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Concentration dependence of the sol-gel transition point and the network formation of polymer gels

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We report the experimental and the numerical studies on the sol-gel transition phenomena of polymer gels in terms of the solution effect. We found that the sol-gel transition boundaries of polymer chemical gels are described by a linear function of the polymer concentration. These results can be successfully explained by the percolation model of thermally reversible physical gels, provided that we estimate that contribution of isolated bonds and subtract it from this model. We also extend this model to explain the molecular weight effect that is peculiar to polymers. The molecular weight dependence of the decrease of the transition boundary for polymer solutions is explained by the effect of both the connectivity and configuration of polymer chains. It is clearly revealed that the concentration dependence of the gel transition boundary for polymer gels can be described in the same framework as physical gels, despite the large difference in the cross-link features. [S1063-651X(96)06212-5]

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I. INTRODUCTION

Polymer gels have been extensively studied from experimental and the theoretical points of view. The three-dimensional network structure is the characteristic feature of gels, and polymer gels have many unique properties that are not observed in polymer solutions [1]. Phase-transition phenomena between the gel phase and the sol phase, which corresponds to the polymer solution, have been investigated mainly on the basis of critical behavior. It is well known that the percolation model gives excellent predictions for various critical properties of the sol-gel transition, which are different from those predicted by the Flory-Stockmayer-type mean-field theory [2,3]. Since then, a large number of investigations have been made on various critical properties of the sol-gel transition, such as correlation length, cluster size, and elastic properties [4–15]. The universality of the critical phenomena associated with the cluster growth of the sol-gel transition has been confirmed in a wide range of gels. On the other hand, it is reported that the critical properties of elasticity depend largely on the precise form of the elastic energy of gels. Therefore, gels do not belong to the same universality class for all kinds of critical behavior [15].

While detailed studies on various critical phenomena have been explored, little attention has been given to the behavior of the sol-gel transition point itself. We might expect that the behavior of the transition point is more system specific than the critical behavior. However, if we concern ourselves with the concentration dependence of the sol-gel transition point, it seems that there exists some system-independent relation between the gelation point and the polymer concentration. This is because the concentration dependence is related only to the dilution effect. The purpose of this paper is to examine whether there is any universal behavior of this concentration dependence of the sol-gel transition point for many kinds of gels, focusing especially on polymer gels.

Here we briefly mention the classification of gels. Although gels have many varieties, gels can be grouped into physical gels or chemical gels in terms of their cross-linking process. Cross-links of physical gels are produced by the hydrogen bonding or the microcrystallization. Their cross-link energy is weak and the order of k_BT. These physical gels often show thermally reversible sol-gel transitions [16–18]. On the other hand, chemical gels are produced by the strong covalent bonding and their cross-links are irreversible. Some kinds of chemical gels, such as poly (N-isopropylacrylamide) gel, show an interesting volume phase transition [19–22]. Chemical gels do not show a reversible sol-gel transition in principle, but the sol to the gel transition is a common phenomenon for both kinds of gels.

Following the above classification, it is important to compare the results of polymer chemical gels with those of physical gels from the viewpoint of the universality. In the case of physical gels, the concentration dependence of the gelation point can be easily obtained by investigating the phase diagrams of gels. Phase diagrams of physical gels are generally described by temperature and concentration [23,24]. In order to compare the phase diagrams of physical gels with those of other kinds of gels, it is essential to find a more general parameter instead of temperature. The question that we have to consider is the temperature dependence of the cross-link properties. Since there are many experimental results on phase diagrams of physical gels, we have no need to carry out experiments for physical gels.

On the other hand, in the case of chemical gels, we need to carry out experiments with carefully chosen samples that make it easy to analyze the concentration dependence. The reason for this is as follows. Many chemical gels are produced by the condensation of monomers. In order to form interconnected gel networks rather than simple long polymer chains, monomers must have at least three functions. In most typical cases, we need both main monomers, which have many functions, and cross-link monomers, which have two functions. The reaction initiators and the reaction accelerators are also required for the chemical reaction to take place. Thus the transition points of the chemical gelation are often described by these parameters. The participation of many

