Synthesizing Polymers (organic classes)

This Demo will start with the preparation of real polyurethane foam to be shown in class. Mixing two components (polyester polyol and aromatic diisocyanate) results in polycondensation reaction yielding large-volume foam which later solidifies into solid polyurethane. This will be followed by preparation of "silly putty" – a hands-on experiment that all students in the class will do. Adding Elmers School glue (or generic brand School Glue) to a water/borax solution causes a chemical reaction between the glue molecules (polyvinylacetate) and the borax molecules ($Na_2B_4O_7 \cdot 10H_2O$) to produce a highly flexible, cross-linked polymer. This is similar to silly putty (real silly putty is a polymer based on organosiloxy groups and doesn't dry out).

Required Materials (You provide the following items indicated in red and starred):

For the polyurethane foam experiment:

- *** 1 clear plastic disposable cup (or the bottom of a 2 L clear soda bottle) *(you provide)***
- *** 1 wooden stirring rod (e.g. a chopstick) *(you provide)***
- *** old newspapers *(you provide)***
- *** 1 gallon Ziploc bag *(you provide)***
- *** 1 set of food dyes (4 colors)**
- 1 bottle of polyether polyol (polyurethane system part A), 20 mL
- 1 bottle of diisocyanate (polyurethane system part B), 20 mL
- 1 pair of disposable gloves

For the "silly putty" experiment:

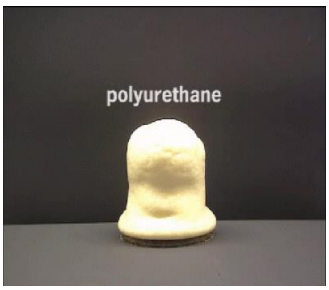
- *** 1 gallon borax water solution in some sort of container (*you provide*)**
- *** eight 4oz school glue containers for a class of 30 students (*you provide*)**
- *** roll of paper towels (*you provide*)**
- *** 15 disposable plastic bowls (*you provide*)**
- *** 30 zip lock plastic bags to store "silly putty" (*you provide*)**
- borax in plastic bag (*we will provide*)

Polyurethane foam demonstration:

Place the disposable container in the middle of your demo area on top of newspapers. Put the gloves on.

Add polyester polyol (polyurethane foam system part A) into the container. You should add few drops of food coloring to the polyol and stir it until it gets uniformly colored.

Pour the diisocyanate (polyurethane foam system part B).



Stir the contents **<u>vigorously</u>** with a stirring rod until reaction begins to occur (for ~ 1 min). *If you did not stir vigorously enough, the volume increase will not be that impressive.*

Once the reaction has started, stop stirring. You will see formation of foam which will expand to about thirty times of the original liquid volume! The container will actually get warm – this indicates an exothermic reaction. The foam will harden in about 15 min and can be cut into pieces.

After the experiment, place empty chemical bottles and gloves into a Ziploc bag, seal it, and bring back to us for proper disposal. The container and all pieces of foam may be thrown in the trash.

Important Safety Notes:

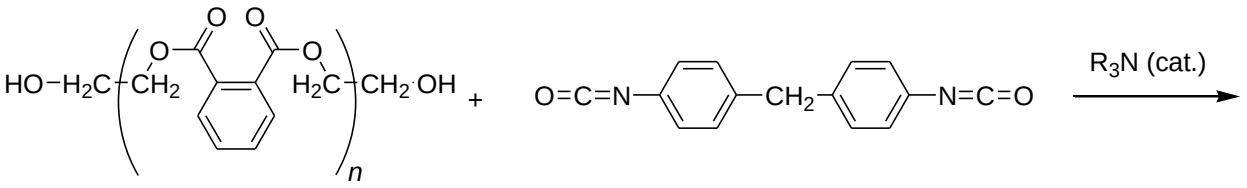
Wear safety goggles for this experiment!

Perform this experiment in a well ventilated area (large-size classroom should be OK).

