

# **SIMULATION OF COMPETITION BETWEEN REACTION AND RELAXATION IN GELATION KINETICS**

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## **ABSTRACT**

Recently, a new type of network formation process in a dilute tetra-functional polymer solution was reported<sup>1</sup>. The percolation process during the gelation in a dilute solution induces large scale phase-separated structures, and the resulting gel becomes turbid. One interpretation for the formation of such phase-separated structures is that the polymer-rich regions which are much larger than precursor polymers are formed during the gelation process. Since the gelation process is essentially nonequilibrium, such a structural formation should be controlled by the kinetics of gelation. In this work, we propose a simple lattice model which can handle the competition between the reaction and the relaxation of polymers. We show that the phase-separation like structures can be reproduced by our simple model when the reaction process is much slower than the relaxation process.

## **MODEL**

To study the gelation process at the long time scale, coarse-grained models are useful. In the previous work<sup>1</sup>, a coarse-grained molecular model in which a tetra-functional polymer is expressed only with five points was utilized. Even with such a coarse-grained model, it is not easy to perform very long time simulations with a very low reaction rate.

To overcome the difficulty, we propose more coarse-grained and simplified model. We model a tetra-functional polymer by just one point, and put them on a two-dimensional square lattice with the lattice constant  $b$ . Initially, polymers (particles) are randomly dispersed on the lattice, and each polymer has four unreacted arms. Two polymers can react and form a covalent bond between them, if they have unreacted sites and the distance between them is short. After the reaction, the number of unreacted sites decreased. A polymer can randomly jump on the lattice. If a polymer is not reacted at all, this random motion can be interpreted as the diffusion. If a polymer is reacted, then it is a part of a cluster or a network. Then the random motion can be interpreted as the relaxation of a cluster or a network.

Both the reaction and jump are stochastic. If we ignore collective motion, we can utilize the Monte Carlo model. We employ the following rules for the Monte Carlo model. At one Monte Carlo trial, a reaction or a jump is randomly attempted. The probability to For the reaction, we

select a polymer randomly, and then select a neighboring site randomly. The nearest neighbor and next near-lest neighbor sites are candidates for the neighboring site. If there is a polymer on the neighboring site, and if two polymers have unreacted arms, the reaction occurs by the following probability:

$$P_{\text{react}} = \min(1, \exp(-E_{\text{bond}}/k_B T)). \quad (1)$$

Here,  $E_{\text{bond}}$  is the elastic energy of a newly created bond and  $k_B T$  is the thermal energy. We employ the elastic energy  $E_{\text{bond}} = k(\Delta r^2 - b^2)/2$ , with  $k$  being the spring constant and  $\Delta r$  being the distance between two polymers.

For the jump, we select a polymer randomly and then select a neighboring site. If the neighboring site is not occupied by a polymer, then the polymer jumps to the neighboring site by the following probability:

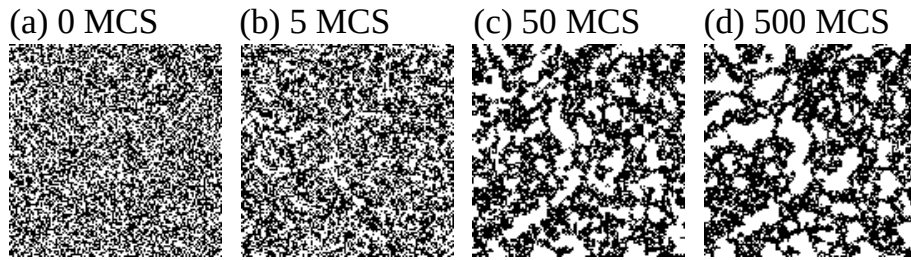
$$P_{\text{jump}} = \min(1, \exp(-\Delta E/k_B T)). \quad (2)$$

$\Delta E$  is the difference of the total bond energy before and after the jump. We express the number of reacted arms of the target polymer as  $n$ , and the distance between this polymer and the  $j$ -th polymer connected to this polymer before and after the jump as  $\Delta r_j$  and  $\Delta r'_j$ . Then we have

$$\Delta E = \sum_{j=1}^n \frac{k}{2} (\Delta r'_j{}^2 - \Delta r_j^2). \quad (3)$$

