Polymer Journal, Vol. 38, No. 5, pp. 405–418 (2006)

REVIEW ARTICLES

Recent Development of Photosensitive Polybenzoxazoles

Ken-ichi FUKUKAWA[1] and Mitsuru UEDA[2,†]

[1]*Materials Research Laboratory, University of California, Santa Barbara, CA 93106-5121, USA*
[2]*Department of Organic & Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-H120, O-okayama, Meguro-ku 152-8552, Japan*

(Received January 16, 2006; Accepted February 23, 2006; Published May 15, 2006)

ABSTRACT: Photosensitive polybenzoxazoles (PSPBOs) have been attracting great attention as insulating materials in microelectronic industry, and can be directly patterned to simplify processing steps. This article reviews recent works on development of PSPBOs. After brief introduction, a typical formulation method of PSPBOs was described, followed by a facile synthetic method of a precursor of PBOs, highly sensitive PSPBOs, highly transparent poly(*o*-hydroxy amide)s (PHAs), an efficient catalyst for low-temperature cyclization of PHA, and finally other applications of PSPBOs. [doi:10.1295/polymj.38.405]

KEY WORDS Photosensitive Polybenzoxazole / Poly(*o*-hydroxy amide) / Photosensitive Compound / Photoacid Generator / Low Temperature Cyclization / Catalyst /

INTRODUCTION

Ongoing improvements in semiconductor technology have contributed greatly to the quality of our lives in the world for several decades. Thermally stable polymers are attracting great interest in the fields of state-of-the-art integrated circuits (ICs) and multi-chip modules (MCMs) because of their excellent thermal properties during manufacture and operation. They have applications as well in the manufacture of high strength-high modulus fibers for bulletproof wear owing to their extremely high mechanical strength.[1–3]

Polybenzoxazoles (PBOs) consisting of alternating phenylene and condensed aromatic heterocyclic rings are representative of thermally stable polymers, and a promising alternative to the polyimides (PIs) that have been commonly used as materials meeting the requirements described above (Figure 1). Both PBOs and PIs possess several outstanding features, such as high thermal stability; low flammability;[4] chemical resistance; and high modulus and strength.[5] In electrical devices, materials are also required to have low dielectric constants to minimize power dissipation.[6] PBOs have an advantage over PIs because of their relatively lower dielectric constants and lower water absorption due to the absence of carbonyl groups in the polymer backbone.

Photosensitive PBO (PSPBO) has been developed to simplify industrial processes significantly: phenolic hydroxyl groups in a precursor polymer of PBO, poly-

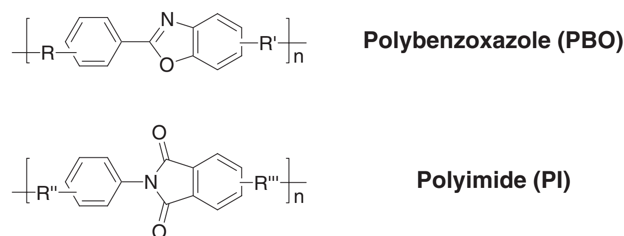


Figure 1. Chemical structure of PBO and PI.

(*o*-hydroxy amide; PHA), provide adequate solubility in an aqueous alkaline developer. In contrast, the precursor of PI, poly(amic acid) (PAA), is not optimally suited as a patternable photosensitive material because its solubility in aqueous alkali is too high. Such photosensitive and thermally stable polymers have been used as buffer coatings to protect bare chips from stresses induced by fillers or thermal mismatches between a passivation layer and molding materials. Even though the PSPBOs and PSPIs have greatly enhanced the progress of microelectronics so far, more technological innovations involving simpler processes, more valuable properties (*e.g.*, transparency, low dielectric constant), higher sensitivity, etc. are still greatly needed in this important area.

In this review article, the latest developments in PSPBOs are presented. The original types of PSPBOs initially developed have been reviewed in the literature.[7–9]

†To whom correspondence should be addressed (Tel: +81-3-5734-2127, Fax: +81-3-5734-2127, E-mail: mueda@polymer.titech.ac.jp).

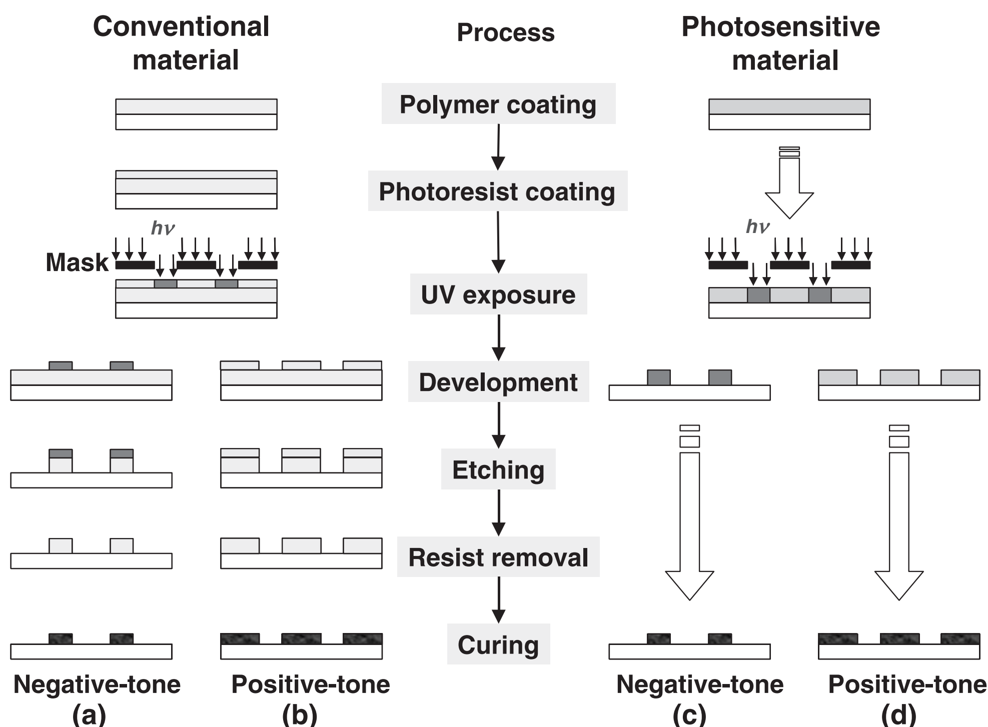


Figure 2. Photolithographic patterning processes in conventional methods (a & b) and using photosensitive materials (c & d).

PROCESS OF PHOTOLITHOGRAPHIC PATTERNING

In a photolithographic process (Figure 2), a photoresist polymer is spun onto a substrate of interest (*e.g.*, a silicon wafer) to form a uniform coating. This coating is then exposed to a specific source of light through a mask that has pattern information to be transferred. The photoresist polymer exposed to the radiation undergoes a chemical change (cross-linking, chain-scission, or polarity change). The step which follows is development, to remove selectively either the exposed or the unexposed regions to shape the pattern of the polymer layer successfully. The polymer is called a positive-tone resist if the exposed regions become more soluble in the developer and a negative-tone resist if the opposite is true. Thus, photolithography provides a large number of options and flexibility to tune the polymers matrices using additives such as photo-sensitizers (*e.g.*, diazonaphthoquinones (DNQs) and photo-acid generators (PAGs)) or cross-linkers. 2.38 wt% tetramethylammonium hydroxide in aqueous solution (TMAHaq) is a commonly used industrial developer.

As these thermally stable polymers are insoluble in organic solvents, they are deposited onto the substrate by spin-casting in the form of their soluble precursors followed by pre-baking to remove residual solvent. After the photolithographic processes involving exposure to radiation and development to form patterns, it is possible to convert the precursor patterns into the corresponding high-temperature polymers by thermal treatment. Figure 3 represents an typical SEM image of PSPBO pattern film.

