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Copolymers of camphorsulfonyloxymaleimide and *t*-BOC protected vinyllactams for applications as single-component resists

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Summary

N-(10-Camphorsulfonyloxy)maleimide (CSOMI) have been copolymerized with two *t*-BOC protected vinyllactams, 3-(*t*-butoxycarbonyl)-1-vinyl-2-pyrrolidinone (BCVP) and 3-(*t*-butoxycarbonyl)-1-vinylcaprolactam (BCVC) to make photoacid-generating polymers P(CSOMI/BCVP) and P(CSOMI/BCVC), respectively. The thermal and photoacidolytic deprotection of the *t*-BOC protected copolymers readily underwent by UV exposure and solubilities of the polymers were remarkably changed thereafter. The polymers were proved to have the capability of a single-component, chemically amplified resist system in the deep-UV region without addition of any photoacid generator, because the polymers themselves photochemically generate a bulky 10-camphorsulfonic acid (SCA). The polymer films gave positive tone images by irradiation with electron beam (EB) and development with aqueous base solutions.

Introduction

There have been reported numerous nonionic photoacid generators (PAG) for applications in chemically amplified resist systems. (1) In particular, a great deal of research efforts have been paid to organic sulfonates which can generate strong sulfonic acids by UV exposure. (2, 3) These sulfonates are considered to be useful PAGs because they are easily synthesized, soluble in a variety of organic solvents, nonionic in character, and adequate in UV absorption. (2, 4) Most of the reported sulfonate PAGs are low-molecular-weight compounds and have been applied in photoimaging as an efficient organic PAG. We have previously reported polymeric photoacid generators based on various sulfonyloxymaleimides which generate corresponding sulfonic acids by deep UV

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(DUV) exposure. (5) These polymeric PAGs were advantageously utilized to design for single-component resists.

Several bulky sulfonate PAGs derived from camphorsulfonic acid (CSA) in a form of triphenylsulfonium salt or naphthalimide and phthalimide were reported to have advantages in thermal stability, nonvolatility and acid diffusion for resist applications. (6) Recently, we have reported new polymeric PAGs based on the alternating copolymers of *N*-(10-camphorsulfonyloxy)maleimide (CSOMI) and styrenes (XSt). (7) In particular, the copolymer P(CSOMI/*t*-BOCSt) consisting of CSOMI and *p*-(*tert*- butyloxycarbonyloxy)styrene (*t*-BOCSt) was found to possess the capability of a single-component resist system by chemical amplification without using any externally added PAG. (7) These single-component resist systems should be free of the compatibility problem arising by addition of a PAG due to its limited solubility in the resist media. In this work a photoacid-generating monomer CSOMI were copolymerized with two t-BOC protected vinyllactams, 3-(*tert*-butoxycarbonyl)-1-vinyl-2-pyrrolidinone (BCVP) and 3-(*t*-butoxycarbonyl)-1-vinylcaprolactam (BCVC). The *t*-BOC protecting groups of BCVP and BCVC units in their polymers were reported to be acidoylitically removable, thereby inducing a significant solubility change of the polymers. (8) The thermal and acidolytic deprotection of the CSOMI polymers were investigated along with preliminary evaluation as a single-component resist system.

Experimental

Materials and Instruments

Furan, maleic anhydride, 10-camphorsulfonyl chloride, caprolactam, hydroquinone (HQ), *n*-butyllithium, *N*-vinylpyrrolidinone and *di-tert*-butyldicarbonate were purchased from Aldrich Chemical Company and used without further purification. Tetrahydrofuran, 1,4-dioxane and diethyl ether purchased from Junsei Chemical Co. were purified prior to use. Hydroquinone was recrystallized from ethanol. Other chemicals were purified by conventional methods. ^{1}H-NMR and ^{13}C-NMR spectra were taken on a Varian Gemini 2000 (200MHz) spectrometer in deuteriochloroform using tetramethylsilane as an internal standard. Infra-red spectra were recoded on a Polaris FT-IR spectrophotometer of Mattson Instrument Co. and elemental analysis was done with a Perkin-Elmer Model 240C elemental analyser. Thermal analysis was carried out on a Du Pont Model 910 DSC and Model 951 TGA at a heating rate of 10℃/min under nitrogen atmosphere. UV absorption spectra were recoded on a JASCO UV/VIS spectrophotometer.

