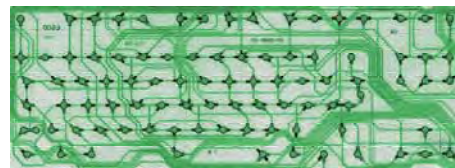


VBT/Bio-inspired Polymer Lesson Plan



Purpose: To introduce students to green chemistry and biomimicry by highlighting a green chemistry technology that improves manufacturing processes using photoresists.

Objectives: Students will ...

- Understand the biological process of sun exposure to skin and how the body deals with UV light
- Understand how chemists have emulated this natural process to develop safer alternatives in a dangerous manufacturing process
- Engage in an experiment which illustrates the uses of this green chemistry technology

Supplies: (per lab group)

- Thymine copolymer (1:4 VBT/VBEA co-polymer solution) – currently only available from Beyond Benign
- 1 plastic transfer pipette
- 1 pre-cut sheet of transparency film (avoid ink-jet transparencies)
- 1 paper towel
- Tape
- 1 coating rod (can also be a Pasteur pipette or glass stirring rod)
- 1 piece of construction paper
- Scissors and hole punchers (for designing the mask)

(Instructor supplies)

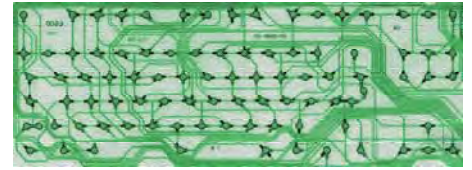
- UV lamp
- Food dye (powder works better than liquid)
- Plastic bowls (1 for water wash step, 1 for food dye wash step)
- Plastic printed circuit film

Classroom Procedure:

This activity works best in a classroom and community setting when students work individually

Safety Precaution: Be careful not to look directly into the UV light or expose your skin to UV light!

1. Put on your eye protection (safety goggles)!
2. Open up the paper towel (if it is the folded type).
3. Tape the paper towel vertically to the table, and tape the transparency film on top of the paper towel.
4. Fill a plastic transfer pipette with the thymine copolymer and apply a thin straight line of liquid at the top of the film, below the tape.
5. To coat the film with the thymine copolymer, place the coating rod horizontally above the line of the copolymer, and draw straight down so the liquid covers the film,



- without rolling the rod (draw down past the bottom of the film so the extra liquid goes on the paper towel).
6. Allow to dry for five minutes.
 7. While drying, make a UV blocking mask using the provided hole punchers and scissors to design your own circuit pattern
 - Your circuit pattern should have at least four informational points to mimic chips and then circuits between them – you may be as artistic as you want!
 8. Place the dried film under the short wave UV lamp for the students with the paper mask on top (Please note: Instructors will be using the UV lamp source; students will not be using the UV lamp. The UV lamp is a hand-held TLC lamp used to look at spots on a TLC plate. In this experiment it is used as it is typically used in a laboratory setting – facing down and not shining the light on skin or eyes).
 9. Wait two minutes, then remove the mask and rinse in a plastic bowl of water.
 10. Place film into the plastic bowl with the food coloring mixture and leave submerged for two minutes (food coloring mixture will be prepared by the instructor before class).
 11. If you keep the tape on the film, you can tape the film to the side of the container of food dye. After this, rinse the film in the water bowl and return to the paper towel to dry.

Cleanup:

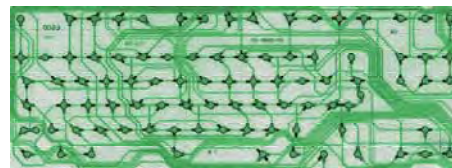
Glass pipettes (used instead of the coating rod) may be rinsed in water and reused or disposed of in the glass disposal box. Glass stirring rods may be rinsed with water and stored away. Replace the cap on the thymine copolymer and throw the plastic transfer pipette in the trash. You may dump the food coloring and water in the plastic bowls down the sink. Leave your film out to dry, and then throw away the paper towel.

