

## Preparing Concentration Dependence of Viscosity in Randomly Branched Systems of Polyacrylamide

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In order to investigate the structure of randomly-branched clusters, the chemically cross-linked sol solutions were synthesized by varying the prepared concentration and the viscosity of them were measured. It was found that the viscosity behavior can be fitted well by a couple of formulae. It means that there are two regions and there is the changing point between the two regions. The regional map which are divided by gelation point and changing point were obtained. In order to investigate the meaning of the changing point, the dilution experiment was carried out. The results suggested that the changing point is the onset concentration above which the strong interaction between the clusters exists.

Key words: viscosity, gelation, branched polymer, entanglement, sols

### 1. INTRODUCTION

The theoretical investigation of sol-gel transition began with the classical Flory-Stockmayer theory [1] and recently-developed by the advent of the percolation theory in connection with the other critical phenomena [2]. For the sol-gel transition, the critical exponents of the number distribution, the molecular weight, the correlation length and so on were calculated theoretically. A number of the experimental investigation has been done for the purpose of the verification [3, 4, 5, 6].

The previous experiments in the sol-gel transition mostly concerned the physically cross-linked system, but hardly concerned the chemically cross-linked system. The physically cross-link system is easy to be treated thermodynamically since the cross-linked points appear and disappear in equilibrium. The experiments often accorded with the theoretical predictions. On the other hand, The chemically cross-linked system is hard to be considered thermodynamically in a rigorous sense since the cross-linked points are irreversibly generated and never disappear. In the chemically cross-linked system, the branched structure contains the frozen complexity that depends on the process of the cross-linking reaction and makes the situation complicated. Moreover in chemically cross-linked system, a kind of topological entanglement that cannot be disentangled forever, may occur by the cross-linking reaction at dense concentrations. The influence of such an entanglement on its properties is interesting; nevertheless it is hard to be described theoretically [7].

Many actual applications, however, are related to chemically cross-linked branched polymers and gels. The structure and properties of them should be investigated. In the present work, the viscosity behavior of the chemically cross-linked sol solution is studied in order to illuminate the structure of the randomly branched polymers.

### 2. EXPERIMENTAL

Samples were synthesized by free radical polymerization in aqueous solution. Pre-reaction solutions consist of monomer acrylamide, cross-linker *N,N'*-methylene-bisacrylamide (Wako Chemicals Co.), and solvent distilled water. The monomer concentrations were 0.00115, 0.00135, 0.00154, and 0.00231 g/ml and cross-linker concentrations were varied from 0 to  $7.12 \times 10^{-4}$  g/ml.

Pre-reaction solutions were about 50ml and bubbled with nitrogen in 45 °C water bath for 30 minutes. Reactions were started by the addition of initiator ammonium-persulfate ( $4.62 \times 10^{-1}$  mg/ml). During the reaction the thermal bath was vibrated 100 rpm by rolling vibrator. Reaction time was 6 hours and then quenched to 1 °C in order to stop the reaction.

Viscosity was measured by 6 kinds of Ubbelode viscometers (1~30000cP) and a falling ball viscometer (>10000cP). The measurement temperature was 30 °C.

### 3. RESULTS AND DISCUSSION

#### 3.1 Divergent behavior of viscosity

Divergence behavior of the viscosity  $\eta$  in the series of the sol solutions is shown in Fig.1. There were 4 series. In each series the prepared concentration of the monomer  $C_{AA}$  was constant. By varying the prepared concentration of the cross-linker  $C_{bis}$ , each series of the sol solutions was prepared. In Fig.1, the closed and open symbols indicate the  $\eta$  determined by Ubbelode viscometers and the falling ball viscometer respectively.

