Temperature swing adsorption of heavy metals on novel phosphate-type adsorbents using thermosensitive gels and/or polymers

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Abstract

A novel thermosensitive adsorbent was developed, which adsorbs and/or desorbs heavy metals through temperature swing process. The gel-type and polymer-type adsorbents, composed of *N*-isopropylacrylamide (NIPA) as a thermosensitive component and 2-methacryloyloxyethyl phosphate (MEP) as an interactive component, were prepared by free-radical copolymerization. For each type of poly(NIPA-*co*-MEP), phase transitions and temperature dependences for the amount of Cu, a model metal ion, adsorbed was examined. The proposed mechanism associated with the temperature swing adsorption of Cu to poly(NIPA-*co*-MEP) is as follows. In the case of the shrinking gel at higher temperatures, two MEP groups are positioned so as to interact with one Cu ion, while in the swelling gel at lower temperatures, Cu is desorbed from isolated MEP groups. In the case of copolymers, at temperatures lower than the lower critical solution temperature (LCST), two MEP groups interact with one Cu ion as well as those in shrunken gels, and at temperatures higher than the LCST, an aggregate of the copolymer, which is strongly hydrophobic, ejects free water along with Cu ion in the shrinking process. The temperature dependences for adsorption to the copolymer are opposite to gels, even in the gel with a low density of crosslinking points.

Keywords**:** Thermosensitive gel, Temperature swing adsorption, *N*-isopropylacrylamide, Heavy metal, Copolymer

1. Introduction

Thermosensitive gels have attracted a great deal of attention for the applications to drug delivery systems, actuators and so on. Poly(*N*-isopropylacrylamide), poly(NIPA), a representative gel, has a lower critical solution temperature (LCST) in the vicinity of 32°C [1,2], i.e. showing hydrophilicity and hydrophobicity in water at lower and higher temperatures, respectively. Novel adsorbents using thermosensitive gels for trapping heavy metals were reported in our earlier papers [3-6], where poly(NIPA) was used as a thermosensitive backbone polymer. A chelating group, which interacts with heavy metals, was introduced into poly(NIPA) with a molecular imprinting technique [7] using a specific metal as the template. The molecular imprinted gel adsorbents reconstruct multi-point adsorption sites at a specific temperature and disrupt them through swelling deformation at a lower temperature. The adsorbents, therefore, are suitable for the temperature swing adsorption (TSA), i.e. the control of adsorption and desorption of a specific heavy metal with the change in temperature. TSA using the adsorbents described here provides an energy-saving and environmentally-friendly process for the separation of both undesirable and valuable heavy metals in aquatic environments and industrial effluents.

The imprinted thermosensitive gel adsorbents functioned efficiently for the selective TSA of a template metal [1-4]. However the amount of chelating groups that can be copolymerized in gels was limited to less than 1 mol% when NIPA is the primary component, since the increase in chelating groups with metals imprinted resulted in a lack of gelation. This leads to a low adsorption capacity. A promising method for preparing the thermosensitive gel adsorbents showing the selective TSA with a large capacity is the use of an interacting group that has an inherently higher selectivity for a specific metal. Thus, the phosphate was the focus of this study. A large number of extractants composed of phosphoric acid and phosphate, of which representatives are di-2-ethylhexylphosphoric acid (DEHPA) [8] and tributylphosphate (TBP) [9], were developed and reported on their metal-selectivity. Concerning the resin, an aminophosphonate-chelating ion-exchange resin, Duolite C467 (Rohm and Haas), selectively loads V from aqueous solutions containing V and Fe [10]. For thermosensitive gels, Nonaka et al. reported that a copolymer consisting of NIPA and acryloyloxypropyl phosphinic acid had an adsorption capacity higher for lanthanides than for transition metals [11].

In this study, preparation and feasibility of TSA of a novel thermosensitive adsorbent was examined. The adsorbent was composed of NIPA, a thermosensitive component, and 2-methacryloyloxyethyl phosphate (MEP), an interactive component. The chemical structures of NIPA and MEP are shown in Fig. 1. Two types of poly(NIPA-*co*-MEP), a gel-type and a polymer-type, were prepared to investigate the effect of polymer structure on adsorption characteristics, where the poly(NIPA-*co*-MEP) gels were cross-linked with *N,N'*-methylenebisacrylamide (MBAA). For each type of poly(NIPA-*co*-MEP), phase transitions and temperature dependences for the amount of Cu, a model metal ion, adsorbed was examined. The mechanism of adsorption of Cu on poly(NIPA-*co*-MEP) is discussed in terms of phase transitions and dissociation of the phosphate group.

2. Experimental

2.1. Preparation of gels and polymers

N-isopropylacrylamide (NIPA), the primary monomer, was supplied by Kohjin Co. and was purified by recrystallization from a benzene/hexane solution prior to use. 2-(methacryloyloxy) ethyl phosphate (MEP) and *N,N'*-methylenebisacrylamide (MBAA) were used without further purification. The gel and copolymer of NIPA-*co*-MEP were prepared by free radical copolymerization. The monomers and the concentrations used are shown in Table 1. In addition, *N,N,N',N'*-tetramethylethylenediamine (10 mol/m^3), an accelerator, and ammonium peroxodisulfate (2 mol/m^3), an initiator, were used. The polymerization was carried out at 10°C for gels and 25°C for copolymers under a nitrogen atmosphere with a reaction time of 24 hours. The resulting gels and copolymers were extensively washed with deionized water to remove the unreacted monomers. In washing the copolymers, a cellulose tubular membrane with a molecular weight cut off, MWCO, of 13000 was used. The gels were cut into cubes having a side length of a few millimeters and were dried in an oven at 50°C. Similarly, to investigate the swelling/shrinking properties, a cylinder-shaped gel was prepared using a glass tube with a 6.0 mm inside diameter.

