Synthesis of Alicyclic Polymers and Characterization of Chemical Amplified Positive Photoresists Having the Same

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ABSTRACT: To investigate the effects of cyclic structures of polymers on the physical properties of photoresist, a series of copolymers consisting of various comonomers selected from 3,6-endo,oxo-1,2,3,6-tetrahydrophthalic anhydride (THPA), bornyl methacrylate (BMA), methacrylic acid (MA), *t*-butyl methacrylate (*t*-BMA), and 2-norborene (NB) was synthesized. The molecular weight, glass transition temperature, and the components of the synthesized copolymers were estimated. Photoresists consisting of the synthesized polymers and photoacid generator were prepared. The dependence of the molecular structures on the developers was investigated. The exposure characteristic curves of the photoresists were studied. The existence of the alicyclic comonomers was clearly found to increase the plasma resistance of the photoresist. The sensitivity, contrast, and exposed real image of the prepared photoresists were all investigated. The results obtained suggest that the alicyclic polymers synthesized in this investigation could be used as positive tone photoresists. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1505–1514, 2005

Key words: copolymerization; chiral; photoresists; synthesis; structure

INTRODUCTION

An increase in the processor speed attained by the development of microelectronic devices with higher integration density in the electronic industry has led to a demand for further improved radiation-sensitive compositions. That is, an improvement in properties, such as resolution of photoresists and dimensional accuracy of images, has been required for satisfying demands in the microelectronic device production industry. According to the Rayleigh's equation

$$R = k\lambda / NA \tag{1}$$

wherein R denotes the ultimate resolution, k is a constant, λ is the wavelength of the light source used in exposure, and NA is the numerical aperture of the illuminating optical system, use of a light source having a shorter wavelength in exposure can most effectively enhance the ultimate resolution. This has been effectively applied to the transition of irradiation technology from g-line (436 nm)[1–3] to i-line (365 nm)[4–6] and has pushed the resolution limits of conventional near-UV irradiation technology[7–9] to <0.30 μm. With the need to produce even smaller features, shorter wavelength radiation, such as deep ultraviolet (DUV) radiation (150–320 nm),[10–12] has been employed. Photons generated from DUV radiation exhibit higher energy than those generated from near UV radiation sources. Therefore, the number of photons per unit energy is smaller, leading to a demand for radiation-sensitive compositions with higher sensitivity.

Radiation-sensitive compositions, called chemically amplified photoresists, are known in the art and are advantageous in that the catalytic imaging process can provide high photosensitivity. By virtue of high photosensitivity and high resolution, the chemically amplified radiation-sensitive compositions are being substituted for conventional radiation sensitive compositions and are being spread.[13–17] The chemically amplified radiation-sensitive compositions comprise a radiation-sensitive acid-generating agent (photoacid generator, PAG), which generates an acid. Upon exposure, this PAG releases an acid which catalyzes a layer dissolution reaction in the case of positive-working photoresists and catalyzes a crosslinking reaction in the case of negative-working photoresists.

The above-described chemically amplified resist can be largely classified into (1) a three-component system made of an alkali-soluble resin, a photoacid generator, and a dissolution-inhibiting compound to the alkali-soluble resin and having an acid-decomposing group[18,19]; (2) a two-component system made of a resin having a group that becomes alkali soluble by being decomposed by the reaction acid, and a photoacid generator[20,21]; and (3) a hybrid system made of a resin having a group that becomes alkali soluble by being decomposed by the reaction acid, a low-molec-

