Photo-reversible and selective Cu^{2+} complexation of a spiropyran-carrying sulfobetaine copolymer in saline solution

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A sulfobetaine copolymer (**1**) carrying a photochromic spiropyran residue was synthesized, which reversibly isomerized between the closed and open forms in pure water and in saline by irradiation with visible light. The thermodynamic stability of the open form of the spiropyran methacrylate (SPMA) units of compound **1** was reduced upon increasing NaCl concentration. In addition, photo-reversible and selective Cu^{2+} complexation in saline solution ([NaCl] = 1.0 wt%) was achieved using compound **1** with metal ions (Cu^{2+}, Zn^{2+}, Ni^{2+}, or Co^{2+}). Covalently cross-linked compound **1** showed selective Cu^{2+} adsorption in pure water. In contrast, the other metal ions were increasingly adsorbed as NaCl concentration increased, resulting in lower selectivity of Cu^{2+} ion adsorption with **1**, *e.g.*, the ratios of adsorption of Cu^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+} with **1** in 10 wt% saline were 73, 20, 10, and 3%, respectively, while only Cu^{2+} adsorption was observed in a solution of 1.0 wt% NaCl. Because the stability of the open form of the SPMA units and the metal complexation of **1** were influenced by NaCl concentration, the electrostatically cross-linked networks of the zwitterionic sulfobetaine units of **1** may be loosened by NaCl addition, resulting in easy entry of metal ions into the network. The order of metal complexation among the four metals corresponded to the Irving–Williams series. Hydrogen-bonded networks of water molecules also may contribute to the relatively ineffective selective adsorption of Cu^{2+} ions by **1** compared to the electrically neutral spiropyran-carrying copolymer of *N*-isopropylacrylamide, **2**.

Introduction

Interest in the design and synthesis of new materials for metal ion sensors, resulting in "one-time" use sensors, has been motivated by non-reversible interactions between a metal ion and its sensing receptor. An important feature for the next generation of metal ion sensing will be reversibility in the recognition process because it contributes to "real-time" metal ion monitoring. The materials showing non-reversible metal adsorption cannot detect a low concentration of the metal ions continuously in the situation after adsorbing high quantities of metal ions. The attractive features of photochromic spiropyrans have prompted a number of studies of derivatives of these compounds and their metal-binding characteristics.[1,2]

Upon irradiation with UV or visible light, spiropyrans isomerize between open and closed forms, respectively.[3] Metal ions can influence this isomerization by association with the open form through electron-rich oxygen atoms. In contrast, visible light produces high concentrations of the closed form, and thus hinders metal binding. Spiropyrans, therefore, have potential for providing photo-reversible metal complexation.

However, some problems of spiropyrans remain as a material for repeated-use metal ion sensing, *i.e.* "real-time" monitoring of metal ions, for biological and environmental applications: (a) high sensitivity to a target metal ion, and (b) photo-reversible function in an aqueous environment with no organic solvent. Some approaches have been reported to overcome the former problem. Winkler and coworkers detected target metal ions in ethanol or benzene by analysis of the metal-complexed spiropyran, based on intensity of fluorescent emission for metal complexes with different metal species.[4] Another well-known approach is modification of spiropyrans with additional ligands for metal chelation at the position *ortho* to the oxygen nucleus of the pyran ring,[5,6] or attachment of crown ethers[7–10] to the molecule to recognize metal size to some extent. Yang and coworkers reported selective Cu^{2+} ion complexation in ethanol–water by synthetic spiropyrans modified with a morpholinomethyl group acting as the chelating functional group.[11]

However, no accounts of spiropyrans showing specific binding to a target metal ion in a purely aqueous environment have been reported because of the difficulty of satisfying the requirements for (a) and (b) with one molecule. The molecular structure of the spiropyrans, especially modification of the pyran ring, is likely to influence the isomerization characteristics of the closed and open forms and their metal complexation characteristics.