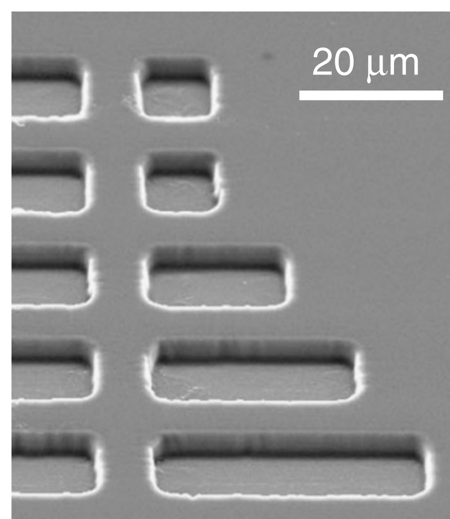
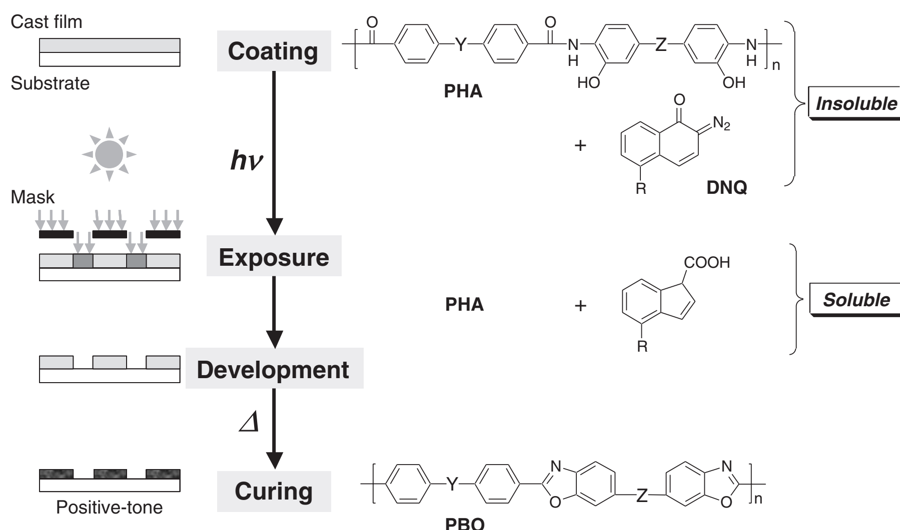


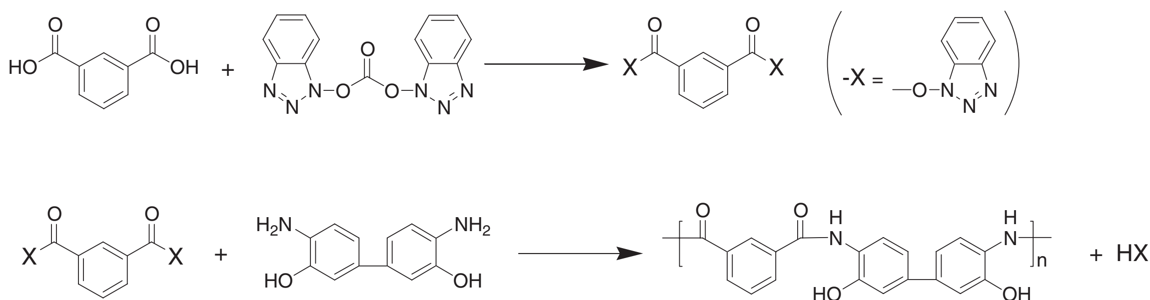
Figure 3. SEM image of PSPBO pattern film.

TYPICAL PREPARATION OF A PSPBO SYSTEM

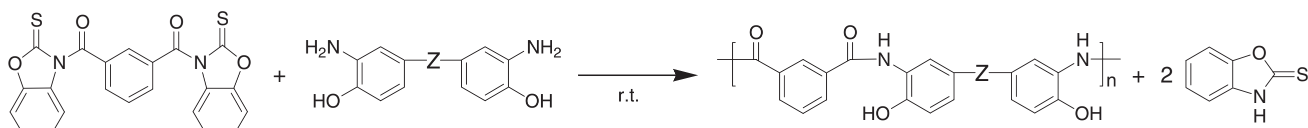
For microelectronics applications such as ICs and MCMs, PBOs are traditionally shaped into micropatterns by transfer of photolithographic patterns of addi-



Scheme 1. Image formation process of PSPBO based on PHA and DNQ.



Scheme 2. Halogen-free method on PHA synthesis.



Scheme 3. Synthesis of PHA from active diamide.

tional photoresist on the polymer layer. To obviate such complex procedures, DNQ, which functions as a dissolution inhibitor, is added to the PHA solution to form a photosensitive polymer solution (Scheme 1) in a typical formulation of PSPBO first developed by R. Rubner.[7–9] The use of PSPBOs allows simple and safe fabrication of electronic devices owing to the elimination of additional photoresist.

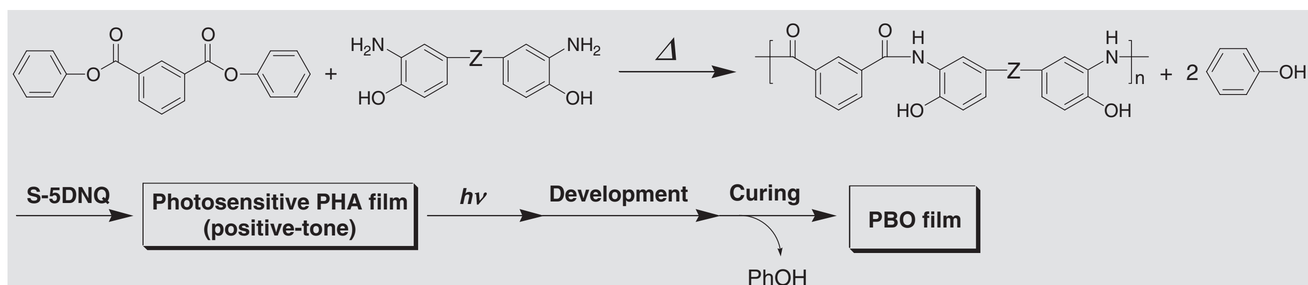
To avoid contamination by chloride ions in microelectronic devices, a chlorine-free synthetic method is generally used to prepare PHA from an aromatic dicarboxylic active diester and bis(*o*-aminophenol). The active ester, *e.g.*, 1-hydroxybenzotriazolyl ester, is prepared from an aromatic dicarboxylic acid and 1-hydroxybenzotriazole in the presence of the activating agent 1,1′-[carbonyldioxy]dibenzotriazole[10] (Scheme 2).

PREPARATION OF PSPBO BY A ONE-POT METHOD *VIA* PHA

As described above, three steps are required to form PSPBO: (i) synthesis of aromatic dicarboxylic active diesters, (ii) polymerization to PHA, and (iii) preparation of the photosensitive polymer solution.

Direct use of a polymerization solution of PHA without isolation steps is very desirable as a facile route to PSPBO. Otherwise, additional procedures to remove by-products followed by re-dissolution of PHA in a solvent are required for resist formulation.

A PHA solution after the polymerization from the active diamide, *N*,*N*′-isophthaloylbis(benzoxazoline-2-thione) and bis(*o*-aminophenol) is capable of direct use for lithographic evaluations (Scheme 3), where



Scheme 4. One-pot Preparation of PSPBO *via* PHA using diphenyl isophthalate.

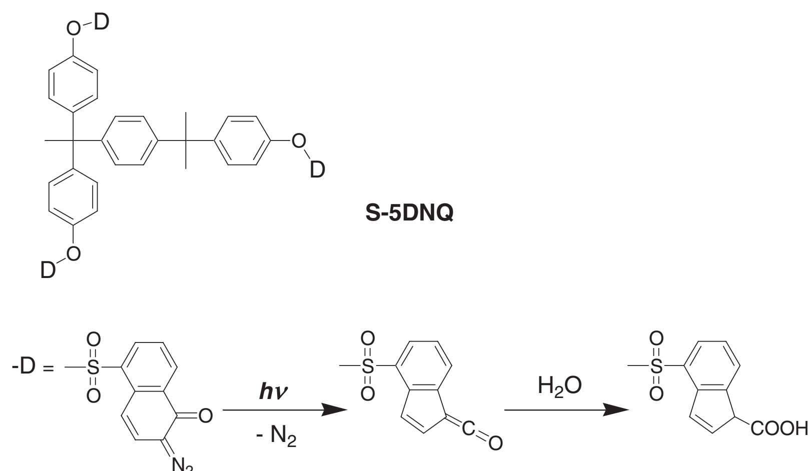


Figure 4. Structure of S-5DNQ.

the active diamide leaving group is eventually removed during the thermal treatment of the positive image in the conversion to PBO.[11]

Another procedure for the simple formulation of PSPBO has been also reported.[12] Polycondensation of bis(*o*-aminophenol) with diphenyl isophthalate to produce PHA (Scheme 4) was studied in detail, and a new synthetic method for PHA and a positive-type PSPBO with 1-{1,1-bis[4-(2-diazo-1-(2*H*)naphthalenone-5-sulfonyloxy)-phenyl]ethyl}-4-{1-[4-(2-diazo-1-(2*H*)naphthalenone-4-sulfonyloxy)phenyl]methylethyl}benzene (S-5DNQ) as a photosensitive compound was developed (Figure 4).

