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Spiropyran-Conjugated Thermoresponsive Copolymer as a Colorimetric Thermometer with Linear and Reversible Color Change

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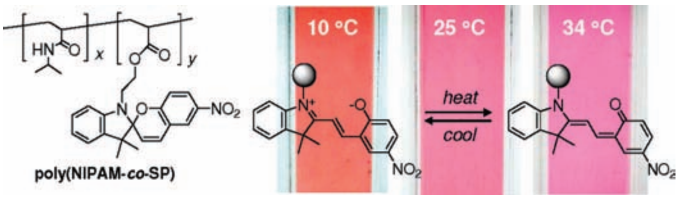
ABSTRACT



A simple copolymer, poly(NIPAM-*co*-SP), consisting of *N*-isopropylacrylamide and spiropyran units, behaves as a colorimetric thermometer exhibiting temperature-responsive linear and reversible bathochromic/hypsochromic shift of the absorption spectra under UV irradiation.

Development of supramolecular systems performing as colorimetric or fluorometric sensory materials has attracted much attention, since they allow prompt detection of analytes by simple spectroanalyses.[1] Of particular interest is the design of temperature sensors. Various molecular systems behaving as colorimetric[2,3] or fluorometric[4] thermometers have been proposed. These optical thermometers allow "remote" sensing of medium temperature, where no electric wires are required to connect the thermometers. These thermometers therefore have advantages over traditional thermometers in applications where electromagnetic noise is strong, sparks could be hazardous, and the environment is corrosive. Among the optical thermometers, colorimetric thermometers are more advantageous because of simplicity of temperature sensing. In particular, a thermometer exhibiting temperature-dependent bathochromic/hypsochromic shift of the absorption spectrum is favorable for accurate sensing. There is, however, only one report of a thermometer showing temperature-dependent absorption shift.[3] In addition, application of this thermometer is limited to the detection of a narrow temperature range ($\Delta T < 5$ °C), and the absorption spectrum does not shift reversibly with the change in temperature.

Spiropyran (SP) derivatives belong to a class of organic photochromes that have been studied intensively and have

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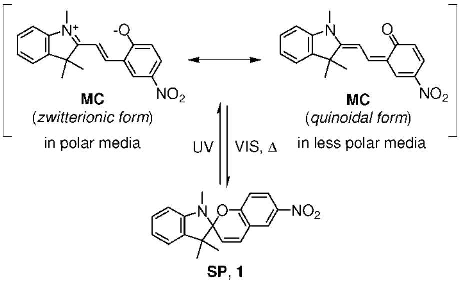
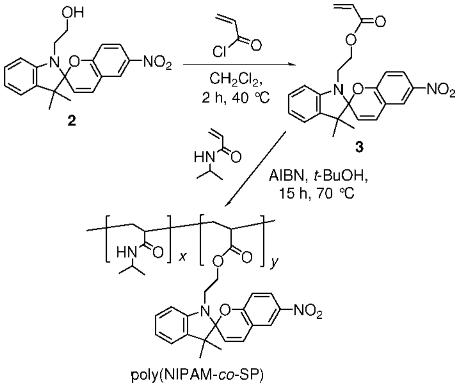
potential application as optical switches,[5] memories,[6] and sensors.[7] These dyes are converted to the colored merocyanine (MC) form upon irradiation with UV light but revert to the colorless SP form upon heating or visible light irradiation (Scheme 1). MC is a resonance hybrid of the zwitterionic and quinoidal forms, and the absorption spectrum of MC depends on the solvent polarity. The zwitterionic MC form is dominant in polar media, whereas the quinoidal MC form exists mainly in less polar media (Scheme 1);[8] the absorption spectrum of the MC species undergoes a bathochromic shift with a decrease in medium polarity (negative solvatochromism).

