

# Preparation and Characterization of Copolymers Containing (+)-Bornyl Methacrylate and Their Racemate for Positive-Tone Photoresist

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**ABSTRACT:** This study investigated the chemical behavior of polymers bearing cycloaliphatic bornyl units along with the steric difference of the chiral (+)-bornyl methacrylate [(+)-BMA] and racemic ( $\pm$ )-BMA, expressed in the physical properties of the copolymers and the resist characteristics. To do this, a series of copolymers containing (+)-bornyl methacrylate [(+)-BMA] and ( $\pm$ )-BMA units was synthesized. Comonomers of *tert*-butyl methacrylate (TBMA), methyl methacrylate (MMA), and maleic anhydride (MA) were used. The thermogravimetric curves, glass-transition temperature ( $T_g$ ), and molecular weight (MW) of the copolymers were evaluated. Exposure characteristics of chemical-amplified positive photoresists comprising various copolymers were investigated. It was found that copolymers bearing ( $\pm$ )-BMA have higher  $T_g$  and better thermostability than those of copolymers containing (+)-BMA units. The copolymers with ( $\pm$ )-BMA units, however, revealed an inert photochemical behavior on the positive-tone photoresist. The patterning properties of the positive photoresist, composed of copolymers bearing (+)-BMA and ( $\pm$ )-BMA, and the photoacid generator (PAG) were also investigated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3538–3544, 2001

**Key words:** Photoresist; Bornyl methacrylate; Chiral; Photoacid generator; Enantiomer; Diastereomer

## INTRODUCTION

Photolithography using deep UV appears to be a viable route for the extension of optical lithography to the dimensions required for the manufacture of submicrometer patterns. Many methods have been tried to improve the solubility change on irradiation in order to obtain higher sensitivity, contrast, and resolution.<sup>1–3</sup> Photoacid generators (PAG) have attracted increasing attention as a catalyst for high-sensitivity photoresist systems, the “chemical ampli-

fication” type, in which generated acids catalyze the thermolyses of hydrophobic groups into hydrophilic groups.<sup>4,5</sup> The combination of a dye and a photoacid generator makes it possible to initiate a number of cationic polymerizations using visible light.<sup>6</sup>

Positive photoresists based on hydroxystyrene-based polymers and photoacid generators are extensively utilized in the field of photolithography.<sup>7–9</sup> The aliphatic nature of the polymer and the low extinction coefficient of the vibronic transition (at 210–220 nm) are characteristics of a very transparent polymer. Acrylic polymers are the new basis for 193-nm resist design because of their excellent optical transparency and easily tailored structure.<sup>10–12</sup>

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To offer flexibility for simultaneously tuning resist performance and realizing increased etch resistance, three-component resists consisting of a methacrylate polymer, an alicyclic dissolution inhibitor compound, and a photoacid generator were developed.<sup>13,14</sup> Copolymers containing racemic isobornyl methacrylate (IBMA) were used as resins for positive-tone photoresist. Introducing cyclic isobornyl groups into the polymers improved the thermal properties of the photoresists.<sup>15</sup> In this study we synthesized acrylic copolymers containing (+)-bornyl methacrylate [(+)-BMA] and its racemate. We investigated the steric difference of the chiral (+)-BMA and achiral ( $\pm$ )-BMA units expressed in the physical properties of the copolymers and the resist characteristics. Thermal properties, polymer transparency, photosensitivity, and imaging quality of the positive-tone photoresists were all estimated.

## EXPERIMENTAL

### Materials

Commercial monomers used in this investigation were obtained from Tokyo Chemical Industries, Ltd. (TKK; Tokyo, Japan). Monomers of *tert*-butyl methacrylate (TBMA), methyl methacrylate (MMA), and maleic anhydride (MA) were purified by distillation technique. (+)-Bornyl methacrylate (BMA) and its racemate ( $\pm$ )-BMA were synthesized according to the procedures described in the literature.<sup>16–17</sup> The initiator azobisisobutyronitrile (AIBN) was purified by recrystallization in ethanol. Triphenylsulfonium hexafluoroantimonate was used as a photoacid generator. Organic solvents used in this investigation were all distilled and dried with molecular sieves prior to use.

