**Bio-Inspired Polymers**

**HIGH SCHOOL**

**Green Chemistry & Sustainable Science**

**Teacher 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 by teachers. Beyond Benign is working to create a teaching kit that includes the material which may be available in the near future.

Please see additional teacher background at the end of the lesson.

**Safety Information:** UV light safety procedure for students; cleanup information in procedure; contact Beyond Benign for SDS for VBT

**Educational Goals:** To understand photoresists and how polymer chemistry is being used in common technology. To introduce students to a technology that has been developed through green chemistry techniques to solve a problem in manufacturing and in creating less e-waste.

**Student Objectives:** Students will …

* Understand the biological process of sun exposure to skin and how the body deals with UV light
* Understand how chemists have used this process in nature to develop a chemical process which solves a societal problem
* Engage in an experiment which illustrates the uses of this green chemistry technology

**Materials:(per lab group)**

* Thymine copolymer (1:4 VBT/VBEA) ONLY CURRENTLY AVAILABLE FROM Beyond Benign
* 1 pipette
* 1 sheet of transparency film
* 1 coating rod (can also be a glass pipette or plastic tube)
* Food dye (liquid or powder)
* 1 piece of construction paper
* Scissors and hole punchers (for designing the mask)
* 1 paper towel
* UV light
* Tape
* An old computer keyboard

**Time Required:** 45-60-minute class period

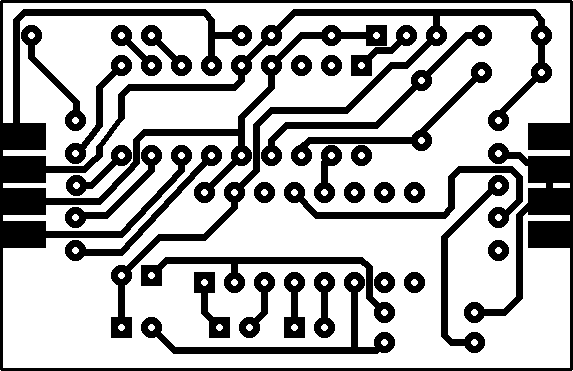
**NGSS Standards Met:**

* **HS-PS3-4.** Plan and conduct an investigation to provide evidence that the transfer of thermal energy when two components of different temperature are combined within a closed system results in a more uniform energy distribution among the components in the system (second law of thermodynamics).
* **HS-PS4-4.** Evaluate the validity and reliability of claims in published materials of the effects that different frequencies of electromagnetic radiation have when absorbed by matter.

**Key Terms**: e-waste; new polymer (VBT), biomimicry

**Teacher Prep:**

* Reading the background information provided.
* Take apart an old computer keyboard until you get to the part that where the circuit is located. It should look like this:

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* You will use this to show students how photoresists are used in computer technology.
* Prepare the food coloring mixture and have multiple containers for the students to dip the film.

**Procedure:**

* Pass around the circuit board and let the students take a look at it.
* Explain to students that chemists at the Warner Babcock Institute for Green Chemistry are currently working on a way to replace toxic monomers used in the preparation of circuit boards of electronics and replace them with a product that is based upon the concepts of biomimicry.
* Hand out the student lab sheet and review
* After all students are finished, discuss the concept of e-waste and the problems of worker exposure regarding the manufacture and dumping of electronics in the developing world. You may use the following YouTube and Teachertube videos to spark conversation on this issue.

<http://www.youtube.com/watch?v=sl2j83LCHss>

<http://www.youtube.com/watch?v=0JZey9GJQP0>

<http://www.teachertube.com/viewVideo.php?video_id=106619&title=WR3A___Fair_Trade_Recycling&vpkey>=

**Disposal Information:** All materials used may put in the trash. Clean up with water.

**Bio-Inspired Polymers: Student Lab**

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

**Procedure:**

* Collect the following materials from the lab supply area.
  + Thymine copolymer (1:4 VBT/VBEA)
  + 1 pipette
  + 1 sheet of transparency film
  + 1 coating rod (can also be a glass pipette or plastic tube)
  + Food dye (liquid or powder)
  + 1 plastic bowl
  + 1 piece of construction paper
  + Scissors and hole punchers (for designing the mask)
  + 1 paper towel
  + UV light
  + Scotch tape
* Tape the paper towel vertically to the table, and tape the film on top.
* Fill a pipette with the thymine copolymer and apply a thin straight line of liquid at the top of the film, below the tape.
* To coat the film, place the coating rod horizontally above the line, 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).
* Allow to dry for five minutes.
* While drying, design your own mask using the provided hole punchers and scissors to make a circuit.
* Your circuit should have at least four informational points to mimic chips and then circuits between them – you maybe as artistic as you want!
* Place the dried film under the short-wave UV lamp with the paper mask on top.
* Wait five minutes, then remove the mask and rinse in cold water.
* Place dried film directly into the food coloring mixture and leave submerged for two minutes.
* 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 with cold water and return to the paper towel to dry.