PHA with number average molecular weight (M_n) of around 8,000 g/mol (including *ca.* 15% PBO moiety) was easily prepared by polycondensation of commercially available 4,4′-(hexafluoroisopropylidene)-bis(*o*-aminophenol) (6FAP) and diphenyl isophthalate in NMP at 185 °C for 24 h. The resist system simply prepared by adding S-5DNQ (30 wt %) to the polymerization solution functioned as a positive-type photoresist. The leaving group, phenol, could be removed by post-baking. The photosensitivity and contrast of this resist were 110 mJ/cm^2 and 5.0 (film thickness, 1.3 µm) with *g*-line radiation, respectively (Figure 5).

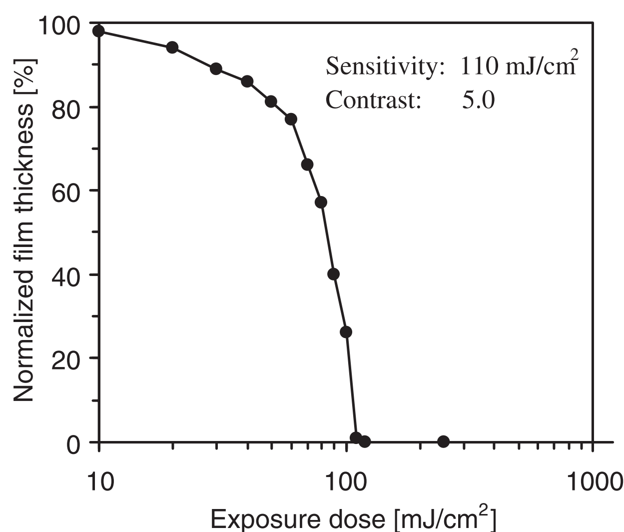
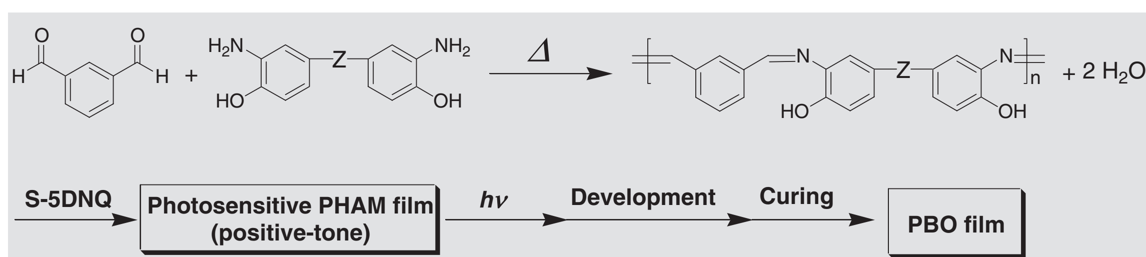


Figure 5. Photosensitivity curve (resist composition: PHA/S-5DNQ = 70/30 (wt), developer: 2.38 wt % TMAHaq, thickness: 1.3 µm).

Such direct resist formulation led to a rather simple method for the preparation of PSPBO compared to the conventional multi-step procedure.



Scheme 5. One-pot Preparation of PSPBO *via* PHAM using isophthalaldehyde.

PREPARATION OF PSPBO BY A ONE-POT METHOD *VIA* PHAM

Another interesting method of synthesizing PSPBO in a simpler manner was inspired by an amphiphilic Schiff-base (or azomethine) derived from bis(*o*-aminophenol) and terephthalaldehyde with the Langmuir-Blodgett method, which provided ultra-thin films of PBO by air oxidation.[13] This methodology was successfully applied to PSPBO (Scheme 5).[14]

A high molecular weight poly(*o*-hydroxyazomethine) (PHAM) was obtained by polycondensation of 6FAP with isophthalaldehyde (IPA) in NMP/toluene under azeotropic conditions. The resist system was simply prepared by direct addition of S-5DNQ (30 wt %) to the polymerization solution, functioning as a positive-type photosensitive resist. The photosensitivity and contrast of this resist were 120 mJ/cm^2 and 2.2 (film thickness, 2.8 µm) with *g*-line radiation, respectively. This positive pattern was finally converted into the corresponding PBO film by thermal treatment at 300 °C in air. The thermal properties of the PBO obtained from PHAM were identical to that from PHA as long as the PBOs had the same structure.

In addition to the facile synthesis of PHAM, the side product in this reaction was only water, lending this PSPBO an environmental advantage over that obtained from PHA, where hydroxybenzotriazole, 2-mercaptobenzoxazole, or phenol are produced as the side product. Environmentally benign processes have a profound impact on industrial manufacturing.

Thus, it was fruitful to investigate the development of PSPBO based on the PHAM/DNQ system in more environmentally friendly solvents such as propylene glycol monomethylacetate (PGMEA), γ-butyrolactone, cyclohexanone, ethyl lactate (EL), etc., in place of the amidic solvents previously used (*e.g.*, *N*-methylpyrrolidone (NMP), *N*,*N*-dimethylacetoamide (DMAc)).[15] EL in particular is known to be a non-toxic, biodegradable organic fluid made from renewable carbohydrates such as cornstarch.

PHAM was synthesized by azeotropic polycondensation of IPA with 6FAP in EL and toluene, and had M_n around 11,000 g/mol. The PHAM solution in EL was stable against hydrolysis when stored at 5 °C, and was thus employed as a photoresist with addition of S-5DNQ (25 wt %) in a manner similar to the procedure described above. The resulting positive pattern image of PHAM film featured 10 µm line-and-space patterns, and was converted into PBO film without deformation by thermal treatment at 350 °C for 1 h in air. The optically estimated dielectric constant of the PBO was 2.76 at 1 MHz.

DEVELOPMENT OF EXTREMELY SENSITIVE PSPBO RESIST

The sensitivity of a photoresist film is one of the most important parameters for designing suitable photoresist materials. Highly sensitive resists are more desirable in order to maximize the throughput of wafers in exposure equipment.

To improve the sensitivity of PSPBO, a chemical amplification system was applied using partially *tert*-butoxycarbonyl (*t*Boc) protected PHA (PtBA) and diphenyliodonium-9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a PAG (Figure 6).[16] Such *t*Boc-protected materials based on poly(hydroxystyrene) derivatives,[17–19] calixarene derivatives,[20,21] or polyimides[22] are commonly employed as positive-type photosensitive polymers owing to their reliability of chemical amplification under the control of PAGs and post-exposure bake (PEB) temperatures.

PHA capped with norbornene amide (PHA-NA) was prepared by polycondensation of 6FAP and diphenyl isophthalate as described above in different feed ratios, followed by treatment with 5-norbornene-2-carboxylic anhydride as an end-capping agent. Subsequently, the PHA-NA obtained was converted to *t*Boc protected polymer PtBA-NA by reaction with di-*tert*-butyl dicarbonate. The photosensitivity and contrast of this resist film of 50% protected PtBA-NA containing 30 wt % DIAS were 60 mJ/cm^2 and 2.5 (film thickness, 1.0 µm) with *i*-line light, respectively, when the film was subjected to PEB at 120 °C for 5 min. This yielded a more than 6,000-fold difference in dissolution rate between the exposed and unexposed areas. A fine posi-

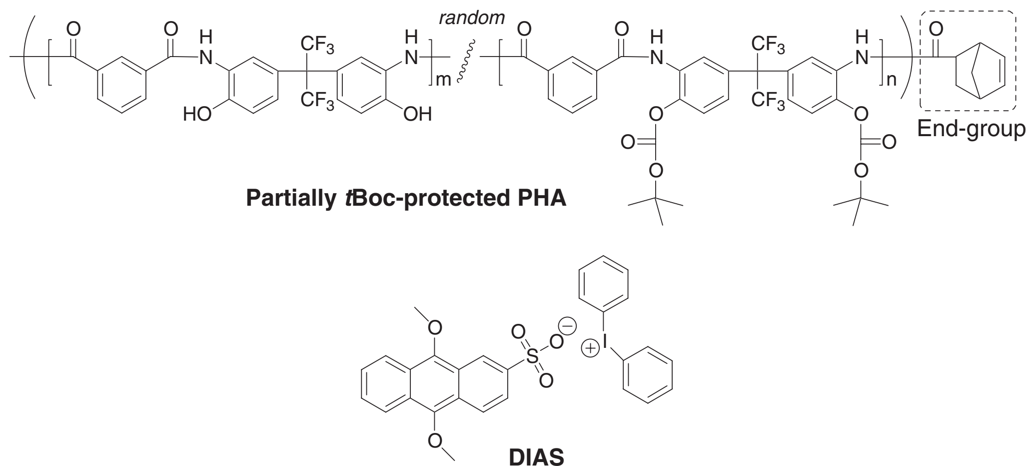


Figure 6. Positive-type chemically amplified PSPBO based on PtBA-NA and DIAS.

