

Effects of Synthesis Temperature and TEMED Concentration on the Swelling Behavior of PAAm Gel

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The authors have investigated the swelling behaviors of several PAAm hydrogels which are synthesized at several temperatures and with some concentrations of *N,N,N',N'*-tetramethylethylenediamine (TEMED), because the gels' swelling degrees are deeply related to their network structures determined by the reaction fashions in their synthesis processes and because the heavy metal adsorption functionalities of their ionized homologues, which is important for the application for purifying environments, seem affected considerably by the swelling ratios. By the investigation in the present study, it has been revealed that the swelling degree of the PAAm gel in these conditions have received considerable effects by the TEMED concentration and synthesis temperature.

Key words: PAAm gel, swelling degree, TEMED, temperature, environmental purification

1. INTRODUCTION

The heavy metals are known to bring about serious environmental problems. In Japan, the most famous incident caused by the heavy-metal pollution is the Itai-Itai Disease, which initiated the movement against progress of the environmental pollution. In 1968, the Ministry of Health and Welfare in Japan announced that the Itai-Itai Disease seemed to occur by cadmium discharged from the Kamioka mine to the Jintsu River, since when public attention have been attracted on the heavy metal pollution and the worry about such an environmental problem has been widespread [1,2]. In these circumstances, the heavy metals in industrial-plant outflows have been severely controlled by ordinance. With these measures, recently, the environmental conditions on the heavy metal pollution have been much better. However, one should not forget that the heavy metals already discharged to the environment would not decompose automatically and that the polluted area has spread by diffusion rather than disappear from the environment [3, 4].

By ordinance, the industrial waste-fluid which contain the heavy metals are classified as a specially controlled industrial waste [5]; the heavy metals in the waste fluids are precipitated in hydroxide forms in the waste-treatment facilities of the industrial plants, which are transported to and are stored in either of Strictly Controlled Type Landfill Site or Controlled Type Sanitary Landfill Site depending on their toxicities and/or chemical stability [5]. Though, usually these procedures are performed without any trouble, the

toxic-waste-fluid leakage from these landfill sites is apprehended because the shielding apparatuses of the landfill sites can be broken by the influence of acid rain [7] going through the process described as follows: In the Least Controlled Landfill Site, the fluid containing the heavy metals can ooze out with the wastes-and-acid-rain reaction and goes under the final landfill site and can contaminate the underground water. In the Controlled Type Sanitary Landfill Site, the heavy metal waste fluid can flow outside through the rent of the shielding sheet. In Strictly Controlled Type Landfill Site, their concrete walls are easy to be corroded by acid rain, therefore the harmful fluid polluted by the heavy metal can escape to the outside from the wall crevices.

In these circumstances, they crave for quick and easy methods which can capture the heavy metals with high efficiency in order to prevent the toxic heavy metals from spreading in the environment and the authors have been convinced that some hydrogels can be usable for such applications.

Some hydrogels show characteristic features by the interactions between their internal parts: network polymers and solvent; one of the most famous phenomena is the volume phase transition [8-10]. In some volume phase transitions, their features change remarkably by introducing ion-groups. In the case of *N*-isopropylacrylamide/acrylic acid gel, the addition of carboxyl-groups induces a discontinuous volume change [11,12]. Such characteristics are very interesting and have been investigated extensively. Besides the drastic transition features, the ion-group introduction to

the hydrogels develops the ion capturing function. By utilizing this property, Jacson *et al.* devised a metal-ion detector by an interpenetrating network hydrogel composed of poly(vinyl alcohol) and *N*-isopropyl-acrylamide/acrylic acid [13]. However, they did not pay attention to the ion-adsorption-amount efficiency of the hydrogel.

In the previous studies [14-16], the authors demonstrated that the ionized gel is promising as a heavy-metal adsorbent with high adsorption efficiency. The advantages of the ionized gel as an ion-capturing material over other ones are as follows:

- The transporting expenses can be considerably cut down because the (organic) hydrogels are composed of relatively light elements (such as H, C, N and O) compared with the heavy metals. Therefore, the weight of the captured heavy metals per that of the adsorbent can be far larger than inorganic adsorbents like zeolites.
- The networks of the chemical hydrogels are made of covalent bonds which are not easily destroyed in a wide range of temperature, pressure and pH, etc. Therefore, they can capture the heavy metals in various conditions.

