Synthesis and Characterization of Novel Copolymers with Acid-Labile Ketal Moieties Derived from Camphor

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ABSTRACT: Novel diastereomeric acrylic ketal monomers derived from (+)-camphor and (±)-camphor were synthesized. To investigate the applications of the camphor derivatives on positive-tone photoresists, the acrylic ketal monomers were copolymerized with methyl methacrylate, methacrylic acid, and *n*-butyl methacrylate. The optical activities of the chiral monomers and polymers were all evaluated. After UV irradiation and postexposure baking, the optical activity of the polymers decreased because of the decomposition of the acid-labile pendant chiral groups. The existence of alicyclic camphyl groups increased the etching resistance of the photoresists. The thermogravimetric properties of the copolymers, the exposure curves, the lithographic evaluation of the positive-tone photoresists, and the effects of alicyclic groups on the plasma etching resistance of the copolymers were all investigated. A resolution of a line-and-space pattern of 0.3 μm was achieved. Acid-catalyzed dehydration crosslinking was also found in this system. Sufficient UV irradiation and heat treatment could cause the acid-catalyzed dehydration crosslinking of pendant carboxyl groups and thereby increase the efficiency of the thermal resistance of the polymers. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2969–2978, 2003

Key words: photoresists; degradation; crosslinking

INTRODUCTION

The electronics industry has enjoyed rapid growth since the early 1960s because of higher and higher integration levels of transistors on single chips.[1] This trend was and still is largely fueled by the progress of photolithographic technologies. For the fabrication of sub-quarter-micrometer semiconductor devices, a chemically amplified resist for deep-UV lithography is one of the most important technologies.[2–5] Many efforts to improve inherent resist performance as well as process stability have been reported. The degree of difficulty in the transition from 248-nm lithography to 193-nm lithography falls somewhere between these past two lithography transitions of 436 to 365 nm and 265 to 248 nm. The optical properties of current 248-nm deep-UV resists are very different at the 193-nm exposure wavelength. Typical *p*-hydroxystyrene-based deep-UV resists, which express good dry-etching resistance, cannot be used for ArF lithography because of their strong optical absorbance at 193 nm.[6–8]

Acrylic polymers have methacrylate backbones and sufficient transparency at 193 nm and can serve as the basis for 193-nm photoresists. However, the disadvantage of acrylic polymers is that they have poor dry-etching resistance in the subsequent plasma steps because of the low carbon density of the polymer chains.[9–13] Methacrylate polymers containing alicyclic hydrocarbons, which are introduced into the side chains, are being studied to improve dry-etching resistance.[14–16] Cycloolefin polymer derivatives and silicon moieties in the polymer chains also enhance dry-etching resistance and adhesion on a substrate without additive materials.[17,18] Camphor is an alicyclic compound, and monomers derived from camphor are expected to have positive effects on the dry-etching resistance of photoresists.

In a series of previous investigations, it has been found that pendant carboxyl groups are crosslinked in the presence of an acid catalyst.[19–22] To improve the photosensitivity and maintain the high thermostability and dry-etching resistance, in this study we synthesized a series of chiral and achiral alicyclic borneol derivatives and introduced them onto the polymer side chains as acid-labile groups for positive-tone photoresists. A series of methacrylic copolymers were synthesized from methacrylic acid (MAA), methyl methacrylate (MMA), *n*-butyl methacrylate (BMA), and (+)- and (±)-camphyl ketal monomers with various feed molar ratios. The following were also investigated: the thermogravimetric properties of the copolymers, the exposure curves, the lithographic evaluation of the positive-tone photoresists, and the effects of alicyclic groups on the plasma etching resistance of the copolymers.

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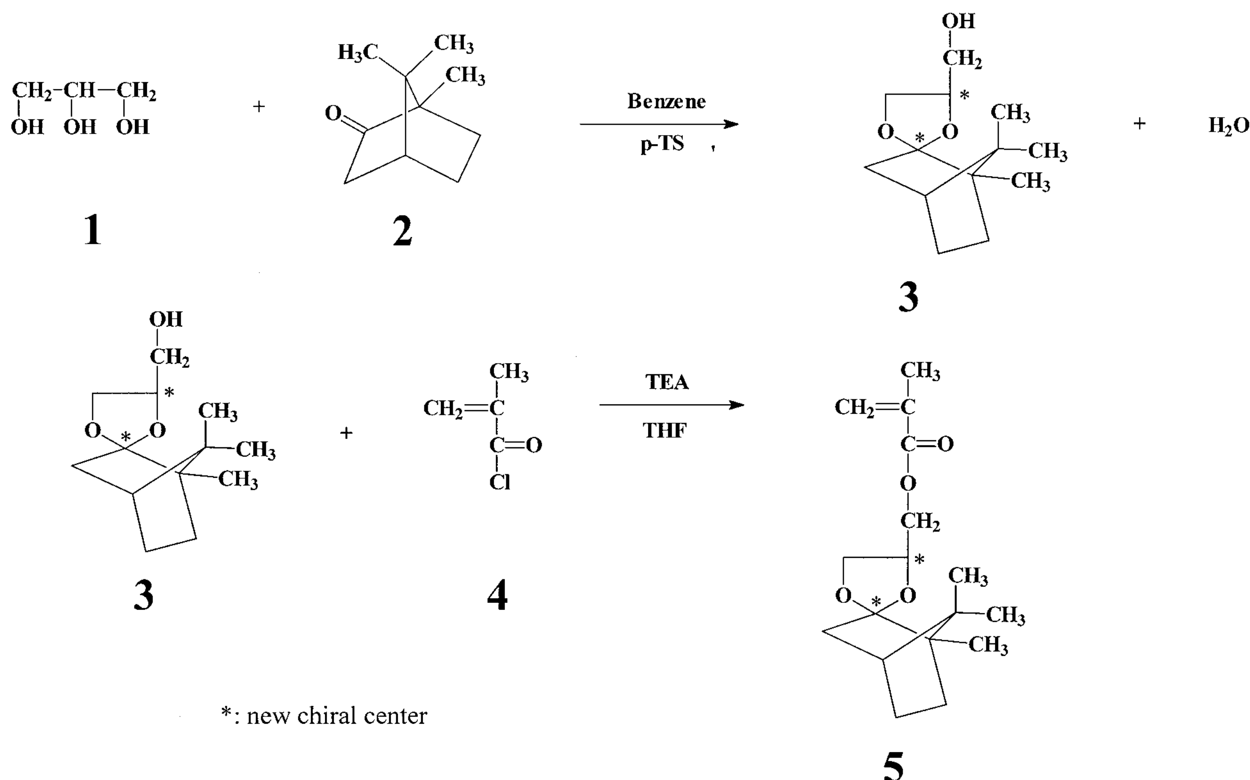