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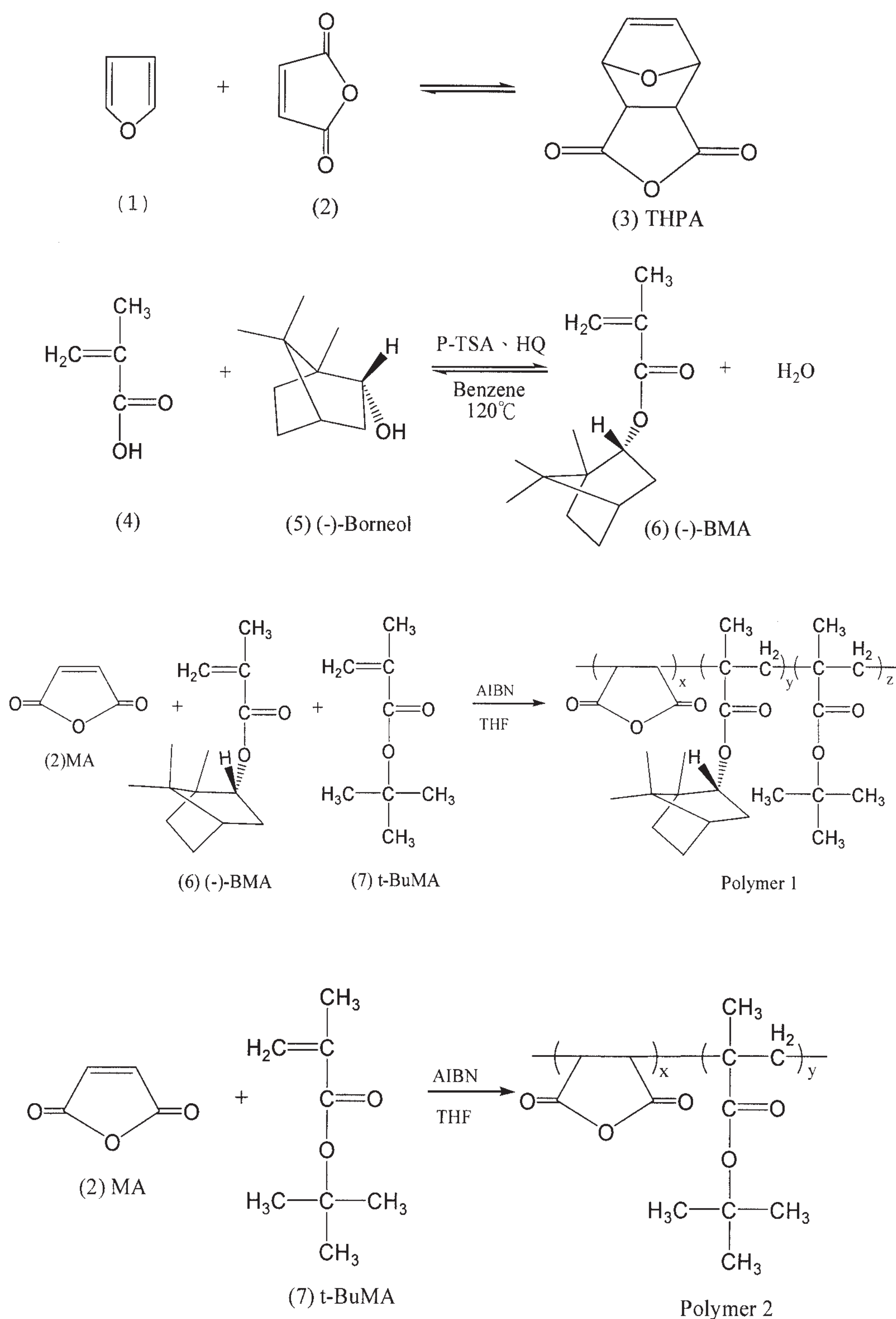
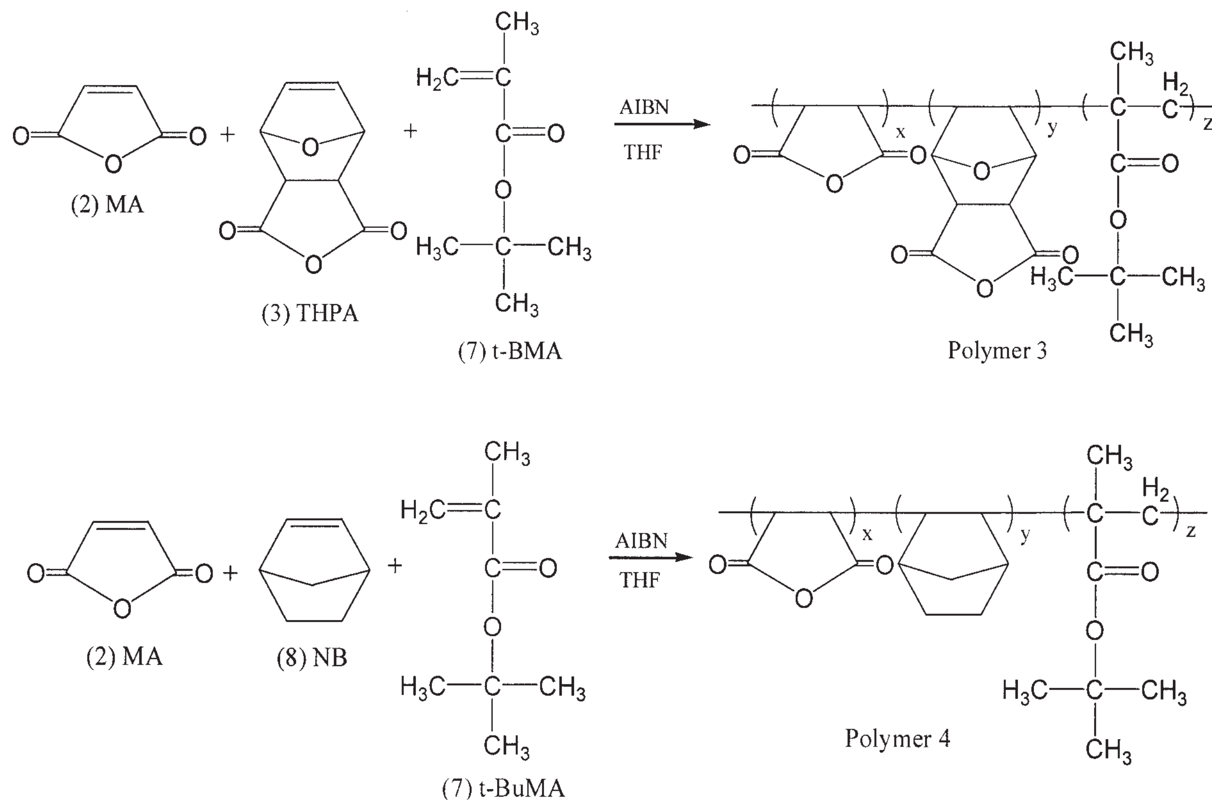


Scheme 1 Synthesis of functional monomers and polymers.

ular dissolution inhibiting compound having an acid decomposing group, and a photoacid generator.[22,23] In these positive-working chemically amplified resists of the two-component system, the three-component system, and the hybrid system, an acid is generated from the photoacid generator by light exposure, and after heat treatment, by developing, resist patterns are obtained. There remains a need in the art for a positive photoresist composition having both high resolution and high sensitivity. There also remains a need in the art of composition for positive photoresist, which is useful in deep-UV image resolution techniques. More-



Scheme 2 Preparation of polymer 3 and polymer 4.

over, there remains a need in the art for positive photoresist dissolution inhibitors capable of providing high sensitivity.

In our previous articles, we synthesized various functional monomers and polymers and studied their applications on the liquid crystal membranes, photoresists, and plastic rods.[24–27] In this article, we synthesized alicyclic copolymers with various alicyclic comonomers. The dependence of feed monomers, molar ratio, and initiator concentration on the molecular weight and thermoproperties were investigated. Developing resistance and exposure characteristic curves of the polymers with photoacid generators were also studied. Real patterns obtained through the photoresists with copolymers synthesized in this investigation were estimated.

