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Multiple switching photochromic poly(*N*-isopropylacrylamide) with spironaphthoxazine hydrogel

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Abstract

Radical polymerization was used to synthesize a multiple switching photochromic poly(*N*-isopropylacrylamide) with spironaphthoxazine hydrogel (PNIPA–SPO), which undergoes thermally controlled, reversible switching from solution phase to gel phase at the lower critical solution temperature. The internal microstructure of the PNIPA–SPO hydrogel with a fibrous, three-dimensional structure was investigated by SEM. A complicated multiple switch in PNIPA–SPO hydrogel was realized by light, thermal and proton stimulation, which makes its application promising in the fields of opto- and electronic smart materials, logic gate, nanomachines, sensors and other molecular photonic devices.

Keywords: Multi-switching; Photochromic; Spironaphthoxazine; Hydrogel; Copolymer; Poly(*N*-isopropylacrylamide)

1. Introduction

The design and creation of molecular systems that show chemical and physical changes in response to external stimuli is a topic of current interest because of their potential applications as sensing and switching devices [1–5]. In particular, the intelligent hydrogels whose properties can be controlled reversibly or irreversibly in response to changes in external chemical, photochemical, thermal stimuli or sound [6–10] have attracted much attention in recent years. Such smart responsive systems are highly desirable in thermo- and mechano-responsive sensor materials or applications like drug delivery or catalysis, or nano- and mesoscopic assemblies with interesting optical and electronic properties and so on [11,12]. Among various types of super-smart hydrogel systems, poly(*N*-isopropylacrylamide) (PNIPA) gels [13,14] are the most practical application promising polymers because they undergo an abrupt volume change at a critical temperature (the lower critical solution temperature, LCST). They can be utilized in designing thermoresponsive optical and electronic-biology materials. Several groups exploited these features for the development of "smart" polymers [15–20]. However, it is a tremendous challenging task to design controllable hydrogel systems based on reversible changes by external stimuli.

Some PNIPA copolymers with photochromic units including azobenzene or spiropyran derivatives have been reported [21–23], in which the PNIPA copolymers were controlled by temperature, light, or chemicals as external stimuli. Among various types of photochromic compounds, spirooxazines (SPO) [24–26] are well-known photochromic compounds that have been attracting much interest from the viewpoint of fundamental elucidation of photochemical reactions and potential applications in optical memories. Photochromism in spirooxazine compounds generally involve the UV-induced dissociation of the spiro C–O bond, from the oxazine ring to form a planar structure. We have developed a series of interesting photochromic spirooxazine polymers [27–30]. As an attempt to obtain a new functional PNIPA hydrogel copolymer with potential photonics application, we have designed and synthesized a photochromic poly(*N*-isopropylacrylamide) with spironaphthoxazine hydrogel copolymer (shown in Scheme 1, PNIPA–SPO).

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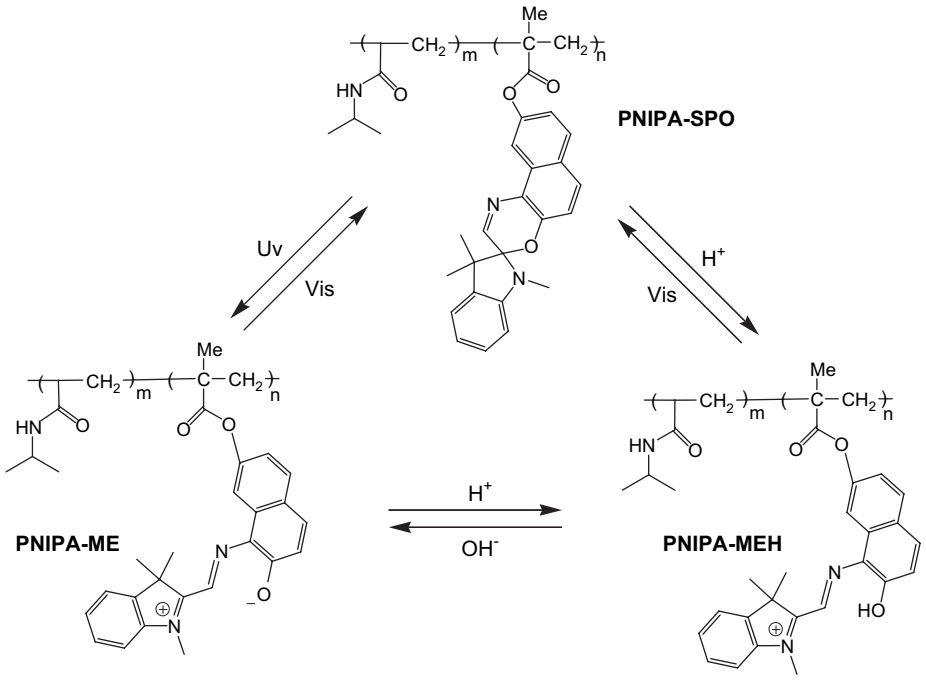


