

Micellization and Gelation of Associating Polymers

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Micellization and thermoreversible gelation of associating polymers are studied by a Monte Carlo simulation method for an off-lattice bead-spring model in three dimensions with attention to competition between micellization and intermolecular cross-linking. For polymers with many associative groups along the chain, intramolecular flower micelles are formed along the chain due to an attractive interaction between associative groups. The intramolecular micellization competes with intermolecular cross-linking. The effect of the intramolecular micellization on the sol/gel transition is studied by the lattice theory of network-forming polymer solutions. MC computer simulations for many chains are also carried out to study relative populations of six fundamental chain categories and gelation in telechelic associating polymers. The effect of chain stiffness on the sol-gel transition and the structure of networks of telechelic associating polymers are also discussed.

Keywords: associating polymers, sol/gel transition, micellization, thermoreversible gelation, computer simulation

1 INTRODUCTION

Associating polymers are polymers carrying associative groups which interact with each other through associative interactions, such as hydrogen bonds, hydrophobic interaction. It is known that associating polymers exhibit a variety of condensed phases by competition of various phase transitions induced by associative interactions, typical examples of which are microphase-separated phases, gels, and liquids crystals.

We here focus on micellization (especially formation of flower micelles) in associating polymers and how such micellization affects the sol/gel transition. For example, if many associative groups are placed along the chain backbone, intramolecular micelles are formed by intramolecular association. In this case, complex phase behavior as functions of polymer concentration and temperature is expected by competition between intra- and intermolecular association. At low polymer concentrations, intramolecular association in the form of flower-like micelles is dominant, but with increase in the concentration, intermolecular association begins to take place, and such bridge chains eventually form networks. This behavior is experimentally observed in water-soluble polymers partially modified by hydrophobic groups [1, 2, 3] and in triblock copolymers in selective solvents [4]. To clarify molecular mechanism of such intra- and intermolecular association, we study micelliza-

tion and gelation of associating polymers by Monte Carlo simulations [5] and by the lattice theory of network-forming polymer solutions [5, 6].

2 MODELS OF COMPUTER SIMULATION

As a model chain, we employ an off-lattice bead-spring model in three dimensions. The potential energy for a polymer chain with n beads consists of the following three terms:

$$H = H_b + H_\theta + H_{nb}. \quad (2.1)$$

Here, H_b is the conventional finitely extensible nonlinear elastic (FENE) potential:

$$H_b = - \sum_{i=1}^{n-1} \frac{1}{2} k_b (l_{\max} - l_0)^2 \ln \left[1 - \left(\frac{l_i - l_0}{l_{\max} - l_0} \right)^2 \right], \quad (2.2)$$

where k_b is the spring constant, l_i , l_0 , and l_{\max} are the length of bond i , the equilibrium bond length, and the maximum bond length, respectively. The bond angle θ_i between successive bonds is maintained close to the equilibrium value θ_0 by the bending potential H_θ :

$$H_\theta = \sum_{i=2}^{n-1} \frac{1}{2} k_\theta (\cos \theta_i - \cos \theta_0)^2. \quad (2.3)$$

Finally, H_{nb} represents interaction between the beads that are not directly connected by a spring:

$$H_{nb} = \sum_{i < j}^{(nb)} u(r_{ij}), \quad (2.4)$$

where u is the pair-potential, r_{ij} is the distance between the beads i and j , and $\sum_{i < j}^{(nb)}$ indicates a summation over all distinct pairs of non-bonded beads. Excluded volume interaction with hard-sphere diameter σ is assumed to act between all non-bonded beads. In addition, we introduce another kind of beads, called "sticker" in this paper, for the associative groups which interact via the following square-well potential with each other:

$$u(r_{ij}) = \begin{cases} \infty, & r_{ij} < \sigma \\ -\varepsilon, & \sigma \leq r_{ij} < d \\ 0, & d \leq r_{ij}, \end{cases} \quad (2.5)$$

Parameters in the model are chosen as follows. The length is scaled by the hard-sphere diameter σ . To avoid bond crossing, we set $l_0 = 1$, $l_{max} = 1.2$ and $\beta k_b = 50$. In the present study, d is fixed at 1.2.

