Thermodynamics of Reversibly Associating Polymer Solutions

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We conducted computer simulations on the phase behavior and gelation of solutions of reversibly associating polymers. The sol-gel transition, near the critical temperature for polymer-solvent phase separation, has thermodynamic signatures reminiscent of the micellization of surfactant solutions. At high temperatures, gelation is a continuous transition. Consequently, the behavior of the sol-gel transition is more complicated than previously thought. [S0031-9007(99)09379-5]

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Associating polymers are chain molecules containing a small fraction of "sticker" groups along the backbone. The rheological properties of these heteropolymers vary widely, from a viscous solution at low polymer concentration, to a weakly elastic solid at higher concentrations where the polymer forms a gel [1–4]. Consequently, these materials are ubiquitous in real life, e.g., in food, enhanced oil recovery, and in biological tissues [5,6]. The critical feature in the behavior of these materials is the formation of thermoreversible gels, which are disordered supramolecular assemblies spanning the system [7–15]. Two conflicting viewpoints have been proposed to explain the physics of the sol-gel transition: Tanaka *et al.* [11–13] suggest that the reversible gelation of an associating polymer in a solvent is a third order thermodynamic transition. In contrast, since gelation has an obvious connection with percolation, others have argued that it is not associated with thermodynamic singularities [10,14,16]. Past computer simulations on solutions of associating polymers [17–19], which do not examine the possibility of thermodynamic singularities associated with the sol-gel transition, cannot address this controversy.

We consider polymer chains on a cubic lattice with periodic boundary conditions in all three directions. Chain lengths of $N = 500$ are considered, where stickers are regularly placed ten monomers apart. Each chain thus contains $r = 51$ stickers. The lattice consists of chains and holes, a system which is isomorphic with an incompressible polymer solution. Nearest neighbor pairs of chain monomers have interaction energies as follows: $\epsilon_{ss} = -6\epsilon$ and $\epsilon_{sm} = \epsilon_{mm} = -\epsilon$, where the subscript s stands for a sticker, while m denotes a nonsticky monomer. The energy of interaction of any species with a hole is identically zero. The reduced temperature is defined as $T^\star = k_BT/\epsilon$. We determined the phase coexistence of these solutions by the histogram reweighting method [20–23]. For a system of volume V in the grand canonical ensemble the probability of its occurrence with energy, E, and number of particles, N_p, $f(N_p, E)$, is

$$f(N_p, E) \equiv \frac{\Omega(N_p, V, E)\,\exp[-\beta E + \beta\mu N_p]}{\Xi(\mu, V, T)}. \quad (1)$$

$\beta \equiv 1/k_BT$, μ is the chemical potential, and $\Xi(\mu, V, T)$ is the grand partition function. $\Omega(N_p, V, E)$ is the microcanonical partition function. One performs a series of grand canonical Monte Carlo simulations with a fixed value of T and μ in each one. The systems are equilibrated through a combination of local reptation moves (80%), and chain insertion/removal which is performed using the configurational bias method (20%). Typical simulations are 5×10^7 elementary steps in length. Combining these simulations yields an estimate of $\Omega(N_p, V, E)$ to within an arbitrary constant, from which system thermodynamics are derived.

