ORIGINAL ARTICLE

Sol-gel transition behavior near critical concentration and connectivity

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A polymer cross-linking system undergoes a phase transition from liquid to solid at a critical point, which is called the sol-gel transition. The sol-gel transition is often understood in the context of the lattice-based percolation model. Two parameters govern the sol-gel transition including the connectivity and polymer concentration. In this study, we independently tuned these parameters and experimentally accessed the sol-gel transition point as a function of connectivity and concentration using a model gel system (tetra-polyethylene glycol gel). The connectivity required to percolate the system continuously increased as the polymer concentration decreased, which is completely different from that predicted by the site-bond percolation model. The viscoelastic behavior at the critical points indicates that the fractal dimension of the percolation clusters deviated from the prediction of the lattice-based percolation model as the polymer concentration decreased. These results indicate that the lattice assumption cannot be applied for a gelling system prepared far below the overlapping concentration.

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INTRODUCTION

When we cross-link a polymeric liquid, a sol-gel transition occurs, and an infinite three-dimensional (3D) polymer network is formed. In the vicinity of the critical point, various physical quantities exhibit unique power law behaviors. Many earlier studies have discussed the power law behaviors of the cluster growth,^{1–7} elastic modulus,^{8–10} viscosity^{11,12} and viscoelastic properties^{13–17} with regards to percolation.^{18,19}

The percolation models approximate the space dimension as lattices and predict the network formation process. The two main classes of percolation models include the bond-percolation model and the site-percolation model. The bond-percolation model treats the situation in which all the lattice sites are occupied and the bonds between neighboring sites are formed at random. The bond-percolation model is often used to predict the network formation process from a molten and concentrated polymer system.^{1–9,11–17} However, the applicability of the bond-percolation model to a dilute system is limited because a massive amount of diluent exists in the system, and the sites (monomer units) do not fill the space. The site-percolation model involves sites that are partly occupied, and the bonds between the occupied sites are ‘certainly’ formed. This model seems to be a candidate for predicting the sol-gel transition in dilute systems. However, this situation cannot be reached experimentally because the connectivity between neighboring sites is not perfect in reality. To predict the sol-gel transition of a dilute system, we need to consider the effects of both the concentration and connectivity. This situation can be modeled using the site-bond percolation model.²⁰ In this model, we can tune both the site occupation and bond formation.

However, to the best of our knowledge, application of the site-bond percolation model to a dilute system has not been examined experimentally, which may be because of the difficulty with independent control of the polymer connectivity and polymer concentration in the real system. To validate the applicability of the site-bond percolation, we need to develop a new system that enables us to tune the connectivity and concentration independently.

Recently, we successfully designed and fabricated a new class of model networks (that is, tetra-polyethylene glycol (tetra-PEG) gel).^{21–25} Tetra-PEG gels are formed by AB-type cross-link-coupling of two types of tetra-arm PEGs with amino groups and activated ester groups. The elementary reaction of the gelation reaction obeyed the second order reaction of amine and activated ester, suggesting that the prepolymers are premixed homogeneously and react efficiently.^{26,27} We directly estimated the connectivity based on the reaction conversion using infrared spectroscopy to determine the ratio of the reacted ends to all the reactive ends. The reaction conversion can be precisely tuned and was as high as 95%.^{28,29} Characterization using small-angle neutron scattering measurements indicated that almost no global heterogeneity existed in the regions up to 200 nm in size.³⁰ The analyses of the small deformation and the fracture test indicated that the elasticity of the tetra-PEG gels simply originated from the chemical cross-links, and the contribution from entanglement couplings between network strands was negligible.²⁹ Based on these results, the tetra-PEG gel is a promising model system with high homogeneity and controllability.

In this study, we investigated the sol-gel transition point as a function of connectivity and concentration. Here, we discuss the

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Figure 1 Schematic representation of the experimental design.

applicability of the site-bond percolation model to the sol-gel transition of a dilute system using the tetra-PEG gel as a model system (Figure 1). We constructed a sol-gel phase diagram tuning the prepolymer volume fraction of the tetra-arm prepolymers (ϕ_0), ranging from $\phi^*/6$ to ϕ^* , where ϕ^* is the overlapping polymer volume fraction of the prepolymer. To tune the connectivity, we mixed tetra-PEG prepolymers with an unbalanced stoichiometry at each polymer volume fraction. In the vicinity of the critical points, we observed the power law behavior of the viscoelasticity. In addition, we compared the experimental results with the predictions from the percolation models and assessed their applicability to the sol-gel transition. These experimental results will contribute to the fundamental understanding of the sol-gel transition phenomena.

