

Crosslinkable Positive-Tone Photoresist Comprising Polymers with Pendant Carboxyl Groups

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ABSTRACT: Poly(methacrylic acid-co-*t*-butylmethacrylate-co-bornylmethacrylate) was synthesized and its application to a crosslinkable positive photoresist was investigated. The existence of pendant alicyclic bornyl groups increased the thermostability of copolymers; however, a decrease in the acid-catalyzed deprotection of pendant *t*-butyl groups led to a decrease in the sensitivity of the positive-tone photoresist. The thermostability of the relief polymeric patterns of the positive-tone photoresist was appreciably improved effectively because of the acid-catalyzed dehydration crosslinking of pendant carboxyl groups. Thermogravimetric properties of binder resins, exposure characteristics, and sensitivity and resolution of the photoresist were all investigated. Lithographic evaluation of the curable positive-tone photoresists was also estimated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1014–1020, 2001

Key words: photoacid generator (PAG); photoresist; bornylmethacrylate; acid-catalyzed dehydration; alicyclic groups

INTRODUCTION

Photosensitive polymers are widely used as protection and insulation layers in semiconductor manufacturing. The solubility change of polymeric compositions following irradiation with ultraviolet (UV) light is a key factor in the application of these polymers to a photoresist because photopatterning utilizes the solubility differences between irradiation and nonirradiation portions. A photoacid generator (PAG) has been used as a catalyst for the thermolyses of carbonate groups into hydroxy groups of the chemically amplified resist systems.^{1–4} Polyhydroxystyrene derivatives, which express a great dry-etching resistance, are incapable of ArF resist because of their strong absorbance at the 193 nm wavelength.^{5, 6}

Acrylic polymers with a methacrylate backbone and sufficient transparency at the 193 nm

wavelength have been developed.^{7, 8} However, the acrylic polymer has a disadvantage of poor dry-etching resistance because of low carbon density in the polymer chain. To improve the dry-etching resistance, alicyclic hydrocarbons were introduced onto the methacrylate polymers.^{9–12} Alternating copolymer of norbornene and maleic anhydride has been introduced to a matrix resin for ArF lithography.¹³ A silicon moiety in the polymer chain can increase the dry-etching resistance, and also some silicon-containing methacrylate polymers bearing acid-labile side groups were synthesized.^{14, 15}

In our previous paper, we reported a novel crosslinking method for a negative-tone photoresist comprising pendant carboxyl groups in the presence of photoacid.¹⁶ Alicyclic bornyl groups were also introduced onto copolymers to improve the thermal properties.¹⁷ To further improve the thermal properties of the relief polymeric resist materials, in this article, we synthesized a series of copolymers with carboxyl groups and acid-labile *t*-butyl groups to design a crosslinkable posi-

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tive photoresist. Effects of alicyclic moieties and acid-catalyzed dehydration crosslinking on the thermal properties of copolymers were investigated. Thermogravimetric properties of binder resin, exposure characteristics, and sensitivity and resolution of the photoresist were all investigated. Lithographic evaluation of the curable positive-tone photoresists was also estimated.

EXPERIMENTAL

Materials

Commercial monomers used in this investigation were obtained from Tokyo Chemical Industries (TCI), Ltd. Monomers of *tert*-butyl methacrylate (TBMA) and methacrylic acid (MAA) were purified by distillation technique. (+)-Bornyl methacrylate (BMA) and its racemate (\pm)-BMA were synthesized according to the procedures described in the literature.^{18, 19} The initiator azobisisobutyronitrile (AIBN) was purified by recrystallization in ethanol. Triphenylsulfonium hexafluoroantimonate was used as a photoacid generator (PAG). Organic solvents used in this investigation were all distilled and dried with molecular sieves prior to use.

Measurements

The UV-visible (UV-vis) 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 is defined as the changes of photoresist film thickness per

development time. The resist pattern profiles were evaluated with Jeol JSM-35 and JAX-840 scanning electron microscopes. Thermal properties and functional groups of polymers were evaluated and analyzed with a Du Pont 910 differential scanning calorimeter (DSC), Perkin-Elmer TGA-7 thermogravimetric analyzer, and Jasco Fourier transform infrared (FTIR) spectrometer. Elemental analyses were calculated with a Heraeus CHN-O rapid elemental analyzer.