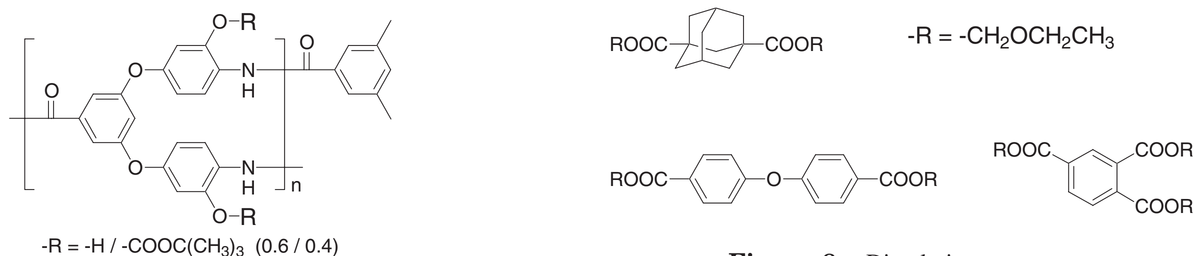
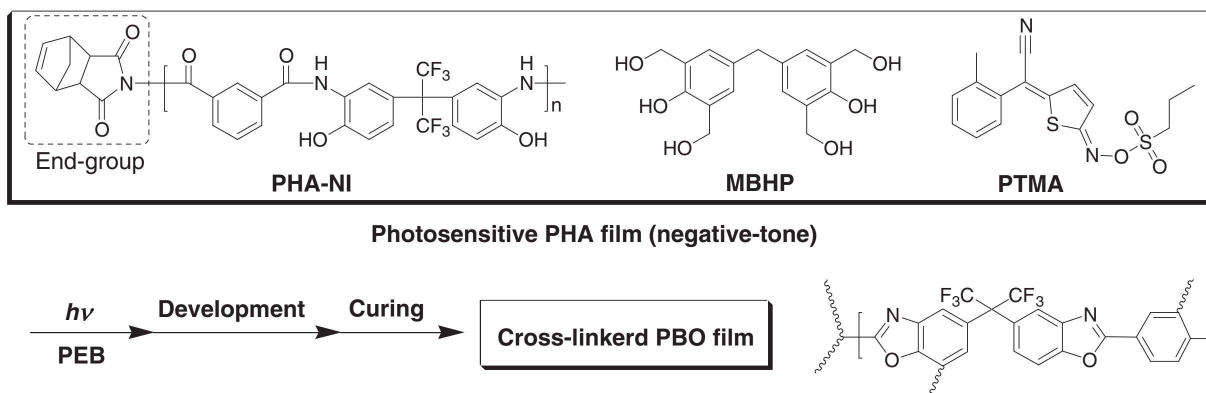


Figure 7. Hyper-branched PtBA.

Figure 8. Dissolution reversers.



Scheme 6. Highly sensitive negative-type chemically amplified PSPBO.

tive image featuring 6 µm line-and-space patterns was obtained. Moreover, by heat treatment at 350 °C for 1 h, this positive image produced cross-linked PBO while retaining its original shape, indicating high durability during thermal processing. Similar methodology using hyper-branched PtBA (40% protection with *t*Boc group) was also applicable to chemically amplified PSPBO (Figure 7).[23] A tetrahydropyranyl group in the place of the *t*Boc group has been utilized for the synthesis PSPBOs as well.[24]

A three-component positive-type PSPBO system consisting of PHA, PAG, and an acid-labile dissolution reverser has been developed (Figure 8), where the dissolution reverser acted as a dissolution inhibitor to 2.38 wt % TMAHaq before photo-irradiation, and a dissolution promoter after photo-irradiation.[25]

A negative-type chemically amplified PSPBO has also been reported,[26] which was based on PHA capped with norbornene imide (PHA-NI), 4,4′-methylenebis-[2,6-di(hydroxymethyl)]phenol (MBHP) as a cross-linker,[27–29] and (5-propylsulfonyloxyimino-5*H*-thiophen-2-ylidene)-(2-methylphenyl)acetonitrile (PTMA) as a PAG[30] (Scheme 6).

PHA-NI was easily prepared as described above except using 5-norbornene-endo-2,3-dicarboxylic anhydride as an end-capping agent. The photochemical

reaction of PTMA, followed by PEB treatment (110 °C for 3 min) induced an effective cross-linking reaction of MBHP with PHA-NI. This mechanism of acid-catalyzed cross-linking was attributed to the benzylic carbocation species, which further underwent electrophilic aromatic substitution to produce a network polymer. The resist consisting of PHA-NI (85 wt %), MBHP (10 wt %) and PTMA (5 wt %) functioned as a negative-type photosensitive polymer, providing very high photosensitivity and contrast of 20 mJ/cm^2 and 9.8 (film thickness, 1.1 μm) with *g*-line radiation, respectively, as shown in Figure 9. The negative image of the polymer film after development was converted to the corresponding PBO image by thermal treatment, and the resulting PBO had a low dielectric constant of 2.75 at 1 MHz by optical estimation. A similar procedure was exploited using hyper-branched PHA for chemically amplified PSPBO as well.[31]

DEVELOPMENT OF PSPBO WITH HIGH TRANSPARENCY AND LOW DIELECTRIC CONSTANT BY INTRODUCTION OF ALICYCLIC COMPONENT

Although a low dielectric constant and high photosensitivity are required to increase circuit speed and to maximize the throughput of wafers in exposure equipment, respectively, most reported materials fall into one of two categories: possessing acceptable thermal stability but only a modicum of photosensitivity[32,33] or vice versa.

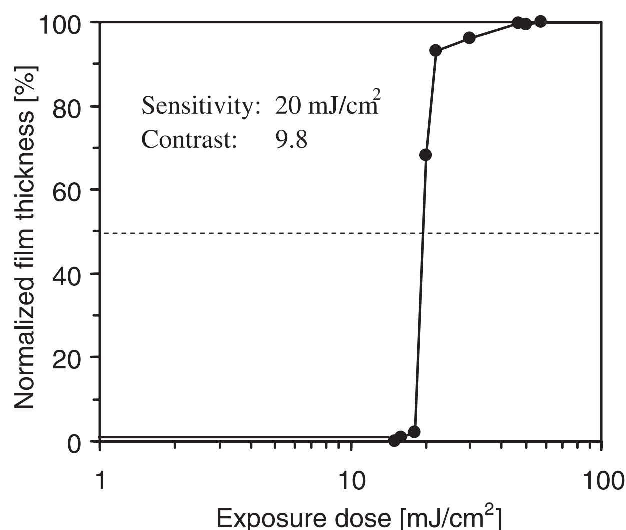


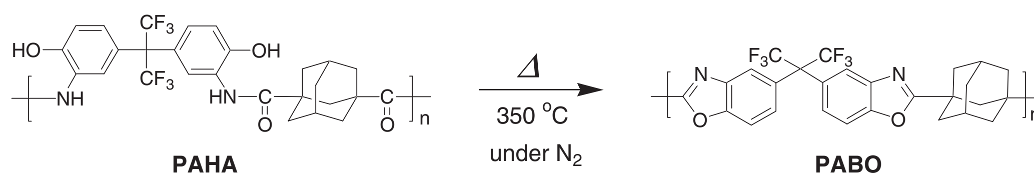
Figure 9. Photosensitivity curve (resist composition: PHA-NI/MBHP/PTMA = 85/10/5 (wt), developer: 2.38 wt % TMAHaq, thickness: 1.1 μm).

In terms of these aspects, alicyclic PBOs (PABOs) are interesting materials for applications in optoelectronics and interlayer dielectrics.[34] Adamantyl units are effective in decreasing both conjugation in the main chain and molecular density because of the sp^3 character of their carbons and bulkiness, respectively,[35,36] producing PABO with high transparency and a low dielectric constant, while maintaining high thermal stability.

