Facile Synthesis of Photosensitive Poly(semi-alicyclic benzoxazole) and Subsequent Low-Temperature Cyclization of Poly(*o*-hydroxy amide)

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ABSTRACT: A positive-type photosensitive polybenzoxazole (PSPBO) based on partially *tert*-butoxycarbonyl (*t*Boc) protected poly(semi-alicyclic *o*-hydroxy amide) (PAtBA) and a photoacid generator, (5-propylsulfonyl-oxyimino-5*H*-thiophene-2-ylidene)−(2-methylphenyl)acetonitrile (PTMA), has been developed for a promising material in microelectronics. PAtBA was prepared from poly(semi-alicyclic *o*-hydroxy amide) (PAHA) and di-*tert*-butyl dicarbonate in the presence of catalytic diethylmethylamine in cyclohexanone and used directly for lithographic evaluation. The *t*Boc protection to PAHA and thermal behavior of PAtBA were characterized by thermogravimetric analysis (TG), ^{1}H NMR, UV−vis, and FTIR spectrometry. As a result of photolithographic evaluation, the PSPBO precursor, PAtBA-20 containing 10 wt % PTMA, showed a sensitivity of 35 mJ/cm^2 and a contrast of 12.8, when it was exposed to a 365 nm light (*i*-line), postbaked at 110 °C for 5 min, and developed with a 2.38 wt % aqueous tetramethylammonium hydroxide solution (TMAHaq) at 25 °C. A fine positive image of 7.8 μm line-and-space pattern was printed in a film which was exposed to 50 mJ/cm^2 of *i*-line by contact-printing mode and fully converted into the corresponding polybenzoxazole (PABO) pattern upon heating at 250 °C, confirmed by SEM and FTIR spectroscopy. Thus, PTMA is effective as a thermoacid generator for low-temperature cyclization of PAtBA into the PABO as well to meet practical requirement in the industry.

Introduction

Photosensitive polybenzoxazoles (PSPBOs)[1−4] are attracting materials in a field of microelectronics industry owing to not only remarkably thermal and mechanical properties, which are comparable to photosensitive polyimides (PSPIs), but also low dielectric characters unlike PSPIs.[5−7] By using PSPBOs or PSPIs, the processing steps are simplified for the fabrication of electronic devices containing metal wiring embedded in these thermally stable polymers. Otherwise, an additional photoresist is required to make a pattern of the thermally stable polymers, involving complicated process steps. Capability of development in an aqueous alkaline solution (e.g., aqueous tetramethylammonium hydroxide solution; TMAH$_{aq}$) is also beneficial for an environmental benign process. Especially, PSPBOs have an advantage over PSPIs because poly(*o*-hydroxy amides) (PHAs), precursors of polybenzoxazoles (PBOs), possess phenolic hydroxyl groups, providing adequate solubility to an aqueous alkaline developer.

We have reported the synthesis of semi-alicyclic PHA (PAHA) with high transparency (99% T at 365 nm) and the corresponding PBO (PABO) having a low dielectric constant ($\epsilon = 2.55$).[8] PAHA was then employed as both (a) positive-type PSPBO consisting of PAHA, 1,3,5-tris[(2-vinyloxy)ethoxy]benzene (TVEB) as an acidolytic de-cross-linker, and diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a photoacid generator (PAG)[8] and (b) negative-type PSPBO based on PAHA, oxybis(3,4-dihydroxymethyl)benzene (OBHB) as a cross-linker, and (5-propylsulfonyloxyimino-5*H*-thiophen-2-ylidene)−(2-methylphenyl)acetonitrile (PTMA) as a PAG[9] in chemical amplification systems. Because of the introduction of an adamantyl unit in the polymer, the dielectric constant of PABO effectively lowered because of the decreasing molecular density and conjugation in the main chain.

Another attracting aspect for development of PSPBO is lower cyclization temperature of PHAs. Up until now, PSPBO based on a PHA derived from 4,4′-(hexafluoroisopropylidene)−bis-(*o*-aminophenol) (6FAP) and 4,4′-oxybis(benzoic acid) derivatives with a photosensitive compound (e.g., diazonaphthoquinone) has been widely used,[10,11] in which the image of the PHA is finally converted into that of PBO by thermal treatment at 350 °C. Such a high-temperature process is hardly accessible to the conventional electronic applications containing thermally unstable components, such as glass−epoxy resin and glass−benzotriazole resin in a built-up or package board.

Recently, sulfonic acids were found to work as effective catalysts for low-temperature cyclization of the PHA.[12] Especially, PTMA acts not only as an excellent PAG in *i*-line (365 nm) or *g*-line (436 nm) regions[13] but also as a thermoacid generator to lower the cyclization temperature down to 250 °C. Thus, compared to the noncatalytic procedure at 350 °C, the significant decreasing of the cyclization temperature will lead to versatile developments of the PSPBO system with PTMA, producing more useful applications in the microelectronics industry.

