Effects of Primary Structure of Reactive Polymers on Network Structure and Mechanical Properties of Gels

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The effects of the primary structure of multifunctional reactive polymers on the network structure and the mechanical properties of gels formed by crosslinking the reactive polymers with crosslinkers are studied by a coarse-grained molecular dynamics simulation. When functional groups are randomly arranged on the polymers, the network structure, such as the number densities of elastically effective chains and entanglements, and the mechanical properties depend on the number average molecular weight of the polymers; however, these properties are almost independent of the molecular weight distribution and the functional group number distribution of the polymers. The control of the arrangement of functional groups on the polymers improves the uniformity and the mechanical properties. By changing the arrangement from a random one to a periodic one, the number of elastically effective chains and the shear modulus increase, and the occurrence of entanglement is suppressed. The detailed analysis of the network structure reveals that the improvement of the mechanical properties is mainly due to the reduction of intramolecular crosslinking.

1 Introduction

Polymer gels are materials in which three-dimensional crosslinked network polymers hold a large amount of solvent. Therefore, polymer gels exhibit both solid-like and liquid-like properties [1, 2, 3]. In addition, various functional polymer gels can be synthesized by appropriately modifying polymers constituting the gels [4, 5]. Due to such properties, polymer gels have been researched and developed for applications in a wide field such as biomedical material, sanitary material, drug delivery system, and soft robotics [6, 7].

The free radical copolymerization of monomers and crosslinkers is a widely used method for synthesizing industrial polymer gels. Since crosslinking points are randomly introduced into the network polymers synthesized by such method, the networks have structural inhomogeneity that reduces the mechanical strength and the transparency of gels[8, 9, 10]. In order to control the network structure, a lot of researches on gels formed by selectively crosslinking the functional groups of pre-synthesized reactive polymers, which have the controlled primary structure, have been carried out [11, 12, 13, 14, 15, 16, 17]. Sakai and coworkers have succeeded in the synthesis of homogeneous gels by the end-coupling reaction of two types of tetra-arm star polymers, and have shown the enhancement of mechanical strength 11, 12. 13]. End-linking gels formed by crosslinking telechelic reactive polymers, which carry functional groups at both ends, with multifunctional crosslinkers have been reported to have relatively uniform structures 14, 15, 16]. Ida and coworkers have found that gels synthesized by crosslinking linear reactive polymers having multiple activated ester groups with diamines have more uniform structures than the gels formed by the radical copolymerization [17]. In the gels of crosslinked linear reactive polymers, they have also reported that the crosslinking density can be easily controlled by using monoamines in addition to diamines[18], and that the monomer arrangement of the polymers affects the macroscopic physical properties [19]. The gel preparation methods of crosslinking the reactive polymers which have the controlled primary structure are able to vary the physical properties of gels in a wide range. Therefore, the understanding of the relation between the primary structure of the reactive polymers and the properties of gels is important not only for gel science but also for applications.

In this paper, we mainly focus on the gels formed by crosslinking the multifunctional linear reactive polymers, and study the effects of the primary structures of the reactive polymers (such as the average molecular weight, the molecular weight distribution, the functional group number distribution, and the ar-

rangement of the functional groups on the polymers) on the network structure and the mechanical properties of the gels by a computer simulation. Numerous computer simulations of crosslinking of linear polymers have been conducted [20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31]. Computational studies have shed light on the effects of the crosslinking density on the microscopic structures such as the distribution of the length of network strands connecting the crosslinking points [21, 27, 28], the conformation of the strands [28, 29, 31], the bonding structure of the strands [20, 21, 23, 29, 31]. The verifications of theoretical models for the elasticity of the polymer networks have been performed by evaluating the contributions of the crosslinking and trapped entanglements in the networks [22, 24, 27, 30]. These studies have revealed that, although the mechanical properties of gels can be fitted by the theoretical models, the detailed structures such as the efficiency of the crosslinking and the trapped entanglement factor [32] are different form the theoretical descriptions [27, 30]. Furthermore, simulations have clarified other mechanisms related to the polymer networks such as the toughening mechanism of interpenetrating networks with chemical and physical crosslinks^[25], the enhancement of the crosslinking efficiency by improving the dispersion degree of the crosslinking points [26], and the effects of crosslinking rate on the network structure [28]. Most of the previous studies were concerned with the crosslinking of linear polymers with monodisperse molecular weight distributions, in which the networks were formed by random crosslinking between polymers [21, 22, 23, 24, 27] or the crosslinking of telechelic polymers and crosslinkers [29, 30]. Although some studies have been reported the relation between the strand length distribution in the networks and the physical properties [33, 34], the effects of controlling the arrangement of the functional groups on the polymers, that is, the controlling the strand length, have been rarely studied. Therefore, we consider that further studies are required to understand the effects of the detailed primary structures of the multifunctional linear reactive polymers on the network structure and the mechanical properties of the gels.

