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# Analysis of photo-induced hydration of a photochromic poly(*N*-isopropylacrylamide) – Spiropyran copolymer thin layer by quartz crystal microbalance

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**Abstract**

We investigated hydration and swelling behavior of a solid state photoresponsive copolymer in water by using a quartz crystal microbalance technique with dissipation measurement (QCM-D technique). On the gold film electrode of a quartz resonator, we deposited a thin layer of a pNSp–NIPAAm, which is a poly(*N*-isopropylacrylamide) (pNIPAAm) polymer partially modified with a photochromic chromophore, 6-nitrospiropyran (NSp). Using QCM-D measurements, we found that at a temperature of 19 °C both water adsorption and changes in the viscoelasticity of the solid pNSp–NIPAAm layer were induced when pNSp–NIPAAm was irradiated by 365 nm ultraviolet light, which triggers the photoisomerization of the NSp chromophore and makes the structure of the chromophore hydrophilic. At temperatures between 25 and 35 °C, this photo-induced hydration was not observed. These observations suggest that the photoisomerization of the NSp chromophores triggered the photo-induced hydration only when pNIPAAm component is sufficiently hydrophilic, at a temperature of 19 °C.

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**Keywords:** Quartz crystal microbalance; QCM; QCM-D; Photofunctional polymer; Spiropyran; Hydration

**1. Introduction**

Photofunctional copolymers utilizing photosensitive chromophores have been developed, and thin

layers of such copolymers immobilized on basal substrates give rise to photoresponsive phenomena, such as photo-induced surface relief formation [1,2] and the photocontrol of gas permeability [3,4]. The changes in the hydrophilicity or electric charge upon light irradiation of photofunctional copolymers dissolved in water also have been reported [5–9]. These phenomena have been applied to the development

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of functional surfaces on which cell adhesion can be photocontrolled [10,11] as well as a gel-functionalized, photoresponsive permeable membrane, in which the gel's hydration and swelling can be controlled by light irradiation and temperature changes [12]. To investigate the photoresponsive change in the hydration state of poly(*N*-isopropylacrylamide) (pNIPAAm) modified with a spiropyran chromophore, Sumaru et al. used the turbidity change of a dilute aqueous solution of the copolymer [9]. However, this method cannot detect changes in a polymer's hydration state when the changes are only slight (i.e. not substantial enough to induce phase transitions), nor can the method detect changes in the hydration state of solid polymers immobilized on a basal solid. Although contact angle measurement is a well-known method for evaluating surface properties of materials [13–15], it is not sensitive enough to detect small changes in surface hydrophilicity.

In recent years, the quartz crystal microbalance (QCM) technique has been shown to be a sensitive and practical tool for real-time measurement of mass adsorption from solution onto a quartz resonator [16,17]. In the QCM technique, the adsorbed mass is proportional to the decrease in the quartz crystal's resonant frequency, as expressed by the Sauerbrey relation [18]. Furthermore, it has been reported that the technique can be applied to evaluation of the hydration states of a hydrophilic species such as protein [19] and pNIPAAm [20] in water. Höök et al. indicated that the mass of water incorporated in a hydrated protein layer can be estimated by the shift in resonant frequency when the hydration state is changed [19]. However, observation of the changing QCM resonant frequency does not permit the precise determination of adsorbed water mass when the adsorbed layer is viscoelastic [21] since the resonant frequency is also affected by the viscoelasticity of the adsorbed layer [22]. In order to measure the viscoelasticity of a polymer using QCM, information regarding the dissipation factor of QCM measurements must be known in addition to the resonant frequency [23,24]. Höök et al. indicated that the simultaneous, real-time measurement of resonant frequency and dissipation factor by a new QCM technique that includes dissipation measurement (QCM-D technique) [25] is effective to evaluate the hydration state of viscoelastic adsorbed layers [19,21].

In this study, by using the QCM-D technique, we investigated the hydration and swelling behavior of

a solid state, thin layer of pNIPAAm partially modified with a photochromic dye, 6-nitrospiropyran, which responds to light irradiation and temperature changes. We observed that UV irradiation-induced swelling of the copolymer in water exhibits a temperature dependence, with swelling being induced at 19 °C.