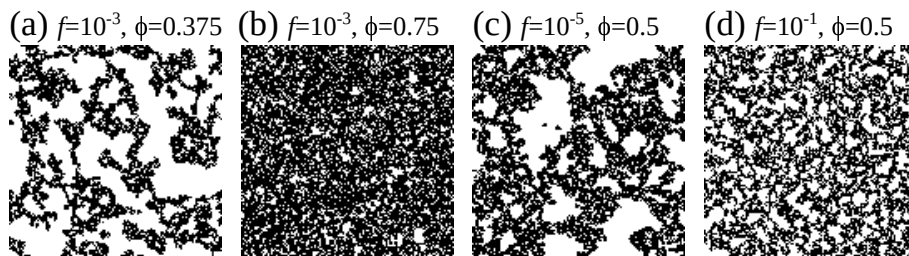
## RESULTS

We perform lattice Monte Carlo simulations with some different parameter sets. We set the lattice constant  $b = 1$ , the spring constant  $k = 1$ , and the thermal energy  $k_B T = 1$ . The nubmer of lattice sites is  $128^2$ . We change the probability to attempt the reaction event  $f$  and the occupied fraction of polymers  $\phi$ . By tuning  $f$ , we can control the competition between the reaction and relaxation processes. **Fig. 1** shows the structural evolution in a simulation with  $f = 10^{-3}$  and  $\phi = 0.5$ . After 500 Monte Carlo steps (MCS), most of arms are reacted and percolated network structure is formed. We observe that the density fluctuation grows as the simulation proceeds. Finally we observe a pattern which is similar to those observed in the phase separation process<sup>2</sup>. Unlike the normal phase separation process, however, the spatial scale of the density fluctuation does not grow after the reaction is completed. This means that the pattern observed in our model is essentially frozen (or arrested). Although our model is highly simplified, we consider that it can qualitatively capture the kinetics of the gelation-induced structural formation.



**Figure 1:** Snapshots of a simulation with  $f = 10^{-3}$  and  $\phi = 0.5$ . (a) The initial state, and (b) 5 Monte Carlo steps (MCS), (c) 50 MCS, and (d) 500 MCS. Polymers are visualized as black dots.

**Fig. 2** shows the snapshots at 500 MCS with different values of  $f$  and  $\phi$ . In **Fig. 2(a)** and **(b)**, we fix the reaction probability  $f$  and change the polymer fraction  $\phi$ . If  $\phi$  is small (the dilute condition), we observe a clear phase-separation like pattern. But if  $\phi$  is large, the density fluctuation is suppressed and the pattern seems to be close to homogeneous. In **Fig. 2(c)** and **(d)**, we fix the polymer fraction  $\phi$  and change the reaction probability  $f$ . If  $f$  is small (the reaction is slow compared with the structural relaxation), we observe a large phase-separation like pattern. On the other hand, if  $f$  is large, the characteristic length scale of the phase-separation pattern is small. From these simulation results, we consider that the gelation-induced pattern is controlled by the competition between the reaction and structural relaxation. If the polymer fraction is small and/or the reaction probability is low, clusters and networks can easily relax into compact forms before the reaction proceeds. Then we observe dense polymer-rich regions. If the polymer fraction is large and/or the reaction probability is high, reaction occurs before clusters and networks relax. In this case, the formation of polymer-rich regions is suppressed, and we observe rather homogeneous structure.



**Figure 2:** Snapshots of a simulation with different reaction probabilities and polymer fractions after 500 Monte Carlo steps. The same reaction rate ( $f = 10^{-3}$ ) with the different fraction: (a)  $\phi = 0.375$  and (b)  $\phi = 0.75$ . ( $\phi = 0.5$  corresponds to **Fig. 1(d)**.) The same polymer fraction ( $\phi = 0.5$ ) with the different reaction probability: (c)  $f = 10^{-5}$  and (d)  $f = 10^{-1}$ . ( $f = 10^{-3}$  corresponds to **Fig. 1(d)**.)

## ACKNOWLEDGMENTS

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## REFERENCES

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