Synthesis and Characterization of Chiral Polyacrylates and Their Applications as Positive Tone Photoresists

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ABSTRACT: To estimate the effects of diastereomeric copolymers as photoresists, diastereomeric copolymers containing chiral and racemic bornyl methacrylates (BMAs) were synthesized. Both alicyclic BMAs were synthesized from (−)-borneol and (±)-borneol, and then copolymerized with *t*-butyl methacrylate (*t*-BMA), tetra-hydro-pyranyl methacrylate (THPMA), and α-methacry-loxy-γ-butyrolactone (MABL). The glass transition temperature of the copolymers was found to increase with an increase in the content of alicyclic bornyl groups in the copolymers. To investigate the effect of both the alicyclic butyrolactone and the bornyl groups on photosensitivity, thermal property, and etching resistance, the synthesized alicyclic copolymers were used to prepare photoresists with photoacid generators. The sensitivity and the contrast of the photoresists were calculated. This investigation demonstrated that the existence of alicyclic butyrolactone and bornyl groups increases the etching resistance of photoresists. It was also found that high stereo hindered bornyl structures disturb and restrict the mobility of the polymer chain, leading to an increase in the thermal stability of the polymers. A real pattern recording of photoresists with PR3 composition was performed; an optimal sensitivity of 20 mJ/cm^2 and resolution of 1 μm of positive tone photoresists with 1 μm thickness was achieved. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3776–3785, 2008

Key words: copolymerization; synthesis; photoresists; chiral

INTRODUCTION

There is great interest in organic films, stemming from their varied applications in corrosion resistance, nonlinear optics, information storage, microelectronic circuit fabrication, biosensors, and even drug delivery systems.[1–3] In the early days of research on 193 nm resists, the focus was mainly on acrylic polymers.[4,5] To improve the resistance of polymers against etching and hydrophilicity, many polymers with cyclic structures, such as cyclo-olefin-*co*-maleic anhydride (COMA), cyclo-olefin copolymer, and COMA-*co*-acrylate were developed.[6–11] However, these polymers were not easily synthesized. For example, synthesis must be catalyzed by rare elements such as transition metals. After the synthesis, it is difficult to remove metallic ions from the synthesized polymer.[12,13] Moreover, the synthesized products have excessively high absorbance and poor hydrophilicity, and thus, it is necessary to develop new polymers that lack these disadvantages.

Vinyl ether-maleic anhydride (VEMA) has advantages that can overcome the limitations of the aforementioned copolymers. For example, VEMA can be synthesized using a much easier method of radical polymerization. Resists made by VEMA have excellent adhesion to substrates, better resistance against etching than the acrylates, and lower absorbance than norbornene-series of polymers. In recent years, a few VEMA-related studies have been published.[14–18]

Because of the strong absorption of aromatic rings, which provide dry-etch resistance, conventional chemical-amplified resists based on phenol resin (248 nm) are completely opaque at 193 nm.[19–22] Thus, to solve these problems, new polymers exhibiting low optical density at 193 nm are necessary. Generally speaking, an appropriate polymer compound for creating photoresists for 193 nm lithography needs to meet five basic requirements: (1) high transparency for a 193 nm light source; (2) good thermoplasticity, e.g., high glass transition temperature (T_g); (3) high etch resistance; (4) good adhesion and development for its composition; and (5) it must contain acid-labile functional groups.

Positive working resists are generally utilized for semiconductor manufacturing. UV lithography at 365 nm (I-line) using novolak polymers and diazo-naphthoquinones as dissolution inhibitors is a currently established chip technology that has a resolution limit of about 0.35–0.30 μm. Lithography in the

far UV at 248 nm using *p*-hydroxystyrene polymers has also been established and has a resolution limit of 0.35–0.18 µm. There is a strong impetus for future photolithography at even shorter wavelengths, to decrease the resolution limit with decreasing wavelength (i.e., a resolution limit of 0.18–0.12 µm for 193 nm imaging). Photolithography using a 193 nm exposure wavelength (ArF excimer laser) is a leading candidate for future microelectronic fabrication using 0.18 and 0.13 µm patterns. Photolithography using a 157 nm exposure wavelength (obtained using an F_2 laser source) may be used for future microelectronic fabrication using design devices of 0.100 µm or less. The opacity of traditional near UV and far UV organic photoresists at 193 nm and shorter wavelengths precludes their use in single-layer schemes at these wavelengths.

To study the characteristics of functional monomers and polymers, a series of chiral dopants and cholesteric liquid crystal cells were synthesized and fabricated.[23–30] In earlier work, a novel crosslinking method for a negative tone photoresist comprised of pendant carboxyl groups in the presence of a photoacid was reported.[31] It is well known that high C/H content polymers can express high etching resistance for a photoresist.[32–36] In this investigation, functional polymers for photoresists were designed consisting of acid-labile, high C/H ratio containing alicyclic and steric hindered groups. To investigate the effect of alicyclic groups and configurational structures on photosensitive polymers, copolymers containing both chiral and racemic alicyclic units derived from borneol were synthesized and copolymerized with acid-labile comonomers. The molecular weight, copolymer composition, and thermal properties of the polymers were also determined. Positive tone photoresists consisting of synthesized polyacrylates bearing alicyclic segments were prepared. Sensitivity, contrast, resolution, and etching resistance of the photoresists were also investigated.

