of the colored photomerocyanine species, which reverts quickly the closed-ring colorless spirooxazine form. Therefore, various methods to stabilize the photomerocyanine form have been developed [8–10]. However, the realization of practical optical information storage on using spirooxazine derivatives is challenging, in part due to the difficulty in making the open-ring photomerocyanine form of the spirooxazine molecule stable enough to ensure that the recorded data can be maintained for a comparatively long time. In addition, it is very difficult to realize read/write/erase process by light energy independently because the information can be easily destroyed when the information is read by light energy. Recently, Tian's group [11] reported a novel spironaphthoxazine molecule with a much more stable open-ring photomerocyanine form by incorporating a ferrocene moiety in the parent spirooxazine (abbreviated as SOFC) and successfully demonstrated 2D and 3D optical storage in the SOFC-doped poly(methyl methacrylate) (PMMA) film. However, the demand to further develop the new and stable high-density optical storage material is necessary. Hydrogel is popular smart materials that can hold large volumes of water, but shrink in volume in the environmental conditions, such as pH, ionic strength, temperature, electric field, and light [12]. This special character of hydrogel can be applied to miniaturize of an

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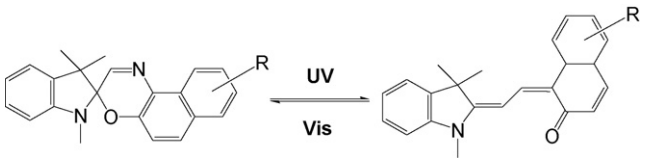


Scheme 1. Photochromism mechanism of a typical spironaphthoxazine. Left: Closed form (colorless). Right: TTC; open form (colored).

existing 3D or 2D object or pattern in the size range of hundreds of nanometers for organic photonic devices [13]. By taking advantage of the idea, we developed a bistable photoswitching in poly(*N*-isopropylacrylamide) with spironaphthoxazine hydrogel (abbreviated as PNIPA-SPO-BIS) as a new recording media for optical information storage, which have successfully demonstrated erasable and rewritable optical information on the hydrogel. Scheme 2 represents the structure and photochemical isomerization of the PNIPA-SPO-BIS.

2. Experimental

Melting points were determined using an Electrothermal IA 900 apparatus and were uncorrected. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using an electron energy of 70 eV and the direct probe EI method. ^{1}H NMR spectra was recorded in $CDCl_3$ using a Varian Inova 400 MHz FT NMR Spectrometer using TMS as internal standard. The UV–vis spectra and transmittance were obtained on a Agilent 8457 UV–vis spectrophotometer. The transmittance of the solution was measured at a wavelength of 500 nm with a thermostatically controlled cuvette. LCST values were also determined by spectrophotometric detection of the changes in transmittance (λ_{max} = 500 nm) of aqueous polymer solutions heated at a constant rate (0.2 °C min^{-1}). Values for the LCST of polymer solutions were determined as the temperature corresponding to the breaking point of optical transmittance. A high-pressure mercury lamp (Ushio, SP3-250D) was used as the UV radiation source and was calibrated with a monochromator at 366 nm. Scanning electron microscopy (SEM) images of xerogels were obtained using a Hitach S-530 scanning electron microscope. Infrared spectra of powders were obtained at room temperature on a Nicolet Fourier IR spectrometer using KBr pellets.

2.1. Materials

N-Isopropylacrylamide (NIPA, Aldrich) was purified by recrystallization from a mixture of toluene/hexane (1/4) and dried in vacuum. 2,2-Azobis-(isobutyronitrile) (AIBN) was recrystallized from methanol. The other chemicals were of the highest grade available and were used without further purification.