Preparation of Copolymers

Copolymers were obtained by the 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 by a freeze-thaw technique and then sealed off. After completion of the polymerization, copolymers were precipitated from a large amount of water/methanol (1:1 in volume) solution, and then thoroughly washed with distilled water.

Exposure Method

Photosensitive solution was obtained by dissolving copolymers (1.0 g) and triarylsulfonium hexafluoroantimonate (PAG, 9.0×10^{-2} g) in 10 mL of THF. The photosensitive solution was filtered with a 0.45- μ m filter, spin coated onto a silicon wafer plate at 1000 rpm for 10 s and then at 2500 rpm for 20 s, and then prebaked at 90 °C for 3 min. The photoresist was exposed with a Karl Suss MJB-3 aligner. After exposure, the resist was post-exposure-baked (PEB) at 100 °C for 10 min, and then developed with a 30-s immer-

Table I Results of Copolymerization of (\pm)-BMA and (+)-BMA with Various Achiral Comonomers^a

Copolymer	MAA ^b	TBMA ^c	(\pm)-BMA ^d	(+)-BMA	Copolymer Evaluation ^e				
					<i>x</i>	<i>y</i>	<i>z</i>	T_g (°C)	MW $\times 10^{-4}$
1	10 ^f	10	0	0	1	1.07	0	184.9	7.34
2	20	10	0	10	2	0.93	0.87	179.5	6.06
3	20	10	10	0	2	0.93	0.87	184.3	6.21

^a Copolymerized in THF, at 60°C, for 12 h, in the presence of 1 wt % AIBN.

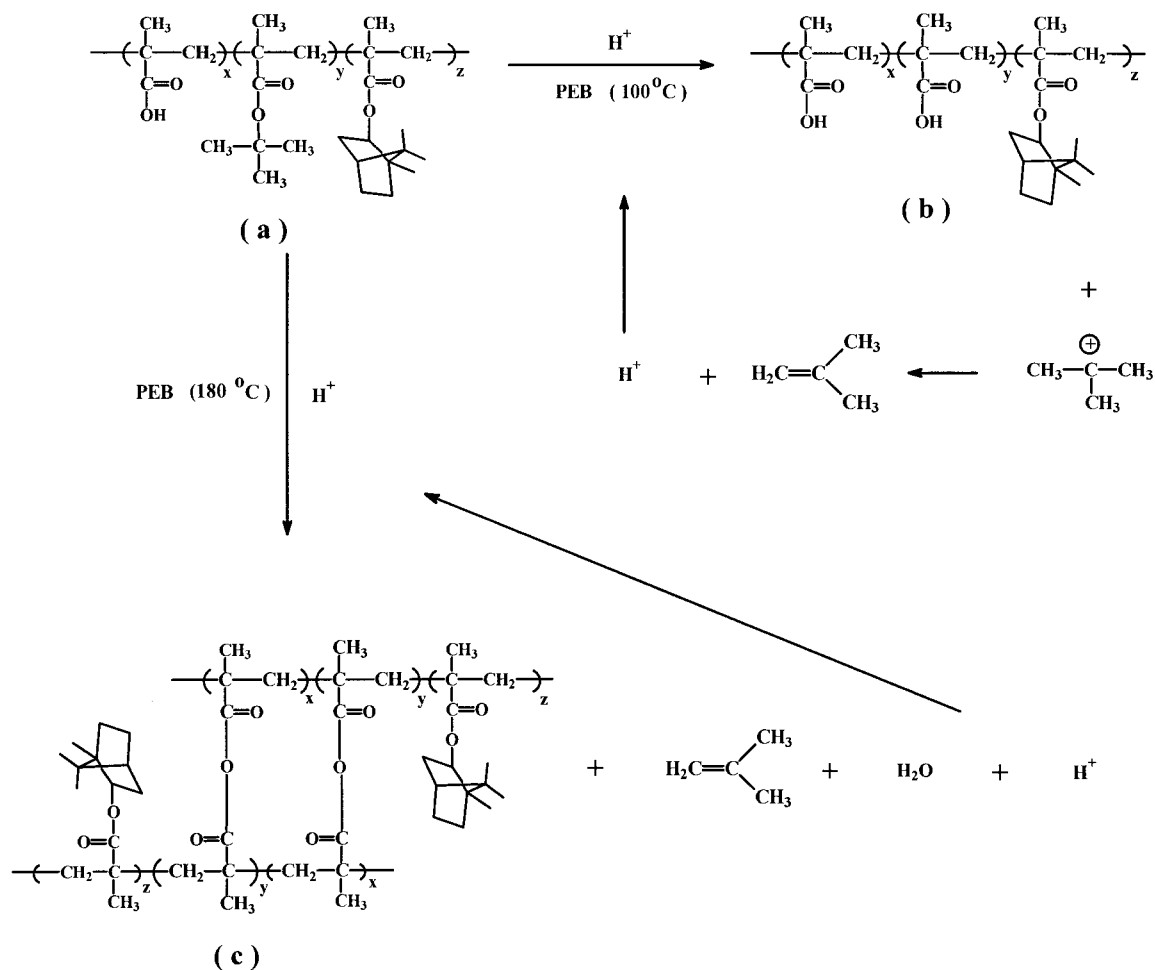
^b Methacrylic acid.