Scheme 1. The structure and multiple switching process of photochromic PNIPA–SPO copolymer associated with the three states PNIPA–SPO, PNIPA–ME, and PNIPA–MEH.

This novel photochromic hydrogel copolymer exhibits excellent reversible photochromic behavior in solution and hydrogel phase and undergoes reversible switching process from solution phase to gel phase at a critical temperature (LCST) by thermal controlling. In addition, this polymer is sensitive to acid and base in water solution, which is promising multiple molecular switches by light, thermal, proton and base stimuli.

2. Experimental

Melting points were determined using an Electrothermal IA 900 apparatus and were uncorrected. Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Mass spectra were recorded on a JMS-700 high resolution mass spectrometer using an FAB ion source. A multi-channel photodiode detector (MCPD, Otsuka Electronics) was used to obtain visible absorption spectra of PNIPA–SPO. ^{1}H NMR spectra was recorded in $CDCl_3$ using a Varian Inova 400 MHz FT-NMR spectrometer using TMS as internal standard. The weight-average molecular weights (M_n) and polydispersity (M_w/M_n) of the polymer was measured on a PL-GPC model 210 chromatograph at 25 °C using THF as the eluent and standard polystyrene as the reference. Infrared spectra of power were obtained at room temperature on a Nicolet Fourier IR spectrometer using KBr pellets. The UV–vis spectra and transmittance were obtained on an Agilent 8457 UV–vis spectrophotometer. The transmittance of the solution was measured at a wavelength of 500 nm with a thermostatically controlled cuvette. The measurements took place in the temperature range from 10 to 65 °C with a heating/cooling rate of 1 °C/min. Scanning electron microscopy (SEM) images of xerogels were obtained using a Hitachi S-530 scanning electron microscope. The multiple switching process photographs were demonstrated in NMR tube.

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. 9′-Hydroxy-1,3,3-trimethylspiro[indoline2,3′-[3*H*]naphtha[2,1-*b*][1,4]oxazine] **1** was prepared using previously described procedures [31].

2.2. Synthesis of the spironaphthoxazine-methyacryloyl monomer *3*

9′-Hydroxy-1,3,3-trimethylspiro[indoline2,3′-[3*H*]naphtha-[2,1-*b*][1,4]oxazine] (2.5 g, 7.62 mmol) was added to 50 ml of anhydrous dichloromethane(CH_2Cl_2) in a 100 ml round bottomed flask. Triethylamine (1.20 g, 11 mmol) was added and the reaction was stirred for half an hour. Then methacryloyl chloride (1.0 g, 8.8 mmol) was dissolved in 10 ml of anhydrous dichloromethane and added dropwise to the reaction under N_2 atmosphere, cooled to 0 °C. The reaction was stirred at 0 °C for a further hour, and then at room temperature for 24 h. The product was washed with 100 ml 0.5 M NaOH, 100 ml water, 100 ml 0.5 M HCl, 100 ml water, 100 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 to obtain the purified white

powder. Yield 2.54 g, 85%; m.p. 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, $m/z = 412$.

