Novel Functional Polymers from *N*-(Tosyloxy)maleimide. Photochemical Acid Generation in Solid-State and Application as Resist Materials[1]

Kwang-Duk Ahn,* Chan-Moon Chung, and Deok-Il Koo

Functional Polymer Laboratory, Polymer Research Division, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea

Received January 27, 1994. Revised Manuscript Received March 25, 1994®

N-(Tosyloxy)maleimide (TsOMI) has been synthesized and used to make a novel functional maleimide polymer, and the photochemical and thermal properties of its styrenic copolymers were investigated. The *N*-(tosyloxy)maleimide unit in the alternating copolymers was designed for photochemical acid generation and the copolymers generated *p*-toluenesulfonic acid by deep-UV irradiation over 30 mol % based on the TsOMI content. The photochemical acid generation was much enhanced when hydroquinone was added. A *t*-BOC-protected copolymer, poly[TsOMI-*alt*-*p*-(((*tert*-butyloxy)carbonyl)oxy)styrene], showed the capability of a single-component resist system in the deep-UV region based on the chemical amplification concept. The single-component resist rendered negative- and positive-tone images by developing with suitable solvents.

Introduction

Chemically amplified deep-UV resists are one promising class of materials for achieving very high sensitivity as well as high resolution.[2] In designing a resist system based on the chemical amplification concept it has to incorporate two basic components, namely, an acid-labile compound or polymer and a photoacid generator (PAG) which should generate a strong acid by UV irradiation in the solid state. Among the various chemically amplified resist systems, the polymer side-chain deprotection system has attracted much attention because of their capability to deliver good resolution with high sensitivity while retaining main-chain integrity. In this case, the deprotected polymers show a remarkable change in polarity after deprotection of the side chains, thereby inducing a large difference in solubility. A typical protecting group is (*tert*-butyloxy)carbonyl (*t*-BOC) group which is readily removable by (acid-catalyzed) thermolysis.

The functional polymaleimides, which are copolymers of various N-functionalized maleimide monomers, provide desirable properties and in addition offer high thermal stability.[3] A few copolymers of N-protected maleimide monomers have been synthesized to investigate their applicability as thermally stable resist materials in the deep-UV region based on the chemical amplification concept. Those N-substituted functional polymaleimides are the styrenic copolymers of *N*-((*tert*-butyloxy)carbonyl)maleimide (*t*-BOCMI),[3–5] *t*-BOC-protected *N*-(*p*-hydroxyphenyl)maleimide,[6] and *N*-(*tert*-butoxy)maleimide (*t*-BuOMI).[7]

There have been reported numerous photoacid generating systems from the well-known onium salt PAGs to pure organic PAGs for more adaptable resist materials.[2b,c] In this study a novel functional maleimide monomer was designed for photochemical acid generation by introducing a *p*-toluenesulfonyl (Ts) group. The *N*-tosyl-substituted maleimide units in the polymers are considered to be a potential photoacid generator since *N*-(tosyloxy)phthalimide was reported to generate *p*-toluenesulfonic acid (TsOH) when irradiated with ultraviolet light.[8,9] In fact, *N*-(tosyloxy)phthalimide was utilized as an organic PAG for generation of TsOH in a well-known *t*-BOC resist system based on a polymer of *p*-(((*tert*-butyloxy)carbonyl)oxy)styrene (*t*-BOCSt).[9] Similarly, a maleimide derivative, *N*-(trifluoremethanesulfonyloxy)-2,3-diphenylmaleimide was also reported to be a useful nonmetallic PAG.[10]

There have been only a few examples of the polymeric photoacid-generating systems. These include the copolymers of 2-nitrobenzyl styrenesulfonate[11] or 9-fluorenylideneiminostyrenesulfonate,[12] which produce a polymer-bound or polymeric sulfonic acid on deep-UV exposure in the solid state. Both of these copolymers with *t*-BOCSt were investigated as a single-component resist system. The copolymer of 2-nitro-α-methylbenzyl methacrylate and

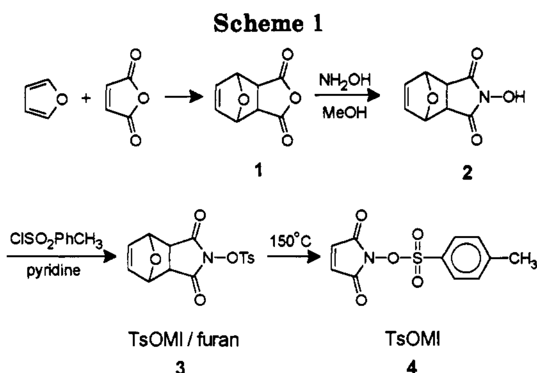
® Abstract published in *Advance ACS Abstracts*, August 15, 1994.

