

# Preparation of Hyperbranched Polyester Photoresists for Miniaturized Optics

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**ABSTRACT:** Hyperbranched polymers containing carboxyl and acryloyl groups were prepared through a one-step synthesis with metatrimellitic anhydride, epichlorohydrin, and methylacrylic acid glycidic ester. The photo-sensitivity coefficients of the polymer resists varied with the resin acid values and formulas. The linear depth was the reverse of the contrast. When the contrast was less than 0.49, the linear depth could reach 43  $\mu\text{m}$ . The hyperbranched poly-

ester resists were used to prepare microlens arrays. Moreover, there was a slight discrepancy between the element profile and simulated profile of the formed resists. The etching depth could reach 50  $\mu\text{m}$ . © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1259–1263, 2004

**Key words:** hyperbranched; resists; optics

## INTRODUCTION

Photoresists are key processing materials of microelectronics, miniaturized mechanics, and miniaturized optics. The miniaturized photoelectronic mechanics system has developed greatly in recent years. Accordingly, the performance requirements of resists have become increasingly stringent. Current resists used in the processing of miniaturized optic elements have the following disadvantages:<sup>1–3</sup> commercial negative resists have some difficulties in controlling the shape; gelatin resists have poor reproducibility, with an etching depth of less than 30  $\mu\text{m}$ ; and positive resists have low UV transmissivity and are not suitable for deeper etching. Therefore, a resist with advantages such as good reproducibility, high light transmissivity, deep etching, and easy shaping is needed for the processing of miniaturized optic elements. Hyperbranched polymers not only have unique spherical shapes and a large number of functional end groups but also have some unique properties different from those of linear polymers, including simple preparation and low cost.<sup>4</sup> Consequently, researchers have shown increasing interest in hyperbranched polymers.<sup>5,6</sup> Much research has been focused on saturated hyperbranched polymers,<sup>7</sup> but few applications for

radiation curing have been reported. Moreover, hyperbranched polymers used in miniaturized optics have not been reported. Therefore, we report here some special hyperbranched polymers with alkaline solubility that can be light-cured. The hyperbranched polymers were prepared by a one-step method with metatrimellitic anhydride, epichlorohydrin, and methylacrylic acid glycidic ester. Studies were conducted on the photo-sensitivity and linearity of the polymer resists. Moreover, a microlens array with a slight discrepancy between the element profile and simulated profile of the formed resists was obtained by the application of the resists to the processing of miniaturized optic elements.

## EXPERIMENTAL

### Synthesis of the hyperbranched alkaline-soluble and light-sensitive polymers

This article reports the synthesis of hyperbranched polyesters with metatrimellitic anhydride, epichlorohydrin, and methylacrylic acid glycidic ester.<sup>8,9</sup> The hyperbranched polyesters were prepared with metatrimellitic anhydride and epichlorohydrin. Then, the hyperbranched alkaline-soluble and light-sensitive polymers were synthesized through the incorporation of the acryloyl groups into the hyperbranched polyester molecules through the reaction of methylacrylic acid glycidic ester with the carboxyl groups outside the hyperbranched polyester molecules.

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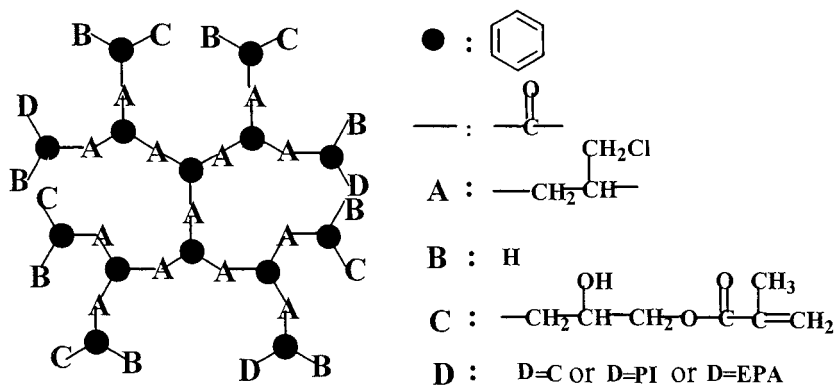


Figure 1 Representative structures of hyperbranched polyesters.

### Preparation of the resists and processing of the microlens array

The negative photoresist was prepared through the mixing of a hyperbranched polyester (78.5%), a polyfunctional acrylic ester as a crosslinking agent (15%), and other reagents (6.5%), including a radical photoinitiator and auxiliary reagents.