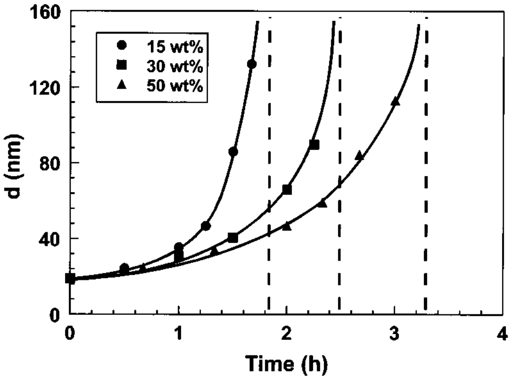

FIG. 1. Network formation processes of PVME solutions for three different concentrations. Here *d* is the hydrodynamic diameter of polymer clusters. The vertical dashed lines are the gel transition points.

parameters makes our analysis considerably more difficult. This point is not a serious problem for the studies of critical phenomena since we can observe the critical behavior by simply choosing one of these parameters as a variable. In general, critical exponents depend only on the dimension of the system and they are less affected by the detailed features of the network structure of gels or parameters. The critical exponents are related to the universal properties and hide various details of the samples. However, in order to study the concentration dependence of the sol-gel transition point of polymer gels, it is required that the system is composed of only one type of main molecule and that there exists only one parameter to represent the cross-link extent. Although this restriction is severe, we found that chemical gel samples of the poly-(vinyl methyl ether) aqueous solutions are suitable for our purposes.

In this paper, we first report the experimental results of the concentration dependence of the sol-gel transition point for polymer chemical gels. Then we compare these results with those of physical gels. We show that the concentration-dependent behavior of polymer gels can be explained in the same framework as physical gels, if we take into account some cross-link features of polymer solutions. We also discuss the molecular weight effect for the gel transition boundary.

II. EXPERIMENT

We used poly-(vinyl methyl ether) (PVME) and water solutions as samples. The weight-averaged molecular weight of PVME is 92 000. The formation of cross-links due to the γ-ray irradiation leads to gels [25,26]. The radiation source was Co^{60} and the dose rate was 2.38 J/kg s (8.56 kGy/h). No apparent dose rate dependence in the gelation processes was observed below this rate. A γ ray that hits a polymer can make a cross-link point. When it hits a water molecule, it also makes a cross-link point because the OH radical produced can behave as a radical initiator in this solution. Therefore, the total exposure is roughly proportional to the amount of cross-link seeds for the first-order approximation within the concentration region we used. In order to prevent the temperature increase due to the irradiation process, sample cells were immersed in the water jacket whose temperature was always kept at 25 °C.

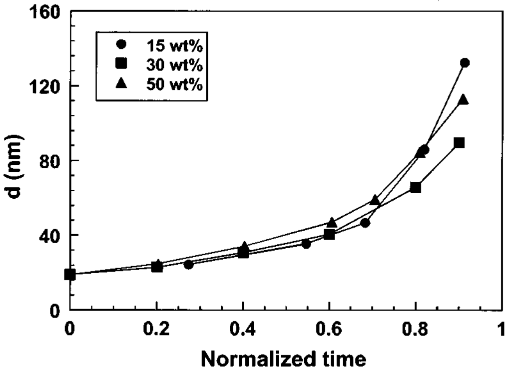

FIG. 2. Normalized plot of the network formation process of PVME solutions.

The experimental method to determine the gelation point in these polymer chemical gels is an essential point. In many experiments, it is widely adopted to measure the viscoelastic properties of samples for the determination of the gelation point [9–11]. When sol solutes consist of low molecules, the rheological method, such as the falling-ball method, is a simple and effective experimental tool. However, in the case of concentrated polymer solutions, solutions become viscoelastic when their concentration is higher than the overlapping threshold due to the entanglement effect. The falling-ball method is directly related to the absolute values of elasticity, and this causes a systematic error for concentrated polymer solutions. To avoid this problem, the rheological measurement of the frequency spectrum of viscoelasticity is more adequate for the rheological determination of the gelation point, since the viscoelasticity shows the power law in frequency given by

$$G(\omega)\sim\omega^{\Delta} \tag{1}$$

at the critical gel transition point [27,28]. This method is especially effective for thermally reversible gels. However, for chemical gels, there is another simple method to determine the gelation point. We can directly measure the average cluster size that diverges at the sol-gel transition point. In this method, we have to dilute samples in order to measure the size of one molecule. The irreversibility of chemical cross-links during the dilution enables us to carry out this kind of experiment. When the average cluster size diverges at the gelation point, the following phenomena are also observed in our experiments, which reinforce our determination of the gelation point: (i) a large polymer network that is insoluble to water appears; (ii) it becomes difficult for the sample to flow and so keeps its shape. These phenomena are taken into account for the determination of the gelation point.