(1) A part of this work was presented at International Conference on Advanced Materials (ICAM-93) of IUMRS held in Tokyo on Aug 31 to Sept 3, 1993.

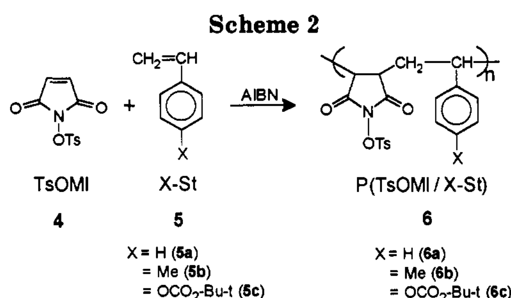
(2) (a) Ito, H.; England, W. P.; Ueda, M. *J. Photopolym. Sci. Technol.* **1990**, *3*, 219. (b) Reichmanis, E.; Houlihan, F. M.; Nalamasu, O.; Neenan, T. X. *Chem. Mater.* **1991**, *3*, 394. (c) Lamola, A. A.; Szmanda, C. R.; Thackeray, J. W. *Solid State Technol.* **1991**, *Aug*, 53.
(3) Ahn, K.-D.; Lee, Y.-H.; Koo, D.-I. *Polymer* **1992**, *33*, 4851.
(4) Chatterjee, S.; Jain, S.; Lu, P. H.; Khanna, D. N.; Potvin, R. E.; McCaulley, J. A.; Rafalko, J. *Polym. Eng. Sci.* **1992**, *32*, 1571.
(5) Sebald, M.; Berthold, J.; Beyer, M.; Leuschner, R.; Nolscher, Ch.; Scheler, U.; Sezi, R.; Ahne, H.; Birkle, S. *Proc. SPIE* **1991**, *1466*, 227.
(6) Turner, S. R.; Ahn, K.-D.; Willson, C. G. In *Polymers for High Technology*; ACS Symposium Series No. 346, Bowden, M. J., Turner, S. R., Eds.: American Chemical Society: Washington, DC, 1987; Chapter 17, p 200.
(7) Ahn, K.-D.; Koo, D.-I. In *Polymers for Microelectronics*; ACS Symposium Series No. 537, Thompson, L. F., Willson, C. G., Tagawa, S., Eds.; American Chemical Society: Washington, DC, 1994; Chapter 9, p 124.
(8) Cadogan, J. I. G.; Rowley, A. G. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1069.
(9) Brunsvold, W.; Kwong, R.; Montgomery, W.; Moreau, W.; Sachdev, H.; Welsh, K. *Proc. SPIE* **1990**, *1262*, 162.
(10) Brunsvold, W.; Montgomery, W.; Hwang, B. *Proc. SPIE* **1991**, *1466*, 368.
(11) Hanson, J. E.; Reichmanis, E.; Houlihan, F. M.; Neenan, T. X. *Chem. Mater.* **1992**, *4*, 837.
(12) Shirai, M.; Kinoshita, H.; Tsunooka, M. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 451.

0897-4756/94/2806-1452$04.50/0 © 1994 American Chemical Society

Scheme 1



Scheme 2



t-BOCSt was also known to generate polymeric carboxylic acid and was reported as a single-component resist.[13]

It is of particular interest that the photochemical acid generation from PAGs and the subsequent acid-catalyzed deprotections occur all in solid-state polymer films. In the acid-catalyzed reactions the freely separated sulfonic acid would be preferred to polymer-bound sulfonic acids because the nonbound acids can diffuse effectively in the resist medium. In this article we report the synthesis and properties of a new kind of functional polymaleimide designed as a photoacid-generating polymer and preliminary evaluation on its capability of a single-component resist system.

Results and Discussion

Synthesis and Copolymerization of TsOMI. *N*-(Tosyloxy)maleimide (TsOMI, **4**) was prepared by a retro-Diels–Alder reaction as described in Scheme 1. The maleic anhydride/furan adduct **1** reacted with hydroxylamine to give *N*-hydroxymaleimide/furan adduct **2**, which then reacted with *p*-toluenesulfonyl chloride. The resulting TsOMI/furan adduct **3** was thermolyzed at 150 °C to obtain the desired TsOMI (**4**) in a yield of 57% as white crystals with mp 150 °C. The structure of TsOMI was confirmed by ^{1}H NMR, ^{13}C NMR, IR, mass spectra, and elemental analysis.

