Structure Analysis of Chemical Gel Using Monte Carlo Simulation

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We studied the structure of gel using Monte Carlo simulation with modeled radical reactions. Simulation is performed using beads-spring model in three dimensional continuous space. For the criterion of gel, we apply the concept of percolation to our clusters; we calculate the maximum size in all directions for each cluster, and sum up the number of percolated direction for all percolated clusters in a system. We call this the number of percolation. We obtained structure information of system from plotting the average number of percolation. We can determine whether the system has percolated clusters, and also whether the polymer network has inhomogeneous structure.
Key words: gel, Monte Carlo, simulation, radical, structure

1. INTRODUCTION

Chemically cross-linked gel is a very useful material, and many experimental studies have been done [1,2,3]. However, gelation process and structure are not fully understood. The classical theory of sol-gel transition is given by Flory[4] and Stockmayer[5]. Theoretical investigations of gelation have been performed using percolation model[6]. In the system of physically cross-linked gel, cross-linked points can change reversibly between bonded and non-bonded states. In this case, gelation process is treated by the equilibrium theory and the mean field theory. Experimental results are well interpreted by the theory.

On the other hand, in the system of chemically cross-linked gel, the cross-linked points do not annihilate, generation process is irreversible, and the structure of the system has inhomogeneities. For establishing theory, we need to study the kinetics of gelation mechanism. Monte Carlo simulations have been used to study gelation using percolation model[7,8]. However, there is some difficulty, for example, the irreversibility of chemically cross-linked gel.

In this paper we study a model of radical reaction gelation in continuum system using Monte Carlo method. We calculated kinetic gelation by changing the numbers of linkers and monomers, and investigated different structures.

2. MODEL

We simulated radical polymerization process with cross linkers in the continuous system. Basic components of our model are radicals, monomers and linkers. The radicals and the monomers were modeled as particles. A linker is a bonded pair of monomers. The connectivity of a monomer in a bonded pair is similar to that of a single monomer. We did not include the production of radicals from the initiators in our model. Fixed numbers of radicals are dispersed in the initial configuration. A radical reaction is terminated by recombination. Other termination mechanisms such as disproportionation and chain transfer with solvent are ignored in our model.

We distinguish the particle before and after the reaction. We call the former "active" particle, e.g. active monomer. We called the latter "non-active" particle, e.g. non-active linker.

For the potential between radicals and active monomers, we use the following Lennard-Jones potential,

$$V_{R-act} = \epsilon \{ (\frac{r_0}{r})^{12} - 2(\frac{r_0}{r})^6 \} \qquad (1)$$

Here, $\epsilon = 0.3$ with unit temperature. r_0 is diameter, and r is distance between particles.

For the interaction between non-active particles or between radical and non-active particle, we use the following potential.

$$V_{other} = \epsilon (\frac{r_0}{r})^{12} \qquad (2)$$

Radical reactions generate bonds. Spring potential is used between bonded particles.

$$V_{bond} = C_b \epsilon \frac{(r - r_0)^2}{r_0^2} \qquad (3)$$

Here, we use $C_b = 500$.

In our simulation, each particle has a chance of movement in one time step. Maximum distance of movement is 20% of the particle radius. In one particle movement process, we use three random numbers for radius and two angles. A possible new particle position is chosen randomly. We compare the potential energy before the move and after the move. We decide if the particle movement is accepted or rejected, by Metropolis sampling. Moreover, we introduced parallel movement of polymers. Maximum distance of this movement is 2% of the particle radius.