### Measurements

The UV-visible spectra of films of the photoresist on quartz substrates were measured with a Jasco UV-vis 7850 double-beam spectrometer. The photoresist was exposed with a Karl Suss MJB-3 aligner. The film thickness was measured with a Tencor Instrument alpha step-200 film-thickness monitor. Dissolution rate was defined as the changes of photoresist film thickness per development time. The resist pattern profiles were evaluated using Jeol JSM-35 and JAX-840 scanning electron microscopes. The thermal properties and functional groups of the polymers were evaluated

and analyzed with a DuPont 910 differential scanning calorimeter and a PerkinElmer TGA-7 thermogravimetric analyzer and with a Jasco FTIR spectrometer, respectively. Elemental analyses were calculated with a Heraeus CHN-O rapid elemental analyzer.

### Preparation of Copolymers

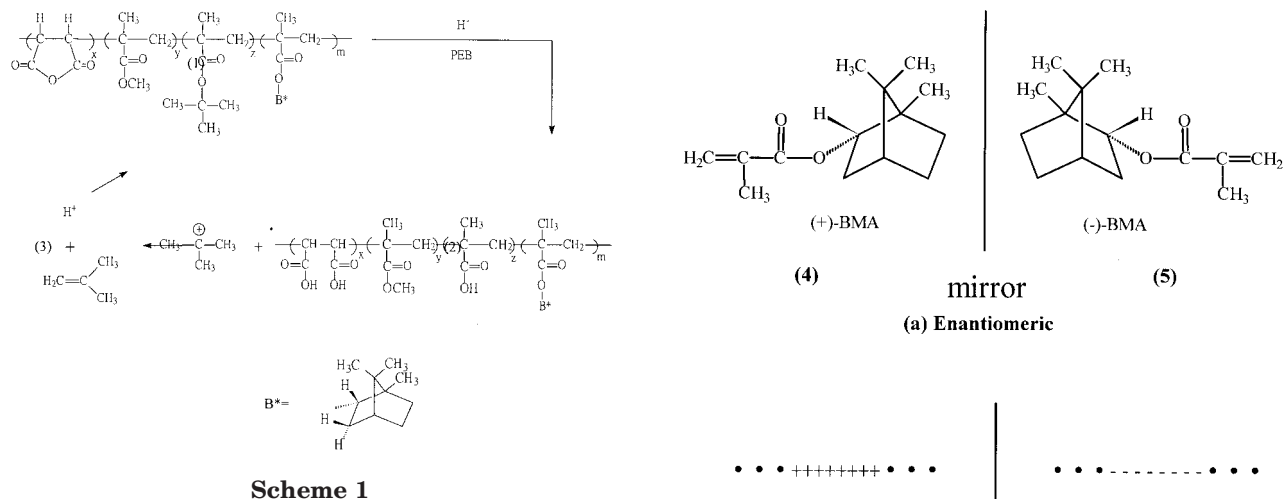
Copolymers were obtained by copolymerization of monomers in tetrahydrofuran (THF) in the presence of 1 wt % AIBN at 60°C for 12 h. Comonomers were poured into a glass polymerization tube equipped with a sealing cap, which was degassed in vacuum using a freeze–thaw technique and then sealed off. After complete polymerization, the copolymers were precipitated out from a large amount of water–methanol solution (1:1 in volume) and then washed completely with distilled water.

### Exposure Method

Photosensitive solution was obtained by dissolving copolymers (1.0 g), and triphenylsulfonium hexafluoroantimonate (photoacid generator,  $9.0 \times 10^{-2}$  g) in 10 mL of THF. The photosensitive solution was filtered with a 0.45  $\mu\text{m}$  filter and then was spin-coated onto a silicon wafer plate, first at 1000 rpm for 10 s and then at 2500 rpm for 20 s. The solution was then prebaked at 90°C for 3 min. The photoresist was exposed with a Karl Suss MJB-3 aligner. After exposure the resist was postbaked (PEB) at 100°C for 10 min and then developed by a 30-s immersion in a 6 wt % sodium carbonate developer.