The cluster size of the solutes was measured by means of dynamic light scattering. The laser source was an argon-ion laser and its wavelength was 488 nm. We adopted the homodyne method. All light-scattering measurements were carried out at a temperature of 25 °C and at a fixed scattering angle of 90°. The hydrodynamic radius of the cluster was obtained using Einstein-Stokes equation

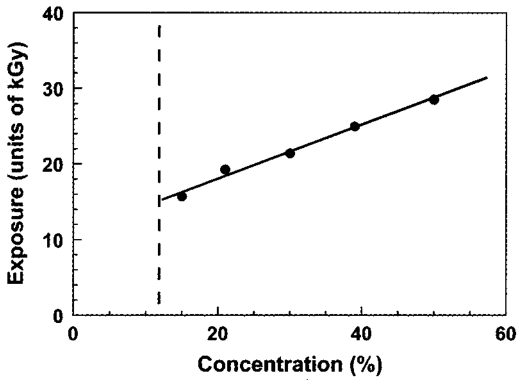

FIG. 3. Critical gelation exposure for various polymer concentrations. In a lower-concentration region than the dashed line, no gel or only partially formed gels are obtained.

$$\xi_H=\frac{k_B T}{6\pi\eta_0 D},\tag{2}$$

where D is the diffusion constant obtained from the relaxation time and η_0 is the viscosity of the solvent. We regard this hydrodynamic radius of polymer solutions as an index to the average cluster size of sol molecules.

III. RESULTS

Figure 1 shows the growth of the cluster size in the gelation process obtained by the dynamic light scattering measurements. The horizontal axis indicates the elapsed time from the start of the irradiation. In this figure, the network formation processes of three different concentrations are shown. Three vertical dashed lines indicate the sol-gel transition points for each sample. According to this result, the time required for the gelation takes longer as the concentration of the sample increases. In order to compare these gelation processes, we normalized the horizontal axis as shown in Fig. 2. Here the time scale is normalized against the gelation time of each sample. This figure indicates that the network formation processes agree with the same master curve irrespective of the sample concentration.

Now we can obtain the concentration dependence of the sol-gel transition point of PVME solutions. As shown in Fig. 3, the gel transition boundary is well expressed by a linear function of the polymer concentration. The vertical dashed line in Fig. 3 indicates that below this concentration the infinite gel network was not obtained. The important point to notice is that we consider only the infinite gel network in our experiments and we disregard the finite gel-like networks. Specifically, we can observe small fragments of gels at the concentration region that is slightly lower than this threshold. However, gels obtained in this concentration region are fragments that do not fill the whole volume of the original polymer solutions. We call these gels the partially formed gels, whose gel network is not infinite. This threshold is about 12 wt % for our PVME solution, and this value is similar to the overlapping concentration c^* of this polymer solution. This result suggests that the infinite polymer gel network can be obtained when polymer chains collide with each other almost anywhere in a solution in its sol phase.

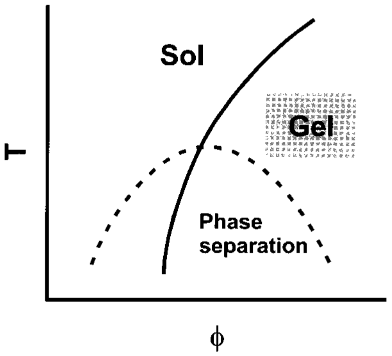

FIG. 4. Schematic phase diagram of typical thermally reversible physical gels.

IV. DISCUSSION

A comparison of results of polymer chemical gels with those of physical gels will provide a clear picture for the concentration dependence of the sol-gel transition point. There have been many studies of phase diagrams of physical gels from both the experimental and theoretical points of view [16–18,23,24]. We summarize the phase diagram of ordinary thermally reversible gels as shown in Fig. 4. The gel phase exists in the lower-temperature and higher-concentration region. The dashed line shown in Fig. 4 indicates the phase-separation boundary. It is also an interesting property of some physical gels, which enables us to observe the competition phenomena between the gelation process and the phase separation process. In order to compare the phase diagram of physical gels with other kinds of gels that do not have a temperature factor in their phase diagram, it is convenient to replace temperature by the bonding probability. The cross-links of physical gels usually originate in the hydrogen bonding or the microcrystallization. Its bonding probability between two molecules becomes higher as the temperature decreases. The bonding probability p_b is defined as the probability that the connection between two molecules is formed under the condition that these two molecules are present at nearest neighbors. This probability is given, using the two-state model, by

