Three-Dimensional Printing Using a Photoinitiated Polymer

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Microstereolithography (μSL) is the construction or printing of very small three-dimensional (3D) objects based on computer-designed models. Several methods exist that accomplish this construction, each with its particular limitations *(1)*. Rapid prototyping methods use a "print head", typically consisting of a nozzle or an energy source, such as a laser, to trace a cross-sectional area back-and-forth along the x and y axes, creating a layer pixel-by-pixel. The finished layer is moved along the z axis, and then the next layer is created in the same manner. This process requires devices with complex positional control.

Projection microstereolithography (PμSL) uses a data projector to create each layer simultaneously rather than sequentially by row (Figure 1). Researchers at University of California—Berkeley and the Nano-CEMMS center at the University of Illinois are performing PμSL by creating polymer layers on the order of 400 nm *(1, 2)*. Many applications exist for this technique of nanoscale and microscale manufacturing, including micro-bioreactors to support tissue growth, micromatrices for drug delivery and detection, and biochemical integrated circuits that could eventually simulate biological systems *(1, 3)*. We describe the use of the technique in a classroom or laboratory setting at the high school or college level to create 3D objects familiar to the students (Figure 2).

Chemical Considerations

In PμSL, photocurable polymers such as 1,6-hexanediol diacrylate (HDDA) can be used for the fabrication of 3D objects. HDDA polymerizes via an addition mechanism (Scheme 1). When a photoinitiator, such as phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, absorbs photons of ultraviolet (UV) wavelengths, species with free radicals are produced. Ordinary data projectors emit enough UV light to produce free radicals from the photoinitiator. These free radicals react with the HDDA monomers to initiate polymerization.

Because UV radiation is being used to change the solubility of a chemical, PμSL could be considered a form of maskless photolithography that is capable of producing true 3D objects *(4)*. In this case, the mask is replaced by a black background from the projector. The white images from the projector include the UV light needed to induce polymerization, so red light from the projector should be used to confirm proper focusing and alignment. A dark room for the development of photographic plates uses a similar idea, utilizing red light because it is not energetic enough to cause electrons to be excited away from their associated atoms.

The free radical species attacks the double bond at the end of the HDDA monomer, attaching to the terminal carbon atom and causing a radical to be formed on the second carbon atom. This new carbon radical then attacks a terminal double-bonded carbon of an adjacent HDDA molecule to continue the propagation of the chain *(5)*.

Chain propagation continues until two of the chains react with each other and terminate growth *(6)*. Because the HDDA monomers have another double bond beyond the one that was broken apart by the free radical in the addition reaction, extensive cross-linking occurs, in essence forming a large single molecule. Because the resulting cross-linked molecules are much larger than their component monomers, the created polymers are less soluble then the surrounding solution and gelate into a solid object.

Mechanical Considerations

By lowering the stage on which the layer of solid is produced (Figure 3), layers of polymers can be added to each other to create a 3D object. The thickness of these layers can be controlled by varying the concentration of 1-phenylazo-2-naphthol, also known as Sudan I. Beer's law tells us that the absorbance of light is related to the concentration of the absorbing molecule. Sudan I absorbs light in the ultraviolet and short-wavelength visible spectrum, with maximum absorbance occurring at 418 nm. The more Sudan I added, the thinner the polymer layers. We have generated good results with between 0.4 mM and 1.6 mM Sudan I (between 0.005 and 0.040 g of Sudan I in a 100 mL solution of monomer and initiator.) A teacher could have students test different concentrations of Sudan I to investigate Beer's law.

Limitations

One limitation of PμSL is that a connection must exist between each of the successive layers when creating the objects. Great care should be taken when planning the cross sections of the objects so that this is achieved. Another limitation with PμSL is the resolution. Objects created in the college classroom have features of 300−500 μm in width owing to limitations in the projection systems. In all forms of PμSL, limitations exist on the proximity that fine details can have to each other because stiction problems occur owing to the capillary action *(7)*. These problems can be partially avoided by controlling the vertical sizes of fine details (Figure 2). Another limitation comes from the exothermic nature of the reaction. Large cross sections tend to bubble as

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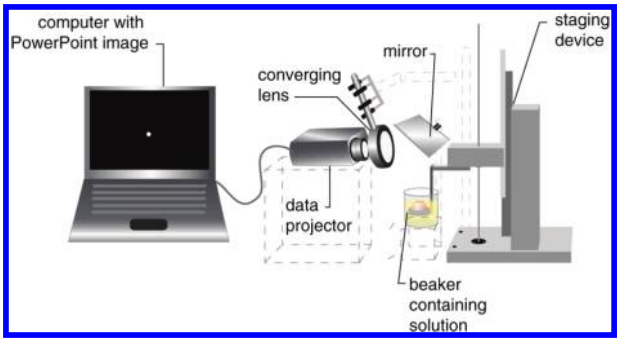


Figure 1. PowerPoint images of slices of the object to be printed are projected at a thin layer of monomer. Successive layers are made by lowering the polymerized shape into a beaker of the monomer to build up a 3D object. The lens and front-surface mirror should be mounted as close to the projector as possible.

