Dimensions of Cross-Linked Polymers Formed in Living Vinyl/Divinyl Copolymerization

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ABSTRACT: A new kinetic theory for network formation in living copolymerization of vinyl and divinyl monomers is proposed. This theory is based on the distribution of cross-linked units in the primary polymer molecule along the direction of growth. The formed cross-linked structure, such as the molecular weight distribution and the spatial distribution of cross-linked polymer chains, is investigated under the classical ring-free model. The molecular weight distribution can be multimodal if the Poisson distribution is valid for the primary polymer molecules. The radius of gyration is found to be smaller than that for the random cross-linking of linear polymer chains having the most probable distribution at the Θ state. The fractal dimension of the cross-linked polymer molecules is less than 3 except for extremely large polymer molecules, i.e., gel molecule in practice.

Introduction

On the basis of the pioneering work of Flory and Stockmayer,[1–4] various statistical approaches[5–13] have been developed for polymeric network formation. These theories have enjoyed the simplicity of a mean-field theory; however, they lack the space dimensionality in which to be embedded. In polymeric network formation, the spatial distribution of cross-linked polymer chains possesses significant effects on cross-linking and cyclization reactions that should be highly dependent on both molecular size and structure. Especially, the spatial distribution is the essence of cyclization reactions since they are controlled by the conformational statistics of the sequence of bonds. Various models for the cyclization reactions have been proposed;[14–23] however, elucidation of the long-range correlation in nonlinear polymerization seems to be a formidable task at the present stage. On the other hand, the percolation type computer simulations[24–36] account for the chain distribution in space. However, realistic simulations of polymeric network formation that must account for the diffusion and mobility during polymerization require an excessive amount of calculations even for an extremely small reaction volume with a limited time interval. It seems that both types of models need refinements in order to clarify the complicated phenomenon of polymeric network formation.

For linear polymers, ionic polymerization possesses advantages in regulating the molecular structure, such as the molecular weight distribution and the stereoregularity, over free-radical polymerizations. Living polymerization is an interesting technique to obtain a narrow distribution of the primary polymer molecule and may be useful to produce nonlinear polymers with a controlled structure. Anionic living nonlinear polymerizations have been studied both experimentally and theoretically,[37–42] and several studies suggest that cyclization is important in these systems.[39–42]

In this paper, first we propose a kinetic theory for the living copolymerization of vinyl and divinyl monomers, neglecting the structural dependence of cross-linking reactions. Then the molecular constitution of the formed cross-linked polymers is simulated to investigate the molecular weight distribution and the spatial distribution of the cross-linked polymer chains under the classical ring-free model.[1–4] The present study may be simplistic to elucidate the network formation in real systems; however, it can provide a reasonable start point to complement the weakness of the mean-field approaches, i.e., the space dimensionality and the long-range correlation problems. The objective of the present study is at least 2-fold: (1) to develop a model for living cross-linking copolymerization that accounts for the heterogeneity of the cross-link points along the primary polymer molecules; (2) to clarify the statistical properties of cross-linked polymers formed with a very narrow primary polymer distribution in contrast to that formed with a broader distribution, which may provide useful information in designing the polymer networks with higher quality.

Theoretical Section

We are to consider an ideal living polymerization; the initiation is instantaneous and there are no chain transfer reactions. Formulation of the molecular weight distribution in living copolymerization is not an easy task even for linear polymers.[43] However, at least when the mole fraction of one component is much smaller than unity, the chain length distribution of the linear copolymers would be approximated well by the Poisson distribution. The weight fraction distribution of the polymer molecules is given by:[44]

$$W(r) = \frac{e^{-\eta}\eta^{r-1}}{(r-1)!} \tag{1}$$

where r is the chain length (degree of polymerization) and η is the number-average chain length that is given by:

$$\eta = \frac{[M]_0}{[I]_0}x \tag{2}$$

where $[M]_0$ is the initial monomer concentration, $[I]_0$ is the initiator concentration, and x is the total monomer conversion. (Note that the initiator units are not included in counting the chain length r in eq 1.) In order to simplify our discussion, we are to consider the cases where the mole fraction of divinyl monomer is small and use eq 1 for the chain length distribution of the primary polymer molecules.

In the present analysis, we further assume that the reactivity of the active centers as well as the pendant double bonds is independent of chain length.

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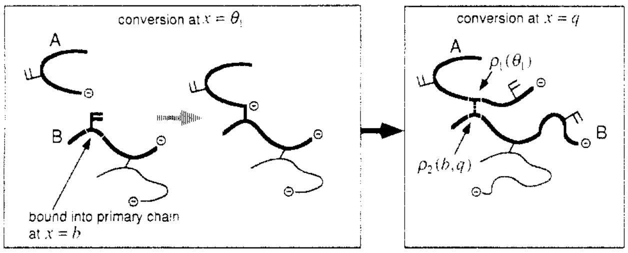

Figure 1. Schematic drawing of the process of cross-linking. The linear polymer chains shown in bold lines (A and B) are the primary polymer molecules. At $x = q$, the probability that the unit incorporated into the polymer chain at $x = b$ possesses a cross-linkage is given by eq 3.

Cross-Linking Density Distribution along the Primary Polymer Molecule. In living copolymerization, the kinetic effects of the cross-link formation are engraved on each primary polymer chain; the location of cross-linked units along the primary chain is nonrandom, although the expected cross-linking density of one primary chain is the same for all chains as shown later. This is a clear difference from free-radical cross-linking copolymerizations in which nonrandomness appears in the difference of the cross-linking density among the primary polymer molecules depending on the birth time of each primary chain. In order to quantify such nonrandomness due to the kinetically controlled network formation in free-radical systems, the cross-linking density distribution was proposed.[45-49] Formally, the same equations apply to the present reaction system although the physical meaning of the independent variables must be modified.

