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Reversible and Efficient Proton Dissociation of Spirobenzopyran-Functionalized Poly(*N*-isopropylacrylamide) in Aqueous Solution Triggered by Light Irradiation and Temporary Temperature Rise

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Various researches have been carried out to develop the functional polymers whose ion dissociation can be controlled by the light irradiation.[1,2] Very recently, Kimura et al. reported that selective extraction of alkali metal ions was switched with light by using vinyl polymers incorporating a crowned spirobenzopyran at the side chain.[2] In this paper, we describe the efficient and reversible proton dissociation in an aqueous solution of spirobenzopyran choromophore introduced in poly(*N*-isopropylacrylamide) (pNIPAAm) which is triggered by both light irradiation and temporary temperature rise.

The polymer we used in this study (pSPNIPAAm) was pNIPAAm incorporating 3.0 mol % acryl ester of 1′,3′,3′-trimethyl-6-hydroxyspiro(2*H*-1-benzopyran-2,2′-indoline). In acidic conditions, spirobenzopyran at the polymer side chain was in the protonated open-ring form (McH) with a strong absorption band at 422 nm (molar absorption coefficient is 18.9 mM^{-1} cm^{-1}).[3] In the process of isomerization from the McH form to the closed-ring form, it is considered to dissociate a proton (Figure 1).[4−6] On the other hand, pNIPAAm, which consists of the main chain of pSPNIPAAm, is thermoresponsive as well known and exhibits drastic dehydration at temperatures higher than the critical temperature (~32 °C).

Figure 2 shows the change in specific conductance (K) and absorbance at 422 nm (A_{422}) of 0.10 wt % pSPNIPAAm aqueous solution (chromophore concentration: 0.25 mM) containing 0.26 mM HCl at 20 °C when it was irradiated repeatedly with blue light (400−440 nm, 30 mW). Before the irradiation, A_{422} indicated that 76% of all the chromophores were in McH form. After the first irradiation for 1 min, A_{422} decreased remarkably, indicating that most chromophores, which had been in McH form, were isomerized to the colorless closed-ring form. Simultaneously, K increased by 79%, suggesting strongly the efficient proton dissociation. After the light was turned off, K and A_{422} approached gradually to the values before the irradiation. As a result of curve-fitting analysis, this relaxation behavior turned out to have a major mode with the time scale of 1.5 h and a minor and slow mode with the time scale of 1 day. Since the interval of irradiations (~20 h) was not long enough, K and A_{422} just before the second or third irradiation did not return to the initial values before the first irradiation due to the minor and slow relaxation mode. However, more than 50% of the chromophores were isomerized repeatedly by the light, and the conductance increased correspondingly, indicating that the photoresponsive process was reversible.

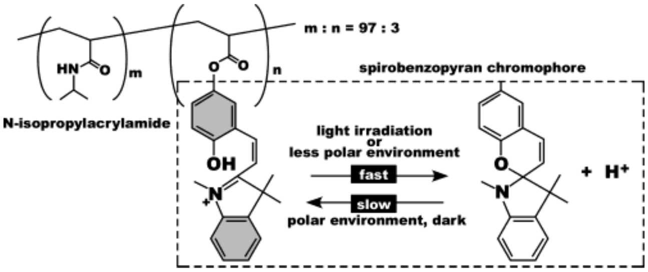

Figure 1. Chemical structure of pSPNIPAAm and characteristics of its components: pNIPAAm main chain and spirobenzopyran side chain.

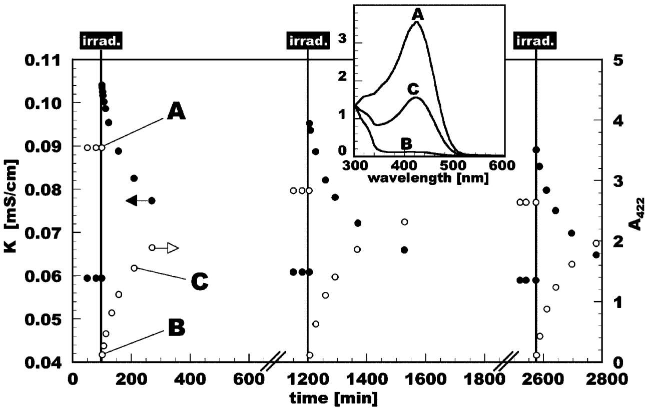

Figure 2. Change in specific conductance (closed circles) and absorbance at 422 nm (open circles) of 0.10 wt % pSPNIPAAm aqueous solution (chromophore concentration: 0.25 mM) containing 0.26 mM HCl at 20 °C as irradiated repeatedly with blue light. Inset: absorbance spectra of the solution (A) before, (B) just after, and (C) 2 h after the first irradiation.