2.2. Measurements of swelling diameter of hydrogels and spectrophotometric analysis of aqueous solution of polymers

The swelling diameter of the cylinder-shaped gel was measured as a function of temperature. The ratio of the diameter to the length of the gel was 1:1. The gel was initially immersed in water at 10°C. The diameter, at equilibrium, was measured with a microscope. The temperature was then increased, in increments, and the diameter was measured at each temperature.

To investigate the phase transition of the polymer, the transmittance through an aqueous solution of the polymer was taken as a measure of the turbidity and was measured with a spectrophotometer at the specific temperature. The concentration of the polymer solution used was 5 kg-dry polymer/m^3 and distilled water was used as the reference. The transmittance of the solution was measured at 600 nm, taking into account of the sensitivity for its change.

2.3. Adsorption experiments

The dry gel, 0.05 – 0.2 g, and an aqueous solution of $CuCl_2 \cdot 2H_2O$ in 15 – 20 cm^3 were mixed in a vial, in which the initial concentration of Cu was 1.0 mol/m^3 and the pH was ca. 5.2. The vial was first shaken in a water bath at 10°C for one day to allow the gel to swell. The vial was held at the desired temperature for one day, which was a sufficient period for equilibrium to be attained. The initial and equilibrium concentrations of Cu in the solutions were measured by inductively coupled plasma spectroscopy, ICP (SPS3000, Seiko Instrument Inc.). The equilibrium amount of Cu adsorbed on the gel, which is the net amount of Cu interacted with polymer, was determined from the mass balance on the basis of the assumption that the concentration of free Cu, i.e. non-interacted Cu with polymer in water retained in hydrogel was the same as that in the solution out of gels.

The experiments on the adsorption of Cu on the copolymers were carried out in basically the same manner as was used for the gels. Two types of solutions, 5 cm^3 of a 2 wt% aqueous solution of polymer and 40 cm^3 of a 0.5 mol/m^3 aqueous solution of Cu, were brought into contact via a tubular cellulose membrane with a MWCO = 6000. The polymers in the inner solution did not diffuse via the membrane, while Cu ions diffused from the outer solution to the inner solution. The outer solution was stirred in adsorption experiments. The equilibrium amount of Cu adsorbed on the polymer was determined from the decreased amount of Cu ions in the outer solution.

2.4. Measurements of dissociation of phosphate groups

In order to determine the dissociation constant for phosphate groups in the MEP monomer and NIPA-*co*-MEP polymer (POLY), a pH titration was carried out with aqueous NaOH at 25°C. The pH values were measured with a pH meter. The conditions were as follows; for the MEP monomer, an aqueous 0.01 kmol/m^3 MEP solution of 25 cm^3 and an aqueous 0.01 kmol/m^3 NaOH solution, while for NIPA-*co*-MEP polymer (POLY), an aqueous 1.21 wt% polymer solution of 35 cm^3 and an aqueous 0.005 kmol/m^3 NaOH solution.

3. Results and Discussion

3.1. Phase transitions of hydrogels and polymeric aqueous solutions

Figure 2 shows the change in transmittance with temperature for 5 kg-dry polymer/m^3 NIPA-*co*-MEP polymeric aqueous solutions. The polymers tested were POLY and poly(NIPA) without MEP. The transmittance through an aqueous solution of poly(NIPA) is ca. 1 and 0 at temperatures lower or higher than ca. 33°C of the LCST, respectively. The values of 1 and 0 indicate that the transparent and non-transparent solutions are caused, respectively, by the solubilization and insolubilization of poly(NIPA). Aqueous solution containing POLY also had an LCST. The LCST for POLY is higher that for poly(NIPA). This is attributed to the hydrophilicity of MEP at pH 5.29 of the solution tested as in the cases of poly(NIPA) copolymerized with the hydrophilic acrylic acid [12] and acrylamide [13], respectively. The transmittance through the POLY aqueous solution increases again with an increase in temperature over 50°C, since the dispersed state of the aggregates of insoluble polymer is changed to the bulk state.

Figure 3 shows the temperature dependence for the swelling diameter of the cylinder-shaped NIPA-*co*-MEP gel (GEL) in water. The gel swells and shrinks reversibly with the change in temperature. The swelling diameter decreases with an increase in temperature. Drastic change in diameter was observed at ca. 35°C, similarly to the copolymer.

3.2. Temperature dependence for the amount adsorbed

Figure 4 shows the temperature dependence for the amount of Cu adsorbed to the NIPA-*co*-MEP copolymers and gels. The amount of Cu adsorbed on GEL increases in a stepwise manner with an increase in temperature in the range 30 – 40°C. In this temperature range, the swelling diameter of cylindrical GEL changes sharply, as shown in Fig. 3. Thus the change in the size of the gel-network has an important effect on adsorbability.

The amount of Cu adsorbed to POLY remains constant at temperatures lower than 40°C and then decreases substantially with increasing temperature. As shown in Fig. 2, POLY is insoluble at temperatures higher than ca. 33°C of the LCST and the aggregate is formed over 50°C. The hydrophobicity of POLY increases with an increase in temperature above the LCST and the strong aggregation of the polymer caused by the hydrophobicity leads to poor adsorbability.

The amounts of Cu adsorbed to GEL and POLY are largely dependent on temperature. It should be noted that the adsorption behavior of the gel and the copolymer are different, i.e. the amount of Cu adsorbed to GEL increases with an increase in temperature, while that to POLY decreases. The mechanism of adsorption will be discussed later for each situation. Although the contents of MEP in GEL and POLY are almost the same (see Table 1), the maximum amount of Cu adsorbed on GEL is smaller than that on POLY. The lower adsorbability of GEL can be attributed to the dual role of the crosslinking points, which prevent the gel-network from deforming and function as the obstacle to adsorption.

