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Photoregulated optical switching of poly(*N*-isopropylacrylamide) hydrogel in aqueous solution with covalently attached spironaphthoxazine and D-π-A type pyran-based fluorescent dye

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ABSTRACT

A thermoresponsive poly(NIPAM-*co*-SPO-*co*-fluorophore) hydrogel comprising poly(*N*-isopropylacrylamide) that was partially modified using an electron donor-π-conjugated-electron acceptor (D-π-A) pyran-based fluorescent dye using radical copolymerization as well as a photochromic spironaphthoxazine unit displayed a lower critical solution temperature transition from 28 to 50 °C in aqueous solution. The poly(NIPAM-*co*-SPO-*co*-fluorophore) copolymer exhibited excellent photochromic behavior in both aqueous solution and hydrogel state. The fluorescence intensity of the poly(NIPAM-*co*-SPO-*co*-fluorophore) was temperature-dependent. The relationship between fluorescence intensity change and size of the polymer aggregates was determined using dynamic light scattering. Reversible modulation of fluorescence intensity was achieved using alternating irradiation with UV and visible light. The internal microstructure of the poly(NIPAM-*co*-SPO-*co*-fluorophore) hydrogel was investigated using SEM.

1. Introduction

Of various types of photochromic compound, spironaphthoxazines (SPO) [1–3], have attracted much interest from the viewpoint of fundamental elucidation of photochemical reactions and potential application as optical memory. Photochromism in spironaphthoxazine compounds generally involves the UV-induced dissociation of the spiro C—O bond, from the oxazine ring to form a planar structure. Several poly(*N*-isopropylacrylamide) (PNIPAM) copolymers containing photochromic units such as azobenzene or spiropyran derivatives have been reported [4–6], in which the PNIPAM copolymers were controlled by temperature, light or chemical stimuli. AIn the context of thermoresponsive polymers, PNIPAM and its copolymers exhibit a lower critical solution temperature (LCST) in aqueous solution by means of which, their hydration-dehydration states change reversibly and rapidly in response to a small temperature change [7,8]. This endothermic phase transition is accompanied by a release of water bound to the polymer chain. In previous papers [9,10], the present research groups has reported bistable photoswitching in poly(*N*-isopropylacrylamide) with photochromic spironaphthoxazine hydrogel for optical data storage applications. D-π-Apyran-based, fluorescent dyes such as 4-(dicyanomethylene)-2-methyl-6-(4-(dimethylamino)styryl)-4*H*-pyran (DCM) have been developed as both photo- and electro-luminescent materials for applications in dye lasers [11], sensors [12] and dye-sensitized solar cells [13]. Their fluorescence properties are highly sensitive to changes in external environment such as polarity and pH, owing to their intrinsic intramolecular charge transfer character [14,15]. In previous research [16], we reported the synthesis, photophysical properties and unusual, aggregation-induced fluorescence changes within copolymers comprising a novel pyran-based fluorophore. This paper concerns the synthesis and characterization of a poly(*N*-isopropylacrylamide) hydrogel consisting of *N*-isopropylacrylamide, spironaphthoxazine and D-π-A type pyran-based fluorescent dye units as the thermosensitive, photochromic and fluorophore components, respectively. Importantly, modulated fluorescence signalling was achieved by photochromic switching the spironaphthoxazine component of the polymer.

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2. Experimental

Melting points were determined using Electrothermal IA 900 apparatus and were uncorrected. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using an electron energy of 70 eV employing a 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 M_n and polydispersity (M_r/M_n) of the polymer was measured using a PL-GPC model 210 chromatograph at 25 °C using THF as eluent and standard polystyrene as reference. Fluorescence spectra were measured on a Shimadzu RF-5301PC fluorescence spectrophotometer; UV–vis spectra and transmittance were obtained on a Agilent 8457 UV–vis spectrophotometer. LCST values were determined by spectrophotometric detection of the changes in transmittance ($\lambda_{max} = 465$ nm) of aqueous polymer solutions heated at a constant rate (0.2 °C min^{-1}) using a thermostatically controlled cuvette. Dynamic light scattering (DLS) measurements were carried out on a Wyatt Technology Dynapro Titan instrument using the 828.6 nm line of a laser as excitation source. A high-pressure mercury lamop (Ushio, SP3-250D) was used as UV radiation source and was calibrated with a monochromator at 366 nm. Scanning electron microscopy (SEM) images of the hydrogel were obtained using a Hitachi S-530 scanning electron microscope.