In order to elucidate the effects of the primary structures of the reactive polymers on the properties of gels, we prepare several types of networks with varying the primary structures. We calculate the number of elastically effective chains [35, 36], that of entanglements [37], and the shear modulus. We analyze the bonding structure of the network strands, the probability for a strand to form a loop structure, and the spatial correlation between the crosslinking points in order to understand the molecular mechanisms of the effects of the primary structures. We discuss the effects of the arrangement of the functional groups by the comparisons between the results of random reactive polymers which have a random arrangement of the functional groups and those of periodic reactive polymers which have a periodic arrangement of the functional groups. In recent years, the syntheses of polymers with precisely controlled monomer sequences have been reported [38, 39]. We think that the studies of the periodic reactive polymers provide insights into the development of novel gels formed by crosslinking polymers which have such controlled monomer sequences. We show that the results of the networks composed of the random reactive polymers qualitatively agree with the results of the Miller-Macosko theory [40, 41]. However, the results of the periodic reactive polymers significantly deviate from those of the corresponding random reactive polymers due to the change in the number of intramolecular crosslinks. In order to deepen the understanding of the effects of the primary structures, we also compare the results of this study with those of the networks formed by crosslinking reactive polymers with different architectures [42].

2 Simulation Model

In this study, we employed the bead-spring model called the Kremer–Grest model[43, 44, 45] for the linear reactive polymers and modeled the crosslinker by a single bead. The reactive polymers consisted of functional beads and non-functional beads, and formed the networks by generating bonds between the functional beads on the polymers and the crosslinkers (**Figure 1**). Each functional bead on the polymers can form one bond with the crosslinker, and each crosslinker can form two bonds with the polymer functional beads. Hence, the crosslinkers serve as bifunctional crosslinkers and act as four-branch crosslinking points in the networks when those form the bonds with the polymers as shown in Figure 1. We used the mass m of one bead as a unit of mass. We fixed the ratio $r = \left(\sum_n \sum_f f N_{n,f}\right) / \left(\sum_n \sum_f n N_{n,f}\right)$ of the total number of polymer functional beads to the total number of polymer beads at r = 0.05. Here, $N_{n,f}$ is the number of f-functional reactive polymers consisting of n beads. We set the number N_c of crosslinkers to the stoichiometric amount $N_c = \left(\sum_n \sum_f f N_{n,f}\right)/2$.

In order to study the effects of the primary structures of the reactive polymers such as the average molecular weight, the molecular weight distribution, the functional group number distribution, and the arrangement of the functional groups on the network properties, the following seven types of the polymers were used: P80-1, P160-1, P240-1, P96-1.7, P160-1.7, P160-1m, P160-1p. Here, the number following "P" and the number after hyphen represent the number average molecular weight and the polydispersity index of the reactive polymers, respectively. The alphabet "m" at the end means that the functional group number distribution of the polymers is monodisperse, and "p" means that the arrangement of the functional groups is periodic. Table 1 lists the data of each reactive polymer: the number average molecular weight \overline{M}_n , the weight average molecular weight \overline{M}_w , the polydispersity index $\overline{M}_w/\overline{M}_n$, the number average number of functional groups $\overline{f}_n \equiv \left(\sum_f \sum_n f N_{n,f}\right) / \left(\sum_f \sum_n N_{n,f}\right)$, the weight average number of functional groups $\overline{f}_w \equiv \left(\sum_f \sum_n f^2 N_{n,f}\right) / \left(\sum_f \sum_n f N_{n,f}\right)$, and the polydispersity index of the number of functional groups $\overline{f}_w/\overline{f}_n$. The polymers P96-1.7 and P160-1.7 consisted of 20*l* beads (*l* is an integer of $l \geq 1$) and had molecular weight distributions similar to the Schulz–Zimm distribution [46, 47] (Figure S1 in the Supporting Information). For the polymers other than P160-1m and P160-1p, the functional groups were randomly arranged on the polymers, and we restricted for each reactive polymer to have at least one functional group. For P160-1m and P160-1p, the number of functional groups was fixed at 8. In P160-1m, the functional groups were randomly arranged on each polymer. For P160-1p, we periodically arranged the functional groups on each polymer so that the number $n_{\rm ff}$ of bonds between adjacent functional beads was constant, that is, $n_{\rm ff} = 20$ (Figure S2(a) in the Supporting Information). In contrast, since the functional groups of the polymers except P160-1p were randomly distributed on the polymers, the distributions $P(n_{\rm ff})$ of the bond number $n_{\rm ff}$ showed the exponential distribution: $P(n_{\rm ff}) =$ $u^{n_{\rm ff}-1}(1-u) \simeq (1/\overline{n}_{\rm ff})e^{-n_{\rm ff}/\overline{n}_{\rm ff}}$ (Figure S2(b) in the Supporting Information). Here, u is the probability for a bead to connect to a non-functional bead that is not a bead at a polymer end, and $\overline{n}_{\rm ff} = 1/(1-u)$ is the average number of bonds between adjacent functional beads. In this study, five independent systems were generated for each condition, and the average of the results of the five systems was used as the simulation result for each condition.

The excluded volume effect between each pair of beads was introduced by the Weeks–Chandler–Anderson (WCA) potential which is the truncated and shifted Lennard–Jones potential[48]:

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

Here, r_{ij} is the distance between the *i*-th bead and *j*-th bead, ε is the strength of the WCA potential, and σ is the unit length of the WCA potential. In this study, ε and σ were used as a unit of energy and length, respectively. We used $\varepsilon/k_{\rm B}$ and $\tau \equiv \sigma \sqrt{m/\varepsilon}$ as a unit of temperature and time, respectively. Here, $k_{\rm B}$ is the Boltzmann constant. In this study, we fixed the reduced temperature at $k_{\rm B}T/\varepsilon = 1$.