^c *tert*-Butyl methacrylate.

^d (\pm)-Bornyl methacrylate.

^e Composition of copolymers (*x*, *y*, *z*) were estimated by elemental analyses.

^f Feed millimoles of monomers.



Scheme 1

sion in 6 wt % sodium carbonate developer. The residue polymeric materials of the pattern matrix were then exposed to UV light and then further

heat treated at 180 °C for 10 min. In this stage, the dehydration of pendant carboxyl groups that occurred led to the crosslinking of polymers.

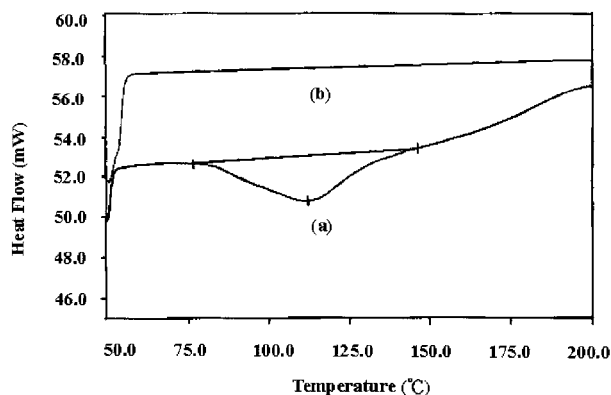


Figure 1 DSC thermograms of photoresist comprising copolymer 2 and PAG treated with various conditions: (a) UV exposed, and (b) UV exposed and then PEB heat treatment at 180 °C for 60 min.

RESULTS AND DISCUSSION

In our previous paper, we reported that the existence of alicyclic bornyl groups would increase the glass transition temperature (T_g) of copolymers.¹⁷ As shown in Table I, however, thermal improvement of bornyl groups on the copolymers synthesized in this investigation are not evident. The T_g s of the three polymers are not so different. Monomer content of MAA in copolymer 1 is 50 mol %. A large amount of hydrogen bonding may exist in copolymer 1. Introduction of alicyclic groups into the copolymer will decrease the content of carboxyl groups and lead to a decrease in hydrogen bonding. Effects of hydrogen bonding in copolymer 1 may cancel out the improvement of