TsOMI readily copolymerized with styrene monomers (X-St) **5** such as styrene (St), *p*-methylstyrene (MeSt), and *p*-(((*tert*-butyloxy)carbonyl)oxy)styrene (*t*-BOCSt) to give copolymers **6** of P(TsOMI/St), P(TsOMI/MeSt), and P(TsOMI/*t*-BOCSt) in high conversions with high molecular weights using an AIBN radical initiator as shown in Scheme 2. The results of radical copolymerizations of the TsOMI monomer with styrene monomers **5** are summarized in Table 1. Copolymerizations of TsOMI with styrene monomers were carried out with 1:1 molar feed ratio at 55 °C in dioxane and the copolymers obtained were confirmed to have an alternating structure from the ^{1}H NMR spectral analyses. Under these conditions, the homopolymerizations of TsOMI only resulted in oligomer formation. The molecular weights of the copolymers **6** were controlled by adjusting the concentration of the radical initiator and the monomer in polymerizations.

(13) Schwalm, R. *J. Electrochem. Soc.* **1989**, *136*, 3471.

Table 1. Radical Copolymerizations of TsOMI (4) with Styrenes

polymer[a]	AIBN[b]	M/S,[c] g/mL	time, h	conversion, %	inherent viscosity,[d] dL/g
P(TsOMI)	1	0.25	18	15	*e*
P(TsOMI/St) **6a**	1	0.25	3	91	0.55
P(TsOMI/MeSt) **6b**	*f*	0.27	6	85	0.71
	1	0.33	3	88	0.92
P(TsOMI/*t*-BOCSt) **6c**	1	0.25	3	87	0.58
	1	0.50	2	86	0.81

[a] All the copolymers have an alternating structure. Copolymerizations were carried out in 1:1 molar feed ratio at 55 °C in dioxane. [b] Mole percent of the initiator AIBN to the combined monomers. [c] Ratio of the total monomers to the volume of dioxane. [d] Inherent viscosities measured at a concentration of 0.20 g/dL in dioxane at 25 °C. [e] Oligomeric precipitates formed in methanol by homopolymerization, but no measurable viscosity value. [f] Polymerization without using initiators (spontaneous polymerization at 55 °C).

Table 2. Thermal Properties of the Copolymers 6[a]

polymer	deprotected polymer	mass loss calcd	mass loss found	T_{dp}, °C	T_g, °C	T_{dc}, °C
P(TsOMI/St) **6a**					172	273
P(TsOMI/MeSt) **6b**					172	270
P(TsOMI/t-BOCSt) **6c**	P(TsOMI/HOSt)	21	21	171	198	266

[a] Thermal analysis done at a heating rate 10 °C/min in a nitrogen stream. T_{dp} = deprotection temperature of the side-chain *t*-BOC groups measured by DSC. T_g = glass transition temperature of (deprotected) polymers measured by DSC. T_{dc} = onset decomposition temperature measured by TGA.

The radical copolymerizations of TsOMI with styrene monomers (X-St) proceeded much more easily than previously reported other photoacid-generating monomers.[11-13] For example, the nitrobenzyl ester monomers generally gave low conversions (less than 50%) with difficulties in the control of copolymer composition.[11,14] Alternating copolymers were always obtained in the radical copolymerizations of TsOMI and styrene monomers with high conversions (more than 85%). It is well-known that an electron-rich monomer (styrene) and an electron-poor monomer (TsOMI) lead to an alternating copolymer structure in radical copolymerizations.[15] Spontaneous polymerization is also possible in these monomer pairs without any initiator, as in the case of the polymerization of TsOMI and MeSt (Table 1).[16]

Thermal Properties. The copolymers **6** showed thermal decomposition (T_{dc}) beginning at about 270 °C and T_g's at about 170 °C in DSC analysis as summarized in Table 2. The values of T_{dc} and T_g of **6** are somewhat low compared to the styrenic copolymers of *t*-BOCMI.[3] The DSC thermogram of P(TsOMI/*t*-BOCSt) **6c** revealed an endothermic event (T_{dp}) due to the deprotection of the side-chain *t*-BOC groups at 171 °C. Around this temperature the mass loss of the copolymer **6c** in the TGA thermogram was estimated to be 21%, which is the same amount as the theoretically calculated mass loss due to the evolution of carbon dioxide and isobutylene from the copolymer as shown in Figure 1a. This indicates that the

(14) Schwalm, R., private communication.
(15) Turner, S. R.; Anderson, C. C.; Kolterman, K. M. *J. Polym. Sci., Polym. Lett. Educ.* **1989**, *27*, 253.
(16) Hall, H. K.; Padias, A. B. *Acc. Chem. Res.* **1990**, *23*, 3.