EXPERIMENTAL PROCEDURE

Fabrication of the critical solution

Tetra-amine-terminated PEG (tetra-PEG-NH₂) and tetra-OSu-terminated PEG (tetra-PEG-OSu) were purchased from NOF Co. (Tokyo, Japan). Here, -OSu stands for *N*-hydroxysuccinimide. The molecular weight (M_w) of tetra-PEG-NH₂ and tetra-PEG-OSu was 20 kg mol⁻¹. We combined stoichiometrically unbalanced amounts of tetra-PEG-NH₂ and tetra-PEG-OSu to control the reaction conversion in the final state. We prepared the samples using various initial polymer volume fractions ($\phi_0 = 0.034, 0.017, 0.011, 0.0087, 0.0070$ and 0.0061). To determine the critical gelation molar ratios, the tetra-PEG-OSu to total tetra-PEG molar ratios (r) were varied at each concentration, as shown in Table 1. Tetra-PEG-NH₂ and tetra-PEG-OSu were dissolved in a phosphate D₂O buffer (pH 7.4) and a phosphate-citric acid D₂O buffer (pH 5.8), respectively. The ionic strengths of the buffer solutions were tuned from 5–35 mM in proportion to the concentration of the amine group. The two solutions were mixed and maintained for at least 12 h to achieve reaction completion.

Viscoelastic measurement

The solution with tetra-PEG-NH₂ and tetra-PEG-OSu was poured into the interstice of the double cylinder of a rheometer (MCR302; Anton Paar, Graz, Austria). The storage modulus (G') and loss modulus (G'') were measured 12 h after mixing. The angular frequency (ω) dependence of G' and G'' was measured with a strain amplitude (γ) of 10–200% at 25 °C. The value of γ was determined so that the measurement could be performed in the linear viscoelastic region.

Nuclear magnetic resonance (NMR) measurement

The ¹H NMR spectra were measured using a JEOL Alpha series (400 MHz) spectrometer. ¹H NMR (δ_{ppm} , D₂O): 1.75 (q, CH₂CH₂CH₂NH₂, $J = 6.50$), 1.58 (q, CH₂CH₂CH₂NHCO, $J = 6.65$), 1.41 (m, CH₂CH₂CH₂CH₂CH₂) and 1.14 (m, CH₂CH₂CH₂CH₂CH₂).

Table 1 The polymer volume fraction of tetra-PEG prepolymers (ϕ_0) and the range of the molar ratio of tetra-PEG-OSu (r) of the critical solutions

$\phi_0 [-]$	$r [-]$
0.034	0.11, 0.13, 0.15, 0.17, 0.19, 0.21
0.017	0.17, 0.19, 0.21, 0.23, 0.25, 0.27
0.011	0.22, 0.24, 0.26, 0.28, 0.30, 0.32
0.0087	0.27, 0.29, 0.31, 0.33, 0.35, 0.37
0.0070	0.32, 0.34, 0.36, 0.38, 0.40, 0.42
0.0061	0.40, 0.42, 0.44, 0.46, 0.48, 0.50

Abbreviations: tetra-PEG, tetra-polyethylene glycol; tetra-PEG-OSu, tetra-OSu-terminated PEG.

RESULTS AND DISCUSSION

Change in viscoelastic properties in the vicinity of the sol-gel transition point

Figure 2 shows the ω dependence of G' and G'' for mixtures of tetra-PEG prepolymers with various stoichiometric ratios (r) at $\phi_0 = 0.034$. When $r < r_c$ ($r_c = 0.18$), G'' was $> G'$ in the studied range, and the ω dependence of G'' exhibited the following relationship: $G'' \sim \omega^1$. This tendency is similar to the typical terminal relaxation of polymer solutions.³¹ When $r > r_c$, G' was $> G''$, and a plateau region for G' was observed at a low frequency, indicating that the system is percolated and in the gel state. At $r = r_c$, the curves of G' and G'' overlapped with each other, and a power law behavior was observed, indicating the criterion of the sol-gel transition reported by Winter and Chambon.¹⁷ According to this criterion, we also determined the critical gelation molar ratios (r_c) at other polymer volume fractions ($\phi_0 = 0.017, 0.011, 0.0087, 0.0070$ and 0.0061). Figure 3 shows the phase diagram of this system. The critical gelation molar ratio (r_c) increased with a decrease in ϕ_0 and approached stoichiometry ($r = 0.50$), which suggests that a higher reaction conversion is required to percolate the system in the dilute solution region.

