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Short Communication

**Sol-gel transition of alginate solution by addition of calcium ions:
alginate concentration dependence of gel point**

Zheng-Yu Wang (*), Qing-Zhi Zhang, Mikio Konno and Shozaburo Saito

Department of Molecular Chemistry and Engineering, Faculty of Engineering, Tohoku University, Aramaki Aoba, Aoba-ku Sendai 980, Japan

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Abstract. — Polyelectrolyte concentration dependence of gel point was experimentally investigated for alginate solution by addition of calcium ions. A power law relation was found between the gelation threshold f_c and alginate concentration C with an exponent of -0.65 ± 0.05 . It was shown that the experimental results can be explained in terms of the scaling theories developed for vulcanization process and polyelectrolytes in semi-concentrated solutions. Based on the scaling analysis, a good agreement was obtained between the experimental and theoretical exponents.

1. Introduction.

Gelation phenomena have been studied for a very long time both theoretically and experimentally. The theory of gelation of polymers was developed half a century ago by Flory [1] and Stockmayer [2]. This classical theory gives for the f -functional random polycondensation a very satisfactory prediction of the gel point. During the last decade, many researchers have carried out analysis of the gelation process, following the scaling concepts first proposed by de Gennes [3] and Stauffer [4]. These authors established an analogy between the gelation and percolation processes. This allows us to consider the gelation process as a second order phase transition, where the fraction of cross-links, f , is equivalent to temperature. The gel point corresponds to the amount $f = f_c$ of cross-links for which an infinite cluster is formed. However, not all the solvent effects were taken into account by these approaches, although it is known that solvent effects play a significant role in the conformation of polymer chains.

A theoretical work of Daoud [5] based on scaling theory has provided a connection between solution and melt states for a special case of gelation of chains. The process in the melt,

(*) *Present address:* Research School of Chemistry, The Australian National University, GPO Box 4, Canberra ACT 2601 Australia.

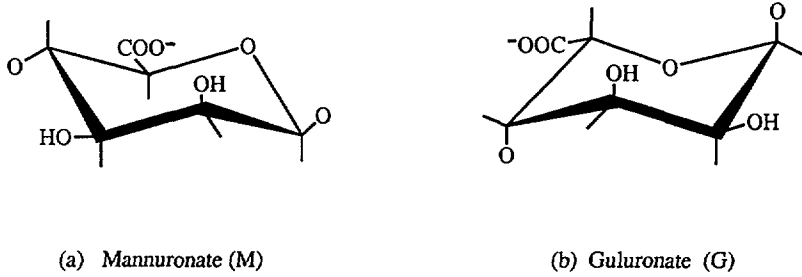


Fig. 1. — Constituent monomer units of alginate: (a) mannuronate (M) and (b) guluronate (G).

usually called vulcanization, was first studied by Flory [1] who showed, based on mean field approximation, that the gelation threshold, f_c , is determined by

$$f_c \approx N^{-1} \quad (1)$$

for a large linear macromolecule comprised of N monomers, and each of these monomers is considered as a basic unit having one cross-link site. The mean field treatment has been shown by the Gennes [3, 6] to be valid for predicting the behavior of vulcanization in the melt state. Daoud [5] has made a generalization to semidilute solutions by considering a blob, instead of a monomer, as a basic unit having one cross-link site. This is because in semidilute solutions a given chain no longer has N contacts with the other chains, but a smaller number, depending on the polymer concentration, C . Each of the blobs is made of g monomers and has a length ξ , called correlation length, with

$$\xi \sim g^v \sim C^{-m} \quad (2)$$

The values of v and m are dependent on the properties of polymer and solvent. As a result, vulcanization may then be described as a percolation process of polymer chains, each having $N' = N/g$ units. Thus the gelation threshold f_c becomes

$$f_c \approx 1/N' = N^{-1}g. \quad (3)$$

From equations (2) and (3), f_c can be expressed by

$$f_c \sim \xi^{1/v} \sim C^{-m/v} \quad (4)$$

For a neutral polymer in a good solvent, $v = 3/5$ and $m = 3/4$ are obtained and these values lead to $f_c \sim C^{-5/4}$ which was derived by Daoud [5]. This scaling relation has been observed in the gelation processes induced by cross-linking of neutral polymers (polystyrene) [7] and by ion complexation of polyhydroxy compounds (galatomannans) [8].