For all the series, the  $\eta$  rises as the prepared  $C_{bis}$  increase. In the lower  $C_{bis}$  region, as the  $C_{bis}$  increases, the branched-polymers are formed and the molecular weight grows, and then the  $\eta$  gradually increases. In low  $C_{bis}$  region, as the increment of the  $\eta$  depends strongly on the growth of the molecular weight, the  $\eta$  behavior in this region is considered to obey

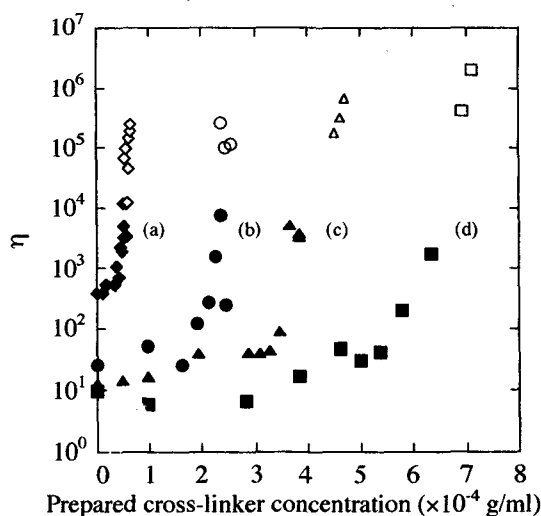


Fig.1: Divergency of the viscosity  $\eta$  against the prepared  $C_{bis}$ . The monomer concentrations are (a) 0.00231 (b) 0.00154 (c) 0.00135 (d) 0.00115g/ml. Closed symbols indicate the results of Ubbelode viscometer and open symbols indicate the results of ball falling viscometer.

approximately to the Mark-Howink-Sakurada's formula. In the higher  $C_{bis}$  region, the size of the clusters constructed by the branched polymer grows. The  $\eta$  diverges toward the gelation point and obeys to the power-law function of the distance to the gelation point. In the present study, the gelation point is defined as the diverged point of the  $\eta$ . We try to determine the dependence of the gelation points on  $C_{bis}$ .

The divergence behavior of  $\eta$  was analyzed by the fitting to experimental formulae. An example of the analysis of  $\eta$  as a function of  $C_{bis}$  is shown in Fig. 2. We first tried to fit  $\eta(C_{bis})$  to an experimental formula

$$\eta = s \times (C_g - C_{bis})^\beta \quad (1)$$

where  $s$  is constant,  $\beta$  is an exponent and  $C_g$  is the gelation point. This fitting didn't go well in low  $C_{bis}$  range and the determined  $C_g$  were unreasonable. Therefore we next divided whole plots into two regions. In the lower  $C_{bis}$  region,  $\eta(C_{bis})$  was fitted to an experimental semi-linear formula

$$\eta_1 = p + q \times C_{bis}^r \quad (2)$$

where  $p$ ,  $q$  are constants and  $r$  is an exponent. In the higher  $C_{bis}$  region,  $\eta(C_{bis})$  was fitted to a power-law formula as Eq.(1):

$$\eta_2 = s \times (C_g - C_{bis})^\beta \quad (3)$$

Figure 2 shows a result of the fitting analysis with the formulae of  $\eta_1$  and  $\eta_2$ . It was found that the fitting went well. The obtained  $r$  and  $\beta$  were 1.66 – 4.51 and 5.80 – 13.0. These  $\beta$  and  $r$ , however are no quantitatively meaning in the consideration of the dispersion of the experimental values. For all the series of the samples,

