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Development of Photosensitive Polyimide and Polybenzoxazole

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感光性ポリイミド・感光性ポリベンズオキサゾールの開発

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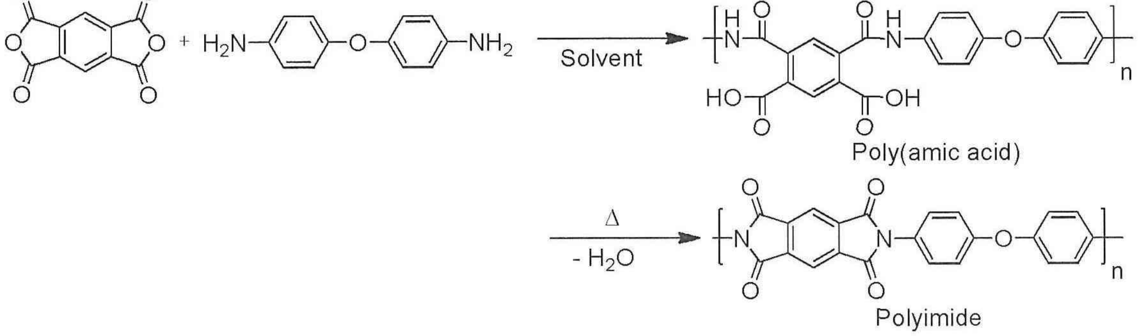
Contents

Chapter 1

General Introduction

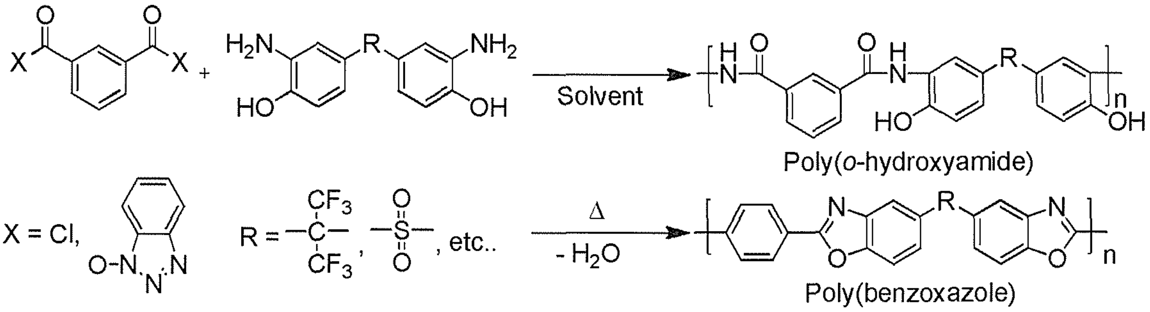
1-1. Introduction

In 1960, a typical polyimide (PI) “Kapton” was developed by DuPont. Kapton was prepared by thermal cyclodehydration reaction of a precursor polymer, poly(amic acid) which was obtained from pyromellitic dianhydride and 4,4'-oxydianiline (Scheme 1-1).[1] Soon after, various PIs were synthesized by changing dianhydrides and diamines.[2] PIs generally show high thermal stability, mechanical property and chemical resistance due to the rigid main chain structures. Therefore, PIs are widely used as heat resisting materials, electronic materials, protective films, and molding materials in electronics, aerospace and nuclear industry fields.



Scheme 1-1. Synthesis of poly(amic acid) and polyimide.

In the late 1970s, polybenzoxazoles (PSPBOs) were developed by a research program sponsored by the U.S. Air Force, which was directed toward the development of new structural materials having low density, high strength, high modulus, and long-term retention of these properties at elevated temperatures.[3] First, PBOs were expected to apply to a high mechanical strength fiber and Toyobo Co., Ltd. and the Dow Chemical Company developed a basic manufacturing technology in 1993. PBOs also have rigid main chain structures like PIs, and are expected for the same applications as PIs. PBO used as a fiber can be prepared by polycondensation of 4,6-diaminoresorcinol and terephthalic acid in poly(phosphoric acid) with a liquid crystal spinning method.[4] In contrast, general PBOs used as a film are formed from the precursor polymers, poly(*o*-hydroxyamide)s (PHAs) which are synthesized from bis(*o*-aminophenol) and dicalboxylic acid derivative, following by cyclodehydration reaction (Scheme 1-2).



Scheme 1-2. Synthesis of poly(*o*-hydroxyamide) and polybenzoxazole.

1-2. Applications of PIs and PBOs in Electronics Fields

PIs were initially used as heat resisting materials in aerospace fields, and in the 1970s, and then PIs were applied to a flexible printed circuit board and an insulating material with the developments in electronics fields. High mechanical and electrical properties of PIs are suitable not only for insulating materials but also for electronic materials, so that PIs are used as surface protection films (α-ray shield, passivation layer, buffer coat, junction coat, etc.) in integrated circuits (ICs). Figure 1-1(a) shows the cross-section view of a plastic leaded chip carrier (PLCC). PLCC is basically composed of a Si die, bonding wires connecting between the Si die and leadframes, resin mold, and leadframes which directly make contacts to the circuit board. The buffer coat materials utilizing PIs and PBOs are placed on the Si die to protect bare chips from stresses induced by filler or thermal mismatches, and require fabricating micro-size via holes to put bonding wires through to the Si die. Moreover, PIs and PBOs are used as an interposer in chip size package (CSP), which is almost the same size as the Si die (Figure 1-1(b)). The interposer, which sets on between Solder bumps and Si die of CSP, works as the insulating layer and the rewriting layer. During rewriting Cu lines, PI and PBO films as the interposer also require forming micro-size patterns.

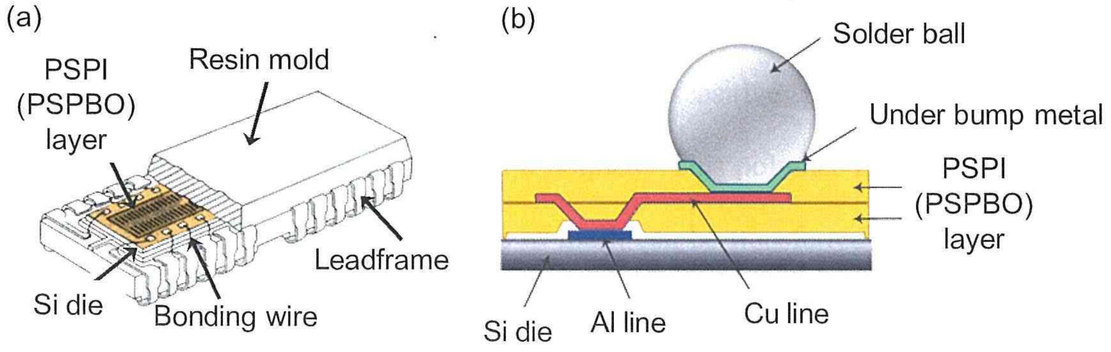


Figure 1-1. (a) cross-section view of PLLC and (b) cross-section view of CSP.

1-3. Photolithografic Process of Photosensitive Polyimides (PSPIs) and Photosensitive Polybenzoxazoles (PSPBOs)

Although there are several methods to fabricate reliefs on a film surface, photolithography technique can adequately provide micro-size via holes on PI or PBO films. There are two main types of the fabrication method of via hole using photolithography technique. One is to make a PI or PBO pattern by etching through a pattern of photoresist, which is known as a conventional method, and the other is to use photosensitive PIs (PSPIs) or PBOs (PSPBOs).[5] It should be noted that "PSPI" or "PSPBO" involves not only a photopatternable PI or PBO with photoactive agents, but also a photopatternable precursor polymer such as PAA, poly(amic ester), or PHA with photosensitive compounds.

The each step of photolithographic processes is shown in Figure 1-2. In a conventional method (Figure 1-2(a) and (b)), A pattern of PIs or PBOs are formed through photolithographic patterns of an additional photoresist coated on a PI or PBO layer by the plasma etching or the development using a hydrazine solution. Subsequently, a process of removing photoresist is required. On the other hand, PSPIs and PSPBOs enable to simplify a patterning process because a photoresist layer is unnecessary (Figure 1-2(c) and 1-2(d)). The patterning processes of PSPIs and PSPBOs are expounded as follows. First, a film of a photosensitive polymer is formed by spincoating on a substrate, and dried on a hotplate. This polymer film is exposed to a UV light through a mask, so that images of mask can be transferred to the film. As the source of UV light, wavelength at 436 nm (*g*-line), 405 nm (*h*-line) or 365 nm (*i*-line) from an ultrahigh pressure mercury lamp is usually utilized for the lithography with PSPIs and PSPBOs. The irradiation causes photochemical reactions to photosensitive compounds, and then the polarity of the polymer films at the exposed areas is changed by the following reactions, such as deprotection, polarity change of a dissolution inhibitor, chainscission, cross-linking, and cyclization upon a post-exposure baking (PEB) (if necessary). By the development with an organic solvent or an alkaline aqueous solution, the dissolution contrast between the exposed and unexposed areas is obtained. When the film at the exposed areas is dissolved in the developer, that resist system is categorized in a positive-type (Figure 1-2(c)). On the other hand, a negative-type refers when the film at the exposed areas becomes insoluble in the developer (Figure 1-2(d)). There are many factors to obtain a large dissolution contrast between the exposed and unexposed areas. For examples, photochemical reactions at the UV irradiation depend on the transparency of matrix polymers and the quantum yield of photosensitive compounds. The deprotection, cross-linking, chainscission, and so on are affected by a PEB process. Exposure doses at each wavelength and casting solvents are also important factors. The fine and clear pattern of photosensitive polymers can be obtained by optimizing these conditions.

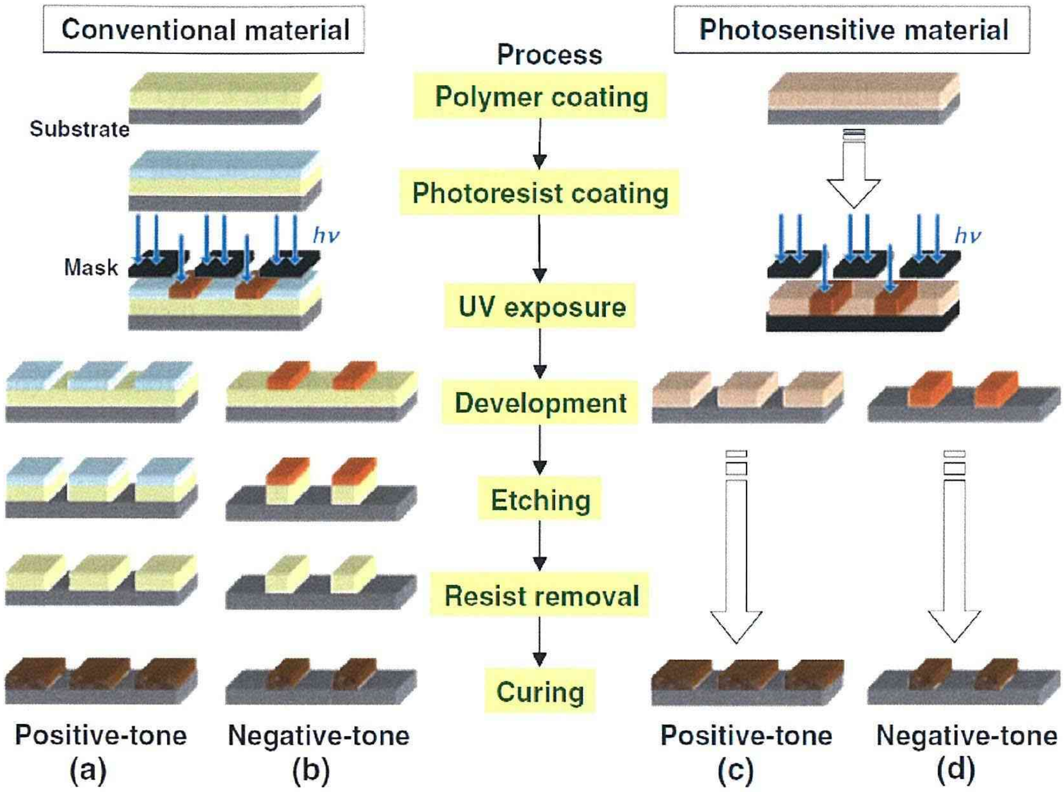
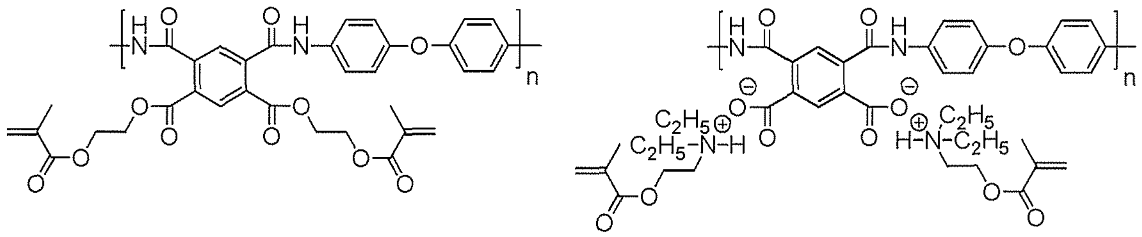


Figure 1-2. Photolithographic patterning processes of conventional materials using photoresists (a: Positive-tone & b: Negative-tone) and photosensitive materials (c: Positive-tone & d: Negative-tone).

1-4. Major Examples of PSPIs

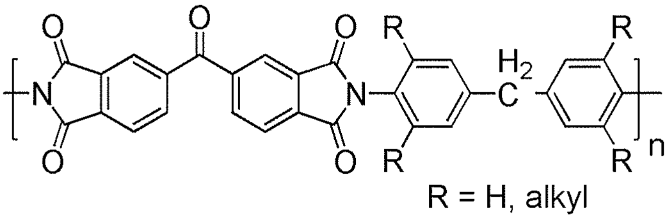
1-4-1. Cross-linking Type by Methacryloyl Pendant Groups (Negative Image). Typical and commercial PSPIs are based on PAA derivatives, where methacryloyl pendant groups as cross-linking sites is introduced to PAA through ester or acid-amine ionic linkage as shown in Scheme 1-3.[6] The cross-linking reaction is occurred at the exposed areas by UV irradiation, so that the cross-linked matrix polymer becomes insoluble in an organic solvent developer which is the mixture of polar solvents such as *N*-methyl-2-pyrrolidinone and alcohol. After dissolving PAA at the unexposed areas by development, the negative image is obtained. The cross-linked methacryloyl groups in PAA are thermally decomposed during the curing process.

Yoda et al. reported the difference of the processes in photo cross-linking reactions between ester type PSPI and ionic bond type PSPI.[7] The cross-linking reactions of methacryloyl unit in ester type PSPI started from the radical generated from photoradical generator by UV irradiation. On the other hand, the charge-transfer complex between PAA of ionic bond type PSPI and a sensitizer, such as *N* -phenyldiethanolamine, is formed, during UV irradiation. The radical formed from the charge-transfer complex becomes the triplet state, and change to the anion radical pair formed in pyromellitic diamide part of the PAA. This charge separation by UV irradiation is considered to be imaging formation mechanism. In addition, this system shows higher sensitivity than that of the ester type PSPI, because the polymer structure itself works as a sensitizer.



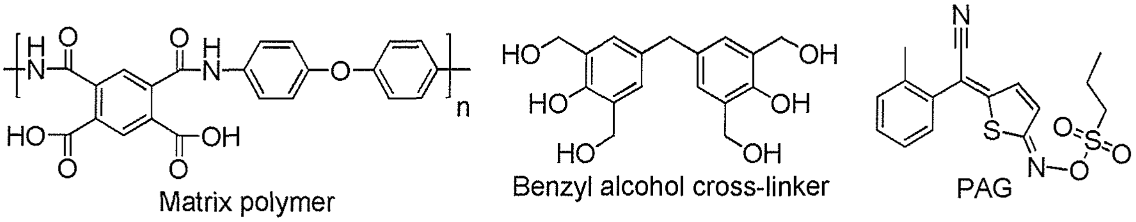
Scheme 1-3. Structures of cross-linking type PSPIs with methacryloyl pendant groups.

1-4-2. Cross-linking Type by Benzophenone Unit in PI (Negative Image). A PI polymerized from benzophenone tetracarboxylic anhydride (BTDA) and *o*-alkyl substituted diamine utilized photocross-linking reactions without sensitizers (Scheme 1-4).[8] The exposed areas become insoluble by radical coupling through hydrogen abstraction of BTDA. After the development by the polar solvents, this PSPI gives the negative images.



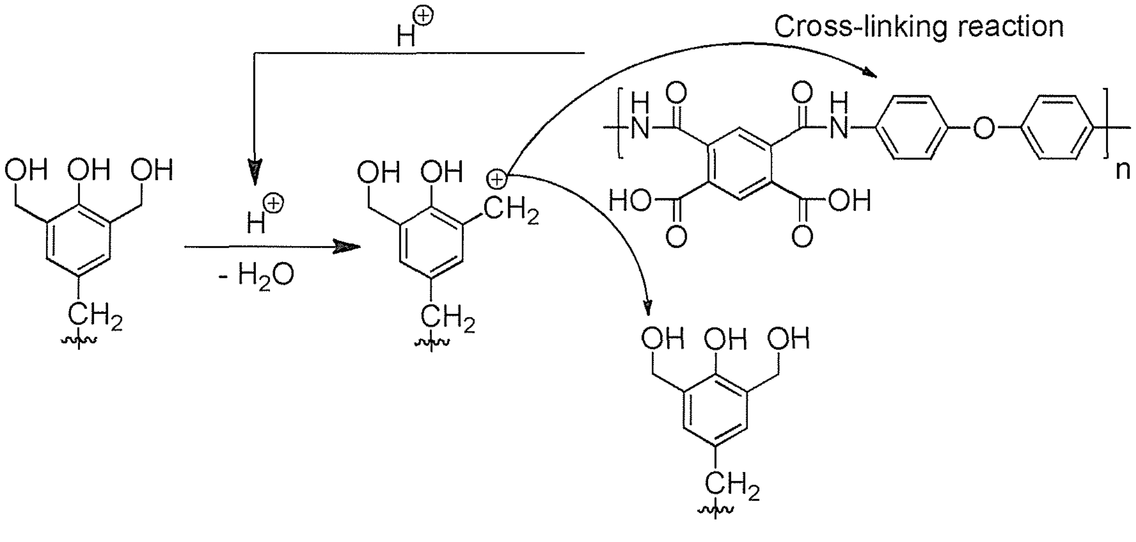
Scheme 1-4. Structure of cross-linking type PSPI with benzophenone units.

1-4-3. Chemically Amplified Cross-linking Type by Benzyl Alcohol Cross-linker (Negative Image). Recently, the patterning processes of PSPIs are required to reduce the environmental burdens with growing focus on environmental problems. Therefore, it is hoped that an organic solvent as the developer is switched to an alkaline aqueous solution, such as commercially available tetramethylammonium hydroxide aqueous solution (TMAHaq). Scince PAAs can easily dissolve in TMAHaq because of carboxylic units in PAAs, PAAs can be used as a matrix polymer of PSPIs which is developable in TMAHaq. Watanabe et al. reported a TMAHaq developable PSPI based on a PAA, a benzyl alcohol type cross-linker and a photoacid generator (PAG) (Scheme 1-5).[9]



Scheme 1-5. Stuructures of PAA as a matrix polymer, benzyl alcohol cross-linker, and PAG for a chemically amplified cross-linking type PSPI.

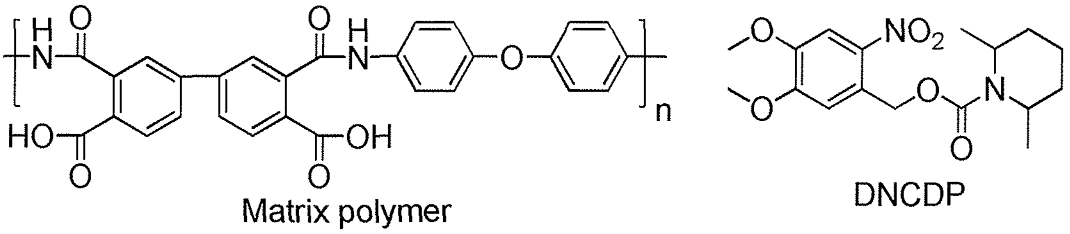
At the exposed areas, the proton generated from PAG reacts catalytically with the benzyl alcohol type cross-linker to generate a benzyl cation. The cross-linking reaction occurs via the benzyl cation during a PEB process (Scheme 1-6). This resist system is called "a chemically amplified system" because the generated proton behaves as the catalyst. After the development, this PSPI gives negative images and shows high sensitivity because of adopting the chemically amplified system.



Scheme 1-6. Cross-linking reaction of benzyl alcohol type cross-linker with acid catalyst.

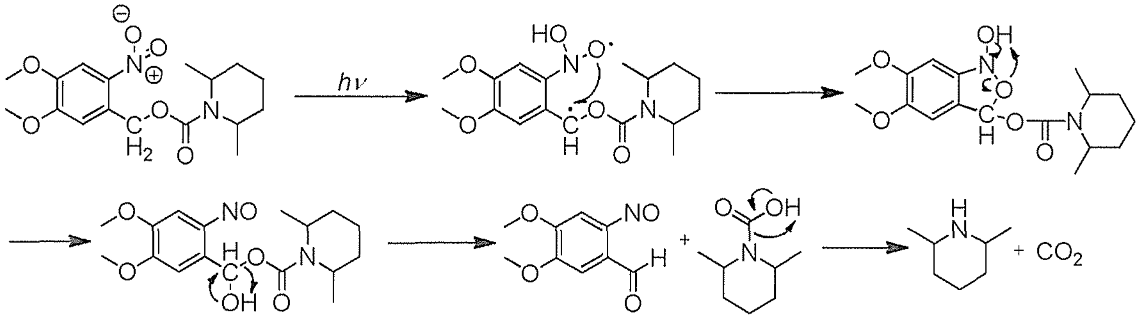
1-4-4. Chemically Amplified Low-temperature Imidization Type by Photobase Generator (PBG) (Negative Image).

Fukukawa et al. reported a PSPI consisting of a PAA and {[(4,5-dimethoxy-2-nitrobenzyl)oxy]carbonyl} 2,6-dimethylpiperidine (DNCDP) as a PBG (Scheme 1-7).[10]



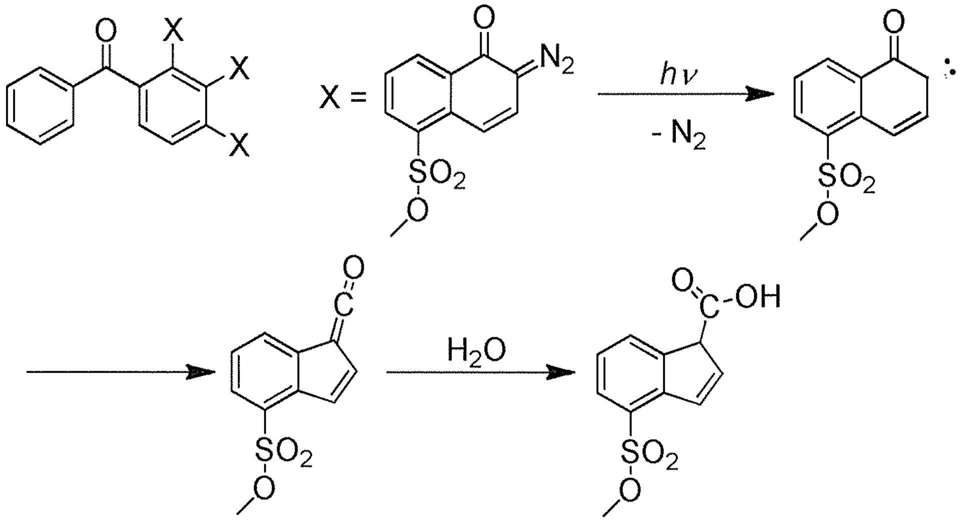
Scheme 1-7. Structure of PAA as a matrix polymer and DNCDP for a chemically amplified low-temperature imidization type PSPI.

This PSPI can also be developed in TMAHaq and adopts the chemically amplified system. Scheme 1-8 shows a photochemical cleavage mechanism of DNCDP at the exposed areas. 2,6-Dimethylpiperidine generated from DNCDP catalyzes the imidization of PAA, and the partially imidized PAA at the exposed areas no longer dissolved in TMAHaq. This PSPI achieved a simple formation of PSPI and low-temperature imidization at 200 °C. In addition, using PBG is effective to overcome the copper corrosion problem after the patterning process.



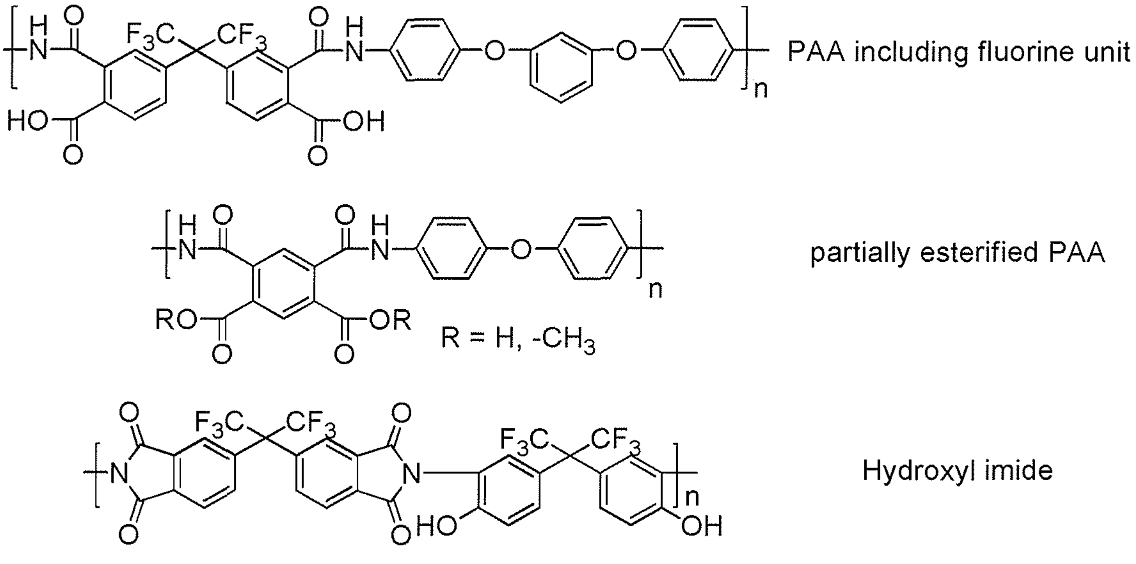
Scheme 1-8. Photochemical cleavage mechanism of DNCDP.

1-4-5. Dissolution Inhibitor Type by Diazonaphthoquinone (DNQ) Derivatives (Positive Image). Positive working photoresists based on novolac resins with DNQ derivatives have been widely used for LSI manufacturing since 1990s. Although DNQ itself is highly hydrophobic compound, DNQ can be transformed into indenecarboxylic acid under UV irradiation (Scheme 1-9). As a result, resist films at the exposed areas can be developed in TMAHaq.



Scheme 1-9. Photochemical transformation of DNQ derivative.

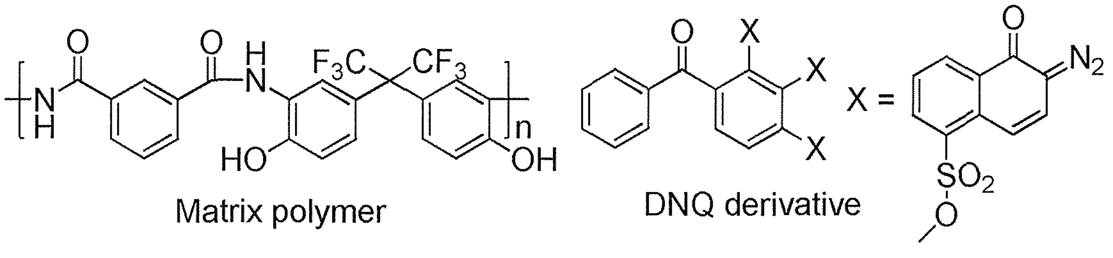
Positive-type PSPIs consisting of PAAs and DNQ derivatives were expected, but it is difficult to form PSPIs because of high solubility of PAA in TMAHaq. Consequently, PSPIs consisted of DNQ derivatives and matrix polymers, which were designed to decrease the dissolution rate to TMAHaq such as a PAA including fluorine units,[11] a partially esterified PAA,[12] and a hydroxyl imide[13] with DNQ derivatives (Scheme 1-10). These PSPIs showed good positive images, although it is complex to prepare such matrix polymers.



Scheme 1-10. Structures of matrix polymers to decrease the dissolution rate in TMAHaq.

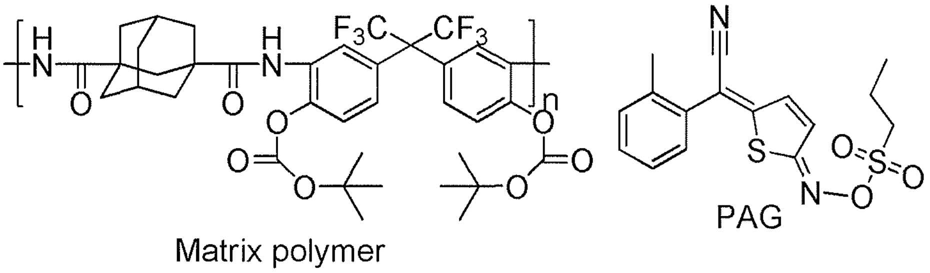
1-5. Major Examples of PSPBOs

1-5-1. Dissolution Inhibitor Type by DNQ Derivatives (Positive Image). Positive-type and TMAHaq developable PSPBOs are easily constructed from PHAs and DNQ derivatives as dissolution inhibitors, because PHAs have phenolic units in polymer structures as same as novolac (Scheme 1-11).[14] The PSPBOs using DNQ derivatives are commercially utilized as the interposer materials due to an adequate dissolution rate in TMAHaq.



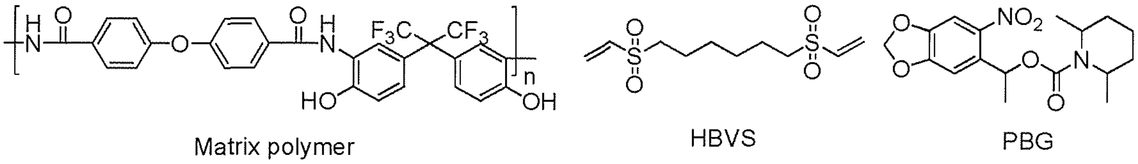
Scheme 1-11. Structures of PHA as a matrix polymer and DNQ derivative for positive-type PSPBO.

