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Estimation of Critical Point in Branching Reactions: Further Examination of Gel Point Formula

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The theory of gel point in real polymer solutions is examined with the empirical correlation between the reciprocal of the percolation threshold and the coordination number given by the percolation theory. Applying a larger value of the relative frequency of cyclization, an excellent agreement is obtained between the present theory and the percolation result. This suggest that while the ring distribution on lattices is similar to that in real systems, ring production is more frequent in the lattice model than in real systems. To confirm this conjecture, we derive the ring distribution function of the lattice model as a limiting case of $d \to \infty$, and show that the solution is in fact identical to the asymptotic formula of $C \to \infty$ in real systems except for the coefficient $\mathscr{C}$, which has a maximum at $d = 5$, in support of the above conjecture. To examine the validity of the asymptotic solution for the lattice model, we apply it to the critical point problem of the percolation theory, showing that the solution works well in high dimensions greater than six.

KEY WORDS: Branching reactions; critical point; dimensional invariant; cyclic distribution on lattices; analogy and difference between real systems and model reactions on lattices.

1. INTRODUCTION

In the previous report we have presented analytic expressions of the gel point as a function of the inverse concentration, the result being in good agreement with the observations. In this report we further examine the theoretical result through the comparison with the percolation simulation.

It was not until 1957, 16 years after Flory's first paper(1) on gelation has appeared, that the percolation theory was introduced by Broadbent

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and Hammersley.(2) Nineteen more years later, the theory was first applied to polymer chemistry as a realistic model of branching process which takes into account ring formation and excluded volume effects.(3, 4) The percolation model has unveiled many a novel feature of gelation, to which most polymer chemists had been unaccustomed then: critical exponents, dimensionality, cluster shape, and so forth.(5, 6) It has further furnished some empirical correlations.(7) Well-known is the linear relationship(8) between the percolation threshold (the gel point) and coordination number z (functionality f) which we are now going to take up for the purpose of reexamination of the preceding theory by the author and coworkers.(9c)

2. THEORETICAL BACKGROUND

We derive an approximate solution of the gel point according to the preceding works. In the limit of an infinite initial monomer concentration C, the concentration of cyclics $[\Gamma]$ in real polymer solutions asymptotically converges on the form:(9, 10)

$$[\Gamma]_{C \to \infty} = \sum_{j=1}^{\infty} \varphi_j [(f-1) D]^j / 2j \qquad (R-A_f) \tag{1}$$

with D being the extent of reaction, f the functionality and φ_j the relative frequency of cyclization of j-chains to intermolecular reaction. φ_j is associated with the cyclization probability $\mathscr{P}$ by the relation:

$$\varphi_j = \frac{1}{v} \mathscr{P} \tag{2}$$

$\mathscr{P}$ being the probability that one end on a chain enters into a volume v with the radius of a bond length ℓ around the other end. In concentrated solutions, $\mathscr{P}$ has the Gaussian form:

$$\mathscr{P} = \int_0^{\ell} S_d \cdot \left(\frac{d}{2\pi \langle r_j^2 \rangle} \right)^{d/2} \exp\left(-\frac{d}{2\langle r_j^2 \rangle} r^2 \right) \cdot dr$$

where d is dimension and S_d the surface area of a d-dimensional sphere. Note that Eq. (1) is valid and makes sense only below the classical gel point D_{co}, for beyond this point the right hand side sum diverges.

The general solution of $[\Gamma]$ has not been found yet. When we consider a high concentration regime, however, it is reasonable to think that Eq. (1) is a good approximation of $[\Gamma]$. Based on this idea, we replace D in Eq. (1) by D_c to obtain a provisional equality. Experiments have shown that the sol-gel line is a smooth and continuous function of C. So, one may, expand the resultant equation around $D_c = D_{co}$ into the Taylor series. Collecting the leading two terms, and making use of the critical relation, $(f-1)\,D_{co} = 1$, one gets the approximate expression of $[\Gamma]$

$$Z(D_c) = [\Gamma] \cong \sum_{j=1}^{\infty} \varphi_j/2j + \sum_{j=1}^{\infty} \varphi_j/2D_{co} \cdot (D_c - D_{co}) \tag{3}$$

which is valid for all dimensions greater than 3, since it may occur in the two dimension that the second term of the right hand side diverges; e.g., $\sum_{j=1}^{\infty} j^{-1} \rightarrow \infty$.

