

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

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## **Introduction**

Thermally stable photosensitive polymers (TS-PSP) such as photosensitive polyimides (PSPIs) were widely used as passivation or insulation layers of semiconductor devices or multichip modules (MCMs) because of their simple process compared to conventional photoresist. Poly(*o*-hydroxyamide) (PHA) as a precursor of polybenzoxazole (PBO) has been also considered as a positive type photosensitive polymer because of its appropriate dissolution rate in aqueous alkaline solution.<sup>1-4</sup> On the other hand, hyperbranched polymers have some interesting properties compared to their linear one such as good solubility, low viscosity and high functionality. Here, we describe the novel application of the hyperbranched polybenzoxazoles to photosensitive polymer based on *t*-BOC protected hyperbranched poly(*o*-hydroxyamide)s.

## **Experimental Section**

### **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 pyridine, di-*tert*-butyl-dicarbonate (DTBDC) (0.1 - 1.5 mmol) and  $\gamma$ -butyrolactone (5 mL). The reaction mixture was stirred at room temperature for 4 h. The resulting product was precipitated in water (400 mL) and isolated by filtration. The light brown powder was resolved in THF (10 mL) and re-precipitated in hexane (400 mL).

**Lithographic Evaluation.** HB-tbocPHAs and 20 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 light with a filtered high-pressure mercury lamp. Imagewise exposure was carried out in the contact mode with a photomask. Post exposure bake 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 sec.

## Results and Discussion

### Synthesis of HB-tbocPHAs.

The HB-tbocPHAs were synthesized by two consecutive reactions: the polycondensation of the AB<sub>2</sub> monomer to afford hyperbranched poly(o-hydroxy-amide) (HBPHA), and subsequent protection of hydroxy group with t-BOC group as shown in Scheme 1.

A series of partially t-BOC protected HBPHAs was 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 experimental t-BOC Content of the polymers was well corresponded to the calculated molar input of DTBDC as shown in Figure 1. The HB-tbocPHAs showed excellent solubility for the common organic solvents such as DMF, THF,  $\gamma$ -butyrolactone and cyclohexanone as shown in Table 1. The solubility of the polymers increased with increasing the t-BOC contents. The 100 % substituted polymer, HB-tbocPHA-100, was soluble even in chloroform and partially soluble in toluene. This enhanced solubility would be originated from the introduction of bulky t-BOC group.

### Scheme 1. Synthesis of polymers.

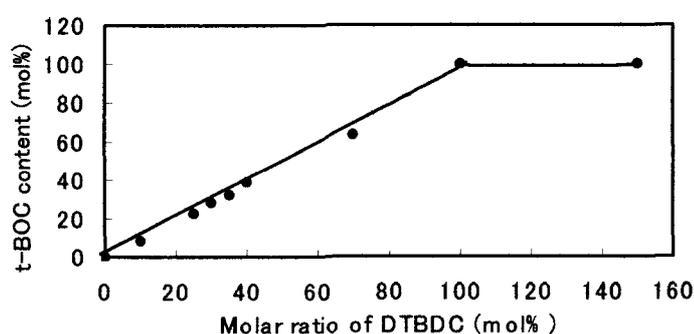
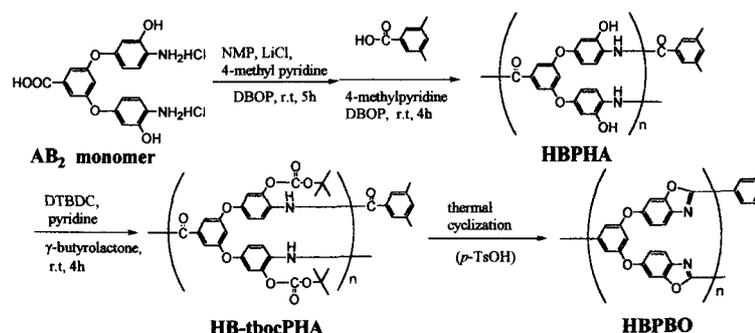


Figure 1. t-BOC content vs. molar ratio of DTBDC.

Table 1. Solubility of partially t-BOC protected HBPHAs

Polymer	DMF	THF	GBL <sup>a</sup>	Cyclohexanone	CHCl <sub>3</sub>	PGMEA	Toluene
HBPHA	++	++	++	++	-	-	-
HB-tbocPHA-10	++	++	++	++	-	-	-
HB-tbocPHA-25	++	++	++	++	-	-	-
HB-tbocPHA-30	++	++	++	++	-	-	-
HB-tbocPHA-35	++	++	++	++	+-	-	-
HB-tbocPHA-40	++	++	++	++	+-	-	-
HB-tbocPHA-70	++	++	++	++	++	+-	-
HB-tbocPHA-100	++	++	++	++	++	++	+-

<sup>a</sup> GBL,  $\gamma$ -Butyrolactone; ++ soluble at room temperature; +- partially soluble; - insoluble.

### Lithographic Evaluation.

Dissolution rate (DR) of matrix polymer in the resist design is one of the key factor to control the performance of photoresist. We investigated the relationship between the t-BOC contents and dissolution rates of the polymers in 2.38 wt% TMAH aqueous solution. The DR dramatically decreased with increasing the t-BOC content (Figure 2).

