Lecture 10:
Gelation

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1 Suggested reading

- *Polymer Physics* – Rubinstein and Colby: Chapter 6

2 Gelation

To date, we have discussed the behavior of individual polymer chains alone and in solution with solvents or other polymer chains. These materials behave as liquids either at room temperature or upon heating. We are often interested in making materials that transition from a liquid to a solid and will refer to these materials as **networks** and **gels**. In contrast to polymer solutions or blends, networks and gels are joined together by intermolecular or interchain **cross-links** and, in many cases, these materials can not return to liquids through simple heating or addition of an appropriate solvent. As we will discuss below, the amazing process of **gelation** produces infinite molecular weight polymer species that can be viewed as a single molecule that has solid-like properties. We encounter many such materials that undergo a sharp transition from a liquid to a solid during everyday life. In cooking an egg, we transition from a liquid solution of proteins to a cross-linked protein 'rubber'. In making Jello or Götterspiese an aqueous solution of protein is transformed into a water-swollen solid gel. When fixing a broken vase with an Epoxy resin, liquid precursors are reacted into a solid fixative. In the case of Götterspiese, the crosslinks form through microcrystallization of the gelatin proteins upon cooling and, in the Epoxy resin covalent bonds are formed linking polymer chains together. In either case, the final material after gelation consists of polymer **strands** joined together by cross-links.

If we consider starting the gelation process from a solution of soluble chains, the cross-linking process induces the formation of larger and larger branched polymer chains. Up to a critical point, this mixture of growing chains will remain soluble and are referred to as the **sol**. At a critical extent of cross-linking, at least one large molecule is formed that spans the whole systems and, if the cross-linking is covalent in nature, the large molecule will not dissolve in any solvent but only swell or shrink. These 'infinite molecular weight' polymers are referred to as the **gel** or **network** and is often surrounded by finite, soluble polymer chains. The extent of cross-linking at which the soluble polymers transform into a solid gel is referred to as the **sol-gel transition** or **gelation** and the critical point at where a gel first appears is called the **gel point**.

The earliest studies of the sol-gel transition occurred during the early days of polymer science and the initial quantitative description of gelation, which rely on mean-field approaches, were developed in the 1940s by Flory and Stockmayer. At the end of this lecture we will briefly describe the Flory-Stockmayer Theory. Many other fields have also approached this fascinating problem and as we discuss below the general problem of **percolation**, a more general phenomenon for connectivity transitions, applies to many fields of modern research. For the purposes of this course, we will not explore the mathematics of gelation and percolation in rigorous depth, but discuss the ideas to understand how we can estimate the gel point for a given solution of functional polymer chains. We are most interest in whether or not gelation will occur and, if so, what the properties of the resultant network or gel will be.

There are two main classes of gelation. Those that occur through **physical** cross-linking, such as with Götterspiese, or through **chemical** cross-linking, such as with the Epoxy resin. Within the class of physical gels, one can form **strong physical gels** that are cross-linked by **strong physical bonds** between polymer chains that act effectively as permanent bonds for a set of experimental conditions. However, as the bonds are physical in nature, changes in the external conditions can cause the properties to change and cease acting like a gel. For most purposes, we will treat a strong physical gel as a chemical gel. In contrast, **weak physical gels** are formed in a manner with highly reversible cross-links and the bonds have finite lifetimes and can be thought of as continuously breaking and reforming. These **reversible gels** are not truly solids but if the association lifetime of the cross-links are sufficiently long they behave as solids on observable time scales. On the other hand, chemical gels are formed through covalent linkages between polymer chains and always results in a strong gel. Such chemical gels can be formed through several gelations processes, including condensation, vulcanization, and addition polymerization.

Condensation reactions are typically formed by two complementary reactants that are selective for each other. This is a common model system for chemical gelation and used extensively in the formation of modern

materials. The reaction proceeds as the **functional** end of one species reacts with the functional end of another species and this proceeds until a network is formed or the reaction is stopped. Throughout this discussion, we will use the term **functional group** or **functionality**. We take the functionality of an end group to be the number of other species that it can react with. This will be more clear when we discuss chemistries of network formation, but suffice it to say that in a condensation reaction each end group has functionality = 1 as it can react with one and only one other species. The math for condesnation gelation is described by the **critical percolation** model. **Vulcanization** was original described for the cross-linking of rubber and refers to the cross-linking of long polymer chains that are already overlapping each other. This process is well-described by the **mean-field percolation** model that we discuss briefly below. The mechanisms of condensation gelation and vulcanization are similar in many aspects. **Addition polymerization** occurs when a free radical propogates through a series of polymerizable groups, leaving behind a trail of chemical bonds. As opposed to being a step-wise process as in condensation reactions, additional polymerization results in a high correlation of formed bonds on the path of a given free radical. In this case, species with multiple polymerizable groups can serve as cross-links as each group can be reacted through forming a chain on either end. In addition polymerization, each polymerizable group has a functionality = 2 as it can react with the incoming monomer as well as pass the radical onto another monomer forming a link in a growing polymer chain. The model describing network formation in an addition polymerization is called **kinetic gelation**.

