

Cite this: DOI: 00.0000/xxxxxxxxxx

Comparison of gels synthesized by controlled radical copolymerization and free radical copolymerization: molecular dynamics simulation[†]

Tsutomu Furuya* and Tsuyoshi Koga*

Received Date

Accepted Date

DOI: 00.0000/xxxxxxxxxx

The structures of gels synthesized by controlled radical copolymerization (CRP) and conventional free radical copolymerization (FRP) were studied by a coarse-grained molecular dynamics simulation. It was confirmed that the CRP gel has a larger number of elastically effective chains and fewer cyclic structures and entanglements than the FRP gel, *i.e.*, the network structure of the CRP gel is more uniform than that of the FRP gel. However, the difference in the shear modulus between the two gels was small due to the opposing changes in the number of elastically effective chains and that of entanglements. The relatively uniform structure of the CRP gel is attributed to the suppression of intramolecular cross-linking by the fast initiation and slow propagation, and the development of cross-linked structures in the post-gel region due to the limited termination. The effects of these CRP characteristics were studied in detail. From the results, it was found that all of these characteristics of CRP cooperatively act to improve the homogeneity of the structure of the CRP gel.

1 Introduction

Polymer gels, in which three-dimensional cross-linked network polymers retain large quantities of solvent molecules, are important materials used in many applications.^{1–3} Free radical polymerization (FRP) of monomers in the presence of cross-linkers is widely used as an industrial method for producing polymer gels,^{1,2,4,5} because it can be carried out under mild conditions with a wide variety of monomers. However, in conventional FRP, since the growth and cross-linking of polymers heterogeneously proceed at the same time due to the slow initiation and fast propagation, the control of the network structure of the obtained gel is difficult.^{4–6}

In order to control the structure of gels synthesized by radical polymerization, many studies using controlled radical polymerization (CRP) have been actively conducted.^{7–17} These studies have shown that CRP gels have a more uniform structure than FRP gels. For example, in CRP, gelation uniformly proceeds without the heterogeneous formation of microgels commonly observed in FRP,^{8,9,11} and the gelation points of CRP systems are closer to the theoretical values,^{18,19} which are calculated assuming an ideal structure, than those of FRP systems.^{7,8,10,14} Analysis

of the gelation process and the spatial inhomogeneity of gels using dynamic light scattering also indicated that CRP gels are more homogeneous than FRP gels.^{9,15,16} CRP gels exhibit high transparency^{13,15} and improved toughness^{14–16} and swelling properties^{12,14–16} due to the relatively uniform structure. In CRP, polymers uniformly grow with conformational relaxation because of the fast initiation and slow propagation of CRP. The uniform structure of CRP gels is considered to be attributed to the uniform polymer growth, which suppresses the formation of cyclic structures by intramolecular cross-linking. However, some experiments reported that there was no significant difference between the structure of CRP gels and that of FRP gels.^{20–22} Therefore, we think that a further careful analysis is necessary to understand the formation mechanism of the uniform structure of CRP gels.

Various simulations have been performed to investigate the structure formation mechanism of CRP gels at the molecular level.^{23–29} This is because it is difficult to experimentally or theoretically clarify the time evolution of the detailed structure of gels. A series of studies of Matyjaszewski's group have reported the effects of the initial composition on the gelation point and the molecular mechanisms of gelation.^{23–26} The simulated gelation points showed good agreement with the experimental results, and increasing the cross-linker content or the solute concentration increases the number of intermolecular cross-links and promotes gelation. They also revealed that not only the ratio of intramolecular to intermolecular cross-links but also the changes in the reactivity of monomers and cross-linkers due to spatial constraints affect the gelation point.^{26,29} In addition, practical prob-

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan. E-mail: furuya.tsutomu.4a@kyoto-u.ac.jp, koga.tsuyoshi.6m@kyoto-u.ac.jp

[†] Electronic Supplementary Information (ESI) available: the details of the simulation method and the supplementary data of the simulation. See DOI: 00.0000/00000000.

lems such as the repair mechanism of severed gels utilizing the living property of CRP have been computationally studied.²⁸ For the structural change by varying the synthesis method from FRP to CRP, the decrease in the polydispersity index of the molecular weight between cross-linking points, *i.e.*, the homogenization of the cross-linked structure has been reported by a kinetic Monte Carlo simulation.²⁷ However, there are not many simulations that systematically compare FRP gels and CRP gels.

In this study, we aim to understand the molecular mechanism by which a more uniform structure is formed in CRP gels than in FRP gels. We systematically compare the structural formation process, network structure, and mechanical properties of CRP gels and FRP gels using a coarse-grained molecular dynamics (CGMD) simulation. Furthermore, we examine the effects of each of the CRP characteristics: the fast initiation, slow propagation, and suppressed termination. We conduct the calculations using the model systems in which one of the CRP characteristics is introduced into FRP, and compare the structures of the gels obtained by these model systems and CRP. We think that these results provide important information for understanding the factors that control the structure of gels synthesized by radical polymerization.

2 Simulation Model

In this study, the CRP system contains monomers, cross-linkers, and initial dormant species represented by a bead-spring model^{30–33} at the initial stage (Fig. 1a). The monomer and the initial dormant species are modeled with a single bead. The cross-linker consists of three beads, the beads at both ends are functional beads with the same reactivity as the monomer, and the central bead is an inactive bead. The polymers are formed by stochastic reaction models^{28,33–36} during the CGMD simulation.

The CRP is assumed to consist of the reversible activation, propagation, and termination (Fig. 2a–c). Assuming that the reversible activation is always in equilibrium, we set the probability that a propagating end is a radical at time t to P_a and the probability that a propagating end is a dormant species to $1 - P_a$. The CRP is initiated when the initial dormant species become the radicals. The propagation proceeds with probability p_p when the distance r between a radical and a functional bead (unreacted monomer or unreacted end of a cross-linker) becomes less than or equal to r_c . Here, r_c is the cut-off radius of the reactions. The propagation forms a new bond between the radical and the functional bead, and transforms the radical and the functional bead into an inert bead and a propagating end, respectively. The termination proceeds with probability p_t between a pair of radicals with a distance $r \leq r_c$, both radicals involved in the termination then change to inert beads. We set the probability that the termination proceeds as the combination and the probability that the termination proceeds as the disproportionation to $p_t^{(c)}$ and $p_t^{(d)} = 1 - p_t^{(c)}$, respectively. When the combination occurs, a new bond is formed between the beads. The detailed calculation method of the CRP is shown in the ESI†.