2.2. Synthesis of 1,3,3-trimethyl-6′-hydroxyspiro-[2H]-indol-2, 30-[3H]-naphth[2,1-b][1,4] oxazine (**3**)

9′-Hydroxy-1,3,3-trimethylspiro[indoline2,3′-[3H]naphtha[2,1-*b*][1,4] oxazine] (**3**) was prepared using previously described procedures [14,15]. mp 211.5–214 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.36 (s, 6H), 2.76 (s, 3H, –NCH_3), 6.6 (d, 1H, *J* = 7.40 Hz), 6.84 (t, 1H, *J* = 7.46 Hz), 7.02 (d, 1H, *J* = 8.68 Hz), 7.22 (t, 1H *J* = 7.40 Hz), 7.58 (d, 1H, *J* = 8.60 Hz), 7.65 (t, H, *J* = 8.56 Hz), 7.71 (s, 1H) 7.88 (s, 1H). Elemental analysis: C, 76.89; H, 4.97; N, 8.59%. $C_{22}H_{20}N_2O_2$ requires: C, 76.72; H, 5.85; N, 8.13%.

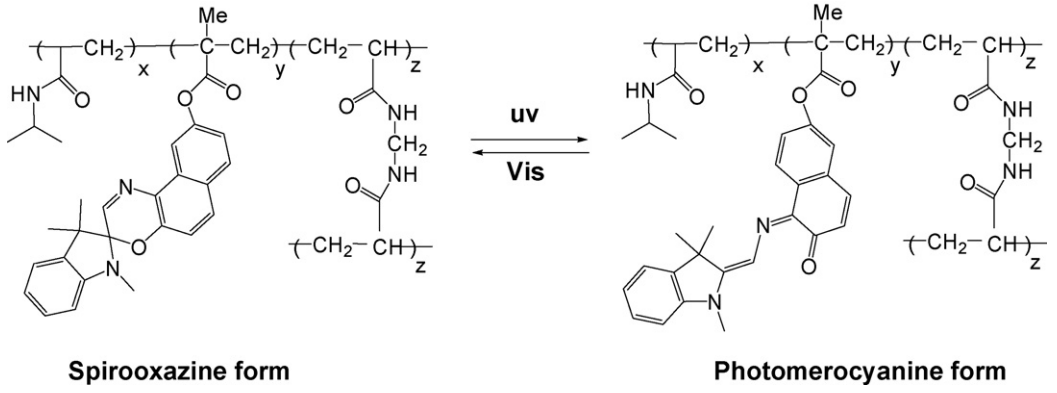
2.3. Synthesis of the spironaphthoxazine-methyacryloyl monomer (**5**)

9′-Hydroxy-1,3,3-trimethylspiro[indoline2,3′-[3H]naphtha[2,1-*b*][1,4] oxazine] (**3**) (1.25 g, 3.81 mmol) was added to 25 ml of anhydrous dichloromethane in a 50 ml round bottomed flask. Triethylamine (0.6 g, 5.5 mmol), was added and the reaction was stirred for half an hour. Then methacryloyl chloride (0.50 g, 4.4 mmol), was dissolved in 5-ml anhydrous dichloromethane and added dropwise to the reaction under N_2 atmosphere, cooled to 0 °C. The reaction was stirred at ice temperature for a further hour, and then at room temperature for 24 h. The product was washed with 50 ml 0.5 M NaOH, 50 ml water, 50 ml 0.5 M HCl, 50 ml water, 50 ml brine and dried with $MgSO_4$. The final solution was rotary evaporated to produce crude compound. This crude product was then recrystallized using methanol. Yield 1.27 g, 85%. mp 143 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.26 (s, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.70 (s, 1H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.16 (m, 1H), 7.08 (d, *J* = 7.52 Hz 1H), 7.00 (d, 1H), 6.90 (m, 1H), 6.58 (d, 1H), 6.41 (s, 1H), 5.79 (s, 2H), 2.76 (s, 3H), 2.10 (s, 3H), 1.56 (s, 3H, CH_3), 1.34 (s, 3H, CH_3). FAB-MS, *m*/*z* = 412. Elemental analysis: C, 76.00; H, 5.97; N, 7.0%. $C_{26}H_{24}N_2O_3$ requires: C, 75.71; H, 5.86; N, 6.79%.