The process of cross-linking reaction in living copolymerization is schematically shown in Figure 1, which shows that a cross-linkage is formed at conversion, $x = \theta_1$, by consuming the pendant double bond on the primary polymer molecule, B. A cross-link point is defined as a unit that bears a tribranch point,[1-4] so two cross-link points are formed in one cross-link reaction. The cross-link points are divided into two types, ρ_1 and ρ_2 as shown in the figure. (The cross-link point of type 1, ρ_1, corresponds to the instantaneous cross-linking density in free-radical polymerization, and ρ_2 corresponds to the additional cross-linking density.[45-49]) The cross-link point of type 1 is formed by consuming the pendant double bonds located on other polymer molecules, while type 2 is formed by consuming the pendant double bonds on its own primary polymer molecule. Generally, it may be impossible to distinguish these two types of cross-link points experimentally; however, from the point of view of the kinetics of network formation it is important to distinguish these types mathematically; ρ_1 is the function of the time of the cross-link formation, while ρ_2 is the function of both the time at which the divinyl monomer is incorporated into the primary polymer molecule and the present time. Here, $\rho_2(b,q)$ gives the probability that a unit incorporated into the polymer chain at conversion $x = b$ forms a cross-linkage in the conversion interval $b < x \leq q$. The probability that the unit incorporated into the polymer chains at conversion $x = b$ is a cross-link point when the conversion at the present time $x = q$ is given by the sum of two possibilities: $\rho_1(b)$ and $\rho_2(b,q)$.

$$\rho(b,q) = \rho_1(b) + \rho_2(b,q) \tag{3}$$

The derivation of the fundamental equations for each type of cross-linking density is essentially the same as that for free-radical polymerizations.[45,46] For a batch cross-linking copolymerization, they are given by:

$$\rho_1(b) = \left(\frac{k_p{*}^0(b)}{k_p(b)}\right)\left(\frac{b}{1-b}\right)\{\bar{F}_2(b) - \bar{\rho}_2(b) - \bar{\rho}_c(b)\} \tag{4}$$

$$\frac{\partial\rho_2(b,q)}{\partial n} = \left(\frac{k_p{*}^0(q)}{k_p(q)}\right)\left\{\frac{F_2(b) - \rho_2(b,q) - \rho_c(b,q)}{1-q}\right\} \tag{5}$$

where $k_p{*}^0$ and k_p are the pseudokinetic rate constants for cross-linking and propagation reactions, respectively. F_2 is the mole fraction of divinyl monomer bound into the polymer chains instantaneously (within a very small time interval), and ρ_c is the cyclization density that is the mole fraction of pendant double bonds wasted by cyclization reactions. All superscript bars in eq 4 are used to designate the accumulated values at a given conversion.

By application of the above equations, it is possible to calculate the cross-linking density distribution along the primary polymer molecules, and using such distribution functions the location of cross-link points can be determined. Examples of the calculated cross-linking density distribution is shown in Figure 2 where the conversion of the present time is $q = 0.281$. (This conversion level will be used as the conversion at the gel point in the later section.) The kinetic parameters used are summarized in Table 1. The condition C1 corresponds to Flory's simplifying assumptions for vinyl/divinyl copolymerization,[4] namely, (1) the reactivities of all types of double bonds are equal, (2) all double bonds react independently, and (3) there are no cyclization reactions in finite molecules. Note that the reactivity ratios shown in Table 1 are defined with respect to the monomeric unit, not the double bond. The kinetic parameters used in condition C2 are approximately those for the anionic copolymerization of styrene and *p*-divinylbenzene reported by Worsfold.[39] In light of a very narrow primary polymer distribution formed in living polymerization, the x-ordinate corresponds to the location along the primary polymer molecule as it stands. The probability of possessing a cross-link point (including both types 1 and 2) at the given location is shown by the bold curves, and that for the cross-link point of type 1 is shown as the broken curves; therefore, the cross-linking density of type 2 is shown as the height in between. Under Flory's simplifying assumptions (C1), the probability of possessing a cross-link point is the same for all monomeric units along the primary polymer molecules, so a statistically homogeneous network is formed. (Note that a homogeneous network does *not* mean a uniform network.) Under condition C2, primary polymer chains have a tendency that the cross-linked points are gathered in one side. In the present calculations, the cyclization is neglected; however, it is reasonable to consider that the cyclization would be more significant under condition C2 if it were allowed since the pendant double bonds also tend to be concentrated at the same side.

Distribution of the Number of Cross-Link Points in the Primary Polymer Molecule. Under Flory's simplifying assumptions, the expected cross-linking density is the same for any location, so the distribution of the number of cross-link points for each primary polymer molecule is simply given by the binomial distribution. The probability that a primary polymer molecule with chain length r and cross-linking density ρ possesses i cross-link points, $P_x(i)$, is given by:

$$P_x(i) = \binom{r}{i}\rho^i(1-\rho)^{r-i} \tag{6}$$

On the other hand, when the variance of the cross-linking density distribution is large as in the case of condition C2,

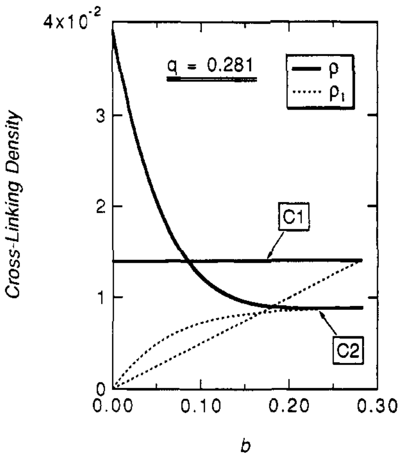

Figure 2. Calculated cross-linking density distribution under conditions shown in Table 1 at the present conversion, $q = 0.281$.