Scheme 1. Photoisomerization of SP Derivatives



Our colorimetric thermometer presented here is a simple copolymer, poly(NIPAM$_x$-*co*-SP$_y$) ($x/y = 15/1$), consisting of poly-*N*-isopropylacrylamide (NIPAM) and SP units (Scheme 2). It is well-known that polyNIPAM in water shows reversible coil-to-globule phase transition associated with hydration/dehydration of the polymer chain by temperature.[9] PolyNIPAM has a polar character at low temperature (coil), but a rise in temperature leads to the formation of a less polar domain inside the polymer associated with polymer aggregation (globule). Our thermometer employs the heat-induced polarity change of polyNIPAM. Upon UV irradiation, the polymer shows linear and reversible bathochromic/hypsochromic shift of the MC absorption with the change in temperature. This allows the accurate sensing of the temperature of a solution over a wide temperature range (10−34 °C) by measuring λ_{max} of the MC absorption.

Scheme 2. Synthesis of Poly(NIPAM$_x$-*co*-SP$_y$) ($x/y = 15/1$)



As shown in Scheme 2, poly(NIPAM-*co*-SP) is easily obtained by copolymerization of NIPAM monomer and acryl-modified SP derivative **3**, which is synthesized by reaction of **2**[10] with acryloyl chloride (Supporting Information, experimental procedure). Figure 1a shows the absorption spectra of poly(NIPAM-*co*-SP) in water. Without UV irradiation (blue line), the solution shows almost no absorption at >450 nm at any temperature, as is usually observed for related SP compounds.[5−7] UV irradiation ($\lambda = 254$ nm), however, creates strong absorption at 450−650 nm, assigned to the generation of the MC form.[11] At 10 °C, λ_{max} of the MC absorption is 519 nm. A rise in temperature leads to a continuous bathochromic shift of the band; λ_{max} at 34 °C is 546 nm ($\Delta\lambda_{10-34\,°C} = 27$ nm). As shown in Figure 1b, the solution color at 10 °C is orange but changes to pink and then to purple at 34 °C.

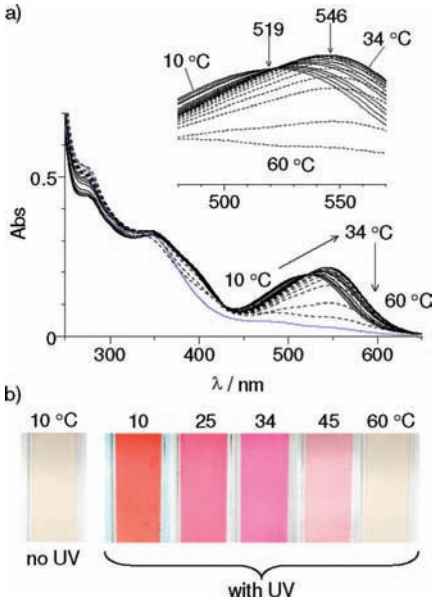


Figure 1. (a) Absorption spectra of poly(NIPAM-*co*-SP) in water (0.4 g L^{-1} containing 190 μM SP unit) measured (blue) without UV irradiation at 10 °C and (black) with UV (254 nm) irradiation during heating sequence. The measurement was started after UV irradiation at 10 °C for 5 min. The spectra at each temperature were obtained after stirring the solution for 1 min at the designated temperature with continued UV irradiation. At each temperature, the solution attains the photostationary state. (b) Photographs of the polymer solutions.

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Figure 2 (○) summarizes the change in λ_{max} with temperature. λ_{max} increases linearly with a rise in temperature at 10−34 °C, suggesting that the polymer allows accurate temperature sensing by measuring λ_{max} of the absorption band. As shown in Figure S2 (Supporting Information), the absorption spectra of unpolymerized SP compounds **1** and **2** (Schemes 1 and 2), scarcely change with temperature, indicating that the bathochromic shift of poly(NIPAM-*co*-SP) is driven by the phase transition behavior of polyNIPAM.

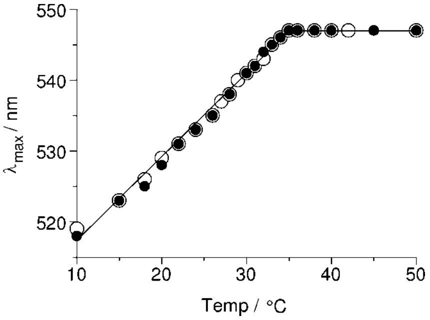


Figure 2. Change in λ_{max} of poly(NIPAM-*co*-SP) in water with temperature. The measurements were carried out during (○) heating or (●) cooling sequences under UV irradiation (254 nm). The measurements were started after UV irradiation at 10 or 50 °C for 5 min. The spectra at each temperature were obtained after stirring the solution for 1 min at the designated temperature with continued UV irradiation. At each temperature, the solution attains the photostationary state. Absorption spectra measured during the cooling sequence are shown in Figure S3 (Supporting Information).