1-5-2. Chemically Amplified Deprotection Type by PAG (Positive Image). PSPBOs using DNQ derivatives normally show low sensitivity (200–400 mJ/cm^2) and it is difficult to form a thick pattern, because DNQ derivatives itself strongly absorb the UV light. To improve photosensitivity, chemical amplified systems were introduced in PSPBOs.[15] Fukukawa et al. reported a positive-type PSPBO which was consisted of partially protected PHA and PAG (Scheme 1-12).[16] In this report, *tert*-butoxycarbonyl (*t*-Boc) units were selected as the protection group, which can be easily decomposed by acids generated from PAG. At the exposed areas, *t*-Boc units of partially protected PHA are de protected by acids generated from PAG during the PEB process. The exposed areas selectively dissolved in TMAHaq at the development process to obtain positive images.



Scheme 1-12. Structures of *t*-Boc protected PHA as a matrix polymer and PAG for a chemical amplified deprotection type PSPBO.

1-5-3. Chemical Amplified Cross-linking Type by Michael-reaction Type Cross-linker with PBG (Negative Image). Chemical amplified PSPBOs generally employed PAG, because there are many decomposed reactions of protecting units and cross-linking reactions by acid catalyst. However, the acids generated from PAG in PSPBOs corrode the copper wirings in the circuits. To overcome this issue, PSPBOs without using PAGs attract much attention. Mizoguchi et al. developed a chemically amplified PSPBO consisting of a PHA, 1,6-bis(vinyl sulfone)hexane (HBVS) as a cross-linker and PBG (Scheme 1-13).[17] Michael additional reaction between HBVS and phenolic unit of PHA promoted by base catalyst generated from PBG at the exposed areas. This PSPBO showed high sensitivity and contrast due to the chemically amplified system.



Scheme 1-13. Structures of PHA as a matrix polymer, HBVS as a cross-linker, and PBG for Michael-reaction cross-linking type PSPBO.

1-6. Current Trends of PSPIs and PSPBOs

Many combinations and mechanisms of PSPIs and PSPBOs have been reported in the past. However, the further developments of PSPIs and PSPBOs are strongly demanded for the rapid development in microelectronics. The followings are the properties which are required to PSPIs and PSPBOs in the future.

1-6-1. Environmental Compatibility. The environmentally-friendly manufacturing systems are strongly demanded in the world. Accordingly, the environmentally-friendly fabrication and patterning processes are required in microelectronics field without exception. The development by alkaline aqueous solution such as TMAHaq is one of the environmentally-friendly patterning processes. The preparation of PAAs is acceptable for the environment, because PAA can be synthesized from dianhydrides and diamines by ring-opening polyadition reaction. In contrast, PHAs for PSPBOs are prepared from bis(*o*-aminophenol)s and dicarboxylic active diesters which are obtained using the expensive activating agent. Therefore, the facile preparation of PHAs is highly required.

1-6-2 High Photosensitivity and Contrast. The fine patterning images of PSPIs and PSPBOs are required with the developments of high-density packaging. To obtain the fine patterns, PSPIs and PSPBOs should have the property of high photosensitivity and contras. Introducing the chemical amplified system in PSPIs and PSPBOs is the most effective method.

1-6-3 Simple Formation of PSPIs and PSPBOs. There are several PSPIs and PSPBOs consisting of the matrix polymer which is synthesized by the complicated synthetic routes.[18] The preparation of these polymers is not only expensive, but also opposed to the environmental compatibility. Consequently, it is preferable that PSPIs and PSPBOs are directly formed from a principle PAA or PHA and additives, such as dissolution inhibitor, cross-linker, PAG, PBG, etc.

1-6-4 Low-Temperature Curing Process. Recently, a high-density packaging of ICs is required for high-functionalization and miniaturization of electronic devices. Figure 3 shows top and side-section views of a multi chip module (MCM). As can be seen, two or more Si dies or CSPs are mounted and interconnected on a substrate. Typical curing temperature of PSPIs and PSPBOs at 350 °C damages MCM substrates and Si dies, because low-heat resistance materials are used in MCM. Therefore, the performance of low-temperature cyclization of PAAs and PHAs is an effective solution to this problem.

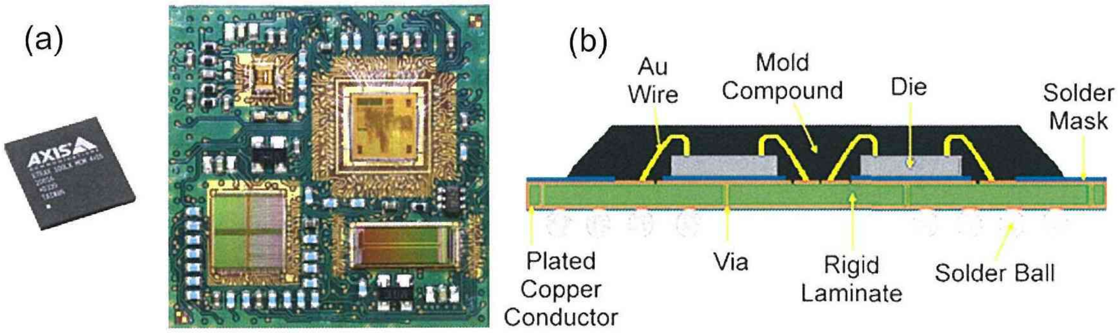


Figure 1-3. (a) Top and (b) side-section views of MCM.

1-6-4 Low Coefficient of Thermal Expansion (CTE). System in package (SIP), also known as a Chip Stack MCM, composes of a number of Si dies stacked in a single package or module, which is one of the high-density packaging technologies (Figure 4).[19] To enclose several Si dies in the traditional size of IC package, a Si wafer for Si die is ground thin. The thickness of the Si wafer for typical ICs is around 700 μm, but that for SIPs is only 70~90 μm. Therefore, high-temperature curing of general PSPIs and PSPBOs causes warpage of thinner Si wafers, because there are differences between the CTE of Si wafer and typical PIs (PBOs). One of the methods to overcome the warpage is the low-temperature cyclization of PAAs and PHAs. However, this method has limitations in reducing thermal strain even at low curing temperature, because the typical matrix polymers of PSPIs and PSPBOs have a relatively high CTE. Accordingly, PSPIs (PSPBOs) using Low-CTE PIs (PBOs) are highly demanded.

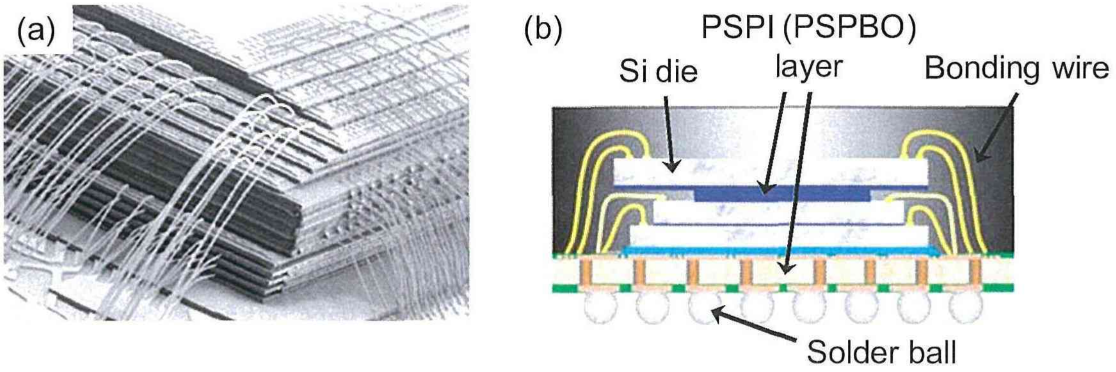


Figure 1-4. (a) A scanning electron microscop image of 24 stacked dies, (b) side-section view of SiP.

1-7. Purposes of This Work

PSPIs and PSPBOs for the next generation electronic devices should be developed with considering the aforementioned trends. Thus, this dissertation aimed to develop new efficient synthetic methods for PAAs and PHAs and simple PSPIs and PSPBOs formulation method. The results are summarized in eight chapters.

In Chapter 1, general introduction is described including recent trends of PSPIs and PSPBOs.

In Chapter 2, to develop a simple method of PHA, a direct synthesis of active diester from dicarboxylic acid and *p*-nitrophenol, and the preparation of PHA are described.

In Chapter 3, developments of novel dissolution inhibitors for PSPBO were described. Moreover, the chemical amplified positive-type PSPBOs based on PHA, these dissolution inhibitors, and PAG are described. These dissolution inhibitors provided a simple PSPBO formulation.

In Chapter 4, a low-temperature curable positive-type PSPBO based on PHA, 9,9-bis(4-*tert*-butoxycarbonyloxyphenyl)fluorene as a dissolution inhibitor, PAG, and isopropyl *p*-toluenesufonate (ITS) as a thermoacid generator is described, in which thermal cyclization reaction is accelerated by ITS at low temperature.

In Chapter 5, for the easy preparation of semi-alicyclic PAA, the facile synthesis of semi- alicyclic PAAs from *trans*-1,4-cyclohexanediamine and aromatic tetracarboxylic dianhydrides using acid catalysts was described.

In Chapter 6, low-CTE PSPI based on PBG and semi-alicyclic PAA for the Chip Stack MCM, which is prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride and CHDA, is formulated in negative-tone chemical amplification. The PAA in this resist system is prepared by using the method described in Chapter 5.

In Chapter 7, to obtain the positive tone of PIs, a novel patterning system of PI using PSPBO as a top-layer is described.

Finally, these research themes are concluded in chapter 8 (General conclusion), and therein the prospects of these studies are described.

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Chapter 2

Direct Synthesis of Active Diester from Dicarboxylic Acid and *p*-Nitrophenol and Synthesis of Poly(*o*-hydroxyamide)

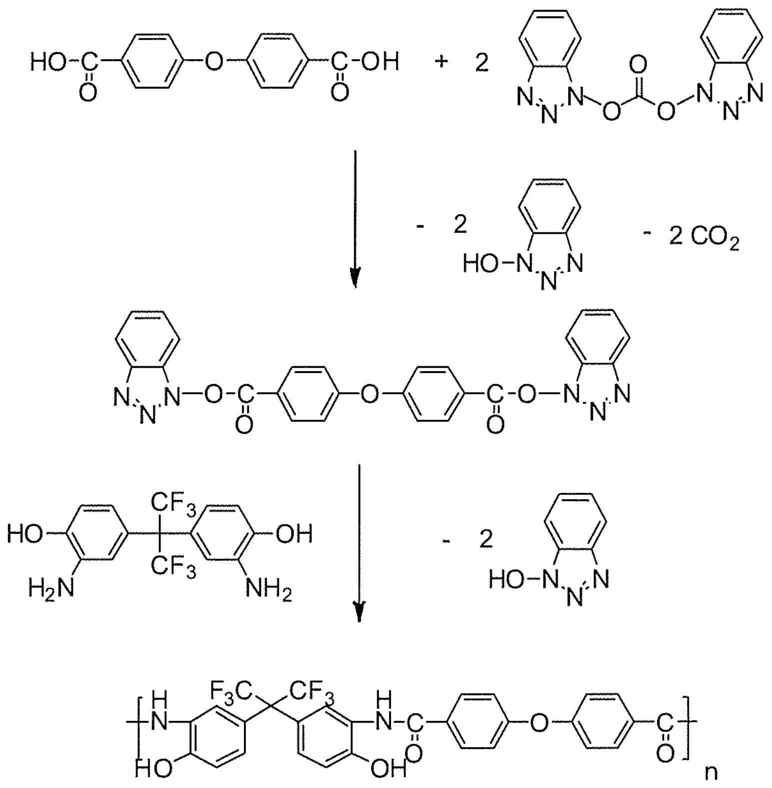
ABSTRACT: A direct synthetic method of active *p*-nitropheny diester from an aromatic dicarboxylic acid and p-nitrophenol catalyzed by *p*-toluene sulfonic acid has been developed. The active diester, 4,4'-oxybis(*p*-nitrophenylbenzoate) was prepared readily in octane under azeotropic conditions. Polycondensation of active 4,4'-oxybis(*p*-nitrophenylbenzoate) with bis(*o*-aminophenol) produced poly(*o*-hydroxyamide) with the number average molecular weight of 12000.

2-1. Introduction

Recently, photosensitive polybenzoxazoles (PSPBOs) are applied as protection and insulation layers in manufacturing semiconductors. With recent miniaturization of integrated circuit and utilization of very thin conductor lines, narrow spaces, and very thin insulation, insulating materials with lower dielectric constants are required for high speed and frequency multilayer printed circuit boards.[1-4]

The most promising PSPBO is composed of a polybenzoxazole (PBO) precursor, poly(*o*-hydroxyamide) (PHA), and a diazonaphthoquinone sensitizer. The phenolic hydroxyl groups of PHA are desirable as base-soluble functional groups for aqueous alkaline developable photosensitive resists. Furthermore, the phenolic hydroxyl groups that increase dielectric constants completely disappear after thermal cyclization of PHA to PBO.

Scheme 2-1 shows the synthetic route of PHA. To avoid a contamination of chlorine ions into microelectronics devices, a chlorine-free synthetic method is generally applied to prepare PHA as the PBO precursor from an aromatic dicarboxylic active diester and bis(*o*-aminophenol).[1b]



Scheme 2-1. Synthetic route of PHA.

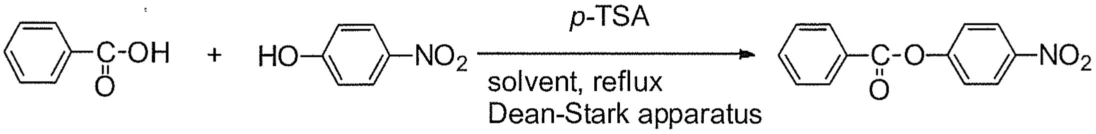
The active diester is prepared from an aromatic dicarboxylic acid and an activating agent, 1,1'-carbonyloxydibenzotriazole (COBT). Although this method reduces significantly chlorine content compared to the conventional acid chloride method, COBT is an expensive reagent, especially for industrial large-scale synthetic use. Therefore, finding an alternative route for active diesters is important to expand the scope of PSPBO. A straightforward method is the direct diester synthesis from dicarboxylic acids and phenols in the presence of catalysts. However, this direct synthesis is difficult because in the ester formation the equilibrium in the C–O bond making process is not favorable compared to that from an aliphatic alcohol.[5] The nucleophilicity of phenols is lower than that of alcohols, and the active esters are easily hydrolyzed with water because of higher acidity of phenols (pK_a: 7–10 than alcohols pK_a: 15). The direct coupling of aromatic carboxylic acids and aryl halides or the carbonylation of aryl halides using a palladium catalyst to generate the corresponding aryl esters is also difficult.[6] Thus, few reports have been published on the direct ester synthesis.[7]

In the previous paper, we reported a convenient synthesis of aliphatic polyesters by the distanoxane-catalyzed polycondensation of aliphatic dicarboxylic acids and aliphatic diols in solvents under azeotropic conditions.[8] The solvent was chosen on the basis that it could not dissolve the polyesters, so that the polymerization could proceed in a two-phase system of solvent and molten polymer to maintain a high reaction concentration. Azeotropic conditions are also required for driving the equilibrium constant toward the formation of the polymer. This finding prompted us to apply this system to direct synthesis of active diesters from dicarboxylic acids and phenols.

Here we report the successful direct synthesis of active diester from an aromatic dicarboxylic acid and *p*-nitrophenol catalyzed by *p*-toluenesulfonic acid (*p*-TSA) and PHA synthesis by polycondensation of the active diester and bis(*o*-aminophenol).

2-2. Results and Discussion

2-2-1. Model Reaction. A *p*-nitrophenyl ester is a typical active ester for the synthesis of aromatic amides. Thus, reaction of benzoic acid with *p*-nitrophenol was carried out in several high boiling hydrocarbons in the presence of *p*-TSA under azeotropic conditions (Scheme 2-2). The results are summarized in Table 2-1.



Scheme 2-2. Preparation of *p*-nitrophenylbenzoate.

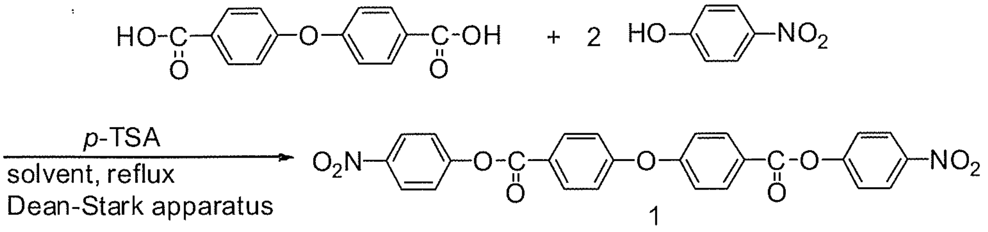
Table 2-1. Preparation of *p*-nitrophenylbenzoate from benzoic acid and *p*-nitrophenol[a].

Run	Solvent	Temp (°C)	Time (h)	Yield (%)
1	nonane	151	7	97
2	cyclooctane	151	24	58
3	octane	127	24	97
4	heptane	98	24	54

[a] Reaction conditions: 10 mmol of benzoic acid, 15 mmol of p-nitrophenol, 1 mmol of *p*-TSA, 20 mL of solvent.

Reactions proceed in a two-phase system of octane or nonane and molten reactants, giving desired *p*-nitrophenylbenzoate in quantitative yields.

2-2-2. Synthesis of Di(*p*-nitrophenyl ester). On the basis of the model reaction, the *p*-TSA-catalyzed esterfication of aromatic dicarboxylic acid, 4,4‘-oxybis(benzoic acid) with *p*-nitrophenol was investigated (Scheme 2-3). The results are summarized in Table 2-2.



Scheme 2-3. Preparation of 4,4‘-oxybis(*p*-nitrophenylbenzoate), 1.

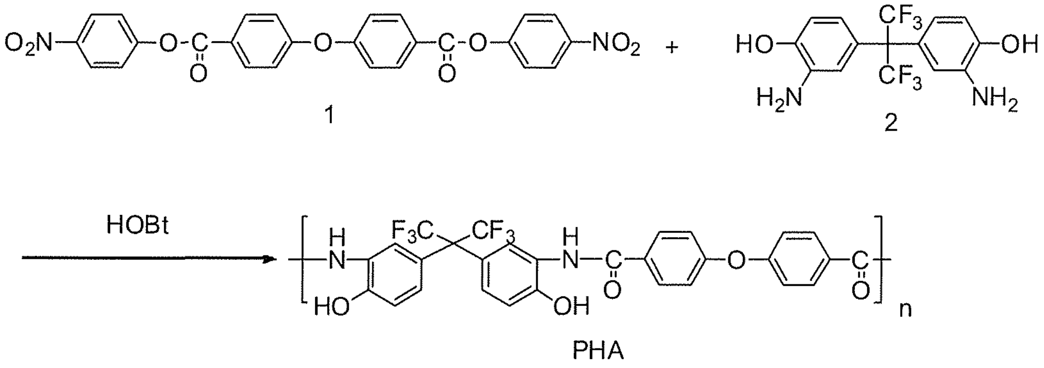
Table 2-2. Preparation of 1 from 4,4‘-oxybis(benzoic acid) and *p*-nitrophenol[a].

Run	Solvent	Temp (°C)	Yield (%)
1	nonane	151	91
2	cyclooctane	151	91
3	octane	127	44

[a] Reaction conditions: 10 mmol of 4,4‘-oxybis(*p*-nitrophenylbenzoate), 40 mmol of *p*-nitrophenol, 1 mmol of *p*-TSA, 50 mL of solvent; time: 24 h.

Reactions also produced the desired active diester, 4,4‘-oxybis(*p*-nitrophenylbenzoate) (1) in high yields. The structure of the diester was identified by IR and NMR spectroscopy.

2-2-3. Synthesis of PHA. 1-Hydroxybenzotriazole (HOBt) catalyzes the polycondensation of di(*p*-nitrophenyl isophthalate) with aromatic diamines,[9] and the chemoselective synthesis of PHA is achieved by polycondensation of isophthaloyl dichloride with 3,3‘-dihydroxybenzidine in the presence of lithium chloride.[10] Based on these findings, polycondensation of 1 and 4,4‘-(hexafluoroisopropylidene)bis(*o*-aminophenol) (2) was carried out in NMP in the presence of HOBt (Scheme 2-4). The results are summarized in Table 2-3.



Scheme 2-4. Preparation of poly(*o*-hydroxyamide).

Table 2-3. Preparation of poly(*o*-hydroxyamide) from 1 and 2[a].

Run	HOBt (mol %)	M_n[b]	M_w/M_n[b]	Yield (%)
1	20	10000	2.2	63
2	40	12000	2.0	89

[a] Reaction conditions: polymerization temperature 90 °C, time 72 h, concentration 25 wt %, solvent NMP.

[b] Determined by GPC (DMF, PSt).

Polycondensation proceeded smoothly at 90 °C to give the desired PHA with a number-average molecular weight of 12 000[11] and a polydispersity of 2.0. Chemoselective polyamidation was observed in the presence of HOBt. The structure of the polymer was identified as the corresponding PHA by ^{1}H NMR and IR spectroscopy.

2-3. Conclusion

In summary, we developed the facile synthesis of active *p*-nitropheny diester from aromatic dicarboxylic acid and *p*-nitrophenol catalyzed by p-TSA, and PHA with high molecular weights could be obtained by polycondensation of active diester and bis(*o*-aminophenol). This process will provide a potentially efficient and versatile route for the synthesis of PHA.

Acknowledgment. We thank Tokyo Institute of Technology Center for Advanced Materials Analysis for elemental analysis.

2-4. Experimental

2-4-1. Materials. Heptane, octane, cyclooctane, and nonane were obtained commercially and use as received. *N*-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation. 4,4'-(Hexafluoroisopropylidene)bis(*o*-aminophenol) was recrystallized from tetrahydrofuran and hexane.

2-4-2. Preparation of *p*-Nitrobenzoate. 4-Nitrophenol (15 mmol, 2.1 g), benzoic acid (10 mmol, 1.2 g), and *p*-toluenesulfonic acid monohydrate (1.0 mmol, 0.19 g) were placed in a 50 mL two-necked round-bottom flask equipped with a Dean-Stark apparatus and condenser (Figure 1). The solvent (20 mL) was added and the mixture was refluxed under nitrogen. Reaction was monitored by IR spectroscopy, and the solvent was then removed by evaporation. The residue dissolved in NMP (50 mL) was reprecipitated in aqueous sodium bicarbonate solution (500 mL). The precipitate was dried *in vacuo* at 50 °C for 12 h. M.p. 142-143°C (lit.142-144 °C. *J. Org. Chem.*, **1985**, *50*, 560). Anal. Calcd for $C_{13}H_9NO_4$: 243.21. C, 64.20; H, 3.73; N, 5.76; O, 26.31. Found: C, 64.69; H, 3.83; N, 5.67; O, 25.81.

IR (KBr):ν (cm^{-1})=1739 (C=O), 1592 (Ar, C-H), 1519 (NO_2), 1346 (NO_2). ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm)=7.43 (d, Ar*H*, 2H), 7.55 (t, Ar*H*, 2H), 7.69 (t, Ar*H*, 1H), 8.21 (d, Ar*H*, 2H), 8.33 (d, Ar*H*, 2H).

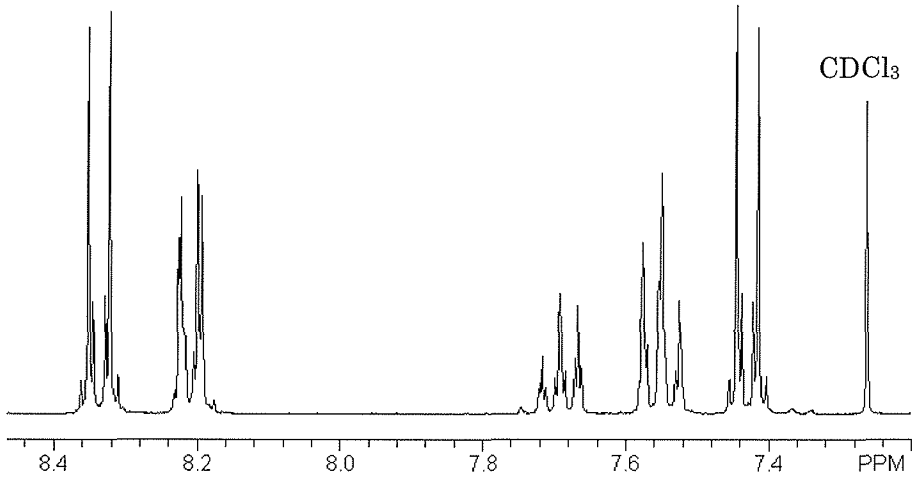


Figure 2-1. ^{1}H NMR spectrum of *p*-nitrobenzoate.

2-4-3. Preparation of 4,4'-Oxybis(*p*-nitrophenyl benzoate). 4-Nitrophenol (40 mmol, 5.5 g), 4,4'-oxiybis(benzoic acid) (10 mmol, 2.6 g), and *p*-toluenesulfonic acid monohydrate (1.0 mmol, 0.19 g) were placed in a 100 mL two-necked round-bottom flask equipped with a Dean-Stark apparatus and a condenser. The reaction was carried out as described above. The product was recrystallized from toluene to produce pale orange needles. M.p. 208-210 °C. Anal. Calcd for $C_{26}H_{16}N_2O_9$: 500.41. C, 62.40; H, 3.22; N, 5.60; O, 28.78. Found: C, 62.60; H, 3.59; N, 5.43; O, 28.38.

IR (KBr):ν (cm^{-1})=1731 (C=O), 1592 (Ar, C-H), 1523 (NO_2), 1349 (NO_2), 1241 (Ar-O-Ar). ^{1}H-NMR (300 MHz, DMSO-d_6) δ (ppm)=7.38 (d, Ar*H*, 4H), 7.68 (d, Ar*H*, 4H), 8.30 (d, Ar*H*, 4H), 8.41 (d, Ar*H*, 4H)

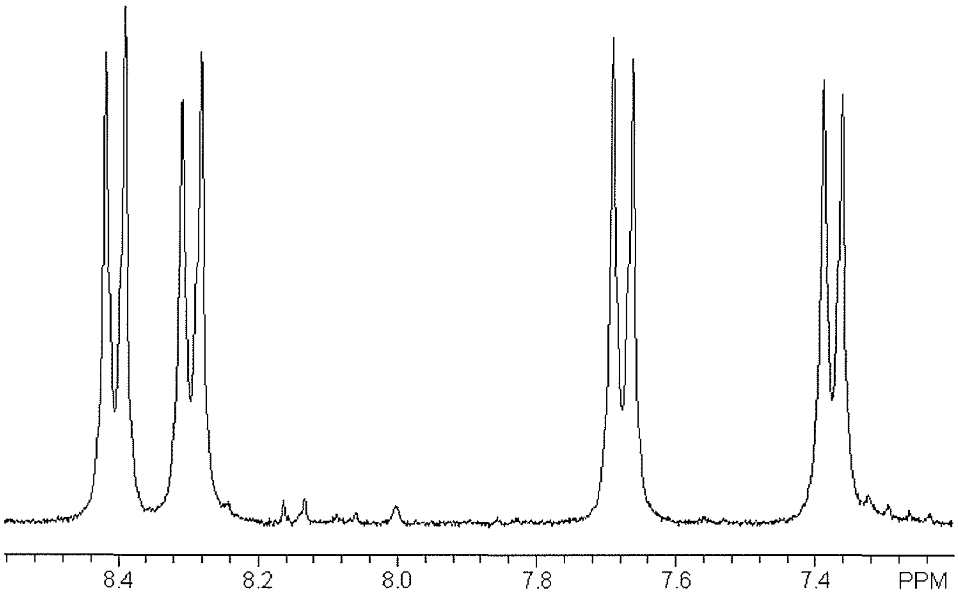


Figure 2-2. ^{1}H NMR spectrum of 4,4'-oxybis(*p*-nitrophenylbenzoate).

2-4-4. Synthesis of Poly(*o*-hydroxyamide). 4,4'-(Hexafluoroisopropylidene)bis(*o*-aminophenol) (1.00 mmol, 0.366 g) in NMP (2.8 mL) were placed in a 10 mL round-bottom flask. To this solution was added active ester **1** (1.00 mmol, 0.500 g) and 1-hydroxybenzotriazole monohydrate (0.40 mmol, 0.063 g) at room temperature. This solution was stirred at 90 °C for 72 h. The resulting polymer solution was poured into aqueous sodium bicarbonate solution (200 mL). The precipitate was filtered and dissolved in NMP. The solution was poured into H_2O / methanol solution (1/1 in volume, 200mL). The precipitate was filtered and dried *in vacuo* at 100 °C for 12 h.

IR (Film):ν (cm^{-1})=1654 (C=O), 1596 (Ar, C-H), 1245 (Ar-O-Ar). ^{1}H-NMR (300 MHz, DMSO-d$_6$) δ (ppm)=7.04 (s, Ar*H*, 4H), 7.22 (d, Ar*H*, 4H), 7.98 (s, Ar*H*, 2H), 8.07 (d, Ar*H*, 4H), 9.55 (s, N*H*CO, 2H), 10.26 (s, ArO*H*, 2H).

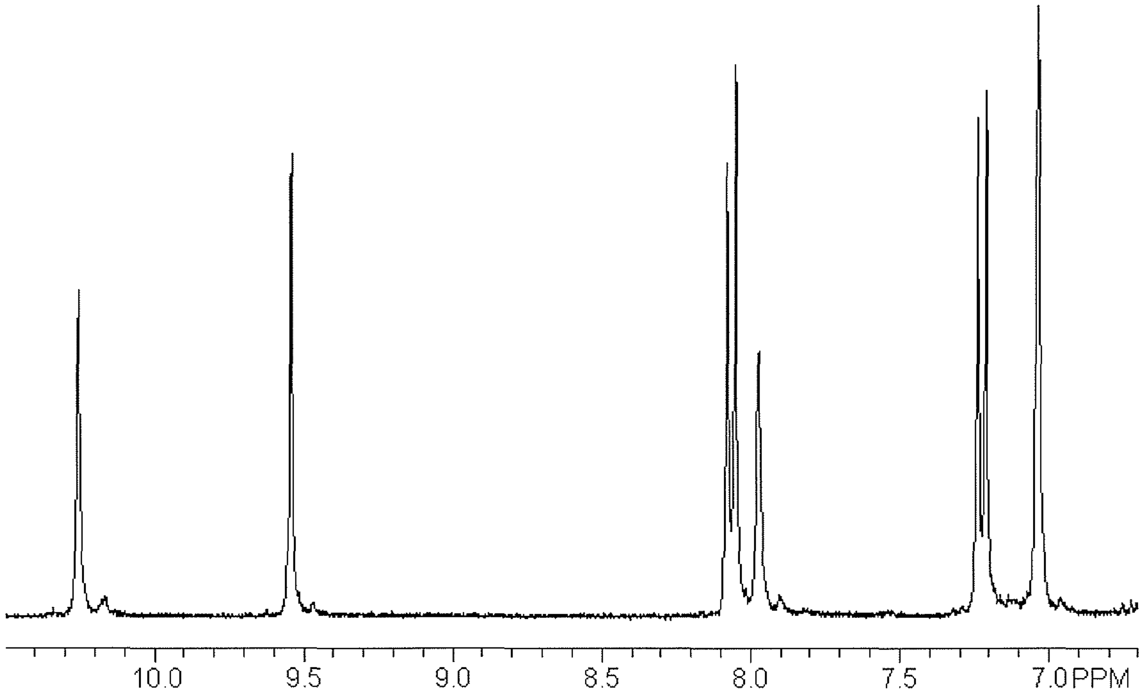


Figure 2-3. ^{1}H NMR spectrum of poly(*o*-hydroxyamide).