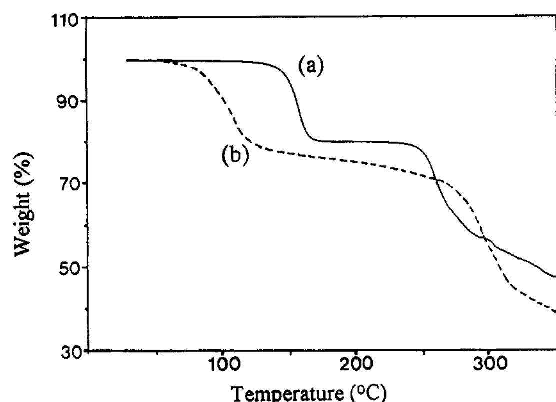
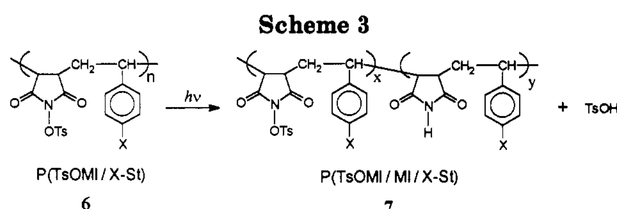


Figure 1. TGA thermograms of (a) P(TsOMI/t-BOCSt) and (b) the same polymer which was exposed to 260-nm deep UV (75 mJ/cm^2) for photoacid generation in the film state.

Scheme 3



thermal deprotection of the *t*-BOC groups from the copolymer **6c** occurs at 171 °C, generating the corresponding copolymer P(TsOMI/HOSt) with *p*-hydroxystyrene (HOSt) units.

The deprotection of the *t*-BOC groups of **6c** was found to begin around 60 °C in Figure 1b and be completed at the temperature near 100 °C when the polymer was subjected to deep-UV exposure with 75 mJ/cm^2 (refer to Scheme 4). By comparison of curves (a) and (b) in Figure 1, the thermal deprotection of *t*-BOC groups of **6c** resulted in the same mass loss of 21% with or without UV exposure, which confirms the photochemical generation of TsOH and the subsequent acidolytic deprotection in solid state. The deprotected copolymer P(TsOMI/HOSt) shows T_g at 198 °C in DSC analysis and has a different solubility from the starting copolymer **6c** due to the large polarity change of the side chains (vide infra).

Photoacid Generation. Some *N*-hydroxymaleimide sulfonates like *N*-(tosyloxy)phthalimide were reported to produce TsOH when irradiated with UV light.[8,9] The photochemical conversion of TsOMI units to maleimide (MI) along with generation of TsOH from the copolymers **6** in solid state as described in Scheme 3 was confirmed by the change in pH of polymer solutions in THF and by identification of TsOH in HPLC. The amount of generated TsOH from the partial photolysis of TsOMI moieties when exposed to deep-UV in the film state was measured by a colorimetry with the change in absorption intensity at 607 nm of the polymer solutions in methylene chloride using a merocyanine dye.[17–20] The large extinction coefficient of the free dye allows determination of very small quantities of acid (10^{-9} mol) with average error of less than 10%.[18]

(17) Gaines, G. L. *Anal. Chem.* **1976**, *48*, 450.
(18) McKean, D. R.; Schaedeli, U.; MacDonald, S. A. *J. Polym. Sci., Polym. Chem.* **1989**, *27*, 3927.
(19) McKean, D. R.; Schaedeli, U.; Kasai, P. H.; MacDonald, S. A. *J. Polym. Sci., Polym. Chem.* **1991**, *29*, 309.
(20) Shirai, M.; Kinoshita, H.; Tsunooka, M. *Eur. Polym. J.* **1992**, *28*, 379.