The application of spiropyran-carrying copolymers has been reported for use in aqueous solution.[12,13] The spiropyran units in the copolymers can perform limited functions, *i.e.*, target metal complexation, because water solubility of the copolymers is achieved with the other co-monomer unit. Here, photo-reversible and selective Cu^{2+} complexation of spiropyran-carrying sulfobetaine copolymer, **1** (Scheme 1), is described in water and in saline solution without an organic solvent, where photo-reversible and Cu^{2+} selective complexation occurs at the spiropyran unit, and the copolymer exhibits high solubility in saline solution

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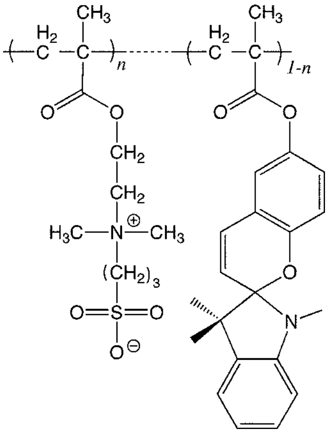


Scheme 1 The chemical structure of **1**.

owing to the sulfobetaine unit. McCormick, and coworkers reported that zwitterions in sulfobetaine polymers remain in their diionic form over a broader pH range than the carboxy betaine polymers.[14] The spiropyran units in the copolymers favor protonation over metal complexation while in the open form. Thus, having the sulfobetaine unit as the other co-monomer allows the spiropyran unit to form a metal complex efficiently. The sulfobetaine copolymers with photo-reversible and selective Cu^{2+} complexation show promise for useful applications in cell biology, molecular biology, and biochemistry due to the ability to function in saline solution.

Results and discussion

Solubility and photochromism of 1 in saline solution

One feature of polymeric betaines is the tendency of the zwitterionic fragments to form a cyclic structure involving the cationic and anionic groups of neighboring monomer units (intragroup), or a head-to-tail stacking (interchain) structure within single macromolecules and interchain ion contacts between neighboring macromolecules. The consequent proximity of the anionic and cationic groups causes the appearance of electrostatically cross-linked networks.[15–17] Therefore, polymeric betaines are usually sparingly soluble in pure water.[18]

A homopolymer of sulfobetaine, one of the co-monomer units of **1**, is insoluble in pure water. The copolymer of **1** containing 1.0 mol% of spiropyran methacrylate (SPMA) units was also insoluble because the hydrophobic closed form of SPMA is dominant in the equilibrium between the closed and open forms in ordinary solvents, involving water.

The addition of electrolytes, such as NaCl and KCl is often used to solubilize polymeric betaines because of the interference of the dissociated electrolytes with the electrostatically cross-linked networks constructed by the zwitterionic fragments. A transparent aqueous solution of compound **1** was prepared by adding **1** to saline solution ([NaCl] = 1.0 wt%, pH ≈ 7.0) at 25 °C. The absorption spectrum of the saline solution of **1** showed a strong band at 530 nm (Fig. 1) attributed to the open form of the SPMA units.[19] This band was photo-bleached by irradiation with visible light (>420 nm), but reappeared upon standing in the dark. Further addition of NaCl to the solution suppressed the thermodynamic stability of the open form of the SPMA units, as indicated by a trend in decrease in intensity of the 530 nm band at 3.0 and 10 wt% aqueous NaCl (Fig. 2). Interfering with the electrostatic interaction, which constructed the cross-linked network with oppositely charged groups in the sulfobetaine units, causes hydration of **1** in response to NaCl addition, leading to an unfavorable environment for thermodynamic stability of the open form of SPMA units. Bergbreiter and coworkers reported that sodium salts, whether kosmotropes or chaotropes, could increase the surface tension of the interface of water and the hydrophobic portions of poly(*N*-isopropylacrylamide), P(NIPAAm).[20] Compound **1** also contains both hydrophobic and hydrophilic portions similar to P(NIPAAm). The subsequent high surface tension of the **1**/water interface upon NaCl addition results in hydrophobic hydration of **1**, which can explain the decrease in the number of SPMA units in the open form.

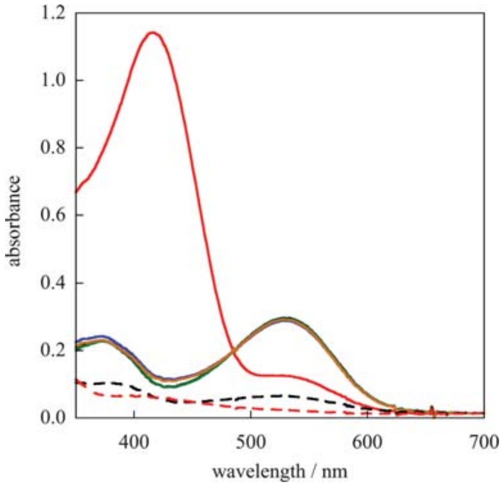


Fig. 1 Absorption spectra of saline solutions ([NaCl] = 1.0 wt%) of **1**. Solutions contained: no metal ions (black), or 1.0 mM Cu^{2+} (red), Zn^{2+} (blue), Ni^{2+} (green), or Co^{2+} (yellow) ions at 25 °C. [SPMA unit] = 0.1 mM at equilibrium (—); after visible light irradiation (---).

