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Gel-Sol Transition in Biopolymers

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Determination of the gelation point is briefly discussed, and it is shown that there are many exceptions which do not obey the criterion proposed by Winter and Chambon. Some specific problems in the gelation in physical gels which are related with non-equilibrium state are pointed out. The recent development in understanding the gelation mechanism of curdlan suspension and konjac glucomannan solution is reviewed.
Keywords: gelation point, rheology, DSC, curdlan, konjac glucomannan

1. INTRODUCTION

Gels and gelling process of biopolymers have attracted much attention both from scientific interest and industrial applications in food, cosmetics, pharmaceutical, biomedical and other related fields. Recent developments in the hydrocolloid gels of various polysaccharides and proteins such as gellan gum, methylcellulose, xyloglucan, curdlan, konjac glucomannan, casein, β -conglycinin, β -lactoglobulin have been reviewed [1]. After a brief review of the determination of the gelation point, some problems, a non-equilibrium character of physical gels, like syneresis is described. Recent further development of the study on the gelation mechanism of curdlan and konjac glucomannan are described in the present work.

2. DETERMINATION OF THE GELATION POINT AND SOME PROBLEMS IN PHYSICAL GELS

Gel is an intermediate state between liquid and solid. There have been many trials to define a gel [2]. The most well-known trial is due to Winter-Chambon [3]. They proposed a criterion for the gelation point as follows: the storage and loss moduli, G' and G'', of the dispersion should show the same frequency dependence at the gelation point,

$$G' \sim G'' \sim \omega^n$$

$$\tan \delta = G''/G' = \tan(n\pi/2)$$

where the relaxation exponent n was first proposed as 0.5, and then later $0.1 \leq n < 1$ have been reported.

It has been shown that this criterion is well satisfied for gelation of various systems such as poly(vinyl chloride) (PVC) - bis(2-ethylhexyl) phthalate (DOP) [4], α , ω -dimethyl silyl poly (propylene oxide) - n-butyl acetate [5], ovalbumin - water [6], ι -carrageenan -water [7], gellan - water [8]. The reported values for relaxation exponent are 0.75 for PVC - DOP irrespective of the molecular weight M and the concentration C, 0.66 for α, ω-dimethyl silyl poly(propylene oxide) - n-butyl acetate also independent of M and C, however it ranged from 0.08 to 0.16 for 15~89% ovalbumin at 5~45℃. The exponent n decreased with increasing concentration in an ι -carrageenan - water system; n=0.42 for 1.0% gel and n=0.32 for 3.0% gel. The exponent was 0.5 for 2.0~3.0% sodium type gellan gels, but it was impossible to find the critical state by the observation of the frequency dependence of G' and G'' for a 3.5% sodium type gellan gel which showed a drastic change between 42 and 43℃.

Some systems of xanthan-water [9], curdlan-water [10], bovine serum albumin(BSA) - water [11-13] have been shown not to satisfy the above criterion. In these systems, $G' > G''$ even before the gel point. This rheological behaviour is called a weak gel behaviour [14]. It is not well understood why these systems behave like a solid, and what kind of repulsive forces are responsible for the stabilization of the system. Tobitani and Ross-Murphy determined a gelation time for BSA in water at which the storage modulus began to increase steeply at a constant temperature because in this system $G' > G''$ even before the gel point [12-13]. Rodd et al recently studied the dependence of linear viscoelastic critical strain and stress on extent of gelation for a solution of xanthan gum in the presence of trivalent aluminum ions, which forms a gel with increasing temperature, and showed that the linear viscoelastic strain approaches zero near the gelation point [15]. Clark and Ross-Murphy pointed out that it is very difficult to distinguish a weak gel from a true gel or an elastic gel only by small deformation rheological measurements. Weak gels are not destroyed by a large strain, whilst an elastic gel is destroyed [14].

