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Chemically Amplified Photosensitive Polybenzoxazoles Based on *tert*-Butoxycarbonyl Protected Hyperbranched Poly(*o*-hydroxyamide)s

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ABSTRACT: We describe the synthesis, characterization, and lithographic performance of positive-working chemically amplified photosensitive polybenzoxazoles (PSPBOs) composed of partially *tert*-butoxycarbonyl (t-BOC) protected hyperbranched poly(*o*-hydroxyamide)s (HB-tbocPHAs) and diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a photo-acid generator (PAG). The HB-tbocPHAs as precursors of PSPBOs were synthesized from hyperbranched poly(*o*-hydroxyamide)s (HBPHAs), which were prepared by self-polycondensation of an AB_2 type monomer. A series of HB-tbocPHAs having the t-BOC content of 8−100 mol % were successfully prepared by controlling the feed amount of di-*tert*-butyl dicarbonate (DTBDC). HB-tbocPHAs had adequate dissolution rate in tetramethylammonium hydroxide (TMAH) aqueous solution as well as excellent solubility in common organic solvents. HB-tbocPHA having 39 mol % t-BOC group showed the optimum dissolution rate in 2.38 wt % TMAH aqueous solution and good adhesion on a silicon wafer. The thermal deprotection of the t-BOC group and conversion to polybenzoxazole (PBO) of HB-tbocPHA in the presence of strong acid such as *p*-toluenesulfonic acid (p-TsOH) were investigated by using FT-IR, DSC, and TGA to examine the acid effect. Both the deprotection of t-BOC groups and the conversion to PBO were accelerated in the presence of p-TsOH. The photolithographic performance of the resist formulated with HB-tbocPHA and 20 wt % of DIAS was evaluated. The resist showed 115 mJ/cm^2 of sensitivity and 2.2 of contrast with 365 nm light when it was developed in 2.38 wt % TMAH aqueous solution at room temperature. The fine positive pattern was obtained at the 200 mJ/cm^2 of i-line exposure. The patterned film was successfully converted to polybenzoxazole without any distortion by thermal treatment at 300 °C for 1 h.

Introduction

Thermally stable photosensitive polymers (TS-PSP) such as photosensitive polyimides (PSPIs) are widely used as passivation or insulation layers for semiconductor devices or multichip modules (MCMs) because of their simple process compared to conventional photoresists. TS-PSP was first reported by Kerwin et al. in 1971[1,2] and has since been under widespread investigation.[3−10] Poly(*o*-hydroxyamide) (PHA) as a precursor of polybenzoxazole (PBO) has also been considered as a positive type photosensitive polymer because of its appropriate dissolution rate in aqueous alkaline solution.[11−14] These types of photosensitive polymers are combined with diazonaphthoquinone (DNQ) as a sensitizer. On the other hand, as an advanced design of photoresist, systems involving chemically amplification have been attracting much attention because of their high sensitivity.

Hyperbranched polymers have some interesting properties compared to their linear counterparts such as good solubility, low viscosity, and high functionality. Although numerous reports on the synthesis and characterization of hyperbranched polymers have been published during the past decade,[15−19] only a few reports were concerned with their application as photosensitive polymers.[20] Previously, we reported the synthesis and characterization of hyperbranched polybenzoxazoles via poly(*o*-hydroxyamide) precursors.[21,22] In this paper, we describe the application of hyperbranched polybenzoxazoles as photosensitive polymers starting from t-BOC protected hyperbranched poly(*o*-hydroxyamide)s.

Results and Discussion

Synthesis of Partially *tert*-Butoxycarbonylated Poly(*o*-hydroxyamide)s. We have prepared partially t-BOC protected HBPHAs (HB-tbocPHAs), which can act as a matrix polymer for positive-working photoresists when mixed with a photoacid generator. The acid generated by UV exposure of the resist attacks and deprotects the acid-labile t-BOC groups to form phenolic moieties. This polarity or solubility change between the exposed and unexposed areas results in pattern formation after a developing process. The HB-tbocPHAs were synthesized by two consecutive reactions: the polycondensation of an AB_2 monomer to afford hyperbranched poly(*o*-hydroxyamide) (HBPHA) and subsequent protection of the hydroxyl groups with t-BOC groups as shown in Scheme 1. The HBPHA was soluble in aprotic solvents, tetrahydrofuran (THF), γ-butyrolactone (GBL), and cyclohexanone (Table 1). The weight-average molecular weight (M_w) of HBPHA was 52 000 with a polydispersity of 1.4. The inherent viscosity (η_{inh}) was 0.13 dL/g. The conversion of end-capping reaction for amino groups was 90%, which was calculated from the comparison of methyl peaks at 2.3 ppm and aromatics at 6.6 ppm by ^{1}H NMR analysis (spectrum b in Figure 1).