The FRP system contains monomers, cross-linkers, and initiators consisting of two beads (Fig. 1b), and the FRP consists of the initiation, propagation, and termination (Fig. 2b–d). The FRP is

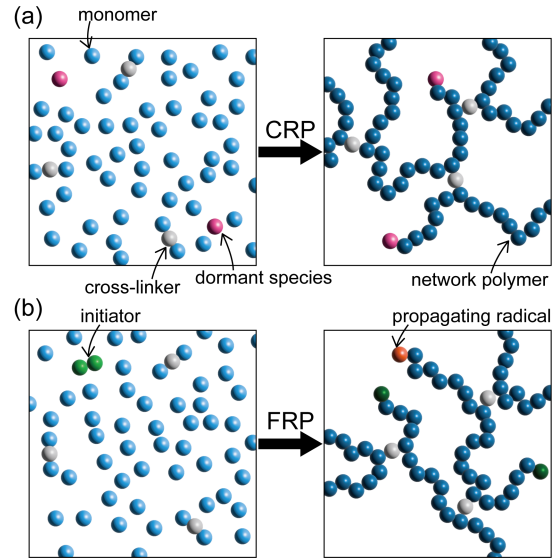


Fig. 1 Schematic illustration of network formation by (a) controlled radical copolymerization (CRP) and (b) conventional free radical copolymerization (FRP).

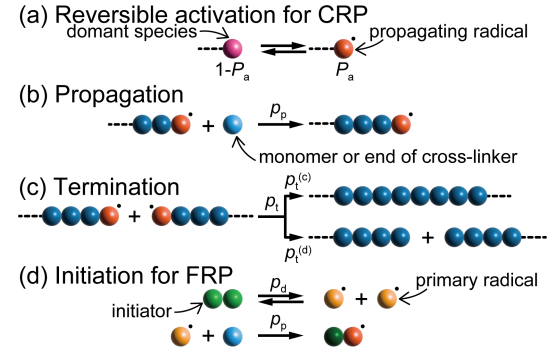


Fig. 2 Elemental reactions in the radical polymerization model.

initiated when the initiators decompose with probability p_d and change to the primary radicals. The propagation and termination proceed in the same manner as in the CRP. However, we assumed that the decomposition of the initiator is reversible, *i.e.*, a pair of primary radicals become an initiator by the combination, when they come into contact with each other. The detailed calculation method of the FRP is shown in the previous study.³³

In order to change the CRP-like properties, the following three values were used for the activation probability P_a : $P_a = 0.1$, 0.02 , and 0.01 . The equilibrium of the reversible activation is usually biased toward the left side in Fig. 2a,^{37,38} therefore, we think that the smaller P_a is, the higher the CRP-like properties are. Since P_a in real CRPs is estimated to *ca.* 1×10^{-5} from the literature,³⁷ the effects of the CRP-like properties of real CRPs are thought to be greater than those in the simulation.

In this study, unless otherwise noted, the reaction probabilities p_d , p_p , and p_t were set to $p_d = 1 \times 10^{-7}$, $p_p = 0.5$, and $p_t = 1$, respectively. These probabilities were adjusted in the previous study³³ so that the FRP simulation reproduces some features of the kinetics of FRP³⁸ (Section S2.1 in the ESI†). We have confirmed that the CRP simulation also reproduces some features of

the kinetics of CRP^{37,38} (Fig. S2†). Although the termination in the FRP simulation is slower than that in real FRPs, we focused on the slow initiation and fast propagation of FRP, and used the above probabilities to avoid unrealistically long calculation times. The probabilities of the combination and the disproportionation were set to $p_t^{(c)} = 0$ and $p_t^{(d)} = 1$, respectively, with reference to the experimental results of polyacrylamide systems, in which the termination was reported to be mainly the disproportionation.³⁹

We here explain the differences between the CRP model and the FRP model. In the CRP, since the dormant species are placed at the initial stage, uniform polymerization immediately begin. However, the propagation is slow and the termination is significantly suppressed, because most of the propagating ends are the dormant species due to the reversible activation. In the FRP, the initiation, which depends on the stochastic initiator decomposition, is slow and heterogeneous. Once polymerization starts, the propagation and termination rapidly proceed, because all the propagating ends are the radicals.

We used the following interactions between beads. The Weeks–Chandler–Andersen (WCA) potential⁴⁰ was used for the non-bonded interactions between the beads: $U_{nb}(r_{ij}) = 4\epsilon_{wca}[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6 + 1/4]$ for $r_{ij} \leq 2^{1/6}\sigma$, where r_{ij} is the distance between the i -th and j -th beads; ϵ_{wca} is the potential strength; and σ is the collision diameter. In this simulation, ϵ_{wca} , σ , $\tau \equiv \sigma\sqrt{m/\epsilon_{wca}}$, ϵ_{wca}/k_B , and m are used as units of energy, length, time, temperature, and mass, respectively. Here, k_B is the Boltzmann constant and m is the mass of one bead. Using this unit system, we set the cut-off radius r_c to $r_c = \sigma$, and fixed the temperature T at $T = \epsilon_{wca}/k_B$. In addition to the WCA potential, we introduced the finitely extensible non-linear elastic (FENE) potential⁴¹ into the interactions between the bound beads: $U_b(r_{ij}) = -(1/2)k_b r_0^2 \ln[1 - (r_{ij}/r_0)^2]$. In order to prevent the crossing of the polymers, the spring constant k_b was set to $k_b = 30\epsilon_{wca}/\sigma^2$ and the maximum bond length r_0 was set to $r_0 = 1.5\sigma$.^{30–32} A cosine harmonic potential was applied to the bond angles of the cross-linkers to prohibit bonding between the ends of the same cross-linker: $U_\theta(\theta_i) = (1/2)k_\theta(\cos\theta_i - \cos\theta_0)^2$. Here, θ_i is the angle between the two bonds of the i -th cross-linker; $k_\theta = 100\epsilon_{wca}$ is the spring constant; and $\theta_0 = \pi$ is the equilibrium bond angle.