3 PERIODIC ASSOCIATING POLYMERS

3.1 Intramolecular Micellization

We first investigate the effect of the attractive interaction on the conformation of a single polymer chain. In a simulation box, we generate a molecule with the degree of polymerization $n = 41$ carrying $n_s = 11$ stickers. The stickers are periodically placed along the chain with the period p , which is fixed at $p = 4$ in the present study. The behavior of periodic associating polymers with a relatively short chain length was studied by the bond fluctuation method in two dimensions [7]. In the present paper, we investigate conformational change for longer polymer chains using the off-lattice MC method in three dimensions to clarify mechanism of intramolecular micellization observed in experiments, which will be explained later.

We study the polymer conformation by varying strength of attractive interaction $\beta\varepsilon$. We find that, for $\beta\varepsilon$ larger than a certain threshold value

(about 3.5 for the present molecular parameters), the stickers are strongly bonded and form a single aggregate. This behavior is similar to the coil-globule transition observed for homopolymers in solutions. However, the characteristic feature of periodic associating polymers is that the aggregates are surrounded by non-attractive beads as shown in Fig.1(a). These aggregates can therefore be regarded as microphase-separated intramolecular micelles.

In Fig.1(b), a typical snapshot obtained by the simulation for $n = 81$ and $n_s = 21$ is presented. In this case, there are two intramolecular micelles. We consider that these intramolecular micelles are thermodynamically stable at this temperature because the attractive interaction between stickers is screened by the surrounded non-attractive beads. Therefore, there seems to be an upper bound in the number of stickers contained in one micelle. This bound strongly depends on the period p of the stickers along the chain and the potential width $d - \sigma$.

The existence of the upper bound suggests that, if we use a longer polymer chain, several flower micelles are formed along the chain. In fact, experimental observation of a structure formed by a train of flower micelles along a chain was reported for amphiphilic graft copolymers in a selective solvent [8]. An example of pearl-necklace structures obtained in our simulation is shown in Fig.1(c).

3.2 Gelation

We next consider the effect of intramolecular micellization on gelation. On the basis of the behavior of a single chain, we expect that an aggregate of the associative groups forms an intermolecular cross-linking region between the two molecules, if stickers of a molecule are involved in an intramolecular aggregate formed in another molecule. In principle, since each aggregate is formed by many stickers, the aggregates can become multiple cross-linking regions in many chain systems. If the polymer concentration increases in such systems, the gelation should take place.

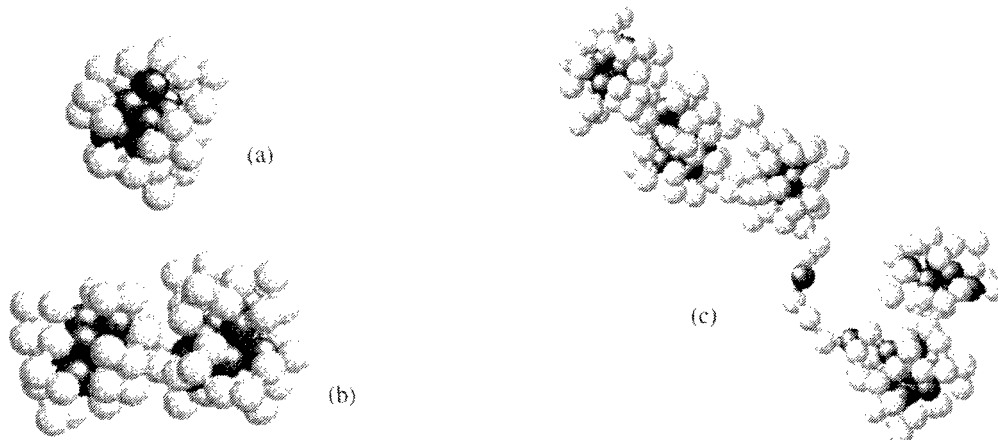


Fig.1 Intramolecular micelles of periodic associating polymers. (a) $n=41$, (b) $n=81$, (c) $n=201$.