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

2.3. Synthesis of poly(N-isopropyacrylamide) with spironaphthoxazine copolymer (PNIPA–SPO)

The *N*-isopropylacrylamide monomer **4** (2.26 g, 20 mmol), spirooxazine-methyacryloyl monomer **3** (82.4 mg, 0.2 mmol), and the initiator 2,2′-azobis(isobutyronitrile) AIBN (32.8 mg, 0.2 mmol) were dissolved in anhydrous THF (20 ml). After this the 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 yield as white powder.

Yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.19 (br), 7.63–7.7 (br), 6.89–7.07 (br), 6.4–6.6 (br), 4.0 (br), 3.73–3.8 (m), 2.74 (br), 1.33–2.33 (m). GPC: M_n: 8766, M_w: 14,917, M_w/M_n: 1.70.

IR: (KBr, disc): $\nu = 3304$, 3075, 2972, 2934, 2875, 1650, 1544, 1459, 1387, 1367,1172, 1130, 645.

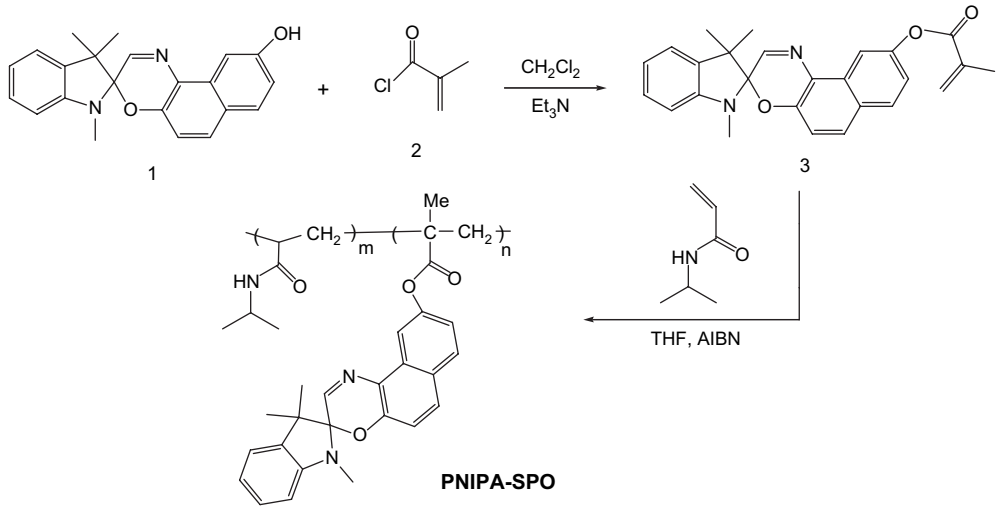
3. Results and discussion

3.1. The design and synthesis of PNIPA–SPO hydrogel

In our design and synthesis strategy, we took the following points into consideration (as shown in Scheme 1): at first, poly(*N*-isopropylacrylamide) (PNIPA) is thermoresponsive hydrogel polymer and exhibits a lower critical solution (LCST) due to the presence of both hydrophilic amide groups and hydrophobic isopropyl groups in its side chains. Second, incorporation of the photochromic spirooxazine unit in the polymer system could lead to smart polymer sensitive to light and pH. So, the PNIPA–SPO hydrogel copolymer would show a cooperative responsive to several stimuli, i.e. light irradiation and changes in temperature and acid and base. The basic strategy employed for the synthesis of photochromic PNIPA–SPO hydrogel copolymer was based on the radical polymerization reaction as shown in Scheme 2, the key intermediate monomer **3** was synthesized by reacting 1,3,3-trimethyl-6′-hydroxyspiro-[2*H*]-indol-2,30-[3*H*]-naphtha[2,1-*b*][1,4] oxazine **1** with methacryloyl chloride. Then the monomer **3** was reacted with NIPA monomer in a solution of distilled tetrahydrofuran (THF) by free-radical polymerization, with 2,2-azobis(isobutyronitrile) (AIBN) as an initiator. The chemical structures of all the intermediates are characterized by ^{1}H NMR, FAB-MS. The ^{1}H NMR spectrum of PNIPA–SPO copolymer is shown in Fig. 1. The characteristic peaks 5.0–6.0 ppm corresponding to the vinyl groups of monomers disappeared completely. The characteristic peaks 6.6–8.1 ppm corresponding to the proton of aromatic ring in spirooxazine and NMR measurement revealed that the fraction of the spirooxazine units in the synthesized PNIPA–SPO hydrogel copolymer was about 1.0 mol%, which agreed well with the molar ratio of the monomers in the initial solution. In addition, the PNIPA–SPO hydrogel copolymer was also determined by gel permeation chromatography (GPC).