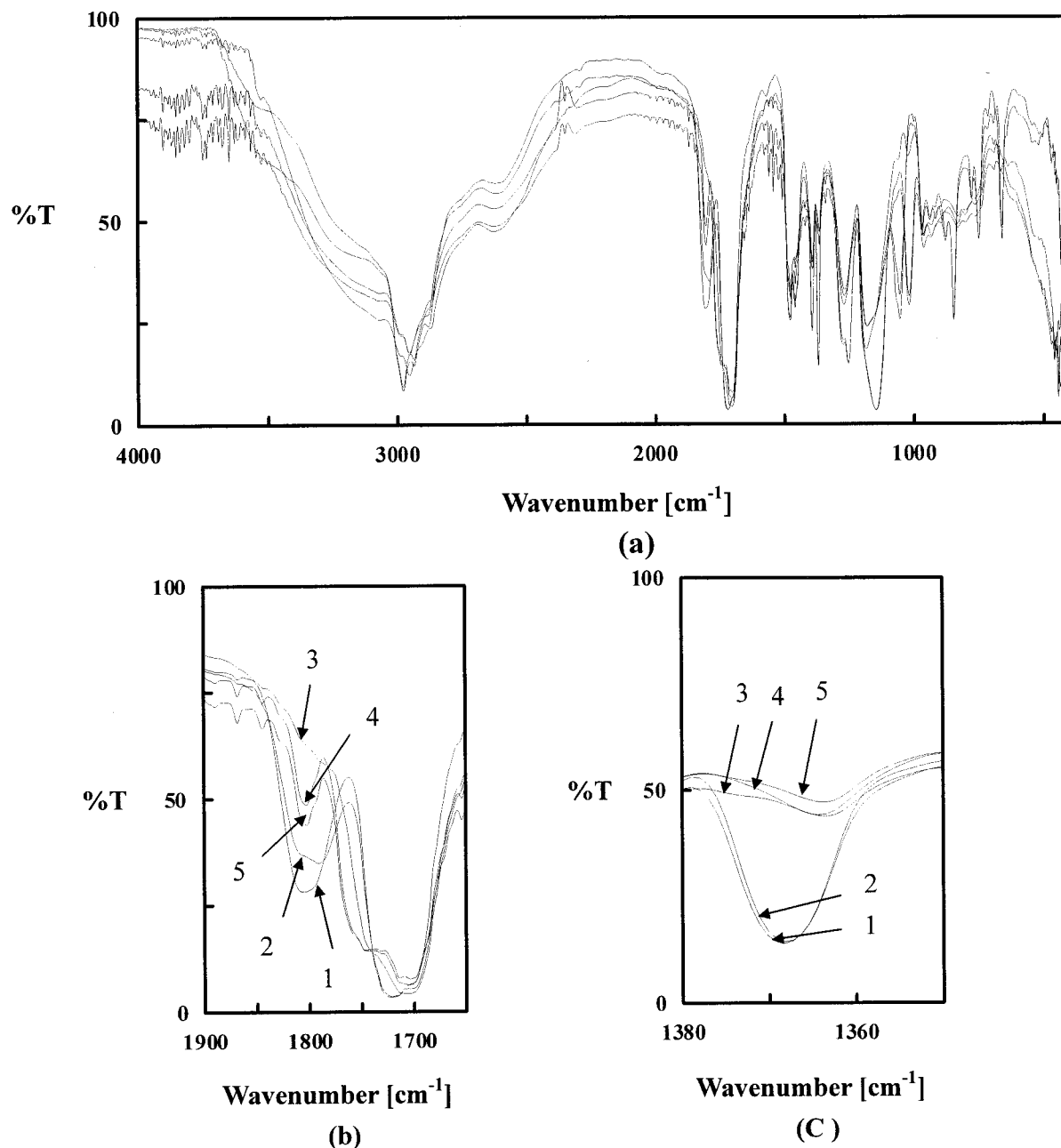


Figure 2 FTIR spectra of photoresist comprising copolymer 1 and PAG treated with various conditions: (1) copolymer 1 with PAG film, (2) UV exposed, (3) UV exposed and PEB at 100 °C for 30 min, (4) UV exposed and PEB at 180 °C for 10 min, and (5) UV exposed and PEB at 180 °C for 30 min.

the alicyclic bornyl groups in copolymers 2 and 3. The compositions of the copolymers are all estimated. Copolymer 2 is a chiral polymer because of the (+)-bornyl groups. The optical activity, $[\alpha]_D = +20.6$ ($C = 0.1$ dg/mL, THF), was estimated with a Jasco DIP-360 automatic digital polarimeter. The copolymer structure is shown in Scheme 1.

