Development of Photoresponsive Shrinking Gels

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1. Introduction

Polyacrylamide (PAAm) gels are known to show a discontinuous volume phase transition with pH, temperature, solvent composition, ionic composition, and a small electric field [1,2]. PAAm gels swollen by water are transparent solids in the range above pH-5. However, they become shrunken near pH-5 and are in the collapsed state in the low pH regions. Thus, since interfacial pressure of swollen PAAm gels can be diminished by the addition of acid solution to them, we could expect the PAAm gels to work mechanically.

Irie and Kungwatchakun reported a synthesis of photosensitive gels by introducing leucocyanide derivatives, which produce ion pairs at irradiation, to PAAm gels [3-5] and first showed that copolymer gels of leucocyanide derivatives and N-isopropylacrylamide display a discontinuous volume phase transition when they are irradiated by uv light. However, quite a few works have been published so far on photoresponsive gel systems using volume phase transition phenomenon by irradiating chromophores introduced into gel systems [6,7]: some rather have used light as a source of local heating [8].

Here we present a new type of photoresponsive gel system using phenol moieties. Phenol is a very weak acid of pKa-10 in the ground state but its pKa is known to become as low as 4 in the singlet excited state [9,10], meaning that phenol can work as a relatively strong acid at irradiation and can change its microenvironment to be acid temporarily. In this paper, we report our success that hydrogels of PAAm incorporated with phenol moieties can be collapsed only by irradiating uv light.

2. Experimental

2.1. Preparation of PAAm gels having phenol side-chains

The PAAm gels with phenol moieties (Fig. 1) were prepared by copolymerization of acrylamide (AAm), N,N'-methylenebisacrylamide (MBAAm) as a cross-linker, p-tert-butoxystyrene (BST), and either sodium acrylate (SA) or sodium methacrylate (SM) as an ion regulator using N,N,N',N'-tetramethylethylenediamine as an accelerator and ammonium persulfate as an initiator. BST was kindly provided by Hokko Chemical Co. The ratio of [AAm]:[MBAAm]:[SA] (or [SM]) was constant to be 54:1:3 and the fraction of BST was changed. Mixture of DMF and water with volume ratio of 2:3 was used as solvent. The solution was kept at pH-8.6, flushed with nitrogen, and stirred at room temperature for 24 h. The protecting group of hydroxy group of a phenol moiety was removed by adding concentrated hydrochloric acid to the crude gels and heating at 60°C for 3 h. The gels were washed with water using dialysis method until

![Chemical structure of PAAm gel A.](image_url)

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Table 1. Molar fraction of components of the PAAm gels used

<table>
<thead>
<tr>
<th>sample</th>
<th>AAm</th>
<th>MBAM</th>
<th>SA</th>
<th>SM</th>
<th>Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(6.5)</td>
<td>87</td>
<td>1.6</td>
<td>4.8</td>
<td>-</td>
<td>6.5</td>
</tr>
<tr>
<td>A(1.6)</td>
<td>92</td>
<td>1.7</td>
<td>5.1</td>
<td>-</td>
<td>1.6</td>
</tr>
<tr>
<td>A(0.41)</td>
<td>93</td>
<td>1.7</td>
<td>5.1</td>
<td>-</td>
<td>0.41</td>
</tr>
<tr>
<td>M(4.1)</td>
<td>89</td>
<td>1.7</td>
<td>-</td>
<td>5.1</td>
<td>4.1</td>
</tr>
<tr>
<td>M(0.63)</td>
<td>92</td>
<td>1.7</td>
<td>-</td>
<td>5.1</td>
<td>0.63</td>
</tr>
</tbody>
</table>

(mol%)

fluorescence of phenol moieties was not detected in water any more. The fraction of phenol group introduced to the gels was determined by uv absorption and fluorescence measurements using 4-isopropylphenol as a monomer model compound. Table 1 shows the sample prepared and used in the present study. All the samples were evaporated and dried under vacuum. Any samples used were prepared by swelling dried samples with distilled and filtered water in the dark.

2.2. Measurements and Irradiation

Uv absorption spectra were measured on a Shimadzu UV-2200. Fluorescence spectra and fluorescence excitation spectra were measured at 25°C on a Hitachi F-4500 spectrofluorometer. In order to irradiate gel samples, a PAN uv lamp PUV-1 (Tokyo Kagaku Kikai) was used as an excitation source without classifying the light by wavelength.

Results and Discussion

All the gels having phenol groups were ascertained to be swollen by water above pH-6 while they were collapsed in the pH range lower than pH-5.1. We first tried to check whether our gels were collapsed by irradiation of uv light or not. Figure 2(A) shows the picture of M(4.1) swollen by water with a swelling weight ratio (= (weight of swollen gel)/(weight of dried gel)) of 500. Although 1g of a gel with a swelling weight ratio of 500 lost 80 mg of water on the average in an hour, the appearance did not change so much. Figure 2(B) displays the change of the same gel shown in Fig. 2(A) by irradiating uv light for 30 min. Most water was removed and the gel was completely collapsed. Figure 2 demonstrates that our PAAM gels having phenol moieties can be collapsed by uv irradiation. H⁺ ions are assumed to be released from excited phenol side-chains and to induce the shrinking of PAAM gels.