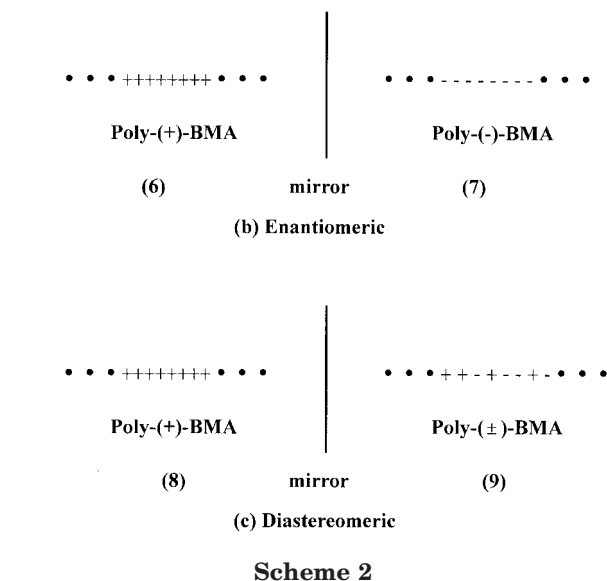
## RESULTS AND DISCUSSION

To investigate the photochemical behavior of polymers bearing cycloaliphatic bornyl units, a series of copolymers containing (+)-BMA and ( $\pm$ )-BMA units was synthesized. Scheme 1 shows the copolymer structure and the mechanism of photochemical degradation of the copolymer in the presence of photo-induced acid. The UV-generated acids catalyzed the thermolyses of hydrophobic *t*-butyl groups into hydrophilic carboxylic groups. The existence of the anhydride unit increases the hydrophilicity of the copolymer for positive-tone characteristics. The aliphatic nature of the copolymer and the low extinction coefficient of the vibronic transition ( $\lambda_{\text{max}}$  at 210–220



nm) are characteristics of a very transparent polymer for deep UV light. The results of the copolymerization of MA, MMA, TBMA, and ( $\pm$ )-BMA are summarized in Table I. As can be seen, the glass-transition temperature ( $T_g$ ) increased with an increasing amount of ( $\pm$ )-BMA units, a result of an increase in the rigid structure of the bornyl moieties. A high  $T_g$  may improve the thermal properties of the copolymers and increase the latitude to perform higher postexposure bakes.

In theory, enantiomers have identical physical properties, except for the direction of rotation of the plane of polarized light. Scheme 2(a) shows the enantiomorphism of (+)-BMA and (-)-BMA monomers. A mixture of equal parts of enantiomers is called racemic modification; an example is ( $\pm$ )-BMA. Polymerization of (+)-BMA and (-)-BMA in achiral environment should lead to the formation of enantiomeric chiral polymers of poly(+)-BMA and poly(-)-BMA. In this investigation, however, copolymerization of each (+)-BMA and ( $\pm$ )-BMA with various achiral comonomers



produced diastereomeric copolymers containing different physical properties. Scheme 2(a-c) shows the relationships between the enantiomeric (+)-BMA/(-)-BMA, poly(+)-BMA/poly(-)-BMA, and diastereomeric poly(+)-BMA/poly( $\pm$ )-BMA pairs, respectively.

To investigate the steric difference of the stereoisomeric comonomers, expressed in the physi-

**Table I** Results of Copolymerization of Comonomers<sup>a</sup>

Sample	MA <sup>b</sup>	MMA <sup>c</sup>	TBMA <sup>d</sup>	( $\pm$ )-BMA <sup>e</sup>	$T_g$ (°C)	$M_w \times 10^{-4}$
1	10 <sup>f</sup>	10	10	0	135.5	6.08
2	10	10	10	10	154.0	7.50
3	10	10	10	50	160.2	6.50
4	10	10	10	100	165.6	7.50

<sup>a</sup> Copolymerized in THF at 60°C for 12 h in the presence of 1 wt % AIBN.