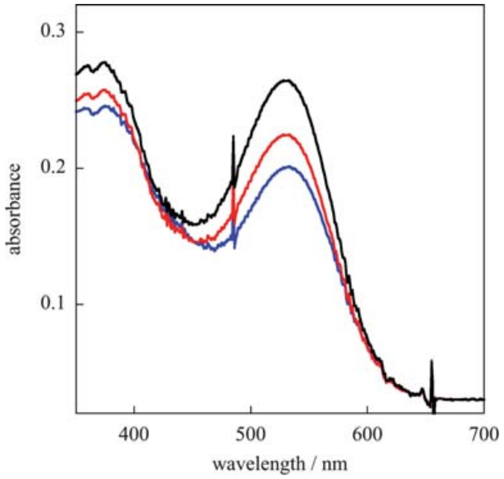
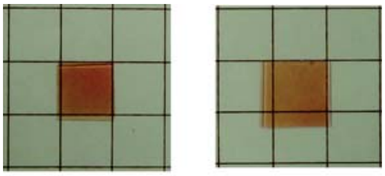


Fig. 2 Absorption spectra of saline solutions of **1** with different NaCl concentrations: 1% (black), 3% (red), and 10 wt% NaCl (blue) at 25 °C.



(a) in pure water (b) 1.0wt%

(c) 5.0wt%

Fig. 3 A hydrogel of covalently cross-linked **1** in aqueous NaCl solution: (a) 0 wt% NaCl (pure water); (b) 1.0 wt% NaCl; and (c) 5.0 wt% NaCl at 25 °C. The plate printed with the grid (1 cm × 1 cm squares) was behind the gel.

A covalently cross-linked copolymer of **1** was also prepared with methylenebisacrylamide as a cross-linker by radical copolymerization in trifluoroethanol. The transparent hydrogel obtained from this copolymer in pure water produced a maximum absorption band at a wavelength of 530 nm (not shown), which was identical to the saline solution of **1**. The non-turbid nature of the hydrogel without addition of NaCl (Fig. 3a) indicates that the polymer chains of the covalently cross-linked copolymer were distributed efficiently in a purely aqueous medium compared to the covalently non-cross-linked copolymer, because the cross-linked structure of the copolymer prevents the zwitterionic sulfobetaine units from entering their intra- and intertether areas, or from forming stacked layers within single macromolecules or interchain ion contacts between neighboring macromolecules. The polymerization process accompanied by cross-linking may place sulfobetaine co-monomers in electrostatically unfavorable conformations as they became a part of the propagating polymer chains in the gel structure. In addition, reversible swelling/shrinking of the hydrogel by changing the concentration of NaCl was observed, as shown in Fig. 3. The size of the hydrogel immersed in 5.0 wt% NaCl solution was 2.2-fold larger than that in pure water. The reversible behavior also supports the presence of electrostatic interactions between the oppositely charged groups of the zwitterionic sulfobetaine units of **1** in aqueous solution.

Metal complexation of the copolymer in saline solution

Four metal chlorides ($CuCl_2$, $ZnCl_2$, $NiCl_2$, and $CoCl_2$), all salts of first-row transition metals, were added separately into a saline solution ([NaCl] = 1.0 wt%) of **1**. No change was seen in the absorption spectra of any of the solutions, except for the $CuCl_2$ solution as shown in Fig. 1, indicating that no metal complexes of **1** with Zn^{2+}, Ni^{2+}, or Co^{2+} are formed. Only the solution containing Cu^{2+} ions contained an absorption band near 420 nm along with a decrease in the intensity of the 530 nm band.