Using the above potentials, the motion of each bead was calculated by integrating the following Langevin equations by the velocity Verlet method⁴² with timestep $\Delta t = 5 \times 10^{-3}\tau$:

$$m \frac{d^2 \mathbf{r}_i(t)}{dt^2} = \mathbf{F}_i(t) - m\zeta \frac{d\mathbf{r}_i(t)}{dt} + \mathbf{W}_i(t), \quad (1)$$

where $\mathbf{r}_i(t)$ is the position vector of the i -th bead at time t ; $\mathbf{F}_i(t)$ is the force acting on the i -th bead at t ; $\zeta = 0.5/\tau$ is the friction coefficient; and $\mathbf{W}_i(t)$ is the random force acting on the i -th bead at t satisfying $\langle \mathbf{W}_i(t) \rangle = 0$ and $\langle \mathbf{W}_i(t) \cdot \mathbf{W}_j(t') \rangle = 6m\zeta k_B T \delta_{ij} \delta(t - t')$.

The simulation of the network formation was performed according to the following procedure. We first placed n_m monomers, n_x cross-linkers, n_{p-x} dormant species, and n_i initiators at random in the cubic simulation box with periodic boundary conditions. Here, $n_i = 0$ for the CRP, and $n_{p-x} = 0$ for the FRP. The molecules were homogeneously mixed by the simulation of $t = 5 \times 10^2 \tau$ with-

out processing the reactions. The simulation was then conducted until the monomer conversion α reached a target value while calculating the reaction process at each time step. We here note that the conversion α_x of the functional group of the cross-linker is lower than α , but there is no difference in α_x between the FRP gel and the CRP gel (Fig. S5†). We fixed the numbers n_m and n_x of monomers and cross-linkers at $n_m = 1 \times 10^5$ and $n_x = 2650$, respectively. We adjusted n_{p-x} in the CRP and n_i in the FRP so that the number average molecular weights $M_{n,p}$ of the primary chains in the corresponding systems were almost equal, because the network structure and physical properties significantly depend on $M_{n,p}$.⁴³ Here, the primary chains are the polymers obtained by the scission of the cross-linkers in the network. The volume V of the simulation box was set so that the monomer volume fraction $\phi_m = n_m \sigma^3 \pi / 6V$ was $\phi_m = 0.1$. The detailed simulation conditions are shown in Table S1†.

In this study, we performed ten independent runs for all conditions, and used the average value for each condition as the simulation result.

3 Results and Discussion

3.1 Comparison of CRP gel and FRP gel

We first present the results of well-developed gels with the monomer conversion $\alpha = 95\%$. Fig. 3 shows the number density v_x of elastically effective chains formed by cross-linking, the number density v_{le} of elastically effective chains generated by entanglements trapped in the network, and the shear modulus G for the FRP gel and the CRP gels with varying the activation probability P_a . Here, in order to obtain the networks with the number average molecular weight $M_{n,p}$ of the primary chains of *ca.* 1.0×10^3 , the initial initiator concentration $[I]_0$ for the FRP gel and the initial dormant species concentration $[P-X]_0$ for the CRP gels were set to $[I]_0 \simeq 6.7 \times 10^{-4}$ ($n_i = 350$) and $[P-X]_0 \simeq 1.9 \times 10^{-4}$ ($n_{p-x} = 100$), respectively. These $[I]_0$ and $[P-X]_0$ correspond to 0.35 mol% and 0.1 mol% based on monomers, respectively, which are close to the reported experimental concentrations.^{8,9,12,15} We measured v_x using the Scanlan–Case criterion^{44,45}. As shown in the ESI†, v_{le} was calculated with reference to Langley’s criterion⁴⁶ after the analysis of entanglement by the method of Everaers *et al.*⁴⁷ The shear modulus G was calculated by the simulation in which the uniaxial deformation was applied to the network. Specific calculations were performed in the same way as in the previous study.³³ The error bars in the figures represent 95% confidence interval.

As seen in Fig. 3, by changing the gel synthesis method from the FRP to the CRP, v_x increases, and v_{le} decreases. The decrease in P_a , *i.e.*, the enhancement in the CRP-like properties increases the difference between the structure of the CRP gel and that of the FRP gel. However, under the conditions shown in Fig. 3, G hardly changes. This is thought to be due to the cancellation of the effects of the increasing v_x and decreasing v_{le} .

In order to analyze the local cross-linked structure in detail, we depict the result of classifying network strands, which are polymer chains connecting adjacent cross-linking points, into bridges, loops, and dangling ends (Fig. 4). By changing the synthesis

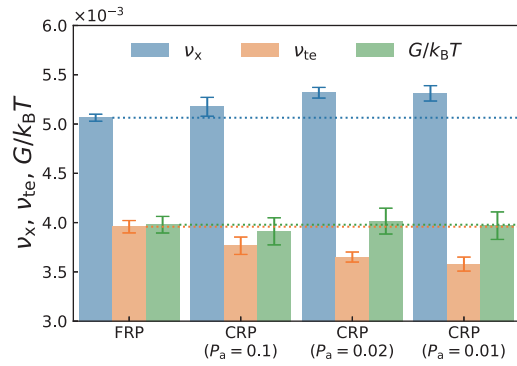


Fig. 3 Number density ν_x of the elastically effective chains formed by cross-linking, number density ν_{te} of the elastically effective chains generated by the trapped entanglements, and shear modulus G of gels with $M_{n,p} \simeq 1.0 \times 10^3$. The monomer conversion is $\alpha = 95\%$. Dotted lines indicate the average values of the FRP gel.

method from the FRP to the CRP and decreasing P_a , the number of bridges increases, and the number of loops decreases. Since $M_{n,p}$ is almost the same in all the gels, the number of dangling ends rarely varies.⁴³ The differences in the cross-linked structure between the gels with almost the same composition are caused by kinetic effects.³³ The increase in ν_x due to the change in the synthesis method from the FRP to the CRP is attributed to the change of the network strands from the loop, which is a defect in the cross-linked structure, into the bridge.