EXPERIMENTAL

Materials

Maleic anhydride (MA), hydroquinone, 2-norborene (NB), and n-butyl mercaptan were purchased from

TABLE I
Results of Polymerization of Polymer 1[a]

Run	$[M]_0$[b]	$x_0/y_0/z_0$[c]	Yield (%)	M_w	M_w/M_n	T_g (°C)	$x/y/z$[d]
1	2	0/50/50	80	76,000	2.69	146.2	0/52/48
2	2	0/50/50	70[e]	32,000	2.03	140.7	0/42/58
3	2	0/50/50	76[f]	27,700	1.80	125.7	0/40/60
4	0.25	0/50/50	35[f]	9900	1.52	105.1	0/41/59
5[g]	1	0/50/50	57	4000	1.34	125.7	0/52/48
6	2	33/33/34	97	13,400	2.78	167.3	21/29/50
7[g]	1	33/33/34	80	8600	1.85	156.8	19/32/49

[a] In THF at 60°C for 24 h, 1 mol % AIBN was used.
[b] Feed monomer concentration.
[c] Molar ratio of feed monomers, x_0 = MA, y_0 = (−)-BMA, z_0 = t-BMA.
[d] Polymer composition, estimated by elemental analysis.
[e] AIBN 5 mol % and [f]10 mol % were used.
[g] n-Butyl mercaptan 0.5 mol % was used as a chain transfer agent.

TABLE II
Results of Polymerization of Polymer 2[a]

Run	$[M]_0$[b]	Yield (%)	M_w	M_w/M_n	T_g (°C)	x/y[c]
1	2	55	22,000	2.03	120.6	35/65
2	0.25	53	12,800	1.96	105.1	48/52
3	1[d]	86	2600	1.92	97.4	48/52

[a] Equal molar feed monomers in THF at 60°C for 24 h, 1 mol % AIBN was used.
[b] Feed monomer concentration, x_0/y_0 = MA/t-BuMA.
[c] Polymer composition, estimated by elemental analysis.
[d] 0.5 mol % *n*-butyl mercaptan was used as a chain transfer agent.

Tokyokasei Co. (Tokyo, Japan). Furan, (−)borneol, methacrylic acid, *p*-toluenesulfonic acid monohydrate, acrylic acid, *t*-butyl methacrylate (*t*-BMA), propylene glycol monomethyl ether acetate, and tetramethylammonium hydroxide (TMAH) were purchased from Acros Co. (Fair Lawn, NJ) and were used without further purification.

Measurements

The UV–visible spectra of films of the photoresist on quartz substrates were measured with 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 by using a JEOL JSM-35 and JAX-840 scanning electron microscope. Thermal properties and functional groups of polymers were evaluated and analyzed by using a DuPont 910 differential scanning calorimeter, a Perkin–Elmer TGA-7 thermogravimetric analyzer, and a Jasco FTIR spectrometer, respectively. Elemental analyses were calculated with a Heraeus CHN—O rapid elemental analyzer.

3,6-Endo,oxo-1,2,3,6-tetrahydrophthalic anhydride (THPA)[(3)]

Furan (17 g, 0.25 mol) and maleic anhydride (24.5 g, 0.25 mol) were added to 10 mL ethyl ether in a flask equipped with a condenser. The mixture was stirred at room temperature for 30 min. The resulted white precipitate was filtered and then washed with water three times.

Yield = 70%. FTIR (KBr): 1780 cm^{-1} (C═O); ^{1}H-NMR ($CDCl_3$) δ: 6.5 ppm (d, 2H, HC═C), 5.3 ppm (d, 2H, HCO), 3.2 ppm (d, 2H, CHCO). ANAL. CALCD FOR $C_8H_6O_4$ (166): C, 57.80%; H, 3.60%. FOUND: C, 57.66%; H, 3.68%.

(−)-Bornyl methacrylate [(−)-BMA][(6)]

(−)-Borneol (15.4 g, 0.1 mol), methacrylic acid (25.8 g, 0.3 mol), *p*-toluene sulfonic acid (2 g), and 200 mL benzene were put in a reaction bottle equipped with a Dean–Stark head and stirrer. The mixture was stirred at reflux for 24 h. After completion of the reaction, the mixture was cooled down to room temperature and then washed with 5 wt % sodium carbonate aqueous solution and dried on magnesium sulfate. After filtration, the solution was distilled at 120°C under 6 Pa.

Yield = 75%. FTIR (KBr): 1740 cm^{-1} (C═O). ANAL. CALCD FOR $C_{14}H_{22}O_2$(222): C, 75.68% H, 9.91%. FOUND: C, 75.36%; H, 9.98%.

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 using a freeze–thaw technique and then sealed off.

TABLE III
Results of Polymerization of Polymer 3[a]

Run	$[M]_0$[b]	$x_0/y_0/z_0$[c]	Yield (%)	M_w	M_w/M_n	T_g (°C)	$x:y:z$[d]
1	2	0/100/0	3	—	—	69.52	—
2	2	33/33/34	13	8400	1.83	—	28/10/62
3[e]	2	33/33/34	53	2250	1.84	102	30/2/68
4	1[f]	33/33/34	52	2000	1.5	101	27/9/64

[a] In THF at 60°C for 24 h, 1 mol % AIBN was used.
[b] Feed monomer concentration.
[c] Molar ratio of feed monomers, x_0 = MA, y_0 = THPA, z_0 = t-BMA.
[d] Polymer composition, estimated by elemental analysis.
[e] AIBN 2 mol % was used.
[f] *n*-Butyl mercaptan 0.5 mol % was used as a chain transfer agent.

TABLE IV
Results of Polymerization of Polymer 4[a]

Run	$[M]_0$[b]	$x_0/y_0/z_0$[c]	Yield (%)	M_w	M_w/M_n	T_g (°C)	$x/y/z$[d]
1	2	0/50/50	8	67,100	1.38	128.7	—
2	2	33/33/34	37	12,500	2.18	154.5	34/9/57
3	1	33/33/34	34	8200	1.76	150.4	31/4/65
4	1[e]	33/33/34	38	5300	1.49	143.2	33/8/59

[a] In THF at 60°C for 24 h, 1 mol % AIBN was used.
[b] Feed monomer concentration.
[c] Feed molar ratio of monomers, x_0 = MA, y_0 = NB, z_0 = t-BuMA.
[d] Polymer composition, estimated by elemental analysis.
[e] *n*-Butyl mercaptan 0.5 mol % was used as a chain transfer agent.