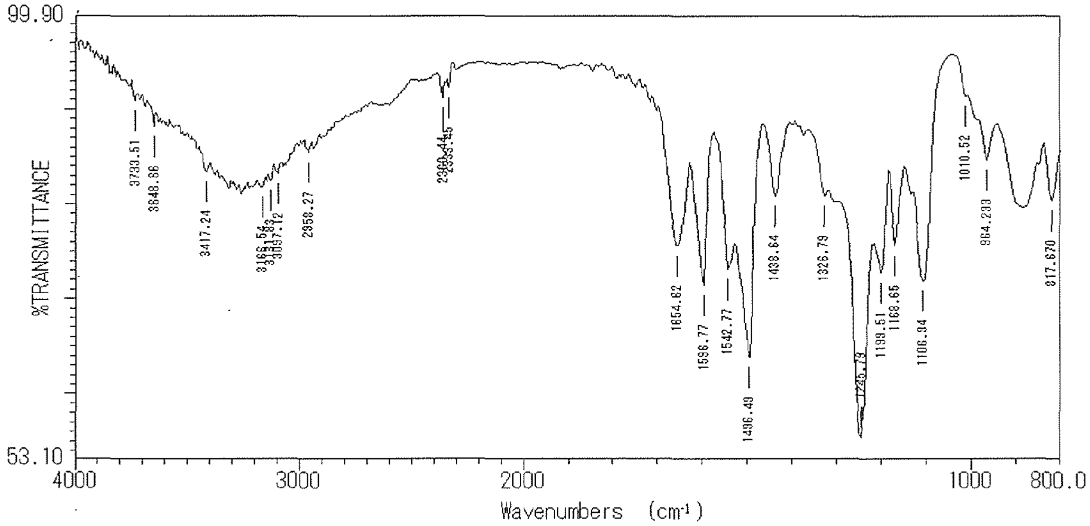


Figure 2-4. FT-IR spectrum of poly(-*o*-hydroxyamide).

2-4-5. Measurement. Infrared spectra (FTIR) were taken with a Horiba FT-210 spectrophotometer. The ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER GPX300 spectrometer (^{1}H at 300 MHz). M_n and M_w were determined by GPC with JASCO PU-2080Plus with two polystyrene gel columns (TSK GELs; GMH$_{HR}$-M) at 40 °C in DMF at a flow rate of 1.0 mL/min, calibrated with polystyrene standards. Elemental analysis was performed by a YANACO CHN corder MT-6 in Tokyo Institute of Technology Center for Advanced Materials Analysis.

2-5. References and Notes

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(11) SEC measurements are crude estimations.

Chapter 3

Photosensitive Polybenzoxazole Based on a Poly(*o*-hydroxy amide), a Dissolution Inhibitor, and a Photoacid Generator

ABSTRACT: A positive-type photosensitive polybenzoxazole (PSPBO), based on a poly(*o*-hydroxy amide) (PHA), the dissolution inhibitor (DI) 9,9-bis(4-*tert*-butoxycarbonyloxyphenyl)fluorene (*t*-Boc BHF), and the photoacid generator (5-propylsulfonyloxyimino-5*H*-thiophene-2-ylidene)-(2-methylphenyl)acetonitrile (PTMA), was developed. Several new tert-butoxycarbonylated compounds as DIs for PSPBOs were prepared from phenolic compounds having a cardolike structure with di-tert-butyl dicarbonate in the presence of 4-dimethylaminopyridine. Among them, *t*-Boc BHF and 5,5',6,6'-tetra(*tert*-butoxycarbonyl)-3,3,3',3'-tetramethyl-1,1-spirobiindane acted as excellent DIs, giving a large dissolution contrast between the exposed and unexposed areas in a 2.38 wt % tetramethylammonium hydroxide solution (TMAHaq)/5 wt % *iso*-propanol (*i*-PrOH). The dissolution behavior of this PSPBO system was studied in relation to the PTMA and *t*-Boc BHF loadings and postexposure baking temperature. A

PSPBO consisting of PHA (77 wt %), *t*-Boc BHF (20 wt %), and PTMA (3 wt %) exhibited a sensitivity of 34 mJ/cm2 and a contrast of 5.8 when exposed to 365-nm light (*i*-line) and developed with an aqueous alkaline developer, 2.38 wt % TMAHaq/5 wt % *i*-PrOH. A clear, positive image with 6 μm features and a 10 μm-thick pattern with high sensitivity and contrast was produced by contact printing and converted into polybenzoxazole patterns upon heating at 350 °C for 1 h.

3-1. Introduction

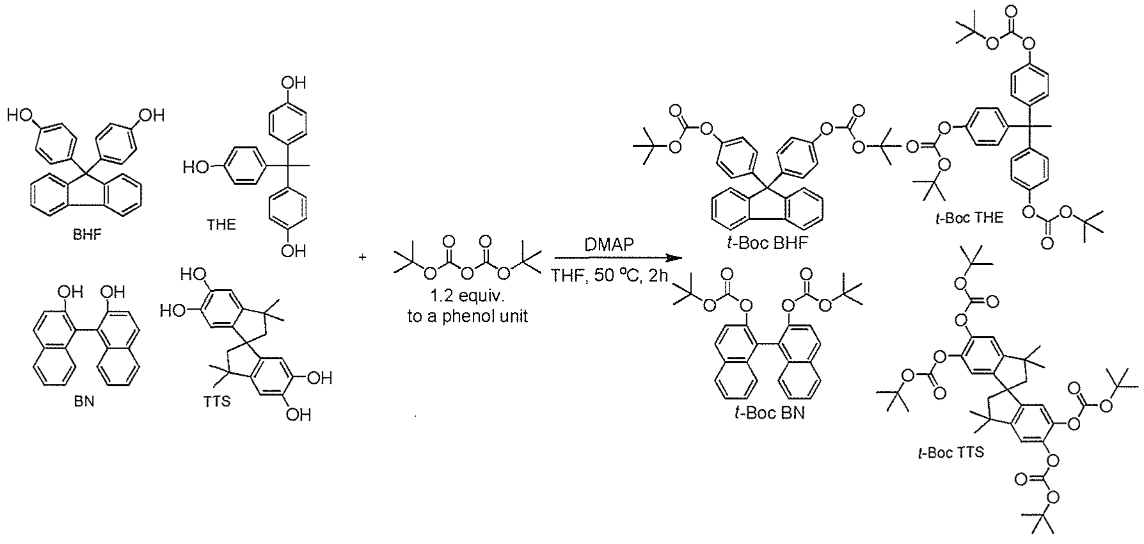
Photosensitive, thermally stable polymers such as photosensitive polyimides and photosensitive polybenzoxazoles (PSPBOs) are attracting attention because of their high mechanical strength, thermal stability, and low dielectric constant. They are used as buffer coatings to protect bare chips from stresses induced by filler or thermal mismatches between a passivation layer and molding materials and can simplify industrial processes significantly by preventing the need for additional photoresists.[1-15]

In general, PSPBOs are formulated from a polybenzoxazole (PBO) precursor, poly(*o*-hydroxy amide) (PHA), and the photosensitizer diazonaphthoquinone (DNQ).[1-11] A phenol group of PHA provides adequate solubility in the alkaline developer, a 2.38 wt % tetramethylammonium hydroxide solution (TMAHaq). Furthermore, the hydroxyl groups that increase the dielectric constant completely disappear after the thermal cyclization of PHA. The aforementioned resist formulation is convenient because it involves the simple addition of DNQ to a solution of PHA. However, the sensitivity of these conventional PSPBOs is low (300 mJ/cm^2), even with a 20-25 wt % loading of DNQ. Moreover, thick resist patterns are difficult to make with these PSPBOs because of the strong absorbance of DNQ at 365nm. To overcome these problems of PSPBOs, a chemically amplified technique has been developed for a design of PSPBOs coupled with a photoacid generator (PAG), for which a partially *tert*-butoxycarbonylated (*t*-Boc) PHA is used as a polymer matrix.[16, 17] For this method, *t*-Boc groups must be introduced into PHA through polymer reactions; that is, two extra steps, such as the modification of PHA with di-*tert*-butyl dicarbonate and the isolation of *t*-Boc PHA, are required, and they are tedious. Recently, Minegishi et al.[18] reported a more convenient method that is widely applicable and provides an easy resist formulation involving a three-component system consisting of PHA, a PAG, and a dissolution reverser based on acid-labile esters. However, the dissolution contrast (DC) to 2.38 wt % TMAHaq between the exposed and unexposed areas is nearly 10; a high DC is required to obtain a fine pattern. In a previous article,[19] we briefly reported that the dissolution inhibitor (DI) 9,9-bis(4-*tert*-butoxycarbonyloxyphenyl)fluorene (*t*-Boc BHF) worked well, giving a large DC between the areas exposed and not exposed to 2.38 wt % TMAHaq for a chemically amplified PSPBO based on a PHA and a PAG. These findings prompted us to develop a new PSPBO having the ability to make a 10 μm-thick pattern with high sensitivity and contrast.

In this study, we report a new positive-working, alkaline-developable, thermally stable, and photosensitive polymer based on a PHA, a DI, and a PAG, (5-propylsulfonyloxyimino-5*H*-thiophene-2-ylidene)-(2-methylphenyl)acetonitrile (PTMA); the synthesis of several *t*-BOC-protected DIs is also reported. This new PSPBO containing new DIs shows very high sensitivity and contrast in the presence of only 3 wt % PTMA, giving a large DC of approximately 500 times between the exposed and unexposed areas in 2.38 wt % TMAHaq/5 wt % *iso*-propanol (*i*-PrOH) after postexposure baking (PEB) at 120 °C for 3 min. Furthermore, a fine pattern could be delineated in a 10 μm-thick film with only 87 mJ/cm^2 doses. Thus, the newly developed PSPBO system, meeting practical requirements in industrial applications, such as a simple resist formulation, high sensitivity, and thick pattern formation, will be a strong candidate for next-generation PSPBOs.

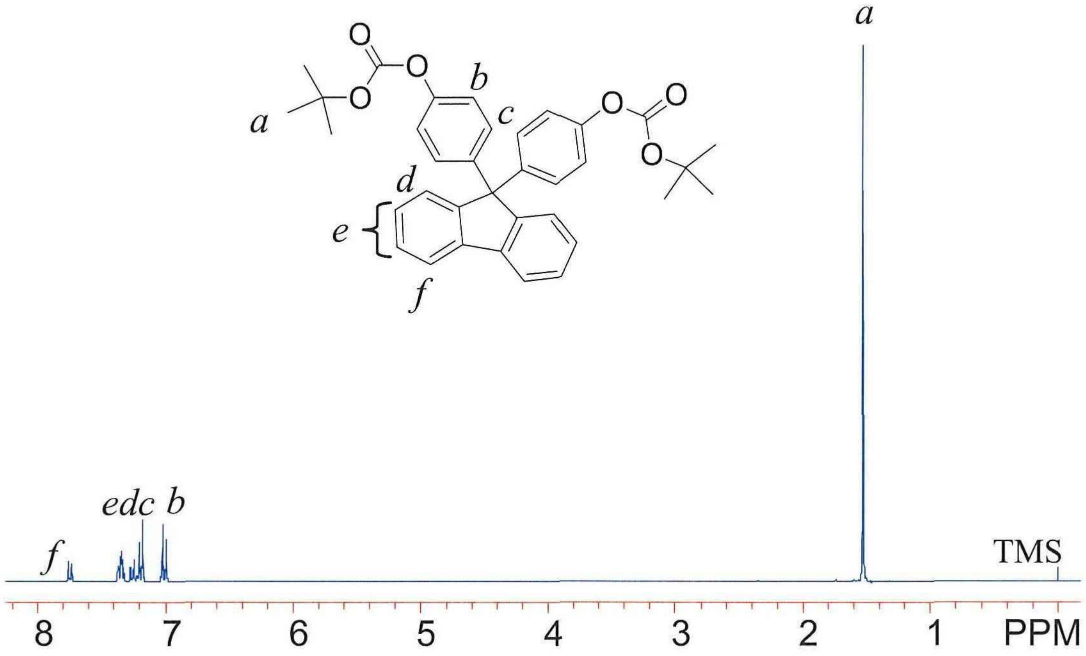
3-2. Results and Discussion

3-2-1. Synthesis of the DIs and PHA. A DI is required to have high hydrophobicity and good compatibility with PHA; after deprotection, it should act as a dissolution promoter to 2.38 wt % TMAHaq. Thus, phenolic compounds with a cardolike structure, such as 9,9-bis(4-hydroxyphenyl)fluorene (BHF), 1,1,1-tris(4-hydroxyphenyl)ethane (THE), 1,1'-bi-2-naphthol (BN), and 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobiindane (TTS), were selected. A *t*-Boc group was chosen as an acid-sensitive protecting group with high hydrophobicity. The reaction of phenolic compounds with di-*tert*-butyl dicarbonate in the presence of 4-dimethylaminopyridine (DMAP) produced the corresponding *t*-Boc compounds (i.e., *t*-Boc DIs) in good yields (Scheme 3-1).



Scheme 3-1. Synthesis of *t*-Boc DIs.

The structures of the *t*-Boc DIs were characterized with IR and ^{1}H NMR spectroscopy. The IR spectra of the *t*-Boc DIs showed characteristic carbonate absorption near 1760 cm-*1*. The 1H NMR spectrum of *t*-Boc BHF is shown in Figure 3-1; the inset indicates the assignment of each resonance. All peaks agreed with the assignment to the expected structure of *t*-Boc BHF. The deprotection temperatures of the *t*-Boc DIs were determined by Thermogravimetry (TG) (Figure 3-2) and are summarized in Table 3-1.



The deprotection temperatures were approximately 180 °C.

Figure 3-1. ^{1}H NMR spectrum of *t*-Boc BHF in $CDCl_3$ at 25 °C.

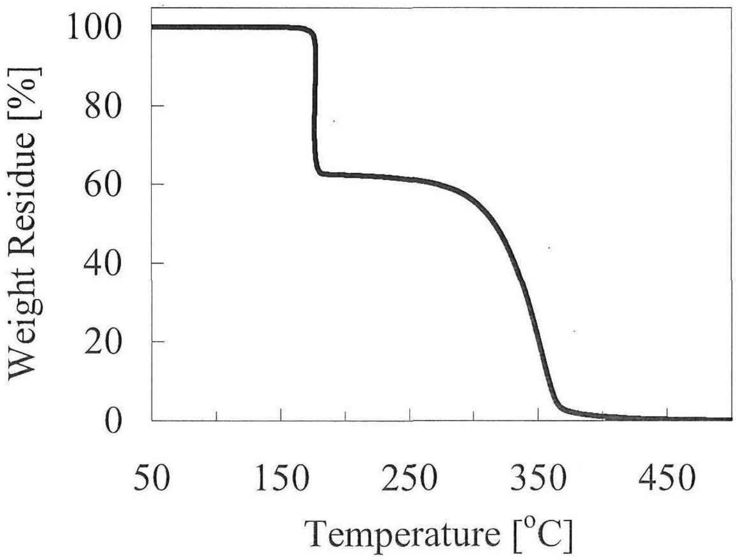


Figure 3-2. TG of *t*-Boc BHF.

Table 3-1. Deprotection temperatures of *t*-Boc DIs.

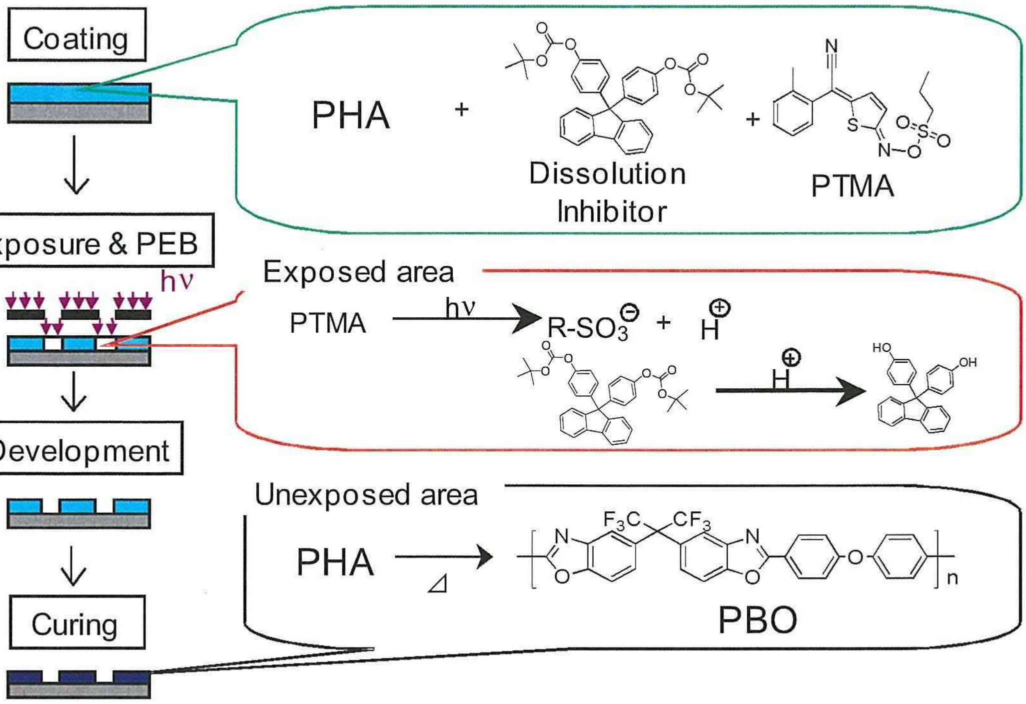
DI	Deprotection temperature [°C][a]
t-Boc BHF	176
t-Boc THE	184
t-Boc BN	196
t-Boc TTS	185

[a] The temperature was determined at a heating rate of 5 °C min^{-1} under nitrogen.

The PHA matrix polymer was prepared from 4,4'-(hexafluoroisopropylidene)bis(*o*-aminophenol) (6FAP) and 4,4'-oxybis(benzoyl chloride) according to a previous report.[9] The number- and weight- average molecular weights (M_n and M_w, respectively) of PHA were 7400 and 16,000, respectively.

3-2-2. Lithographic Evaluation for the PHA/*t*-Boc DI/PTMA Resist System. The patterning process using the positive-type PSPBO based on PHA, *t*-Boc DI, and PTMA is shown in Scheme 3-2.

To obtain contrasting pattern profiles from exposed and unexposed areas, the effects of the PEB temperature and PAG and *t*-Boc DI loadings were investigated. Films were obtained by the spin casting of diluted solutions of PHA, t-Boc DI, and PTMA in cyclohexanone on silicon wafers, which were then prebaked at 100 °C for 5 min in air. These photosensitive polymer films were irradiated with UV light (100 mJ/cm^2) at 365 nm (*i*-line) with a filtered super-high-pressure mercury lamp, baked after exposure at a set temperature for 3 min, and developed with TMAHaq/5 wt % *i*-PrOH at 25 °C.



Scheme 3-2. Patterning process of PSPBO using *t*-Boc DI.

The effect of the PEB temperature was examined because PEB is crucial for a chemically amplified resist system. To clarify the dissolution behaviors of photosensitive films containing *t*-Boc BHF and PTMA in both exposed and unexposed areas, the dissolution rate was estimated from the change in the film thickness before and after development. As shown in Figure 3-3, a large DC between the exposed and unexposed areas in 2.38 wt % TMAHaq/5 wt % *i*-PrOH was obtained in a PEB temperature range of 100-120 °C. PEB temperatures greater than 130 °C could induce the thermal decomposition of t-Boc BHF, resulting in greater solubility in 2.38 wt % TMAHaq/5 wt % *i*-PrOH.

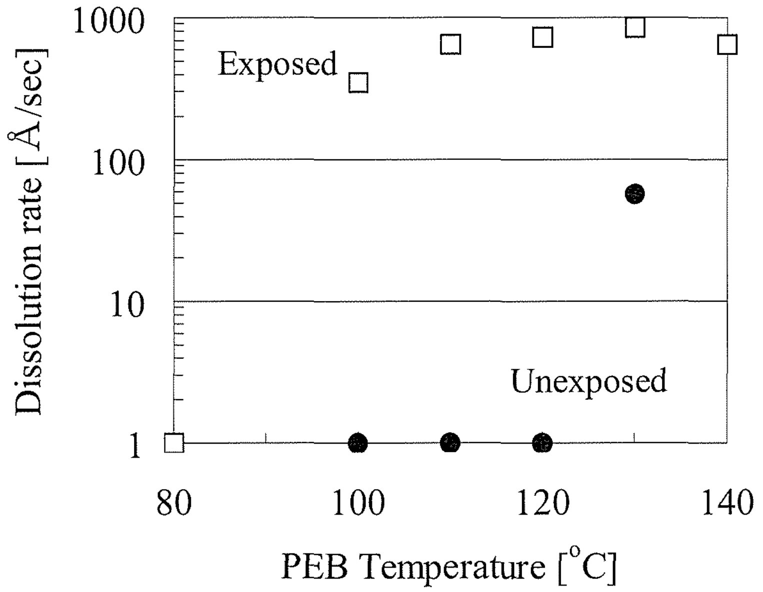


Figure 3-3. Effect of PEB temperature on dissolution rate for PHA/*t*-Boc DI/ PTMA (77/20/3 wt/wt/wt) resist system in exposed (□) and unexposed (●) areas. The *i*-line exposure and PEB time were fixed at 100 mJ/cm^2 and 5 min, respectively.

The effect of the PTMA loading to PHA on the dissolution rate of the film was investigated, as shown in Figure 3-4. A total of 5 wt % PTMA to PHA, which corresponded to a weight ratio of PHA (77 wt %), *t*-Boc BHF (20 wt %), and PTMA (3 wt %), produced a large DC, which indicated that the photogenerated acid decomposes *t*-Boc BHF effectively to give BHF by the PEB treatment. Subsequently, the effect of the *t*-Boc BHF loading on the dissolution rate of the film was studied under similar conditions. The results are shown in Figure 3-5. The dissolution rate of the unexposed area decreased with increasing *t*-Boc BHF content, becoming nearly zero with a 25 wt % *t*-Boc BHF loading to PHA [corresponding to PHA (77 wt %), *t*-Boc DI (20 wt %), and PTMA (3 wt %)], whereas the exposed area with a 30 wt % t-Boc BHF loading was dissolved in the developer. The DC between the exposed and unexposed areas in 2.38 wt % TMAHaq/5 wt % *i*-PrOH reached a value near 500. Finally, the effects of various *t*-Boc DIs on the dissolution rate between exposed and unexposed areas in 2.38 wt % TMAHaq/5 wt % *i*-PrOH were investigated, as shown in Figure 3-6. A large DC was obtained in the presence of *t*-Boc BHF and *t*-Boc TTS having a cardo structure.

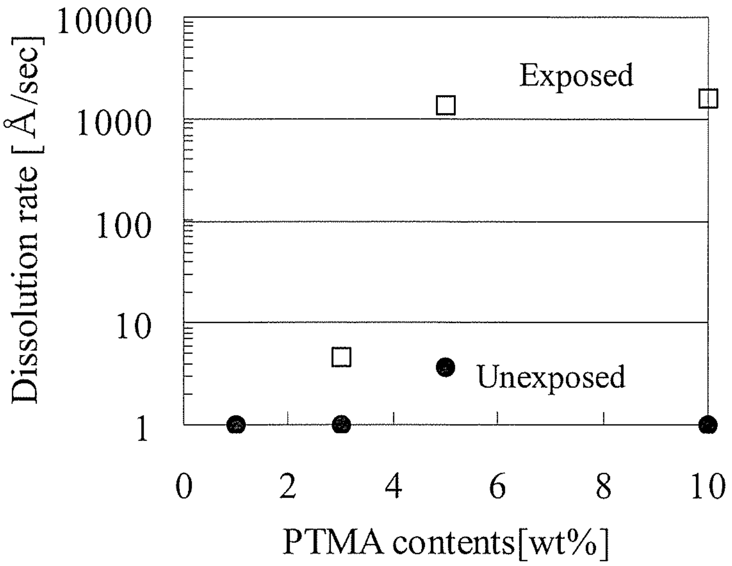


Figure 3-4. Effect of PTMA loading on PHA for dissolution rate for PHA/*t*-Boc DI (75/25 wt/wt) resist system in exposed (□) and unexposed (●) areas. The *i*-line exposure, PEB temperature, and time were 100 mJ/cm^2, 120 °C, and 5 min, respectively.

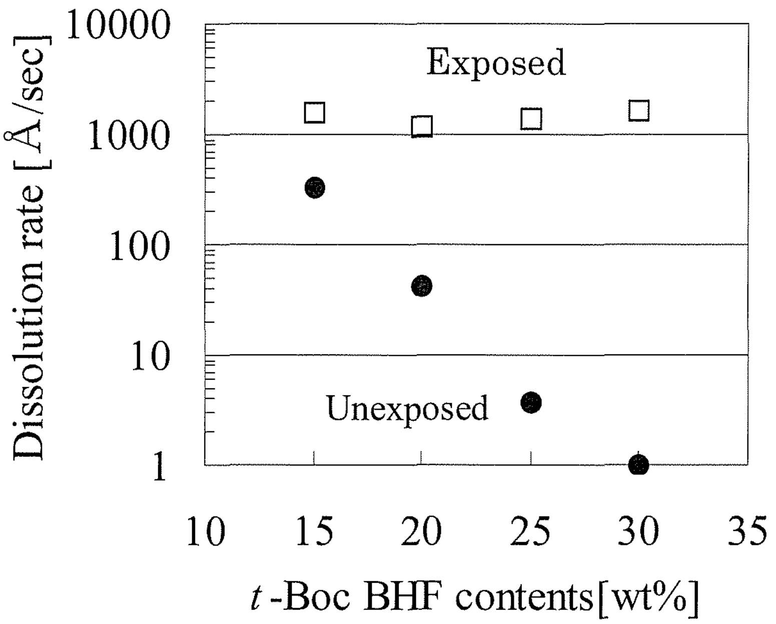


Figure 3-5. Effect of *t*-Boc BHF loading on the dissolution rate for PHA/PTMA (95/5 wt/wt) resist system in exposed (☐) and unexposed (●) areas. The *i*-line exposure, PEB temperature, and time were 100 mJ/cm^2, 120 °C, and 5 min, respectively.

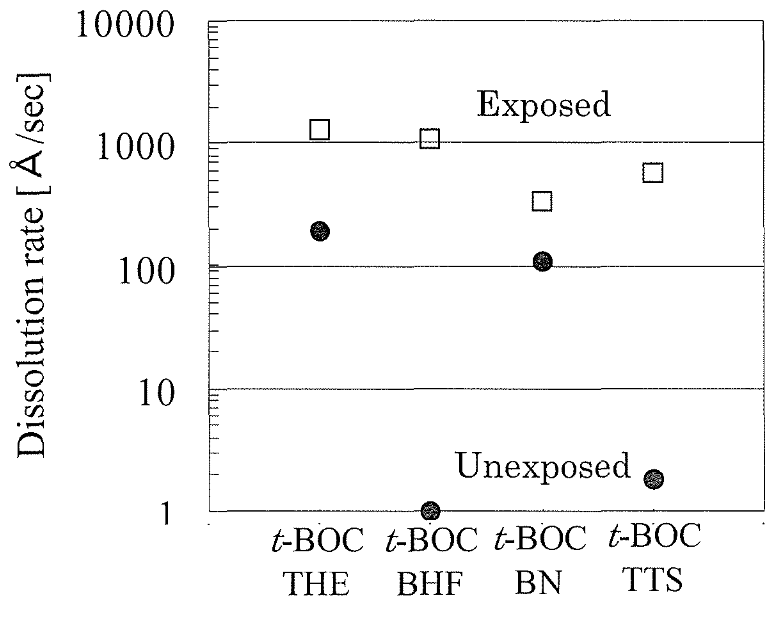


Figure 3-6. Effect of various *t*-Boc DIs on the dissolution rate for PHA/*t*-Boc DI/PTMA (77/20/3 wt/wt/wt) resist system in exposed (☐) and unexposed (●) areas. The *i*-line exposure, PEB temperature, and time were 100 mJ/cm^2, 120 °C, and 5 min, respectively.

On the basis of these preliminary optimization studies involving PTMA, *t*-Boc DI loadings, and the PEB temperature, a PSPBO consisting of PHA (77 wt %), *t*-Boc DI (20 wt %), and PTMA (3 wt %) was formulated. The photosensitivity curve of resist films 1.2 μm thick is shown in Figures 3-7 and 3-8. The resists containing *t*-Boc BHF and *t*-Boc TTS possessed outstanding sensitivity of 34 and 85 mJ/cm^2 and good contrast of 5.8 and 8.6, respectively, with the *i*-line.

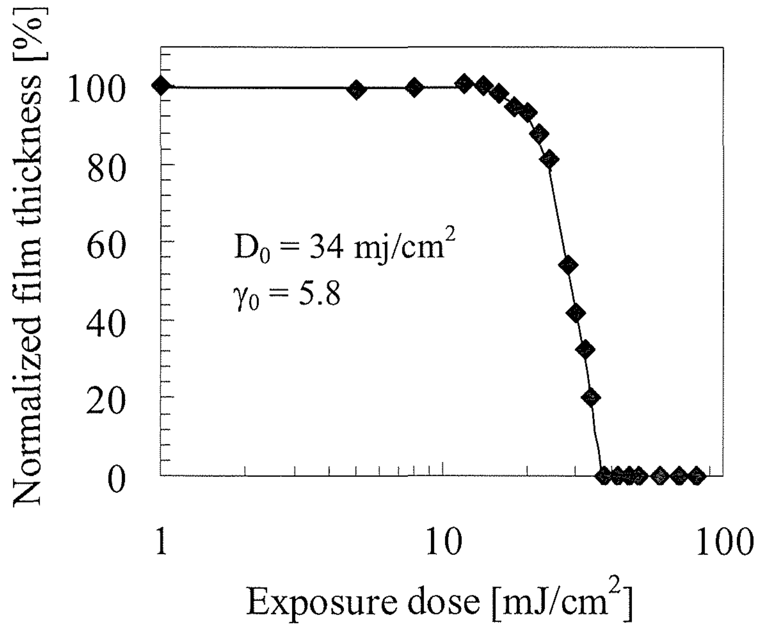


Figure 3-7. Characteristic photosensitive curve for the PHA/*t*-Boc BHF/PTMA (77/20/3 wt/wt/wt) resist system. The PEB temperature and time were 120 °C and 5 min, respectively.