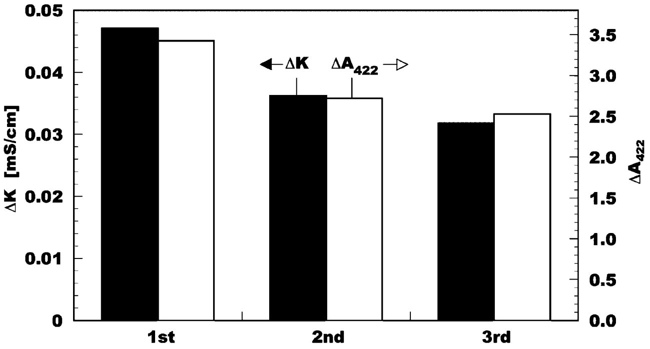

Figure 3. ΔK (black bars) and ΔA_{422} (white bars) of 0.10 wt % pSPNIPAAm aqueous solution containing 0.26 mM HCl at 20 °C in each irradiation. Relative scale of each parameter is arbitrary.

With respect to the response of K and A_{422} to the light irradiations shown in Figure 2, their absolute differential values before and just after each irradiation (ΔK and ΔA_{422}) are shown in Figure 3. In all cases, $\Delta K/\Delta A_{422}$ were in good agreement with one another, indicating that the change in the conductance value was proportional to the amount of the isomerized chro-

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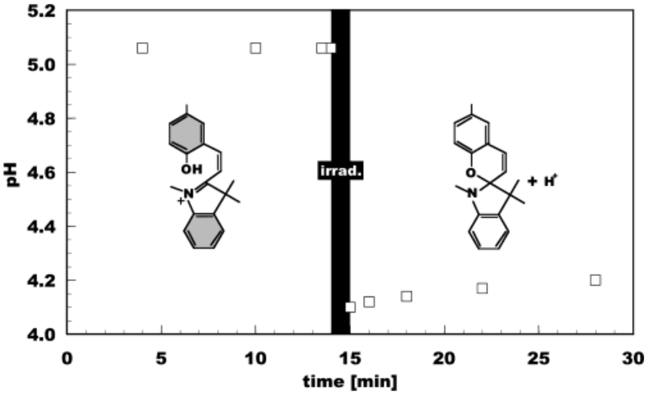

Figure 4. pH change of 0.10 wt % pSPNIPAAm aqueous solution (chromophore concentration: 0.24 mM) containing 0.14 mM HCl and 0.11 mM NaCl at 20 °C when it was irradiated with blue light for 1 min.

mophores. From the values of ΔA_{422} and molar absorption coefficient of McH, the concentration of the chromophores isomerized from McH form to closed-ring form in the first irradiation was estimated to be 0.18 mM (74% of the total chromophore concentration). On the other hand, assuming the differential molar conductance accompanied by the proton dissociation from McH to be 0.3 mS cm^{-1} mM^{-1} as its feasible value at 20 °C, the concentration of proton dissociated through photochromism of McH was calculated from ΔK to be 0.16 mM, which is close to the concentration of the isomerized chromophores estimated above from ΔA_{422}. This estimation suggested that the photoinduced proton dissociation was nearly stoichiometric, and most of the chromophores in the closed-ring form were not protonated even in such acidic conditions. As to this point, Menger and Perinis reported that no protonation at the tertiary amine of spirobenzopyrans with electron-withdrawing substituents in the closed-ring form was detectable by NMR even at acidic conditions.[4]

