

# Studies of 2-Hydroxyethyl Methacrylate and Ethyl Acrylate Copolymers as Negative Photoresists

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## Synopsis

The potential of 2-hydroxyethyl methacrylate and ethyl acrylate copolymers as negative photoresists was studied. Negative photoresist solution was prepared by esterification of copolymers with cinnamoyl chloride. The effects of photosensitizer concentration, copolymer composition, and exposure time were investigated. A resolution of 30  $\mu\text{m}$  was attained from these photoresists.

## INTRODUCTION

Photoresists used in photofabrication processes can be described as photosensitive coatings which, after application to a substrate and irradiation through a master image or pattern, undergo a selective change in solubility.<sup>1</sup> In negative photoresist, areas which are exposed to light in the uv range are rendered insoluble, whereas the unexposed areas still retain their solubility.

Photoresists are a necessary part of the engineering of every microelectronic device and may be considered a tool required for device fabrication. As devices require smaller and smaller geometries, the photoresist portion of the device processing may become the limiting factor in the ultimate device size.

Several negative photoresist systems have been reported in the literature.<sup>2-4</sup> Most of these systems are based on cinnamate derivatives of polymers because the photodimerization of cinnamic acid in the solid state can yield crosslinked products.<sup>5-7</sup> Esterification is the most common method of introducing cinnamoyl groups into polymers having OH groups. Cellulose, polycondensation products of epichlorohydrin and 2,2'(4,4'-dihydroxy diphenyl)propane, polyesters from glycerol and phthalic anhydride, and poly(vinyl alcohol) are the most frequently used polymers.<sup>8</sup>

In the present work we report the preparation of photosensitive polymers based on 2-hydroxyethyl methacrylate (HEMA) and ethyl acrylate (EA) copolymers. Two copolymers having different HEMA content were prepared, and corresponding cinnamate derivatives were obtained by esterification. The effects of photosensitizer concentration and exposure time on image formation were also investigated.

## EXPERIMENTAL

## Preparation of Copolymers

HEMA (Eastman Kodak) was purified by distilling under reduced pressure and stored at low temperature (5–10°C). EA (Koch-light) was purified by three washings with 5% NaOH saturated with NaCl and then several times with distilled water saturated with NaCl. After drying thoroughly over anhydrous sodium sulfate, it was distilled. Benzoyl peroxide (BDH) was purified by the precipitation method, (Benzoyl peroxide was dissolved in chloroform solution and filtered, and then methanol was added to precipitate it. The precipitate was washed with methanol and dried in a vacuum dessicator.)

The copolymerization of HEMA and EA was carried out in a two-necked, pear-shaped flask at 70°C in nitrogen atmosphere. Benzoyl peroxide (0.2% w/v) was used as the initiator. After a time calculated to keep the conversion below 10%, the contents of the flask were poured into *n*-heptane with constant stirring. The precipitated polymer was filtered and then purified by dissolving in dimethylformamide and precipitated in water. It was then dried at 60°C under vacuum. The composition of the copolymer was determined by an acetylation method reported earlier.<sup>9</sup> Two copolymers having different compositions of HEMA and EA were prepared. The details of the reaction conditions are given in Table I. The molecular weight distributions of these copolymers were studied by gel-permeation chromatography. Waters Associates model ALC/GPC-244 was employed for the study. The chromatogram was recorded by differential refractive index measurements using differential refractometer model R401. The flow rate of 1.5 ml/min was maintained, and the chart speed was 6 in./hr. The unit was operated with dimethylformamide as the carrier solvent with 10<sup>3</sup>-, 10<sup>4</sup>- and 10<sup>5</sup>-Å Styragel columns. The molecular weights  $\bar{M}_n$  and  $\bar{M}_w$  were calculated from the resulting chromatograms by a manual method.<sup>10</sup> The polydispersities of the samples are given in Table I.

## Preparation of Cinnamoyl Derivatives

Cinnamoyl chloride was prepared by reacting cinnamic acid (0.1 mol) with thionyl chloride (0.2 mol) in the presence of pyridine (0.5 ml). The reaction was carried at 70°C for 24 hr under reflux. Excess thionyl chloride was removed by distillation. The crude cinnamoyl chloride was distilled under vacuum in a dark room under yellow light. The fraction boiling at 130°C at 10 mm Hg was collected. It was stored in a dark bottle covered with black paper.

