Chemically Amplified Photosensitive Poly(benzoxazole)

Kazuya Ebara, Yuji Shibasaki, and Mitsuru Ueda*

*Department of Organic and Polymeric Materials
Graduate School of Science and Engineering, Tokyo Institute of Technology,
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan
mueda@polymer.titech.ac.jp*

A novel chemically amplified photosensitive poly (benzoxazole) (**PBO**) precursor based on partially *tert*-butoxycarbonylated (*t*-BOC) poly (*o*-hydroxyamide) having norbornene end-capping groups **5** and diphenyliodonium-9,10-dimethoxyanthracene-2-sulfonate (**DIAS**) as a photo-acid generator has been developed. The resist showed a sensitivity of 60 mJ cm⁻² and a contrast of 2.5 when it was exposed to 365 nm light, followed by post-baking at 120 °C for 5 min and developing with 2.38 wt% aqueous tetramethylammonium hydroxide (TMAH) solution at 25 °C. A fine positive image featuring 10 μm line and space patterns was obtained on the film exposed to 100 mJ cm⁻² of UV-light at 365 nm by the contact mode. By heat treatment at 350 °C for 1 h, this positive image gave the cross-linked **PBO** retaining its original shape that indicated high durability during thermal process.

Keywords: Photosensitivity, Poly(benzoxazole), Photoacid generator, Norbornene end-capping, Chemical amplification

1. Introduction

Photosensitive poly(benzoxazole)s (**PBO**)s are attracting great attention as photosensitive and thermally stable polymers because of their high mechanical strength, thermal stability, and low dielectric constant. One of the most promising system is a formation composed of a **PBO** precursor, poly(*o*-hydroxyamide) (**PHA**) and a diazonaphthoquinone photosensitizer [1–3]. Hydroxyl groups of the **PBO** precursor are desirable as base-soluble functional groups for alkaline developable photosensitive resists just like novolac-resin resists. Furthermore, hydroxyl groups, which usually increase the dielectric constant, can be transformed into benzoxazoles by thermal treatment of **PHA**.

In a previous paper, we reported a novel direct resist formulation method for photosensitive **PBO**, where the polymerization solution from diphenyl isophthalate **1** and bis(*o*-aminophenol) **2** was mixed with diazonaphthoquinones for the formulation of resist [4]. Its sensitivity was 110 mJ cm⁻² with 365 nm light. The sensitivity of a

photoresist to exposure is important parameters for the design of photoresist materials. Highly sensitive resists that require low exposure doses are desirable to maximize the throughput of wafers in exposure tools.

Photosensitive polymers with high sensitivity have been developed using polyimides having *tert*-butoxycarbonyloxy (*t*-BOC) substituents in conjunction with a photo-acid generator (chemical amplification system) [5]. To improve the sensitivity of photosensitive **PBO**s, the chemically amplified technique is applied. Furthermore, polymers with low molecular weights are reported to be preferred in the lithographic process [6].

This article describes the development of a novel chemically amplified photosensitive **PBO** precursor based on partially *t*-BOC protected **PHA** having norbornene end-capping groups.

2. Experimental

2.1. Materials

Diphenyl isophthalate (**1**) and 4,4'-(hexafluoroisopropylidene)bis(*o*-aminophenol

) (2) were recrystallized from toluene and hexane/tetrahydrofuran (THF), respectively. 1-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation from calcium hydride and stored over 4A molecular sieves. Diphenyliodonium-9,10-dimethoxyanthracene-2-sulfonate (DIAS) was prepared according to the reported procedure [5] (Scheme 1). Other reagents and solvents were used as received.