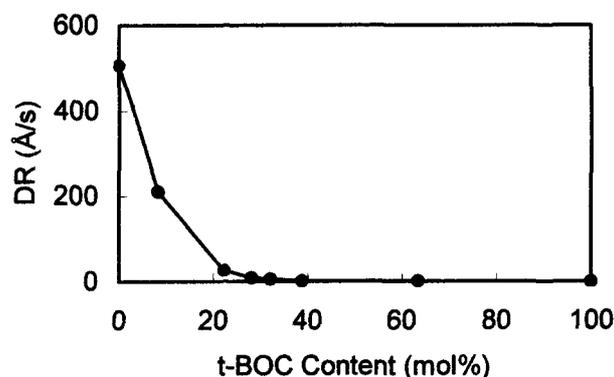


Figure 2. DR of partially t-BOC protected HBPHAs.

Adhesion of polymer film to substrate is also important factor as well as DR of polymer. The adhesion of the polymers on silicon wafer 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 the t-BOC content above 63 %. This phenomenon is probably due to the reduction of hydrophilicity of the polymers at the higher t-BOC content. Therefore, HB-tbocPHA-40, which had a good adhesion as well as adequate DR, was selected as a matrix resin of photoresist in this study.

The sensitivity ( $E_{th}$ ) and contrast ( $\gamma$ -value) of the resist composed of HB-tbocPHA-40 and 20 wt% of DIAS against the polymer were evaluated to be 115 mJ/cm<sup>2</sup> and 2.2 for 365 nm (i-line) light as shown in Figure 3.

Figure 4 (a) shows the scanning electron micrograph of the positive pattern obtained from 1um-thickness resist film composed of HB-tbocPHA-40 and 20 wt% of DIAS against the polymer. The clear positive pattern with 30 um L/S (line/space) was obtained at the 200 mJ/cm<sup>2</sup> of i-line exposure. The corresponding PBO pattern was obtained by thermal curing of the patterned film at

Table 2. Properties of HB-tbocPHAs with various t-BOC contents

Polymer	t-BOC content (mol%)	DR <sup>a</sup> (Å/s)	Adhesion
HBPHA	0	508	○
HB-tbocPHA-10	8.4	212	○
HB-tbocPHA-25	22.4	27	○
HB-tbocPHA-30	28.1	9.5	○
HB-tbocPHA-35	32.1	5.6	○
HB-tbocPHA-40	38.9	1.4	○
HB-tbocPHA-70	63.4	1.8	×
HB-tbocPHA-100	100	0.0	×

<sup>a</sup> DR, dissolution rate in 2.38 wt% TMAH aqueous solution at 25 °C.

300 °C for 1h in a oven as shown in Figure 4 (b). The patterned films shrink ca. 32.8 % after thermal curing process. Film shrinkage after thermal curing due to the thermal cyclodehydration as well as degradation of t-BOC group in the polymer. However, any distortion or deformation of the pattern was not observed after thermal curing.

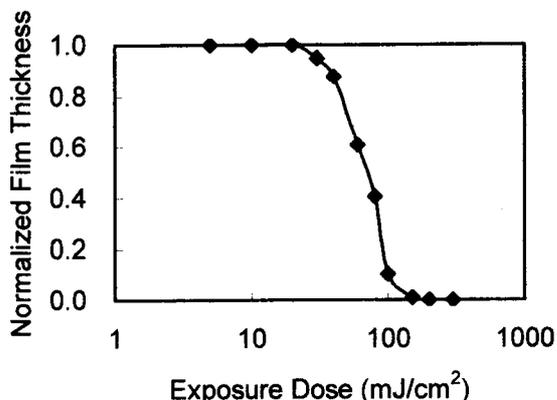


Figure 3. Characteristic curve of the resist.

### Conclusion

A series of partially t-BOC protected HBPHAs was successfully prepared from HBPHA, which were prepared by self-polycondensation of AB<sub>2</sub> type monomer. HB-tbocPHA-40 having the 39 mol% of t-BOC group showed the adequate dissolution rate in alkaline developer and good adhesion on silicon wafer as well as good solubility in common organic solvents.

HB-tbocPHA / DIAS system shows reasonable photospeed (115 mJ/cm<sup>2</sup>), contrast ( $\gamma = 2.2$ ) and good pattern profiles upon 365 nm irradiation. The patterned film was successfully converted to polybenzoxazole without any distortion by thermal treatment at 300 °C for 1h.

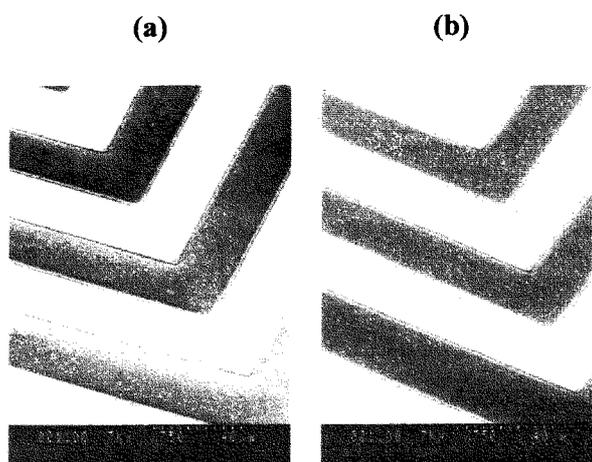


Figure 4. SEM micrograph of positive pattern profile for the HB-tbocPHA-40 / DIAS system (a) before thermal curing, and (b) after thermal curing at 300 °C for 1 h.

### References

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