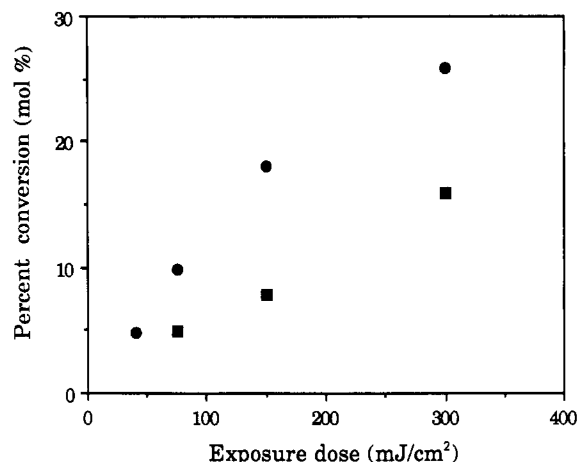
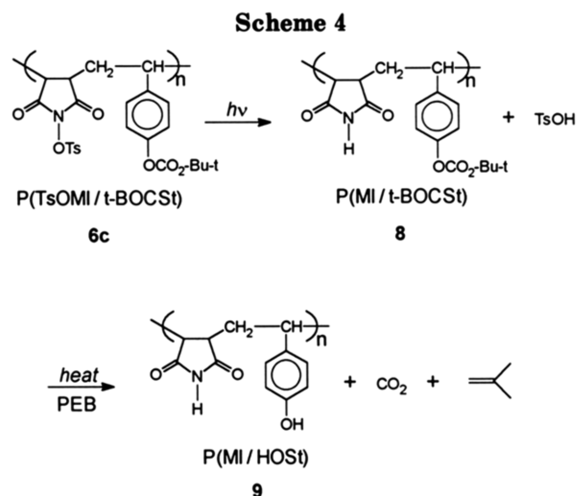


Figure 2. Photochemical TsOH generation in the copolymer of P(TsOMI/St) **6a** by colorimetry: ■, for **6a** film; ●, for **6a** film containing 10% hydroquinone.

The percent conversion of TsOMI units in the copolymer P(TsOMI/St) **6a** at various doses was calculated based on the amount of generated TsOH and is shown in Figure 2. In some cases 30 mol % photochemical conversion of TsOMI units was observed depending on the irradiation time. Upon combining 5–10% of hydroquinone (HQ) as an additive, the acid generation was remarkably enhanced as reported by Brunsvold and co-workers.[9] The upper curve in Figure 2 is the result for the polymer **6a** containing 10% HQ and reveals the increased generation of TsOH at the same dose. Some deviations in the measurements of the acid generation were encountered because precipitates were formed in methylene chloride solutions when the conversion exceeded 25 mol %. Above 30 mol % conversion of TsOMI units in the copolymers **6**, a complete change in solubility was observed as the photoproduct became soluble in an aqueous solution of 4% (1.0 N) NaOH and insoluble in organic solvents such as anisole and methylene chloride. The structural change due to the photochemical TsOH generation was also confirmed by ^{1}H NMR and IR spectral analyses.

Deprotection of *t*-BOC Groups in P(TsOMI/*t*-BOCSt) by TsOH Generated in Situ. Upon exposure to deep-UV the TsOMI units of P(TsOMI/*t*-BOCSt) **6c** are transformed into maleimide units concurrently generating TsOH, which is utilized to catalyze the deprotection of the side-chain *t*-BOC groups on subsequent heating as described in Scheme 4. The transparent film of **6c** was irradiated with UV light and was subjected to heat treatment at 100 °C for 5 min to bring about the acidolytic deprotection of *t*-BOC groups. As a result the complete deprotection of *t*-BOC groups occurred to produce the copolymer P(MI/HOSt) **9** with *p*-hydroxystyrene (HOSt) units. In fact, the deprotected copolymer was found to have a structure composed of MI, TsOMI, and HOSt units, namely, P(TsOMI/MI/HOSt) **7** because of the partial photolysis of TsOMI units. The acidolytic deprotection of **6c** was confirmed by TGA as shown in Figure 1b and also IR spectral change. The TGA thermograms of the copolymer **6c** before and after the UV exposure in Figure 1 imply *in situ* generation of TsOH from the TsOMI units and the complete acidolytic deprotection of *t*-BOC groups of the *t*-BOCSt units by the photogenerated TsOH in solid state. The effectiveness of the acid-catalyzed deprotection was further verified by DSC analyses. In DSC thermograms the endothermic peaks (T_{dp}) of the copolymer **6c**