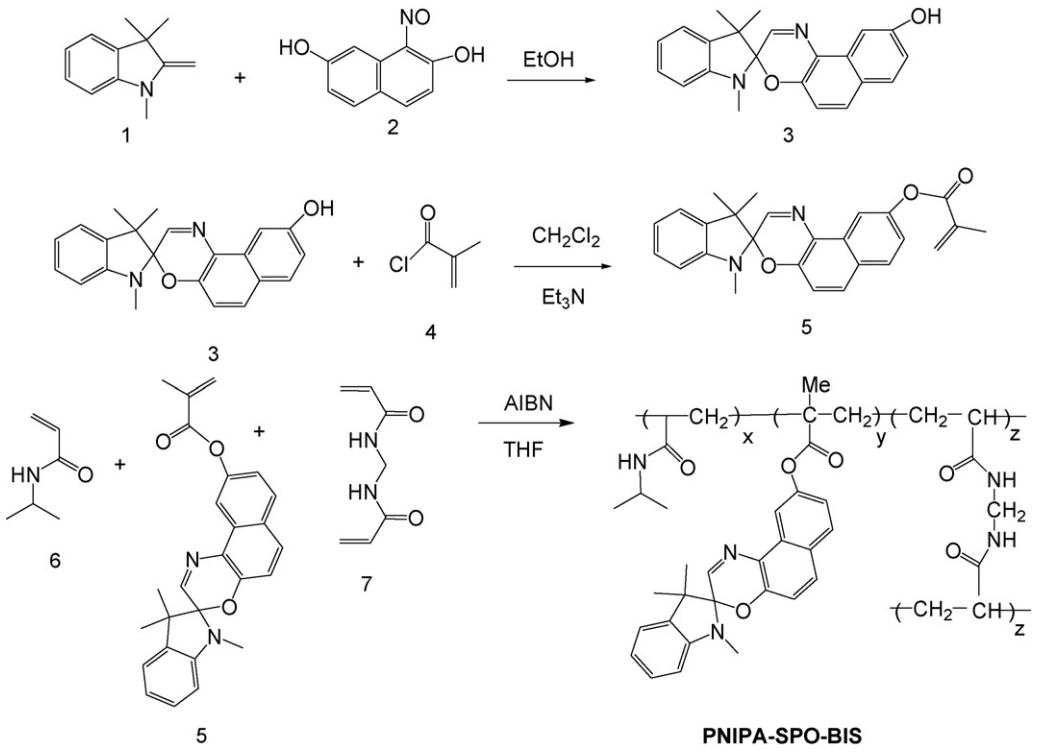
IR (KBr, disc): ν = 2970, 1730, 1631, 1607, 1510, 1484, 1444, 1381, 1359, 1318, 1256, 1207, 1190, 1166, 1124, 1081, 1032, 976, 946, 902, 823, 748.

2.4. Synthesis of poly(N-isopropylacrylamide) with spironaphthoxazine copolymers (PNIPA-SPO-BIS)

The *N*-isopropylacrylamide monomer (**6**) (3.73 g, 33 mol), spirooxazine-methyacryloyl monomer (**5**) (135 mg, 0.33 mmol), the crosslinker *N*,*N*′-methylenebisacrylamide (**7**) (16.4 mg, 0.33 mmol)



Scheme 2. Photoisomerizing behavior of PNIPA-SPO-BIS hydrogel. Left: Spirooxazine form; right: photomerocyanine form.



Scheme 3. The synthetic routes of photochromic PNIPA-SPO-BIS copolymer.

(BIS), and the initiator 2,2′-azobis(isobutyronitrile) AIBN (32.8 mg, 0.2 mmol) were dissolved in anhydrous THF (20 ml). After this mixture was shaken for 5 min at ambient temperature, and the reaction mixture was degassed by subjecting it to freeze–thaw cycle three times. After being heated for 3 days at 65 °C, the resultant mixture was poured into ether and precipitated with ether four times. The resulting copolymer was dried in vacuum to give satisfactory yields as pink powder. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.15 (br), 7.65 (br), 6.5–7.20 (br), 5.55 (br), 3.62 (br), 2.7–1.60 (m). Gel permeation chromatography (GPC): Mn: 23,585, Mw: 48,430, MP 62,949, Mw/Mn: 2.0.