Scheme 1 Structure of DIAS

2.1.2. Synthesis of 5-norbornene-2-carboxylic anhydride (4)

To a solution of 5-norbornene-2-carboxylic acid (1.464 g, 10 mmol) and triethylamine (TEA) (0.536 mL, 10 mmol) in dichloromethane (10 mL) was added dropwise a solution of diphenylphosphoryl chloride (1.22 g, 5 mmol) in dichloromethane (10 mL). After 1 h the mixture was poured into water. The organic layer was separated, washed with water, and dried over MgSO_4 . The solvent was evaporated under reduced pressure. The crude oil was distilled under vacuum (142–145 °C / 10 mmHg). The yield was 45 %. IR (KBr): ν (cm^{-1}) 2950 (CH_2), 1808, 1734 (C=O), 1700 (C=C), and 713 ($-\text{CH=CH}-$). ^1H NMR (CDCl_3): δ (ppm) 6.23–5.99 (m, 4H), 3.25–2.96 (m, 6H), 2.19–1.89 (m, 2H), 1.53–1.29 (m, 6H), 7.85 (s, 1H), 7.64 (t, $J = 8.0$ Hz, 1H), 7.01 (brs, 4H).

2.1.3. Synthesis of end-capped poly(*o*-hydroxyamide) (3)

Monomers 1 (0.636 g, 1.8 mmol), 2 (0.732 g, 2.0 mmol), and NMP (5.6 mL) were placed in a 10 mL round-bottom flask under N_2 . The solution was heated at 185 °C for 6 h and then cooled to room temperature. End capping reagent 4 (0.155 g, 0.6 mmol) in NMP (1 mL) was added to this solution and reacted further for 3h, and poured into an aqueous methanol solution (1 : 1 in volume ratio 200 ml) to precipitate the polymer. The obtained polymer was washed with water and dried in *vacuo* over P_2O_5 . The yield was 94 %. IR (KBr): ν (cm^{-1}) 3300 (OH), 1654 (C=O), 1608(Ar), and 1253 (CF_3). ^1H NMR ($\text{DMSO}-d_6$): δ (ppm) 10.0 (brs, 2H), 9.62

(s, 2H), 8.51 (s, 2H), 8.12 (d, $J = 8.0$ Hz, 2H), 7.85 (s, 1H), 7.64 (t, $J = 8.0$ Hz, 1H), 7.01 (brs, 4H).

2.1.4. Synthesis of poly[*o*-(4-*tert*-butoxycarbonyloxy)hydroxyamide] (5b) : General procedure

To a solution of polymer 3 (0.496 g 1.0 mmol) and *N,N*-dimethylaminopyridine (DMAP) (0.014 g 0.05 mmol) in NMP was added di-*tert*-butyl dicarbonate (0.218 g, 1.0 mmol). The solution was stirred for 1 h at room temperature, and was poured into 1M aqueous hydrogen chloride solution (200 mL). The precipitate was collected by filtration, washed with water and dried in *vacuo* at 60 °C for 24 h. The yield was 94 %. IR (KBr): ν (cm^{-1}) 3300 (OH), 2950 (CH_3), 1766, 1654 (C=O), 1608(Ar), and 1253 (CF_3). ^1H NMR ($\text{DMSO}-d_6$): δ (ppm) 10.0 (brs, 2H), 9.70–9.62 (m, 1H), 8.51 (s, 1H), 8.14–8.1 (m, 2H), 8.12 (t, $J = 8.0$ Hz, 1H), 7.80 (s, 1H), 7.65 (t, $J = 8.0$ Hz, 1H), 7.42 (t, $J = 8.0$ Hz, 1H), 7.22 (s, 1H), 7.01 (brs, 2H), 1.39 (s, 9H).

2.2 Dissolution rate

DIAS was added to a polymer solution (30 wt% of the total solid) to construct a photosensitive polymer. The polymer film spin-cast on a silicon wafer was pre-baked at 80 °C for 3 min, and then exposed to a filtered super-high pressure mercury lamp at 365 nm. The exposed film was developed with a 2.38 wt% aqueous tetramethylammonium hydroxide (TMAH) solution at 25 °C, and rinsed in water. The changes in the film thickness against the exposure energy were measured by a Detak³ surface profiler (Veeco Instrument Inc.).

2.3. Photosensitivity

A 1.0 μm -thick polymer film on a silicon wafer was exposed to radiation at a wavelength of 365 nm through the filtered super high-pressure mercury lamp, developed with a 2.38 wt% aqueous TMAH solution at 25 °C, and rinsed with water. A characteristic curve was obtained by a normalized film thickness against exposure energy. Imagewise exposure through a mask was carried out in a contact-printing mode.

