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Characteristic Phase Transition of Aqueous Solution of Poly(*N*-isopropylacrylamide) Functionalized with Spirobenzopyran

Kimio Sumaru,*,† Mitsuyoshi Kameda,† Toshiyuki Kanamori,† and Toshio Shinbo‡

Research Center of Advanced Bionics, National Institute of Advanced Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan, and Institute for Materials and Chemical Process, National Institute of Advanced Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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ABSTRACT: A novel functional copolymer was synthesized by modifying poly(*N*-isopropylacrylamide) with spirobenzopyran. The phase transition properties of the aqueous solution of this copolymer exhibited a logic-gate response to the light irradiation and to increased temperature, which has three different modes depending on the pH of the solution. Especially, a great increase in turbidity was observed even in dilute aqueous solution containing only 0.10 wt % of the copolymer although the copolymer contained spirobenzopyrans by only 1.1 mol %. It was confirmed also that the spirobenzopyran residues were isomerized by the influence of thermally induced phase transition of the same system. The main chain of thermoresponsive polymer and photoresponsive chromophores, which are linked closely together, affected each other.

Introduction

Modification of thermoresponsive polymers with sensitive groups that respond to various stimuli[1] has led to the development of functional copolymers that respond not only to temperature changes but also to other physical and chemical stimuli. Above all, light irradiation can be applied to the target in a local, contactless, and immediate manner, and therefore, photocontrol of the extent of polymer chain including its phase transition in solutions has been studied with various practical applications. In a pioneering study in this field, Irie et al.[2] synthesized poly(*N*-isopropylacrylamide) (pNIPAAm) partly modified with azobenzene chromophores and showed that the lower critical solution temperature (LCST) of its aqueous solution is shifted by light irradiation.[2] Later, Kröger et al.[3] found the photoinduced LCST shift of 20 °C for an aqueous solution of azobenzene-modified poly(*N*,*N*-dimethylacrylamide).

The swelling and shrinking of hydrogels have also been actively studied by using thermoresponsive polymers partly modified with ionic groups. Ilavsky et al.[4] reported that incorporating sodium methacrylate into a hydrogel of poly(*N*,*N*-diethylacrylamide) increased the phase-transition temperature. Brazel et al.[5] analyzed changes in the degree of swelling and the network mesh size of a hydrogel of pNIPAAm containing sodium methacrylate in response to changes in temperature and pH.

In addition, by introducing benzo[18]crown-6 as a side chain of pNIPAAm, Irie et al.[6,7] synthesized a functional polymer and obtained selective responses to the presence of specific ionic species. Later, by modifying a porous base membrane with the same polymer by plasma graft copolymerization, Yamaguchi et al.[8] and Ito et al.[9] constructed a membrane device whose permeability is controllable by both the presence of specific ions and changes in temperature.

Recently, Desponds et al.[10] proposed a new scheme for synthesizing functional copolymers and synthesized pNIPAAm partly modified with azobenzene chromophores and carboxyl groups as an example. Although they reported a photoinduced LCST shift at only one pH value, they suggested that this polymer responds to three different stimuli: light irradiation and changes in temperature and pH. In this strategy of adding various stimulus-responsive groups to a polymer, however, each kind of group acts on the polymer main chain in a parallel manner, and only simple additive effects are expected.

Instead of such a simple effect, we schemed to develop a polymer that would show a cooperative response to several stimuli, i.e., light irradiation and changes in temperature and pH, and synthesized a novel functional copolymer by modifying pNIPAAm with a spirobenzopyran. This chromophore is considered to have four different stable forms, and the proportion of each form varies in response to both the pH of the solution and whether it is irradiated with light.[11] Especially the photoisomerization of the chromophore resulted in a large change in its chemical structure and physical properties,[11−14] and effective photosensitivity of the polymer is expected even at small modification ratios.

On the basis of the detailed inspection of the spirobenzopyran residues, we systematically analyzed phase transitions in aqueous solutions of this new copolymer in the various conditions of light irradiation, temperature, and pH. We also discussed the isomerization of the chromophores affected by the thermally induced phase transition of the polymer main chain.

Experimental Section

Synthesis of pSPNIPAAm Copolymer. We synthesized the spirobenzopyran monomer by treating 1′,3′,3′-trimethyl-6-hydroxyspiro(2*H*-1-benzopyran-2,2′-indoline) with acrylic anhydride. The NIPAAm-based copolymer partly modified with a spirobenzopyran (pSPNIPAAm) was synthesized in a solution of distilled tetrahydrofuran (THF) by free-radical polymerization, with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator. The initial molar concentration of NIPAAm monomer,

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† Research Center of Advanced Bionics.

‡ Institute for Materials and Chemical Process.

* Corresponding author. E-mail: k.sumaru@aist.go.jp.