EXPERIMENTAL

Materials

Methacrylic acid (MAA; 99.5%) and propylene glycol monomethyl ether acetate (98.0%) were purchased from Tokyo Chemical Industry (TCI, Japan). Triethylamine (TEA, 99.0%), *p*-toluenesulfonic acid monohydrate (99.0%), 3,4-dihydro-2H-pyran (DHP, 99.0%), hydroquinone (99.0%), methyl methacrylate (MMA; 99.0%), (−)-borneol (98.0%), *t*-butyl methacrylate (*t*-BMA; 98.0%), α-bromo-γ-butyrolactone (95.0%), and tetramethylammonium hydroxide (TMAH) were purchased from Acros Chemical (Geel, Belgium), and were used without further purification. Tetrahy-

drofuran (THF; Tedia), Benzene (Tedia, Fairfield, OH), and other solvents were used without any further purification. 2,2′-Azobisisobutyronitrile (AIBN, 98%) was also purchased from Acros Chemical and was freshly recrystallized from methanol.

Measurements

FTIR spectra were recorded on a Jasco VALOR III (Tokyo, Japan) FTIR spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AMX-400 (Darmstadt, Germany) high-resolution NMR spectrometer. Optical rotations were measured at 30°C in THF using a Jasco DIP-370 polarimeter with the D-line of sodium (λ = 589 nm) with a reading to ±0.001°. The measurements were performed using 1% solutions of substances in THF. Elemental analyses were conducted with a Heraeus CHN-O (Darmstadt, Germany) rapid elemental analyzer. Gel permeation chromatography (GPC) measurements were carried out at 40°C on a Hitachi L-4200 (Osaka, Japan) instrument equipped with a TSK gel GMH and G2000H columns using $CHCl_3$ as an eluent. The rate of the elution was 1.0 mL/min; the instrument was calibrated with a polystyrene (PS) standard. Differential scanning calorimetry (DSC) was conducted with a Perkin-Elmer DSC 7 at a heating and cooling rate of 10°C/min in nitrogen atmosphere. Thermal decomposition temperature data were recorded under nitrogen atmosphere at a heating rate of 40°C/min with a thermogravimetric analyzer (TGA) Perkin-Elmer TGA 7. The UV–visible spectra of films of the photoresist on quartz substrates were measured with a Jasco V-550 UV-VIS spectrophotometer. The photoresist was exposed with the help of a Karl Suss MJB-3 aligner. The film thickness was measured with a Tencor Instrument alpha step-200 film thickness monitor. The dissolution rate is defined as changes in the photoresist film thickness per development time. Scanning electron microscope (SEM) microphotographs were measured with a JEOL HR-FESEM JSM-6700F (Osaka, Japan) instrument.

Synthesis of tetrahydropyranyl methacrylate (1)

A mixture was prepared by dissolving MAA (20 g, 0.2 mol) and pyridinium-*p*-toluenesulfonate (PPTS) (0.3 g, 1.2 mmol) in 120 mL of dichloromethane in a 250-mL flask equipped with a condenser and 23.4 g (0.2 mol); DHP was then added dropwise. The mixture was stirred at room temperature for 6 h. After completion of the reaction, the resulting product was washed with an aqueous solution of 5% potassium hydrogen carbonate. The oily phase was separated and dichloromethane was removed by using a rotary
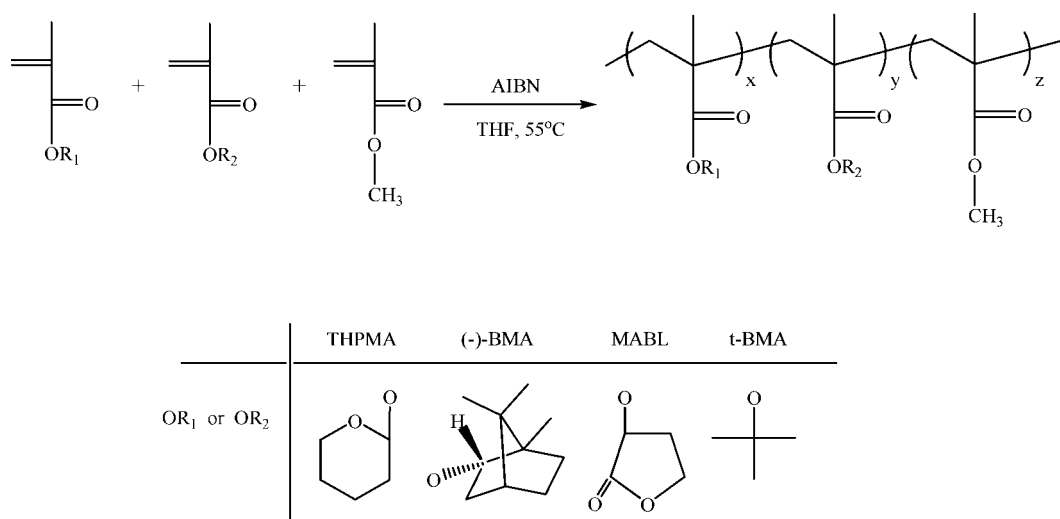
Scheme 1 Molecular structures of comonomers and copolymers.

evaporator. The crude product was then distilled at 50°C under 0.3 torr. An oily product was obtained.