2.4. Measurement

The infrared spectra were recorded on a Horiba FT-210 spectrophotometer. ^1H -NMR spectra were recorded on a Bruker GPX300 (300MHz) spectrometer. UV spectra were obtained on a Jasco V-650 spectrophotometer. Thermal analyses were performed on a Seiko thermal analyzer at a heating

rate of 10 °C /min for thermogravimetry (TG). Molecular weights were determined by a gel permeation chromatograph (GPC) with polystyrene calibration using a Tosoh HPLC-8120-G equipped with consecutive TSK gel columns GMH_{HR} - M and GMH_{HR} - L at 40 °C in DMF containing 0.01 mol / L LiBr. The film thickness was measured by a Dektak³ surface profiler (Veeco Instrument Inc).

3. Results and Discussion

3.1 Polymer synthesis

As described in the introduction, a low molecular weight polymer is needed to get a high resolution without sacrificing thermal stability. End-capping groups that lead to cross-linked network without gas evolution are useful to control molecular weights. Norbornene-terminated imide (bisanidiimide) resins have been used in industry [7]. Thus, a norbornene group as an end-capping was selected in this study.

PHA was prepared from **1** and **2** with their molar ratio of 0.9 : 1 in NMP at 185 °C for 6 h, and then converted end-capped PHA **3** by treating with 5-norbornene-2-carboxylic anhydride **4** as an end-capping agent (eq. 1).

The structure of **3** was characterized by IR and ¹H NMR spectroscopy.

The IR spectrum of **3** exhibited characteristic absorptions at 3300, 1654, 1253 cm⁻¹ due to the O-H, C=O (amide), and C-F stretchings, respectively. Figure 1 shows the ¹H NMR spectrum of polymer **3** with the assignment of each peak. Signals assignable to terminal norbornene protons (peaks 8-10) were observed at 6.0, 2.9, 1.3 ppm, respectively.

The molecular weight of polymer **3** was determined by GPC in DMF at 40 °C. The chromatogram showed a unimodal distribution with M_n and M_w of 4000 and 5800, respectively, with polystyrene standards.

Figure 1. ¹H NMR spectrum of polymer **3** in DMSO-*d*₆

To obtain a chemical amplification system of PBO precursor, **3** was converted to the corresponding partially *t*-BOC protected polymer **5** by treatment with di-*tert*-butyl dicarbonate in the presence of DMAP (eq. 2) (Table 1)

Table 1. Synthesis of polymer **5**

Polymer	Protect feed <i>t</i> -Boc / OH	Yield (%)	Molecular weight ^{a)}	
			M_n	M_n / M_w
5a	80 / 20	95	4600	1.4
5b	50 / 50	94	4400	1.4
5c	30 / 70	94	4200	1.3

a) Measured by GPC in DMF eluent.

The structure of polymers **5** was fully characterized by IR and ¹H NMR spectroscopy. Characteristic *tert*-butoxycarbonyl and alkyl bands were observed at 1766 (C=O) and 2950 cm⁻¹ (C-H), respectively, in the IR spectrum of **5**. The ¹H NMR spectrum showed signals corresponding to *tert*-butyl protons (1.4 ppm) and aromatic protons (7-8.5 ppm) (Figure 2). The *t*-BOC protected ratios determined by signals at 10.3 (amide) and 1.4 (*tert*-butyl) in ¹H NMR spectrum showed a good agreement with the values from the feed ratios.

Figure 2. ^1H NMR spectrum of polymer **5b** in $\text{DMSO}-d_6$

3.2. Lithographic evaluation

The UV-visible spectrum of polymer **5b** film is shown in Figure 3, where a strong absorption at 300 nm due to $\pi \rightarrow \pi^*$ transition of aromatic groups and no absorption above 350 nm were observed. Thus, DIAS having a strong absorption in the range of 300–420 nm was selected as a photo-acid generator.