3.2. Thermo-sensitive properties of PNIPA–SPO hydrogel

The PNIPA–SPO copolymer was soluble in water at or below room temperature. Optically transparent aqueous solutions of this polymer can be prepared at a concentration of approximately 8.0×10^{-4} g/mL. As expected, the aqueous solution became turbid during heating above a certain temperature, indicating the occurrence of an LCST. Fig. 1 shows the



Scheme 2. The synthetic routes of photochromic PNIPA–SPO hydrogel copolymer.

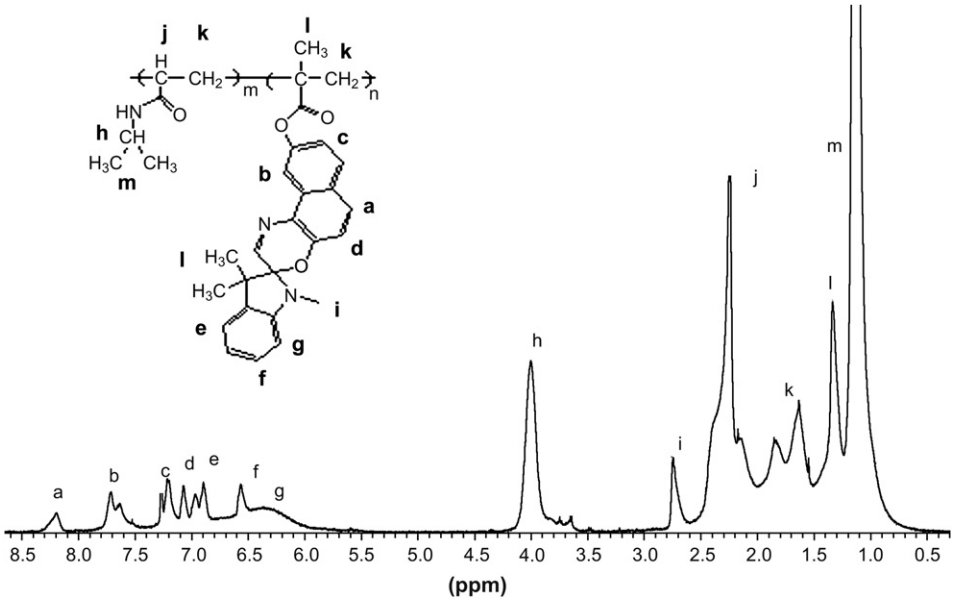


Fig. 1. ^{1}H NMR spectrum of PNIPA–SPO copolymer in $CDCl_3$ at room temperature.