Scheme 1

EXPERIMENTAL

Materials

MAA, MMA, BMA, methacryloyl chloride, (+)-camphor, and (±)-camphor were purchased from Acros (Geel, Belgium) and purified by general methods. Triarylsulfonium hexafluoroantimonate, used as an ionic photoacid generator (PAG), was purchased from Aldrich (Madison, WI). The initiator azobisisobutyronitrile (AIBN) was purified by recrystallization in ethanol. The organic solvents used in this investigation were all distilled and dried with molecular sieves before use.

(+)-3 and (±)-3 ketal derivatives

In a 250-mL flask, camphor (0.5 mol) was refluxed with glycerol (55 g, 0.6 mol) in 100 mL of benzene in the presence of *p*-toluenesulfonic acid monohydrate for 30 h with a Dean–Stark head. After the reaction, the organic layer was separated and washed with dilute sodium hydroxide and water. The resulting mixture was dried over magnesium sulfate and evaporated. The product was obtained as a colorless, oily compound in a yield of 70–75%.

^{1}H-NMR ($CDCl_3$, δ): 0.65, 0.75, 0.85 (9H, —CH_3, s), 1.2–2.2 [6H, C—CH_2—C; 1H, $(C—)_3CH$, m], 2.94 [1H, $(C—)_2OCH$, m], 3.4–4.0 (4H, O—CH_2—C; 1H, —OH, m). ELEM. ANAL. Calcd. for $C_{13}H_{22}O_3$ (226): C, 69.03%; H, 9.73%. Found: C, 69.05%; H, 9.58%.