After completion of the polymerization, copolymers were precipitated from a large amount of water/methanol (1 : 1 in volume) solution and then washed with distilled water completely.

Exposure method

Photosensitive solution was obtained by dissolving copolymers (1.0 g) and triarylsulfonium hexafluoroantimonate (photo acid generator, 9.0×10^{-2} g) in 10 mL THF. The photosensitive solution was filtered with a 0.3-μm filter and then spin coated onto a silicon wafer plate by 1000 rpm for 10 s and 2500 rpm for 20 s. The polymer film 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 (PEB) at 120°C for 10 min and then developed with a 30-s immersion in 0.1 wt % sodium carbonate developer. Scheme 1 shows the synthesis of functional monomers and polymers.

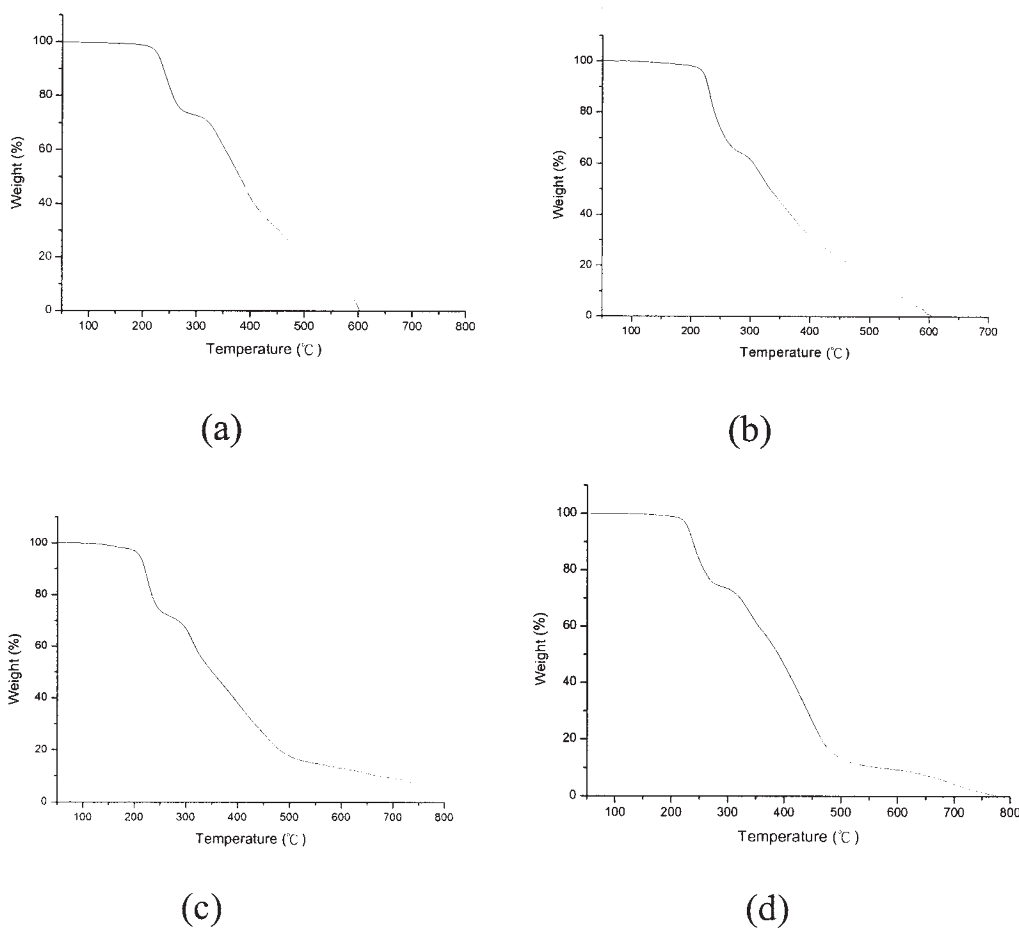


Figure 1 TGA curves of polymers (a) 1, (b) 2, (c) 3, and (d) 4.