To confirm Cu^{2+}-selective adsorption and desorption by **1** in saline solution *via* light irradiation, the metal ion concentration was measured upon photo-reversible isomerization of **1**. As shown in Fig. 3, the color of covalently cross-linked **1** was similar to that of the solutions of the soluble non-cross-linked **1**, *i.e.*, while there was no change in absorption spectra of the cross-linked copolymer after addition of Zn^{2+}, Ni^{2+}, or Co^{2+}; only the solution containing Cu^{2+} showed the appearance of an absorption band near 420 nm and a decrease in intensity of the 530 nm band (Fig. 1). Metal ion measurement of the solution (initial metal chloride concentration: 3.0 μg mL^{-1}, [NaCl] = 1.0 wt%) was performed using inductively coupled plasma atomic emission spectroscopy, ICP-AES, before and after irradiation with visible light (Table 1). Only the solution containing Cu^{2+} showed a change in metal ion concentration before and after visible light irradiation. Inefficient desorption of complexed Cu^{2+} ions from the hydrogel due to irradiation with visible light is due to slow diffusion from inside the gel, indicated by the colorless solution under visible light irradiation.

Table 1 Concentration of metal ions in saline solution of **1** before and after irradiation with visible light, measured by ICP-AES[a]

	Cu^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}
In the dark	1.3	2.9	2.9	3.0
After visible light irradiation	1.7	3.0	2.9	3.0

[a] Unit: μg mL^{-1}, initial concentration of metal chlorides was 3.0 μg mL^{-1}, which was one tenth of the concentration of SPMA units of **1**. [NaCl] = 1.0 wt%, at 25 °C.

The intensity of the 420 nm band of the solution of **1** containing Cu^{2+} increased with NaCl concentration, while the 530 nm band decreased in intensity (Fig. 4). The change in the intensity of the bands at 420 nm and 530 nm accompanied by Cu^{2+} complexation was evaluated in terms of the equilibria of the isomerization reaction of SPMA units and Cu^{2+} complexation with the open form of the SPMA units. Since the concentration of the SPMA units remained constant (0.1 mM), the sum of the concentrations of the closed and the non-complexed open forms decreases as Cu^{2+} complexation increases. The reversible isomerization of SPMA units is an equilibrium between the closed

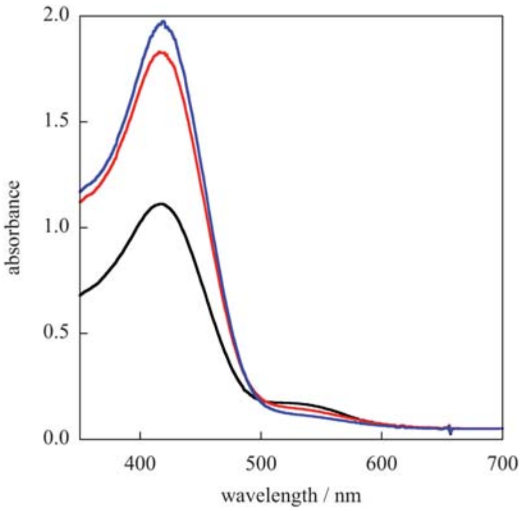


Fig. 4 Absorption spectra of a saline solution of **1** containing Cu^{2+} (1.0 mM) at different concentrations of NaCl at 25 °C. Concentration of NaCl: 1.0 wt% (black); 5.0 wt% (red); and 10 wt% (blue). [SPMA unit] = 0.1 mM.

form (CF) and the open form (OF) (eqn (1)), and concentration of the non-complexed open form is determined by its equilibrium constant in saline of i% NaCl, K_i. Thus, concentration of the closed form of SPMA units also decreases in proportion to the concentration of the non-complexed open form with K_i.

$$\mathrm{CF} \xrightleftharpoons{K_\mathrm{i}} \mathrm{OF} \tag{1}$$

In contrast, similar but small changes in the intensity of the 420 and 530 nm bands for all solutions of **1** containing the Zn^{2+}, Ni^{2+}, or Co^{2+} were also observed at 5.0 and 10 wt% of NaCl at 25 °C. A high NaCl concentration contributes to metal complexation of the SPMA units with inefficient metal ion selectivity.