**Clean-up:**

* Place the glass pipettes in the glass disposal. Replace the cap on the thymine copolymer and throw the pipette in the trash (if it is plastic). You may dump the food coloring down the sink. Leave your film out to dry, and then throw away the paper towel.

**Post Questions:**

Use information from the lab and the “Toxic Trade” article to answer the following questions.

Define e-waste.

List 3 e-waste toxins and the possible adverse health effects.

How does VBT mimic human skin?

Identify and explain three green chemistry principles addressed in the VBT lesson.

How do the green chemistry principles addressed in the VBT lesson align with the international, national and local efforts to reduce e-waste?

What else can be done to reduce e-waste?

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| **Background Reading**  **TOXIC TRADE: THE REAL COST OF ELECTRONICS WASTE EXPORTS FROM THE UNITED STATES** |
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| Source: EarthTrends Environmental Essay Competition Winner Author: Layne Nakagawa Editor: Amy Cassara and Tom Damassa Date: June 2006 |
| http://earthtrends.wri.org/images/spacer.gif |
| Electronic waste, or "e-waste", is a broad term that refers to end-of-life consumer electronics, including televisions, computers and monitors, audio/stereo equipment, VCRs, DVD players, video cameras, telephones, fax and copy machines, mobile phones, wireless devices, and video game consoles. In 2003, the United States alone generated 2.8 million tons of electronic waste and only recovered (re-used or recycled) 290 thousand tons, leaving the rest to enter into the municipal waste stream (EPA 2003).  One of the largest obstacles in recycling e-waste is the lack of proper domestic facilities to sort and handle the various materials, many of which are hazardous. In the United States, waste is frequently exported to developing countries, allowing producers and consumers to take advantage of very low labor costs (as low as $1.50 per worker per day in China) and less stringent environmental and occupational regulations (Puckett et al. 2002: 10). However, the dismantling of e-waste, particularly in parts of Asia and Africa, poses a significant health risk to workers and their communities (Puckett et al. 2002: 11). The promotion of responsible federal regulation, legitimate recycling programs, and corporately sponsored take-back agreements would work towards preventing the export of tons of e-waste and ultimately protect these overseas communities from the environmental and health impacts of the hazardous materials.  **E-Waste Toxins**  E-waste contains a number of toxic substances, including plastics and heavy metals such as lead, cadmium, and mercury, which can cause serious adverse health effects.  Lead can be found in circuit boards and monitor cathode ray tubes (CRTs). Lead is particularly dangerous to the environment because of its ability to accumulate and persist in plants, animals, and microorganisms (Puckett et al. 2002: 11). The bioaccumulation of lead in the human body is particularly harmful because its primary target is the central nervous system. Lead can cause permanent damage to the brain and nervous system, causing retardation and behavioral changes. Infants and young children are particularly susceptible because of the impairment of cognitive and behavioral development it can cause (Ryan et al. 2004: 19A).  Cadmium can be found in SMD (surface mount device) chip resistors, infrared detectors and semiconductors (Puckett et al. 2002: 11). Like lead, cadmium is particularly toxic to humans because it accumulates in the human body and poses an environmental danger due to both acute and chronic toxicity (Puckett et al. 2002: 11). Renal damage is the most common effect of cadmium toxicity. Cadmium that enters the system through the gastrointestinal tract resides in human kidneys with a half-life of 10-20 years (Nordberg et al. 1985).  Mercury is the most prevalent toxic metal found in e-waste. It is in circuit boards, switches, medical equipment, lamps, mobile phones, and batteries. Mercury transforms into methylmercury in water, where it can accumulate in living organisms, typically via fish, concentrating in large fish and humans at the top of the food chain (Puckett et al. 2002: 11). Mercury is readily absorbed by the human body, ultimately inhibiting enzymatic activity and leading to cell damage (Boyer et al. 1959).  The most abundant component of e-waste is plastics. Plastics comprise almost twenty-three percent of a typical desktop computer (Microelectronics 1995). They are used for insulation, cables and housing for all electronic devices; the variety of products available for recovery complicates the de-manufacturing process. Due to the complex recovery process, large amounts of plastic e-waste are disposed of through landfills, incinerators and open burning, allowing toxic substances to leach into the environment.  **Case Study: Guiyu, China**  The town of Guiyu is located in the Chaozhou region of the greater Guangdong Province in southeast China. "Since 1995, Guiyu has been transformed from a poor, rural, rice-growing community to a booming e-waste processing center. While rice is still growing in the fields, virtually all of the available building space has given way to providing many hundreds of small and often specialized e-waste recycling shelters and yards" (Puckett et al. 2002: 17).  Along with this new e-waste recycling comes serious environmental and occupational health hazards. Hazardous recycling operations include toner sweeping, the open burning of dismantled computers, CRT cracking and dumping, circuit board recycling, acid stripping of chips, and plastic chipping and melting (Puckett et al. 2002: 20). The workers are at risk of inhaling the toxic fumes from the burning of the materials and ingesting contaminated water and food. They may also be exposed to toxins through dermal contact due to the lack of sufficient protective equipment.  Please see the [Basel Action Network website](http://www.ban.org/photogallery/index.html) to view a photo gallery of e-waste in Guiyu, China.  Large amounts of imported e-waste material and process residues never get recycled and are simply dumped in open fields; along riverbanks, ponds, and wetlands; in rivers; and in irrigation ditches (Puckett et al. 2002: 23-24). This indiscriminate dumping has exacerbated contamination of drinking water sources and sediments. Water samples from the Liangjiang River outside of Guiyu, China show cadmium and lead levels to be well above World Health Guidelines and EPA Drinking Water Standards (table 1).  **Table 1.** Guiyu Sample Results and Water Quality Comparison. Adapted from Puckett et al., 2002.   |  |  |  |  | | --- | --- | --- | --- | | **Metal** | **Liangjiang River, Guiyu (mg/L)** | **World Health Guideline (mg/L)** | **EPA Drinking Water Standard (mg/L)** | | Cadmium | 0.01 | 0.003 | 0.005 | | Mercury | < 0.001 | 0.001 | 0.002 | | Lead | 1.9 | 0.01 | 0.015 |   **International, National, and Local Efforts to Eliminate E-waste**  The Basel Convention is the leading international authority on regulating the reduction of e-waste. On March 22, 1989 the Basel Convention was established to control "transboundary movements of hazardous wastes and their disposal" between countries (UNEP 1989). Signatories to the Convention are not allowed to import or export any electronic components that may contain toxic chemicals. Currently, there are 167 participants of the Basel  Convention. Afghanistan, Haiti, and the United States have not yet ratified the document (UNEP 2006).  Since the inception of the Basel Convention, European communities have presented a detailed document that specifies methods for regulating e-waste. The Directive on Waste Electrical and Electronic Equipment, or WEEE Directive, was presented and accepted by the European Parliament on January 27, 2003. The directive's purpose was to prevent e-waste from becoming a problem by reusing or recycling recoverable electrical parts (European Parliament 2003a). An amendment to the original directive forced producers to internalize external costs, such as recycling and proper disposal, instead of burdening the consumer with costs for proper disposal (European Parliament 2003b).  In 2001, Japan implemented their Specified Home Appliance Recycling Law, which requires manufacturers to take back their electronic products and home appliances (Ministry of the Environment 2005). The national law also makes it illegal to dump any electronic waste or home appliance in municipal landfills or roadsides (Ministry of the Environment 2005).  In 2003, the Organization for Economic Co-operation and Development (OECD) completed the Environmentally Sound Management of Waste report, which advises countries on collecting, disposing, storing, and recovering their hazardous electronic waste (OECD 2003). This report, however, can only make recommendations to waste facilities about environmental management systems; auditing environment, health and safety measures; and monitoring and recording emissions and waste generation (OECD 2003). The report cannot force countries to implement these measures.  In North America, The Commission for Environmental Cooperation created a proposal in 2004 similar to the WEEE Directive that was introduced in Europe. The proposal was not well-received by electronics-related industries (EPA 2004). Adoption of the proposal to the Commission did not take place (EPA 2004), meaning that it is still legal to allow U.S. export of hazardous e-waste (Puckett et al. 2002: 6).  **Table 2.** International Efforts in Reducing E-Waste.   |  |  |  |  |  | | --- | --- | --- | --- | --- | | **Participating Countries** | **Governing Body** | **Initiative** | **Date Adopted** | **Reference** | | 167 countries of the UN (excluding Afghanistan, Haiti, and the US) | United Nations Environment Programme | *Basel Convention*: No transboundary movement of hazardous waste | 1989 | (UNEP, 1989) | | The European Union | European Parliament | *WEEE Directive*: Reuse/recycle electronic parts; manufacturers internalize take back/recycling costs | 2003 | (European Parliament, 2003) | | Japan | Ministry of the Environment, Government of Japan | *Home Appliance Recycling Law*: Home appliance manufacturers must take back and recycle end-use products | 2001 | (EPA, 2004) | | Intended for OECD countries | Organization for Economic Co-operation and Development (OECD) | *Environmentally Sound Management of Waste*: Reclaim e-waste | 2003 | (OECD, 2003) |   The U.S. stance on the Basel Convention has not stopped private organizations and local governments within U.S. national boundaries from introducing local policies to regulate electronic equipment. Some corporations have played a proactive role in the e-waste debate by providing electronic recycling programs: Dell, Hewlett-Packard (HP), NEC, Toshiba Gateway, eMachines, IBM, and Lexmark for individual consumers, and Xerox and Pitney Bowes for large-scale office equipment customers (SVTC 2004a,b). The following states have initiatives in place: California passed the 2003 Electronic Waste Recycling Act; in 2000, Massachusetts banned CRTs from landfills; in 2003, Minnesota passed a bill that banned CRT disposal in mixed solid waste; and in 2006, Maine became the first state to force television and computer monitor manufacturers pay for recycling and proper disposal (Associated Press 2005).  The strictest regulations so far in the U.S. have been passed in Washington state. As of October 1, 2005, it was illegal to dump any used electronics in Seattle or in King County, Washington (Priorities 2006). The King County Solid Waste Division will not accept any electronics in municipal landfills; instead, their Waste Acceptance Rule directs consumers to drop off used electronics to participating Take it Back Network Electronics Recyclers (King County 2005a,b). Priorities for a Healthy Washington is a state-organized campaign supported by a variety of businesses and public interest groups who are in favor of Senate Bill 6428: Washington State's Electronic Waste Recycling Bill (Priorities 2006). SB 6428 passed on March 6, 2006. Instead of putting the burden on consumers to pay for recycling, this bill expects manufacturers to include electronic recycling fees as part of their own business costs.  **Recommendations**  While a few U.S. states have taken the initiative to manage their e-waste, there is no guarantee that the trend will encourage all states to do the same. A national commitment to e-waste regulation should include the ratification of the Basel convention by the United States, and expand on existing regulations in federal laws such as the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA) by banning hazardous waste exports entirely. Adequate resources need to be allocated for both the implementation and enforcement of e-waste policies. Like the WEEE Directive, there should be a formal document not only banning e-waste creation and trade within U.S. borders, but Canada, Mexico, and the U.S. should also coordinate a formal document that bans e-waste creation and trade within North America.  In addition to government action, private industry can expand its role in managing e-waste. Recycling is one of many solutions, but it can only play a limited role when hazardous inputs are involved. Product substitutions can be implemented wherever possible in order to reduce the amount of poisons in the manufacturing of electronics (SVTC 2004b). Producers can also take the initiative of managing their products over their entire life-cycle. If manufactures and distributors assumed the responsibility for the costs of collecting, managing, and disposing of discarded electronics, they could be reflected in product prices. The cost of "life-cycle responsibility" could be offset by market incentives for manufacturers of electronics to reduce such costs by designing products that are clean, safe, durable, reusable, repairable, upgradeable, and easy to disassemble and recycle (Puckett et al. 2002: 37).  *About the author (June, 2006): Ms. Nakagawa is a graduate student at the Evergreen State College, earning a Master's degree in Environmental Studies.* |

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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.

PHOTORESIST

**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 recollected 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 cationic 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).

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FD & C

Anionic Dye

VBT/VBEA cationic   
co-polymer

Transparency Film

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

**Reference**

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