HEMA-EA copolymers were dissolved in a minimum volume of dimethyl-

TABLE I  
Preparation of HEMA-EA Copolymers<sup>a</sup>

Sample	E1	E2
Volume of HEMA in initial monomer feed (ml)	2	6
Volume of EA in initial monomer feed (ml)	18	14
Conversion (%)	8.1	8.2
HEMA in copolymer (%)	40	80
Polydispersity ( $\bar{M}_w/\bar{M}_n$ )	1.5	2.5

<sup>a</sup> Conditions: benzoyl peroxide, 0.2% (w/v); temperature, 70°C.

formamide. To this an equal volume of pyridine was added. Excess cinnamoyl chloride was then added dropwise to the polymer solution (molar ratio 2:1) with constant stirring. The solution was kept at 30°C for 24 hr and then poured in a beaker containing water and stirred. The precipitated cinnamoyl derivative of the copolymer was washed several times with sodium bicarbonate to remove residual cinnamic acid. It was then quickly washed with ethanol and dried under vacuum.

### Preparation of Photoresist Solution

A 5%–10% solution of cinnamoyl derivative of the polymer was prepared in acetone. Novolak was added to the cinnamoyl derivative of the polymer to increase the adhesion. It was prepared by polymerizing phenol and formaldehyde in a molar ratio of 1.22:1 in the presence of an acid catalyst as described elsewhere.<sup>11</sup> Crystal violet was used as photosensitizer. The details of the various photoresist solutions are given in Table II.

A thin film of the photoresist solution was deposited on a copper-coated glass substrate by a spin-coating method. 8–10 drops of photoresist solution and a spinning time of 15–20 sec were used. After coating the photoresist, prebaking was done at 50–60°C for a period of 15 min. A photomask was then placed in contact with the substrate, and the assembly was exposed to UV light of 3600 Å (Philips MLV 300 WE 220-240V). The exposure time was varied from 0.5 to 3 min.

The substrate was then placed in a mixture of trichloroethylene and acetone. The image was formed after 1–2 min. After development was complete, the plate was thoroughly rinsed in developing solution and dried. Postbaking was done at 50–60°C for 10–15 min. The copper was then etched by putting the substrate in ferric chloride solution (approx. 6%). Copper was dissolved from the areas that were not protected by photoresist. The substrate was washed with water, then with acetone and then dried.

The pattern thus obtained on the glass substrate was used to study the surface topology by scanning electron microscope. The substrate was mounted on a small disk with the help of an adhesive (Quickfix). It was scanned from one end to the other with various magnifications using an S4-10 Cambridge Stereoscan scanning electron microscope at 10 kV.

TABLE II  
Composition of Various Photoresist Solutions Prepared from the Cinnamoyl Derivative of HEMA-EA Copolymers (Samples E1 and E2)<sup>a</sup>

Sample No.	Copolymer Sample	Concentration of Cinnamoyl Derivative (% w/v)	Concentration of Photosensitizer (% w/w) <sup>b</sup>
H1	E2	10	1.0
H2	E2	10	0.6
H3	E2	10	0.2
H4	E2	5	1.0
H5	E1	10	1.0

<sup>a</sup> Solvent, acetone; concentration of Novolak, 7% (w/v).

<sup>b</sup> With respect to the cinnamoyl derivative.

## RESULTS AND DISCUSSION

The effect of exposure time on image formation was studied for solution H1. When the exposure time was less than 0.5 min or greater than 3 min, development of the image was found to be poor (Fig. 1, photographs a and b). Low exposure may not be sufficient for enough crosslinking to occur, and long exposure may degrade the polymer. The resolution was found to be better at an exposure time of 2 min, being approximately  $30\ \mu\text{m}$ .

On analyzing the samples at different magnifications, it was observed that the H1 sample gave the best resolution (Fig. 1, c-f). No pinholes or breaks in the image were observed. Photograph g was taken at a higher magnification, and no undercutting is observed. A very blurred image was obtained with the H5 solution, indicating poor resolution.

Sample H1 solution, which was prepared from the two copolymer sample was found to give the best results. This may be due to the high content of HEMA in the copolymer. This would lead to a high degree of esterification of the copolymer by cinnamoyl chloride. The crosslinking efficiency was thus increased,