For the elastic energy potential of each pair of bonded beads, we employed the finitely extensible nonlinear elastic (FENE) potential[49]:

$$U_{\text{fene}}(r_{ij}) = -\frac{1}{2}k_{\text{b}}r_0^2 \ln\left[1 - \left(\frac{r_{ij}}{r_0}\right)^2\right].$$
 (2)

Here, $k_{\rm b}$ is the spring constant and r_0 is the maximum bond length. We set $k_{\rm b} = 30$ and $r_0 = 1.5$ in order to avoid the crossing of the polymers [43, 44, 45].

We next explain the generation of the bonds between the functional beads on the polymers and the crosslinkers. The following FENE-C potential was introduced between an unreacted functional bead and a crosslinker which can form additional bonds [49, 50]:

$$U_{\rm a}(r_{ij}) = \begin{cases} U_{\rm fene}(r_{ij}) - U_{\rm s}(r_{ij},\Delta r) - U_{\rm fene}(r_{\rm c}) + U_{\rm s}(r_{\rm c},\Delta r) & \text{for } r_{ij} \le r_{\rm c} \\ 0 & \text{for } r_{ij} > r_{\rm c} \end{cases}$$
(3)

Here, r_c is the cut-off radius of the FENE-C potential, and $U_s(r_c, \Delta r)$ is a smoothing function that acts at $r_c - \Delta r < r_{ij} \leq r_c$ and ensures $dU_a/dr_{ij} = 0$ at $r_{ij} = r_c$. In this study, we fixed $r_c = 1.2$ and $\Delta r = 0.02$. The FENE-C potential forms a transient bond between a functional bead and a crosslinker at $r_{ij} \leq r_c$. We changed the FENE-C potential between the beads connected by the transient bond to the shifted FENE potential $(U_{\text{fene}}(r_{ij}) - U_{\text{fene}}(r_c) + U_s(r_c, \Delta r) \text{ for } r_{ij} < r_0)$ when the distance r_{ij} between the beads of interest became $r_{ij} \leq r_c - \Delta r$. By this procedure, we generated permanent bonds between the functional beads and the crosslinkers without discontinuities in force and energy.

The motion of each bead was calculated by the following Langevin equation:

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

where $\mathbf{r}_i(t)$ is the position vector of the *i*-th bead; $\mathbf{F}_i(t) = -\partial U_i(t)/\partial \mathbf{r}_i(t)$ is the force acting on the *i*-th bead; $U_i(t)$ is the sum of the potential energies working on the *i*-th bead; ζ is the friction coefficient; and $\mathbf{W}_i(t)$ is the random force with $\langle \mathbf{W}_i(t) \rangle = 0$ and $\langle \mathbf{W}_i(t) \cdot \mathbf{W}_j(t') \rangle = 6m\zeta k_{\rm B}T\delta_{ij}\delta(t-t')$. In this study, we set $\zeta = 0.5\tau^{-1}[43, 44, 45]$, and integrated the Langevin equation by the velocity Verlet method[51] with timestep $\Delta t = 0.005\tau$.

In the calculation of the network formation, we first placed $N_{\rm p} = \sum_n \sum_f N_{n,f}$ polymers and N_c crosslinkers at random in the cubic simulation box with periodic boundary conditions. We next performed the simulation of $t = 5 \times 10^3 \tau$ without the bond formation between the functional beads and the crosslinkers in order to homogeneously mix the polymers and the crosslinkers. We then carried out the simulation with the bond formation between the polymers and the crosslinkers until the conversion α became a constant value, that is, the network formation was completed. In order to investigate the effects of the concentration at the network formation stage on the network structure and the mechanical properties, we prepared the network with systematically varying the volume fraction $\phi = \left(N_c + \sum_n \sum_f nN_{n,f}\right) v_b/V$ of the polymers and the crosslinkers. Here, $v_{\rm b} = \pi \sigma^3/6$ and V are the volume of one bead and that of the simulation box, respectively. In this simulation, although there were some variations in the P96-1.7 and P160-1.7 systems, we fixed the total number of beads at $N_c + \sum_n \sum_f nN_{n,f} \simeq 3.69 \times 10^4$, and changed the volume fraction ϕ by adjusting V. As shown in Figure S3 in the Supporting Information, the conversions α were 95 % or more under all conditions, and the differences between the different polymer systems were within 1 %. Although α slightly increased with increasing ϕ , we thought that the effects of the difference in α were not significant.

In order to study the relation between the network structure and the mechanical properties, we also conducted the simulation under the uniaxial deformation. We applied the uniaxial deformation to the simulation box, that is, the lengths of the simulation box were changed from the initial length $L_0 = V^{1/3}$ to λL_0 in the x-direction and to $L_0/\sqrt{\lambda}$ in the y- and z-directions. Here, λ is the one-dimensional deformation ratio. The simulation box was deformed by repeating a deformation process and a relaxation process until λ was reached a target value. In the deformation process, we performed the simulation of $t = 50\tau$ while changing λ at the deformation rate $d\lambda/dt = 2 \times 10^{-3}\tau^{-1}$. In the subsequent relaxation process, we carried out the simulation of $t = 1.25 \times 10^4 \tau$ under a constant λ . The mechanical properties at each λ were calculated from the average values at $1 \times 10^4 \tau \leq t \leq 1.25 \times 10^4 \tau$ in the relaxation process. We confirmed that the nominal stress reached almost a constant value at $t \geq 1 \times 10^4 \tau$ in the relaxation process after the deformation process (Figure S4 in the Supporting Information).