Here, we applied the major two strategies such as facile development of PSPBO and thermal cyclization of PHA at lower temperatures for development of new PSPBO system. Partially *tert*-butoxycarbonyl (*t*Boc) protected PAHA (PAtBA) was utilized for positive-type PSPBO with PTMA, which is different photolithographic system referred above.[8,9] The *t*Boc-protected materials based on poly(hydroxystyrene) derivatives,[14−16] calixarene derivatives,[17,18] polyimide,[19] or even PHA/PBOs[20,21] are commonly employed as positive-type photosensitive polymers, owing to reliability of chemical amplification under the control

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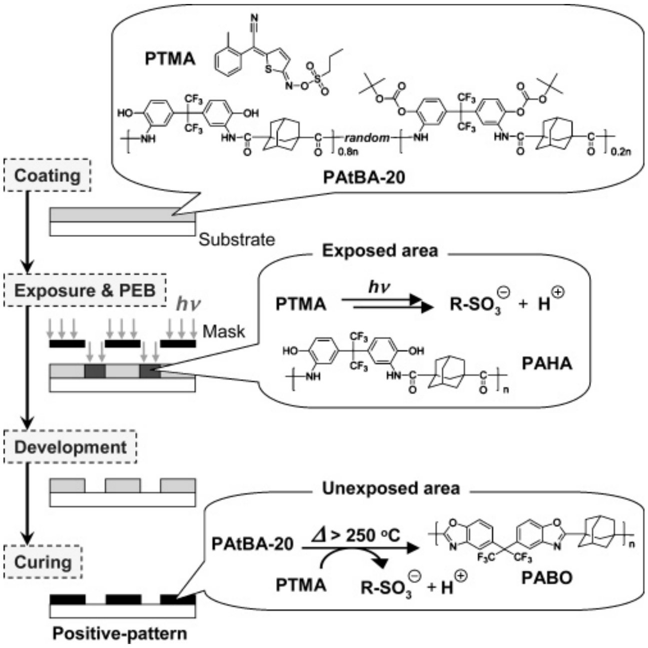
Scheme 1. Patterning Process and Subsequent Low-Temperature Cyclization Using Positive-Type PSPBO Based on Partially Protected PAtBA and PTMA



of PAGs and postexposure bake (PEB) temperatures. The formation of positive pattern of PHA, however, plays a key role to accomplish the low-temperature cyclization because PTMA should be remained intact in the film until the thermal treatment after the image formation, as shown in Scheme 1. In contrast, it seems to be almost impossible to make a PBO pattern lower than 300 °C for the strategy of negative-type PSPBO due to exhausting PTMA in the film at the stages of UV exposure, followed by the development with an aqueous developer.

Moreover, facile preparation of partially protected PAtBA in a solution makes applicable for direct photolithographic evaluations and pattern formations. Usually, *t*Boc-protection reaction was carried out with (*N*,*N*-dimethylamino)pyridine (DMAP) as a base catalyst, even though removal of the base and purification procedure should be required.[22] On the other hand, PAtBA was prepared from PAHA with di-*tert*-butyl dicarbonate in the presence of a catalytic amount of a volatile base such as diethylmethylamine and used directly for image formation. The subsequent low-temperature cyclization into PABO pattern at 250 °C proceeded successfully with an acetic acid treatment after development with TMAHaq. As a consequence, the direct use of the partially protected PAtBA solution simplified the photolithographic process, and the following thermal treatment at 250 °C will promote PSPBO for diverse applications.

Experimental Section

Materials. 5,5′-(Hexafluoroisopropylidene)−bis(2-hydroxyadamantanecarboanilide) (**1**) and PAHA were prepared as described previously.[8] The number- and weight-average molecular weight (M_n and M_w) of PAHA was 12 600 and 22 100 (M_w/M_n 1.8) measured by GPC with polystyrene standards. A photoacid generator, PTMA,[13] was kindly donated by Ciba Specialty Chemicals, stored in a refrigerator, and used without further purification. Di-*tert*-butyl dicarbonate (97% purity, Aldrich), diethylmethylamine (Aldrich), cyclohexanone (Wako), 2-methoxyethanol (Wako), and the other chemicals were used as received unless noted.

Synthesis of 5,5′-(Hexafluoroisopropylidene)−Bis(2-*tert*-butoxycarbonyloxyadamantanecarboanilide) (PAtBA Model Compound, 2). To a solution of **1** (0.256 g, 0.371 mmol) and di-*tert*-butyl dicarbonate (0.170 g, 0.779 mmol) in cyclohexanone (1.46 g, to be a 15 wt % solution) was added diethylmethylamine (9.4 μL, 0.0779 mmol). The solution was stirred at room temperature for 10 h. A portion of the solution was taken out for ^{1}H NMR spectroscopy at each desired reaction period (0, 1, 3, 5, and 8 h). Then, the reaction mixture was poured into water. The precipitate was filtered and washed with water, followed by drying in vacuo at 80 °C. The collected white solid was purified by recrystallization from hexane. The yield was 0.235 g (71%). IR (KBr, ν, cm^{-1}): 2935 and 2857 (Ali), 1766 and 1650 (C=O), 1604 (Ar), 1253 (CF$_3$). ^{1}H NMR (DMSO-d_6, δ, ppm): 1.47 (s, 18H, C(CH_3)$_3$), 1.69 (s, 12H, CHCH_2CH), 1.88 (s, 12H, COC(CH_2)$_3$, 2.00 (s, 6H, CH), 7.11 (d, J = 9.3 Hz, 2H, Ar), 7.35 (d, J = 8.7 Hz, 2H, Ar), 7.59 (s, 2H, Ar), 8.89 (s, 2H, NHCO). ^{13}C NMR (DMSO-d_6, δ, ppm): 27.3, 28.1, 28.5, 36.8, 39.7, 42.2, 85.2, 121.9, 125.0, 126.9, 130.5, 131.6, 141.7, 151.0, 176.2. Elemental Analysis: Calcd for $C_{47}H_{56}F_6N_2O_8$: C, 63.36; H, 6.34; N, 3.14. Found: C, 63.34; H, 6.64; N, 3.10.

