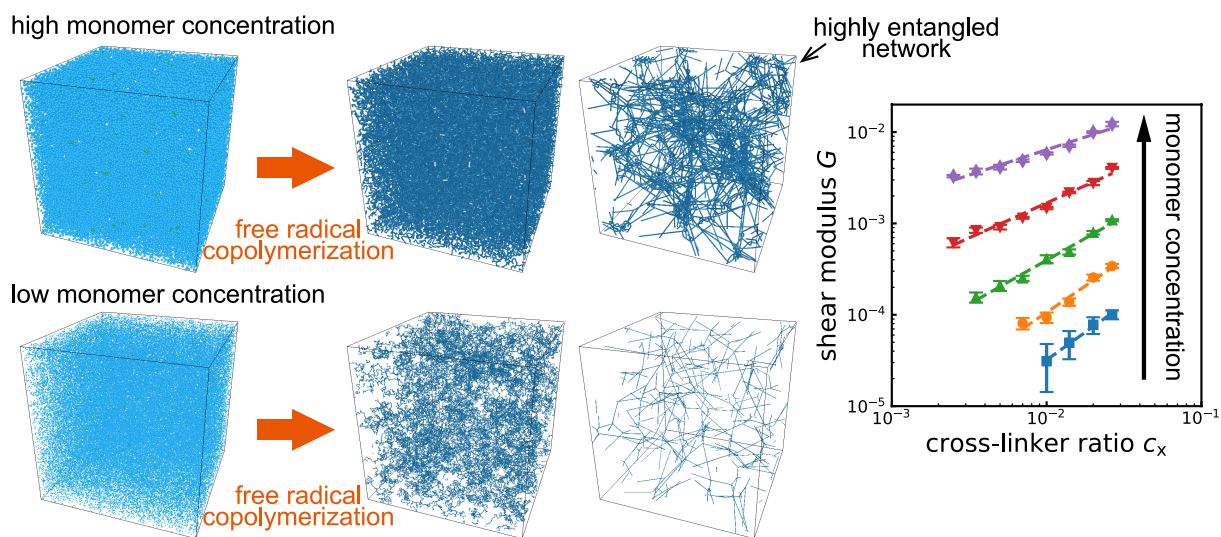


Graphical Abstract

Molecular Simulation of Polymer Gels Synthesized by Free Radical Copolymerization: Effects of Concentrations and Reaction Rates on Structure and Mechanical Properties

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Highlights

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- Gels formed by free radical copolymerization are studied by a simulation.
- The effects of concentrations and reaction rates on network structure are studied.
- At high monomer concentrations, the shear modulus increases due to entanglement.
- Slowing down the propagation rate improve the uniformity of network structure.
- Structural changes due to changes in concentrations or reaction rates are clarified.

Molecular Simulation of Polymer Gels Synthesized by Free Radical Copolymerization: Effects of Concentrations and Reaction Rates on Structure and Mechanical Properties

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ABSTRACT

The effects of polymerization concentrations and elementary reaction rates on the network structure and mechanical properties of gels synthesized by free radical copolymerization of monomers and cross-linkers are studied by a coarse-grained molecular dynamics simulation. The shear modulus, the number of elastically effective chains, and the number of trapped entanglements are calculated with varying the concentrations. The results reveal that the experimentally reported high cross-linking efficiency of the gels formed at high monomer concentrations and low cross-linker concentrations is due to the large number of trapped entanglements. The molecular mechanisms of changes in the network structure due to changes in the concentrations are elucidated by analyzing the detailed structure of network strands connecting adjacent cross-linking points. The results with systematically varying the elementary reaction rates indicate that the decrease in the propagation rate suppresses the formation of cyclic structures and reduces the influence of the trapped entanglements, *i.e.*, improves the structural uniformity of the gels.

1. Introduction

Polymer gels are composed of three-dimensionally cross-linked network polymers and a large number of solvent molecules, and are used in a wide range of application fields such as food[1], sanitary products[2], and medical materials[3]. Since the physical properties of polymer gels are closely related to the structure of the network polymers, understanding and controlling the network structure is necessary to obtain gels with desired properties. In recent years, it has been reported that high toughness gels with controlled structures are obtained by cross-linking reactive polymers[4, 5, 6]. However, free radical copolymerization (FRCP) of monomers and cross-linkers is still widely used as a gel synthesis method in industry due to its advantages such as versatility and productivity[7, 8]. Therefore, deepening our understanding of the structure formation of the network polymers in FRCP is important not only for gel science but also for the development of new industrial gels.

In conventional FRCP, polymers non-uniformly grow and are randomly cross-linked; hence, the network structures of gels formed by FRCP are difficult to control and become heterogeneous[7, 9]. Such structural heterogeneity reduces the physical properties of FRCP gels such as mechanical strength and transparency.

In order to control the structure and physical properties of FRCP gels, a lot of research has been conducted on various factors such as polymerization concentrations[10, 11, 12, 13, 14], the molecular weight of polymers[10], reaction rates[12, 14, 15], the type of monomers[12, 15], and the

size of cross-linkers[16, 17]. For example, the shear modulus G monotonically increases with increasing monomer concentration and cross-linker concentration[11, 13]. On the other hand, the cross-linking efficiency ϵ_G calculated from G and the cross-linker concentration (hereafter, we call it “mechanical cross-linking efficiency”), which is used to experimentally evaluate structural homogeneity, shows complicated behavior[11, 13]. With increasing the cross-linker concentration, ϵ_G increases at low monomer concentrations, but decreases at high monomer concentrations[13]. Under a constant cross-linker concentration, ϵ_G non-monotonically varies with increasing the monomer concentration[11]. Furthermore, recently, Norioka and coworkers have reported that FRCP gels synthesized at high monomer concentrations and low cross-linker concentrations exhibit ϵ_G greater than one, and indicate excellent toughness[18]. The relationships between the behavior of ϵ_G and various structural defects (such as intramolecular cross-links, multiple cross-links, and entanglements) have been discussed from the experimental results[11, 13, 18]. However, since it is difficult to experimentally analyze detailed network structures at the molecular level, we think that simulation studies are necessary to clarify the molecular origin of the behavior of ϵ_G associated with the structure formation of FRCP gels.

Experimental studies also reported that the reaction rates of FRCP affect the structure and physical properties of FRCP gels[7, 12, 14]. These studies clarified that the decrease of the polymerization rate by changing the types of initiators[14] and monomers[12] improves the homogeneity of the network structure. In addition, the structure of gels synthesized by controlled radical copolymerization (CRCP) was reported to be more uniform than that of FRCP gels[2, 19, 20]. Generally, in FRCP, a relatively slow initiation heterogeneously proceeds, and propagations rapidly proceed,

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whereas in CRCP, a fast initiation uniformly proceeds, and the propagation rate is slow[21]. Such difference in the elementary reaction rates is considered to be one reason of the relatively uniform structure of CRCP gels. From these results, we think that the elementary reaction rates are also important for understanding the structure formation of FRCP gels.