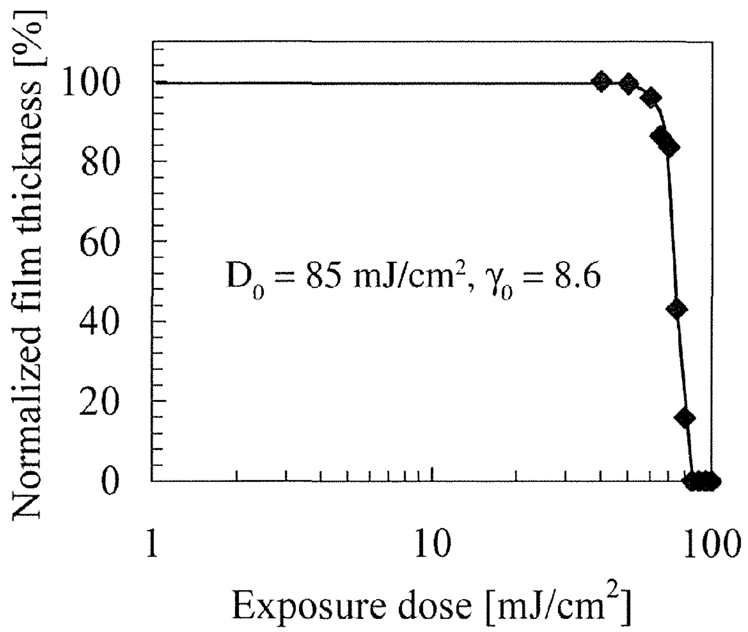


Figure 3-8. Characteristic photosensitive curve for the PHA/*t*-Boc TTS/PTMA (77/20/3 wt/wt/wt) resist system. The PEB temperature and time were 120 °C and 5 min, respectively.

Figure 3-9 shows the SEM micrograph of a contact-printed image obtained with the system described: the resist layer was exposed to 100 mJ/cm^2, postbaked at 120 °C for 3 min, and developed with 2.38 wt % TMAHaq/5 wt % *i*-PrOH at 25 °C. A clear, positive pattern with a 6 μm feature could be observed when a 2.8 μm-thick film was used. The printed pattern was converted to the PBO pattern without deformation via heating at an elevated temperature up to 350 °C for 1 h under nitrogen (Figure 3-10). The formation of PBO was confirmed by the IR spectrum, in which the characteristic oxazole ring absorption appeared at 1616 cm^{-1} and absorptions due to hydroxyl and carbonyl groups at 3300 and 1650 cm^{-1}, respectively, disappeared in the PHA spectrum.

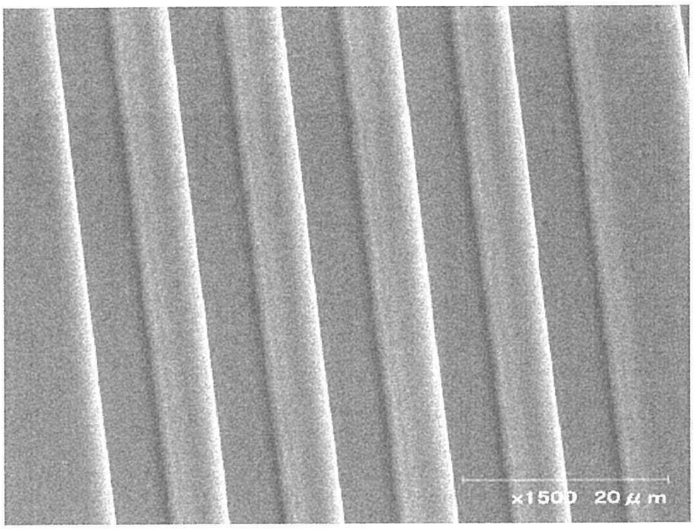


Figure 3-9. SEM image of positive-pattern 2.8 μm-thick film based on PHA/*t*-BocBHF/PTMA (77/20/3 wt/wt/wt).

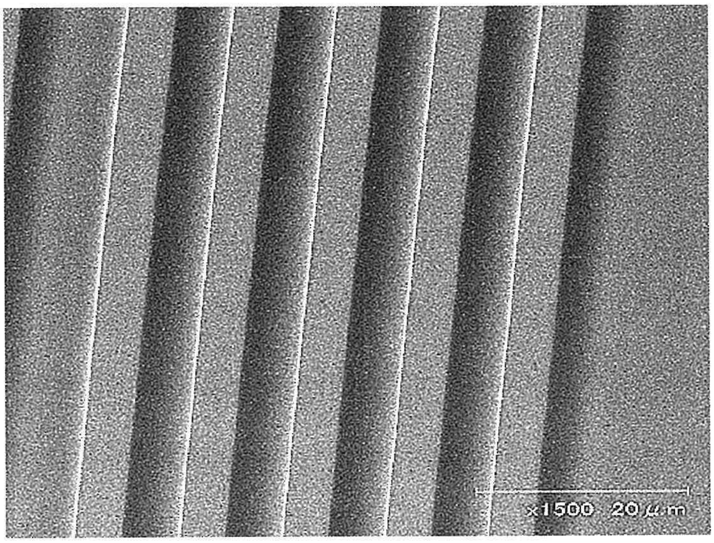


Figure 3-10. SEM image of PBO pattern cured at 350 °C for 1 h.

The resist system was used to produce a thick pattern. The 20 μm image was made in a 10 μm-thick film by PEB at 120 °C for 3 min after exposure to 87 mJ/cm^2 of *i*-line, which was followed by development with 2.38 wt % TMAHaq/5 wt % *i*-PrOH at 25 °C for 80 s. Adequate resolution and edge sharpness can be seen clearly in Figure 3-11.

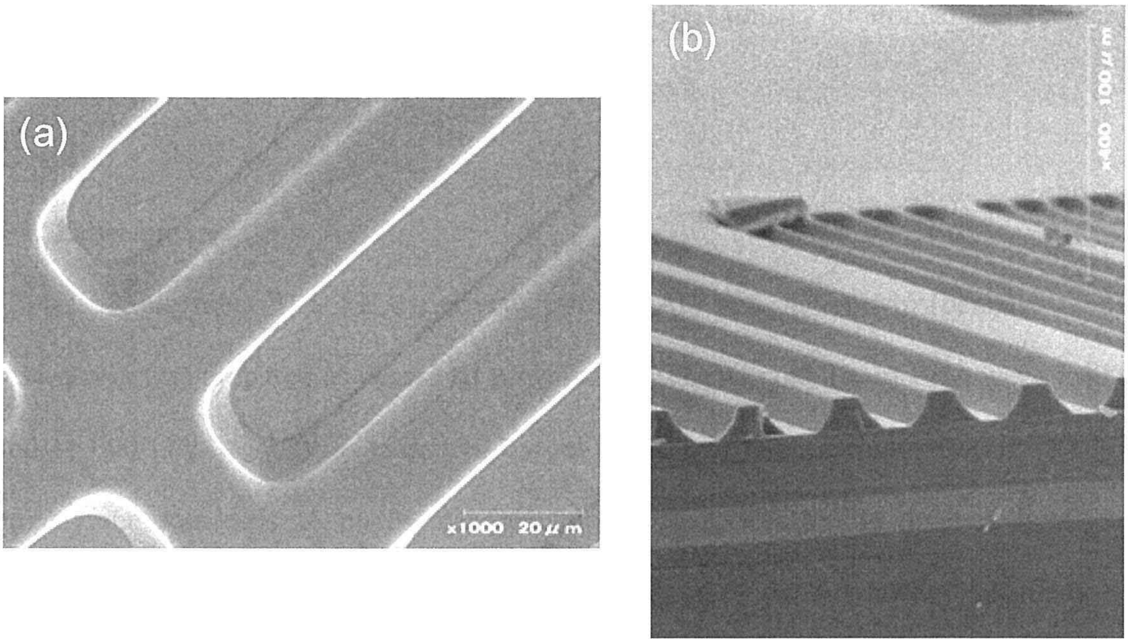


Figure 3-11. SEM image of positive-pattern 10 μm-thick film based on PHA/*t*-BocBHF/PTMA (77/20/3 wt/wt/wt); (a) top and (b) cross-section view.

3-3. Conclusion

Several *t*-Boc DIs for PSPBOs were prepared from phenolic compounds having a cardolike structure with di-*tert*-butyl dicarbonate in the presence of DMAP. Among them, *t*-Boc BHF was successfully formulated in a positive-type, alkaline-developable PSPBO based on a PHA, PAG, and PTMA. The new resist system showed high sensitivity and contrast of 34 mJ/cm^2 and 5.8, respectively, with *i*-line exposure. The clear positive image after development was converted to a PBO image by a thermal treatment. A thick pattern also was depicted with this PSPBO system. This new formulation method provides a PSPBO with high sensitivity in comparison with conventional PSPBOs with DNQ as a DI.

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Science Research (no. 18350059) from the Japanese Ministry of Education, Science, Sports, and Culture, which is gratefully acknowledged.

3-4. Experimental

3-4-1. Materials. The PHA derived from 6FAP and 4,4'-oxybis(benzoic acid) derivatives was prepared as described previously.[20] The M_n and M_w of PHA were 7,400 and 16,000 (M_w/M_n 2.2), as measured by gel permeation chromatography (GPC) with polystyrene standards. A photo-acid generator, PTMA was kindly donated by Ciba Specialty Chemicals, stored in a refrigerator, and used without further purification. Di-*tert*-butyl dicarbonate (97% purity, Aldrich), DMAP (Aldrich), cyclohexanone (Wako), cyclopentanone (Wako), and the other chemicals were used as received unless otherwise noted.

3-4-2. Synthesis of 9,9-Bis(4-*tert*-butoxycarbonyloxyphenyl)fluorene (*t*-Boc BHF). Di-*tert*-butyl dicarbonate (1.49 g, 6.84 mmol) was added to a solution of 9,9-bis(4-hydroxyphenyl)fluorene (1.00 g, 2.85 mmol) and DMAP (0.0018 g, 0.015 mmol) in THF (20 mL), and then stirred at 50 °C for 2 h. The solution was poured into methanol/H_2O (4:1 v/v) and the precipitate collected. The precipitate was recrystallized from hexane/THF (5:1 v/v) as white crystals (1.33 g, 84%). Decomposition temperature (D.P) 176 °C; IR (KBr, v, cm^{-1}): 1755 (C=O). ^{1}H NMR ($CDCl_3$, □, ppm): 7.75 (d, 2H, Ar$\underline{H}$), 7.35 (m, 4H, Ar$\underline{H}$), 7.27 (d, 2H, Ar$\underline{H}$), 7.19 (d, 4H, Ar$\underline{H}$), 7.00 (d, 4H, Ar$\underline{H}$), 1.54 (s, 18H, $COC(C\underline{H}_3)_3$). Elemental analysis: Calcd. for $C_{35}H_{34}O_6$: C, 76.34; H, 6.22; O, 17.43; Found C, 76.17; H, 6.65; N, 0.1, O, 17.08.

3-4-3. Synthesis of 1,1,1-Tris(4-*tert*-butoxycarbonyloxyphenyl)ethane (*t*-Boc THE). This compound was prepared from 1,1,1-tris(4-hydroxyphenyl)ethane (3.06 g, 10.0 mmol) and di-*tert*-butyl dicarbonate (7.85 g, 36.0 mmol) as described above. The product was recrystallized from hexane/THF (6:1 v/v) as white crystals (5.15 g, 85%); m.p. 162-163 °C. IR (KBr, *v*, cm^{-1}): 1755 (C=O). ^1H NMR ($CDCl_3$, □, ppm): 7.07 (d, 12H, ArH), 2.13 (s 3H, CH_3), 1.56 (s, 27H, $COC(CH_3)_3$). Elemental analysis: Calcd. for $C_{35}H_{42}O_9$: C, 69.29; H, 6.98; O, 23.73; Found C, 69.49; H, 7.15; O, 23.34.

3-4-4. Synthesis of 1,1'-*tert*-Butoxycarbonyl-bi-2-naphthyl (*t*-Boc BN). This compound was prepared from 1,1'-bi-2-naphthol (4.02 g, 15.0 mmol) and di-*tert*-butyl dicarbonate (7.19 g, 33.0 mmol) as described above. The product was recrystallized from hexane/toluene (1:1 v/v) as white crystals (5.72 g, 78%). D.P. 196 °C. IR (KBr, *v*, cm^{-1}): 1751 (C=O). ^1H NMR (DMSO-d_6, □, ppm): 8.16 (d, 2H, ArH), 8.07 (d, 2H, ArH), 7.58 – 7.5 (m, 4H, ArH), 7.35 (t, 2H, ArH), 7.07 (d, 2H, ArH), 1.13 (s, 18H, $COC(CH_3)_3$). Elemental analysis: Calcd. for $C_{30}H_{30}O_6$: C, 74.06; H, 6.21; O, 19.73; Found C, 74.41; H, 6.27; O, 19.32.

3-4-5. Synthesis of 5,5'6,6'-*tert*-Butoxycarbonyl-3,3,3',3'-tetramethyl -1,1'-spirobiindane (*t*-Boc TTS). This compound was prepared from 5,5'6,6'-tetrahydroxy-3,3,3',3'-tetramethyl -1,1'-spirobiindane (5.10 g, 15.0 mmol) and di-*tert*-butyl dicarbonate (14.4 g, 66.0 mmol) as described above. The product was recrystallized from hexane/toluene (1:1 v/v) as pale yellow crystals (12.6 g, 84%). D.P. 185 °C. IR (KBr, *v*, cm^{-1}): 1766 (C=O). ^1H NMR ($CDCl_3$, □, ppm): 7.02 (s, 2H, ArH), 6.70 (s, 2H, ArH), 2.30 (q, 4H, CH_2), 1.55 (s, 18H, $COC(CH_3)_3$), 1.51 (s, 18H, COC($C\underline{H}_3$)$_3$), 1.36 (s, 6H, $C\underline{H}_3$), 1.32 (s, 18H, $C\underline{H}_3$). Elemental analysis: Calcd. for $C_{41}H_{56}O_{12}$: C, 66.47; H, 7.62; O, 25.91; Found C, 67.07; H, 7.68; N, 0.08, O, 25.17.

3-4-6. Dissolution Rate. DI and PTMA were added to a PHA solution in cyclohexanone (for *t*-Boc BHF, *t*-Boc BHE) or cyclopentanone (for *t*-Boc BN, *t*-Boc TTS) to construct a photosensitive polymer. The polymer film was spin-cast from the solution (15 wt % concentration) on a silicon wafer and prebaked at 100 °C for 5 min, then exposed to a filtered super-high-pressure mercury lamp at 365 nm (*i*-line), followed by post-exposure baking at 80 – 140 °C for 5 min. The exposed film was developed with 2.38 wt% TMAHaq/5 wt% *i*-PrOH at 25 °C to determine dissolution rate (Å/sec).

3-4-7. Photosensitivity. The polymer film with 1.2 μm thickness on a silicon wafer was exposed to light at a wavelength of 365 nm, developed with 2.38 wt% TMAHaq/5 wt% *i*-PrOH at 25 °C for 10 sec, and rinsed in water. A characteristic curve was obtained by plotting normalized film thickness as a function of exposure dose (mJ/cm^2). The image exposure was obtained as a contact print.

3-4-8. Measurements. Infrared spectroscopy (IR) was done using a Horiba FT-210 spectrophotometer. The ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER GPX300 (300 MHz) spectrometer. TG was performed using a Seiko TG/DTA 6300 at a heating rate of 5 °C/min under nitrogen. M_n and M_w were determined by GPC using a Hitachi LaChrom with two polystyrene gel columns (TSK GELs; GMH_{HR}-M) at 40 °C in THF at a flow rate of 1.0 mL/min, calibrated with polystyrene standards. Film thickness on silicon wafers was measured by a Veeco Instrument Dektak^3 surface profiler. The scanning electron microscope (SEM) photos were taken with a Technex Lab Tiny SEM 1540 scanning electron microscope with 15 kV accelerating voltage for imaging.

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Chapter 4

Photosensitive Poly(benzoxazole) Based on Poly(*o*-hydroxy amide), Dissolution Inhibitor, Thermoacid Generator, and Photoacid Generator

ABSTRACT: A positive-type photosensitive polybenzoxazole (PSPBO) based on a poly(*o*-hydroxy amide) (PHA), a dissolution inhibitor (DI) 9,9-bis(4-*tert*-butoxycarbonyloxyphenyl)fluorene (*t*-Boc BHF), a thermoacid generator (TAG) isopropyl *p*-toluenesufonate (ITS), and a photoacid generator (PAG) (5-propylsulfonyloxyimino-5*H*-thiophene-2-ylidene)-(2-methylphenyl)acetonitrile (PTMA) has been developed. ITS was easily prepared by reaction of *p*-toluenesulfonyl chloride with isopropyl alcohol. The dissolution behavior of the PSPBO system was studied in relation to PTMA loadings, and post exposure baking (PEB) temperature and time. The PSPBO consisting of PHA (73 wt %), *t*-Boc BHF (18 wt %), ITS (7.5 wt %), and PTMA (1.5 wt %) exhibited a sensitivity of 33 mJ/cm^2 and a contrast of 5.1 when exposed to 365 nm light (*i*-line) and developed with an aqueous alkaline developer, 2.38 wt% tetramethylammonium hydroxide solution/2.5 wt% *iso*-propanol. A clear positive image with 3 μm features was produced by contact-printing and converted into a poly(benzoxazole) (PBO) pattern upon heating at 250 °C for 20 min. Thus, the ITS is

effective as a TAG for improving the sensitivity and low temperature cyclization of PHA into the PBO as well to meet practical requirement in the industry.

4-1. Introduction

Photosensitive polybenzoxazoles (PSPBOs)[1-5] are used as buffer coatings to protect bare chips from stresses induced by fillers or thermal mismatches between a passivation layer and molding materials. These compounds possess high mechanical strength, thermal stability, and low dielectric constants. They have been developed to simplify processes in which a precursor of polybenzoxazoles (PBOs), poly(*o*-hydroxy amide) (PHA), is used as a polymer matrix. The phenolic hydroxyl groups in PHA promote solubility of 2.38 wt% tetramethylammonium hydroxide solution (TMAHaq), used as the aqueous alkaline developer. Previously, PHA obtained from 4,4'-(hexafluoroisopropylidene)bis(*o*-aminophenol) (6FAP) and 4,4'-oxybis(benzoic acid) derivatives was used because of its high transparency at a wavelength of 365 nm (*i*-line). A conventional PSPBO was formulated by adding the photo-sensitizer diazonaphthoquinone (DNQ) to PHA.[6]

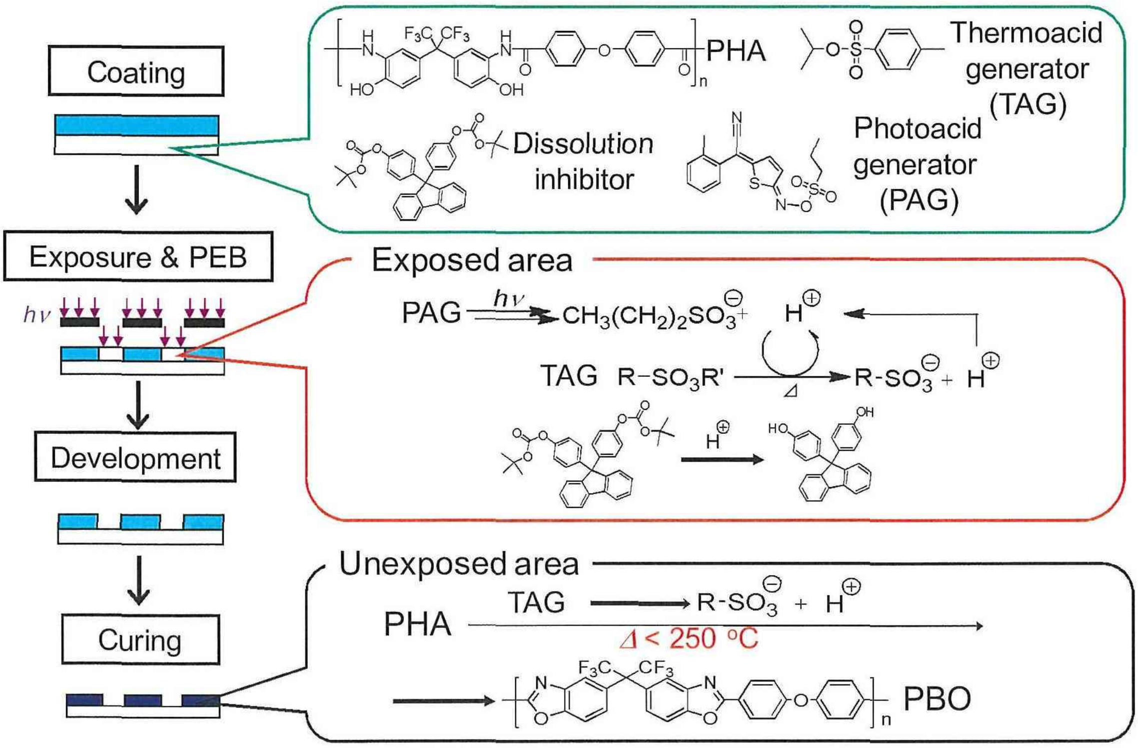
The sensitivity of photopolymers is important in the design of photoresist materials. The conventional PSPBO based on DNQ, however, possesses low sensitivity (>100 mJ/cm^2) and a strong absorbance at 365 nm, and is difficult to use for thick patterns. To overcome these problems, a chemically amplified technique was introduced to develop PSPBOs coupled with a photoacid generator (PAG),[7] for which 9,9-bis(4-*tert*-butoxycarbonyloxyphenyl)fluorene (*t*-Boc BHF) was used as a dissolution inhibitor (DI).[8] This three-component, positive-type, alkaline-developable PSPBO showed the sensitivity and contrast of 34 mJ/cm^2 and 5.8, respectively with *i*-line exposure, to produce a 20 μm image in 10 μm-thick film. A positive image of PHA is converted into that of PBO by thermal treatment at 350 °C. This high-temperature process is not applicable to conventional electronic applications containing one or more thermally unstable organic components, such as glass-epoxy resin or glass-bis(maleimide)-triazine resins that may be present in a built-up or package board. Thus, a significant decrease in the cyclization temperature of PHA allows versatile development of a PSPBO system, producing more useful applications in the microelectronics industry.

Recently, sulfonic acids were found to work as effective catalysts for low-temperature cyclization of PHA.[9] This finding was applied to develop a low-temperature curable PSPBO coupled with a PAG [5-propylsulfonyloxyimino-5*H*-thiophene-2-ylidene-(2-methylphenyl)acetonitrile] (PTMA), for which DNQ or partially *tert*-butoxycarbonyl (*t*-Boc)-protected PHA was used as the DI or polymer matrix.[10,11] The former PSPBO, however, cannot be applied for thick patterns, and *t*-Boc groups must be introduced to PHA through polymeric reactions in the latter PSPBO, which is troublesome. A more convenient method that is widely applicable and provides easy resist formulation involves a four-component system consisting of PHA, a PAG, a DI, and a thermoacid generator (TAG) based on acid-labile sulfonates.

For practical use of these acids, development of latent acid catalysts for low-temperature cyclization of PHA is more desirable. Latent catalysts are compounds stable under ambient conditions, which function only after specific external stimulation such as heating or photo-irradiation. Sulfonate derivatives are known to function as latent acid generators both by thermal treatment and photo irradiation.[12,13] Recently, Arimitsu et al. demonstrated a novel photoproliferation for a chemically amplified photoresist in order to improve the sensitivity.[14] We anticipated that such a latent thermo-sensitive acid catalyst will enhance both storage stability and processability of

PHA solutions because of non-reactivity at storage temperatures, while the cyclization of PHA is promoted within a specific range of elevated temperatures.

This report describes the successful development of an alkaline-developable, chemically amplified positive-type PSPBO based on a PHA, DI (*t*-Boc BHF), TAG (isopropyl *p*-toluenesufonate, ITS), and PAG (PTMA). A patterning process and subsequent low-temperature cyclization using PSPBO is shown in Scheme 4-1.



Scheme 4-1. Patterning process and subsequent low-temperature cyclization using positive-type PSPBO.

The formulation of PSPBO is simple, involving the addition of *t*-BocBHF, ITS, and PTMA to a PHA solution. The PSPBO solution is spin-coated and baked in the usual way. Then, the film is exposed to UV light to produce propanesulfonic acid from PTMA. Upon post-exposure bake (PEB) treatment of the PSPBO film, propanesulfonic acid catalyzes decomposition of ITS to yield propene and *p*-toluenesulfonic acid. These sulfonic acids induce a cascade of deprotection reactions of *t*-Boc BHF to produce 9,9-bis(4-hydroxyphenyl)fluorene (BHF). The exposed and baked film then can be developed with 2.38 wt% TMAHaq to provide a positive image. The subsequent low-temperature cyclization into the PBO pattern at 250 °C proceeds with *p*-toluenesulfonic acid produced from thermal decomposition of ITS. As a consequence, the direct formulation of chemically amplified PSPBO simplifies the photolithographic process, and the following thermal treatment at 250 °C will promote PSPBO for a variety of applications.

4-2. Results and Discussion

4-2-1. Synthesis of TAG. TAG is required for compatibility with PHA and good thermal stability during pre-baking treatment. It decomposes near 150 °C to produce a sulfonic acid. While TAG decomposes easily with a photo-generated acid, the sensitivity of PSPBO is improved with a small amount of PAG. To satisfy these requirements for TAG, its design was based on sulfonate compounds able to decompose thermally with the production of stable carbocation species, giving olefins and sulfonic acids. TAGs, isopropyl methanesufonate (IMS), and ITS were prepared by reaction of isopropyl alcohol with methanesulfonyl chloride and p-toluenesulfonyl chloride in the presence of pyridine in dichloromethane. DI

4-2-2. Thermal Decomposition of TAGs. The relation between the decomposition percentage of TAGs and heating time at each temperature is shown in Figures 4-1 and 4-2. The thermal decomposition behavior of TAGs was followed by ^{1}H NMR spectroscopy. IMS is stable at 100 °C, and decomposes completely upon thermal treatment at 125 °C for 20 min. At 150 °C, complete decomposition occurred within 5 min. In contrast, ITS was more stable than IMS, and decomposed completely within 10 min at 150 °C. No mixture of TAGs and the corresponding sulfonic acids was observed in the ^{1}H NMR spectra, which suggests that the thermo-generated sulfonic acid promotes decomposition of TAGs.

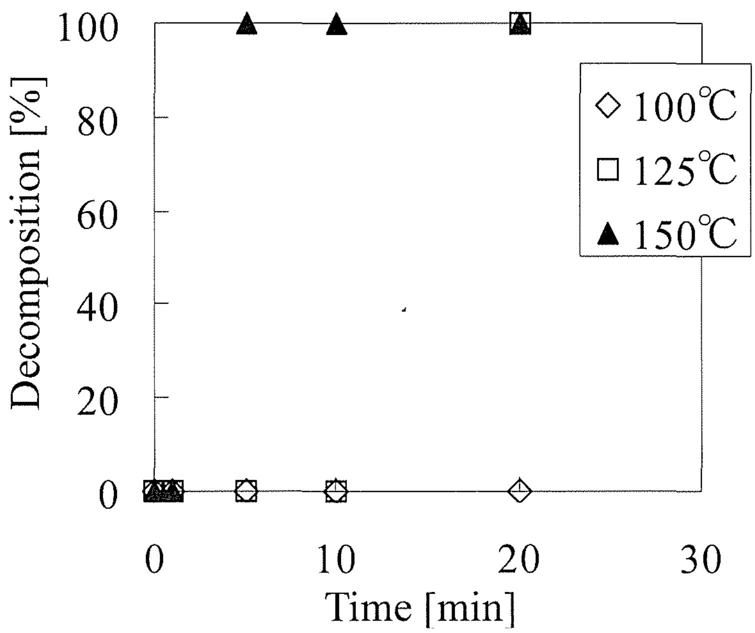


Figure 4-1. Relationship between the decomposition percentage of IMS and the heating time at each temperature.

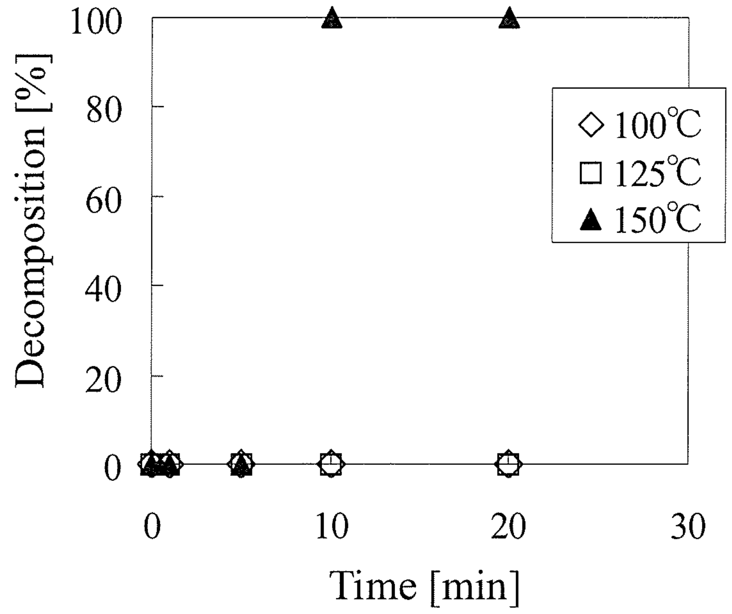


Figure 4-2. Relationship between the decomposition percentage of ITS and the heating time at each temperature.