Table 1. Calculation Conditions Investigated

	C1	C2
initial mole fraction of divinyl monomer, f_2^0	0.0254	0.01
reactivity ratios, r_1 and r_2	0.5, 2.0	0.05, 20.0
reactivity of pendant double bonds, k_p^{*0}/k_p	1	0.8
$[M]_0/[I]_0$	250	250
cyclization density, ρ_c	0	0

determination of $P_x(i)$ is not a trivial problem. Suppose the probability of possessing a cross-link point for the jth unit along the primary polymer molecule is p_j ($\cong\rho(q\times j/r,q)$ where q is the conversion at the present time). For example, the probability that a primary polymer molecule with chain length r possesses one cross-link unit is given by:

$$P_x(1) = (\prod_{j=1}^{r}(1-p_j))\left(\sum_{k=1}^{r}\frac{p_k}{(1-p_k)}\right) \tag{7}$$

When the cross-linking density is small enough, it may be reasonable to guess the distribution can be approximated by the binomial distribution as follows:

$$P_x(i) = \binom{r}{i}\bar{\rho}^i(1-\bar{\rho})^{r-i} \tag{8}$$

where $\bar{\rho}$ is the average cross-linking density.

The applicability of eq 8 was examined using the Monte Carlo simulation method assuming $p_j = \rho(q\times j/r,q)$. Figure 3 shows the comparison of the Monte Carlo simulation results for both types 1 and 2 (by generating 1×10^4 primary polymer molecules) with the binomial distribution (eq 8) at $q = 0.281$ whose cross-linking density distribution is shown in Figure 2 (C2), and excellent agreement is observed. Note that the use of an average value is valid even for each type of cross-link point. Figure 4 shows the case for condition C2 at the present conversion $q = 0.8$ when the cross-linking density level is much higher with a broader cross-linking density distribution than at $q = 0.281$. Again, the binomial distribution completely agrees with the simulated results. The use of eq 8 is now verified.

Molecular Weight Distribution. Since the number of the cross-link ponts in each primary polymer molecule can be approximated by the binomial distribution, the weight-average chain length development during polymerization is simply given by:[1-4,50,51]

$$P_w = \frac{P_{wp}}{1-\bar{\rho}P_{wp}} \tag{9}$$

where P_{wp} is the weight-average chain length of the primary polymer molecules that is equal to $1 + \eta$ in the present case.

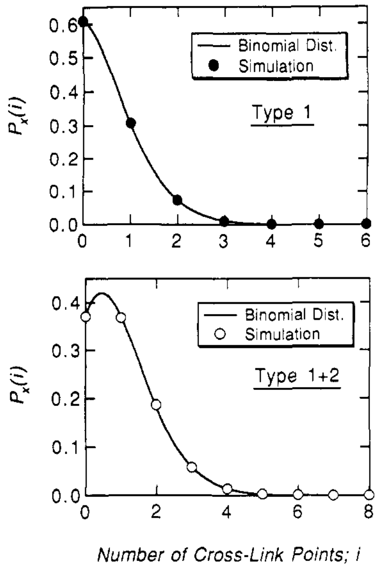

Figure 3. Comparison of the calculated distribution of the number of cross-link points on a primary polymer molecule with chain length $r = 70$ ($=[M]_0q/[I]_0$) under condition C2 at $q = 0.281$. The solid curve shows the binomial distribution using the average cross-linking density, while keys show the Monte Carlo simulation results.

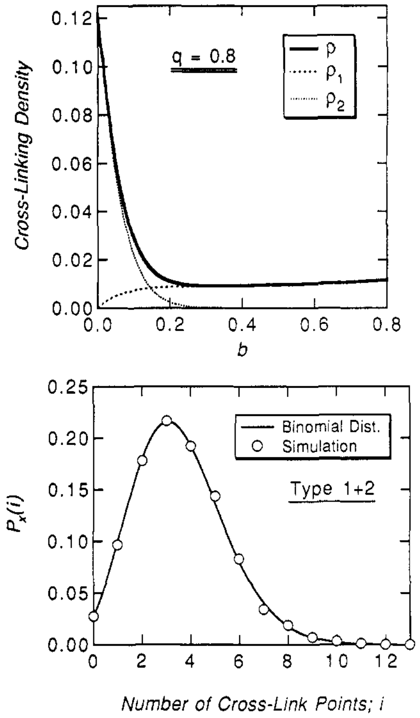

Figure 4. Calculated cross-linking density distribution under condition C2 at $q = 0.8$ and comparison of the calculated number of cross-link points on a primary polymer molecule with chain length $r = 200$ ($=[M]_0q/[I]_0$).

