Effects of Monomer Constituents, Crosslinker Concentration and Ambient Temperature on the Turbidity of Poly(acrylamide-co-maleic acid) Gel

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As well as the ingredient compositions, strongly temperature dependent features of the turbidities of poly(acrylamide/malic acid) (AAm/MA) gels have been found in the light transmissivity measurements ($\lambda$ = 600 nm). In addition, nano-scale fractal structures in the turbid gels have been recognized by the small angle X-ray scattering (SAXS) measurements at room temperature; and from a positive correlation between the degree of the turbidity and the fractal dimension derived from the SAXS profiles, it has been concluded that the origin of the increase in the light scattering intensity is caused by the densification of the network polymers.

Key words: gel, malic acid, turbidity, inhomogeneity, SAXS

1. INTRODUCTION

Composed of solvent and three-dimensional cross-linked polymer network, properties of gels are much affected by the interactions between these two components [1, 2], among which the electrostatic interaction between the ionized terminal groups suspended to the gel network and solute ions in the solvent often plays an important role for the interesting and useful properties of the hydrogels [1]. The authors have been investigating the positive-heavy-metal-ion capturing properties of hydrogels ionized by acrylic acid, a monocarboxylic acid [3]. In addition, the authors once adopted maleic acid (MA), a dicarboxylic acid, as an ionizing ingredient aiming at promotion of the capturing efficiency. However, in some experimental conditions, a copolymer hydrogel containing MA (acrylamide/maleic acid [AAm/MA] gel) was observed to show turbidity [4] indicating emergence of an inhomogeneity which can be undesirable for the heavy-metal-ion capturing functionality. Therefore, detailed investigations on the conditions for occurrence of the turbidity seem to be important for developing the new heavy-metal capturing hydrogels. Under these circumstances, in the present study, the temperature dependences of the light transmissivities have been investigated for the AAm/MA gels with a variety of total monomer concentrations, crosslinker concentrations and MA molar ratios. In addition, the measurements of the small angle X-ray scattering of those AAm/MA gels have been also performed at room temperature in order to make clear the correspondence between their turbidities and nano-structures.

2. EXPERIMENTALS

Necessary amounts of acrylamide (AAm), maleic acid (MA) and N,N'-methylenbisacrylamide (BIS, cross-linker) monomers were dissolved in each of the 25 ml distilled water for preparing the mixture solutions with different ingredient compositions in a range of 0.7, 1.4, 2.1 M in (AAm+MA) concentration, 6:1, 5:2, 4:3 in AAm:MA molar ratio and 12, 25, 37 mM in BIS-concentration. After these preparations, 0.0135 g of ammonium persulfate (APS, reaction initiator) was dissolved in each of the pre-gel solutions. Then, the respective solutions were poured into glass test tubes of 12 mm in diameter and 75 mm in height to conduct gelation; then they had been left in an incubator kept at 60 °C for 24 hours. Before putting in the incubator, all of the pre-gel solutions were transparent while, after the reaction period, some of them gained opaqueness, of which the degree varied with the total monomer concentration, the AAm:MA molar ratio and the BIS concentration. As the result of the gelation, formed were cylindrical hydrogels of 10.5 mm in diameter and 50 mm in height.

For investigating the turbidimetric properties of the obtained AAm/MA gels, their light transmissivities at 600 nm were measured in a temperature range from 60 °C to 5 °C (in descending order); more in detail, each of the test tubes containing the AAm/MA gels had been dipped in a temperature-controlled water bath for a while in order to wait for reaching a condition of thermal equilibrium. After then, in order to prevent wide change in the specimen’s temperature, the transmissivity of each of the AAm/MA gels was measured at speed after quickly placing the gel-containing test tube in the measurement chamber of a spectrophotometer (APEL PD-303).
The light transmissivity of the each gel $T_{gel}$ was evaluated by the formula:

$$T_{gel} = \frac{I_{gel} - I_0}{I_{water} - I_0}$$

where $I_0$ is the output from detector measured with the light source off, $I_{gel}$ and $I_{water}$ are those measured with setting the test tubes containing AAm/MA gel and distilled water, respectively, after turning on the light source.

The small angle X-ray scattering (SAXS) experiments were performed with a SAXS apparatus installed at a beam-line (BL40B2) in SPring-8 (Harima, Japan) at room temperature (~25 °C). An X-ray beam of 1.488 Å in wavelength was used as a light source. For measuring the SAXS profiles, prepared were the disk-shaped specimens with 5 mm in diameter and 1 mm in thickness. Preventing the AAm/MA gel specimens from dehydration, they were sandwiched and sealed with two kapton films before placed in the sample stage of the SAXS apparatus. Ion chambers were placed at the rear and in front of the specimen for further data analyses such as derivation of its X-ray transmittance. The intensity fluctuation of the incident X-ray beam had been less than 0.05 % during the SAXS measurements. The measurement time for all specimens was set to be 10 seconds. By utilizing the

![Fig. 1 Temperature dependences of the light transmissivity ($\lambda=600$ nm) of 0.7 M AAm/MA gels with different BIS concentrations and MA molar ratios. The symbols, □, × and ▲, correspond to the data of gels with 12, 25 and 37 mM in BIS-concentration (see also text).](image1)