Preparation:

Prepare at least two dye stations. Sprinkle some of the dye in a plastic bowl and fill the bowl with water. For best results use FD&C food dye, this dye is much more concentrated than food dyes you find at the store. Wear gloves when handling films in the dye mixture. Although the food dye is safe, the concentrated dye will stay on your skin for a couple of days.

Also if you are not in a room where students can easily access a sink for the rinsing step make sure to also have 2 bowls with water for the rinsing step.

VBT Bio-Inspired Polymer Background Information



This lesson is based on research and development currently underway at the Warner-Babcock Institute for Green Chemistry. The material VBT is a product of the Warner-Babcock Institute for Green Chemistry and is unavailable for purchase. Beyond Benign is working to create a teaching kit that includes the material which may be available at www.beyondbenign.org in the near future.

A great deal of information has emerged recently on the risks of exposing unprotected skin to too much sunlight. Several causes have been proposed for this cellular damage. One mechanism involves the reaction of DNA with UV light. One of the heterocyclic bases of DNA, thymine, has been linked to this photoreaction.

When thymine is irradiated with UV light (the kind of light that the ozone layer protects us from), it undergoes a dimerization reaction in which it couples with a neighboring thymine in the DNA chain (Figure 1) (1).

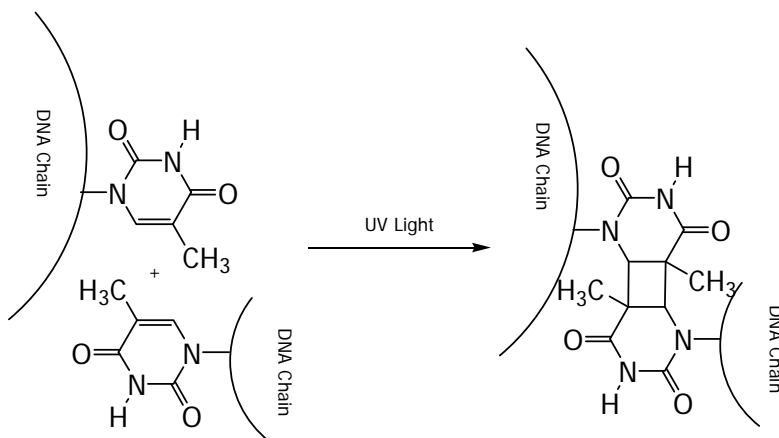


Figure 1. Photodimerization of thymine in DNA.

In our bodies, the dimerization process creates a “kink” in our DNA. There is an enzyme in our bodies that recognizes these kinks and cuts them out of the DNA strand. A second enzyme then comes along and repairs the DNA strand, replicating missing DNA in order to fill in the gap. In our bodies, we luckily have this repair mechanism to eliminate thymine dimers that form from too much exposure to the sun. When this mechanism breaks down, however, this can lead to mutations, other carcinogenic events and even skin cancer (2). With the depletion of the ozone layer, more UV light is getting to the surface of the earth. The increase in UV light will correspond to an increased rate of skin cancer.

Researchers at the Warner Babcock Institute for Green Chemistry have identified an enzyme that is capable of recognizing thymine dimers and essentially “unzips” them. This enzyme, called DNA photolyase, is found in e-Coli bacteria and other microorganisms.

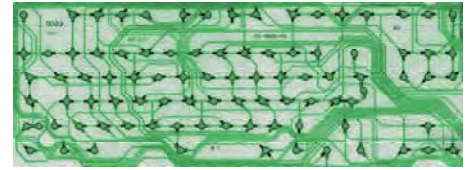
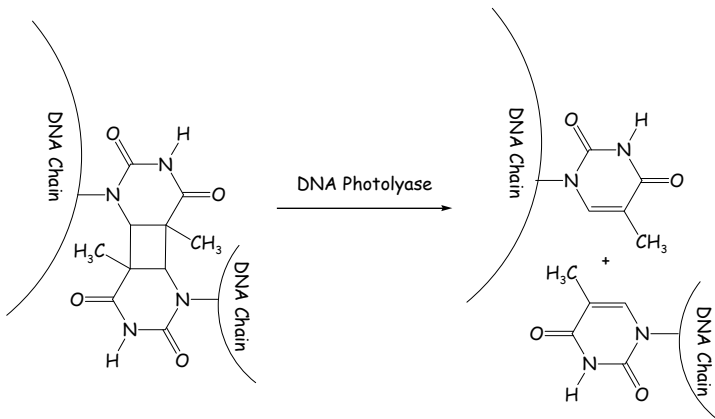


Figure 2. “Unzipping” of photodimer by DNA photolyase.