Syntheses of PAtBAs; General Procedure. For a synthesis of 100% *t*Boc-protecting PAHA (PAtBA-100), to a solution of PAHA (0.771 g, containing 2.78 mmol unit of OH group) and di-*tert*-butyl dicarbonate (0.609 g, 2.79 mmol) in cyclohexanone (4.37 g, to be a 15 wt % solution) was added diethylmethylamine (67.3 μL, 0.556 mmol, to be 0.200 equiv of OH group on PAHA). For other *t*Boc-protecting PAHA (denoted as PAtBA-*x*; x = 20, 35, 50, and 70) with different *t*Boc-protection ratios (20−70%), di-*tert*-butyl dicarbonate was added as much as *x* percentage of OH group on PAHA fed in the reaction. The solution color was gradually changed from yellowish to less clear pale after the addition of diethylmethylamine. The solution was stirred at room temperature for 10 h. If any, the reaction mixture was poured into water to precipitate. The white powder was collected by filtration and washed with water, followed by drying in vacuo at 80 °C. For a direct photolithographic evaluation, the reaction mixture was used without further processing (e.g., precipitation, extraction, and so on).

Dissolution Rate. PTMA (5 or 10 wt % of the total polymer weight) was added to a PAtBA solution in cyclohexanone (15 wt % concentration) to construct a photosensitive polymer. The polymer film spin-cast from the solution on a silicon wafer was prebaked at 80 °C for 3 min and then exposed to a filtered super-high-pressure mercury lamp at 365 nm (*i*-line), followed by postexposure baking at a set of temperatures (100−120 °C) for 5 min each. The exposed film was developed with 2.38 wt % TMAH$_{aq}$ at 25 °C. The dissolution rate (Å/s) of the film was determined from changes in the film thickness before and after the development.

Photosensitivity. A 1.8 μm thick photosensitive polymer film on a silicon wafer was exposed to *i*-line and then developed with 2.38 wt % TMAH$_{aq}$ at 25 °C for 45 s, followed by rinsing with water. A characteristic curve was obtained by plotting a normalized film thickness as a function of exposure dose (unit: mJ/cm^2).

Degree of Cyclization from *t*Boc-Protected PAHA into PABO. PAtBA or the photosensitive polymer film spin-cast on a silicon wafer was baked at 110 °C for 5 min as mimic of PEB. The each film thickness was about 0.80 μm. The film was then heated on a hot plate at a set of temperatures (150−350 °C) for 15 min each. PABO film was prepared by heating at elevated temperature up to 350 °C and held at that temperature for 1 h under nitrogen as a reference. Absorption intensities on a FTIR spectrum at 1045 cm^{-1} (A_{1045}) assignable to C−O stretch of benzoxazole group and at 609 cm^{-1} (A_{609}) assignable to silicon wafer as invariable standard was measured, and the degree of cyclization was determined using the following equation:[23]

$$\text{degree of cyclization [\%]} = (A_{1045}/A_{609[\text{samp}]} - A_{1045}/A_{609[\text{init}]})/(A_{1045}/A_{609[\text{PABO}]} - A_{1045}/A_{609[\text{init}]}) \times 100 \quad (1)$$

Subscripts between brackets followed A_{1045}/A_{609} in the equation indicate states of the film; e.g., [samp] is the polymer sample at each heating temperature level (150−300 °C), [init] is initially prebaked polymer film at 110 °C in air, and [PABO] is the fully cured PABO at 350 °C for 1 h under nitrogen.