Yield = 70%. FTIR (KBr pellet, v_{max}/cm^{-1}): 1116, 1158 (C—O), 1637 (C=C), 1725 cm^{-1} (C=O). ^{1}H NMR (CDCl$_3$, δ in ppm): 1.58–1.89 (6H, m, CH$_2$), 1.98 (3H, s, CH$_3$), 3.70–3.96 (2H, t, CH$_2$O), 5.62 (1H, d, CH=C), 6.06 (1H, t, OCHO), 6.19 (1H, d, CH=C). C$_9$H$_{14}$O$_3$ (170) Cald.: C 63.53; H 8.24. Found: C 63.62; H 8.21.

Synthesis of (−)-bornyl methacrylate (2)

(±)-Borneol (15.4 g, 0.1 mol), MAA (17.2 g, 0.2 mol), *p*-toluenesulfonic acid (1 g), hydroquinone (0.5 g), and 200 mL benzene were placed in a reaction bottle equipped with a Dean-Stark head and stirrer. The mixture was stirred and refluxed for 24 h. After completion of the reaction, the mixture was cooled down to room temperature and then washed with an aqueous solution of 5 wt % sodium hydrogen carbonate, and then dried on magnesium sulfate. After filtration, the solution was distilled at 120°C under 6 torr.

Yield = 75%. FTIR (KBr pellet, v_{max}/cm^{-1}): 1636 (C=C), 1717 (C=O), 2876, 2947 cm^{-1} (C—H). ^{1}H NMR (DMSO-d_6, δ in ppm): 0.77–0.95 (9H, m, CH$_3$), 1.15–2.27 (7H, m, CH$_2$), 1.85–1.90 (3H, s, CH$_3$), 4.79–4.83 (1H, t, HCO), 5.62 (1H, d, CH=C), 6.0 (1H, d, CH=C). [α]$_D$ = −41.3° (THF, c = 0.01 mg/mL). C$_{14}$H$_{22}$O$_2$ (222) Cald.: C 75.68; H 9.91. Found: C 75.36; H 9.98.

(−)-Bornyl methacrylate [(±)-BMA] was synthesized using procedures similar to those described above. The product revealed the same physical properties as those of (−)-BMA. However, it revealed no specific rotation.[33]

Synthesis of α-methacryloxy-γ-butyrolactone (3)

α-Bromo-γ-butyrolactone (16.4 g, 0.1 mol), MAA (17.2 g, 0.2 mol), and 150 mL of methyl isobutyl ketone were placed in a 250-mL reaction bottle equipped with a condenser. TEA (30.3 g, 0.3 mol) was added dropwise to the above mixture in the reaction bottle at room temperature. This mixture was then stirred at room temperature for 10 h. After completion of the reaction, the precipitate was removed by filtering. The filtrate was washed with an aqueous solution of 5 wt % sodium hydrogen carbonate and then dried on magnesium sulfate. After removing the methyl isobutyl ketone, the residue was distilled at 88°C under 0.3 torr.

Yield = 70%. FTIR (KBr pellet, v_{max}/cm^{-1}): 1160 (C—O), 1635 (C=C), 1727, 1785 (C=O), 2921, 2970 cm^{-1} (C—H). ^{1}H NMR (CDCl$_3$, δ in ppm): 1.93 (3H, s, CH$_3$), 2.27–2.75 (2H, m, CH$_2$), 4.25–4.49 (2H, t, CH$_2$O), 5.42–5.47 (1H, t, OCHO), 5.65 (1H, d, CH=C), 6.17 (1H, d, CH=C). C$_8$H$_{10}$O$_4$ (170) Cald.: C 56.47; H 5.88. Found: C 56.41; H 5.92.

Preparation of copolymers

Copolymers were obtained by the copolymerization of monomers in 2-ethoxy ethanol in the presence of 1 mol % AIBN at 55°C for 6 h. These comonomers were poured into a glass polymerization tube equipped with a sealing cap, which was degassed in vacuum by using a freeze–thaw technique, and then sealed. After completion of polymerization, the copolymers were precipitated from a large amount of water/methanol (1 : 1 volume) solution, thoroughly washed with distilled water, and then were dried *in vacuo*. The structures of copolymers are shown in Scheme 1.

TABLE I
Results of Polymerization of THPMA, (−)-BMA, and MMA[a]

Polymer	$x_o/y_o/z_o$[b]	AIBN (mol %)	Yield[c] (%)	M_w[d] ($\times 10^4$)	M_w/M_n[d]	T_g[e] (°C)	$x/y/z$[f]	$[\alpha]_D$[g]
P1	50/0/50	1	84	4.63	1.92	116	30/0/70	0
P2	33/33/34	1	68	5.80	1.63	135	29/31/40	−12.5
P3	33/33/34	10	59	2.57	2.13	124	30/29/41	−18.3
P4[h]	33/33/34	1	42	0.90	1.65	133	25/32/43	−21.7
P5[h]	50/25/25	1	33	0.89	1.54	127	44/26/30	−10.6
P6[i]	33/33/34	1	72	5.20	1.65	125	30/29/41	0
P7[i]	33/33/34	10	52	2.41	2.21	112	32/26/42	0
P8[h,i]	33/33/34	1	65	0.78	1.82	114	26/28/46	0

[a] In THF at 55°C for 6 h.
[b] Feed molar ratio of monomers.
[c] Isolated polymers.
[d] Determined by GPC.
[e] Glass transition temperature, determined by DSC at 10°C/min under N_2.
[f] Polymer composition, evaluated by elemental analysis.
[g] Specific rotation of polymers, measured at 30°C.
[h] n-Butyl mercaptan 0.5 mol % was added as chain transfer agent.
[i] (±)-BMA was used.