3.3. Temperature swing adsorption

The feasibility of TSA, i.e. the control of adsorption and desorption by changing the temperature, was investigated. The results of the TSA experiments between 30 and 40°C for GEL and between 30 and 60°C for POLY, based on the temperature dependence of Cu adsorption in Fig. 4, are shown in Fig. 5. In Fig. 5 (a), the amount of Cu adsorbed to GEL is high at 40°C and low at 30°C, that is, the NIPA-*co*-MEP gel adsorbs and desorbs reversibly. In Fig. 5 (b), the amount of Cu adsorbed to POLY decreases when the temperature is increased and then increases again when the temperature is lowered. However, the amount adsorbed in the second run at 30°C is somewhat smaller than that for the initial run of 30°C. That can be attributed to the fact that the aggregation of the polymer once formed at 60°C was not completely disrupted at 30°C due to the absence of stirring in cellulose tubular membrane containing the polymer.

3.4. Dissociation of phosphate groups

To explain the temperature dependence for Cu adsorption on poly(NIPA-*co*-MEP), an understanding of the interaction of MEP and Cu is important. The dissociation of phosphate groups, shown in Eqs. (1) and (2), in the NIPA-*co*-MEP polymer (POLY) and MEP monomer was investigated.

$$\mathrm{R-PO_3H_2} \;\leftrightarrow\; \mathrm{H^+} \;+\; \mathrm{R-PO_3H^-} \tag{1}$$

$$\mathrm{R-PO_3H^-} \;\leftrightarrow\; \mathrm{H^+} \;+\; \mathrm{R-PO_3{}^{2-}} \tag{2}$$

Figure 6 shows the pH titration curves for aqueous solutions containing POLY and MEP monomer with aqueous NaOH at 25°C. For the MEP monomer, the two-step dissociation corresponding to Eqs. (1) and (2) can be clearly observed. On the other hand, the curve for POLY shows no drastic change in pH at the equivalence point. This low sensitivity is due to the small content of MEP in POLY. The dissociation constants, K_{a1} and K_{a2} [kmol/m^3], for Eqs. (1) and (2) were determined by curve fitting based on the following Eqs. (3) – (6).

$$K_{\mathrm{a1}} = [\mathrm{H^+}][\mathrm{R-PO_3H^-}]/[\mathrm{R-PO_3H_2}] \tag{3}$$

$$K_{\mathrm{a2}} = [\mathrm{H^+}][\mathrm{R-PO_3{}^{2-}}]/[\mathrm{R-PO_3H^-}] \tag{4}$$

$$[\mathrm{R-PO_3H_2}]_0 = [\mathrm{R-PO_3H_2}]+[\mathrm{R-PO_3H^-}]+[\mathrm{R-PO_3{}^{2-}}] \tag{5}$$

$$[\mathrm{Na^+}]+[\mathrm{H^+}] = [\mathrm{R-PO_3H^-}]+2[\mathrm{R-PO_3{}^{2-}}]+[\mathrm{OH^-}] \tag{6}$$

where Eqs. (5) and (6) are the mass balance and the electroneutrality, respectively. The subscript “0” in Eq. (5) denotes the initial concentration of phosphate groups. The values of K_{a1} and K_{a2} obtained were $K_{a1} = 7.0 \times 10^{-3}$ and $K_{a2} = 1.6 \times 10^{-7}$ for the MEP monomer and $K_{a1} = 1.2 \times 10^{-7}$ and $K_{a2} = 1.6 \times 10^{-11}$ for POLY, respectively. The regression curves based on these dissociation constants are shown in Fig. 6.

The mole fraction of phosphate group dissociated can be calculated using the dissociation constants obtained. Figure 7 shows the dissociation diagram for the phosphate group in POLY and MEP monomer as a function of pH at 25°C. The phosphate groups in both POLY and the MEP monomers are undissociated at lower pH. This explains the observed phenomena that the NIPA-*co*-MEP gel (GEL) did not adsorb any Cu at the pH = 2.06. A two-step dissociation then occurs as the pH increases. The phosphate group in POLY is dissociated at a higher pH than that in the MEP monomer. This can be attributed to the smaller amount of free water around the phosphate group in POLY due to the presence of polymer chains in comparison with the case of MEP monomer.

3.5. Adsorption mechanism

The proposed mechanisms for Cu to be adsorbed to the poly(NIPA-*co*-MEP), GEL and POLY, are as follows: GEL adsorbs and desorbs Cu at 40°C and 30°C, respectively, as shown in Fig. 5 (a). GEL shrinks and swells at 40°C and 30°C, respectively, as shown in Fig. 3. The two-step dissociation of the phosphate group in POLY occurs at quite high pH ranges, as shown in Fig. 7. Therefore the first stage of dissociation of the phosphate group in GEL should occur at pH = ca. 5.2, the pH where the adsorption experiment was carried out. From these results, the mechanism of TSA for Cu on NIPA-*co*-MEP gels is what is schematically shown in Fig. 8. In the shrinking gel at higher temperatures, two MEP groups are brought into the vicinity and interact with one Cu ion. On the other hand, in the swelling gel at lower temperatures, Cu is desorbed from isolated MEP groups. However, taking into account the fact that

GEL is not completely desorbed by the temperature swing, only a limited portion of the MEP contributes to the TSA. In other words, a portion of the MEP continues to exist in pair and adsorbs Cu ions, irrespective of the gel swelling pattern.