4-2-3. Degree of Cyclization of PHA into PBO by IR Spectroscopy. The effect of TAGs on low-temperature cyclization of PHA to PBO was investigated using IR spectroscopy. The PHA solutions containing 10 wt% TAGs in 2-methoxyethanol were spin-coated on a silicon wafer, pre-baked at 100 °C for 5 min, and heated at each temperature for 15 min. A fully cured PBO film was prepared for each sample by increasing the temperature to 350 °C and then holding it for 1 h under nitrogen. IR spectra of the film are shown in Figure 4-3 after pre-baking and heating at 250 or 350 °C (as the reference). At a temperature of 250 °C or higher, the spectra exhibit characteristic absorption bands at 1045 and 1620 cm^{-1} corresponding to a benzoxazole ring. A band at 1654 cm^{-1} due to the amide group and a band near 3400 cm^{-1} due to the hydroxyl group of PHA disappear. Eventually, the IR spectrum obtained after thermal treatment at 250 °C for 15 min is identical to that of a fully cured PBO film (350 °C for

1 h). Thus, PHA is readily converted to the corresponding PBO in the presence of 10 wt% TAG. The degree of cyclization in the presence of ITS is less than that using IMS in the temperature range of 150-200 °C, but becomes greater than that using IMS above 210 °C (Figure 4-4). This behavior may be explained by high mobility at low temperatures and easy volatilization at higher temperatures of IMS compared to ITS. Based on these results, ITS was selected as the TAG for further investigation. The mechanism of acid-catalyzed cyclization involved sulfonic acid acceleration of the phenolic hydroxyl group attack on an amide carbonyl unit through protonation of the oxygen of the amide group. The degree of cyclization was calculated from the eq 1 as described in the Experimental section and is shown in Figure 4-4. An absorbance band at 1045 cm^{-1} (A_{1045}) assignable to C-O stretching of a benzoxazole group occurred in the IR spectrum upon an increase in temperature, while the band at 609 cm^{-1} (A_{609}) assignable to the silicon wafer was used as a non-interactive standard.

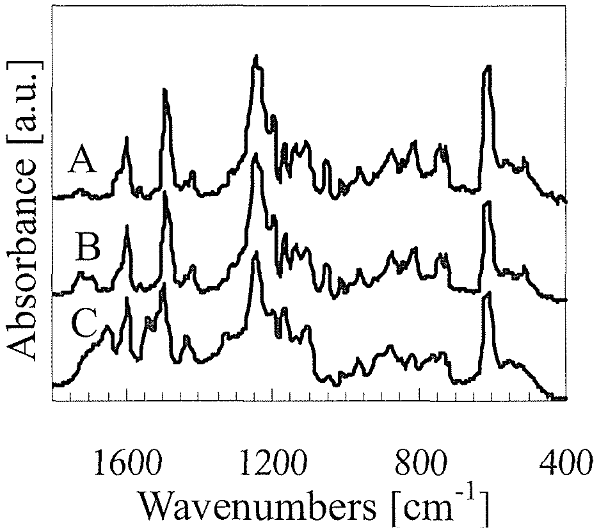


Figure 4-3. FT-IR spectra of PHA films containing 10 wt% IMS on a silicon wafer: (A) reference film baked at 350 °C for 1 h without IMS, (B) baked film at 250 °C for 15 min, (C) as-made film.

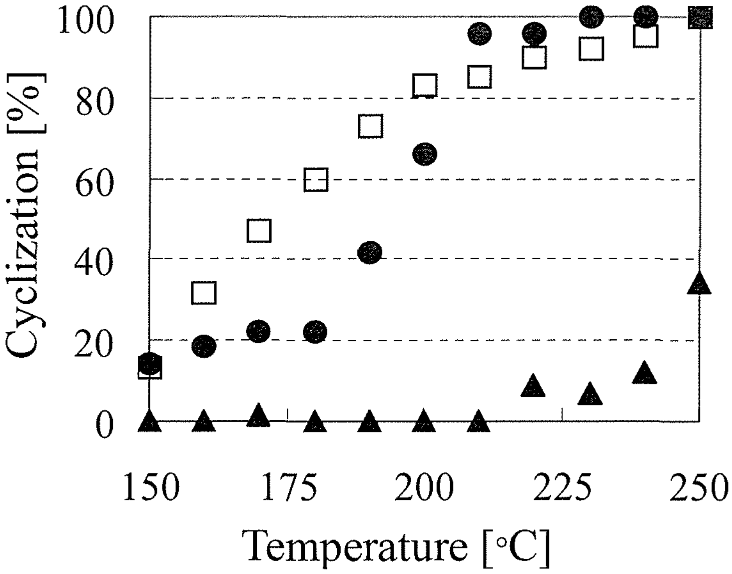


Figure 4-4. Degree of cyclization of PHA containing 10 wt% TAGs into PBO at different temperatures. IMS (□), ITS (●), and no-additive (▲).

4-2-4. Lithographic Evaluation of the PHA/DI/TAG/PAG System. The PHA matrix polymer was prepared from 6FAP and 4,4'-oxybis(benzoyl chloride) according to a method reported previously.[9] The number- and weight-average molecular weights (M_n and M_w) of PHA were 7,400 and 16,000, respectively.

Preliminary optimization studies of processing conditions and composition ratios of DI, TAG, and PAG to PHA for formulation of new PSPBOs were conducted using *t*-BocBHF and PTMA as the DI and a PAG, respectively, according to a previous report.[8] Films were obtained by spin-casting a diluted solution of PHA, DI, TAG, and PTMA in cyclohexanone on a silicon wafer, and then pre-baked at 100 °C for 5 min in air. This photosensitive polymer film was irradiated with UV light (100 mJ/cm^2) at 365 nm (*i*-line) using a filtered super-high-pressure mercury lamp, baked after exposure at a set temperature for 3 min, and developed with TMAHaq/2.5 wt% *iso*-propyl alcohol (*i*-PrOH) at 25 °C.

PEB temperature is crucial for chemically amplified resist systems because diffusion of the generated acids in the films is a key process. To clarify the dissolution behaviors of PSPBO films containing *t*-Boc BHF, ITS, and PTMA in both exposed and unexposed areas, the dissolution rate was estimated by the change in film thickness before and after development. As shown in Figure 4-5, a large difference in dissolution (dissolution contrast, DC) of approximately 800 times between the exposed and unexposed areas in 2.38 wt% TMAHaq/2.5 wt% *i*-PrOH was obtained for PEB at a temperature range of 120 °C, indicating that the photo-generated acid decomposes *t*-Boc BHF effectively to give BHF by PEB treatment. PEB temperatures greater than 130 °C may induce thermal decomposition of *t*-Boc BHF, resulting in greater solubility in 2.38 wt% TMAHaq/2.5 wt% *i*-PrOH.

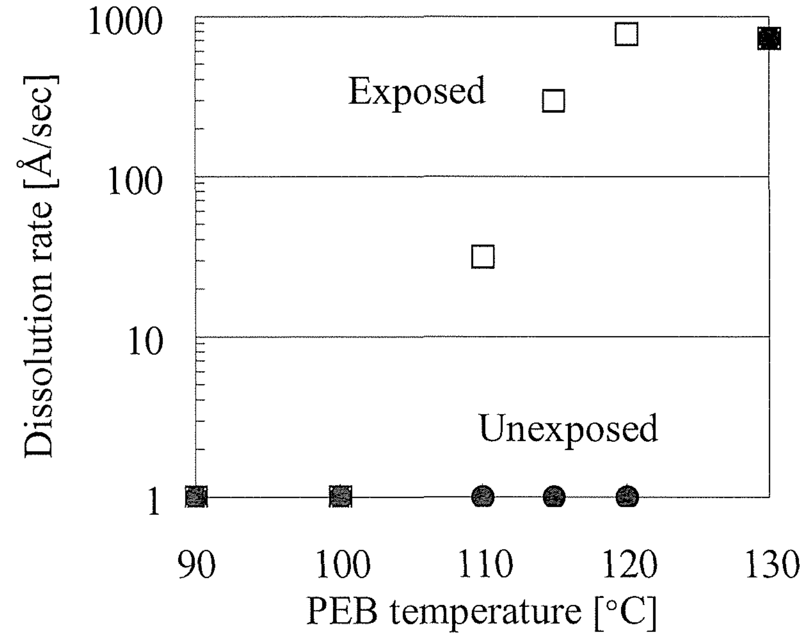


Figure 4-5. Effect of PEB temperature on dissolution rate for PHA/*t*-Boc BHF/ITS/ PTMA (73/18/7.5/1.5 wt/wt/wt/wt) resist system in exposed (□) and unexposed (●) areas. The *i*-line exposure and PEB time were fixed at 100 mJ/cm^2 and 3 min, respectively.

The effect of PEB time on dissolution rate of the film was investigated as shown in Figure 4-6. PEB times of 3-4 min were adequate to produce a large DC between exposed and unexposed areas. Further PEB treatment may induce decomposition of TAG, resulting in no DC between the exposed and unexposed areas.

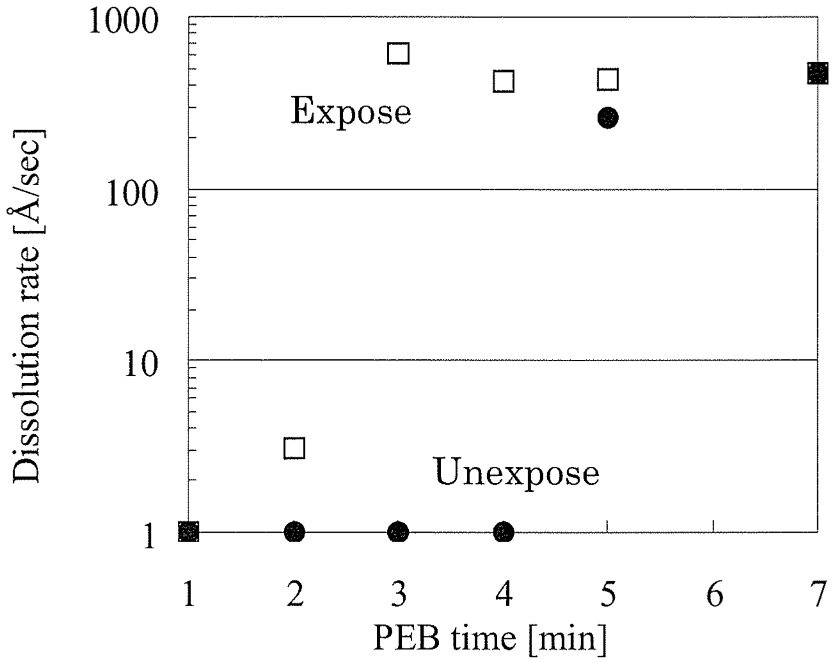


Figure 4-6. Effect of PEB time on dissolution rate for PHA/*t*-Boc BHF/ITS/ PTMA (73/18/7.5/1.5 wt/wt/wt/wt) resist system in exposed (□) and unexposed (●) areas. The *i*-line exposure and PEB temperature were fixed at 100 mJ/cm^2 and 120 °C, respectively.

The effect of PTMA loading of PSPBO on the dissolution rate of the film is shown in Figure 4-7. Even with 1wt% loading of PTMA to PSPBO, a large DC was obtained, indicating that the photo-generated acid catalyzes a cascade of ITS decomposition, followed by effective deprotection of *t*-Boc BHF by PEB.

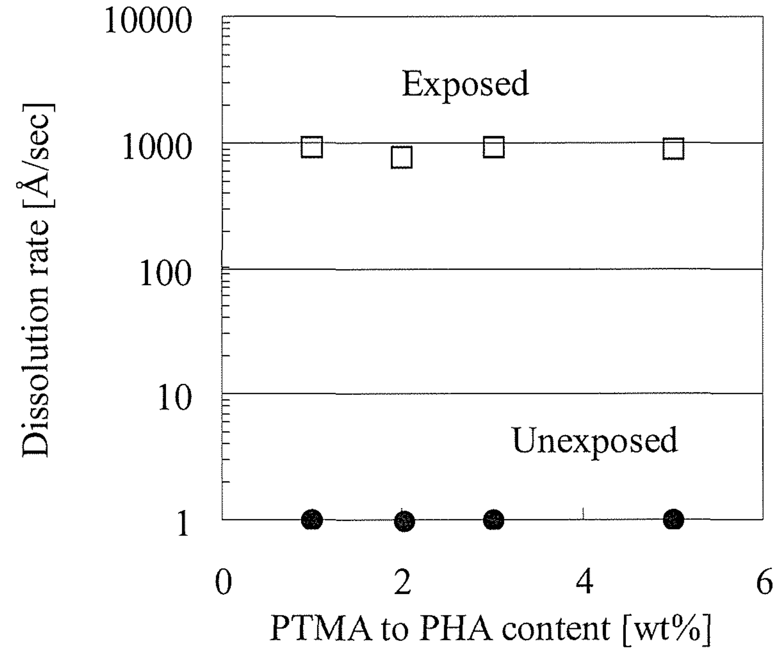


Figure 4-7. Effect of PTMA loading on PHA for dissolution rate for PHA/*t*-Boc BHF/ITS/ PTMA resist system in exposed (□) and unexposed (●) areas. The *i*-line exposure, PEB temperature, and time were 100 mJ/cm^2, 120 °C, and 3 min, respectively.

Based on the studies involving PTMA loadings, and PEB temperature and time, a PSPBO consisting of PHA (73 wt %), t-Boc BHF (18 wt %), ITS (7.5wt %), and PTMA (1.5 wt %) was formulated. The photosensitivity curve of resist films 1.2 mm thick is shown in Figure 4-8. The resist containing *t*-Boc BHF and ITS possessed outstanding sensitivity (D_0) of 33 mJ/cm^2, and good contrast (γ_0) of 5.1.

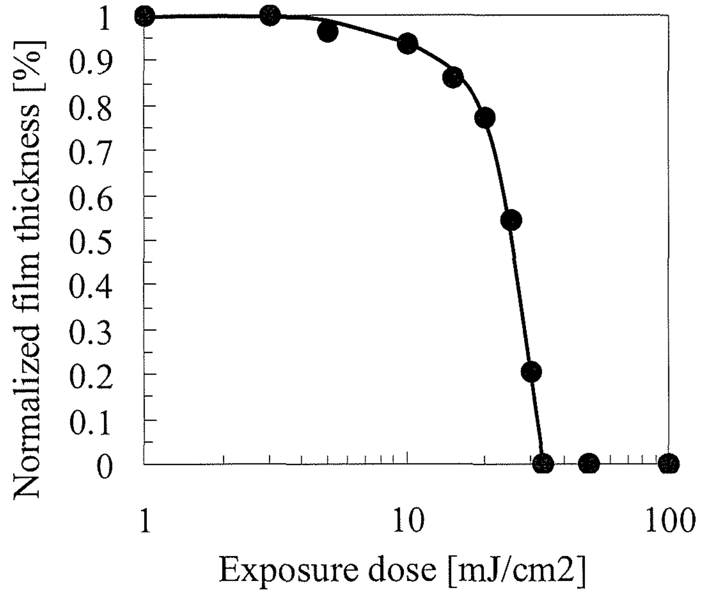


Figure 4-8. Characteristic photosensitive curve for the PHA/*t*-Boc BHF/ITS/ PTMA (73/18/7.5/1.5 wt/wt/wt) resist system. The PEB temperature and time were 120 °C and 3 min, respectively.

Figure 4-9 shows the scanning electron micrograph of a contact-printed image obtained with the system described: the resist layer was exposed to 50 mJ/cm^2, post-baked at 115 °C for 3 min, and developed with 2.38 wt% TMAHaq/2.5 wt% *i*-PrOH at 25 °C. A clear, positive pattern with a 3 μm feature was observed using a 3 μm thick film.

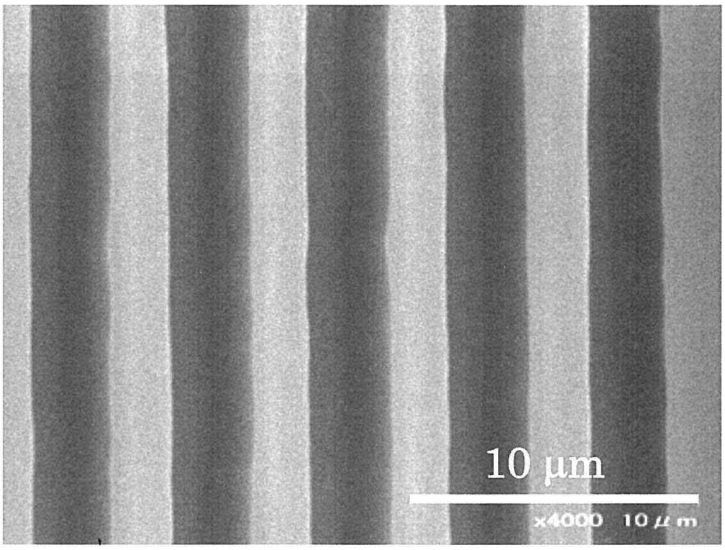


Figure 4-9. SEM image of positive-pattern 3-μm-thick film based on PHA/*t*-Boc BHF/ITS/ PTMA (70.4/21.1/7.1/1.4 wt/wt/wt/wt).

4-2-5. Low-Temperature Cyclization of PHA. The printed pattern was converted to a PBO pattern without deformation by heating at temperatures up to 150 °C for 10 min and 250 °C for 20 min under nitrogen (Figure 4-10). The formation of PBO was confirmed by IR spectroscopy, in which the characteristic oxazole ring absorption appeared at 1616 cm^{-1} and absorptions due to hydroxyl and carbonyl groups at 3300 and 1650 cm^{-1}, respectively, in the PHA spectrum disappeared.

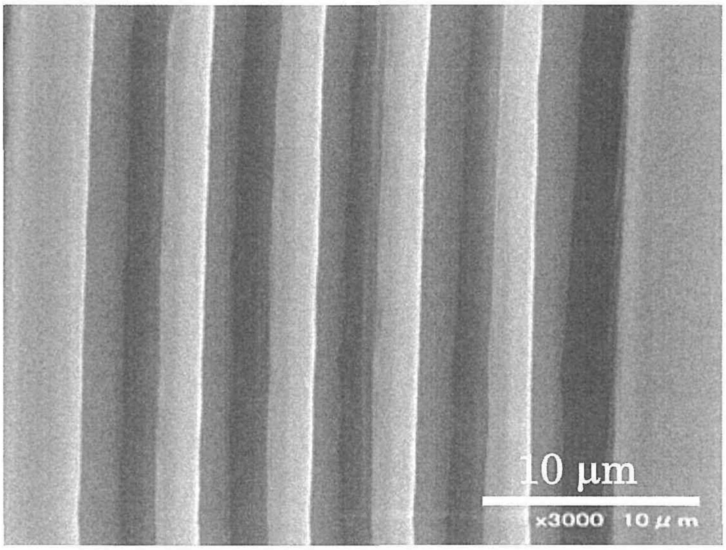


Figure 4-10. SEM image of PBO pattern cured at 250 °C for 20 min under nitrogen.

The resist system was used to produce a thick pattern. The 20-μm image was made in 10 μm thick film by PEB at 115 °C for 3 min after exposure to 70 mJ/cm^2 of *i*-line, followed by developing with 2.38 wt% TMAHaq/2.5 wt% *i*-PrOH at 25 °C for 110 s. Adequate resolution and edge sharpness can be seen in Figure 4-11.

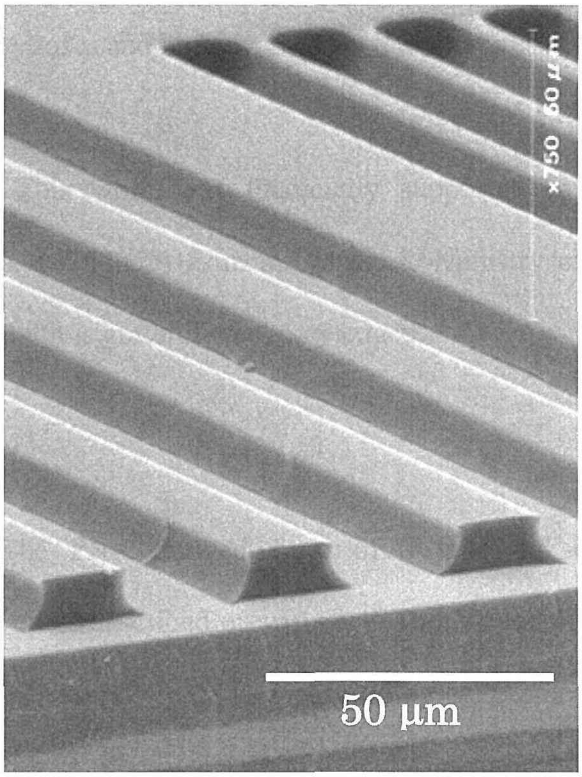


Figure 4-11. SEM image of positive-pattern 10-μm-thick film based on PHA/*t*-Boc BHF/ITS/ PTMA (70.4/21.1/7.1/1.4 wt/wt/wt/wt).

4-3. Conclusion

Two TAGs (IMS and ITS), which improve the sensitivity and transparency at the *i*-line region of PSPBO, and accomplish low-temperature cyclization of PHA to PBO, were prepared from isopropyl alcohol and methanesulfonyl chloride or *p*-toluenesulfonyl chloride. ITS satisfied the requirements for TAG, and was used for formulation of a positive-type alkaline developable PSPBO based on a PHA, *t*-Boc BHF, and PTMA.

The new resist system showed high sensitivity and contrast of 33 mJ/cm^2 and 5.1, respectively, with *i*-line exposure. Furthermore, the clear positive image after development was converted to a PBO image by low-temperature treatment. A thick pattern also was obtained with the PSPBO system. This new formulation method provides a more efficient and versatile process compared to the standard route that requires large exposure doses and high cyclization temperatures.

Acknowledgements. This work was financially supported by a Grant-in-Aid for Science Research (No. 18350059) from the Japanese Ministry of Education, Science, Sports, and Culture, which is gratefully acknowledged.

4-4. Experimental

4-4-1. Materials. The PHA derived from 6FAP and 4,4'-oxybis(benzoic acid) derivatives was prepared as described previously.[10] The M_n and M_w of PHA were 7,400 and 16,000 (M_w/M_n=2.2), respectively, as measured by gel permeation chromatography (GPC) with polystyrene standards. The photo-acid generator PTMA was donated by Ciba Specialty Chemicals and stored in a refrigerator. *t*-Boc BHF was prepared from BHF and di-*tert*-butyl dicarbonate.[8] 2-Methoxyethanol and other chemicals were used as received unless otherwise noted.

4-4-2. Synthesis of Isopropyl Methanesufonate (IMS).[15] Pyridine (8.15 mL, 100 mmol) was added dropwise over 15 min to a solution of isopropanol (3.83 mL, 50.0 mmol) and methanesulfonyl chloride (3.23 mL, 41.7 mmol) in dichloromethane (100 mL) at 0 °C. The resulting solution was stirred at 0 °C for 1.5 h, then at room temperature for 1.5 h, followed by dilution with dichloromethane (200 mL). The solution was washed successively with 1M hydrochloric acid solution and aqueous 20% potassium hydrogen carbonate solution, dried over anhydrous magnesium sulfate, filtered, and concentrated at reduced pressure using a rotary evaporator to afford oil which was distilled under reduced pressure to yield IMS (3.1 g, 53%) as a clear, colorless liquid. Infrared (IR) (KBr, ν, cm^{-1}): 1350 and 1176 cm^{-1} (-SO_3-). ^{1}H NMR ($CDCl_3$, δ, ppm): 4.98 (m, 1H, C$\underline{H}$(CH_3)$_2$), 3.02 (s, 3H,CH_3), 1.45 (d, 6H, CH(C$\underline{H}_3$)$_2$).

4-4-2. Synthesis of Isopropyl *p*-Toluenesufonate (ITS).[16] This compound was prepared from isopropanol (8 mL, 104 mmol) and *p*-toluenesulfonyl chloride (8 mL, 104 mmol) as described above. The product was a clear, colorless liquid (5.50 g, 49%). IR (KBr, ν, cm^{-1}): 1361 and 1176 cm^{-1} (-SO_3-). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.81 (d, 2H, ArH), 7.36 (d, 2H, ArH), 4.76 (m, 1H, C$\underline{H}$(CH_3)$_2$), 2.47 (s, 3H, CH_3), 1.29 (d, 6H, CH(C$\underline{H}_3$)$_2$).

4-4-3. Thermal Decomposition of TAGs. 0.5 g of IMS or ITS was placed in a flask, heated at 100, 125, and 150 °C under nitrogen for 1, 5, 10, and 20 min. The aliquot of each sample was transferred into a NMR tube, dissolved in $CDCl_3$, and the degree of the decomposition was determined from the integral ratio of the methyl group of IMS or ITS and that of the corresponding sulfonic acid.

4-4-4. Degree of Cyclization from PHA into PBO. The PHA or the photosensitive polymer film spin-casted on a silicon wafer was baked at 100 °C for 5 min as a mimic of PEB. The thickness of each film was approximately 1.2 μm. The film was heated on a hotplate at a series of temperatures from 150 to 250 °C for 15 min each. The PBO film was prepared by heating at a temperature up to 350 °C; the film was held at that temperature for 1 h under nitrogen as a reference. Absorption intensities on the IR spectrum at 1045 cm^{-1} (A_{1045}) assignable to C-O stretch of benzoxazole group and at 609 cm^{-1} (A_{609}) assignable to silicon wafer as invariable standard was obtained, and the degree of cyclization was determined using the following eq 1,[11]

$$\text{Cyclization [\%]} = (A_{1045}/A_{609\,[\text{samp}]} - A_{1045}/A_{609\,[\text{init}]})$$

$$/(A_{1045}/A_{609\,[\text{PBO}]} - A_{1045}/A_{609[\text{init}]}) \times 100, \quad (1)$$

where the subscripts between the brackets following A_{1045}/A_{609} indicate the state of the film; e.g., [samp] is the polymer sample at each heating temperature level (150-250 °C); [init] is initially pre-baked polymer film at 110 °C in air; [PBO] is the fully cured PBO at 350 °C for 1 h under nitrogen.

4-4-5. Dissolution Rate. DI, TAG, and PTMA were added to a PHA solution in cyclohexanone to construct a photosensitive polymer. The polymer film was spin-casted from the solution (15 wt% concentration) on a silicon wafer and prebaked at 100 _C for 5 min, then exposed to a filtered super-high-pressure mercury lamp at 365 nm (*i*-line), followed by post-exposure baking at 80-140 °C for 3 min. The exposed film was developed with 2.38 wt% TMAHaq/2.5 wt% *i*-PrOH at 25 °C to determine dissolution rate (Å /sec).

4-4-6. Photosensitivity. The polymer film of 1.2-μm thickness on a silicon wafer was exposed to light at a wavelength of 365 nm, developed with 2.38 wt% TMAHaq/2.5 wt% *i*-PrOH at 25 °C for 33 s, and rinsed in water. A characteristic curve was obtained by plotting normalized film thickness as a function of exposure dose (mJ/cm^2). The image exposure was obtained as a contact print.

4-4-7. Measurements. IR spectra were obtained using a Horiba FT-720 spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker GPX300 (300 MHz) spectrometer. M_n and M_w were determined by GPC using a Hitachi LaChrom with two polystyrene gel columns (TSK GELs; GMHHR-M) at 40 °C in tetrahydrofuran (THF) at a flow rate of 1.0 mL/min, calibrated with polystyrene standards. The film thickness on silicon wafers was measured with a Veeco Instrument Dektak^3 surface profiler. Scanning electron microscope (SEM) photos were taken with a Technex Lab Tiny SEM 1540 instrument with 15 kV accelerating voltage for imaging. Pt/Pd was spattered on a film prior to obtaining the SEM pictures.

4-5. References and Notes

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Chapter 5

Facile Synthesis of Semi-aromatic Poly(amic acid)s from *trans*-1,4-Cyclohexanediamine and Aromatic Tetracarboxylic Dianhydrides

ABSTRACT: A facile synthetic method to give semi-aromatic poly(amic acid)s (PAAs) with high molecular weights from *trans*-1,4-cyclohexyldiamine (CHDA) and aromatic tetracarboxylic dianhydrides has been developed. The polymerization of CHDA and various aromatic tetracarboxylic dianhydrides was preceded smoothly in the presence of acetic acid at room temperature, giving PAAs with higher inherent viscosities compared with the corresponding polymerization in the absence of acetic acid.

5-1. Introduction

Polyimides (PIs) are a class of polymers used extensively in a variety of industrial fields because of the excellent properties such as high thermoxidative stability, high mechanical strength, excellent electrical properties, and high chemical resistance. In the electronics applications they 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.[1] PIs are generally prepared by thermal or chemical imidization of poly(amic acid)s (PAAs), which are synthesized from aromatic diamines and aromatic tetracarboxylic dianhydrides in solutions. Recently, much attention has been paid to semi-aromatic PIs with high transparency and low dielectric constant in the application as optoelectronics and interlayer dielectric materials.[2] Formation of inter- or intramolecular charge-transfer complexes, which increases the dielectric constant and lowers the transparency, will be reduced by introducing alicyclic structures. Moreover, a bulky alicyclic unit effectively decreases a molecular density, giving a semiaromatic PI with a lower dielectric constant.[3] Semi-aromatic PIs are easily prepared from aromatic diamines and alicyclic tetracarboxylic dianhydrides.2 On the other hand, the synthesis of semi-aromatic PIs from aromatic tetracarboxylic dianhydrides and aliphatic or alicyclic diamines is rather difficult.[4] The carboxylic acids of PAAs form salts or gels with aliphatic or alicyclic diamines because the basicity of aliphatic or alicyclic diamines (pK_a of the ammonium ion: 10.7) is much higher than that of aromatic diamines (pK_a of the ammonium ion: 4.6). This salt formation and gelation prevents the formation of high-molecular-weight PAAs. Several techniques involving a high-temperature polymerization[5] and a N-silylation method[6] have been reported to avoid the formation of salt in the synthesis of PAAs. However, the high-temperature polymerization is not versatile, and in the latter case the silyl residues are usually remained in the final compounds even after the thermal treatment, which limits this method for the electronics applications. Therefore, an alternative method to prepare high-molecular-weight PAAs from aromatic tetracarboxylic dianhydrides and aliphatic or alicyclic diamines is still challenging to expand the scope of PIs.

Generally speaking, a salt formed from a strong base and a weak acid acts as a weak base in a solution. Thus, we expected that the polymerization of aromatic tetracarboxylic dianhydrides with aliphatic or alicyclic diamines would proceed when the resulting salts are dissolved in solutions. The salts from aliphatic or alicyclic diamines and monocarboxylic acids such as acetic acid would have higher solubility in organic solvents than those from aliphatic or alicyclic diamines and PAAs.

In this paper, we report a successful synthetic method of high-molecular-weight semiaromatic PAAs from aromatic tetracarboxylic dianhydrides and *trans*-1,4-cyclohexyldiamine (CHDA) in the presence of acetic acid. It is well-known that the polymerization of aromatic tetracarboxylic acids with CHDA is completely inhibited by the salt formation between PAAs and CHDA.[4,5] Therefore, CHDA was selected as an alicyclic diamine. Our method usually gives PAAs with higher inherent viscosities compared with the conventional low-temperature solution polymerization of CHDA with aromatic tetracarboxylic dianhydrides.