Computer simulation is useful for the analysis of the network structure of gels at the molecular level. Numerous simulation studies have been conducted to understand the molecular mechanisms of the network formation in FRCP gels[22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32]. These simulations showed the decrease of the average length of strands connecting adjacent cross-linking points with increasing the cross-linker concentration[23], the reduction of the polymerization rate due to gelation[24], the non-monotonic change of the number of defects in the network structure (such as dangling ends and loops) with increasing conversion[25, 26, 28, 30, 31, 32], and the delayed gelation due to the defects in the network structure[22, 26, 27, 31, 32]. The effects of the difference in reactivity between monomers and cross-linkers[28, 29] and those of the cross-linker functionality[24, 25] were also reported. The relationships between the structures of FRCP gels and their physical properties such as the elastic modulus and the glass transition temperature have been studied[26, 28, 29, 31]. However, more exhaustive research is needed to elucidate the molecular origin of the complicated experimental results such as the behavior of ϵ_G . Furthermore, although some simulations showed the effects of the reaction rates on the structure of FRCP gels[24, 32], systematic simulations concerned with each elementary reaction rate have been rarely performed.

In this paper, we systematically study the effects of the polymerization concentrations and the elementary reaction rates on the network structure and mechanical properties of FRCP gels by a coarse-grained molecular dynamics (CGMD) simulation. We first confirm that our simulation reproduces some features of the classical kinetics of free radical polymerization (FRP) by using linear polymer polymerization systems, because the effects of the reaction rates on the structure and physical properties of FRCP gels were reported. We then calculate the shear modulus G and the detailed structure (such as the number of elastically effective chains[33, 34], the number of entanglements[35, 36, 37], and the structure of the network strands which are polymer chains connecting adjacent cross-linking points[37]) of the FRCP gels with systematically varying the polymerization concentrations. From these results, we clarify the molecular mechanisms of the experimentally reported behavior of ϵ_G . Finally, we discuss the effects of each elementary reaction rate on the structure formation of the FRCP gels from the simulation results with systematically varying the elementary reaction rates. We think that these results deepen the understanding of the structure formation mechanisms and the relationship between the structure and mechanical properties of FRCP gels, and provide important knowledge for the development of new materials using FRCP gels.

2. Simulation Model

In this simulation, we represented molecules with a coarse-grained model[38, 39, 40], and used a model based on a cut-off distance and reaction probabilities for chemical reactions[30, 41, 42]. This is because calculations over wide scales of space and time are required to study the relationship between the structure and mechanical properties of FRCP gels. We employed a bead-spring model for the monomer, cross-linker, initiator, and polymer (Fig. 1a). The monomer, cross-linker, and initiator consisted of one, three, and two beads, respectively. The monomer beads and the end beads of the cross-linkers were set to functional beads with the same reactivity, and the center beads of the cross-linkers were set to non-functional beads. The initiator was set to generate two primary radical beads by decomposition. The polymers were formed by the FRCP in the CGMD simulation.

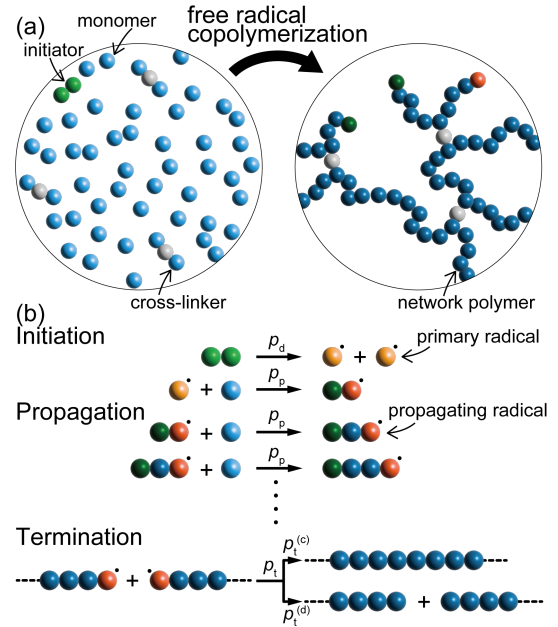


Figure 1: (a) Schematic illustration of network formation by free radical copolymerization and (b) elemental reactions in the free radical polymerization model. Cyan beads indicate the monomers and the ends of the cross-linkers, which are the functional beads. Green beads indicate the initiators. Orange and red beads indicate the primary and the propagating radicals, respectively. Dark blue, dark green, and gray beads indicate the inactive beads.

In the calculation of the FRCP, we considered the following three types of stochastic elementary reactions: the initiation, propagation, and termination (Fig. 1b). The initiator first decomposes with a probability p_d and generates two primary radicals. The propagation proceeds with a 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 the cut-off distance r_c ; a new bond is formed between the two beads, and the radical and the functional bead become an inactive bead and a new

propagating radical, respectively. A cross-linker two ends of which are reacted cross-links the polymers and serves as a four-branched cross-linking point (Fig. 1a). The termination proceeds with a probability p_t when a radical pair come in contact with each other at $r \leq r_c$, and both radicals change into inactive beads. The probabilities of combination and disproportionation occurring in the termination are $p_t^{(c)}$ and $p_t^{(d)} = 1 - p_t^{(c)}$, respectively. When the combination occurs, a new bond is generated between the radicals participating in the termination. In this study, we assumed that the decomposition of the initiator is reversible; the termination between primary radicals always proceeds with the combination, and the molecule obtained by the combination of the two primary radicals is effective as an initiator. Although FRP includes chain transfer reactions and initiations from chain-transferred radicals, they were not considered in this study for simplicity. The detailed reaction process is shown in Supporting Information.

In the simulation with the FRCP, the reaction process was performed every Θ CGMD steps of timestep Δt to simultaneously calculate the motion of each bead and the FRCP. The rate constant k_d of the initiator decomposition, which is a first order reaction, is given by $k_d = p_d/\Theta\Delta t$; hence, k_d is proportional to p_d/Θ . It should be noted that the initiation rate is affected by other simulation parameters such as p_t and Θ , because the initiator efficiency f depends on the diffusion and the combination rate of the primary radicals. The reaction rate constants k_p and k_t of the propagation and the termination, which are second order reactions, are more complex than k_d , because they are affected by the collision frequency of the beads involved in the reactions. When the effective reaction probability p_x/Θ ($x = p$ or t) is small, the rate constant k_x is expressed as $k_x \simeq K_x p_x/\Theta$ using the rate of collision K_x between the chemical species of interest. When p_x/Θ is sufficiently large, the reaction becomes diffusion-controlled, and k_x approaches a certain constant value[43]. Thus, k_x is proportional to p_x/Θ for small p_x/Θ and does not depend on p_x/Θ for large p_x/Θ (Fig. S4 in Supporting Information).