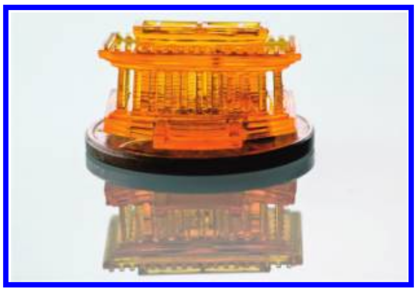
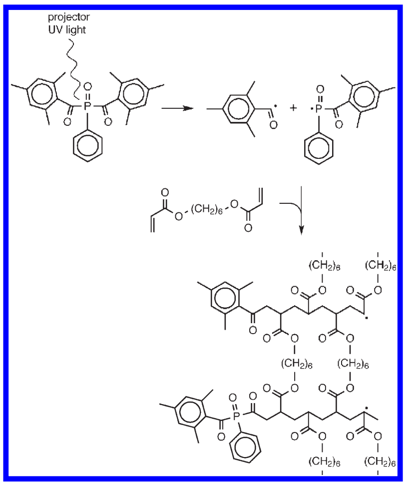


Figure 2. This is a representation of the Lincoln Memorial in Washington, DC. The object is resting on a penny for size comparison. Designed by Matt Ragusa.

Scheme 1. Reaction Scheme for the Initiator Being Split by Ultraviolet Light and Subsequent Polymerization of 1,6-Hexanediol Diacrylate



the polymerization reaction generates so much heat that the object expands. The supporting material includes a discussion of ways to deal with this problem, for example, by using shorter illumination times.

Integrating the Activity into the Curriculum

In this activity, students create a three-dimensional object using a data projector, a series of images from PowerPoint, and a solution containing a photoinitiator and a monomer.

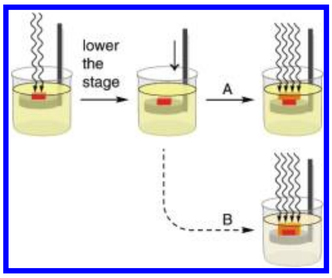


Figure 3. A UV absorber, Sudan I, is added to modify the optical absorption depth so light causes polymerization only on top of the solution (yellow solution in the figure). The stage is lowered so fresh monomer flows over the top of the polymerized shape, and light is used to polymerize the next layer (beaker A). Without the UV absorber (beaker B, colorless solution) the large absorption depth prevents production of overhanging structures.

The equipment involved in this experiment is either present in most educational settings or easily obtained.

To understand how these 3D objects are being created, students will examine the underlying chemical principles:

- UV light from the data projector causes free radicals to be formed.
- Free radicals are reactive species with an unpaired electron.
- Free radicals react with monomers to start a chain reaction that terminates when the chain with a free radical reacts with another free radical.
- Substances that absorb UV light inhibit the formation of free radicals.

Polymerization is often initiated through the creation of free radical species, which, in turn, may be formed by the exposure of an initiator to UV light. Thus, this experiment would fit well into a unit on polymers, but it also could be incorporated into a unit on electromagnetic radiation. One possible line of further study in the classroom could be to explore the correlation between Sudan I concentration and the depth of UV penetration. 3D printing could be integrated into a calculus course with the emphasis placed upon thinking of three dimensions as an infinite number of cross sections. Additionally, the scaling of the object from its size on the screen to its size as an actual object could create a connection to lower-level mathematics classes. The determination of the focus could be one exercise in optics for a physics class; however, multiple physics applications exist. Also, the task of manipulating PowerPoint to create these objects builds a connection to computer instruction. Another interdisciplinary connection would be the construction and perhaps design of the staging device (Figure 4) required for this experiment, which could be completed in industrial technology courses. Lastly, the creation or design of the objects could be used in an art class to discuss lithography as projection microstereolithography creates a new medium for self-expression. This, in turn, could generate a discussion of the connections among science, technology, and society.

