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Research Article

Network Dimension Theory and Its Application to Miniemulsion Vinyl/Divinyl Copolymerization

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Abstract: Newly developed network dimension theory is used for rapid estimation of the root-mean-square radius of gyration R_g of each polymer molecule formed during vinyl/divinyl copolymerization. The R_g-value is used for describing the enhancement of intramolecular crosslinking or the cyclization reactions. The model is applied to the miniemulsion copolymerization, and both conventional free-radical polymerization and ideal living polymerization are considered. Some of important characteristics of network architecture formed in these two types of polymerization mechanisms that cannot be predicted based on the classical chemical kinetics can be reproduced by the model successfully. For example, such unique characteristics as the pendant double bonds are consumed from the start of polymerization in conventional free-radical polymerization but not so in living polymerization can be elucidated. The present kinetic model provides useful insights into the size- and structure-dependent network formation.

Keywords: Crosslinking, Emulsion polymerization, Gelation, Graph diameter, Radius of gyration

1. Introduction

Classical chemical kinetics (CCK), which employs the product of average concentrations of functional groups, has been a standard tool for describing chemical reaction rates. When applying CCK to the polymeric network formation during the pre-gelation period, one of the drawbacks is that it cannot describe the intramolecular crosslinking reaction. In an infinitely large reaction system consisting of an infinite number of molecules, the weight fraction of a single sol polymer molecule is always zero. Therefore, the molar ratio of the pendant double bonds located on its own sol polymer molecule is zero because an infinite number of pendant double bonds must exist in the whole reaction system. This is the basic assumption of the classical Flory-Stockmayer gelation theory [1] from the point of view of the chemical kinetics. The cycle formation is allowed only within the gel molecule that possesses a nonzero weight fraction in the reaction system.

In a real system, the cyclization or intramolecular crosslinking reaction occurs because the pendant double bonds on its polymer molecule must always stay close to the active center. Figure 1 shows a three-dimensional representation of a crosslinked polymer molecule with an active center (red) at the chain end. The green sphere represents the radius of gyration of this crosslinked polymer architecture. The pendant double bonds (blue) on its own polymer molecule are enriched within a volume around the active center, compared with the other pendant double

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bonds located in other polymer molecules that exist far away. Not all pendant double bonds are equal in terms of the kinetics of crosslinking and cyclization.

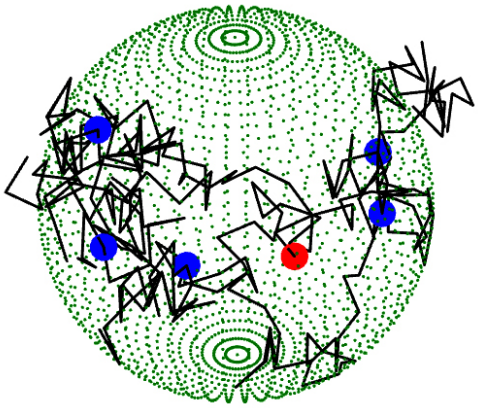

Figure 1 Schematic representation of a crosslinked polymer molecule. The red dot represents the active center, and the blue dots are the pendant double bonds. The sphere indicated by small green dots has the radius of gyration for this particular architecture.

A simple model to account for the concentration enrichment effect is to use the three-dimensional size of a growing polymer molecule [2]. The mean-square radius of gyration R_g^2 would be a reasonable measure for the three-dimensional size of a polymer molecule. Thanks to the development of graph theory, it is nowadays possible to determine R_g^2 of network polymers in the unperturbed state in a straightforward manner [3]. Any well-defined network, such as that generated by Monte Carlo (MC) methods, can be used for the calculations. On the other hand, however, directly calculating the R_g^2 of large networks requires intensive computations and may not be suitable for direct MC simulation of molecular build-up processes.