<sup>b</sup> Maleic anhydride.

<sup>c</sup> Methyl methacrylate.

<sup>d</sup> *tert*-Butyl methacrylate.

<sup>e</sup> ( $\pm$ )-Bornyl methacrylate.

<sup>f</sup> Millimoles of monomers.

**Table II Results of Copolymerization of Each (+)-BMA and ( $\pm$ )-BMA with Various Achiral Comonomers<sup>a</sup>**

Sample	MA <sup>b</sup>	MMA <sup>c</sup>	TBMA <sup>d</sup>	( $\pm$ )-BMA <sup>e</sup>	(+)-BMA	$T_g$ (°C)	$M_w \times 10^{-4}$
5	10 <sup>f</sup>	10	20	0	0	139.1	7.05
6	10	10	30	0	10	143.9	7.23
7	10	10	30	10	0	120.9	7.45
8	10	10	90	0	10	129.4	6.43

<sup>a</sup> Copolymerized in THF at 60°C for 12 h in presence of 1 wt % AIBN.

<sup>b</sup> Maleic anhydride.

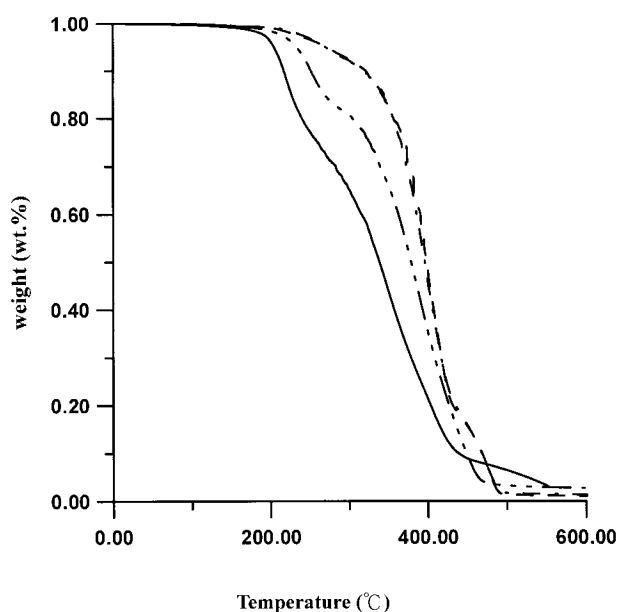
<sup>c</sup> Methyl methacrylate.

<sup>d</sup> *tert*-Butyl methacrylate.

<sup>e</sup> (+)-Bornyl methacrylate.

<sup>f</sup> Millimoles of monomers.

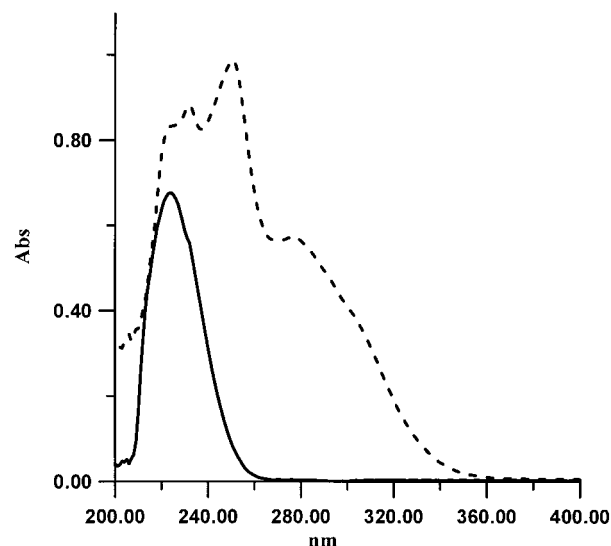
cal properties of the copolymers, (+)-BMA and ( $\pm$ )-BMA were used as comonomers, and three kinds of copolymers (sample 5, 6, and 7) were prepared. As shown in Table II, introducing achiral ( $\pm$ )-BMA into the copolymers gives a better thermal property than that of a (+)-BMA-containing copolymer. These results suggest that the copolymers of 6 and 7 are different, although both are diastereomers and both (+)-BMA and ( $-$ )-BMA have identical reactivity for copolymerization. Table II shows the different molecular weight in response to the identical reactivity of the (+)-BMA and ( $\pm$ )-BMA monomers.