5-2. Results and Discussion

5-2-1. Selection of Monocarboxylic Acids. As monocarboxylic acids, bromoacetic acid, benzoic acid, and acetic acid were selected. The polymerization of 4,4'-biphthalic anhydride (BPDA) with CHDA was carried out in *N,N*-dimethylacetamide (DMAc) in the presence of these monocarboxylic acids at room temperature for 6 h (Figure 5-1). The acidity of monocarboxylic acids and the results of the polymerization are summarized in Table 5-1. No polymer was obtained without monocarboxylic acids, which indicates the salt from the PAA and CHDA is not soluble in DMAc at room temperature. The polymer with sufficiently high viscosity is obtained in the presence of benzoic acid and acetic acid. On the other hand, bromoacetic acid afforded the polymer with a moderate viscosity because the formation of the resulting salt has a weaker nucleophilicity compared to that of the salts from benzoic acid and acetic acid.

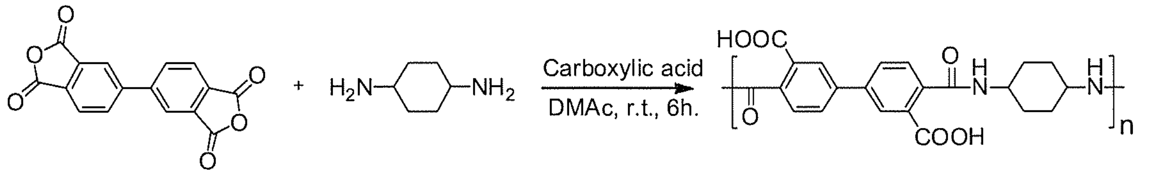

Figure 5-1. Synthesis of semiaromatic PAA consisting of BPDA and CHDA.

Table 5-1. Preparation of PAA from BPDA and CHDA in the presence of various of monocarboxylic acids.[a]

Acid	Bromoacetic acid	Benzoic acid	Acetic acid	No additive
pK_a	2.90	4.20	4.76	-
Inherent viscosity [dL/g][b]	0.40	0.96	1.26	-

[a] Polymerization was carried out with 1.0 mmol of each monomer and 2.2 mmol of the acid in DMAc (15 wt %) at room temperature for 6 h.

[b] Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

5-2-2. Change of Molecular Weight with Time. To investigate the solution stability of the resulting PAA, the polymerization of BPDA with CHDA was carried out in DMAc in the presence of acetic acid at room temperature, and the inherent viscosities (η_{inh}) of PAA was monitored at the set time (Figure 5-2). The heterogeneous solution of the CHDA–acetic acid salt is turned into the viscous and homogeneous solution in 30 min after BPDA was added. Then the η_{inh} of PAA decreases as the time passes and becomes a constant value in 30 h. This slow decrease of the viscosity is explained by the equilibrium reaction between PAA and the corresponding anhydride and amine in the solution and has been observed in all kinds of aromatic PAAs.[7]

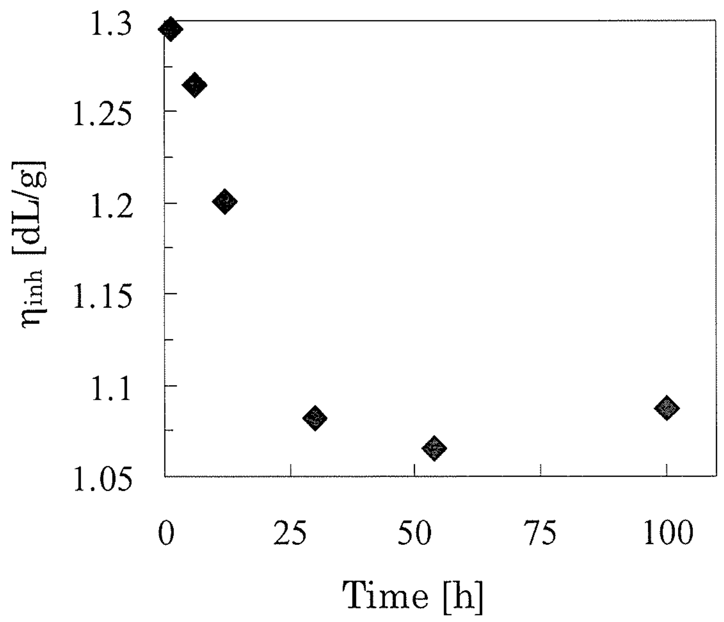

Figure 5-2. Viscosity change of PAA solution in DMAc.

5-2-3. Amounts of Acetic Acid. The polymerization of BPDA with CHDA was carried out in DMAc in the presence of various amount of acetic acid at room temperature for 6 h, and the each η_{inh} of PAAs is summarized in Table 5-2. The polymerization does not proceed in the presence of 0.5 equiv of acetic acid for CHDA because the salt formation of CHDA with PAA occurs. A high-molecular-weight PAA is obtained when more than 1 equiv of acetic acid is used. These results suggest that acetic acid more than 1 equiv to CHDA is required to suppress the salt formation from PAA and CHDA. However, the excess amount of the acid interferes with the polymerization, resulting in a rather low viscous polymer. Acetic acid is not good solvent for PAA; thus, a large amount of acetic acid prevents the homogeneous polymerization and gives the low-molecular-weight PAA.

Table 5-2. Effect of the amount of acetic acid on the polymerization of BPDA with CHDA.[a]

Acetic acid [equiv.]	0.5	1.0	2.2	4.0	8.0
Inherent viscosity [dL/g][b]	-	1.20	1.26	0.88	0.63

[a] Polymerization was carried out with 1.0 mmol of each monomer in DMAc (15 wt %) at room temperature for 6 h.

[b] Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

5-2-4. Polymerization with Other Aromatic Tetracarboxylic Dianhydrides. To investigate the versatility of our new method, the polymerization of other dianhydrides such as 4,4'-oxydiphthalic anhydride (ODPA), 3,3',4,4'-benzophenonetetracarboxylic anhydride (BTDA), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) with CHDA was carried out in the presence of acetic acid. Table 5-3 summarizes the results of the polymerization. In all of the cases, acetic acid acts as an inhibitor for the salt formation between the carboxylic acids of PAAs with CHDA in monomers or oligomers, resulting in higher-molecular-weight PAAs compared with the conventional solution polymerization.

Table 5-3. Preparation of PAAs from various tetracarboxylic dianhydrides and CHDA in the presence of acetic acid.[a]

Aromatic tetracarboxylic dianhydride	Additive [dL/g][b]	
	none	Acetic acid
BPDA	-	1.26
BTDA	0.47	1.55
ODPA	0.63	0.98
6FDA	0.50	1.63

[a] Polymerization was carried out with 1.0 mmol of each monomer and 2.2 mmol of acetic acid in DMAc (15 wt %) at room temperature for 6 h.

[b] Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

5-3. Conclusion

A new synthetic method to produce semi-aromatic PAAs with high molecular weights from CHDA and aromatic tetracarboxylic dianhydrides has been developed. The polymerization of the organic salt consisting of CHDA and acetic acid with various aromatic tetracarboxylic dianhydrides was carried out and gave PAAs with high inherent viscosities compared with the polymerization of CHDA with aromatic tetracarboxylic dianhydrides in the absence of acetic acid. This new method can be applied for the PAA synthesis from aliphatic or alicyclic diamines with aromatic tetracarboxylic dianhydrides on an industrial scale.

5-4. Experimental

5-4-1. Materials. CHDA (mp 72–73 °C) purchased from Tokyo Chemical Industry Co., Ltd., was purified by recrystallization from hexane and dried in vacuo at room temperature for 24 h before use. BPDA (mp 299 °C by DTA), ODPA (mp 226–227 °C), BTDA (mp 223–224 °C), and 6FDA (mp 247–248 °C) purchased from Tokyo Chemical Industry Co., Ltd., were purified by recrystallization from acetic anhydride and dried in vacuo at 160 °C for 24 h before use. DMAc was purified by vacuum distillation. The structures of the monomers used are shown in Figure 5-3. The inherent viscosities (η_{inh}) of the PAAs were measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

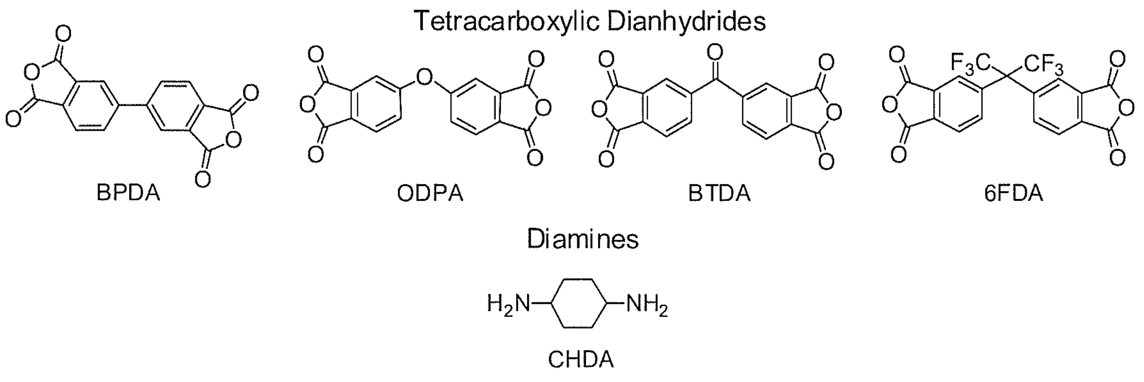

Figure 5-3. Structures and abbreviations of monomers.

5-4-2. Typical Polymerization Procedure. CHDA (0.114 g, 1.00 mmol) was charged in a 5 mL vial pot at 70 °C and dissolved in DMAc to adjust the concentration of 15 wt %. The solution was cooled down to room temperature, and then acetic acid (0.132 g, 2.20 mmol) was slowly added. After 10 min, a solid aromatic tetracarboxylic dianhydride (1.00 mmol) was added into the solution, and the solution was stirred at room temperature for the set time. The η_{inh} of the PAAs were measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

5-5. References and Notes

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Chapter 6

Low-*CTE* Photosensitive Polyimide Based on Semi-alicyclic Poly(amic acid) and Photobase Generator

ABSTRACT: A negative-type photosensitive polyimide (PSPI) based on semi-alicyclic poly(amic acid) (PAA), poly(*trans*-1,4-cyclohexylenediphenylene amic acid), and {[(4,5-dimethoxy-2-nitrobenzyl)oxy]carbonyl} 2,6-dimethylpiperidine (DNCDP) as a photobase generator has been developed as a next generation buffer coat material. The semi-alicyclic PAA was synthesized from 3,3',4,4'-biphenyltetracarboxylic dianhydride and *trans*-1,4-cyclohexyldiamine in the presence of acetic acid, and the PAA polymerization solution was directly used for PSPI formulation. This PSPI, consisting of PAA (80 wt%) and DNCDP (20 wt%), showed high sensitivity of 70 mJ/cm^2 and high contrast of 10.3, when it was exposed to a 365 nm line (*i*-line), post-exposure baked at 190 °C for 5 min, and developed with 2.38 wt% tetramethylammonium hydroxide aqueous solution containing 20 wt% *iso*-propanol at 25 °C. A clear negative image of 6 μm line and space pattern was printed on a film which was exposed to 500 mJ/cm^2 of *i*-line by a contact printing mode and fully converted to poly(*trans*-1,4-cyclohexylenebiphenylene imide) pattern upon heating at 250 °C for 1 h. The PSPI film had a low coefficient of thermal expansion of 16 ppm/K compared to

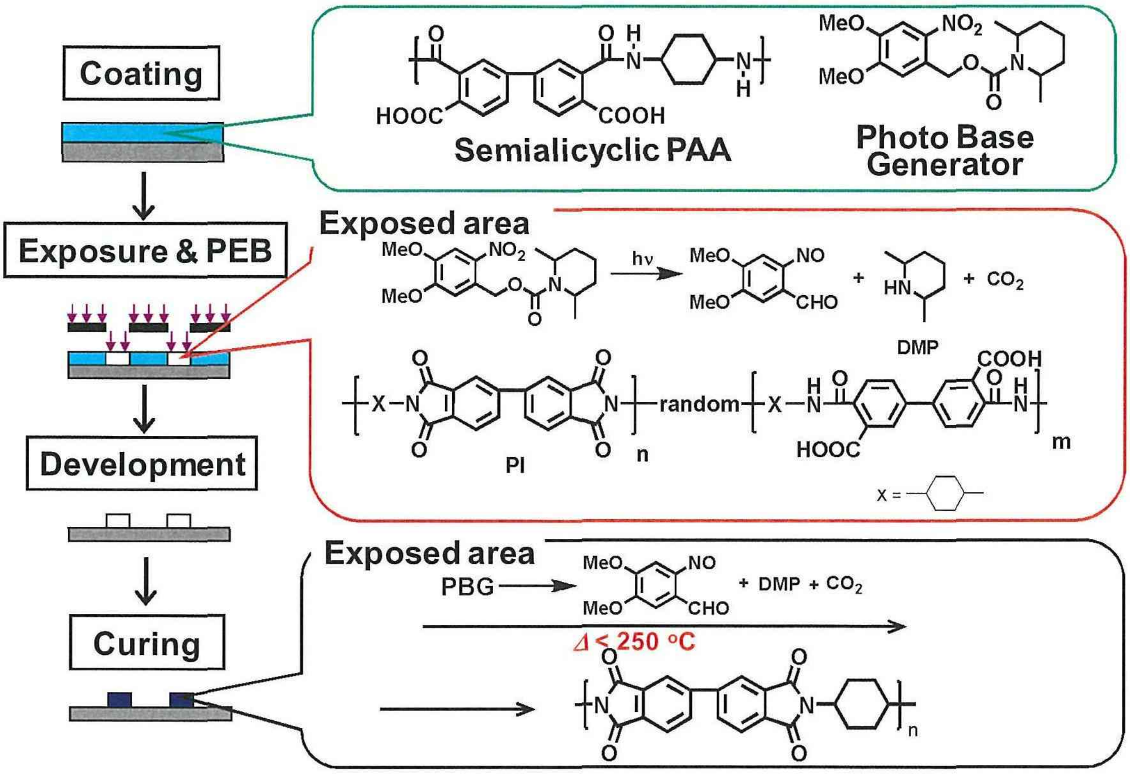
typical PIs, such as prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride and 4,4'-oxydianiline.

6-1. Introduction

Polyimides (PIs) have been widely studied as insulating materials,[1,2] optical applications,[3,4] and piezoelectric materials.[5] Moreover, photosensitive PIs (PSPIs) have been used in the semiconductor industry as interlevel insulators, buffer coat materials, α-ray shielding layers, and so on, because of their excellent thermal stability, high mechanical properties, and relatively low dielectric constants. Furthermore, they simplify processing and avoid the use of photoresist in the microelectric industry.[6-23] The commercially available PSPIs usually consist of poly (amic acid) (PAA) derivatives with methacryloyl pendant groups as cross-linking sites.[6,7] However, PSPIs are further expected to improve their performance with the increase developments in the semiconductor industry. For examples, a chemically amplified system in PSPI has been introduced to show high sensitivity,[16] Kim and coworkers reported a positive-working PSPI which can be developed in alkaline aqueous solution.[22]

Recently, silicon substrates are stacked in a memory chip to achieve high-density packaging, and those in multi-chip packages are thinner than the usual ones due to fitting them in the traditional packaging size.[24] Future PSPIs as buffer coat materials require a lower imidization temperature because high-temperature curing causes warpage of thinner silicon wafers. In previous works, we have developed several PSPIs which can be imidized at low temperature.[25,26] However, the matrix polymer of these PSPIs is a PAA prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA), which has a relatively high coefficient of thermal expansion (*CTE*). Therefore, these PSPIs have limitations in reducing thermal strain even at low curing temperature and PSPIs using low-*CTE* polyimides (PIs) are highly demanded. Although low-*CTE* PIs can be obtained from monomers having rigid structures, PI films prepared from BPDA and 1,4-phenylenediamine, for example, are brittle due to their rigidity, arising a difficulty to apply them to PSPIs.

Hasegawa and coworkers reported the properties of poly(*trans*-1,4-cyclohexylenebiphenylene imide) prepared from BPDA and *trans*-1,4-cyclohexyldiamine (CHDA), which showed high thermal stability, a low-dielectric constant, high transparency and low *CTE* because of its rigid and semi-alicyclic structure.[27,28] Moreover, the film formed from a highly viscous poly(*trans*-1,4-cyclohexylenebiphenylene amic acid) solution was flexible, which is suitable for a PSPI system. Accordingly, PAA from BPDA and CHDA is excellently suitable to a matrix polymer of PSPI, which can resolve the warpage of thinner silicon wafers. As PAAs can be imidized at low temperature in the presence of a base catalyst,[25] a PSPI could be constructed using the polymerization solution of PAA from BPDA and CHDA with a photobase generator (PBG). In this paper, we report a low-*CTE* PSPI based on semi-alicyclic PAA, prepared from BPDA and CHDA, as a matrix polymer and {[(4,5-dimethoxy-2-nitrobenzyl)oxy]carbonyl} 2,6-dimethylpiperidine (DNCDP) as a PBG. The patterning process of this PSPI is shown in scheme 6-1. The PSPI resist solution is spin-coated on a silicon wafer and prebaked. The film is exposed to a 365 nm line (*i*-line) through a photomask to produce 2,6-dimethyl piperidine (DMP) from DNCDP. Upon PEB treatment of the PSPI film, DMP catalyzes the imidization of PAA. The dissolution rate of the exposed area to 2.38 wt% tetramethylammonium hydroxide aqueous solution (TMAHaq) containing 20 wt% *iso*-propanol (*i*PrOH) decreases and a negative pattern is formed. Finally, partial PI film is converted to complete PI film by thermal treatment at 250 °C This pattern formation method provides a versatile process, such as direct resist formulation from a varnish of the PAA, base-catalyzed low-temperature imidization, and low-*CTE* PI film preparation for buffer coat materials.

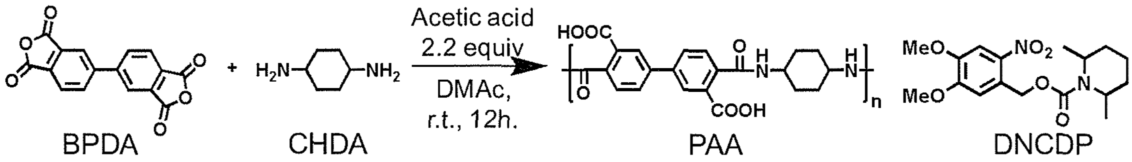


Scheme 6-1. Patterning process of Low *CTE* PSPI.

6-2. Results and Discussion

6-2-1. Synthesis of PAA from BPDA/CHDA. Generally, it is rather difficult to prepare semi-alicyclic PAAs from aromatic dianhydrides and alicyclic diamines. The carboxylic acids of PAAs easily generate salts or gels with alicyclic diamines because the basicity of alicyclic diamines (p*K*a of the ammonium ion: 10.7) is much higher than that of aromatic diamines (p*K*a of the ammonium ion: 4.6). This ionic interaction prevents the synthesis of PAAs. We previously reported a facile method for the synthesis of PAA from BPDA and organic salts consisting of CHDA and acetic acid.[29] This polymerization proceeded in homogeneous state without gel formation and yielded

PAA with high molecular weight. The synthetic scheme of PAA from BPDA and CHDA, and the structure of DNCDP are shown in scheme 6-2. The inherent viscosity of PAA was intentionally set as low as 0.24 dL/g so that high dissolution contrast was expected. The PAA polymerization solution containing acetic acid was directly used for the PSPI formulation.



Scheme 6-2. Structures of BPDA/CHDA PAA and DNCDP.

6-2-2. Lithographic Evaluation. PSPI was formulated by mixing the PAA polymerization solution with DNCDP, as shown in Scheme 6-1.To clarify the dissolution rate between the exposed and unexposed areas to 2.38 wt% TMAHaq containing 20 wt% *i*PrOH, the effects of DNCDP loading, PEB temperature, PEB time and exposure dose were investigated. The PSPI films were obtained by spin-casting on a silicon wafer, and then pre-baking at 100 °C for 5 min in air. These PSPI films were irradiated with UV light at *i*-line using a filtered super high-pressure mercury lamp, PEB at a set temperature for a prescribed period of time, and developed with 2.38 wt% TMAHaq containing 20 wt% *i*PrOH at 25 °C. The partially imidized PAA by the PEB process at the exposed area was slightly soluble in 2.38 wt% TMAHaq. To reduce the solubility of the partial imidized PAA, 20 wt% *i*PrOH was added to 2.38 wt% TMAHaq solution. The dissolution rate was estimated from the change in the film thickness before and after development.

First, the effect of DNCDP loading on the dissolution rate of the film was investigated (Figure 6-1), where each film was prebaked at 100 °C for 5 min, exposed to 500 mJ/cm^2, and then PEB at 190 °C for 5 min. The dissolution rate of the exposed area becomes almost zero in the case of 20 wt% DNCDP loading, and the dissolution contrast (DC) between the exposed and unexposed areas in 2.38 wt% TMAHaq containing 20 wt% *i*PrOH reaches 3000 times. It should be mentioned that the low-temperature imidization at the exposed area was not affected by acetic acid, because most acetic acids might be evaporated in the pre-baking process. Moreover, DNCDP did not decompose by the PEB process, because it was stable up to 250 °C.[9]

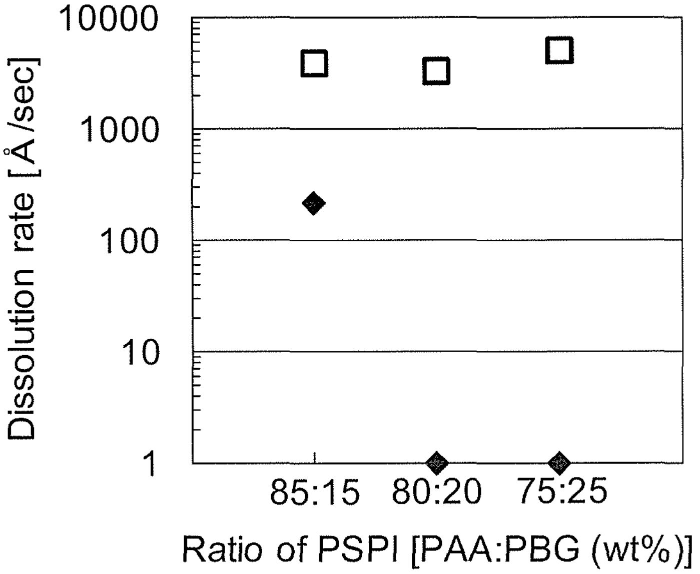


Figure 6-1. Effect of DNCDP loading to PAA on the dissolution rate for the resist system under exposed (◆) and unexposed area (□). The pre-bake, the *i*-line exposure and PEB conditions were fixed to 100 °C for 5 min, 500 mJ/cm^2 and at 190 °C for 5 min, respectively.

The PEB temperature is a very important parameter for this PSPI system, because the degree of imidization depends strongly on the curing temperature. PSPI consisting of PAA (80 wt%) and DNCDP (20 wt%) was formulated, and then the effect of PEB temperature on the dissolution rate was investigated (Figure 6-2). A large DC between the exposed and unexposed areas is observed and reaches 3000 times at 190 °C. The DI at each temperature is summarized in Table 6-1. PAA film with over 34% imidization does not dissolve in 2.38 wt% TMAHaq containing 20 wt% *i*PrOH. The DI at the unexposed area also increases with increasing the PEB temperature, and the dissolution rate at the unexposed area decreases.

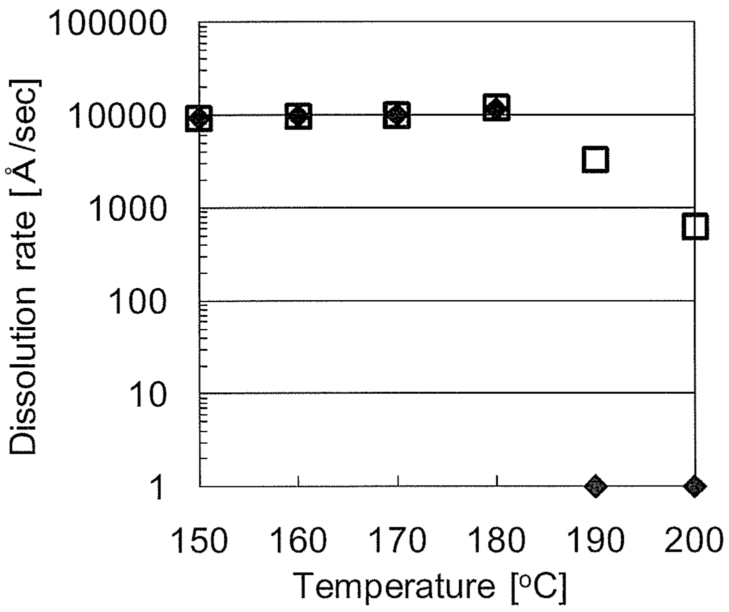


Figure 6-2. Effect of PEB temperature on the dissolution rate for the PAA/DNCDP (80/20 w/w) resist system under exposed (◆) and unexposed area (□). The pre-bake, the *i*-line exposure and PEB time were fixed to 100 °C for 5 min, 500 mJ/cm^2 and for 5 min, respectively.

Table 6-1. The degree of imidization at each PEB temperature. [a]

Temperature [°C]	150	160	170	180	190	200
Exposed area	2	3	8	12	34	54
Unexposed area	0	0	2	6	13	24

[a] Conditions preparation of PSPI films: The resist films (PAA/DNCDP, 80/20 (w/w)) was pre-baked at 100 °C, exposed the *i*-line at 500 mJ/cm^2, post-exposure baked at the set temperature for 5min. The degree of imidization was calcurated by eq (1).

In a similar way, the effect of PEB time on the dissolution rate was investigated under the same condition (Figure 6-3). The dissolution rate at the exposed area gradually decreased with increasing the PEB time, and became almost zero under condition of 5 min PEB time. Table 6-2 shows the DI at each PEB time. It indicates that a small difference in the degree of imidization strongly affects on the dissolution rate.

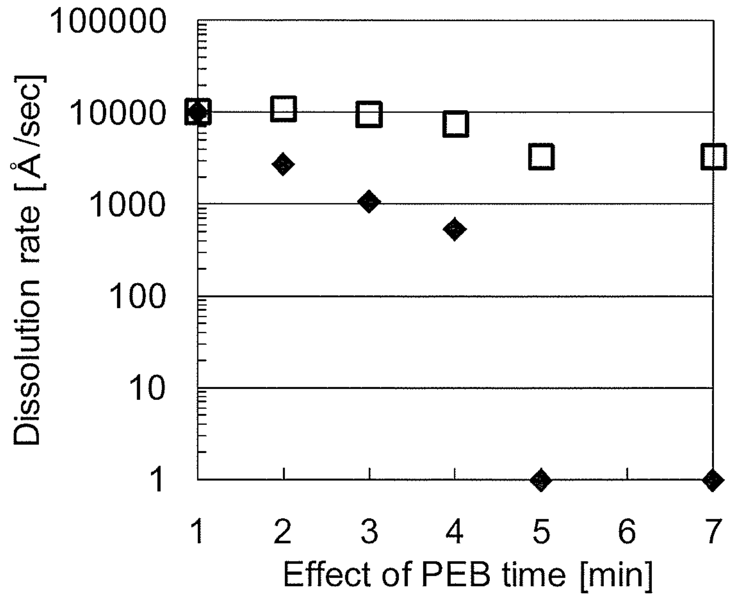


Figure 6-3. Effect of PEB time on the dissolution rate for the PAA/DNCDP (80/20 w/w) resist system under exposed (◆) and unexposed area (□). The pre-bake, the *i*-line exposure and PEB temperature were fixed to 100 °C for 5 min, 500 mJ/cm^2 and at 190 °C, respectively.

Table 6-2. The degree of imidization at each PEB time. [a]

Time [min]	1	2	3	4	5	7
Exposed area	8	18	23	29	34	37
Unexposed area	3	5	9	11	13	17

[a] Conditions preparation of PSPI films: The resist films (PAA/DNCDP, 80/20 (w/w)) was pre-baked at 100 °C, exposed the *i*-line at 500 mJ/cm^2, post-exposure baked at 190 °C for the set time. The degree of imidization was calcurated by eq (1).

Based on these preliminary optimization studies, PSPI containing PAA (80 wt%) and DNCDP (20 wt%) was formulated. The photosensitivity curve of the resist film with 1.7 μm-thick film is shown in Figure 6-4. This resist has excellent sensitivity (D_0) of 70 mJ/cm^2 and high contrast ($\square_0$) of 10.3 with *i*-line exposure. These findings indicate that a photogenerated DMP effectively catalyses the imidization of PAA by PEB treatment, producing a large DC between the exposed and unexposed areas.

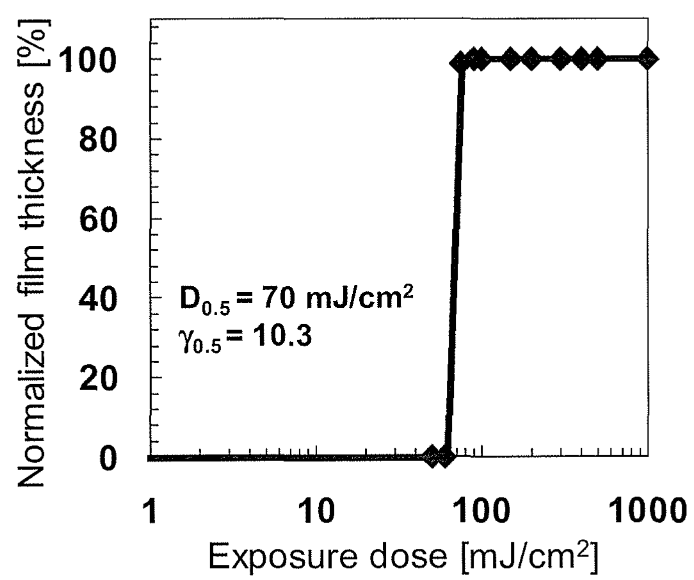


Figure 6-4. Characteristic photosensitive curve for the PAA/DNCDP (80/20 w/w) resist system in 1.7 μm film thickness. The pre-bake and PEB were fixed to 100 °C for 5 min and at 190 °C for 5 min, respectively.

6-2-3. Low-Temperature Imidization of PSPI. To conduct the complete imidization of this PSPI, PSPI solution containing PAA (80 wt%) and DNCDP (20 wt%) was spin-coated on a silicon wafer, pre-baked on a hotplate at 100 °C for 20 min, and then post-exposure baked at each temperature (110~250 °C) for 20 min after exposure to 500 mJ/cm^2 of *i*-line. A reference PI film was also prepared by heating at 350 °C for 1 h under nitrogen. Figure 6-5 shows the DI of PSPI film with DNCDP and the pristine PAA film. In this study, two bands at 1365 and 609 cm^{-1} due to the C-N stretching of an imide group and a silicon wafer, respectively, were used for the estimation of the DI. The imidization of PSPI film is completed at 250 °C due to the presence of photogenerated DMP from DNCDP. In contrast, additive-free PAA film reaches 80 % of imidization at 250 °C. The cleavage percentage of DNCDP with exposure to 500 mJ/cm^2 was around 17 %, estimated by data in the previous report of photosensitive polybenzoxazole using PBG.[30] It is indicated that low-temperature imidization of this PSPI completed in the presence of a small amount of DMP. In a previous work, the PAA film from BPDA and ODA containing a base catalyst could enforce imidization at 200 °C.[25] This PSPI film, however, required high thermal treatment at 250 °C to complete the imidization. It is assumed that DMP generated from DNCDP as a base catalyst vaporizes at around 200 °C, judging from the very slow imidization rate at these temperatures. Therefore, a non-volatile base from PBG should be developed to conduct lower-temperature imidization in PSPI.