Note that the critical extent of reaction is separable,

$$D_c = D(inter) + D(ring)$$

The unification of the tree theory and the cyclization theory can in principle be achieved by calculating the above respective terms independently. For simplification, we here introduce the independence assumption between intermolecular reaction and cyclization which asserts that the gel point shifts upward exactly by the portion of functional units wasted by cyclization. Then, it follows that

$$D_c \cong D_{co} + D(ring) \tag{4}$$

Let γ be the reciprocal, $1/C = V/M_0$, of the initial monomer concentration where M_0 is the total number of monomer units of the $R - A_f$ model and V the volume. $D(ring)$ can be equated with $2[\Gamma]/fC$, since only two functional units are wasted every cyclization independently of the size of rings. Substituting Eq. (3) into Eq. (4), and rearranging the resultant equation, one arrives at an approximate expression of the gel point in real polymer solutions:

$$D_c = \frac{1}{f-1} \left\{ \frac{1 - \dfrac{f-1}{f} \sum\limits_j (1 - 1/j)\, \varphi_j \cdot \gamma}{1 - \dfrac{f-1}{f} \sum\limits_j \varphi_j \cdot \gamma} \right\} \qquad (R - A_f) \tag{5}$$

3. COMPARISON WITH PERCOLATION RESULTS

Let us apply the above result to the empirical correlation known by the percolation theory. Prior to the comparison, we rewrite Eq. (5) in the reciprocal of the gel point, $\mathcal{U} = 1/D_c$, to get

$$\mathscr{U} = (f-1)\left\{\frac{1-\dfrac{f-1}{f}\sum_j \varphi_j \cdot \gamma}{1-\dfrac{f-1}{f}\sum_j (1-1/j)\,\varphi_j \cdot \gamma}\right\} \tag{6}$$

Looking at $\mathscr{U}$ as a function of f alone, we see $\mathscr{U}$ varies linearly with increasing f in proportion to $f-1$, in accordance with the empirical rule of the percolation theory.

To make sure this, $\mathscr{U}$ is plotted as against f in Fig. 1, together with the calculated values ($\times$, $1/p_c^{bond}$) in the 3-d percolation simulation(7, 8) on various lattices. The initial concentration $C = 8$ mole/ℓ, hence $\gamma = 0.125$, was chosen so that it corresponds to the melt polymerization in the three dimensional space where C ranges from ≈ 5 to 10 mole/ℓ in general. Taking the trial value $\sum_j \varphi_j \cong 5$, and assuming $\sum_j \varphi_j \cong 5 \sum_j \varphi_j / j$ valid for the excluded volume chain ($\varphi_j \propto j^{-2}$) of $j \geqslant 3$ on the 3-d lattice,(11, 12) the excellent agreement between the theory (solid line) and the percolation results is found (Appendix). If we extend the concept of gelation to the imaginary regime of $f \leqslant 2$, we realize that the theoretical line must intercept the f axis at $f = 1$ where the divergence of the gel point occurs. Since no cyclization is possible in monofunctional systems, the classical gel point formula applies, that is, $D_{co} = 1/(f-1) \to \infty$ as $f \to 1$.

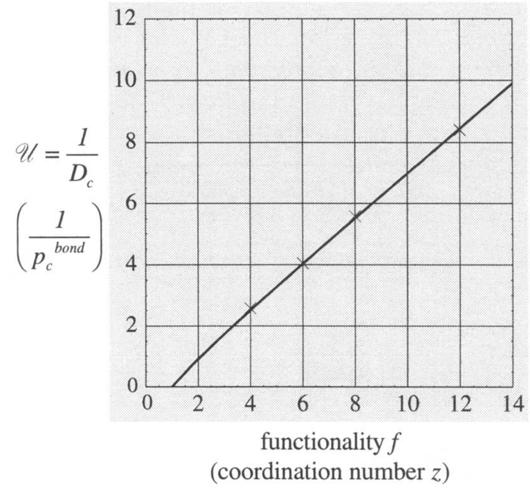

Fig. 1. The correlation between the reciprocal of the gel point (percolation threshold) and the functionality (coordination number). $\times$: calculated(7) (by the percolation theory); —: theoretical line by Eq. (6).

The consistency with the percolation results suggests that Eq. (5) has the sound basis as an approximate formula. The numerical value applied above ($\sum_j \varphi_j \cong 5$), on the other hand, seems exceedingly large, compared to the observed values ($\lesssim 1$) in real systems.[13] This becomes more evident when we look at the fact that smaller rings, which would occupy an essential part of the ring fraction, are always forbidden on lattices. Thus it is suggested: while (i) the ring distribution on lattices will be similar to that in real systems, (ii) the production of rings is more frequent in the lattice model. This problem of the overproduction of rings of the lattice model has already been conjectured by Burchard.[14] We now inspect these points in detail in the following.