3 Results and Discussion

3.1 Network Structure

In order to study the effects of the primary structure of the reactive polymers on the network connectivity, we show the number density ν_{eff} of the elastically effective chains in **Figure 2**. We here used the Scanlan–Case criterion[35, 36] to count the number of elastically effective chains. We focused on a path between the crosslinking points, and judged that the path is elastically effective when the ends of the path are both connected to the crosslinking points that carry at least three paths leading to the network matrix.

As shown in Figure 2(a) and 2(b), the number density ν_{eff} of the elastically effective chains increases with increasing the number average molecular weight \overline{M}_n . However, the change in ν_{eff} accompanying the change in \overline{M}_n reduces in the high \overline{M}_n region. From the comparison of P160-1, P160-1.7, and P160-1m, we find that ν_{eff} is independent of the molecular weight distribution and the functional group number distribution in the random reactive polymer systems in which the functional groups are randomly arranged on the polymers. According to Miller–Macosko's theory shown in the Supporting Information, ν_{eff} of well-developed gels with a high conversion α mainly depends on the reciprocal $(\overline{M}_n)^{-1}$ of the number average molecular weight, and decreases with increasing $(\overline{M}_n)^{-1}$. The behavior of ν_{eff} in the networks of the crosslinked random reactive polymers can be qualitatively explained by the theory; ν_{eff} increases with increasing \overline{M}_n , and the \overline{M}_n dependence of ν_{eff} reduces in the high \overline{M}_n region. Since $(\overline{M}_n)^{-1}$ is proportional to the number of polymer ends, the effect of \overline{M}_n indicates the influence of the polymer ends.

From Figure 2(c), we find that the gel of P160-1p which has the periodic arrangement of the functional groups exhibits higher number densities ν_{eff} of the elastically effective chains than the gels made of the random reactive polymers with the same number average molecular weight \overline{M}_{n} . The increase in ν_{eff} due to the periodic arrangement of the functional groups decreases with increasing the volume fraction ϕ . In order to investigate the mechanisms of the increase in ν_{eff} , we classified the network strands which are parts of the polymers connecting the adjacent crosslinking points into the following three categories according to the local bonding structure: bridge chain, loop chain, and dangling chain. Figure 3 shows the relative populations of each chain category. As seen in Figure 3(a) and 3(b), the periodic arrangement of the loop chains. The change of the bonding structure from the loop chain to the bridge chain rises ν_{eff} . At the high ϕ , the increase in ν_{eff} with the bonding structure change reduces, since the relative population of the loop chain decreases. The bonding structures in the gels of the crosslinked random reactive polymers are independent of the molecular weight distribution and the functional group number distribution, but depend on \overline{M}_{n} ; the numbers of bridge chains and loop chains rise with increasing \overline{M}_{n} due to the reduction of the influence of the polymer ends.

It should be note that, as seen in Figure 2, the minimum value of the volume fraction ϕ in the simulation results depends on the polymer model, because the minimum gelation concentration ϕ^* differs for each polymer model. At low ϕ , since the number of loop chains increases, the number of functional groups which is effective for gelation decreases. Therefore, below ϕ^* , the reactive polymers do not exhibit gelation. For the random reactive polymers, ϕ^* mainly depends on the weight average number of functional groups \overline{f}_w ; ϕ^* decreases with increasing \overline{f}_w . The reduction of the number of loop chains due to the periodic arrangement of the functional groups promotes the gelation; thus, ϕ^* decreases.

In order to consider the difference in the loop formation between the random reactive polymer systems and the periodic reactive polymer systems, we show the ratio $R_{\ell}(n_{\rm cc}) = N_{\ell}(n_{\rm cc})/N_{\rm b}(n_{\rm cc})$ of the number of loop chains to the number of bridge chains in **Figure 4**. Here, $n_{\rm cc} = n_{\rm ff}+2$ is the number of bonds between the adjacent reacted crosslinkers along the polymer, and $N_{\ell}(n_{\rm cc})$ and $N_{\rm b}(n_{\rm cc})$ are the numbers of loop chains and bridge chains consisting of $n_{\rm cc}$ bonds, respectively. The loop ratio $R_{\ell}(n_{\rm cc})$ is independent of the primary structure of the polymers and decreases according to the power law $n_{\rm cc}^{-a}$ with an exponent $a \simeq 1.4-1.6$ (the results of $R_{\ell}(n_{cc})$ at other volume fractions ϕ are shown in Figure S5 in the Supporting Information). This exponent well agrees with the exponent 3/2 in Jacobson–Stockmayer's theoretical study of the Gaussian chain[52]. From the results of $R_{\ell}(n_{cc})$, we find that the short strands form many loop structures in the random reactive polymers, whereas the number of loop chains in the P160-1p system is small due to the absence of the short chain.