Scheme 4



were clearly observed at 109 °C without HQ and 84 °C in the presence of 10% HQ after DUV exposure with 75 mJ/cm^2. These endothermic events corresponding to the deprotection of *t*-BOC groups occurred at significantly low temperatures compared with the simple thermal deprotection at 171 °C. In this case, the amount of generated TsOH was estimated to be about 5 mol % by the partial photolysis. The copolymers with MI units usually have high T_g's at above 200 °C. In fact, the copolymer P(MI/HOSt) was already reported to have very high T_g with 280 °C.[3]

Application of P(TsOMI/*t*-BOCSt) as a Single-Component Resist. The copolymers **6** are usually soluble in organic solvents such as chloroform, cyclohexanone, THF, and anisole but insoluble in toluene, methanol, and aqueous alkaline solutions. The *t*-BOC copolymer **6c** showed a significant change in solubility when it was converted to the copolymer P(TsOMI/MI/HOSt) **7** or P(MI/HOSt) **9** after deep-UV exposure and thermal deprotection. P(MI/HOSt) is insoluble in chloroform, cyclohexanone, and anisole but soluble in aqueous alkaline solutions such as 4% sodium hydroxide solution. All the TsOMI copolymers **6** have a good transparent film-forming property, and **6c** has an optical density of 0.47/μm at 250 nm. The **6c** film containing 10% HQ has an optical density of 0.52/μm at 250 nm and the value increases slightly by deep-UV exposure. The optical density of **6c** is considered somewhat high to obtain high-resolution images in the deep-UV region. In this regard, the terpolymer system of TsOMI is one plausible way to reduce the absorption.

P(TsOMI/t-BOCSt) **6c** was employed as a single-component, chemically amplified resist without adding any photoacid generator. Negative-tone image patterns were successfully obtained from **6c** when developed with anisole after 260-nm deep-UV exposure with 75 mJ/cm^2 and the postexposure bake (PEB) treatment at 70 °C for 3 min on a hot plate. Positive-tone images were possible by development with 4% aqueous NaOH solution. A microscopic photograph of 1.0-μm dot patterns is shown in Figure 3 and a SEM photograph of 1.5-μm line and space patterns is shown in Figure 4. The two photographs were obtained in negative-tone images because positive-tone images usually suffered from a poor adhesion problem.

The *t*-BOC protected copolymer **6c** exhibited higher sensitivity in image-making than the previously reported single-component resist systems in which PEB temperatures were higher than 120 °C.[11-13] This improved sensitivity is attributable to easy diffusion of separated

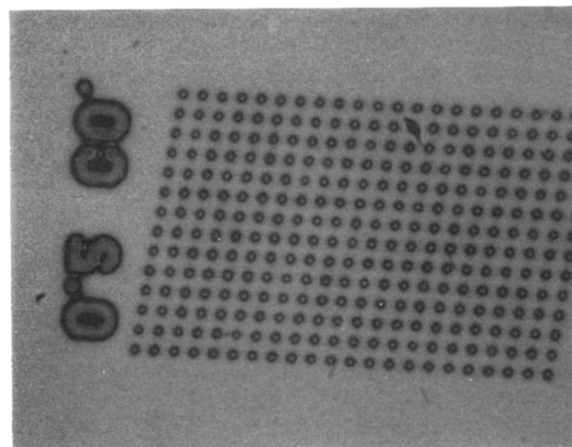


Figure 3. Microscopic photograph of 1.0-μm dot patterns in P(TsOMI/*t*-BOCSt) **6c** containing 10% hydroquinone: exposure to 260-nm light (75 mJ/cm^2) by a contact mode; PEB at 70 °C for 3 min.

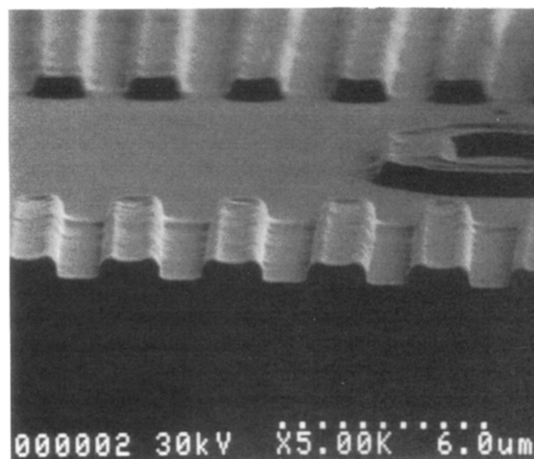


Figure 4. SEM photograph of 1.5-μm line and space patterns in P(TsOMI/*t*-BOCSt) **6c** containing 10% hydroquinone: exposure to 260-nm light (75 mJ/cm^2) by a contact mode; PEB at 70 °C for 3 min.

free TsOH from the polymer chains in solid state compared with the previous resist systems which generate only polymer-bound benzenesulfonic acids.[11,12] A study on terpolymers consisting of TsOMI, *t*-BOCSt, and maleimide or *t*-BOCMI is underway to improve photosensitivity, developing conditions, and thermal properties for lithographic applications.