4. RING DISTRIBUTION FUNCTION

It has been pointed out frequently[5, 7] that there are two specific features in the percolation model: (i) one is that molecules are fixed on a lattice; (ii) the second is that the theory does not incorporate solvent molecules. Thus it has been recognized that the theory essentially simulates the melt polymerization.

While the site-bond percolation[15, 16] has been devised to improve the second problem, the deviation has been found in the $p_b - \phi_s$ curvature between the percolation results and the observed values in real systems. Hence, the question arose as to whether the percolation model really simulates branching reactions.[6] To consider this problem, it is useful to analyze the difference of the chemical processes between the real system and the percolation model.

4.1. Real system

Consider a branching reaction in the real system, and pay attention to a functional unit on a branched molecule. Let the functional unit belong to a j-chain. Then, let us consider a transition from $i-1$ bonds to i bonds. The functional unit in question must undergo either intermolecular reaction or cyclization. So, the transition probability can be written for a j-ring as

$$p\{ring\ j\} = \frac{v_{R_j}}{v_L + v_R}$$

and for intermolecular reaction as

$$p\{inter\} = 1 - \sum_{j=1}^{\infty} p\{ring\ j\} = \frac{v_L}{v_L + v_R}$$

where v denotes the chemical velocity; the subscript R_j j-rings, R the sum of all rings from 1 to ∞ and L intermolecular reaction. As experiments have shown, cyclization undergoes the first order reaction of concentration, whereas intermolecular reaction the second order. In terms of statistical physics, the cyclization rate can be equated with the cyclization probability of j-chains multiplied by the number of chances ϕ_j of cyclization and therefore

$$v_{R_j} = \mathscr{P} \times \phi_j$$

while the intermolecular reaction rate is the probability υ/V of a given unreacted functional unit entering a small volume υ around the other unit, multiplied by the number of all pairs, $(1/2)\{fM_0(1-D)\}^2$, so that

$$v_L = (1/2)\{fM_0(1-D)\}^2 \upsilon/V$$

It has been known that ϕ_j approaches to the asymptotic form with increasing C:

$$\phi_{j(C\to\infty)} = (1/2)\, fM_0(f-1)(1-D)^2\,[(f-1)\,D]^{j-1}$$

Moreover, because of the relation $v_R/v_L \propto C^{-1}$, one has

$$p\{ring\ j\} \to v_{R_j}/v_L, \qquad \text{as} \quad C\to\infty$$

By the relationship (2), the transition probability reduces to

$$p\{ring\ j\} \cong \varphi_j(f-1)[(f-1)\,D]^{j-1}/fC, \qquad \text{for} \quad C\to\infty \tag{7}$$

Note that $p\{ring\ j\}$ is equivalent to the number fraction, δN_{R_j}, of j-rings to be formed in the transition of $i-1\to i$. Making use of the definition $\delta i = (fM_0/2)\cdot\delta D$, one has from Eq. (7)

$$\delta[\Gamma]_{C\to\infty} = \delta\sum_j^{\infty} N_{R_j}/V = \frac{1}{2}\sum_j^{\infty}\varphi_j(f-1)[(f-1)\,D]^{j-1}\cdot\delta D$$

Integrating this equation, we arrive at the simple expression of Eq. (1) for the number concentration of rings. This is the basic way of the derivation of the ring distribution function[9] in the real system.

In turn, let us focus our attention on the

4.2. Lattice Model

Let $P(r)$ be the end-to-end distance probability distribution function. The chain is fixed on a lattice, so the conformation is fixed and timeinvariant. By simulating many other chains of the same size, however, it is possible that the theory correctly takes into account the conformational change in effect. Thus, within the framework of the approximation, the lattice theory correctly estimates the cyclization probability $\mathscr{P}$.

To derive an analytic solution of ring distribution on lattices, let us first assume that the relative rate of cyclization to intermolecular reaction is a monotonic decreasing function of dimension. The validity of this hypothesis becomes evident according to the derivation.