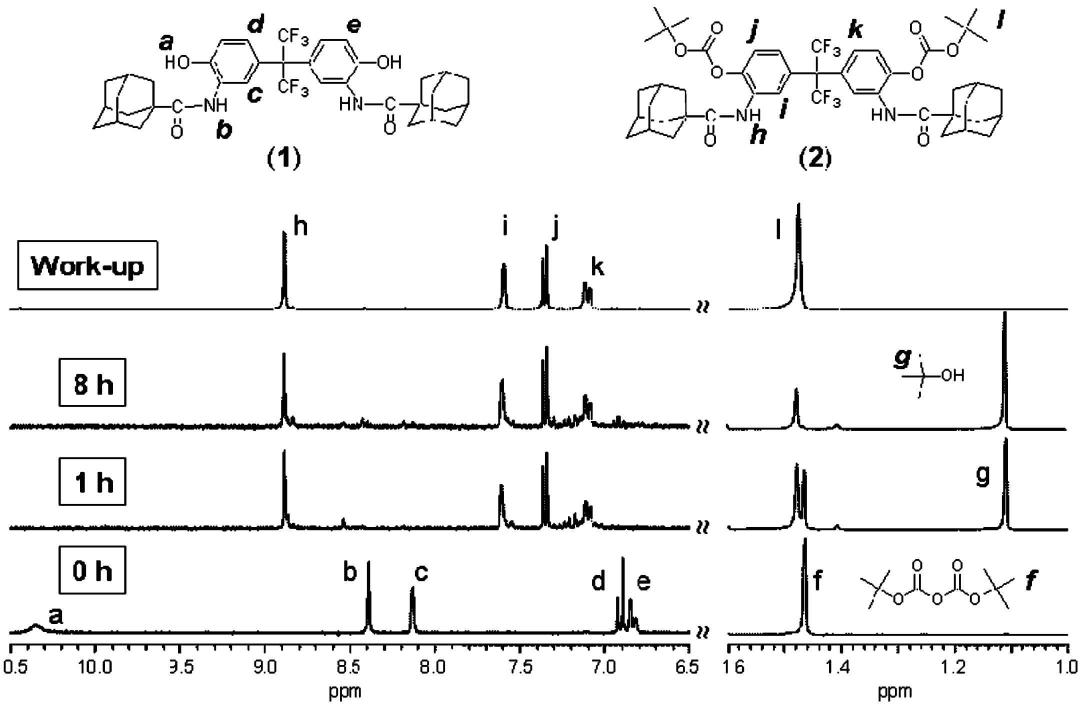
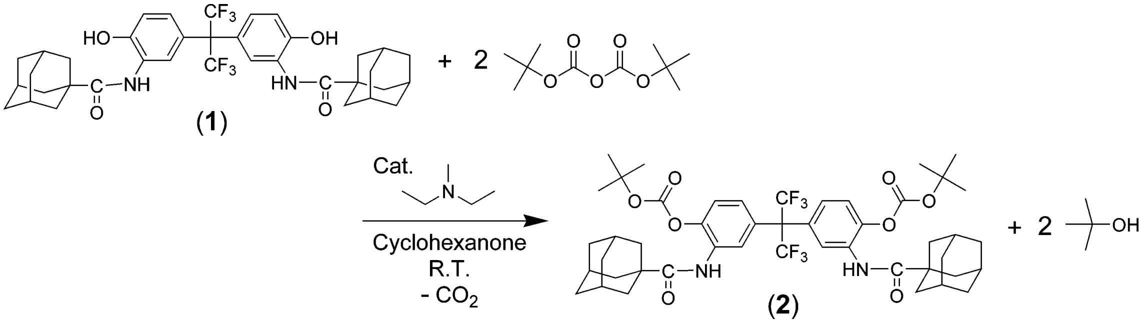


Figure 1. ^{1}H NMR spectra in distinctive areas for *t*Boc-protection reaction of PAHA model compound **1** in the presence of diethylmethylamine (see Scheme 2). Each spectrum shows arbitrary intensity and reaction time after addition of the base.

Scheme 2. Model Reaction for *t*Boc Protection to PAHA in the Presence of Diethylmethylamine



Measurements. Infrared spectroscopy (FTIR) was taken with a Horiba FT-210 spectrophotometer. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker GPX300 spectrometer (^{1}H at 300 MHz and ^{13}C at 75 MHz). Thermogravimetry (TG) was performed on a Seiko TG/DTA 6300 at a heating rate 2.5 °C/min under a nitrogen stream. Ultraviolet−visible (UV−vis) spectroscopy was performed on a Jasco V-650 spectrophotometer. M_n and M_w were determined by a GPC with Tosoh HLC-8120 equipped with two polystyrene gel columns (TSK GELs; GMH_{HR}-M and GMH_{HR}-L) at 40 °C in DMF (containing 0.01 M LiBr) at a flow rate of 1.0 mL/min, calibrated with polystyrene standards. The film thickness on silicon wafers was measured by Veeco Instrument Dektak^3 surface profiler. The field emission scanning electron microscope (SEM) was taken with Technex Lab Tiny-SEM 1540 in 15 kV accelerating voltage for imaging. Pt/Pd was spattered on a film in advance of the SEM observation.

Results and Discussion

Model Reaction for *t*Boc Protection with PAHA. For a *t*Boc protection of phenolic hydroxyl groups, DMAP is used as a common base catalyst.[22] Therefore, removal procedure of the base (typically, precipitation into water) is required because DMAP is nonvolatile (bp 162 °C at 50 mmHg). On the other hand, *tert*-butyl alcohol which is a byproduct from the protection reaction tends to be easily vaporized on a soft heating to 100 °C (bp 83 °C). As for more simple procedures for PSPBO, facile preparation of photosensitive polymers should be established. Here, we selected a volatile base such as diethylmethylamine (bp 63−65 °C) for the alternative to DMAP. The evaporation of the amine is also important in a lithographic evaluation so that a PAG can work effectively. Otherwise, the photochemically generated acid from the PAG will be quenched by the amine.

To clarify the *t*Boc-protection reaction with diethylmethylamine, model compound **1** was reacted with di-*tert*-butyl dicarbonate in the presence of diethylmethylamine (10 mol % of di-*tert*-butyl dicarbonate) in cyclohexanone, a common resist solvent (Scheme 2). The reaction mixture was sampled at desired period and measured by ^{1}H NMR spectrometry (DMSO-d_6), as shown in Figure 1. The reaction proceeded smoothly with the base catalyst in a few hours. After the reaction for 8 h, the original signal of di-*tert*-butyl dicarbonate (1.47 ppm) disappeared in the spectrum, and signals due to the reacted *tert*-butyl group of compound **2** (1.48 ppm) and byproduct of *tert*-butyl alcohol (1.11 ppm) appeared clearly. The latter signal was then removed after workup procedures as precipitation, filtration, and vacuum-drying.