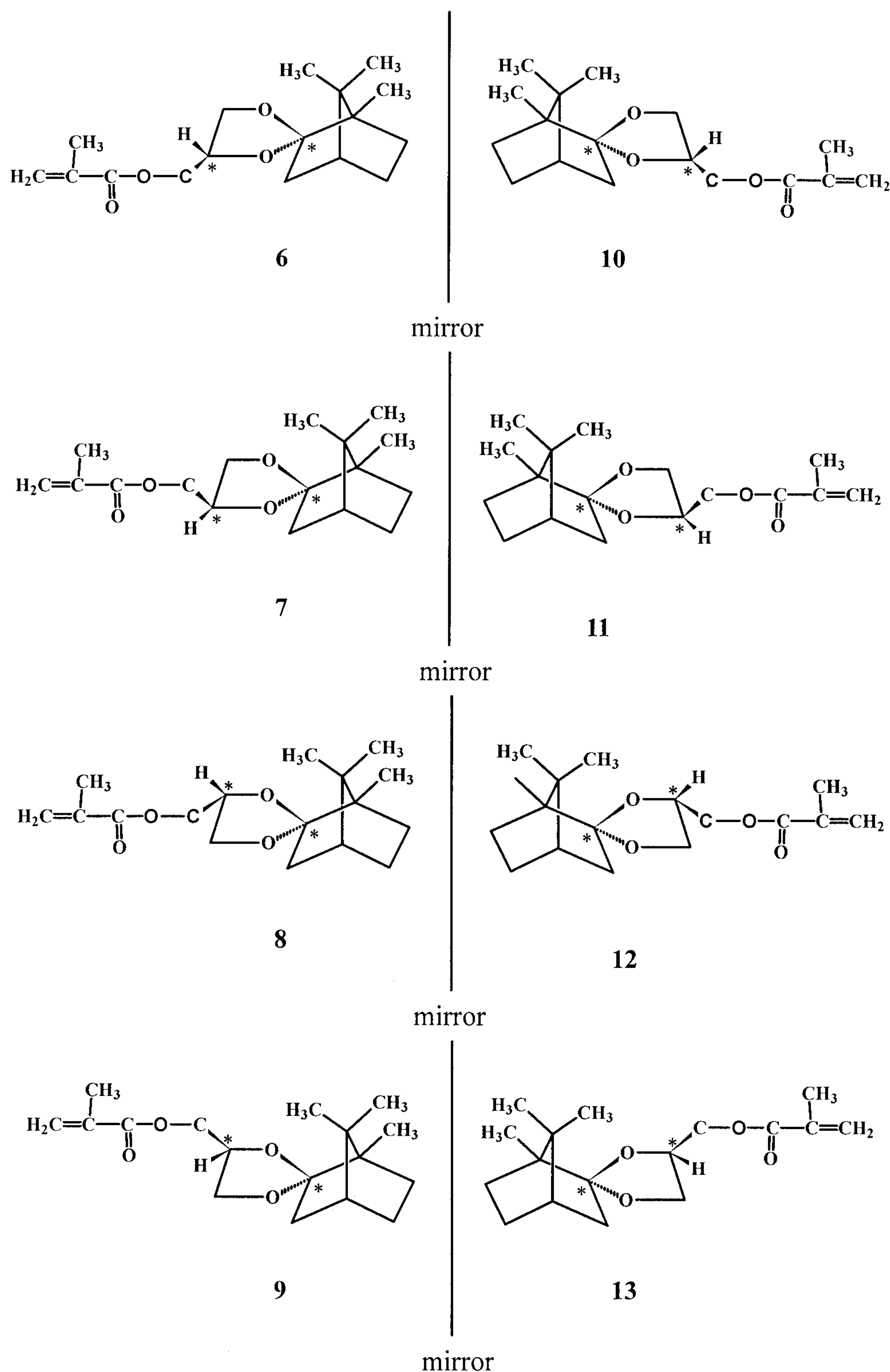
(+)-5 and (±)-5

In a 250-mL, round-bottom flask, (+)-**3** or (±)-**3** (0.1 mol) in 50 mL of dry benzene was added to 0.15 mol (15.2 g) of triethylamine at room temperature with vigorous swirling. Methacryloyl chloride (0.11 mol, 11.5 g) was added dropwise, and the mixture was reacted for 1 h at 0°C. The reaction mixture was kept cold in an ice–water bath and was stirred for 10 h. After the reaction was complete, the precipitated triethylamine salt was filtered off. The filtrate was washed two times with dilute aqueous sodium bicarbonate and then three times with water. It was then dried over anhydrous magnesium sulfate and distilled *in vacuo*. A pale yellow, oily product was obtained in a yield of 77%.

^{1}H-NMR ($CDCl_3$, δ): 0.66, 0.73, 0.85 (9H, —CH_3, s), 1.95 (3H, C═C—CH_3, s), 1.3–2.3 [6H, C—CH_2—C; 1H, $(C—)_3CH$, m], 3.09 [1H, $(C—)_2OCH$, s], 3.4–4.1 (4H, O—CH_2—C, m), 5.8, 6.2 (2H, CH_2═C, s). ELEM. ANAL. Calcd. for $C_{17}H_{26}O_4$ (294): C, 69.39%; H, 8.84%. Found: C, 69.3%; H, 8.57%.

Polymerization

The copolymers were synthesized by free-radical copolymerization in tetrahydrofuran (THF) in the presence of 1 wt % AIBN at 60°C for 12 h. The comonomers were poured into a glass polymeriza-



Scheme 2

tion tube equipped with a sealing cap, which was degassed *in vacuo* with a freeze–thaw technique and then sealed off. After the polymerization was complete, the resulting mixture was precipitated by the reaction mixture being poured into a large amount of distilled water, and then the copolymer was col-

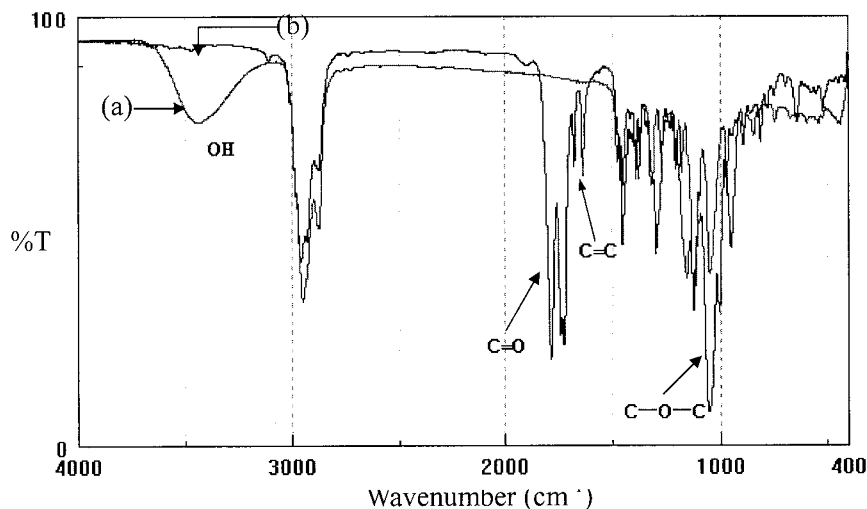
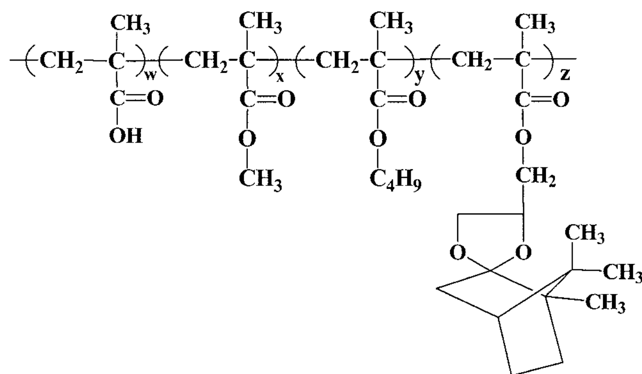


Figure 1 FTIR spectra of (a) (+)-**3** and (b) (+)-**5**.

lected on a suction filter and washed two times with distilled water.

Measurements

For the evaluation of the sensitive wavelengths of the polymers, the ultraviolet–visible (UV–vis) spectra of the photoresist films 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 with a KrF light source. The film thickness was measured with a Tencor Instrument Alpha Step 200 film thickness monitor. The dissolution rate was defined as the change in the photoresist film thickness with the development time. The resist pattern profiles were evaluated with 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, a PerkinElmer TGA-7 thermogravimetric analyzer, and a Jasco Fourier transform infrared (FTIR) spectrometer. Elemental analyses were calculated with a Heraeus CHN-O rapid elemental analyzer. A TOA pH meter was used to measure the pH values of the developing aqueous solutions.