As mentioned, the thermodynamic stability of the open form of SPMA units of **1** decreased in the more concentrated NaCl solutions, showing a decrease in the intensity of the 530 nm band. Since both the stability of the open form of SPMA units and the metal complexation of **1** were closely connected to the NaCl concentration, the NaCl may loosen the electrostatically cross-linked networks of the zwitterionic sulfobetaine units of **1**, allowing the metal ions easy entry into the network. The order of metal complexation among the four metals followed the Irving–Williams series, which refers to the relative stabilities of complexes formed by a metal ion.[21]

Calculation of amount of metal ion adsorption with 1

SPMA-coordinating Cu^{2+} complexes exist with different SPMA coordination numbers, such as OF–Cu^{2+} and $(OF)_2$–Cu^{2+}. The amounts are dependent upon the equilibria among the Cu^{2+} complexes (OF + Cu^{2+} ⇄ OF–Cu^{2+} and OF–Cu^{2+} + OF ⇄ $(OF)_2$–Cu^{2+}). The dominant metal complexes can be determined by Job's method.[22] However, the quantity of Cu^{2+} ions adsorbed on **1** cannot be easily calculated by spectroscopic analysis of the 420 nm band. Filley and coworkers reported that the molar absorption coefficients of the metal complexes of spiropyrans were not proportional to the number of spiropyran ligands, *i.e.*, the molar absorption coefficient of $(OF)_2$–Metal is not twice that of OF–Metal.[23] In contrast, the 530 nm band is due to the non-complexed open form of the SPMA units of **1**. The quantity of the non-complexed open form of the SPMA units is related to the concentration of the closed form of the SPMA units through the equilibrium constant (K_i) for isomerization between closed and open forms in saline (i% of NaCl). Therefore, the 530 nm band absorbance is appropriate for estimating the total amount of all Cu^{2+} complexes of **1** because the quantity of the Cu^{2+} complexes involving $(OF)_2$–Cu^{2+} and OF–Cu^{2+} can be calculated by subtraction of the sum of the closed and the non-complexed open forms from the initial concentration of SPMA units.

Three types of SPMA units of **1** in saline solution containing metal ions exist: the closed form (CF), the non-complexed open form (OF), and the metal-complexed open form (MF), which involves metal complexes with different binding ratios, *e.g.*, OF–Metal and $(OF)_2$–Metal. The total concentration of the SPMA units ([SPMA]) of **1** is constant, as follows:

$$[\mathrm{SPMA}] = [\mathrm{CF}] + [\mathrm{OF}] + [\mathrm{MF}] \tag{2}$$

Concentrations of the SPMA units of **1** before and after addition of metal ions are:

$$[\mathrm{CF}]_\mathrm{b} + [\mathrm{OF}]_\mathrm{b} = [\mathrm{CF}]_\mathrm{a} + [\mathrm{OF}]_\mathrm{a} + [\mathrm{MF}]\ (= [\mathrm{SPMA}]) \tag{3}$$

where $[CF]_b$ and $[CF]_a$, or $[OF]_b$ and $[OF]_a$ are the concentrations of CF or OF before and after the addition of metal ions, respectively. Eqn (3) can be rewritten as:

$$[\mathrm{MF}] = ([\mathrm{CF}]_\mathrm{b} + [\mathrm{OF}]_\mathrm{b}) - ([\mathrm{CF}]_\mathrm{a} + [\mathrm{OF}]_\mathrm{a}) \tag{4}$$

where [MF] is the concentration of the total generated metal complexes of SPMA units after metal ion addition.

Isomerization of the SPMA units of **1** between CF and OF is a reversible reaction with an equilibrium constant (K_i) in i% NaCl solution as follows:

$$K_\mathrm{i} = [\mathrm{OF}]/[\mathrm{CF}] \tag{5}$$

This leads to eqn (6):

$$\begin{aligned}[\mathrm{MF}] &= (K_\mathrm{i}^{\,-1} + 1)\big([\mathrm{OF}]_\mathrm{b} - [\mathrm{OF}]_\mathrm{a}\big)\\ &= (K_\mathrm{i}^{\,-1} + 1)(1 - \mathrm{x})[\mathrm{OF}]_\mathrm{b}\\ &= (1 - \mathrm{x})\big([\mathrm{CF}]_\mathrm{b} + [\mathrm{OF}]_\mathrm{b}\big)\\ &= (1 - \mathrm{x})[\mathrm{SPMA}]\end{aligned} \tag{6}$$