The purpose of this study is to present some experimental data on the polymer concentration dependence of gel point for a *polyelectrolyte* system. Our results show that the scaling relation of equation (4) also holds when applied to polyelectrolyte solutions and the exponents v and m can be evaluated from a scaling analysis developed by de Gennese, *et al.* [9] and Odijk [10] for polyelectrolyte systems without added salt. The polyelectrolyte used in this study is alginate which is a linear polysaccharide of (1 → 4) linked β -D-mannuronate(M) (Fig. 1a) and α -L-guluronate(G) (Fig. 1b) residues arranged in a non-regular blockwise pattern. Alginate aqueous solution is well known to undergo sol-gel transition by addition of various divalent cations which act as cross-linkers [11]. The critical behavior of viscosity for this system has been investigated and presented in a previous paper [12].

2. Experimental.

Sodium alginate used for this study was purchased from Kimitsu Chemical Industries Co. Japan which was obtained from *Lessonia Nigrescens*. An average molecular weight of 2.1×10^5 was determined by means of gel permeation chromatography by using water-soluble columns (Asahipack, GSM-700H). Pullulan standard samples were used for calibration. In order to obtain the ratio of mannuronate to guluronate residues, a sample was hydrolyzed in 0.3 M hydrochloric acid at 100 °C for 10 h as described by Haug *et al.* [11], followed by a ^{13}C -NMR measurement using an inverse gated decoupling technique. A value of 1.5 was determined for M/G by this method. The alginate samples were dissolved in distilled water at a polymer concentration of 5 wt%. The solution was first dialyzed twice (3 hours each time) in distilled water using cellulose tubular membranes (molecular weight cut-off = 12,000), and then further dialyzed for 3 hours in deionized water. The dialyzed product was centrifuged at 20,000 rpm (38,460G) for 20 minutes to remove any water-insoluble substances, and finally freeze-dried to obtain a purified sample.

Samples for sol-gel transition measurements were prepared at room temperature by mixing 10 ml of alginate aqueous solution with a certain concentration and 1 ml of calcium chloride solution with different concentrations. All samples were homogeneous after magnetic stirring for 1 hour. We define the stoichiometric ratio $f = [\text{Ca}^{2+}] / [\text{residues of alginate}]$ as a factor which controls the gelation process, with the assumption that ratio f is proportional to the fraction of cross-links formed. Sol-gel transition experiments were performed by viscosity measurements using an Ostwald-type capillary viscometer at 30 ± 0.02 °C. The efflux time for the lowest viscosity sample was more than 150 seconds. Relative viscosity η_{rel} , defined as a ratio between the viscosities of the solutions with and without Ca^{2+} addition, was used as a measure for describing the extent of gel formation.

3. Results and discussion.

Figure 2 shows the variations of relative viscosity versus fraction of cross-links, f , for various alginate concentrations. The range of concentration in alginate solutions is from 0.45 wt% to 8.5 wt%. It is shown that the lower the alginate concentration, the greater the value of f for gel formation, indicating a strong dependence of polymer concentration on sol-gel transition. This result qualitatively corresponds to the fact that there exist more contact sites between polymer chains in concentrated solution than in dilute solution, as a result a smaller value of f is required for concentrated solution to form the gel phase. For a more quantitative analysis, variation of gelation threshold f_c as a function of alginate concentration was plotted in figure 3. The procedure of determination of f_c has been described in a previous paper [12], which involves using a linear plot between $-\eta_{\text{rel}}^{-1} (d\eta_{\text{rel}}^{-1}/dC)^{-1}$ against C . The error in the estimation was within 5 %. The double logarithmic plot of f_c versus C can reasonably be approximated by a single straight line, suggesting that the power law relation between f_c and C is satisfied over the concentration range of this study. The slope obtained from figure 3 was found to be -0.65 ± 0.05 , which is very different from the value of -1.25 as predicted and measured for neutral polymer systems.

