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Negative-Working Photosensitive Polybenzoxazoles Based on Hyperbranched Poly(*o*-hydroxyamide)s

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ABSTRACT: The negative-working photosensitive polybenzoxazole (PSPBO) composed of hyperbranched poly(*o*-hydroxyamide) (HBPHA), 2,6-bis(hydroxymethyl)-*p*-cresol (BHMP) as a cross-linker and diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a photoacid generator (PAG) was developed and evaluated. The HBPHA as a precursor of PSPBO was prepared by self-polycondensation of an AB_2 type monomer. The acid-catalyzed cross-linking of the BHMP in the presence of strong acid such as *p*-toluenesulfonic acid (*p*-TsOH) was investigated by using DSC and TGA. The cross-linking of BHMP was accelerated in the presence of *p*-TsOH, whereas cross-linking was not observed until it reached 140 °C without acid. The photolithographic performance of the resist (XPR-721) formulated with 70 wt% of HBPHA, 20 wt% of BHMP, and 10 wt% of DIAS was evaluated. The resist showed high sensitivity ($E_{th}{}^{1/2}$ = 56 mJ cm^{-2}) and good contrast ($\gamma^{1/2}$ = 4.6) with 365 nm light when it was developed in 1.19 wt% tetramethylammonium-hydroxide (TMAH) aqueous solution at room temperature. The fine negative 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 350 °C for 1 h.

KEY WORDS Polybenzoxazoles / Hyperbranched Polymer / Photosensitive Polymer / Negative Type Photoresist / Poly(*o*-hydroxyamide)s / Cross-Linking / Photoacid Generator (PAG) /

Photosensitive polymers (PSP) such as photosensitive polyimides (PSPIs) have been utilized for various applications, especially in the field of electronic device production. The main advantage of using photosensitive polymers as passivation coating or inter-layer dielectrics in semiconductor devices are their simple process compared to conventional photoresist.

Negative type photosensitive polyimide was first reported by Kerwin *et al.* in 1971.[1,2] Several types of negative-working PSP were developed by a lot of research groups such as covalent type PSPIs by Rubner *et al.*,[3] ionic type PSPIs by Yoda *et al.*,[4] base-catalyzed type PSPIs by Mckean *et al.*[5] and simple blend systems consisted of polyamic acids (PAA), acrylic monomers and photo initiators by Nishizawa *et al.*[6] In 1994, Fréchet reported a negative type resist system composed of poly(4-hydroxystyrene) (PHS), photoacid generator (PAG), and polyfunctional benzylic alcohols as cross-linkers.[7] They found that benzylic alcohols act as excellent cross-linkers in the presence of acid showing good lithographic performance. In 1996, Ueda also reported similar resist system using the poly(hydroxyimide) (PHI), 2,6-bis(hydroxymethyl)-*p*-cresol (BHMP) as a cross-linker and PAG.[8] Both of the systems suggest that *p*-hydroxyphenyl unit of the PHI reacts easily with electrophilic benzylic carbocation.

On the other hand, poly(*o*-hydroxyamide) (PHA), precursor of polybenzoxazole (PBO), has been also considered as a matrix polymer for alkaline developable photosensitive polymer because of its appropriate dissolution rate in aqueous alkaline solution.[9–14]

Previously we reported chemically amplified positive-working photosensitive polybenzoxazoles[15] based on *tert*-butoxycarbonyl (*t*-BOC) protected HBPHA and photoacid generator (PAG). In this paper, we describe a novel negative type photoresist system based on hyperbranched poly(*o*-hydroxyamide), PAG and cross-linker. The fine negative-patterned profiles of hyperbranched polybenzoxazoles (HBPBOs) were obtained by thermal conversion of photosensitive HBPHAs.