Control of *t*Boc-Protection Reaction with PAHA and Characterizations. Since the minimum ratio of the *t*Boc group attached in PAHA is desirable for lithographic evaluation in a chemical amplification system, control of the protection ratio

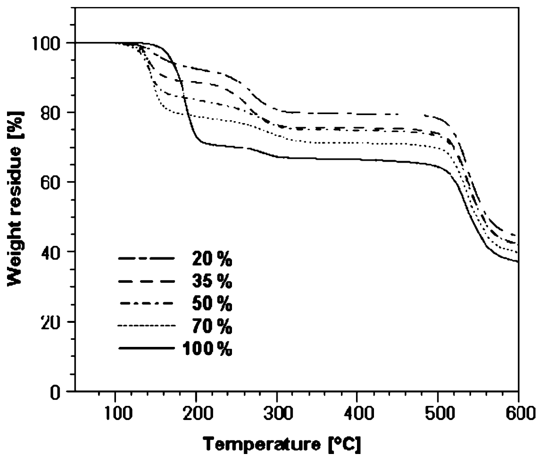


Figure 2. TG traces of partially protected PAtBAs with various protection ratios, measured at a heating rate of 2.5 °C/min under nitrogen.

Table 1. Characterization of Series of PAtBAs

PAtBA-*x*	weight loss [wt %][a]		proton ratio (tBu/[Ar + NH])[b]		UV−vis at
x	calcd	exptl	calcd	exptl	310 nm [%*T*][c]
20	6.7	7.1	0.45	0.44	47.8
35	11.2	11.3	0.79	0.75	53.7
50	15.3	16.0	1.13	1.16	61.3
70	20.2	20.8	1.58	1.60	74.6
100	26.5	28.2	2.25	2.33	93.5

[a] Weight loss was determined at 190 °C (except 220 °C for PAtBA-100) by TGA at a heating rate of 2.5 °C/min under nitrogen (Figure 2). [b] Proton ratio of *tert*-butyl group (*t*Bu: 1.41−1.43 ppm) and multiaromatic and amino signals (Ar + NH: 6.80−9.05 ppm) was calculated from each ^{1}H NMR spectrum (DMSO-d_6, 40 °C). [c] Transmittance was measured by UV−vis spectrometry in 2-methoxyethanol (1.0×10^{-3} [M]; Figure 3).

was studied. The reaction of PAHA with a various feed ratio of di-*tert*-butyl dicarbonate (20, 35, 50, 70, and 100 mol %) to the phenol groups in the presence of catalytic diethylmethylamine was carried out in a similar way as the model reaction described above. A series of partially protected PAtBAs were obtained by precipitation into water, followed by vacuum-drying at 80 °C.

To estimate the protecting ratio of the resulted polymers, thermogravimetric analysis was conducted. The *t*Boc group releases a quantitative amount of isobutene and carbon dioxide around 180 °C. The traces of TGs are shown in Figure 2, indicating all polymers have three plateaus: normal condition (<130 °C), after thermal decomposition of *t*Boc group (180−250 °C), and after thermal cyclization into PABO (<330 °C). It is reasonable for 100% protected PAtBA to decompose at higher temperature than the others because of no acidic phenol moiety in the polymer.[18] The gradual slopes in the middle plateaus and the subsequent decreasing trends up to 320 °C are ascribed to a thermal dehydration of PAHA to PABO. All polymers also show similar decomposition behaviors around 520 °C, which corresponds to that of fully cured PABO as reported.[8] The observed weight losses are in good agreement with calculated ones (Table 1). Since the ^{1}H NMR spectrum of partially protected PAtBAs provided complicated multiple signals because of a mixture of several compounds, the proton ratio of the *tert*-butyl group (*t*Bu: 1.41−1.43 ppm) to whole aromatic and amino groups (Ar + NH: 6.80−9.05 ppm) was estimated. As summarized in Table 1, the experimental proton ratios nearly correspond to the theoretical values.

Further characterization by UV−vis spectrometry (Figure 3) was performed for each PAtBA to measure its transparency, which is an important parameter to conduct *i*-line photolithography. Because of low transparency of cyclohexanone below 350 nm, UV−vis spectra of the PAtBAs in 2-methoxyethanol were measured down to 280 nm at a concentration of 1.0 mM. It is noteworthy that the transparency increases with increasing the *t*Boc-protection ratio of PAtBAs (Table 1); however, all the polymers show remarkably high transparency in the *i*-line region (>99% *T*) as well as nonprotected PAHA.[8] The expanding the clear UV region is explained by increasing twist of the polymer main chain, which suppresses both formation of charge-transfer complex and intramolecular hydrogen bonding. Indeed, introduction of the alkyl or *t*Boc group to PHA is effective to get higher transparency than unsubstituted PHA by theoretical and experimental analyses.[4,11,24]