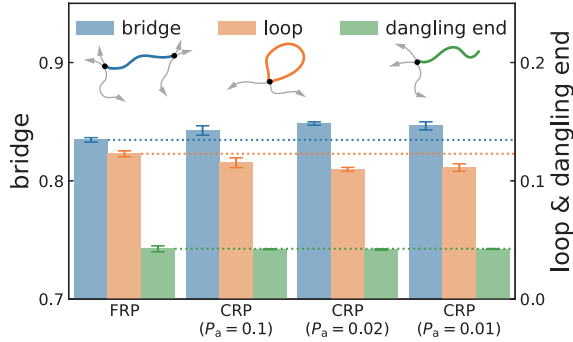


Fig. 4 Relative populations of bridges, loops, and dangling ends in gels with $M_{n,p} \simeq 1.0 \times 10^3$. The monomer conversion is $\alpha = 95\%$. Dotted lines indicate the average values of the FRP gel.

From the results in Figs. 3 and 4, we find that the CRP gels have the relatively uniform network structures compared to the FRP gel as reported in the experimental studies.^{7–17} We have confirmed that ν_x and the number of bridges increase, and ν_{te} and the number of loops decrease, by changing the synthesis method from the FRP to the CRP and decreasing P_a , even in the gels with different $M_{n,p}$ (Fig. S6†). Although the trend of the change in G appears to depend on $M_{n,p}$, the change in G is small and can be explained by the number of elastically effective chains formed by cross-linking and the trapped entanglements. (Fig. S7†). In addition, we have confirmed that the same results as in this study are obtained even when the termination is mainly the combination, i.e., $p_t^{(c)} = 1$ and $p_t^{(d)} = 0$ (Fig. S8†).

In order to elucidate the homogenization mechanisms of the network structure by changing the synthesis method, the structural analysis results of clusters formed during the network formation process of the FRP gel and the CRP gel with $P_a = 0.01$ are shown in Fig. 5. Here, $\varepsilon \equiv \alpha - \alpha^*$ is the distance from the gelation conversion α^* ; M_n and M_w are the number average molecular weight and weight average molecular weight of clusters formed in the sol fraction, respectively; and ν_p is the number density of clusters in the sol fraction. In this study, we regard the minimum conversion α at which a cluster connects to images in adjacent simulation boxes in all three directions as the gelation conversion α^* .^{48,49} Although M_n and M_w in the FRP are larger than those in the CRP in the low ε region, in both systems, M_n and M_w show the maximum values near the gelation point ($\varepsilon \simeq 0$) and then decrease (Fig. 5a). The behavior of ν_p and the cross-linked structures of the network strands are greatly changed by changing the synthesis method (Figs. 5b and 5c). In the FRP, ν_p and the cross-linked structures only show slight changes around the gelation point, whereas in the CRP, ν_p and the number of dangling ends significantly decrease with gelation, and the number of bridges greatly increases.

The differences in the behavior of ν_p and the cross-linked structures of the strands between the FRP and the CRP are due to the difference in the gelation mechanism. As shown in Fig. 6a, in the CRP, a large number of sparsely cross-linked clusters, i.e., branched polymers are first formed by the fast and uniform initiation and slow propagation. The gelation of the CRP system occurs by intermolecular cross-linking of such branched polymers. On the other hand, in the FRP (Fig. 6b), a small number of densely cross-linked clusters (hereafter, we call it “microgel”) are formed in the pre-gel region due to the slow and heterogeneous initiation and fast propagation. The gels spanning the simulation box are formed by cross-linking between such microgels. Due to the microgel formation, M_n and M_w of the FRP exhibit large values even in the low ε region (Fig. 5a).

The density fluctuations generated during the network formation process also change depending on the difference in the gelation mechanism. Fig. 7 shows the structure factor $S(q)$ at various ε . The detailed calculation method of $S(q)$ is shown in the ESI†. In the CRP, although the strength in the wide-angle region gradually rises with the progress of the polymerization, the strength in the small-angle region is almost constant. In contrast, in the FRP, since the heterogeneous microgel formation generates long-period density fluctuations, the strength in the small angle region significantly increases before gelation and decreases in the post-gel region. We here note that the strength in the small angle region of the FRP gel is higher than that of the CRP gel even in the post-gel region (Fig. 10d). The occurrence of entanglement is considered to be promoted in the high-density regions caused by the large density fluctuations; hence, the number density ν_{te} of the elastically effective chains generated by the trapped entanglements of the FRP gels indicates a high value. We have confirmed that, even in the pre-gel region, the number of entanglements in the FRP is larger than that in the CRP (Fig. S9†).

The differences between the CRP and the FRP also affect the manner of cross-linking in the network formation process. Fig. 8

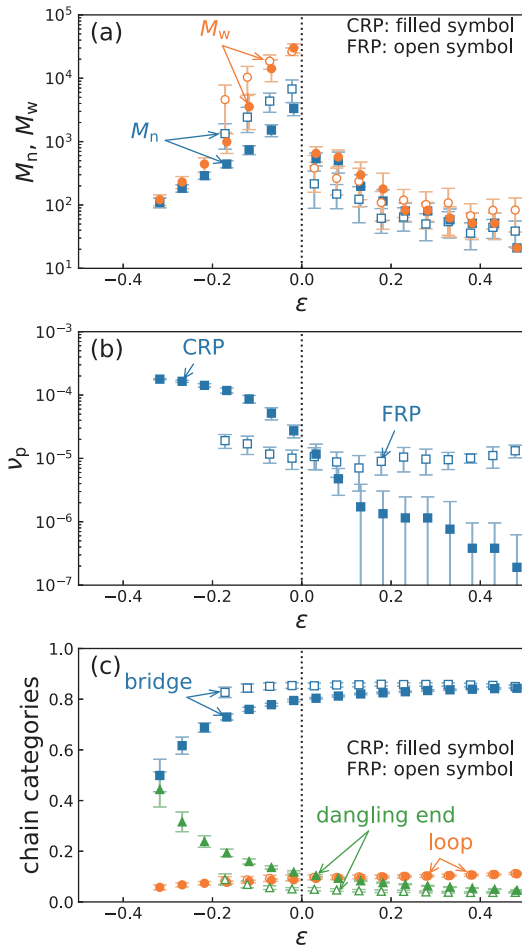


Fig. 5 Structural changes of clusters during the network formation process by the FRP and the CRP with $P_a = 0.01$. (a) Number average molecular weight M_n and weight average molecular weight M_w of clusters in the sol fraction. (b) Number density ν_p of clusters in the sol fraction. (c) Relative populations of bridges, loops, and dangling ends in clusters. $M_{n,p} \simeq 1.0 \times 10^3$ at $\alpha = 95\%$.