2.1. Materials

2,6-Dimethylpyran-4-pyrone, allyl cyanoacetate and 4-(diphenylamino)benzaldehyde, Fisher's base, 2,7-dihydroxy naphthalene and methacryloyl chloride were purchased from Aldrich. *N*-Isopropylacrylamide (Aldrich) was purified by recrystallization from a mixture of toluene/hexane (1/4) and dried under vacuum. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. All other chemicals were of the highest grade available and were used without further purification. Solvents were analytically pure and were employed without any further drying or purification. The spironaphthoxazine **6** was prepared from 9′-hydroxy-1,3,3-trimethylspiro[indoline-2,3-[3H]naphtha[2,2-b][1,4-oxazine and methacryloyl chloride according to the method described previously [17,18] (Scheme 1).

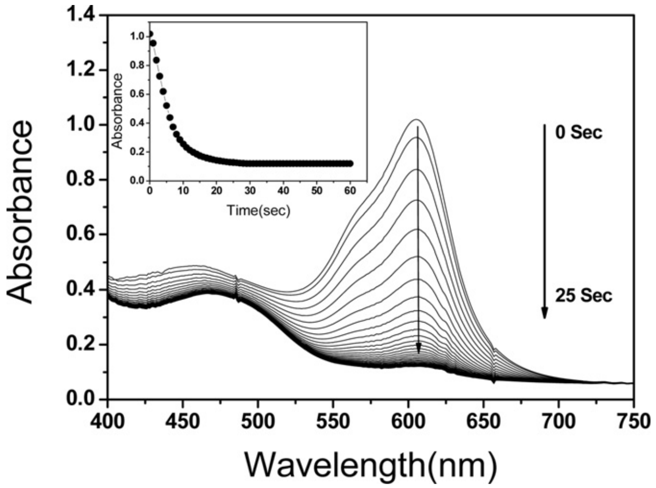
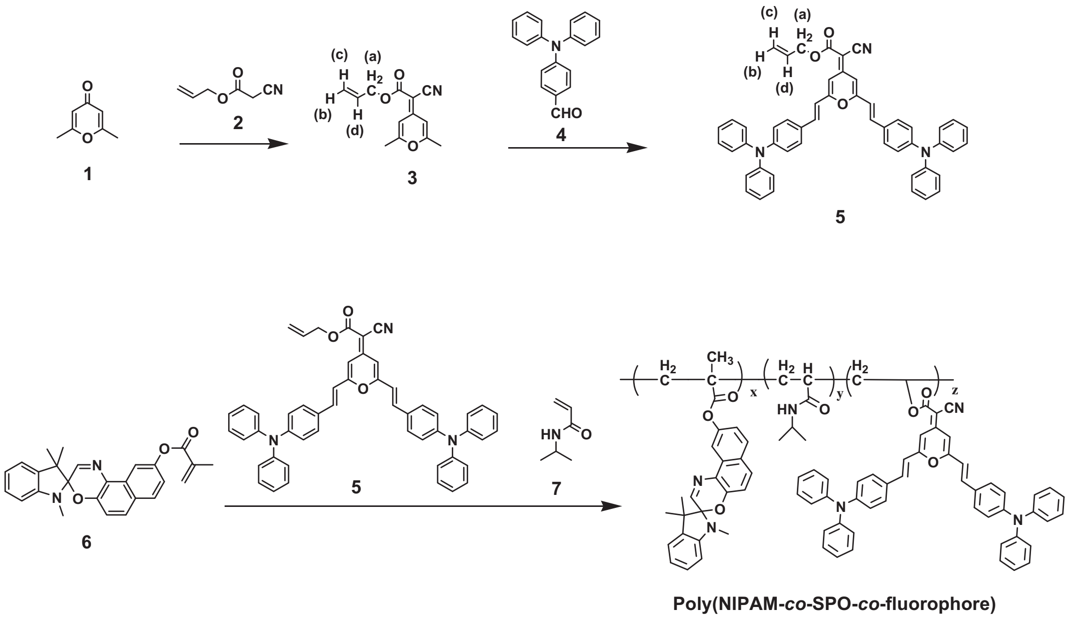


Fig. 1. UV–vis absorption spectral changes of poly(NIPAM-*co*-SPO-*co*-fluorophore) in water (0.2 g/mL) upon irradiation with UV light. The inset figure shows the decolouration at 605 nm.