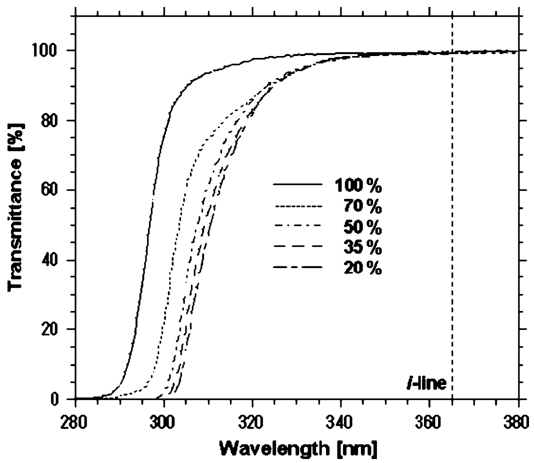


Figure 3. UV−vis spectra of partially protected PAtBAs with various protection ratios in 2-methoxyethanol (1.0×10^{-3} [M]).

Lithographic Evaluation for the PAtBA-20/PTMA Resist System. The introduction of *t*Boc groups to PAHA means construction of a chemical amplification resist with a PAG such as PTMA which is easily soluble in common organic solvents and sensitive to *i*-line exposure.[13] The film of PAtBA containing PTMA (10 wt %) was prebaked at 80 °C for 3 min in air. To this film was irradiated UV light of *i*-line by a filtered super-high-pressure mercury lamp and then postexposure baked (PEB) at a set of temperatures (100−120 °C) for 5 min. The exposed film was immediately developed with a 2.38 wt % TMAH_{aq} at 25 °C and rinsed with water. The dissolution rate was estimated from the change of the film thickness before and after the development.

To determine the minimum *t*Boc protection of PAHA for the photolithographic evaluation, the series of PAtBA-*x* ($x = 0$, 20, 35, 50, 70, and 100) films were soaked into the TMAH_{aq} developer. The resulted dissolution rates are shown in Figure 4. No dissolution is observed on the films of PAtBAs protected more than 50% of OH group in PAHA. On the other hand, PAtBA-20 dissolves in the developer at a rate of 1 Å/s,[25] which is 10^3 times smaller than the dissolution rate of PAHA ($x = 0$). Therefore, PAtBA-20 was selected for the further investigation in the respects of both less weight loss and quicker response to the deprotection reaction of the *t*Boc group.

Because PEB is crucial for chemically amplified resist system, thus to clarify dissolution behaviors of the photosensitive film (contained 10 wt % PTMA) in both exposed and unexposed areas, the effect of PEB temperature was studied, as shown in Figure 5. The dissolution rate in the exposed area increases with increasing the PEB temperatures. On the other hand, the rates of unexposed area are held as a constant of 1 Å/s up to 110 °C and then increase dramatically at higher temperatures. As

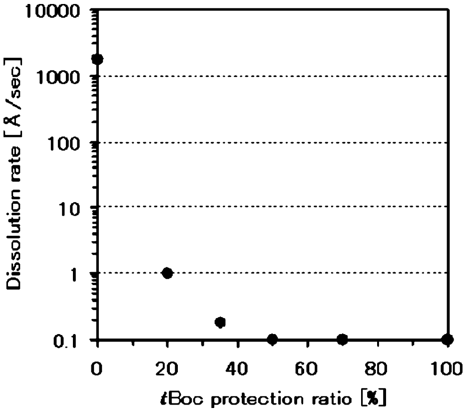


Figure 4. Effect of *t*Boc-protection ratio of PAHA on the dissolution rate. A 2.38 wt % of $TMAH_{aq}$ was used as a developer.

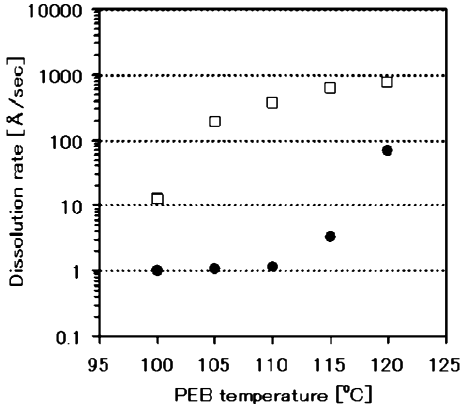


Figure 5. Effect of PEB temperature on the dissolution rate for PAtBA-20/PTMA (90/10 w/w) resist system in exposed (□) and unexposed area (●). The *i*-line exposure and PEB time were fixed as 60 mJ/cm^2 and for 5 min, respectively. A 2.38 wt % of $TMAH_{aq}$ was used as a developer.

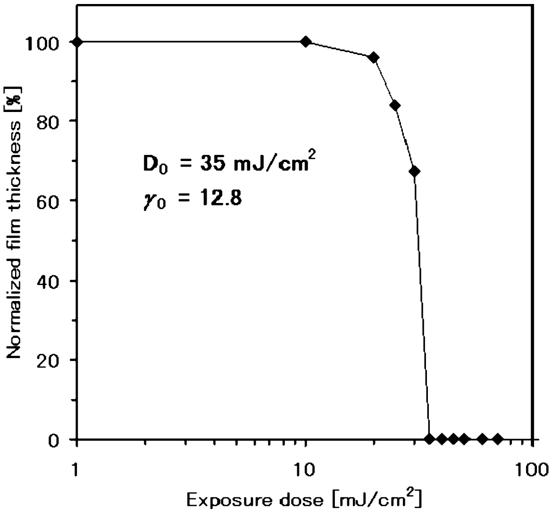


Figure 6. Characteristic photosensitive curve for PAtBA-20/PTMA (90/10 w/w) resist system directly prepared. The photosensitivity (D_0) and contrast (γ_0) in 1.8 μm thick film are shown.