At temperatures lower than 40°C, the amount of Cu adsorbed to the NIPA-*co*-MEP polymer, POLY, is a large constant value but decreases substantially with an increase in temperature, as shown in Fig. 4. Figure 9 shows the photos of an aqueous solution containing POLY during the adsorption experiment. The NIPA-*co*-MEP polymer is soluble in water at temperatures below 30°C and is insoluble around 35°C of the LCST. The NIPA-*co*-MEP polymer undergoes aggregation at 40°C and the size of aggregate decreases with an increase in temperature. From these results, the mechanism of the TSA of Cu on NIPA-*co*-MEP copolymers is what is schematically shown in Fig. 10. At temperatures lower than the LCST, two MEP groups in the copolymer interact with one Cu ion, similar to those in shrunken gels. Around the LCST, MEP in the copolymer still adsorbs Cu although the copolymer is insoluble in water. The fact that Cu is adsorbed to the copolymer at 40°C suggests that the hydrophobicity of the copolymer is not so strong and that free water is present, essential for the adsorption of Cu, around MEP. At temperatures higher than the LCST, as can be expected from the shrunken aggregate of the copolymer, free water around MEP is ejected and Cu ion is taken away along with it.

3.6. Effect of crosslinking on adsorbability

The temperature dependences for Cu adsorption on gel and copolymer are different, as shown in Fig. 4. The difference in the structures of gels and copolymers, the presence or absence of the crosslinking points, can be the key factor. Therefore in the case where the density of the crosslinking points in the gels is decreased, the temperature dependence for Cu adsorption to the gels may resemble that for copolymers. From this viewpoint, the amount of Cu adsorbed to NIPA-*co*-MEP gels prepared using different concentrations of the MBAA crosslinker was investigated. The results are shown in Fig. 11. Temperature dependence is the same for MBAA = 10, 30 and 60 mol/m^3. The amounts adsorbed to the gels of MBAA = 120 and 240 mol/m^3 are somewhat smaller than the values for 60 mol/m^3. This can be attributed to the relative decrease in MEP content in the gels caused by the increase in MBAA content. In conclusion, even though there are a few crosslinking points in a gel, the temperature dependences for adsorption to gels and polymers can be different. In other words, the steric formation of gel-network crosslinked is limited, while that of the polymer is unlimited.

Conclusions

A novel thermosensitive adsorbent for the TSA of heavy metals was developed. Gel-type and polymer-type adsorbents were prepared by the copolymerization of NIPA, a thermosensitive component, and MEP, an interactive component. The NIPA-*co*-MEP gel swells and shrinks reversibly in water in accordance with the temperature swing between 30 and 40°C. The amount of model metal Cu adsorbed to the gel increased with increasing in temperature between 30 and 40°C. This thermosensitive change in the amount of Cu adsorbed was reversible. Taking into account the phase transitions and the dissociation of phosphate group, in the shrinking gel at 40°C, two MEP groups become positioned in the vicinity, interacting with one Cu ion, while in the swelling gel at 30°C, Cu is desorbed from an isolated MEP group. The solubility phenomenon of

NIPA-*co*-MEP polymer is reversible; it is soluble or insoluble in water at temperatures lower or higher than ca. 35°C of the LCST. The amount of Cu adsorbed by the copolymer decreases with an increase in temperature from 30 to 60°C. The amount adsorbed to the copolymer, as well as that on the gel, changes reversibly as a result of temperature swing. In the desorption process at 60°C, the thermosensitive polymer, which shrinks extensively as a result of the enhanced hydrophobic interactions compared with the thermosensitive gel-network, expels free water along with Cu ions. The gel-type and polymer-type adsorbents demonstrate the feasibility of TSA, but their adsorption and desorption by temperature swing is opposite. Even in the gel with a low density of crosslinking points, the temperature dependences for adsorption to the gels and copolymers are different.

Acknowledgment

The authors wish to acknowledge the support of a Grant-in-Aid for Scientific Research from JSPS (Japan Society for the Promotion of Science) (Grant No. 16760607).

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Figure captions

Fig. 1 Chemical structures of NIPA (left) and MEP (right)

Fig. 2 Transmittance against temperature for aqueous solutions of NIPA-*co*-MEP polymer (POLY) and NIPA polymer (poly(NIPA))

Fig. 3 Swelling diameter of cylinder-shaped NIPA-*co*-MEP gel (GEL) in water as a function of temperature.

Fig. 4 Amount of Cu adsorbed to NIPA-*co*-MEP gel (GEL, open key) and copolymer (POLY, closed key) as a function of temperature.

Fig. 5 Changes in the amount of Cu adsorbed to poly(NIPA-*co*-MEP) by temperature swing. (a) GEL, between 30 – 40°C. (b) POLY, between 30 – 60°C.

Fig. 6 pH titration curves for aqueous solutions containing (a) NIPA-*co*-MEP polymer (POLY) and (b) MEP monomer with aqueous NaOH at 25°C. Solid curves are the calculated values.

Fig. 7 Calculated mole fraction of species of dissociated phosphate group in (a) NIPA-*co*-MEP polymer (POLY) and (b) MEP monomer as a function of pH at 25°C.

Fig. 8 Schematic diagram of the temperature swing adsorption of Cu to NIPA-*co*-MEP gels.

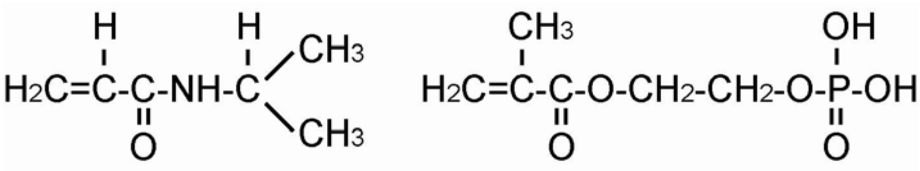
Fig. 9 Photos of aqueous solutions containing NIPA-*co*-MEP polymer (POLY) during the adsorption experiment.

Fig. 10 Schematic diagram of temperature swing adsorption of Cu to NIPA-*co*-MEP copolymers.

Fig. 11 Amount of Cu adsorbed to NIPA-*co*-MEP gels prepared using different concentrations of MBAA as a function of temperature.