We have computed the phase coexistence for chains of length $N = 500$, with and without stickers, dissolved in solvent (Fig. 1). The inclusion of the stickers shifts the critical temperature to higher values, in agreement with intuition [24]. Next, we focus on locating the sol-gel transition line for this model system. We consider systems in the *canonical* ensemble, i.e., fixed N_p, V, T, where each simulation spans 5×10^7 elementary moves with 80% reptation moves and 20% chain regrowth using the configurational bias method. We define that two chains have "clustered" if a pair of nearest neighbors corresponds to an intermolecular sticker-sticker contact. The distribution of all of the cluster sizes is then derived. In the gel state the probability distribution function for cluster sizes is bimodal, with one peak in the sol and the other in the gel. The volume fraction of monomers in the gel, $\phi_{\rm gel}$, is the appropriate "order parameter" for the sol-gel transition. From Fig. 2 it is clear that $\phi_{\rm gel} > 0$ for $\phi \geq 0.025 \pm 0.002$ at $T^\star = 3.85$. Thus, we identify $\phi_{\rm sg} = 0.025$ as the sol-gel transition [25]. Another estimate for $\phi_{\rm sg}$ draws inspiration from micellization of surfactant molecules, and utilizes the fact that the volume fraction of unassociated chains, $\phi_{\rm mono}$, changes slope at $\phi = \phi_{\rm sg}$ [26]. Figure 2b uses this idea, and demonstrates that $\phi_{\mathrm{sg}} \approx 0.026 \pm 0.004$, in good agreement with the results presented in Fig. 2a. In Fig. 1 we plot the locus of sol-gel transitions as a function of temperature. Note that this transition persists out to high temperatures (e.g., $T^{\star} = 25$), as expected by de Gennes [16]. We speculate that this occurs because chains, at high enough ϕ, stochastically form clusters because stickers on different chains can be adjacent to each other even though there is essentially no preference for them to aggregate at high temperatures. However, the "gel" at high temperatures would not possess unusual rheological properties, such as being like an elastic solid at short time scales. These results merely restress the fact that our structurally based definition of a gel cannot be utilized to comment critically on the dynamic properties of the resulting structure.

Some salient features of these results are addressed here. First, the radius of gyration of unperturbed chains of $N = 500$ is $R_G \approx 14$ lattice units. The overlap concentration, $\phi^{\star} = N/(4/3)\pi(R_G)^3 \approx 0.04$, is somewhat higher than the location of the sol-gel transition. The critical point for liquid-liquid phase separation, however, occurs at a much higher polymer concentration, in qualitative agreement with mean-field predictions [14]. Second, it appears to be accepted in the current literature that the sol-gel transition occurs through the exchange of intramolecular sticker pairing for intermolecular associations. Figure 3, however, shows no evidence for this phenomenon since the fraction of stickers participating in intramolecular associations is independent of ϕ. Consequently, we are forced to conclude that our systems are in the limit of a large number of weak stickers, where the entropic penalty for complete intramolecular sticker pairing even for isolated chains is larger than the enthalpic gain at this temperature. Further corroboration for these ideas stems from the fact that intramolecular sticker pairs account for only 1% of all the stickers in the system (Fig. 3). Understanding the transition from the "weak" sticker to the strong sticker limit is an issue which we are currently working on. Third, we have also computed the number averaged molecular weight of the sol phase for $\phi > \phi_{\mathrm{sg}}$ and find at $T^{\star} = 4.5$ that this quantity decreases monotonically with ϕ. This result is in qualitative accord with the Flory theory for the post-gel regime which allows for the possibility of cycle formation, but not the Stockmayer model which assumes that the gel phase has a treelike structure. These results therefore assert that intramolecular cycles are important in the post-gel regime [7,8]. Fourth, the results from Fig. 3 can be used to comment critically on the validity of Flory and Stockmayer's theories of gelation, both of which assume that no intramolecular sticker associations are permitted in the pre-gel regime. Further, both assume that pairs of chains do not bond multiple numbers of times with each other. Under these assumptions the sol-gel transition occurs when $f_s(r - 1) = 1$, where $f_s = \phi_{\mathrm{ass}}/2$, where ϕ_{ass} is the fraction of stickers participating in intermolecular pairs. By considering only the intermolecular sticker pairs in Fig. 3, the mean-field estimate for the sol-gel transition is $\phi_{\mathrm{mf}} = 0.022$, a result which is in remarkable agreement with the "exact" estimates obtained from simulation. While we conclude that the mean-field theory for gelation is surprisingly accurate in locating the sol-gel transition for this case of weak stickers, it is also important to note that the number of intramolecular sticker pairs are roughly 30% the magnitude of the number of intermolecular sticker pairs at ϕ_{sg} (Fig. 3). Ignoring these pairs can therefore lead to an inaccurate understanding of this physical situation. A final point is that, especially