$$\begin{aligned}p_b&=\exp\left(-\frac{-\Delta E}{k_B T}\right)\Bigg/\left[1+\exp\left(-\frac{-\Delta E}{k_B T}\right)\right]\\&\approx 1-\exp(-\Delta E/k_B T),\end{aligned}\tag{3}$$

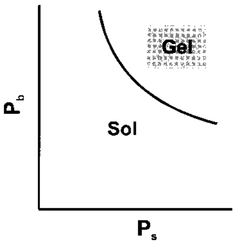

FIG. 5. Schematic phase diagram of physical gels. Here the vertical axis is replaced by the bonding probability, using Eq. (3).

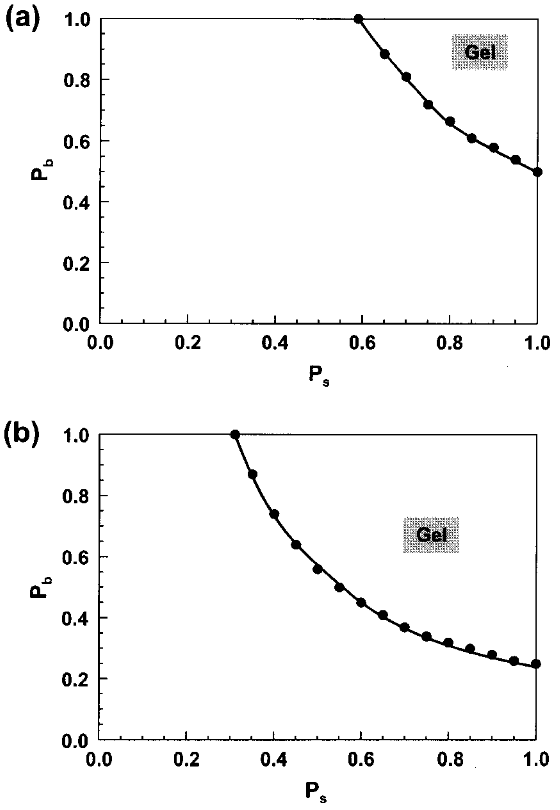

FIG. 6. Sol-gel transition boundary for the site-bond percolation model: (a) two-dimensional square lattice and (b) three-dimensional simple cubic lattice.

where ΔE is the decrease of energy due to the formation of a cross-link. Using this bonding probability p_b, the phase diagram of thermally reversible physical gels can be schematically shown as in Fig. 5.

This reduced phase diagram and the critical behavior of gels have already been explained by the percolation model. This theory is based on the lattice model and it takes into account the excluded-volume interaction and the possibility of the formation of loops that are ignored in a classical mean-field-type theory. The bond percolation model corresponds to the gelation model without solvent. There are two kinds of percolation models that include the effect of a solvent. One is the correlated percolation model in which monomers do not randomly distribute on the percolation lattice because of the attractive force between monomers [23,29,30]. The other is the site-bond percolation model, which focuses on the dilution effect [31,32]. Since we mainly investigate the dilution effect, we adopt the site-bond percolation model here. The site-bond percolation model is a two-parameter model that combines the site percolation and the bond percolation. The occupied sites and the unoccupied sites correspond to monomers and solvents, respectively. The probability of the site occupancy p_s and that of the bond occupancy p_b are given independently. Two sites are regarded as connected only if both sites are occupied and the bond is linked. When there is an infinite cluster, this state is defined as the gel phase. Figure 6 shows the phase diagram of gels obtained by this model. Figure 6(a) is the phase diagram for two-dimensional systems and Fig. 6(b) is the phase diagram for three-dimensional systems. The gel phase region in two-dimensional systems is extremely limited compared to that in three-dimensional systems since there are fewer ways to detour the vacant region. We use calculations for three-dimensional systems since our systems are three dimensional. The phase boundary of Fig. 6(b) obtained by the site-bond percolation model qualitatively predicts the phase diagram of physical gels, which is shown in Fig. 5.