In the authors' previous investigation [14], they demonstrated that poly(acrylamide/sodium acrylate) (PAAm/SA) gel can be utilized as a positive heavy-metal adsorbent with high efficiency. The Cu(II) ion-capturing features are shown in Fig.1 [14]. As shown in the figure, the Cu(II) adsorption amount increases with the its concentration and become saturated after a certain value; the maximum captured Cu(II) weight shows an exponential saturation feature with the SA fraction in the PAAm/SA gel. The Cu(II) capturing efficiency in the previous experiment was estimated to be ~20wt% of the polymer network, which

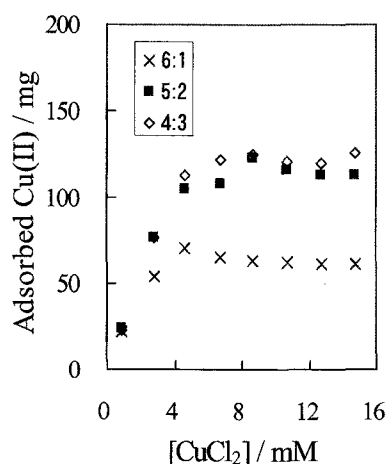


Fig. 1 CuCl₂ concentration dependence of the recovered Cu(II) weight to 10 g of the PAAm/SA (700 mM) pregel solution [14].

The symbols, ×, ■ and ◇ denote the data of the PAAm/SA gels with molar ratios AAm:SA=6:1, 5:2, 4:3, respectively.

is a considerably high value as an adsorbent compared with other adsorbent like zeolites and so on. The authors also demonstrated the positive heavy-metal adsorption functionality of the sodium carboxymethylcellulose gel [15] made by γ -ray irradiation [17,18]. The characteristics of this material in addition to those of the PAAm/SA gel are non-toxicity, biodegradability and availability at low price.

The authors also developed the negative-ion-capturing hydrogels in addition to the abovementioned positive-ions-adsorbing ones because there are many harmful heavy-metal ions with a negative polarity in the environment such as Cr₂O₇²⁻ and SeO₄²⁻. As for chromium, the chromium metal itself is not harmful and is used for the tableware plating. However, it becomes toxic in the form of the trivalent- or hexavalent-ion form. The natural form of the chromium ion is trivalent and is not so toxic, while the hexavalent chromium ion is generated artificially and very harmful; there is a great possibility of becoming not only dermatitis or neoplasm but also cancer if the skin is stained with the hexavalent chromium. In addition, the hexavalent chromium is easy to evaporate, which make the influence on health more serious because it can be absorbed from the digestive organs, lungs, the skin, etc. In the previous study [16], the heavy-metal-anion absorption feature of dimethyl-aminoethylmethacrylate quaternised with methyl chloride (DMAEMAMeCl) / acrylamide (AAm) gels were investigated as the first examination of the negative-ion capturing hydrogel, in which the usability of the DMAEMAMeCl/AAm gel for a heavy-metal-anion capturing material was clearly demonstrated. Besides, the comparison of the captured heavy-metal amounts of PAAm/SA [14], CMC-Na [14] and DMAEMAMeCl /AAm [16] gels observed in the previous studies, revealed almost the same ion-capturing efficiency, and needless to say, much higher than that of

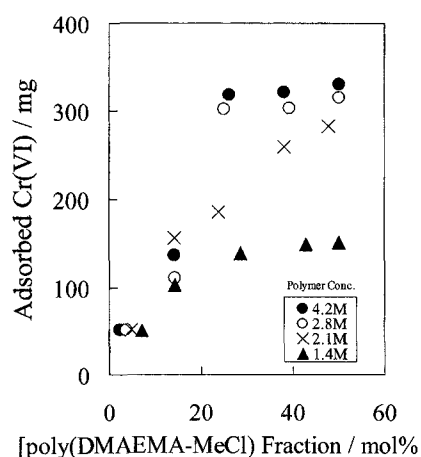


Fig. 2 Adsorbed Cr(VI) amount change with the [poly(DMAEMAMeCl)]:[AAm] molar ratio and ingredient's concentration of poly(DMAEMA-MeCl)/AAm copolymer gel to 10 g of the pregel solution [16].

other adsorbents such as zeolite, ion-exchange resins and so on.

From these experimental results of the previous studies, the authors have confidence that these hydrogels can be usable for the environmental purifying applications. However, the authors also noticed a problem in the previous studies, the small diffusion constant of water in the gels, which is very important problem for quick capturing of the heavy-metal ions by as many internal ionized-groups as possible. Before the present study, because the ion-capturing efficiencies of the gels depend heavily on their structures, there had been several attempts to improve the efficiency such as extending the surface area of the gels by making the volume of the gels smaller [19] or increasing the spacing of networks in the gels by their decreasing crosslink densities [20]. However, these methods are not for suitable for the practical of the gels in a field because the gels made by these method are not easy to handle and/or fragile. In these circumstances, the authors have adopted the other methods which utilize the inhomogeneity introduced in the gel's synthesis process, namely, making the porous gels with internal channels which enable the ambient water to penetrate into the middle of the hydrogel block quickly. Along this line, the authors prepared porous PAAm/SA gels with prescribing an excessive amount of cross-linker in the preparation process because it is known that the PAAm/SA hydrogel becomes turbid above a certain cross-linker concentration due to network polymer inhomogeneity with a scale of light wavelength in the previous studies [21-27]. However, in the previous study [28], a considerable elasticity increase was also observed around the cross-linker concentration around which the gel's turbidity occurs. This feature is not favorable for the present application of the hydrogels because the large elasticity will inhibit the swelling process. Therefore, the authors have been seeking for other methods which can increase the swelling degree without causing any side effect. In these circumstances, in the present study, the authors have examined the swelling properties of the PAAm gels with prescribing several amounts of TEMED in the synthesizing procedure at some temperatures and have found that the swelling degree is much affected by this treatment, which can be useful for utilizing the gels for the environmental purifying applications.