Another measure to represent the dimensions of network polymers is graph diameter D. In graph theory, the distance between two vertices is the shortest path, and the diameter is the greatest distance between any pair of vertices or the longest shortest path. In a recent series of investigations on the relationship between R_g^2 and D of various statistical network polymers [4-6], it was found that R_g^2 is proportional to D, and the proportional coefficient a_r is dominated by the cycle rank r, defined as the minimum number of edges that must be removed from the graph to break all its cycles, making it into a ring-free, tree-like architecture. The following universal relationship was found for both random and nonrandom statistical network polymers [6].

$$R_g^2 = a_r D \tag{1}$$

$$a_r = a_{0,\mathrm{ran}} f \left[(1+r)^{-\frac{2}{3}} + \frac{r}{2}\right]^{-0.25} \tag{2}$$

where $a_{0,\mathrm{ran}}$ is the ratio for the ring-free random crosslinked polymers, which is $a_{0,\mathrm{ran}}$ = 0.178 [7], irrespective of the primary chain length distribution. The constant factor f represents the effect of heterogeneity, and f = 1 for a homogeneous random network. The magnitudes of f's determined so far do not deviate significantly from unity, and f = 1 can be used for an approximate estimation.

The computational load of D is much smaller than that of R_g^2, and the use of D is suitable for the application to large network polymers. The estimation of R_g^2 based on Equations (1) and (2) is named as the network dimension theory (NDT) in this article. In a broader sense, the NDT involves the master curve relationship of D and r [8,9] that can be used to design and control network polymers' dimensions. However, the contents of this article could be

understood without the knowledge of the master curve, and interpretation of the simulated results through the master curve relationship is omitted. An important point worth noting here is that the use of NDT enables one to determine R_g^2 through a quick calculation of D.

In the present study, a new model is proposed for the polymeric network formation, in which the concentration enrichment of pendant double bonds inside the volume characterized by R_g^2 is accounted for the intramolecular crosslinking, and the magnitude of R_g^2 is determined from the calculation of D based on the NDT. The proposed model is applied to the miniemulsion vinyl/divinyl copolymerization.

The miniemulsion polymerization proceeds in stabilized monomer droplets, and ideally, it can be modelled as consisting of a large number of independent batch microreactors. Because the size of droplets that are the polymerization loci is small, each polymer molecule possesses a nonzero weight fraction, and therefore, direct application of CCK leads to the formation of network polymer molecules without any modification [9]. The differences in network architecture formed through CCK, and the model based on NDT can be highlighted in a straightforward manner. In addition, by employing the polymerization loci having submicron sizes, direct measurement of the molecular weight distribution is feasible even after forming nanogels experimentally [10].

Both conventional free-radical and ideal living polymerization are considered, and the characteristics of the network architecture formed are discussed in detail, referring to the reported experimental results.

2. Methodology

To represent the enrichment effect of pendant double bonds located on its polymer molecule, the sphere volume whose radius is equal to the root-mean-square radius of gyration R_g is employed. Assuming that one segment consists of n_{seg} units, the total number of units inside the sphere volume v_{unit} is given by the following equation.

$$v_{\mathrm{unit}} = \frac{4\pi}{3}\left(n_{\mathrm{seg}} R_g\right)^3 \tag{3}$$

The effective volume v_{e} for cyclization reaction could be represented by the following equation, by introducing an expansion factor α.

$$v_{\mathrm{e}} = \alpha v_{\mathrm{unit}} = \frac{4\pi\alpha}{3}\left(n_{\mathrm{seg}} R_g\right)^3 \tag{4}$$

The magnitude of α can be larger or smaller than unity. In the present simulation study, α = 1 is used. Note that v_{e} is represented by the number of monomeric units.

In the simulation, the graph diameter D is determined for the polymer molecule having an active center, and v_{e} is calculated by using Equations (1), (2), and (4). In this article, f = 1 is used for Equation (2). For the newly growing chain whose segment length is not larger than unity, D = 1 is employed.

To simplify the model, monodisperse polymer particles are assumed, although the actual miniemulsion polymerization tends to form a large particle size distribution. The total number of monomeric units in a particle is set to be N_{M} = 2 x 10^5, which corresponds to a particle whose diameter is about 40 nm, assuming that the density is 1 g/cm^3 and the molecular weight of a monomeric unit is 100.

The volume of a single particle is denoted by V, which is represented by the number of units in this article. For the cases without using solvent, $V = N_{\mathrm{M}}$. When solvent is introduced for dilution, the V-value larger than N_{M} is used.