We here study the effects of the ratio r of the number of the functional beads to the number of polymer beads on the total number N_{ℓ} of loop chains in the networks. The distribution $P(n_{\rm ff})$ of the number of bonds between the functional groups is mainly determined by the ratio r, and the loop ratio $R_{\ell}(n_{\rm cc})$ depends on the number of bonds; hence, N_{ℓ} varies by changing r. From the results of $R_{\ell}(n_{\rm cc})$ and the theoretical study[52], we assume that the number $N_{\ell}(n_{\rm cc})$ of loop chains consisting of $n_{\rm cc}$ bonds is given by $N_{\ell}(n_{\rm cc}) = CN_{\rm b}(n_{\rm cc})n_{\rm cc}^{-3/2}$ where C is a prefactor determined by conditions such as the volume fraction ϕ . In the well-developed networks ($\alpha \simeq 1$), the sum $N_{\ell}(n_{\rm cc}) + N_{\rm b}(n_{\rm cc})$ of the numbers of loop chains and bridge chains is almost equal to the number of strands whose number of bonds is equal to $n_{\rm ff} = n_{\rm cc} - 2$. For the crosslinked random reactive polymers, the sum is given by $N_{\ell}(n_{\rm cc}) + N_{\rm b}(n_{\rm cc}) \simeq N_{\rm sub}u^{n_{\rm ff}-1}(1-u)$. Here, $N_{\rm sub}$ is the total number of strands, and $u = 1 - \overline{n_{\rm ff}}^{-1}$ is the above-mentioned probability for a bead to connect to a non-functional bead that is not a bead at a polymer end. The total number N_{ℓ} of loop chains in the networks consisting of the random reactive polymers is given by

$$N_{\ell} = \frac{CN_{\rm sub}}{\overline{n}_{\rm ff}} \sum_{n_{\rm ff} \ge 1} \frac{(1 - \overline{n}_{\rm ff}^{-1})^{n_{\rm ff} - 1} (n_{\rm ff} + 2)^{-3/2}}{1 + C(n_{\rm ff} + 2)^{-3/2}}.$$
(5)

On the other hand, in the crosslinked periodic reactive polymers, N_{ℓ} is calculated by the following equation:

$$N_{\ell} = \frac{CN_{\rm sub}(\overline{n}_{\rm ff} + 2)^{-3/2}}{1 + C(\overline{n}_{\rm ff} + 2)^{-3/2}}.$$
(6)

Figure 5 shows the ratio N_{ℓ} of the total number of loop chains to that of strands as a function of the average bond number $\overline{n}_{\rm ff}$. We here set the prefactor C to $C \simeq 1.96$ from the simulation results shown in Figure 4. As seen in Figure 5, N_{ℓ} in the periodic reactive polymers is less than that in the random reactive polymers except when all the beads are functional groups ($\overline{n}_{\rm ff} = 1$). The networks made of the random polymers have the strands the lengths of which are shorter than the average $\overline{n}_{\rm ff}$. Since the loop formation probabilities of such short strands are high, N_{ℓ} increases. From these results, we find that the change of the arrangement of the functional groups from a random one to a periodic one generally reduces the number of loops and enhances the network connectivity. We also show the results of N_{ℓ} at other volume fractions ϕ in Figure S6 in the Supporting Information.

We analyzed the entanglements of the polymers in the networks by the method of Everaers *et al*[37]. In the method of Everaers *et al.*, all ends of polymers are spatially fixed, the intramolecular excluded volume effects are then turned off, and the temperature T is gradually lowered to zero. By this method, we can calculate the number of intermolecular contact points (entanglements) when the ends of the polymers are connected by the shortest paths (primitive paths) without crossing between the polymers. Almost all the reactive polymers and the crosslinkers are contained in one huge molecule when the system forms the gel network; hence, if we automatically turn off the intramolecular excluded volume effects, almost all the excluded volume effects disappear, and the polymers freely cross. In order to avoid the free crossing between the polymers, we only turned off the relatively short-range intramolecular excluded volume effects, that is, the intra-strand excluded volume effects and the excluded volume effects between the strands attached to the same crosslinking point. From the network structure after this calculation, we counted the number density ν_{en} of the bridge chains generated by the entanglements[42]. The detailed calculation method is shown in the Supporting Information.

The number density $\nu_{\rm en}$ of the bridge chains generated by the entanglements is plotted against the volume fraction ϕ in **Figure 6**. In the gels of the random reactive polymers, $\nu_{\rm en}$ increases with increasing the number average molecular weight $\overline{M}_{\rm n}$. This increase in $\nu_{\rm en}$ is due to the decline of the influence of

the polymer ends which prevent the formation of the bridge chains. From Figure 6, we confirm that ν_{en} is independent of the molecular weight distribution and the functional group number distribution.