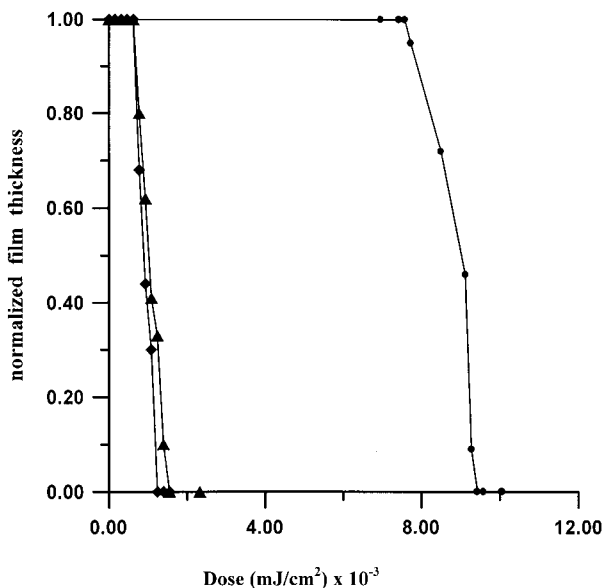
**Figure 1** Effects of ( $\pm$ )-BMA units on the thermostability of copolymers: ( $\pm$ )-BMA content: (—) 0 wt %; — · · · —: 25 wt %; — — —: 62 wt %; — — —: 77 wt %.

The effects of ( $\pm$ )-BMA units on the thermostability of the copolymers are shown in Figure 1. The thermal resistance of the copolymers increased with an increasing content of ( $\pm$ )-BMA units. The results, as shown in Figure 1 and samples 6 and 7 in Table II, suggest that copolymerization of racemic ( $\pm$ )-BMA with other comonomers may cancel the chiral effects from the existence of racemates, leading to decreased steric hindrance between the polymer chains. The physical property  $T_g$  and the thermal resistance of the copolymers will increase with increasing steric hindrance between the polymer chains.

Figure 2 shows the UV spectra of the photoacid generator (PAG) triphenylsulfonium hexafluoroantimonate with copolymer 7 from Table II. The



**Figure 2** UV spectra of photoacid generator (PAG) and copolymer 7: (—) copolymer 7; (— — —) photoacid generator.

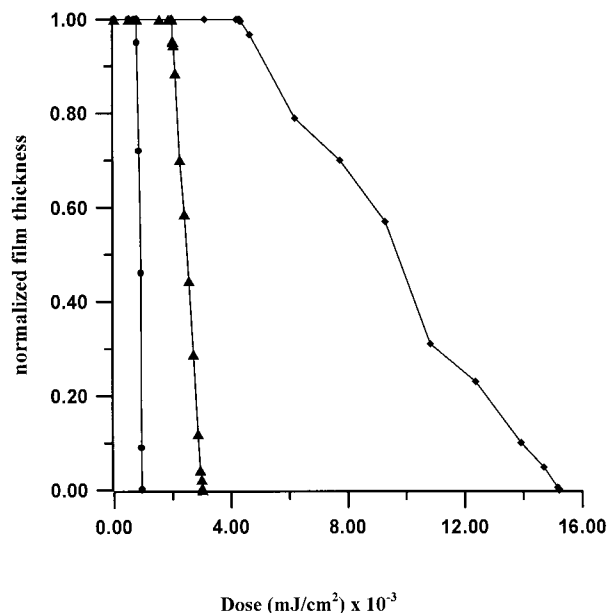


**Figure 3** Exposure characteristic curves of positive photoresist comprising various copolymers: (◆) copolymer 5; (▲) copolymer 6; (●) copolymer 7.

results suggest that deep UV (around 250 nm) of the KrF excimer laser is available for this resist system. The UV spectra of copolymers synthesized in this investigation have no obvious difference.

