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## Sol–gel transition and phase separation in ternary system of gelatin–water–poly(ethylene glycol) oligomer

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### ABSTRACT

The phase behaviors are studied in the ternary system of gelatin–water–poly(ethylene glycol) oligomer. It is found that both the phase separation and the sol–gel transition occur simultaneously when the poly(ethylene glycol) oligomers are added to the aqueous gelatin solution. The phase separation boundary is found to shift in the higher temperature than the sol–gel transition line when the higher molecular weight oligomers of poly(ethylene glycol) coexist in the solution. The competition of these two transitions creates two new phases in the system, the phase separated solution of gelatin and poly(ethylene glycol) and the opaque gelatin gel in which the density fluctuation due to the phase separation is frozen in.

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### 1. Introduction

The phases and the phase transition of the biopolymer solutions draw much attention from both the practical as well as the scientific point of view. Among others, gelatin is one of the most familiar biopolymers that is used in a wide variety of science and technology. Gelatin is highly soluble in water since it consists of the polyelectrolyte that prepared from the collagen. It is well known that the aqueous solution of gelatin shows a sol–gel transition upon cooling. The relationship between the sol–gel transition and the molecular properties of gelatin has been studied in detail so far [1,2]. The phase behavior of the gelatin solution is also studied in the ternary system of gelatin–water–methanol in which the system shows the phase separation and the sol–gel transition simultaneously [3]. The results are discussed in terms of the site-bond correlated-percolation model for the polymer solution that correctly describes the phase behaviors in the gelatin system [4,5]. The similar phase behavior is observed in the aqueous agarose system, which is also a typical biopolymer from algae, and analyzed in the similar manner in detail [6]. Although the phase behaviors of the biopolymer systems are studied, the information gained so far is clearly limited for the full understanding of the phase behaviors in biopolymer systems.

The phase behaviors of the polymer solution are controlled by many physical parameters such as the temperature, the quality of the solvent, and the pH [7,8]. In the cases of the aqueous gelatin solution, the quality of the solvent is changed by the addition of the third liquid component,

methanol, to the aqueous solution in the previous study [3]. It has been also reported that the phase separation can be induced by adding water-soluble polymer such as poly(ethylene glycol) (PEG) to aqueous gelatin solution [9–11]. Though, many interesting experimental results are deduced, the systematic understanding of the phenomenon is not obtained yet. Here, therefore, we are going to report on the phase transitions of the ternary system of gelatin–water–PEG. Both solutions of gelatin and PEG are homogeneous when they are solely dissolved into water [12,13]. It, however, is separated into two phases when they are coexist in solution. The previous studies suggest that the phase separation in gelatin–water–PEG strongly depends on the molecular weight of PEG that is added to the solution. Since, the molecular weights of the PEG used in the previous studies is rather high, i.e., 6000 to 20 000 or more. It is, therefore, inevitable that the molecular weight distribution of PEG affects the overall phase behaviors of the system. In this study, first of all, we used PEG oligomers to obtain the exact molecular weight effects on the phase behaviors of the ternary system of gelatin–water–PEG. We believe that the effects of the addition of PEG on the phase transition can be clearly shown by using these PEG oligomers.

### 2. Experimental

Alkali-treated (type-B) gelatin is obtained from Merck (No. 1040781000; Darmstadt, Germany). The average molecular weight determined by gel permeation chromatography is 69 100. The isoelectric point of the sample was 4.9.

The PEG oligomers used in this study are di-ethylene glycol (EG-2), tri-ethylene glycol (EG-3), and tetra-ethylene glycol (EG-4), and these are obtained from Wako Pure Chemical Industry (Osaka, Japan). The larger molecular weight oligomers, PEG-400 and PEG-1000, are

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obtained from Nichiyu Corporation (Tokyo Japan) and Sanyo Chemical Industry (Kyoto, Japan). The molecular weights of the low molecular weight oligomers are 106 (EG-2), 150 (EG-3), and 194 (EG-4). The numbers of the monomer unit in the PEG-400 and PEG-1000 are ranging from 7 to 9 for PEG-400 and 22 for PEG-1000 according to the manufacturer. Hence, the molecular weights are estimated to be about 370 (8-mer; PEG-400) and 986 (22-mer; PEG-1000). These samples are used as obtained.

The sample solutions are prepared as follows. Firstly, the oligomers of PEG are dissolved into water, which is purified by Milli-Q system, at desired concentrations. Then gelatin is dissolved into these PEG solutions at a temperature of 60 °C. The concentration of the PEG oligomer is fixed at 10 wt.% in this study while the concentration of gelatin is changed up to 30 wt.%.

The sample solutions thus obtained are transferred into a temperature controlled bath at a temperature of 60 °C. It is well known that the gelatin is easily degraded by the autocatalysis reaction in the solution state. The sample solution, therefore, should not be exposed to higher temperature for long time. The temperature is, therefore, lowered at a rate of about 10 °C/h. This cooling rate is not enough to determine the phase diagram in the equilibrium state but is necessary to avoid the possible degradation of gelatin. The phase separation temperature is defined as the temperature at which the sample becomes opaque in the cooling process of the solution by naked eye observation. In addition to this, the turbidity of the solution is also measured as a function of the temperature independently for the crosscheck of the phase separation temperature determined by the naked eye inspections. After the determination of the phase separation temperature of the solution, the samples are kept at the temperature of 15 °C for 12 h to ensure the gelation. Then the temperature is gradually increases at a rate of 5 °C/h to determine the melting temperature of the gel. The melting point of gel is determined by the falling ball method. The Teflon ball of about 16 mg is used in this study.