For the initial configuretion, all particles are dispersed randomly and simulated several thousands of

(a)

(a)

(b)

(b)
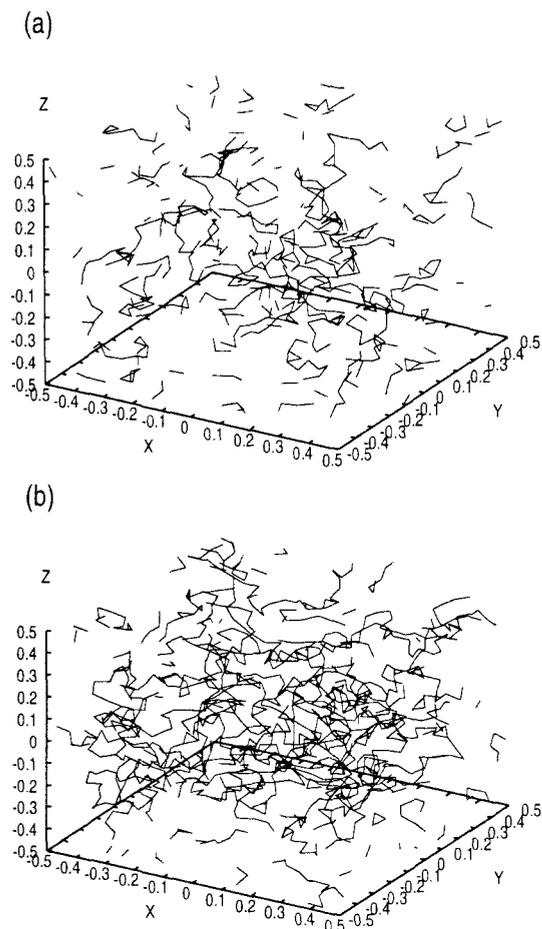
Figure 1: Snapshot of simulation at n_r=40, n_m=1125 and n_l=200 after (a) 10^4 steps (b) 10^5 steps. Lines indicate bonds formed by radical reactions.

steps without radical reactions. Radical reaction gelation strongly depends on the initial configuration. We prepared several different initial configurations using different seeds of random numbers. Radical reaction of our model is controlled by the distance between radical and active particle. If that distance is less than the particle radius, then the radical reaction occurs.

3. RESULTS

We have performed simulation with the number of monomers (n_m) 375, 750, 1125, 1500 and 1825, and the number of linkers (n_l) 50, 100, 150, 200 and 250. We simulated 25 sampling points. For each sampling point, we have performed several independent simulations. Simulation space is cubic using periodic boundary condition. The radius of particle to 0.025 with system box size scaled to 1.

A snapshot of simulation is shown in Fig. 1. Polymer growth by radical reaction is seen in the beginning of simulation in Fig. 1(a), and we find few clusters constructed from linked polymers. On the other hand, at the end of the simulation in Fig. 1(b), the polymers have grown to a large and complicated cluster. In Fig. 1(b), we see two large clusters. One is percolated in the x and z direction, and the other is
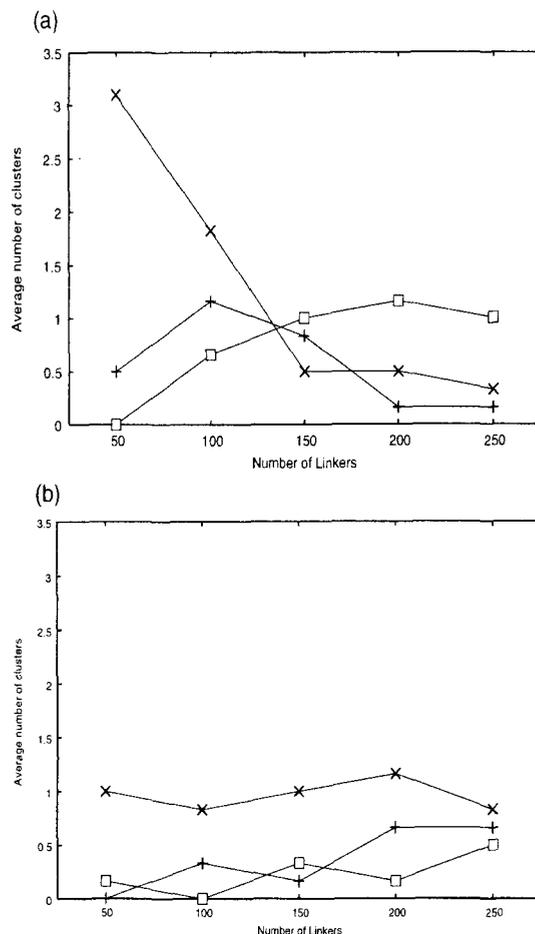
Figure 2: Average number of clusters plotted for each dimension for (a) n_m = 1875; (b) n_m = 1125. × are plotted for one-dimensional cluster. + are plotted for two-dimensional cluster. □ are plotted for three-dimensional cluster.

