

Preparation and characterization of a photochromic hydrogel

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ABSTRACT

A new type of photochromic hydrogel, spiropyran (SP)-Polyvinylpyrrolidone (PVP)-poly (N-isopropyl acrylamide) (PNIPAM) hydrogel with functionalized SP chemically incorporated, was synthesized. The molecular structure of synthesized products was given by nuclear magnetic resonance (NMR) spectra and infrared spectrum (IR). The photochromism of the hydrogel was evidenced by photography and characterized by ultraviolet-visible (UV-Vis) spectroscopy. The photochromic reversibility of the hydrogel was tested through observing its responses to the alternating UV irradiation to dark environment. The fluorescence micrographs showed the fluorescent effect as well as confirmed the photochromic properties of the hydrogel, and indicated that the chemical incorporation made the functionalized SP distribute well in the gel. Copyright © 2011 VBRI press.

Keywords: Photochromism; polymeric hydrogel; spiropyran.



Mo Chen obtained his Bachelor degree from Hebei University in 2004. At present, he is working in North China Institute of Science and Technology. His major research is focus on synthesizing photochromic compound and developing multifunctional products for biological applications.



Xiaoqiang Li obtained his Ph.D. degree from Donghua University in March, 2010. Currently, he is working in Ibaraki University (Japan) as an assistant researcher. Dr. Li's main research interests include fabrication of biofunctional nanofibers for Tissue Engineering from electrospun nanofibers, and development of drug-delivery systems by emulsion or coaxial electrospinning.

Introduction

Most of hydrogels are water-swollen polymeric materials that maintain a distinct three-dimensional structure and be of high interest for technical and medical applications [1]. Their classification based on the source, crosslinking function, presence of pores and their applications. Among various hydrogels, poly (N-isopropylacrylamide) (PNIPAM) is a typical thermo-sensitive polymeric material

that demonstrates a lower critical solution temperature (LCST) at 32 °C in aqueous solution. While temperature and pH are well-known signals that induce responses in polymer hydrogels, the use of light as another type of signal has not yet found a wide application. Some researchers have investigated various functional hydrogels [2-7]. In their work, the photochromic or thermal-light doubly sensitive or even multi-responsive hydrogels were prepared by modifying polymer hydrogels with chromophores such as azobenzene, spirobenzopyran, etc. Upon the irradiation of UV or visible light, isomerization of the chromophores in the polymer hydrogels gives rise to phase transition and thus induces responses in the hydrogels.

Photochromic materials had abstracted great interest due to their wide applications. Especially in biological applications, the use of light offers unique opportunities, as light fluxes are easy to control temporally and are less likely to perturb delicate biological structures than most other stimuli [8-10]. As a class of structurally diverse photochromic compounds, spiropyran (SP) play a special role since their photoinduced and reversible ring-opening to the corresponding merocyanines is accompanied not only by a significant structural change from a non-planar to a planar structure but also by a large polarity increase [11]. The low water-solubility of SP limits its potential to be applied in aqueous biological environments. Hence they are

often conjugated to biomaterials so that to equip these materials with photochromic properties [12]. However, incorporation of SP to the well-studied PNIPAM hydrogel was seldom reported. PNIPAM hydrogel has good hydrophilicity and biocompatibility, which make it a promising material for photochromic switching or fluorescent labeling in biological applications if combined with suitable chromophores.

In the present study, a novel functionalized SP was synthesized and incorporated into PNIPAM hydrogel to produce a photochromic hydrogel, the photosensitivity of which is reflected in color changes and fluorescence induced by the isomerization of SP rather than phase transition. The molecular structure of the functionalized SP and the synthesized hydrogels were given by nuclear magnetic resonance (NMR) and Infrared (IR) spectra. Various methods were applied to characterize the photochromic properties and fluorescent effect of the photochromic hydrogels.