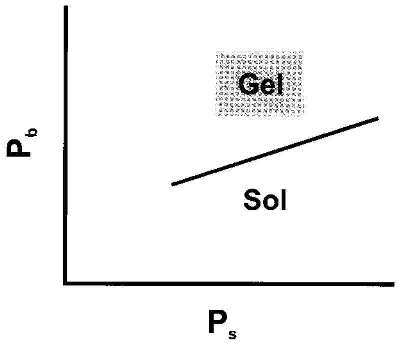

FIG. 7. Schematic picture for the results of PVME solutions. The cross-link ratio p_b is given by p_b=(number of occupied bonds)/(number of all bonds). In the site-bond percolation model, the number of all bonds is a constant irrespective of the polymer concentration.

Now we will discuss the concentration dependence of polymer chemical gels. Experimental results that we obtained for PVME solutions are schematically shown in Fig. 7. In this figure, the horizontal axis indicates the concentration and the vertical axis indicates the bonding probability in the sense of the percolation model. The bonding probability is calculated as the ratio of the number of occupied bonds over the number of total lattice bonds. Here the number of occupied bonds is proportional to the total exposure, whereas the number of all lattice bonds is a constant irrespective of the sample concentration in the site-bond percolation model. The phase diagram of polymer gels shown in Fig. 7 is different from that in Fig. 6(b). Where does this difference come from? In the site-bond percolation model, sites and bonds are randomly allocated in the lattice. As a result, there are many occupied bonds that have no or only one occupied site in its both ends. These isolated bonds in the site-bond percolation model correspond to the chemical reaction seeds that fail to make the bond formation. However, in polymer gels, there are very few such isolated bonds because the solution is concentrated so that it is easy for bonding reaction seeds to find another polymer and make cross-links during their lifetime. Therefore, the bonding probability of our experiments, which is shown in Fig. 7, shares only the portion of the bonding probability of the original site-bond percolation model. In other words, the bonding probability p_b in the site-bond percolation model overestimates the bond connectivity ratio of polymer chemical gels. This excess estimation of the bonding probability Δp is simply given by

$$\Delta p = p_b(1 - p_s^2), \qquad (4)$$

since the site connectivity and bond connectivity are independently determined by the random number generator for

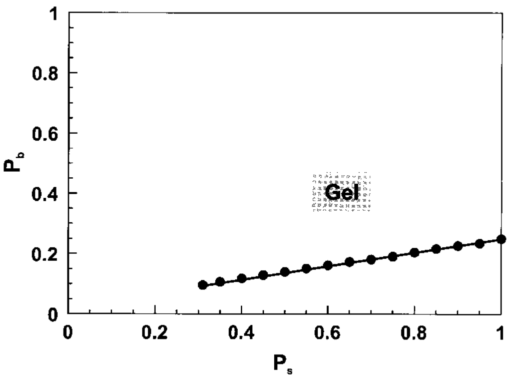

FIG. 8. Phase diagram for polymer chemical gels with the correction of Eq. (4).

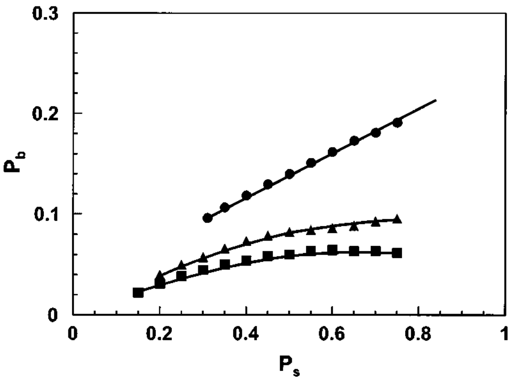

FIG. 9. Phase boundary for polymer chemical gels with different chain length. Circles, simple molecule; triangles, four-step molecule; squares, ten-step molecule.

every place. If we subtract this contribution of isolated bonds Δp from the original model, the phase diagram of Fig. 6(b) is replaced by a new phase diagram as shown in Fig. 8. This gives the sol-gel transition boundary that is nearly a linear function of sample concentration. The calculated phase boundary quantitatively explains the results of experimental data. Therefore, the difference in the concentration dependence of the sol-gel transition point between physical gels and polymer chemical gels comes from the estimation of the bonding probability.