As can be seen in Scheme 1, the acid-catalyzed decomposition of *t*-butyl groups occurred at 100

°C, leading to an increase in the hydrophilicity of copolymers. Moreover, acid-catalyzed dehydration of pendant carboxyl groups occurred at 180 °C, leading to the crosslinking of copolymers. The treatment temperatures were determined by DSC analyses.

The DSC thermograms of photoresist comprising copolymer 1 and PAG treated with various conditions are shown in Figure 1. The photoresist

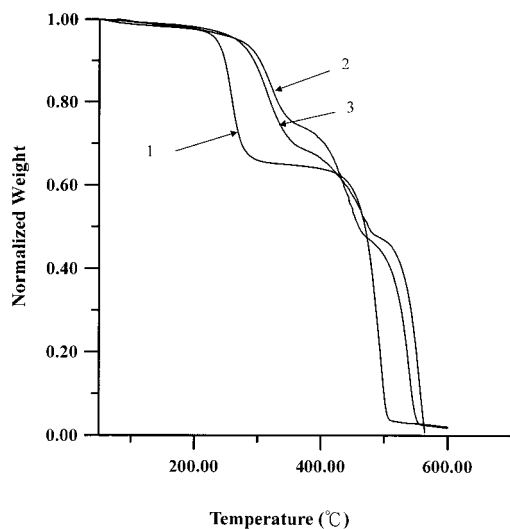


Figure 3 Effects of pendant alicyclic bornyl groups on the thermostability of copolymers without any PAG added: (1) copolymer 1 (no BMA content), (2) copolymer 2 (25% (+)-BMA content), (3) copolymer 3 (25% (±)-BMA content).

used in curve a was only exposed to UV light without any PEB treatment. The photoresist used in curve b was exposed to UV light and then post baked at 180 °C for 60 min. As shown in curve a, an endothermic broad peak appears at ~80–145 °C because of the deprotecting of pendant *t*-butyl groups. The exothermic phenomenon shown at <150 °C may be due to the acid-catalyzed dehydration of pendant carboxyl groups. As shown in Figure 1, however, the phenomena is not seen in curve b after a complete PEB heat pretreatment of the photoresist.

To investigate the reaction mechanism of the photoresist, the FTIR spectra of copolymers before and after UV irradiation and heat treatment were measured. The FTIR spectra of photoresist comprising copolymer 1 and PAG treated with various conditions are shown in Figure 2. Curve 1 and 2 show the results of polymer film before and after UV exposure. The curves are not so different because the UV irradiation can only cause the decomposition of PAG molecules. After PEB at 100 °C for 30 min, as shown in curve 3, *t*-butyl group absorption around 1368 cm^{-1} obviously decreased. After a heat treatment at 180 °C for 10 and 30 min, the absorption at ~1800 cm^{-1} increased and the absorption at ~1740 cm^{-1} was broadened. These results may due to the formation of anhydride structure of the acid-catalyzed dehydration of the pendant carboxyl groups.

The effect of alicyclic bornyl groups on the thermostability of copolymers without any PAG added

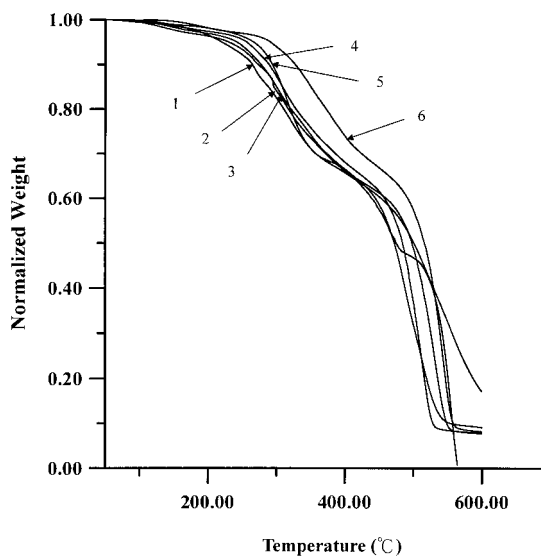


Figure 4 Effects of PEB time at 180 °C on the thermostability of photoresist comprising copolymer 1 and PAG. PEB time: (1) 0 min, (2) 5 min, (3) 10 min, (4) 20 min, (5) 30 min, and (6) 60 min.