Experimental

Materials

All of the materials used for NO_2SP synthesis in this study are chemically pure degree. N-isopropylacrylamide (analytically pure) was provided by Acros Co., Belgium; potassium persulfate (KPS) and N,N,N',N' -tetramethyldiamine (TEMED) were provided by Shanghai Chemical Reagent, Analytic Reagent; absolute ethanol was purchased from AAPER Alcohol and Chemical Company; N,N' -Methylenebis (acrylamide) (BIS), polyvinylpyrrolidone (PVP) and N-vinylpyrrolidone (NVP) were purchased from Aldrich. The functionalized NO_2SP was synthesized in our own lab.

Synthesis of SP-P (NIPAM-co-NVP) hydrogel

NVP was dissolved in water and bonded to NIPAM using KPS and TEMED as the catalysts to form carbon bond. 0.5 g NO_2SP was dissolved in 5.0 g ethanol, which then was added to a NIPAM and NVP aqueous solution (20 g, $\text{cNIPAM} = \text{cNVP} = 4 \text{ wt}\%$). After the solution being completely mixed, 0.03 g BIS was added. The reaction was allowed to continue for 2 h in the dark at room temperature. The resultant SP-P (NIPAM-co-NVP) hydrogel was immersed in an ethanol/water ($w/w = 20/80$) mixture for a week and then in deionized water for another week in the dark at room temperature. The immersion process was carried out four times until the supernatant became completely colorless. The IR spectra of hydrogel samples (PNIPAM, P (NIPAM-co-NVP) and SP-P(NIPAM-co-NVP)) were obtained on a NEXUS 670 Infrared-Raman Spectrometer (Nicolet, US).

Characterization

The hydrogel samples were powdered and mixed with KBr to make samples. The IR spectra of the samples were obtained on a NEXUS 670 Infrared-Raman Spectrometer (Nicolet, US). UV exposure at 365 nm for the samples was provided by a UV lamp (Blak-Ray Model B, 100 AP) at a distance of 30 cm. The UV light intensity received by the

samples was 1.2 W/cm^2 . The samples were shaped to fit in quartz cures. The absorbance as a function of wavelength was measured using a Lambda 35 UV-Vis spectrophotometer (PerkinElmer, US). The samples were powdered or cut into strips. The fluorescent effect of the samples was observed by a fluorescent microscope (UL 100HG, Olympus, Japan).

Results and discussion

The IR spectra of different samples are shown in **Fig. 1**. The absorption peak of -C=C- in benzene ring at about 1450 and 1580 cm^{-1} and the peak of C=O at 1680 cm^{-1} can be clearly seen for the SP-P(NIPAM-co-NVP) sample, which did not appear in the spectra of the PNIPAM and P(NIPAM-co-NVP) samples, significantly indicated that the functionalized SP had been incorporated into the hydrogel.

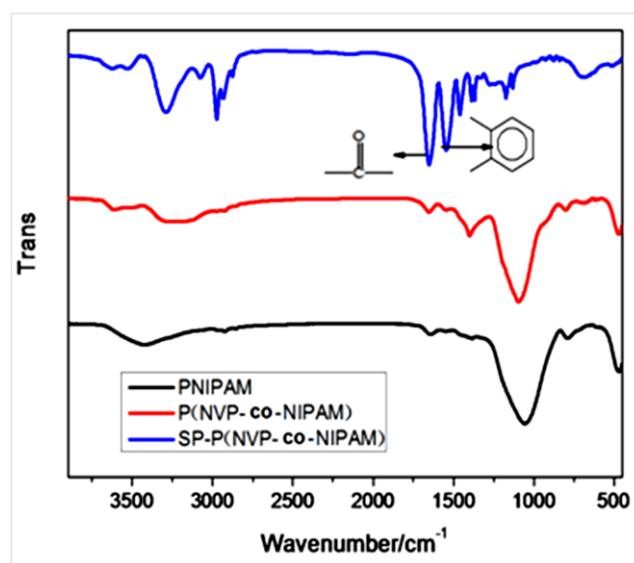


Fig.1. IR spectra of PNIPAM, P (NIPAM-co-NVP), SP-P (NIPAM-co-NVP) hydrogels.