Conversion of r_c to p^*

To discuss the exact reaction conversion at the critical gelation point (p^*), we need to convert r_c to p^* . We performed ¹H NMR measurements to directly estimate the amounts of reacted amide and unreacted amino groups. The signals from the β carbon of the unreacted amino groups and the β carbon of the amide bonds were observed at 1.75 p.p.m. (peak intensity = a) and 1.58 p.p.m. (peak intensity = b), respectively. The $a + b$ sum corresponds to the number of feed amino groups. Because the molar ratio of the amino groups to the activated ester groups was $(1 - r)/r$, the total number of feed reactive groups including amino and activated ester groups

Figure 2 The value of G' and G'' as a function of ω in $\phi_0=0.034$ (circle; G' , triangle; G''). The solid line shows the following relationship: $G' \sim \omega^1$. The dashed lines are the fitted curves showing the following relationship: $G'' \sim \omega^{0.69}$. The curves were shifted sideways (factor A) to avoid overlap.

Figure 3 Phase diagram of off-stoichiometric tetra-polyethylene glycol (tetra-PEG) system (circle, gel; cross, sol). The solid line shows the boundary line between the sol and gel phases.

corresponds to $(a+b)/(1-r)$. Because $2b$ of the species react among all the reactive species, the connectivity (p) can be expressed as follows:

$$p = \frac{2b(1-r)}{a+b} \quad (1)$$

Figure 4 shows a plot of p as a function of r . p proportionally increased with an increase in r in each graph. Notably, the values of p are the equilibrium values because the activated esters dissociated and lose their reactivity. For $\phi_0=0.034$, the slope of the linear fit was ~ 2.0 . When all the activated ester groups react with the excess amino groups, the slope was 2. This result indicates that approximately all tetra-PEG-OSu that exist in the solution react with excess tetra-PEG-NH₂. This reaction conversion is comparable to that of the stoichiometric system,^{21,28,29,32} which suggests that the reaction proceeds efficiently even under stoichiometrically unbalanced conditions. The slope slightly decreased with a decrease in ϕ_0 , suggesting a decrease in the reaction conversion under dilute conditions. The values of p^* were determined as p at r_c for each ϕ_0 .

Comparison with the site-bond percolation model

Figure 5 shows the concentration-dependence of p^* . Here, the polymer volume fraction (ϕ_0) is normalized by the overlapping volume fraction ($\phi^*=0.034$) predetermined by rheometry.²⁹ The value of p^* decreased with an increase in ϕ_0/ϕ^* , suggesting that higher connectivity is needed to form a 3D network in the region of lower ϕ_0/ϕ^* . In our system, the lowest concentration at which a gel

was formed (critical concentration) was $\sim \phi^*/6$. This result is different from the expectation from previous studies, which identified the critical concentration as the overlapping concentration.^{33,34} Our results indicate that gelation occurred far below the overlapping concentration of the polymers, and the non-gelation that was observed in previous studies may be caused by experimental problems that inhibit gelation, such as low-reaction efficiency and progressive intramolecular reactions. The overlapping of the polymers at the starting condition may not be so important because ϕ^* , which is determined by the molecular weight of the polymer in the system, decreases as the reaction progresses. When the reaction proceeds, the polymers are connected to each other, and the average molecular weight of polymers increases. Because an increase in the molecular weight of a polymer (M) decreases the overlapping volume fraction as $\phi^* \sim M^{-0.80}$ (for real linear polymer),³⁵ ϕ_0/ϕ^* increased as the reaction progressed and finally became >1 , at which point the system was filled with polymers.

To further discuss the relationships between p^* and ϕ_0/ϕ^* , we use the site-bond percolation model.²⁰ This model has two independent parameters (that is, the occupied site fraction (p_s) and the connected bond fraction between the neighboring sites (p_b)). For simple bond percolation and site percolation, the exact values of p_s and p_b have been estimated for various lattices. However, for site-bond percolation, the exact solution is not available. Based on Monte Carlo simulations for site-bond percolation on several two-dimensional and 3D lattices^{19,36} as well as renormalization group studies,³⁷ the following empirical relationship has been proposed.