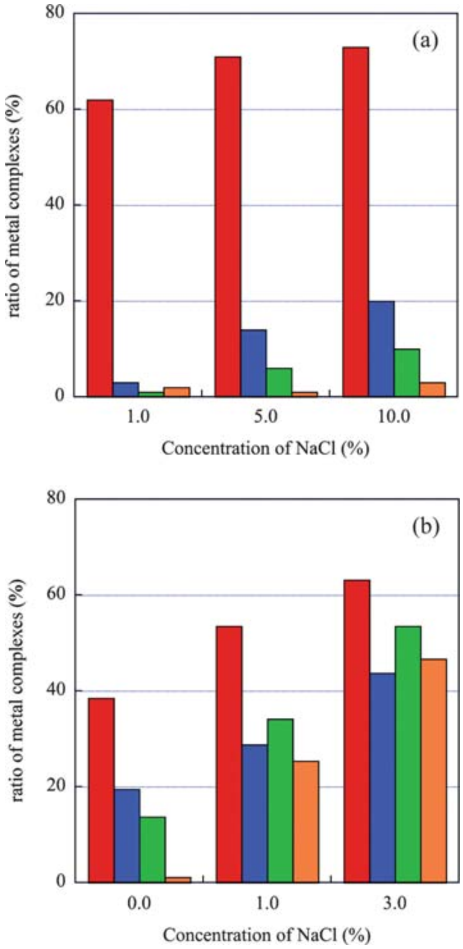


Fig. 5 The ratios of metal ion complexes to spiropyran units of copolymers **1** (a) and **2** (b) in solutions with different NaCl concentrations. The graphs show the adsorption of: Cu^{2+} (red), Zn^{2+} (blue), Ni^{2+} (green), and Co^{2+} (yellow).

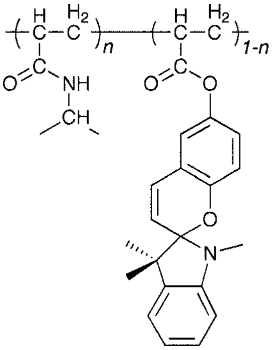
where x is the ratio of the 530 nm band intensity after metal ion addition to that before the addition, *i.e.*, $[OF]_a = x[OF]_b$. The value of x, measured from the absorption spectra, varies between 0 and 1. The absorbance at 550 nm was used as the initial absorbance for the aqueous solution containing **1** before addition of metal ions to estimate the amount of metal adsorption by **1** in saline.[24]

Fig. 5a shows ratios of the amount of metal complex to total SPMA units of **1** at 25 °C. A case with extremely low or high metal complexation is difficult to analyze because of the accuracy of x. Therefore, the initial Cu^{2+} solution was prepared with three-fold greater concentration than the concentration of SPMA units of **1** due to the relatively high ability of Cu^{2+} to complex with **1**, whereas the concentration of the other three metal ions was ten-fold greater than that of the SPMA units. Nevertheless, selective and photo-reversible Cu^{2+} adsorption was complete in saline ([NaCl] = 1.0 wt%). Increasing NaCl concentration in the solutions increased the amount of metal complexation for all of the metal ions, as shown in Fig. 5a. This resulted in a lower effective selectivity for Cu^{2+} ion adsorption with **1** at 10 wt% NaCl.

Cu^{2+} ion adsorption with electrically neutral copolymer of acryl amide

An electrically neutral water-soluble copolymer, poly(*N*-isopropylacrylamide-*co*-spiropyran acrylate), **2** (Scheme 2), was compared to the selective Cu^{2+} ion adsorption with **1**. Zwitterionic-type polyeletrolytes have a small positive *N* value. The *N* value is the number of H-bonds disrupted because of the presence of one monomer residue in the polymer. The *N* value of zwitterionic polyeletrolytes is similar to that for electrically neutral polymers.[10] Thus, the difference in the metal complexation between **1** and **2** could reveal the contribution of electrostatically cross-linked networks of sulfobetaine units to selective Cu^{2+} ion adsorption by **1**.

Poly(*N*-isopropylacrylamide), P(NIPAAm), is a thermosensitive polymer, showing a phase transition at the lowest critical solution temperature (LCST). Such a polymer is sensitive to the surrounding conditions, *e.g.*, temperature, pH, and ion strength of aqueous solutions, accompanied by a large structural change in polymer chains. According to Maeda and co-workers, the LCST of P(NIPAAm) varies with NaCl concentration in aqueous solution (LCST of 32 °C in pure water and 10 °C in 10 wt% NaCl).[25] The effect of dissociated NaCl ions on the phase transition of aqueous polymer solutions is indirect and can be explained by changes in the structure and properties of water. The LCST of **2**, comprising 2 mol% spiropyran acrylate (SPAA) units and 98 mol% NIPAAm units, was 28 °C, which is lower than that for P(NIPAAm) due to the hydrophobic SPAA units in the copolymer.[12]



Scheme 2 Chemical structure of **2**.