## 2. Experimental

### 2.1. Synthesis and characterization of the spiropyran-modified poly(*N*-isopropylacrylamide)

We synthesized the spiropyran monomer (*N*-(3-[3-(3,3-dimethyl-6'-nitrospiro-(2H-1'-benzopyran-2,2'-indol-1-yl)-propionylamino)-propyl]-2-methylacrylamide)) containing the photochromic dye 6-nitrospiropyran (NSp) according to published literature procedures [26,27]. The *N*-isopropylacrylamide (NIPAAm)-based copolymer containing the spiropyran residue (pNSp–NIPAAm) (Fig. 1) was synthesized in a solution of distilled tetrahydrofuran by free-radical polymerization with 2,2'-azobis(isobutyronitrile) as an initiator. The initial molar ratio of NIPAAm monomer, spiropyran monomer, and initiator in the reaction solution was 95:5:1. The reaction solution was stirred at 65 °C for 4 d under vacuum and precipitated in diethyl ether, and the pNSp–NIPAAm precipitate was collected and dried under vacuum, giving a brownish white powder. The weight-average molecular weight was determined to be  $3.9 \times 10^4$  g/mol by gel permeation chromatography using a Shodex LF-804 column (Showa Denko, Tokyo, Japan) with a

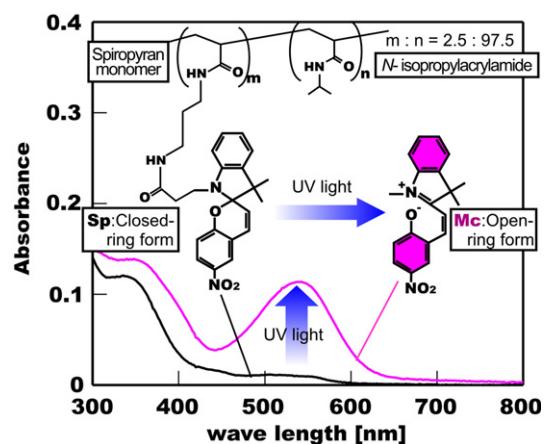


Fig. 1. Chemical structure of pNSp–NIPAAm and absorbance spectra of 0.005 wt% pNSp–NIPAAm aqueous solution measured both before and after UV irradiation at 19 °C.

polyethylene glycol standard and 10 mM LiBr in *N,N*-dimethylformamide as the eluent. The fraction of the spiropyran units was estimated to be 2.5 mol% by NMR measurement. Absorbance and turbidity spectra of aqueous copolymer solutions (or dispersions) were measured using a UV-vis spectrophotometer (V570, JASCO, Tokyo, Japan). Photoisomerization of NSp chromophores contained in a 0.005 wt% polymer solution was monitored using the 540 nm absorbance peak, which we attribute to the presence of the open-ring, or merocyanine (Mc), form of the chromophore. As a measure of phase transition, the dissolution temperature ( $T_d$ ) of the pNSp–NIPAAm dissolved in water was defined as the temperature at which the turbidity of a 0.05 wt% aqueous pNSp–NIPAAm solution began to decrease when the solution was cooled from 35 to 15 °C, as monitored by turbidity at 700 nm, where NSp does not absorb any light.

## 2.2. Theory of QCM-D for measurement of polymer hydration

In the ordinary QCM technique, a resonant frequency shift is proportional to the mass adsorbed on the quartz resonator,  $\Delta m$  [ng cm<sup>-2</sup>], through the Sauerbrey relation, given below [18].

$$\Delta m = -\frac{C}{n} \Delta f_n \quad (1)$$

$C$  is the mass sensitivity constant, equal to 17.7 ng cm<sup>-2</sup> Hz<sup>-1</sup> in this study, and  $\Delta f_n$  [Hz] is the resonant frequency at an overtone number  $n$  (e.g. 1, 3, 5, 7 . . .). The technique has been applied to evaluation of the hydration state of hydrophilic species such as proteins [19] and pNIPAAm [20]. These papers have shown that hydration of the chemical overlayer formed on the resonator can be monitored as the decrease of resonant frequency ( $f$ ). Höök et al. have reported that Eq. (1) has some uncertainty when a viscoelastic layer, such as a hydrophilic protein layer, is formed on the resonator surface [21]. QCM can also provide information about changes in the layer's viscoelasticity, which can be related to the dissipation of the oscillation [23,24]. The ratio of the lost energy to the stored energy for each oscillation frequency is defined as the dissipation factor ( $D$ ) [28]. In this study, we evaluated the hydration and dehydration behavior of a pNSp–NIPAAm thin layer adsorbed at a gold-coated resonator surface in water through simultaneous measurement of  $f$  and  $D$  by the quartz crystal

microbalance technique implemented with dissipation factor (QCM-D technique). In order to reduce the influence of bulk water on the observed measurements, we carried out all measurements at the highest harmonic ( $n = 7$ ), since measurements at lower harmonics ( $n = 1, 3, 5$ ) are largely affected by the bulk water in contact with the resonator surface [22].