2.2. Synthesis of the flurophore monomer ***5***

2.2.1. Allyl-cyano-2-(2,6-dimethyl-4H-pyran-4-ylidene)acetate ***3***

A mixture of 2,6-dimethylpyran-4-pyrone (3 g, 24 mmol) **1**, allyl cyanoacetate **2**, (3 g, 24 mmol) and acetic acid (12.5 mL) was refluxed for 24 h. The crude solid obtained was filtered, washed with methanol and recrystallized from methanol several times. Yield: 32%; mass (m/z) 231 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 6H), 4.65 (dt, $J_{ab} = 1.6$ Hz, $J_{ac} = 1.6$ Hz, $J_{ad} = 5.2$ Hz, 2H), 5.20 (dd, $J_{ac} = 1.6$ Hz, $J_{bc} = 1.6$ Hz, $J_{bd} = 10.4$ Hz, 1H), 5.36 (dd, $J_{ac} = 1.6$ Hz, $J_{bc} = 1.6$ Hz, $J_{cd} = 17.2$ Hz, 1H), 5.94–6.03 (m, 1H), 6.59 (s, 1H), 7.87 (s, 1H). Anal. calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.17; H, 5.72; N, 6.03%.



Scheme 1. Synthesis of a D-π-A charge transfer dye, **5**, and poly(NIPAM-*co*-SPO-*co*-fluorophore).

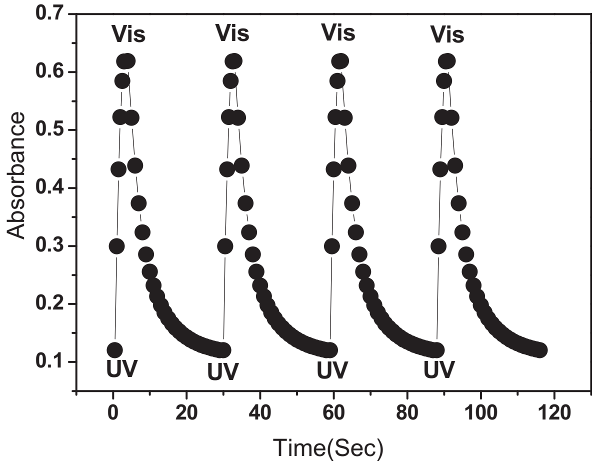


Fig. 2. Cyclic absorbance changea at 605 nm of poly(NIPAM-*co*-SPO-*co*-fluorophore) in water (0.2 g/mL) following UV and visible light irrafiation.

2.2.2. Allyl-2-(2,6-bis((E)-4-(diphenylamino)styryl)-4H-pyran-4-ylidene)-2-cyanoacetate 5

A solution of allyl-2-cyano-2-(2,6-dimethyl-4*H*-pyran-4-ylidene)acetate **3** (1 g, 4.3 mmol), 4-(diphenylamino)benzaldehyde **4** (1.4 g, 5.2 mmol), and piperidine (0.3 mL) in 1-propane (50 mL) was refluxed for 24 h using a Dean–Stark trap. After cooling the reaction mixture, the resulting precipitate was filtered, washed well with 1-propanol and dried. The reaction mixture was evaporated to remove solvent and separated by column chromatography using chloroform. Yield: 30%; mp 229–231 °C; mass (m/z) 741 (M^+). ^1H NMR (400 MHz, $CDCl_3$): δ 4.69 (dt, J_{ab} = 1.6 Hz, J_{ac} = 1.6 Hz, J_{ad} = 5.6 Hz, 2H), 5.23 (dd, J_{ac} = 1.6 Hz, J_{bc} = 1.6 Hz, J_{bd} = 10.8 Hz, 1H), 5.37 (dd, J_{ac} = 1.6 Hz, J_{bc} = 1.6 Hz, J_{cd} = 17.2 Hz, 1H), 5.87–5.94 (m, 1H), 6.60 (d, *J* = 6.8Hz, 1H), 6.64 (d, *J* = 6.8Hz, 1H), 6.73 (s, 1H), 7.02–7.35 (m, 30H), 8.04 (s, 1H). Anal. calcd for $C_{51}H_{39}N_3O_3$: C, 82.57; H, 5.66; N, 5.30. Found: C, 81.84; H, 5.78; N, 5.44%.