Scheme 3

Lithographic evaluation

A photoresist solution was made by the dissolution of 1.5 g of a copolymer and 0.15 g of a PAG in 10 mL of THF. The photosensitive solution was filtered through a 0.3-μm filter, spin-coated onto a clean silicon wafer surface at 1000 rpm for 10 s and at 2500 rpm for 20 s, and prebaked at 80°C for 2 min. A 1–3-μm-thick film was obtained. The photoresist was exposed with a Karl Suss MJB-3 aligner. After the exposure, the resist was subjected to postexposure baking (PEB) at 100°C for 2 min. It was then developed with a 20-s immersion in a 0.1 wt % sodium carbonate developer. A clear pattern was obtained when it was rinsed completely with distilled water. The relief polymeric materials were then exposed to UV light and further heat-treated at 120°C for 10 min. During this stage, the dehydration of pendant carboxyl groups that occurred led to the crosslinking of the copolymers. The resolution of the photoresist was estimated with scanning electron microscopy (SEM).

TABLE I
Chiral and Achiral Compounds Synthesized in this Investigation

Monomer	Yield (%)	$[\alpha]^{25}$ [a]
(+)-**3**	61	23.8
(+)-**5**	89	9.1
(±)-**3**	59	— [b]
(±)-5	83	—

[a] C = 10 mg/mL in THF.
[b] Achiral compound.

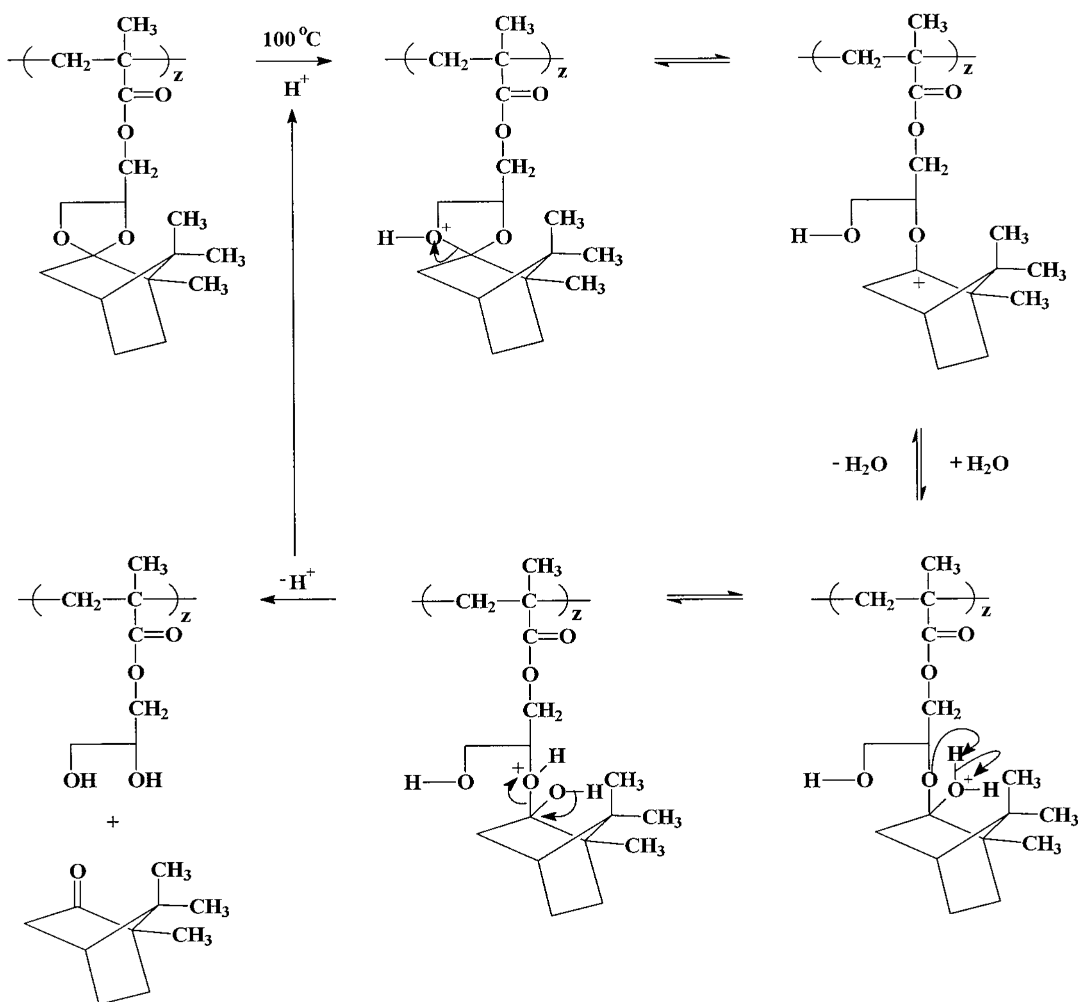
TABLE II
Results of the Copolymerization of (+), and (±)-5 with Various Comonomers[a]

Polymer	MAA	MMA	BMA	(+)/(±)-**5**	Yield (%)	M_w/M_n	$M_w \times 10^{-4}$ [b]
1	20[c]	20	20	10[d]	75	1.9	2.3
2	20	20	20	20	70	2.3	2.2
3	20	20	20	40	65	2.0	1.2
4	20	20	20	10[e]	83	2.0	2.5
5	20	20	20	20	73	1.55	1.1
6	20	20	20	40	80	1.19	2.4

M_w = weight-average molecular weight; M_n = number-average molecular weight.
[a] In THF at 60°C for 12 h, in the presence of 1 wt % AIBN.
[b] By gel. permication chromatography with polystyrene standards.
[c]mmol of monomers.
[d](+)-**5.**
[e](±)-**5.**