is shown in Figure 3. Below 200 °C, the thermostability of the polymers is not very different. Existence of bornyl groups will increase the steric hindrance, decrease the mobility of the polymer chain, and lead to positive improvement of thermodegrading at higher temperature. As mentioned in our previous paper,¹⁷ copolymers 2 and

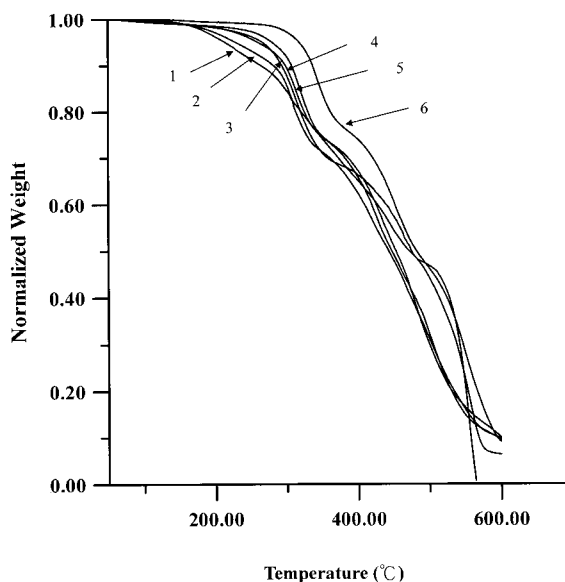


Figure 5 Effects of PEB time at 180 °C on the thermostability of photoresist comprising copolymer 2 and PAG. PEB time: (1) 0 min, (2) 5 min, (3) 10 min, (4) 20 min, (5) 30 min, and (6) 60 min.

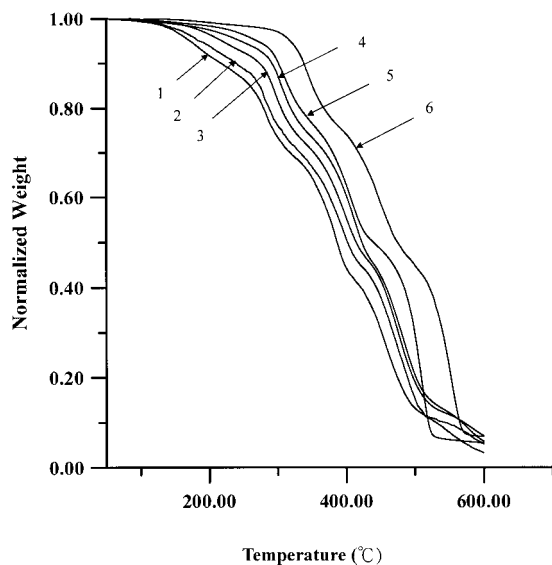


Figure 6 Effects of PEB time at 180 °C on the thermostability of photoresist comprising copolymer 3 and PAG. PEB time: (1) 0 min, (2) 5 min, (3) 10 min, (4) 20 min, (5) 30 min, and (6) 60 min.

3 have a diastereomeric relationship and show a different thermostability (see Figure 3).

To investigate the acid-catalyzed dehydration that occurred in the second stage, copolymer 1 with PAG photoresist was irradiated with UV light for 60 s and then PEB at 180 °C for various times. As can be seen in Figure 4, thermostability increase with increasing the PEB heat treatment time. In the initial stage of the PEB heat treatment, *t*-butyl groups will decompose. This phe-