Fig. 2 shows the color change and UV-Vis spectra of PNIPAM and SP-P (NIPAM-co-NVP) hydrogels under the irradiation of 365 nm UV light for different times. In **Fig. 2** (a), a represents the PNIPAM gel after UV irradiation for 30 s; B, C and D are the SP-P (NIPAM-co-NVP) gels after irradiation for 0, 10 and 30 s, respectively. The PNIPAM gel was colorless and transparent as shown in picture-A **Fig. 2** (a) as it was unirradiated. In contrast, the SP-P (NIPAM-co-NVP) gel exhibited a light yellow color when subjected to irradiation for 10 s. With the increase of irradiation time, the color of the gel getting darker, and was reddish brown when the irradiation time reached at 30 s. As mentioned in the Experimental section, the SP-P (NIPAM-co-NVP) gels were first immersed in an acetone/water mixture for 1 h and then fully washed in water. Therefore, the color shown in the pictures was ascribed to the incorporated SP. The color changes indicated that the SP was still photo-chemically active and endowed the hydrogel with photochromism after incorporated into it. It can be seen in **Fig. 2** (b) that, without UV irradiation, there was no absorbance over the whole wavelength range in

UV-Vis spectrum for the PNIPAM gel, as evidenced by picture-A in **Fig. 2 (a)**. For the SP-P (NIPAM-co-NVP) gel, an absorption peak appeared at 568 nm and increased with increased irradiation time, in good accordance with the results of **Fig. 2 (a)**. Before irradiation, a fraction of SP molecules were in the merocyanine form (open ring), though most of the SP molecules were in the spiro (closed-ring) form. The existence of mero isomers led to a small absorption peak at 568 nm. Under irradiation, some spiro isomers converted to the mero (open-ring) form, making the absorption peak increase with prolonged irradiation time. The hydrogel exhibited obvious photochromic properties after the incorporation of SP. Incorporating SP molecules into the PNIPAM hydrogel could enhance the applicability of photochromic materials in aqueous environment.

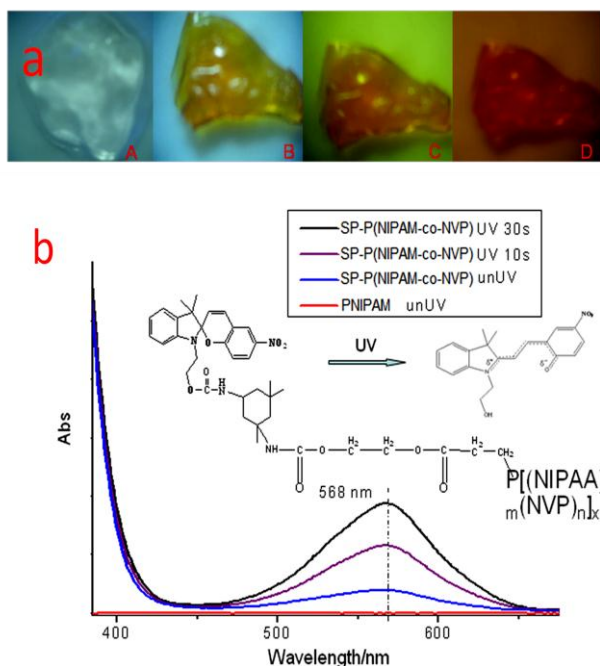


Fig. 2. (a) Color changes and (b) UV-Vis spectra of hydrogels irradiated by 365 nm UV light for different times.

The 568 nm light transmittance of SP-P (NIPAM-co-NVP) gel in response to alternating UV irradiation and darkness is shown in **Fig. 3**. As discussed above, SP was in the spiro form in the dark, whose absorption band lies in UV region. The SP-P (NIPAM-co-NVP) gel was thus nearly colorless and transparent with a transmittance of around 82.5 %. When exposed to 365 nm UV light, the transformation of SP to the mero form made the gel turn into reddish brown, leading to a dramatic decrease of transmittance. Moreover, for several cycles in the data range, the modulation of the transmittance was fully reversible without any sign of fatigue effect, demonstrating the great potential of such hydrogels for on-and-off switching applications.