percolated in the z direction.

The definition of percolation we used is the following. We calculated the cluster length in the x, y, and z direction. Then if the cluster length is larger than the system size, we call this percolation.

From the structure of cluster, we analyzed the dimension of percolation. The average numbers of percolation are calculated from several simulations. In Fig. 2(a) we show the case of large n_m. For small n_l, we find more one-dimensional clusters than high-dimensional clusters. The cluster cannot develop to a large cluster, since the number of linkers in one polymer is small in this case, and the chance of linking among polymers is small. When n_l increases, the chance of linking also increases. And the dimension of cluster becomes higher than in the small n_l case. But the number of clusters decreases. When the number of linkers is 250, the average number of three-dimensional clusters is nearly 1, and we find few clusters of lower-dimensionality. This indicates that most polymers are linked, and one large cluster is formed.

In Fig. 2(b), we show the case of small n_m. The structure of the system is much different from the

(a)

(b)
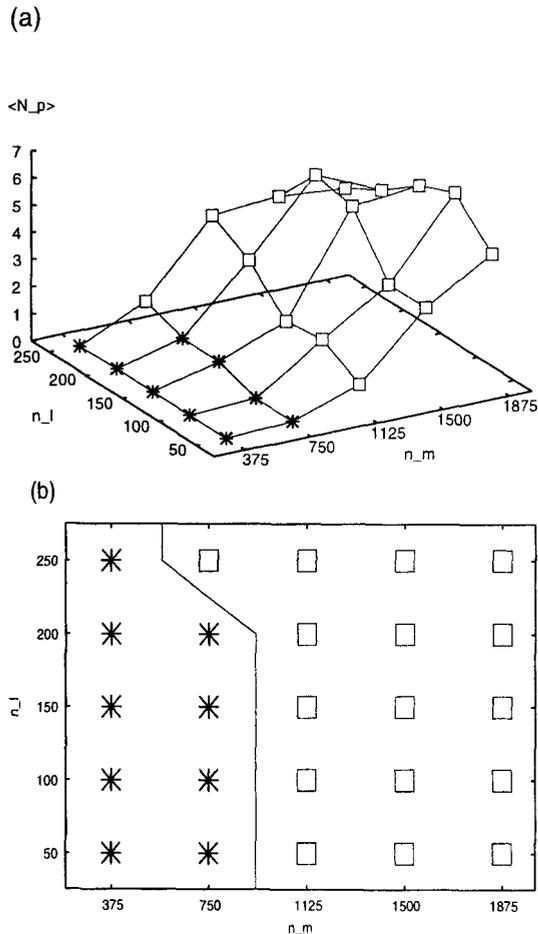
Figure 3: (a)Average number of percolation as a function n_m and n_l. (b)Phase diagram. The symbol $*$ means $< N_p >$ is smaller than 1. The symbol $\square$ means $< N_p >$ is larger than 1.

case of large n_m. We find more one-dimensional clusters than in the case of large n_m. However, when n_l is large, the number of each dimensional cluster is not so different. This result is because n_m is less than the chain overlap concentration. For small n_m, the degree of polymerization is small, and a cluster is hard to grow to a large cluster. Only a small number of polymers succeed to link to other polymers, and form percolated cluster. Under this condition, irreversibility of chemical gelation appears strongly, and percolated clusters are very unstable, and have inhomogeneity.