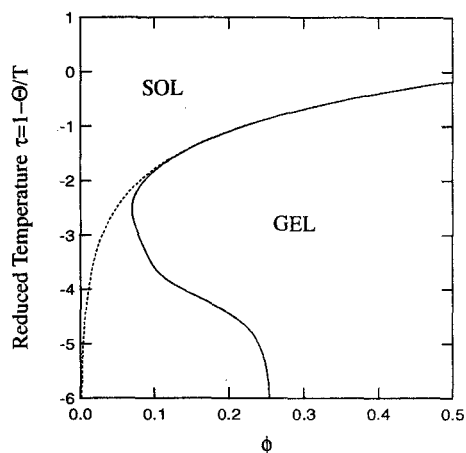


Fig.2 Sol/gel transition curve for periodic associating polymers: $n=101$, $p=5$, $s=5$.

It is important to note that the effective number of associative groups on a chain decreases by the formation of intramolecular micelles because the cores of such micelles are regarded as composite associative groups if they are not saturated. In this case, gelation is suppressed by intramolecular micellization.

Here we study the effect of intramolecular micellization on gelation by the lattice theory of network-forming associating polymers. In the theory, intramolecular micellization is taken into consideration by introducing the conformational free energy for polymer chains into the total free energy of the system. Details of the theory are presented in Ref.[6].

Figure 2 shows the sol/gel transition curve obtained by the theory as a function of the dimensionless temperature $\tau \equiv 1 - \Theta/T$, where Θ is Flory's theta temperature of our polymer solu-

tions. The broken line corresponds to the case where intramolecular association does not take place. Here we use $n = 101$ and the period p of the associative groups is 5. The number of associative groups in a intramolecular micelle and the multiplicity of junctions, *i.e.*, the number of groups combined into the junction, are both fixed at $s = 5$. At a high temperature region ($\tau \geq -2$), the gelation volume fraction ϕ^* decreases with decrease of τ as in the case without intramolecular association indicated by the broken line. On the other hand, ϕ^* rapidly increase with decrease of τ at a low temperature region ($\tau \leq -2$) due to the intramolecular micelle formation. Figure 2 shows that there is an optimal temperature of gelation where ϕ^* becomes minimal. Therefore, at a fixed concentration, the solution gels on heating, but it goes back to sol on further heating.

4 TELECHELIC ASSOCIATING POLYMERS

We next consider cluster formation and gelation in telechelic polymers. Since a telechelic associating polymer is a polymer chain carrying two hydrophobes at both its ends, it forms a single loop by intramolecular association. Therefore, polymer chains in the solution are classified into 6 types as shown in Fig.3, *i.e.*, isolated open chain, isolated loop, cluster consisting only of loops (called "flower micelles"), bridge chain, dangling chain, dangling loop in a cluster. In this case, loop formation competes with intermolecular association.

Characteristic structures formed in telechelic polymer solutions, *i.e.*, flower micelles and networks, are presented in Fig.4 and 5, respectively. In these figures, the non-associative beads are replaced by bonds to give a clear picture. In Fig.5, the cross-linking points are decorated by many small loops.

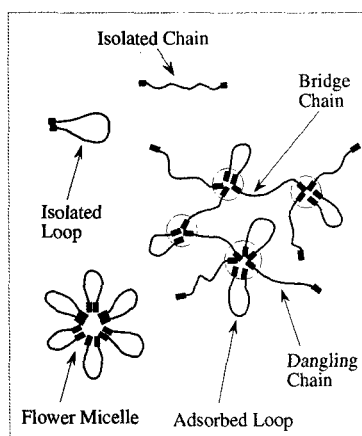


Fig.3 Six chain categories in telechelic associating polymer solutions.