A series of partially t-BOC protected HBPHAs were synthesized from HBPHA. The t-BOC content of HB-tbocPHA could be adjusted by the feed amount of di-*tert*-butyl dicarbonate (DTBDC) in the substitution reaction. The t-BOC content of the polymers could be calculated by the integration ratio of the *tert*-butyl peak

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Scheme 1. Synthesis of Polymers

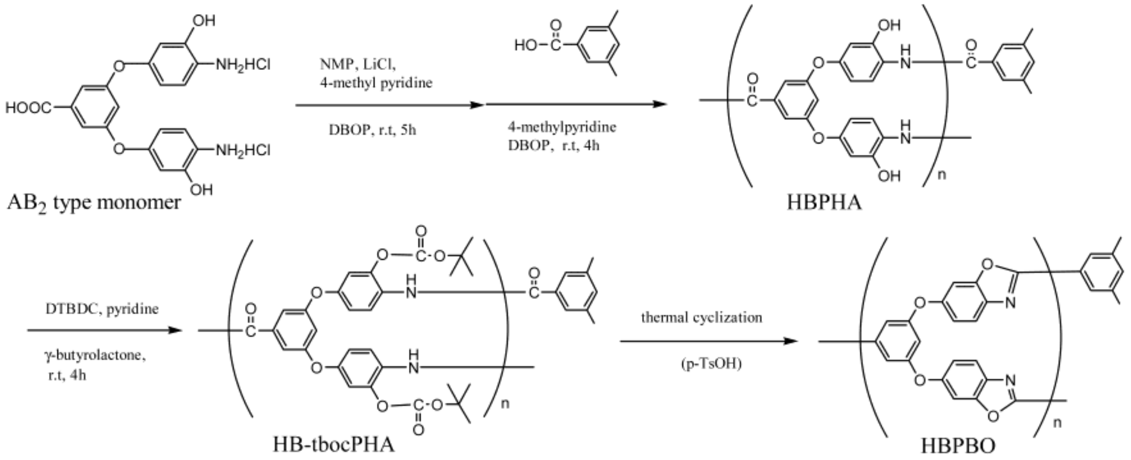


Table 1. Solubility of Partially t-BOC Protected HBPHAs[a]

polymer	DMF	THF	GBL[b]	cyclohexanone	$CHCl_3$	PGMEA[c]	toluene
HBPHA	++	++	++	++	−	−	−
HB-tbocPHA-10	++	++	++	++	−	−	−
HB-tbocPHA-25	++	++	++	++	−	−	−
HB-tbocPHA-30	++	++	++	++	−	−	−
HB-tbocPHA-35	++	++	++	++	+−	−	−
HB-tbocPHA-40	++	++	++	++	+−	−	−
HB-tbocPHA-70	++	++	++	++	++	+−	−
HB-tbocPHA-100	++	++	++	++	++	++	+−

[a] ++, soluble at room temperature; +−, partially soluble; −, insoluble. [b] GBL = γ-butyrolactone. [c] PGMEA = propylene glycol monomethyl ether acetate.