EXPERIMENTAL

Materials

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 was used after distillation with calcium sulfate. Lithium chloride (LiCl) and potassium carbonate were dried at 130°C and 200 °C *in vacuo*, respectively and kept under nitrogen. 3,5-Dihydroxybenzoic acid (Tokyo Kasei, > 98%) was used after recrystallization with water. 4-Methylpyridine was purified by distillation in the presence of potassium hydroxide. (2,3-Dihydro-

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2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP) was prepared according to the literature[16] and purified by recrystallization with hexane. 2,6-Bis(hydroxymethyl)-*p*-cresol (BHMP, Aldrich, > 95%), 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, 3,5-bis(4-amino-3-hydroxyphenoxy)benzoic acid dihydrochloride, was prepared *via* three steps starting from 3-fluoro-6-nitrophenol and 3,5-dihydroxybenzoic acid according to the same manner as described in our previous report.[17]

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 806 M and KD 802 columns in DMF containing lithium bromide ($0.01\,\mathrm{mol\,L^{-1}}$) as an eluent. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a Seiko DSC 6200 and TG/DTA 6200 at a heating rate of $10\,°\mathrm{C\,min^{-1}}$ under nitrogen. Inherent viscosity was measured at a concentration of $0.5\,\mathrm{g\,dL^{-1}}$ with an Ostwald type viscometer in DMAc at 30 °C. UV spectra were obtained on a JASCO V-560 spectrophotometer. Film thickness was measured on a Dektak 3 system of Veeco Instruments Incorporation. Resist films were exposed to 365 nm light with a i-line filtered super high-pressure mercury lamp (250 W). Pattern profiles were obtained with a Hitachi S-800 scanning electron microscope (SEM).

Synthesis of Hyperbranched Poly(o-hydroxyamide) (HBPHA)

HBPHA was prepared by polycondensation of the AB_2 type monomer (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. 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 additional 4 h: 67% yield; weight-average molecular weight, $M_\mathrm{w} = 51500$, polydispersity index, $M_\mathrm{w}/M_\mathrm{n} = 1.4$; inherent viscosity, $\eta_\mathrm{inh} = 0.13\,\mathrm{dL\,g^{-1}}$.

Lithographic Evaluation

HBPHA (70 wt%), BHMP (20 wt%), and DIAS (10 wt%) were dissolved at 20 wt% in cyclohexanone. After filtration through 0.2 μm of disk-type filter, the photoresist solution was spun on a silicon wafer with 1.0 μm thickness 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 i-line filtered high-pressure mercury lamp. Imagewise exposure was carried out in the contact mode with a photomask. Post exposure bake (PEB) of resist film was carried out at 120 °C for 5 min. Finally, the patterned film was developed in 1.19 wt% TMAH aqueous solution at 25 °C for 60 s.

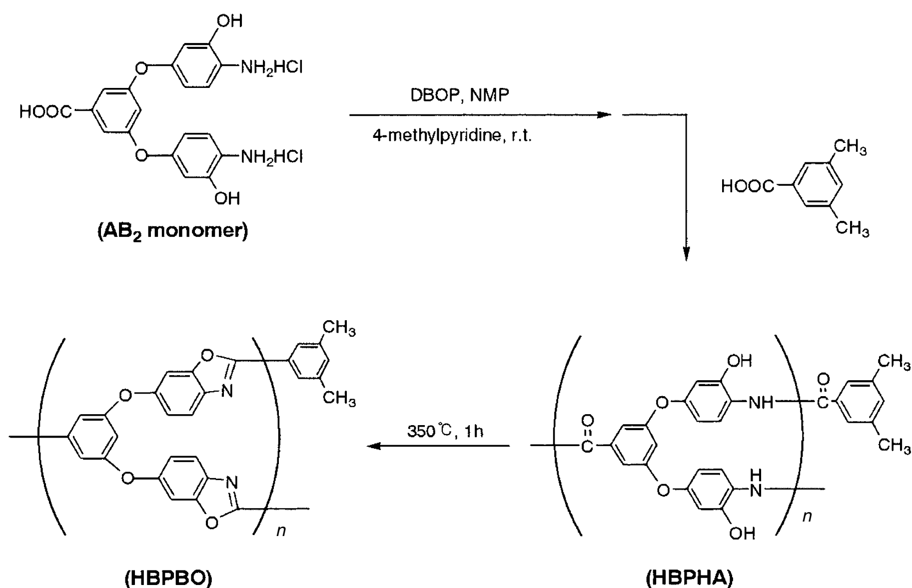
RESULTS AND DISCUSSION

Synthesis of Poly(o-hydroxyamide)