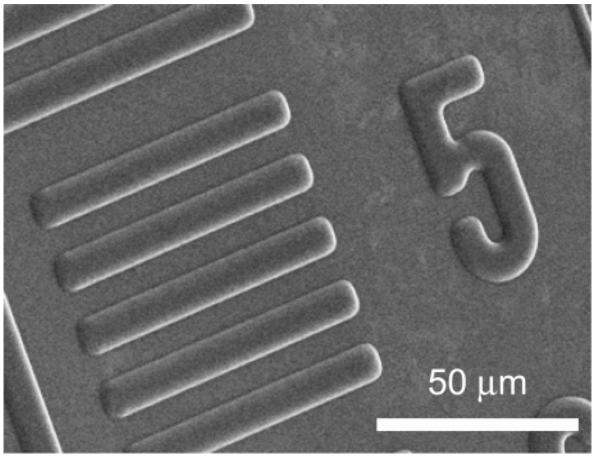


Figure 7. SEM image of positive-pattern of 1.8 μm thick film based on PAtBA-20/PTMA (90/10 w/w).

expected from the results of TG analysis, this behavior is attributed to the thermal decomposition of *t*Boc group to be more soluble in $TMAH_{aq}$. The largest difference of the dissolution rates between the two areas was obtained at PEB of 110 °C for 5 min, resulting in about 320 times.

Based on the preliminary optimizations described above, the system of photosensitive polymer consisting of PAtBA-20 (90 wt %) and PTMA (10 wt %) in cyclohexanone was formulated, where the PAtBA-20 solution prepared from PAHA and di-*tert*-butyl dicarbonate in the presence of diethylmethylamine was used for the direct evaluation. A photosensitivity curve in 1.8 μm film thickness was obtained, as depicted in Figure 6. This resist system reveals a photosensitivity (D_0) of 35 mJ/cm^2 and contrast (γ_0) of 12.8 with *i*-line exposure. The PAtBA/PTMA resist system is more sensitive than the previously evaluated positive-type resist consisting of PAHA/TVEB/DIAS (D_0, 40; γ_0, 4.0),[8] even though both were prepared in a one-pot manner. A SEM image in Figure 7 (film thickness, 1.8 μm) was obtained in contact-printing mode under the optimized condition (PEB at 110 °C for 5 min, *i*-line exposure of 50 mJ/cm^2), producing a clear positive-tone pattern with 7.8 μm line-and-space resolution. Besides, facile preparation of the resist system for PSPBO was established even though the trace of diethylmethylamine might be remained in the film as expected to quench the photochemically generated acid from PTMA.

Degree of Cyclization into PABO by IR Spectroscopy. For low-temperature cyclization of PHA to PBO, the effect of PTMA in the positive-type PAtBA-20 resist system was studied by FTIR spectroscopy. The films containing PTMA (0, 5, or 10 wt %) were prebaked at 80 °C for 3 min and postexposure baked at 110 °C for 5 min, followed by soaking into 2.38 wt % $TMAH_{aq}$ for 45 s as a mimic of the development. A fully cured PABO film was prepared for each of samples by the following thermal treatment: increasing the heating temperature up to 350 °C and then held at that temperature for 1 h under nitrogen. FTIR spectra of the unexposed film consisting of PAtBA-20/PTMA (90/10 w/w) are shown in Figure 8 under the conditions such as PEB (110 °C), development and acetic acid treatment (D & A), heated at 150, 200, 250, and 350 °C (as the reference). At 200 °C or higher temperatures, the spectra exhibit characteristic absorption bands at 1045 and 1620 cm^{-1} corresponding to benzoxazole, while a band at 1654 cm^{-1} due to the amide group and a band around 3400 cm^{-1} for hydroxyl groups of PAHA disappear. Eventually, the FTIR spectrum obtained by the thermal treatment at 250 °C for 15 min is identical to that of the fully cured PABO film (350 °C for 1 h). Thus, PAtBA-20 is readily converted to the corresponding PABO in the presence of 10 wt % PTMA. We assume the mechanism of the acid-catalyzed cyclization to be that sulfonic acids would accelerate the attack of a phenolic hydroxyl group on an amide carbonyl unit through protonation on the oxygen of the amide group. However, it seems to be difficult to predict the proper mechanism because the cyclization process involves several interrelated elemental reactions, causing dynamic change of

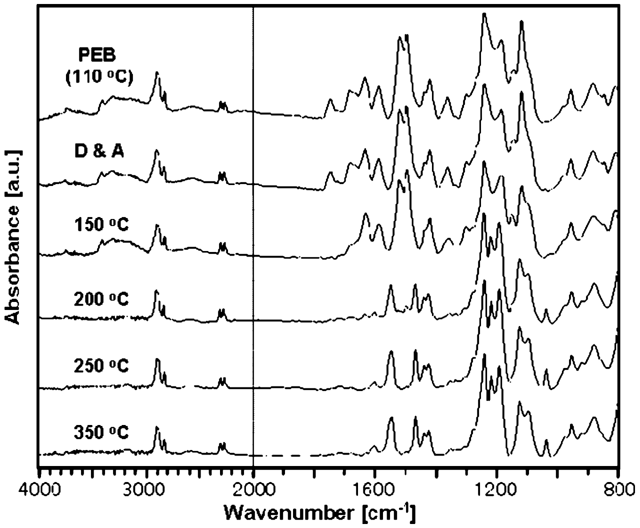


Figure 8. FTIR spectra of PAtBA-20/PTMA (90/10 w/w) resist film on a silicon wafer at different temperatures. "D & A" means steps of development with TMAH$_{aq}$ for 45 s and 20 wt % acetic acid treatment for 10 s.