RESULTS AND DISCUSSION

As shown in Scheme 1, (+)-**5** and (±)-**5** were synthesized from (+)-camphor and (±)-camphor, respectively. An asterisk marks the generation of two new asymmetric carbons. The molecular structures were identified with ^{1}H-NMR and FTIR spectroscopy. Scheme 2 shows the stereoisomers that formed during the synthesis of chiral monomer **5**. In theory, from (+)-camphor and (±)-camphor, four diastereomers of **6–9** and eight steric isomers of **6–13** could be synthe-



Scheme 4

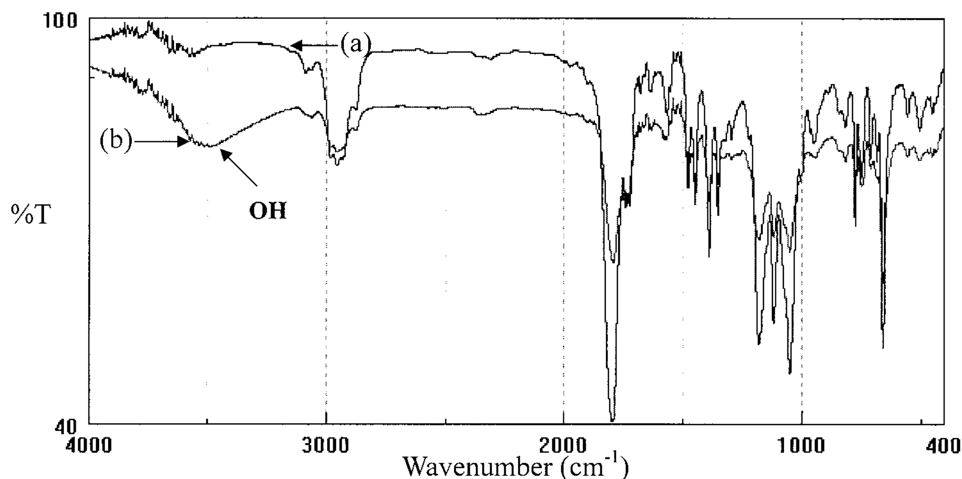


Figure 2 FTIR spectra of poly[(+)-**5**-*co*-MMA-*co*-*n*-BMA] with 10 wt % PAG (a) before and (b) after UV irradiation and subsequent PEB.

sized, respectively. Among these monomers, **6** and **10**, **7** and **11**, **8** and **12**, and **9** and **13** were enantiomer pairs. Each enantiomer pair had the same physical properties, including NMR and IR spectra. Diastereomeric monomers **6–9** should have very similar but not identical physical properties. All these steric isomeric monomers (**6–13**) in Scheme 2, however, had the same elemental analysis values. In studying the preparation and acid-catalyzed deprotection properties of the ketal compounds, we synthesized compounds **3** and **5**, as shown in Scheme 1, without further separation. As can be seen in Figure 1(a), compound **3** showed C—O—C and OH absorption at 1050 and 3450 cm^{-1}, respectively. After esterification, in Figure 1(b), the OH stretching absorption around 3450 cm^{-1} completely disappeared. Multiple C═O and C═C stretching bands appeared around 1784 and 1731 cm^{-1} and 1632 and 1678 cm^{-1}, respectively. The results suggest that several diasteromeric monomers existed in the products. ^{1}H-NMR and elemental analyses described in the Experimental section also supported the formation of the steric isomers.

Scheme 3 shows the copolymer structure synthesized in this investigation. Alicyclic camphyl groups with ketal structure were introduced onto the polymer side chains as acid-labile groups. Table I shows the results of the syntheses of compound **3** and monomer **5**. The optical activity of **3** and **5** was estimated to be $[\alpha]_D = +23.8$ ($C = 0.1$ dg/mL, THF) and $[\alpha]_D = +9.1$ ($C = 0.1$ dg/mL, THF), respectively. The compounds synthesized from racemic camphor were all achiral products. The results of the polymerization are summarized in Table II. Because the copolymers contained four components, the compositions of the synthesized copolymers could not be estimated from the elemental analyses. The compositions shown in Table II are feed comonomers molar ratios. All the polymers synthesized in Table II could be dissolved in alkaline aqueous solutions.

Scheme 4 shows the mechanism of the deprotection of the acid-labile ketal groups on the polymer side chains. To investigate the acid-catalyzed deprotection of the copolymers, we evaluated the FTIR spectra of poly[(+)-**5**-*co*-MMA-*co*-MAA-co-*b*-BMA] with 10 wt % PAG with and without UV irradiation and subsequent baking at 100°C for 2 min. As can be seen in Figure 2, the strength of the OH absorption increased after UV irradiation and PEB because of the decomposition of ketal groups.

The thermal properties and optical activities of the copolymers are summarized in Table III. After UV irradiation and PEB, there was an obvious decrease in the optical activity of the membranes. The results suggest that the chiral camphyl groups bonded on the polymer side chains were decomposed. In theory, the optical activity decreases with decreasing content of the chiral groups in the polymer. These results are

TABLE III
Thermal Properties and Optical Activities of the Polymers

Polymer	T_{dp} (°C)[a]	T_{dc} (°C)[b]	$[\alpha]^{25}$ [c]	
			Before UV	After UV[d]
1	92	208	1.8	0.9
2	89	178	3.5	1.3
3	88	155	6.8	2.1
4	97	221	—	—
5	93	215	—	—
6	99	209	—	—

[a] T_{dp} = deprotection temperature measured by differential scanning calorimetry.
[b] T_{dc} = decomposition temperature measured by TGA.
[c] Specific rotation, $C = 10$ mg/mL in THF.
[d] After UV irradiation and PEB.