IR (KBr, disc): ν = 3307, 3077, 2973, 2934, 2876, 1651, 1545, 1459, 1387, 1367, 1172, 1130, 655.

3. Results and discussion

3.1. The design and synthesis of PNIPA-SPO-BIS hydrogel copolymer

In our design and synthesis strategy, we took the following points into consideration. Scheme 3 represents the synthetic routes of the PNIPA-SPO-BIS. At first, we chose two monomer types to prepare the polymer network of the gel, each of which plays a different role. Poly(*N*-isopropylacrylamide) (PNIPA) is thermo-responsive hydrogel polymer and exhibits a change in its hydrophilicity in response to temperature[16,17], whereas

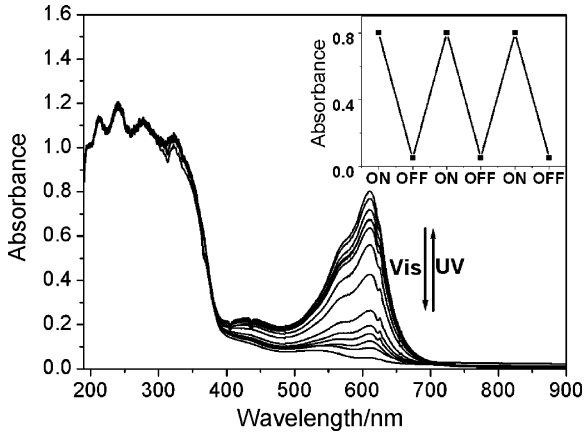


Fig. 1. UV–vis absorption spectra changes of PNIPA-SPO-BIS copolymer in water solution (2.5×10^{-4} mol l^{-1}) upon irradiation with UV and visible light. The inset shows absorption monitoring of cyclical on and off (by alternative irradiation with UV and visible light) photoconversions of PNIPA-SPO-BIS copolymer (at λ_{max} = 605 nm).

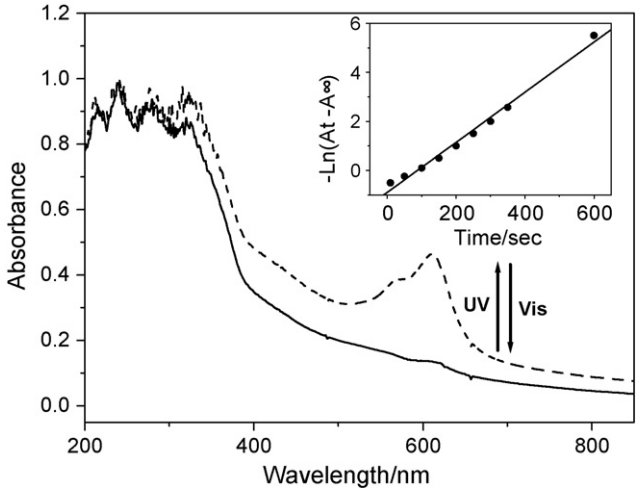


Fig. 2. UV–vis absorption spectra changes of PNIPA-SPO-BIS copolymer in hydrogel state (2.5×10^{-4} mol l^{-1}) upon irradiation with UV and visible light at 28 °C. The inset shows plot of $-\ln(A_t - A_\infty)$ as function of time according to Eq. (1) for the decoloration of PNIPA-SPO-BIS hydrogel (at λ_{max} = 615 nm).