HBPHA as a matrix polymer of negative-working photoresist was prepared by the polycondensation of the AB_2 monomer as shown in Scheme 1. The weight average molecular weight (M_w) of HBPHA was 51500 with a polydispersity of 1.4. The inherent viscosity (η_inh) was $0.13\,\mathrm{dL\,g^{-1}}$. 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. It was reported that the generated acid from PAG by UV irradiation reacts with the hydroxy group of BHMP to form benzyl cation and subsequently accelerates cross-linking reactions between the BHMP and poly(4-hydroxystyrene) (PHS) by Fréchet.[18] They revealed that the reaction involving cross-linkers such as BHMP is proceeded *via* both a direct *C*-alkylation as well as an initial *O*-alkylation followed by a subsequent acid-catalyzed rearrangement to the final *C*-alkylated product in the BHMP/PHS system. Since HBPHA contains aromatic carbons at the ortho position of the hydroxy groups, the same cross-linking reaction through the *C*-alkylation could be expected in the HBPHA/BHMP/PAG resist system.

Thermal Behavior of BHMP

In this study, we made choice of BHMP as an acid-catalyzed cross-linker. As a preliminary research, we have investigated the thermal cross-linking behavior of BHMP with or without acid by DSC measurements (Figure 1). The self-crosslinking reaction of BHMP was observed in the range of 140–206 °C in the absence of *p*-TsOH as a broad endothermic peak. It implies that the PEB temperature of this resist system have to be below 140 °C. On the other hand, the broad endothermic peak was observed at 87–138 °C in the presence



Scheme 1. Synthesis of hyperbranched polybenzoxazoles *via* poly(*o*-hydroxyamides).

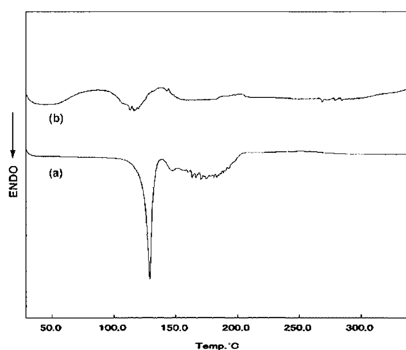


Figure 1. DSC thermogram of (a) BHMP and (b) their mixture (BHMP/*p*-TsOH = 2/1 wt%).

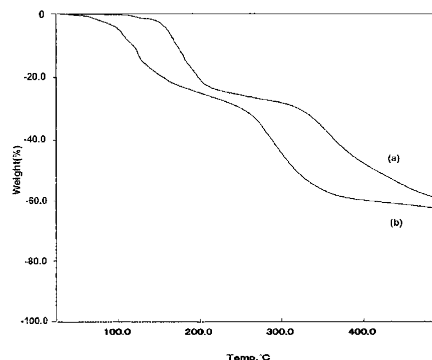


Figure 2. TGA thermogram of (a) BHMP and (b) mixture (BHMP/*p*-TsOH = 2/1 wt%).

of *p*-TsOH (BHMP/*p*-TsOH = 2/1 wt%). It is clear that the acid accelerates the self-crosslinking reaction of BHMP. The accelerated crosslinking might proceed during the PEB process at 120 °C. The TGA thermogram of BHMP showed two step weight loss (Figure 2). The first step weight loss (20.9 wt%) at 149–207 °C is probably due to the elimination of water during the cross-linking. However, the weight loss (20.9 wt%) was not consistent with the calculated weight loss of 10.7 wt%. It was not clear, but we guess the weight loss at this region is due to not only the elimination of water but also the degradation of unreacted or low molecular weight materials. The temperature for the second step weight loss was higher than 300 °C. The good thermal stability is demanded for the application of permanent dielectric layers with high-temperature polymers.

Lithographic Evaluation

Diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) was used as a photoacid generator (PAG), since it showed high absorbance in the range of 330–440 nm with maximum absorbance at 390 and 413 nm in the UV-vis spectra. The mechanism of cross-linking of BHMP with HBPHA was shown in Figure 3. DIAS is photochemically decomposed to give 9,10-dimethoxyanthracene-2-sulfonic acid, benzene and iodobenzene. Generated acid subsequently reacts with BHMP and induces cross-linking reactions between the BHMP and HBPHA.