Table 1 Concentrations of monomers in pre-gel solutions [mol/m^3] and theoretical values of the MEP content in NIPA-*co*-MEP copolymers [mmol/g-dry polymer]

Sample name	[NIPA]	[MEP]	[MBAA]	[MEP]/[NIPA]	MEP content
GEL	1200	10	60	0.83 mol%	0.0674
POLY	750	6.25	0	0.83 mol%	0.0720



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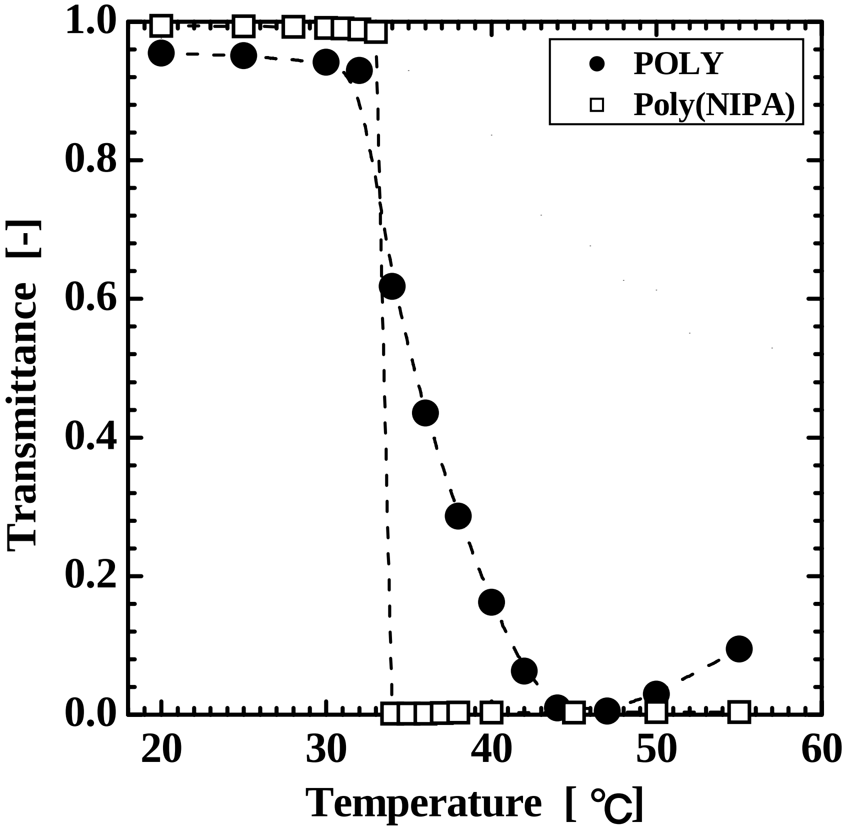

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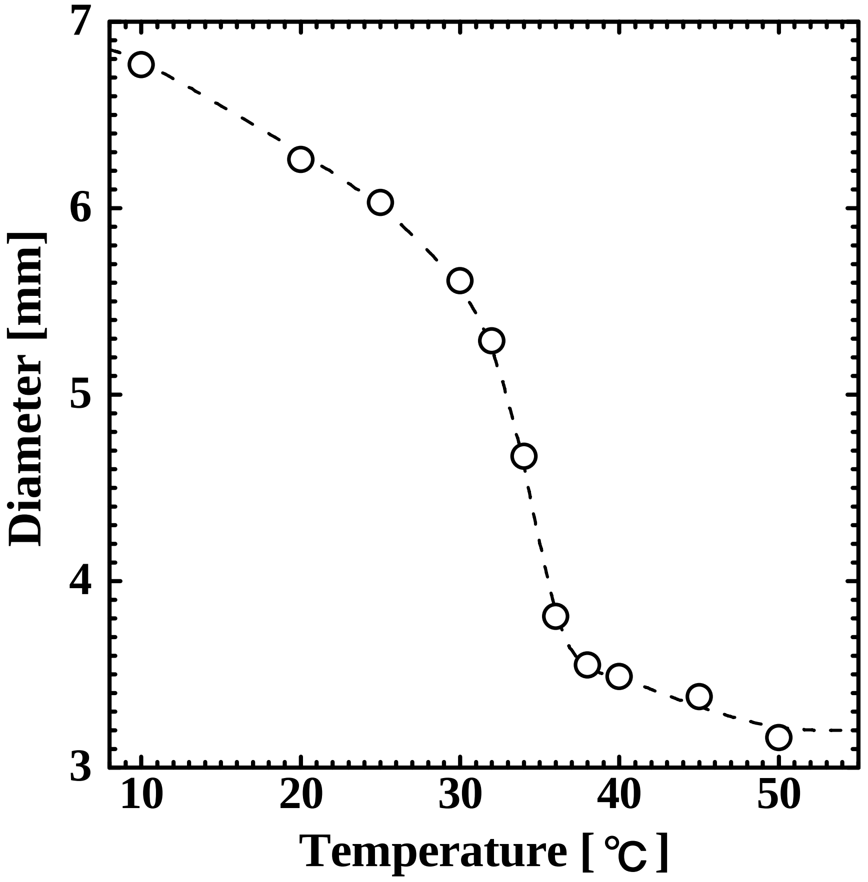