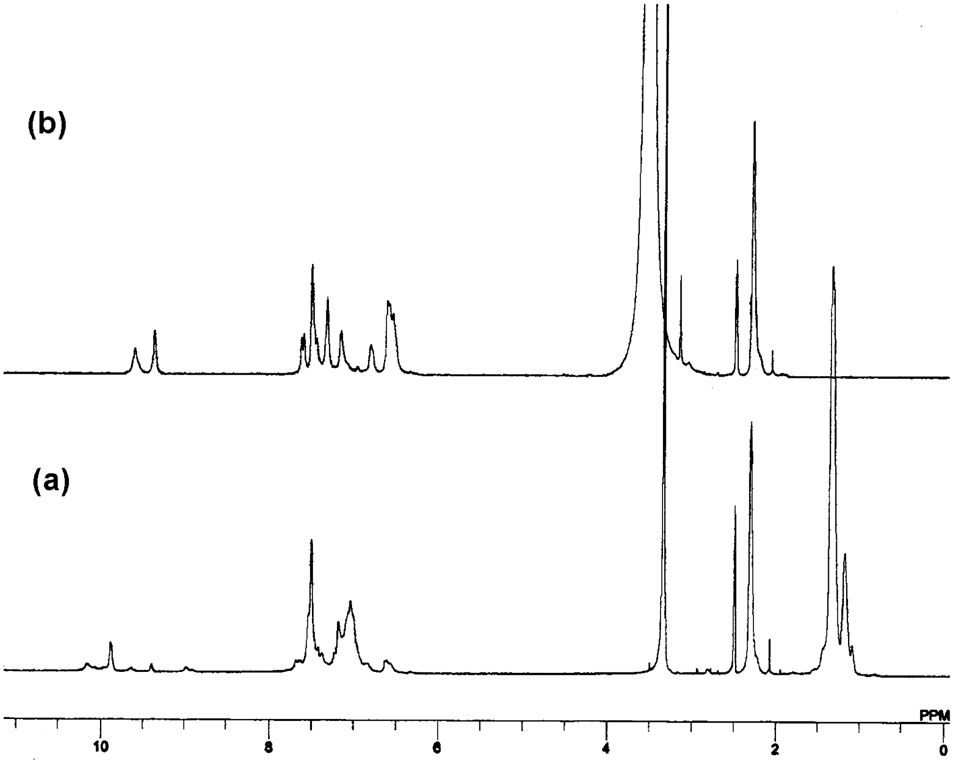


Figure 1. ^1H NMR spectra of (a) HB-tbocPHA-100 and (b) HBPHA.

at 1.33 ppm to the methyl peak at 2.3 ppm in ^1H NMR spectra. The experimental t-BOC content of the polymers corresponded well to the calculated molar input of DTBDC (Table 2). The HB-tbocPHAs showed excellent solubility in common organic solvents such as DMF, THF, γ-butyrolactone, and cyclohexanone as shown in Table 1. The solubility of the polymers increased with increasing t-BOC contents. The 100% substituted polymer, HB-tbocPHA-100, was soluble even in chloroform and partially soluble in toluene. This enhanced solubility can be attributed to the introduction of bulky t-BOC groups.

Thermal Conversion of HB-tbocPHAs to HB-PBO. We have monitored the deprotection of t-BOC

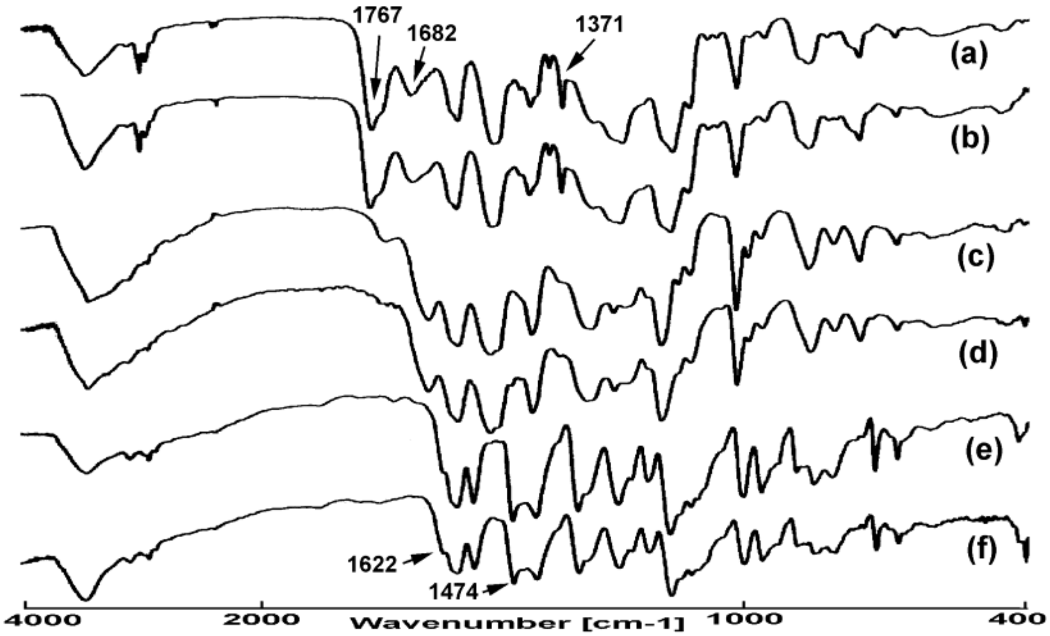


Figure 2. FT-IR spectra of HB-tbocPHA-100 with heat treatment at (a) rt, (b) 100 °C, (c) 150 °C, (d) 200 °C, (e) 250 °C, and (f) 300 °C for 1 h in vacuo.