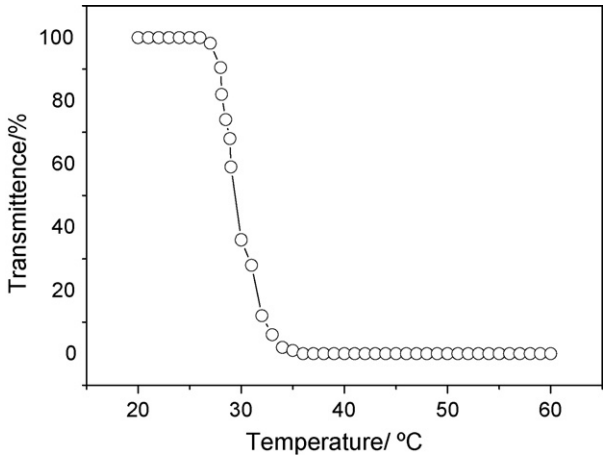


Fig. 3. Temperature dependence of the transmittance of a solution of PNIPA-SPO-BIS copolymer in water.

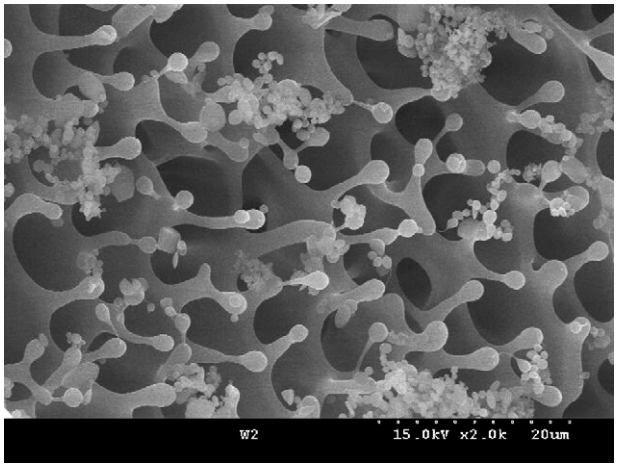


Fig. 5. SEM image of PNIPA-SPO-BIS hydrogel. (The gels were prepared from freeze-dried in water, PNIPA-SPO-BIS = 0.5 wt%).

the minor monomer, methyacryloyl-spironaphthoxazine (SPO) undergoes reversible photochromic reactivity under irradiation with UV and visible light, respectively. The basic strategy employed for the synthesis of photochromic PNIPA-SPO-BIS hydrogel copolymer was based on the radical polymerization reaction from the two key monomers methyacryloyl-spironaphthoxazine (**5**) and *N*-isopropylacrylamide (NIPA, **6**) using *N*,*N*′-methylenebisacrylamide (BIS, **7**) as a crosslinker. The chemical structures of all the intermediates are characterized by ^{1}H NMR, MS. The PNIPA-SPO-BIS are identified by ^{1}H NMR spectroscopy, FIT-IR spectroscopy and be determined by GPC.

3.2. Photochromism of PNIPA-SPO-BIS hydrogel copolymer

In water, PNIPA-SPO-BIS hydrogel showed excellent photochromic behavior. Fig. 1 shows the UV–vis absorption spectra changes of PNIPA-SPO-BIS copolymer in water solution (2.5×10^{-4} mol l^{-1}) upon irradiation with UV (365 nm) and visible light (>510 nm). Irradiation a colorless solution of PNIPA-SPO-BIS with UV light led to the appearance of a new absorption band at round 605 nm and the colorless solution of PNIPA-SPO-BIS turned to blue. The colorless closed-ring form of PNIPA-SPO-BIS converts to the corresponding, intensively colored open-ring merocyanine form due to the cleavage of the spiro-C–O bond. This process results in an extended π-conjugation system in spirooxazine unit. And after visible light irradiation the original absorption spectra were converted back to that of the initial closed-ring isomer of PNIPA-SPO-BIS. The inset shows absorption monitoring of cyclical on and off photoconversions of PMMA-SPO-BIS hydrogel in water solution. It can be repeated more than 20 times without any essential loss in color characteristics in repeated on and off process.