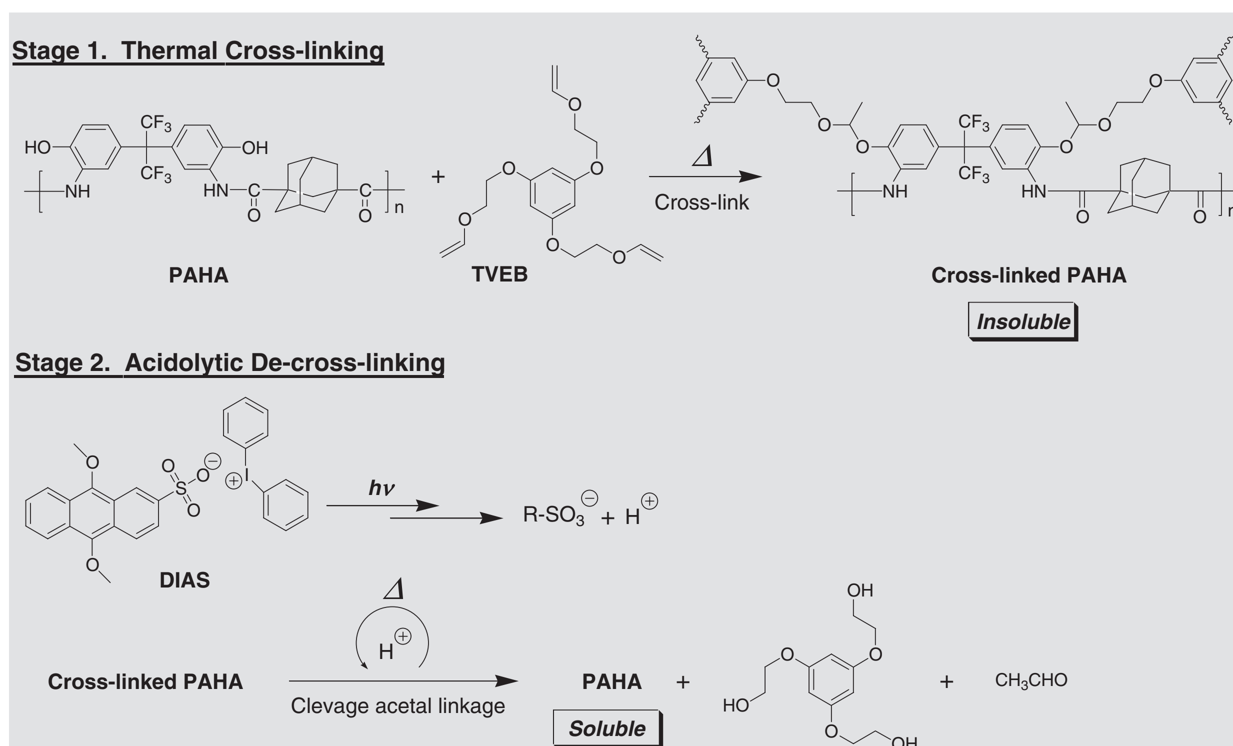
Alicyclic PHA (PAHA) containing adamantyl units in the main chain had excellent transparency above 320 nm. Thermal treatment of PAHA easily produced PABO (Scheme 7). The glass-transition temperature (T_g) and 5% weight-loss temperature (T_{d5}) of the PABO were 302 and 518 °C, respectively, under nitrogen. The optically estimated dielectric constant was 2.55 at 1 MHz, significantly lower than that of conventional aromatic PBOs.

PAHA containing 15 wt % 1,3,5-tris[(2-vinyloxy)-ethoxy]benzene (TVEB) and 5 wt % DIAS was formulated as a positive-type photosensitive polymer in conjunction with chemical amplification. TVEB and DIAS acted as acidolytic de-cross-linker and PAG, respectively (Scheme 8). At the pre-bake stage, the vinyl ether group of TVEB reacted with the phenol group of PAHA at certain temperatures to form a cross-linked network with a weak acetal linkage. Then, after photo-irradiation of PEB, the cross-linked junctions were cleaved with acid catalysis by the PAG. This material showed a photosensitivity of 40 mJ/cm^2 and contrast of 4.0 with *i*-line exposure (film thickness, 2.0 μm). The positive image of PAHA film formed by a contact-printing mode was successfully converted to the corresponding PABO image by thermal treatment at 350 °C.

Another type of chemically amplified negative-type PSPBO based on PAHA, oxybis(3,4-dihydroxymethyl)benzene (OBHB) as a novel cross-linker, and PTMA has been developed to improve sensitivity as well.[37]



Scheme 7. Semi-alicyclic PHA (PAHA) and PBO (PABO).



Scheme 8. Mechanism of positive-type chemically amplified PSPBO using acidolytic de-cross-linker, TVEB.

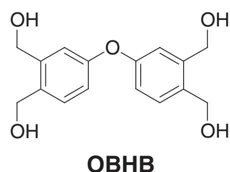


Figure 10. Phenol-free cross-linker, OBHB.

As for cross-linkers, MBHP has been used extensively for negative-tone chemically amplified photosensitive materials so far. However, the phenolic hydroxyl groups of MBHP remaining after thermal treatment may increase the dielectric constant of these films. Thus, a new cross-linker without phenol units is more desirable. The cross-linking reaction involving OBHB (Figure 10) proceeded through electrophilic substitution on the matrix polymer and itself.

The resist system was formulated by mixing PAHA (85 wt %), OBHB (10 wt %) and PTMA (5 wt %) in cyclohexanone, and acted as an alkaline-developable chemically amplified negative-type resist. It showed a photosensitivity of 14 mJ/cm^2 and contrast of 2.4 with *i*-line exposure (film thickness, 2.2 µm). The resulting PABO patterned film with clear 7 µm-feature resolution (Figure 11) also successfully showed a lower dielectric constant (optically estimated $\varepsilon = 2.62$ at 1 MHz) than that of films incorporating MBHP ($\varepsilon = 2.67$) due to the absence of phenolic hydroxyl groups in OBHB.

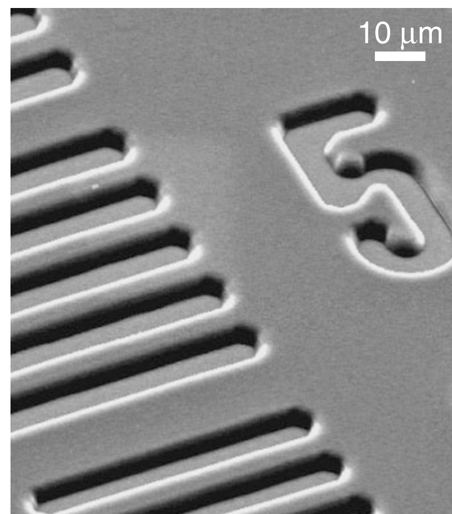
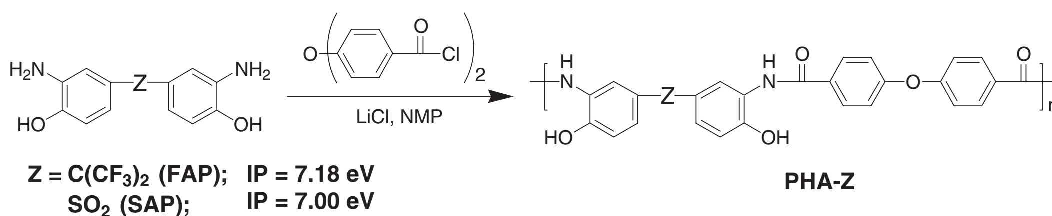


Figure 11. SEM image of negative-type semi-alicyclic PSPBO (resist composition: PAHA/OBHB/PTMA = 85/10/5 (wt), thickness: 4.1 µm).

FLUORINE-FREE AROMATIC PHA WITH *I*-LINE TRANSPARENCY FOR PSPBO

Until now, PSPBO based on PHA derived from 6FAP and 4,4′-oxybis(benzoic acid) derivatives with a photosensitive compound such as DNQ has been widely used because of its high transparency at 365 nm, whereas wholly aromatic PHAs are generally not transparent at 365 nm. To expand the areas of



Scheme 9. Synthesis of PHA-Z (Z = F, S).

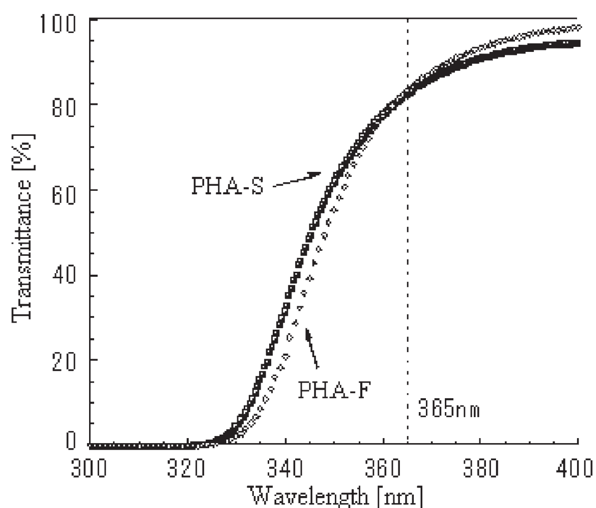


Figure 12. Transparency of PHA-Z (Z = F, S) in *i*-line region (measured in DMAc solution, 1.0×10^{-3} mol/L).