In this study, we fixed the reaction interval Θ at $\Theta = 1$ in order to be able to calculate fast reactions, and used the following reaction probabilities except for the calculation of the effects of the elementary reaction rates: $p_d = 1 \times 10^{-7}$, $p_p = 0.5$, and $p_t = 1$. Under these conditions, the relationship $k_t \geq k_p \gg k_d$ is obtained, and the propagation and the termination are considered to be diffusion-controlled. Although $k_t \gg k_p$ in real FRPs[21], satisfying this relationship requires a very long computation time due to the large decrease in p_d and p_p . Therefore, we here focused on the slow initiation and set the probabilities as described above. In this study, we assumed a polyacrylamide system and set the termination between the propagating radicals to be mainly disproportionation[44], i.e., $p_t^{(c)} = 0$ and $p_t^{(d)} = 1$.

We next explain the interactions that act on the beads. The Weeks-Chandler-Anderson (WCA) potential[45] was

used for the non-bonding interactions between the beads:

$$U_{\text{wca}}(r_{ij}) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 + \frac{1}{4} \right] & r_{ij} \leq 2^{1/6}\sigma \\ 0 & r_{ij} > 2^{1/6}\sigma \end{cases} \quad (1)$$

Here, r_{ij} is the distance between the i th bead and the j th bead, ϵ is the potential strength, and σ is the collision diameter. In this simulation, ϵ and σ are used as units of energy and length, respectively. The units of time, temperature, and mass in the simulation are $\tau \equiv \sigma\sqrt{m/\epsilon}$, ϵ/k_B , and m , 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 distance r_c for the FRCP to $r_c = \sigma$, and fixed the temperature T at $T = \epsilon/k_B$.

In addition to the WCA potential, the finitely extensible non-linear elastic (FENE) potential[46] was introduced into the interactions between the bound beads:

$$U_b(r_{ij}) = -\frac{1}{2}k_b r_0^2 \ln \left[1 - \left(\frac{r_{ij}}{r_0} \right)^2 \right], \quad (2)$$

where k_b is the spring constant and r_0 is the maximum bond length. In order to prevent the crossing of the bonds during the simulation, we set $k_b = 30\epsilon/\sigma^2$ and $r_0 = 1.5\sigma$ [38, 39, 40].

In order to avoid the cyclization due to the bond formation between the ends of the same cross-linker, we employed the following bending potential for the bonds of the cross-linkers:

$$U_\theta(\theta_{ijk}) = \frac{1}{2}k_\theta (\cos \theta_{ijk} - \cos \theta_0)^2. \quad (3)$$

Here, θ_{ijk} is the instantaneous bond angle formed by three consecutive beads, k_θ is the spring constant, and θ_0 is the equilibrium bond angle. In this simulation, we set $k_\theta = 100\epsilon$ and $\theta_0 = \pi$.

Using these potentials, the motion of each bead was calculated by the following Langevin equation:

$$m \frac{d^2 \mathbf{r}_i(t)}{dt^2} = \mathbf{F}_i(t) - m\zeta \frac{d\mathbf{r}_i(t)}{dt} + \mathbf{W}_i(t), \quad (4)$$

where $\mathbf{r}_i(t)$, $\mathbf{F}_i(t)$, and $\mathbf{W}_i(t)$ are the position vector of the i th bead at time t , the force acting on the i th bead, and the random force acting on the i th bead, respectively, and ζ is the friction coefficient. Here, $\mathbf{W}_i(t)$ satisfies $\langle \mathbf{W}_i(t) \rangle = 0$ and $\langle \mathbf{W}_i(t) \cdot \mathbf{W}_j(t') \rangle = 6m\zeta k_B T \delta_{ij} \delta(t - t')$. In this study, we set $\zeta = 0.5/\tau$, and integrated the Langevin equations by the velocity Verlet method[47] with timestep $\Delta t = 0.005\tau$.

In the simulation with the FRCP, first, we randomly placed n_m monomers, n_x cross-linkers, and n_i initiators in the cubic simulation box of volume V with periodic boundary conditions. We next performed the simulation of 1×10^5 steps ($t = 5 \times 10^2 \tau$) without processing the FRCP to homogeneously mix the molecules. We then conducted the

simulation while performing the trial of the FRCP (Fig. S1 in Supporting Information) $n = n_m + 3n_x + 2n_i$ times at each time step. At this stage, the calculations for the network formation were performed until the monomer conversion α reached 95%. The calculations of linear polymer polymerization systems without the cross-linkers were performed for 2×10^7 steps ($t = 1 \times 10^5 \tau$) or until there were no more reactive beads. In this study, the number n_m of monomers was fixed at $n_m = 1 \times 10^5$, and the volume fraction $\phi_m = n_m \pi \sigma^3 / 6V$ of the monomer was varied by adjusting V . On the other hand, the concentrations of the cross-linker and the initiator were varied by changing n_x and n_i , respectively.

In order to study the mechanical properties of the obtained networks, the simulations of the networks under the uniaxial deformation were performed without the reactions. In this study, we applied the uniaxial deformation to the networks by changing the lengths of the simulation box from L_0 to λL_0 in the x -direction and from L_0 to $L_0 / \sqrt{\lambda}$ in the y - and z -directions. Here, $L_0 = V^{1/3}$ is the initial length of the simulation box, and λ is the one-dimensional deformation ratio. Specifically, the networks were deformed by repeating a deformation process and a relaxation process. In the deformation process, the simulation of 1×10^4 steps ($t = 50\tau$) was performed while changing λ at the deformation rate $|d\lambda/dt| = 2.0 \times 10^{-3}/\tau$. In the subsequent relaxation process, the simulation of 2.1×10^6 steps ($t = 1.05 \times 10^4 \tau$) under a constant λ was carried out. After λ reached a target value by repeating the deformation and relaxation processes, the time development of the nominal stress $\sigma_N(t)$ was calculated by the simulation of 2.2×10^7 steps ($t = 1.1 \times 10^5 \tau$) under the target λ . The nominal stress $\sigma_{N,eq}$ at the equilibrium state ($t \rightarrow \infty$) was estimated by plotting $\sigma_N(t)$ against the reciprocal $1/t$ of the time and fitting $\sigma_N(t)$ with $\sigma_N(t) = A/t + \sigma_{N,eq}$. The shear modulus G was then calculated by fitting $\sigma_{N,eq}$ in the range of $0.6 \leq \lambda \leq 1.4$ with the neo-Hookean model $\sigma_{N,eq} = G(\lambda - \lambda^{-2})$. The detailed calculation method is shown in Supporting Information.

We performed three independent runs for the calculation of the kinetics of FRP and the effects of the polymerization concentrations on the structure and shear modulus of the FRCP gels, and seven independent runs for the calculation of the effects of each elementary reaction rate on the structure of the FRCP gels. We used the average of these independent runs as the simulation results for each condition.