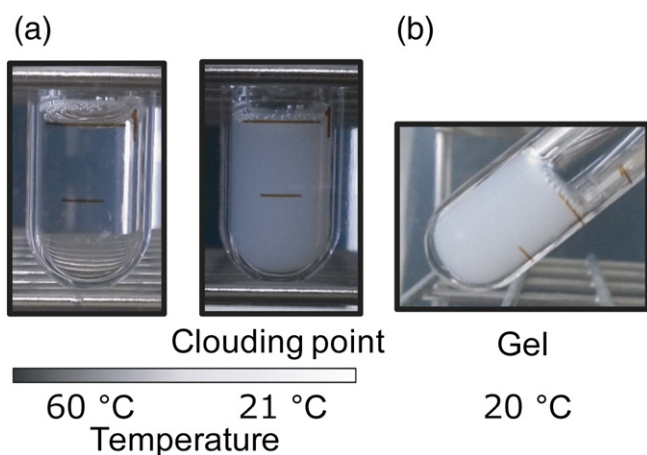
### 3. Results

In Fig. 1, we show the snapshots of the solution that is taken in the cooling process of the solution. The concentrations of gelatin and PEG-400 are 5.0 wt.% and 10 wt.%, respectively. The transparent solution at a temperature of 60 °C becomes opaque at about 21 °C. It is also found that the gel is formed in this case. The gel thus obtained is completely opaque as shown in this figure. The results indicate that the gelatin solution shows the phase separation as well as the gelation when PEG

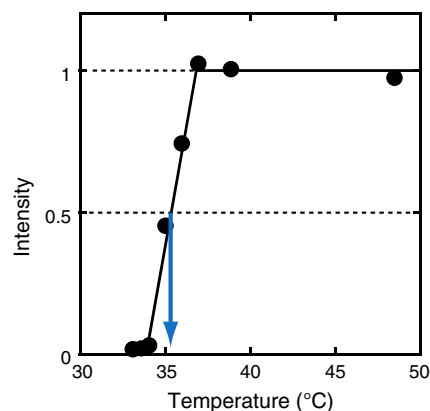
coexists in the solution. The turbidity of the solution, which is prepared at a concentration of 5 wt.% of gelatin and 10 wt.% of PEG-1000, is measured as a function of the temperature for the crosscheck of the cloud point temperature. The results are given in Fig. 2. The cloud point of the solution is determined to be 35 °C by the naked eye inspection as shown in Fig. 3(c), while it becomes 36 °C by the turbidity measurement. The temperatures of the cloud point that determined by two independent methods agree rather well. Therefore, the cloud point of the solution is mainly determined by the naked eye inspection of the solution. The melting temperature of the gel thus formed is found to be higher than the cloud point of the solution. Since the cooling rate is rather fast, the exact gelation temperature could not be determined in the cooling process. Alternatively, we determine the gelation temperature of the solution by quenching the solution to the various temperatures lower than the melting temperature to compare with the melting point of the gel. It is found that the gelation temperature of the solution, which determined by the quenching method, is slightly lower than the melting temperature of the gel. However, the difference between the gelation and the melting temperatures is found to be less than 2 °C. We, therefore, believe that the sol–gel transition line of the solution is not too far from the melting temperature line of the gel. In fact, the hysteresis of the gelation process and the melting process is reported to be small in the case of the gelatin solution [1,2]. Such a kinetic effect should be studied in detail but is not the purpose of the present study. Here we tentatively regard the melting temperature line of the gel as the sol–gel transition line of the system.

The typical phase diagrams thus obtained are given in Fig. 3. The results with EG-2, PEG-400, and PEG-1000 are shown in Fig. 3. It is clear that, only sol–gel transition is observed at above 10 °C in the system of gelatin and EG-2. In contrast, the phase separation of the solution appears in the lower concentration region of gelatin when PEG-400 coexists in the solution. In addition to this, it is also found that the phase separation line shifts to the higher temperature region when PEG-1000 coexists while the position of the peak is not much affected by the molecular weight of PEG. This behavior of the phase separation line is similar with the one observed in the ternary system of gelatin–water–methanol where the phase separation line shift to the higher temperature region with the increase of methanol concentration in the solution [3].

It is clear from Fig. 3, that the low molecular weight PEG oligomer, EG-2, does not induce the phase separation of the solution, and the solution only shows the sol–gel transition when the concentration of PEG oligomer is 10 wt.%. The similar results are obtained in the cases of EG-3 and EG-4. In these oligomers, therefore, only the melting



**Fig. 1.** Phase behaviors of a gelatin–water–PEG oligomer system at different temperatures. The polymer composition is gelatin 5.0 wt.% and PEG-400 10 wt.%. (a) The transparent solution at a temperature of 60 °C becomes turbid when it is cooled to 21 °C. The cooling rate is 10 °C/h. (b) The solution transforms into the gel at about 20 °C. The gel is turbid due to the frozen-in inhomogeneity, but does not flow when tilted.



**Fig. 2.** The temperature dependence of the transmitted light intensity. The transmitted light intensity is plotted as a function of the temperature. The intensity is normalized by the average transmitted light intensity of the homogeneous solution. The concentration of gelatin is 5 wt.% and that of PEG-1000 is 10 wt.%, respectively. The cloud point of the solution is determined to be 35 °C by the naked eye inspection while that determined from these results is 36 °C. See also Fig. 3(c).

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