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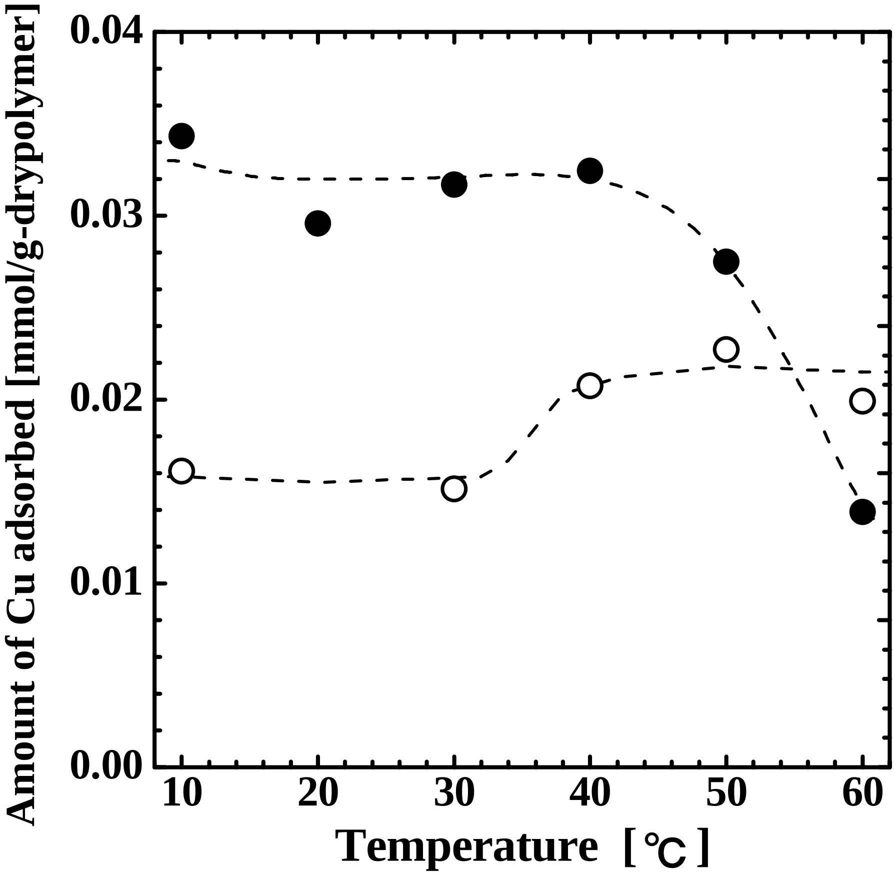

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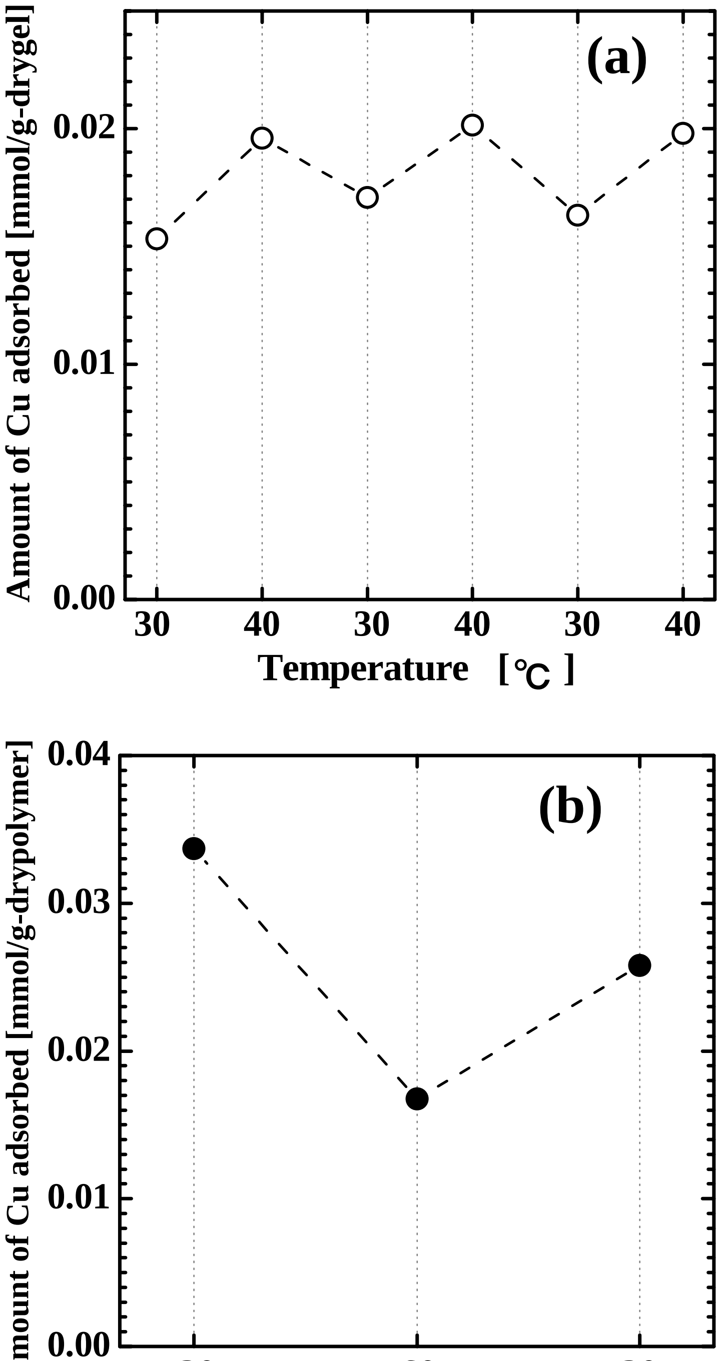