In general, for a solution of polymeric species to be able to form a network or gel the average functionality f has to be greater than 2. If all species have at most $f = 2$, one can only form linear chains. Below, we will discuss the criteria for gelation as a function of extent of reaction using a mean-field approach.

3 Percolation

Before looking at the details of gelation, it is worth noting that the mathematics and physics of **percolation** as a general approach to understanding systems that undergo connectivity transitions. This can include household examples of water percolating through ground coffee beans, the spread of a forest fire, or even the spread of a contagious disease (note that a forest is static translationally while a population of living creatures which is dynamic). One approach to addressing these problems is through the **bond percolation** model. A lattice is populated with the species of interest and a degree of connectivity between the species of interest. We then consider the presence or absence of a bond between two neighboring sites on the lattice. Percolation occurs when one can draw a path across the whole domain by connecting formed bonds. One can then define a **percolation threshold** p_c that will guarantee that a path can be drawn across the sample in every case. These percolation theories are still an active area of research, including here at ETH, and can be used to understand not only the phenomenon described above, but also phase transitions from a mathematical perspective.

4 Mean-field model of gelation

One method of presenting the mean-field model of gelation is by placing monomers at the sites of an infinite **Bethe lattice**. In this way, the functionality of the monomers is taken into account by incorporating this into the structure of the Bethe lattice. For a species with 3 functionalities (trifunctional) there are 3 possible bonds at each lattice site. This propagates in all directions for an infinite number of 'generations'. In this approach, we place a functional group at each lattice site and assume that a bond is formed between neighboring sites with probability p or unreacted with probability $1 - p$. As before, we take a mean-field approach and assume that the probability p is independent of all surrounding monomer pairs. Further, we do not allow intermolecular looping. That is functionalities of the same generation cannot react.

We can then calculate the gel point for such a lattice. The general approach is to focus on one lattice site and move progressively outwards. At the gel point we require that we can continue to move along the lattice with formed bonds in all directions. If we assume that the original lattice ('parent' site) has formed a bond with one of it's neighbors ('grandparent' site) then we can calculate the average number of additional bonds the parent site forms with the $f - 1$ remaining neighbors (potential 'children'). The probability that a bond is formed with each potential child site is p and so the average number of bonds between parent and children sites is $p(f - 1)$. In a similar fashion, we can consider the average number of bonds that the child site forms with its remaining neighbors (potential 'grandchildren'), which is also $p(f - 1)$. This process can be considered iteratively out in all directions.

If the average number of bonds $p(f - 1)$ is less than one ($p < 1/(f - 1)$), then each new generation will have, on average, less members and the 'family' will die out. This corresponds to the formation of finite-sized branched polymers. If, however, the average number of bonds is greater than one ($p > 1/(f - 1)$), then each

generation has, on average, more members than the previous generation and the descendants grow indefinitely, forming an infinitie genealogical branched family tree or infinite network. The transition between these two cases is defined as the gel point:

$$p_c = \frac{1}{f-1}. \tag{1}$$

Below the gel point $p < p_c$ there are only soluble branched polymers and above the gel point $p > p_c$ there exists at least one infinite polymer, called the gel.

One major consideration is to calculate the **sol fraction** P_{sol} and **gel fraction** P_{gel} as a function of p. To calculate this, we define Q as the probability that a randomly selected lattice site is not connected to the gel through a randomly chosen path. This can occur either by not being connected to the neighbor with probability $1 - p$ or by being connected to a neighbor that is not connected to the gel through any of its neighboring sites pQ^{f-1}. Continuing in this vein of logic, we can develop a **recurrence relation** for the probability that a randomly selected site is not connected to the gel:

$$Q = 1 - p + pQ^{f-1}. \tag{2}$$

We can also write that the sol fraction P_{sol} is the probability that a randomly selected site is not connected to the gel through any of its f neighbors:

$$P_{sol} = Q^f \tag{3}$$

which implies,

$$Q = P_{sol}^{1/f}. \tag{4}$$

Combining Eqs. 4 and 2 provides a relation between the sol fraction and the extent of reaction p that is general for any functionality lattice f:

$$P_{sol}^{1/f} = 1 - p + pP_{sol}^{(f-1)/f}. \tag{5}$$

By definition we can solve for the gel fraction:

$$P_{gel} + P_{sol} = 1. \tag{6}$$

There is always one solution to Eq. 5 below the gel point with $P_{sol} = 1$. There is also a second solution for every $f \geq 3$. For $f = 3$, the second solution of Eq. 5 can be found:

$$P_{sol} = \left(\frac{1-p}{p}\right)^3 \quad \text{for } f = 3 \text{ and } p > p_c. \tag{7}$$

A more general formulation for the critical gel point p_c is developed from the Flory-Stockmaye Theory, which we will not develop here, that accounts for a general system of two species with functionalities f_A and f_B and a stoichiometric ratio between the reactive groups r and is written as:

$$p_c = \frac{1}{\sqrt{r(f_A - 1)(f_B - 1)}}. \tag{8}$$

We will use the general form of the gel point when we discuss the formation of gels from multiply species of differing functionality. Note that for the Bethe lattice described above we are considering a stoichiometric ratio $r = 1$ and $f_A = f_B = f$ and Eq. 8 converges to Eq. 1 in this case.