Figure 4 shows the pH change of 0.10 wt % pSPNIPAAm aqueous solution (chromophore concentration: 0.24 mM) containing 0.14 mM HCl and 0.11 mM NaCl at 20 °C when it was irradiated with blue light temporarily for 1 min. The pH value, which had exceeded 5 before the irradiation, decreased after the irradiation by about 1, indicating that the activity of proton increased by 10 times. Since we estimated roughly the pK_a of McH to be 6−7,[3] this result suggested that pK_a change brought about to the chromophore through photoisomerization is greater than 2. Also for the pH value, relaxation behavior was observed after the light was turned off. Together with the results of conductance measurement, it was confirmed experimentally that pSPNIPAAm dissociates protons in aqueous solution quite efficiently in response to the visible light irradiation. Since the dipole moments of two isomers of spirobenzopyran are widely different, and the activation energy in the isomerization is relatively low, the isomerization ratio of spirobenzopyran is greatly influenced by the surrounding dielectric environment.[7] As a matter of fact, we found in the previous study that McH incorporated into pNIPAAm isomerized quickly to the closed-ring form even in the darkness when the pNIPAAm main chain dehydrates due to the thermally induced phase transition.[3] To investigate the effect of the isomerization through this mechanism on proton dissociation, we monitored K and the absorbance spectrum of 0.10 wt % pSPNIPAAm aqueous solution (chromophore concentration: 0.24 mM) containing 0.48 mM HCl as its temperature was raised from 10 to 60 °C temporarily and cooled back to 10 °C (Figure 5). A_{422} decreased remarkably in the temporary rise of temperature, indicating that isomerization of McH to closed-ring form was caused by the thermally induced dehydration of the pNIPAAm main chain. Although K increased correspondingly to the temperature rise, this is mainly due to the temperature dependence of ion conductivity itself. However, the value of K just after the temperature rise ("B" in Figure 5) was greater than the initial value ("A") by 0.041 mS mM^{-1} cm^{-1}, suggesting the efficient proton dissociation.

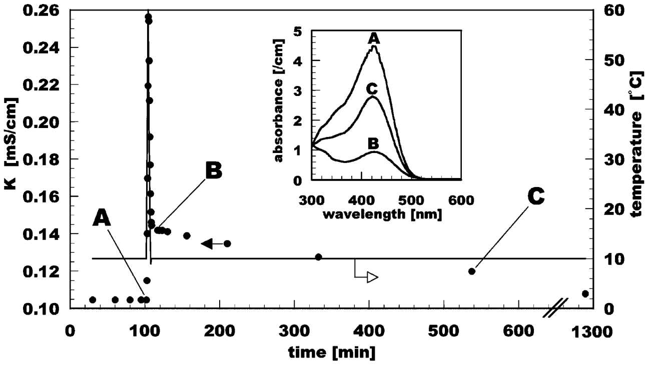

Figure 5. Change in specific conductance (closed circles) of 0.10 wt % pSPNIPAAm aqueous solution (chromophore concentration: 0.24 mM) containing 0.48 mM HCl as its temperature (solid line) was raised from 10 to 60 °C temporarily and brought back to 10 °C. Inset: absorbance spectra of the solution (A) before, (B) just after, and (C) 7 h after the temporary temperature rise.

From the experimental results described above, we conclude that the spirobenzopyran chromophore incorporated into pNIPAAm as a side chain exhibited the efficient photoresponsive proton dissociation in an acidic aqueous solution. It was confirmed also that the proton dissociation was brought about by the thermally induced dehydration of the pNIPAAm main chain. In our previous study, we found in the similar copolymer that the spirobenzopyran incorporated into pNIPAAm by only 1 mol % triggered the dehydration of the whole polymer chain in a certain temperature range.[3] Together with that result, it was revealed that the hydration of polymer and the isomerization of chromophore accompanied by the efficient proton dissociation interact with each other in the aqueous solution of pSPNIPAAm. This unique mechanism will provide a new principle for the development of stimuli-responsive polymers.

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Supporting Information Available: Experimental procedures for the synthesis of pSPNIPAAm and the characterization of aqueous polymer solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Irie, M.; Kunwatchakun, D. *Macromolecules* **1986**, *19*, 2476.
(2) Kimura, K.; Sakamoto, H.; Uda, R. M. *Macromolecules* **2004**, *37*, 1871.
(3) Sumaru, K.; Kameda, M.; Kanamori, T.; Shinbo, T. *Macromolecules* **2004**, *37*, 4949.
(4) Menger, F. M.; Perinis, M. *Tetrahedron Lett.* **1978**, *47*, 4653.

(5) Williams, R. M.; Klihm, G.; Braslavsky, S. E. *Helv. Chim. Acta* **2001**, *84*, 2557.
(6) Willner, I.; Lion-Dagan, M.; Marx-Tibbon, S.; Katz, E. *J. Am. Chem. Soc.* **1995**, *117*, 6581.
(7) Drummond, C. J.; Furlong, D. N. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3613.

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