This report focused on the influence of NaCl concentration on the thermodynamic stability of the open form of the SPAA units of **2**. The absorbance of the 530 nm band attributed to the open form decreased as the NaCl concentration increased, whereas the intensity of the 295 nm band increases with the concentration of the closed form of the SPAA units. The change in the absorption spectra of a saline solution of **2** was the same as that for **1**. Therefore, NaCl addition to a solution of **2** also suppressed thermodynamic stability of the open form of the SPAA units, indicating that dissociated NaCl electrolytes could increase the cost of hydrophobic hydration, *i.e.*, increase the surface tension of the polymer/water interface.[20]

Three aqueous solutions were prepared with varying NaCl concentrations: 0, 1.0, and 3.0 wt%. Absorption spectra of the saline solutions of **2** upon addition of a metal ion (Cu^{2+}, Zn^{2+}, Ni^{2+}, or Co^{2+}) were measured at 10 °C, a temperature far from the LCST to avoid generation of a precipitate of **2**. Quantitative analysis to determine metal adsorption by **2** in saline solution was conducted as shown in Fig. 5b. Even under conditions disadvantageous for the adsorption of Cu^{2+} ions ($[Cu^{2+}] : [SPAA] = 3 : 1$) for comparison with the other metal ions ($[Metal^{2+}] : [SPAA] = 10 : 1$), absorption of Cu^{2+} ions was greatest among the four metal ions. Upon increasing the NaCl concentration, adsorption of all of the metal ions by **2** improved, while the selectivity of metal ion adsorption decreased.

The change in metal adsorption as a function of NaCl concentration for **2** was similar to that for **1**. These results indicate that the open form of the spiropyran units of **1** and **2** is less thermodynamically stable in the hydrophobic hydrated environment resulting from the addition of NaCl electrolytes. The consequent hydration results in lower levels of H-bonded arrangements of water molecules, leading to greater opportunities for the spiropyran units to come into contact with metal ions, in contrast to increased H-bonding in dilute NaCl solution. This could improve metal adsorption by the spiropyran units of **1** and **2**, and decrease metal ion selectivity. Breaking the H-bonded structure by addition of NaCl probably also occurs for **1** to the same extent as **2** because zwitterionic polybetaines have a *N* value similar to that for electrically neutral polymers. However, increasing the NaCl concentration to 10 wt% did not significantly improve the amount of metal complexes of **1**, except for the level of Cu^{2+} complexation in comparison to **2**, as shown in Fig. 5. This indicates that electrostatically cross-linked networks of sulfobetaine units are better at protecting against metal ion entry than the H-bonding networks of water molecules. Some reports described the interaction between spiropyrans and Cu^{2+} ions, leading to selective Cu^{2+} complexation.[11,26] There may be a similar interaction between the sulfobetaine units of **1** and Cu^{2+} ions.

Experimental section

Materials

[2-(Methacryloyloxy)ethyl]-dimethyl-(3-sulfopropyl)-ammonium hydroxide (reagent grade) was purchased from Sigma-Aldrich, Inc. *N*-Isopropylacrylamide was purchased from Wako Pure Chemical Industries, Ltd. and used after recrystallization. 1′,3′,3′-Trimethyl-6-hydroxyspiro(2*H*-1-benzopyran-2,2′-indoline) was purchased from Acros Organics. *N*-Isopropylacrylamido (NIPAAm, Wako Pure Chemical Industries, Ltd.) was purified by recrystallization from benzene–*n*-hexane.

1′,3′,3′-Trimethyl-6-methacryloylspiro[2*H*-1-benzopyran-2,2′-indoline] (SPMA)

1′,3′,3′-Trimethyl-6-hydroxyspiro(2*H*-1-benzopyran-2,2′-indoline) (6.8 g) was reacted with methacryloyl chloride (1.3 mL) at 0 °C in chloroform (10 mL) with triethylamine (1.9 mL) for an hour. The solvent was removed *in vacuo*, followed by extraction (chloroform–water). The residue was purified by column chromatography on silica gel with chloroform as the eluent (R_f = 0.67, chloroform) to give SPMA in 51% yield (4.3 g); MS *m*/*z* 361 (M^+, 100%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (3H, s, CCH_3), 1.30 (3H, s, CCH_3), 2.03 (3H, s, methacryloyl-CH_3), 2.72 (3H, s, NCH_3), 5.70 (1H, d, J = 10.3 Hz), 5.71 (1H, dd, J = 0.6, 1.5 Hz, methacryloyl-H), 6.30 (1H, dd, J = 0.7 Hz, methacryloyl-H), 6.5–7.1 (8H, m, Ar–H).