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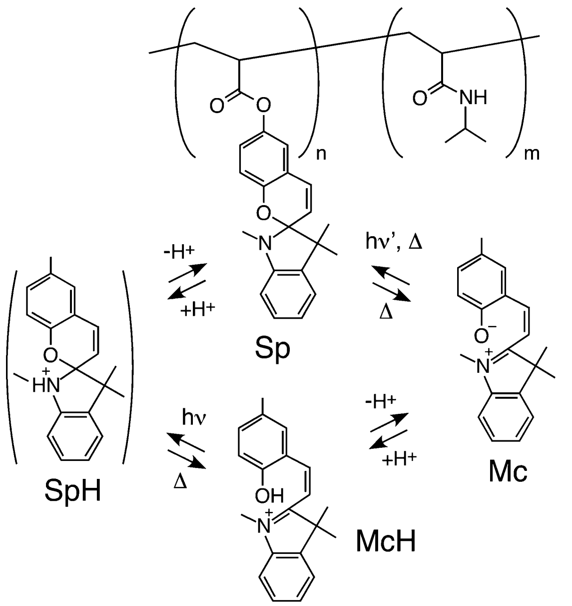

Figure 1. Photoisomerization and protonation of spirobenzopyran chromophore in pSPNIPAAm.

acrylated spirobenzopyran monomer, and initiator in the reaction solution were 2.0, 0.020, and 0.020 M, respectively. After deaeration by freezing and thawing, the reaction solution was polymerized by incubation at 60 °C for 12 h. The resulting solution was poured into diethyl ether, and the precipitate was collected and dried under vacuum to give pSPNIPAAm as a white powder (Figure 1, top). The molecular weight was determined by gel permeation chromatography (GPC; column, Shodex KF-805) at 25 °C with THF as the eluant; the weight-average and number-average molecular weights of pSPNIPAAm, estimated on the basis of polystyrene standards, were 22 000 and 7800, respectively. NMR and UV−vis absorbance measurements revealed that the fraction of the spirobenzopyran units in the synthesized pSPNIPAAm was 1.1 mol %, which agreed well with the molar ratio of the monomers in the initial solution.

Characterization of pSPNIPAAm Aqueous Solution. Absorbance/turbidity spectra of pSPNIPAAm in aqueous solution were measured with ~2.5 mL samples containing HCl and NaOH at various concentrations in a cuvette with an optical path length of 10 mm in a UV−vis spectrometer having a thermoregulated cell holder. To examine the proton dissociation of the chromophore introduced to pSPNIPAAm, NaOH was added to the aqueous solution of pSPNIPAAm (0.20 wt %) containing 0.50 mM HCl, which had been equilibrated at 25 °C. Then the solution was cooled to 0 °C, and the change of absorption spectra was measured swiftly at the temperature while NaOH was added in portions. Temperature dependence measurements were carried out for well-stirred solutions raising the temperature of the system stepwise. The UV−vis absorption spectra were collected after the spectra stabilized at each temperature. The typical rate of temperature increase was 1 °C/h. Dynamic light scattering (DLS) measurements were carried out with an Otsuka ELS-800 electrophoretic light scattering spectrophotometer having a thermoregulated cell holder. The light irradiation to the sample solutions were carried out with a Hamamatsu Photonics LC6 Xe light source and Ushio ModuleX ultrahigh-pressure Hg light source. In the spectroscopic measurements and DLS measurements, light from the Xe light source was guided to the well-stirred sample solutions, in a thermoregulated cell holder in the spectrometers, through a set of filters and a liquid-fiber light guide. The wavelength and total intensity of the irradiating light were 400−440 nm and 30 mW, respectively, for the irradiation to the samples in acidic or neutral conditions and 480−520 nm and 60 mW for basic conditions. In the observation of the appearance of the solution affected by light irradiation, the ultrahigh-pressure Hg light source and a set of filters were used to irradiate visible light on a well-stirred sample solution in a constant-temperature bath. The wavelength and intensity of the irradiating light were 400−440 nm and 20 mW/cm^2, respectively.

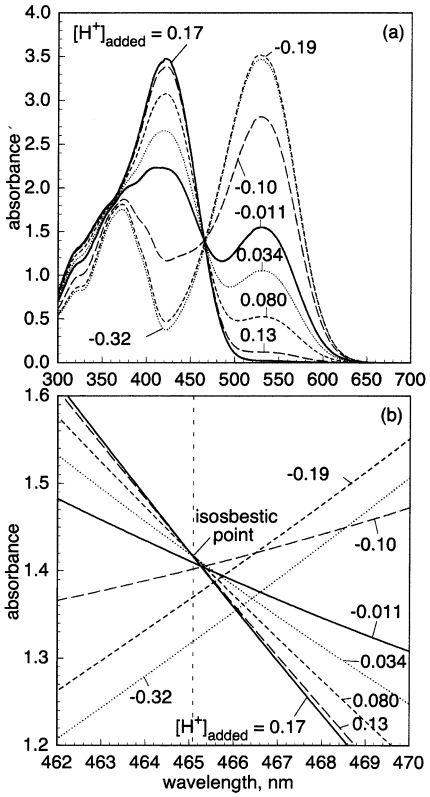

Figure 2. Absorption spectra of 0.20 wt % pSPNIPAAm in aqueous solution containing various concentrations of $[H^+]_{added}$. (a) Full spectra and (b) expanded view of the spectra at the isosbestic point.