We formed the membrane by spinning the resultant resist for 5 s at a speed of 500 rpm and for 10 s at a speed of 1000 rpm and by drying it for 40 min at 100°C. The microlens array photoresist elements, with an area of  $200\ \mu\text{m} \times 200\ \mu\text{m}$ , were prepared through the exposure of the membrane with a contact transfer exposure technique and then through etching with 0.6% tetramethyloxammonia several times.

### Characterization

The structures of the photoresists were characterized with a UV 240 UV spectrometer (Shanghai Analytical Instruments Factory, Shanghai, China), a Nicolet 560 IR spectrometer (Thermo Nicolet, Wisconsin) (the sample was tableted with KBr), and a Varian Unity Inova 400 NMR spectrometer (California) to obtain the UV spectra, IR spectra, and  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra. The molecular weight was determined with an HP 1100 high-performance liquid chromatograph and a gel permeation chromatograph (Hewlett-Packard, USA). Tetrahydrofuran was used as the solvent, and polystyrene was used as the standard sample.

After the stepwise exposure of the same resist membrane for 30, 60, and 300 s, the curve of the membrane thickness and exposure energy was obtained through the determination of the various membrane thicknesses with an Alpha-Step 500 step instrument (Tencor Corp., California) after complete etching for various predetermined intervals. The exposure curve was then obtained through the normalization of the membrane thickness and the exposure time. For the exposure, the lamp power was 300 W, and the lamp dis-

tance was 50 cm. An exposure instrument from the Research Institute of Optoelectronic Technology of the Chinese Academy was used.

## RESULTS AND DISCUSSION

### Synthesis of the hyperbranched alkaline-soluble and light-sensitive polymers

The vibration absorption peaks of the acryloxy group are very distinct at 815 and  $1663\ \text{cm}^{-1}$ . From the  $^1\text{H}$ -NMR spectrum, it can be seen that the hydrogen proton, which is at the double bond of the acryloxy group, exists at  $\delta = 6.3$ . Moreover, the absorption peaks of the carboxyl carbon and carbonyl carbon also exist at  $\delta = 164\text{--}166$  in the  $^{13}\text{C}$ -NMR spectrum. Consequently, it can be concluded that the resist polymer contains the carboxyl and acryloxy groups. The gel permeation chromatography analytical results indicate that the average molecular weight of the polymer is 4900. The UV spectrum shows that the light absorption wavelength of the polymer is 320 nm, indicating the slight shielding effect of UV absorption for the photoinitiator. The ideal structures of the polymers are given in Figure 1.

### Exposure characteristics

The exposure parameters of the hyperbranched polyester resists include the critical gel exposure energy ( $E_0$ ) and contrast ( $\gamma$ ). The resin acid value and the composition of the resist greatly affect  $E_0$  and  $\gamma$ .  $\gamma$  increases as the resin acid value increases. In addition, it decreases as the content of the photoinitiator increases. The linear depth, denoted as the depth range of the linear variation between the membrane thickness and exposure energy, decreases as the resin acid value increases and increases as the content of the photoinitiator increases. Moreover, the linear depth is also related to the etching and exposure conditions. The solution rate of the incompletely crosslinked mol-

TABLE I  
Properties of the Photoresists

	A	B	C
Acid value (KOH mg/g)	97.7	157.7	97.7
Irgacure 651 (%)	6.0	6.0	3.0
$E_0$ (mJ/cm <sup>2</sup> )	2.0	1.0	5.0
$\gamma$	0.49	0.56	0.76
Linear depth ( $\mu\text{m}$ )	0-43	0-30	0-24

ecules in the exposed part during the etching process increases as the resin acid value increases, and this leads to a reduction in the linear depth. On the contrary, the crosslinking density of the exposed part increases with an increase in the content of the photoinitiator, which leads to a reduction of the etching rate for the exposed part, indicating an increase in the etching depth and linear depth. The linear depth can reach 43  $\mu\text{m}$  through the optimization of the resist formula, the etching liquid and its concentration, the etching time, and the amount of exposure. The characteristic exposure parameters are summarized in Table I. The surface-profile curves of the membrane thickness versus the exposure energy of resist A are shown in Figure 2. Table I shows that the linear depth increases as  $\gamma$  decreases.

