

Molecular Simulation of Effects of Network Structure on Fracture Behavior of Gels Synthesized by Radical Polymerization

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Abstract

The synthesis of high-strength gels with many entanglements by radical polymerization with high monomer and low cross-linker concentrations has recently been reported by several groups. In order to elucidate the toughening mechanism of such high-strength gels, the fracture behavior of gels synthesized by radical polymerization is studied by a coarse-grained molecular dynamics simulation. The simulation results qualitatively reproduce the reported experimental results; the gels formed with high monomer and low cross-linker concentrations have a small number of elastically effective chains due to cross-linking, but many polymer entanglements, and exhibit high toughness without sacrificing the shear modulus. In the tough gels, the structural changes that suppress the orientation of the polymer chains in the elongation direction and stress concentration are confirmed. Analysis of the relationship between network structure and fracture behavior reveals that the chain length between cross-linking points and the number of entanglements are important for the toughness of the gels.

Introduction

Polymer gels, which consist of three-dimensionally cross-linked network polymers and solvents, are important materials used in a wide range of fields such as food,¹ sanitary products,² soil treatment agents,³ and biomedical materials,⁴ and are the subject of active research.⁵⁻⁷ Improving the mechanical strength of gels is one of the main research topics to further expand their range of applications.⁸ Since the mechanical strength of gels is closely related to the structure of network polymers, high-strength gels with characteristic network structures synthesized by unique methods have been reported.⁹⁻¹⁸ Typical examples include slide-ring (SR) gels with movable cross-linking points formed by cross-linking polyrotaxanes,^{9,10} nanocomposite (NC) gels using clays as multiple cross-linking points,^{12,13} double-network (DN) gels in which hard and brittle gels and soft and ductile gels interpenetrate,^{14,15} and tetra-poly(ethylene glycol) (PEG) gels with uniform structures formed by end-linking of tetra-arm PEGs.^{16,17}

Understanding the methodology for obtaining high-strength gels using general synthesis methods rather than specialized methods is important for expanding the range of applications of polymer gels. Industrially, network polymers are often synthesized by free radical polymerization (FRP) of monomers in the presence of cross-linkers, since a wide range of monomer species and synthesis conditions can be used.^{7,19,20} A lot of research has been conducted with systematically varying the synthesis conditions, including polymerization concentrations,²¹⁻²³ reaction rates,²⁴ and types of monomers and cross-linkers^{24,25} to understand and control the structure and properties of FRP gels. However, the propagation of polymers heterogeneously and stochastically proceeds in FRP, various defects, such as dangling chains, loops, entanglements, and density fluctuations, are formed in the network structure;^{7,20,26} thus, the control of the structure of FRP gels is difficult.

In recent years, a new methodology to improve the mechanical strength of FRP gels by actively utilizing entanglements, which are a type of inhomogeneity in the gels, has been reported.²⁷⁻²⁹ These studies have shown that FRP gels synthesized with high monomer and

low cross-linker concentrations exhibit high elastic moduli and high toughness.^{27,28} The high-strength FRP gels indicate high elastic modulus due to the large number of entanglements trapped in the network, which act as physical cross-linking points, although the number of covalent cross-linking points is small.^{27,28} The improvement in toughness is attributed to reduced stress concentration under large deformation due to the structural changes involving the movement of trapped entanglements.²⁷⁻²⁹ Although the proposed strengthening mechanism seems reasonable, it is necessary to consider effects other than entanglements, since the length of strands, which are polymer chains connecting adjacent cross-linking points, and density fluctuations also change with the changes in concentrations at the synthesis of FRP gels. Clarifying the extent of the effect of entanglements on the toughening of FRP gels is important in determining whether to actively use entanglements in the development of high-strength FRP gels.

The fracture behavior of gels has been computationally studied, because simulation is useful for investigating the relationship between the detailed network structure of gels and their physical properties.³⁰⁻³⁶ Simulations to understand the unique mechanical strength of high-strength gels, such as SR gels,³³ NC gels,³⁰ DN gels,³¹ and tetra-PEG gels,³⁴⁻³⁶ have been actively conducted. In studies focusing on the inhomogeneities in the network structure, Arora *et al.* reported that the gel formed by cross-linking of tetrafunctional cross-linkers and telechelic functional polymers decreases the maximum stress with increasing loop chains but increases the extension at which the network breaks.³² Argun and Statt actively varied the inhomogeneities of gels and reported that gels with large density fluctuations exhibit lower toughness.³⁷ However, since few studies have focused on the effect of entanglements on the toughening of FRP gels, we think that more detailed studies are needed.

In this study, we investigate the influence of the network structure on the fracture behavior of the gels synthesized by radical polymerization by a coarse-grained molecular dynamics (CGMD) simulation. We first prepare the FRP gels with different monomer and cross-linker concentrations and confirm that their fracture behavior agrees with the experimental re-

sults.²⁷ By analyzing the structural changes under deformation, we elucidate the toughening mechanism of the gels with many entanglements. We compare the fracture behavior of gels synthesized by controlled radical polymerization (CRP) with that of the FRP gels to evaluate the effects of factors other than the entanglements, such as the solid content concentration, strand length, and density fluctuations. The comparison of the deformation ratios at the onset of the bond breaking estimated from the network structure and those obtained from the simulation is used to clarify the effect of entanglements on the fracture behavior of the gels. We think that the results of this study provide useful information for increasing the strength of gels synthesized by radical polymerization.

Simulation

Gel formation

The FRP and CRP gel models were prepared in the same way as in the previous studies.^{38,39} In the FRP gel, the monomer, cross-linker, and initiator are represented by a bead-spring model^{40–42} consisting of one, three, and two beads, respectively, and the network polymer is created by stochastic elementary reactions: the initiation, propagation, and termination (see Figure S1 in the Supporting Information (SI)). The beads at both ends of the cross-linker have the same reactivity as the monomer, while the center bead is an inert bead. In the initiation, the initiator decomposes with probability $p_i = 1 \times 10^{-7}$ to produce two primary radical beads. The propagation and termination proceed with probabilities $p_p = 0.5$ and $p_t = 1$, respectively, when the distance between a pair of reactive beads is less than or equal to $r_r = \sigma$. Here, σ is the collision diameter of the Weeks–Chandler–Andersen (WCA) potential⁴³ described below, and the termination is assumed to be the disproportionation based on the experimental results of polyacrylamide systems.⁴⁴ In the CRP gel, instead of the initiator and the initiation in the FRP gel, the initial dormant species represented by a single bead and the reversible activation were introduced to create the network polymers. The reversible

activation is assumed to be always in equilibrium, and the probability of a propagation end being a radical at time t is set to $P_a = 0.01$. The details of the polymerization model are presented in Section S1.1 in the SI and in our previous works.^{38,39} The reaction probabilities p_i , p_p , p_t , and P_a were adjusted to reproduce some features of the reaction kinetics of FRP and CRP,^{45,46} such as the time evolution of the conversion index, the concentration dependences of the polymerization rate and the average molecular weight (Figure S3–S6 in the SI). In addition, we have confirmed that the intensity of the structure factor $S(q)$ of the FRP gel increases in the small-angle region with decreasing the monomer concentration or increasing the cross-linker concentration (Figure S19 in the SI). These results qualitatively reproduce the results of scattering experiments of FRP gels.^{21,22} However, as discussed in the SI, in order to avoid enormous computation time, the termination is slower than in real systems, and the probability that the propagation end is a radical is higher than in real CRPs.