As revealed by Figure 6(c), the change of the arrangement of the functional groups from the random one to the periodic one reduces the number density $\nu_{\rm en}$ of the bridge chains generated by the entanglements. The random crosslinking in the network formation process causes the fluctuation of the crosslinking density, that is, regions with high and low crosslinking densities are created[8, 9, 10]. We consider that the reduction in $\nu_{\rm en}$ is due to the change of the fluctuation of the crosslinking density, that is, the spatial correlation between the crosslinking points. In order to quantify the spatial correlation between the crosslinking points, we calculated the binary cluster integral $\beta_{\rm cc}$ by the following equation[26, 53]:

$$\beta_{\rm cc} \equiv 2\pi \int_0^\infty [1 - g_{\rm cc}(r)] r^2 dr.$$
⁽⁷⁾

Here, $g_{cc}(r)$ is the radial distribution function of the crosslinking points. The negative β_{cc} means that an apparent attractive interaction acts between the crosslinking points, that is, the crosslinking points tend to aggregate. On the other hand, the positive β_{cc} indicates the tendency of the crosslinking points to disperse. **Figure 7** shows β_{cc} as a function of the volume fraction ϕ . The gels consisting of the random polymers exhibit smaller β_{cc} than that of the P160-1p gel. Thus, the crosslinking points in the gels of the random polymers tend to aggregate more than in the gel of P160-1p, and the fluctuations of the crosslinking density in the former are larger than that in the later. We consider that the entanglement densities ν_{en} of the gels made of the random polymers indicate high values, since the occurrence of the entanglement is promoted in high density regions. The large density fluctuation in the crosslinked random polymers is thought to be caused by the random arrangement of the functional groups and the formation of many loop chains that are intramolecular crosslinks.

3.2 Mechanical Properties

We next study the relation between the mechanical properties and the primary structure of the reactive polymers. In **Figure 8**, we plot the shear modulus G against the volume fraction ϕ . Here, the shear modulus G is calculated by fitting the nominal stress $\sigma_{\rm N}$ under the uniaxial deformation to the neo-Hookean model $\sigma_{\rm N} = G(\lambda - 1/\lambda^2)$. The detailed calculation method is shown in the Supporting Information. The shear modulus G shows the same trend as the number density $\nu_{\rm eff}$ of the elastically effective chains; G increases with increasing the number average molecular weight $\overline{M}_{\rm n}$, and is independent of the molecular weight distribution and the functional group number distribution. The periodic arrangement of the functional groups rises G.

We here estimate the shear modulus G from the network structures for the understanding of the relation between the mechanical properties and the network structures. In this study, we take account of the following contributions to G: the contribution G_{eff} from the elastically effective chains formed by crosslinking and the contribution G_{te} from the entanglements trapped in the networks. The contributions G_{eff} and G_{te} are evaluated by using the phantom network model[54, 55]:

$$G_{\rm eff} = \left(\nu_{\rm eff} - \mu_{\rm eff}\right) k_{\rm B} T,\tag{8}$$

$$G_{\rm te} = \left(\nu_{\rm te} - \mu_{\rm te}\right) k_{\rm B} T. \tag{9}$$

Here, μ_{eff} is the number density of the elastically effective crosslinking points that carry at least three paths leading to the network matrix, and μ_{te} and ν_{te} are the number densities of the trapped entanglements and the elastically effective chains generated by the trapped entanglements, respectively. We calculate μ_{te} and ν_{te} with reference to Langley's research[32]. In Langley's research, when two strands involved in an entanglement have paths to the network matrix at both sides of the entanglement, the entanglement is judged to be trapped in the networks and elastically effective. Therefore, in this study, we consider that an entanglement in the simulation is trapped in the network when two or more strands involved in the entanglement of interest are the elastically effective chains. Figure 9 shows the shear modules G calculated by the simulation under the uniaxial deformation, the contribution G_{eff} from the elastically effective chains, the contribution G_{te} from the trapped entanglements, and the sum $G_{\text{eff}} + G_{\text{te}}$ of the contributions. Since G and $G_{\text{eff}} + G_{\text{te}}$ indicate the same level of values, we think that the contributions from the elastically effective chains and the trapped entanglements can be evaluated by G_{eff} and G_{te} at a reasonable level (the results of the other gels are shown in Figure S7 in the Supporting Information). The upward deviation of $G_{\text{eff}} + G_{\text{te}}$ at the high volume fractions ($\phi \ge 0.25$) is considered to be due to the overestimation of the entanglements analyzed by the contact between the primitive paths. For the P160-1p gel, $G_{\text{eff}} + G_{\text{te}}$ is larger than G at the intermediate volume fractions ($0.025 \le \phi \le 0.1$). This deviation is thought to be caused by the overestimation of the fluctuation of the crosslinking points in the phantom network model. In the intermediate concentration region, G of the P160-1p gel indicates values between the shear modulus $G_{\text{eff}} + G_{\text{te}}$ of the phantom network model and that ($\nu_{\text{eff}} + \nu_{\text{te}}$) $k_{\text{B}}T$ of the affine network model[1, 56] (Figure S8 in the Supporting Information). Hence, we consider that the fluctuation of the crosslinking points is suppressed to some extent because of the high crosslinking efficiency of the gel formed by crosslinking the periodic reactive polymers.