Table 2. Properties of HB-tbocPHAs with Various t-BOC Contents

polymer	calcd molar input of DTBDC	t-BOC content[a] (mol %)	DR[b] (Å/s)	adhesion[c]
HBPHA	0	0	508	○
HB-tbocPHA-10	10	8.4	212	○
HB-tbocPHA-25	25	22.4	27	○
HB-tbocPHA-30	30	28.1	9.5	○
HB-tbocPHA-35	35	32.1	5.6	○
HB-tbocPHA-40	40	38.9	1.4	○
HB-tbocPHA-70	70	63.4	1.8	×
HB-tbocPHA-100	100	100	0.0	×

[a] Estimated by using ^{1}H NMR spectra. [b] DR = dissolution rate in 2.38 wt % TMAH aqueous solution at 25 °C. [c] Adhesion on silicon wafer: ○, good; ×, peeling.

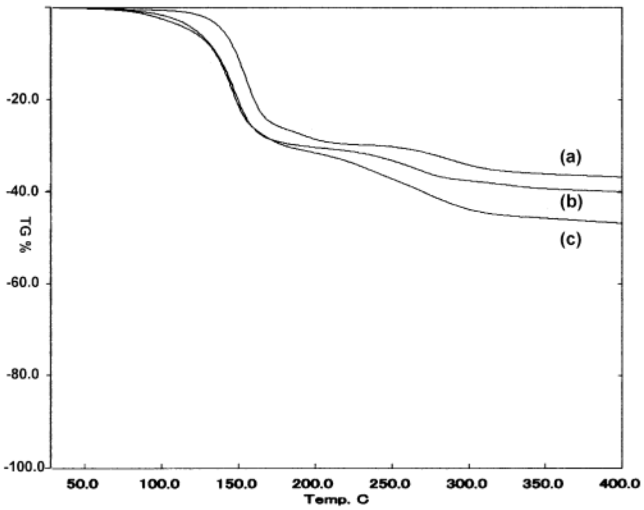


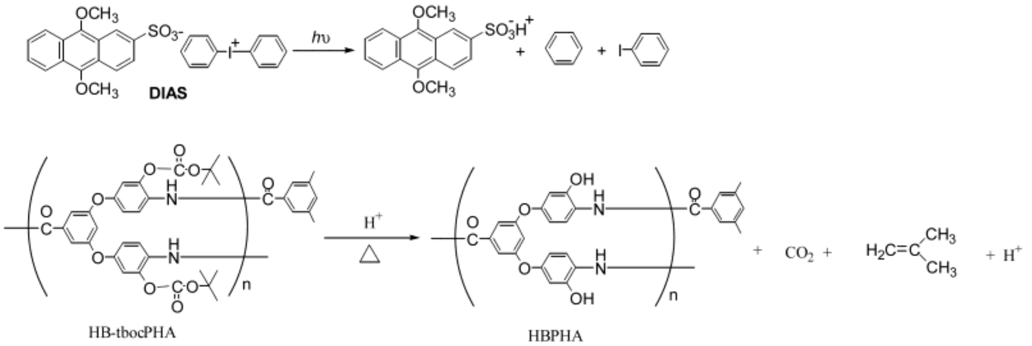
Figure 3. TGA thermogram of (a) HB-tbocPHA-100, (b) **S1** (a mixture of HB-tbocPHA-100 and 10 mol % of p-TsOH), and (c) **S2** (a mixture of HB-tbocPHA-100 and 5 mol % of DIAS).

groups and thermal conversion of HB-tbocPHA to HBPBO with temperature variation by FT-IR as shown in Figure 2. The characteristic carbonate and *tert*-butyl peaks of t-BOC group at 1767 and 1371 cm^{-1} and amide peak at 1682 cm^{-1} were observed in spectrum a of Figure 2. The peak intensities decreased gradually with temperature and disappeared completely at higher temperature, whereas two new characteristic peaks for benzoxazole at 1622 and 1474 cm^{-1} were clearly observed above 250 °C. The IR spectra in Figure 2 clearly indicated that the decomposition of the t-BOC groups in the polymers took place between 150 and 200 °C, and the conversion of the precursor to PBO was completed after thermal treatment at 250 °C for 1 h in vacuo. To elucidate detailed thermal behavior, the polymers were analyzed by DSC and TGA measurements, which are given in the Supporting Information.