The photoreaction has been found to have some benefit in our skin and has been used for medical purposes. UV irradiation has been employed to treat serious cases of psoriasis and some forms of cancer (called PUVA phototherapy). The UV light essentially damages the DNA of the fastest replicating cells (the psoriatic or cancerous cells) and eliminates them.

Synthetic polymers that incorporate thymine take advantage of this photoreaction. Water-soluble polymers can be made that contain thymine in the chain (4). When the polymer is irradiated with UV light, the same reaction occurs that links two adjacent thymine molecules together, and it is transformed into a material that resists dissolution in water. This type of material is called a photoresist (5).

The microelectronics industry is based in large part on photoresist technology in the manufacture of printed circuit boards, integrated circuit chips, and other components. Photolithography and other forms of imaging are also based on photoresists. The basic procedure is outlined in Figure 3. The soluble material is coated on a solid support. Irradiation through a mask or by a laser causes the regions where light hits the surface to turn insoluble. These areas “resist” being washed away. After the photoresist is removed, copper or other conductive materials are deposited on the solid support to generate the final image.

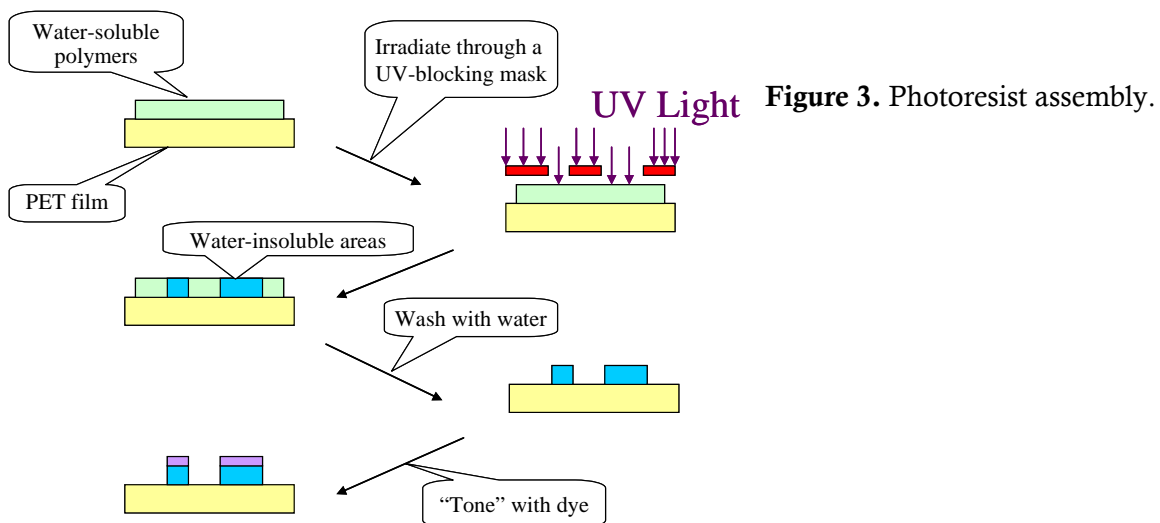
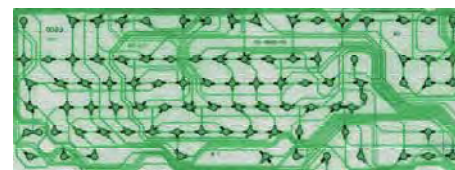


Figure 3. Photoresist assembly.