The molecular weight distribution can be simulated easily using the Monte Carlo sampling technique proposed earlier;[47-49] however, since the connection between primary polymer chains can be considered random, the problem is less complicated. It is straightforward to show that the Schulz–Zimm distribution[52,53] (eq 10) agrees well with the Poisson distribution given by eq 1 when the number-average chain length η is large enough.

$$W(r) = \frac{\sigma^\sigma}{\eta\Gamma(\sigma)}\left(\frac{r}{\eta}\right)^\sigma \exp\left(-\frac{\sigma r}{\eta}\right) \tag{10}$$

where σ is a parameter indicating the narrowness of the distribution breadth and reduces to $\sigma = \eta$ if the Poisson distribution is approximated by eq 10. On the basis of the

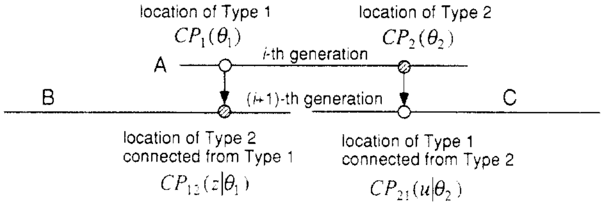

Figure 5. Schematic drawing for the concept of various types of connection probabilities.

integro-differential equation proposed by Saito[50,51] that describes the molecular weight distribution development during random cross-linking, Kimura[54,55] obtained the series solution for the primary polymer molecules with the Schulz–Zimm distribution. Recently, it was recognized that a correction is required in his solution, and the weight fraction distribution in which the cross-linking density is ρ is given by:[56]

$$W(r,\rho) = \frac{1}{\eta}\left(\frac{r}{\eta}\right)^{\sigma} \exp\left[-(\sigma + \rho\eta)\frac{r}{\eta}\right] \times \left(\sum_{k=0}^{\infty} \frac{\sigma^{(k+1)(\sigma+1)}(\rho\eta)^k}{(k+1)!\Gamma[(k+1)(\sigma+1)]}\left(\frac{r}{\eta}\right)^{k(\sigma+2)}\right) \tag{11}$$

Incidentally, the k value in eq 11 corresponds to the number of cross-linkages in a polymer molecule,[57] so one obtains the fractional chain length distribution containing k cross-linkages using eq 11.

Location of Cross-Link Points in the Primary Polymer Molecule. Now we have information on (1) the chain length distribution of the primary polymer molecules and (2) the number of cross-link points of both types 1 and 2 on each primary polymer molecule. With one more piece of information, that is the location of the cross-linkages among the primary polymer molecules that could be obtained from the cross-linking density distribution, it becomes possible to simulate the cross-linked structure of each nonlinear polymer molecule formed in living copolymerization.

We have to formulate probability functions of four types. After the determination of the number of cross-link points of type 1 and type 2 using the binomial distribution, we have to determine (1) the location of cross-link points of type 1 and (2) that of type 2. Next, we have to determine how each type of cross-link point is connected to the other primary polymer molecules; (3) the location of the cross-link point of type 2 in the next generation that is connected from the type 1 cross-link point in the previous generation, and (4) the location of that cross-link point of type 1 that is connected from the type 2 cross-link point in the previous generation. Figure 5 shows the schematic drawing for the concept of four types of probabilities.

We are to consider the molecular constitution at the present conversion, ψ. When the given primary polymer molecule possesses a cross-link point of type 1, the probability that the cross-linkage is formed in the conversion interval 0 to θ_1 is given by:

$$CP_1(\theta_1) = \frac{\int_0^{\theta_1} \rho_1(b)\,\mathrm{d}b}{\int_0^{\psi} \rho_1(b)\,\mathrm{d}b} \tag{12}$$

Since this cross-linkage is formed at $x = \theta_1$ by consuming the pendant double bond located on another primary polymer molecule, the divinyl monomer unit on the primary polymer molecule B in Figure 5 must be incorporated into the chain prior to $x = \theta_1$. The probability that this divinyl monomer unit is incorporated into the primary polymer molecule B in the conversion interval 0 to z ($0 < z < \theta_1$) is given by:

$$CP_{12}(z|\theta_1) = \frac{\int_0^{z} \frac{\partial\rho_2(b,q)}{\partial q}\Big|_{q=\theta_1} \mathrm{d}b}{\int_0^{\psi} \frac{\partial\rho_2(b,q)}{\partial q}\Big|_{q=\theta_1} \mathrm{d}b} \tag{13}$$

On the other hand, when the given primary polymer molecule possesses a cross-link point of type 2, the probability that the given divinyl monomer unit is incorporated into the primary polymer molecule A in the conversion interval 0 to θ_2 is given by:

$$CP_2(\theta_2) = \frac{\int_0^{\theta_2} \rho_2(b,\psi)\,\mathrm{d}b}{\int_0^{\psi} \rho_2(b,\psi)\,\mathrm{d}b} \tag{14}$$

Since the given divinyl monomer unit is incorporated into the chain at $x = \theta_2$, this cross-linkage must be formed after $x = \theta_2$. The probability that this cross-linkage is formed in the conversion interval θ_2 to u ($\theta_2 < u < \psi$) is given by:

$$CP_{21}(u|\theta_2) = \frac{\int_{\theta_2}^{u} \frac{\partial\rho_2(\theta_2,q)}{\partial q}\,\mathrm{d}q}{\int_{\theta_2}^{\psi} \frac{\partial\rho_2(\theta_2,q)}{\partial q}\,\mathrm{d}q} = \frac{\rho_2(\theta_2,u)}{\rho_2(\theta_2,\psi)} \tag{15}$$

By application of eqs 12–15, the connectivity among primary polymer molecules can be determined. The whole molecular constitution can be simulated based on the Monte Carlo sampling technique[47–49] with the following steps. (1) One primary polymer molecule is selected randomly on the weight basis as the primary polymer molecule that belongs to the zeroth generation, and the chain length of this primary polymer molecule is determined from eq 1. Note that the zeroth generation always consists of one primary polymer molecule. (2) Determine the number of cross-link points for both types 1 and 2 using the binomial distribution given by eq 8. Obviously, $\bar{\rho}_1$ and $\bar{\rho}_2$ are used to determine the cross-link points of each type. (3) Determine the location of cross-link points (that is given by the conversion level as an independent variable) on the primary polymer molecule that belongs to the zeroth generation from eqs 12 and 14, and the location for the connected cross-link points on the first generation by application of eqs 13 and 15. (4) Then, the chain length of each primary polymer molecule that belongs to the first generation is determined again from eq 1. The number of cross-link points for both types 1 and 2 are given by eq 8. Note that except for the primary polymer molecule in the zeroth generation, $r - 1$ is used instead of r since one unit is used to connect with the previous generation although this procedure may be neglected for long primary polymer molecules. The location of the cross-link points is determined by using eqs 12–15. The processes shown in item 4 are reiterated until all primary polymer molecules fail to be connected to the next generation. In the present paper, we are to use the Monte Carlo sampling technique only for the sol polymer molecules.