Next we examined what is dependent on the collapsing time of gel samples by uv light. The decaying time of gels by uv light was measured as follows. A gel swollen by water was prepared in a quartz test tube whose diameter is 1 cm. The test tubes were set upside-down and irradiated at 2.1×10^{18} quanta/s. We measured the time required for water to ooze from the irradiated gel or for some parts of the gel sample to move. Figure 3 shows the relationship between collapsing time of gel by irradiation and swelling weight ratio. Each point is the average value of two or three experiments: for example, in the case of A(1.6) with a swelling weight ratio of 500, the collapsing time was measured to be 19 min and 16 min. By taking into account distribution of phenol moiety being not uniform in gels, these values are evaluated to be reproducible enough.

The results of Fig. 3 indicate that the collapsing time of each gel is strongly dependent on concentration of phenol moiety in the area irradiated. In the state of high swelling ratio, all the photons of irradiation light can be absorbed by phenol moieties, so the sample with high content of phenol (M(4.1)) was collapsed more quickly than...
the samples with lower content of phenol (M(0.63)). The order of the collapsing time was the same as that of phenol fraction of each gel sample. On the contrary, in the case of low swelling ratio such as 100, because the concentrations of phenol moieties of any samples are higher than the photons given by irradiation ($2.1\times10^4$ quanta/s), the collapsing times turned out to be nearly the same.

As a matter of fact, the swollen gels prepared from A(6.5) were found not to be collapsed even after irradiation for 6 h in spite of high fraction of phenol moieties. In order to examine this cause, we measured fluorescence spectra of phenol moieties in each gel with different swelling ratios. Figure 4 shows the difference of phenol fluorescence in A(6.5) and A(1.6) with a swelling weight ratio of 1000. Below this concentration, the fluorescence spectra of phenol moieties of A(6.5) were identical with one another in shape. The shape of phenol fluorescence of A(1.6) agrees with that of 4-isopropylphenol, a monomer model, together with the fluorescence shapes of A(0.41), M(0.63) and M(4.1), meaning that this fluorescence shape with a peak at 305 nm is of a phenol group being independent of other groups. However, the phenol fluorescence of A(6.5) in Fig. 4 has a peak at 320 nm and is different from the spectrum for an isolated phenol group such as a dilute solution of 4-isopropylphenol. The excitation spectra of the fluorescence of the A(6.5) hydrogel were found to be identical with one another. The same fluorescence behavior was observed for poly(p-vinylphenol) in a mixture of water and tetrahydrofuran. Thus, the fluorescence of A(6.5) hydrogel can be assumed to be from an excimer formed between side-chain phenol groups. Because the fraction of phenol moieties in PAAm gels is so high that some phenol groups can interact with each other, proton cannot be released from a phenol group even for a temporal time.

On the other hand, the efficiency of photoresponsivity of PAAm gels having a methacrylate group (PAAm M) was found to be higher than that of PAAm gels having an acrylate group (PAAm A) (Fig. 3). This difference is assumed to be due to distribution of phenol groups in gels. When PAAm gels were prepared, phenol groups were introduced to them as a p-tert-butylstyrene (BSt), which is not polar at all. It is assumed to be more uniform in a PAAm gel with less polar methacrylate groups than in a PAAm gel with more polar acrylate groups. Since solvents used for the preparation are polar, BSt's, namely phenol moieties, are considered to be introduced into PAAm M more uniformly and to work more effectively as a supplier of a proton to PAAm gels. This assumption is supported by the fact that the excimer fluorescence was observed for an A(6.5) hydrogel (Fig. 4), but not detectable at all for an M(4.1) hydrogel. As a matter of fact, if 6.5 mol% of phenol were dispersed uniformly in a gel with a swelling ratio of 1000, no excimer formation would have been observed. The existence of an excimer fluorescence is a proof that local concentration of the phenol side-chain introduced into A(6.5) is quite high.
Fig. 5. Fluorescence spectra change of A(1.6) hydrogel with a swelling ratio of 1000 when it was irradiated at 279 nm: excitation wavelength for fluorescence measurement is 279 nm. Except the spectrum for 1 h in the dark, all the spectra were obtained after irradiating for the time described. After irradiating for 3 h, the gel was kept for 1 h in the spectrofluorometer without irradiation.

Protons released from phenol groups at irradiation should be back to phenol groups in the ground state. However, since local microenvironment in a gel around a phenol side-chain is not uniform and simple, the shrinking process of the gels is assumed to be predominant than the recombination process between a phenol anion and a proton. In order to examine what is taking place in the gel, we measured time change of fluorescence spectra of A(1.6) hydrogel with a swelling ratio of 1000 (Fig. 5). The gel was irradiated at 279 nm by an excitation beam of the spectrofluorometer with 5.8 x 10^10 quanta/s. The fluorescence intensities of phenol side-chains were found to decrease with a time of irradiation. This large decrease indicates that photodegradation of phenol groups took place in any case. However, because the fluorescence intensities of phenol groups turned out to be recovered more or less after leaving the gel in the dark, it is clear that the decrease of the fluorescence as shown in Fig. 5 is not only due to photodegradation but also to release and transfer of protons from phenol side-chains.

In conclusion, we have successfully presented in the present paper that the PAAm hydrogels having a small amount of phenol side-chains can be shrunk by irradiation of phenol moieties. We hope that this system will be useful for the development of a photoresponsive gel that can do the work at irradiation of light.

References