The following interactions were used between beads. The WCA potential⁴³ was applied between all beads: $U_{\text{wca}}(r_{ij}) = 4\varepsilon [(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6 + 1/4]$ for $r_{ij} \leq 2^{1/6}\sigma$. Here, r_{ij} is the distance between the beads i and j , ε is the potential strength, and σ is the collision diameter. The units of energy, distance, mass, temperature, and time in the simulation are then ε , σ , m , ε/k_B , and $\tau \equiv \sigma\sqrt{m/\varepsilon}$, respectively. Here, m is the mass of one bead and k_B is Boltzmann's constant. The finitely extensible non-linear elastic (FENE) potential⁴⁷ was applied between the bound beads in addition to the WCA potential: $U_{\text{fene}}(r_{ij}) = -(1/2)k_b r_0^2 \ln [1 - (r_{ij}/r_0)^2]$. In order to prevent bond crossing, the spring constant k_b was set to $30\varepsilon/\sigma^2$ and the maximum bond length r_0 was set to 1.5σ .^{40–42} The following bending potential was introduced into the bond angles of the cross-linkers to prohibit intramolecular reactions between the cross-linker ends: $U_{\text{bend}}(\theta_i) = (1/2)k_{\text{bend}}(\cos \theta_i - \cos \theta_0)^2$, where θ_i is the bond angle of the cross-linker i , $k_{\text{bend}} = 100\varepsilon$ is the spring constant, and $\theta_0 = \pi$ is the equilibrium bond angle.

Using the above potentials, the motion of the beads was calculated by integrating the

following Langevin equations by the velocity Verlet method⁴⁸ with timestep $\Delta t = 5 \times 10^{-3}\tau$:

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

Here, $\mathbf{r}_i(t)$ is the position vector of the bead i at time t ; $\mathbf{F}_i(t)$ is the force acting on the bead i based on the above potentials; $\zeta = 0.5/\tau$ is the friction coefficient; $\mathbf{W}_i(t)$ is the random force acting on the bead i satisfying $\langle \mathbf{W}_i(t) \rangle = 0$ and $\langle \mathbf{W}_i(t) \cdot \mathbf{W}_j(t') \rangle = 6mk_B T \zeta \delta_{ij} \delta(t - t')$; and T is the temperature, which was fixed at ε/k_B in this study.

The gels were created by stochastic progression of the elementary reactions while calculating the motion of the beads. Specifically, n_m monomers, n_x cross-linkers, n_i initiators for the FRP, and n_d initial dormant species for the CRP were randomly placed in the cubic simulation box of volume V with periodic boundary conditions. In order to uniformly mix the molecules, the simulation was performed for 500τ without processing the reactions. The network polymers were then formed by performing the simulation with the calculations of elementary reactions at each time step until the conversion α reached 95%. In this study, the number n_m of monomers was fixed at 1×10^5 , and the monomer concentration was adjusted by changing V . The cross-linker concentration was varied by changing the number n_x of cross-linkers. The number n_i of initiators for the FRP was fixed at 350 throughout this study. On the other hand, the number n_d of initial dormant species for the CRP was adjusted so that the number average molecular weight $M_{n,p}$ of the primary chains, which are the polymers obtained by the scission of the cross-linkers in the network, was almost equal to that of the corresponding FRP gel, since the effects of $M_{n,p}$ on the structure and physical properties are significant.⁴⁹ The detailed simulation conditions are shown in Table S1 in the SI. In the following, the monomer concentration is expressed as the monomer volume fraction $\phi_m = n_m \sigma^3 \pi / 6V$ and the cross-linker concentration is expressed as the ratio $c_x = n_x / n_m$ of the number n_x of cross-linkers to the number n_m of monomers.

Using the prepared gels, we evaluated the number density ν_x of the elastically effective

chains formed by chemical cross-linking, the number density ν_{te} of the elastically effective chains generated by the entanglements trapped in the network, and the equilibrium shear modulus G . ν_x was calculated by counting the number of elastically effective chains using the Scanlan–Case criterion.^{50,51} In order to measure ν_{te} , we analyzed all entanglements by the method of Everaers *et al.*⁵² and then extracted the entanglements trapped in the network by using Langley’s criterion.⁵³ G was calculated by fitting the nominal stress $\sigma_{n,eq}$ at the equilibrium state, which is estimated from the time evolution of the nominal stress σ_n under small deformation (the uniaxial deformation with the one-dimensional deformation ratio λ of 0.6–1.4), to the neo-Hookean model $\sigma_{n,eq} = G(\lambda - \lambda^{-2})$. The detailed calculation methods are shown in Section S1.3 in the SI.

Fracture behavior of gel

In the simulation of the fracture behavior of the gels, the potentials between the bound beads were changed from the FENE potential to a FENE potential with a cutoff radius to handle bond breaking, *i.e.*, the FENE-C potential:⁴⁷

$$U_{fene-c}(r_{ij}) = \begin{cases} U_{fene}(r_{ij}) - U_s(r_{ij}, \Delta r) & r_{ij} \leq r_{cut} \\ U_0 & r_{ij} > r_{cut} \end{cases}. \quad (2)$$

Here, r_{cut} is the cutoff radius, $U_s(r_{ij}, \Delta r)$ is a smoothing function acting at $r_{cut} - \Delta r < r_{ij} \leq r_{cut}$ to ensure the continuity of the force $dU_{fene-c}(r_{ij})/dr_{ij}$, and $U_0 = U_{fene}(r_{cut}) - U_s(r_{cut}, \Delta r)$. In this study, we set $r_{cut} = 1.4\sigma$ and $\Delta r = 0.1\sigma$. When the bond length of a bond exceeds r_{cut} , the bond is broken, and the beads connected by the bond become inert beads. Even if the distance between these beads becomes less than or equal to r_{cut} , the bond is not reformed. The potential energy difference ΔU_{cut} between the minimum potential energy $U_{fene-c}(r_{eq}) + U_{wca}(r_{eq})$ at the equilibrium bond length $r_{eq} \simeq 0.961\sigma$ and the potential energy $U_{fene-c}(r_{cut}) + U_{wca}(r_{cut})$ at bond breaking is *ca.* 38.1ε . The bond breaking rate due to

thermal fluctuations is estimated to be approximately $\exp(-\Delta U_{\text{cut}}/k_{\text{B}}T) \simeq 3 \times 10^{-17}\tau^{-1}$. Since this rate is very slow compared to the deformation rate used in this study (1×10^{-4} – $2 \times 10^{-3}\tau^{-1}$), we consider that bond breaking due to thermal fluctuations occurs negligibly. We have also confirmed that the bonds are not broken by thermal fluctuations during the simulation under the small deformations for $t = 1.1 \times 10^5\tau$. In the previous simulations of gel fracture, although quartic potentials were often used between bound beads,^{31,33} we here used the FENE-C potential to directly correspond to the simulation at the undeformed state. Although the difference in the potential causes small quantitative differences in the fracture behavior of the gels, it does not change the qualitative results (Section S3 in the SI).