$$\frac{\log p_s^* + \log p_b}{\log p_s^* + \log p_b^*} = 1 \quad (2)$$

where p_s^* and p_b^* are the critical fractions in the pure bond and site problems, respectively. Equation (2) indicates that the critical point of the site-bond percolation model is determined by the distance from the critical points of the site and bond percolations. For a 3D diamond lattice, $p_s^*=0.43$ and $p_b^*=0.39$.³⁸ Because these critical values barely change with the lattice structure, we do not lose any generality with this assumption. Here, it is important to note that we cannot directly compare p_b and the experimentally estimated reaction conversion (p). The value of p is estimated as the ratio of the reacted arms to all the arms. However, p_b is the probability to form a bond with a neighboring site 'only if the neighboring site is occupied'. The experimentally estimated p corresponds to $p_b p_s$. The relationship between the theoretical prediction of p^* ($=p_b p_s$) and p_s is shown in Figure 5 as a solid line. One of the features of the model prediction is a discontinuous change in p^* at $p_s=0.43$. At $p_s=0.43$, all the neighboring sites are bonded ($p_b=1$ and $p^*=0.43$), and the system is just percolating. Below this point, no gel was formed even when all the neighboring sites are connected. However, in the $p_s>0.43$ region, p^* slightly decreased with an increase in p_s and reached the value of the bond-percolation model ($=0.39$) at $p_s=1$.

Based on the definition of ϕ^* , it may be natural to find a similarity between p_s and ϕ_0/ϕ^* because both conditions units fill the space. Here, we accept the assumption that ϕ_0/ϕ^* corresponds to p_s and compare the experimental data and the model prediction. When we focus on the $\phi_0/\phi^* \approx 1$ region, the experimentally estimated p^* ($=0.36$) is close to $p_b^*=0.39$, which suggests the applicability of the bond-percolation model to the system around ϕ^* . However, a qualitative discrepancy exists in the vicinity of the site-percolation threshold ($\phi_0/\phi^*=p_s^*$): p^* shows a continuous change as a function of ϕ_0/ϕ^* . p^* predicted by the site-bond percolation model shows a discontinuous change as a function of p_s . This discrepancy suggests the

Figure 4 The reaction conversion (p) as a function of r in (a) $\phi_0=0.034$, (b) $\phi_0=0.017$, (c) $\phi_0=0.011$, (d) $\phi_0=0.0087$, (e) $\phi_0=0.0070$ and (f) $\phi_0=0.0061$. The dashed line is the fitted curve (circle, experimental conversion; cross, critical conversion estimated by the fitting curve).

Figure 5 The critical reaction conversion (p^*) as a function of the polymer volume fraction at a preparation state normalized by the overlapping fraction (ϕ_0/ϕ^*). The solid line represents the prediction from the site-bond percolation model.

inapplicability of the site-percolation model to the sol-gel transition far below ϕ^* , which may originate from the limitation of the lattice model.

Viscoelasticity at the critical point

In the previous section, we discussed the phase diagram of the relationships between the critical reaction conversion (p^*) and the polymer volume fraction at the preparation state (ϕ_0). The site-bond percolation model failed to describe the phase diagram, especially in the low ϕ_0 region. To investigate the reason for this failure, we

investigated the network structure at p^* using rheometry. Figure 6 shows the ω dependence of G' and G'' at the critical point at various preparation concentrations ($\phi_0=0.0087-0.034$). Under each critical condition, a power law relationship ($G' \approx G'' \sim \omega^u$) was observed. The power (u) relates to the percolated structure. We estimated the values of u from the slope and plotted against ϕ_0/ϕ^* in Figure 7. The value of u decreased from 0.83 to 0.69 with an increase in ϕ_0 . Similar tendencies have been observed in previous studies. Winter and Chambon found that stoichiometrically unbalanced end-linked elastomers exhibited higher exponent values ($0.5 < u < 1$),¹³ and the stoichiometrically balanced end-linked elastomers (polydimethylsiloxane,¹⁷ polyurethane³⁹) exhibited a specific value of $u=0.50$. Takahashi *et al.* reported that the end-linked PDMS elastomers exhibited a higher exponent at the critical point when the functional groups of the precursor chains ends were less active.⁴⁰ According to these results, an increase in the effective network concentration tends to decrease the power of the critical behavior.