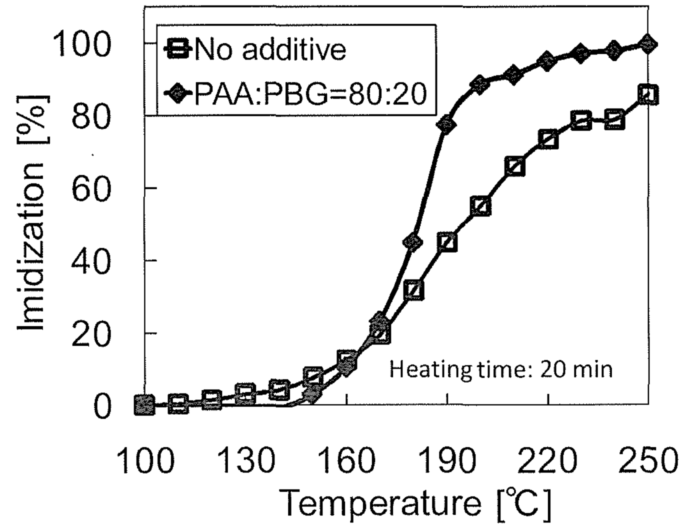


Figure 6-5. The degree of imidization of the PAA film containing DNCDP (20 wt%) (◆) and no additive (□) estimated from Fourier-transferred Infrared Spectroscopy (FT-IR).

6-2-4. Image Formation of PSPI. The SEM image in Figure 6-6a reveals the result of a negative PAA pattern after a series of treatments, such as exposure to 500 mJ/cm^2 of *i*-line, post baking at 190 °C for 5 min and developing to 2.38 wt% TMAHaq containing 20 wt% *i*PrOH. A clear negative pattern with a 6 μm feature could be obtained when a 1.4-μm thick film was used. The printed PAA pattern was converted to the PI pattern by heating at an elevated temperature up to 250 °C for 1 h under nitrogen (Figure 6-6b). The film thickness decreased from 1.4 to 1.0 μm and no damage of the formed patterns was found. The formation of PI was confirmed by FT-IR spectroscopy, in which the peak assignable to the C-N stretching of imide groups at 1365 cm^{-1} appeared and the absorption of carboxylic acid at 1716 cm^{-1} disappeared.

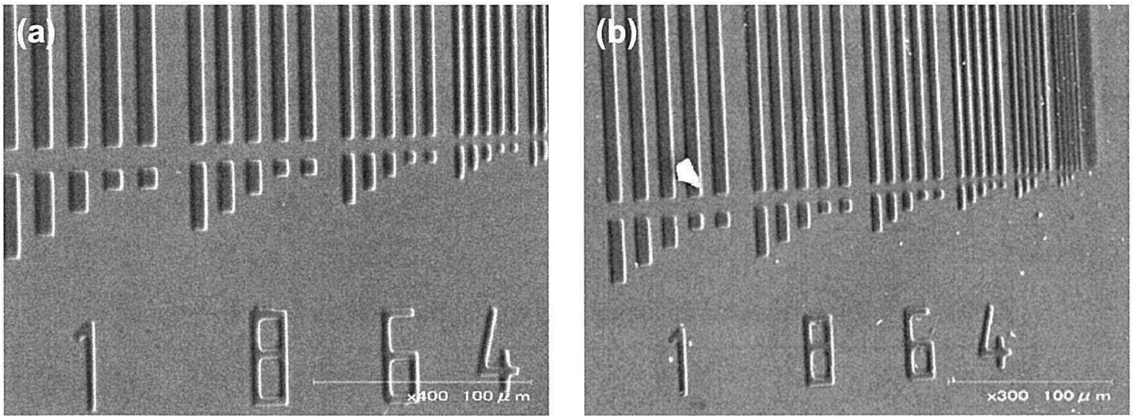


Figure 6-6. SEM images of negative-patterns: (a) a 1.4 μm-thick PAA film based on the PAA/DNCDP (80/20 w/w) resist system. The pre-bake, the *i*-line exposure and PEB were fixed to 100 °C for 5 min, 500 mJ/cm^2 and at 190 °C for 5 min, respectively, (b) a 1.0 μm-thick PI film cured at 250 °C for 1h under nitrogen.

6-2-5. Refractive Index and Dielectric Constant. A dielectric constant (ε) is one of the important properties of PSPIs as insulator materials. The ε of polymer film at 10 MHz is calculated from the average refractive index (n_{AV}) of the film according to a modification of Maxwell's equation, $\varepsilon = 1.1\, n^2_{AV}$.[31] The PAA and PSPI solutions were spin-casted on a quartz plate and the films were imidized by heating. Table 6-3 shows the refractive indices and the optically estimated ε values of the PI and PSPI films. Generally, the ε value of PSPIs becomes higher than the matrix PI because photoactive compounds have high polar character. The average refractive indices (n_{AV}) of both films are determined as 1.657 and 1.647, respectively, which are translated into ε values of 3.03 and 2.99, respectively. These results suggest that the incorporation of DNCDP in PSPI does not affect the ε value very much. A high Δn value of PI film is observed as compared to that of PSPI film due to the orientation of PI by high-temperature curing. This result suggests that the intermolecular orientation of PSPI film is suppressed by low-temperature imidization.

Table 6-3. Refractive Indices and dielectricconstants of polymer films.

Film[a]	n_{TE}	n_{TM}	n_{AV}	Δn[b]	ε
PI	1.716	1.539	1.659	0.177	3.03
PSPI	1.670	1.601	1.648	0.069	2.99

[a] Conditions preparation of PSPI films: The resist films (PAA/DNCDP 80/20, (w/w)) was pre-baked at 100 °C, exposed the *i*-line at 500 mJ/cm^2, post-exposure baked at 190 °C for 5min. Secondly, the resist films was cured at 250 °C for 1 h under nitrogen. Conditions preparation of PI films: The films cured at 350 °C for 1 h under nitrogen.

[b] Birefringence: $\Delta n = n_{TE} - n_{TM}$.

6-2-6. Thermal and Mechanical Properties of PSPI. The thermal stability and mechanical properties of PI and PSPI were investigated by Dynamic mechanical thermal analysis (DMA). The DMA curves of PI film cured at 350 °C for 1 h, and PSPI film exposed to 500 mJ/cm^2 and cured at 250 °C for 1 h, are shown in Figure 6-7. The initial storage moduli (*E'*) of PI and cured PSPI at ca 50 °C are 1.4 and 1.1 GPa, and their loss moduli (*E"*) at the same temperature are 133 and 124 MPa, respectively. The T_g of PI, determined from the peak temperature of the tanδ plots, is observed at 359 °C, whereas the T_g of PSPI is observed at 329 °C. It is assumed that the T_g of PSPI is slightly lower than that of PI probably due to the residues of DNCDP in the PSPI film. It is noteworthy that the PSPI film has a mechanical property similar to the pristine PI film. The *CTE* values of PI and PSPI films measured by TMA were 10 ppm/K and 16 ppm/K, respectively. Because of low-temperature curing and the residue of the PBG, the *CTE* value of the PSPI film is slightly higher than that of the pristine PI film. This *CTE* value, however, is enough low for the next generation PSPIs.

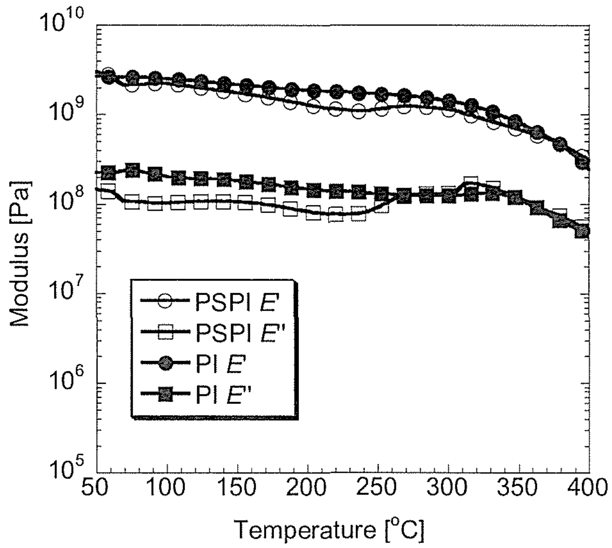


Figure 6-7. DMA curves (storage modulus *E'* and loss modulus *E"*, 1 Hz, 2 °C/min, in air) of PSPI and cured PI films.

6-3. Conclusion

In this paper, low-*CTE* semi-alicyclic PI prepared from BPDA and CHDA could be formed as PSPI, which is suitable as a buffer coat in multi-chip packages. This negative-type PSPI consisted of a PAA from BPDA and CHDA with DNCDP as a PBG. This PSPI system has the following advantageous points and satisfactory properties: (i) direct formulation of PSPI from the PAA polymerization solution, (ii) high sensitivity of 70 mJ/cm^2 and high contrast of 10.3 with *i*-line exposure, (iii) low-temperature imidization at 250 °C, and (iv) the low-*CTE* film of 16 ppm/K. Furthermore, this PSPI exhibits high thermal stability and good mechanical properties, and is suitable for next generation PSPIs.

6-4. Experimental

6-4-1. Materials. *N,N*-Dimethylacetamide (DMAc) was purified by vacuum distillation. CHDA purchased from Tokyo Chemical Industry Co., Ltd. (TCI) was recrystallized from *n*-hexanes under nitrogen and dried *in vacuo* at room temperature. BPDA purchased from TCI was dried *in vacuo* at 180 °C for 12 h before use. DNCDP was prepared according to the reported procedure.[19] TMAHaq purchased from AZ Electronic Materials (JAPAN) K. K. *i*PrOH purchased from GODO Co., Ltd. and was used in unrefined.

6-4-2. Synthesis of Poly(amic acid) from BPDA and CHDA. CHDA (0.114 g, 1.00 mmol) was placed in a 5 ml vial pot and dissolved in DMAc to adjust the concentration of 15 wt%. Acetic acid (0.132 g, 2.20 mmol) was slowly added to the diamine solution. After 10 min, BPDA (0.294 g, 1.00 mmol) was added into the solution, and the solution was stirred at room temperature for 12 h. The yield was quantitative. The inherent viscosity of this PAA was 0.24 dL/g at a concentration of 0.5 dL/g in DMAc at 30 °C.

6-4-3. Degree of Imidization. The polymer solution containing acetic acid was diluted with DMAc to a concentration of 15 wt%, followed by the addition of DNCDP. This solution was spin-coated on a silicon wafer, baked at 100 °C for 20 min in air. The film thickness was about 1.0~1.2 μm. Then, the films were baked on a hot-plate at each temperature (110~250 °C) for 20 min. A reference PI film was prepared by heating at 350 °C for 1 h under nitrogen. Absorption intensities on a FT-IR spectrum at 1365 cm^{-1} (A_{1365}) assignable to the C-N stretching of an imide group and at 609 cm^{-1}(A_{609}) assignable to a silicon wafer were measured, and the degrees of imidization (DI) were determined using the following equation;

$$\text{Imidization (\%)} = (A_{1365} / A_{609(\mathrm{samp})} - A_{1365} / A_{609(\mathrm{init})}) / (A_{1365} / A_{609(\mathrm{imid})} - A_{1365} / A_{609(\mathrm{init})}) \times 100 \qquad \text{eq (1)}$$

Subscripts between parentheses followed A_{1365} /A_{609} in the equation indicate the states of the polymer films; e.g. (samp) indicates the polymer sampled at each heating temperature level (110~250 °C); (init) indicates initially prebaked PAA at 100 °C; (imide) indicates the fully cured at 350 °C for 1 h in nitrogen.

6-4-4. Dissolution Rate. DNCDP was dissolved in a PAA polymerization solution to formulate a photosensitive polymer. The polymer film was spin-casted from the solution on a silicon wafer and prebaked at 100 °C for 5 min, then exposed to a filtered ultra-high-pressure mercury lamp at *i*-line, followed by PEB at 150 – 200 °C for 5 min or PEB at 190 °C for 1 -7 min. The exposed film was developed with 2.38 wt% TMAHaq containing 20 wt% *i*PrOH at 25 °C, and then measured change of film thickness before and after the development to determine the dissolution rate (Å/sec).

6-4-5. Photosensitivity. A 1.7 □m thick photosensitive polymer film was prepared from a varnish consisting of 80 wt% PAA and 20 wt% DNCDP, followed by spin-coating on a silicon wafer and then prebaked at 100 °C for 5 min. This film was exposed to *i*-line using a filtered supper-high-pressure mercury lamp, followed by PEB at 190 °C for 5 min, then developed with 2.38 wt% TMAHaq containing 20 wt% *i*PrOH at 25 °C for 15 s, and subsequently rinsed with distilled water. The characteristic photosensitivity curve was obtained by plotting a normalized film thickness as a function of exposure dose (unit: mJ/cm^2). Image-wise exposure was carried out in a contact-printing mode.

6-4-6. Measurements. The FT-IR spectra were obtained on a Horiba FT-210 spectrophotometer. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER GPX300 (300 MHz) spectrometer. DMA was performed on a Seiko DMS 6300 at a heating rate of 2 °C/min with a load frequency of 1 Hz in the air using the PI or thermally cured PSPI films (10 mm long, 5 mm wide, and 25 μm thick). The glass transition temperatures (T_gs) were determined as the peak temperature of tanδ plots. CTE of the PI and PSPI films (10 mm long, 4 mm wide, and 26 μm thick) was measured as an average with around 100~200 °C by thermo mechanical analysis (TMA) on a Seiko TMA /SS 6100. Film thickness on silicon wafer was measured by a

Veeco Instrument Dektak^3 surface profiler. The scanning electron microscope (SEM) photos were taken with a Technex Lab Tiny SEM 1540 scanning electron microscope with 15 kV accelerating voltage for imaging. Refractive indices of PI and the PSPI films formed on quartz substrates were measured at a wavelength of 1320 nm at room temperature with a Metricon model PC-2000 prism coupler. The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of PI films were measured with a prism coupler equipped with a half-waveplate in the light-path and a He-Ne laser light source (wavelength: 633 mm). n_{TE}/ n_{TM} and birefringence (Δn) were calculated as a difference between n_{TE} and n_{TM}. The average refractive index was calculated according to equation: $n_{AV} = [(2n_{TE}^2+n_{TM}^2)/3]^{1/2}$. The dielectric constant at 10 MHz frequency was calculated from the following empirical equation, $\varepsilon= 1.1\ n^2_{AV}$, where n_{AV} is an average refractive index.

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Chapter 7

Pattern Formation of Polyimide by Using Photosensitive Polybenzoxazole as a Top Layer

ABSTRACT: A versatile method for positive-type patterning of polyimide (PI) based on a two-layer photosensitive polybenzoxazole (PSPBO) and poly(amic acid) (PAA) film has been developed to provide a promising material in the field of microelectronics. This patterning system consisted of a pristine PAA thick bottom-layer and a poly(*o*-hydroxy amide) (PHA) thin top-layer with 9,9-bis[4-(*tert*-butoxycarbonylmethyloxy)phenyl]fluorene (TBMPF) as a dissolution inhibitor, and (5-propylsulfonyloxyimino-5*H*-thiophene-2-ylidene)-(2-methylphenyl)-acetonitrile (PTMA) as a photoacid generator (PAG). The PHA and PAA were prepared from 4,4'-(hexafluoroisopropylidene)-bis(*o*-aminophenol) and 4,4'-oxybis(benzoic acid) derivatives, and 3,3',4,4'-biphenyltetracarboxylic dianhydride and 4,4'-oxydianiline, respectively, in *N,N*-dimethylacetamide. This two-layer system based on PHA (150-nm thickness) and PAA (1.5-μm thickness) showed high sensitivity of 35 mJ/cm^2 and high contrast of 10.3 when exposed to a 365 nm line (*i*-line), postbaked at 100 °C for 2 min, and developed in a 2.38 wt% tetramethylammonium hydroxide aqueous solution/5 wt% *iso*-propanol at 25 °C. A clear positive image of a 4-μm line-and-space pattern was

printed on a film which was exposed to 100 mJ/cm^2 of *i*-line by a contact printing mode and fully converted to the corresponding PBO/PI pattern upon heating at 350 °C, confirmed by FTIR spectroscopy. This two-layer system could be applied to the patterning of various PAAs.

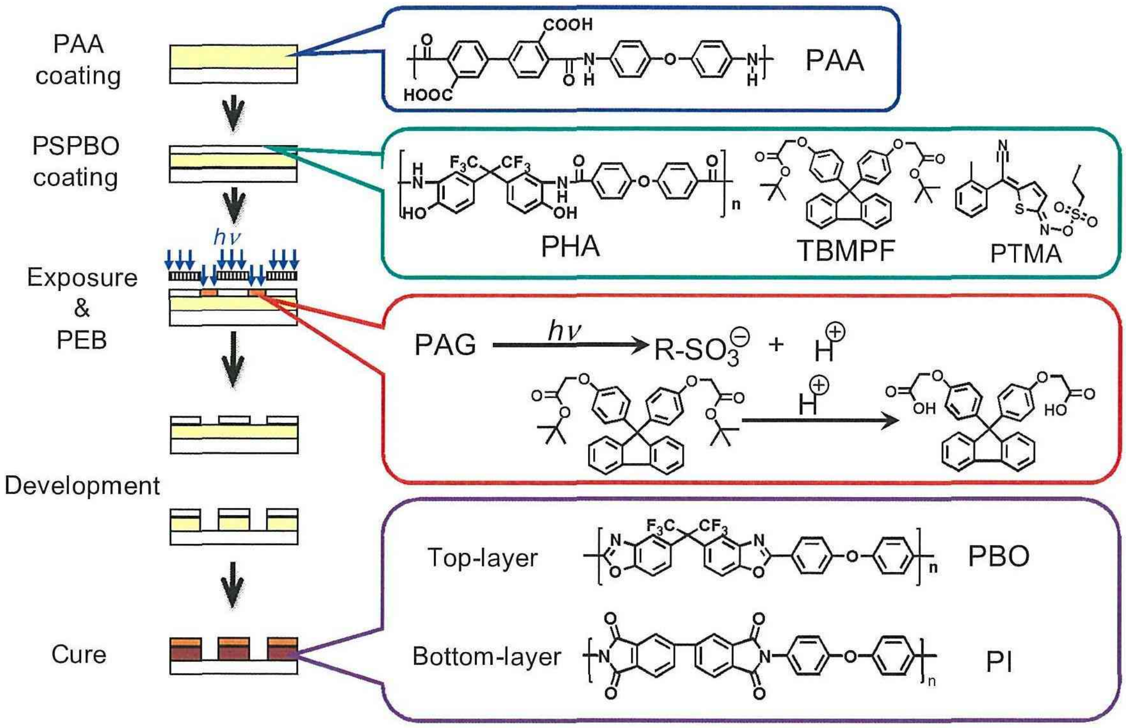
7-1. Introduction

Protecting and insulating materials for microelectronics require essential properties such as high thermal stability, high mechanical property, insulating performance, and so on. Polyimides (PIs) and poly(benzoxazole)s (PBOs) are an important class of advanced materials and fulfill the above requirements, so photosensitive PIs (PSPIs) and PBOs (PSPBOs), which are formed by the addition of a photosensitizing agent to PIs and PBOs, have been widely used in microelectronics fields.[1-12]

In general, PSPBOs are easily formulated from a precursor, poly(*o*-hydroxy amide) (PHA), and the photo-sensitizer, diazonaphthoquinone (DNQ) as a dissolution inhibitor.[13-15] Since the phenol group of PHA provides adequate solubility in an alkaline developer such as a 2.38 wt% tetramethylammonium hydroxide aqueous solution (TMAHaq), positive images are obtained at the exposed area. Furthermore, PSPBOs introducing a chemically amplified system normally show high sensitivity.[16-19]

On the other hand, it is difficult to form TMAHaq-developable positive-type PSPIs based on a PI precursor, poly(amic acid)s (PAAs), because the dissolution rate of PAAs in a TMAHaq solution is too high to obtain proper dissolution contrast between exposed and unexposed areas due to the high acidity of the carboxylic acid in PAA. A few TMAHaq-developable positive-type PSPIs have been reported,[20-22] where highly fluorinated or partially esterified PAAs are used to reduce the dissolution rate in TMAHaq. Recently, we have developed a chemically amplified positive-type PSPI which could be developed in a TMAHaq solution and showed good sensitivity.[23] This PSPI was directly formulated from a PAA-polymerized solution, a vinyl ether crosslinker, a thermobase generator and a photoacid generator (PAG). Although the formulation of this PSPI is facile, the physical properties are strongly affected by the residues of the crosslinker and the PAG. Additionally, these residues will cause out-gassing from films and fretting metal lines. These are generally unavoidable phenomena of PSPIs, because PSPIs include several additional compounds other than PAAs. On the other hand, photoresists were previously used for the patterning of PIs, and then the resists were removed after an etching process.

Herein we use PSPBO as a photoresist for PAA patterning, which is unnecessary to remove after development, and report the successful development of a TMAHaq-developable, chemically amplified, positive-type patterning of PI using a novel two-layer system based on a pristine PAA thick bottom-layer and a PSPBO thin top-layer consisting of 9,9-bis[4-(*tert*-butoxycarbonyl-methyloxy)phenyl]fluorene (TBMPF)[24] as a dissolution inhibitor, and (5-propylsulfonyloxyimino-5*H*-thiophene-2-ylidene)-(2-methylphenyl)acetonitrile (PTMA) as a PAG. The patterning process of this two-layer system is shown in Scheme 7-1.



Scheme 7-1. Patterning process of two-layer system.

Firstly, the PAA solution is spin-coated on a silicon wafer and baked in the usual way. Then, the thin layer of PSPBO consisting of PHA, TBMPF and PTMA is formed onto the thick PAA film and dried by pre-baking. This film is exposed to UV light to generate propanesulfonic acid from PTMA. Upon post-exposure bake (PEB) treatment of the film, the acid hydrolyzes the *tert*-butyl ester of TBMPF and gives the corresponding carboxylic acid. The exposed compartment of the PSPBO layer is developed with 2.38 wt% TMAHaq to provide a positive image. Subsequently, the PAA sublayer is developed under the patterns of PSPBO. As a result, a positive PAA image is obtained. These PSPBO-PAA patterns are converted to PBO-PI patterns by thermal cyclization. As a consequence, a pristine PAA pattern is obtained because there are no additives to PAA, so the problems of out-gassing and fretting metal lines due to PAG are solved. In addition, it is not necessary to remove the PSPBO layer as a thin top-layer after the formation of the PAA pattern due to its utility as a buffer coating material. TMAHaq-developed and positive-type patterns of PIs could be obtained from various PAAs by using this two-layer system.

7-2. Results and Discussion

7-2-1. Decomposition Percentages of TBMPF in PSPBO Film. A positive-type PSPBO based on PHA, TBMPF, and PTMA was the selected base of our previous work.[24] First, the relationship between the decomposition percentages of TBMPF and the dissolution rates of PSPBO at each temperature was studied. PSPBO films consisting of PHA (74 wt%), TBMPF (22 wt%) and PTMA (4 wt%) were exposed to 200 mJ/cm^2 of *i*-line and post-exposure baked at a set temperature for 2 min. Subsequently, these films were dissolved in DMSO-d_6 and the molar ratios of TBMPF and the corresponding carboxylic acid were calculated from the integration of the methylene signal by ^{1}H nuclear magnetic resonance (NMR) spectra. (Figure 7-1) The decomposition percentages and the corresponding dissolution rates are summarized in Table 7-1; they increase by increasing the PEB temperature. TBMPF almost decomposed above a PEB temperature of 130 °C. Actually, the large dissolution contrast (DC) between the exposed and the unexposed areas was observed at a PEB temperature of more than 130 °C in our previous work.[24]

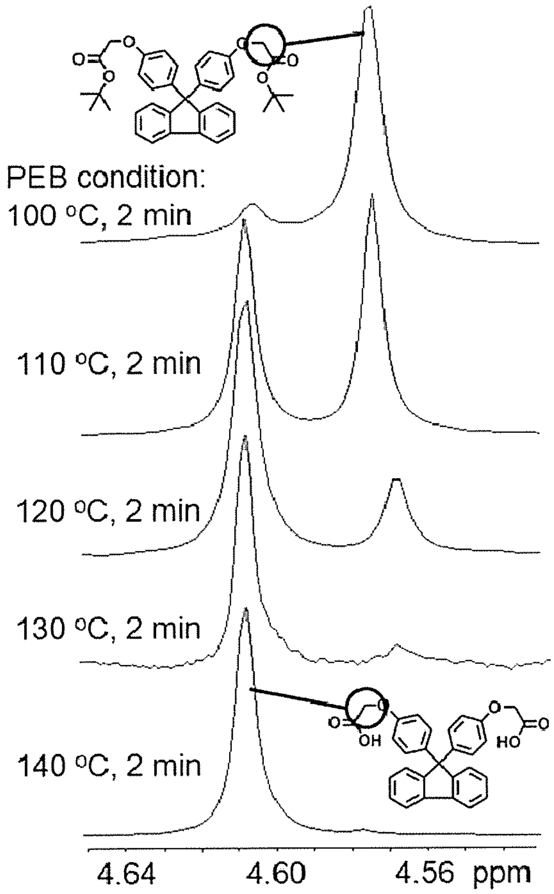


Figure 7-1. ^{1}H NMR spectra of TBMPF and the corresponding carboxylic acid at each PEB temperature.

Table 7-1. The decomposition percentage of TBMPF and the dissolution rate of PSPBO.[a]

PEB temperature [°C]	100	110	120	130	140
Decomposition Percentage [%][b]	15	48	77	94	100
Dissolution rate [Å/sec]	25	356	1129	1944	2663

[a] Conditions preparation of PSPBO films: The resist films (PHA/TBMPF/PTMA, 74/22/4 (w/w/w)) was pre-baked at 100 °C, exposed the *i*-line at 200 mJ/cm^2, post-exposure baked at the set temperature for 2min.

[b] The decomposition rate was calculated from integral ratio of methin peak of TBMPF and the corresponding calboxylic acid.

7-2-2. Lithographic Evaluation. To obtain contrasting pattern profiles from the exposed and unexposed areas, the effects of PEB temperature, PEB time, PSPBO layer thickness and exposure dose were investigated in detail. The 1.5-μm-thick PAA films were obtained by spin-casting from diluted polymerization solutions of PAA on a silicon wafer, and then pre-baked at 100 °C for 2 min in air. Subsequently, PSPBO thin film consisting of 74 wt% PHA, 22 wt% TBMPF, 4 wt% PTMA was prepared by spin-coating from their cyclohexanone solution on PAA film, and then pre-baked under the same condition while drying the PAA film. The thickness of the PSPBO layer was around 150 nm, measured by a surface profiler. These two-layer photosensitive films were irradiated with UV light at the *i*-line using a filtered super-high-pressure mercury lamp, baked after exposure at a set temperature, and developed with TMAHaq/5 wt% *i*PrOH at 25 °C. To improve compatibility between the developer and PHA containing a high hydrophobic hexafluoroisopropylidene unit, 5 wt% *i*PrOH was added to a 2.38 wt% TMAHaq solution. To clarify the difference in the dissolution behavior between the exposed and unexposed areas, the dissolution rates were estimated by the change in film thickness before and after development.

The PEB temperature is crucial for chemically amplified resist systems because the decomposition percentage of TBMPF and the following dissolution rate depend on the PEB temperature. As shown in Figure 7-2, the largest DC between the exposed and unexposed areas in 2.38 wt% TMAHaq/5 wt% *i*PrOH is obtained with PEB at 130 °C. The dissolution rates at the exposed areas treated at a PEB temperature slightly above 140 °C decrease. It is supposed that imidization occurs in the PAA layer at that cure temperature. On the other hand, the films of the unexposed areas are dissolved at a PEB temperature of 100-110 °C. The developing times at the PEB temperatures of 100 and 110 °C were 8 and 11 sec, respectively, which were longer than that (2 sec) at other temperatures. This indicates that the developer could slowly penetrate into a PSPBO layer due to longer developing time, although the PSPBO layer has high hydrophobicity.

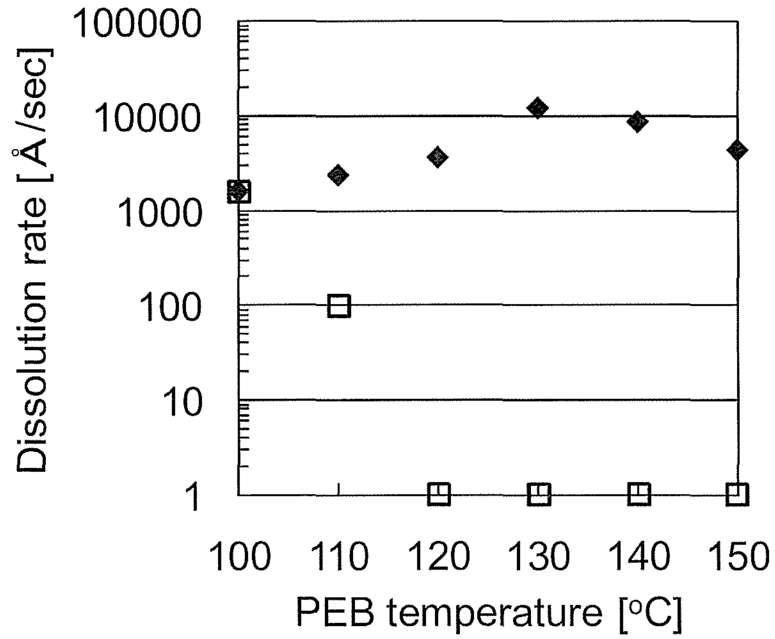


Figure 7-2. Effect of PEB temperature on the dissolution rate for the two-layer resist system based on the PSPBO (150 nm)/PAA (1.5 μm) under exposed (◆) and unexposed area (□). The PSPBO was constructed of PHA, TBMPF, and PTMA (74/22/4 w/w/w). The pre-bake, the *i*-line exposure and PEB time were fixed to 100 °C for 2 min, 200 mJ/cm^2 and for 2 min, respectively.

The effect of PEB time on the dissolution rate of the film was investigated, as shown in Figure 7-3. The dependence of the dissolution rate on PEB time is not observed at a PEB temperature of 130 °C. The sulfonic acid generated from PTMA diffuses efficiently within a short PEB time because the PSPBO layer is very thin.