Consider a high dimension where it has been known that the end-to-end distance distribution can be well approximated by the Gaussian function. The cyclization probability is the probability that one end of a chain enters into a volume with the radius of a bond length ℓ. In this case, ℓ can be equated with the size of unit cell. Since immediate reversals are forbidden, there are $f-1$ paths for the end monomer site to react, of which only one path can lead to the other end. The fraction of unoccupied paths is $(f-1)(1-D)$; hence in order for cyclization to occur, $\mathscr{P}$ must be divided by the factor $(f-1)(1-D)$, so that

$$P_{cy}=\frac{\mathscr{P}}{(f-1)(1-D)}=\frac{1}{(f-1)(1-D)}\int_0^{\ell} P(r)\,S_d\cdot dr \tag{8}$$

In the real polymer solutions, this factor did not appear explicitly since that was canceled out exactly by the same factor appearing in the intermolecular reaction term, so that it was unnecessary to introduce the new quantity P_{cy}. However, P_{cy} is essential for the lattice theory, as becomes clear in the following.

The total number of chances of cyclization is identical with the one derived on the basis of the tree approximation of $C\to\infty$. Only, in the lattice model it corresponds, by the hypothesis, to the solution of $d\to\infty$. Hence,

$$\phi_{j(d\to\infty)}=(1/2)\,fM_0(f-1)(1-D)^2\,[(f-1)\,D]^{j-1}$$

The cyclization rate can be equated with the product: $P_{cy}\times\phi_{j(d\to\infty)}$, and therefore

$$v_{R_j}=\left\{\frac{\mathscr{P}}{(f-1)(1-D)}\right\}\times\left\{\frac{1}{2}M_0 f(f-1)(1-D)^2\,[(f-1)\,D]^{j-1}\right\} \tag{9}$$

Then, let us proceed to the calculation of the intermolecular reaction rate. For this purpose we are interested in the number of *unreacted* functional units. The probability of a randomly chosen functional unit being *unreacted* is $1-D$, while there are $fM_0(1-D)$ such functional units altogether. A given *unreacted* functional unit possesses only one chance to react; it can form a bond with the nearest neighbor alone which, thanks to the specific feature of lattices, is always unoccupied by the probability 1. Hence, the intermolecular reaction rate becomes

$$v_L = (1/2)\, fM_0(1-D) \times 1$$

The expression asymptotically becomes exact as $d \to \infty$ where cyclization is suppressed entirely. Thus, in the lattice model, clusters grow according to the first order reaction of the concentration; no intermolecular reaction occurs in the ordinary sense, in contrast to the case in the real polymer solutions.

On the other hand, as $d \to \infty$, $\mathscr{P} \to 0$ and hence $v_R/v_L \cong 0$, corresponding to the limiting case of $C \to \infty$ in the real system. The transition probability then reduces to $\cong v_{R_j}/v_L$ and yields

$$p\{ring\ j\} \cong \frac{1}{(f-1)}\mathscr{P}(f-1)^j D^{j-1}, \qquad \text{for} \quad d \to \infty \tag{10}$$

With $\delta i = (fM_0/2) \cdot \delta D$, carrying out the integration of Eq. (10) one gets the asymptotic expression of the total ring concentration on lattices

$$[\Gamma]_{d \to \infty} = \left(\frac{f}{f-1}\right) C \sum_j \mathscr{P}[(f-1)\, D]^j/2j$$

Since $f \to \infty$ with $d \to \infty$, it further reduces to

$$[\Gamma]_{d \to \infty} = C \sum_j \mathscr{P}[(f-1)\, D]^j/2j, \qquad \text{for} \quad d \to \infty \tag{11}$$

At first sight, it may appear that there is a marked difference between Eq. (1) and Eq. (11); so the result is not in harmony with the foregoing findings concerning the linear rule between D_c^{-1} and f. However, this is not the case.

Consider the d-dimensional hyper-cubic lattice. Then $C = (1/\ell)^d$ (Appendix). For a long chain, one has $d\ell^2/2\langle r_j^2 \rangle \cong 0$; then $\mathscr{P}$ is separable and yields $\mathscr{P} \cong P(0)\, \nu \equiv \varphi_j \nu$, where ν has the form $\mathscr{C}\, \ell^d$ with $\mathscr{C}$ being the coefficient. Thus, C and ν essentially cancel out each other, resulting in the familiar form:

$$[\Gamma]_{d \to \infty} = \mathscr{C} \sum_j \varphi_j [(f-1)\, D]^j/2j \tag{11'}$$

Comparing Eq. (11′) with Eq. (1), it turns out that while the microscopic feature of the chemical process is entirely different in both the systems, the branching reaction proceeds, in effect, in the same manner between the lattice model and the real system, except for only one point that the amount of rings is different, by the factor $\mathscr{C} = 2\pi^{d/2}/d\Gamma(d/2)$, varying with dimension as $4\pi/3(d=3)$, $\pi^2/2(d=4)$,..., which has a maximum at $d=5$, beyond which it rapidly decreases to 0. This behavior of $\mathscr{C}$ never means that the cyclic formation becomes maximum at $d=5$; instead, the product $\mathscr{C} \times \varphi_j$ is a steeply decreasing function of d and so is the $[\Gamma]$, in harmony with the foregoing hypothesis.