## 2.3. Evaluation of the pNSp–NIPAAm thin layer by QCM-D

In this study, we used a QCM-D system (QCM-D 300, Q-sense AB, Göteborg, Sweden) in order to measure  $f$  and  $D$  simultaneously. At first, we installed a gold-coated quartz resonator (QX301, Q-sense AB) in the axial flow chamber (QAFC302, Q-sense AB) and measured  $f$  at 25 °C. Then, a thin layer of the pNSp–NIPAAm copolymer was prepared by spincoating a pNSp–NIPAAm solution in isopropanol on the resonator, followed by drying at 60 °C for 1 h. We measured  $f$  of the copolymer-coated resonator in the axial flow chamber at 25 °C. The thickness of the pNSp–NIPAAm layer formed on the resonator was calculated from Eq. (1) using the difference in  $f$  between the uncoated resonator and the pNSp–NIPAAm-coated resonator, assuming the density of the copolymer layer to be 1.1 g/cm<sup>3</sup>.

The resonator with the pNSp–NIPAAm layer was installed in the window chamber (QWiC301, Q-sense, AB), enabling light irradiation on the surface of the resonator in water (Fig. 2). Water was purified with a Milli-Q Biocel system (Millipore, MA, USA). The surface of the resonator was irradiated with ultraviolet (UV) light (365 nm wavelength, 50 mW/cm<sup>2</sup> intensity at the resonator surface) or visible (VIS) light (>500 nm wavelength, 50 mW/cm<sup>2</sup> intensity at the resonator surface). Light from the light source (LC6, Hamamatsu Photonics, Japan) was guided through the glass window of the chamber using a set of filters and a liquid fiber light guide. The temperature of the resonator was accurately controlled ( $\pm 0.01$  °C). To estimate the loss of copolymer from the resonator surface during the measurement, the pNSp–NIPAAm-coated resonator was dried at 60 °C for 1 h following measurement, and  $f$  of the dried resonator was measured in the axial flow chamber.

For each experiment, an uncoated resonator was used as a negative control. As a non-thermoresponsive control, we also prepared a resonator with a

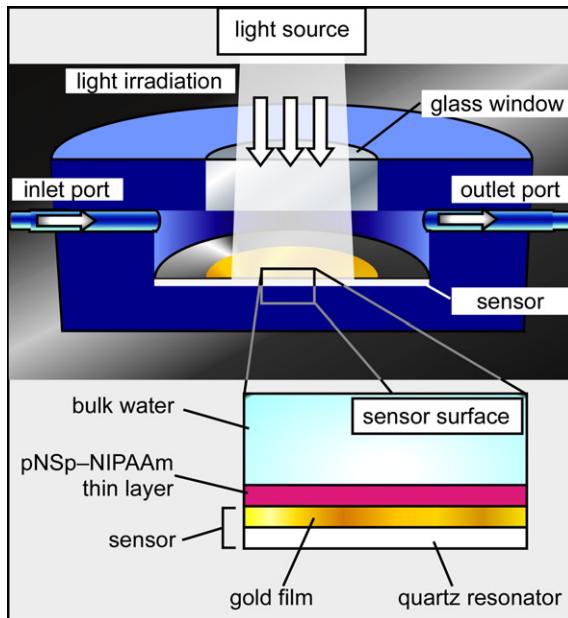


Fig. 2. Schematic illustration of the experimental setup for investigating photoresponse of polymer thin layers in water by the quartz crystal microbalance technique with dissipation measurement (QCM-D technique).

surface coated with a thin layer of polystyrene. The polystyrene layer's thickness was similar to that of the pNSp-NIPAAm-coated resonator.

### 3. Results and discussion

#### 3.1. Thermally induced hydration of the pNSp-NIPAAm layer in the dark

As shown in Fig. 1, the NSp contained in the pNSp-NIPAAm adopts either of two stable states in a neutral condition: the open-ring state, known as the merocyanine (Mc) form, or the closed-ring state, known as the spiro (Sp) form [29]. The colorless, hydrophobic Sp chromophore is isomerized into the red and relatively hydrophilic Mc form through irradiation with 365 nm UV light. Fig. 1 shows the absorbance spectra of a pNSp-NIPAAm aqueous solution before and after UV irradiation. The absorbance peak appearing at 540 nm after UV irradiation indicates that photoisomerization of the NSp chromophores from the Sp form to the Mc form has progressed. From the turbidity measurement results (data not shown), we estimated the dissolution temperature ( $T_d$ ) of pNSp-NIPAAm in water to be 22 °C both with and without UV irradiation: pNSp-NIPAAm was soluble in water

below 22 °C, yet it was insoluble above that temperature. These observations indicate that the pNSp-NIPAAm aqueous solution had a lower critical solution temperature (LCST) around 22 °C, which was lower than that of the pNIPAAm aqueous solution (31 °C), suggesting that the hydrophobic spiro-pyran chromophore suppressed the hydration of the pNIPAAm component in the pNSp-NIPAAm.