One remaining possibility that may cause the intrinsic difference between physical gels and chemical gels in the concentration dependence of the sol-gel transition boundary is the effect of reversibility of cross-links. Physical gels exist in the thermal equilibrium state. Their cross-links between molecules are so weak that they are always in competition with the entropy effect, which is directly related to the concentration. On the contrary, chemical gels are produced by nonequilibrium chemical reaction process. The transition boundaries are less affected by this dissolution effect. However, this effect seems to appear only when we examine the transition lines very precisely, and detecting it experimentally would be difficult.

The next question related to the sol-gel transition of polymer gels is how the polymer chain length affects the transition boundary. The sol-gel transition point varies with the molecular weight even if the volume fraction of polymers is the same. Usually, the configuration of the flexible polymer chains is represented by the trajectory of the self-avoiding random walk. This model takes into account the excluded-volume effect, and the number of steps corresponds to the degree of polymerization. The configuration of the flexible polymer chains is roughly the globular form whose radius is $N^{\nu}a$, where N is the degree of polymerization, ν is some scaling exponent, and a is the effective length per monomer. Therefore, it may be reasonable to adopt the approximation that one polymer occupies one site in the percolation model. However, in order to explain the molecular weight effect of polymer gels, we must add another factor to the original percolation model. The combined model of the percolation and the self-avoiding random walk is the simplest model for the description of the gelation process of polymer solutions. The actual simulation procedure is as follows. The number of polymer chains N_p is given by

$$N_p = N_s p_s / N_L , \tag{5}$$

where N_s is the total number of sites, p_s is the probability of site occupation, and N_L is the length of polymer chains, which is equal to the number of steps in the random walk. We disregard the molecular weight distribution in our calculation. We arranged these N_p polymer chains on the lattice one by one. For each polymer arrangement, we first assign the position of one end of the polymer chain by a random number and then the self-avoiding random walk of the step length N_L starts from there. If the trajectory goes into the dead end before its step length reaches N_L, the arrangement of this polymer is canceled. The arrangement of this polymer chain restarts from a new starting point, which is again randomly assigned. Strictly speaking, the configuration of the first polymer chain assigned to the lattice is the same as that of the polymer chain in a dilute solution since there are no other polymers. The configuration of polymers that are assigned later is affected by the entanglement effect, since many polymer chains already exist. However, we also disregard this effect for convenience. We used these initial arrangements as polymer solutions before the gelation. So the gelation of these polymer solutions can be regarded as another type of percolation model with some kind of correlated distribution. We then simulate gelation process by assigning bonds using the bond linking probability p_b.

Figure 9 shows the results of the phase boundary of polymer gels that correspond to the step lengths 1, 4, and 10, respectively. These calculations were carried out under the condition that the total number of lattice points is 1×10^6. This figure indicates that when polymer chains become longer, the sol-gel transition occurs at the lower bonding probability. In addition, this figure also indicates that the transition boundary of a higher molecular weight sample weakly depends on the concentration. We also investigate the total lattice size effect. The transition boundary for the polymer chains of step length 10 in a lattice size of $40\times40\times40$ is identical to those obtained at a larger lattice whose size is $100\times100\times100$. Therefore, the transition lines of polymer solutions are independent of the ratio of their chain length to the total size of the system and they are determined only by the value of the chain length. This suggests that our calculations are carried out under the condition that the lattice size is large enough compared to the effective

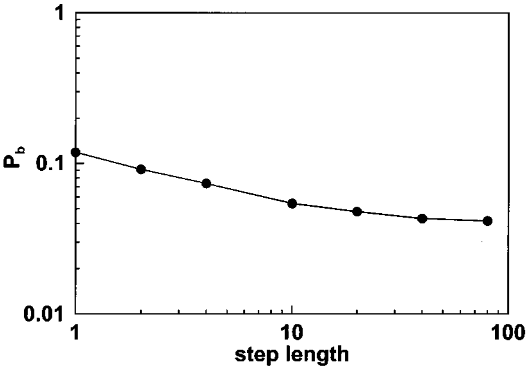

FIG. 10. Molecular weight dependence of the gel transition point of polymer solutions. The volume fraction of polymers is 0.4.