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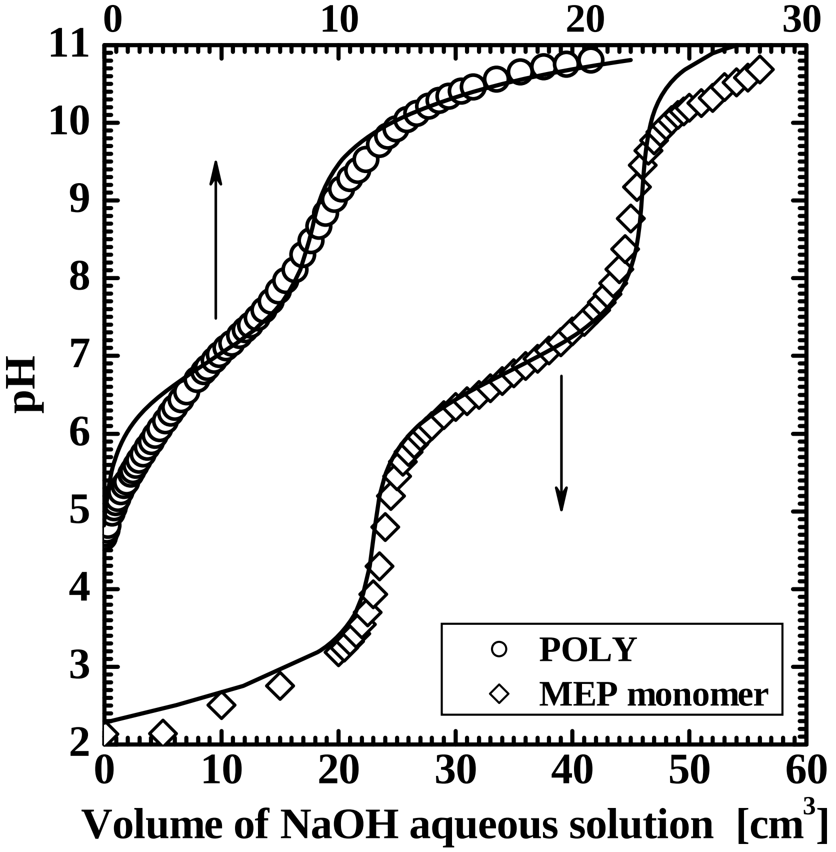

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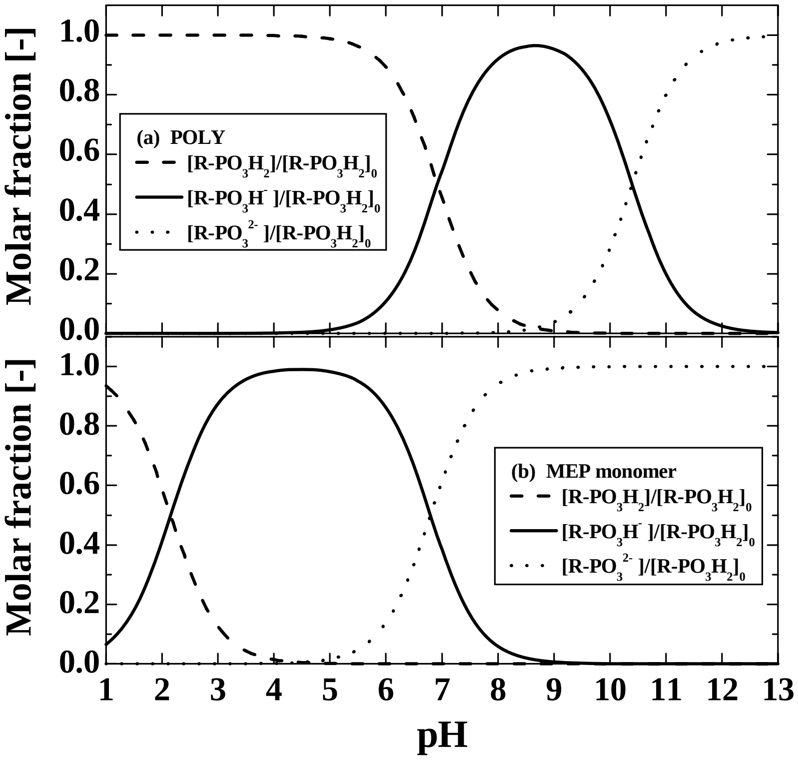

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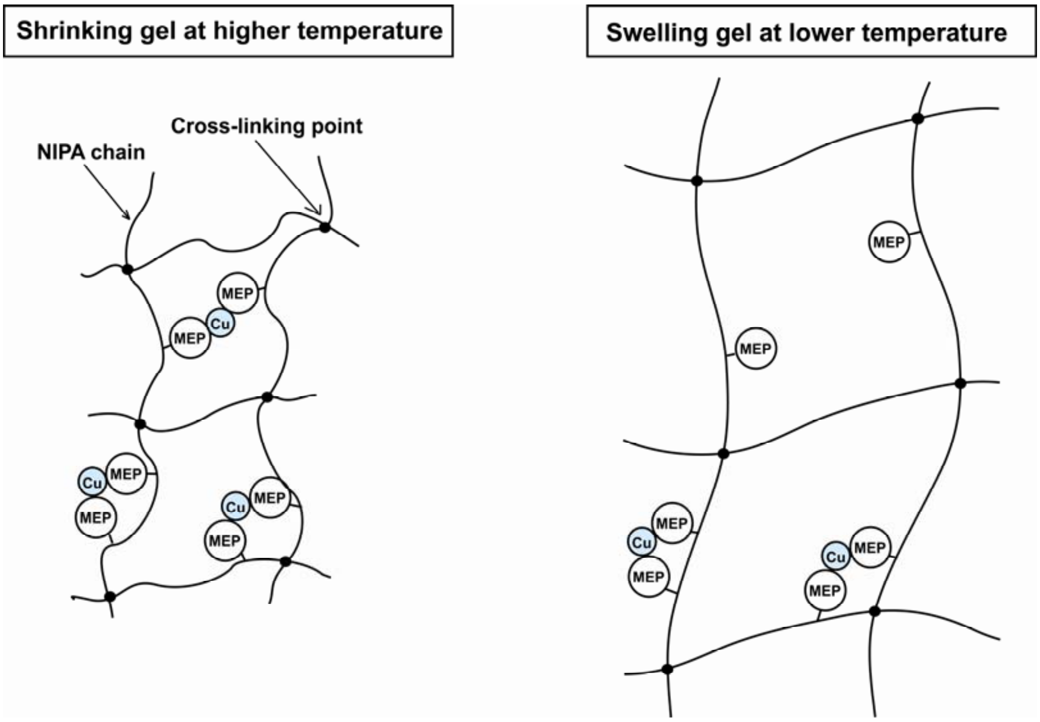