Acid Effect on the Thermal Behavior of HB-tbocPHAs. It has been reported that PAG generate acid during the thermal decomposition process.[23] Therefore, elucidation of the acid effect on the thermal behavior of HB-tbocPHA is important as preliminary research. The degradation behavior of HB-tbocPHA to form HBPBO in the presence of 10 mol % of *p*-toluenesulfonic acid (p-TsOH) (**S1**) or 5 mol % of DIAS (**S2**) was investigated by using DSC and TGA. The DSC thermogram is available in the Supporting Information. Figure 3 shows the TGA thermogram of the HB-tbocPHA, **S1** and **S2**. Both first step weight losses for **S1** and **S2** were observed in the range of 117−163 °C, while the second step weight losses of **S1** and **S2** were observed at 232−283 and 218−301 °C, respectively. The data suggest that the acid was generated by thermal decomposition of the DIAS in **S2**, and a strong acid, such as p-TsOH, or the generated acid from DIAS accelerated the thermal cyclization of HB-tbocPHA. Therefore, we can expect that the generated acid from PAG in photolithography would promote PBO formation as well as deprotection of t-BOC groups.

Lithographic Evaluation. The dissolution rate (DR) of the matrix polymer in resist design is one of the key factors in order to control the performance of a photoresist. The relationship between the t-BOC content and dissolution rate of the polymers was investigated in 2.38 wt % TMAH aqueous solution. The DR decreased

Scheme 2. Photochemical Reaction Mechanism of DIAS



dramatically with an increase in the t-BOC content as shown in Table 2. The HBPHA without a t-BOC group showed 508 Å/s of DR under the conditions described in the Experimental Section. When the t-BOC content reached 40%, the DR of polymer was below 2 Å/s, which seems to be sufficient for use as a matrix polymer for photoresists. The adhesion of the polymers on silicon wafers was examined and judged by bare eyes during the developing process. As shown in Table 2, the adhesion of HB-tbocPHA on silicon substrate was good up to 39% of t-BOC content. However, the polymer films peeled off at t-BOC contents above 63%. This phenomenon is probably due a reduction of the hydrophilicity of the polymers at the higher t-BOC contents. Therefore, HB-tbocPHA-40, which had good adhesion as well as adequate DR, was selected as the matrix resin for photoresists in this study.

Diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) was used as a photoacid generator (PAG) because it showed high absorbance in the range 330−440 nm with absorbance maxima at 390 and 413 nm in the UV−vis. spectra. The mechanism of photochemical reaction of DIAS and deprotection of the t-BOC groups is shown in Scheme 2. DIAS is photochemically decomposed to give 9,10-dimethoxyanthracene-2-sulfonic acid, benzene, and iodobenzene. The acid generated subsequently deprotects the t-BOC group of the HB-tbocPHA during the postexposure bake (PEB), yielding HBPHA, isobutene, and carbon dioxide.

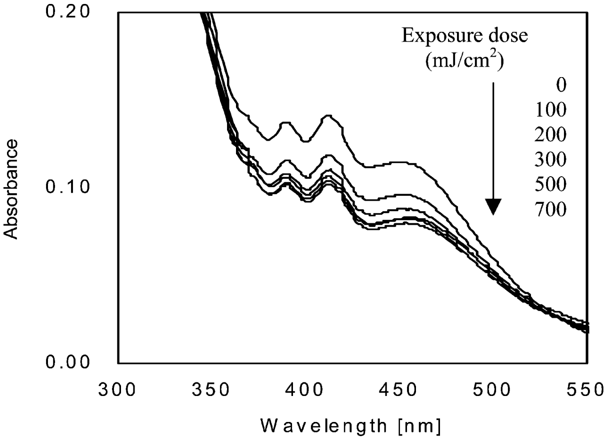


Figure 4. UV−vis spectral change of the resist composed of HB-tbocPHA-40 and 20 wt % of DIAS upon irradiation with 365 nm light.

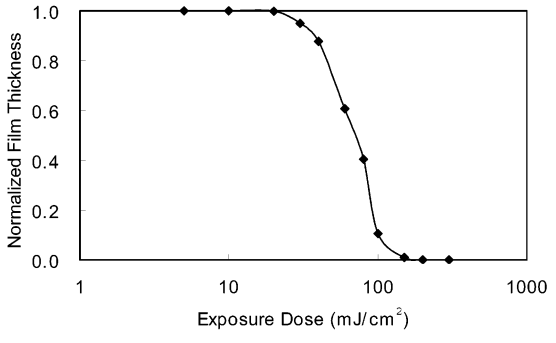


Figure 5. Characteristic curve of the HB-tbocPHA-40/DIAS system.

The UV−vis spectral change of the resist film composed of HB-tbocPHA-40 and 20 wt % DIAS against the polymer is shown in Figure 4. The characteristic absorbances at 390, 413, and 450 nm decrease with an increase in the exposure dose, implying that the resist system can be applied as g-line (436 nm) and i-line (365 nm) resists.