presents the ratios $\xi_{\text{inter}} \equiv \mu_{\text{inter}}/\mu_{\text{total}}$ and $\xi_{\text{intra}} \equiv \mu_{\text{intra}}/\mu_{\text{total}}$ of the number of intermolecular cross-linking points and the number of intramolecular cross-linking points to the number of all cross-linking points. Here, μ_{total} , μ_{inter} , and μ_{intra} are the number densities of all the cross-linkers incorporated in the polymers, the cross-linkers cross-linking different primary chains, and the cross-linkers both ends of which are bound to the same primary chain, respectively. In the CRP with the uniform and fast initiation, the probability of the intermolecular cross-linking is high because there are many primary chains before gelation. The intramolecular cross-linking occurs more easily in the FRP than in the CRP due to the heterogeneous and rapid polymer growth in the FRP. Thus, the CRP exhibits larger ξ_{inter} and smaller ξ_{intra} in the pre-gel region than the FRP. Since the intramolecular cross-linking reduces the spatial size of the primary chain, we think that high ξ_{intra} of the FRP also contributes to the enhancement of the density fluctuations. Furthermore, in the post-gel region, ξ_{inter} of the CRP increases faster than that of the FRP. From these results, we consider that the CRP gel can significantly develop

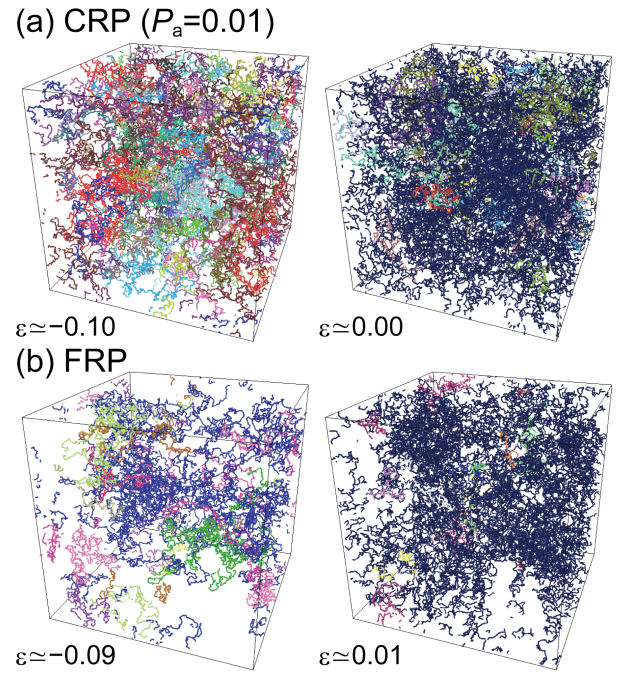


Fig. 6 Structures of clusters formed by (a) the CRP with $P_a = 0.01$ and (b) the FRP at each distance ε from the gelation conversion. Different clusters are shown in different colors.

cross-linked structure even in the post-gel region due to the suppressed termination. The relatively high number density ν_x of the elastically effective chains formed by cross-linking of the CRP gel is attributed to the high ξ_{inter} in the pre- and post-gel regions.

3.2 Effects of Characteristics of CRP on Network Structure

In this section, we discuss in detail the effects of each characteristic of CRP. We here perform the calculations using the following three model systems in which one characteristic of CRP is introduced into the FRP: FRPfi, FRPsp, and FRPwot. FRPfi is a system with a fast initiation, in which the decomposition probability p_d of the initiator is set to $p_d = 1$. For FRPsp, the propagation probability p_p is set to $p_p = 0.025$, and the propagation rate is slower than that of the CRP with $P_a = 0.01$ (Fig. S10a†). FRPwot is a system without terminations, of which the termination probability p_t is equal to zero. The reaction probabilities of each model system other than the reaction probabilities specified here are the same as the basic FRP. Although the molecular weight distribution of the primary chains differs between the CRP gel and the FRP gel, we have confirmed that the difference in the molecular weight distribution does not significantly affect the network structure.⁴³

We plot the number density ν_{e} of the elastically effective chains generated by the trapped entanglements against the number density ν_x of the elastically effective chains formed by cross-linking for well-developed gels with $\alpha = 95\%$ (Fig. 9). Here, the data for each system shows the results with varying the number average molecular weight $M_{n,p}$ of the primary chains by changing the initial initiator concentration $[I]_0$ or the initial dormant species concentration $[P-X]_0$. The shift of the data in the lower right direction in Fig. 9 indicates a decrease in the number of defects

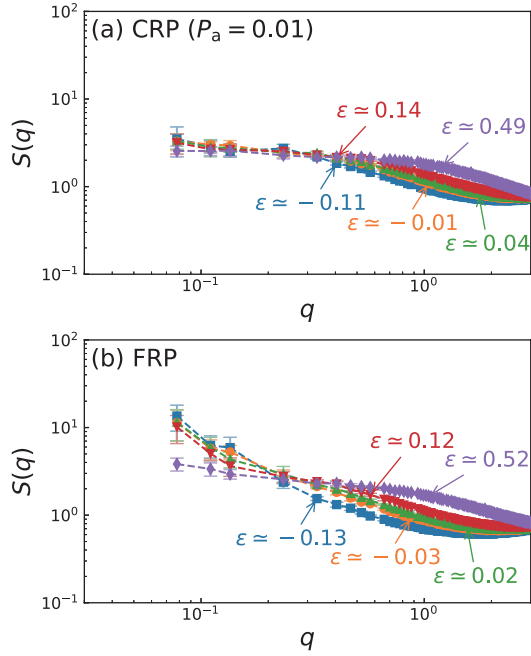


Fig. 7 Structure factors $S(q)$ at each distance ε from the gelation conversion of (a) the CRP ($P_a = 0.01$) system and (b) the FRP system.