Fig. 4 shows the fluorescent effect of hydrogels under different conditions. The chromophores (fluorophores) were protected by the hydrogel from the external environment. Therefore, the quenching of their

fluorescence could be avoided. As expected, the PNIPAM gel did not fluoresce upon excitation by green light (520 – 570 nm). The unirradiated SP-P (NIPAM-co-NVP) gel emitted weak fluorescence. When kept in the dark, only a very small amount of SP molecules were in the mero form. The fluorescence resulted from electron transition of the mero isomers was thus fairly weak. Under UV irradiation, however, certain amounts of spiro isomers converted to mero isomers. More electrons were excited and transitioned back to the ground state, leading to stronger fluorescence. With the increase of irradiation time, the fluorescence grew stronger. Furthermore, the whole hydrogel strip emitted fluorescence of the same intensity (**Fig. 4 E**), suggesting that SP distributed uniformly in the hydrogel.

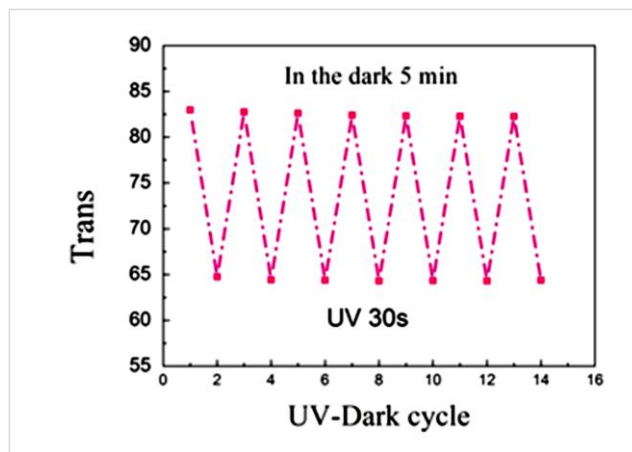


Fig. 3. Modulation of light transmittance at 568 nm for the SP-P (NIPAM-co-NVP) gel with alternating UV and darkness: In each cycle, the sample was irradiated by 365 nm UV light for 30 s (low transmittance) and kept in darkness for 5 min (high transmittance).

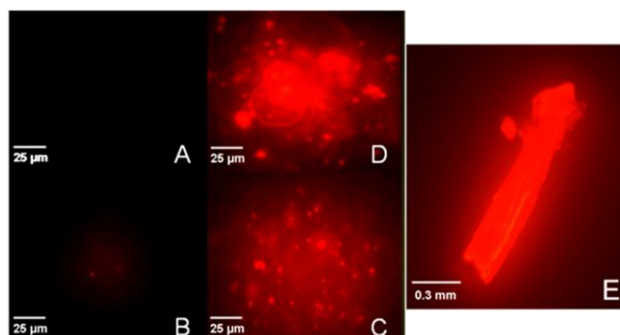


Fig. 4. Fluorescent effect of various gels under different irradiation conditions: A PNIPAM gel irradiated by 365 nm UV light for 10 s; B SP-P(NIPAM-co-NVP) gel before UV irradiation; C SP-P(NIPAM-co-NVP) gel irradiated by 365 nm UV light for 10 s; D SP-P(NIPAM-co-NVP) gel irradiated by 365 nm UV light for 20 s. The wavelength of the exciting light was in the range of 520-570 nm when observing fluorescence.

The functionalized SP molecules were incorporated into the hydrogel via reaction of double bonds, making them much less likely to aggregate and affect the properties of the gel. The red fluorescence could be elicited by green light after the hydrogel was irradiated by UV light for

several seconds, indicating that SP-P (NIPAM-co-NVP) gel can be used in fluorescence labeling.

Conclusion

A photochromic SP-P (NIPAM-co-NVP) hydrogel with a functionalized SP incorporated was synthesized. The pictures and the UV-Vis results suggested that the hydrogel possessed excellent photochromic properties and can be hopefully used in aqueous systems. It is found from the rapid responses of the hydrogel to the alternating UV irradiation and dark cycles that it had great potential for light-triggering switching applications. The fluorescence micrographs demonstrated fluorescent effect and photochromism of the hydrogel, which make it possible to be used for biological fluorescence labeling. The SP distributed uniformly in the gel, ensuring its good photochromic properties.

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