The UV spectrum of the matrix polymer (HBPHA) is shown in Figure 4. The polymer showed high transparency at i-line (365 nm) as well as g-line (436 nm). Therefore, HBPHA could be used as a matrix polymer upon irradiation with 365 nm light. The UV-vis spectral change of the resist (XPR-721) composed of HBPHA (70 wt%), BHMP (20 wt%), and DIAS (10 wt%) is shown in Figure 5. The characteristic absorbance of DIAS at 389, 414, and 456 nm decreased with increasing the exposure dose.

The conversion of HBPHA precursor to HBPBO was confirmed by using FT-IR and TGA. The IR spectra of patterned film before and after thermal curing were

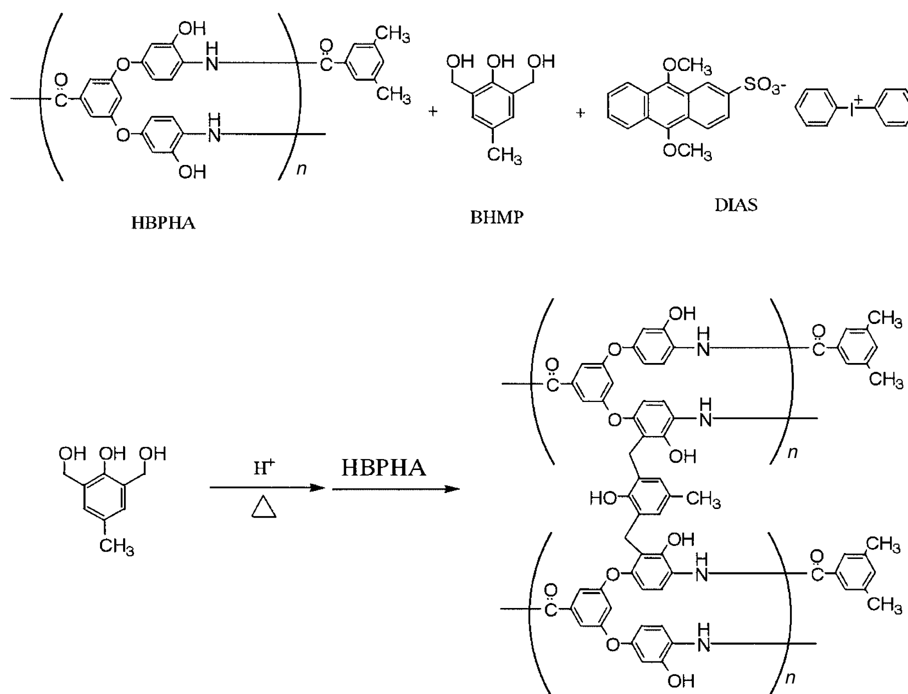


Figure 3. Cross-linking mechanism of BHMP with HBPHA.

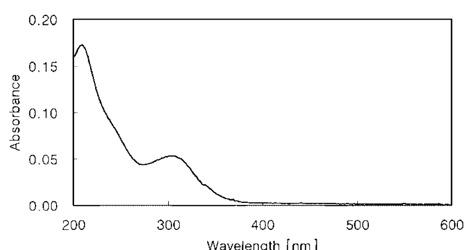


Figure 4. UV-vis spectrum of the matrix polymer (HBPHA). Film thickness: 0.2 ìm.

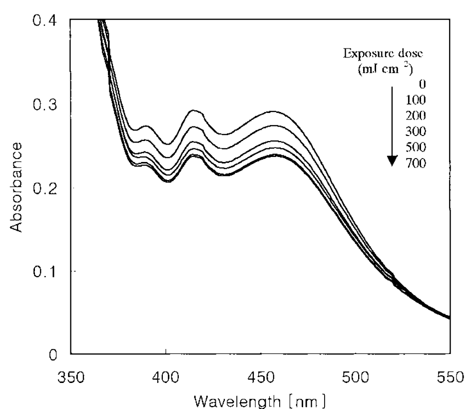


Figure 5. UV-vis spectral change of the resist XPR-721 (film thickness: 0.2 ìm) upon irradiation with 365 nm light.