Conclusions

Functional polymaleimides P(TsOMI/X-St) were obtained in an alternating structure by radical copolymerizations of a novel functional maleimide TsOMI with styrene monomers (X-St) and used as a polymeric photoacid generator. By UV irradiation P(TsOMI/X-St) generated free TsOH which was more than 30 mol % based on TsOMI units in the solid state. The photoacid generation capability of TsOMI polymers was remarkably improved when hydroquinone was used as an additive. The alternating copolymer P(TsOMI/*t*-BOCSt) was investigated as a single-component, chemical amplification resist system. Photoacidolytic deprotection of the *t*-BOC groups was observed at the temperature below 100 °C when exposed to deep UV while thermal deprotection occurred at 171 °C without UV exposure. The deprotected polymers with the structure of P(TsOMI/MI/HOSt) after

exposure and postbake at 100 °C showed complete change in solubilities and high T_g's at above 200 °C. The copolymer P(TsOMI/*t*-BOCSt) was found to have potential for application as a single-component resist with dual-tone images.

Experimental Section

Materials and Instruments. *p*-Hydroquinone (HQ), maleic anhydride, styrene (St), and *p*-methylstyrene (MeSt) were purchased from Aldrich Chemical Co. *p*-(((*tert*-Butoxy)carbonyl)-oxy)styrene (*t*-BOCSt) was kindly donated by Eastman Kodak Co. The styrene monomers were purified by distillation. Other chemicals were purified by conventional methods.

^{1}H NMR spectra were taken on a JEOL PMX-60 SI spectrometer or a Varian Gemini 300-MHz spectrometer in deuteriochloroform using tetramethylsilane as an internal standard. ^{13}C NMR spectra were also obtained with a Varian gemini spectrometer in deuteriochloroform. IR spectra were recorded on an Polaris FT-IR spectrophotometer (Mattson Instrument Co.) and mass spectra were taken on a JEOL JMS-DX 303 spectrometer. Elemental analysis was done with a Perkin-Elmer Model 240C elemental analyzer. Thermal analysis was carried out on a DuPont Model 910 DSC and Model 951 TGA at a heating rate of 10 °C/min under nitrogen atmosphere. Solution viscosities of polymers were measured with a Cannon-Fenske viscosity tube (no. 50) or an Ubbelohde viscometer tube mounted on an automatic measuring apparatus (Schott-Gerate GmbH) at 25 °C in dioxane. UV absorption spectra were recorded on a Shimadzu UV-240 spectrophotometer. Exposure of the polymer films was made on a Hybralign Series 400 Exposure System of Optical Associates Inc. equipped with a 500-W short-arc Hg-Xe lamp and optics tuned to 260 nm or a UV illuminator of Ushio Inc. equipped with a 500-W high-pressure mercury lamp.

***N*-(Tosyloxy)maleimide (TsOMI) 4.** The *N*-hydroxymaleimide/furan adduct **2**, *N*-hydroxy-3,6-epoxy-1,2,3,6-tetrahydrophthalimide, was prepared according to the known procedure.[7,21] The maleic anhydride/furan adduct 1, 3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride, was first prepared by a Diels-Alder reaction and then reacted with hydroxylamine. To a solution of the adduct **2** (36.23 g, 0.20 mol) in a mixture of pyridine (150 mL) and tetrahydrofuran (300 mL) was added toluenesulfonyl chloride (38.13 g, 0.20 mol). After stirring at room temperature for 30 min the solution was poured into distilled water to precipitate the crude product. The colorless fine crystals of TsOMI/furan adduct **3**, *N*-toluenesulfonyloxy-3,6-epoxy-1,2,3,6-tetrahydrophthalimide, with mp 165 °C, were obtained by recrystallization from acetone in a yield of 85% (57.28 g).