Fractal dimension at the critical point

According to dynamics scaling theory,¹⁴ a general expression for u is as follows:^{16,41}

$$u = \frac{z}{z+k} \quad (3)$$

Here, z and k are the critical exponents for the equilibrium elastic modulus and zero-shear viscosity near the critical point, respectively. When the hydrodynamic interaction is completely screened out and the excluded volume effect is dominant, equation (3) is reduced to the following form:⁴²⁻⁴⁴

$$u = \frac{d}{D+2} \quad (4)$$

Here, D and d represent the fractal dimension and the spatial dimension ($d=3$), respectively. Using equation (4), we estimated D from u for each critical point and plotted them as a function of ϕ_0/ϕ^* in Figure 8. The value of D at $\phi_0/\phi^*=1$ ($D \approx 2.3$) is close to the prediction from the conventional-percolation model in 3D space for the diamond lattice ($D=2.5$).¹⁷ When the values of ϕ_0/ϕ^* decreased, D deviates downward from the prediction of the percolation model. Notably, the site-bond percolation model always predicts $D=2.5$ for the 3D diamond lattice. The 3D diamond lattice has only a family of percolated structures with $D=2.5$ regardless of p_s . This deviation also indicates the inapplicability of the lattice-based percolation model to the concentration region below ϕ^* . To understand the sol-gel transition in the dilute region, we need to remove the restriction of lattices.

Several off-lattice models have been proposed to account for the deviation of the network forming process from the percolation model. The aggregation model is a popular model for considering the network forming process.^{45,46} The two subtypes of aggregation processes include monomer-cluster and cluster-cluster aggregation models. The monomer-cluster aggregation model considers the growing process in which monomer particles freely diffuse and adsorb onto a spatially immobilized cluster.⁴⁷ On the other hand, the cluster-cluster aggregation model considers a growing process in which the clusters and monomers diffuse and are connected to each other. The growth process is dominated by the association between the clusters.^{45,46} These models seem appropriate for dilute systems because the effect of diffusion is expected to become important especially in the dilute region, where clusters cannot find the reactive neighbors without diffusion. On the basis of 3D Monte Carlo simulations, the

Figure 6 The values of G' and G'' as a function of ω for samples prepared at (a) $\phi_0=0.034$, (b) $\phi_0=0.017$, (c) $\phi_0=0.011$ and (d) $\phi_0=0.0087$. The dashed lines are the fitted curves showing the following relationship: $G' \approx G'' \sim \omega^u$. The curves were shifted sideways (factor A) to avoid overlap.

Figure 7 The ϕ_0/ϕ^* dependence of u .

fractal dimensions of the percolation cluster have been estimated for the monomer-cluster (3.00 for reaction limited, and 2.50 for diffusion limited) and cluster-cluster (2.10 for reaction limited, and 1.78 for diffusion limited) aggregation processes.^{46,48} Our experimental value at $\phi_0 = \phi/4^*$ ($D=1.6$) is close to that predicted by the diffusion-limited cluster-cluster aggregation process ($D=1.76$). This agreement suggests that the network formation process shifts from the bond-percolation model to a diffusion-limited cluster-cluster aggregation process with a decrease in ϕ_0 . To further examine this hypothesis, the size distribution of the clusters during the gelation should be studied. However, this investigation is beyond the scope of this paper.

Finally, we make a conjecture on the percolated network structure formed at $\phi_0 = \phi/4^*$. Despite a low ϕ_0 , the reaction conversion was as high as 0.8, indicating that a large portion of the polymers can find reactive neighbors. To achieve such a high conversion with limited reactive neighbors, intramolecular reactions must occur between neighboring polymers. This prediction is supported by the abnormally low-fractal dimension ($D=1.6$), which is close to that of the real chain ($D=1.7$). When intramolecular reactions occur between neighboring polymers, multi-cyclic structures are most likely formed (Figure 9). This structure is locally oriented and may have a fractal dimension that is similar to that of a real chain. This locally oriented structure efficiently expands the network structure and enables the system to percolate with a limited number of polymers. The existence of this cyclic structure has been strongly suggested in our previous studies as well.^{21,22,28,29,32,49,50}

Figure 8 The ϕ_0/ϕ^* dependence of D . The dashed line represents the prediction of the percolation theory.

Figure 9 Schematic illustration of the chain-like structure formed at a low-preparation concentration. The right inset shows the chain-like structure formed by intramolecular reactions.

CONCLUSION

We investigated the sol-gel phase diagram by independently tuning the connectivity and concentration using the tetra-PEG gel system with unbalanced stoichiometry. We obtained the following results: (1) the constructed phase diagram indicates that the reaction conversion required to percolate a system continuously increased with a decrease in the polymer concentration; and (2) the fractal dimension of the percolation clusters deviated from the prediction of the percolation model with a decrease in the concentration. These results validate the lattice-based percolation model around the overlapping concentration and indicate a failure of this model far below the overlapping concentration. In the region far below the overlapping concentration, diffusion of the polymers becomes important, and a multi-cyclic structure may be formed. These data will aid in elucidating the gelation process of polymer gels.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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