Results and Discussion

Molecular Weight Distribution (MWD). We are to consider the conditions shown in Table 1. The calculated average cross-linking density development is shown in

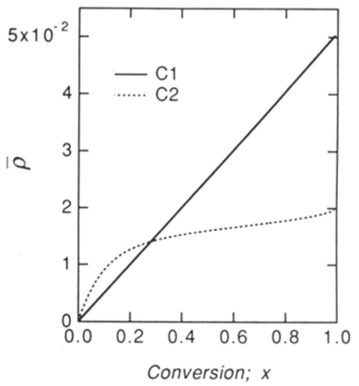

Figure 6. Average cross-linking density development under the conditions shown in Table 1.

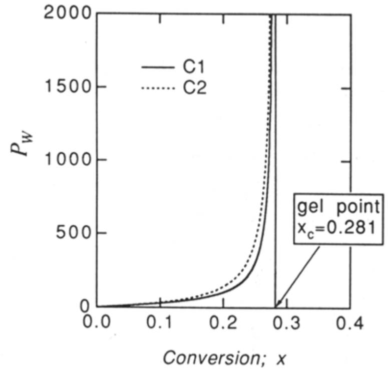

Figure 7. Weight-average chain length development.

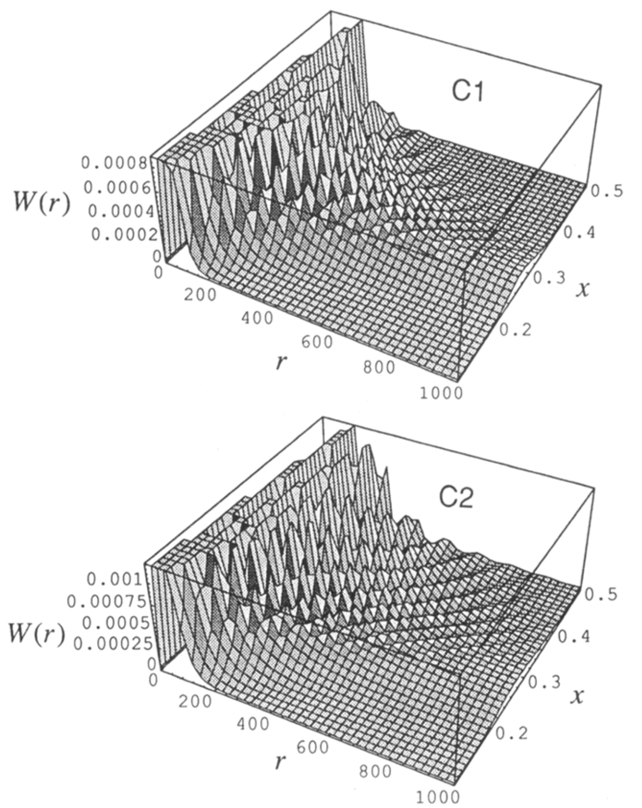

Figure 8. Weight fraction distribution ($W(r)$) development during polymerization.

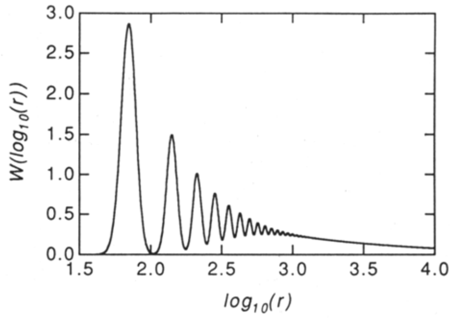

Figure 9. Weight fraction distribution ($W(\log r)$) at the gel point (x_c = 0.281).

Figure 6. Under condition C1 (Flory's simplifying assumptions), the average cross-linking density increases linearly, while it is nonlinear under condition C2. The average cross-linking density is the same for both conditions at $x = 0.281$. We set the calculation conditions shown in Table 1 in order to make the gel point at this point, $x_c = 0.281$, deliberately. The weight-average chain length development is shown in Figure 7.

The MWD can be calculated from eq 11 (although it is also possible to use the Monte Carlo sampling technique[56]). Figure 8 shows the weight fraction distribution ($W(r)$) development during polymerization. Multimodal distributions are obtained, and each peak moves toward larger chain lengths since the primary polymer chains that constitute the cross-linked polymer molecules grow larger as polymerization proceeds. The change in the MWD is smooth irrespective of the pre- and postgelation periods. The height of each peak decreases in the postgelation period. Figure 9 shows the weight fraction distribution ($W(\log r)$) at the gel point. Note that the x-ordinate is the logarithmic scale in Figure 9, while it is normal scale in Figure 8. The weight fraction distribution in logarithmic scale ($W(\log r)$) is important due to the formal relationship with the elution curve obtained in gel permeation chromatography (gpc). Since the average cross-linking density is the same at the gel point, the MWD is the same for both conditions.

