Clouding Properties of Maleic Acid/Acrylamide Gels

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Clouding-feature observations were made for several maleic acid/acrylamide (MA/AAm) gels with different fractions of MA and cross-linker concentrations for the first time. In the investigations, both of the conditions were found to considerably influence the turbidity of the MA/AAm gels. In addition, it was also found that turbidity of some MA/AAm gels changes with temperature, which indicates the inhomogeneity alteration.

Key words: turbidity, maleic acid, acrylamide, gel, inhomogeneity

1. INTRODUCTION

Gel is a kind of two-component system made up of solvent and network. Because of this structural characteristic, the interactions between the two constituents affect considerably properties of the gel [1,2], which are very interesting and seem also to be utilizable for the industrial applications as a smart material [3-5]. Besides, some gels also show curious structural features in the dehydrated state, such as micro-phase separation, of which the structure is quite sensitive to environmental conditions [6,7].

As well as these features, the gels exhibit remarkable property related to configuration of the network: some gels become turbid with a small change in the concentration of cross-linker. The turbidity is known to be related to a spatial inhomogeneity of the gel network and many studies have been reported [8-18]. Because such a property change is very interesting from both of the viewpoints of the light scattering mechanism and nanostructural network configuration, the authors carried out investigations of two hydrogels, sodium acrylate/acrylamide (SA/AAm) and sodium acrylate/N-isopropylacrylamide (SA/NIPA) gels, in the previous studies; and observed various property changes at critical cross-linker concentrations where the gels become turbid [19,20].

In the present study, the authors have made observations for the clouding properties of maleic acid/acrylamide (MA/AAm) gel, for the first time, in order to examine the effect of plural carboxyl groups on the turbidity properties (an MA molecule has two carboxyl groups). In the turbidity investigations of the MA/AAm gels with several MA-ratios and the cross-linker concentrations.

2. EXPERIMENTALS AND RESULTS

The 6 sets of the 1.4 M aqueous solutions of molar ratios of AAm:MA = 6:1, 5:2, 4:3 and 3:4 were prepared as the pre-gel solutions of the MA/AAm gels. Then, different amounts of N,N’-methylenebisacrylamide (BIS, cross-linker), corresponding to 0.12, 0.14, 0.16, 0.18, 0.20 and 0.22 wt%, were added to pre-gel solutions of the respective AAm:MA molar ratios. After then, 0.04 wt% of ammonium persulfate was put into the pre-gel solutions in order to initiate gelation. After these procedures, the pre-gel solutions had been left intact at 50 °C for 24 hrs.

While all the mixture solutions were transparent in the early periods of the gelling process, some of the specimens after gelation became turbid with different degrees depending on BIS concentration and the molar ratios of AAm and MA (Table I). Table I shows the clouding feature of MA/AAm gels with several BIS concentrations and AAm:MA molar ratios at room temperature (~25 °C). Broadly speaking, the MA/AAm gels with higher BIS concentrations are more turbid, of which the feature is similar to the AAm and SA/AAm gels. However the value of the BIS concentration (~0.20 wt%) where the clouding occurs is much smaller in the MA/AAm gels than those in the SA/NIPA (~1.5 wt% in the 0.2 M / 0.5 M composition) and SA/AAm (~2.5 wt% in the 0.2 M / 0.5 M composition) gels [19,20]. As for the MA-ratio dependence of their turbidity, the MA/AAm gels with higher ratio are more turbid than those with the lower ones while the SA/AAm gels show the opposite clouding features on SA-ratio dependence.

After the observation at room temperature, the influence of temperature on the turbidness was examined by monitoring the clouding properties of an MA/AAm gel (0.6 M:0.8 M in [MA]/[AAm] ratio and 0.14 wt% in BIS concentration) at several temperatures.
Figure 1 shows the clouding features of the MA/AAm gel observed at 50, 25 and 3 °C in descending order after having been left for 24 hrs at each temperature. Immediately after the gelation, at 50 °C, the MA/AAm gel was transparent. Similarly, the gel was still transparent at 25 °C. On the other hand, the occurrence of the strong opaqueness was observed at 3 °C. In order to examine the reversibility of this phenomenon, the observations of the turbidity were carried out at 3 and 50 °C in ascending order. In the observation, the MA/AAm gel was found to regain transparency within 1 hr after the temperature of the MA/AAm gel was set at 50 °C as shown in Fig. 2. This feature clearly demonstrates the temperature dependent and reversible turbidity occurs in the MA/AAm gel.

Table I  The clouding features of the MA/AAm gels with several cross-linker (BIS) concentrations and AAm/MA molar concentrations at room temperature (~25 °C).

<table>
<thead>
<tr>
<th>BIS conc. (wt%)</th>
<th>AAm/MA</th>
<th>0.12 %</th>
<th>0.14 %</th>
<th>0.16 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 M / 0.2 M</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
</tr>
<tr>
<td>1.0 M / 0.4 M</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
</tr>
<tr>
<td>0.8 M / 0.6 M</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
</tr>
<tr>
<td>0.6 M / 0.8 M</td>
<td>×</td>
<td>×</td>
<td>×</td>
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</table>

<table>
<thead>
<tr>
<th>BIS conc. (wt%)</th>
<th>AAm/MA</th>
<th>0.18 %</th>
<th>0.20 %</th>
<th>0.22 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 M / 0.2 M</td>
<td>○</td>
<td>○</td>
<td>△</td>
<td></td>
</tr>
<tr>
<td>1.0 M / 0.4 M</td>
<td>○</td>
<td>○</td>
<td>△</td>
<td></td>
</tr>
<tr>
<td>0.8 M / 0.6 M</td>
<td>○</td>
<td>△</td>
<td>△</td>
<td></td>
</tr>
<tr>
<td>0.6 M / 0.8 M</td>
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</table>

Fig. 1  The clouding property of an MA/AAm gel (0.6 M:0.8 M in [MA]:[AAm] ratio and 0.14 wt% in BIS concentration) at several temperatures observed with decreasing temperature.