The fracture behavior of the gel was analyzed by applying the uniaxial deformation to the gel. In this study, the uniaxial deformation was applied by changing the lengths of the simulation box from L_0 to λL_0 in the x -axis direction and from L_0 to $L_0/\sqrt{\lambda}$ in the y -axis and z -axis directions at a constant deformation rate $d\lambda/dt$. Here, $L_0 = V^{1/3}$ is the initial length of the simulation box, and λ is the one-dimensional deformation ratio. The simulation of the fracture of the gel was carried out until the connectivity of the gel in the x -axis direction was lost (the rupture of the gel) or λ reached 18.

Unless otherwise noted, the simulation results in this study are the average of ten independent runs, and the error bars or shaded regions in the figures indicate the 95% confidence interval.

Results and discussion

Tough gel synthesized with high monomer and low cross-linker concentrations

In order to reproduce the experimental results that gels synthesized with high monomer and low cross-linker concentrations become tough without sacrificing the elastic moduli,^{27,28} the FRP gels with almost the same equilibrium shear modulus G were formed by adjusting the

cross-linker ratio c_x while varying the monomer volume fraction ϕ_m . In this study, we fixed G at *ca.* 4×10^{-3} to investigate a wide range of ϕ_m at c_x near the experimentally reported range (1×10^{-5} – 0.05).^{27,28} We present the relationship between G and both ϕ_m and c_x in Figure S8 in the SI. For the FRP gels with almost the same G formed by adjusting c_x , the number density ν_x of the elastically effective chains formed by cross-linking decreases with increasing ϕ_m , while the number density ν_{te} of the elastically effective chains generated by the entanglements trapped in the network increases (Figure 1).

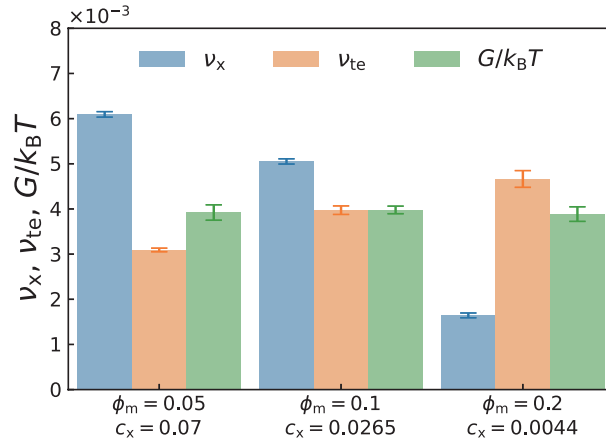


Figure 1: Number densities ν_x and ν_{te} of the elastically effective chains formed by cross-linking and those generated by the trapped entanglements, and shear modulus G of the FRP gels prepared by adjusting the cross-linker ratio c_x while varying monomer volume fraction ϕ_m to obtain almost the same G . The error bars indicate the 95% confidence interval.

When these gels are subjected to large deformation, the gel made with a high ϕ_m and low c_x clearly shows improved toughness compared to the gel made with a low ϕ_m and high c_x . Figure 2 shows the nominal stress σ_n and the ratio f_{bb} of the number of bonds broken during the deformation to the total number of bonds in the gel at the initial state when the uniaxial deformation is applied to the gel at the deformation rate of $d\lambda/dt = 1 \times 10^{-4}$. The results up to the minimum of the gel rupture deformation ratios λ_r calculated in ten independent simulations are shown in Figure 2, where λ_r is defined as the deformation ratio at which the gel network loses its connectivity in the x -direction. Since the compared gels have almost the same G , when $d\lambda/dt$ is slow, the gels show approximately the same σ_n at small deformation

ratios ($\lambda \lesssim 2$). With increasing λ , σ_n rapidly increases, the bond breaking begins, σ_n exhibits the maximum, and the gel then ruptures. With increasing ϕ_m , the deformation ratio λ^* at the onset of bond breaking, the deformation ratio λ_p indicating the maximum σ_n , and λ_r shift to the larger λ side (the gel formed with $\phi_m = 0.2$ do not rupture at $\lambda \leq 18$). The λ^* and λ_p for the gel made at $\phi_m = 0.2$ are about 10 and about 14, respectively, both about three times larger than those for the gel made at $\phi_m = 0.05$ ($\lambda^* \simeq 3.4$ and $\lambda_p \simeq 4.2$). Here, λ^* is estimated from the intersection of the fitted line in the region where f_{bb} is almost proportional to λ and the horizontal axis. These simulation results show that, similar to the experimental results,^{27,28} the gel can be toughened without sacrificing the elastic modulus by creating the gel with a high monomer concentration and a low cross-linker concentration.

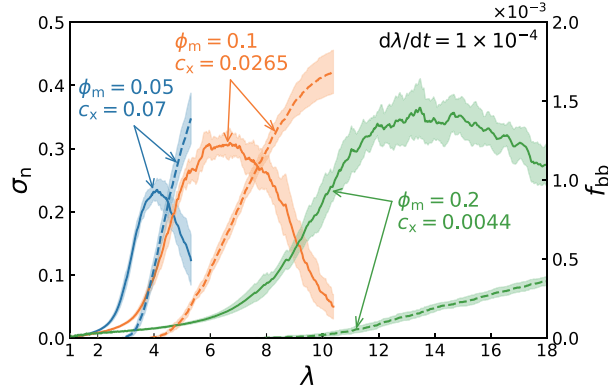


Figure 2: Nominal stress σ_n (solid lines) and proportion f_{bb} of broken bonds (dashed lines) shown as functions of the deformation ratio λ . The deformation rate $d\lambda/dt$ is equal to 1×10^{-4} . The shaded regions indicate the 95% confidence interval.

The fracture behavior is qualitatively the same at different $d\lambda/dt$, but $d\lambda/dt$ dependence of σ_n is more pronounced for the gels formed with higher ϕ_m . Figure 3 shows the stress-strain curves and the proportion f_{bb} of broken bonds for various $d\lambda/dt$. Even if $d\lambda/dt$ changes, the concentration dependence of the fracture behavior shows the same trend as Figure 2. Although λ_r shows a slight increasing trend with increasing $d\lambda/dt$, λ^* and λ_p are almost independent of $d\lambda/dt$ (Figure S9 in the SI). With increasing $d\lambda/dt$, σ_n increases, and the deformation ratio at which σ_n rapidly increases shifts to the smaller λ side. The changes

in σ_n due to the change in $d\lambda/dt$ are larger for the gels formed at higher ϕ_m . The high σ_n at fast $d\lambda/dt$ is considered to be caused by the deviation of the structure from the optimal structure under deformation. Since the gels formed with high ϕ_m and low c_x , which contain many entanglements, exhibit a long relaxation time (Figure S7 in the SI), the structural deviation from the optimal structure and the increase in σ_n become large at fast $d\lambda/dt$. In addition, λ_r , which depends on $d\lambda/dt$, is thought to be related to the structure with the long relaxation time.