Result and Discussion

Characteristics of Spirobenzopyran Residue. As shown in Figure 1, four different stable states are presumed for spirobenzopyran introduced for a side chain of pSPNIPAAm: a colored merocyanine with an open-ring structure (Mc) and a colorless spiro form with a closed-ring structure (Sp) and the protonated forms of each (McH and SpH). We found that the absorption band of $\lambda_{max} = 422$ nm attributed to McH[15] increased gradually and reached equilibrium after HCl was added to an aqueous solution of pSPNIPAAm in darkness at 25 °C. The absorbance value was hardly affected by changes in [HCl] at concentrations greater than 0.2 mM or by temperature changes at temperature in the range from 0 to 25 °C, which strongly suggests that all the chromophores are in the McH form under these conditions.

In the examination of the proton dissociation of McH, the absorbance attributed to McH decreased as NaOH was added to the solution, which had initially contained excess HCl (see Experimental Section), and another absorbance of $\lambda_{max} = 530$ nm attributed to free Mc increased. The experimentally obtained spectra at various concentrations of added proton ($[H^+]_{added}$ = [concentration of added HCl] − [concentration of added NaOH]) are shown in Figure 2. Under the condition of $[H^+]_{added} > 0$ mM, an isosbestic point was found at 465 nm. This result indicated that McH was converted into Mc, keeping the sum of the concentrations of McH and

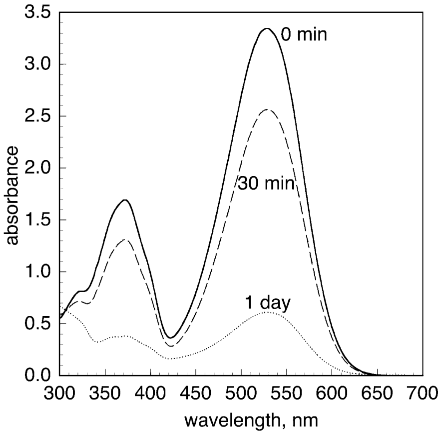

Figure 3. Absorption spectra of 0.20 wt % pSPNIPAAm in aqueous solution at $[H^+]_{added} = -0.32$ mM: solid line, just after addition of NaOH at 0 °C; dashed line, after allowing the solution to remain at 0 °C for 30 min; dotted line, after allowing the solution to remain at 0 °C for 1 day.

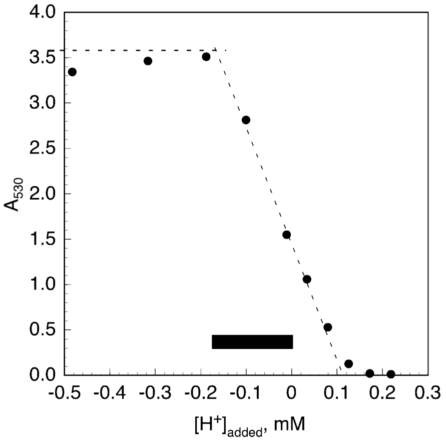

Figure 4. A_{530} plotted against $[H^+]_{added}$. A bar indicates the theoretical $[H^+]_{added}$ range in which titration of choromophore contained in the solution should be completed.

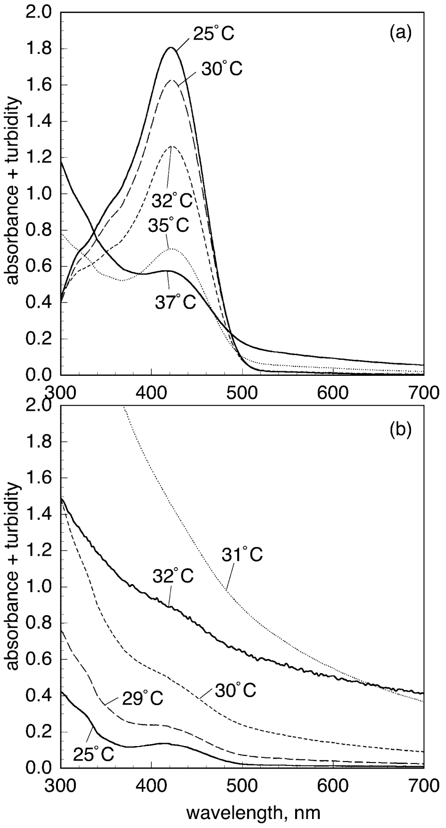

Figure 5. Absorbance/turbidity spectra of 0.10 wt % pSPNIPAAm aqueous solution at $[H^+]_{added} = 0.2$ mM (pH ≈ 4): (a) in the dark and (b) under light irradiation.