It is well known that it takes a very long time for the storage modulus of gelatin solutions to reach an equilibrium value [2]. Since it does not reach an equilibrium modulus even after 100hours at ambient temperatures, we can obtain at most a "pseudo-equilibrium modulus". This situation is not specific for only gelatin but also true for other physical gels of water soluble polymers.

In addition to this problem, the syneresis occurs quite often in the study of physical gels. As the swelling sometimes change drastically the elastic property of gels, syneresis also changes it dramatically. From the viewpoint of the concentration dependence of the elastic modulus, the elastic modulus of gels should increase when the concentration increases if the network structure does not change . Nagasaka and Taneya [16] have found that the elastic modulus of agar gels decreased as a result of the syneresis. In spite of the increase of the concentration resulting from syneresis, it is believed that the chain molecules spanning the three dimensional network became into a loosened state from an extended state.

Most polysaccharides are known to form a gel via the aggregation of rods or helices. A problem arises for the stiffness of chains to form a gel even at a low concentration <1%. For example, a typical concentration of a cubic agar jelly in a Japanese traditional dessert Mitsumame is about 1%. Although the details of the gelation mechanism of polysaccharides such as agarose, carrageenan, gellan remain a matter of debate, it is believed that helices should be formed before the gelation occurs. Koga and Tanaka [17] recently have shown by a computer simulation that the critical concentration for gelation decreases with increasing persistent length of polymeric chains. Conversely, solutions of flexible chains, like pullulan or polyethylene oxide, do not form a gel even at quite a high concentration. However, since it is known that these polymer solutions produce a film when the solvent water is evaporated, they should form a gel before becoming a solid film. It is evident that solutions of monomers of these polymers, glucose or ethylene glycol do not form a gel even if solvents are evaporated. These substances with low molecular weights are known to form a crystal. Therefore, there should be a critical molecular weight of polymers below which no gel is formed. It is therefore important to study systematically the effects of flexibility and molecular weight on the gelling ability of polymer solutions, and accumulate the knowledge to get the insight of the gelation. Gel-sol transition of some biopolymers, gellan, conglycinin, methyl cellulose has been reviewed recently [1]. It is also important to study the relation between the helix-coil transition and gel-sol transition in some helix forming polymers such as gellan which will be described in the forthcoming paper [18]. In the present paper, the recent development of the understanding of the gelation of curdlan and konjac glucomannan is reviewed.

3. GELATION OF CURDLAN AQUEOUS SUSPENSION

Curdlan, β-1,3 glucan produced by *Alcaligenes faecalis*, is not soluble in water but soluble in alkaline condition or in dimethyl sulfoxide (DMSO) [19]. Fig. 1 shows the frequency dependence of 2% curdlan in water and in DMSO at 40℃. While a curdlan solution in DMSO behaves like a typical concentrated polymer solution where the entanglement of chain molecules plays an important role and the crossover of G' and G'' is seen at a certain frequency, curdlan suspension in water behaves like a solid where $G' > G''$ at all the accessible frequencies. Although $G' > G''$, a 2% curdlan in water is not a gel but a sol. This is a so-called weak gel. When it is heated at 70℃, it turns into a gel in which mechanical loss tan δ is far smaller than in a sol state.

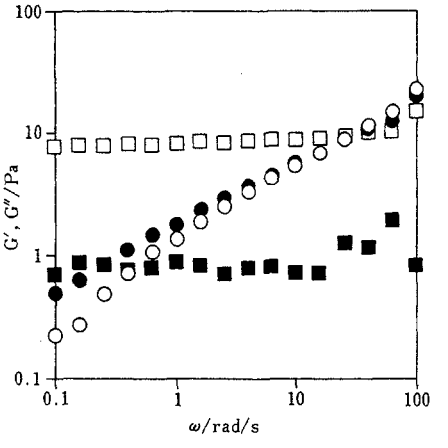

Fig. 1 Mechanical spectra of a 2% aqueous suspension (square) and a 2% DMSO solution (circle) of curdlan. Open symbols for storage moduli and solid symbols for loss moduli. Temperature, 40℃. From ref. [10].