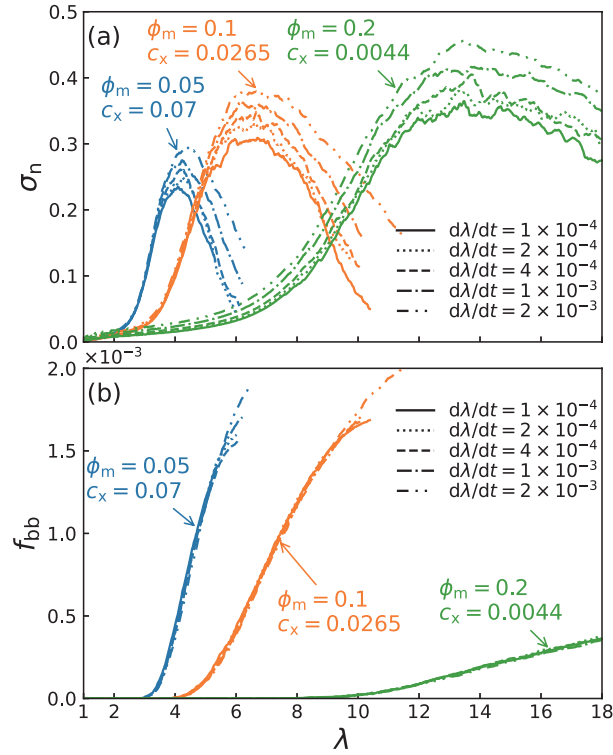


Figure 3: (a) Nominal stress σ_n and (b) proportion f_{bb} of broken bonds shown as functions of the deformation ratio λ for various deformation rates $d\lambda/dt$.

The stress-strain curves in this study are reproduced by the slip-link model with the finite chain extensibility proposed by Edwards and Vilgis.⁵⁴ The reduced stress $\sigma_n/(\lambda - \lambda^{-2})$ is plotted against λ^{-1} for comparison with the theoretical model (Figure 4). In Figure 4, we present σ_n at $d\lambda/dt = 0$, determined by extrapolating the relationship between σ_n and $d\lambda/dt$ for each λ . The equilibrium nominal stresses $\sigma_{n,eq}$ obtained from long-time simulations and used for the calculation of G are also shown. The Edwards–Vilgis theory includes param-

ters representing the contribution of cross-links to the shear modulus G_c , the contribution of entanglements to the shear modulus G_e , the reciprocal of the maximum deformation ratio α' , and the slip-link slippage parameter η . When the parameters G_c , G_e , and α' , estimated from the simulation results ($G_c = \nu_x - \mu_x$, where μ_x is the number density of elastically effective cross-linking points, $G_e = G - G_c$, and $\alpha' = 1/\lambda^*$), are used with the theoretical value of $\eta \simeq 0.2343$,⁵⁵ the theoretical results overestimate the strain-softening due to entanglements (dotted lines in Figure 4). The overestimation of stress-softening in theories compared to simulations has been reported in previous studies.^{56,57} The difference in the mobility of entanglements is thought to be one of the reasons for the discrepancy between theory and simulation. The Edwards–Vilgis model deals with the slippage of a single entanglement to achieve mechanical equilibrium. However, in the simulation with multiple entanglements, the collisions between entanglements restrict slippage and hinder the achievement of mechanical equilibrium.^{57,58} Treating all the theoretical parameters as fitting parameters yields good agreement between the theoretical and simulation results (solid lines in Figure 4). G_c obtained from the fitting is higher than that estimated from the simulation results, while G_e is lower. The fitting results of η for the gels formed with $\phi_m = 0.1, 0.2$ are close to the theoretical value, but that for the gel formed with $\phi_m = 0.05$ is nearly zero; hence, in the last gel, it is possible that the displacement of entanglements is significantly suppressed. Although similar results are obtained from analyses using other theoretical models,^{55,58–60} the Edwards–Vilgis model provides the best fit to this simulation (Figure S13 in the SI).

The toughening of gels prepared at high ϕ_m and low c_x is considered to be related to the changes in the network structure during the deformation. In order to understand the toughening mechanism, we performed the load-unload tensile tests (Figure 5). Here, we focused on structural changes other than bond breaking; thus, after applying the elongation deformation to the gel at a constant deformation rate ($d\lambda/dt$) until the deformation ratio $\lambda \simeq 0.8\lambda^*$, where the bonds are not broken, we then applied the compression deformation at the same deformation rate ($-d\lambda/dt$) until $\lambda = 1$. The gels show hysteresis in σ_n of the

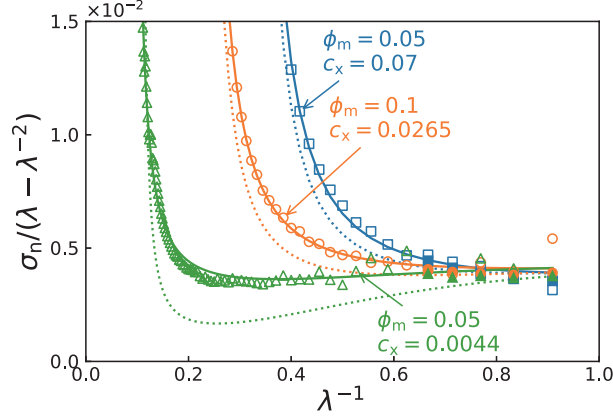


Figure 4: Reduced stress $\sigma_n/(\lambda - \lambda^{-2})$ shown as a function of the reciprocal λ^{-1} of the deformation ratio. Open symbols indicate σ_n at $d\lambda/dt = 0$ obtained by the relationship between σ_n and $d\lambda/dt$. Filled symbols indicate the equilibrium nominal stresses $\sigma_{n,eq}$ obtained from long-time simulations. Solid and dotted lines represent the theoretical results using the parameters obtained by fitting and those determined from the simulation results, respectively.

load-unload test. The hysteresis can be attributed to the energy dissipation due to the changes in the network structure caused by the deformation. Since the hysteresis reduces with decreasing $d\lambda/dt$, we think that the hysteresis is caused by the deviation of the structure from the equilibrium structure at each λ . As seen in Figure 5, the increase in ϕ_m causes the increase in hysteresis (Figure S14 in the SI). Therefore, the gels with high ϕ_m more significantly change their structures during the deformation. It should be noted that, in the experimental studies, the high-strength gels with many entanglements only exhibit small hysteresis.^{28,29} We think that the difference in the hysteresis between the simulation and experiments is due to the difference in $d\lambda/dt$, which in the simulation is much faster than in the experiments.