To investigate flexible polymer networks, the initial mole fraction $f_{2,0}$ of divinyl monomer is set to be small and $f_{2,0}$ = 0.01 and 0.0145 are used. The latter value is used for comparison with experiments. Note that subscript 1 is used for the vinyl monomer, and 2 is for the divinyl monomer. The initial total number of vinyl monomers (M_1) in a particle is $n_{1,0} = N_{\mathrm{M}}(1 - f_{2,0})$ and that of divinyl monomer (M_2) is $n_{2,0} = N_{\mathrm{M}} f_{2,0}$.

In the present model, the substitution effect on the reactivity of a pendant double bond is neglected, and the reactivity of a pendant double bond is assumed to be the same as for the double bond in a divinyl monomer. The reactivity of a double bond in a divinyl monomer is β times larger than that in the vinyl monomer. When the CCK is applied with β = 1, the formed crosslinked architecture is homogeneous and randomly crosslinked. In this article, the simulated results solely with β = 1 are shown, and the other cases can be found elsewhere [2].

The pendant double bonds are categorized into two types; those on its own polymer molecule whose number is represented by n_c, and those on the other molecules n_x. The probabilities p_1, p_2, p_c, and p_x that an active center reacts with a double bond in M_1, M_2, a pendant double bond on its own molecule to cause cyclization, and that in another molecule to form intermolecular crosslink are given respectively as follows.

$$p_1 = \frac{n_1}{n_1 + 2\beta n_2 + \beta(V/v_e)n_c + \beta n_x} \tag{5}$$

$$p_2 = \frac{2\beta n_2}{n_1 + 2\beta n_2 + \beta(V/v_e)n_c + \beta n_x} \tag{6}$$

$$p_c = \frac{\beta(V/v_e)n_c}{n_1 + 2\beta n_2 + \beta(V/v_e)n_c + \beta n_x} \tag{7}$$

$$p_x = \frac{\beta n_x}{n_1 + 2\beta n_2 + \beta(V/v_e)n_c + \beta n_x} \tag{8}$$

Note that one divinyl monomer possesses 2 double bonds in it, so the factor 2 is needed for the reaction with divinyl monomer.

In the present calculation by using the NDT model, when the magnitude of v_e is larger than V, $v_e = V$ is used. In addition, after the formation of a clear nanogel molecule, $v_e = V$ is used for the nanogel molecule. Note, however, the determined v_e-value is used for other than the nanogel molecule throughout the polymerization. For the CCK model, no enrichment occurs and (V/v_e) = 1.

When the event represented by the probability p_1 occurs, the number n_1 of M_1 is decreased by one. For the event with p_2, the number n_2 of M_2 is decreased by one, and the number of pendant double bonds in the growing chain is increased by one. For the events with p_c and p_x, the number of pendant double bonds in the primary chain that caused the intra- or intermolecular reaction is decreased by one. In this article, the conversion x is represented by the consumption of monomers, not the double bond.

$$x = 1 - \frac{n_1 + n_2}{n_{1,0} + n_{2,0}} \tag{9}$$

In the conventional miniemulsion free-radical polymerization (FRP), the zero-one system is assumed for simplicity, and only one polymer radical exists in a particle during the growth period. The double bond is added one by one to a single active center in the particle. The most probable distribution is used for the primary polymer chains, whose number-based distribution $N(P)$ is given by:

$$N(P) = \frac{1}{P_{np}} \exp\left(-\frac{P}{P_{np}}\right) \tag{10}$$

where P_{np} is the number-average chain length of the primary chains.

For the ideal living polymerization, the initial number of potential active centers, equal to the number of primary chains, is kept constant during polymerization. Representing the number-average primary chain length at 100% conversion by R, the total number of primary chains in a particle is given by N_M/R.

After determining the molecular architecture by the MC simulation method, the graph diameter D is determined using the commercial software Mathematica, with a standard command for the undirected graph, "GraphDiameter". Using the number n_s of segments (edges) and the number n_v of vertices of a polymer molecule, the cycle rank r is calculated from [3]:

$$r = n_s - n_v + 1 \tag{11}$$

3. Results and discussion

An interesting characteristic of conventional free-radical polymerization is that a certain percentage of pendant double bonds are consumed from the beginning of polymerization, which means an infinite reactivity of pendant double bonds if CCK is applied. Figure 2 shows some of the reported pendant double bond (PD) conversion at zero monomer conversion, x = 0 [11-15]. On the other hand, it is known that living radical polymerization leads to zero PD conversion at x = 0 [16].