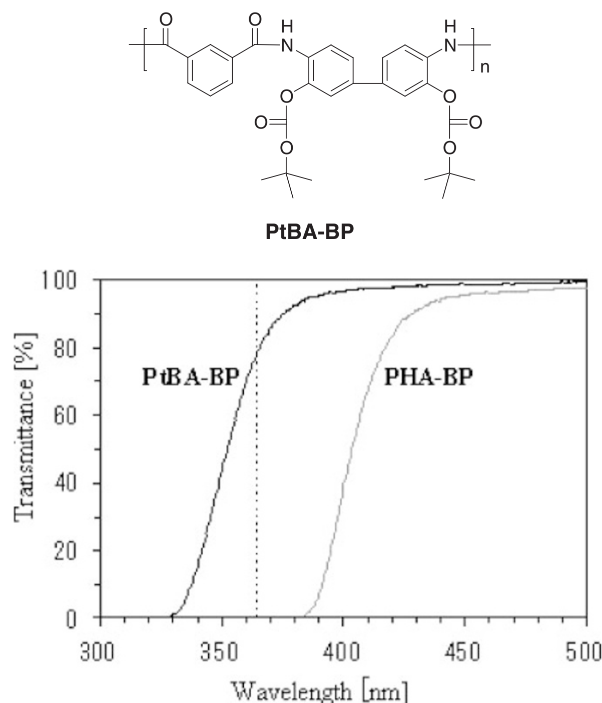


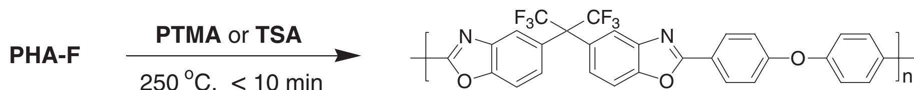
Figure 13. Transparency of PtBA-BP and PHA-BP (measured in DMAc, 1.0×10^{-3} mol/L).

application and to create a library of PSPBOs, a novel PHA transparent at 365 nm is essential.

Time-dependent density functional theory (TD-DFT) calculations using B3LYP hybrid functionals with the 6-311++G(d,p) basis set are a very useful tool for predicting the absorption spectra of hydroxyamide compounds derived from various aminophenol moieties.[38] The TD-DFT calculation is based on the transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). This transition is responsible for the absorption at the longest wavelength. Even though the HOMO and LUMO are spatially separated in the molecule, the absorptions appearing in the *i*-line region are closely related to the typical charge-transfer transition between the benzoic acid and the *o*-hydroxyamide rings. Hence, the introduction of electron withdrawing groups effectively lowers the HOMO levels, and thus increases the band gaps, causing hypsochromic (blue) shifts of the absorptions originating from the HOMO→LUMO transition. The degree of electron-donating character of each bis(hydroxylamine) is estimated from its ionization potentials (IPs) estimated by TD-DFT calculation.

PHA-S containing sulfonyl groups in the main chain was prepared from 4,4′-sulfonylbis(*o*-aminophenol) (SAP) (IP, 7.00 eV) with 4,4′-oxybis(benzoic acid) (*OBBC*) by simple polycondensation (Scheme 9) and showed high transparency at 365 nm compared to that of PHA-F derived from 6FAP (IP, 7.18 eV) (Figure 12), as predicted by TD-DFT calculations. Thus, PSPBO based on PHA-S (81 wt %), TVEB (14 wt %), and PTMA (5 wt %) provided a photosensitivity and contrast of 14 mJ/cm^2 and 2.7, respectively (film thickness, 1.5 µm), when the film was irradiated with *i*-line light followed by PEB at 120 °C for 5 min.

TD-DFT calculations also indicated that OH-protected PHA led to high transparency in the 365 nm region. Indeed, *t*Boc substitution of OH groups, suppressing the formation of intramolecular hydrogen bonds, was suitable not only for enhancing transparency and solubility, but also for the formulation of chemically amplified PSPBO.[39] Fluorine-free PHA-BP derived from 3,3′-dihydroxybenzidine and isophthaloyl chloride was prepared, and its OH moieties protected with *t*Boc groups. Figure 13 shows the



Scheme 10. Low-temperature cyclization of PHA-F with PTMA or TSA.

structure and transparency of 100% protected PtBA-BP (1.0 mM in DMAc), exhibiting 80 percent transmittance (%T) at 365 nm, attributed to the complete *t*Boc protection of OH groups in PHA. In contrast, the unsubstituted PHA allowed no transmittance in this region. The PtBA-BP will be applied for formulation of PSPBO as a matrix in conjunction with a PAG.

It is noteworthy that methyl- or dimethoxy-substitution at the *ortho*-position to amide groups in PHA yielded a material with higher transparency than that of unsubstituted PHA. This high transparency could be explained as arising from twisting of the polymer main chain induced by substituted groups, restricting formation of charge-transfer complexes and intramolecular hydrogen bonds.[40]

CATALYSTS FOR LOW-TEMPERATURE CYCLIZATION OF PHA

The photolithographic image of PHA is finally converted into its PBO counterpart by thermal treatment at around 350 °C. Such a high-temperature process is hardly applicable to conventional electronics containing thermally *un*stable components, for example, glass-epoxy resins and glass-bismaleimide-triazine resins in a built-up or package board. Moreover, heat-induced strain in silicon wafers is not negligible as the surface area of the wafer increases. Thus, processes at temperatures below 250 °C are preferred in the semiconductor industry.

Sulfonic acids have been found be effective catalysts for the low-temperature cyclization of PHAs (Scheme 10).[41,42] In particular, PTMA acted not only as an excellent PAG in the *i*-line or *g*-line regions but also as a thermo-acid generator to lower the cyclization temperature down to 250 °C rapidly when the film was loaded with 10 wt % PTMA. Therefore, compared to the uncatalyzed procedure at 350 °C, the significant decrease in cyclization temperature will lead to versatile developments of PSPBO systems with PTMA, producing more useful applications in a variety of areas.

The degree of cyclization was determined by the specific absorption at 1051 cm^{-1} assignable to the C–O stretch of benzoxazole in its infrared spectrum. The progress of cyclization at 250 °C in the presence of various catalysts including PTMA, *p*-toluenesulfonic acid (TSA), and 1-{1,1-bis[4-(2-diazo-1-(2*H*)-naphthalenone-4-sulfonyloxy)-phenyl]ethyl}-4-{1-[4-(2-diazo-1(2*H*)naphthalenone-4-sulfonyloxy)phenyl]-methylethyl}benzene (S-4DNQ) is shown in Figure 14. DNQs are commonly used as photo-dissolution inhibitors for photosensitive polymers. S-4DNQ as shown in Figure 15 produces a strong sulfonic acid by photo-irradiation or thermal treatment. Cyclization was complete in a few minutes in the presence of 10 wt % PTMA or TSA, while no cyclization occurred without additives at 250 °C. Even though S-4DNQ would be expected to work as a catalyst for the low-temperature cyclization of PHA, the degree of cyclization only reached around 60% after 2 h at 250 °C. This may be explained by thermal cross-linking of DNQ decomposition products, which suppressed the diffusion of sulfonic acid moieties.

By using PTMA as an effective thermo-acid generator to lower the cyclization temperature of PHA

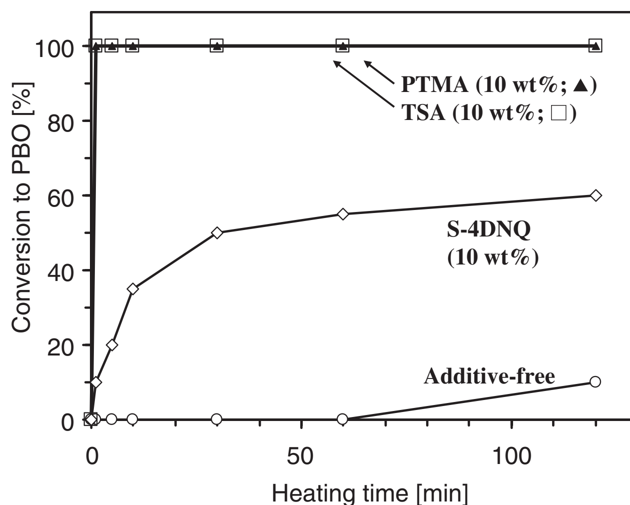


Figure 14. Degree of cyclization of PHA-F at 250 °C with various additives.

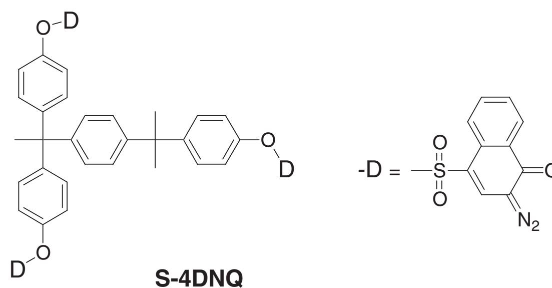


Figure 15. Chemical structure of sulfonic acid generative DNQ (S-4DNQ).