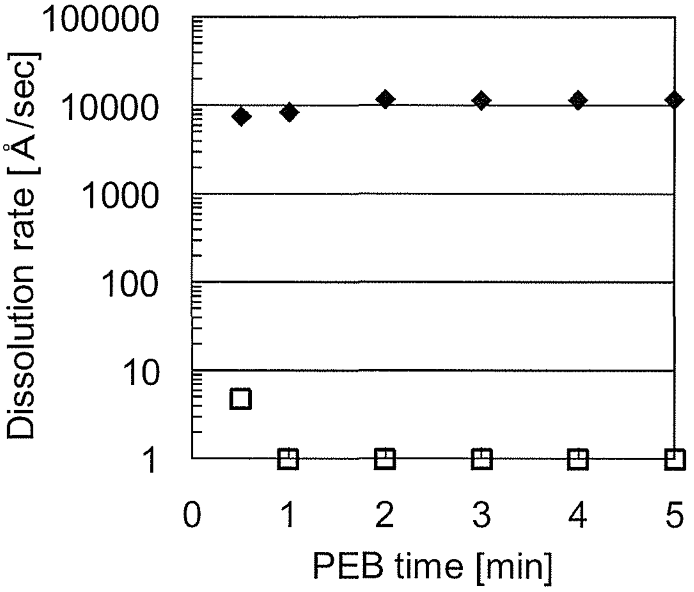


Figure 7-3. Effect of PEB time on the dissolution rate for the two-layer resist system based on the PSPBO (150 nm)/PAA (1.5 μm) under exposed (◆) and unexposed area (□). The PSPBO was constructed of PHA, TBMPF, and PTMA (74/22/4 w/w/w). The pre-bake, the *i*-line exposure and PEB temperature were fixed to 100 °C for 2 min, 200 mJ/cm^2 and at 130 °C, respectively.

The effect of the PSPBO layer thickness on the dissolution rate is shown in Figure 7-4. Even in a 20-nm thickness of a PSPBO layer, a large DC is obtained. It is assumed that the developer could not penetrate into the PSPBO layer because of a short developing time (within 2 sec).

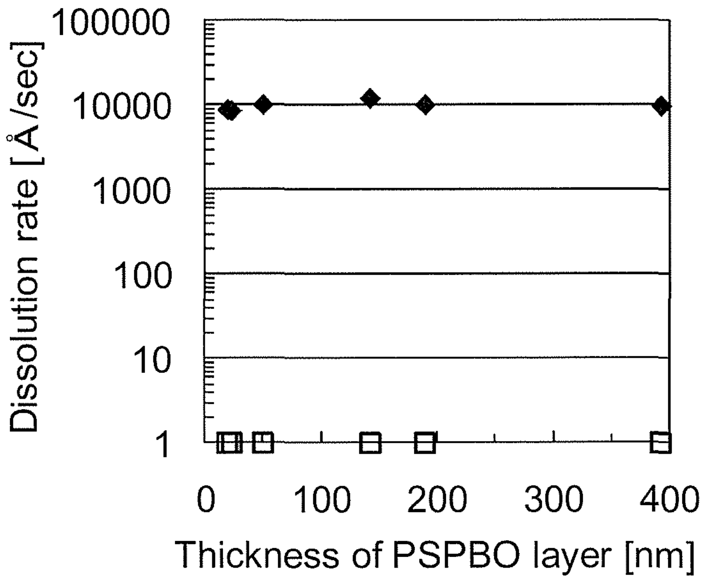


Figure 7-4. Effect of PSPBO layer thickness on the dissolution rate for the two-layer resist system based on the PSPBO/PAA (1.5 μm) under exposed (♦) and unexposed area (□). The PSPBO was constructed of PHA, TBMPF, and PTMA (74/22/4 w/w/w). The pre-bake, the *i*-line exposure and PEB were fixed to 100 °C for 2 min, 200 mJ/cm^2 and at 130 °C for 2 min, respectively.

Based on studies involving PEB temperature and time, a PSPI consisting of a 1.5-μm-thick PAA bottom-layer and a 150-nm-thick PSPBO top-layer consisting of PHA (74 wt%), TBMPF (22 wt%), and PTMA (4 wt%) was formulated. The photosensitivity curve of resist films is shown in Figure 7-5. This PSPI shows high sensitivity (D_0) of 35 mJ/cm^2 and good contrast (γ_0) of 10.3.

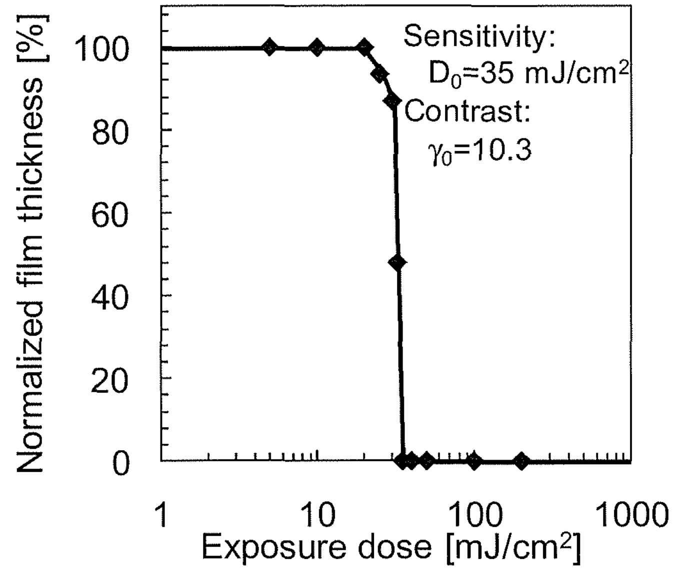


Figure 7-5. Characteristic photosensitive curve for two-layer resist system based on the PSPBO (150 nm)/PAA (1.5 μm). The pre-bake and PEB were fixed to 100 °C for 2 min and at 130 °C for 2 min, respectively.

7-2-3. Image Formation of Two-layer System. Figure 7-6a shows the SEM image of a patterned film obtained with a system described as follows: the resist layer was exposed to 100 mJ/cm^2 of *i*-line, post-baked at 130 °C for 2 min, and developed with 2.38wt% TMAHaq/5wt% *i*PrOH at 25 °C for 2 sec. A clear and positive pattern with a 4-μm feature could be observed when using a 2.0-μm-thick film, in which the thickness of the PSPBO layer was 200 nm. The printed pattern was cured to the PBO/PI film by heating at an elevated temperature up to 350 °C for 1 h under nitrogen (Figure 7-6b). The formation of the PBO/PI film was confirmed by IR spectrum. The film thickness was changed to 1.4 μm and the PBO/PI pattern shrank slightly because of a cyclodehydration reaction. Figure 7-7 shows cross-section views of the non-cured and the cured two-layer film. A boundary line between the PAA and PSPBO layers is clearly observed, which indicates that the PSPBO layer is not miscible with the PAA layer (Figure 7-7a). After the curing process, the resulting PI pattern is covered with the PBO top-layer and the merged layer is observed between the PBO and PI both layers (Figure 7-7b). The peeling-off phenomenon between the PBO and PI layers is not observed, which indicates this two-layer pattern is integrated with each other together by thermal curing process.

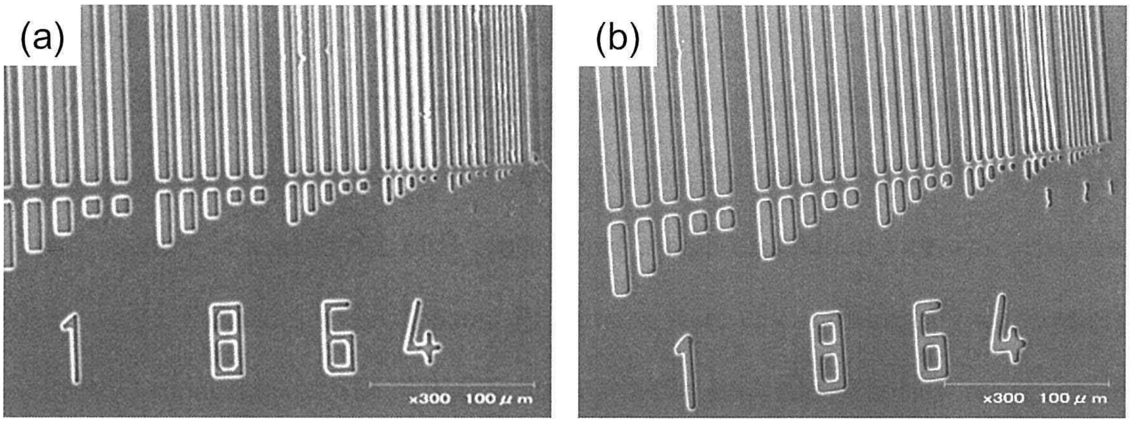


Figure 7-6. SEM images of positive-patterns: (a) a 2.0 μm-thick two-layer film based on the PSPBO (200 nm)/PAA (1.8 μm). The PSPBO was constructed of PHA, TBMPF, and PTMA (74/22/4 w/w/w). The pre-bake, the *i*-line exposure and PEB conditions were fixed to 100 °C for 2 min, 200 mJ/cm^2 and at 130 °C for 2 min, respectively, (b) a 1.4 μm-thick PI/PBO film cured at 350 °C for 1h under nitrogen.

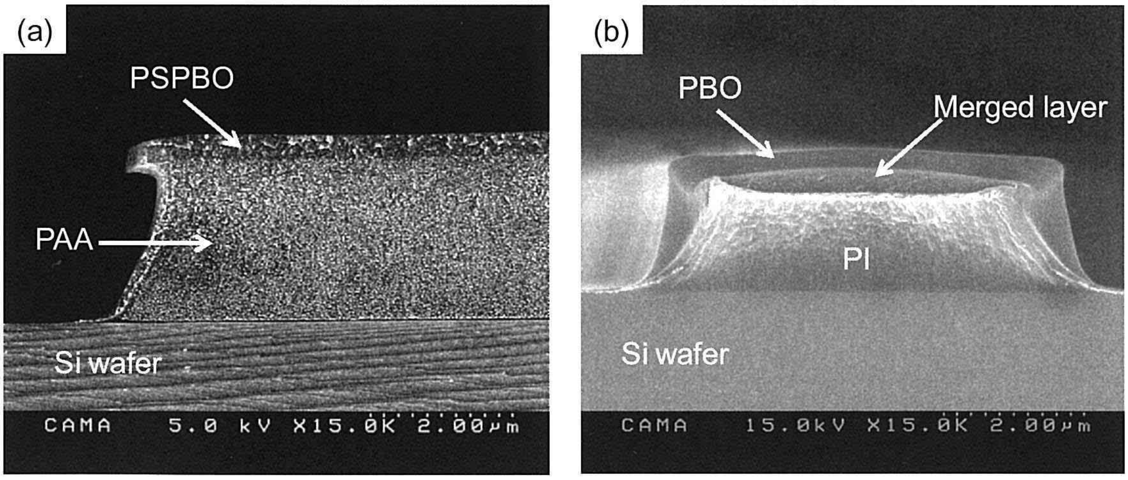


Figure 7-7. Cross-section views of the two-layer film observed by SEM: (a) PSPBO/PAA film, (b) PBO/PI film after the curing process at 250 °C for 30 min and then 350 °C for 30 min under nitrogen.

7-3. Conclusion

A novel PI patterning system consisting of isolated PAA and PSPBO layers has been developed. TBMPF as a dissolution inhibitor for PSPBO was immediately hydrolyzed in the presence of acid in the PEB process and a high dissolution rate was achieved. Positive-type and alkaline-developable PI patterns were easily formed by spin-casting the PSPBO consisting of PHA, TBMPF, and PTMA on PAA film. The new resist system showed high sensitivity and contrast of 35 mJ/cm^2 and 10.3, respectively with *i*-line exposure. Furthermore, the clear positive image after development was converted to a patterned PBO/PI film. The new pattern formation of PI provides a more efficient and versatile process compared to that using conventional PSPIs that requires a large amount of a photosensitizing agent or matrix polymers having complex structures.

Acknowledgement. We thank Mr. Jun Koki (Center for Advanced Materials Analysis, Tokyo Institute of Technology) for taking experiments of SEM images.

7-4. Experimental

7-4-1. Materials. *N,N*-Dimethylacetamide (DMAc) was purified by vacuum distillation. 4,4'-Oxydianiline (ODA) purchased from Tokyo Chemical Industry Co., Ltd (TCI) was recrystallized from tetrahydrofuran (THF) under nitrogen. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA) purchased from TCI was dried *in vacuo* at 180 °C for 12 h before use. The TBMPF and PHA derived from 4,4'-(hexafluoroisopropylidene)bis(*o*-aminophenol) and 4,4'-oxybis(benzoic acid) derivatives were prepared as described previously.[17] The number- and weight-average molecular weights (M_n and M_w) values of PHA were 7,400 and 16,000 (M_w/M_n 2.2), respectively, as measured by gel permeation chromatography (GPC) with polystyrene standards. PTMA used as a PAG was kindly donated by Ciba Specialty Chemicals, stored in a refrigerator, and other reagents and solvents were obtained commercially and used as received.

7-4-2. Synthesis of Poly(amic acid) from BPDA and ODA. BPDA (0.273 g, 0.93 mmol) was added to a solution of ODA (0.200 g, 1.00 mmol) in DMAc (2.68 mL). The mixture was stirred at room temperature for 12 h to give a viscous clear solution. The yield was quantitative. The inherent viscosity of this PAA was 0.70 dL/g at a concentration of 0.5 g/dL in DMAc at 30 °C.

7-4-3. Decomposition Percentage of TBMPF. A PSPBO solution consisting of PHA (74 wt%), TBMPF (22 wt%) and PTMA (4 wt%) in cyclohexanone was casted on a Si wafer by spin-coater. The polymer film was prebaked at 100 °C for 2 min, then exposed to 200 mJ/cm^2 of 365 nm (*i*-line) by a filtered ultra-high-pressure mercury lamp, followed by PEB at the set temperature for 2 min. Decomposition percentages of TBMPF at each temperature were calculated from the integration of the methylene signal by ^{1}H NMR. Dissolution rates of PSPBO film referred to a previous work.[24]

7-4-4. Dissolution Rate. TBMPF and PTMA were added to a PHA solution in cyclohexanone. The polymer film was casted from the solution (6 wt% concentration) on a Si wafer and prebaked at 100 °C for 2 min, then exposed to 200 mJ/cm^2 of *i*-line, followed by PEB at 100 – 150 °C for the set time. The exposed film was developed with 2.38 wt% TMAHaq/5 wt% *i*PrOH at 25 °C and measured the change of film thickness before and after the development to determine the dissolution rate (Å/sec).

7-4-5. Photosensitivity. A 1.3-□m thick PAA film and then a 250-nm thick PSPBO film consisting of 74 wt% PHA, 22 wt% TBMPF and 4 wt% PTMA was prepared by spin-coating on a silicon wafer and prebaked at 100 °C for 2 min. This film was exposed to *i*-line using a filtered supper-high-pressure mercury lamp, post-exposure baked at 130 °C for 2 min. Development of the exposed film was carried out with the developer of 2.38 wt% TMAHaq at 25 °C for 2 s, and subsequently rinsed with distilled water and dried with drier. The characteristic sensitivity curve was obtained by plotting a normalized film thickness against the exposure dose (unit: mJ/cm^2). Image-wise exposure was carried out in a contact-printing mode.

7-4-6. Measurements. The Fourier-transferred Infrared Spectroscopy (FT-IR) spectra were recorded on a Horiba FT-720 and the ^{1}HNMR spectra were recorded on a BRUKER GPX300 (300 MHz) spectrometer. Viscosity measurements were carried out by using an Ostwald viscometer at 30 °C in DMAc. The film thickness on a silicon wafer was measured by a Veeco Instrument Dektak^3 surface profiler. The scanning electron microscopy (SEM) photos were taken with a Technex Lab Tiny-SEM 1540 scanning electron microscope with 15kV accelerating voltage for imaging. Pt/Pd was spattered on film in advance of the SEM measurement. The cross-section view of the film was measured by HITACHI S4500 with 1.0kV accelerating voltage and carbon vapor deposition for imaging.

7-5. References and Notes

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Chapter 8

General Conclusion

The conclusions of each chapter and future prospects of photosensitive polyimides (PSPIs) and photosensitive poly(benzoxazole)s (PSPBOs) are described in this chapter.

In Chapter 1, backgrounds and current trends of PSPIs and PSPBOs are described.

In Chapter 2, the environmentally compatible and facile synthesis method of active *p*-nitrophenyl diester has been developed. This method which formed a phase separation between melting *p*-nitrophenol and hydrocarbon solvent accelerated the esterification reaction and azeotropic dehydration. As the results using this method, 4,4'-oxybis(*p*-nitrophenyl benzoate), which was synthesized from 4,4'-oxybisbenzoic acid and *p*-nitrophenol with catalytic *p*-toluenesulfonic acid in good yield. Furthermore, poly(*o*-hydroxyamide) (PHA) with high molecular weight could be obtained by polycondensation of 4,4'-oxybis(*p*-nitrophenyl benzoate) and 4,4'-(hexafluoroisopropylidene)bis(*o*-aminophenol). This process will provide a potentially efficient and versatile route for the synthesis of PHA for PSPBOs.

In Chapter 3, several dissolution inhibitors, which were prepared from phenolic compounds having a cardo-like structure with di-*tert*-butyl dicarbonate, have been developed for PSPBOs. The PSPBO consisting of PHA, 9,9-bis(4-*tert*-butoxycarbonyloxyphenyl)fluorene (*t*-BocBHF) as a dissolution inhibitor, and photoacid generator (PAG) showed high sensitivity and contrast of 34 mJ/cm^2 and 5.8, respectively, under the *i*-line exposure. Moreover, clear positive PHA patterns were obtained after the development and could be converted to PBO by the thermal cyclization.

In Chapter 4, low-temperature curable PSPBO has been developed by using *t*-BocBHF studied in Chapter 3 and thermoacid generator, isopropyl *p*-toluenesufonate (ITS). This positive-type PSPBO consisting of PHA, *t*-BocBHF, ITS, and PAG showed high sensitivity and contrast of 33 mJ/cm^2 and 5.1, respectively, under the *i*-line exposure. Furthermore, the clear positive images after development were converted to the PBO images by low-temperature treatment at 250 °C. A thick pattern was also obtained with this PSPBO system. ITS acted as an acid proliferator at the exposed areas during the post-exposure baking process, and as a cyclization catalyst for the curing process. Through the developments described in Chapter 3 and 4, we have achieved the facile formation of low-temperature curable positive-type PSPBO.

In Chapter 5, a facile synthesis method of semi-alicyclic poly(amic asid)s (PAAs) prepared from various aromatic tetracarboxylic dianhydrides and *trans*-1,4-cyclohexyldiamine (CHDA) with equivalent amount of acetic acid has been developed. This acetic acid prevented the salt formation between PAA and CHDA, so that the molecular weights of PAAs can be increased, showing high inherent viscosities, compared to the polymerization system without acetic acid. This new method can be applied for the PAA synthesis from aliphatic or alicyclic diamines with aromatic tetracarboxylic dianhydrides in industrial scale.

In Chapter 6, by expanding the study in Chapter 5 to PSPI, low- coefficient of thermal expansion (CTE) PSPI has been developed. This PSPI consisted of photobase generator

(PBG) and semi-alicyclic PAA, which was prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride and CHDA using the method introduced in Chapter 5, showed high sensitivity of 70 mJ/cm^2 and high contrast of 10.3 under the *i*-line exposure. The clear negative PI patterns were obtained after the development and then the curing process was performed at 250 °C. Moreover, the imidized film of this PSPI showed low-CTE at 16 ppm/K. This PSPI is suitable for the next generation PSPIs.

In Chapter 7, a novel PI patterning system consisting of isolated PAA as a bottom-layer and PSPBO as a top-layer has been developed. Positive and alkaline-developable PAA patterns were easily formed under the patterns of PSPBO and could be converted to PBO-PI pattern by thermal cyclization. This new resist system showed high sensitivity and contrast of 35 mJ/cm^2 and 10.3, respectively, under the *i*-line exposure. The new pattern formation of PI could be applied to various PAAs.

Throughout the whole researches as described above, the simple fabrication of PSPIs and PSPBOs for the next generation is remarkable points. Chapter 2 and 5 described facile and environmental-friendly preparation of PAA and PHA for PSPIs and PSPBOs by simple methods. These methods can be easily adapted to industrial field and moreover be applied to synthesize other products for other purposes. Simple formulations of low-temperature curable PSPBO (Chapter 4) and low-CTE PSPI (Chapter 6) are suitable for the next-generation buffer coating and interposer materials. Furthermore, the two-layer system using PSPBO can simplify forming micro patterns of any kind of PI.s

The future targets for PSPIs and PSPBOs are described to the following. First, PHAs are still prepared from active diester and bis(*o*-aminophenol), although the facile synthesis method of PHAs for PSPBOs has been developed in Chapter 2. Accordingly, PHA polymerized from dicarboxylic acid and bis(*o*-aminophenol) is an ideal matrix polymer for PSPBO in industrial field. This subject is surely tough and challenging, because the direct and selective amidation reaction between dicarboxylic acid and bis(*o*-aminophenol) has to occur during polymerization. Conceivably, this reaction can be achieved by the effective azeotropic technique as shown in Chapter 2 and reaction inhibitor of esterification. Second, a positive-type PSPBO using PBG is attractive in industrial and academic fields, because it can avoid the corrosion of copper circuits and has never been reported. To form positive-type PSPBO, the phenolic units of PHA have to be protected by any protection group, which can be deprotected with base catalyst. Acetyl or *p*-nitrophenyloxycarbonyl group can be used as such a protection group. However, the nucleophilic reaction occurs between the protection group and the base generated from PBG, because typical PBGs generate primary or secondly amines. If a PBG is able to produce a tertiary amine, positive-type PSPBO using PBG is easily obtained with preventing the nucleophilic reaction. Finally, the development of dissolution inhibitor for alkaline developable positive-type PSPI is a challenging subject because positive-tone of PI has an advantage by the shape of patterns and the formulation of PSPI using dissolution inhibitor is quite simple. However, the dissolution rate of PAAs in the alkaline developer is too high to obtain proper dissolution contrast between exposed and unexposed areas due to the high acidity of the carboxylic acid in PAA. Consequently, a steroid alcohol derivative of which hydroxyl group is protected can be utilized as dissolution inhibitor for PSPI due to its high hydrophobicity.

I wish to conclude this thesis, and hope that some of developments and findings in this study will be utilized practically in the field of microelectronics and also that one can enjoy an affluent daily life based on many benefits from them.

Appendix

List of Publications (Concerning This Thesis)

(1) **“Direct Synthesis of Active Diester from Dicarboxylic Acid and *p*-Nitrophenol and Synthesis of Poly(*o*-hydroxyamide)”** Ogura, T.; Ueda, M. *Macromolecules* **2006**, *39*, 3980.

(2) **“Three Components Positive Type Photosensitive Poly(benzoxazole) Based on Poly(*o*-hydroxy amide), a Dissolution Inhibitor and a Photo Acid Generator”** Ogura, T.; Ueda, M. *J. Photopolym. Sci. and Technol.*, **2006**, *19*, 291.

(3) **“Photosensitive Polybenzoxazole Based on a Poly(*o*-hydroxyamide), a Dissolution Inhibitor, and a Photoacid Generator”** Ogura, T.; Ueda, M. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 661.

(4) **“Photosensitive Poly(benzoxazole) Based on Poly(*o*-hydroxy amide), Dissolution Inhibitor, Thermoacid Generator, and Photoacid Generator”** Ogura, T.; Yamaguchi, K.; Shibasaki, Y.; Ueda, M. *Polym. J.* **2007**, *39*, 245.

(5) **“Facile Synthesis of Semiaromatic Poly(amic acid)s from *trans*-1,4-Cyclohexanediamine and Aromatic Tetracarboxylic Dianhydrides”** Ogura, T.; Ueda, M. *Macromolecules* **2007**, *40*, 3527.

(6) “**Low-*CTE* Photosensitive Polyimide Based on Semi-alicyclic Poly(amic acid) and Photobase Generator**” Ogura, T.; Higashihara, T.; Ueda, M. *J. Polym. Sci., Part A: Polym. Chem.* In Published.

(7) **“Pattern Formation of Polyimide by Using Photosensitive Polybenzoxazole as**

a Top Layer" Ogura, T.; Higashihara, T.; Ueda, M. *Macromolecules* In Submitted.

Other Publications

(1) **"Synthesis of Transparent Poly(*o*-hydroxy amide) Derivative in *i*-line Region for Photosensitive Polybenzoxazole"** Ogura, T.; Fukukawa, K.; Shibasaki, Y.; Ueda, M. *J. Photopolym. Sci. and Technol.*, **2005**, *18*, 319.

(2) **"Thermo-base Generator for Low Temperature Solid-phase Imidation of Poly(amic acid)"** Fukukawa, K.; Ogura, T.; Shibasaki, Y.; Ueda, M. *Chem. Lett.*, **2005**, *34*, 1372.

(3) **"Optically Transparent Sulfur-Containing Polyimide-TiO2 Nanocomposite Films with High Refractive Index and Negative Pattern Formation from Poly(amic acid)-TiO_2 Nanocomposite Film"** Liu, J.; Nakamura, Y.; Ogura, T.; Shibasaki, Y.; Ando, S.; Ueda, M. *Chem. Mater.* **2008**, *20*, 273.

(4) **"Development of Negative-type Photosensitive Polyimide, Based on Poly(amic acid)s, Photo Base Generator and Thermal Base Generator"** Ogura, T.; Mizoguchi, K.; Ueda, M. *J. Photopolym. Sci. and Technol.*, **2008**, *21*, 125.

(5) **"Direct Patterning of Poly(amic acid) and Low-temperature Imidization Using a Crosslinker, a Photoacid Generator, and a Thermobase Generator"** Ogura, T.; Higashihara, T.; Ueda, M. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 3362.

(6) **"Development of Photosensitive Poly(benzoxazole) Based on a Poly(*o*-hydroxy amide), a Dissolution Inhibitor, and a Photoacid Generator"** Ogura, T.; Higashihara, T.; Ueda, M. *J. Photopolym. Sci. and Technol.*, **2009**, *22*, 429.

(7) **A Negative-type Photosensitive Poly(3-hexylthiophene) with Cross-linker and Photoacid Generator"** Endo, K.; Ogura, T.; Higashihara, T.; Ueda, M. *Polym. J.*,

2009, *41*, 808.

List of Presentations (Concerning This Thesis)

(1) **"Direct Synthesis of Active Diester From Dicarboxylic Acids and Phenols"** Ogura, T.; Ueda, M. *55th SPSJ Annual Meeting* Nagoya, May **2006** (poster).

(2) **"Three Components Positive Type Photosensitive Poly(benzoxazole) Based on Poly(*o*-hydroxy amide), a Dissolution Inhibitor and a Photo Acid Generator"** Ogura, T.; Ueda, M. *The 23rd Conference of Photopolymer Science and Technology* Chiba, June **2006** (oral).

(3) **"Novel Thermal Acid Generators for Low Temperature Cyclization of Poly(*o*-hydroxyamide) and Their Application for Photosensitive Polymer"** Ogura, T.; Yamaguchi, K.; Ueda, M. *PolyCondensation 2006* Istanbul, Turkey, August **2006** (poster).

(4) **"Three-Components Positive Type Photosensitive Poly(benzoxazole) Based on Poly(*o*-hydroxy amide), Dissolution Inhibitor and Photo Acid Generator"** Ogura, T.; Shibasaki, Y.; Ueda, M. *Asian Conference and 7th Japan-China Seminar on Polyimides and Advanced Aromatic Polymers* Tokyo, September **2006** (poster)

(5) **"Positive Type Photosensitive Poly(benzoxazole) Based on Poly(*o*-hydroxy amide), Photo Acid Generator, Dissolution Controller, and Thermal Acid Generator"** Ogura, T.; Shibasaki, Y.; Ueda, M. *55th SPSJ Symposium on Macromolecules* Toyama, September **2006** (oral)

(6) **"Facile Synthesis of Semi-Aromatic Poly(amic acid)s"** Ogura, T.; Shibasaki, Y.; Ueda, M. *56th SPSJ Annual Meeting* Kyoto, May **2007** (poster).

(7) **"Development of Photosensitive Polyimide Using Poly(amic acid) of Low-CTE**

Polyimide" Ogura, T.; Higashihara, T.; Ueda, M. *The 17th Japan Polyimide and Aromatic Polymer Conference* Morioka, October **2009** (poster).

Other Presentations

(1) **"Low Temperature Imidization of Poly(amic acid) Using Thermal Base Generators"** Ogura, T.; Fukukawa, K.; Shibasaki, Y.; Ueda M. *54th SPSJ Annual Meeting* Yokohama, May **2005** (poster).

(2) **"Synthesis of Transparent Poly(*o*-hydroxy amide) Derivative in *i*-line Region for Photosensitive Polybenzoxazole"** Ogura, T.; Fukukawa, K.; Shibasaki, Y.; Ueda, M. *The 22nd Conference of Photopolymer Science and Technology* Chiba, June **2005** (oral).

(3) **"Thermo-Base Generator for Low Temperature Solid-Phase Imidization of Poly(amic acid)"** Ogura, T.; Fukukawa, K.; Shibasaki, Y.; Ueda, M. *2005 International Chemical Congress of Pacific Basin Societies* Honolulu, USA, December **2005** (poster).

(4) **"Positive Type Photosensitive Poly(imide) Based on Poly(amic acid), Cross-linker, Photo Acid Generator, and Thermal Base Generator"** Ogura, T.; Higashihara, T.; Ueda, M. *58th SPSJ Annual Meeting* Kobe, May **2009** (poster).

(5) **"Development of Photosensitive Poly(benzoxazole) Based on a Poly(*o*-hydroxy**

amide), a Dissolution Inhibitor, and a Photoacid Generator" Ogura, T.; Higashihara, T.; Ueda, M. *The 26th Conference of Photopolymer Science and Technology* Chiba, July **2009** (oral).

(6) **"Synthesis of Dissolution Inhibitor for Photosensitive Polybenzoxazole"** Ogura, T.; Higashihara, T.; Ueda, M. *238th ACS National Meeting* Washington DC, USA, August **2009** (poster).

Patents

(1) **"Method for Synthesizing Polyamic Acid and Polyimide"** Ueda, M.; Ogura, T.; Nishimura, S. *PCT Int. Appl.* **2007**, 17 pp.

(2) **"Manufacture of Copper-clad Laminates Involving Dimension-stable Polyimide Insulator Layers and Manufacture of Coverlays and Flexible Printed Boards Therefrom"** Nishimura, S.; Ueda, M.; Ogura, T. *PCT Int. Appl.* **2007**, 21pp.

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Tomohito Ogura