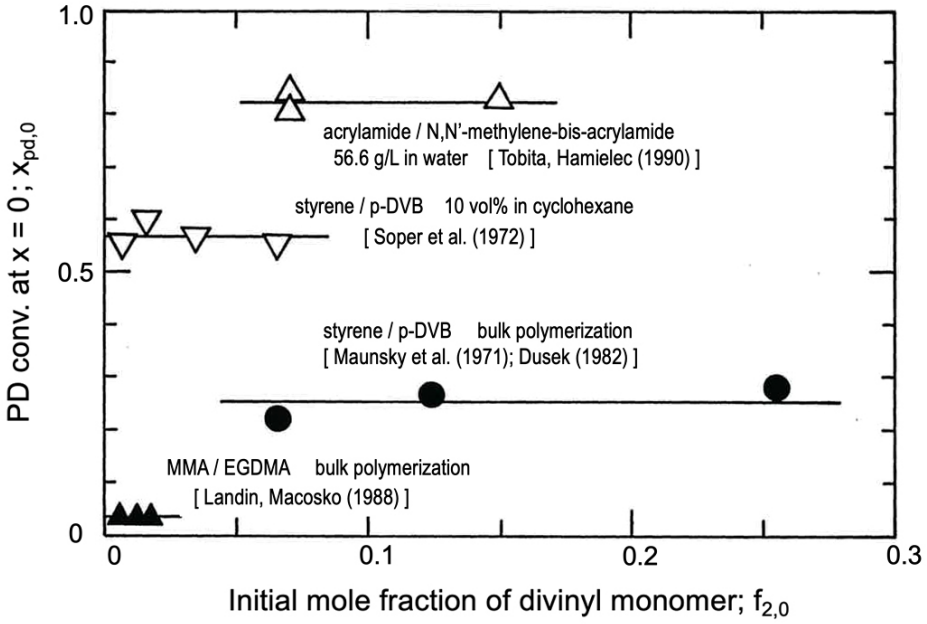

Figure 2 Effect of initial mole fraction of divinyl monomer, $f_{2,0}$ on the pendant double bond conversion at zero monomer conversion.

Figure 3 shows the simulated results of the NDT model for conventional free-radical polymerization (FRP) and ideal living polymerization with the conditions of $f_{2,0}$ = 0.01 and n_{seg} = 5. For FRP, the number-average primary chain length is set to P_{np} = 100. For ideal living polymerization, the number-average primary chain length at x = 1 is R = 200, which means that P_{np} = 100 at x = 0.5. The present simulation results successfully reproduce the unique characteristics that the pendant double bonds are consumed from the start of polymerization in FRP but not in living polymerization. Note that in the CCK model, no PDs are consumed at x = 0 in both FRP and living polymerization [2].

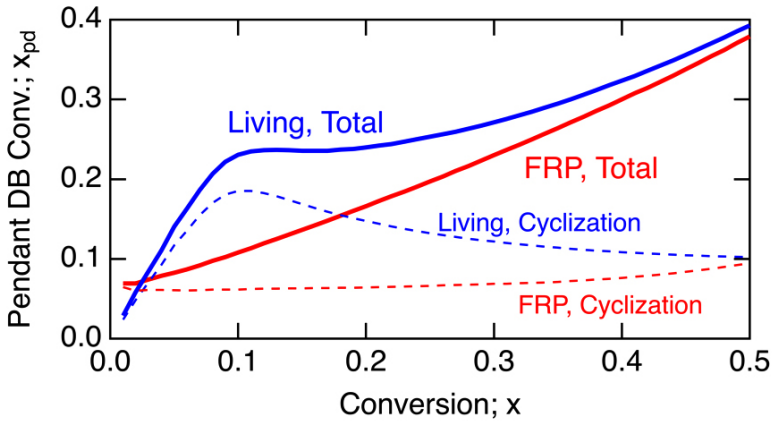

Figure 3 Development of the pendant double bond conversion simulated by using the NDT model.