3. Results and Discussion

3.1. Free Radical Polymerization of Linear Polymer

We first present the results of the polymerization of linear polymers in the systems without the cross-linkers (the number of cross-linkers $n_x = 0$) to confirm the behavior of the FRP model in this study. Fig. 2 shows the time developments of the concentrations of each species, the number average molecular weight $\bar{M}_n$, the weight average molecular weight $\bar{M}_w$, the polydispersity index (PDI) $\bar{M}_w/\bar{M}_n$, the monomer conversion $\alpha = 1 - [M]/[M]_0$, and the conversion

index (CI) $\ln([M]_0/[M])$. Here, $[M]_0$ and $[M]$ are the initial monomer concentration and the concentration of the unreacted monomer at time t , respectively. In Fig. 2, $[M]_0$ and the initial initiator concentration $[I]_0$ are set to $[M]_0 \simeq 0.19$ (the monomer volume fraction $\phi_m = 0.1$) and $[I]_0 \simeq 6.7 \times 10^{-4}$ (the ratio of the number of initiators to that of monomers $c_i \equiv n_i/n_m = 3.5 \times 10^{-3}$), respectively.

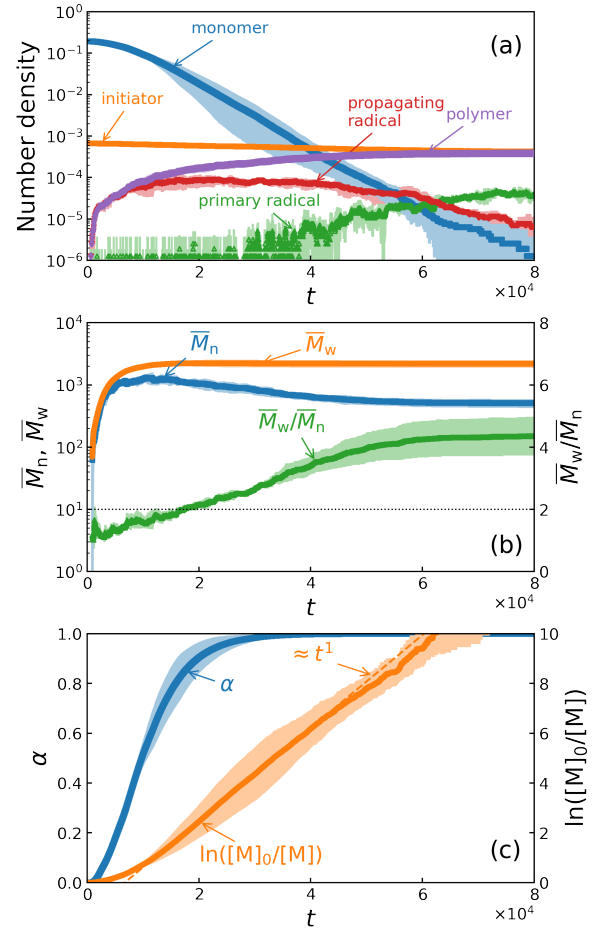


Figure 2: Time developments of (a) the number densities of each species, (b) the number average molecular weight $\bar{M}_n$, the weight average molecular weight $\bar{M}_w$, the polydispersity index $\bar{M}_w/\bar{M}_n$, (c) the monomer conversion α , and the conversion index $\ln([M]_0/[M])$. The initial number densities of the monomer and the initiator are $[M]_0 \simeq 0.19$ and $[I]_0 \simeq 6.7 \times 10^{-4}$, respectively.

The time evolution results of the system are consistent with the kinetics of FRP[21, 48]. As seen in Fig. 2a, the concentration of the propagating radical is almost constant in the range of $1 \times 10^4 \lesssim t \lesssim 4 \times 10^4$; thus, this time range is considered to correspond to the steady state in the kinetics of FRP[21]. The PDI in the early steady state is almost equal to 2 (Fig. 2b), and the CI in the steady state is approximately proportional to t .

We find that the polymerization rate R_p is proportional to $[I]_0^a [M]_0^b$ and the reaction orders a and b are $a \simeq 0.6$ and $b \simeq 0.9$ – 1.2 , respectively (Fig. 3). Here, R_p is calculated from the

average of $-d[M]/dt$ in the initial stage ($0.1 \leq \alpha \leq 0.4$) of FRP. These results are in good agreement with the kinetics of FRP ($a = 1/2$ and $b = 1$)[21]. We have also confirmed that the concentration dependence of the average molecular weight at the steady state agrees with the kinetics of FRP (Fig. S5 in Supporting Information). From these results, we think that this simulation well reproduces some features of the kinetics of FRP.

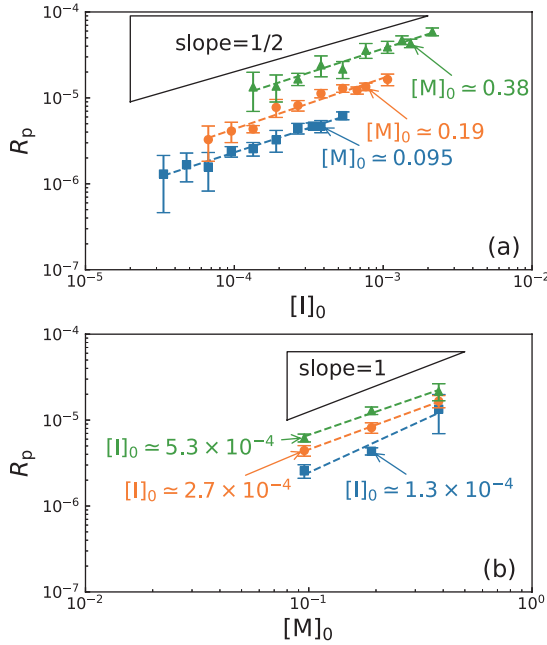


Figure 3: Polymerization rate R_p shown as functions of (a) the initial number density $[I]_0$ of the initiator and (b) the initial number density $[M]_0$ of the monomer.

The results of the preliminary simulation with varying the reaction probabilities are shown in Supporting Information.

3.2. Effects of Monomer Concentration and Crosslinker Ratio

We next explain the results of the FRCP gels. In the following, we fix the initiator ratio at $c_i = 3.5 \times 10^{-3}$.

Fig. 4 depicts the shear modulus G and the mechanical cross-linking efficiency $\epsilon_G \equiv v_G/v_{id}$ at various monomer volume fractions ϕ_m as functions of the cross-linker ratio $c_x \equiv n_x/n_m$. Here, v_G is the apparent number density of elastically effective chains calculated by using G of the simulation results and the affine network model $G = v_G k_B T$, and $v_{id} \equiv 2n_x/V$ is the ideal number density of elastically effective chains. In Fig. 4, we also show the results of fitting the simulation results with $G \approx c_x^\gamma$ in order to understand the trend.