In addition, we measured the absorption spectra changes of PNIPA-SPO hydrogel to obtain an insight into their photochromic properties in gel phase, which show similarly photochromic performance as in solution. When the PNIPA-SPO-BIS copolymer in water solution was heated to at 28 °C, the PNIPA-SPO-BIS solution change to the transparent gel phase. Irradiation a colorless hydrogel of PNIPA-SPO-BIS with UV light, the colorless PNIPA-SPO hydrogel turned to blue and a new absorption band appeared at around 615 nm and gradually increased and reached a photostationary state (shown in Fig. 2). When subsequent irradiation of the closed of PNIPA-SPO hydrogel with visible light, the system gradually returned to the initial hydrogel status. This allowed the absorption to be monitored at λ_{max} (615 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)):

$$\ln\left(\frac{A_t - A_\infty}{A_i}\right) = kt \quad (1)$$

In the present case, where A_i is the absorbance at 615 nm, and A_t is the absorbance at 615 nm at any time t after UV irradiation. A_∞ and k refer to absorbance at 615 nm after 1 h and first-order color changing rate constant, respectively. In the thermal color changing

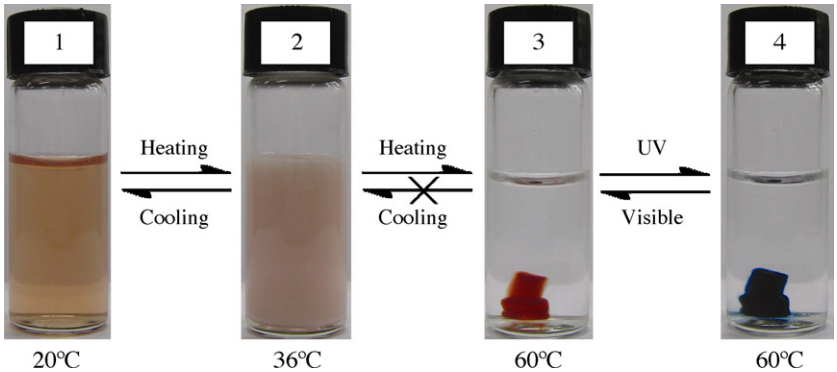


Fig. 4. The bistable switching photos of PNIPA-SPO-BIS hydrogel in solution and gel by thermal and light stimuli at different temperature. (**1**) Sol (20 °C); (**2**) gel (36 °C); (**3**) spirooxazine form of gel (60 °C); (**4**) photomerocyanine form of gel (60 °C). Photoswitching photos were obtained from the PNIPA-SPO-BIS gel in water at 60 °C by using UV light (365 nm) and visible light (>500 nm). The concentration of the PNIPA-SPO-BIS copolymer in water solution is 0.5% (w/v).