In the present NDT model, the effect of chain flexibility can be accounted for by the magnitude of n_{seg}, i.e., the number of units that constitute the random flight segment. Basically, the magnitude of n_{seg} would be smaller for flexible chains. Figure 4 shows the effect of n_{seg} on the pendant double bond conversion at x = 0, $x_{pd,0}$ in FRP. The n_{seg}-value used here is for the cyclization reaction in which the instantaneous conformation is important and may not necessarily be equal to the n_{seg}-value at an equilibrium relaxed state. Anyway, however, the magnitude of $x_{pd,0}$ increases by reducing the n_{seg}-value, i.e., for more flexible chains.

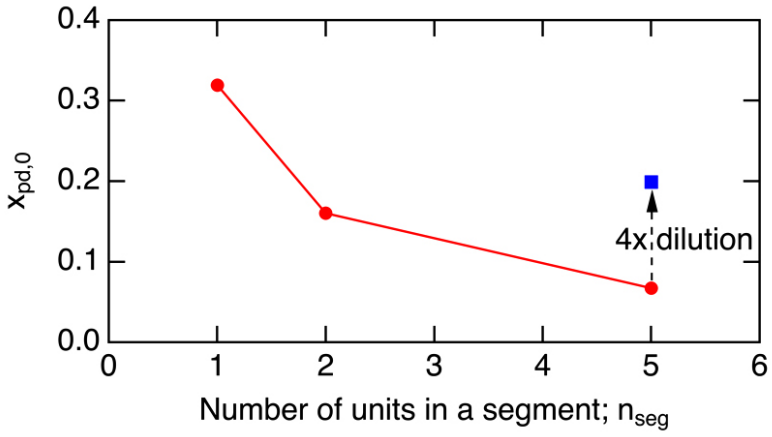

Figure 4 Effect of chain flexibility and dilution by solvent on the pendant double bond conversion at x = 0 in FRP.

The effect of dilution by solvent could be accounted for by making V larger than N_M. Remember that the magnitude of v_e and V are represented by the number of monomeric units in this article. In Figure 4, the case with $V = 4N_M$ is shown, for which N_M = 2×10^5, $f_{2,0}$ = 0.01, n_{seg} = 5, and P_{np} = 100 are used. The $x_{pd,0}$-value increases with dilution, which conforms to the experimental results [11-13].

The published experimental data [10] of miniemulsion polymerization that compare the conventional FRP and the nitroxide-mediated radical polymerization are referred to examine the validity of the present NDT model. In the experiments, miniemulsion copolymerization of n-butyl methacrylate and ethylene glycol dimethacrylate were examined. Since the chemical structure of all types of double bonds is the same, it would be reasonable to assume β = 1. The initial mole fraction of divinyl monomer employed in the experiment was $f_{2,0}$ = 0.0145, which is used for the present simulation method.

In the conventional FRP, the experimental results [10] showed that a clear nanogel molecule is observed in the measured molecular weight distribution (MWD) at conversion as low as 3%. The MWD reported therein is a sharp single peak, and the sharp peak moves toward higher MW as the polymerization proceeds. Similar behavior can be found in the simulation with P_{np} = 1000 and n_{seg} = 5, as shown in Figure 5(a), in which the nanogel peak emerges at x = 0.05, and a sharp peak moves toward higher MW. On the other hand, for the nitroxide-mediated radical polymerization (NMP), the R-value used was 200, and a sharp, high molecular weight peak, which corresponds to the formed nanogels, emerges in the reported MWD profile at x = 0.44, and moves toward larger MW as the polymerization proceeds. In the present simulation, the nanogel peak appears at x = 0.5, and a sharp peak moves toward larger MW with the progress of polymerization, as shown in Figure 5(b). The qualitative behavior is similar to those reported in experiments both for FRP and living polymerization [10]. Note that the MWD profiles at high conversions are narrower than experiments since monodisperse particles are used in the simulation.