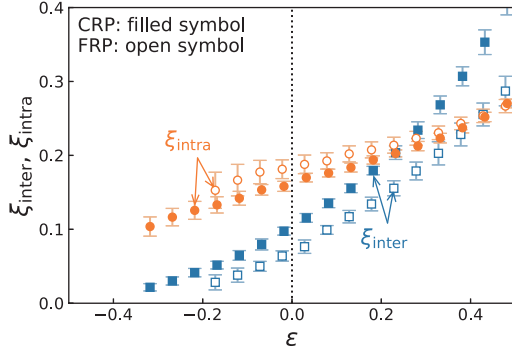


Fig. 8 Proportions ξ_{inter} and ξ_{intra} of the intermolecular cross-links and the intramolecular cross-links in the clusters formed by the CRP with $P_a = 0.01$ and the FRP.

such as the loops and entanglements, *i.e.*, the homogenization of the network structure. As discussed in the previous section, since the density fluctuations are related to the cross-linked structures and entanglements, the results regarding density fluctuations (Fig. 10d), which are spatial inhomogeneities, are consistent with the trends in Fig. 9.

In Fig. 9, the results of the FRPfi gel and the FRPwot gel almost overlap with the basic FRP gel, whereas the data of the FRPsp gel is shifted to the lower right. Therefore, we find that the slow propagation independently homogenizes the network structure, but the fast initiation or the prohibition of the termination alone does not improve the homogeneity of the structure. However, the FRPsp gels have more heterogeneous structures than the CRP gels, although the polymerization rate of FRPsp is slower than that of the CRP with $P_a = 0.01$. In addition, the results in the previous section suggest the effects of the fast initiation and the

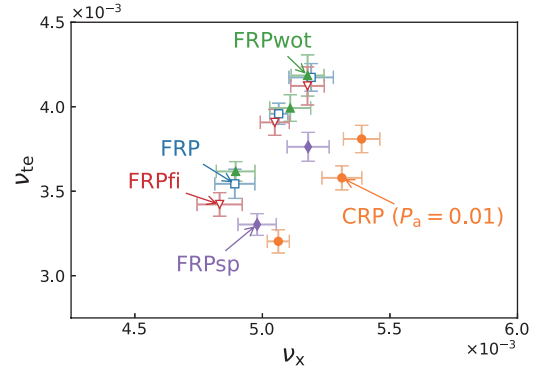


Fig. 9 Number density ν_{te} of the elastically effective chains generated by the trapped entanglements plotted against the number density ν_x of the elastically effective chains formed by cross-linking. The monomer conversion is $\alpha = 95\%$.

suppressed termination on the network structure. Therefore, we next conduct more detailed analyses for each system.

Fig. 10 shows the number density ν_p of clusters in the sol fraction, the ratios ξ_{inter} and ξ_{intra} of the intermolecular and intramolecular cross-linking points, and the maximum intensity S_{max} of the structure factor $S(q)$, which is the intensity at the minimum q , as functions of the distance ε from the gelation point. In Fig. 10, the initial initiator concentration $[I]_0$ for each model system is set as follows so that $M_{n,p}$ becomes *ca.* 1.0×10^3 at $\alpha = 95\%$: $[I]_0 \approx 9.5 \times 10^{-5}$ ($n_i = 50$) for FRPfi, $[I]_0 \approx 1.4 \times 10^{-4}$ ($n_i = 75$) for FRPsp, and $[I]_0 \approx 1.1 \times 10^{-3}$ ($n_i = 550$) for FRPwot. The snapshots of the network formation process and the cross-linked structures of the network strands are shown in the ESI.†

As seen in Figs. 10b and 10c, ξ_{intra} of FRPsp is smaller than that of the FRP, while ξ_{inter} of FRPsp is almost equal to that of the FRP. Therefore, the occurrence of the intramolecular cross-linking is suppressed by slowing down the propagation rate. In the FRP, since the propagation is fast and diffusion-controlled (Fig. S10b†), the propagating ends have a high probability to react with nearby beads. After one end of a cross-linker is incorporated into a polymer, the propagating end of the polymer has a high probability to react with the other end of the cross-linker, *i.e.*, form an intramolecular cross-link. On the other hand, in FRPsp, the propagating ends can react with a wide range of beads due to the slow propagation which is not diffusion-controlled (Fig. S10b†); hence, the probability of forming intramolecular cross-links reduces.

We find that the density fluctuations formed in the network formation process of the FRPsp gel are smaller than those of the FRP gel, because S_{max} of FRPsp indicates smaller values than that of the FRP (Fig. 10d). The small density fluctuations in FRPsp are considered to be due to the decrease in the number of intramolecular cross-links. In FRPsp, the occurrence of entanglement, which is considered to be promoted in high-density regions, is suppressed due to the small density fluctuations. However, ν_p of FRPsp almost overlaps with that of the FRP (Fig. 10a), *i.e.*, the gelation in FRPsp occurs by cross-linking between heterogeneously formed microgels. The development of cross-linked struc-

tures in the post-gel region is inhibited by the termination. Therefore, the structure of the FRPsp gel is more heterogeneous than that of the CRP gel.