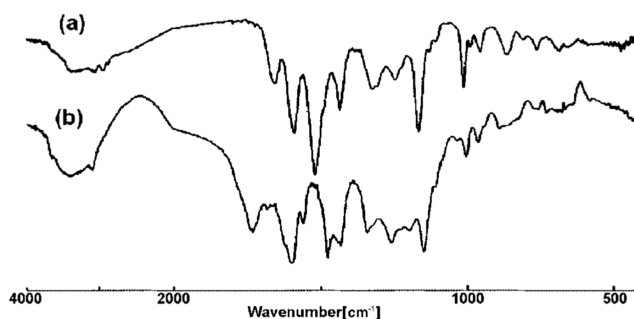


Figure 6. IR spectra of patterned film after development: (a) before thermal curing, (b) after thermal curing at 350 °C for 1 h.

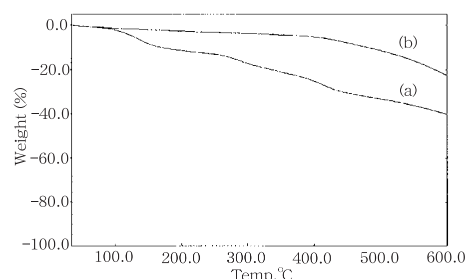


Figure 7. TGA thermogram of XPR-721: (a) before thermal curing, and (b) after thermal curing at 350 °C for 1 h.

shown in Figure 6. The characteristic amide peak at 1654 cm^{-1} in Figure 6a was disappeared after thermal curing and new peaks were observed at 1730 cm^{-1} as well as at 1620 cm^{-1} and 1476 cm^{-1}, which is a characteristic benzoxazole peak (spectrum b in the Figure 6). The peak at 1730 cm^{-1} seemed to be due to the reactive quinone methide intermediate[19] of BHMP.

TGA thermograms of XPR-721 before and after thermal curing are shown in Figure 7. The thermogram a shows three step weight loss. The first step weight loss started at 100 °C, indicating that vaporization of residual solvent began at this temperature, followed by vaporization of BHMP and degradation of DIAS at around 156 °C. The second step weight loss was occurred in the range of 266–391 °C which is due to

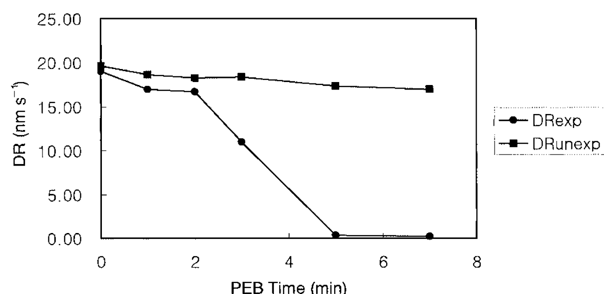


Figure 8. PEB time effects on the dissolution rate of the resist film (PEB temperature: 120 °C). (DRexp: dissolution rate of the exposed resist film, DRunexp: dissolution rate of the unexposed resist film.)

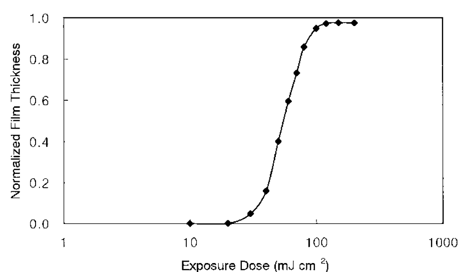


Figure 9. Characteristic curve of the XPR-721.

the elimination of water during the thermal cyclization. And, the decomposition of polybenzoxazole started at 391 °C. The resist after thermal curing at 350°C for 1 h shows one step weight loss at 412°C. The IR and the TGA results indicate that the HBPHA precursor was fully converted to HBPBO after thermal curing at 350 °C for 1 h.