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℃ in dioxane. Film thickness was measured by P-10 Surface Profiler of Tencor Instruments.

Exposure of the polymer films was made on a UV illuminator of Ushio Inc. equipped with a 500-W high-pressure mercury lamp in conjunction with an Oriel narrow-band-pass filter for 250nm. Electron beam lithography was performed on a Cambridge Instrument EBMF 10.5 at 30KeV in Inter-University Semiconductor Research Center of Seoul National University.

Polymerization

Three monomers CSOMI, BCVP and BCVC were prepared according to the previously reported procedure. (7, 8) Copolymerizations were carried out using 2mol% AIBN in dioxane at 60℃ for 5h. The CSOMI monomer and the vinyllactam comonomers were charged in 1:1 molar ratio to obtain two alternating copolymers P(CSOMI/BCVP) and P(CSOMI/BCVC).

To a 10ml reaction vessel with a nitrogen inlet and an outlet placed were CSOMI (1.01g, 3.08mmol), BCVC (0.73g, 3.05mmol) and AIBN (0.02g, 0.12mmol) in 3.8ml dioxane. The copolymerization was carried out for 5h at 60℃ under nitrogen. The product was diluted with dioxane and precipitated into 300ml of methanol. The white powdery copolymer P(CSOMI/BCVC) was obtained in a yield of 85% (1.48g) after drying in vacuo at 40℃. The inherent viscosity of the polymer was measured to be 0.38dℓg^{-1} in dioxane at 25℃. BCVP was also copolymerized with CSOMI following the same procedures. The results of elemental analyses of two copolymers were compared with the value of the copolymers by assuming an alternating structure. P(CSOMI/BCVP) : Anal. Calcd : C, 55.7 ; H, 6.36 ; N, 5.20 ; S, 5.95. Found : C, 55.1 ; H, 6.46 ; N, 5.15 ; S, 6.02. P(CSOMI/BCVC) : Anal. Calcd : C, 57.2 ; H, 6.76 ; N, 4.94 ; S, 5.66. Found : C, 55.3 ; H, 6.87 ; N, 4.90 ; S, 5.99.

Image-making

A 15wt% solution of P(CSOMI/BCVC) containing 5wt% hydroquinone with respect to the polymer in cyclohexanone was filtered with a membrane filter of 0.2-㎛ pore size. The solution was applied onto silicon wafers at 2500-3000rpm for 30sec using a spin-coater of Headway Research. The resist films were prebaked at 80℃ for 90sec and the film thickness was measured to be about 0.7 ㎛. The films were irradiated with 30KeV electron beam and underwent post-exposure bake at temperatures varying from 110 to 120℃ on a hot plate. Immersion development was carried out using a diluted 2.38wt% TMAH solution at room temperature. Positive-tone images were obtained by developing for 20sec and subsequent rinse with pure water.

Results and Discussion

Copolymerizations of CSOMI

The electron poor monomer CSOMI was readily copolymerized with a *t*-BOC protected, vinyllactam monomer BCVP or BCVC using AIBN as a radical initiator to render acid-labile, photoacid-generating polymers. The CSOMI monomer and the vinyllactam comonomers were charged in 1:1 molar ratio to obtain two copolymers P(CSOMI/BCVP) and P(CSOMI/BCVC) in high yield. The copolymers prepared in this study are described in Scheme 1 and the results of the copolymerizations are summarized in Table 1. The copolymers were found to have alternating composition by NMR and elemental analysis. *N*-Vinylpyrrolidinone (VP) ia known to be electron donating and VP usually give alternating copolymers with electron-accepting monomers. (9)

