

Part I

Reversible Gelation and Glass

Transition:

Towards a microscopic model of
reversible polymer gel

Chapter 1

Introduction: Gel and gelation

A (polymer) gel is a macroscopic network of polymer chains joined at a number of connection sites. These joints can be either irreversible chemical bonds or reversible physical associations, which are called chemical (irreversible) or physical (reversible) gels. Chemical associations are usually introduced by crosslinking (e.g., vulcanization), while physical gels can involve many different types of interactions, such as hydrophobic interactions, hydrogen bonds, and electrostatic interactions between certain segments of the polymer chains.

In most cases the joints in a gel network are localized¹ and result from short-range interactions. But short-range connections have to be linked by long chains to form a macroscopic network. The assembly of long polymers by short-range connections result in a spatially extended network which is non-uniform. These two features, i.e., **local joints** connected by arms with **finite spatial extensions**, characterize most gel-forming systems.

Comparing to an ordered crystal, we find that microscopic structures in a gel network are highly random with no long-range order. The non-uniform yet aperiodic structures make a polymer gel share both liquid and solid properties. Within short time scales, the non-uniform micro-structures should have solid-like elasticity and exhibit fixed mechanical shapes. But over a long time span, the aperiodic structures in a gel are not thermally stable compared to periodic crystals; these structures should evolve slowly and exhibit liquid-like responses, such as finite shear viscosities. These features are reminiscent of another class of disordered materials—glasses.

1.1 Preparation of gels

We first briefly review the conventional ways to prepare chemical and physical polymer gels. A straightforward way to introduce chemical links is to add polyfunctional units (with 3 or more functional groups) that serve as branches in a network. Such polyfunctional units are interconnected

¹An exception is the network generated by topological entanglements, such as in melts of very long polymer chains, or a series of interconnected rings (de Gennes, 1979).

with polymer chains generated by di-functional monomers. Alternatively one can add crosslinking agents to the system which will form inter- and intra-chain connections. A typical example is vulcanized rubber, where sulphur molecules act as the crosslinking agents (Doi, 1996).

For polymer gels prepared via crosslinking, the connections are permanent and the gelation process is irreversible. It was Flory (1953) who first calculated the amount of crosslinkers that are necessary to generate a macroscopic network (Flory-Stockmayer model) and studied the elasticity of this network (“rubber elasticity” theory). The basic model for this crosslinked network is percolation, and it is known that Flory’s mean-field theory is accurate.

Reversible physical interactions that can induce gelation include hydrophobic interactions, electrostatic interactions, and hydrogen bonds. A typical example is a solution of associating A-B-A triblock copolymers where A segments associate with each other. At low concentrations, these triblock copolymers form micelles with A segments aggregating in the core and B segments in the corona. As the concentration of polymers increases, more micelles are formed with bigger sizes and finally these micelles overlap and interconnect with each other, some A-B-A chains serving as linkers among the micelles. In this case the connections are not permanent and the gelation process is reversible, i.e, the gel can dissociate when connections are turned off or reduced in number. This reversible property makes physical gel an ideal candidate for drug delivery or intelligent materials responsive to physical stimuli such as pH, temperature, or radiation (Petka et al., 1998; Shen et al., 2006).

Besides these traditional methods, connections can also be introduced via topological constraints. For example, in a concentrated solution of long polymers, polymer chains are strongly entangled; if the concentration is high enough, the topological joints can support a macroscopic network within the time scale of chain reptation. This is demonstrated by the elastic response of these systems. The open ends of polymers can also be closed to form rings, then these rings can interconnect with each other to form the so-called “Olympic” gel (Raphaël et al., 1997). This type of gel has permanent, but non-local junctions, and these junctions are topological in nature, therefore their property should resemble irreversible polymer gels; furthermore, as the junctions are non-local, this kind of material should have even better elasticity than crosslinked networks.