To investigate the dissolution behavior of exposed and unexposed areas of XPR-721 during the developing process, the effects of the post-exposure bake (PEB) time on the dissolution rate (DR) were studied (Figure 8). The resist (XPR-721) was spin-coated at 1 μm thickness, pre-baked at 100 °C for 3 min and exposed 200 mJ cm^{-2} at 365 nm irradiation, subsequently carried out PEB at 120 °C for variable time and finally developed with 1.19 wt% of TMAH aqueous solution at 25 °C. DR was calculated by the thickness difference of the resist film before and after the development. The dissolution rate of the exposed area decreased with increasing PEB time, while unexposed area was almost unchanged. The maximum dissolution contrast was achieved at the PEB time of 5 min. It suggests that the thermal crosslinking reaction of acid-catalyzed cross-linked polymer has great influence on the DR of the polymer. The sensitivity ($E_{th}^{1/2}$) and contrast ($\gamma^{1/2}$) of the negative-working resist (XPR-721) were evaluated to be 56 mJ cm^{-2} and 4.6 for 365 nm light as shown in Figure 9. This resist system showed higher sensitivity compared to conventional linear photosensitive polymer[8] which maybe due to their hyperbranched structure.[20]

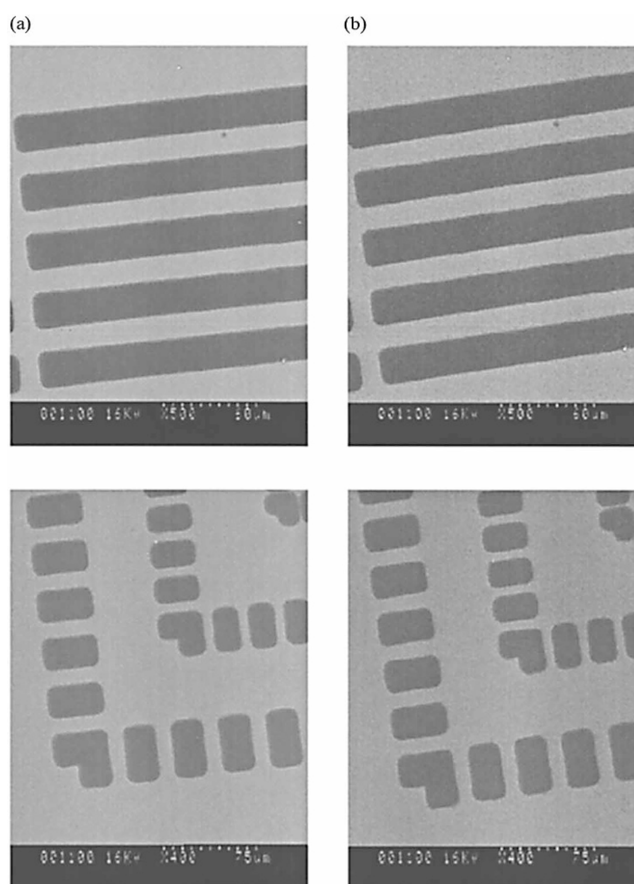


Figure 10. Scanning electron micrograph of negative pattern profile for the XPR-721: (a) before thermal curing, and (b) after thermal curing at 350 °C for 1 h.

Figure 10a shows the scanning electron micrograph of the negative pattern obtained from 1 μm-thickness resist film before thermal curing. The clear negative pattern with 15 μm L/S (line/space) was obtained at the 200 mJ cm^{-2} of i-line exposure with pre-bake at 100°C for 3 min and PEB at 120 °C for 5 min. The corresponding PBO pattern was obtained by thermal curing of the patterned film at 350 °C for 1 h in an oven as shown in Figure 10b. The film thickness reduced in *ca.* 15.3% after the thermal curing process. The film shrinkage is due to the thermal cyclodehydration as well as degradation of PAG. However, any distortion or deformation of the PBO pattern was not observed after the thermal curing at 350 °C for 1 h.

CONCLUSION

We developed and evaluated the new negative-working photosensitive polybenzoxazoles based on hyperbranched poly(*o*-hydroxyamide), BHMP as a cross-linker and DIAS as a PAG. XPR-721 composed of HBPHA (70 wt%), BHMP (20 wt%), and DIAS (10 wt%) shows high photosensitivity ($E_{th}^{1/2}$ =

56 mJ cm^{-2}), good contrast ($\gamma^{1/2} = 4.6$) and fine pattern profiles upon 365 nm irradiation. The patterned film was successfully converted to polybenzoxazole without any distortion by thermal treatment at 350°C for 1 h.

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