In consequence, the above result shows: while (i) the branching reaction proceeds essentially in the same manner in both the systems, (ii) in lower dimensions, the ring production tends to be more frequent in the lattice model than in the real systems, in accordance with the findings in Section 3.

4.3. Application to Simulation Results

Let us apply Eq. (11) to the percolation result. According to the bond percolation simulation at the six dimension, it has been shown numerically that $p_c^{bond} = 0.094$. For the hypercubic lattice, $f = 2d = 12$, and the mean square end-to-end distance without excluded volume effects is

$$\langle r_j^2 \rangle \doteq \frac{f}{f-2} j\ell^2 - \frac{2(f-1)}{(f-2)^2} \ell^2$$

Note that as $f \to \infty$, $\langle r_j^2 \rangle \to j\ell^2$; with increasing d, therefore, the lattice chain tends to behave like a freely joined chain. Summing up even number rings alone (corresponding to odd bond numbers: $j = 3, 5, 7,..., 2k+1,...$), the immediate integration of Eq. (11) yields, for $\ell = 1$,

$$C \sum_{k=1}^{\infty} \mathscr{P}(r \leqslant \ell) \cong 0.092$$

$$C \sum_{k=1}^{\infty} \mathscr{P}(r \leqslant \ell)/(2k+1) \cong 0.025$$

Replacing the corresponding terms in Eq. (5) with these, one gets

$$D_c = \frac{1}{12-1} \times \frac{1 - \frac{11}{12} \times (0.092 - 0.025)}{1 - \frac{11}{12} \times 0.092} \cong 0.093$$

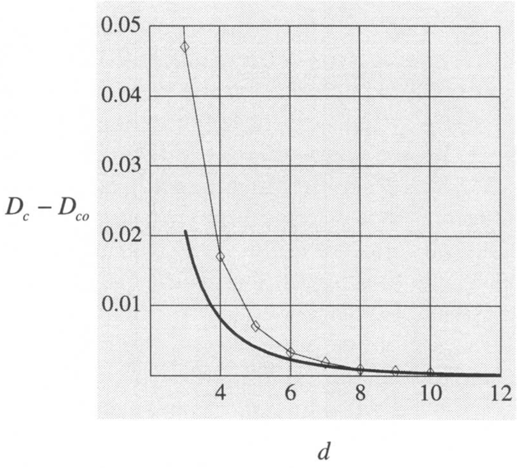

Fig. 2. Dimensionality dependence of the gel point. ◇: observed points based on the percolation theory in hyper-cubic lattices. —: theoretical line calculated from Eqs. (5) and (11) for $\ell = 1$.

whereas, with $\varphi_j \cong P(0)$, Eq. (11′) yields $D_c \cong 0.095$. These are close to the observed value 0.094.(7, 8) The results are summarized in Fig. 2 as a function of d. Diamonds (◇) denote the observed values on the hyper-cubic lattices, and the heavy line (—) the present theory based on Eq. (11). As we can see, both the curves rapidly converge on the same prediction with increasing d, showing that Eq. (11) works well for $d \geqslant 6$.

5. DISCUSSION

When one compares the mathematical structures of Eqs. (1) and (11), an unexpected interpretation arises. As a space-freedom expands, it becomes a rarer event for one end on a chain to encounter the other end for cyclization. Thus, it follows that as the dimensionality increases, the cyclization probability $\mathscr{P}$ decreases strongly, and so does the $[\Gamma]$ of Eq. (11). This is the behavior of cyclization that the lattice theory predicts by Eq. (11). However, for the real system described by Eq. (1), it is the relative frequency φ_j that determines the amount of rings and not $\mathscr{P}$. Unlike $\mathscr{P}$, the quantity φ_j is not such a monotonic decreasing function of d. By the foregoing relation (2) between φ_j and $\mathscr{P}$, we can show that φ_j once goes down with increasing dimensionality to attain a minimum point, then again goes up indefinitely. There is a minimum point of φ_j around $d \approx \pi \langle r_j^2 \rangle$; beyond this point it turns to an increasing function. In Fig. 3 is shown an example of d-dependence of φ_j based on the numerical integration

