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Thermoreversible Gelation Strongly Coupled to Polymer Conformational Transition

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Summary: Thermoreversible gelation of polymers driven by the coil-to-helix transition in chain conformation is theoretically studied. For pairwise association of single helices, there are three fundamental types of self-assemblies as a result of competition between helix growth and helix association: Type I network (random coils connected by paired short helices), Type II network (helices connected by short random coils) and pairing (pairs of long helices without branching). Two distinct phase diagrams showing sol/gel transition and coil/helix transition are derived for weak and strong association.

Introduction

Most natural polymers undergo conformational transition preceding gelation. Activation of the particular functional groups on a polymer chain accompanied by a proper three dimensional conformation change is a necessary prerequisite for the interchain cross-linking. For instance, water-soluble natural polymers such as agarose and κ-carrageenan first change their conformation from the random coil state to a partially helical state, and then helical parts aggregate to form network junctions (Figure 1).[1-4] Recently, a similar two-step mechanism of gelation through coil-to-helix transition was confirmed for synthetic polymers with stereo-regularity.[5,6] It was found that, in solutions of syndiotactic poly(methyl methacrylate) in toluene, a fast intramolecular conformational change is followed by an intermolecular association leading eventually to gelation. The main purpose of this study is to derive possible phase diagrams in which two phase transitions, sol/gel transition and coil/helix transition, interfere.

Thermoreversible Gelation Induced by Coil/Helix Transition

A large body of experimental and theoretical study on the problem of single-chain coil/helix transition now exists,[7] but there is room for the theoretical study of gelation of many chains induced by coil/helix transition. We consider a single polymer chain with total number η statistical units from which j_ζ sequences of ζ contiguous chain

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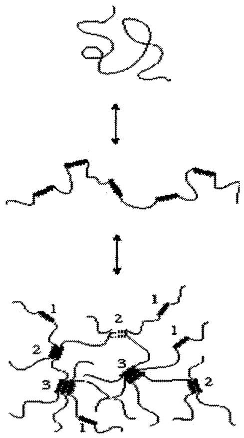

Figure 1. Thermoreversible gelation by association of partial helices on polymers. Pairwise or triple association of helices form network junctions connecting random chains. If a polymer chain carries many short helices, its functionality is high but association energy of each helix is small. On the contrary, if a polymer chain has small number of long helices, its functionality is low but association energy is large. Therefore, there should be a competition between helix growth and helix association. Network structure varies depending upon the length distribution of helices on a chain.

segments are selected for helix formation. The total number of $W(\eta,\{j\})$ of possible arrangement of j_ζ non-overlapping sequences of length ζ is then given by

$$W(n,\{j\}) = (n-\sum \zeta j_\zeta)!/\{\prod j_\zeta !\}(n-\sum \zeta j_\zeta - \sum j_\zeta)\,. \tag{1}$$

The canonical statistical weight of a polymer conformation carrying such helices is then given by

$$e^{-\Delta A(\{j\})/k_B T} = W(n,\{j\})\prod \eta_\zeta^{j_\zeta}\,, \tag{2}$$

where η_ζ is the weight for a helix of the length ζ. In order to focus on the many-chain problem concerning the connectivity of the solution as a whole (see Figure 1), we here employ for a single chain the simplest Zimm-Bragg model of the coil/helix transition, for which η_ζ is given by $\eta_\zeta = \sigma s(T)^\zeta$, where s is given by $s(T) \equiv \exp(\varepsilon_H/k_B T)$ in terms of the hydrogen-bonding energy ε_H between the neighboring groups on a chain for helix formation.

A characteristic feature of gelation by such sequence selection lies in that, for the pairwise association, the total number of helices on a chain must be equal to or larger than 3 in order for the solution to gel. For triple association, it must be equal to or larger than 2. Therefore, as the sequence ζ becomes longer by lowering the temperature, the effective functionality becomes smaller, and, at a certain critical value of ζ, the solution goes back to a non-gelling system. This simple consideration suggests that gelation becomes easiest in the intermediate temperature region where the coil/helix transition takes place.

In what follows we consider pairwise association of single helices as the simplest model system. We apply our recent theory of network-forming polymer solution[8,9] in which functionalities of polymers change depending upon their conformation. We start from the lattice-theoretical free energy of functional polymers, and minimize the total free energy of the solution to find the most probable molecular-weight distribution functions of clusters formed by the polymers whose conformations are given by the statistical weight eq. (2). This process is most systematically done by imposing multiple equilibrium conditions on the chemical potentials of clusters. The equilibrium conditions between the random-coil state and partial helix state are also imposed. Then, from the obtained distribution function, we calculate the weight-average molecular weight of the clusters, and from its divergence point we identify the sol/gel transition point. (We employ conventional definition of the gel point such that the largest cluster percolates onto the entire solution.) The tendency of helix pairing is described by the association constant $\lambda(T) \equiv \lambda_0 \exp(\varepsilon_A / k_B T)$, where ε_A is the association energy between the helices. The competition between the helix growth and helix association can be described by the ratio $b \equiv \varepsilon_A / \varepsilon_H$, *i.e.* the strength of association energy relative to the hydrogen-bonding energy. If b is large, we expect Type I networks, while, if b is small, we expect Type II networks, or pairing in the extreme case (see Figure 2).