The sensitivity (E_{th}) and contrast (γ value) of the resist composed of HB-tbocPHA-40 and 20 wt % of DIAS against the polymer were evaluated to be 115 mJ/cm^2 and 2.2, respectively, for 365 nm light as shown in Figure 5.

Figure 6a shows the scanning electron micrograph of the positive pattern obtained from a 1 μm thick resist film composed of HB-tbocPHA-40 and 20 wt % of DIAS against the polymer. The clear positive pattern with 30 μm L/S (line/space) was obtained with 200 mJ/cm^2 of i-line exposure. The corresponding PBO pattern was obtained by thermal curing of the patterned film at 300 °C for 1 h as shown in Figure 6b. The patterned films shrink ca. 32.8% after the thermal curing process, presumably due to the thermal cyclodehydration as well as the degradation of the t-BOC groups in the polymer.

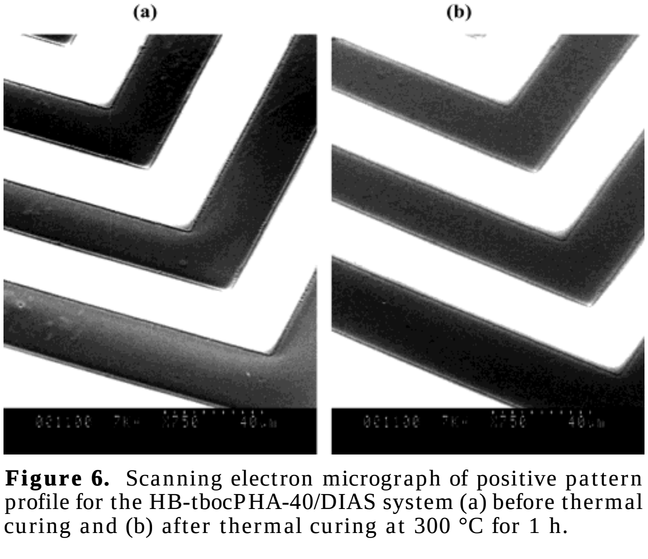


Figure 6. Scanning electron micrograph of positive pattern profile for the HB-tbocPHA-40/DIAS system (a) before thermal curing and (b) after thermal curing at 300 °C for 1 h.

However, no distortions or deformations of the pattern were observed after thermal curing.

Conclusion

A series of partially t-BOC protected HBPHAs were successfully prepared from HBPHA, which were prepared by self-polycondensation of AB$_2$ type monomer. The acid generated from DIAS accelerated the thermal conversion of HB-tbocPHA to HBPBO as well as the deprotection of the t-BOC groups. HB-tbocPHA-40 having 39 mol % of t-BOC groups showed an adequate dissolution rate in alkaline developer and good adhesion on silicon wafers as well as good solubility in common organic solvents. The HB-tbocPHA/DIAS system showed reasonable photospeed (115 mJ/cm^2), contrast ($\gamma = 2.2$), and good pattern profiles upon 365 nm irradiation. The patterned film was successfully converted to polybenzoxazole by thermal treatment at 300 °C for 1 h without any pattern distortion.

Experimental Section

Chemicals. *N*,*N*-Dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), toluene, and *N*-methyl-2-pyrrolidinone (NMP) were dried with calcium hydride and then distilled under reduced pressure. Acetone and γ-butyrolactone (GBL) were used after distillation from calcium sulfate. Lithium chloride (LiCl) and potassium carbonate were dried at 130 and 200 °C in vacuo, respectively and kept under nitrogen. 3,5-Dihydroxybenzoic acid (Tokyo Kasei, >98%) was used after recrystallization from water. Triethylamine (TEA), pyridine, and 4-methylpyridine were purified by distillation in the presence of potassium hydroxide. 2,3-Dihydro-2-thioxo-3-benzoxazolylphosphonic acid diphenyl ester (DBOP) was prepared according to a reported procedure[24,25] and purified by recrystallization from hexane. Di-*tert*-butyl dicarbonate (DTBDC, Aldrich, >99%), diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS, Aldrich, E.G), 5-fluoro-2-nitrophenol (Tokyo Kasei, >98%), 3,5-dimethylbenzoic acid (Tokyo Kasei, >99%), cyclohexanone (Aldrich, 99.8%), and the other reagents were used as received. The AB$_2$ type monomer was prepared as described in a previous report.[22]