2.3. Synthesis of Poly(NIPAM-co-SPO-co-fluorophore)

The thermosensitive and photochromic hydrogel was prepared by free radical copolymerization. *N*-Isopropylacrylamide **7** (3 g, 0.27 mmol), allyl-2-(2,6-bis((*E*)-4-(diphenylamino)styryl)-4*H*-pyran-4-ylidene)-2-cyanoacetate **5** (0.1 g, 0.13 mmol),spironaphthoxazine

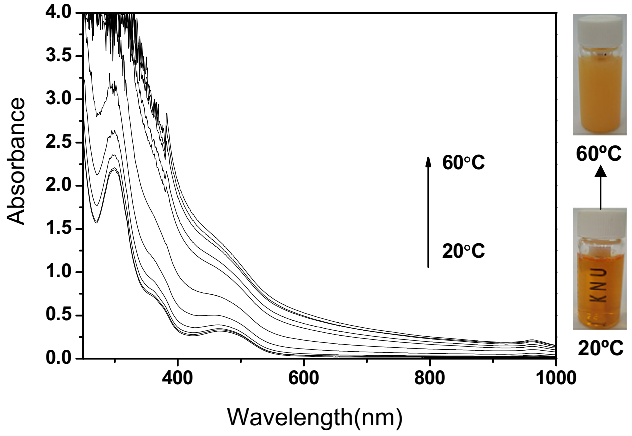


Fig. 3. Absorption spectra of poly(NIPAM-*co*-SPO-*co*-fluorophore) in water (0.2 g/mL) at various temperatures.

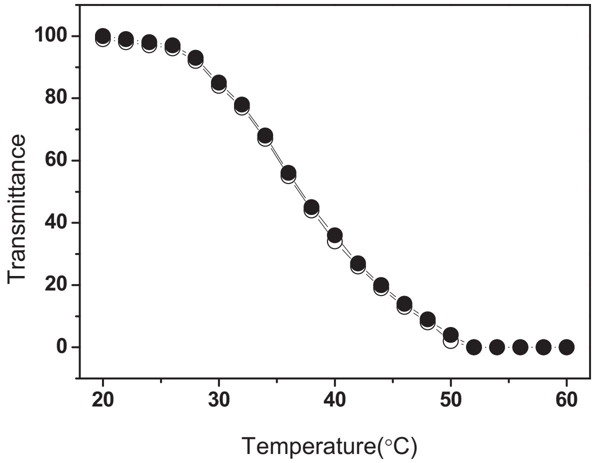


Fig. 4. Transmittance of a solution of poly(NIPAM-*co*-SPO-*co*-fluorophore) in water (0.2 g/mL).●, heating; ○, cooling.

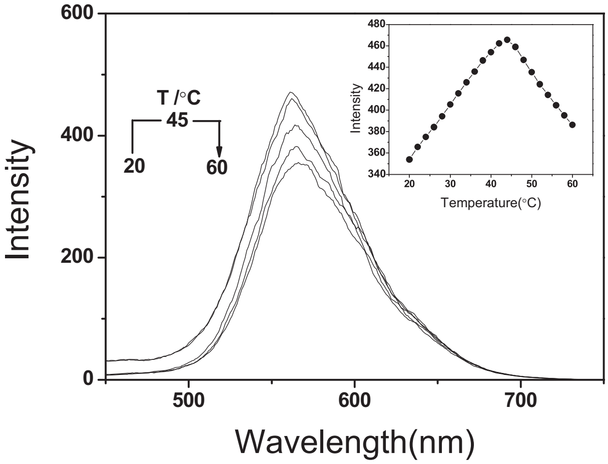


Fig. 5. Fluorescence spectral changes of poly(NIPAM-*co*-SPO-*co*-fluorophore) in water (0.2 g/mL) at various temperatures. The insect shows the fluorescence intensity at 565 nm.