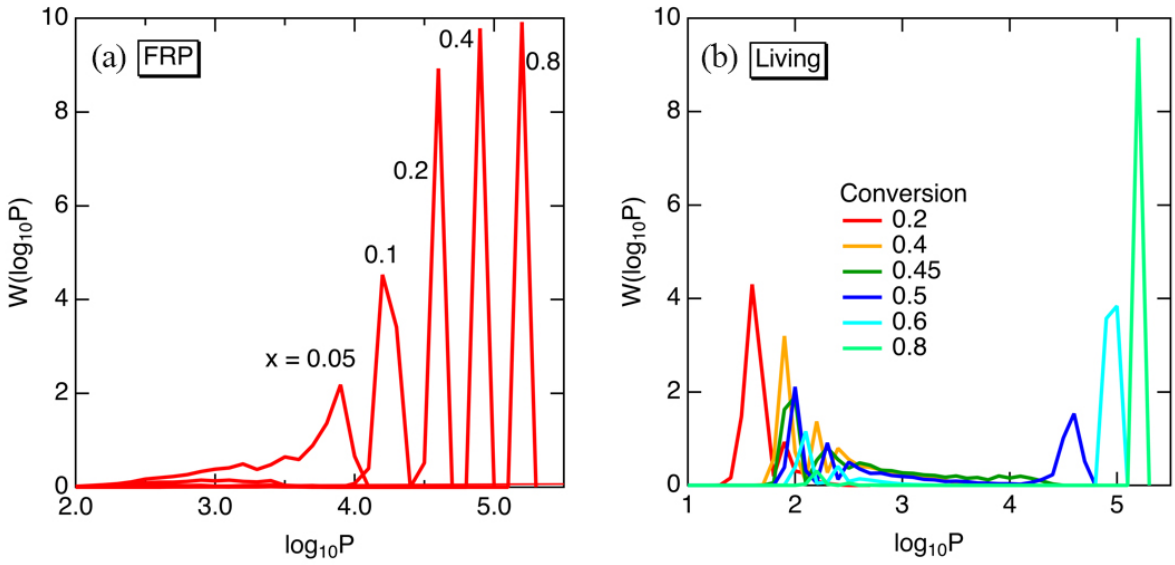

Figure 5 Simulated weight fraction distribution development for (a) FRP and (b) ideal living polymerization that agrees qualitatively with the experimental results [10]. In the figure, P is the chain length, which is the number of monomeric units in a polymer molecule.

To evaluate the spatial dimensions of nonlinear polymers without the effect of molecular weights, the g-ratio of R_g^2 with respect to that, the corresponding linear molecule is commonly used [17].

$$g = \frac{R_g^2}{R_{g,\mathrm{linear}}^2} = \frac{6R_g^2}{n_{\mathrm{s}}} = 6\left(\frac{R_g^2}{D}\right)\left(\frac{D}{n_{\mathrm{s}}}\right) = 6a_r d \tag{12}$$

where n_{s} is the number of segments in the given polymer molecule, and $d = D/n_{\mathrm{s}}$ means the fraction of segments located in the diameter chain. The d-value of the generated network can be determined with a quick calculation, and g can be obtained by using the a_r shown in Equation (2) in a straightforward manner. Note that f = 1 is used for the present calculation.

Figure 6 compares the g-ratios of the network polymers obtained at x = 0.8. The dimensions of the living polymers are larger. The experimental results showed [10] that the swelling ratio is larger for the NMP nanogels rather than the FPR. Although the g-ratio in the unperturbed state is not equivalent to the swelled state, the comparison of dimensions could be correlated, at least qualitatively.

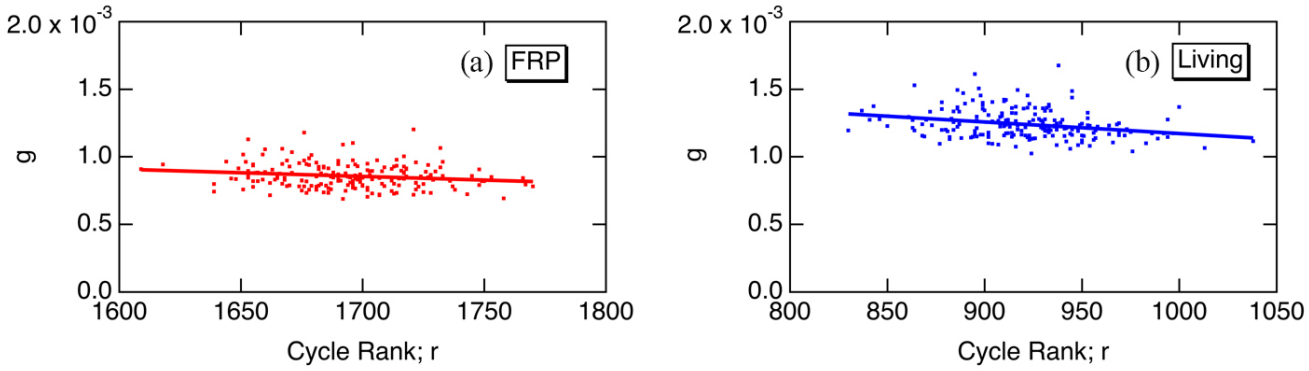

Figure 6 Comparison of dimensions of network polymers obtained at x = 0.8. A total of 200 particles are simulated. The solid line is the regression line.