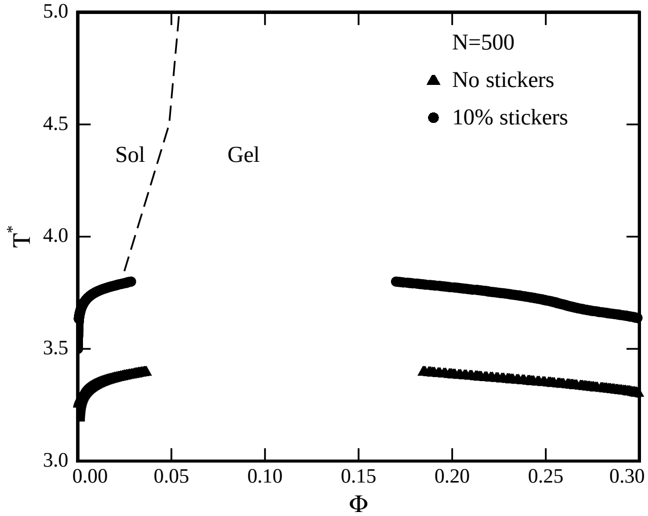

FIG. 1. Phase behavior of chains of length $N = 500$ with and without stickers. No points are shown in the vicinity of the critical point due to the finite system size. The sol-gel transition is shown as a dashed line.

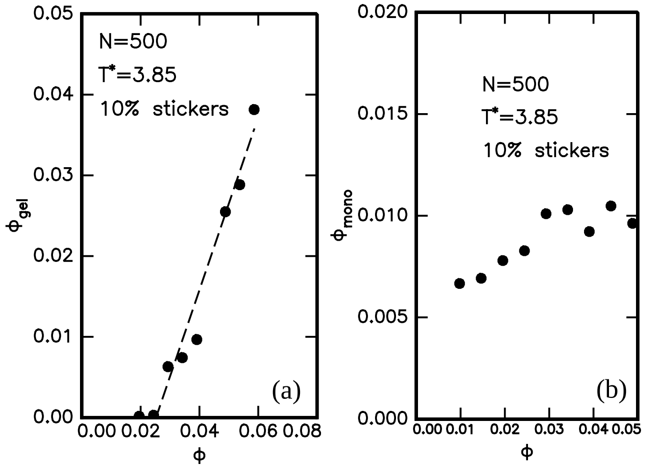

FIG. 2. (a) Determination of the sol-gel transition by plotting ϕ_{gel} as a function of ϕ. The line is a best fit straight line. (b) Determination of the sol-gel transition by plotting ϕ_{mono} as a function of ϕ.

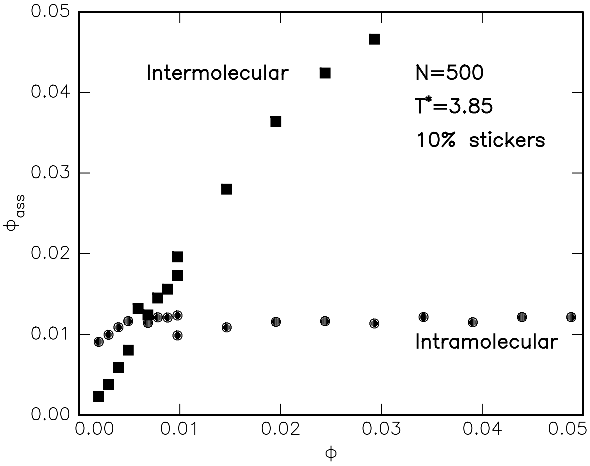

FIG. 3. Fraction of association groups participating in intramolecular and intermolecular associations, ϕ_{ass}, as a function of ϕ.

close to the critical point, both phases in equlibrium are gels. At lower temperatures, a more normal sol-gel coexistence results. These results are qualitatively in accord with mean-field predictions [14].