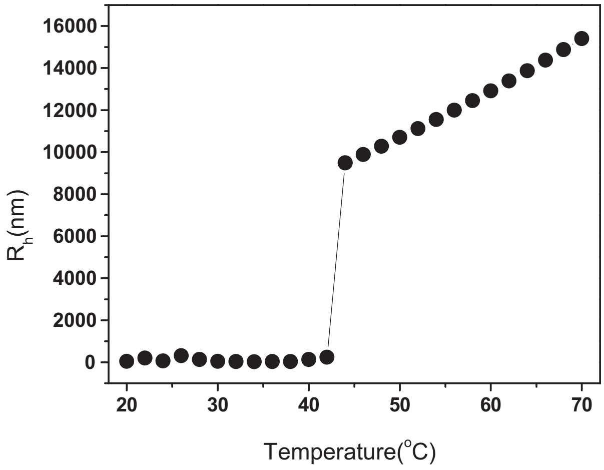


Fig. 6. Hydrodynamic radius(R_h) of poly(NIPAM-*co*-SPO-*co*-fluorophore) in water (0.2 g/mL) at various temperatures.

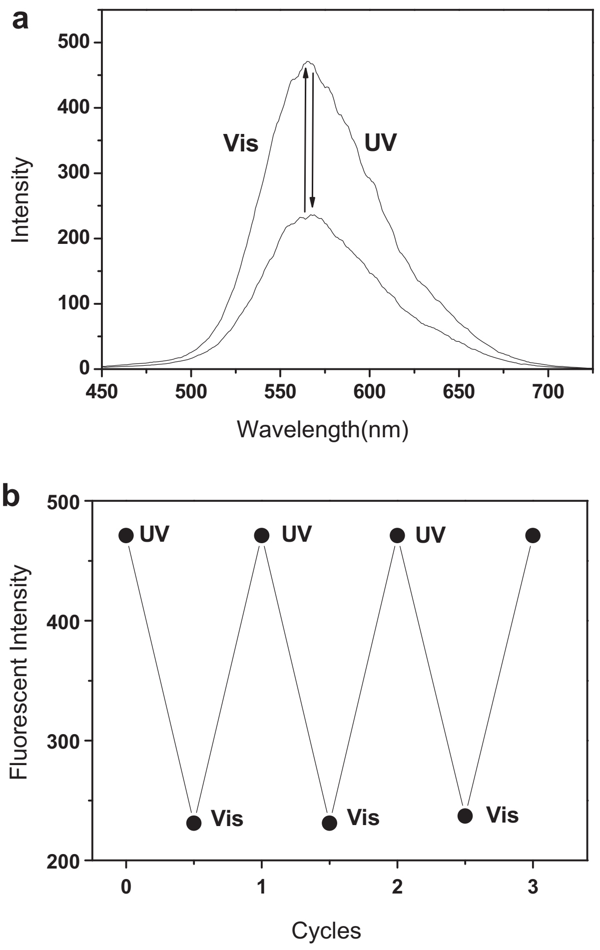


Fig. 7. (a) Fluorescence spectra of poly(NIPAM-*co*-SPO-*co*-fluorophore) on each photostationary state by alternating irradiation with UV and visible light. (b) Fluorescence switching. Fluorescence of poly(NIPAM-*co*-SPO-*co*-fluorophore) under 445 nm excitation is switched on and off with alternating UV and visible irradiation.

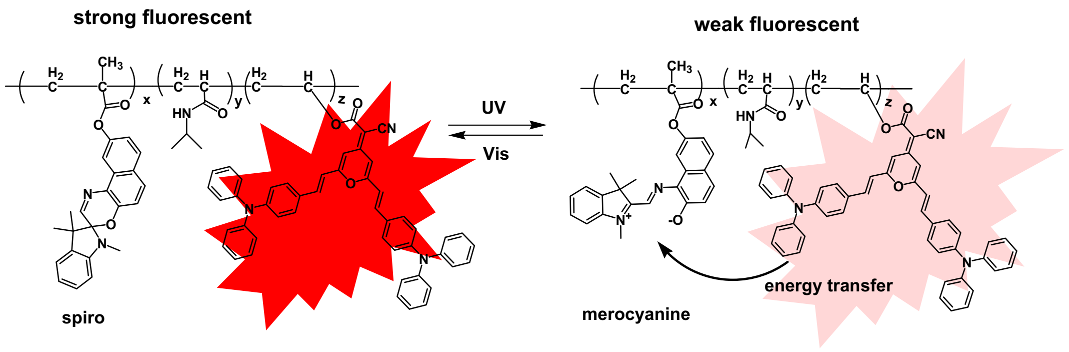
(SPO) (0.005 g, 0.13 mmol) **6** and 2,2′-azobis-(isobutyronitrile) (0.06 g, 0.4 mmol) were dissolved in anhydrous THF (20 mL) under dry nitrogen. After heating for 3 days at 65 °C, the resultant mixture was precipitated from ether and the resulting polymer was dried under vacuum to give an orange-colored powder. Yield: 30%; Gel permeation chromatography (GPC): Mn: 19800, Mw: 22000, MP: 16300, Mw/Mn: 1.11.