Figures 8 and 9 show multimodal distributions. Most conventional theories for network formation usually provide only the average chain lengths or the moments of the MWD. When the MWD is multimodal, the averages are clearly insufficient to represent the MWD and the full MWD is required to investigate the polymeric network formation. On the other hand, it may be very difficult to observe so many peaks experimentally due to the following reasons. (1) Multimodal peaks are obtained only for the primary polymer chains with very narrow distributions. For example, if the polydispersity index (PDI = P_w/P_n) for the primary polymer molecules is larger than 1.1, even the second peak cannot be observed as reported elsewhere.[56] If the primary polymer distribution becomes broader for some reason, it would be difficult to obtain so many peaks shown here. (2) The MWDs are usually determined by the use of a gpc. In a gpc technique, the polymer molecules are fractionated according to their hydrodynamic volume, not the molecular weights. Even the polymer molecules with the same molecular weight can possess completely different configurations in nonlinear polymers. This makes each peak broader in gpc except for the peak at the smallest chain length that is for linear polymers. Furthermore, the occurrence of cyclizations would change the hydrodynamic volume significantly.

Spatial Distribution of Cross-Linked Polymer Molecules. Since each cross-linked polymer molecule can be observed directly in the Monte Carlo sampling technique, the spatial distribution can be examined by embedding the polymer molecule in the three-dimensional space. We are to consider the polymer molecules formed at the gel point where polymer molecules with any size can be obtained. A reasonable start point to consider the distribution in space would be to assume a Θ state; each primary polymer molecule is drawn as the trajectory of

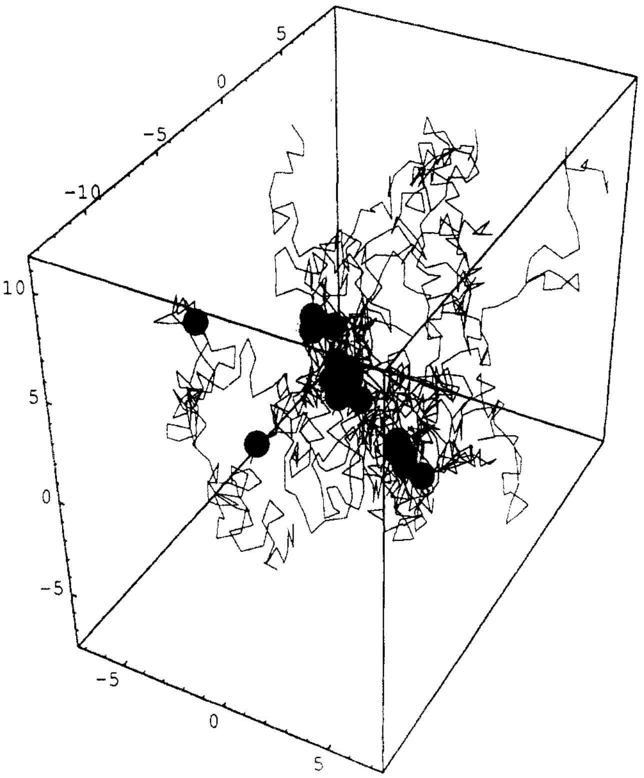

Figure 10. Example of the spatial distribution of a cross-linked polymer molecule formed under condition C2 with the structure a given in Figure 11. The dots show the spatial distribution of the cross-linkages.

the Brownian motion. This kind of approach may be too simple to describe the real networks; however, it is hoped that the present analysis gives fundamental information on the spatial distributions. Figure 10 shows an example of the spatial distribution whose connection among primary polymer molecules is given in Figure 11a.

Radius of Gyration. We selected 15 types of cross-linked polymer molecules and made close examinations. Two of the selected cross-linked structures are shown in Figure 11. We determined the mean-square radius of gyration under conditions C1 and C2 by generating a large number of cross-linked polymer molecules having the same chain length. In the simulation, the chain lengths of primary polymer molecules and the number of cross-link points on each polymer molecule is preserved for each type of cross-linked polymer (that means the structure shown in Figure 11 is preserved), while the location of cross-link points along each primary polymer molecule is recalculated every time a new polymer molecule is simulated using the probability functions, eqs 12–15. Therefore, the obtained mean-square radius of gyration is not the radius of gyration for a particular cross-linked polymer molecule but a kind of average radius of gyration for polymers that are equal in chain length but different in configurations formed under conditions C1 and C2.

Zimm and Stockmayer[58] developed the functional forms for the radius of gyration in a Θ state theoretically for many branch shapes. For random cross-linking of primary polymer molecules having the most probable distribution, the root-mean-square radius of gyration for the cross-linked polymers is given by:[58]

$$\langle s^2\rangle^{1/2} = \langle s^2\rangle_l^{1/2}\left\{\left(1+\frac{m}{6}\right)^{1/2}+\frac{4m}{3\pi}\right\}^{-1/4} \tag{16}$$

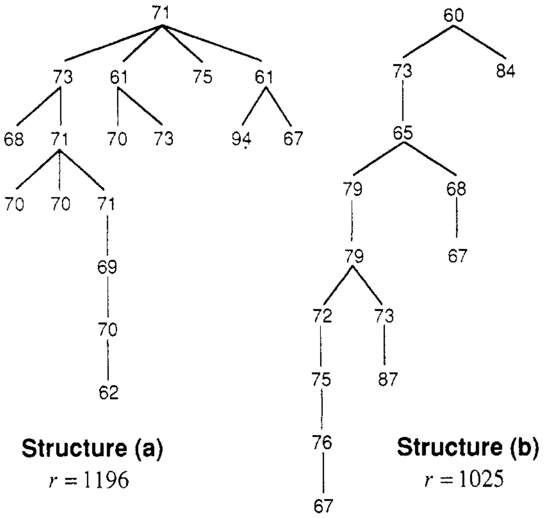

Figure 11. Example of the simulated cross-linked polymers. Each number indicates the chain length of the primary polymer molecule.