Mc constant (see Supporting Information). When $[H^+]_{added}$ was negative, however, the absorbance at this wavelength decreased as the amount of added NaOH increased (Figure 2b).

While the sample remained at 0 °C at an $[H^+]_{added}$ value of −0.32 mM, the absorbance in the wavelength range 300−650 nm decreased considerably as the time proceeded (Figure 3). In an equilibrium state (1 day after addition of NaOH), only 20% of choromophore remained in the Mc form. This experimental result suggested that Mc tends to isomerized thermally to Sp in an alkaline environment, and this isomerization caused small deviation of absorbance value at 465 nm, which was observed for negative $[H^+]_{added}$ value in Figure 2 (see Supporting Information).

The absorbance values at 530 nm (A_{530}) are plotted against $[H^+]_{added}$ in Figure 4. As NaOH was added to the solution, the value of A_{530} increased only in the $[H^+]_{added}$ range from 0.1 to −0.2 mM, exhibiting the typical tendency observed in acid−base titration. Upon further addition of NaOH, however, A_{530} decreased gradually due to the thermal isomerization of Mc to Sp as discussed above. A bar in the figure indicates the theoretical $[H^+]_{added}$ range in which titration of chromophore contained in the solution should be completed. Although the $[H^+]_{added}$ range in which A_{530} varied most actually was in approximate agreement with that calculated from the concentration of contained chromophore, the A_{530} value at $[H^+]_{added} = 0$ mM was about 30% of its maximum value, indicating that the chromophores in the merocyanine form were protonated to a certain extent under this condition. We estimated pK_a of McH roughly to be 6−7 from the results of absorption measurements in several buffer solutions, and pH measurements at the point of color change supported this estimation. We consider that this pK_a value, which is considerably small for phenol with ester group in the para position, is due to the resonance stabilization of phenolate ion[16] and to the electrostatic repulsion of proton by the positive charge of neighboring ammonium.[17] Therefore, Mc is not a strong base enough to take proton away from water molecules. As a result, it was suggested that our pSPNIPAAm prepared and purified as described above contained some proton source such as carboxyl groups by one per every 300 monomer units.

Phase Transition of pSPNIPAAm Solution. Here, we discuss the effects of irradiation with visible light and of temperature changes on the phase transition of 0.10 wt % pSPNIPAAm in aqueous solution under several conditions of $[H^+]_{added}$. Figure 5 shows the absorbance/turbidity spectra of the pSPNIPAAm aqueous solution at $[H^+]_{added} = 0.2$ mM (pH ≈ 4). As temperature raised gradually from 0 °C in darkness (Figure 5a), the absorbance attributed to McH ($\lambda_{max} = 422$ nm) did not change at the temperatures lower than 25 °C and decreased remarkably only around the phase separation temperature. This result suggests strongly that a part of McH groups isomerized to the colorless spiro form, which has a relatively hydrophobic closed-ring structure, due to the thermally induced phase

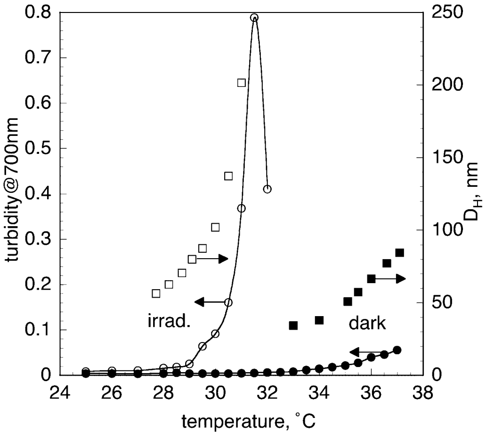

Figure 6. Temperature-dependent turbidity at 700 nm and D_H values of 0.10 wt % pSPNIPAAm aqueous solution at $[H^+]_{added}$ = 0.2 mM (pH ≈ 4): open symbols, under light irradiation; closed symbols, in the dark.

transition. Although the solution started to become turbid at 32.0 °C, the turbidity did not increase much even when the temperature increased up to 37.0 °C. The chromophores, which remained in McH form even at the temperature, were considered to stabilize the hydration of pSPNIPAAm quite effectively. On the other hand, under the irradiation with the light in the wavelength range 400−440 nm (Figure 5b), the absorbance at 422 nm was reduced considerably, indicating that McH groups were isomerized effectively to spiro form. The solution started to become turbid at 29.0 °C, and the turbidity increased sharply as temperature raised a few more °C, in good contrast to the nonirradiated condition.