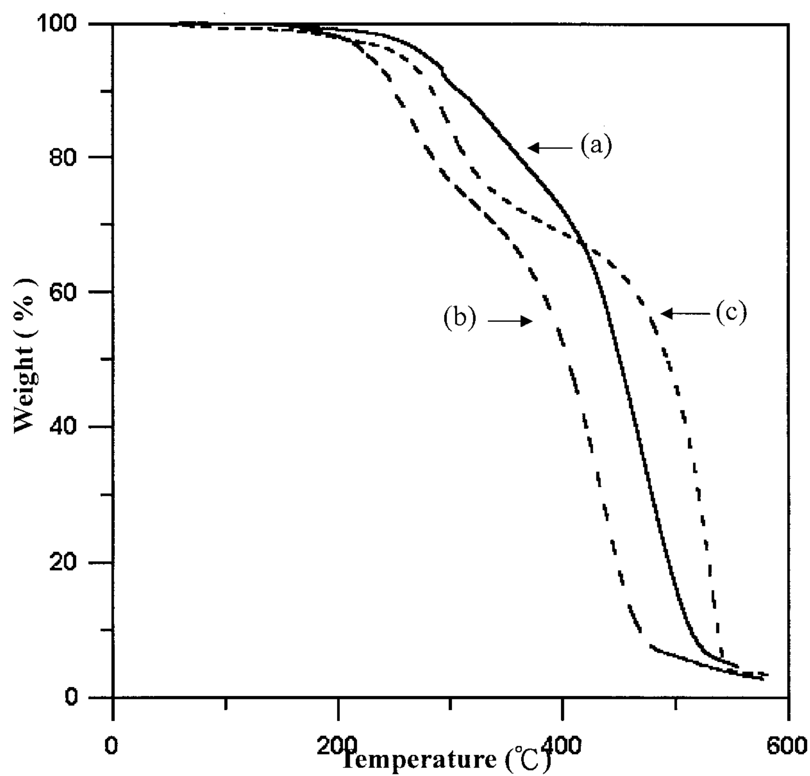


Figure 3 TGA curves (20°C/min) in nitrogen: (a) polymer **1**, (b) polymer **2**, and (c) polymer **3**.

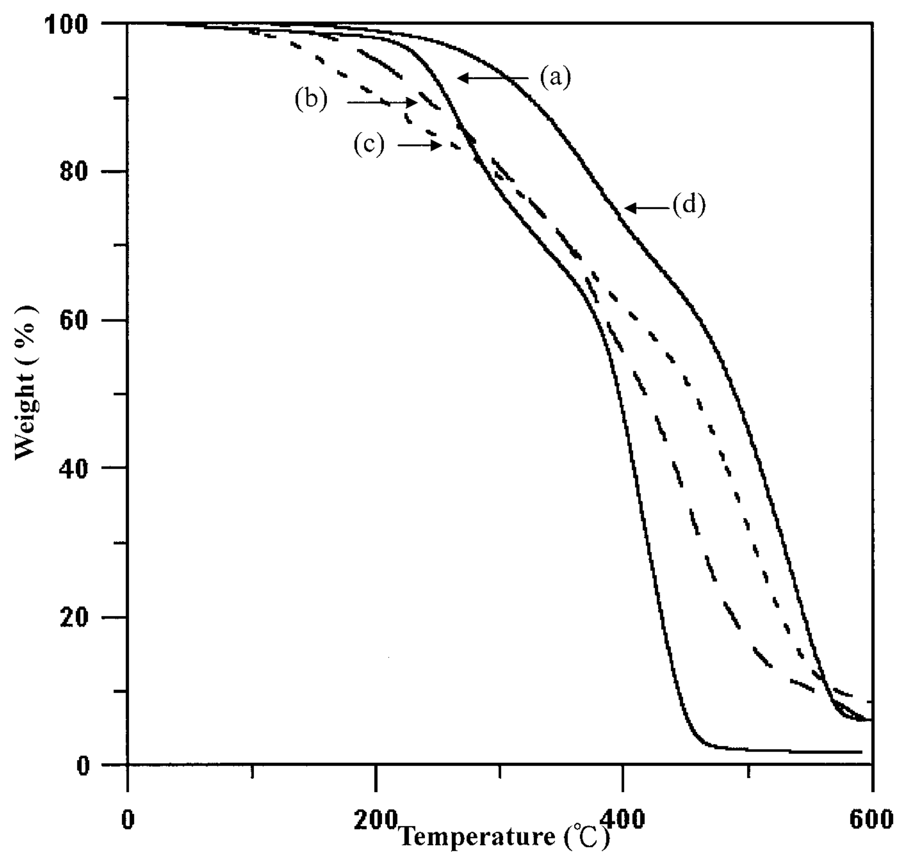


Figure 4 TGA curves of polymer **2**: (a) the neat polymer, (b) **2** with 10 wt % PAG before UV irradiation, (c) **2** with 10 wt % PAG after UV and PEB at 100°C for 2 min, and (d) **2** with 10 wt % PAG after UV irradiation and PEB at 120°C for 30 min.