Exposure method

A photosensitive solution was prepared by dissolving copolymers (1.0 g) and triarylsulfonium hexafluoro-antimonate [photoacid generator (PAG), 9.0 $\times 10^{-2}$ g] in 10 mL of THF. The photosensitive solution was filtered by a 0.3-μm filter, then spin coated on a silicon wafer plate at 1000 rpm for 10 s and then at 2500 rpm for 20 s. The polymer film thus obtained was prebaked at 90°C for 3 min. The photoresist was exposed with a Karl Suss MJB-3 aligner. After exposure, the resist was postbaked at 120°C for 10 min, and then developed by immersing it in 2.38 wt % TMAH developer for 30 s.

RESULTS AND DISSCUSSION

Physical properties of polymers

To estimate the differences caused by various configurational factors, both chiral and racemic alicyclic monomers derived from borneol were synthesized and copolymerized with acid-labile comonomers. The molecular structures of comonomers and copolymers are shown in Scheme 1. The results of polymerization are summarized in Tables I–IV. The chiral (−)-BMA was synthesized through the esterification of MAA and the corresponding hydroxyl group [(−)-borneol] using p-toluenesulfonic acid as a catalytic system in dry benzene. The synthesized chiral (−)-BMA was then copolymerized with other comonomers. The synthesized monomers were identified with FTIR, NMR, and elemental analysis.

Table I shows the results of polymerization of tetrahydropyranyl methacrylate (THPMA), (−)-BMA, (±)-BMA, and MMA. The composition of the polymers was calculated using elemental analysis and the result was further confirmed by ^{1}H NMR analyses. The weight-average molecular weights (M_w) of these synthesized polymers, determined by GPC using monodispersed PS as a calibration standard, were in the range of 6.5×10^3 to 6.59×10^4 g/mol, with a polydispersity index in the range of 1.29–2.31. The specific rotation of the chiral polymers was esti-

TABLE II
Results of Polymerization of THPMA, MABL, and MMA[a]

Polymer	$x_o/y_o/z_o$[b]	AIBN (mol %)	Yield[c] (%)	M_w[d] ($\times 10^4$)	M_w/M_n[d]	T_g[e] (°C)	$x/y/z$[f]
P9	33/33/34	1	53	5.29	2.16	104	29/27/44
P10	33/33/34	10	37	2.31	2.31	103	27/30/43
P11[g]	33/33/34	1	30	0.73	1.56	98	24/34/42
P12[g]	50/25/25	1	26	0.79	1.45	102	48/22/30

[a] In THF at 55°C for 6 h.
[b] Feed molar ratio of monomers.
[c] Isolated polymers.
[d] Determined by GPC.
[e] Glass transition temperature, determined by DSC at 10°C/min under N_2.
[f] Polymer composition, evaluated by elemental analysis.
[g] n-Butyl mercaptan 0.5 mol % was added as chain transfer agent.

TABLE III
Results of Polymerization of *t*-BMA, (−)-BMA, and MMA[a]

Polymer	$x_o/y_o/z_o$[b]	AIBN (mol %)	Yield[c] (%)	M_w[d] (×10⁴)	M_w/M_n[d]	T_g[e] (°C)	$x/y/z$[f]	$[\alpha]_D$[g]
P13	33/33/34	1	71	6.59	1.92	198	24/43/33	−22.6
P14	33/33/34	10	49	3.21	1.62	194	21/45/34	−15.7
P15[h]	33/33/34	1	21	0.84	1.67	191	23/42/35	−17.9
P16[h]	50/25/25	1	15	0.77	1.29	193	46/29/25	−17.3
P17[i]	33/33/34	1	73	6.14	2.05	190	26/40/34	0
P18[i]	33/33/34	10	54	3.02	1.84	188	18/42/40	0
P19[h,i]	33/33/34	1	58	0.72	2.11	182	28/35/37	0

[a] In THF at 55°C for 6 h.
[b] Feed molar ratio of monomers.
[c] Isolated polymers.
[d] Determined by GPC.
[e] Glass transition temperature, determined by DSC at 10°C/min under N_2.
[f] Polymer composition, evaluated by elemental analysis.
[g] Specific rotation of polymers, measured at 30°C.
[h] *n*-Butyl mercaptan 0.5 mol % was added as chain transfer agent.
[i] (±)-BMA was used.

mated and the results are summarized in Table I. Polymer 1 (P1) is an achiral polymer that contains no chiral segments. Polymerization of racemic (±)-BMA produced only optically inactive polymers P6 to P8. The glass transition temperature (T_g) was recorded using DSC at 10°C/min in an inert (nitrogen gas) atmosphere. The addition of the chain transfer agent *n*-butyl mercaptan showed a reduction in the molecular weight. For polymers P4 and P5, the glass transition temperatures were found to be higher than that of P1, although the molecular weights of these polymers were much lower. The results suggest that the existence of the stereo-hindered bulky bornyl group might disturb and restrict the mobility of the polymer chains, leading to an increase in the glass transition temperatures.[37] Similar phenomena could also be seen for P2 and P3 polymers (Table I). A comparison of glass transition temperatures between the chiral copolymers (P2, P3, and P4) and the racemic copolymers (P6, P7, and P8) revealed that the temperatures of the chiral copolymers were 10–19°C higher than the racemic copolymers. This might be due to differences in molecular weight, molecular arrangement order, or polymer composition.[38] Chiral polymers consist of only one configurational form of the molecule. Contrary to this, optically inactive racemic polymers consist of a pair of enantiomers. The molecular stacking order of the enantiomeric monomers might be different and may dictate the thermal stability of the polymers. The relationship between each set of polymers P2/P6, P3/P7, and P4/P8 can be considered diastereomeric, and reveals different physical properties.