Conventional photoresist processes are not very good for the environment or for workers preparing the materials. Typical materials are organic-solvent-dependent monomers that undergo polymerization upon irradiation. These often-toxic monomers are recaptured in the wash stage, requiring strict monitoring of waste and solvent evaporation (6). The process can be visualized by imagining many small individual molecules that undergo conversion into a huge networked material (Figure 4).

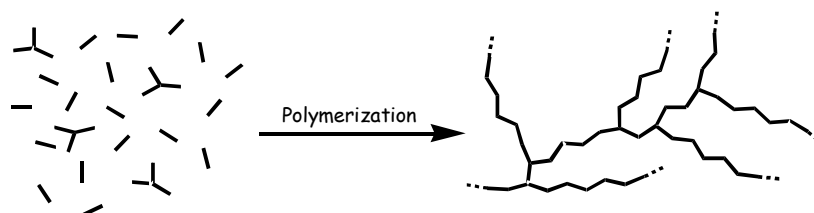


Figure 4. Polymerization process.

Thymine-based polymers are advantageous for several reasons. First, they are water-soluble, which avoids the need for organic solvents, an environmentally beneficial objective on its own. Second, a polymerization reaction is not necessary. These water-soluble nontoxic polymers are already polymerized. The photoreaction initiates a cross-linking mechanism by which neighboring strands are “tied” together through thymine dimers (Figure 5). The formation of networks in this way makes them insoluble.

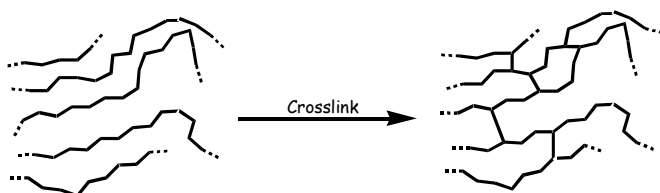
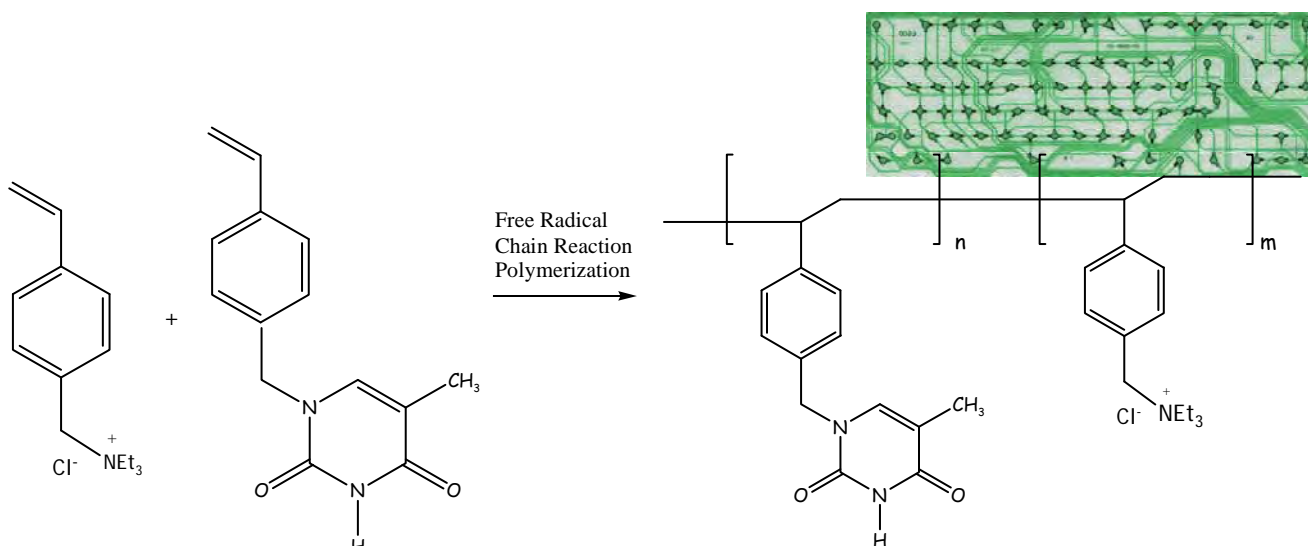


Figure 5. Cross-linking of polymer chains.