Preparation of the microlens array

The transfer simulated-profile light-etching technique, which has been developed since the begin-

ning of the 1980s, has the following advantages in the processing of miniaturized optic elements: it demands a short exposure time, and a larger area and a deeper microlens array can be prepared simultaneously. However, this technique demands a wider linear depth. Moreover, it is easy to control the surface profile of the resist. Therefore, there is no such resist to meet the requirements of this technique. In this article, some new resists are reported. The hyperbranched polyester resists can prevail over other resists under otherwise identical conditions through the application of the aforementioned technique. Excellent results can be obtained. A slight discrepancy occurs between the element profile and simulated profile of the formed resists. Furthermore, the surface profile is fairly good. The etching depth can reach 50  $\mu\text{m}$ . Results have been obtained with an Alpha-Step 500 step instrument (200  $\mu\text{m} \times 200 \mu\text{m}$ ) through the etching of the hyperbranched polyesters for 8 min with the transfer simulated-profile light-etching technique (Fig. 3). A comparison of the computer-simulated and practical surface profiles of the microlens is shown in Figure 4.

CONCLUSIONS

The prepared hyperbranched polyester resists were applied to the processing of miniaturized optic elements to obtain a microlens array with a slight dis-

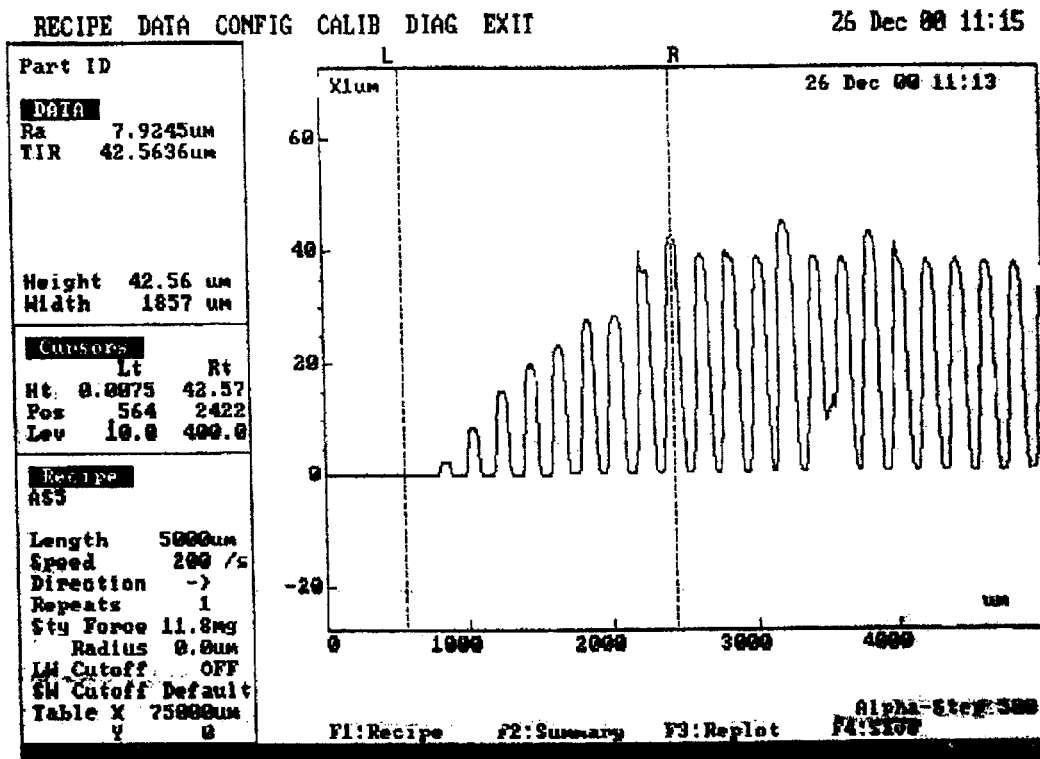


Figure 2 Surface-profile curves of the etching versus the exposure energy of the resin of resist A (etching time = 4 min).