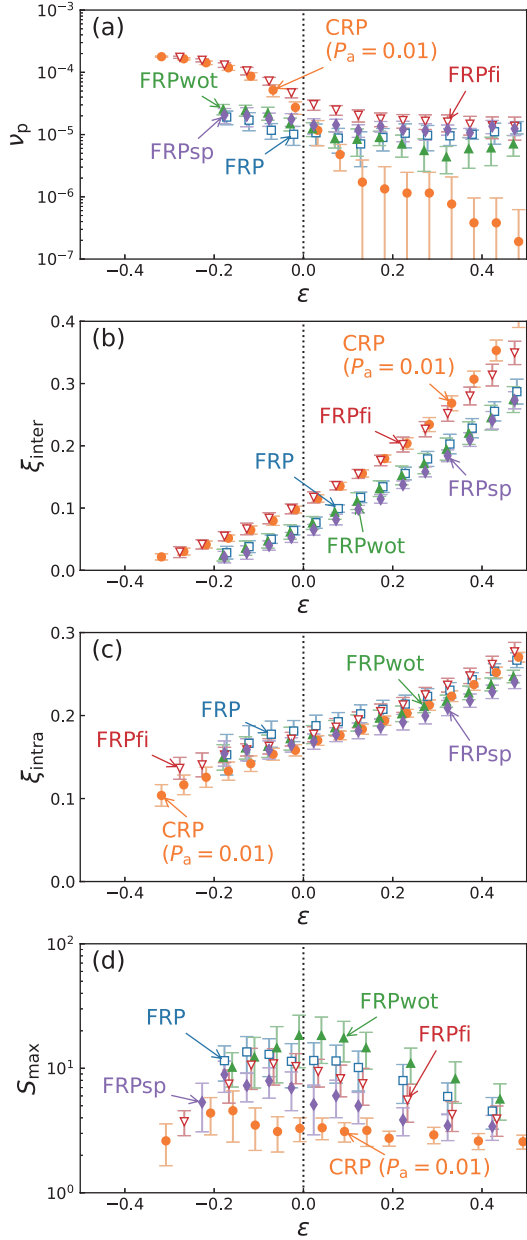


Fig. 10 (a) Number density ν_p of clusters in the sol fraction, (b) proportion ξ_{inter} of the intermolecular cross-links, (c) proportion ξ_{intra} of the intramolecular cross-links, and (d) maximum intensity S_{max} of the structure factor $S(q)$. $M_{n,p} \simeq 1.0 \times 10^3$ at $\alpha = 95\%$.

Similar to the CRP, FRPfi with the fast initiation shows a sharp drop in ν_p around the gelation point; thus, the gelation of FRPfi is caused by cross-linking between branched polymers (Fig. 10a). In the pre-gel region, due to the gelation mechanism of cross-linking between branched polymers, FRPfi exhibits relatively high ξ_{inter} , which is comparable to that of the CRP (Fig. 10b). However, the difference in ξ_{inter} between FRPfi and the CRP expands in the post-gel region. This expanding difference is accounted for

by the inactivation of propagating ends by the termination, which prevents the development of cross-linked structures in the post-gel region like the CRP gels. The higher ν_p of FRPfi in the post-gel region compared to the CRP indicates free inactivated polymers that are not incorporated into the gel network. In addition, in FRPfi, where the propagation is fast, ξ_{intra} and the density fluctuations are larger than those in the CRP (Figs. 10c and 10d); therefore, the entanglement occurs more easily than in the CRP.

The results shown in Fig. 10 indicate that FRPwot without the termination exhibits non-uniform gelation due to cross-linking between microgels, and the manner of cross-linking is similar to that of the FRP. In the CRP, since the termination is suppressed, the cross-linked structure quickly develops in the post-gel region, but in FRPwot, no such trend is observed. This is considered to be because the propagating ends in FRPwot are confined in the high-density regions formed during the non-uniform gelation, and become ineffective for cross-linking.

Although the fast initiation and the prohibition of the termination do not seem to affect the network structure from the results in Figs. 9 and 10, we have confirmed that they also contribute to the formation of the relatively uniform structure of the CRP gel. As shown in the ESI†, gels formed by a model system incorporating these two characteristics of CRP into the FRP, *i.e.*, FRPfi without the termination or FRPwot with the fast initiation, have more uniform structures than the FRPfi gels and the FRPwot gels.

From the above results, we considered that the characteristics of CRP, the fast initiation, slow propagation, and suppressed termination, cooperatively act to improve the structural homogeneity of the CRP gel. The fast initiation promotes uniform polymer growth and intermolecular cross-linking in the pre-gel region. The slow propagation suppresses intramolecular cross-linking. The uniform polymer growth, the promotion of intermolecular cross-linking, and the suppression of intramolecular cross-linking reduce the density fluctuations and the number of entanglements during gelation. The suppressed termination develops the network structure in the post-gel region. However, systems with only one of these characteristics show limited effects or almost no effect on improving the structural homogeneity.

Finally, we mention the effects of temperature T . Although we have fixed T at $\epsilon_{\text{wca}}/k_B$ in this study, we think that the CRP gel is more homogeneous than the FRP gel even at different T . In the FRP at low T , even if the propagation is slow and the bimolecular termination is negligible, since the slow initiation heterogeneously proceeds, gelation occurs by cross-linking the microgels. Therefore, the structure of the FRP gel is considered to be more heterogeneous than that of the CRP gel. At high T , the initiation of the FRP becomes fast, which results in relatively uniform gelation of the system. However, the initiation of the CRP is also fast, and the propagation and termination of the CRP are slower than those of the FRP due to the propagating ends existing as dormant species. Thus, we think that the CRP gel has a more uniform structure than FRP gel.

4 Conclusions

We have studied the structure of gels synthesized by CRP and FRP by the CGMD simulation. From the comparison of the CRP

gel and the FRP gel, we have found that the former has a larger number of elastically effective chains and a smaller effect of entanglements, *i.e.*, a more uniform structure than the latter. The simulation results qualitatively agree with the experimentally reported results comparing CRP gels and FRP gels.^{7–17} By analyzing the network formation process of model systems that have one of the characteristics of CRP, we have clarified the molecular mechanisms that make the structure of the CRP gel relatively uniform. We have shown that the systems with only one of the CRP characteristics have limited effects or almost no effect on improving the structural uniformity. Therefore, we have found that the characteristics of CRP, the fast initiation, slow propagation, and suppressed termination, cooperatively contribute to the improvement of the structural homogeneity of the CRP gel.

In this study, although we have discussed only the structure and equilibrium mechanical properties of CRP gels and FRP gels, it has also been reported that the two differ in fracture behavior.^{14,16} We are planning to analyze the effects of the difference in polymerization mechanisms on the fracture behavior of gels.

Author Contributions

Tsutomu Furuya: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Visualization, Writing - original draft. **Tsuyoshi Koga:** Resources, Software, Supervision, Writing - review & editing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by JSPS KAKENHI (Grant-in-Aid for Early-Career Scientists), Grant Number JP20K14429.