Temperature change affected the QCM measurements of a thin layer of pNSp-NIPAAm in water in the dark (Fig. 3). After the stepwise temperature decrease from 35 to 30 °C or from 30 to 25 °C,  $\Delta f_7$  decreased and reached thermal equilibrium within 10 min. Since similar behavior was observed also for an uncoated resonator, such changes in  $\Delta f_7$  in response to temperature changes were mainly attributed to changes in viscosity and density of the bulk water in contact with the resonator surface [30]. Therefore, to extract the contribution of the polymer layer formed on the resonator, the difference in  $\Delta f_7$  between the uncoated and polymer-coated resonators ( $\Delta\Delta f_7$ ) was calculated by subtracting  $\Delta f_7$  observed for the uncoated resonator from each corresponding datum obtained for the polymer-coated resonator.

The values of  $\Delta\Delta f_7$  for the polystyrene-coated resonator, which had been expected to have no thermoresponse, remained near 0 Hz following each temperature change; for the pNSp-NIPAAm-coated resonator, only a temperature decrease from 25 to

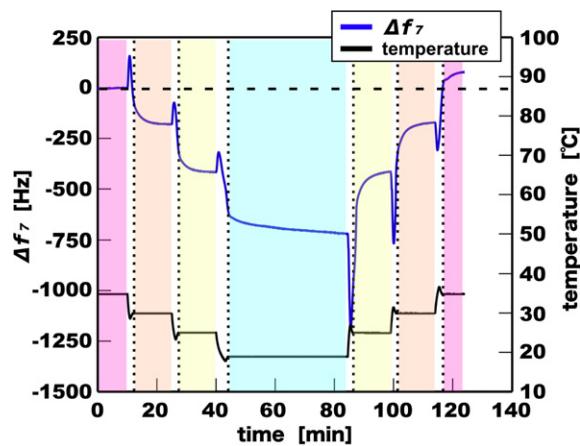


Fig. 3. Time courses of the resonant frequency at the 7th harmonic,  $\Delta f_7$  (blue line), observed for a pNSp-NIPAAm-coated resonator in water in the dark as the temperature (black line) was varied stepwise between 35 and 19 °C (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

19 °C elicited a continuously decreasing  $\Delta\Delta f_7$  over time (Fig. 4). In these experiments, a decrease in  $\Delta f_7$  was related to an increase in mass measured at the resonator because the influence of dissipation was slight as observed using dissipation measurements. Therefore, the decrease in  $\Delta\Delta f_7$  obtained for the pNSp–NIPAAm-coated resonator concurrent with the temperature decrease from 25 to 19 °C should be considered to be due to the hydration of the pNSp–NIPAAm thin layer formed on the resonator. The fact that the solubility of pNSp–NIPAAm increases at 22 °C and below further supports this conclusion, since an increasing solubility suggests an increase of water uptake into the copolymer.

### 3.2. Evaluation of photo-induced hydration of pNSp–NIPAAm by QCM-D

In response to UV irradiation at 19 °C in water,  $\Delta f_7$  of both the pNSp–NIPAAm-coated and uncoated resonators rapidly increased: in case of the uncoated resonator, immediately after the cessation of UV irradiation,  $\Delta f_7$  returned to its initial value (Fig. 5). Similar behavior was observed for a resonator coated with polystyrene, which is expected to be non-UV-responsive since it is almost transparent at 365 nm. Benkoski et al. attributed