3: ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 2.50 (s, 3 H, Me), 2.96 (s, 2 H, 2 -CO-CH-), 5.15 (s, 2 H, 2 -O-CH-), 6.59 (s, 2 H, 2 =CH-), 7.56 (d, 2 H, benzene), 7.90 (d, 2 H, benzene). IR (KBr) ν (cm^{-1}) 3100 (olefinic CH), 1800, 1750 and 1740 (imide), 1180 (sulfone), 1150 (C-O-C).

Into a round-bottomed flask in an oil bath heated at 150 °C was placed 6.70 g of the adduct **3** and thermolysis was performed for 30 min under reduced pressure. The residue in the flask was dissolved in acetone and the insolubles were filtered off. Recrystallization from acetone gave the desired TsOMI (**4**) as white crystals with mp 150 °C in a yield of 57% (3.04 g). 4: ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm) 2.53 (s, 3 H, Me), 7.03 (s, 2 H, 2 =CH-), 7.57 (d, 2 H, benzene), 7.95 (d, 2 H, benzene). ^{13}C NMR δ (ppm); 21.80 (Me), 130.30, 131.03, 134.23 and 148.05 (benzene), 164.82 (C=C), 206.18 (C=O). IR (KBr) ν (cm^{-1}); 3100 (olefinic CH), 1825, 1748, and 1710 (imide), 1180 (sulfone). GC/MS *m/e* 267 (M, 1), 155 (90), 97 (8), 91 (100). Anal. Calcd for $C_{11}H_9NO_5S$: C, 49.43; H, 3.39; N, 5.24; S, 12.00. Found: C, 49.31; H, 3.46; N, 5.37; S, 11.93.

Polymerizations. All the radical polymerizations were carried out at 55 °C in dioxane under nitrogen atmosphere. TsOMI and styrene monomers **5** were charged in 1:1 molar ratio with 1 mol % of AIBN initiator (with respect to the combined monomers). The polymers were obtained by precipitating into *n*-hexane or methanol and drying in vacuo. The structure of obtained polymers was fully characterized by spectroscopy and the thermal deprotection of the side-chain *t*-BOC groups of the copolymer P(TsOMI/*t*-BOCSt) **6c** was investigated by TGA an DSC.

Measurement of Photogenerated Acid. The quantitative measurement of the photogenerated *p*-toluenesulfonic acid from P(TsOMI/St) **6a** in the film state was performed by employing a colorimetric method.[17-20] A merocyanine dye, 1-*n*-hexadecyl-4-[(4-oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine, was prepared according to the known procedure.[17,20] A polymer solution of 10 wt % P(TsOMI/St) in cyclohexanone was spin-coated onto silicon wafers and then dried at 90 °C for 3 min. The films of the same polymer containing 10% of hydroquinone with respect to the polymer were also prepared to investigate the influence of the additive in photoacid generation. Both the TsOMI polymer films before and after exposure were dissolved in a methylene chloride solution of the blue form of the dye which has an absorption maximum at 607 nm ($\epsilon = 7.00 \times 10^4$ L/mol cm). The decrease in absorbance of the polymer solution at 607 nm was measured to calculate the acid concentration. The results of acid generation were estimated in mole % based on TsOMI units of the copolymers. The exposure doses were calculated based on intensity of the 0.5 mW/cm^2 on a power meter tuned with a probe of 260-nm wavelength.

Image-Making with P(TsOMI/*t*-BOCSt) 6c. A resist solution of 10 wt % P(TsOMI/*t*-BOCSt) in cyclohexanone was prepared and filtered with a membrane filter of 0.45-μm pore size. The solution was applied onto silicon wafers at 2000-2500 rpm for 30 s with a Headway Research Spin-coater. The films of the polymer were prebaked at 90 °C for 3 min, and the film thickness was measured to be about 0.90 μm. The resist films were imagewise-exposed by a contact mode with various doses at 260-nm deep-UV light on a OAI Exposure System and postbaked at temperatures varying from 70 to 140 °C on a hot plate to effect the deprotection of *t*-BOC groups. Immersion development was carried out using organic solvents or aqueous alkaline solutions at room temperature. Negative-tone images were obtained by development with anisole for 1 min and positive-tone images resulted with 4% (1.0 N) aqueous NaOH solution for 1 min.

Acknowledgment. The authors are deeply grateful to the Korea Ministry of Science and Technology for the financial support of the research project on advanced resist materials.

(21) Narita, M.; Teramoto, T.; Okawara, M. *Bull. Chem. Soc. Jpn.* 1971, *44*, 1084.