Figure 6 shows the temperature-dependent turbidity at 700 nm of the solution under the same condition. The tendency varied with the condition of light irradiation. Although the value of turbidity measured for the irradiated solution decreased drastically as the temperature increased from 31.5 to 32.0 °C, this was due to sedimentation of precipitated pSPNIPAAm as a result of photoinduced dehydration, not to redissolution of the copolymer. Also, the temperature-dependent data of hydrodynamic diameter (D_H) observed by means of DLS are shown in Figure 6. D_H, which corresponds to the size of aggregates, is considered to reflect the aggregation state of the system[18] and showed a good agreement with the tendency of turbidity in both light and darkness. This supports the analysis in this study monitoring the phase transition through the turbidity change.

Figure 7 shows photoinduced changes in the absorbance/turbidity spectra when the same sample was irradiated with visible light after standing in darkness at 31.5 °C. The solution, which had been transparent in the dark, became markedly turbid, and the absorbance at 422 nm disappeared after the light irradiation for only a few minutes. The molar content of chromophores in pSPNIPAAm was relatively small (1.1 mol %) compared with previously reported photosensitive copolymers containing more than 3 mol % of chromophore.[2,3] Nevertheless, the photoinduced increase in turbidity was considerable, and the experimental data in Figure 7 appear noisy because of the presence of large precipitates.

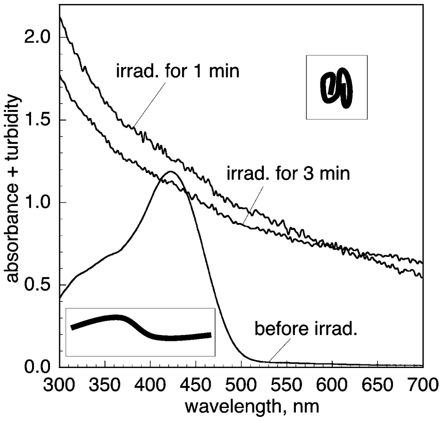

Figure 7. Photoinduced change in the absorbance/turbidity spectra of 0.10 wt % pSPNIPAAm aqueous solution at $[H^+]_{added}$ = 0.2 mM (pH ≈ 4) accompanied by the irradiation with visible light after standing in the dark at 31.5 °C.

Figure 8 shows the change in appearance of 0.10 wt % pSPNIPAAm acidic solution brought about by light irradiation. The solution at $[H^+]_{added}$ = 0.5 mM (pH ≈ 3), which had been kept in the darkness, was irradiated with blue light at 31.5 °C. Before the irradiation (a), the solution was transparent and was colored yellow due to the light absorption by McH, and the yellow color was lightened distinctly after light irradiation for 20 s (b). After an additional 5 s irradiation (c), the yellow color faded and the solution became slightly opaque. The turbidity of the solution was increased rapidly on further irradiation (d, e). When the stirring was stopped after irradiation for 50 s in total (f), visually observable precipitates were separated and suspended in the solution, which were sedimented after leaving for 5 min without stirring or irradiating (g). As described above, also Kröger et al. found copolymers whose aqueous solutions exhibit a large photoinduced LCST shift.[3] In their systems, however, the precipitates obtained above LCST were viscous and transparent phases containing a lot of water. In contrast, the precipitate separated from an irradiated pSPNIPAAm acidic solution we found in this study was solid containing a little amount of water, suggesting photoinduced dehydration of copolymer was much more remarkable than the system reported by Kröger et al. With the light irradiation with larger intensity, the photoinduced phase transition of pSPNIPAAm acidic solution was accelerated, indicating that the photoisomerization of spirobenzopyran triggered the dehydration of copolymer in an immediate manner.

Next, we discuss the phase transition of a pSPNIPAAm aqueous solution at $[H^+]_{added}$ = 0 mM (pH ≈ 7). Absorbance/turbidity spectra of the solution are shown in Figure 9. In darkness (Figure 9a), two absorbance peaks attributed to Mc and McH at 422 and 530 nm, respectively, were observed at 25.0 °C, since pSPNIPAAm prepared and used in this study contained some proton source as mentioned above. The absorbance at both peaks was small, suggesting that many of chromophores were in the colorless Sp state and pSPNIPAAm was not photochromic. Practically, the solution exhibited similar behavior either in the dark or under light irradiation of 400−440 nm wavelength (Figure 9b).