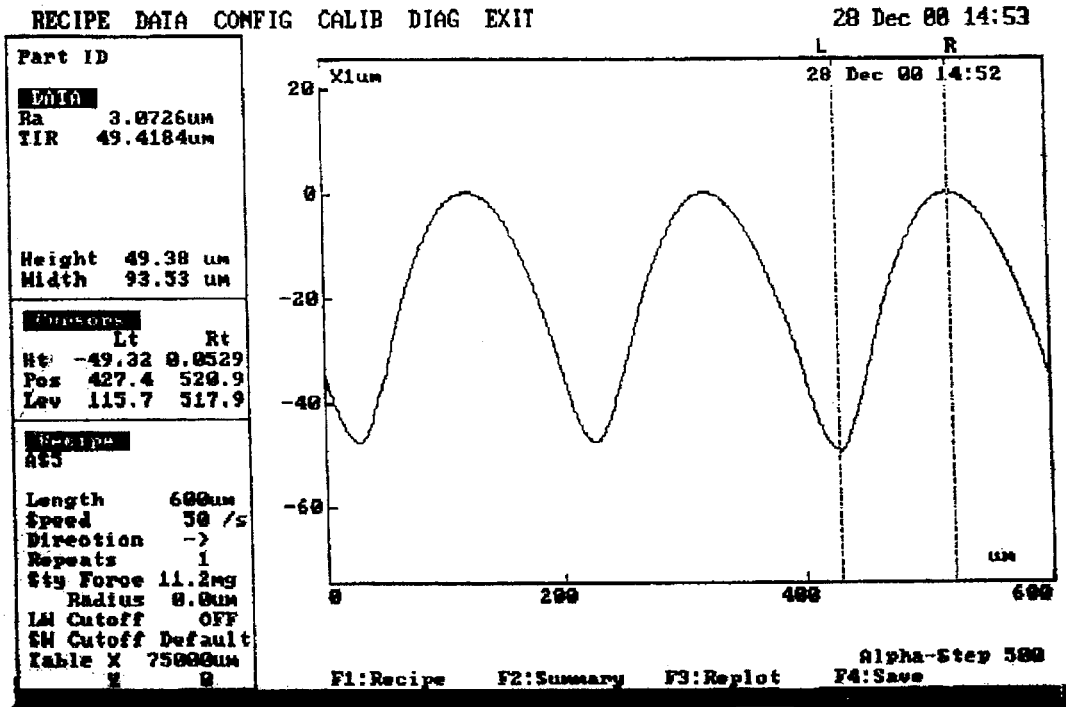


Figure 3 Surface-profile curves of the microlens array fabricated with the hyperbranched resist.

crepancy between the element profile and simulated profile of the formed resists. The etching depth could reach 50  $\mu\text{m}$ . Consequently, it can be concluded that the hyperbranched polyester resists have advantages

such as good reproducibility, high light transmissivity, wide linear depth, deep processing, and repetitive etching. Moreover, it is easy to control the surface profile. These hyperbranched polyester resists provide

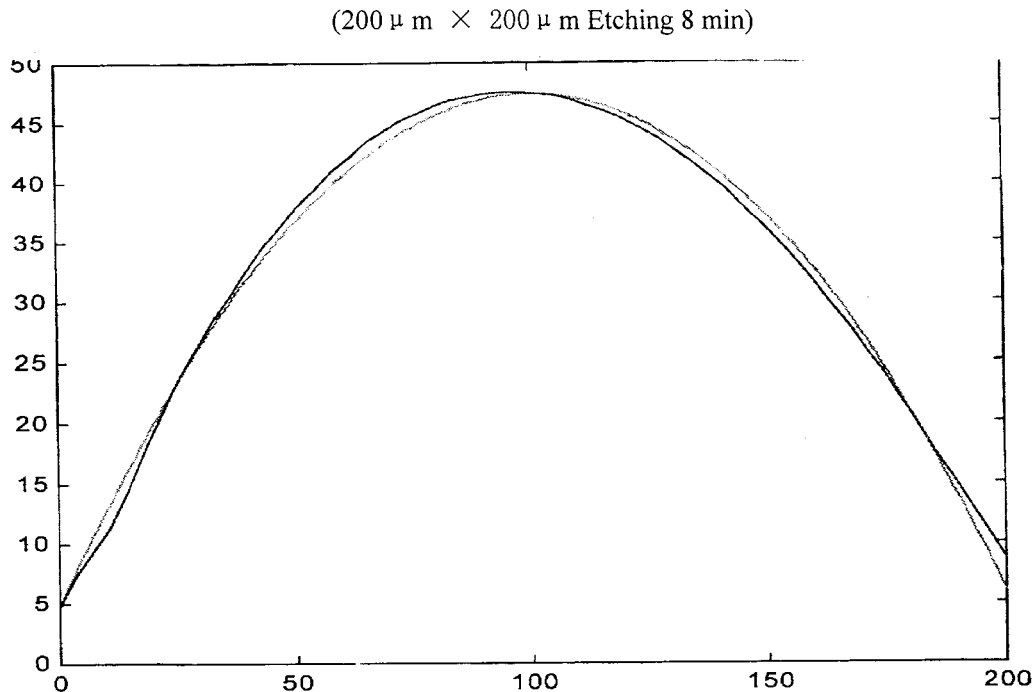


Figure 4 Comparison of computer-simulated and practical surface profiles of the microlens. The broken line represents the ideal shape, and the solid line represents the practical shape.

a new type of prospective functional material for the miniaturized optic element processing industry. In the meanwhile, they also widen the application range of hyperbranched polymers.

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