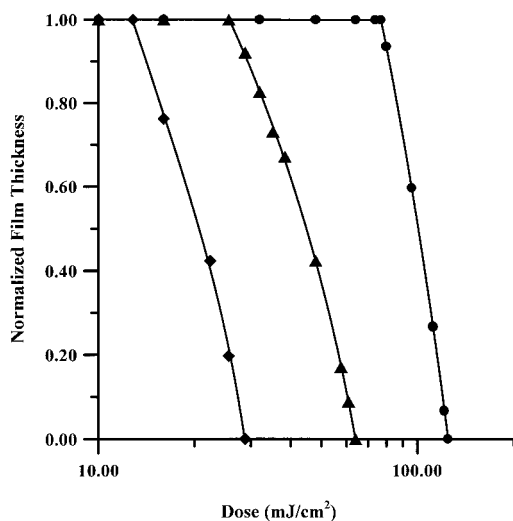
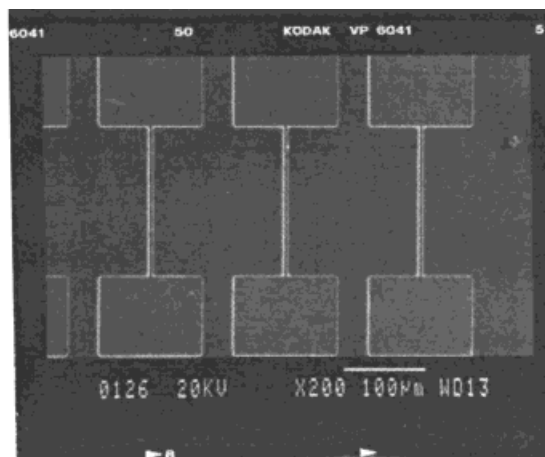
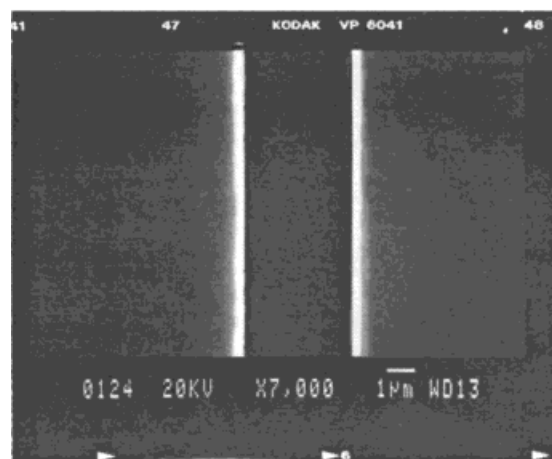


Figure 7 Exposure characteristic curve of positive photoresist comprising various copolymers. Key: (◆) copolymer 1; (▲) copolymer 2; (●) copolymer 3.



(a)



(b)

Figure 8 Scanning electron micrographs of the patterns from copolymer 1 with PAG.

nomenon can be seen in curve 1; in this case, the polymer did not undergo any PEB heat pretreatment. After a sufficient PEB heat treatment at 180 °C for 60 min, as shown in curve 6, decomposition of *t*-butyl groups and dehydration crosslinking of pendant carboxyl groups all occurred completely, indicating great thermostability.

PEB heat treatment effects on the thermostability of copolymers 2 and 3 are shown in Figures 5 and 6, respectively. The results are similar to those observed in Figure 4. However, the thermostability of the copolymers 2 and 3 is worse than that of copolymer 1. The existence of alicyclic bornyl groups may interfere with the acid-catalyzed dehydration of carboxyl groups and lead to the decrease of the thermostability. The results shown in Figures 4–6 suggest that the thermostability of the relief polymeric patterns of the

positive-tone photoresist will be effectively improved by the dehydration crosslinking of pendant carboxyl groups.

The exposure characteristic curves of the photoresists comprising the copolymers 1, 2, and 3 are shown in Figure 7. Copolymer 1 has a better sensitivity than copolymers 2 and 3. The existence of alicyclic bornyl groups in copolymers 2 and 3 may interfere the acid-catalyzed decomposition of *t*-butyl groups and thereby lead to the decrease of the sensitivity. The lithographic evaluation of the crosslinkable positive-tone photoresist with copolymer 3 was also investigated. The scanning electron micrographs (SEMs) of the patterns examined (3- μ m pattern resolution) are shown in Figures 8a and b.

CONCLUSION

The thermostability of the relief polymeric patterns of the positive-tone photoresist can be effectively improved effectively by dehydration crosslinking of pendant carboxyl groups. The existence of alicyclic bornyl groups increases the thermostability of polymers. However, these groups may interfere the acid-catalyzed deprotection of pendant *t*-butyl groups and lead to the decrease of sensitivity of the positive-tone photoresist. Alicyclic bornyl groups also interfere with photoacid-catalyzed dehydration crosslinking of pendant carboxyl groups.

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