1.2 Gelation

Gelation is the formation of gel out of uniform solutions, which is usually marked by a transition from liquid-like behavior to solid-like behavior, for example, finite elastic modulus. Both physical gelation and chemical gelation have generated considerable interest in statistical physicists.

Sol-gel transition is a natural example of percolation (Stauffer et al., 1982), which is characterized by the emergence of a macroscopic cluster. The gelation point is identified as the critical point of

percolation, which is characterized by a threshold bond (or site) occupancy probability. If more bonds are occupied than the critical value, the system is percolated (in the gel phase), with an emergent macroscopic network and small clusters; below the critical threshold, only finite clusters are present and the system is in the sol phase. Near the threshold, physical properties including the probability distribution of finite clusters are universal and can be calculated from the percolation model.

In the classical model by Flory and Stockmayer (see Flory, 1953), the crosslinked network (e.g., vulcanized rubber) is assumed to be an infinitely large branched tree (without cycles), which is the mean-field limit of the percolation model (i.e., percolation on a Cayley tree). The Flory-Stockmayer model can be solved analytically and makes good predictions regarding the gelation point and elastic properties. Furthermore, as each crosslinker (multi-functional unit) is surrounded by many monomers, cycle structures are rare, therefore the Flory-Stockmayer model is accurate even near the critical threshold (de Gennes, 1979). Later, Coniglio et al. (1979, 1982) modified the model to account for the presence of solvent molecules. In this “site-bond correlated percolation” model, lattice sites are occupied by monomers as well as solvent molecules and a bond can be formed between neighbor monomers only. In addition, enthalpic monomer-monomer interactions are introduced as near-neighbor correlations. In this model there is a sol-gel transition as well as a phase coexistence as in normal polymer solutions due to the enthalpic interaction. The sol-gel transition intersects the phase coexistence at a tricritical point which depends on the solvent property (see Tanaka et al., 1979).

The “site-bond correlated percolation” model provides a natural extension to reversible gelation: permanent links can be replaced by reversible monomer interactions and gelation can be defined as a “transient” percolation of these reversible connections. Based on this model, Tanaka and co-workers (Tanaka, 1989, 1990; Tanaka and Matsuyama, 1989; Tanaka and Stockmayer, 1994) extended the model by Coniglio et al. (1982) to study the thermodynamics of reversible gelation. The polymer solution is treated following the mean-field theory of Flory and Huggins (Flory, 1953) and the reversible gelation is treated as a micellation. Later on, Semenov, Rubinstein and co-workers (Semenov et al., 1995b; Semenov and Rubinstein, 1998a) studied a similar model, but with different assumptions on the infinite cluster in the gel phase. Both models predict similar phase diagrams to those observed in Tanaka et al. (1979), but the different assumptions for the post-gel regime, which result in different cluster-size distributions, also lead to different predictions of the thermodynamic nature of gelation. Tanaka’s theory predicted that reversible gelation is a third-order thermodynamic transition while Rubinstein’s theory suggested that it is not a thermodynamic transition at all. The assumption for the post-gel regime in a reversible gel phase essentially depends on the nature of gelation and the life-time of the infinite cluster. Is the real gel phase is indeed reversible as implied by the Rubinstein model? Or does it signal some new kind of transition which resembles critical

percolation? Is the reversible gel more like a big micelle, or is it similar to a percolated network? What defines gelation in a percolation network with reversible connections?

Although the definition of irreversible gel as a macroscopic network is unambiguous and results in successful predictions, the percolation picture raises questions in the case of reversible gelation. In particular, how to consistently account for the enthalpic monomer interactions and the emergence of a macroscopic network is not obvious at all. Actually, the recent work by Zilman and Safran (2002) on self-assembled networks revealed that in a system of self-assembling chains, the percolation transition is purely topological, with no thermodynamic signature or dynamic crossover. This is clearly at odds with experimental characterization of reversible gels by their solid-like dynamic properties, which distinguish them from the liquid-like sol phase. Furthermore, the simulation results by Kumar and co-workers (Kumar and Panagiotopoulos, 1999; Kumar and Douglas, 2001) showed that for associating polymers with weak connections (associating energy comparable to $k_B T$), gelation is characterized by a change of dynamic properties, which marks a distinct transition line from the percolation transition. All these facts suggest that we should abandon the percolation picture, but build a model of reversible gelation from the microscopic monomer interactions.