Scheme 1

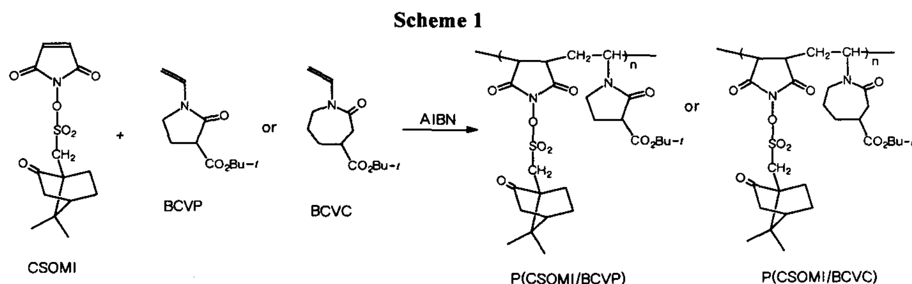


Table 1. Copolymerization Results of CSOMI with *t*-BOC Vinyllactams[a]

Polymer	Yield (%)	Inherent viscosity[b] (g/dℓ)	Mass loss[c] Calcd.	Mass loss[c] Found	T_{dp}*(℃)
P(CSOMI/BCVP)	82	0.38	18.7	17	210
P(CSOMI/BCVC)	85	0.36	17.8	15	205

[a]Copolymerization in 1:1 molar feed ratio using AIBN (2mol%) at 60℃ for 5h in dioxane.
[b]Inherent viscosities measured at a concentration of 0.2g/dℓ in dioxane at 25℃.
[c]The mass loss is calculated by assuming the alternating structure.
*Thermal analysis done at a heating rate 10℃/min in a nitrogen stream and the deprotection temperature (T_{dp}) of the side-chain *t*-BOC groups measured by DSC.

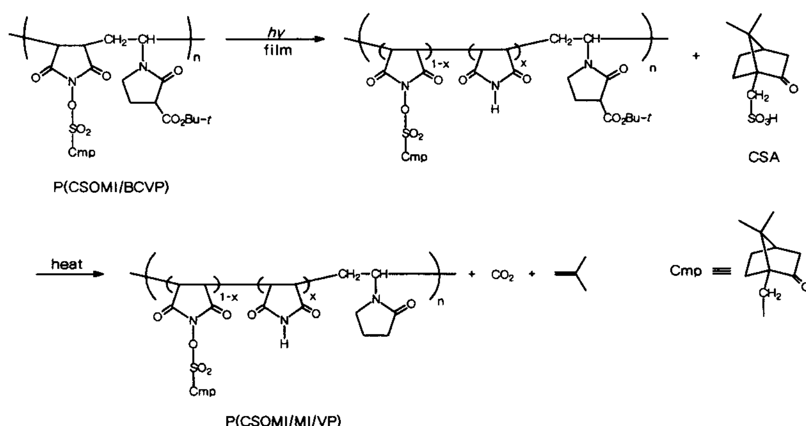
Thermal and Photoacidolytic Deprotection

The thermograms of two *t*-BOC protected copolymers revealed endothermic events in the range of 200-210℃ due to the deprotection of *t*-BOC groups in DSC. The TGA curve of P(CSOMI/BCVP) shown in Fig. 1 (a) indicates that the polymer is thermally stable up to 180℃ and then it undergoes precipitous mass loss, evolving isobutylene and carbon dioxide due to the spontaneous thermolysis of the *t*-BOC groups. By the thermal deprotection, the BCVP units in