The heat-induced bathochromic shift of the polymer is due to the formation of a less polar domain by polymer aggregation,[9] leading to isomerization of MC from zwitterionic to quinoidal form. The formation of a less polar domain is confirmed by ^{1}H NMR analysis of the polymer in D_2O. Figure 3 (☐) shows temperature-dependent change in the integrated intensity of C*H* resonance of the polymer chain and the NIPAM unit. The intensity decreases with a rise in temperature, indicating that the polymer indeed becomes less polar with polymer aggregation.[4d,e] The polymer aggregation is further confirmed by dynamic light scattering analysis.[9c] Also shown in Figure 3 (○), the formation of polymer particles is detected at >25 °C (detection limit, 3 nm), and the particle size increases with a rise in temperature. These findings clearly indicate that, as shown in Scheme 3, the heat-induced polymer aggregation leads to growth of the less polar domain. This promotes isomerization of MC from zwitterionic to quinoidal form, resulting in continuous bathochromic shift of the absorption band.[12]

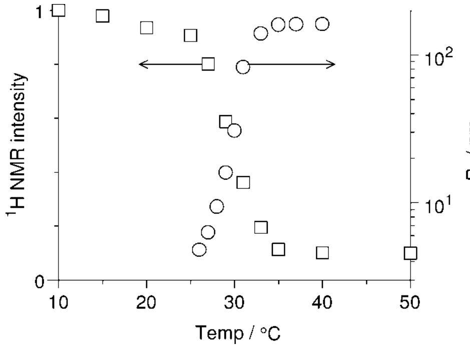
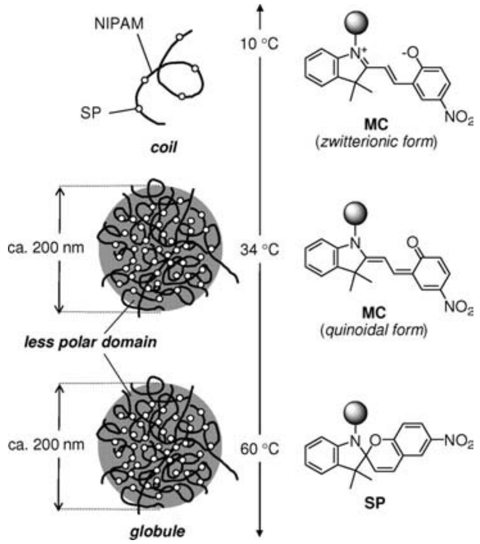


Figure 3. (☐) Temperature-dependent change in integrated intensity of C*H* resonance of the polymer chain and the NIPAM unit determined by ^{1}H NMR analysis of poly(NIPAM-*co*-SP) in D_2O, where the intensity at 10 °C is set as 1. (○) Change in hydrodynamic radius (R_h) of the polymer determined by dynamic light scattering analysis under UV irradiation. The ^{1}H NMR and R_h distribution data are shown in Figures S4 and S5 in Supporting Information.

Scheme 3. Mechanism of Bathochromic/Hypsochromic Shift of Absorption Spectra of Poly(NIPAM-*co*-SP) in Water under UV Irradiation



As shown in Figure 2, the bathochromic shift of the absorption spectra stops at >34 °C. This is because polymer

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(11) As shown in Figure S1 (Supporting Information), evolution of the MC absorption upon UV irradiation of the poly(NIPAM-*co*-SP) solution occurs within 5 min at any temperature, as is the case with unpolymerized SP compound.

aggregation terminates at this temperature range. As shown in Figure 3 (□), decrease in the ^{1}H NMR intensity of the polymer stops at >34 °C. In addition, as shown in Figure 3 (○), increase in R_h of the polymer particle also stops at >34 °C. These data clearly suggest that the growth of the less polar domain stops at >34 °C and, hence, suppresses further shift of the absorption band. At this temperature range, absorbance of MC decreases with a rise in temperature (Figure 1a); the solution color fades accordingly (Figure 1b). This is due to the thermal reversion of MC to the colorless SP form enhanced at higher temperature.[13] As shown in Figure S7 (Supporting Information), color fading of the polymer solution, when left in the dark after 5 min of UV irradiation, is indeed accelerated at higher temperature.[14]