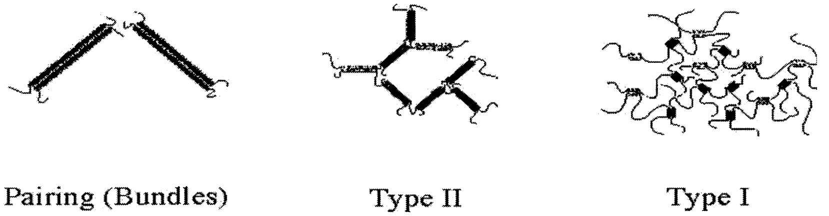

Figure 2. Three fundamental types of association. When the length of a helix reaches the total chain length, pairing (or bundle formation in more general multiple association) of helices occurs. When chains carry small number of long helices, networks of rigid-rod helices connected by short random chains are formed (Type II). The elastic properties of Type II network are highly nonlinear and non-affine. When chains carry many short helices, networks of random coils connected by point-like cross-links are formed (Type I). The elastic properties of Type I networks show those of ordinary affine networks.

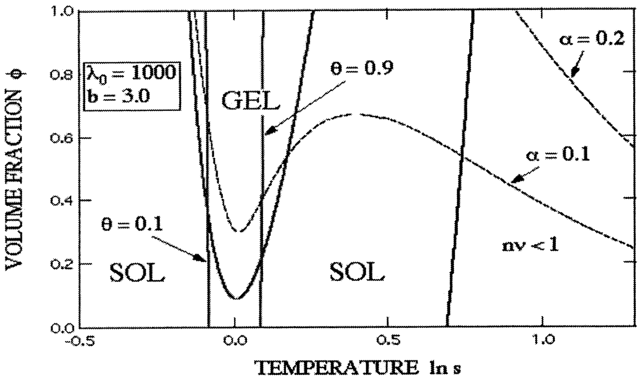

Figure 3. Phase diagram showing sol/gel transition and coil/helix transition in the weak association case (*b*=3.0). Solid line shows sol/gel transition line. The two lines indicated by θ are the contours at constant helix content (0.1 and 0.9). Broken lines show the contours at constant reactivities. The vertical thick solid line at the right side shows the boundary at which the average number of helices on a chain becomes less than one.

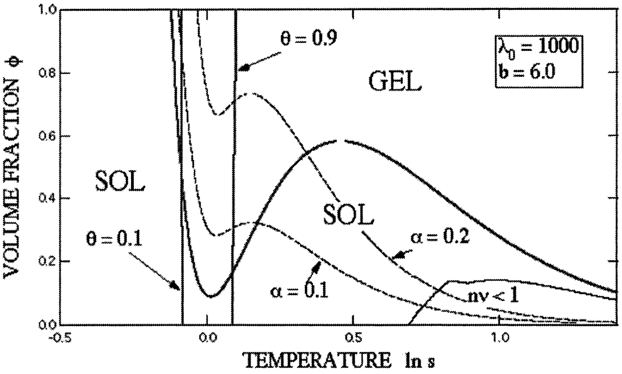

Figure 4. Phase diagram showing sol/gel transition and coil/helix transition in the strong association case (*b* = 6.0). Lines are the same as in left figure.

Figures 3 and 4 show theoretically calculated typical phase diagrams for weak association and strong association, respectively. The temperature is measured in terms of ln $s = \varepsilon/k_B T$ as in the literature[7] on coil/helix transition, so that it decreases as one moves rightward along the horizontal axis. The vertical axis shows the polymer volume fraction.

In the weak association, the sol/gel transition takes place across the coil-to-helix transition temperature region where the number of helices become large (Fig. 3). The coil-to-helix transition region is shown by the two lines showing the contour with constant helix content θ, *i.e.* $\theta = 0.1$ and $\theta = 0.9$. In the postgel regime, networks of Type I are formed. At high concentration in the postgel regime, transition from random coil to helix takes place inside the network because the transition region is mostly confined in the postgel regime. At low temperatures, a polymer chain carries only one long helix below the line indicated. These rod-like helices may form various anisotropic mesophases either in isolated or paired form, but such phase transitions are not studied in the present theory. The broken lines show the contours at constant reactivity (*i.e.* the number of paired helices divided by the total number of helices) $\alpha = 0.1$ and $\alpha = 0.2$.

In strong association, the gel region is largely expanded. Across the coil/helix transition region, Type I networks are formed, but just below the transition region, helices grow and Type II networks are formed (Fig. 4). At low temperatures, although the helix content becomes nearly full, there are only relatively short helices to reduce the network free energy by increasing the number of helices. Networks of short helices connected by the paired helices are formed. They can be called "reentrant Type I" networks. At low concentration, however, helices can grow because of the small probability of association, and pairing of long helices is possible. Therefore, if we increase the polymer concentration at low temperature, there should be another transition from the pairing state to the network state. This is a new transition characteristic of thermoreversible gelation induced by coil/helix transition

Conclusions

It is shown that two fundamentally different types of polymer networks are formed depending upon the strength of helix-forming tendency and of association among helices, and accordingly, two different phase diagrams are possible. At sufficiently low temperatures, gelation is prevented in both cases because the length of helices reaches the total length of a polymer. There should be a transition from pairing state to network state at such low temperatures with increase in the polymer concentration. Typical phase diagrams are calculated for the simplest case of pairwise association of single helices. Our theory can readily be generalized to multiple association, and also to double helices to compare with the experimental observation of biopolymer gels. Theoretical details will be reported in a forthcoming paper.

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