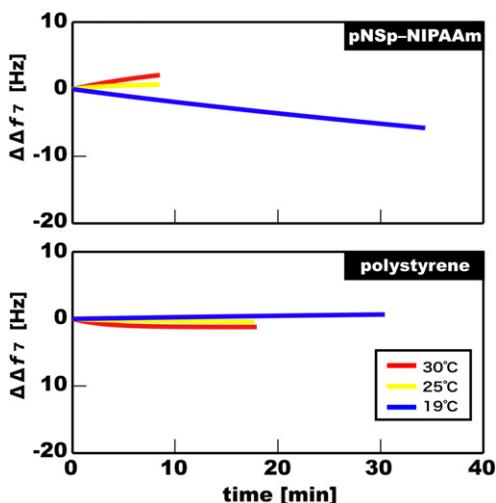


Fig. 4. Time courses of the resonant frequency difference,  $\Delta\Delta f_7$ , observed for the pNSp–NIPAAm-coated resonator (upper plot) or the polystyrene-coated resonator (lower plot) in water in the dark following stepwise temperature decreases from 35 to 30 °C (red lines), from 30 to 25 °C (yellow lines), and 25 to 19 °C (blue lines) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

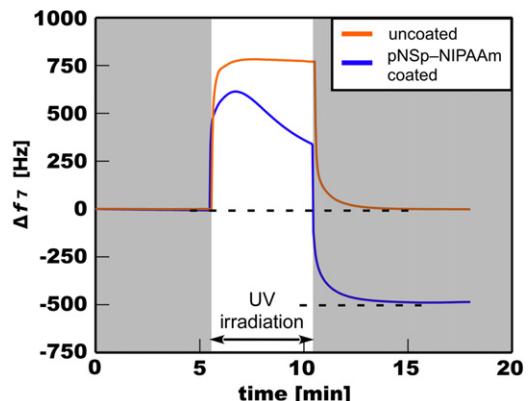


Fig. 5. Change in  $\Delta f_7$  values observed for the pNSp–NIPAAm-coated resonator (blue line) and the uncoated resonator (orange line) in response to temporal UV irradiation at 19 °C in water. Dotted lines indicate the baselines of  $\Delta f_7$  before and after irradiation (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

such changes in  $\Delta f$  to the increase in the surface temperature induced by UV irradiation [31].

The  $\Delta f_7$  values for the pNSp–NIPAAm-coated resonators after UV irradiation decreased substantially relative to those observed before the irradiation. The decrease in  $\Delta f_7$  can be attributed to the change of the pNSp–NIPAAm layer formed on the resonator, because results obtained for uncoated and polystyrene-coated resonators reveal that surface temperature did not influence  $\Delta f_7$  following UV irradiation. Furthermore, such a decrease in  $\Delta f_7$  was not observed following VIS irradiation, which cannot isomerize NSp. The decreasing rate of  $\Delta f_7$  during UV irradiation was estimated to be more than 500 times larger than that observed in the dark at the same temperature (19 °C), as shown in Fig. 4. These results strongly suggest that UV irradiation facilitates hydration of the pNSp–NIPAAm layer in water at 19 °C.

For a detailed analysis of the hydration behavior of the pNSp–NIPAAm layer, we investigated the influence of irradiation using  $\Delta\Delta f_7$  and  $\Delta\Delta D_7$ , which is defined as the  $\Delta D_7$  obtained for the pNSp–NIPAAm-coated resonator minus that for the uncoated resonator at each temperature. The time course of the temperature changes was similar to that of the non-irradiated experiment shown in Fig. 3. In the UV irradiation experiment, the pNSp–NIPAAm-coated resonator was irradiated with UV light at 19 °C. Fig. 6 shows the comparison between the experiments with and without UV irradiation.

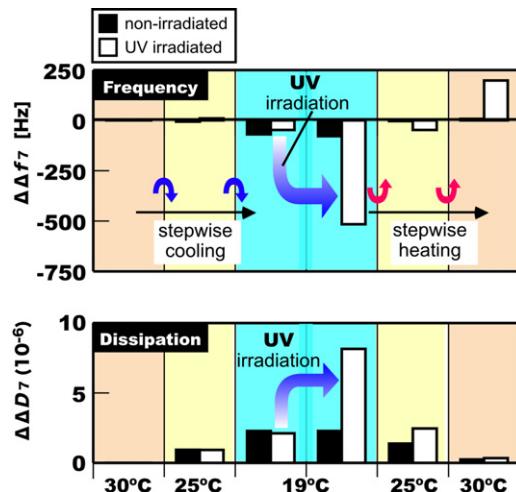


Fig. 6.  $\Delta\Delta f_7$  (upper plot) and  $\Delta\Delta D_7$  (lower plot) observed after each stepwise temperature change and temporal UV light irradiation at 19 °C.