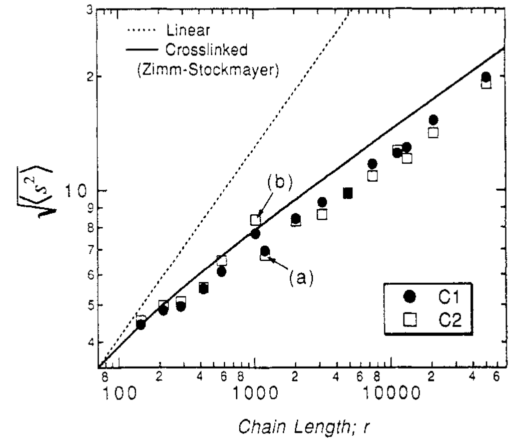

Figure 12. Comparison of the calculated root-mean-square radius of gyration. The dotted line shows the radius of gyration for linear polymers (eq 17), while the solid curve is for cross-linked polymers calculated from eq 16. The keys are the simulated results for living copolymerization.

where m is the average number of cross-linkages within the polymer molecules that possess the same chain length, and $\langle s^2\rangle_l^{1/2}$ is the radius of gyration for the linear polymers having the same chain length. For linear polymers with n segments, $\langle s^2\rangle_l^{1/2}$ is given by:

$$\langle s^2\rangle_l^{1/2} = l\left(\frac{n}{6}\right)^{1/2} \tag{17}$$

where l is the length of a segment.

In the present analysis, we consider that one segment consists of one monomeric unit ($n = r$) and l as the unit length ($l = 1$). Since the primary chain length distribution is very narrow, the relationship between the chain length r and the number of cross-linkages m is simply given by:

$$r = \eta(m + 1) \tag{18}$$

Figure 12 shows the comparison of the root-mean-square radius of gyration from eq 16 and the simulated ones as a function of chain length. In the simulation, the root-mean-square radius of gyration for a given chain length is determined by simulating at least 50 cross-linked polymer molecules. Clearly, the radius of gyration is smaller for the narrower primary polymer distributions than that with the most probable distribution ($P_{wp}/P_{np} = 2$). This would be due to the fact that the larger primary chains possess a significant effect on the $\langle s^2\rangle^{1/2}$ values. The polymer molecules shown as a and b correspond to those shown in Figure 11. The chain length of these two polymers does not differ much; however, the radius of gyration is significantly different. As shown in Figure 11,

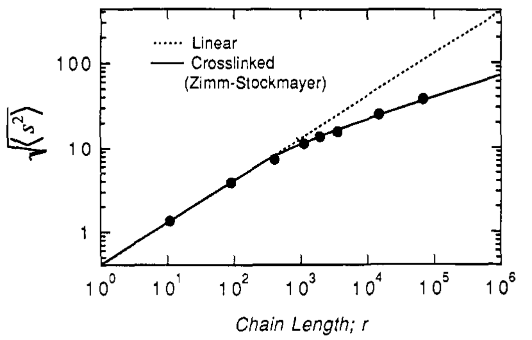

Figure 13. Calculated root-mean-square radius of gyration for the polymer molecules obtained from random cross-linking of primary polymers with the most probable distribution. The number-average chain length of the primary polymer molecules is 200, and the average cross-linking density of the reaction system is 2.5×10^{-3}.

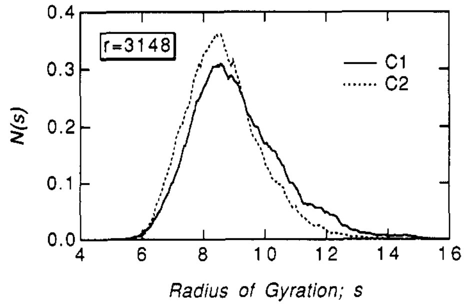

Figure 14. Distribution of the radii of gyration for the cross-linked polymer molecules with chain length r = 3148 containing 43 cross-linkages.

polymer a possesses cross-link points in a more concentrated form than that for polymer b. The concentration of cross-linkages in three-dimensional space is represented well in Figure 10. The effect of the difference in the configuration of the cross-linked polymers is found to be significant especially for the polymers with the intermediate sizes although such differences may not be significant for polymers with both small and large numbers of cross-linkages.

Incidentally, Figure 13 shows the case in which primary polymers with the most probable chain length distribution are cross-linked randomly. Good agreement with eq 16 is obtained; this is direct proof that eq 16 is correct. As shown in Figure 13, all points fit very well with eq 16 irrespective of their configurational differences, and it seems reasonable to consider the difference in the configuration (as shown in Figure 11) possesses smaller effects on the radius of gyration for broader primary polymer chain length distributions. More detailed investigation concerning the cross-linking of broader primary polymer distributions will be reported separately.

Let us compare the effects of the reaction conditions C1 and C2 on the radius of gyration. Under condition C2, there is a tendency that the cross-linkages are formed at one side of the primary polymer molecule than the center part as shown in Figure 2. When the number of cross-linkages is very small, this makes the radius of gyration larger as shown in Figure 12 since the formed polymers may tend to be more like linear polymers. On the other hand, as the number of cross-linkages increases, the condition C2 tends to make highly cross-linked regions, which makes the radius of gyration smaller for C2 gradually as shown in Figure 12.