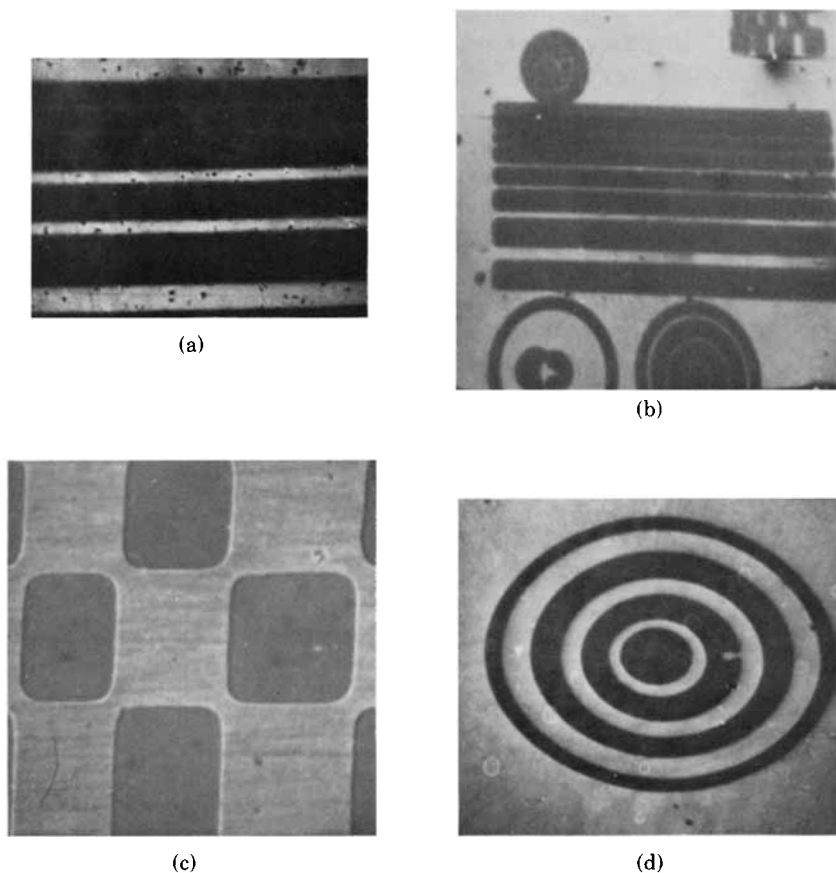
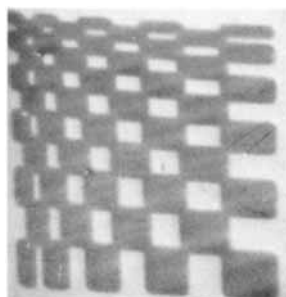


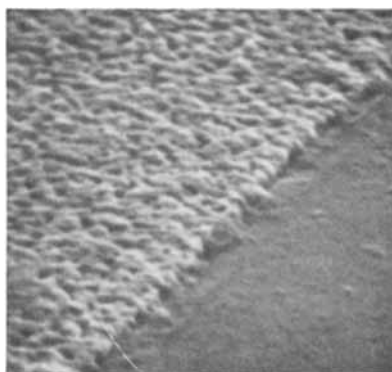
Fig. 1. Scanning electron micrographs of the resolution patterns of the various photoresists. (a) Resist H1 with exposure time of 0.5 min. (320 $\times$ ). (b) Resist H1 with exposure time of 3 min. (118 $\times$ ). (c) Resist H1 with exposure time of 2 min. (1075 $\times$ ). (d) Resist H2 with exposure time of 2 min. (300 $\times$ ). (e) Resist H3 with exposure of 2 min. (74 $\times$ ). (f) Resist H4 with exposure of 2 min. (240 $\times$ ). (g) Resist H1 with exposure time of 2 min. (40,000 $\times$ ).



(e)



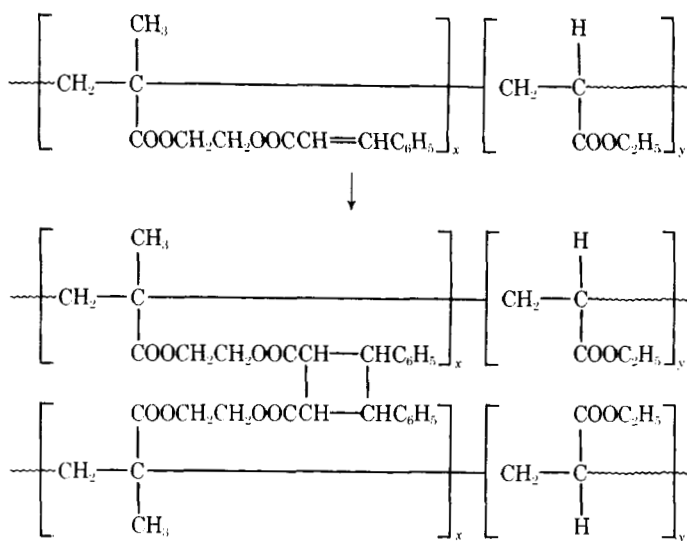
(f)



(g)

Fig. 1. (Continued from previous page.)

as is illustrated by the following scheme:



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