It must be noted that the temperature-dependent linear shift of the absorption band at 10−34 °C occurs reversibly regardless of the heating/cooling sequence. As shown in Figure 2 (●), the λ_{max} profile obtained by cooling sequence is exactly the same as that obtained by the heating sequence (○). This is because structure change of the polymer occurs reversibly by temperature.[15] As is usually observed for related SP compounds,[16] visible light irradiation of the polymer leads to disappearance of the MC absorption due to isomerization of MC to the colorless SP form. As shown in Figure 4, at both 10 and 34 °C, the MC absorption bands, assigned to zwitterionic and quinoidal forms, disappear upon 5 min of visible light irradiation. Sequential UV irradiation of the solution, however, leads to regeneration of the absorption, where λ_{max} and absorbance do not change during the repeated UV/visible light irradiation. This indicates that the polymer allows repeated temperature sensing just by turning on UV light.

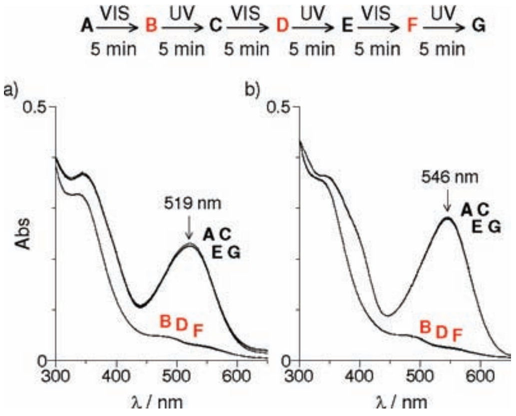

Figure 4. Change in absorption spectra of poly(NIPAM-*co*-SP) in water upon sequential irradiation of UV and visible light at (a) 10 and (b) 34 °C.

It is well-known that SP compounds are decomposed by UV irradiation.[17] As shown in Figure S9 (Supporting Information), prolonged UV irradiation of the polymer solution leads to decrease in MC absorption, indicating that parts of the SP moieties on the polymer are decomposed. However, λ_{max} of the MC absorption does not change during UV irradiation, indicating that partial decomposition of the SP moieties does not significantly affect the temperature sensing.

In summary, we have found that the simple copolymer poly(NIPAM-*co*-SP), when irradiated with UV light in water, behaves as a colorimetric thermometer exhibiting linear and reversible bathochromic/hypsochromic shift of the absorption spectrum in a wide temperature range (10−34 °C). Colorimetric temperature sensing may be realized by applying the basic concept, and the results presented here may contribute to the development of more efficient and useful temperature sensors.

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Supporting Information Available: Experimental procedures and Figures S1−S12. This material is available free of charge via Internet at http://pubs.acs.org.

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(12) As resported,[8a] λ_{max} of SP compounds, obtained in different solvents unUV irradiation, shows a linear relationship with the normalized Reichardt's solvent polarity parameter, E_T^N (Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319–2358.). As shown in Figure S6 (Supporting Information), λ_{max} of **1** indeed increases linearly with a decrease in E_T^N. Plots of the λ_{max} data for poly(NIPAM-*co*-SP) obtained at 10 °C (519 nm) and 34 °C (546 nm) indicates that a rise in temperature from 10 to 34 °C leads to increase in E_T^N of the inner polymer environment from 0.77 to 0.55, which is similar to the change in solvent from methanol to 2-propanol.

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(14) The thermal reversion rates at each temperature are determined to be 1.24×10^{-3} (25 °C), 2.92×10^{-3} (34 °C), 4.39×10^{-3} (40 °C), and 9.14×10^{-3} s^{-1} (50 °C), respectively. As shown in Figure S8 (Supporting Information), activation energy for the MC → SP isomerization of poly(NIPAM-*co*-SP) is determined by the Arrhenius plots to be 63.4 kJ mol^{-1}.

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