temperature dependence of transmittance at 500 nm for hydrogel prepared from PNIPA–SPO copolymer. When the PNIPA–SPO solution is heated above the LCST value of 31 °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. The transmittance decreases from 100% at room temperature to 0% at 50 °C, and then stabilizes at even higher temperatures. There is no macroscopic phase separation after storage at 50 °C for 24 h when the stabilized PNIPA–SPO hydrogel is cooled below the LCST value of 33 °C from 50 °C and the transmittance starts to increase dramatically. When the PNIPA–SPO hydrogel is cooled at room temperature, it recovers the original PNIPA–SPO solution. The whole process is reversible as shown in Fig. 5. The solution was recovered reversibly when the hydrogel is cooled below the LCST value of about ($T_1 = 33$ °C) (Fig. 2). The PNIPA–SPO hydrogel swelled when cooled below the LCST and collapsed when heated above the LCST. This was because the amide group of NIPA in the polymeric structure had an intermolecular hydrogen bond with the surrounding water at a low temperature, which turned into an intramolecular hydrogen bond over its transition temperature. This caused the hydrogel hydration capacity to decrease and the hydrophobicity of the isopropyl groups of PNIPA–SPO hydrogel to increase. These two effects caused the bonding water in the hydrogel to change into free water, and the gel exhibited a volume-phase transition around its LCST.

3.3. Morphological characterization of internal microstructures of PNIPA–SPO hydrogel

To obtain visual image of microstructure of PNIPA–SPO hydrogel, the morphology of the internal microstructures of the PNIPA–SPO hydrogel was observed by scanning electron microscopy (SEM). To retain the internal microstructure, the PNIPA–SPO hydrogel solution was heated above the LCST value of 31 °C and was no macroscopic phase separation in pure water at 36 °C for 24 h, and then was frozen rapidly in liquid nitrogen. The frozen sample was 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. 3 shows the SEM image of the internal microstructure of PNIPA–SPO hydrogel indicating that the hydrogel has fibrous aggregation with a three-dimensional network structure. This morphology indicated that PNIPA–SPO hydrogels' self-assembly formed stable gel when the temperature is above the LCST of PNIPA–SPO.

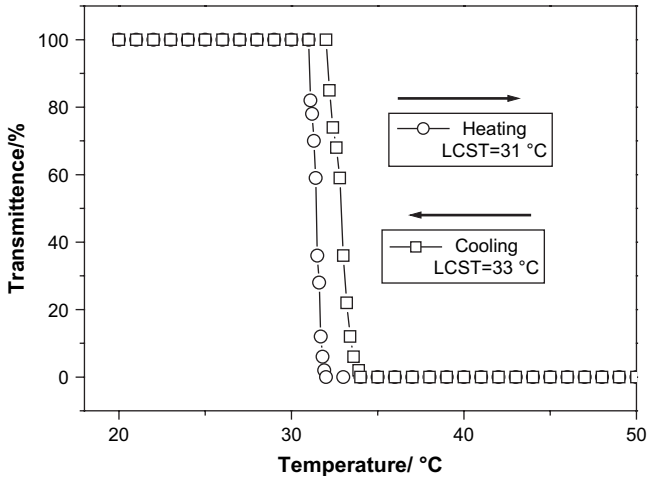


Fig. 2. Transmittance of a solution of PNIPA–SPO copolymer in water (8.0×10^{-4} g/mL) versus temperature during heating and cooling.

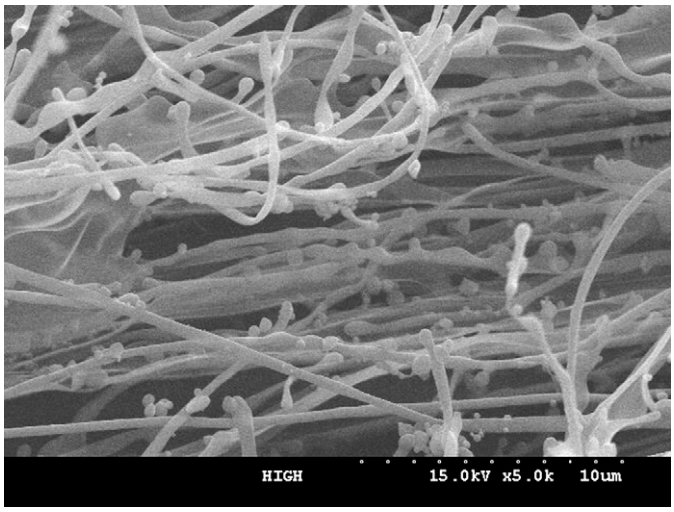


Fig. 3. SEM image of PNIPA–SPO copolymer hydrogel. (The gels were prepared from water, PNIPA–SPO = 0.5 wt%.)