1.3 Features of reversible gelation and relations to the glass transition

In a reversible gel, the network structure can transform through the breaking and rebuilding of connections. Therefore the dynamic property of the gel phase has a liquid-like behavior in addition to solid elasticity, this is especially evident in the long time limit. In real applications gelation is usually defined as when the system exhibits a finite elastic modulus at low frequency range (generally $1\text{Hz} \sim 10^3\text{Hz}$).

Semenov and Rubinstein (1998b) used a scaling argument to study the dynamic responses of the reversible gel phase based on the Zimm dynamics in the semi-dilute regime. The dynamic properties of the gel phase (but not the sol phase, i.e., below the gelation point) depend on the lifetime and the number of reversible junctions. In addition they also calculated the frequency dependence of dynamic modulus and the scaling of viscosity away from the gelation point. Their predictions reflect their assumptions that the reversible gel phase consists of transient network structures and the dynamics of the system is governed by the dissociation of individual junctions but not of the mesoscopic clusters.

However, recent experiments and simulations have shown that the gelation process shares many similarities with the glass transition, and the gel phase is usually characterized by static inhomogeneities with ergodicity breaking; in particular, the dynamic properties depend on small-scale relaxations as well as relaxations at the mesoscopic scale.

Segrè et al. (2001) studied reversible gelation in a weakly attractive colloidal system using light scattering. For all samples with high volume fractions ($> 8\%$), the static light scattering profile exhibits a peak at a finite wave number, implying percolation in the system with a finite correlation length. However, not all the samples are truly solid-like. In those samples at larger volume fractions ($> 11\%$), the scattering profile is stable, and the sample is non-ergodic; for samples at relatively lower volume fractions ($< 11\%$), the speckles around the peak of the scattering profile are not static, but fluctuate with time, reflecting cluster diffusions in the system. The scattering profiles of all these samples are roughly identical, suggesting that similar structures are present in both ergodic and non-ergodic samples; but the relaxation time in non-ergodic samples is infinite, while for quasi-ergodic samples it is large but finite (the scattering profile remains constant for several days). Comparing these behaviors to the glass transition, we see the following features: First, the non-ergodic samples resemble amorphous glasses, which behave like a normal solid but do not have periodic microstructures. Second, gelation is similar to the glass transition as it is a *smooth* transition occurring over a volume fraction range, instead of at a threshold value, and both transitions are accompanied by a crossover in dynamic responses. In addition, the final decay of the dynamic light-scattering function of the system is similar to that observed in structural glasses, characterized by a power-law divergence. The intermediate scattering functions even satisfy the same scaling form as predicted by the mode coupling theory for the glass transition (Götze, 1989).

Shibayama and co-workers (Ikkai and Shibayama, 1999; Shibayama et al., 2000) studied the sol-gel transition in a reversible system consisting of poly(vinyl alcohol), Congo red (PVA/CR), and water. They found that some speckles (random fluctuations in the scattered intensity) in the time average light scattering intensity appear exclusively in the gel state, and disappear when the temperature is increased or the concentration is lowered across the gelation point. These speckling patterns indicate the existence of frozen inhomogeneities, which implies non-ergodicity in the system. In addition, the slow mode in time intensity correlation measured by dynamic light scattering is well fit by a stretched exponential form for the sol phase, and a power law for the gel phase. Similar results have been discovered in the gelatin system (Ren and Sorensen, 1993). These features are similar to the β and α relaxations observed in glasses and predicted by the mode-coupling theory (Götze, 1989).