It is sometimes argued that the dimensions of networks formed by living polymerization are larger than those synthesized by the conventional FRP because the formed network is more homogeneous. On the other hand, however, Figure 7 shows a comparison of g with homogeneous, randomly crosslinked networks whose primary chain length distribution is the same as the living polymerization. It is clearly shown that the g-ratio is larger for the present living polymers whose network architecture is heterogeneous due to the size- and structure-dependent network formation. An important conclusion for the dimensions of statistical network polymers is that, in general, the dimensions of heterogeneous networks are larger than the homogeneous, randomly crosslinked networks [6,8,9]. This is because the dimensions of network polymers are dominated by the loosely crosslinked regions.

Incidentally, as a part of network dimension theory, the relationship between d and r was investigated for various types of statistical networks to find a master curve relationship [8,9], which enables one to make a detailed discussion on how to control the dimensions of network polymers [18].

It was reported [10] that for both NMP and FRP, the radius of gyration decreased as the conversion increased, even though the molecular weights of network polymers became greater with conversion. In the present simulation work, Figure 8 shows the number fraction distribution $N(R_g)$ of the root-mean-square radius of gyration of nanogels obtained at conversion x = 0.6 and 0.8. In the figure, the unit length for R_g is the segment length consisting of 5 monomeric units. The contraction of R_g is clearly shown, and at least qualitatively, the present simulation results agree with the experimentally observed contraction in the later stages of polymerization.

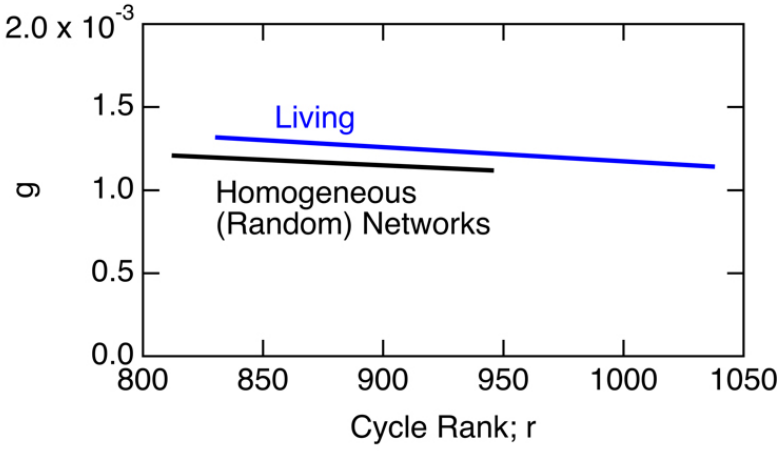

Figure 7 Comparison of g with the homogeneous, randomly crosslinked networks.

Figure 9 compares the ring size distribution, which shows the average number of rings in a nanogel molecule. Note that the approximate particle size of the present simulation is about 40 nm, while those reported in the experiments are about 150 nm [10]. The numbers per nanogel molecule in the experiment would be much larger, but the relative abundance would be the same as the present simulation results. It is worth noting that if the CCK model is used, essentially, no small-sized rings were found [2]. The abundance of small-sized rings is an important characteristic of the NDT model.