To evaluate the effect of butyrolactone groups on the photoresist, polymerization of THPMA, α-methacryloxy-γ-butyrolactone (MABL), and MMA was performed. The results are summarized in Table II. The glass transition temperatures of the polymers were similar. Table II shows that without the existence of chiral stereo-hindered bornyl groups in the polymer, the glass transition temperature of the polymer P1 was lower than that of P2 to P8, even though the molecular weight of P9 was much higher than P4, P5, and P8. However, the glass transition temperature of the polymer P9 was lower than P4 and P8. The results suggest that sterically hindered

TABLE IV
Results of Polymerization of *t*-BMA, MABL, and MMA[a]

Polymer	$x_o/y_o/z_o$[b]	AIBN (mol %)	Yield[c] (%)	M_w[d] (×10⁴)	M_w/M_n[d]	T_g[e] (°C)	$x/y/z$[f]
P20	33/33/34	1	58	5.10	1.40	176	30/44/26
P21	33/33/34	10	42	3.23	1.39	173	27/48/29
P22[g]	33/33/34	1	30	0.77	1.37	171	25/45/30
P23[g]	50/25/25	1	22	0.65	1.35	169	45/29/26

[a] In THF at 55°C for 6 h.
[b] Feed molar ratio of monomers.
[c] Isolated polymers.
[d] Determined by GPC.
[e] Glass transition temperature, determined by DSC at 10°C/min under N_2.
[f] Polymer composition, evaluated by elemental analysis.
[g] *n*-Butyl mercaptan 0.5 mol % was added as chain transfer agent.
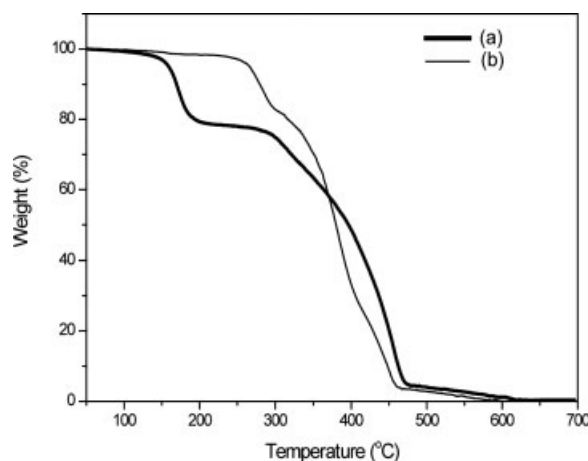
Figure 1 TGA thermogravimetric curves of (a) P9 and (b) P13.

bornyl groups might disturb the mobility of the polymer chain, leading to an increase in glass transition temperatures.

For studying the photosensitivity of the copolymers containing acid-labile isobutyl groups, copolymerization of *t*-BMA, (−)-BMA, and MMA was investigated. The results are presented in Table III. Because of the copolymerization rate of comonomers, the compositions of the copolymers shown in Table III were quite different than those shown in Table I. The bornyl group content in P13 to P19 was much higher than that of P2 to P8. It was observed that stereo-hindered *t*-butyl groups further disturb the mobility of the polymer chain and might raise the glass transition temperature. Table III shows that the glass transition temperatures of the copolymers were higher than 182°C. It was observed that an increase in the glass transition temperature of the polymers enhanced the reliability of the photoresist patterns. Figure 1(a,b) shows the thermogravimetric curves for polymers P9 and P13, respectively. As seen in the curves, the first degrading stage might be caused by the deprotection of both the acid-labile tetrahydropyranyl and *t*-butyl pendant groups. Because of their molecular structures, thermal degradation of the tetrahydropyranyl and *t*-butyl group generates acid residues, thereby leaving a main chain segment. Because of these phenomena, a mass decrease of about 23% for P9 and less than 20% for P13 in the TGA curve could be observed, even though the contents of the tetrahydropyranyl and *t*-BMA were 29% and 24%, respectively. For other polymers, similar degradation of acid-labile groups could be seen in the TGA thermogravimetric curves. As can be seen from the curves, the deprotection of tetrahydropyranyl occurred at a lower temperature and the degradation was faster than that of the *t*-butyl group. Furthermore, for comparing the chiral polymers, racemic (±)-BMA was used to prepare

optically inactive copolymers P17, P18, and P19. As presented in Table III, the molecular weights and the glass transition temperatures of the racemic copolymers were both smaller than those of the chiral polymers. This could be due to reactivity differences between chiral monomers and a pair of enantiomers during polymerization with other comonomers.