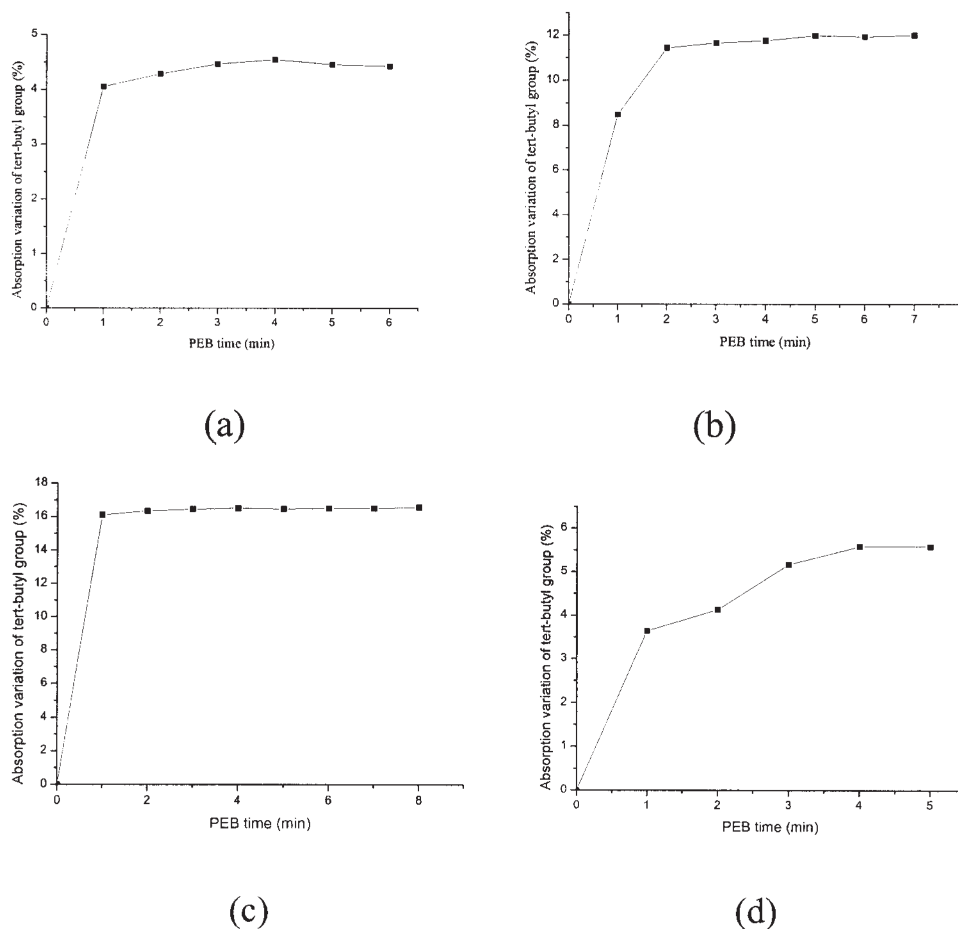


Figure 2 Dependence of PEB time on deprotection of *t*-butyl groups at 120°C for polymers (a) 1, (b) 2, (c) 3, and (d) 4.

RESULTS AND DISCUSSION

Monomers were synthesized and confirmed by using FTIR, ^{1}H-NMR, and elemental analyses. Scheme 2 shows the syntheses and polymerizations of alicyclic comonomers. Four copolymers were prepared and the results are summarized in Tables I-4. As can be seen in Scheme 2, all polymers bore acid labile pendant *t*-butyl groups. This could be used as functional polymers in designing positive tone photoresists. Molecular structures were confirmed by using ^{1}H-NMR, FTIR, and elemental analyses.

Table I shows the results of the polymerization of polymer 1. The existence of high-steric-hindered bornyl groups seems to increase the glass transition temperature of the polymers. High-hindered side-chain groups always inhibit the thermomobility of the

TABLE V
Characteristics of Photoresists

Photoresist	Polymer	Developer[a]	Sensitivity[b]	Contrast[c]	Resistance[d]
PR1	1	2.38%TMAH	162	2.1	1050
PR2	2	5%	189	1.7	1150
PR3	3	H_2O	270	2.5	1265
PR4	4	2.38%TMAH	108	3.3	1080
PMMA	—	—	—	—	2700[e]

[a] Developing aqueous solution.
[b] Resist sensitivity, mJ/cm^2.
[c] Estimated from the slope of characteristic curve.
[d] Plasma etching resistance (Å/min), $CF_4 : O_2 = 50 : 5$ standard cubic centimeters per minute gas flow, 60 mTorr 150 W, 300 s treatment.
[e] Used to compare the plasma resistance of the materials.

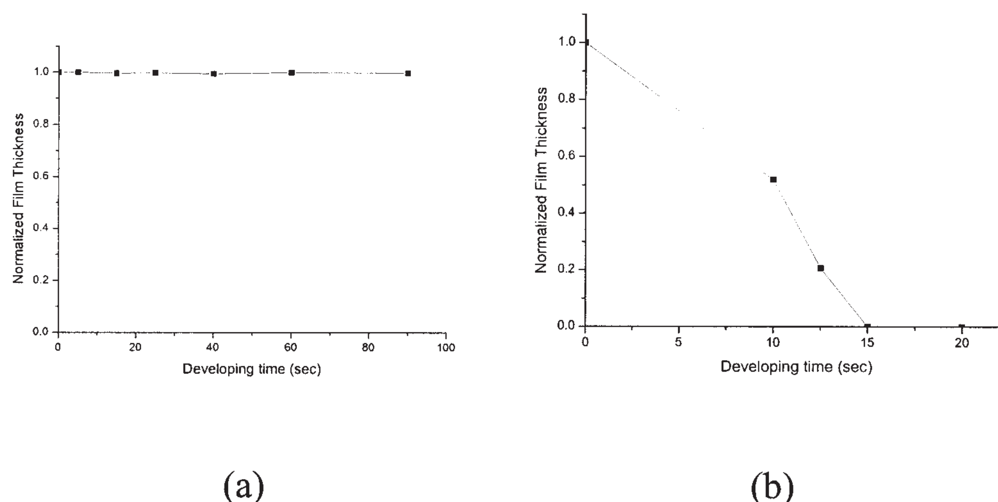


Figure 3 Developing resistance of PR1 normalized film thickness (a) before and (b) after UV exposure in 2.38% TMAH.

polymer chains, which leads to the increase of the glass transition temperature. As can be seen in Table I, molecular weight also clearly affected the glass transition temperature. The higher the initiator concentration, the lower the molecular weight and the glass transition temperature. Normal butyl mercaptan was used as a chain transfer agent in the polymerization of comonomers. It was found to restrain the growth of polymers effectively. Considering the contrast of photoresists, a molecular weight lower than 10,000 is generally considered to be a preferable condition.

Polymer 2 was prepared with equal molar feed comonomers MA(2) and *t*-BuMA.(7) The results are summarized in Table II. The results show that alternative copolymers were obtained under these conditions. This may be due to the high conjugating stability of comonomer MA.(2) It seems difficult to homopolymerize high-resonance monomers. Similarly, as shown in Table III, monomer THPA(3) could not be homopolymerized. As can be seen in Scheme 2, monomer THPA(3) contained two tertiary hydrogens near the C═C double bond. Radical and ionic structures may be stabilized by the big conjugating system around the C═C double bond. Even copolymerized with other comonomers, the component contents of THPA(3) were a little low. The effects of molecular weight and chain transfer agents on glass transition temperatures can also be seen in Tables II and III. The tendencies were quite similar to those in Table I.