3. Results and discussion

The synthetic route of the poly(NIPAM-*co*-SPO-*co*-fluorophore) is depicted in Scheme 1. In our design and synthetic strategy, we took the following points into consideration: at first, poly(*N*-isopropylacrylamide) is thermosensitive polymer hydrogel and shows a lower critical solution temperature (LCST) due to the presence of both hydrophilic amide groups and hydrophobic isopropyl groups in its side chains. Second, incorporation of the photochromic spironaphthoxazine unit in the polymer system could lead to a photoswitching unit. We designed a new D-π-A charge transfer dye, **5**, containing a polymerizable functional allyl group. As shown in Scheme 1, the synthetic method was very simple. The ^{1}H spectrum of **5** verified its well-defined chemical structure. Characteristic NMR peaks due to the allyl group appeared at 5.23(dd), 5.37(dd) and 5.94(m). Reaction of an fluorophore monomer **5**, spironaphthoxazine **6** and *N*-isopropylacrylamide **7** in THF affords a orange-colored powder of poly(NIPAM-*co*-SPO-*co*-fluorophore). The change in electronic absorption spectra of poly (NIPAM-*co*-SPO-*co*-fluorophore) upon UV irradiation in aqueous solution is depicted in Fig. 1.

The visible range absorption increased gradually by UV irradiation which is ascribed to the generation of the open merocyanine form from the closed spiro form. When the sample of poly(NIPAM-*co*-SPO-*co*-fluorophore) was left in the dark at room temperature after irradiation, the absorbance at 605 nm decreased. The original spectral pattern is reversibly recoverd within 20 s. Irradiation of the merocyanine with visible light at wavelength greater than 500 nm resulted in the rapid decolouration and the regeneration of the closed spiro form. This photochromic behavior also exhibited a fairly good reproducibility, as can be seen in Fig. 2, where consecutive colouration–decolouration cycles are shown. UV–vis spectrometry is an easy and widely used method for the determination of the LCST. In Fig. 3 we show the absorption spectra of aqueous poly (NIPAM-*co*-SPO-*co*-fluorophore) solution at different temperature. As solution is heated, it becomes turbid; these temperature-responsive changes are entirely reversible. This kind of gelation behavior induced by temperature is well-known as an LCST, resulting from a balance between hydrogen-bond formation with water and intramolecular hydrophobic forces [5].

The values of transmittance (A465) of aqueous solution containing poly(NIPAM-*co*-SPO-*co*-fluorophore) are plotted against the temperature of the solution in Fig. 4; an obvious transmittance decrease at $<$ 28 °C:LCST = 28–50 °C. The results of thermoresponse of poly(NIPAM-*co*-SPO-*co*-fluorophore) solution characterized by UV–vis spectrometry are comparable with those from fluorescence measurement.



Scheme 2. Schematic representation of fluorescence modulation by photochromic switching. When spiro form is converted to the merocyanine bt UV light, the emission intensity of fluorophore is reduced through energy transfer quenching. After exposure to visible light and photoisomerization from merocyanine to spiro form, the emission intensity is increased.

The temperature-dependent emission spectra of the poly(NIPAM-*co*-SPO-*co*-fluorophore) in temperature range from 20 to 60 °C is shown in Fig. 5. Fig. 5 inset indicates the fluorescence intensity temperature diagram of poly(NIPAM-*co*-SPO-*co*-fluorophore).