We next examine the orientation of the bond vectors to study the changes in the network structure due to the deformation. Figure 6 shows the average orientation correlation $\overline{C}_{\text{bond}} \equiv (1/n_{\text{bond}}) \sum_{i=1}^{n_{\text{bond}}} (3 \cos^2 \theta_{\text{bond},i} - 1)/2$ between the bond vectors and the elongation direction. Here, n_{bond} is the number of bonds in the gel and $\theta_{\text{bond},i}$ is the angle between the i -th bond vector and the elongation direction. Since $\overline{C}_{\text{bond}}$ decreases with increasing the number of broken bonds, the results are shown for $\lambda < 0.9\lambda^*$, where few bonds break.

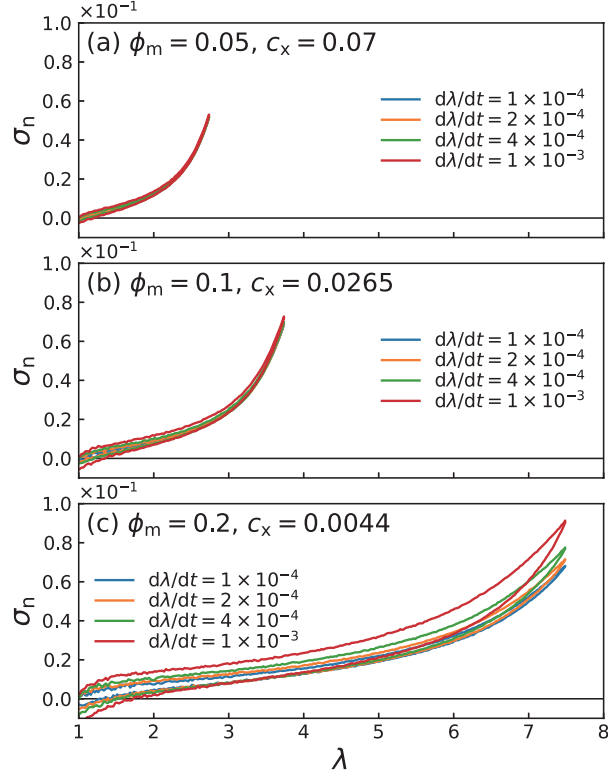


Figure 5: Stress-strain curves of the load-unload tensile test with varying deformation rate $d\lambda/dt$.

In the gels made with high ϕ_m and low c_x , the orientation of bonds in the elongation direction is suppressed, and further relaxation of the orientation is possible by the structural change. In Figure 6, when comparing at the same λ , the higher ϕ_m is, the smaller $\overline{C}_{\text{bond}}$ is, *i.e.* the orientation of bonds is suppressed. Furthermore, while $\overline{C}_{\text{bond}}$ of all the gels decrease with decreasing $d\lambda/dt$, the gel made with $\phi_m = 0.2$ more strongly depends on $d\lambda/dt$ than the other gels. These results indicate that the gels can change the network structures to relax the orientation of bonds, and the gel formed with $\phi_m = 0.2$ shows relatively slow structural changes and relatively large structural deviations from the equilibrium structure at fast $d\lambda/dt$.

Under large deformation, in the gels made with high ϕ_m , the strands are highly oriented, and the stress is uniformly distributed throughout the network. At the maximum deformation ratio for each gel in Figure 6, *i.e.*, the deformation ratio immediately before the

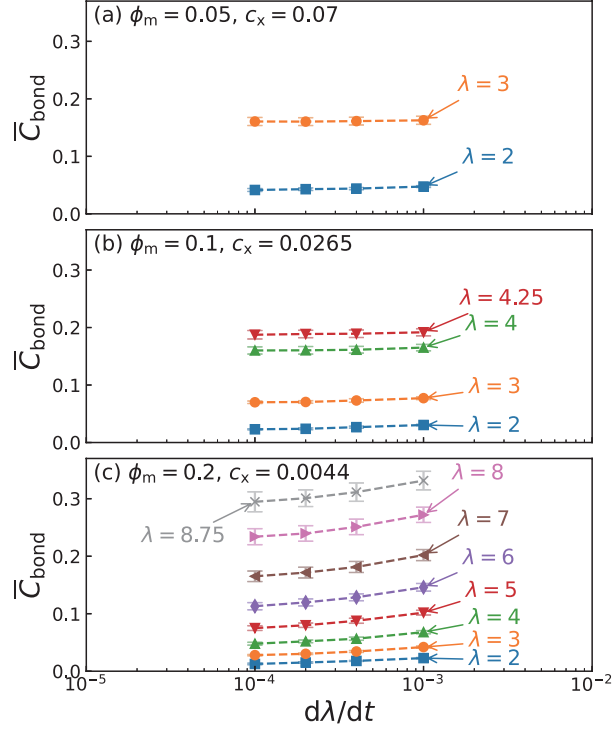


Figure 6: Average orientation correlation $\bar{C}_{\text{bond}}$ between the bond vectors and the elongation direction shown as a function of the deformation rate $d\lambda/dt$.

deformation ratio at which the bond breaking begins, the lower ϕ_m is, the smaller $\bar{C}_{\text{bond}}$ is. The difference in $\bar{C}_{\text{bond}}$ under the large deformation reflects the difference in the distribution of the orientation correlation C_{bond} of each bond (Figure 7a). As seen in Figure 7a, the gels formed with low ϕ_m have many bonds that are not oriented in the elongation direction ($C_{\text{bond}} < 0$) at the deformation ratio just before the onset of bond breaking. On the other hand, the gel made with $\phi_m = 0.2$ has relatively few bonds that are not oriented in the elongation direction, and there are many bonds that are oriented to some extent ($C_{\text{bond}} > 0.4$). Since the stress arises from the oriented bonds, in the gels prepared with low ϕ_m , the stress is concentrated in some bonds (Figure 7b), while in the gel prepared with $\phi_m = 0.2$, the stress is relatively uniformly distributed throughout the network (Figure 7c). In addition, the decrease in $\bar{C}_{\text{bond}}$ accompanying the decrease in $d\lambda/dt$ in the gel formed with $\phi_m = 0.2$ is mainly caused by the decrease in highly oriented bonds (Figure S10 in the SI). Therefore, we consider that the structural change to reduce stress concentration occur in the high-strength

gels created with high ϕ_m and low c_x . Recent studies have revealed that, at high concentrations, SR gels synthesized by cross-linking low coverage polyrotaxanes and tetra-PEG gels with long strand lengths both exhibit extremely high toughness, and show a high orientation of strands in the elongation direction at high deformation ratios, followed by strain-induced crystallization.^{11,18} The structural changes occurring before the crystallization of these tough gels are thought to be similar to those of the high-strength gels in this study. We here note that the orientation of the end-to-end vectors of the elastically effective strands also shows the same trend as Figure 7 (Figure S17 in the SI).