In order to quantify the effects of the primary structure of the reactive polymers on the network structures and the mechanical properties of the gels, we present the following relative results $\nu_{\rm eff}/\nu_{\rm eff}^{\circ}$, $\nu_{\rm en}/\nu_{\rm en}^{\circ}$, $G_{\rm eff}/G_{\rm eff}^{\circ}$, and $G_{\rm te}/G_{\rm te}^{\circ}$ to the results of the P160-1 gel (**Figure 10**). Here, $\nu_{\rm eff}^{\circ}$, $\nu_{\rm en}^{\circ}$, $G_{\rm eff}^{\circ}$, and $G_{\rm te}^{\circ}$ are the results of the P160-1 gel, and the distances from one to the relative results indicate the magnitude of the effects. From Figure 10(a) and 10(c), we find that the effects of the structural change of the reactive polymers on $\nu_{\rm eff}$ and $G_{\rm eff}$ are approximately equal. As shown in Figure 10(b) and 10(d), the effects of the primary structure on $\nu_{\rm en}$ and $G_{\rm te}$ are qualitatively the same, but quantitatively different; the effect of $\overline{M}_{\rm n}$ on $G_{\rm te}$ is larger than that on $\nu_{\rm en}$, and the effect of the functional group arrangement on $G_{\rm te}$ is smaller than that on $\nu_{\rm en}$. In this study, $G_{\rm te}$ is calculated from the number density of the entanglements trapped in the network. The probability for an entanglement to be trapped in the network (trapped entanglement factor[32]) $T_{\rm e}$ depends on the formation efficiency of the elastically effective chains, that is, $T_{\rm e}$ increases with increasing $\nu_{\rm eff}$ (Figure S9 in the Supporting Information). Since the increase in $\overline{M}_{\rm n}$ rises $\nu_{\rm eff}$ and $\nu_{\rm en}$, the effect of $\overline{M}_{\rm n}$ on $G_{\rm te}$ becomes greater than that on $\nu_{\rm en}$. On the other hand, the gel of the periodic polymer P160-1p exhibits low $\nu_{\rm en}$, but shows high $\nu_{\rm eff}$; hence, $G_{\rm te}$ of the P160-1p gel becomes relatively large.

We here discuss the effects of the primary structure of the reactive polymers in actual gels expected from the simulation results. As discussed above, the simulation results indicate that the changes in the network structure and the mechanical properties with increasing the average molecular weight of the reactive polymers decrease in the high average molecular weight region. The actual gels are usually synthesized from polymers the degree of polymerization of which is higher than those of the polymers in the simulation [17]. Therefore, the effects of the average molecular weight observed in the actual gels are expected to be smaller than the simulation results. On the other hand, regarding the other effects of the primary structure of the reactive polymers such as the molecular weight distribution, the functional group number distribution, and the arrangement of the functional groups, we consider that the actual gels show the same trends as the simulation results. When the number average molecular weight of the polymers used in the actual gel synthesis is constant, the network structure and the mechanical properties hardly change even if the molecular weight distribution and the functional group number distribution change, because the influence of the polymer ends is constant. Since the effects of the arrangement of the functional groups are mainly due to the formation of local loop structures, the structural uniformity and the mechanical properties of the actual gels are enhanced by changing the arrangement from the random one to the periodic one.

3.3 Comparison with Other Preparation Methods

Finally, we compare the results of this study with those of the networks formed by crosslinking reactive polymers by the other methods. By the method shown in the previous study[42], we prepared the fol-

lowing two types of gels: the gels formed by end-linking of two types of tetra-arm star polymers and the gels formed by crosslinking telechelic reactive polymers and tetrafunctional crosslinkers. Hereafter, we call the former "Tetra-gel" and the later "EL-gel". Here, the composition of each network was set to indicate the same crosslinking density when the network was ideally formed, and the calculation of the network formation was performed until the conversion α became a constant value. Tetra-gel corresponds to Tetra-PEG gels synthesized by Sakai and coworkers, which have uniform structures and show excellent mechanical strength[11, 12, 13]. Since the lengths of strands between the crosslinking points are the same, EL-gel is also considered to be more uniform than networks formed by conventional free radical copolymerization[14, 15].

Figure 11 shows the number density $\nu_{\rm eff}$ of the elastically effective chains, the number density $\nu_{\rm en}$ of the bridge chains generated by the entanglements, and the shear modulus G as functions of the volume fraction ϕ . The gel of the random reactive polymer P160-1 exhibits smaller ν_{eff} and G, and larger ν_{en} than Tetra-gel and EL-gel, that is, the gel of P160-1 has a less uniform structure and lower mechanical strength than Tetra-gel and EL-gel. At the low volume fractions ($\phi \leq 0.1$), ν_{eff} and G of the P160-1p gel formed by crosslinking the periodic reactive polymers are comparable to those of EL-gel, and $\nu_{\rm en}$ is smaller than those of Tetra-gel and EL-gel. Thus, the P160-1p gel formed in the low volume fraction region has a fairly uniform structure and moderately high mechanical strength. In the P160-1p gel, the network strand length is uniform as in Tetra-gel and EL-gel, and at least three strands are connected to each crosslinking point. In addition, among multiple-links in which several strands connect one pair of the crosslinking point [42], only double-links can be formed. Since the degree of freedom in the structure formation in the P160-1p gel is relatively low, the formation of the cyclic structures such as the loop chains and the multiple-links is suppressed. We consider that the suppression of the formation of the cyclic structures improves the uniformity of the network structure and the mechanical properties. On the other hand, when the network is formed at the high volume fractions, the crosslinking efficiency and the mechanical strength of the P160-1p gel are lower than Tetra-gel and EL-gel, because the polymer ends always become the dangling chains.