The results of the behavior of ϵ_G qualitatively agree with the experimental results[13, 18]. As shown in Fig. 4, G increases with increasing ϕ_m and c_x . The slope of G , i.e., the exponent γ decreases with increasing ϕ_m . Thus, ϵ_G increases with increasing c_x at the low monomer concentrations ($\phi_m = 0.02, 0.03$), but decreases with increasing c_x at the high

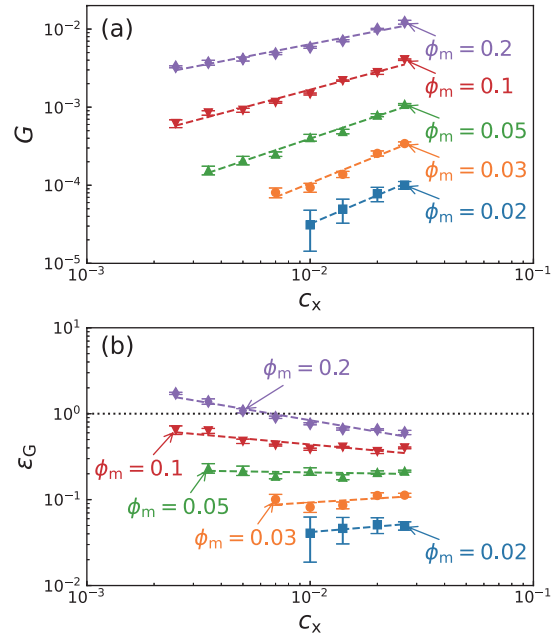


Figure 4: (a) Shear modulus G and (b) mechanical cross-linking efficiency ϵ_G shown as functions of the cross-linker ratio c_x . Dashed lines indicate the results of fitting the simulation results with $G \approx c_x^\gamma$.

monomer concentrations ($\phi_m = 0.1, 0.2$)[13]. Furthermore, the gels formed at the high ϕ_m and the low c_x exhibit ϵ_G greater than one[18]. From these results, we consider that the mechanical properties of the FRCP gels formed in this simulation reproduce some features of the real FRCP gels.

In order to understand the molecular mechanisms of the behavior of ϵ_G , we here calculate the number of elastically effective cross-linking points and that of entanglements trapped in the network from the network structure. In this study, the number of elastically effective cross-linking points is calculated by using the Scanlan-Case criterion[33, 34]. The cross-linking points carrying three or more paths to the network matrix are judged to be elastically effective, and the strands both ends of which are connected to the elastically effective cross-linking points are counted as the elastically effective chains. For the trapped entanglement, we first analyze the entanglements of the polymers in the network by the method of Everaers *et al.*[35], and then calculate the number of trapped entanglements with reference to Langley's study[49]; the entanglements where two or more elastically effective chains are involved are counted as the trapped entanglements[37]. The trapped entanglements additionally generate the elastically effective chains. The detailed calculation method is shown in Supporting Information.

The number density v_x of the elastically effective chains formed by cross-linking increases with increasing ϕ_m and c_x (Fig. 5a). The slope of v_x decreases with increasing ϕ_m , but is greater than one under all the conditions. Therefore, we find that the cross-linking efficiency $\epsilon_x \equiv v_x/v_{id}$ calculated

from the network structure increases with increasing c_x under all the conditions.

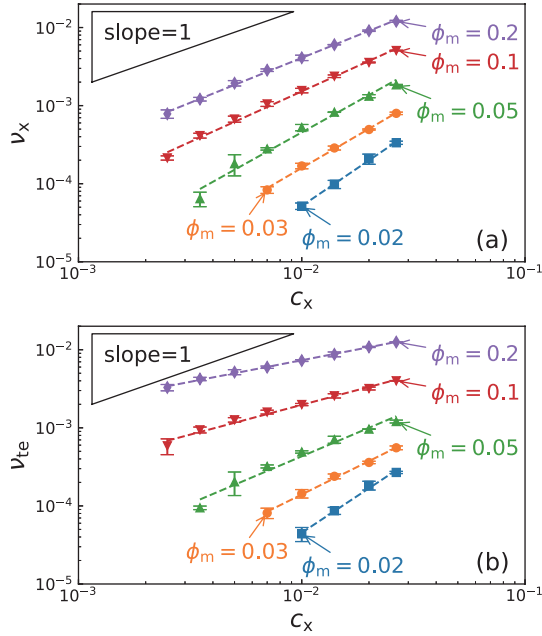


Figure 5: (a) Number density ν_x of the elastically effective chains formed by cross-linking and (b) number density ν_{te} of the elastically effective chains generated by the trapped entanglements shown as functions of the cross-linker ratio c_x .

Similar to ν_x , the number density ν_{te} of the elastically effective chains generated by the trapped entanglements also increases with increasing ϕ_m and c_x , and its slope decreases with increasing ϕ_m (Fig. 5b). However, the slope of ν_{te} becomes smaller than one at the high monomer concentrations ($\phi_m = 0.1, 0.2$), i.e., the formation efficiency $\varepsilon_{te} \equiv \nu_{te}/\nu_{id}$ of the elastically effective chains by the trapped entanglements decreases with increasing c_x in the high ϕ_m region. Therefore, the decrease in ε_G with increasing c_x at the high ϕ_m is attributed to the entanglements trapped in the network.

In order to evaluate the influence of the entanglements, the ratio ν_{te}/ν_x is shown in Fig. 6. The ratio ν_{te}/ν_x , i.e., the influence of the entanglements increases with increasing ϕ_m and decreasing c_x . Especially, at the high monomer concentrations ($\phi_m = 0.1, 0.2$), we find that the entanglements have a great influence, since ν_{te}/ν_x is greater than one for almost all c_x . The simulation results are consistent with the experimental results of Norioka *et al.*[18]

Let us now study the relationship between the shear modulus G and the network structure. In Fig. 7, G is plotted against the shear modulus $G_x + G_{te}$ evaluated from the network structure. Here, G_x and G_{te} are the contributions of the elastically effective cross-linking points and the trapped entanglements, respectively. By using the phantom network model[50, 51], G_x and G_{te} are calculated by

$$G_x = (\nu_x - \mu_x) k_B T, \quad (5)$$

$$G_{te} = (\nu_{te} - \mu_{te}) k_B T, \quad (6)$$

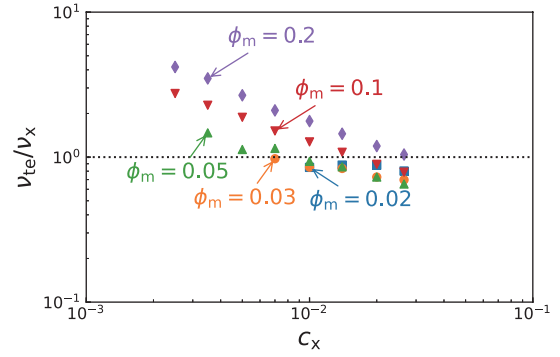


Figure 6: Ratio ν_{te}/ν_x of the number of elastically effective chains generated by the trapped entanglements to that of elastically effective chains formed by cross-linking shown as a function of the cross-linker ratio c_x .

where μ_x and μ_{te} are the number densities of the elastically effective cross-linking points and the trapped entanglements, respectively.