In the present simulation method, very detailed information can be obtained easily. Figure 14 shows the distribution of the radii of gyration obtained by simulating 1000 polymer molecules.

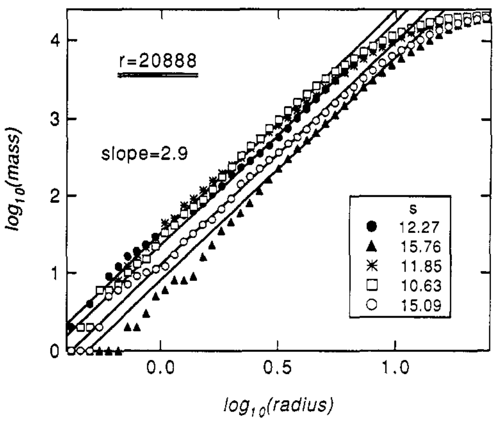

Figure 15. Mass–radius relationship for the cross-linked polymer molecule with chain length r = 20888 under condition C2.

Fractal Dimension. It is clearly shown in eq 16 that the fractal dimension of randomly cross-linked polymer molecules is 4 at the large chain length limit. This is one of the reasons for the argument that the ring-free model is unrealistic. However, the fractal nature of the real world comes into play only for a limited size range. Judging from Figures 12 and 13, it is expected that the dominant size of yardstick to determine the fractal dimension must be much larger than $\langle s^2 \rangle^{1/2} = 10$ in order for the fractal dimension to be 4 since the slope changes with chain length for $\langle s^2 \rangle^{1/2} < 10$. We determined the fractal dimension of the cross-linked polymer molecules from the mass–radius relationship;[59] the relationship between the number of units within the distance from the center of mass.

$$N_{\text{units}}(R) \propto R^D \tag{19}$$

where R is the distance from the center of mass and D is the fractal dimension.

Figure 15 shows an example of the mass–radius relationship (r = 20888 formed under condition C2). There certainly exists a region of a linear relationship for log(mass) ~ log(radius) irrespective of the difference in structure. (Note that the location of cross-link points on each primary polymer molecule is changed for all simulated cross-linked polymer molecules.) In the present system, the weight fraction of polymer molecules with chain length smaller than 5000 is $W(r{<}5000) = 0.91$ and that smaller than 1×10^4 is $W(r{<}1{\times}10^4) = 0.94$, so the polymer molecule shown in Figure 15 (r = 20888) is considered a very large polymer molecule. However, (1) the dominant yardstick is smaller than 10, and (2) the fractal dimension is smaller than 3; i.e., the molecule does not fill up the three-dimensional space even when the present statistical distribution continues forever.

The radius of gyration is larger for condition C2 than for condition C1 for smaller polymers, while it is smaller for larger polymers as shown in Figure 12, so it may be expected that the fractal dimension is larger for condition C2. Figure 16 shows the comparison of the fractal dimension as a function of chain length. The fractal dimension of condition C2 for smaller polymers is smaller than that of condition C1 probably due to a larger contribution of linear polymer parts whose fractal dimension is 2. The fractal dimension becomes larger for condition C2 in the intermediate chain length range; however, the difference is diminished for extremely large polymer molecules. For extremely large polymer molecules it may be reasonable to guess that the highly cross-linked regions formed in C2 are distributed homogeneously in the three-dimensional space. The fractal dimension becomes larger than 3 only for the chain length larger

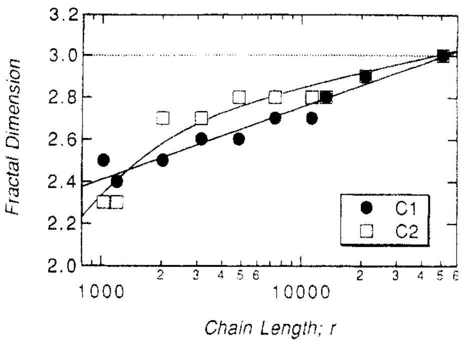

Figure 16. Fractal dimension of the cross-linked polymers as a function of chain length.

than 5×10^4 that includes more than 1400 cross-link points (700 cross-linkages) in the present reaction system. This fact implies that the ring-free structure is not prohibited in the three-dimensional space except for extremely large polymer molecules that may be regarded as gel molecules in practice. Since the ring formation is permitted within gel fraction even in the framework of the ring-free model,[1-4,60] it seems reasonable to consider the ring-free model (or Flory's treelike model) does not break down due to the ring formation required from the limitation of space availability; i.e., the Malthusian packing paradox[60,61] resulting from the impossibility of accommodating all units in space plays a role only for the gel molecule in practice. Even when the ring formation due to the Malthusian packing paradox is negligible for sol fractions, cyclization due to the conformational statistics of the sequence of bonds would occur. The present simulation method in the three-dimensional space may provide a reasonable start point to clarify such long-range correlations in cross-linked polymers.

Conclusions

In this paper, a new kinetic theory for network formation in living cross-linking copolymerization that considers the history of the generated structure is proposed. This theory is based on the distribution of cross-linked units along the primary polymer molecule. The molecular weight distributions can be multimodal in living cross-linking copolymerization although such distributions may be difficult to be observed experimentally. The radius of gyration is found to be smaller than that for the random cross-linking of linear polymer chains having the most probable distribution. The fractal dimension of the cross-linked polymer molecules is less than 3 except for extremely large polymer molecules, and the ring-free model may not break down due to the Malthusian packing paradox. Closer investigation of the spatial distribution of cross-linked polymers would be required in order to build a more realistic model for polymeric network formation.

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