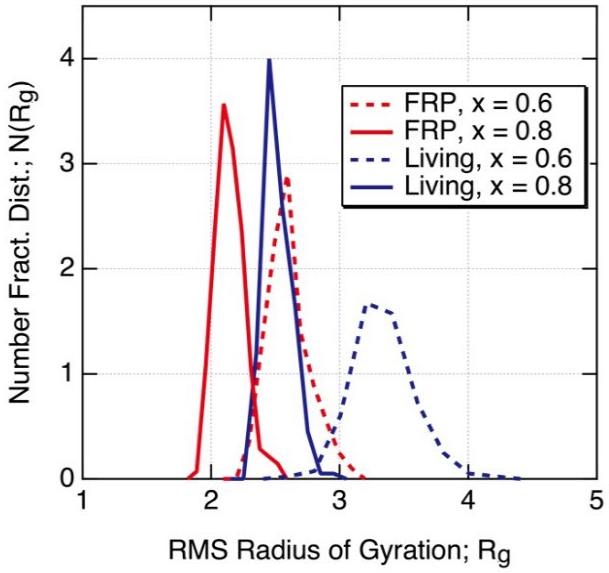

Figure 8 Comparison of the number fraction distribution $N(R_g)$ of the root-mean-square radius of gyration.

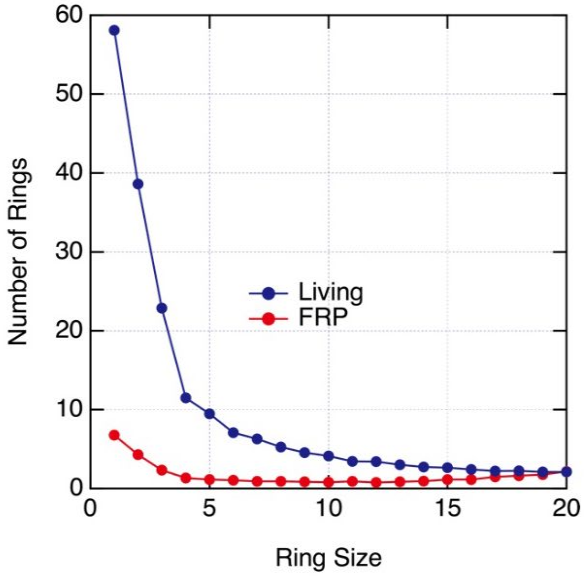

Figure 9 Comparison of the ring size distribution in a nanogel molecule formed at x = 0.8.

The number of small-sized rings is much larger in a living polymer. The small rings are mainly formed at the chain ends, and the living polymer possesses many chain ends due to smaller primary chain lengths. For the FRP, the only detectable small cluster in the experiment may be the ring of size 1. In the present model, such rings are formed when the cyclization reaction is caused by the monomeric units located in the adjacent segments. Because one segment consists of 5 monomeric unis, the characteristic length of such rings might be approximately equal to one segment length, which is about 5×2.5 = 12.5 Å in the present simulation. For an FRP, the experiment [10] found the clusters having a size of 9.5 Å, connected by long portions. Because the average number of such clusters in a nanogel molecule in the present simulation is less than 10, the average length between the clusters is expected to be large.

For the living polymers, Figure 9 shows that a much larger number of rings having n_s < 5 are formed. In the experiment [10], the clusters having a size of 16 Å are formed in the NMP, which may correspond to these small rings. Because the total number of such small rings is large, the average distance between the rings would be smaller than the FRP nanogels.

It was reported [10] that the structure of nanogels synthesized by miniemulsion NMP consists of "relatively open domains connected by relatively short chains segments", whereas that of FRP is formed by "densely crosslinked structures connected by long chain portions". It is not clear whether the small rings observed in the present simulation results actually correspond to "open domains" and "densely crosslinked structures" in the above description. However, the present simulation shows the possibility of forming such heterogeneous structures by the rings.

4. Conclusion

The network dimension theory developed recently enables one to quickly estimate the root-mean-square radius of gyration R_g, based on the calculation of graph diameter D. A new model that accounts for the concentration enrichment effect of pendant double bonds located on its own polymer molecule during vinyl/divinyl copolymerization is proposed. The model is applied to the miniemulsion copolymerization, and both conventional free-radical polymerization and ideal living polymerization are investigated. A well-known difference between these two types of network formation is that the pendant double bonds are consumed from the beginning of polymerization in conventional free-radical polymerization but not so in living polymerization. The present model can reproduce such differences successfully.

The published experimental data [10] on the structural development of network architecture in miniemulsion nitroxide-mediated radical polymerization and conventional free-radical polymerization are used to compare with the present model. The model agrees, at least qualitatively, with the experimental findings. The present model provides valuable insights into the size- and structure-dependent network formation kinetics and promises to develop more realistic models for complex gelation phenomena.

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