Kumar and co-workers (Kumar and Panagiotopoulos, 1999; Kumar and Douglas, 2001) conducted Monte Carlo simulations on the phase behavior and gelation of reversibly associating polymers. Their results showed that at high temperatures (the sticker attraction energy comparable to $k_B T$), the “gel” structure characterized by geometric percolation (connected network) does not possess the characteristic rheological properties of a gel, e.g., elasticity at short time scales. Instead, the change of dynamic properties occurs near the so-called “clustering transition,” which leads to an abrupt increase in cluster lifetimes over a small temperature range. This transition is similar to vitrification

in glass-forming liquids. Furthermore, the diffusivity data fit well with the Vogel-Fulcher form, which is known to describe the relaxation in fragile glasses.

The above results show that (1) reversible gels are characterized by the breaking of ergodicity (static inhomogeneities); (2) relaxations in the system near gelation are quite similar to those in supercooled liquids near the glass transition, usually characterized by a power law for the glassy state and a stretched-exponential function for the viscous liquid state; (3) in the “weak” interaction case (association energy comparable to $k_B T$), physical gelation is characterized by a dynamic transition, usually occurring after the geometric percolation.

The similarity between reversible gelation and glass transition is also evident from the microscopic perspective. Consider the solution of associating polymers. At low concentration, polymers associate to form micelles; as concentration increases, more micelles are formed with larger aggregation number, and finally these micelles overlap with each other to form a macroscopic network connected by associating polymers. Gelation should resemble the microphase order-disorder transition in the associating polymer solution. However, as these micelles have different sizes, and moreover, the micelles from associating polymers are “soft” rather than “rigid,” their packing may be random and share similarities with random close packing of spheres and the jamming transition, both of which are believed to occur in certain glass transitions. These microscopic similarities between polymer gels and soft (fragile) glasses are also reflected on their similar mechanical responses, including non-equilibrium relaxations and partial breaking of ergodicity.

Here we propose that reversible gelation is essentially related to the microphase transition in the system, and can be viewed as a “glass transition” alternative to the ordering transition, or, put in other words, a transition from the disordered liquid phase to a solid-like state with random structures that may be still slowly evolving. The central idea in studying the glass transition is the free energy landscape, which is introduced to separate physical relaxations at different length and time scales. In this picture, gelation or glass transition is characterized by ergodicity breaking in the system, which results in solid-like responses; but the system has liquid-like micro-structures, and therefore can still evolve. We hope this new paradigm for reversible gelation could yield better insights into their thermodynamic nature.

In Chapter 2 we study the thermodynamics of associating polymer solutions and work out the mean-field phase diagram in this system. We recover the phase diagram as observed in Tanaka et al. (1979) and obtained in the papers by Coniglio et al. (1982), Tanaka (1989), and Semenov and Rubinstein (1998a), but the gelation line is identified as the microphase transition spinodal with no *a priori* assumption of the network. We may tentatively conclude that gelation is related to this microphase transition, at least in the mean-field sense. In Chapter 3 we adapt the replica approach by Schmalian, Wolynes, and co-workers (Westfahl et al., 2001; Schmalian and Wolynes, 2000) and study the phase diagram in the system of diblock copolymer melts. Even though diblock

copolymer melt is essentially different from associating polymer solutions, they both have the feature of microphase transition. In fact, it is believed that in copolymer solutions with non-selective solvents, the microphase transition is likened to the ordering transition in copolymer melt with “diluted” monomer interactions (Fredrickson and Leibler, 1989). Therefore our conclusion regarding the glass transitions in diblock copolymer melts remains qualitatively correct for the gelation in associating polymer solutions. Revealing the possibility of glass transitions in diblock copolymer melts also supports our conjecture that gelation is the glass-transition alternative to the ordering transition in associating polymer solutions.