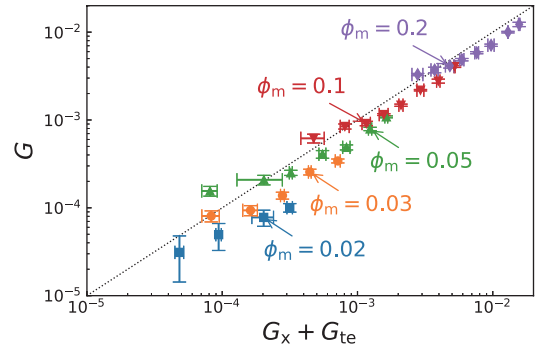


Figure 7: Shear modulus G calculated by the simulation under the uniaxial deformation shown as a function of the shear modulus $G_x + G_{te}$ evaluated from the network structure.

As seen in Fig. 7, G is close to $G_x + G_{te}$ at the high monomer concentrations ($\phi_m = 0.1, 0.2$); hence, the behavior of G in this region is considered to be explained by the elastically effective cross-linking points and the trapped entanglements. The gels formed at the high ϕ_m and the low c_x exhibit high ε_G due to the great influence of the trapped entanglements. Since the cross-linking efficiency ε_{te} related to the trapped entanglements decreases with increasing c_x in the high ϕ_m region, ε_G also decreases.

The discrepancy between G and $G_x + G_{te}$ grows at the low monomer concentrations ($\phi_m \leq 0.05$) (Fig. 7). However, the cross-linking efficiency calculated from $G_x + G_{te}$, which monotonically increases with increasing c_x , qualitatively agrees with ε_G . Therefore, the trend of G can be explained to some extent from the network structure. The overestimation of the number density ν_x of the elastically effective chains formed by cross-linking is considered to be one factor for the discrepancy between G and $G_x + G_{te}$ at the low ϕ_m . As described later (Fig. 8), since the networks formed at the low ϕ_m have sparse cross-linked structures with many dangling ends and loops, we think that

large-scale defects such as super dangling chains and super loops[25, 52], which are not evaluated in this study, also exist in the network. Here, the super dangling chains and super loops denote partial networks consisting of multiple strands that are only connected to one or two true elastically effective cross-linking points of the network, respectively. The elastically effective chains in such large-scale defects are no more elastically effective.

In order to elucidate the molecular mechanisms of the behavior of the cross-linking efficiency ε_x by the chemical cross-linking, we classify the network strands into the bridge chain, loop chain, and dangling chain according to their connectivity (Fig. 8). With increasing ϕ_m , the numbers of loop chains and dangling chains decrease, and the number of bridge chains increases. The reduction of the number of dangling chains is considered to be mainly due to the change in the number average molecular weight $\overline{M}_{n,p}$ of the primary chains, which are the polymers obtained by the scission of the cross-linkers in the network. Since $\overline{M}_{n,p}$ increases with increasing ϕ_m (Fig. S6 in Supporting Information), the influence of polymer ends decreases, and the number of dangling chains declines. The intermolecular cross-linking of the polymers is promoted by increasing ϕ_m ; hence, the number of loop chains, which are the intramolecular cross-links, decreases with increasing ϕ_m . With increasing c_x , the number of dangling chains decreases, and the number of bridge chains increases, while the number of loop chains hardly changes. This is because the rise in c_x increases the total number of strands and thus relatively reduces the influence of polymer ends. Since v_x is approximately proportional to ϕ_m , c_x , and the fraction of the bridge chain, the growth in $\varepsilon_x \propto v_x/c_x\phi_m$ with increasing ϕ_m or c_x is caused by the change of the network strands from the loop chain and the dangling chain to the bridge chain.

We next investigate the molecular mechanisms of the behavior of the cross-linking efficiency ε_{te} related to the trapped entanglements. Fig. 9 shows the number density v_{en} of all the bridge chains generated by the entanglements and the probability $T_e = v_{te}/v_{en}$ (trapped entanglement factor[49]) that an entanglement is trapped in the network. Both v_{en} and T_e increase with increasing ϕ_m and c_x . However, since the change in T_e is smaller than the change in v_{en} , we find that the number density v_{te} of the elastically effective chains generated by the trapped entanglements mainly depends on v_{en} .

The increment in v_{en} with increasing ϕ_m is attributed to the decrease in the entanglement molecular weight M_e [53] and the reduction of the influence of polymer ends with increasing $\overline{M}_{n,p}$. On the other hand, when c_x is varied under a constant ϕ_m , M_e is theoretically constant, and the change in $\overline{M}_{n,p}$ is small (Fig. S6 in Supporting Information). Therefore, we consider that the increase in v_{en} with increasing c_x is due to the entanglements fixed by the introduction of cross-links as shown in Fig. 10. We have confirmed that some entanglements are released by the scission of some cross-links in the network (Fig. S7 in Supporting Information). The growth in v_{en} due to the cross-linking is related to the

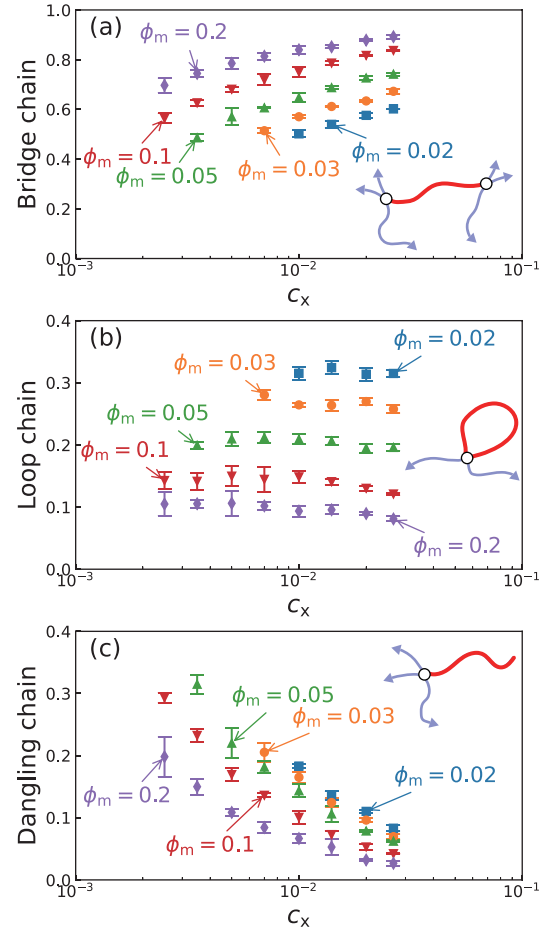


Figure 8: Relative populations of (a) the bridge chain, (b) the loop chain, and (c) the dangling chain shown as functions of the cross-linker ratio c_x .