To compare the photosensitivity of the copolymers shown in Table II, copolymerization of *t*-BMA, MABL, and MMA was performed. The results are summarized in Table IV. Also in this case, due to the high molar content of MABL, the glass transition temperatures of the copolymers were observed to be higher than that of the polymers shown in Table II. As shown in Scheme 1, alicyclic copolymers were expected to reduce the absorption around deep UV and increase the etching resistance when used as a photoresist.[6]

Improvement of photoresist properties

To improve the sensitivity and contrast of photoresists, the molecular weights of polymers used in photoresists are usually lower than 10,000. The data on thermal decomposition temperatures of P4, P8, P11, P15, P19, and P22 are summarized in Table V. The polymer pairs of P4/P8/P11 and P15/P19/P22 had similar acid-labile groups. The thermal stability of P4 was found to be 27°C higher than that of P11. This result suggested that bornyl groups were bulkier and more hindered than butyrolactone. The thermal stability of P4 was observed to be 18°C higher than P8. This might be due to differences in the molecular arrangement order. Essentially, these polymers are different, and the relatively lower molecular weight and different composition of P8 should also be considered. Similar results could also be seen when P15 was compared with P19 and P22. The decomposition temperature of P15 was 11°C and 16°C higher than P19 and P22, respectively. Table V shows that the structural effects on thermal stability were quite consistent and similar to those shown in Tables I–IV. The results suggested that highly stereo-hindered structures might disturb and restrict the

TABLE V
Thermal Properties of Copolymers[a]

No.	Copolymer	T_g (°C)	T_d (°C)[a]
P4	Poly(THPMA-*co*-(−)-BMA-*co*-MMA)	133	188
P8	Poly(THPMA-*co*-(±)-BMA-*co*-MMA)	114	170
P11	Poly(THPMA-*co*-MABL-*co*-MMA)	98	161
P15	Poly(*t*-BMA-*co*-(−)-BMA-*co*-MMA)	191	265
P19	Poly(*t*-BMA-*co*-(±)-BMA-*co*-MMA)	182	254
P22	Poly(*t*-BMA-*co*-MABL-*co*-MMA)	171	249

[a] Decomposed temperature at 5% weight loss measured by TGA.

TABLE VI
Sensitivity and Contrast of Photoresists[a]

Entry	Photoresist	Polymer	Solvent[b]	Sensitivity (mJ/cm^2)	Contrast γ
1	PR1[c]	P4	ECS	126	2.10
2	PR1	P4	ECS	72	4.09
3	PR2	P8	ECS	94	3.82
4	PR3	P11	γ-BLO	60	3.66
5	PR4	P15	ECS	114	3.32
6	PR5	P19	ECS	128	3.16
7	PR6	P22	γ-BLO	96	2.93

[a] In the presence of 10 wt % photo acid generator (PAG), film thickness is 1.5 μm.
[b] 2-Ethoxyethanol (ECS) and γ-butyrolactone (γ-BLO) were used; 15 wt % polymer solutions were prepared.
[c] In the presence of 1 wt % PAG.

mobility of the polymer chain, leading to an increase in the thermal stability of the polymers.

The synthesized copolymers were used to investigate the physical properties of the chemically amplified photoresists. The composition, sensitivity, and contrast of the photoresists are summarized in Table VI. As can be seen from entries 1 and 2 of Table VI, an increase in the amount of acid obviously increased both the sensitivity and the contrast of the photoresists. A higher acidic proton concentration might accelerate the deprotection of the photoresists. Table V shows that both the polymer pairs of P4/P8/P11 and P15/P19/P22 contained the same acid-labile groups. The existence of sterically hindered bornyl groups in entries 3 and 6 of Table VI seemed to decrease the sensitivity but increase the contrast of the photoresists. A comparison of entries (3, 4) and (6, 7) suggests that restriction on side chain mobility might intersect the polymer chains and decrease the solubility of the polymers in the developer, leading to a decrease in sensitivity. A comparison of entries 2 and 5 with entries 3 and 6 of Table

VI reveals that the chiral polymers consisting of only one configurational isomer were higher both in sensitivity and contrast. These results suggest that molecular arrangement order is one of the factors that improve photoresist properties. As described earlier, these basic polymers are diastereomeric and usually reveal different physical properties from each other. Besides the molecular arrangement order, the molecular weight and composition of the copolymers could also be expected to affect the physical properties of the photoresists.

Effects of postexposure baking temperature

The results of the effects of postexposure baking (PEB) temperature on normalized deprotection degree are depicted in Figures 2 and 3. Figure 2 demonstrates that the normalized deprotection temperature of the polymers increased with the PEB temperature and equalized at about 90°C for PR1 and PR3. However, as seen in Figure 3, the normalized deprotection temperature of the polymers in
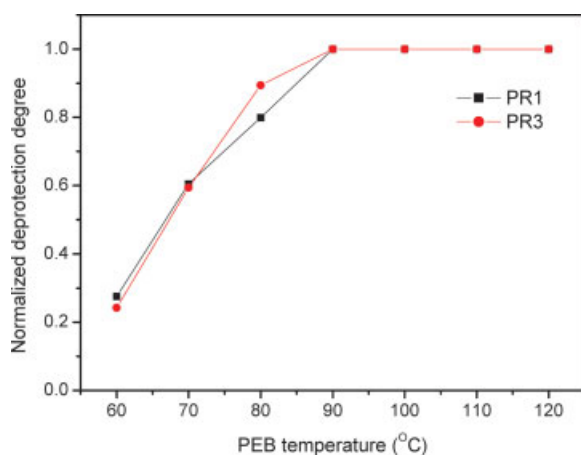

