3.5.2 CROSS-LINKING POLYMERS

Concepts to Investigate: Cross-linking, polymers, cross-linking agents, viscosity, elastomers, thermoplastic polymers, thermoset polymers.

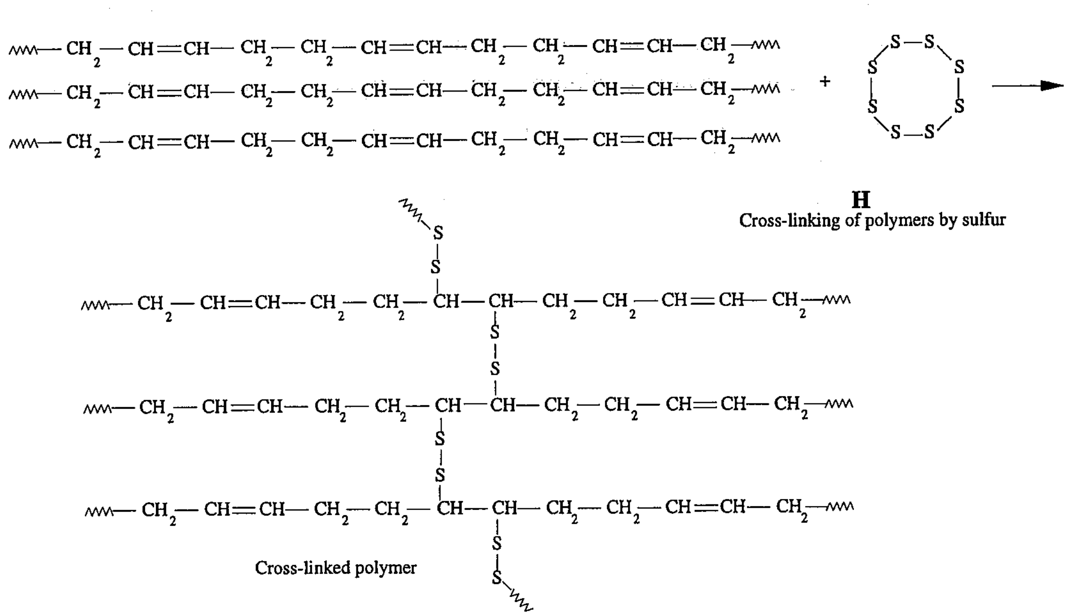
Materials: Part 1: Polyvinyl alcohol; sodium borate decahydrate (e.g. Twenty Mule Team Borax® Laundry Booster), Styrofoam cups, wooden stirring stick, plastic sandwich bags; Part 2: Substitute white glue for polyvinyl chloride.

Safety: *Wear goggles, lab coat and gloves.*

Principles and Procedures: In 1839, American chemist Charles Goodyear discovered that rubber could be made much stronger by heating it in the presence of sulfur. Figure H shows how sulfur can cross-link hydrocarbon polymer chains to form a stronger interlocking mass.

Goodyear recognized the potential industrial applications of his "vulcanization" process and applied for numerous patents. Although Goodyear's discovery was indeed revolutionary, he was unable to make money on the process and died in substantial debt. By the end of the 19th century technological and economic conditions improved, and the need for vulcanized rubber increased with the growing popularity of the bicycle. An Ohio entrepreneur by the name of Frank Seiberling borrowed a few thousand dollars to develop a plant to make bicycle tires made of vulcanized rubber. Seiberling named his company in honor of the man who discovered the vulcanization process. The booming bicycle industry created huge sales and catapulted the Seiberling's Goodyear Tire and Rubber Company into international prominence. The rapid growth of the automotive industry in the twentieth century fostered Goodyear's sales, and by 1996 sales exceeded thirteen billion dollars a year! Polymer-cross-linking has proved to be a very lucrative business.

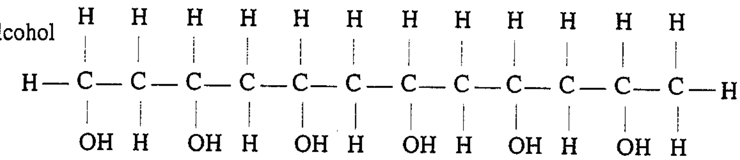
In the following activities, you will be investigating the influence that cross-linking has on the nature of two polymers. Can you think of any possible practical applications for these cross-linked polymers?



H
Cross-linking of polymers by sulfur

polyvinyl alcohol

I



Part 1: "Slime" (cross-linked polyvinyl alcohol): Polyvinyl alcohol (Figure I) is a polymer used extensively in the plastics industry in molding compounds, surface coatings, and chemical-resistant films. Sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) is a mineral used in cleaning compounds such as Twenty Mule Team Borax® Laundry Booster. Both polyvinyl alcohol and sodium borate are water soluble, but when mixed, form a cross-linked polymer. Sodium borate acts as a cross-linking agent to bind polyvinyl alcohol chains together. This solidifies the polyvinyl alcohol and traps water, forming a slimy mass.

Sodium borate dissolves in water to form boric acid, H_3BO_3, which then accepts a hydroxide from water to become $B(OH)_4^-$.