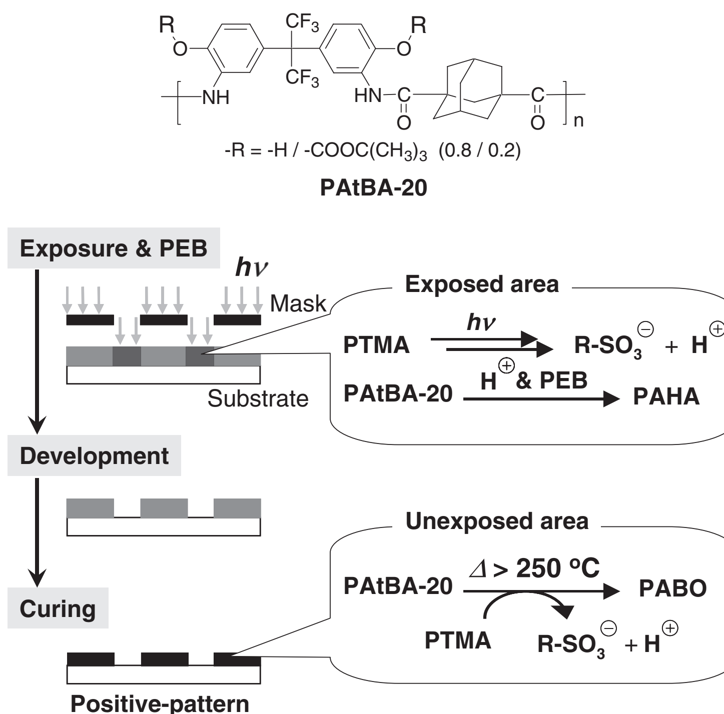


Figure 16. Dual role of PTMA in a positive-type chemically amplified PSPBO system.

down to 250 °C, a PSPBO system was formulated,[43] where the resist film based on PHA-F (75 wt %), S-4DNQ (15 wt %), and PTMA (10 wt %) showed a photosensitivity of 60 mJ/cm^2 with *i*-line exposure (film thickness, 2.4 µm). A positive-tone image featuring an 8 µm line-and-space pattern was obtained, following development with 2.38 wt % TMAHaq. The PHA-F image was successfully converted into a PBO image after 10 min at temperatures as low as 250 °C. In this system, however, use of S-4DNQ was required as a dissolution inhibitor for patterning.

Because of the good performance of PTMA as a catalyst for the cyclization of PHA and photo-patterning, PSPBO with PTMA can be considered another new system without DNQs. Partially (20%) *t*Boc-protected PAHA (PAtBA-20) was utilized for positive-type chemically amplified PSPBO with PTMA (Figure 16).[44] The photolithographic results showed a sensitivity of 35 mJ/cm^2 and a contrast of 12.8, when the PAtBA-20 film (film thickness, 1.8 µm) containing 10 wt % PTMA was exposed to *i*-line radiation. The film thus obtained was fully converted into its corresponding PABO pattern upon heating at 250 °C, allowing PTMA in the unexposed areas of the film to function as a thermo-acid generator.

OTHER APPLICATIONS BASED ON PSPBOS

As PSPBOs are utilized in microelectronics, the differences in coefficients of thermal expansion (CTE) between PBO films and inorganic or metallic materials result in serious thermal stresses. Thus, the stresses accumulated during multiple heat/cool steps might cause device failure through peeling and cracking of the films. To improve the CTEs of PSPBOs, a small amount of nano-dispersed organoclay was added into PSPBO films. The high surface-to-volume ratio of the nano-dispersed clay restricted the thermal expansion and contraction of the polymer molecules.[45] The organoclay was formed by a cation-exchange reaction between Na$^+$ montmorillonite clay and a dodecylamine salt. The addition of 5 wt % clay decreased the CTE of PBO film by 33%. Furthermore, water absorption by the PBO/organoclay nano-composite was decreased by 62% after the addition of this amount of clay.

As PAA has hydrophilic carboxylic acid groups, which are very soluble in TMAHaq, DNQ is not enough to inhibit the dissolution of PAA in alkaline solution. To remedy this problem, PHA was introduced in conjunction with PAA for better control of the dissolution rate in TMAHaq.[46] Thus, a novel positive-working photosensitive poly(imide-benzoxazole) precursor based on poly(amic acid-hydroxyamide) with DNQ was developed (Figure 17).

The photosensitive precursor containing 25 wt % DNQ showed a sensitivity of 256 mJ/cm^2 and contrast of 1.14 (film thickness, 3.0 µm) when the film was developed in 0.6 wt % TMAHaq.

PSPBOs were also applied to specific fluorescence patterning in optelectronics.[47,48] To produce poly(hydroxybenzoxazole) (PHBO), PAGs were exploited to deprotect the *t*Boc group in *t*Boc-blocked PHBO

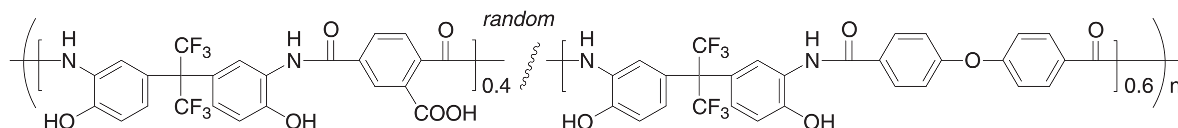
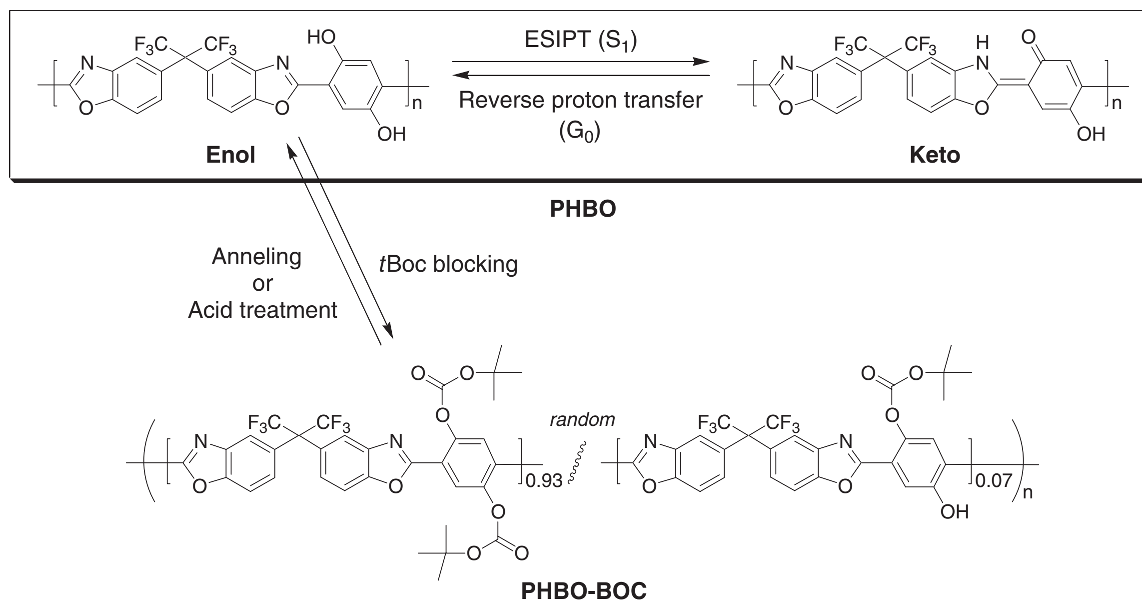


Figure 17. Poly(amic acid-hydroxyamide).



Scheme 11. Schematic diagram of Excited-state Intramolecular Proton Transfer (ESIPT) between PHBO and PHBO-BOC.

(PHBO-BOC). PHBO was considered to be potentially active toward excited-state intramolecular proton transfer (ESIPT) fluorescence because of its intramolecular hydrogen-bonded OH groups (Scheme 11). ESIPT is based on a fast enol to keto prototropy in the excited state between intramolecular hydrogen-bonding interactions.[49] Thus, dual color fluorescence photo-patterning was achieved in a chemical amplification resist with the PAG, where the PHBO area emitted orange fluorescence while the PHBO-BOC region showed green emission.

FUTURE PROSPECTS

In the remarkable examples described above, PSPBOs have been established for use in simple schemes, and developed as high quality photosensitive materials in terms of photosensitivity, transparency, dielectric properties and environmental impact.