Figure 2 Effect of PEB temperature on the normalized deprotection degree of polymers containing acid-labile tetrahydropyranyl groups. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
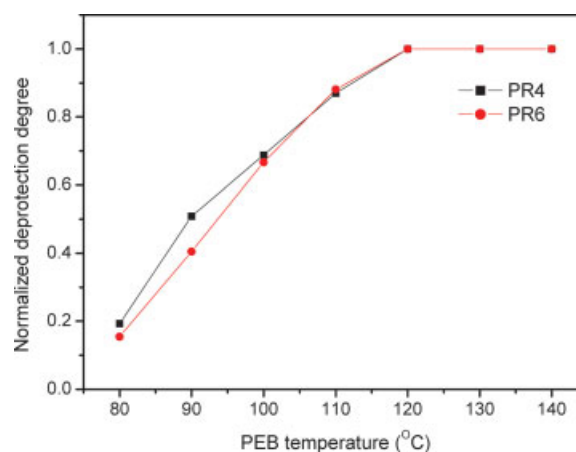

Figure 3 Effect of PEB temperature on the normalized deprotection degree of polymers containing acid-labile t-butyl groups. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
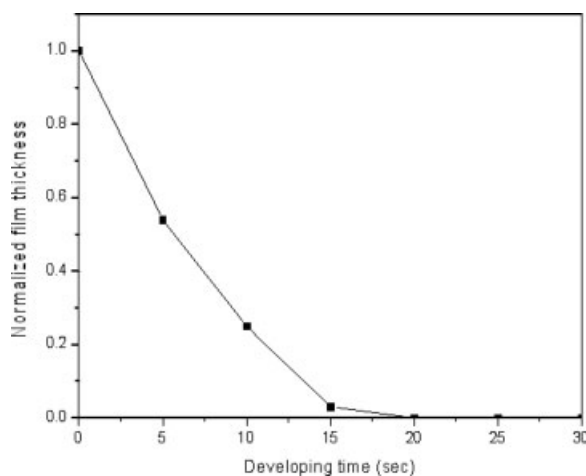
Figure 4 Dependence of normalized PR3 film thickness on developing time after UV exposure and PEB in 2.38% TMAH.

PR4 and PR6 increased with the PEB temperature and equalized at around 120°C. In general, it was observed that an increase in temperature increases both the mobility of the molecules and the acid-catalyzed deprotection of the acid-labile groups. These results reveal that sensitivity towards the deprotection of the acid-labile tetrahydropyranyl groups is faster than that of *t*-butyl groups. The results are consistent with those shown in Figure 1.

It was observed that after UV exposure and post-baking, the deprotected polymers were easily soluble in the developer. Figure 4 shows the dependence of normalized film thickness of the photoresist on developing time. From this curve, an appropriate developing time of 20 s was estimated. An aqueous solution of 2.38% TMAH was used as the developer. In principle, the higher the concentration of alkaline in aqueous solution is, the faster the dissolution rate. Figure 5 shows that increasing the quantity of PAG
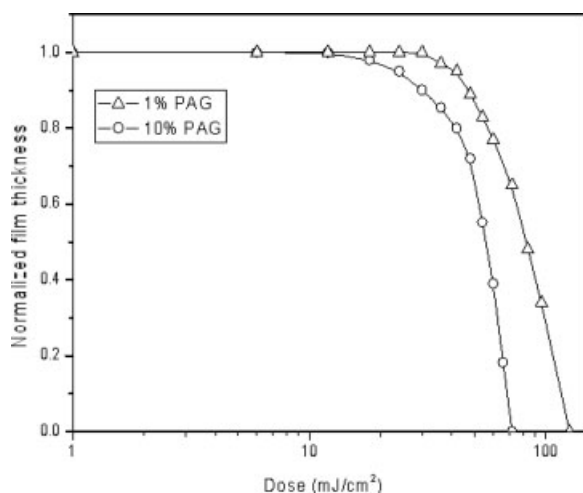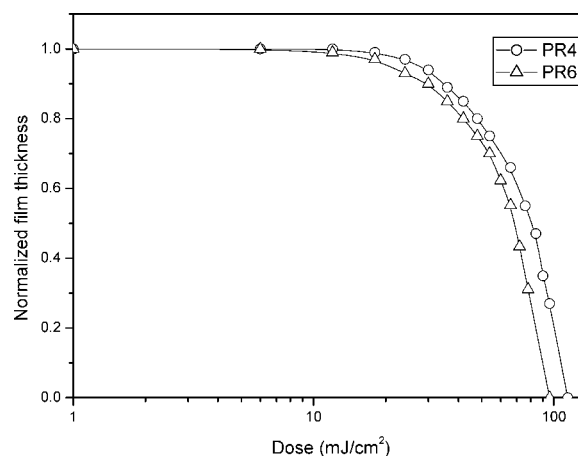

Figure 6 Exposure characteristic curves of PR4 and PR6.

generally accelerates the deprotection of the photoresist, leading to an increase in photosensitivity and contrast.