During the cooling process,  $\Delta\Delta f_7$  did not change much until 25 °C and decreased at 19 °C; however,  $\Delta\Delta D_7$  increased with each cooling step. These results suggest that the pNSp–NIPAAm layer became more hydrophilic when upon cooling to 19 °C. However, a larger decrease in  $\Delta\Delta f_7$  and a larger increase in  $\Delta\Delta D_7$  were observed upon UV irradiation at 19 °C. These results indicate that UV irradiation not only facilitated hydration of the pNSp–NIPAAm layer but also increased the layer's viscoelasticity. Subsequently, when the temperature rose to 30 °C during the stepwise heating process,  $\Delta\Delta f_7$  and  $\Delta\Delta D_7$  for the non-irradiated resonator returned to almost the same level as that observed at 30 °C before the cooling process. Additionally,  $\Delta f_7$  values measured at dried pNSp–NIPAAm-coated resonators before and after the experiment were almost the same, indicating that most of the pNSp–NIPAAm layer without UV irradiation was retained on the surface of the resonator and did not dissolve in water. These results suggest that the pNSp–NIPAAm layer without UV irradiation was dehydrated and became rigid again when the layer was heated to 30 °C. In contrast,  $\Delta\Delta f_7$  of the irradiated pNSp–NIPAAm layer at 30 °C after UV irradiation became much larger than that at 30 °C before UV irradiation. The  $\Delta f_7$  values of the irradiated pNSp–NIPAAm-coated resonators measured in dried states showed that about 40% of the copolymer in the pNSp–NIPAAm layer had been lost in water. These results suggest that UV

irradiation drastically facilitates hydration of the pNSp–NIPAAm layer.

### 3.3. Mechanism of photo-induced hydration of pNSp–NIPAAm

Fig. 7 shows changes in  $\Delta f_7$  caused by UV irradiation at 30, 25, and 19 °C, which were calculated by subtracting a stable  $\Delta f_7$  after UV irradiation from that before the UV irradiation (dotted lines in Fig. 5).  $\Delta f_7$  for the uncoated resonator was not affected by UV irradiation at each temperature.  $\Delta f_7$  for the pNSp–NIPAAm-coated resonator also was not affected by UV irradiation at 25 °C but fell substantially after UV irradiation at 19 °C. Therefore, we propose a mechanism for this photo-induced hydration as follows: hydrophilic NSp generated through UV-induced photoisomerization triggers the uptake of a large amount of water molecules into the pNSp–NIPAAm layer only when the thermoresponsive pNIPAAm component is hydrophilic, i.e. at a temperature of 19 °C.

In Fig. 8, we present a schematic mechanism of hydration of the pNSp–NIPAAm immobilized on the gold surface of a quartz resonator based on the results of this study. When the temperature decreases from 25 to 19 °C, the pNSp–NIPAAm changes from a hydrophobic state (1) to a relatively hydrophilic state in which the pNIPAAm component is ready to hydrate (2), while its immobilization suppresses the hydration of the pNSp–NIPAAm with bulk water. In response to UV irradiation at 19 °C, marked hydration and swelling of the

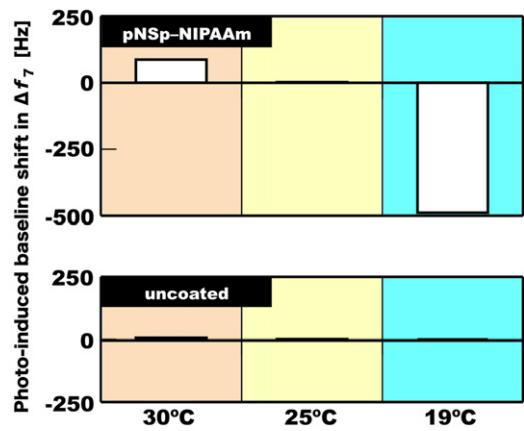


Fig. 7. Baseline shifts in  $\Delta f_7$  induced by UV irradiation of a pNSp–NIPAAm-coated resonator (upper plot) and an uncoated resonator (lower plot) at 30, 25, and 19 °C in water.