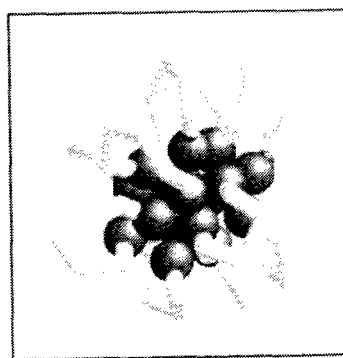


Fig.4 Flower micelle of telechelic associating polymers.

Figure 6 shows relative population of each chain category as a function of the total polymer volume fraction obtained by the MC simulation. The curves are normalized to give unity when summed. The isolated chain and the isolated loop start with the ratio 0.86 to 0.14, but both of them decrease with the polymer volume fraction, because most of them are adsorbed into mixed clusters. The dangling chain and the dangling loop increase with the volume fraction, but the bridge chain eventually dominate at high volume fractions. The gel volume fraction ϕ^* estimated from a percolation probability is about 0.08. Flower micelles slightly appear before the solution gels and its relative population decreases at high polymer volume fractions. This is because loops which form flower micelles change into bridge chains with the polymer volume fraction.

5 CONCLUSIONS AND DISCUSSION

We have studied formation of intramolecular micelles and intermolecular cross-links in associating polymers by both computational and theoretical methods.

In the case of periodic associating polymers, Monte Carlo simulation clarified how intramolecular association take place; the polymer chain forms many microphase-separated flower micelles along the chain that can be regarded as effective functional groups for cross-linking. The sol/gel transition line for such periodic associating polymers are derived by the lattice theory, where intra- and intermolecular association compete with each other. At low temperatures, gelation of periodic associating polymers can be suppressed by intramolecular micellization. In this case, a large gel region appears at intermediate temperatures in the phase diagram.

In the case of telechelic associating polymers,

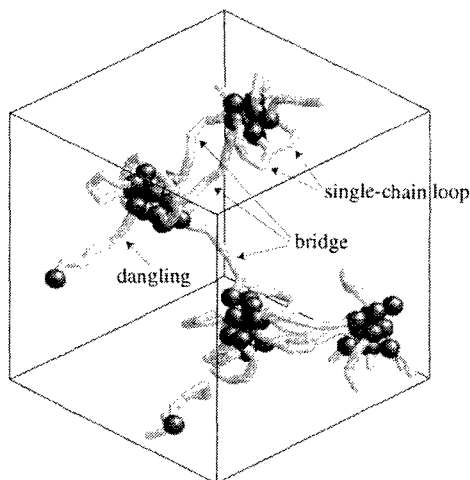


Fig.5 Network of telechelic associating polymers: $n=7$, $\beta\epsilon=4$, $\beta k_0=5$, $\phi=0.03$.

competition between loop formation and intermolecular cross-linking are studied by the MC simulations with special attention to the formation of flower micelles. We clarified how the relative population of bridge chains and loop chains changes with the polymer concentration.

In this paper, we mainly focus on the effect of intramolecular association on phase behavior of gelling associating polymers. Chain stiffness can strongly affect such intramolecular association because it prevents loop formation. Furthermore, characteristic structures are expected in stiff associating polymers by competition between association and orientational ordering of the molecules, which leads to the formation of bundles and liquid crystals. These subjects are now under investigation and will be reported elsewhere.

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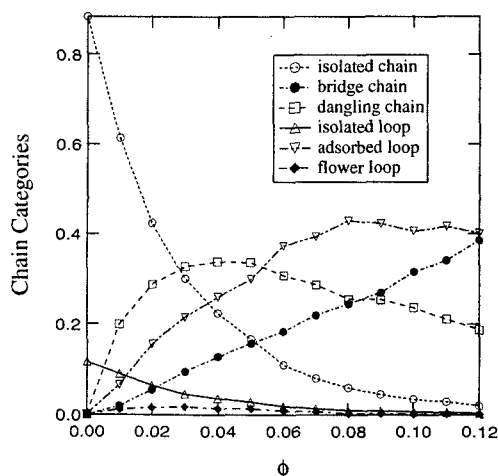


Fig.6 Relative population of each chain category plotted against total polymer volume fraction. $n=7$, $\beta\epsilon=3$, $\beta k_0=0$.