Measurements. ^{1}H NMR spectra were recorded on a JEOL JNM-AL 300 (300 MHz) spectrometer. FT-IR spectra were measured as a KBr pellet with a JASCO FT/IR-460 Plus spectrophotometer. Molecular weights were determined by gel permeation chromatography (GPC) with polystyrene calibration using a SHODEX GPC-104/101 with Shodex KD 806M and KD 802 columns in DMF containing lithium bromide (0.01 mol/L) as the eluent. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a Seiko DSC 6200 and TG/DTA 6200, respectively, at a heating rate of 10 °C/min under nitrogen. Inherent viscosity was measured at a concentration of 0.5 g/dL with an Ostwald type viscometer in DMAc at 30 °C. The UV spectra were obtained on a JASCO V-560 spectrophotometer. The film thickness was measured on a Dektak 3 system of Veeco Instruments Inc. The resist films were exposed to 365 nm light with a filtered superhigh-pressure mercury lamp (250 W). The pattern profiles were obtained with a Hitachi S-800 scanning electron microscope (SEM).

Synthesis of Hyperbranched Poly(*o*-hydroxyamide) (HBPHA). The HBPHA was prepared by polycondensation of AB$_2$ type monomer (**3**, 2.05 g, 5.0 mmol) with DBOP (1.9 g, 5.0 mmol), dried LiCl (0.45 g, 10.0 mmol), and 4-methylpyridine (1.45 mL, 15.0 mmol) in 15 mL of NMP as described in a previous report.[22] The reaction mixture was stirred at room temperature for 5 h. The end-capping solution, composed of 3,5-dimethylbenzoic acid (10.0 mmol), DBOP (3.85 g, 10.0 mmol), 4-methylpyridine (1.0 mL, 10.0 mmol), and 20 mL of NMP, was added slowly to the reaction mixture and stirred for an additional 4 h: 67% yield; weight-average molecular weight, M_w = 51 500; polydispersity index, M_w/M_n = 1.4; inherent viscosity, η_{inh} = 0.13 dL/g.

Preparation of Partially t-BOC Protected Poly(*o*-hydroxyamide)s (HB-tbocPHAs). The partially t-BOC protected HBPHAs were synthesized as shown in Scheme 1. In a 50 mL round-bottomed three-neck flask equipped with a gas inlet were placed HBPHA (0.24 g, 1.0 mmol of OH equivalent), catalytic amount of dried pyridine, DTBDC (0.1−1.5 mmol), and γ-butyrolactone (5 mL). The reaction mixture was stirred at room temperature for 4 h. The resulting product was precipitated from water (400 mL) and isolated by filtration. The light brown powder was redissolved in THF (10 mL) and reprecipitated from hexane (400 mL). The resulting polymer was dried at 30 °C for 1 day in a vacuum oven:

HB-tbocPHA-40 (OH equivalent of HBPHA:DTBDC = 100:40): 91.4% yield; t-BOC content, 38.9 mol %. ^{1}H NMR (DMSO-d_6, ppm) δ: 9.37−10.08 (m, 3H), 7.64−6.60 (m, 16H, Ar−H), 2.31 (s, 6H, methyl), 1.32−1.42 (m, 9H, *tert*-butyl). IR (KBr): 1765 cm^{-1} (carbonate), 1651 cm^{-1} (amide), 1371 cm^{-1} (*tert*-butyl).

HB-tbocPHA-100 (OH equivalent of HBPHA:DTBDC = 100:100): 91.3% yield; t-BOC content, 100.0 mol %. ^{1}H NMR (DMSO-d_6, ppm) δ: 9.42−10.19 (m, 2H), 7.64−6.63 (m, 13H, Ar−H), 2.30 (s, 6H, methyl), 1.10−1.35 (m, 20H, *tert*-butyl). IR (KBr): 1767 cm^{-1} (carbonate), 1685 cm^{-1} (amide), 1371 cm^{-1} (*tert*-butyl).

Acid Effect on the Conversion of HB-tbocPHAs to HBPBO. To investigate the acid effect on the PBO formation, 0.2 g (0.3 mmol) of HB-tbocPHA and 0.03 mmol of *p*-toluenesulfonic acid (p-TsOH) (**S1**) or 0.015 mmol of diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) (**S2**) were mixed in THF and stirred for 0.5 h in the dark room, and then the solvent was evaporated under reduced pressure at room temperature for 24 h. The resulting polymer mixtures were analyzed by using DSC and TGA.