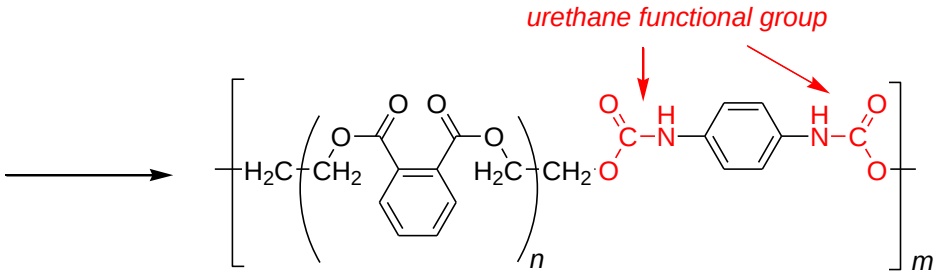
Properly prepared polyurethanes are safe to handle. However, since it is impossible to guarantee the one-to-one ratio of the reactants in the demonstration, the foam prepared may contain some unreacted isocyanate (toxic) and therefore it is unwise to pass the pieces of the foam to children. Touch this foam only with gloves.

Chemistry: Polyurethanes make a valuable contribution to our daily lives – from foam insulation to shoe soles, car seats to abrasion-resistant coatings. All polyurethanes are made using an exothermic reaction of diisocyanates with polyol molecules, containing hydroxyl groups. Relatively few commercial diisocyanates and a range of polyols of different molecular weights and functionalities are used to produce the whole spectrum of polyurethane materials. Depending on the grade, you may want to discuss the underlying chemistry (below) in more or less details. In any case, don't forget to emphasize that this huge variety of different plastics we use in everyday life are made by organic chemists from just a few elements (carbon, hydrogen, oxygen, nitrogen), and few relatively simple compounds. You may want to bring a few of polyurethane-made household things (seat cushions, sponges, pipe insulation, etc.) to demonstrate this.

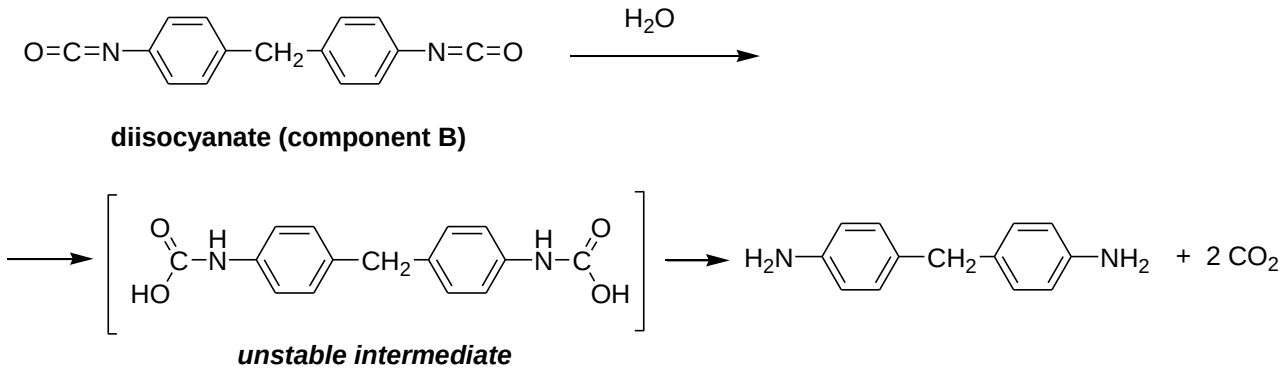
One liquid (off white, part A) contains a polyester polyol, a silicone surfactant, and the catalyst tertiary amine. The other liquid (dark brown, part B) contains diphenylmethane diisocyanate as well as oligomers of diisocyanate. The polycondensation reaction occurs when the two substances are mixed together. In addition, small amount of water (e.g. moisture from the atmosphere) reacts with the diisocyanate in decomposition reaction to produce CO_2 gas. This gas causes the foaming and expansion. After the increase in volume the polymer hardens and forms porous and rigid polyurethane foam.



polyol (component A) **diisocyanate (component B)**



polyurethane



"Silly putty" recipe: 2-3 tablespoons of borax ($Na_2B_4O_7 \cdot 10H_2O$) mixed in 1 gallon of water. It doesn't hurt to add too much borax, as it will not dissolve and just sit on the bottom of the container. If you don't add enough borax (less than 1 *teaspoon*, for example) there may not be enough borax present to fully polymerize the glue molecules. This will lead to a very gooey, slime-like product. For high-school classes, one can have them experiment with the effects of adding variable amounts of borax to the water and to calculate what molarity borax solutions they are preparing. They can then add fixed amounts of glue to these solutions and observe the properties of the polymer produced.