We investigated the difference of structure of gel to analyze the dimensionality of percolated cluster. In Fig. 3 we show the phase diagram of gelation. In order to analyze the microscopic cross-linked polymerization, we define the number of percolation as follows.

$$N_p = N^{(3)} * 3 + N^{(2)} * 2 + N^{(1)} * 1$$

Here, $N^{(3)}$ is the number of percolated cluster having percolation in all three directions, $N^{(2)}$ is the number of percolated cluster having percolation in two directions, and $N^{(1)}$ is the number of percolated cluster having percolation in only one direction.

We calculate the maximum lengths in the x, y and z direction of each cluster, and count the number of direction that is larger than the system size. The dimensionality of cluster determines the number of directions. For example, 1D-percolated cluster means that the length of cluster is larger than the system size in only one direction. If we have a two-dimensional percolated cluster, $N_p = 2$. If we have two three-dimensional clusters, $N_p = 6$. We perform 10 simulations for all sampling points, and we calculate the average N_p of 10 simulations. If the average percolation number is more than one, we say gel is formed.

We perform simulation of polymerization for chemical gelation, and the polymers and the clusters grow randomly. We observe different structures of polymer networks at the same parameter using different seeds of the random number. Many clusters do not grow in all directions equally, because the supply of monomers and linkers is finite, and our simulation is off-lattice.

Many individual percolated clusters are observed in one simulation; some clusters percolated in two directions, e.g. x and y, and a few clusters percolated in three directions, e.g. x, y and z. Usual percolation theory do not distinguish whether the system has two or more percolated clusters or it has one percolated cluster. But we consider the connectivity of polymer networks corresponding to the number of percolated cluster and the number of percolation direction.

In Fig. 3(a), when n_m is small, N_p increases as a function of n_l. When n_m is large, N_p decreases if n_l is high, while N_p increases if n_l is small. We have large N_p when we have many percolated clusters of one- or two-dimension. With the high densities of monomers and linkers, the system has homogeneous polymer networks. On the other hand, if we fix n_m and look at N_p as a function of n_l, we can observe a maximum. At this maximum, the system has many percolated clusters, and forms inhomogeneous networks. For example, for $n_m = 1875$, the maximum is at $n_l = 150$. For $n_m = 1500$, the maximum is at $n_l = 200$.

4. CONCLUSION

We have performed Monte Carlo simulation of gel. By changing the number of monomers and the number of linkers, we analyzed the structure of our system. In this simulation, inhomogeneous and homogeneous polymer networks are observed. Inhomogeneous system is formed by many one- or two-dimensional clusters. And homogeneous network is formed by a three-dimensional cluster. We obtained information of the difference of structure from the average number of percolation. Whether the system has percolated cluster depends on the number of monomers. And whether polymer networks are homogeneous or inhomogeneous depends on the number of linkers.

Further investigation should be performed for cluster growth, and also for the generation of radicals from initiator. We intend to analyze the kinetics of chemical gelation.

References

[1] T. Kanaya, M. Ohkura, K. Kaji, M. Furusaka and M. Misawa, Macromolecules, **27** 5609-5615 (1994)

[2] M. Takeda, T. Norisuye and M. Shibayama, Macromolecules, **33** 2909-2915 (2000)

[3] D. Katayama, H. Furukawa and M. Okada, Transaction of the Materials Reserch Society of Japan **25** 775-778 (2000)

[4] P. J. Flory, J. Am. Chem. Soc., **63**, 3083-3090, 3091-3096, 3096-3100 (1941)

[5] W. H. Stockmayer, J. Chem. Phys., **11**, 45-55 (1943); **12**, 125-131 (1944)

[6] A. Coniglio, H. E. Stanley and W. Klein, Phys. Rev. Lett., **42** 518-522 (1979)

[7] H. J. Herrmann and D. P. Landau, Phys. Rev. Lett., **49** 412-415 (1982)

[8] R. Bansil, H. J. Herrmann and D. Stauffer, Macromolecules **17** 998-1004 (1984)