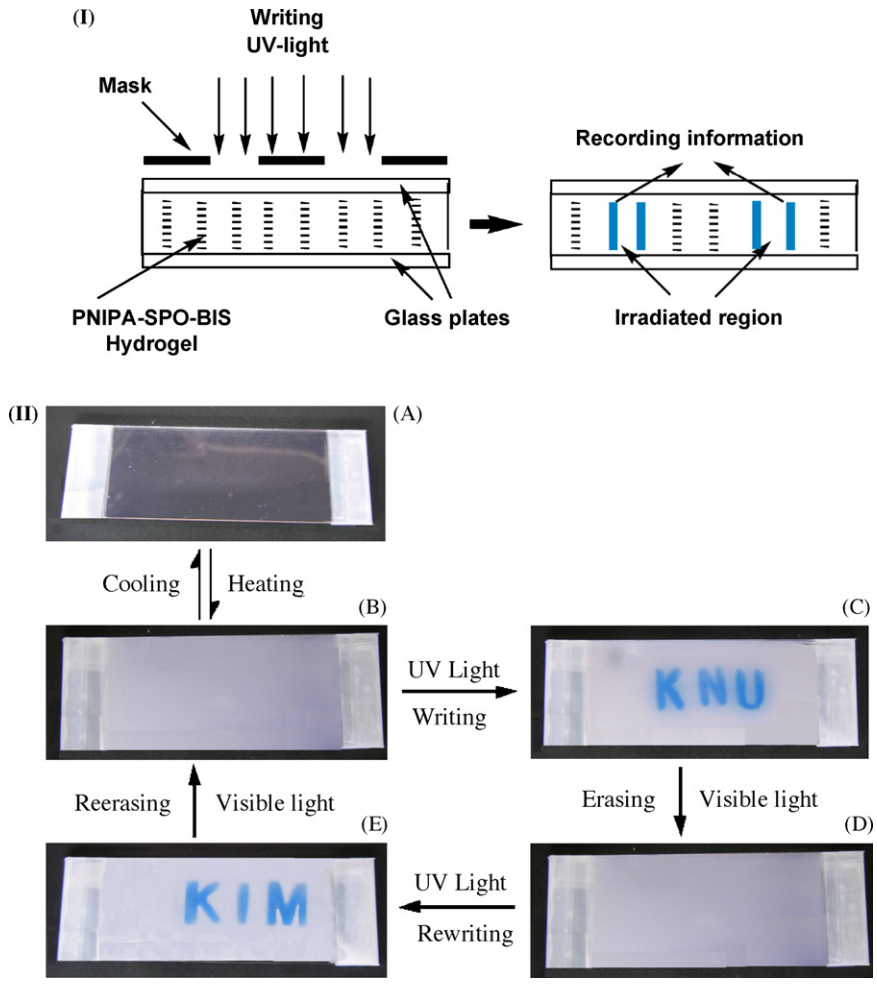


Fig. 6. (I) Principle scheme of the optical data recording on PNIPA-SPO-BIS hydrogel. (II) The switching and optical storage images of PNIPA-SPO-BIS hydrogel. (A) Sol; (B) gel; (C) writing; (D) erasing; (E) rewriting. Photo-rewritable imaging on the PNIPA-SPO-BIS hydrogel by using UV light (365 nm) and visible light (500 nm). The blue regions represent the writing optical data parts irradiated with UV light. The concentration of the PNIPA-SPO-BIS copolymer in water solution is 0.2% (w/v).

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 PMMA-SPO-BIS hydrogel is shown in Fig. 2 (inset). The color changing rate constant $k = 11.0 \times 10^{-3}\ s^{-1}$ was obtained from the slope. In addition, the PMMA-SPO-BIS hydrogel showed excellent fatigue resistance. It can be also repeated more than 20 times without any essential loss in color characteristics in repeated on and off process.

3.3. Thermo-and photoswitching properties of PNIPA-SPO-BIS hydrogel copolymer

We investigated PNIPA-SPO-BIS hydrogel properties in pure water at a concentration of 0.5% (w/v), it undergoes an abrupt volume change at a critical temperature (the lower critical solution temperature, LCST). Fig. 3 shows the temperature dependence of the transmittance of a solution of PNIPA-SPO-BIS copolymer in water. Optically clear aqueous solutions at or below room temperature became turbid during heating above the LCST value of about 30 °C. When the PNIPA-SPO-BIS solution is heated above the LCST value of 30 °C, the transmittance starts to decrease dramatically. This means that, during precipitation of the polymer due to heating above the LCST value, most of polar water molecules are repelled out of the polymer [18]. The transmittance decreases from 100% at room temperature to 0% at 36 °C, and then stabilizes at even higher temperatures. There is no macroscopic phase separation after storage at 40 °C for 24 h. When the stabilized PNIPA-SPO-BIS hydrogel is cooled below the LCST value of 31 °C from 40 °C, the transmittance starts to increase dramatically. When the PNIPA-SPO-BIS hydrogel is cooled at room temperature, it recovers the original PNIPA-SPO-BIS solution. The whole process from **1** state to **2** state is reversible as shown in Fig. 4. However, when the PNIPA-SPO-BIS hydrogel was heated from 40 °C to higher temperature, the volume of PNIPA-SPO hydrogel began to shrink and form an agglomerate and separate wholly from the water at 60 °C, when the PNIPA-SPO-BIS agglomerate was cooled to at room temperature, which cannot recover the original state. This behavior is the typical shrinking change of bulk NIPA copolymer gels in water [19]. Interestingly, we use the UV light to irradiate the PNIPA-SPO-BIS agglomerate hydrogel, the red PNIPA-SPO-BIS agglomerate hydrogel turned to blue and kept the color for 2 h. After visible light irradiation, the blue PNIPA-SPO-BIS agglomerate hydrogel converted back to the initial color. The whole process can repeat more than 15 times and keep the agglomerate from **3** and **4** states (shown in Fig. 4).