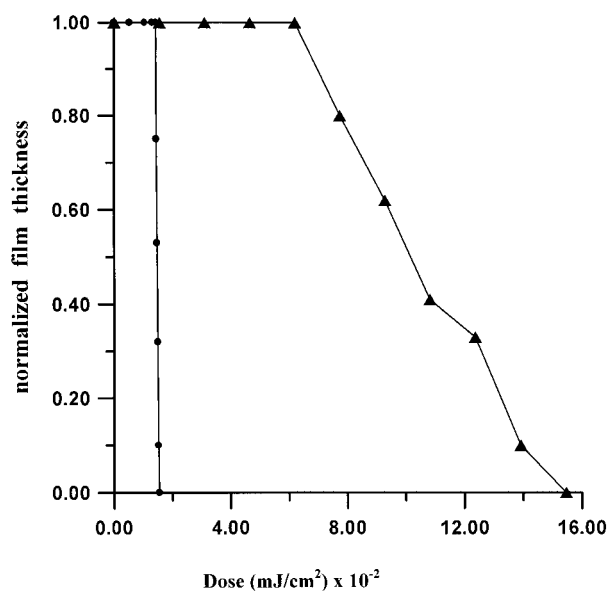
To assess the photochemical behavior of copolymers 5, 6, and 7, lithographic evaluation of copolymers was done using small amounts of photoacid generator (PAG). Figure 3 shows the exposure characteristic curves of positive photoresists comprising various copolymers. As can be seen, the photoresist comprising copolymer 7—bearing ( $\pm$ )-BMA units needs more energy than that of copolymer 6—bearing (+)-BMA units. These results are consistent with those observed in TGA analyses. The steric hindrance in copolymer 7 may be smaller than that of copolymer 6. Furthermore, the same results can be seen in Figure 4, with the irradiation dose increasing with increasing amounts of ( $\pm$ )-BMA units in the copolymer. These results are consistent with those observed in Table I: steric hindrance increased with an increasing content of ( $\pm$ )-BMA in the copolymers.

Figure 5 shows the exposure characteristic curves of the photoresists comprising copolymers 7 and 8. The sensitivity of the positive-tone photoresist was greatly improved by increasing the number of *tert*-butyl methacrylate (TBMA) units in the copolymer. As shown in Scheme 1, the amount of the acid-labile *t*-butyl group in TBMA



**Figure 4** Exposure characteristic curves of positive photoresist comprising copolymers with ( $\pm$ )-BMA unit contents of: (●) 17 wt %; (▲) 30 wt %; (◆) 38 wt %.

units mainly will affect the photochemical behavior of the copolymers. The contrast and sensitivity of the photoresist containing copolymer 8 both improved, although the ( $\pm$ )-BMA units existed in the binder resin. As can be seen in Figure 6, adding hydrophilic ethylene glycol and oxalic acid