Table IV shows the results of the polymerization of polymer 4. As shown in Scheme 2, both monomers THPA(3) and NB(8) have tertiary hydrogens. Because of the resonance stabilization around the double bond, both monomers seem difficult homopolymerize. The composition contents of THPA(3) and NB(8) in both copolymers 3 and 4 were small. The molecular

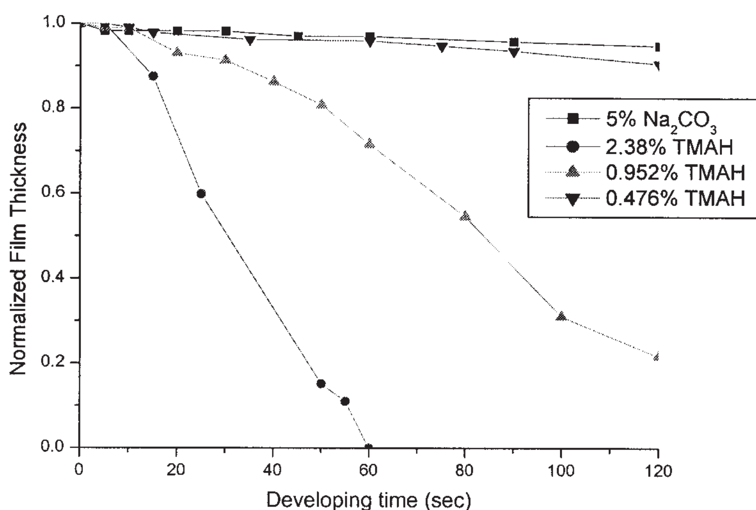


Figure 4 Developing resistance of PR2 film thickness before UV exposure in various developers.

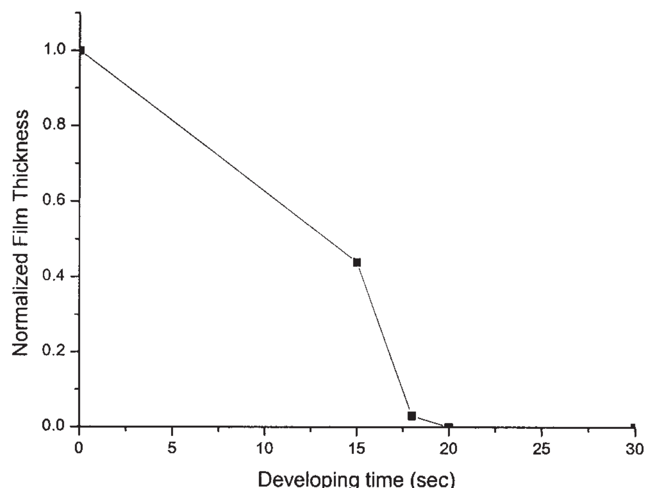


Figure 5 Dependence of normalized PR2 film thickness on developing time after UV exposure and PEB in 5% Na_2CO_3.

weights in Table IV are slightly higher than those in Table III. The results suggest that the polymerization rate of the monomer THPA[(3)] is a little lower than that of NB.[(8)] This may be due to the longer resonance of the plural rings through the oxygen atom, double bond, and tertiary carbons in THPA.[(3)]

The thermal properties of the polymers were evaluated and the results are summarized in Figure 1. As shown in Figure 1, all TGA curves have a first degradation stage. This may be due to the thermodegradation of the pendant *t*-butyl groups. As shown in the figures, the initial thermal degradation occurred ~ 200°C. Generally, photoresist is prebaked and postbaked at ~ 120°C. The thermostability of the polymers is good enough to be used in the field of photoresists. All polymers synthesized in this investigation revealed a high thermal resistance.

To investigate the postexposure baking behaviors of the polymers, the polymers were mixed with PAG. After UV irradiation, the photoresists were postbaked at 120°C for various times. The degradation of the *t*-butyl groups was studied by using a FTIR spectrophotometer and the results are summarized in Figure 2. The acid labile *t*-butyl groups were cut out from the polymers, and, as shown in Figure 2, the absorption variation of the *t*-butyl group increased with the increase of the PEB time. The variation between the curves in Figure 2 may be due to the difference of the glass transition temperatures and the structural characteristics of the polymers.

As can be seen in Scheme 2, the polymer structures synthesized in this investigation are quite different. Hence, they have different solving resistances to the alkaline aqueous developers. The polymers used in the photoresists are summarized in Table V. To estimate the proper developing conditions, various concentrations of sodium carbonate and TMAH aqueous solutions were used. TMAH 2.38% aqueous solution was found to be useful for photoresist 1, as shown in Figure 3(a). Before UV irradiation, polymers should have enough resistance to the developing agent. As shown in Figure 3(b), after UV irradiation, deprotection of *t*-butyl groups increased the solubility of the resist matrix. The curves in Figure 3 show standard characteristics of a positive tone photoresist.

Figure 4 shows the developer resistance of photoresist 2. A concentration of the TMAH aqueous solution $< 0.5\%$ and the 5% sodium carbonate aqueous solution available for photoresist 2. Figure 5 shows the positive tone characteristics of photoresist 2 in 5% sodium carbonate aqueous solution after UV exposure. After UV deprotection, polymer 2 could be dissolved in the developer within 20 s.