1′,3′,3′-Trimethyl-6-acryloylspiro[2*H*-1-benzopyran-2,2′-indoline] (SPAA)

1′,3′,3′-Trimethyl-6-hydroxyspiro(2*H*-1-benzopyran-2,2′-indoline) (4.7 g) was reacted with acryloyl chloride (1.6 g) at 0 °C in toluene (43 mL) with triethylamine (1.8 g) for 15 h. The solvent was removed *in vacuo*, followed by extraction (toluene–water). The residue was purified by column chromatography on silica gel with chloroform as the eluent (R_f = 0.82, chloroform) to give SPAA in 66% yield (3.10 g); mp 88–90 °C; MS *m*/*z* 347 (M^+, 100%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (3H, s, CCH_3), 1.29 (3H, s, CCH_3), 2.71 (3H, s, NCH_3), 5.70 (1H, d, J = 10.3 Hz), 5.97 (1H, dd, J = 1.1, 10.6 Hz, acryloyl-H), 6.28 (1H, dd, J = 10.5, 16.5 Hz, acryloyl-H), 6.56 (1H, dd, J = 0.7, 17.2 Hz, acryloyl-H), 6.5–7.1 (8H, m, Ar–H).

Copolymerization of sulfobetaine methacrylate and SPMA (1)

The radical copolymerization of [2-(methacryloyloxy)ethyl]-dimethyl-(3-sulfopropyl)-ammonium hydroxide (830 mg) and SPMA (10.8 mg) in 2,2,2-trifluoroethanol (2 mL) was performed under a nitrogen atmosphere at 60 °C for 4 h with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator to afford **1**. The molecular weight of the copolymer ($M_w = 7.5 \times 10^5$, M_w/M_n = 2.9) was determined by GPC (OHpak SB-806MHQ) using saline ([NaCl] = 0.4 mol mL^{-1}) as the eluent and Shodex Standard P-82 as the molecular weight standard. The ratio of SPMA in **1** was 1 mol%, as determined by ^{1}H NMR.

Preparation of a cross-linked copolymer of 1

The radical copolymerization of [2-(methacryloyloxy)ethyl]-dimethyl-(3-sulfopropyl)-ammonium hydroxide (1340 mg), SPMA (36 mg) and methylenebisacrylamide (15 mg) in 2,2,2-trifluoroethanol (2 mL) was performed under a nitrogen atmosphere at 60 °C for 5 h with AIBN on a glass plate to afford a cross-linked copolymer membrane of **1**. The obtained copolymer membrane was immersed in water several times to remove the trifluoroethanol.

Copolymerization of NIPAAm and SPAA (2)

The radical copolymerization of NIPAAm and SPAA in ethanol was performed under a nitrogen atmosphere at 60 °C with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator to afford P(NIPAAm-SPAA). The molecular weight for the copolymer was determined ($M_w = 1.3 \times 10^5$, M_w/M_n = 1.4) by GPC (Shodex KF-804L and KF-803L) using tetrahydrofuran as the eluent and polystyrenes as the molecular weight standard. The ratio of SPAA in P(NIPAAm-SPAA) was 2 mol%, as determined by ^{1}H NMR.

General methods

^{1}H NMR spectra were recorded at 500 MHz on a JEOL JNM-ECP500 instrument. UV/visible absorption spectra were acquired on an Agilent 8453 diode array spectrophotometer. Visible light (>420 nm) for photo-irradiation was obtained by passing light from a 500 W Xe lamp (USHIO) through a color filter, SCF-50*S*-42L (SIGMA KOKI).

Conclusions

The zwitterionic copolymer of **1** has electrostatically cross-linked networks of zwitterionic sulfobetaine units, which improve Cu^{2+} ion selectivity as well as the amount of Cu^{2+} ion adsorption. In contrast, H-bonded networks of cross-linked water molecules in the hydration shell of polymer chains of **1** and **2** do not seem to contribute effectively to metal ion selectivity in metal complexation.

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