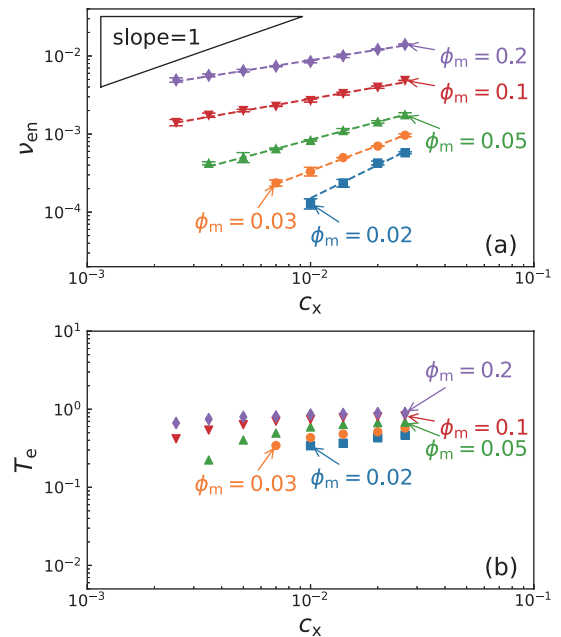


Figure 9: (a) Number density v_{en} of all the bridge chains generated by the entanglements and (b) trapped entanglement factor T_e shown as functions of the cross-linker ratio c_x .

number of effective cross-linking points, which are the ends of the bridge chains. Therefore, at the low ϕ_m , where the number of bridge chains is small and its slope is relatively large, the increase in c_x significantly enhances v_{en} ; thus, ε_{te} increases with increasing c_x . On the other hand, at the high ϕ_m , where the number of bridge chains is large and its change is relatively small, v_{en} gradually increases with increasing c_x , and thus ε_{te} decreases.

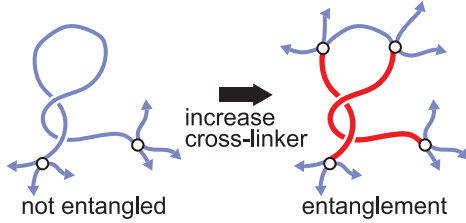


Figure 10: Schematic illustration of the generation of the entanglements by increasing the number of cross-linkers.

In order to discuss the homogeneity of the cross-linked structure, we show the concentration dependence of the strand polydispersity index $\overline{M}_{w,s}/\overline{M}_{n,s}$ in Fig. 11. Here, $\overline{M}_{n,s}$ and $\overline{M}_{w,s}$ are the number average molecular weight and weight average molecular weight of the strands, respectively. $\overline{M}_{w,s}/\overline{M}_{n,s}$ is almost independent of c_x , but decreases with increasing ϕ_m . Therefore, the gels formed at high ϕ_m have relatively uniform cross-linked structures with small $\overline{M}_{w,s}/\overline{M}_{n,s}$ and high cross-linking efficiency ε_x , although many entanglements are present in them. The increase in $\overline{M}_{w,s}/\overline{M}_{n,s}$ with decreasing ϕ_m is thought to be due to the effects of the loop chains and dangling chains. Since different strand types have different molecular weight distributions (Fig. S8 in Supporting Information), $\overline{M}_{w,s}/\overline{M}_{n,s}$ increases with increasing the number of strands other than the bridge chain.

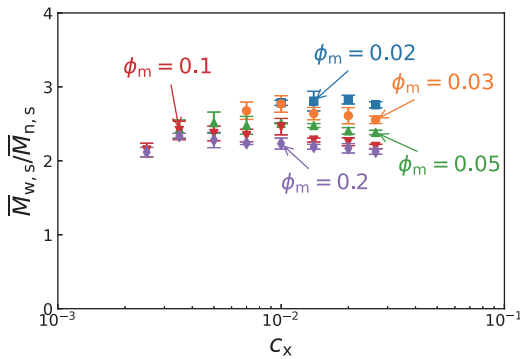


Figure 11: Polydispersity index $\overline{M}_{w,s}/\overline{M}_{n,s}$ of the strands shown as a function of the cross-linker ratio c_x .

3.3. Effects of Elementary Reaction Rates

In this section, we demonstrate the effects of each elementary reaction rate on the network structure of the FRCP gels. We here set the reaction probabilities ($p_d = 1 \times 10^{-7}$,

$p_p = 0.5$, and $p_t = 1$) used in the previous sections as standards, and form the networks with systematically varying each reaction probability. However, since the change in the termination probability between the primary radicals alters the initiator efficiency f , the termination probability between the primary radicals is fixed at one. In the following, we fix the monomer volume fraction and the cross-linker ratio at $\phi_m = 0.1$ and $c_x = 2.65 \times 10^{-2}$, respectively.

Fig. 12 shows the number density v_x of the elastically effective chains formed by cross-linking, the number density v_{te} of the elastically effective chains generated by the trapped entanglements, and the number average molecular weight $\overline{M}_{n,p}$ of the primary chains with varying each reaction probability. The decrease in p_d or the increase in p_p increases v_x , v_{te} , and $\overline{M}_{n,p}$. On the other hand, within the calculation range of p_t in this study, the simulation results are almost independent of p_t . According to the kinetics of FRP, $\overline{M}_{n,p}$ is proportional to the rate constant k_p of the propagation and inversely proportional to the square root of the rate constants k_d and k_t of the initiator decomposition and the termination[21]. The growth in $\overline{M}_{n,p}$ with decreasing p_d or increasing p_p qualitatively agrees with the kinetics of FRP. We have confirmed that each reaction rate constant changes with varying each reaction probability (Fig. S4 in Supporting Information). However, the change in k_t is small because the termination, which proceeds by the collision of polymer ends, is diffusion-controlled over the wide p_t range. The simulation results that are insensitive to p_t are considered to be due to the small change in k_t .

Since $\overline{M}_{n,p}$ affects the network structure as discussed above, we plot the results with varying p_d or p_p against $\overline{M}_{n,p}$ in Fig. 13. As seen in Fig. 13a, in the region of $\overline{M}_{n,p} \leq 7 \times 10^2$, the networks with reduced p_p exhibit larger v_x and smaller v_{te} than the networks with the same $\overline{M}_{n,p}$ and increased p_d . These results indicate that a relatively uniform network structure with high cross-linking efficiency and the suppressed occurrence of entanglement is obtained by slowing down the propagation rate. Orakdogan *et al.* reported that the homogeneity of the network structure is improved by decreasing the polymerization rate[12, 14]. We think that the simulation results are consistent with their experimental results. In addition, it has been recently reported that gels having many entanglements exhibit excellent mechanical properties such as toughness and low friction[18, 54]. Therefore, we think that the enhancement of the occurrence of entanglement by speeding up the propagation improves the mechanical properties of FRCP gels.