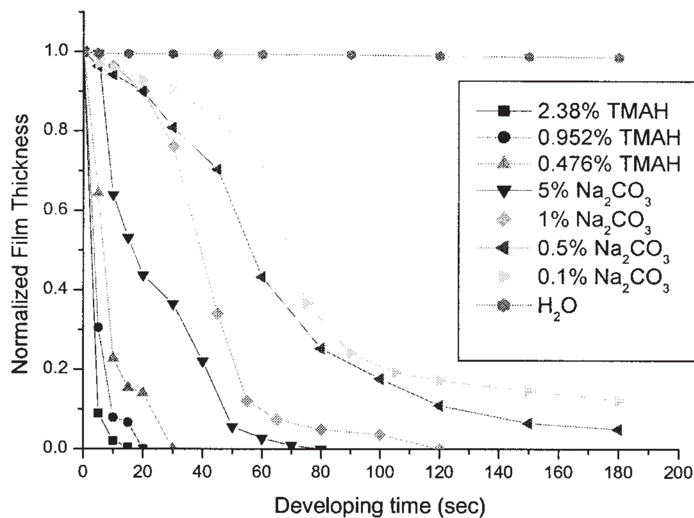


Figure 6 Developing resistance of PR3 normalized film thickness before UV exposure in various developers.

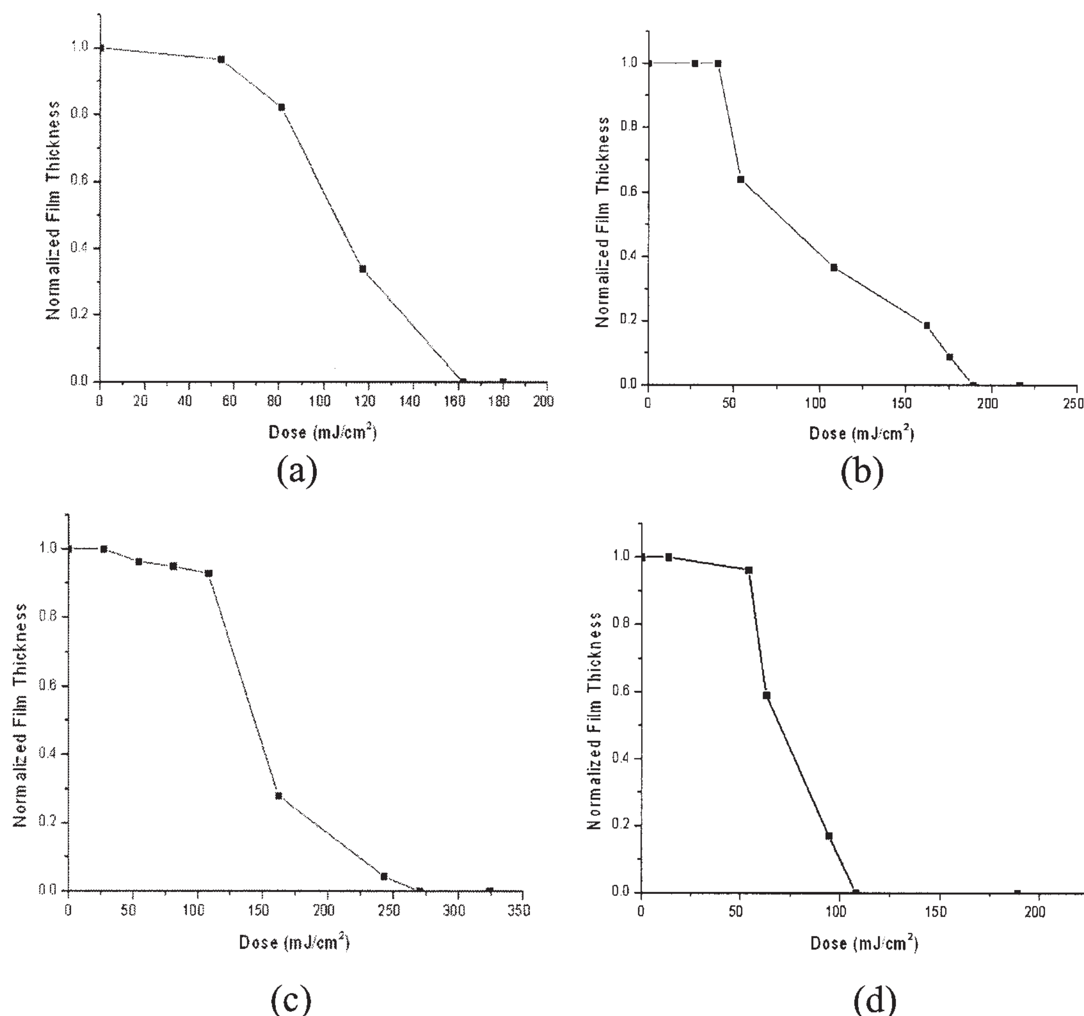


Figure 7 Exposure characteristic curves of (a) PR1, (b) PR2, (c) PR3, and (d) PR4.

The developing agent resistance of photoresist 3 with polymer 3 as the resist matrix is shown in Figure 6. In contrast with the results in the previous figures, even a weak alkaline solution could dissolve the photoresist before UV exposure. This may be due to the instability of the pendant cyclic anhydride ring to the alkaline solution. Hydration of the anhydride ring usually generates hydrophilic carboxylic acids and increases the solubility of the polymers in the alkaline solutions. Pure water was found to be a useful developer for photoresist 3. Available developers used for every photoresist were summarized in Table V. Variation of the content of the pendant cyclic anhydride groups and the structural stability of the polymers may affect the resistance of the photoresist to the basicity of the developers.

The exposure characteristic curves of the photoresists were all evaluated and the results are summarized in Figure 7. The developers used, sensitivity, and plasma resistance of the photoresists were all estimated and summarized in Table V. Contrast was estimated from the slope of the curves in Figure 7. The larger the number, the better the resist contrast. Plasma etching resistance was also evaluated. As shown in Table V, the etching resistance was obviously improved because of the existence of the cyclic structures. The real exposed image patterns with 1.2-μm resolution are shown in Figure 8. The results in this investigation suggest that synthesized alicyclic copolymers could be used for chemically amplified positive tone photoresists.