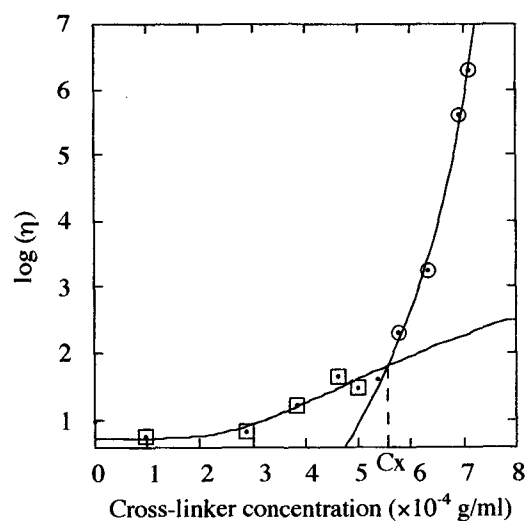


Fig.2: An example of the fitting analysis for the viscosity  $\eta$  as a function of the prepared  $C_{bis}$ . The monomer concentration is constant at 0.00115g/ml. A couple of lines are the fitting curves. In the lower  $C_{bis}$ , the data indicated by  $\square$  were fitted to a semi-linear formula. In the higher  $C_{bis}$ , the data indicated by  $\circ$  were fitted to a power law formula. (See text for detail).

the gelation points  $C_g$ , and the cross-points  $C_x$  of  $\eta_1$  and  $\eta_2$  were determined by the analysis. It is seemed that the obtained  $C_x$  is the characteristic concentration above which the interaction among the clusters of branched polymer becomes effective.

### 3.2 Phase diagram

From the  $C_{bis}$ -dependence of  $C_g$  and  $C_x$ , the regional map of sol-gel transition is obtained (Fig.3). It is found that both  $C_g$  and  $C_x$  can be scaled with  $C_{bis}$  as  $C_g \sim C_{bis}^{3.3}$  and  $C_x \sim C_{bis}^{3.8}$ . There is a closed region between the lines of  $C_g$  and  $C_x$ . In this region the divergence behavior of  $\eta$  is described by  $\eta_2$ . In this region, the clusters of branched polymers interact strongly each other with entanglement and the viscosity rises. It may be considered that the structure of the branched polymers in this region depends on the reaction process.

In the following, we perform the viscosity measurement of diluted sol-solutions in order to investigate the structure of the clusters in this region. If the clusters are isolated by the dilution, the interaction between the clusters should be decrease. The viscosity measurement of the diluted solution should give information about the structure of the isolated clusters. Hence for the preparation of the dilution experiments, the crossover concentration of the linear polymer was determined.

### 3.3 Crossover concentration

The linear polyacrylamide was synthesized by the same method of branched one without the cross-linker. The molecular weight was determined by the inherent viscosity. The Mark-

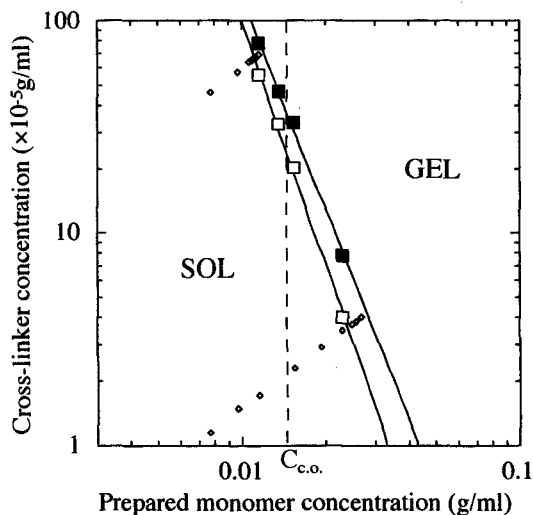


Fig. 3: The phase diagram. Open box symbols indicate the gelation points and closed box symbols indicate the changing points determined from the fitting results. Lines are the fitting curves of the power-law formula. Small diamond symbols indicate the measurement points of the following experiments of the dilution.

Howink-Sakurada's formula  $[\eta] = KM^a$  was used for the calculation of the molecular weight, where the constant  $K = 0.068 \text{ ml/g}$  and the exponent  $a = 0.66$  [8]. The determined molecular weights have the dependence on the prepared monomer concentrations  $C_{AA}$ . The molecular weight increases as  $C_{AA}$ . The gyration radius  $R_g$  and the crossover concentrations were calculated from the molecular weight. The dependence of the crossover concentration on the prepared monomer concentrations is shown in Fig. 4. Thus we determined the concentration  $C_{c.o.} = 0.0145 \text{ g/ml}$  at which the prepared monomer concentration accords with the crossover concentration (Fig. 4).