P(CSOMI/BCVP) are converted to the VP units as the deprotected polymer structure is transformed into P(CSOMI/VP). Accordingly, BCVC units in the copolymer P(CSOMI/BCVC) are also converted to *N*-vinylcaprolactam (VC) units to give P(CSOMI/VC). Upon DUV exposure a bulky sulfonic acid CSA is photochemically generated in some extent (7) Acidolytic deprotection of the *t*-BOC groups induced by the photogenerated acid in P(CSOMI/BCVP) is verified as shown in Fig. 1 (b). The cleavage of the *t*-BOC groups in P(CSOMI/BCVP) begins at about 100℃, transforming the polymer into P(CSOMI/MI/VP) as described in Scheme 2. At the photolysis step only x mole fractions (about 10mol%) of CSOMI units in the polymers are converted to maleimide (MI) units while generating CSA (7). By comparing the curves (a) and (b) in Fig. 1, the thermal and photoacidolytic deprotection of the *t*-BOC groups of P(CSOMI/BCVP) resulted in nearly the same mass loss of 17wt% which corresponds to the theoretically calculated weight loss due to the evolution of carbon dioxide and isobutylene from the copolymer. (8)

Both the copolymers showed very similar thermal and photochemical deprotection behaviors. Upon exposure to 250nm DUV with 100mJ/cm^2 P(CSOMI/ BCVC) revealed a distinctive endothermic event due to the deprotection of *t*-BOC groups at much lower temperature (146℃) in its DSC thermogram as shown in Fig. 2 (b). This implies the acidolytic deprotection by the photogenerated CSA as depicted in Scheme 2. The deprotection temperature (T_{dp}) further decreased to 115℃ when 5wt% hydroquinone (HQ) was added to the polymer as shown in Fig. 2 (a). HQ is known to be an effective additive for generation of CSA in the photocleavage reaction. (5) The acidolytic deprotection temperatures of P(CSOMI/BCVC) considerably lowered as compared with the original thermal deprotection temperature at 205℃ in the absence of CSA before exposure.

Scheme 2



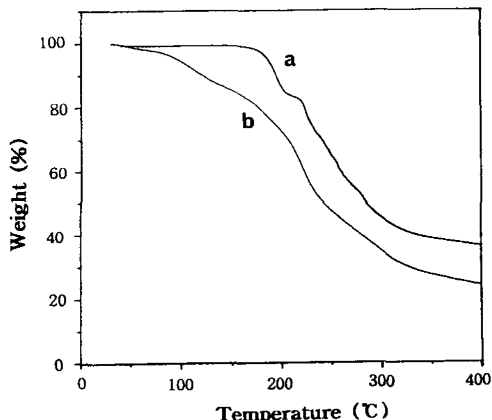


Fig. 1. TGA thermograms of (a) P[CSOMI/BCVP] and (b) the same polymer when exposed to deep UV at 250nm with 100mJ/cm^2 for photoacid generation in the film.

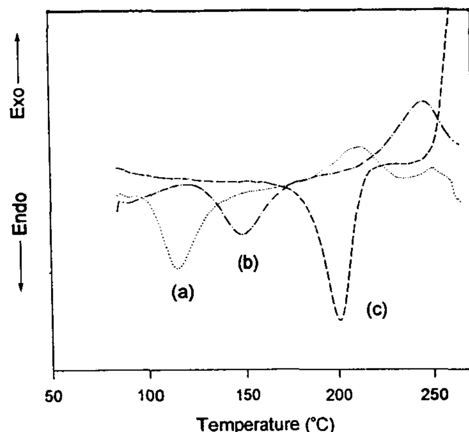


Fig. 2. DSC thermograms of P[CSOMI/BCVC] by exposure to 250nm DUV with 100mJ/cm^2: endothermic peaks appeared at (a) 115℃ with 5wt% HQ, (b) 146℃ without HQ and (c) 205℃ without exposure.

Solubility of Polymers

All of the copolymers are white powders having a good film forming property. The *t*-BOC protected polymers show considerable change in solubility after deprotection due to the large polarity changes. The deprotected polymers were obtained by exposure to DUV and subsequent heating or post-exposure bake (PEB) at 120℃ for 2min in the film state. The copolymers of P(CSOMI/BCVP) and P(CSOMI/BCVC) are very soluble in common organic solvents such as chloroform, toluene, chlorobenzene and dimethylformamide (DMF) but insoluble in aqueous base solutions, hexane and chloroform. The deprotected polymers, P(CSOMI/MI/VP) and P(CSOMI/MI/VC), however, are soluble in aqueous base solutions, THF, methanol, dioxane and DMF but insoluble in organic solvents such as chloroform, toluene and hexane. The good solubilities of the deprotected polymers in aqueous base solutions are of utmost importance in practical applications as resist materials.