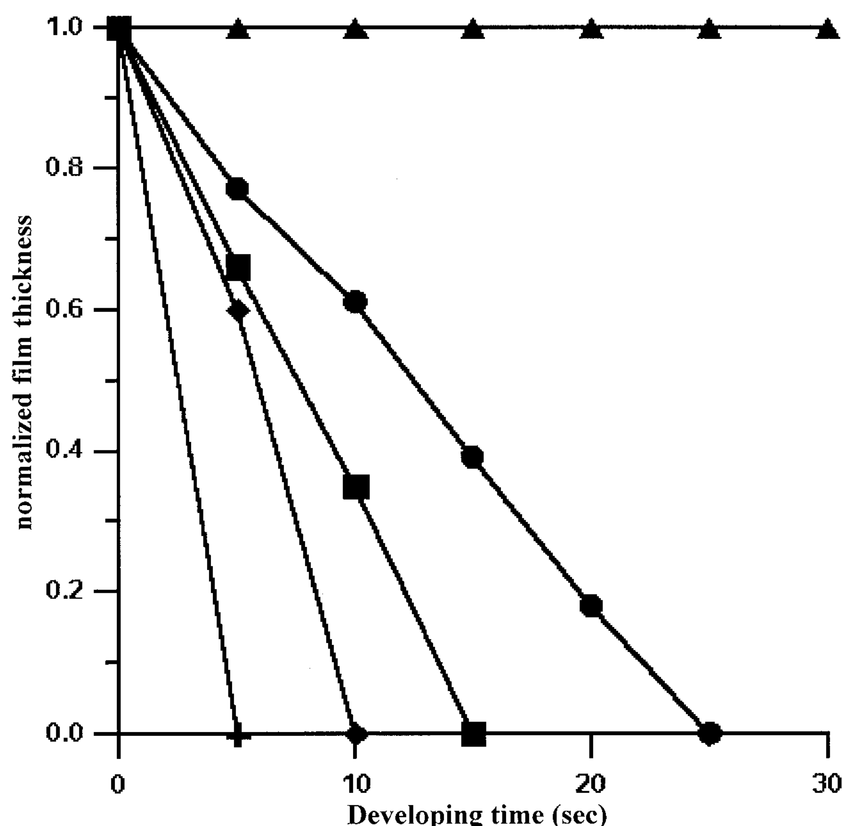


Figure 5 Dependence of the normalized polymer **5** film thickness on the development time in various concentrations of sodium carbonate: (+) 5, (♦) 3, (■) 1, (●), 0.5, and (▲) 0.1 wt %.

consistent with those shown in Figure 2. Moreover, the thermal resistances of the copolymers containing (+)-**5** were lower than those of polymers containing (±)-**5**. As previously described, it seems reasonable that the diastereomeric polymers obtained here had different physical properties.

Figure 3 shows the results of the thermogravimetric analysis (TGA) of polymers **1**, **2**, and **3** in nitrogen. Thermal deprotection occurred at the initial stage. The higher ketal content polymer **2** showed a large weight loss during the initial stage. Polymer **3** contained the highest amount of (+)-**5** and showed some degree of crosslinking due to the esterification of deprotected side groups. After deprotection, dehydrating esterification between carboxyl and hydroxyl groups may have occurred, leading to the crosslinking of the polymers.[20–22]

In investigating the acid-catalyzed dehydration occurring in the second stage, we explored the following three cases: TGA of polymer **2** with 10 wt % PAG before UV irradiation, after UV irradiation, and after UV irradiation followed by PEB at 120°C for 30 min. The results are shown in Figure 4. In comparison with curve a, the initial decomposition temperature of curves b and c decreases in the presence of PAG. The results suggest that both UV irradiation and thermal treatments may cause the generation of acidic protons. The existence of acidic protons may reduce the initial decomposition temperature. After UV irradiation and sufficient PEB at 120°C for 30 min, as shown in curve d, both the deprotection of ketal groups and the dehydration crosslinking of carboxyl groups occurred, effectively leading to the greater thermal resistance of the polymers.

After UV irradiation and PEB treatment, as shown in Scheme 4, camphor was formed as a deprotected product. Camphor could sublimate away from the membrane matrices during the PEB process, despite being a relatively large molecule.

To find a suitable developer, we investigated the solubility of polymer **5** in various concentrations of sodium carbonate. As Figure 5 shows, a 0.1 wt % sodium carbonate aqueous solution was a suitable developer for this system. Under these conditions, the photoresist could not be dissolved in the developer without UV irradiation and PEB treatment. After UV irradiation and PEB treatment, however, all the polymers dissolved completely within a few seconds.

Figure 6 shows the exposure curves of the photoresists consisting of polymers **1–6**. Compared with those polymers containing (±)-**5**, polymers with (+)-**5** expressed higher sensitivity and greater contrast. The results suggest that the deprotection of acid-labile groups in polymers **1–3** was faster than that in poly-