Figure 10 shows the temperature-dependent turbidity at 700 nm of the solution under the same condition. Whether the sample was irradiated with the light or not, the solution greatly became turbid as the temperature was increased above 30.0 °C at $[H^+]_{added}$ = 0 mM (pH ≈ 7). This may have occurred because many of chromphores were in the relatively hydrophobic Sp state regardless of light irradiation. At temperature above

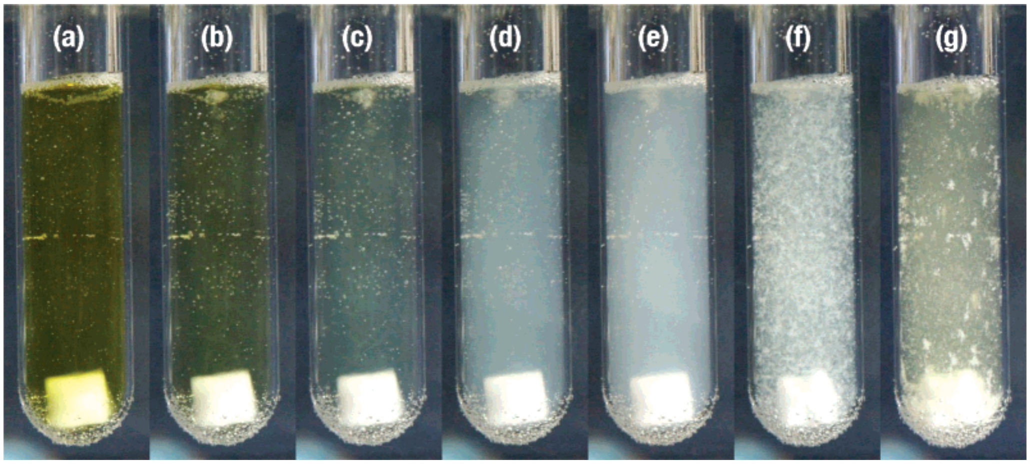

Figure 8. Photoinduced change in the appearance of 0.10 wt % pSPNIPAAm aqueous solution at $[H^+]_{added} = 0.5$ mM (pH ≈ 3) accompanied by the irradiation with visible light after standing in the dark at 31.5 °C. The wavelength and intensity of the irradiating light were 400−440 nm and 20 mW/cm^2, respectively.

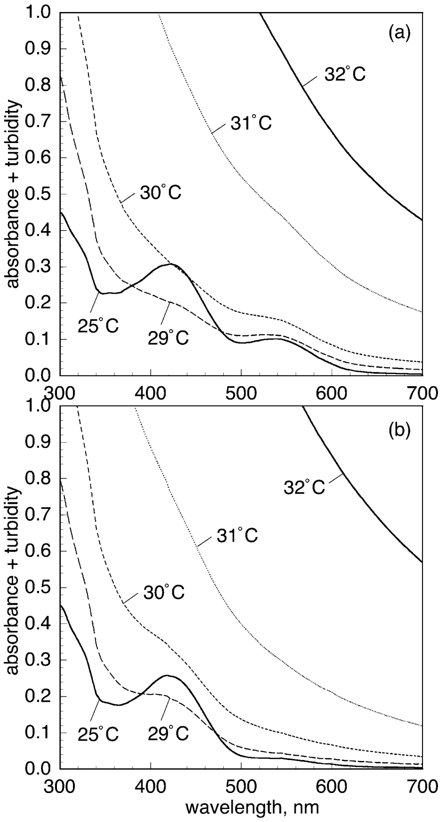

Figure 9. Absorbance/turbidity spectra of 0.10 wt % pSPNIPAAm aqueous solution at $[H^+]_{added} = 0$ mM (pH ≈ 7): (a) in the dark and (b) under light irradiation.

32.0 °C, the appearance of the solution varied depending on whether it was irradiated with the light; while the polymer aggregates remained suspended rather stably in darkness, the optical density decreased due to sedimentation of precipitated polymer during light irradiation.

Subsequently, the absorbance/turbidity spectra obtained for 0.10 wt % pSPNIPAAm aqueous solution at $[H^+]_{added} = -0.3$ mM (pH ≈ 10) are shown in Figure 11. As seen also in Figure 3, the spectra data at 0 °C showed that only about 20% of all the chromophores were in the Mc form, and many of chromophores were in the Sp form having the closed-ring structure in an alkaline environment even in the darkness (Figure 11a).

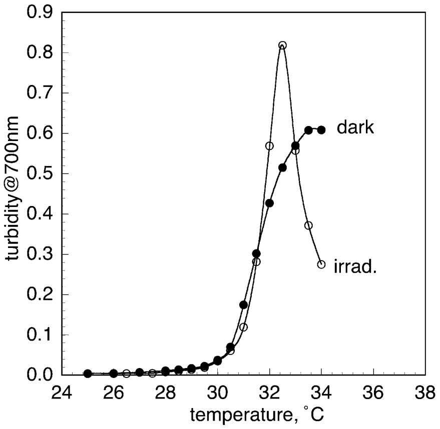

Figure 10. Temperature-dependent turbidity at 700 nm of 0.10 wt % pSPNIPAAm aqueous solution at $[H^+]_{added} = 0$ mM (pH ≈ 7): open symbols, under light irradiation; closed symbols, in the dark.