As has been done for PIs, various monomers for PBOs (*e.g.*, dicarboxylic acid, and bis(*o*-aminophenol)) have been developed for diverse applications, and novel photolithographic mechanisms should be developed as well for more sophisticated PSPBO systems.

To open up further vistas in the development of photosensitive thermally stable materials, a more straightforward synthesis of PHA is required for expanding the scope of PSPBO. For example, if polyamide derived from dicarboxylic acid and diamine (including bis(*o*-aminophenol)) is synthesized with catalysis, not only genuine halogen-free synthesis of polyamide but also direct use of the polymerization solution of PHA for photolithographic patterning could result. Such efforts in this area would certainly lead to low-cost manufacturing and environmentally friendly production strategies.

REFERENCES

1. C. Arnold, *J. Polym. Sci. Part D: Macromol. Rev.*, **14**, 265 (1979).
2. a) R. H. Reuss and B. R. Chalamala, *MRS bull.*, **28**, 11 (2003).
   b) R. H. Reuss and B. R. Chalamala, *MRS bull.*, **28**, 35 (2003).
3. Y. H. So, A. Sen, P. Kim, and V. St Jeor, *J. Polym. Sci., Part A: Polym. Chem.*, **33**, 2893 (1995).
4. H. Zhang, R. J. Farris, and P. R. Westmoreland, *Macromolecules*, **36**, 3944 (2003).
5. M. Hasegawa, J. Kobayashi, and L. Vladimirov, *J. Photopolym. Sci. Technol.*, **17**, 253 (2004).
6. G. Maier, *Prog. Polym. Sci.*, **26**, 3 (2001).
7. R. Rubner, *Adv. Mater.*, **2**, 452 (1990).
8. H. Ahne, R. Rubner, and R. Sezi, *Appl. Surf. Sci.*, **106**, 311

(1996).
9. R. Rubner, *J. Photopolym. Sci. Technol.*, **17**, 685 (2004).
10. M. Ueda, H. Oikawa, and T. Teshirogi, *Synthesis*, 908 (1983).
11. K. Ebara, Y. Shibasaki, and M. Ueda, *J. Photopolym. Sci. Technol.*, **14**, 55 (2001).
12. K. Ebara, Y. Shibasaki, and M. Ueda, *Polymer*, **44**, 333 (2003).
13. N. Ogata, *Pure Appl. Chem.*, **63**, 951 (1991).
14. K. Ebara, Y. Shibasaki, and M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 3399 (2003).
15. K. Fukukawa, Y. Shibasaki, and M. Ueda, *Polym. J.*, **36**, 489 (2004).
16. K. Ebara, Y. Shibasaki, and M. Ueda, *J. Photopolym. Sci. Technol.*, **16**, 287 (2003).
17. H. Ito and C. G. Willson, *Polym. Eng. Sci.*, **23**, 1021 (1982).
18. S. A. MacDonald, C. G. Willson, and J. M. J. Fréchet, *Acc. Chem. Res.*, **27**, 151 (1994).
19. E. K. Lin, C. L. Soles, D. L. Goldfarb, B. C. Trinque, S. D. Burns, R. L. Jones, J. L. Lenhart, M. Angelopoulos, C. G. Willson, S. K. Satija, and W.-L. Wu, *Science*, **297**, 372 (2002).
20. K. Takeshi, R. Nakayama, and M. Ueda, *Chem. Lett.*, **27**, 865 (1998).
21. K. Young-Gil, J. B. Kim, T. Fujigaya, Y. Shibasaki, and M. Ueda, *J. Mater. Chem.*, **12**, 53 (2002).
22. T. Omote, K. Koseki, and T. Yamaoka, *Macromolecules*, **23**, 4788 (1990).
23. C. S. Hong, M. Jikei, R. Kikuchi, and M. Kakimoto, *Macromolecules*, **36**, 3174 (2003).
24. S. L.-C. Hsu, W.-C. Chen, and P.-I. Lee, *Polym. Bull.*, **50**, 295 (2003).
25. T. Minegishi, H. Takusari, and K. Katoh, *J. Photopolym. Sci. Technol.*, **17**, 247 (2004).
26. K. Fukukawa, K. Ebara, Y. Shibasaki, and M. Ueda, in "*Advances in Imaging Materials and Processes*" H. Ito, P. R. Varanashi, M. M. Khojasteh, and R. Chen, Ed., SPE, Mid-Hudson Section, PA 2003, p 339.
27. K. Takeshi, K. Okuyama, Y. Ohba, and M. Ueda, *J. Photopolym. Sci. Technol.*, **13**, 345 (2000).
28. K. Tsuchiya, Y. Shibasaki, M. Suzuki, and M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 2235 (2004).
29. Y. Watanabe, K. Fukukawa, Y. Shibasaki, and M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 593 (2005).
30. T. Asakura, H. Yamato, and M. Ohwa, *J. Photopolym. Sci. Technol.*, **13**, 223 (2001).
31. C. S. Hong, M. Jikei, and M. Kakimoto, *Polym. J.*, **35**, 586 (2003).
32. T. M. Long and T. M. Swager, *J. Am. Chem. Soc.*, **125**, 14113 (2003).
33. W. C. Wang, R. H. Vora, E. T. Kang, K. G. Neoh, C. K. Ong, and L. F. Chen, *Adv. Mater.*, **16**, 54 (2004).
34. K. Fukukawa, Y. Shibasaki, and M. Ueda, *Macromolecules*, **37**, 8256 (2004).
35. Y. T. Chern and H. C. Shieu, *Macromol. Chem. Phys.*, **199**, 963 (1998).
36. Y. Watanabe, Y. Shibasaki, S. Ando, and M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 144 (2004).
37. K. Fukukawa, Y. Shibasaki, and M. Ueda, *Polym. J.*, **37**, 74 (2005).
38. F. Toyokawa, K. Fukukawa, Y. Shibasaki, S. Ando, and M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 2527 (2005).
39. T. Ogura, K. Fukukawa, Y. Shibasaki, and M. Ueda, *J. Photopolym. Sci. Technol.*, **18**, 319 (2005).
40. F. Toyokawa, Y. Shibasaki, S. Ando, and M. Ueda, *Polym. Prepr., Jpn.*, **54**, 1616 (2005).
41. T.-K. Kim, K.-Y. Choi, K.-S. Lee, D.-W. Park, and M.-Y. Jin, *Polym. Bull.*, **44**, 55 (2000).
42. F. Toyokawa, K. Fukukawa, Y. Shibasaki, and M. Ueda, *Chem. Lett.*, **33**, 1342 (2004).
43. F. Toyokawa, Y. Shibasaki, and M. Ueda, *Polym. J.*, **37**, 517 (2005).
44. K. Fukukawa and M. Ueda, *Macromolecules*, in press.
45. S. L.-C. Hsu, C.-Y. Lin, and K.-C. Chang, *J. Appl. Polym. Sci.*, **97**, 2350 (2005).
46. S. L.-C. Hsu, H.-T. Chen, and S.-J. Tsai, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 5990 (2004).
47. S. Park, S. Kim, J. Seo, and S. Y. Park, *Macromolecules*, **38**, 4557 (2005).
48. J. K. Lee and T. S. Lee, *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 1397 (2005).
49. A. Weller, *Prog. React. Kinet.*, **1**, 188 (1961).

Ken-ichi Fukukawa was born in Tokyo, Japan in 1977. He received a Ph. D. degree of Engineering in Organic and Polymeric Materials from Tokyo Institute of Technology in March 2005. His Ph. D. dissertation was Developments of Photosensitive Thermally Stable Polymers involving polyimides and polybenzoxazoles under the supervision of Prof. Mitsuru Ueda. Meanwhile, he worked at Bell Laboratories, Lucent Technologies in New Jersey, USA as a scholarship research assistant from April 2002 for one year with Shu Yang Ph. D. He is currently undertaking a postdoctoral fellowship with Prof. Craig J. Hawker at Materials Research Laboratory in University of California Santa Barbara from May 2005. His current research is focusing on making functional nano-objects based on biocompatible polymers.

Mitsuru Ueda received his B.S., and M.S. degrees in polymer chemistry from Chiba University in 1970 and 1972, respectively, and Ph. D. degree from Tokyo Institute of Technology. He joined Yamagata University in 1972 and promoted a professor in 1989. He moved to Tokyo Institute of Technology in 1999. He published more than 420 papers. His current research interests are the development of new synthetic methods for condensation polymers, low k materials, fuel cell membranes, photosensitive materials for microelectronics, and new advanced resist materials. He is the recipient of the Arthur K. Doolittle Award (1990, ACS), the Award of the society of Polymer Science, Japan (1995), and The Photopolymer Science and Technology Award (2003).