Figure 3. UV-visible spectrum of polymer **5b**

To clarify the dissolution behavior of exposed and unexposed areas, the effects of *t*-BOC protecting ratios in polymer **5** and post exposure bake (PEB) temperatures on the dissolution rate in 2.38 wt% aqueous a tetramethylammonium hydroxide (TMAH) solution were investigated. The films spin-cast on silicon wafers were pre-baked at 80 °C for 3 min, and then exposed to a filtered super-high pressure mercury lamp (365 nm, 100 mJ cm⁻²). The dissolution rate was estimated by measuring the film thickness after the development.

The effect of *t*-BOC protecting ratios in polymer **5** loading with DIAS after exposure of 100 mJ cm⁻² and PEB at 120 °C for 5 min was studied, and the results are illustrated in Figure 4.

Figure 4. Relationship between dissolution rate and *t*-BOC protecting ratio polymer **5** with DIAS

The dissolution rate of the unexposed area decreased gradually with increasing the *t*-BOC protection ratios, and reached zero at the 50 % *t*-BOC protection ratio.

To investigate the PEB temperature effect on the dissolution rate, the dissolution rates both of exposed and unexposed areas at various PEB temperatures were measured. The resist was formulated by mixing polymer **5b** (70 wt%) and DIAS (30 wt%) in ethyl lactate, and the films exposed to 100 mJ cm⁻² at 365 nm light were post-baked at temperatures from 100 to 150 °C for 5 min, and developed with 2.38 wt% aqueous TMAH developer. The results are shown in Figure 5.

Figure 5. Relationship between dissolution rate and PEB temperature for polymer **5b** film containing DIAS

The dissolution rates of the exposed region increased with increasing of PEB temperatures, and that of the unexposed area was rezero below 120 °C. The difference of the dissolution rate between exposed and unexposed parts reached about 10,000 times at 120 °C for 5 min. Thus, the suitable PEB temperature was determined to be 120 °C.

Then, a resist consisting of polymer **5b** and

DIAS was formulated. The sensitivity curve for a 1.0 μm -thick polymer **5b** film was consistent with the dissolution behavior studied above, indicating that the sensitivity (D^0) and contrast (γ^0) were 60 mJ cm^{-2} and 2.5, respectively (Figure 6).

Figure 7 shows a scanning electron micrograph of the contact printed positive image after exposure of 100 mJ cm^{-2} . The resist is capable of resolving a $1 \mu\text{m}$ feature when a $1 \mu\text{m}$ thick film is used.

Figure 6. Exposure characteristic curve for polymer **5b** containing 30 wt% **DIAS**

Figure 7. SEM micrograph of pattern from the system consisting of polymer **5b** and **DIAS**

3.3 Thermal stability of polymer films

The positive image in the polymer film was also converted into that of **PBO** by high-temperature treatment (350°C) for 1 h. The IR spectra of polymer **5b** and thermally treated film **6** are shown in Figure 8.

Figure 8. The IR spectra of polymer **5b** and thermally treated films **6**

The characteristic oxazole ring absorption at 1620 cm^{-1} appeared in polymer **6**, and the absorptions due to the hydroxyl and *t*-BOC groups at 3300 and 1766 cm^{-1} , respectively, in polymer **5b** disappeared.

Figure 9 shows a TGA curve of polymer **5b** film cured at 350°C for 1 h.

Figure 9. TG curve of polymer **5b** film cured at 350°C for 1h under N_2 .

No weight loss of the cured **5b** was observed below 450°C and a 5% weight loss was at 530°C . This curing temperature is higher than that expected for the retro Diels-Alder reaction of norbornene group and elimination of water by formation of oxazole ring. Thus, this result indicated that norbornene groups contributed for the cross-linking reaction.

4. Conclusion

Norbornene end-capped polymer **3** was prepared by polycondensation of **1** and **2**, followed by treatment with **4** as the end-capping agent. Then, polymer **3** was converted to *t*-BOC protected polymer **5** by reaction with di-*tert*-butyl dicarbonate. The resist based on polymer **5b** and

DIAS showed a high sensitivity (60 mJ cm^{-2}) and contrast (2.5) with 365 nm light. The thermally treated positive image revealed a high thermal stability.

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