Since alginate is a polyelectrolyte and we know that polyelectrolyte shows a particular behavior in its solution properties compared with neutral polymer, a different approach is necessary to explain our experimental results. It has been widely accepted that a highly charged polyelectrolyte chain in a salt-free or very low salt concentration solution will be nearly fully stretched due to strong electrostatic repulsion of the like charges along the polymer chain, which

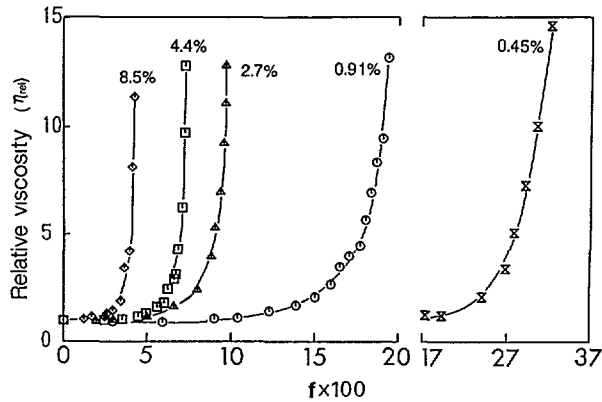


Fig. 2. — Variations of relative viscosity of alginate solution versus fraction of Ca(II) at various alginate concentrations.

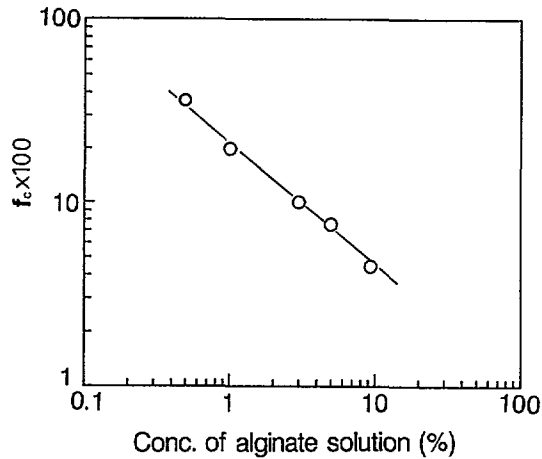


Fig. 3. — Alginate concentration dependence of gelation threshold f_c for Ca(II)-added system. The slope of the straight line is -0.65 .

are only weakly screened. While in the presence of an excess of the added salt, polyelectrolytes can essentially be considered to show a similar behavior to that of neutral polymers in good or θ solvents. As the maximum salt concentration in this study is as low as 0.02 M, we assume that our system can be approximated as one without added salt. For this case, de Gennes *et al.* [9] have developed a scaling theory to take into account the concentration dependences in polyelectrolyte systems. According to this theory, in a semidilute concentration regime where most experimental investigations have been carried out, there is considerable overlap between the chains, leading to a transient network with a correlation length ξ . On scale $r < \xi$, the chains may be considered to be fully extended, thus the relation $\xi \sim g$ is expected. On the other hand, ξ is estimated to decrease with concentration as $C^{-1/2}$ and this has been confirmed

experimentally by neutron spin echo and light scattering measurements [14], so we can write

$$\xi \sim g \sim C^{-1/2} \quad (5)$$

This corresponds to $v = 1$ and $m = 1/2$ in equation (2). Putting these values into equation (4), we then have $f_c \sim C^{-1/2}$ which is quite close to our experimental result.

The scaling concepts for semidilute polyelectrolyte solutions without added salt have been re-considered by Odijk [10] to incorporate a concentration dependence of chain flexibility through persistence length of a wormlike model and counterions screening of the charges. In this case, polyelectrolyte concentration dependence of correlation length ξ has been obtained for the whole concentration range:

$$\xi \sim (L_p + L_e)^{-1/4} C^{-5/8} \quad (6)$$

where L_p is the bare persistence length independent of C , and L_e is the electrostatic persistence length which is given [8] by