Fig. 2 shows a typical result of thermal scanning rheological measurements of a 2% curdlan in water with a heating and a cooling DSC curves at the same scan rate 0.5 ℃/min [20]. Storage modulus G' increased slightly at the temperature range from 30 to 55℃, and then decreased. If the heating is stopped at this temperature range, the suspension forms a thermoreversible gel. The spin-spin relaxation time T_2 of ^{1}HNMR decreased with increasing temperature up to 55℃ indicating the space filling process of the curdlan particles which are swollen by heating [20]. The mobility of the chain molecules became more restricted in this process. The molecular forces which are responsible for gel formation may be

hydrophobic interaction or entanglement of chains protruding from swollen curdlan particles. It is urgently required to confirm this by other techniques. On further heating, an endothermic peak was observed in a DSC curve at 60℃ indicating the enhancement of the chain molecules which appeared as the increase in T_2. This might be caused by the breakage of intra- and inter-molecular hydrogen bonds in microfibrils. Further heating induced a gel formation, and then storage modulus G' increased and the spin-spin relaxation time T_2 decreased. On cooling at the same scan rate to 40℃, G' began to increase steeply, the spin-spin relaxation time T_2 began to decrease and the DSC curve showed an exothermic peak, which should be attributed to the network formation of hydrogen bonds.

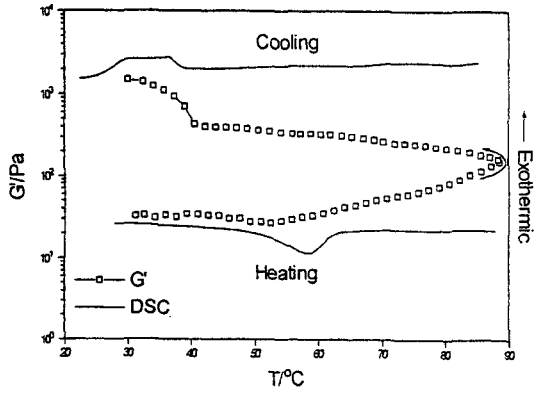

Fig.2 Temperature dependence of storage modulus and heating and cooling DSC curves of 2% curdlan aqueous suspension. Scan rate, 0.5℃/min. From ref. [20].

4. GELATION OF KONJAC MANNAN SOLUTION

It is believed that aqueous solution of konjac glucomannan (KGM), a plant polysaccharide extracted from tuners of *Amorphophallus Konjac* K.Koch (mannose to glucose ratio is reported as 2 to 3 or 1 to 2), forms a gel by adding alkali coagulant because acetyl groups are removed. Only one acetyl group is known to attach to 19 sugar units, however, this small amount of acetyl groups seems to contribute to the solubility of this polymer. Yoshimura et al examined the gelation process of dispersions of KGM with different concentrations and molecular weights in the presence of alkaline coagulant, sodium carbonate, and found that the gelation began earlier and the gelation proceeded faster with increasing molecular weight (Fig.3) or concentration [21]. They also found the decrease in G' after reaching a maximum in the gelation process at a constant temperature, and it was attributed to a slippage in the measuring geometry of the rheological apparatus although it is difficult to exclude completely the possibility of the formation of some fragile network structure in a fast gelation process. Similar phenomena of the maximum of storage modulus in the gelation were reported for milk protein dispersion [22] and κ-carrageenan solutions [23]. However, the maximum of G' reported in carrageenan was ascribed later to the slippage [24].