The polymer that we will use in this experiment is a copolymer of vinylbenzyl thymine (VBT) and vinylbenzyl triethylammonium chloride (VBEA) (Scheme 1). The VBT is used to adhere the polymer to the surface (as in the mechanism explained previously) and the VBEA is the component that makes the polymer dissolve in water since it is a chloride salt.



Scheme 1. Polymerization of VBT and VBEA.

Once coated on the substrate surface, a photoresist can be made using a process described previously. Upon patterning the surface, a dye can be used in order to visualize the pattern. The anionic nature of VBEA allows for the use of food color dyes in this process. It turns out that most FD&C (food, drug and cosmetic) dyes are anionic, allowing for the dye to stick to the surface of the polymer through electrostatic charges (Figure 6).

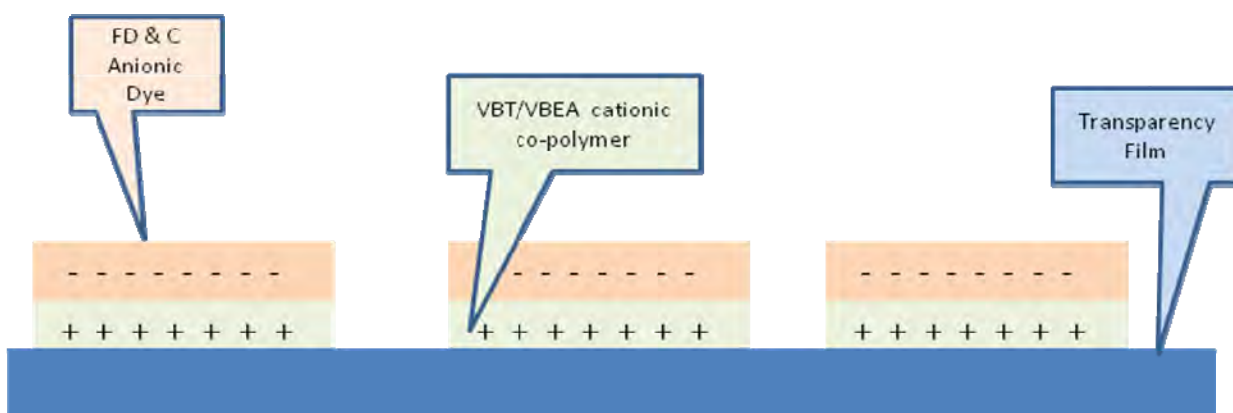


Figure 6. Cross-section of coating, showing electrostatic affinity of the cationic polymer to the anionic dye.

Reference

1. (a) Blackburn, G. M.; Davies, R. J. H. *J. Chem. Soc. C* **1966**, 2239. (b) Lamola, A. A.; Mittal, J. P. *Science* **1966**, 154, 1560.
2. Yamada, H.; Hieda, K. *Photochem. Photobiol.* **1992**, 55, 541.
3. Kim, S.-T.; Malhotra, K.; Smith, C.; Taylor, J.; Sancar, A. *Biochemistry* **1993**, 32, 7065.
4. Cheng, C. M.; Egbe, M. J.; Grasshoff, M. J.; Guarrera, D. J.; Pai, R. P.; Taylor, L. D.; Warner, J. C. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, 33, 2515.
5. (a) Grasshoff, J. M.; Taylor, L. D.; Warner, J. C. U.S. Patent 5,395,731, March 7, 1995. (b) Grasshoff, J. M.; Taylor, L. D.; Warner, J. C. U. S. Patent 5,455,349, Oct 3, 1995. (c) Grasshoff, J. M.; Taylor, L. D.; Warner, J. C. U. S. Patent 5,616,451, April 1, 1997. (d) Grasshoff, J. M.; Taylor, L. D.; Warner, J. C. U. S. Patent 5,708,106, Jan 13, 1998.
6. Frechet, J.; Havard, J.; Lee, S.; Shim, S.; Uranker, E. *Polym. Mater. Sci. Eng.* **1995**, 72, 4.