Materials and Equipment

The solution used during the PμSL process, prepared by dissolving 2.00 g of phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide in 98.0 mL of 1,6-hexanediol diacrylate (HDDA), should be done at least the day before because the photoinitiator is slow to dissolve in the HDDA. A small quantity of Sudan I should be

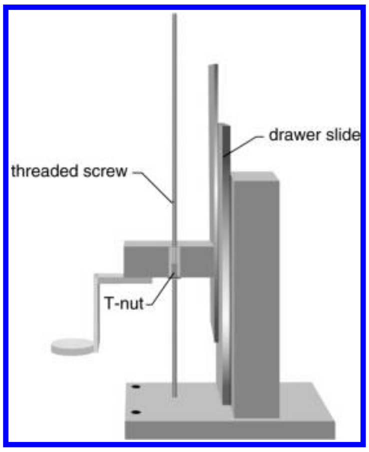


Figure 4. A drawer slide works well to keep the vertical movement of the stage small, smooth, and aligned. A T-nut and threaded rod provide the vertical control as the threaded rod is turned.

added to the HDDA solution to prevent UV light from penetrating too deeply into the solution (Figure 3). All chemicals can be purchased from Sigma-Aldrich. The quantity of Sudan I can be varied in the range between 0.005 and 0.040 g to adjust the thickness of the layers, with an inverse relationship existing between the quantity of Sudan I and the thickness of the layers. In addition to the chemical preparation, the projection setup must be assembled and at least one staging device must be constructed.

The projection setup requires a data projector, a converging lens or magnifying glass, a front-surface mirror, and a staging device (Figure 1). In addition, clamps and ring stands are used to place the lens and mirror appropriately. The lens should be as close as possible to the projector for optimal focal length. The focal length of the lens is an important consideration. A longer focal length provides a large working range for manipulation of the staging device, although a smaller focal length ensures that the needed intensity of light is achieved. Using a lens with a 15 cm focal distance (Edmund Optics, model number NT 32-975), objects of consistently high quality have been produced from images that occupy roughly 1/4 of the computer screen space. The mirror should be positioned near the lens so that the focal plane of the image is parallel to the table. A front-surface mirror is recommended so that secondary images reflected off of the cover glass in a typical mirror can be avoided.

A simple staging device can be constructed using a drawer slide as the basis for its vertical alignment (Figure 4). Twisting a threaded rod attached to a T-nut provides the mechanism for fine vertical control. The T-nut can be attached to the drawer slide with a wooden block. Attached to the wooden block is a stage that comes down about the height of a 50 mL beaker and is capable of being maneuvered inside of the beaker.

A slide show can be prepared using Microsoft PowerPoint, with slides consisting of the cross sections of the object (Figure 5). The slides should have a black background with the cross sections in white. An initial slide with an image that is red instead of white can be used to determine focusing and alignment. The cross-sectional images can be interspersed with blank black backgrounds that can be projected while the staging device's stage is lowered. Each layer should be exposed for 10 s to ensure optimal polymerization.

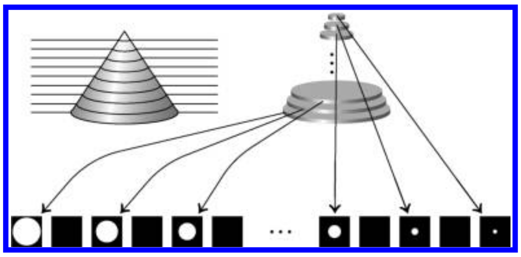


Figure 5. To create an object, the cross sections of the object need to be created as black and white images. Each cross section is interspersed with a black slide; it is during the black slide that the stage is lowered. To align and focus, a black and red image can be used. The red can be seen easily by a person but does not polymerize the solution.

Hazards

1,6-Hexanediol diacrylate, phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide, and Sudan I (1-phenylazo-2-naphthol) are all irritants and skin sensitizers. In addition, Sudan I is mutagenic for mammalian somatic cells and may cause cancer based on animal data. Sudan I is also flammable. Because the data projector has some UV output and is being projected onto a reflective surface, care should be taken to avoid looking directly at the beaker containing the stage while the 3D objects are being created. All waste material should be collected in a nonhalogenated waste container and disposed of appropriately. After the object has been made, exposing it to UV light will cause any unreacted chemical to polymerize. This can be achieved by taking the object out into the sunlight. After this occurs, the objects are safe for students to take home.

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Supporting Information Available

Extensive documentation including a laboratory procedure with photographs of each step of the experiment, sample PowerPoint slides, and hints for success. This material is available via the Internet at http://pubs.acs.org.