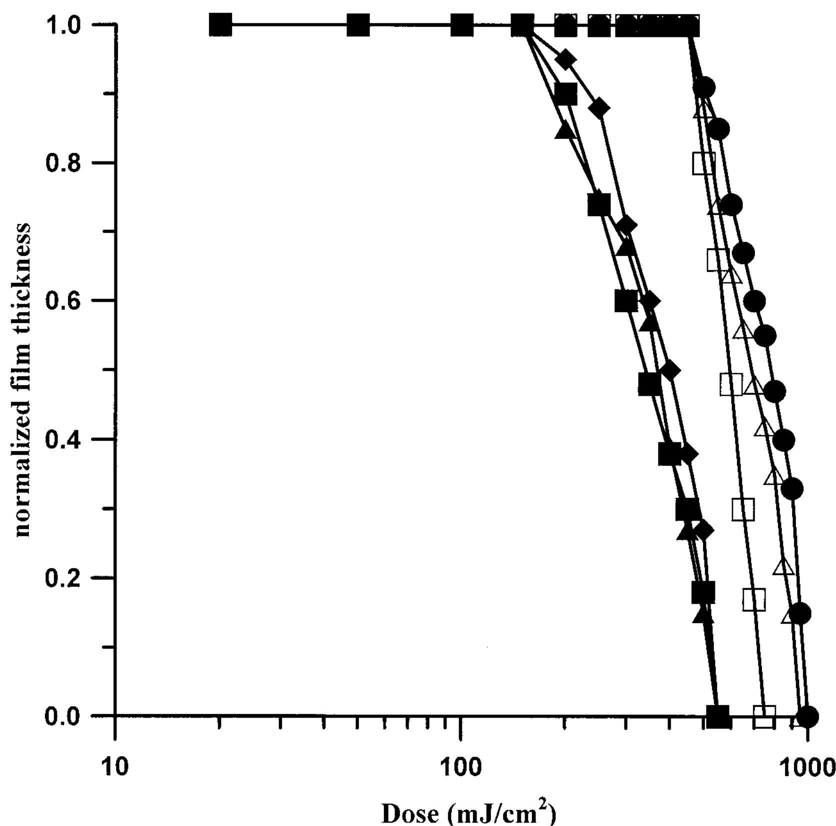


Figure 6 Exposure curves of positive photoresists consisting of various copolymers (developed in 0.1 wt % Na_2CO_3 and subjected to PEB at 100°C for 2 min): (♦) polymer **1**, (▲) polymer **2**, (■) polymer **3**, (●) polymer **4**, (□) polymer **5**, and (△) polymer **6**.

mers **4–6**. The results are consistent with those given in Table III: polymers with lower deprotection temperatures showed higher photosensitivity.

The etching rates of polymers **1–6**, poly(methyl methacrylate) (PMMA), and novolac resin were investigated with CH_4/Ar plasma etching. Figure 7 shows the results of the etching resistance of the polymers normalized to the novolac resin. Polymers **1–6**, containing alicyclic camphyl groups, provided better etching resistance than PMMA. The existence of alicyclic camphyl groups may have increased the etching resistance of the photoresists. The results are consistent with those polymers containing pendant alicyclic moieties described in the literature.[23–25]

SEM images of the lithographic performance were evaluated for polymer **2** (with 10 wt % PAG) spin-coated on a silicon wafer and irradiated with a KrF aligner through a line-and-space photomask. After exposure, the resist film was subjected to PEB at 100°C for 2 min, developed in a 0.1 wt % sodium carbonate developer, and then washed with distilled water. The relief pattern was heat-treated further at 150°C for 5 min. Figure 8 shows the results of lithography, by which a 0.3-μm line-and-space pattern was achieved.

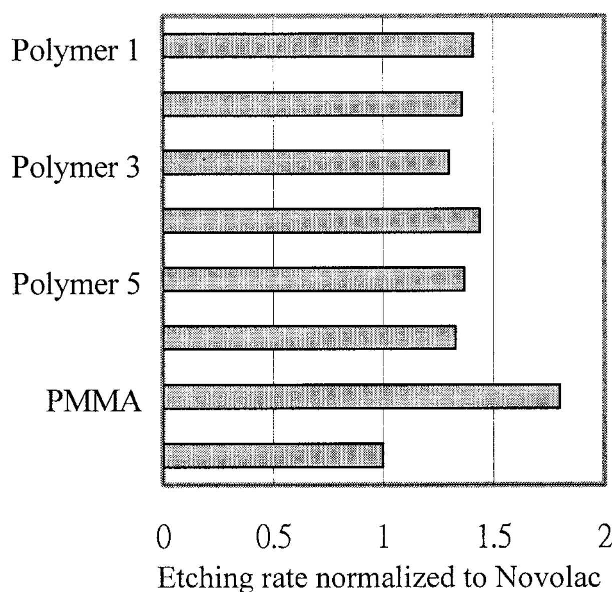
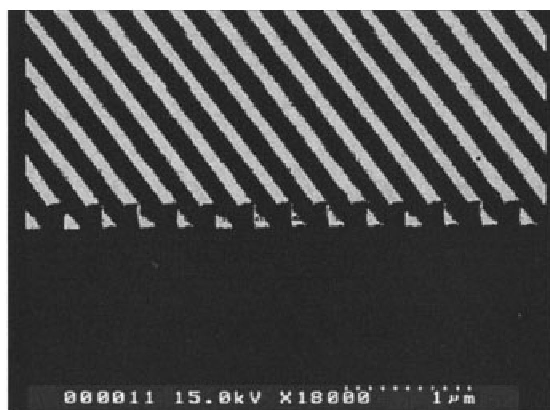
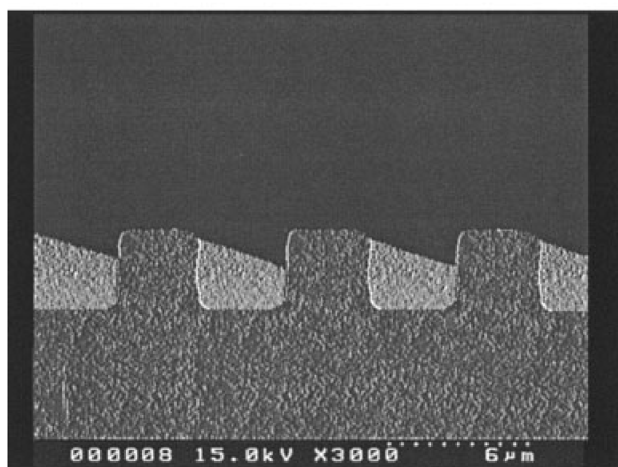


Figure 7 Etching resistance of polymers normalized to novolac resin.



(a)



(b)

Figure 8 SEM photographs of resolution patterns: (a) 0.3-μm line-and-space pattern and (b) 0.375-μm-diameter spot pattern.

CONCLUSIONS

Polymers with pendant ketal groups derived from (+)-camphor and (±)-camphor can be applied as acid-labile positive-tone photoresists. For the photoresist composition in this investigation, both UV irradiation and thermal treatments were shown to cause the generation of acidic protons leading to the deprotection of ketal groups. Diastereomeric copolymers containing (+)-**5** and (±)-**5** showed different physical properties, including thermal stability and photosensitivity. The existence of alicyclic camphyl groups increased the etching resistance of the resists. A 0.3-μm line-and-space pattern was achieved.

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