Similarly to the tendency found for $[H^+]_{added} = 0.2$ mM (pH ≈ 4), the absorption band at 530 nm, which is attributed to the Mc form, decreased as the temperature was increased to 30.0 °C (Figure 11b). In this case, a temperature range in which the absorbance started to decrease was far below the LCST of the solution, and this is an interesting finding that we will discuss separately.[19] In the irradiated sample, this absorption band, which had been suppressed by the light irradiation at 0 °C, increased as the temperature was increased (Figure 11b). This was not due to a shift in the equilibrium of the isomerization between Mc and Sp, but due to the increase in the rate constant for the thermal recovery of Mc from Sp in darkness; in the measurement, it took about 30 s to scan the wavelength range around 530 nm after the light was turned off, and the recovery of Mc from Sp during this period may have affected the experimental results. We confirmed that the recovery of Mc from Sp in darkness is faster at higher temperatures. Putting the data shown in Figure 3 together, these experimental results indicated that the activation energy in the isomerization from Mc to Sp is not much larger than the thermal energy at 0 °C.

Figure 12 shows the temperature-dependent turbidity at 700 nm of the solution under the same conditions. Regardless of the light irradiation, the solution was hard to become turbid, and a distinct increase of the turbidity was not observed even at 36.0 °C. Although Figure 11

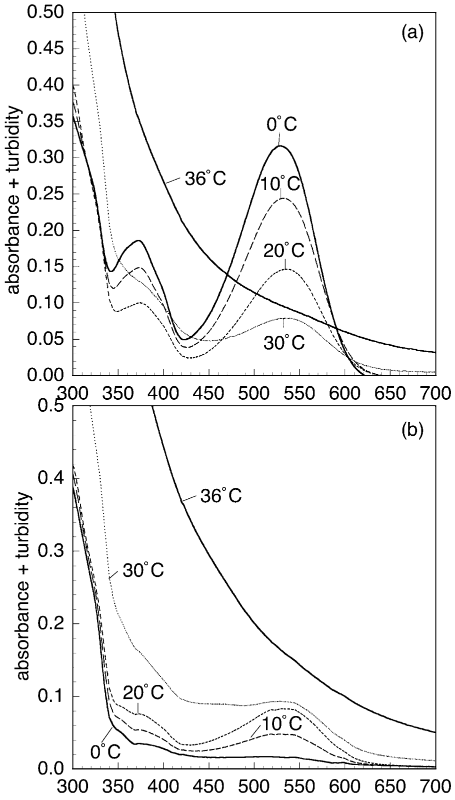

Figure 11. Absorbance/turbidity spectra of 0.10 wt % pSPNIPAAm aqueous solution at $[H^+]_{added} = -0.3$ mM (pH ≈ 10): (a) in the dark and (b) under light irradiation.

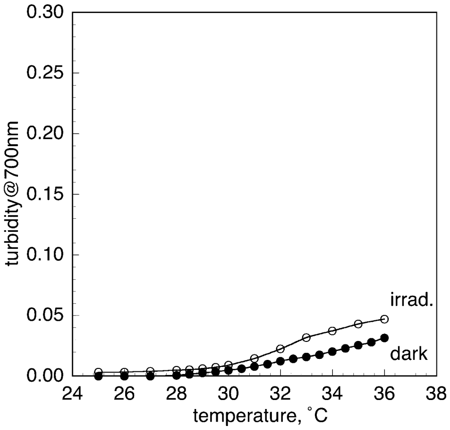

Figure 12. Temperature-dependent turbidity at 700 nm of 0.10 wt % pSPNIPAAm aqueous solution at $[H^+]_{added} = -0.3$ mM (pH ≈ 10): open symbols, under light irradiation; closed symbols, in the dark.

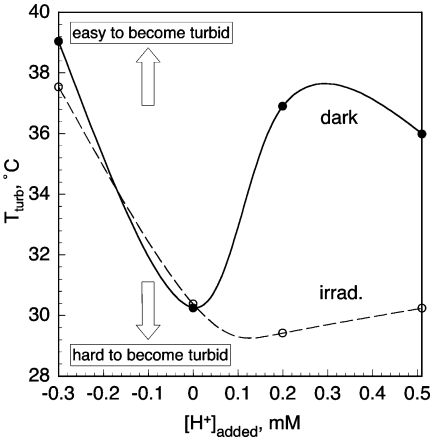

Figure 13. Dependence of T_{turb} on $[H^+]_{added}$ and the condition of light irradiation (see the text for details): open symbols, under light irradiation; closed symbols, in the dark.