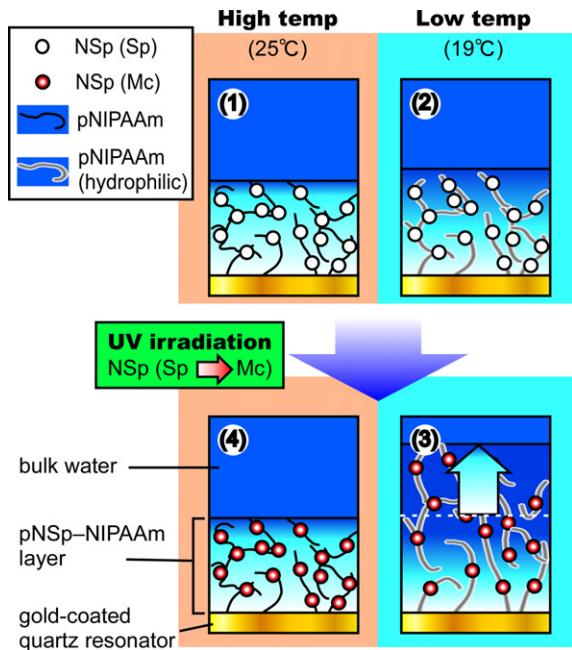


Fig. 8. The presumed mechanism for the photo-induced hydration of a solid pNSp–NIPAAm thin layer in water: (1) the pNSp–NIPAAm was relatively hydrophobic in the dark at 25 °C, (2) at 19 °C in the dark it became more hydrophilic, (3) it became extremely hydrated and swelled under UV irradiation at 19 °C (photo-induced hydration), (4) the photo-induced hydration did not occur even under UV irradiation at 25 °C.

pNSp–NIPAAm is triggered by photoisomerization of the NSp chromophore from its hydrophobic form (Sp) to its hydrophilic one (Mc) (3). However, hydration is not induced at 25 °C (4) since the hydrophilic NSp chromophore is confined within the surrounding hydrophobic environment of the pNIPAAm component.

#### 4. Conclusion

Through QCM-D measurement of pNSp–NIPAAm-coated quartz resonators in water, we found that at a temperature of 19 °C, the pNSp–NIPAAm thin layer rapidly adsorbed a large amount of water molecules and increased in viscoelasticity when it was irradiated with UV light, which induces photoisomerization of NSp from the hydrophobic form to the hydrophilic one. At temperatures between 25 and 35 °C, however, such a photo-induced hydration was not observed. These results suggest that the photoisomerization of the NSp chromophore triggered the photo-induced hydration only when the pNIPAAm component is sufficiently hydrophilic, at a temperature of 19 °C.

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#### References

- [1] Kim DY, Tripathy SK, Li L, Kumar J. Laser-induced holographic surface-relief gratings on nonlinear-optical polymer-films. *Appl Phys Lett* 1995;66(10):1166–8.
- [2] Sumaru K, Yamanaka T, Fukuda T, Matsuda H. Photoinduced surface relief gratings on azopolymer films: Analysis by a fluid mechanics model. *Appl Phys Lett* 1999;75(13):1878–80.
- [3] Aoyama M, Watanabe J, Inoue S. Photoregulation of permeability across a membrane from a graft copolymer containing a photoresponsive polypeptide branch. *J Am Chem Soc* 1990;112(14):5542–5.
- [4] Kameda M, Sumaru K, Kanamori T, Shinbo T. Photore-sponse gas permeability of azobenzene-functionalized glassy polymer films. *J Appl Polym Sci* 2003;88(8):2068–72.
- [5] Irie M, Kunwatchakun D. Photoresponsive polymers .8. Reversible photostimulated dilation of polyacrylamide gels having triphenylmethane leuco derivatives. *Macromolecules* 1986;19(10):2476–80.
- [6] Tomer R, Florence AT. Photo-responsive hydrogels for potential responsive release applications. *Int J Pharm* 1993; 99(2–3):R5–8.
- [7] Kröger R, Menzel H, Hallensleben ML. Light controlled solubility change of polymers – copolymers of *N,N*-dimethylacrylamide and 4-phenylazophenyl acrylate. *Macromol Chem Phys* 1994;195(7):2291–8.
- [8] Despends A, Freitag R. Synthesis and characterization of photoresponsive *N*-isopropylacrylamide cotelomers. *Langmuir* 2003;19(15):6261–70.
- [9] Sumaru K, Kameda M, Kanamori T, Shinbo T. Characteristic phase transition of aqueous solution of poly(*N*-isopropylacrylamide) functionalized with spirobenzopyran. *Macromolecules* 2004;37(13):4949–55.
- [10] Nakayama Y, Furumoto A, Kidoaki S, Matsuda T. Photo-control of cell adhesion and proliferation by a photoinduced cationic polymer surface. *Photochem Photobiol* 2003;77(5):480–6.
- [11] Tada Y, Sumaru K, Kameda M, Ohi K, Takagi T, Kanamori T, et al. Development of a photoresponsive cell culture surface: Regional enhancement of living-cell adhesion induced by local light irradiation. *J Appl Polym Sci* 2006;100(1):495–9.
- [12] Sumaru K, Ohi K, Takagi T, Kanamori T, Shinbo T. Photoresponsive properties of poly(*N*-isopropylacrylamide) hydrogel partly modified with spirobenzopyran. *Langmuir* 2006;22(9):4353–6.