CONCLUSIONS

Copolymerization of monomers selected from THPA, BMA, MA, *t*-BMA, and NB were performed. The molecular weight, glass transition temperatures, and compositions of the polymers were estimated. The developer resistance of the polymers in various solvents was evaluated. Photoresists consisting of synthesized polymers and photoacid generator were prepared. The exposure characteristic curves of the pho-

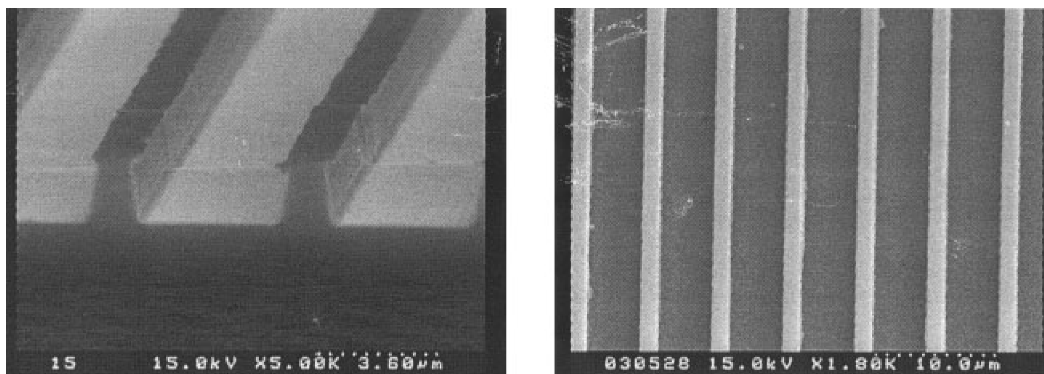


Figure 8 SEM photographs of PR4 resist patterns.

toresists, sensitivity, contrast, and plasma etching resistance of the photoresists were all investigated. The existence of the pendant alicyclic rings was found to obviously increase the plasma etching resistance. Real image patterns with 1.2-μm resolution through masks were achieved.

References

1. Yao, J.; Su, J.; Du, J.; Zhang, Y.; Gao, F.; Guo, Y.; Cui, Z. Microelectron Eng 2000, 53, 531.
2. Chung, J.; Jeng, M. C.; Moon, J. E.; Wu, A. T.; Chan, T. Y.; Ko, P. K.; Hu, C. IEEE Electron Device Lett 1988, 9, 186.
3. Fay, B. Microelectron Eng 2002, 11, 61–62.
4. Kim, H. J.; Kim, D. J.; Ryu, J. K.; Pak, S. S. Appl Surf Sci 2004, 228, 100.
5. Soon, L. J.; Il, H. S. Eur Polym J 2002, 38, 387.
6. Cheng, T. S.; Lee, H. Y.; Lee, C. T.; Chen, H.; Lin, H. T. Mater Lett 2003, 57, 4578.
7. Caddy, M.; Kemp, T. J. Eur Polym J 2003, 39, 461.
8. Dentinger, P. M.; Krafcik, K. L.; Simison, K. L.; Janek, R. P.; Hachman, J. Microelectron Eng 2002, 61–62, 1001.
9. Chuang Yun-Ju, Tseng Fan-Gang, Cheng Jen-Hau, Lin Wei-Keng. Sens Actuators, A 2003, 103, 64.
10. Asano, K.; Choi, Y. K.; King, T. J.; Hu, C. M. IEEE Trans Electron Devices 2001, 48, 1004.
11. Tattersall, P. I.; Breslin, D.; Grayson, S. M.; Heath, W. H.; Lou, K.; McAdams, C. L.; McKean, D.; Rathsack, B. M.; Willson, C. G. Chem Mater 2004, 16, 1770.
12. Jung, J. C.; Jung, M. H.; Lee, G.; Baik, K. H. Polymer 2001, 42, 161.
13. Shah, M.; Allen, N. S.; Salleh, N. G.; Corrales, T.; Edge, M.; Catalina, F.; Bosch, P.; Green, A. J Photochem Photobiol, A 1997, 111, 229.
14. Serafinowski, P. J.; Garland, P. B. J Am Chem Soc 2003, 125, 962.
15. Ortica, F.; Coenjarts, C.; Scaiano, J. C.; Liu, H.; Pohlers, G.; Cameron, J. F. Chem Mater 2001, 13, 2297.
16. Coenjarts, C.; Ortica, F.; Cameron, J.; Pohlers, G.; Zampini, A.; Desilets, D.; Liu, H.; Scaiano, J. C. Chem Mater 2001, 13, 2305.
17. Pawloski, A. R.; Christian, Nealey P. F. Chem Mater 2001, 13, 4154.
18. Nicolau, D. V.; Haguchi, T.; Tanigawa, H.; Yoshikawa, S. Biosens Bioelectron 1996, 11, 1237.
19. Miyagawa, K.; Naruse, K.; Ohnishi, S.; Yamaguchi, K.; Seko, K.; Numa, N., Iwasawa, N. Prog Org Coat 2001, 42, 20.
20. Kim, J. B.; Lee, J. J. Polymer 2002, 43 1963.
21. Lee, J. H.; Ahn, K. D.; Cho, I. Polymer 2001, 42, 1757.
22. Barnes, D. A.; Benedikt, G. M.; Goodall, B. L.; Huang, S. S.; Kalamarides, H. A.; Lenhard, S.; McIntosh, L. H.; Selvy, K. T.; Schick, R. A.; Rhodes, L. F. Macromolecules 2003, 36, 2623.
23. Padmanaban, M.; Alemy, E.; Bae, J. B. J Photopolym Sci Technol 2001, 14, 631.
24. Liu, J. H.; Wang, H. Y. J Appl Polym Sci 2003, 90 (11), 2969.
25. Liu, J. H.; Wang, H. Y. J Appl Polym Sci 2004, 91 (2), 789–799.
26. Liu, J. H.; Wu, F. T. J Polym Res 2004, 11, 1, 43–51.
27. Liu, J. H.; Wang, H. Y.; Ho, C. H. J Polym Res 2003, 10, 13.