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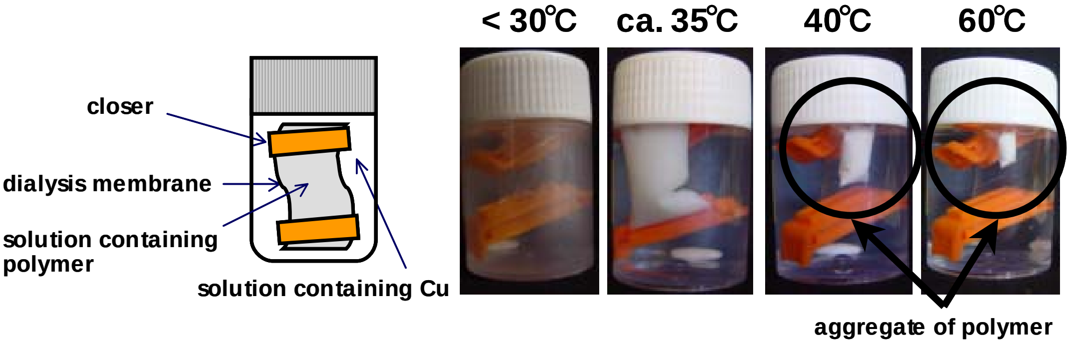

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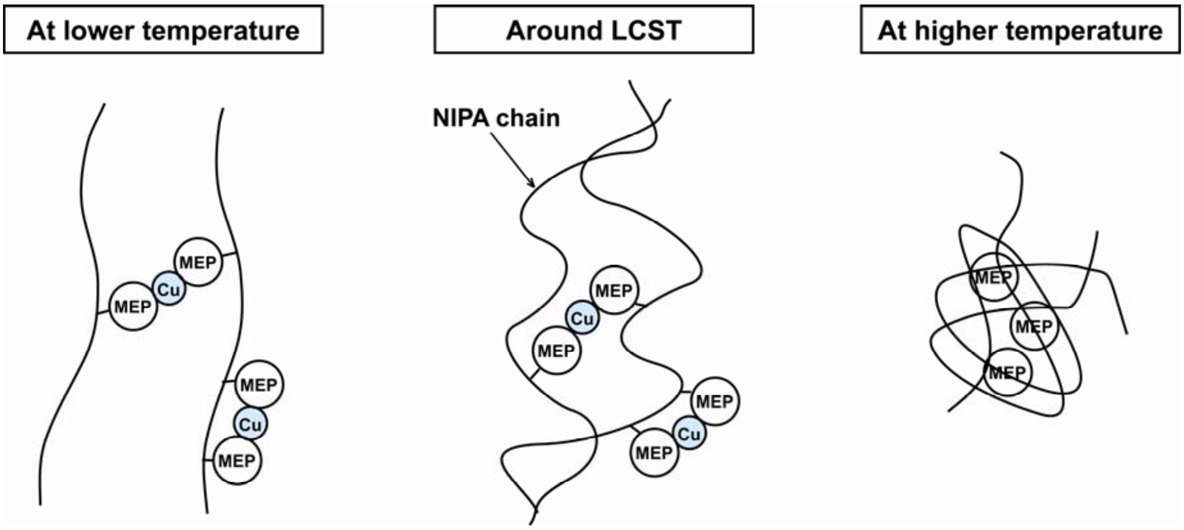

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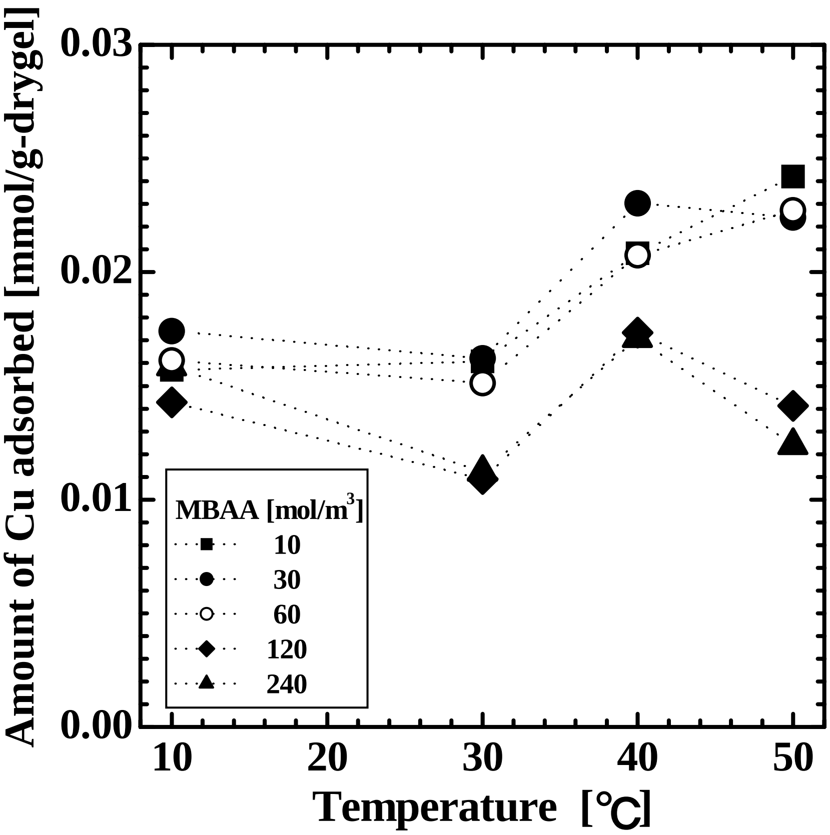

Fig. 11 H. Tokuyama et al.