Applications as Single-Component Resists

The P(CSOMI/BCVC) film exhibits excellent transparency at 250nm and nearly no change upon exposure to DUV and subsequent PEB as shown in the UV spectra of Fig. 3. The major contributor to the UV absorption in the resist film at this wavelength is the added 5wt% hydroquinone as shown in the curve d in Fig. 3. The optical density of P(CSOMI/BCVC) at 250nm in the film state was determined to be 0.04μm^{-1}. The protected polymers show high resistance toward development and the thickness of the unexposed films is remained intact in a

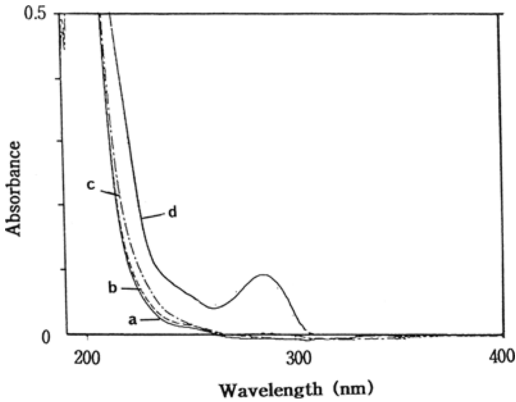


Fig. 3. UV absorption spectra of 1.0㎛ thick P[CSOMI/BCVC] film: (a) as cast, (b) exposure to DUV for 100mJ/cm^2, (c) PEB at 120℃ for 2min and (d) the polymer with 5wt% HQ.

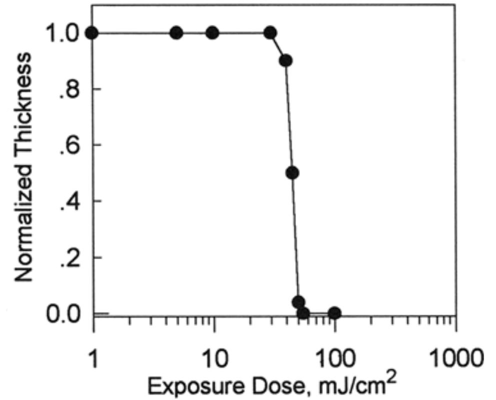


Fig. 4. Plots of normalized thickness P[CSOMI/BCVC] resist vs. exposure dose at 250nm and PEB at 120℃ for 2min.

commercial aqueous base developer, 2.38wt% tetramethylammonium hydroxide (TMAH) solution. Fig. 4 is a typical sensitivity curve for a 0.7㎛ thick resist film of P(CSOMI/BCVC) containing 5wt% HQ. After exposure to 250nm DUV and PEB at 120℃ for 2min the sensitivity of the resist was determined to be about 45mJ/cm^2 with a high contrast (γ) of 9.6.A commercial 2.38wt% TMAH solution was diluted with 4 times of water and the diluted TMAH solution was used as a developer. Positive-tone 0.7㎛ image patterns were delineated by irradiation with 30KeV electron beam as shown in Fig. 5. Negative-tone images were also obtained by development with anisole.

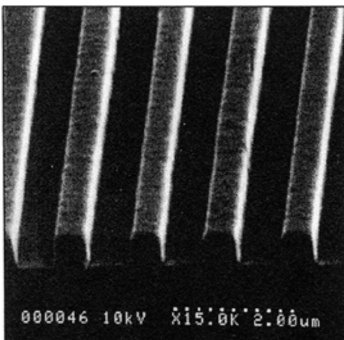


Fig. 5. A SEM photograph of 0.7㎛ coded line and space patterns formed in 0.65㎛ thick P(CSOMI/BCVC) resist irradiated with EB dose of 15μC/cm^2 and followed by PEB at 120℃ for 90sec and development for 20sec.

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