Table 1. Characteristic Response of Phase Transition of pSPNIPAAm Aqueous Solution to Light Irradiation and Change in Temperature and pH

		T (turbidity)[a]		
H (temperature)	*L* (irradiation)	pH < 5	pH ≈ 7	pH > 9
1 (32−36 °C)	1	1	1	0
1 (32−36 °C)	0	0	1	0
0 (<30 °C)	1	0	0	0
0 (<30 °C)	0	0	0	0
logic expression of *T* using *H* and *L*		*HL*	*H*	0

[a] *H*, *L*, and *T* are defined as Boolean variables relating to temperature, light irradiation, and the turbidity of the solution that occurs in response to these stimuli, respectively. *H* is 1 when the temperature is higher than 32 °C and 0 when it is lower than 30 °C; *L* is 1 when the solution is irradiated with light and 0 when it is left in darkness; *T* is 1 when the solution is turbid and 0 when it is transparent.

indicates that most of the chromophores were in the hydrophobic Sp state as well as at $[H^+]_{added} = 0$ mM (pH ≈ 7), the solution at $[H^+]_{added} = -0.3$ mM (pH ≈ 10) did not become turbid easily. With respect to this point, conversion of a very small portion of the monomer units constituting pSPNIPAAm to acrylic acid in the process of polymer synthesis may account for this observation; carboxyl groups dissociated under alkaline conditions, and the resultant net charge enhanced the hydration of the polymer chains.[1,20] As discussed in the previous subsection, pSPNIPAAm prepared and purified in this study was suggested to contain some proton source by one per every 300 monomer units. Although the influence of such a small amount of carboxyl groups should not be great,[4] synergistic effect with the chromophores may have unexpected effects on the phase transition of the system.

To aid in discussing our findings relating to turbidity, here we define T_{turb} as the temperature at which the turbidity (in 10 mm optical path length at 700 nm) of a 0.10 wt % pSPNIPAAm aqueous solution is 0.05. Figure 13 shows the dependence of T_{turb} on $[H^+]_{added}$ and on light irradiation. At $[H^+]_{added} = -0.3$ mM (pH ≈ 10), the solution did not readily become turbid, and T_{turb} was high (about 38 °C); at $[H^+]_{added} = 0$ mM (pH ≈ 7), T_{turb} was low (about 31 °C). At both values of $[H^+]_{added}$ (0 and −0.3 mM), the value of T_{turb} did not depend on whether the sample was irradiated with the light or not. When excess protons were contained (pH = 3−4), however, T_{turb} was changed largely in response to light irradiation. Characteristic phase transitions (turbidity, *T*) of pSPNIPAAm in aqueous solution in response to light irradiation (*L*) and changes in temperature (*H*) are summarized in logical expressions tabulated in Table 1. It is clearly shown that the phase transition has three different modes corresponding to the pH of the solution: At high pH (>9), *T* is 0 regardless of the values of *H* and *L*. When the solution is nearly neutral (pH ≈ 7), *T* is the same as *H* regardless of the value of *L*. Under acidic conditions (pH < 5), *T* is 1 only when both *H* and *L* are 1 and otherwise is 0 (here *T* is the logical product of *H* and *L*).

Conclusion

We synthesized a novel functional copolymer by modifying pNIPAAm with spirobenzopyran moieties and have investigated the cooperative effects of light irradiation and changes in temperature and pH on the phase transition of the aqueous copolymer solution. We found that the copolymer solution exhibits a logic-gate response to light irradiation and the temperature increases, with three different modes depending on the pH of the solution. This unique characteristic is due mainly to interaction between the main chain of the thermoresponsive pNIPAAm and spirobenzopyran moieties, which respond to both light irradiation and pH changes. Such a unique behavior was not found in the earlier studies in which thermosensitive polymers were modified with several different residues in an attempt to obtain an additive effect.

On the other hand, the photoinduced phase transition found in this study was drastic, and increases in turbidity (at 700 nm, 10 mm optical path length) were observed to be up to 0.7 for a dilute aqueous solution containing only 0.10 wt % of the copolymer. It is interesting that such a drastic dehydration of polymer was brought about by the photoisomerization of small proportion (only 1.1 mol %) of chromophores introduced into the pNIPAAm. This was probably due to not only the drastic change in the chemical structure of the chromophores used in this study but also the short distance between the polymer main chain and the chromophores; the spirobenzopyrans were directly connected to the polymer main chain through ester bonds, and so we suggest that photoisomerization of the chromophores directly affected the hydration of the polymer main chain. In addition, we confirmed also that the spirobenzopyran residues were isomerized in response to the influence of the thermally induced phase transition of the copolymer solution. Putting the photoinduced phase transition together, we can conclude that the main chain of the thermoresponsive polymer and the photoresponsive chromophores, which were linked closely together, affect one another. These observations obtained in this study were expected to provide an important clue to design functional copolymers containing various stimuli-responsive components.

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Supporting Information Available: Isosbestic point with respect to proton dissociation of McH. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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