3.4. The multiple switching behavior of PNIPA–SPO hydrogel

Fig. 4 shows the absorption spectral changes of PNIPA–SPO in a water solution and hydrogel by light, proton and base stimuli. Like other spirooxazine molecules, the PNIPA–SPO undergoes reversible photochromic reaction. Irradiation of a water solution of PNIPA–SPO with UV light leads to the appearance of a new absorption band at around 605 nm and the colorless solution of PNIPA–SPO turned blue (shown in Fig. 4: line 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 Scheme 1 (PNIPA–ME). And after visible light irradiation the original absorption spectrum was converted back to the initial closed-ring isomer of PNIPA–SPO. The PNIPA–SPO copolymer showed interesting acid-chromic reaction like photochromic compound spiropyran [32]. The interaction of PNIPA–SPO with proton was investigated in water solution through spectrophotometric titration experiment. Upon equivalent proton addition, the colorless solution of PNIPA–SPO became pink red. In Fig. 4, line 3 shows the titration spectra of PNIPA–SPO with proton. Upon addition of equivalent H^+, the band with a peak at around 520 nm occurred and produced the protonated merocyanine PNIPA–MEH form. And after visible light irradiation the original absorption spectrum was converted back to the initial state of PNIPA–SPO. Interestingly, upon addition of equivalent OH^- in the solution titrated with proton, the pink solution became blue in color. In Fig. 4, line 4 showed the absorption spectra of PNIPA–SPO with proton after titration with base. Upon addition of equivalent OH^-, the maximum absorption peak occurred the large red shift and the band with a peak at round 660 nm is observed. And after titrating with proton the original absorption spectrum was converted back to the pink red state of PNIPA–SPO. And after visible light irradiation the original absorption spectrum was converted back to the initial closed-ring isomer of PNIPA–SPO. When a water solution of PNIPA–SPO was heated above the LCST value, the PNIPA–SPO converted from the solution state to hydrogel state. After cooling to room temperature, the PNIPA–SPO could be recovered in the solution state, the whole process was reversible and could be repeated more than 10 times. In addition, we measured the absorption spectra of PNIPA–SPO hydrogel to obtain an insight into their photochromic properties in gel phase, which resemble photochromic performance in solution. The colorless PNIPA–SPO hydrogel turned blue and a new absorption band appeared at around 615 nm and gradually increased and reached a photostationary state (shown in Fig. 4: line 5 gel (closed); line 6 gel (open)). On subsequent irradiation of the closed of PNIPA–SPO hydrogel with visible light, the system gradually returned to the initial hydrogel status. Therefore, the light, thermal proton and base actions may be exploited to modulate the multiple switches between the species PNIPA–SPO, PNIPA–ME and PNIPA–MEH in solution and hydrogel states.