3.4. Morphological characterization of internal microstructures of PNIPA-SPO-BIS hydrogel

In addition, to obtain visual images of microstructures of PNIPA-SPO-BIS hydrogels, the morphology of the internal microstructures of the PNIPA-SPO-BIS hydrogels were observed by SEM. To retain

the internal microstructures, the PNIPA-SPO-BIS hydrogel solution was heated above the LCST value of 30 °C and there was no evident macroscopic phase separation in pure water for 24 h, and then was frozen rapidly in liquid nitrogen. The frozen samples were freeze-dried for 48 h using a freeze-dryer to completely remove the imbibed water. The freeze-dried samples were then fractured mechanically, and loaded on the surface of the SEM sample holder and putter-coated for 40 s before measurement. Fig. 5 shows the SEM image of the internal microstructure of PNIPA-SPO-BIS hydrogel that the gel has homogeneous porous coral-like microstructure. This morphology indicated that PNIPA-SPO-BIS could form stable hydrogel when the temperature was above the LCST value of PNIPA-SPO-BIS.

3.5. Erasable and rewritable (EARW) properties of PNIPA-SPO-BIS hydrogel for optical data storage

The inherent characteristics of PNIPA-SPO-BIS hydrogel make it possible to use such materials for data recording. A possible procedure for data recording and erasing is presented in Fig. 6(I). Upon UV light irradiation through the mask, the optical data were recorded on PNIPA-SPO-BIS hydrogel irradiation region. When irradiation with visible light on irradiation region, the optical data were erased. To obtain visual bistable photoswitching images of PNIPA-SPO-BIS hydrogels, we make the optical storage device that comprised with two ITO glasses (3 cm × 3 cm) separated by a 0.1 mm thickness spacer of PET film and placed so as to face each other on the inside of the cell, and the edges of the cell were unsealed. The cell was filled with 0.2% (w/v) PNIPA-SPO-BIS hydrogel water solution. Fig. 6(II) shows the process of the bistable photoswitching in PNIPA-SPO-BIS hydrogel for optical data storage. When the solution of PNIPA-SPO-BIS (A) was heated from at room temperature to the LCST value of 30 °C, which could keep stable gel state (B), this process was reversible from solution to gel by thermal controlling and repeated many times. In gel state, the practical capability of rewritable photoimaging on hydrogel was investigated by patterned illumination through photomasks. The word 'KNU' (Kyungpook Nation University, abbreviated) was recorded as a first image (Fig. 6II,C), which was subsequently erased and followed by the recording of a second image, the Korean first surname (KIM). The cycles of writing and erasing was repeated more than 20 times. This successful demonstration of rewritable photoimage suggests the potential application of PNIPA-SPO-BIS hydrogel to rewritable optical memory media or imaging processes.

4. Conclusion

In conclusion, we have successfully designed and synthesized a novel bistable photoswitching in PNIPA-SPO-BIS, which showed excellent photochromic behavior in gel state. Erasable and rewritable (EARW) photoimaging on the hydrogel was successfully demonstrated. A novel optical data storage material based on photochromic hydrogel was developed. These developments are crucial for fundamental studies and eventual technical application for all-photo mode high-density optical data storage. Considering its inherent reversible photoisomerization and high fatigue resistance, PNIPA-SPO-BIS hydrogel copolymer can be suggested as a promising candidate for erasable optical data storage.

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