Dissolution Rates (DR) of the Partially t-BOC Protected HBPHAs. HB-tbocPHAs were dissolved at 20 wt % in cyclohexanone. After filtration of polymer solutions using 0.2 μm disk-type filters, they were spin-coated on a silicon wafer to a 1.8 μm film thickness. The films were baked at 100 °C for 3 min and then developed in 2.38 wt % TMAH solution at 25 °C for 20−60 s and finally rinsed with water. The dissolution rates (DR) of polymers were calculated by the thickness loss for development per given time.

Lithographic Evaluation. HB-tbocPHAs and 10−30 wt % of DIAS against the polymer were dissolved at 20 wt % in cyclohexanone. The solution was spun on a silicon wafer and prebaked at 100 °C for 3 min to form a photoresist film layer. The resist film was exposed to 365 nm (i-line) light with a filtered high-pressure mercury lamp. Imagewise exposure was carried out in the contact mode with a photomask. Postexposure bake (PEB) of resist film was carried out at 120 °C for 3 min. Finally, the resist films were developed in 2.38 wt % TMAH aqueous solution at 25 °C for 60 s.

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Supporting Information Available: DSC and TGA data for the thermal conversion of HB-tbocPHA to HBPBO; acid effect on the thermal behavior of HB-tbocPHAs (DSC thermogram). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kerwin, R. E.; Goldrick, M. R. *Polym. Eng. Sci.* **1971**, *2*, 426.
(2) Curran, R. K.; Goldrick, M. R.; Kerwin, R. E. U.S. Patent 3,623,870, 1971.
(3) Rubner, R. *Siemens Forsh. Entwickl. Ber.* **1976**, *5*, 92.
(4) Loprest, F. J. U.S. Patent 4,093,461, 1978.
(5) Kubota, S.; Moriwaki, T.; Ando, T.; Fukami, A. *J. Appl. Polym. Sci.* **1987**, *33*, 1763.

(6) Khanna, D. N.; Mueller, W. H. *Polym. Eng. Sci.* **1989**, *29*, 954.

(7) Omote, T.; Mochizuki, H.; Koseki, K.; Yamaoka, T. *Macromolecules* **1990**, *23*, 4796.

(8) Seino, H.; Mochizuki, A.; Haba, O.; Ueda, M. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2261.

(9) Itatani, T.; Gorwadkar, S.; Fukushima, T.; Komuro, M.; Itatani, H.; Tomoi, M.; Sakamoto, T.; Matsumoto, S. *Proc. SPIE* **2000**, *3999*, 552.

(10) Jung, E. S.; Segawa, S.; Itatani, T.; Komuro, M.; Itatani, H.; Miyamura, M.; Matsumoto, S.; Aoyagi, M. *J. Photopolym. Sci. Technol.* **2001**, *14*, 61.

(11) Ahne, H.; Rubner, R.; Kuhn, E. European Patent 23,662A1, 1981.

(12) Rubner, R. *Adv. Mater.* **1990**, *2*, 452.

(13) Ahne, H.; Rubner, R.; Sezi, R. *Appl. Surf. Sci.* **1996**, *106*, 311.

(14) Ebara, K.; Shibasaki, Y.; Ueda, M. *J. Photopolym. Sci. Technol.* **2001**, *14*, 55.

(15) Srinivasan, S.; Twieg, R.; Hedrick, J. L.; Hawker, C. J. *Macromolecules* **1996**, *29*, 8543.

(16) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685.

(17) Yang, G.; Jikei, M.; Kakimoto, M. *Macromolecules* **1999**, *32*, 2215.

(18) Thompson, D. S.; Markoski, L. J.; Moore, J. S.; Sendijarevic, I.; Lee, A.; McHugh, A. J. *Macromolecules* **2000**, *33*, 6412.

(19) Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505.

(20) Okazaki, M.; Shibasaki, Y.; Ueno, M. *J. Photopolym. Sci. Technol.* **2001**, *14*, 45.

(21) Hong, C. S.; Jikei, M.; Kakimoto, M. *J. Photopolym. Sci. Technol.* **2002**, *15*, 219.

(22) Hong, C. S.; Jikei, M.; Kakimoto, M. *Polym. J.*, submitted.

(23) Kim, T. K.; Choi, K. Y.; Lee, K. S.; Park, D. W.; Jin, M. Y. *Polym. Bull. (Berlin)* **2000**, *44*, 55.

(24) Ueda, M.; Kameyama, A.; Hashimoto, K. *Macromolecules* **1988**, *21*, 19.

(25) DBOP was prepared by reaction of diphenyl chlorophosphate with 2-mercaptobenzoxazole in the presence of triethylamine and toluene at room temperature for 6 h.

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