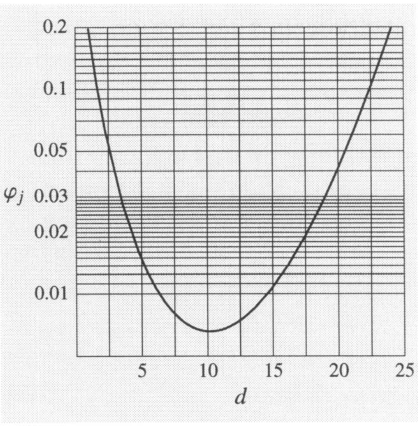

Fig. 3. Dimensionality dependence of the relative cyclization frequency. $\varphi_j = \mathscr{P}/v$ was calculated numerically integrating the Gaussian function of $j = 4$ and $\ell = 1$.

of $\mathscr{P}/v$. In terms of the transition probability, it follows that for the real system

$$\sum_{j=1}^{\infty} p\{ring\ j\} = \frac{v_R}{v_L + v_R} \to \begin{cases} \text{min.} & \text{for} \quad d \approx \pi \langle r_j^2 \rangle \\ 1, & \text{for} \quad d \to \infty \end{cases}$$

which means that in the limit of the infinite dimension, all the products are of cyclic origin. This behavior of cyclization in the real system is not only so unexpected, but also opposed to the prediction by Eq. (11) of the lattice theory. The physical meaning of this difference between the two theories, however, can be easily comprehended as follows:

As the dimensionality increases, the space-freedom expands, so the probability of one end on a chain encountering the other end must decrease, whereas by just the same reason, the probability of two functional units on different molecules encountering must decrease as well. As a result of this competition, the minimum $\varphi_{j,\,\text{min}}$ occurs at some point d_{min}, beyond which cyclization predominates over intermolecular reaction. Thus, at sufficiently high dimensions, the system behaves as if a dilute solution; molecules having a tendency to be more isolated from each other, and cyclization becoming overwhelming.

On the other hand, the collision probability on lattices between two units on different molecules is always fixed to unity because of the structural specificity of lattices.(17) Mathematically, this can be explained by the absence of the v/V term from the intermolecular reaction. For lack of this term, intermolecular reaction on lattices has no dependence on the dimensionality; it is a function of functionality alone, while cyclization depends strongly on d (Section 4.2) according to $\mathscr{P}$, the decreasing function of d. As the dimensionality increases, therefore, the relative rate of cyclization to intermolecular reaction decreases, resulting in the known behavior of the lattice model: $v_R/v_L \to 0$ as $d \to \infty$.

The other salient feature is that Eq. (11) is proportional to the concentration C—for the site-bond percolation, it becomes $C\phi_s$, ϕ_s being the fraction of monomer sites. This means that the fraction of rings ($[\Gamma]/C\phi_s$) is independent of the concentration. Hence, cyclization does not vanish in the lattice model$^{(17)}$ irrespective of the monomer concentration, in contrast to the behavior of the real polymer solutions.

6. CONCLUDING REMARKS

We have applied the analytic expression of the gel point to the empirical correlation between the reciprocal of the gel point and the functionality known by the percolation theory. The present theory embraces the essential features which the empirical formula has revealed. However, in order to obtain the best fitting, it was found that the significant larger value is required for the relative frequency of cyclization, implying that while the branching reaction proceeds, in effect, in the same manner in both the systems, the production of rings is more frequent in the lattice model than in the real systems.

To examine our conjecture, we have derived the ring distribution function on lattices for the limiting case of $d \to \infty$, and showed that the solution is identical with the corresponding distribution function of $C \to \infty$ in the real system, except for the coefficient $\mathscr{C}$ which has the maximum at $d = 5$, in support of the above conjecture.

We have discussed the differences of the chemical process between the polymer theory and the percolation theory: a typical one being that in the lattice model, the fraction of rings is independent of the monomer concentration.

APPENDIX

φ_j and C have the dimensions of *molecules* $\cdot L^{-d}$ (L: length),$^{(13)}$ so that γ has $L^d \cdot$ *molecules*$^{-1}$, resulting in the dimensionless quantity $\varphi_j\gamma$.

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