[13] Klee D, Villari RV, Höcker H, Dekker B, Mittermayer C. Surface modification of a new flexible polymer with improved cell-adhesion. *J Mater Sci: Mater M* 1994;5(9–10):592–5.

[14] Ko TM, Cooper SL. Surface-properties and platelet-adhesion characteristics of acrylic-acid and allylamine plasma-treated polyethylene. *J Appl Polym Sci* 1993;47(9):1601–19.

[15] Tao GL, Gong AJ, Lu JJ, Sue HJ, Bergbreiter DE. Surface functionalized polypropylene: synthesis, characterization, and adhesion properties. *Macromolecules* 2001;34(22):7672–9.

[16] Nomura T, Okuhara M. Frequency-shifts of piezoelectric quartz crystals immersed in organic liquids. *Anal Chim Acta* 1982;142(Oct):281–4.

[17] Martin BA, Hager HE. Velocity profile on quartz crystals oscillating in liquids. *J Appl Phys* 1989;65(7):2630–5.

[18] Sauerbrey G. Verwendung von Schwingquarzen zur Wagung dünner Schichten und zur Mikrowagung. *Zeitschrift für Physik* 1959;155:206–22.

[19] Höök F, Kasemo B, Nylander T, Fant C, Sott K, Elwing H. Variations in coupled water, viscoelastic properties, and film thickness of a Mefp-1 protein film during adsorption and cross-linking: a quartz crystal microbalance with dissipation monitoring, ellipsometry, and surface plasmon resonance study. *Anal Chem* 2001;73(24):5796–804.

[20] Wang ZH, Kuckling D, Johannsmann D. Temperature-induced swelling and de-swelling of thin poly(*N*-isopropylacrylamide) gels in water: combined acoustic and optical measurements. *Soft Mater* 2003;1(3):353–64.

[21] Höök F, Rodahl M, Brzezinski P, Kasemo B. Energy dissipation kinetics for protein and antibody-antigen adsorption under shear oscillation on a quartz crystal microbalance. *Langmuir* 1998;14(4):729–34.

[22] Voinova MV, Rodahl M, Jonson M, Kasemo B. Viscoelastic acoustic response of layered polymer films at fluid–solid interfaces: continuum mechanics approach. *Phys Scr* 1999;59(5):391–6.

[23] Su HB, Chong S, Thompson M. Interfacial hybridization of RNA homopolymers studied by liquid phase acoustic network analysis. *Langmuir* 1996;12(9):2247–55.

[24] Janshoff A, Wegener J, Sieber M, Galla HJ. Double-mode impedance analysis of epithelial cell monolayers cultured on shear wave resonators. *Euro Biophys J* 1996;25(2):93–103.

[25] Rodahl M, Höök F, Fredriksson C, Keller CA, Krozer A, Brzezinski P, et al. Simultaneous frequency and dissipation factor QCM measurements of biomolecular adsorption and cell adhesion. *Faraday Discuss* 1997(107):229–46.

[26] Namba K, Suzuki S. Normal and reverse photochromism of 1-(beta-carboxyethyl)-3,3-dimethyl-6'-nitrospiro[indoline-2,2'-2H-benzopyran] in water–dioxane. *Bull Chem Soc Jpn* 1975;48(4):1323–4.

[27] Willner I, Liondagan M, Marxtibbon S, Katz E. Bioelectrocatalyzed amperometric transduction of recorded optical signals using monolayer-modified Au-electrodes. *J Am Chem Soc* 1995;117(24):6581–92.

[28] Buttry DA, Ward MD. Measurement of Interfacial processes at electrode surfaces with the electrochemical quartz crystal microbalance. *Chem Rev* 1992;92(6):1355–79.

[29] Fissi A, Pieroni O, Angelini N, Lenci F. Photoresponsive polypeptides, photochromic and conformational behavior of spiropyran-containing poly(L-glutamate)s under acid conditions. *Macromolecules* 1999;32(21):7116–21.

[30] Lin ZX, Yip CM, Joseph IS, Ward MD. Operation of an ultrasensitive 30-MHz quartz-crystal microbalance in liquids. *Anal Chem* 1993;65(11):1546–51.

[31] Benkoski JJ, Jesorka A, Kasemo B, Höök F. Light-activated desorption of photoactive polyelectrolytes from supported lipid bilayers. *Macromolecules* 2005;38(9):3852–60.