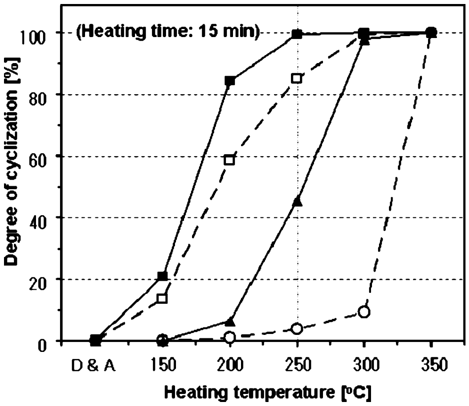


Figure 9. Degree of cyclization into PABO with various conditions: included 10 wt % PTMA and treated with acetic acid (AA) before curing (■), included 10 wt % PTMA without AA treatment (□), included 5 wt % PTMA and treated with AA before curing (▲), and without PTMA & AA treatment (○). "D & A" implies development with TMAH$_{aq}$ and (if required) 20 wt % AA treatment for 10 s.

physical properties (e.g., diffusion rate, chain mobility, solvation, and acidity). The degree of cyclization was calculated from eq 1, as described in the Experimental Section, and is shown in Figure 9. An absorbance band at 1045 cm^{-1} (A_{1045}) assignable to C−O stretching of benzoxazole group was traced in the FTIR spectrum with increasing the temperature, while the band at 609 cm^{-1} (A_{609}) assignable to silicon wafer was contributed as a noninteractive standard.

Further evaluation for low-temperature cyclization of the resist system was conducted in various conditions, and the results are summarized in Figure 9. The only FTIR spectrum of PAtBA-20/PTMA (90/10 w/w) with acetic acid treatment reaches the 100% conversion at 250 °C, which is identical to that of the fully cured PABO film. However, a similar heating procedure but without acetic acid treatment or reducing the amount of PTMA (0−5 wt %) does not reach full conversion into PABO up to 250 °C. These results indicate that thermally generated sulfonic acid from PTMA in unexposed area plays a key role for low-temperature cyclization of PAtBA with appropriate acetic acid treatment. Hence, *t*Boc-protection/deprotection chemistry with PTMA is a suitable method for not only establishment of positive-type chemically amplified PSPBO but also low-temperature cyclization into PBO, which was not successful in the case of a previous PSPBO system based on PAHA, TVEB, and DIAS.

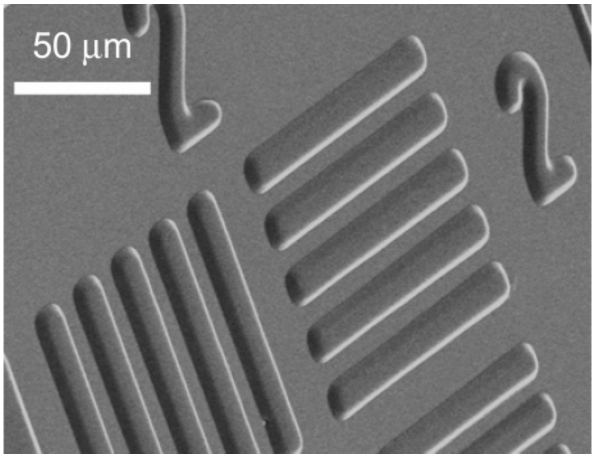


Figure 10. SEM image of PABO pattern cured at 250 °C for 15 min.

A SEM image in Figure 10 reveals the result of positive pattern after the thermal treatment at 250 °C for 15 min. The resist film was capable of resolving of 10 μm-featured pattern where the film was shrunk from 4.4 to 3.6 μm in the vertical direction during the cure. 20% *t*Boc protection is also effective to make the resist system minimize the weight loss and volume shrinkage of the pattern.

Conclusion

The PAtBA-20 solution obtained from PAHA and di-*tert*-butyl dicarbonate in the presence of diethylmethylamine was used directly for formulation of a positive-type PSPBO by adding PTMA. Since PAtBA-20 has a high transparency in the UV−vis region, the new resist system showed the high sensitivity and contrast of 35 mJ/cm^2 and 12.8, respectively, with *i*-line exposure. Because of the critical effect of PTMA also employing as thermoacid generator, the obtained positive image was then easily converted into the corresponding PABO pattern by acetic acid treatment, followed by the thermal treatment up to 250 °C. The facile preparation of the resist system and low-temperature cyclization of PHA will provide more efficient methods for practical use of PSPBO together with thermally unstable components.

References and Notes

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