4 Conclusion

We have studied the effects of the primary structure of the linear reactive polymers on the network structure and the mechanical properties of the gels formed by crosslinking the reactive polymers with the crosslinkers by the coarse-grained molecular dynamics simulation. In the gels of the random reactive polymers which have the random functional group arrangement, the number of elastically effective chains, the number of entanglements, and the shear modulus increase with increasing the number average molecular weight of the reactive polymers, because the influence of the polymer ends is reduced. We have confirmed that the network structures and the mechanical properties of the well-developed gels are independent of the molecular weight distribution and the functional group number distribution of the reactive polymers. The shear modulus calculated by the simulation under the uniaxial deformation well agrees with the shear modulus evaluated from the network structure by using the phantom network model except in the high concentration region. The gel consisting of the random polymers has a less uniform structure and lower mechanical strength than the relatively uniform gels formed by the other methods.

By changing the functional group arrangement of the reactive polymers from the random one to the periodic one, the number of elastically effective chains and the shear modulus increase, and the number of entanglements decreases. We have found that these improvements of the uniformity and the mechanical properties of the gels are due to the suppression of the formation of the loop structures. Furthermore, in the gels consisting of the periodic reactive polymers formed at the intermediate concentrations, the fluctuation of the crosslinking points is suppressed to some extent due to the high crosslinking efficiency. In the low concentration region, the gel of the crosslinked periodic polymers with the tetrafunctional crosslinkers. From these results, we think that the performance of real gels can be dramatically

improved if periodic reactive polymers are synthesized by precision polymer synthesis and are crosslinked to form gels. In this study, we have focused the properties of chemically crosslinked gels. We think that the structure formation and the physical properties of associating polymer solutions showing the thermoreversible gelation and the phase separation also significantly change by controlling the functional group arrangement. We plan to study the effect of the functional group arrangement on the phase behavior of associating polymer systems.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1: Schematic illustration of the network formation by crosslinking reactive polymers with crosslinkers. Red and white circles indicate functional and non-functional beads of the polymers, respectively. Cyan circles indicate the crosslinkers.

polymer	$\overline{M}_{\rm n}$	$\overline{M}_{\rm w}$	$\overline{M}_{\rm w}/\overline{M}_{\rm n}$	\overline{f}_{n}	\overline{f}_{w}	$\overline{f}_{\rm w}/\overline{f}_{\rm n}$
P80-1	80	80	1	4.0	4.7	1.18
P160-1	160	160	1	8.0	8.8	1.10
P240-1	240	240	1	12.0	12.87	1.07
P96-1.7	96	160	1.66	4.8	7.6	1.58
P160-1.7	160	276	1.72	8.0	12.7	1.59
P160-1m	160	160	1	8	8	1
P160-1p	160	160	1	8	8	1

Table 1: Average molecular weight and average number of functional beads of the reactive polymers.



Figure 2: Number density ν_{eff} of the elastically effective chains shown as a function of the volume fraction ϕ .



Figure 3: Relative populations of (a) the bridge chains, (b) the loop chains, and (c) the dangling chains shown as functions of the volume fraction ϕ .



Figure 4: Ratio $R_{\ell}(n_{\rm cc})$ of the number of loop chains to that of bridge chains shown as a function of the number $n_{\rm cc}$ of bonds between adjacent reacted cross-linkers. The volume fraction ϕ is equal to $\phi = 0.1$.



Figure 5: Calculated total number of loop chains N_{ℓ} shown as a function of the average number $n_{\rm ff}$ of bonds between adjacent functional groups of the polymer. The volume fraction ϕ is equal to $\phi = 0.1$.



Figure 6: Number density ν_{en} of the bridge chains generated by the entanglements shown as a function of the volume fraction ϕ .



Figure 7: Binary cluster integral β_{cc} of the cross-linking points shown as a function of the volume fraction ϕ .



Figure 8: Shear modulus G shown as a function of the volume fraction ϕ .



Figure 9: Shear modulus G, contribution G_{eff} from the elastically effective chains, contribution G_{te} from the trapped entanglements, and $G_{\text{eff}} + G_{\text{te}}$ shown as functions of the volume fraction ϕ for (a) P160-1 gel and (b) P160-1 gel.



Figure 10: Relative results (a) $\nu_{\rm eff}/\nu_{\rm eff}^{\circ}$, (b) $\nu_{\rm en}/\nu_{\rm en}^{\circ}$, (c) $G_{\rm eff}/G_{\rm eff}^{\circ}$, and (d) $G_{\rm te}/G_{\rm te}^{\circ}$ of each gel shown as functions of the volume fraction ϕ . $\nu_{\rm eff}^{\circ}$, $\nu_{\rm en}^{\circ}$, $G_{\rm eff}^{\circ}$, and $G_{\rm te}^{\circ}$ are the results of P160-1 gel.



Figure 11: (a) Number density ν_{eff} of the elastically effective chains, (b) number density ν_{en} of bridge chains generated by the entanglements, (c) and shear modulus G shown as functions of the volume fraction ϕ .



The network structure and the mechanical properties of gels formed by crosslinking linear reactive polymers are studied by a coarse-grained molecular dynamics simulation. The effects of the primary structure of the polymers are systematically investigated. The mechanical properties are improved by changing the arrangement of functional groups on the polymers from a random one to a periodic one.