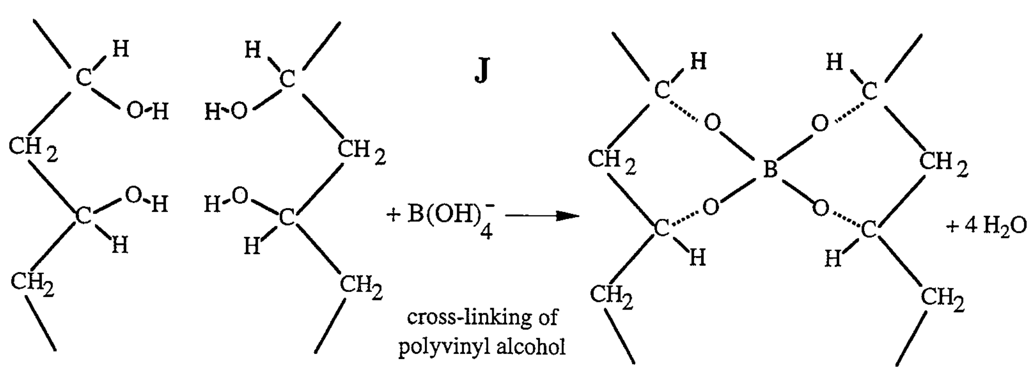
$$H_3BO_3 + 2H_2O \longrightarrow B(OH)_4^- + H_3O^+$$

It is thought that $B(OH)_4^-$ then reacts in a condensation reaction with polyvinyl alcohol as indicated in Figure J. The water from this condensation reaction as well as the excess water from the two solutions gets trapped in the cross-linked polymer, producing the slimy, flexible properties.

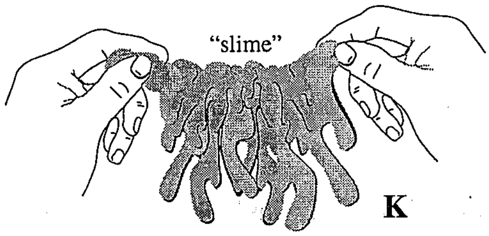
Make a 4% polyvinyl alcohol solution by slowly stirring in 4 grams of polyvinyl alcohol powder into 96 mL of hot (approximately 80°C; not boiling!) distilled water (use a magnetic stirrer if possible). Do not add the polyvinyl alcohol rapidly or it may clump and form a sticky mass. Allow the solution to stand in a covered container. Make a 4% solution of sodium borate by dissolving 0.4 gram of sodium borate decahydrate (borax) in 9.6 mL of distilled water. Pour the polyvinyl alcohol solution into a Styrofoam or plastic cup and stir in the sodium borate solution.

Although the "slime" that develops is nontoxic and can be handled, stretched, and formed into various shapes (Figure K), you may wish to wear gloves to reduce the possibility of skin irritation. Be sure to wash your hands thoroughly after handling the polymerized slime. Repeat the procedure using twice as much sodium borate solution. What effect does the amount of sodium borate solution have on the viscosity (thickness) of the slime? Describe the characteristics of the slime. You can keep the slime sealed in a plastic bag.

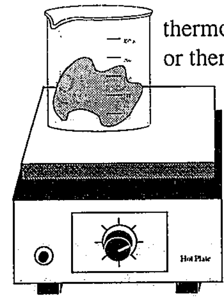
J



cross-linking of polyvinyl alcohol



K



L

Part 2: "Silly Putty": In 1943 a team of chemists developed a new putty-like polymer that could be repeatedly shaped, twisted, tied, stretched, flattened and rolled. The chemists were sure that the highly unusual properties of this polymer would make it useful for some new product, and distributed samples to thousands of engineers. Surprisingly, none of the engineers could find a practical use for this odd material until someone realized that it would make a great toy. Entrepreneurs soon packaged and sold the polymer as "Silly Putty®" which came to be one of the best-loved toys of the second half of the twentieth century. Although the real Silly Putty® is made from a relatively expensive siloxane polymer, we can make a cross-linked polymer that has many of the same properties using simple household materials.

Prepare a glue solution by adding equal quantities of water and white glue (Elmer's® glue works well) to a plastic or paper cup. Prepare a borax (sodium borate decahydrate) solution by dissolving 10 grams of borax in 90 mL of water. If you wish to make colored putty, add a couple of drops of food coloring to the glue solution. Mix equal volumes of the glue and borax solutions and stir for a couple of minutes. Roll the lump around in your hands until it ceases to be sticky.

White glue is a solution consisting of many small hydrocarbon globules suspended in water. It is viscous (thick) because all of the long molecular chains are tangled together just like a pot of stirred spaghetti. Sodium tetraborate acts as a cross-linker and ties the hydrocarbon chains together, resulting in an extremely viscous substance that exhibits properties of both a liquid and a solid. An elastomer has elastic properties and returns to its original shape after being twisted, pulled and compressed. Is the cross-linked glue-based polymer you made an elastomer? Does it bounce? Drop the ball from a height of 50 cm and measure its rebound ratio (Figure E). Compare the rebound ratio with those found by the other students in your class. Did everyone get the same rebound ratio? If your polymer ball cracks when dropped from this height, try measuring the rebound ratio when dropped from 25 cm. Place the ball in a refrigerator for 15 minutes and try bouncing it again. How does temperature affect the elasticity of this substance?

If the rigidity of a polymer decreases as the temperature is raised past a critical temperature, it is said to be a thermoplastic polymer. If, however, the polymer chemically decomposes before it softens, it is known as a thermoset plastic. Place the polymer clump in a beaker and heat gently and slowly on a hot plate (Figure L). Does this appear to be a thermoset or a thermoplastic polymer?