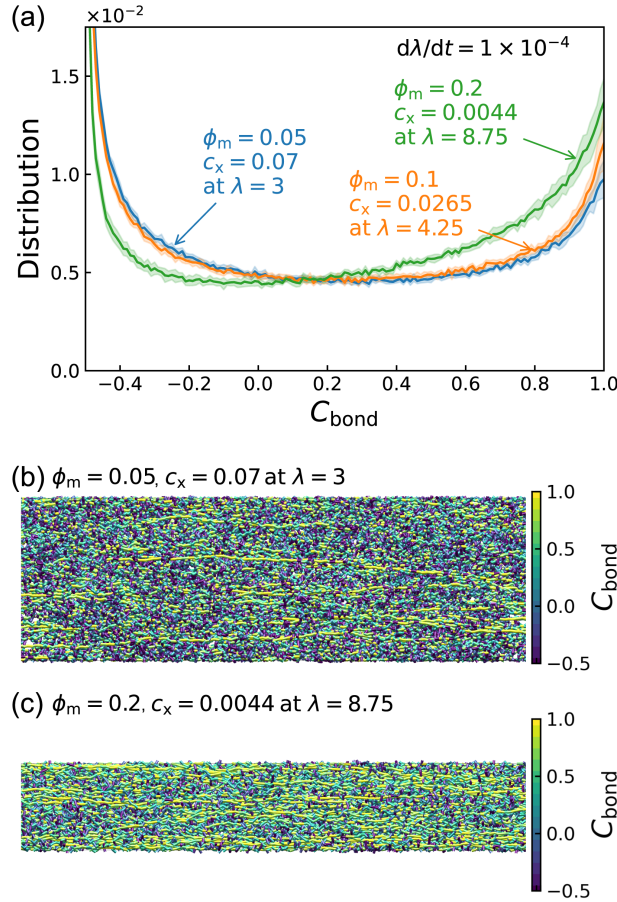


Figure 7: (a) Distribution of the orientation correlation C_{bond} between the bond vectors and the elongation direction near the deformation ratio at the onset of bond breaking. The deformation rate $d\lambda/dt$ is equal to 1×10^{-4} . (b) Part of the network structure at $\lambda = 3$ for the FRP gel formed with $\phi_m = 0.05$ and $c_x = 0.07$ and (c) part of the network structure at $\lambda = 8.75$ for the FRP gel formed with $\phi_m = 0.2$ and $c_x = 0.0044$. The bonds are shown in different colors depending on C_{bond} .

In addition to the structural differences shown in Figure 1, there are other differences between the gels prepared with high ϕ_m and low c_x and those prepared with low ϕ_m and high c_x . First, the length of the strands between the cross-linking points is longer in the former than in the latter (Figure S18a in the SI). Second, the former has a higher solid content concentration and smaller density fluctuations (Figure S20a in the SI). Furthermore, these gels exhibit differences in their network topology such as the bridge, loop, and dangling end (Figure S22a in the SI). While no clear correlation between the relative population of bridges and the fracture behavior is observed, the gels with high toughness indicate a lower proportion of loops and a higher proportion of dangling ends (Figure S22b in the SI). Since these differences may also affect the toughening mechanism, we discuss their effects in the following sections.

Comparison of CRP gel and FRP gel

In this section, we compare the gels prepared by conventional free radical polymerization (FRP) and controlled radical polymerization (CRP) to deepen the understanding of the effects of various structural differences on the fracture behavior. Figure 8 shows the number density ν_x of the elastically effective chains formed by cross-linking, the number density ν_{te} of the elastically effective chains generated by the trapped entanglements, and the equilibrium shear modulus G for the FRP gel and the CRP gel formed with the same solid content concentration ($\phi_m = 0.1$ and $c_x = 0.0265$). As shown in our previous study,³⁹ under these conditions, although G of the two gels are almost equal, the CRP gel has a larger ν_x , a smaller ν_{te} , and smaller density fluctuations than the FRP gel (Figure S20b in the SI). The strand lengths of the two gels are almost the same, and there is no difference in the polydispersity index of the strand lengths (Figure S18b in the SI). Although the CRP gel exhibits a higher number of bridges and a lower number of loops compared to the FRP gel, these differences are smaller than the variations observed among the FRP gels examined in the previous section (Figure S22c in the SI).

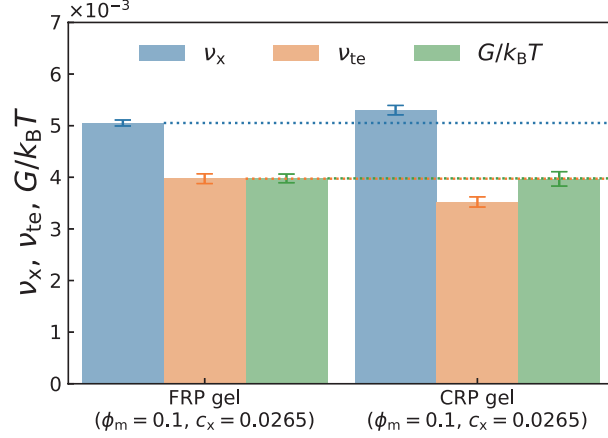


Figure 8: Number densities ν_x and ν_{te} of the elastically effective chains formed by cross-linking and those generated by the trapped entanglements, and shear modulus G of the FRP gel and the CRP gel formed with $\phi_m = 0.1$ and $c_x = 0.0265$. Dotted lines indicate the average values of the FRP gel.

Although the difference is small, the FRP gel tends to have higher toughness than the CRP gel due to the structural changes during deformation. As shown in Figure 9, there is no significant difference in the stress-strain curves of the CRP gel and the FRP gel, but more bonds are broken in the CRP gel than in the FRP gel. The average orientation correlation $\overline{C}_{\text{bond}}$ between the bonds and the elongation direction of the CRP gel is statistically significantly higher than that of the FRP gel in the region of $\lambda \geq 3$ (Figure 10). Furthermore, the hysteresis in the load-unload test is greater for the FRP gel than for the CRP gel (Figure S16 in the SI). From these results, the structural change due to the deformation is more pronounced in the FRP gel than in the CRP gel; therefore, the toughness of the FRP gel is considered to be higher than that of the CRP gel. Note that, since Figure 9 shows the results up to the minimum of the gel rupture deformation ratios λ_r calculated in ten independent simulations, there appears to be a difference in λ_r between the FRP gel and the CRP gel. However, statistical analysis revealed no significant differences in the deformation ratio λ^* at the onset of bond breaking, the deformation ratio λ_p indicating the maximum σ_n , and λ_r (Figure S12 in the SI).

In the comparison of the fracture behavior of the FRP and CRP gels, the entanglement is

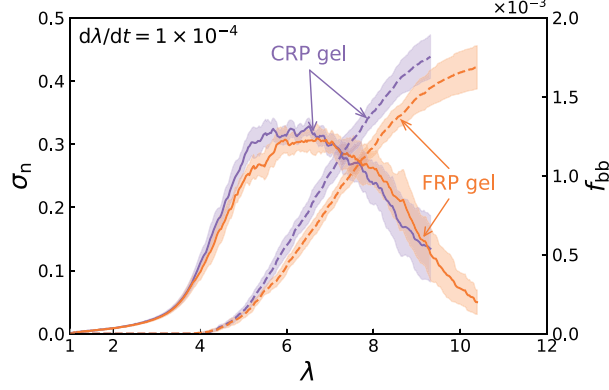


Figure 9: Nominal stress σ_n (solid lines) and proportion f_{bb} of broken bonds (dashed lines) of the FRP gel and the CRP gel formed with $\phi_m = 0.1$ and $c_x = 0.0265$ shown as functions of the deformation ratio λ . The deformation rate $d\lambda/dt$ is equal to 1×10^{-4} .

