

# tested demonstrations



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## Polymer Photophysics: A Negative Photoresist

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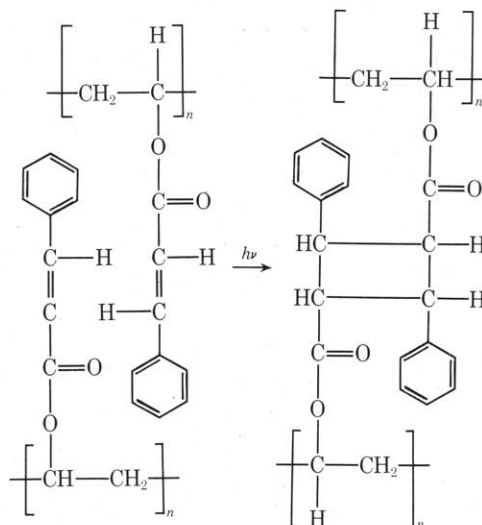
The photochemistry, photophysics, and materials science applications of photoresists have been the subject of several recent review articles and texts, (1). Photoresists, which are used in the fabrication of solid-state electronic components and integrated circuits, consist of a mixture of chemicals generally containing a film-forming polymer and one or more photosensitive compounds. The term photoresist arises from the essential photochemical behavior and chemical resistance of this mixture. When exposed to light of the proper wavelength, a photoresist undergoes photochemical reactions which alter the molecular structure of some of its components and change its solubility. If exposure to light imparts increased chemical solubility, the photoresist is called a positive photoresist. Conversely, if exposure to light imparts reduced solubility, the photoresist is called a negative photoresist. A primary commercial use of photoresists is to precisely define the composition and physical location of electronic components in solid state integrated circuits. Reviews of the basic formulation, utilization and significance, of photoresists are presented in references (1-3).

We wish to describe the formulation of a negative photoresist which can be used as a 15-min classroom demonstration for undergraduate general chemistry or organic chemistry courses and which demonstrates a photochemically initiated polymerization technique of commercial significance.

In this experiment a negative photoresist is formulated that consists of a solution of a photosensitive film-forming polymer or "resin" which is used to create the negative image of an object upon a glass slide (see Note 1). The chemistry of the photoresist and the method of image formation are described below.

### Film-Forming Polymer

Film-forming polymers or "resins" used in negative photoresists generally consist of soluble, intermediate molecular weight (~12,000 g/mol), linear polymers which can undergo photoinitiated crosslinking reactions. Among the different film-forming polymers currently in use commercially are cyclized rubbers, hydrocarbon copolymers and polyvinyl cinnamate derivatives (1, 3). The resins used in negative photoresists must be intrinsically photosensitive or capable of



A photochemical reaction of poly(vinyl cinnamate) to yield a cross-linked polymer derivative of  $\alpha$ -truxillic acid.

photochemical reactions in the presence of additives known as sensitizers to yield highly crosslinked, chemically resistant, insoluble polymers of high molecular weight. Figure 1 illustrates a possible crosslinking mechanism based on the intrinsic photosensitivity of polyvinyl cinnamate, the resin used in this demonstration, to yield an insoluble polymer. The photosensitivity of polyvinyl cinnamate is due to the photochemical reactivity of the cinnamyl group. The  $\pi$  electrons of the conjugated vinyl moiety undergo a photochemically allowed 2 + 2 cycloaddition. As described in references (1-3), the photochemical behavior of such resins can be used to protect selected areas of a substrate (e.g., silicon dioxide, aluminum, zinc) from chemical attack.

Resins used for negative photoresists must be protected from inadvertent heating because these materials may also undergo undesired thermally induced crosslinking. Such thermally activated reactions are difficult to control, and interfere with the formation of specific, well-defined patterns of crosslinked resin.

A solvent is used to deposit the photosensitive film-forming resin uniformly and homogeneously on a substrate. Solvents commonly used include methylene chloride, cyclohexanone, methoxyethyl acetate (cellosolve acetate) or mixtures of similar solvents. Such materials are relatively inexpensive, transparent to near uv radiation, and do not inhibit photochemical reactions.

### Experimental

#### Equipment

Student centrifuge in large box; uv source; glass microscope or 2 x 2 slides; droppers; overhead projector (optional).

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## Reagents

10 ml cellosolve acetate; 0.25 g polyvinyl cinnamate; 10 ml methylene chloride

## Procedure

### Image Formation

Formulate the photoresist by dissolving 0.25 g polyvinyl cinnamate in 10 ml of methylene chloride, (Note 2, 3). Be careful to shield the methylene chloride solution from intense light. This photoresist will yield sharp images when applied in a uniform thickness to glass slides. The application of a uniform thickness of photoresist can be easily achieved by spin-casting. A simple, but extremely effective spin-casting apparatus can be made by taping a glass slide to the top of a student centrifuge. About 1 ml of photoresist is added to the top of the slide and the centrifuge is turned on for a few seconds. A layer of uniform thickness of relatively solvent-free photoresist will remain on the slide. The spin-casting apparatus should be mounted in a (cardboard) box to catch any resultant spray, to shield the photoresist from exposure to light, and to act as a safety barrier in the event that a slide breaks away from its tape mounting during the spin-casting.

Using this technique, coat several slides with a translucent layer of photoresist. Several applications of photoresist may be necessary for the preparation of *each* slide. Spin each slide separately until it appears to be solvent free.

Place a suitable mask (key, paper clip, token, etc. . .), over each of the photoresist-coated slides and expose them for about 10 min to a properly shielded short wavelength uv source, (Note 4). The exposure time may be profitably used to discuss the photophysics and photochemistry of the crosslinking reaction. After exposure, develop each slide by separately placing it on the spin-casting apparatus, and coating it with a thin layer of cellosolve acetate. After 15 sec development, spin-cast the slide for about 20 sec. This will rapidly remove excess solvent and stop further solvation reactions of the cellosolve acetate developer. The images which are produced should be sharp enough to be projected using either an overhead projector (for microscope slides) or a slide projector (for 2 × 2 slides.)

Any unused solvent may be disposed of by slow evaporation in a

well-ventilated fume hood or by disposal in a waste solvent container.

## Notes

1) This demonstration is also available from the authors as a 3-hr laboratory preparation which utilizes the Schotten-Baumann esterification of polyvinyl cinnamate from polyvinyl alcohol and cinnamoyl chloride.

2) Polyvinyl cinnamate may be purchased from a number of different chemical supply houses including Aldrich Chemical Co., 159 Forrest Street, Metuchen, N.J. 08840.

3) **Avoid contact with and use care when handling methylene chloride solutions.** Methylene chloride is reported to be **mildly toxic**, and should be handled with care (4).

4) **Short wavelength uv light, (<360 nm), is particularly dangerous to the unprotected eye.** Any of a variety of properly shielded 50–150 watt Hg or Hg-Xe lamps are convenient sources.

## Acknowledgment

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## Literature Cited

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- (3) DeForest, W. S., "Photoresist Materials and Processes," McGraw-Hill, New York, 1975, pp. 20–47 and references cited therein.
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