In the sol-solution synthesized at the  $C_{AA}$  higher than the  $C_{c.o.}$ , the branched polymers cross over each other independently of  $C_{bis}$ . On the other hand, in the sol solution synthesized at the  $C_{AA}$  lower than the  $C_{c.o.}$ , the opportunities of the crossover between the branched polymers are few if  $C_{bis}$  is small. Although by the addition of the cross-linker the branched polymers are formed and  $C_{AA}$ -dependence of  $C_{c.o.}$  changes, we use the  $C_{c.o.}$  as a characteristic concentration for branched systems.

### 3.4 Dilution experiment

The prepared concentrations of all the samples for the dilution experiments are shown in Fig. 3 with small diamond symbols. A couple of series of the samples were synthesized. For each series, the samples were prepared in the same ratio of  $C_{bis}$  to  $C_{AA}$  varying the total monomer concentrations. The prepared ratios were of 0.0600 and 0.00150 g/g. If the reaction goes ideally, the number of the branch points

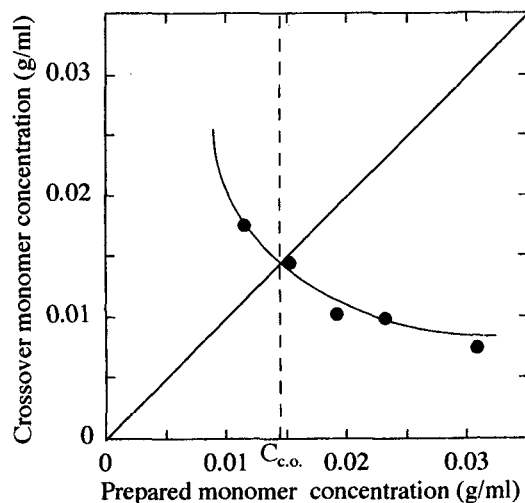


Fig. 4: The crossover concentrations against the prepared monomer concentrations. The prepared monomer concentration is equal to the crossover concentration at  $C_{c.o.}$  (0.0145 g/ml).

per the length of the main chain is constant. For the higher ratio of  $C_{bis}$ , all the samples were prepared at the concentrations lower than  $C_{c.o.}$ . On the other hand, for the lower ratio of  $C_{bis}$ , all the samples were prepared at both the concentrations lower and higher than  $C_{c.o.}$ . At first, the samples were measured as-prepared. Next the samples were diluted with distilled water to the same monomer concentration of 0.00769 g/ml for all samples. This concentration is lower than the  $C_{c.o.}$ . It seems that the clusters in the solution are isolated. The water-added samples were put for several days to be homogeneous and then measured.

Figure 5(a) shows the results of the dilution experiment for the higher ratio series of  $C_{bis}$ . It appears that  $\eta$  of the samples decreases by the dilution. The increasing profile of  $\eta$  don't change after the dilution in this series; before and after the dilution,  $\eta$  gradually increases in the lower concentration region, and then divergently grows over about the  $C_x$ . It should be noted that this divergent behavior of  $\eta$  never disappears after the dilution. It means that there is a kind of strong interact between the clusters that does not disappear by the dilution. Thus it seems that there exist the permanent entanglement. In the diluting experiments, the high concentration samples were hard to be diluted in actual. Therefore the analysis with the fittings were not performed.