Pour enough borax/water solution to cover the bottom 1/3 of whatever bowl you are using to prepare the *"silly putty"*, and squirt in as much Elmer's Glue as you want to make polymer. Note that if you are going to add a lot of Elmer's Glue (more than 8 oz, for example) you will need to have at least a pint (~500 mL) of solution present.

Vigorously mix together the glue and borax water mixture with your fingers while keeping the polymerizing glue *"silly putty"* in the borax water solution. If you squirted the glue into the borax water solution as a thin stream and it sank into the solution, you should only have to mix it vigorously with your fingers for about 30 seconds to 1 minute. If you poured the glue into the solution as a big blob, then it will take considerably longer to mix the borax into the glue and get it all to polymerize into *"silly putty."* Every now and then, pull the blob of glue/silly putty out of the borax water and kneed it up and see if any pockets of liquid glue still exist. If you see liquid glue squirting out of the *"silly putty"*, then it has not yet fully reacted with the borax water. Put it back into the solution and kneed it up some more.

Once it has fully reacted, pull it out of the solution and gently pat it dry with a paper towel. Dry off your hands with a paper towel and it is ready to play with! Store it in a zip-lock plastic storage bag to keep it from drying out. If it gets into clothes or hair, it can be easily washed out with warm water. The *"silly putty"* is pretty much non-toxic (unless you eat way too much of it) and tasteless if eaten. The starting glue and *"silly putty"* are environmentally safe and biodegradable.

Notes: Two students should share each disposable bowl and take turns to prepare the "silly putty".

One 4 oz glue container should provide enough glue for 4 students. A typical class has 30 students in it, so you will need 7-8 glue containers for a class.

Colored "silly putty" can be made by first coloring the glue by adding 5-10 drops of food coloring to the glue and shaking it up like crazy to mix the color into the glue. This takes some time for a full bottle of glue.

A neat variant is to have one student make one color "silly putty", while the second student makes a different color. They can then roll out each colored "silly putty" to make a rope and then braid

them together, break in half, and then each student will have a bi-colored "silly putty". As they play with it, the colors will very slowly blend together to make a new, third color.

Another variant suitable for K-2 grades is to squirt two different color glues into the same bowl at the same time and mix them together. This will generate a new uniformly colored silly putty that is a mixture of the two original colors. This is a very nice hands-on demonstration of color mixing – perfect for kindergarten and first graders!!!

Chemistry:

Elmers Glue is made up of polyvinyl acetate, which reacts with water to some extent to replace some of the acetate groups with OH (alcohol) groups. The B-OH groups on the borax molecules react with the acetate groups on the glue molecules (relatively long polymer chains) to eliminate acetic acid and form new bonds between the borax and two glue molecules. The linking of two glue molecules via one borax molecule is called ***polymer cross-linking*** and it makes a bigger polymer molecule, which is now less liquid-like and more solid.

The bottom figure shows that many of these borax cross-links occur to "glom" together many polymer molecules turning them into a pliable solid "silly putty".

This really isn't the silly putty you buy in the store, since it will dry out. Real silly putty is an organosiloxane polymer that doesn't have any water in it so it doesn't dry out.

You can have the students simulate this chemistry by having about 6 groups of 4 students hold hands and form glue chains. Have them walk around the front of the class. Then send out 6 individual students to act as borax molecules to grab onto two glue chains – one with each hand. Tell the glue chains that once they are grabbed onto by the borax students that they shouldn't try to break free. This should result in all the glue chains being linked together by the borax molecules (students). Now that all the students are linked together they represent the more solid "silly putty" that was formed in the experiment. This is a rather good physical analogy to the chemistry going on.