Fig. 2  The clouding property of an MA/AAm gel (0.6 M:0.8 M in [MA]:[AAm] ratio and 0.14 wt% in BIS concentration) at 3 °C and 50 °C observed with increasing temperature.
In order to examine MA-ratio influence on the newly found temperature dependent turbidity more in detail, several MA/AAm gels of 0.14 wt% in BIS concentration were prepared with setting MA:AAm concentration compositions to 0.2 M:1.2 M, 0.3 M:1.1 M, 0.4 M:1.0 M, 0.5 M:0.9 M and 0.6 M:0.8 M; and their opaque properties were examined at 50 °C and 3 °C after having been left for 24 hrs at the respective temperatures. The effects of the MA:AAm concentration composition and temperature on their turbidity are shown in Fig. 3. As can be easily seen, MA/AAm gels with [MA] ≥ 0.5 M become considerably turbid at 3 °C while all the gels were transparent at 50 °C.

3. DISCUSSION

In the present study, the clouding properties of MA/AAm gels were studied for the first time. It was found that the MA/AAm gel with the network concentration of 1.4 M becomes turbid in a range of MA fraction and BIS concentration shown in Table I at room temperature. Besides, in the present study, the turbidity of some of MA/AAm gels was found to be temperature-dependent and can be reversibly altered with changing temperature.

It is well known that turbidity occurs by the scattering of visible light in the materials which have some inhomogeneities with a scale comparable with the wavelength of visible light. It should be aware that there are several kinds of light scattering mechanisms [21]: If the scatterers are thinly dispersed and their sizes are very small compared with the wavelength of visible light, the scattering properties obey Rayleigh scattering mechanism. However, in the case of Rayleigh scattering, the light scattering intensity is very low therefore this scattering mechanism can be only applied to the light scattered from more of the turbid gels than the solution in the early stage of the gelation. When the sizes of tenuously-dispersed light-scatterers are comparable with the visible-light wavelength, the scattered light intensity becomes stronger than that by Rayleigh scattering mechanism and its directional dependence of the scattered light intensity comes to have sharp peaks, of which the light scattering mechanism is called Mie scattering. However, the main light scattering mechanism of the turbid gel may not be Mie scattering; because usually the size of the light scatterers in the turbid gels are not so large as can be easily observed by the optical microscope and because the scattered-light intensity broadly distributes without fine structures. Taking these features into consideration, the scattered light from turbid gel is thought to be generated through the multiple light-scattering mechanism which often occurs in the materials composed of the scatterers with an inter-scatterer distance being comparable to the coherence length of incident light. Therefore, the light scattering features often observed in turbid materials will depend the distance between the scatterers inside and are also significant properties of the structural states of the materials [22-30].

Let us discuss on the clouding properties of MA/AAm gels observed in the present study. The 1.4 M MA/AAm gels show turbidity in high BIS concentration range as can be noticed from Table I. While such a feature is similar to those of other gels studied in the previous investigation, it is noteworthy that the BIS concentration at which the MA/AAm gel becomes turbid is much smaller than those of the SA/NIPA and SA/AAm gels investigated in the previous studies [19, 20] as mentioned in the preceding section.

The turbidity in AAm gel cross-linked with BIS can be ascribed to the inhomogeneity which occurs due to the different polymerization rates of AAm and BIS monomers [8-18]. Usually, the inhomogeneity in AAm gel becomes higher with increasing BIS/AAm concentration ratio in the pre-gel solution. Usually, the turbidity in the gel occurs when the concentration ratio becomes higher than a certain value $C^*$, which varies with the internal and/or external conditions. One of the conditions which affect the critical value $C^*$ is the ionization of the polymer network. As is known in AAc/AAm gel, introducing ionizing parts into gel network raises $C^*$ by the osmotic pressure generated through the interaction with counterions in solvent [9,10,16,17].

In the present study, it has been found that the $C^*$'s of MA/AAm gels are considerably small compared with the SA/AAm and SA/NIPA gels observed in the previous studies [19,20]. By taking
account of the abovementioned properties on the inhomogeneity and turbidity of the AAm-related gels cross-linked by BIS, it can be naturally come up with that the behavior of the side chain group of MA is not similar to that of SA in the SA/AAm and SA/NIPA gel. In addition, it should be noted that the turbidity occurs in the high MA fraction range shown in Table I. As mentioned in the preceding paragraph, the gels which have more carboxyl end groups was estimated to become more transparent with more number of end groups originating expansion force via the osmotic pressure caused by the interaction with counterions. However, in the present study, it has been observed that the MA/AAm gels become more turbid in the higher MA fraction region shown in Table I. Therefore, the authors have a think that considerably small $C^*$ values in MA/AAm gel compared with other gels and the higher turbidness in the higher MA-ratio region may come from the same origin. As one of the possibility, there can be an attractive interaction between plural carboxyl groups like the hydrogen bonding.

Additionally, one of the most interesting features observed in the present study is that some MA/AAm gels exhibit temperature dependent opaqueness. This phenomenon indicates that the inhomogeneities in these MA/AAm gels are influenced by temperature. Though the origin of the property has not been made thoroughly understood yet, the authors have estimated that the abovementioned interaction between the plural carboxyl groups and/or the change in the ionization may have some relation to the temperature dependent clouding property.

More detailed investigations on the relation between the clouding properties and the interactions between the plural carboxyl groups are currently in progress.

REFERENCES


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