The result for the lower ratio series of  $C_{bis}$  is shown in Fig. 5(b). It seems that there are three characteristic regions of the increasing profile of  $\eta$  before the dilution. The increment rate of  $\eta$  changes around the  $C_{c.o.}$  as the  $C_{bis}$  increases. Again the increment rate changes above about  $C_x$  and  $\eta$  diverges. On the other hand, after the dilution the change of the increment rate of  $\eta$  around the  $C_x$  disappears. It is explained

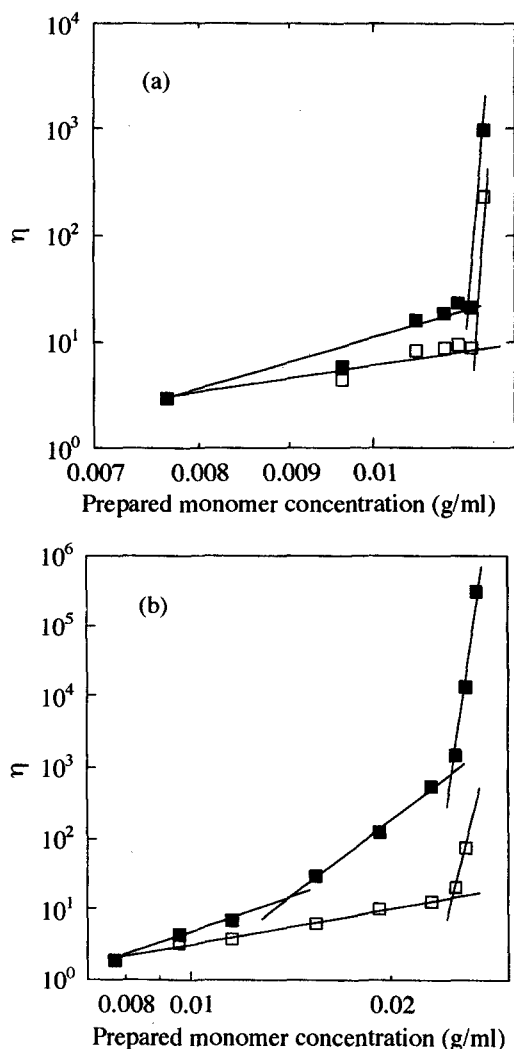


Fig.5: The log-log plots of the viscosity  $\eta$  against the prepared monomer concentration for (a) the higher ratio series (b) the lower ratio series in the dilution experiment. Closed box symbols indicate pre-dilution viscosity and open box symbols indicate after-dilution viscosity. The ratio of the concentration of cross-linker and of monomer is constant, and the total concentrations are varied. The concentration of this measurement is shown in sol-gel phase diagram (Fig.3). Lines are added to guide the eye.

that the clusters of the branched polymers is isolated by the dilution and the increment of  $\eta$  caused by the entanglement between the clusters disappears. The change of the increment rate of  $\eta$  about  $C_x$  line does not disappear by the dilution. This phenomenon accords with the behavior for the high ratio series. It also seems that there exist the permanent entanglement. It suggest that this phenomenon is a characteristic nature of the chemically cross-linked systems. In the discussion of the chemically cross-linked gelation process, the effect of the permanent entanglement should be considered.

#### 4. CONCLUSION

In order to investigate the structure of randomly-branched clusters, the chemically cross-linked sol solutions were synthesized varying the prepared concentration and the viscosity of them were measured. It was found that the viscosity behavior cannot be fitted well by one formula. The viscosity behavior can be fitted well by a couple of formulae. It means that there are two regions and there is the changing point between the two regions. By the fitting, the gelation point  $C_g$  and the changing point  $C_x$  were determined. The regional map which are divided by  $C_g$  and  $C_x$  were obtained. In order to investigate the origin of the concentration  $C_x$  we carried out the dilution experiment. The viscosity of the diluted samples reflects the structure of the isolated clusters. In the synthesis of the samples for the dilution, the ratio of the concentration of cross-linker to that of monomer is constant in the prepared solution, and the total concentration is varied. We first measured the viscosity of the samples in as-prepared solution. Next the samples are diluted to the same concentration lower than the characteristic and we measured the viscosity. It was observed that the divergent behavior appeared above about the  $C_x$  line never disappears by the dilution. This suggests that the  $C_x$  is the onset concentration above which the strong interaction between the clusters of the branched polymers exists.

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