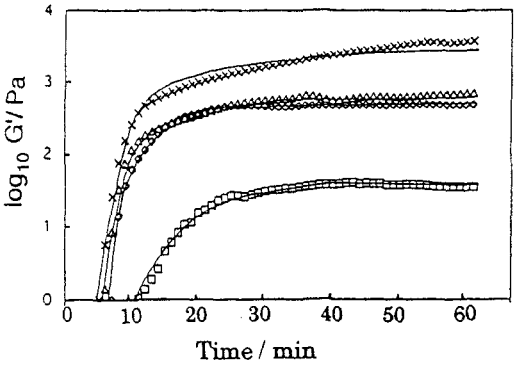

Fig.3 Gelation process of KGM with different molecular weights at 60℃. 1, $M = 2.56\times10^5$; 2, $M = 4.38\times10^5$; 3, $M = 4.44\times10^5$; 4, $M = 5.96\times10^5$. Solid lines were calculated using a first order kinetic equation. From ref. [21].

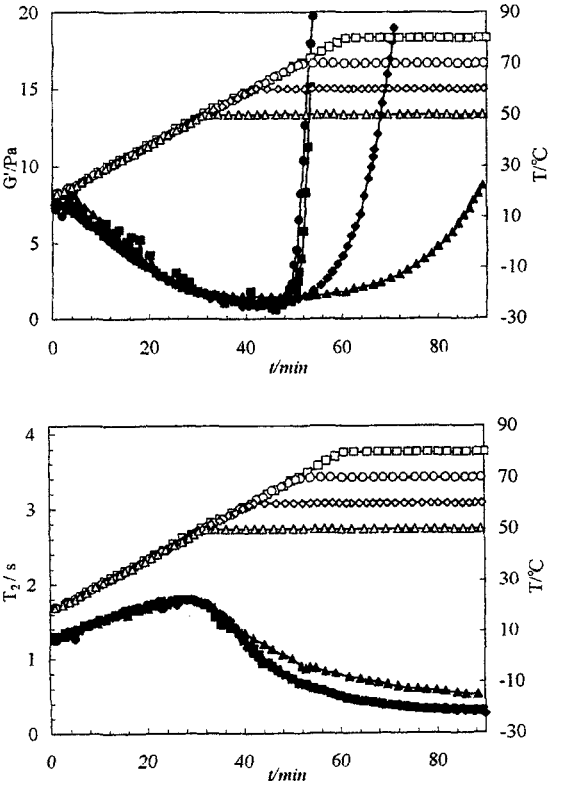

Fig.4 (a) Spin-spin relaxation time T_2 and (b) Storage modulus G' of 1%KGM solution. The temperature was raised from 20℃ to 50, 60, 70 and 80℃ at 1℃/min and kept constant. From ref. [25].

Williams et al studied the gelation process of KGM in the presence of the same alkaline coagulant by NMR and dynamic viscoelastic measurements [25]. The spin-spin relaxation time T_2 of ^{1}HNMR increased with increasing temperature up to 40℃ indicating the solubilization of chain molecules and the enhancement of the molecular motion, which is equivalent to raising the temperature. The storage modulus G' decreased in this temperature range. Further heating led to the gelation of KGM as reported previously.

5. CONCLUSION

Some other aspects in physical gels and gelling processes such as the structure of junction zones and networks, the effects of temperature, molecular weight, concentration, co-solutes on the elastic modulus, interaction between different biopolymers have been reviewed recently [26].

Although it is not easy to prepare the well defined samples of these biopolymers, it is important to do it. It is urgently required to study the gelation of these biopolymers using several fractions with different molecular weight and with narrow molecular weight distribution to understand the influence of the length and the stiffness of the chains on the gelling behaviour. Without studying these problems, questions whether helices can be formed from two or three chains with different lengths or not, and whether the helix-to-coil transition occurs from the end of helix or from the middle or any intermediate point in a helix or not cannot be answered definitely.

It has been proved fruitful to compare the experimental results obtained by different techniques for one common sample as shown in a special issue of Progress in Colloid and Polymer Science, Vol.114 (1999), Physical Chemistry and Industrial Application of Gellan Gum.

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