References

- 1 E. M. Ahmed, *J. Adv. Res.*, 2015, **6**, 105–121.
- 2 K. Varaprasad, G. M. Raghavendra, T. Jayaramudu, M. M. Yallapu and R. Sadiku, *Mater. Sci. Eng. C*, 2017, **79**, 958–971.
- 3 S. Mondal, S. Das and A. K. Nandi, *Soft Matter*, 2020, **16**, 1404–1454.
- 4 S. Seiffert, *Polym. Chem.*, 2017, **8**, 4472–4487.
- 5 Y. Osada, K. Dušek, M. Shibayama and K. Urayama, *Gel Science*, Kodansha, Tokyo, Japan, 2020.
- 6 M. Shibayama, *Macromol. Chem. Phys.*, 1998, **199**, 1–30.
- 7 N. Ide and T. Fukuda, *Macromolecules*, 1997, **30**, 4268–4271.
- 8 N. Ide and T. Fukuda, *Macromolecules*, 1999, **32**, 95–99.
- 9 T. Norisuye, T. Morinaga, Q. Tran-Cong-Miyata, A. Goto, T. Fukuda and M. Shibayama, *Polymer*, 2005, **46**, 1982–1994.
- 10 H. Gao, K. Min and K. Matyjaszewski, *Macromolecules*, 2007, **40**, 7763–7770.
- 11 Q. Yu, S. Xu, H. Zhang, Y. Ding and S. Zhu, *Polymer*, 2009, **50**, 3488–3494.
- 12 J. A. Yoon, C. Gayathri, R. R. Gil, T. Kowalewski and K. Matyjaszewski, *Macromolecules*, 2010, **43**, 4791–4797.
- 13 C. Gonzato, P. Pasetto, F. Bedoui, P.-E. Mazeran and K. Haupt, *Polym. Chem.*, 2014, **5**, 1313–1322.
- 14 R. Henkel and P. Vana, *Macromol. Chem. Phys.*, 2014, **215**, 182–189.
- 15 C. Norioka, A. Kawamura and T. Miyata, *Polym. Chem.*, 2017, **8**, 6050–6057.
- 16 T. Miyajima, Y. Matsubara, H. Komatsu, M. Miyamoto and K. Suzuki, *Polym. J.*, 2020, **52**, 365–373.
- 17 C. W. A. Bainbridge, A. Wangsadijaya, N. Broderick and J. Jin, *Polym. Chem.*, 2022, **13**, 1484–1494.
- 18 P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
- 19 W. H. Stockmayer, *J. Chem. Phys.*, 1944, **12**, 125–131.
- 20 A. J. Scott, A. Nabifar and A. Penlidis, *Macromol. React. Eng.*, 2014, **8**, 639–657.
- 21 R. Scherf, L. S. Müller, D. Grosch, E. G. Hübner and W. Oppermann, *Polymer*, 2015, **58**, 36–42.
- 22 F. Cavalli, C. Pfeifer, L. Arens, L. Barner and M. Wilhelm, *Macromol. Chem. Phys.*, 2020, **221**, 1900387.
- 23 H. Gao, P. Polanowski and K. Matyjaszewski, *Macromolecules*, 2009, **42**, 5925–5932.
- 24 P. Polanowski, J. K. Jeszka and K. Matyjaszewski, *Polymer*, 2010, **51**, 6084–6092.
- 25 P. Polanowski, J. K. Jeszka, W. Li and K. Matyjaszewski, *Polymer*, 2011, **52**, 5092–5101.
- 26 P. Polanowski, J. K. Jeszka, K. Krysiak and K. Matyjaszewski, *Polymer*, 2015, **79**, 171–178.
- 27 S. Hamzehlou, Y. Reyes and J. R. Leiza, *Euro. Polym. J.*, 2016, **85**, 244–255.
- 28 A. Singh, O. Kuksenok, J. A. Johnson and A. C. Balazs, *Soft Matter*, 2017, **13**, 1978–1987.
- 29 J. Lyu, Y. Gao, Z. Zhang, U. Greiser, P. Polanowski, J. K. Jeszka, K. Matyjaszewski, H. Tai and W. Wang, *Macromolecules*, 2018, **51**, 6673–6681.
- 30 K. Kremer, G. S. Grest and I. Carmesin, *Phys. Rev. Lett.*, 1988, **61**, 566–569.
- 31 K. Kremer and G. S. Grest, *J. Chem. Phys.*, 1990, **92**, 5057–5086.
- 32 K. Kremer and G. S. Grest, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 1707–1717.
- 33 T. Furuya and T. Koga, *Polymer*, 2023, **279**, 126012.
- 34 H. Liu, Y.-L. Zhu, Z.-Y. Lu and F. Müller-Plathe, *J. Comput. Chem.*, 2016, **37**, 2634–2646.
- 35 A. Petrov, V. Y. Rudyak, P. Kos and A. Chertovich, *Macromolecules*, 2020, **53**, 6796–6808.
- 36 A. A. Gavrilov and A. V. Chertovich, *Polym. Chem.*, 2022, **13**, 2143–2154.
- 37 A. Goto and T. Fukuda, *Prog. Polym. Sci.*, 2004, **29**, 329–385.
- 38 T. Endo, M. Sawamoto, M. Kamigaito, K. Satoh, S. Aoshima, S. Kanaoka, A. Hirao and K. Sugiyama, *Polymer synthesis*, Kodansha, Tokyo, Japan, 2010, vol. 1.
- 39 E. A. S. Cavell, *Makromol. Chem.*, 1962, **54**, 70–77.
- 40 J. D. Weeks, D. Chandler and H. C. Andersen, *J. Chem. Phys.*, 1971, **54**, 5237–5247.
- 41 M. Kröger, *Phys. Rep.*, 2004, **390**, 453–551.

- 42 D. Frenkel and B. Smit, *Understanding Molecular Simulation 2nd Edition: From Algorithms to Applications*, Academic Press, San Diego, CA, 2002.
- 43 T. Furuya and T. Koga, *Macromol. Theory Simul.*, 2022, **31**, 2200044.
- 44 J. Scanlan, *J. Polym. Sci.*, 1960, **43**, 501–508.
- 45 L. C. Case, *J. Polym. Sci.*, 1960, **45**, 397–404.
- 46 N. R. Langley, *Macromolecules*, 1968, **1**, 348–352.
- 47 R. Everaers, S. K. Sukumaran, G. S. Grest, C. Svaneborg, A. Sivasubramanian and K. Kremer, *Science*, 2004, **303**, 823–826.
- 48 D. R. Rottach, J. G. Curro, G. S. Grest and A. P. Thompson, *Macromolecules*, 2004, **37**, 5468–5473.
- 49 T. Furuya and T. Koga, *Soft Matter*, 2018, **14**, 8293–8305.