length of polymers. In Fig. 10 we show the step length dependence of the gel transition point at the polymer volume concentration of 0.4. The total lattice size for these calculations is 27×10^6. Gel transition points decrease by a power of -0.1 compared to the step length, though it seems that the transition point becomes less sensitive to the step length in the higher step length region. This behavior can be explained as follows. The solutions of a long polymer chain require two corrections for the sol-gel transition point compared with their equivalent low molecular solutions. First is the effect of the connectivity of polymers. Despite the length of polymer chains, one cross-link between polymers connects all occupied sites that belong to both polymers. Therefore, less bonding probability is required for the solutions of longer polymer chain to connect to each other if we consider the probability per one site. The second is the effect of the configuration of polymers. Since we consider the flexible polymer chains that take the globular form, the number of possible cross-link points to another chain is mainly ascribed to the number of surface sites of the polymer chains. The ratio of the surface sites over the inner sites plays an important role. The former effect of connectivity is responsible for the rapid decrease of the bonding probability with the increase of step length in the small step length region. The latter effect of the configuration is responsible for the weak decrease of the bonding probability in the large step length region.

If we renormalize this lattice structure of polymer solutions to the ordinary low molecule percolation problem, the effect of polymer length can be ascribed to the number of functions of one monomer site. The effect of the connectivity of polymers increases this number of functions and the effect of the configuration of polymers suppresses this increase. In the cubic lattice structure, monomers have six neighboring sites. It may be interesting to compare long polymer chains with various low molecular systems that have more than six functions. However, the lattice structures of many functional monomers are generally difficult to constitute, so we cannot point out the similarity or the difference between the polymer model and the many-functional-monomer model in detail at present.

The schematic picture of the concentration dependence of the sol-gel transition line for polymer chemical gels is summarized in Fig. 11. In the lower-concentration region, it is impossible to form a network of infinite size even if all

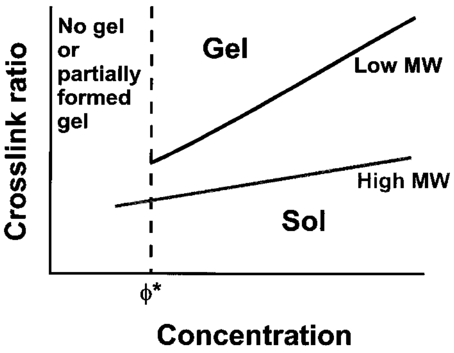

FIG. 11. Schematic picture of the sol-gel transition boundary for polymer chemical gels. The vertical dashed line indicates the critical gel concentration. The gel phase region is above the transition line.

bonds are connected. This region is described as a no-gel or partially formed gel region. Gels appear above this threshold and the sol-gel transition point increases as the polymer concentration becomes dense. Our experimental and numerical results show that the transition boundary is almost a straight line. If it follows such a simple relation, there might be some simple physical reason or meaning. It may be interesting to investigate the fractal structure of critical gels at the transition points for each concentration. As for the molecular weight dependence, solutions of the higher molecular weight polymers have a transition boundary that is located at the lower bonding probability. Its critical threshold also moves to a lower concentration. Our simulations were carried out in a simple cubic lattice. We believe that this outline of behavior of the transition line remains the same for many kinds of lattices, provided that simulations are carried out in three dimensions.

V. SUMMARY

We studied both experimentally and numerically the concentration dependence of the sol-gel transition point of polymer chemical gels. Our experimental results showed that the critical sol-gel transition concentration is around the overlapping concentration of the polymer solution and the transition boundary is a linear function of the polymer concentration. We investigated this dependence through the site-bond percolation model. In the case of polymer chemical gels, the bonding processes of molecules are different from those of physical gels in that the bonding process is a nonequilibrium chemical reaction and the concentration of polymer solutions is above its overlapping concentration. These two factors make the isolated bonds hardly existent in polymer chemical gels. As a result, we need to subtract the contribution of isolated bonds from the original site-bond percolation model. This contribution can be estimated by the ratio of $1-\phi^2$ to the original bonding probability, where ϕ is the concentration of polymers. With this treatment, both physical gels and chemical gels belong to the same class for the concentration dependence behavior. As for the molecular weight effect, the transition occurs at the lower bonding probability as the molecular weight increases. This behavior can be explained by the effect of both connectivity and the configuration of the flexible polymer chains. Polymers behave as if they were many functional monomers. Polymer chemical gels have many different features compared to ordinary physical gels. However, with these modifications, both systems can be successfully described by the same framework of the site-bond percolation model for both the concentration dependence and the molecular weight dependence of the gel transition point.

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