This shows the fluorescence intensity of the poly(NIPAM-*co*-SPO-*co*-fluorophore) is significaltly increased with heating from 20 to 45 °C when the excitation wavelength was 445 nm. The emission enhancement at higher temperature is due to the formation of hydrophobic domain near the isopropylacrylamide units. In contrast, at gt; 45 °C, the fluorescence intensity decreased. The temperature dependence of the size of polymer particles as obtained using dynamic light scattering method is shown Fig. 6.

At 45 °C, the size of the polymer hydrogel is estimated to be 9000 nm, due to a formation of the large hydrophobic polymer aggregates. Within the large polymer particles, the fluorophore units scarcely absorb the excitation beam, thus resulting in emission quenching which is accordance with the formation of the huge hydrophobic domain [19]. Fig. 7(a) shows the fluorescence spectral change of poly(NIPAM-*co*-SPO-*co*-fluorophore) with the excitation wavelength at 445 nm. The fluorescence intensity change was regulated by the photochromic reaction. Before irradiation with UV light, it showed an emission in 565 nm with $\lambda_{\text{max, exi}} = 445$ nm. Upon irradiation, with UV light, the fluorescent intensity of poly(NIPAM-*co*-SPO-*co*-fluorophore) decreased. After irradiation with visible light, the original emission spectra is regenerated. The fluorescence of this polymer obviously depends on the state of the spironaphthoxazine photochromic switching between spiro and merocyanine using alternate irradiation with UV and visible light. From what can be seen in Fig. 7(b), the fluorescence intensity reversibly changed at 565 nm (excitation: 445 nm). The fluorescence quenching in merocyanine is attributed to the energy transfer from the excited fluorophore unit to the opened merocyanine units, because the spectral overlapping in the range of 550–600 nm between the absorption band of the merocyanine and the emission band of the fluorophore. A feasible mechanism for energy transfer and fluorescence switching is shown in Scheme 2.

Fig. 8 shows a few representative SEM image of the internal matrix structure of poly(NIPAM-*co*-SPO-*co*-fluorophore) hydrogel which has irregular fibrous aggregation and homogeneous coral-like microstructure with a three dimensional net work structure. This morphology indicated that poly(NIPAM-*co*-SPO-*co*-fluorophore) could form stable hydrogel when the temperature was above the LCST of poly(NIPAM-*co*-SPO-*co*-fluorophore).

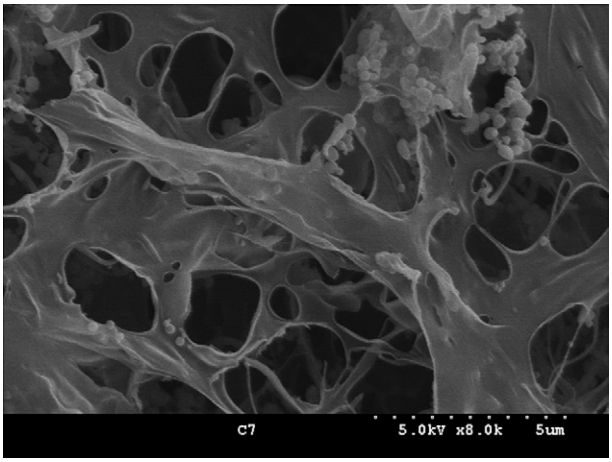


Fig. 8. SEM micrographs of poly(NIPAM-*co*-SPO-*co*-fluorophore).

4. Conclusion

In conclusion, photoswitchable spironaphthoxazine can be integrated with D-π-A type pyran-based fluorophore into the thermoresponsive poly(*N*-isopropylacrylamide). The phase transition temperature for poly(NIPAM-*co*-SPO-*co*-fluorophore) was determined by UV–vis spectroscopic method. The fluorescence intensity of poly(NIPAM-*co*-SPO-*co*-fluorophore) increased in the range at 20–45 °C. This suggests that the hydrophobic domain near the flurophore unit was increased with increasing temperature. In contrast, at gt; 45 °C, the fluorescence intensity decreased, suggesting that the intensity of excitation beam could be reduced by large hydrophobic polymer aggregates. The particle size of the aggregates was estimated to be 9000 nm at 45 °C by dynamic light scattering. We also revealed that the fluorescence intensity of the D-π-A type fluorophore is efficiently regulated by photochromic switching between spiro and merocyanine using alternate irradiation with UV and visible light which can be attributed to energy transfer from the excited fluorophore to the merocyanine.

Acknowledgements

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