![Fig. 2 Temperature dependences of the light transmissivity ($\lambda=600$ nm) of 1.4 M AAm/MA gels with different BIS concentrations and MA molar ratios. The symbols, □, × and ▲, correspond to the data of gels with 12, 25 and 37 mM in BIS-concentration (see also text).](image2)

![Fig. 3 Temperature dependences of the light transmissivity ($\lambda=600$ nm) of 0.7 M AAm/MA gels with different BIS concentrations and MA molar ratios. The symbols, □, × and ▲, correspond to the data of gels with 12, 25 and 37 mM in BIS-concentration (see also text).](image3)
imaging plates, measured were the two-dimensional X-ray intensity distributions scattered from the specimens, from which one-dimensional scattered-X-ray intensity distributions were derived by carrying out the radial integration with FIT2D [5] assuming the specimens to be isotropic. For the analyses of the measured SAXS profiles, the 2D X-ray-intensity distributions from silver behenate was also measured around the same time and was utilized for determining the distance between the specimens and the detector, for estimating the incident X-ray-beam position obscured by a beam stopper, and for scaling the scattering vector [6]. In order to compensate the absorption of the incident X-ray beam by each specimen, the scattered intensity distribution data on the imaging plate were divided by the transmittance derived from the outputs of the ion chambers being set at the rear and in front of the specimen; then, the subtraction of the background intensities were also carried out after the normalization of the data.

3. RESULTS

Figures 1, 2, and 3 show the temperature dependences of the light transmissivity of the AAm/MA gels with 0.7 M, 1.4 M and 2.1 M in total monomer concentration; and, in each of the figures, right-hand, central and left-hand sub-figures correspond to the data of the AAm/MA gels with 6:1, 5:2 and 4:3 in AAm:MA molar ratio; and besides, in each sub-figure, symbols, □, × and ▲ correspond to the data of the gels with 12, 25 and 37 mM in BIS-concentration, respectively.

As can be easily seen from Figs. 1, 2 and 3, turbidity of the AAm/MA gel increases (namely, the transmissivity decreases) with decreasing temperature and with increasing BIS-concentration. However, at high temperature, somewhat complex behaviors are observed in the total monomer concentration and MA molar ratio dependences: As shown in Figs. 2 and 3 (namely, their total molar concentrations are 1.4 and 2.1 M, respectively) the transmissivity becomes lower with increasing MA molar ratio while, in Fig. 1 (0.7 M), gets higher. As for the total monomer concentration dependence, most of the transmissivity of the gels increases with increasing the total

![Fig. 4 The SAXS profiles and the bar graphs of the light transmissivities (λ=600 nm), measured at room temperature, of AAm/MA gels with different total monomer concentrations, MA molar ratios and BIS concentrations. The symbols, □ , × and ▲ , correspond to the data of the gels with 12, 25 and 37 mM in BIS-concentration, respectively.](image-url)
monomer concentration, however that with AAm:MA= 4:3 and 37 mM in BIS concentration shows somewhat complex behavior.

Figure 4 shows the SAXS profiles and the bar graphs of the light transmissivities (l=600 nm), measured at room temperature, of the AAm/MA gels with different total monomer concentrations, MA molar ratios and BIS concentrations. The symbols, □, × and ▲, correspond to the data of the gels with 12, 25 and 37 mM in BIS-concentration, respectively. As indicated in Fig. 4, one can find a strong negative correlation between the intensity in the low scattering-vector regions of the SAXS profile and the light transmissivity.

4. DISCUSSIONS

Turbidity is an optical property being recognized when an incident light is scattered strongly by an inhomogeneous medium. The origin of this property can be ascribed to mainly two origins: large dimensions and/or highly dense populations of the light scatterers. Therefore, the light scattering mechanism cannot be figured out only by the turbidity measurements. Such a situation becomes more complicated when the multiple light scattering occurs because the coherent lengths of visible lights (400 ~ 800 nm) are usually much longer than the distances between the scatterers in the turbid medium. Therefore, structural analyses in scales shorter than the light wavelength should be essential in order to fully understand the light scattering mechanism, though the turbidity measurement is sensitive and handy method to detect the changes in the medium.

In the previous paper, the authors reported that the AAm/MA gels show opaqueness in a range of BIS concentrations and temperatures for the first time [4], however, in the investigations, only a few specimens were observed and the opaqueness was observed only by their appearance. On the other hand, in the present study, the authors have carried out quantitative investigations by measuring turbidity of much more specimens; and, in addition, the SAXS measurements have been carried out in order to examine the correlation between the turbidity and nano-scale structure.

In Fig. 5, depicted are double log plots of the SAXS profiles which show strong scattering in the low q-region. From the figure, clearly noticed are linear dependences of the logarithm of intensity on that of scattering vector, indicating nano-scale fractal structures in the turbid gels [7]. From the characteristics of the fractal structures, there can be no definite structure with a specific dimension in the correspondent scale.

For further quantitative analyses, the authors have defined “cloudiness” as 100-transmissivity in %; and, in Fig. 6, shown is the cloudiness dependence of the fractal dimension derived from Fig. 5. Though the data seem somewhat scattered, perceived is a positive correlation between the fractal dimension and cloudiness. Because the fractal dimension indicates the degree of densification of the structure, this tendency recognized in Fig. 6 can demonstrate that the increase in the opaqueness can be resulted from the densification of the light scatterers, namely, the network polymers in the case of the present study. In other words, the light scattering mechanism is mainly the multiple scattering in which the incident light is scattered many times within the coherent length.

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