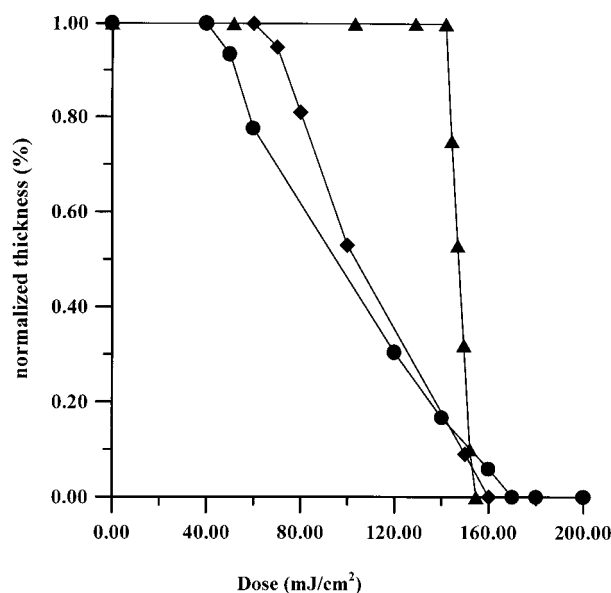


**Figure 5** Improvement of photochemical behavior of copolymers by increasing the amount of TBMA units: (▲) polymer 6; (●) polymer 8.

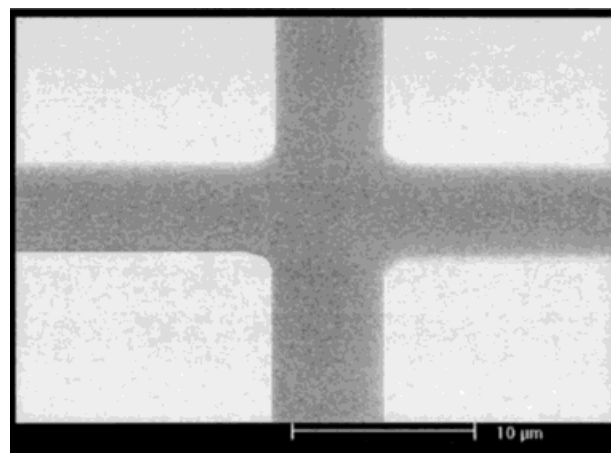
into the copolymers will decrease the contrast of the positive-tone photoresist. The existence of hydrophilic ethylene glycol and oxalic acid may increase the solubility of binder resins and may affect the photochemical reactions in the polymer matrix, leading to a decrease in contrast. A lithographic evaluation of the positive-tone photoresist containing copolymer 8 was also done. A 5- $\mu\text{m}$  pattern resolution was examined, and Figure 7(a,b) shows the scanning electron micrographs of the patterns.

## CONCLUSION

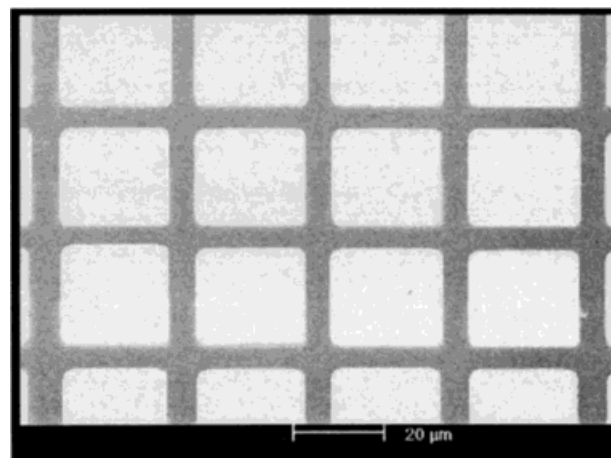
The copolymers bearing (+)-BMA and ( $\pm$ )-BMA units prepared in this investigation can be used as binder resins for a positive-tone photoresist. The copolymers containing ( $\pm$ )-BMA units synthesized in this investigation have a higher  $T_g$  and better thermal stability, but reveal an inert photochemical behavior. The thermal resistance of the copolymers increased with an increasing content of ( $\pm$ )-BMA units. The sensitivity of the photoresist comprising copolymers containing ( $\pm$ )-BMA was improved by increasing the content of the TBMA units. This investigation also prepared and examined a 5- $\mu\text{m}$  pattern resolution of positive-tone photoresist.



**Figure 6** Effects of ethylene glycol and oxalic acid on photochemical behavior of copolymers: (●) Copolymer 6 + ethylene glycol; (◆) Copolymer 6 + oxalic acid; (▲) Copolymer 8.



(a)



(b)

**Figure 7** Scanning electron micrograph of the pattern from PAG-containing copolymer 8.

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