2. EXPERIMENTAL

2.1 Sample Preparation

In the present study, acrylamide (AAm, 700mM), *N,N*-methylenebisacrylamide (BIS, 20mM), *N,N,N,N*-tetramethylethylenediamine (TEMED, 1~5mM) and ammonium persulfate (APS, 1mM) were used as primary monomer, cross-linker, accelerating agent and initiator, respectively. To begin with, 8mL of the mixtures with different TEMED concentration were poured into several test tubes. Then, a polypropylene straw (~5.6mm in diameter) was put into each the test tube. After then, the test tubes were left, for 24hrs, at room temperature, 40, 60, 70 and 80 °C, respectively. After completion of the gelation process, the straws were taken out from test tubes and the column-shaped gels were pushed out from the straws. After both the

10mm-edges of the columns were cut off, two 15mm-samples were cut out and, in order to wash out unreacted ingredients, soaked in 200mL of purified water at room temperature for 48 hrs, during which the ambient water was renewed 3 times. After the washing, the samples were put in a vessel containing pure water.

2.3 Measurement of Equilibrium Swelling Weight

Every-24hr sample-weight measurements were carried out after taking them out from the vessel and wiping up the surface water; then, they were returned to the vessel. The weight measurements were continued until all the weight changes in the last 5-time measurements became within the 5% of the respective weight values and the equilibrium weights were derived by averaging the last five values.

After finishing the weight measurements, all the samples had been dehydrated at room temperature for 10 days, and then at 105°C for 1 day. After the dehydration treatments, the weights of the dried samples were measured five times and the weights of the gel network polymers were obtained by averaging the 5 weight values. With these values, the gels' swelling degrees were derived in the form of the water content (R) which is described by the formula,

$$R = \frac{(w_g - w_p)}{w_p}$$

where w_g is the equilibrium weight of the swollen gel, and w_p , the network-polymer weight. R indicates the water weight which can be hold by 1 g of the network polymer.

3. RESULTS AND DISCUSSION

The polymerization temperature and TEMED concentration dependences of the swelling degree (R) is shown in Fig.3. As can be seen from the figure, R increases remarkably with increasing the polymerization

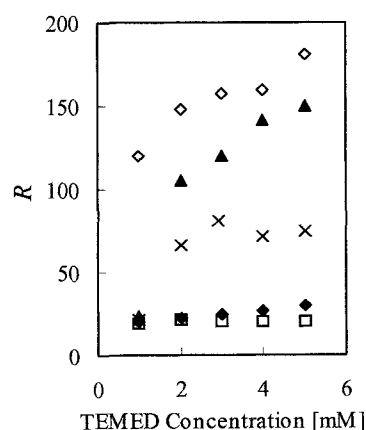


Fig.3 The polymerization temperature (T_p) and TEMED concentration dependences of water content (R). The symbols in the figure refer to T_p 's, \diamond :80°C, \blacktriangle :70°C, \times :60°C, \blacklozenge :40°C and \square :Room Temperature, respectively. (See also text.)

temperature. As a possibility, the authors estimate that these features may be caused by increasing the reaction rate in the gelation process. It is also perceived from Fig.3 that the degree of the influence of the TEMED differs with the polymerization temperature: below 60°C no remarkable effects of TEMED on R are observed while an almost linear dependence on the TEMED concentration is clearly seen above the temperature. However, roughly speaking, the effects of the TEMED concentration and the synthesis temperature seem to be similar. The author estimate that such a similarity in the effects on the swelling process comes from the similar role of both the parameters on the polymerization reaction: both the parameters accelerate the polymerization process. As for the structure, the fast reaction process may introduce a sparse configuration of aggregates as observed in the case of the diffusion limited aggregation, while the slow reaction, dense arrangements of small clusters with small correlation length like the reaction-limited aggregation. Such a structural feature can affect the swelling properties: the sparse configuration enables the ambient water to permeate into the internal part more easily than the dense configuration. However, the detailed features of these phenomena are not clear so far, therefore much more investigations are necessary for the understanding of the whole mechanism. It may be necessary to refer to the environmental applications of the experimental features. In the present investigations, remarkable increase in R is demonstrated by the simple treatment in the present study, which indicates a potential for the high efficiency ion-capturing functionality. The next subject for the practical applications is the examination of the ion-capturing property of the gels made by the present treatments which is in progress now.

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