The exposure characteristic curves of PR4 and PR6 are depicted in Figure 6. Detailed sensitivity and contrast are listed in Table VI. Figure 7(a) shows a
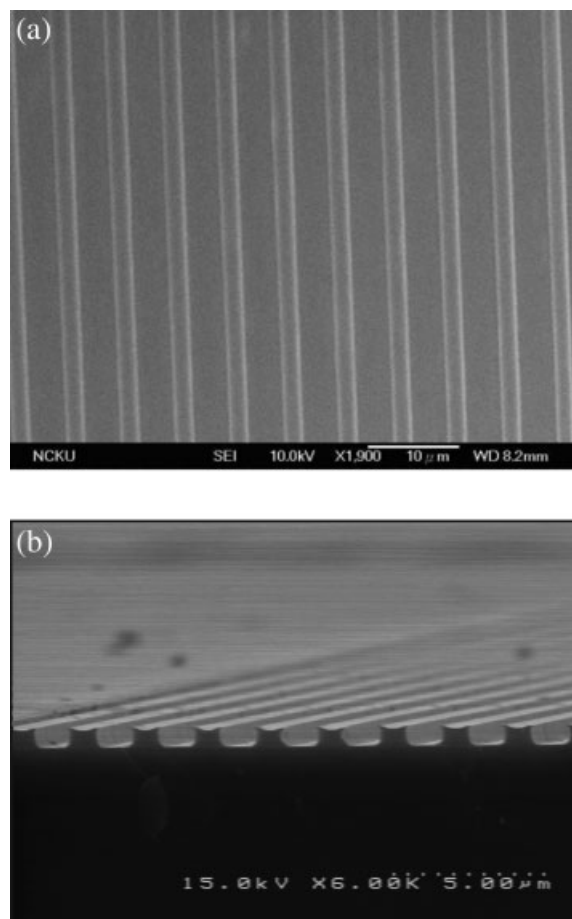

Figure 7 (a) Line and space pattern of PR3 with a 1 μm film thickness, exposed to 20 mJ/cm²; (b) side view of PR3 with 1 μm resolution.

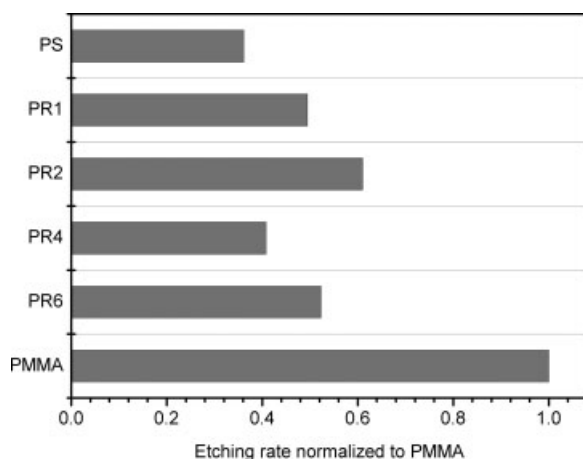**Figure 5** Exposure characteristic curve of PR1.

Figure 8 Etching rate of prepared photoresists normalized to PS and PMMA. $CF_4 : Ar = 50 : 5$ standard cubic centimeters per minute gas flow, 60 mtorr, 300 W, 300 s treatment.

line and space pattern of PR3 with a 1 μm film thickness. As seen in Figure 7(b), an optimal sensitivity of 20 mJ/cm^2 and a positive tone photoresist resolution of 1 μm were achieved with a 1 μm thickness of PR3. The results in this investigation demonstrate that synthesized alicyclic copolymers could be used for chemically amplified positive tone photoresists.

Etching resistance of photoresists

The etching resistance of photoresists PR1, PR2, PR4, and PR6, poly(methyl methacrylate) (PMMA), and PS was investigated with CH$_4$/Ar plasma etching. Figure 8 demonstrates the results of the etching rates of the polymers normalized to PS and PMMA. It was found that the photoresists PR1, PR2, PR4, and PR6 containing alicyclic groups revealed better etching resistance than that of PMMA. It was therefore established that the existence of alicyclic butyrolactone and bornyl groups could increase the etching resistance of the resists. As shown in Figure 8 and Table V, copolymer PR4 revealed the highest thermal and plasma resistance. The results suggest that high sterically hindered chiral bornyl groups might intersect the polymer chains and disturb chain mobility, leading to an increase in thermal stability, etching resistance, and contrast of the photoresists. A chiral polymer is a homopolymer that usually consists of only one of the configurational isomers. A racemic polymer consists of a pair of enantiomers. After polymerization of racemic monomers, the molecular arrangement order is quite different from that of the chiral homopolymer. In theory, the relationship between a chiral polymer and the racemic polymer is not at all enantiomeric. As described in this investigation, both types of polymer usually reveal different physical properties.

CONCLUSIONS

Functional polymers containing acid-labile, alicyclic, sterically hindered segments were synthesized. The existence of sterically hindered alicyclic butyrolactone and bornyl groups in polymers was found to increase their glass transition temperature. The contrast and the etching resistance of photoresists containing chiral polymers bearing bornyl groups were significantly improved. This investigation demonstrates that polymers synthesized from optically inactive racemic monomers are diastereomerically different from those polymers synthesized from chiral monomers. The synthesized diastereomeric polymers revealed different physical properties. The optimal sensitivity of 20 mJ/cm^2 and a resolution of 1 μm with the positive tone photoresist with 1 μm thickness using PR3 were achieved.

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