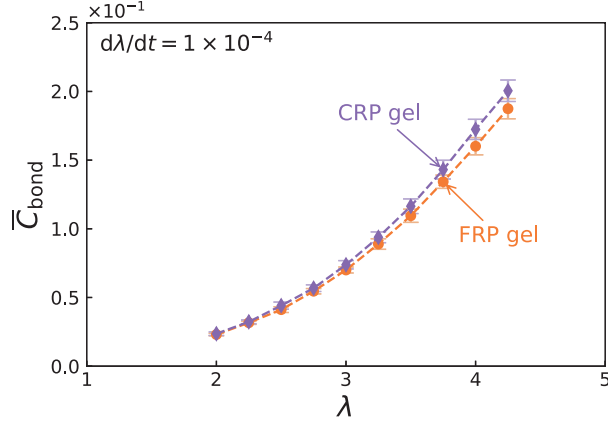


Figure 10: Average orientation correlation $\overline{C}_{bond}$ between the bond vectors and the elongation direction shown as a function of the deformation ratio λ . The deformation rate $d\lambda/dt$ is equal to 1×10^{-4} .

considered to enhance the toughness of gels. The FRP and CRP gels compared in this section have the same solid content concentration and strand length, but differ in the number of entanglements, the magnitude of density fluctuations, and the network topology. The trend that the FRP gel with larger density fluctuations and a higher loop population than the CRP gel exhibits higher toughness than the CRP gel is inconsistent with the results in the previous section, where the gels with higher toughness show smaller density fluctuations and a lower loop proportion. Therefore, the difference in the fracture behavior between the FRP and CRP gels is considered to be mainly due to the differences in ν_x and ν_{te} . The present

findings appear to be inconsistent with the simulation results that reported the increase in the gel rupture deformation ratio λ_r with increasing the number of loops or decreasing density fluctuations.^{32,37} Therefore, we will further discuss these discrepancies after considering the effect of the strand length in the next section.

Effects of strand length and entanglement on toughness

In order to understand the toughening mechanism of gels created with high monomer volume fractions ϕ_m and low cross-linker ratios c_x , we here clarify the effect of each structural difference by evaluating the influence of the strand length. We estimate the ideal deformation ratio λ_{id} at which the bond breaking begins from the average strand length, and compare it with the deformation ratio λ^* at the onset of bond breaking calculated by the simulation.

The ideal deformation ratio λ_{id} at the onset of bond breaking is evaluated by the following procedure. First, the average number N_{eff} of bonds per elastically effective chain in the gel is calculated by the following equation:

$$N_{eff} = \frac{n_{gel}}{(\nu_x + \nu_{te})V} - 1. \quad (3)$$

Here, n_{gel} is the number of beads constituting the gel, the denominator is the total number of elastically effective chains in the gel, and one is subtracted to evaluate the number of bonds between beads. Using this N_{eff} , λ_{id} with the assumption of the affine deformation of strands is evaluated by

$$\lambda_{id}^{(af)} = \frac{r_{cut} N_{eff}}{\langle R^2(N, \phi) \rangle^{1/2}}, \quad (4)$$

where the superscript “(af)” indicate the affine deformation, $r_{cut} = 1.4\sigma$ is the bond breaking length, and $\langle R^2(N, \phi) \rangle$ is the mean squared end-to-end distance of linear polymers with N bonds at the volume fraction ϕ . Considering the fluctuation of cross-linking points based on the phantom network model,⁵⁹ strands with $fN_{eff}/(f-2)$ bonds are assumed to be affinely

deformed; thus, λ_{id} is estimated by

$$\lambda_{\text{id}}^{(\text{ph})} = \frac{r_{\text{cut}} f N_{\text{eff}} / (f - 2)}{\langle R^2 (f N_{\text{eff}} / (f - 2), \phi_{\text{m}}) \rangle^{1/2}}. \quad (5)$$

Here, the superscript “(ph)” indicates the phantom network model and $f = 4$ is the functionality of cross-linking points. When the deformation ratio exceeds λ_{id} , the effective strands whose end-to-end vectors are parallel to the elongation direction break. Although $\langle R^2 (N, \phi) \rangle$ depends on ϕ , since $\langle R^2 (N, \phi) \rangle \approx N^\nu$ ($1 \leq \nu \leq 6/5$), $\lambda_{\text{id}} \approx N_{\text{eff}}^{1-\nu/2}$. Thus, λ_{id} increases with increasing the average stand length N_{eff} , *i.e.*, decreasing c_x .

In order to evaluate the effect of entanglement on the toughness of the gel, $\lambda^*/\lambda_{\text{id}}$ is plotted against $\nu_{\text{te}}/(\nu_x + \nu_{\text{te}})$ in Figure 11. Since λ_{id} mainly depends on the average strand length, the ratio $\lambda^*/\lambda_{\text{id}}$ is considered to indicate effects other than the average strand length. The ratio $\nu_{\text{te}}/(\nu_x + \nu_{\text{te}})$ is the contribution of the entanglements in the number of elastically effective chains. Each data set in Figure 11 shows the results for the gels formed by varying c_x (the detailed conditions are shown in Table S1 in the SI). All the data show the same trend, *i.e.*, $\lambda^*/\lambda_{\text{id}}$ increases with increasing $\nu_{\text{te}}/(\nu_x + \nu_{\text{te}})$. This means that the increase in the number of entanglements delays the onset of bond breaking, *i.e.*, increases the toughness of the gel. From the behaviors of $\lambda^*/\lambda_{\text{id}}^{(\text{af})}$ and $\lambda^*/\lambda_{\text{id}}^{(\text{pf})}$, we find that λ^* tends to shift toward $\lambda_{\text{id}}^{(\text{pf})}$ from $\lambda_{\text{id}}^{(\text{af})}$ as $\nu_{\text{te}}/(\nu_x + \nu_{\text{te}})$ increases. The results suggest that the nonaffine displacement of cross-linking points improves the toughness of the gels with many entanglements. In addition, since the results for the gels formed at different ϕ_{m} almost overlap, we consider that the effect of ϕ_{m} is not significant.