We now address whether any thermodynamic properties of the system are singular when the sol-gel transition is crossed. Tanaka and Stockmayer [12] suggested that the osmotic susceptibility will display a cusplike singularity at the sol-gel transition. In contrast, others have suggested that the free energy and all of its derivatives are continuous through ϕ_{sg}. We use the identity $\frac{\pi V}{k_B T} \equiv \ln \Xi$ to calculate the osmotic pressure of the solution, π. In Fig. 4 we plot π as a function of ϕ at $T^\star = 3.85$ and 4.5, respectively. At the higher temperature the osmotic pressure has a concave dependence on composition. Thus, the osmotic susceptibility, $1/\phi(\partial\phi/\partial\pi)$, decreases monotonically with ϕ, and gelation is continuous. At the lower temperature, which is just above the polymer solution critical temperature, the slope of this plot decreases as one goes from the sol to the gel, i.e., in the range $0.02 \leq \phi \leq 0.04$. A plot of the osmotic susceptibility does show cusplike behavior, but we speculate that this will *not* become a singularity even in the thermodynamic limit. Support for this conjecture comes from the fact that we have varied the box size from $25 \times 25 \times 25$ to $80 \times 80 \times 80$ and found that π, and also the osmotic susceptibility, are independent of system size in this range. These results are highly reminiscent of the behavior of surfactant molecules in the vicinity of the critical micelle concentration (cmc), where the π vs ϕ plots behave in a similar manner. At $T^\star = 3.85$ the chain-chain second virial coefficient, A_2, obtained by examining the $\phi \to 0$ limit of the slope of $\frac{\pi N}{\phi k_B T}$ vs ϕ, is negative. At $T^\star = 4.5$, this quantity is positive. We also remind the reader that the A_2 of chains without stickers would be positive for all temperatures where $T^\star \geq \Theta = 3.71$. Since the backbone is in good solvent, it is clear that the "cooperative" aggregation at $T^\star = 3.85$ is driven only by the sticker groups, in analogy with the micellization of surfactants. In contrast, at $T^\star = 4.5$ there is no such driving force for cooperative aggregation since $A_2 > 0$. Based on the analogy to micellization, it thus appears that gelation will have a much more dramatic consequence on the dynamic properties of gels near the critical temperature for phase separation, compared to gels formed at $T^\star \gg T_c$.

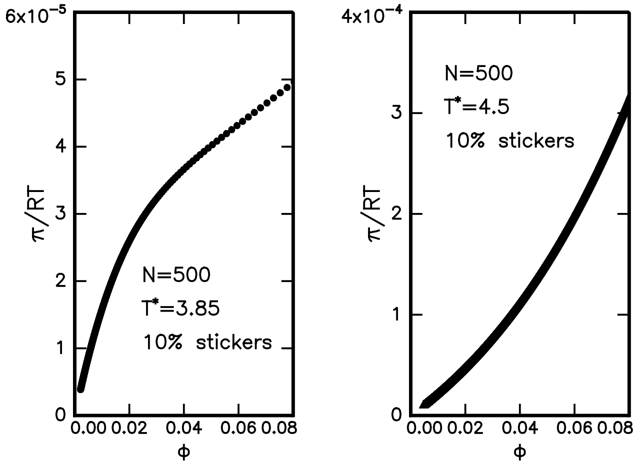

FIG. 4. Plot of π as a function of ϕ.

In summary, we have shown that the sol-gel transition for reversibly associating chains has a thermodynamic signature very reminiscent of the cmc for surfactant solutions, especially below the critical point for liquid-liquid phase separation. However, since no thermodynamic property shows an abrupt change we conclude that reversible gelation is not a higher order thermodynamic transition, even under these conditions. At high temperatures the transition is continuous, and hence purely structural. A critical comparison of our results to the mean-field Flory-Stockmayer theory of gelation shows that this approximate theory is remarkably accurate in predicting the location of the sol-gel transition. These results bear new insights into the behavior of this class of systems, which remain to be experimentally verified, and we shall be focusing on these issues in future work.

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