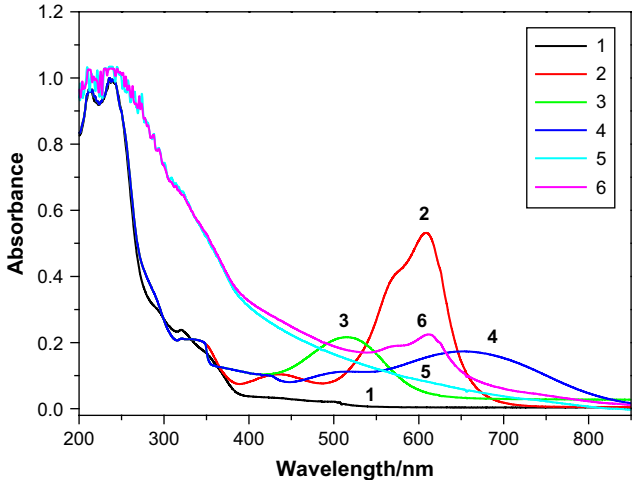


Fig. 4. (1) Absorption spectra of the closed form of PNIPA–SPO copolymer in water solution; (2) absorption spectra of the photostationary state of PNIPA–SPO copolymer upon irradiation with 365 nm light in water solution; (3) absorption spectra of the closed form of PNIPA–SPO copolymer titration with proton in water solution; (4) absorption spectra of the closed form of PNIPA–SPO copolymer titration with H^+ [Sol + H^+] titration with base in water solution (8.0×10^{-4} mol L^{-1}); (5) absorption spectra the closed-ring isomer of PNIPA–SPO copolymer in hydrogel; (6) absorption spectra of the photostationary state of PNIPA–SPO upon irradiation with 365 nm light in hydrogel state.

Fig. 5 showed the whole multiple switching processes with photographic images of PNIPA–SPO in the trigger of light, thermal, base and proton. Upon irradiation with UV light and visible light, the colorless closed spirooxazine form of PNIPA–SPO can be interconverted with the blue color open-ring PNIPA–ME form in the gel or in solution, i.e. photochromic processes both in hydrogel and in solution. The interconversion between the hydrogel phase and solution could be easily achieved by thermal stimuli at a different temperature. In addition, the solution of PNIPA–SPO was both sensitive to proton and base ion, which resulted in obvious changes in the absorption (shown in Fig. 4). The reversible chemical switch could be obtained by proton and base stimuli. The multiple switching

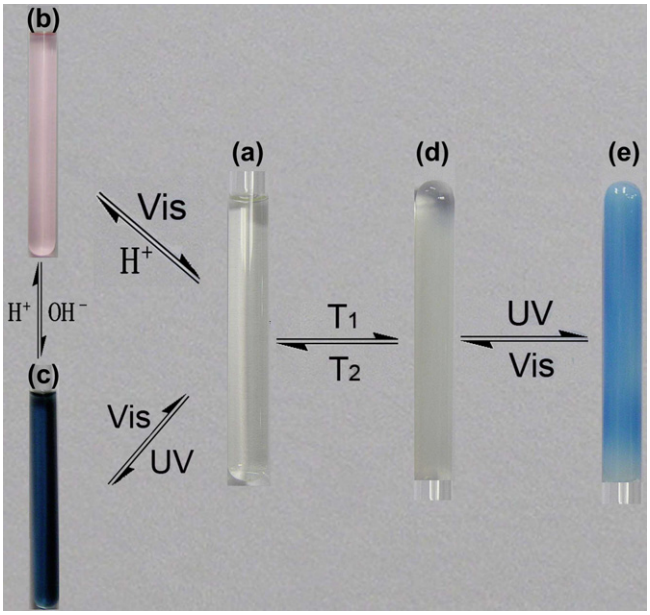


Fig. 5. Multiple switching images of PNIPA–SPO copolymer in NMR tube with the trigger of light, thermal, base, proton. (a) Sol (closed) (b) Sol (closed) $+ H^+$; (c) Sol (closed) $+ H^+ + OH^-$; (d) Gel (closed); (e) Gel (open).

could be repeated more than 10 times. Thus, this system constitutes a multi-mode complete reversible switch by light, thermal stimuli, base as well as proton.

4. Conclusions

In summary, we have demonstrated a multiple switching photochromic poly(*N*-isopropylacrylamide) with spironaphthoxazine copolymer in hydrogel phase and in solution by light, thermal, base, proton stimuli. It exhibits excellent photochromic properties and defined thermo reversible properties in hydrogel system at a critical temperature (LCST). In the same time, we take advantage of the OH^- and proton inducing obviously different absorption of the photochromic PNIPA–SPO hydrogel in water solution sequentially alternating UV–vis light irradiation. Hence, a complicated multiple switch is realized, which makes it promising application in the fields of opto- and electronic smart materials, logic gate, nanomachines, fluorescence sensors and other molecular photonic devices.

Acknowledgements

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