From the analysis of the structure of the network strands, we find that the networks with reduced p_p have fewer loop chains and more bridge chains than the networks with increased p_d (Fig. 13b). When the propagation is fast, the probability for a propagating end to react with nearby reactive beads is high. Therefore, after one end of a cross-linker reacts, the probability of the formation of the loop chain by the reaction between the other end of the cross-linker and the

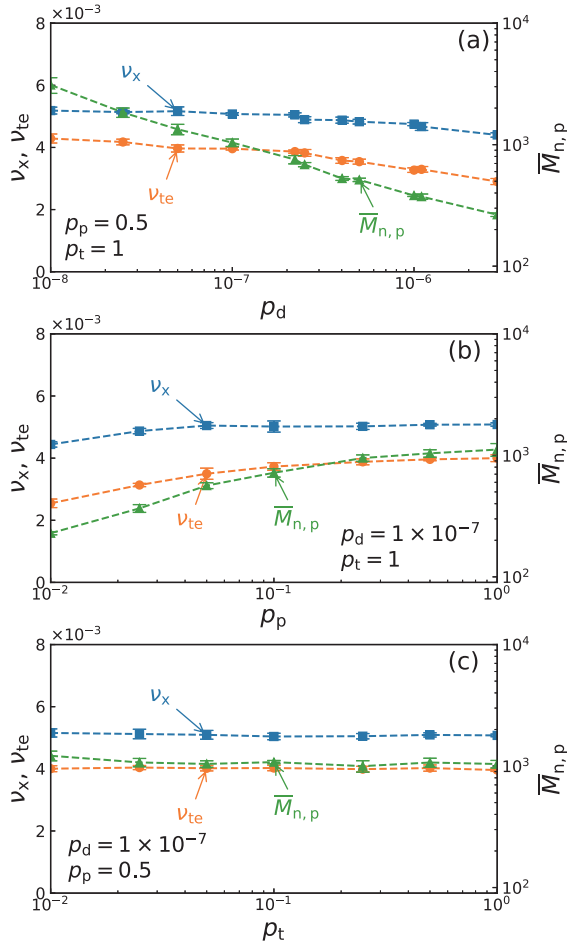


Figure 12: Number density v_x of the elastically effective chains formed by cross-linking, number density v_{te} of the elastically effective chains generated by the trapped entanglements, and the number average molecular weight $\bar{M}_{n,p}$ of the primary chains shown as functions of (a) the decomposition probability p_d , (b) the propagation probability p_p , and (c) the termination probability p_t .

propagating end increases. The formation of the loop chains, which are intramolecular cross-links, promotes density fluctuations, and enhances the occurrence of entanglement[37]. On the other hand, when the propagation is slow, since a propagating end is able to react with monomers in a wide space, the probability of the loop formation decreases. The decline in the number of loop chains rises that of bridge chains; hence, v_x increases. From these results, we consider that the homogenization of the structure of the networks with slow propagations is due to the kinetic structural changes of the network strands. We here note that the polydispersity index $\bar{M}_{w,s}/\bar{M}_{n,s}$ of the strands is almost independent of the reaction rates within the calculation range of this study (Fig. S9 in Supporting Information).

Finally, we mention the effects of the standard reaction probabilities. In this paper, we have used the reaction probabilities under which the propagation is diffusion-controlled as the standard conditions. As shown in Supporting Information, we have confirmed that the similar results are obtained

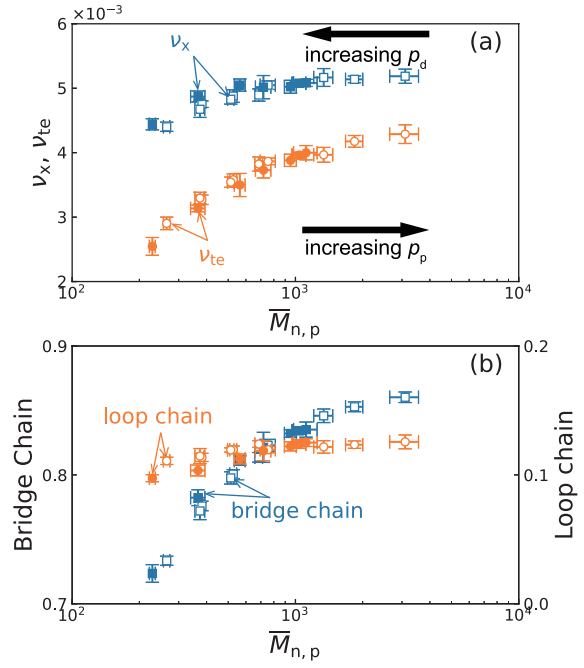


Figure 13: (a) Number density v_x of the elastically effective chains formed by cross-linking and number density v_{te} of the elastically effective chains generated by the trapped entanglements shown as functions of the number average molecular weight $\bar{M}_{n,p}$ of the primary chains. (b) Relative populations of the bridge chain and the loop chain shown as functions of $\bar{M}_{n,p}$. Open and filled symbols indicate the results with varying the decomposition probability p_d and those with varying the propagation probability p_p , respectively.

when the reaction probabilities under which the propagation is not diffusion-controlled are used as the standard conditions.

4. Conclusions

We have studied the network structure and mechanical properties of gels formed by FRCP of monomers and cross-linkers by the CGMD simulation with the FRP model that reproduces some features of the kinetics of FRP. For the gels formed at the low monomer volume fractions ϕ_m , the mechanical cross-linking efficiency ϵ_G calculated from the shear modulus G increases with increasing the cross-linker ratio c_x . However, ϵ_G decreases with increasing c_x when the gels are formed at the high ϕ_m . In addition, the gels formed at the high ϕ_m and the low c_x exhibit very high ϵ_G . These results qualitatively agree with the experimental results[13, 18]. In the gels formed at the low ϕ_m , the formation of the bridge chains is rapidly enhanced with increasing c_x . As a result, the numbers of elastically effective chains and entanglements both significantly increase with increasing c_x ; thus, ϵ_G increases with increasing c_x . On the other hand, in the gels formed at the high ϕ_m , the contribution of the entanglements trapped in the network to G is large, and the number of entanglements gradually increases with increasing c_x . Therefore, ϵ_G decreases with increasing c_x .

We have also studied the effects of the elementary reaction rates on the structure of FRCP gels with systematically varying each elementary reaction rate. We have confirmed that the numbers of the elastically effective chains and trapped entanglements increase due to the increase in the number average molecular weight of the primary chains, when the initiation rate is decreased or the propagation rate is increased. From the comparison of the results with varying the initiation rate and those with varying the propagation rate, we have found that the slow propagations relatively increase the number of elastically effective chains while relatively decreasing the number of trapped entanglements, *i.e.*, make the network structure uniform. Since the formation of the loop chains is suppressed in the gels with the slow propagations, we found that the structure is homogenized by the structural changes of the network strands due to the differences in the reaction rates. We think that the variation in the network structure with changing reaction rates contribute the uniform structure of gels synthesized by CRCP[2, 19, 20]. We plan to study the homogenization mechanism of the network structure by CRCP focusing on the difference in the reaction rates.

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CRedit authorship contribution statement

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

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