We here discuss the influence of the network topology and density fluctuations on $\lambda^*/\lambda_{\text{id}}$. Figure 12 shows $\lambda^*/\lambda_{\text{id}}$ as a function of the relative population r_{loop} of loops in the gels. At a constant ϕ_{m} , $\lambda^*/\lambda_{\text{id}}$ increases with increasing r_{loop} . Since the decrease in c_x increases r_{loop} ³⁸ and reduces density fluctuations (Figure S19b in the SI), the increase in r_{loop} in Figure 12 corresponds to the reduction in density fluctuations. Thus, at a constant ϕ_{m} , the

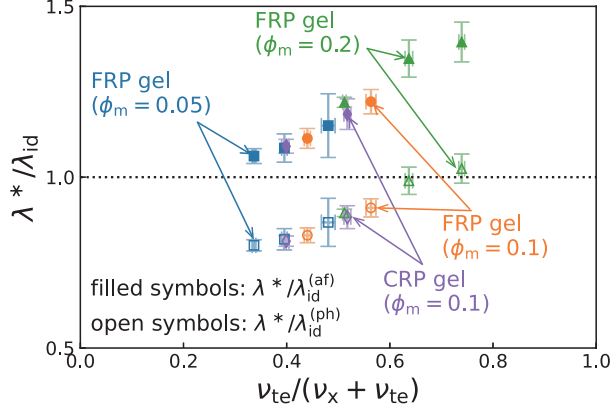


Figure 11: Ratio λ^*/λ_{id} of the deformation ratio λ^* at the onset of bond breaking calculated by the simulation to that λ_{id} estimated by the network structure shown as a function of the ratio $\nu_{te}/(\nu_x + \nu_{te})$ of the number density ν_{te} of the elastically effective chains generated by the trapped entanglements to that $\nu_x + \nu_{te}$ of all the elastically effective chains. Filled and open symbols indicate $\lambda^*/\lambda_{id}^{(af)}$ with the assumption of the affine deformation and $\lambda^*/\lambda_{id}^{(pf)}$ based on the phantom network model, respectively.

reduction in density fluctuations also improves the toughness of the gels (Figure S21 in the SI). These results are consistent with the reported simulation results.^{32,37} However, when considering all λ^*/λ_{id} , including those obtained from the gels formed at various ϕ_m , unlike the entanglement contribution $\nu_{te}/(\nu_x + \nu_{te})$, r_{loop} and density fluctuations exhibit a poor correlation with λ^*/λ_{id} . Therefore, while the network topology and density fluctuations are factors that affect the gel toughness, we consider that λ^*/λ_{id} , which indicates the effects other than the average strand length, is mainly explained by the entanglement.

Assuming that $\lambda^*/\lambda_{id}^{(af)}$ in Figure 11 becomes larger than one mainly due to the entanglement effect, the contribution of the entanglements to the deformation ratio λ^* at the onset of bond breaking is evaluated by $\lambda_{en} = \lambda^* - \lambda_{id}^{(af)}$ (Figure 13). λ^* of the gel formed with $\phi_m = 0.2$ and $c_x = 0.0044$ is about 190% larger than that of the gel formed with $\phi_m = 0.05$ and $c_x = 0.07$. About 110% of this increase is due to the difference in $\lambda_{id}^{(af)}$, *i.e.*, the increase in the average strand length, and about 80% is due to the enhancement effect of abundant entanglements. Therefore, we conclude that the increase in the strand length is the major cause of the toughening of the gels made with high ϕ_m and low c_x in this study, but the effect of the entanglements is also significant.

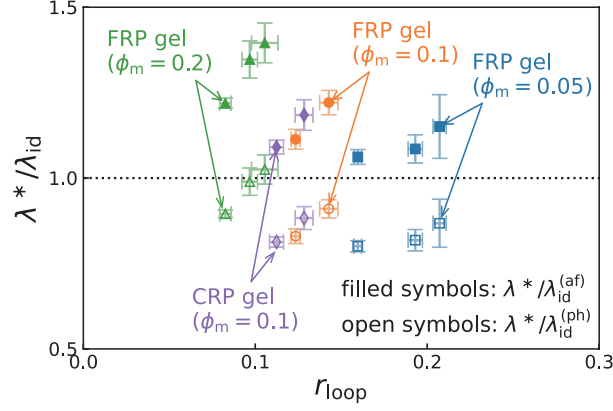


Figure 12: Ratio λ^*/λ_{id} of the simulation bond breaking deformation ratio λ^* to the ideal bond breaking deformation ratio λ_{id} shown as a function of the proportion r_{loop} of loops in the gels.

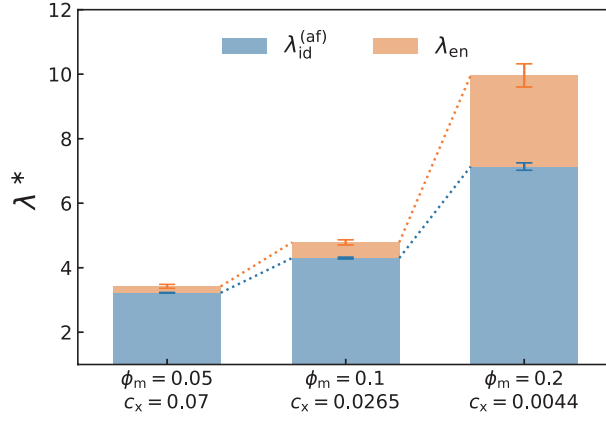


Figure 13: Contribution $\lambda_{id}^{(af)}$ of the average strand length and that λ_{en} of the entanglements to the deformation ratio λ^* at the onset of bond breaking for the FRP gels with approximately the same G .

Conclusions

In this study, the relationship between the fracture behavior and the network structure of gels synthesized by radical polymerization has been investigated by a CGMD simulation. The gels synthesized with high monomer and low cross-linker concentrations contain many entanglements trapped in the network, and the deformation ratios related to the fracture of such gels with many entanglements are found to increase, *i.e.*, the toughness is improved, compared to the gels synthesized with low monomer and high cross-linker concentrations.

These results are qualitatively consistent with the reported experimental results.^{27–29} We have found that the gels synthesized with high monomer and low cross-linker concentrations exhibit improved toughness by changing the network structure to suppress the orientation of polymer chains and the stress concentration on some strands. The influence of the network structure on the toughness of the gels has been investigated in detail by comparing gels prepared by conventional free radical polymerization with those prepared by controlled radical polymerization, and by comparing the simulation results with the deformation ratio at the onset of bond breaking estimated from the network structure. From these results, within the range calculated in this study, we have confirmed that the main reason for the improved toughness of the gels synthesized with high monomer and low cross-linker concentrations is the increase in the average strand length due to the synthesis with low cross-linker concentrations. However, since the effect of entanglement is also significant, it is important to actively increase the number of entanglements to improve the toughness of gels synthesized by radical polymerization.

In this study, we focused on the effect of network structure on the toughness of gels and the toughening mechanism, and studied the fracture behavior of gels without changing the reaction probabilities, *i.e.*, the reactivities of monomers and cross-linkers. Since the changes in the reactivities of monomers and cross-linkers are expected to significantly change the network structure, the effect of entanglement on the fracture behavior of gels will also change. In order to propose methods for synthesizing gels with higher strength, we will explore ways to actively increase entanglement by changing reactivities and gel synthesis methods, and deepen our understanding of the relationship between network structure and fracture behavior.

Supporting Information Available

The following files are available free of charge.

- SI-ma-2024-02875s.pdf: Details of the simulation; supplementary data of the simulation; and the effects of potential between bound beads on the fracture behavior of the gels.

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TOC Graphic