$$L_e = (16\pi Q A C)^{-1} \quad (7)$$

where $Q = e^2/\epsilon k_B T$ is the Bjerrum length (e is the elementary charge and ϵ is the relative permittivity of water) and A is the contour distance between two successive charges along the polymer chains. Since the total concentration of calcium ions for most experiments (polymer concentration: 1 ~ 10 %) in this study was less than 15 % of total concentration of sodium ions in monomolarity (M), we neglected the contribution of divalent ions to the electrostatic persistence length L_e , instead, we only took into account the univalent cation (Na^+) in equation (7). If we use $A = 5 \text{ \AA}$ for alginate [15] and $Q = 7.5 \text{ \AA}$ for water at 30 °C, the values of L_e are estimated in a range of 1.5 ~ 30 Å for the studied concentration regime. On the other hand, the value of L_p for alginate chains has not yet been determined although for poly(styrenesulfonate) chains $L_p = 30 \sim 50 \text{ \AA}$ and $L_p = 12 \text{ \AA}$ have been reported to give the best fit to the experimental data of quasi-elastic light scattering and small angle neutron scattering, respectively [16, 17]. As a first approximation, if we assume that the value of L_p for alginate is of the same order of magnitude as the poly(styrenesulfonate), then $L_e \leq L_p$ is satisfied for the concentration range of 1 ~ 10 wt%. The validity of the condition $L_e \leq L_p$ will be discussed later. Because the concentration dependence of electrostatic persistence length may be negligible under this condition the correlation length ξ in equation (6) can be expressed by $\xi \sim C^{-5/8}$. This corresponds to the limit of highly concentrated polyelectrolyte solutions. Since the relation of $\xi \sim g$ also holds in Odijk's approach, i.e., chain length shorter than ξ may be considered to be fully stretched, the concentration dependence of gel threshold f_c is given by $f_c \sim C^{-0.625}$. This is in good agreement with our experimental result ($f_c \sim C^{-0.65 \pm 0.05}$). The small discrepancy between experimental and theoretical exponents is thought to be due to the following reasons: (i) experimental conditions are not completely ideal for using equation (6), as the theory has been developed for the case without added salt, (ii) there is uncertainty in evaluating the value of L_p for alginate and (iii) the expression of L_e (Eq. (7)) contains a number of assumptions and is known to be only semiquantitatively correct.

A recent result reported by Wang and Bloomfield [18] has shown that there are three reasonably distinct regimes for the dependences of osmotic pressure Π on concentration for polyelectrolyte solutions without added salt and there are no sharp breaks between these regimes but each extends over an appreciable concentration range. In semidilute regime, the power law $\Pi \sim C^{9/8}$ has been observed, implying that correlation length ξ varies as $\xi \sim C^{-3/8}$ which is corresponding to the case $L_e \gg L_p$. On the other hand, in the concentrated regime a much longer concentration dependence of Π has been observed, which is $\Pi \sim C^{9/4}$, implying $\xi \sim C^{-3/4}$. This corresponds to the behavior of neutral polymers in semidilute solution, and

probably also corresponds to the case $L_e \ll L_p$, as Odijk has shown $\xi \sim C^{-5/8}$ for this case (see Eq. (6)). Between the two regimes, a transition (crossover) regime has also been confirmed (it might be called "semi-concentrated" regime), in which ξ should be expressed by $\xi \sim C^{-\alpha}$ ($3/8 < \alpha < 3/4$). The concentration range of this study was 0.05 ~ 0.56 M, which fell onto this transition regime (see Fig. 6 in Ref. [18]).

Since our result can be better interpreted by assuming the relation $\xi \sim C^{-5/8}$ which is very close to that obtained from osmotic pressure experiments for concentrated polyelectrolyte solutions without added salt, the assumption of $L_e \leq L_p$ may be reasonable for this case although we do not know the exact value of L_p for alginate. Taking into account a viscosity result [19] which shows a relationship between absolute viscosity η_{abs} of alginate solution and concentration by $\eta_{\text{abs}} \sim C^3$ for the concentration range 3 ~ 10 %, our results support the conclusion reached by Wang and Bloomfield [18] that a wormlike chain conformation of the sort adopted by neutral polymers in good solvents may be reached in highly concentrated polyelectrolyte solutions without added salt.

In conclusion, our experimental results on sol-gel transition of alginate solution with the addition of calcium ions show that the gel point is significantly affected by alginate concentration and a power law relation was confirmed between the gelation threshold f_c and alginate concentration C with an exponent of -0.65 ± 0.05 . These results can be interpreted by a combination of scaling theories developed for vulcanization process and polyelectrolytes in semi-concentrated solution. Based on the scaling analysis, a good agreement was obtained between the experimental and theoretical exponents.

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