

Hydroxyamide-containing Positive-type Photosensitive Polyimides

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ABSTRACT: A hydroxyamide-containing tetracarboxylic dianhydride was synthesized from trimellitic anhydride chloride and bis(3-amino-4-hydroxyphenyl)sulfone. Poly(amic acid)s (PAAs) were polymerized from this dianhydride with several diamines in N-methyl-2-pyrrolidone (NMP). The reflux of the PAA solutions at 160°C for 3 h allowed to form hydroxyamide-containing polyimides (PHAI)s highly soluble in common organic solvents such as NMP. The PHAI films could be completely converted to poly(benzoxazole imide)s (PBOIs) through cyclodehydration of the hydroxyamide groups upon heat treatment at 300°C. The thermally cured PBOI films showed a high T_g ranging 298–323°C. Other PBOI film properties are also discussed in this paper. The PHAI films were highly transparent at 435 nm but not at 365 nm. This is a problem to be solved for high sensitivity patterning at i-line. The solubility of the PHAI films in TMAH could be controlled by copolymerization using different diamines. The PHAI copolymer film dispersing diazonaphthoquinone (DNQ) as a photosensitizer were uv-irradiated through a photo-mask. Development using a 2.38 wt% TMAH aqueous solution containing 2-propanol gave a fine positive-type pattern with L&S = 20 μm. In this work, novel highly transparent PHAI systems are also discussed.

Keywords: Hydroxyamide-containing soluble polyimides / Positive-type photosensitive polyimide / Poly(hydroxyamide imide)s / Poly(benzoxazole imide)s

1. Introduction

Polyimides (PIs) have been widely utilized in a variety of micro- and opto-electronic applications such as the substrates for flexible printed circuit boards (FPC), chip-on-film, and tape-automated bonding (TAB) assembly systems, buffer-coating films and interlayer dielectrics for LSI chips, high temperature adhesives, light wave guides for their combined excellent properties, i.e., high glass transition temperature (T_g), high resistance to chemicals and radiation, relatively low dielectric constant, and good mechanical properties [1].

Negative-type Photosensitive PI systems are applied to buffer-coating films for simplifying the chip fabrication processes. These systems are formulated from polyimide precursors, poly(amic acid)s (PAAs) and radical-polymerizable acrylate crosslinkers which are covalently or ionically bound to the carboxylic acid groups in PAAs. The acrylate-modified polyimide precursors are usually soluble in common organic solvents. Thus, these can be developed by NMP-containing solutions after uv-exposure through a photo-mask. A problem for the negative-type systems is that the

development systems using such organic solvents are not environmentally friendly.

In this regard, positive-type photosensitive PI systems which can be developed with alkaline solutions (usually 2.38wt% tetramethyl ammonium hydroxide (TMAH) are advantageous since the waste developers can be readily disposed by simple neutralization. The positive-type systems are generally based on a combination between alkali-soluble polymers and diazonaphthoquinone (DNQ) photosensitizer which originally acts a dissolution inhibitor but can be photo-transformed to an indenecarboxylic acid with enhanced solubility in alkaline solutions. DNQ/phenolic resin systems are known as a representative high resolution positive-type photosensitive resin composition. However, application of the DNQ-based principle to PAA systems causes a serious problem: it is often difficult to obtain a sufficiently large difference of the dissolution rates between the exposed and unexposed areas. This is based on the fact that PAAs still possess too high alkali-solubility even if a large amount of hydrophobic DNQ (20–30 wt%)

was dispersed into the PAA films. Thus, positive-type photosensitive PI systems are disadvantageous for high resolution patterning.

In order to solve this serious problem, we have so far studied how the solubility of PAAs in a TMAH aqueous solution can be controlled. Our approaches previously reported are the use of specially designed monomers: imide-containing fluorinated diamines shown in Fig.1 [2]. CBDA/TFMB polyimide system possessing a very

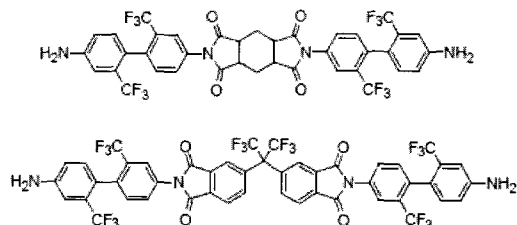


Fig.1 Structures of imide-containing fluorinated diamines used in our previous work.

low dielectric constant and a low coefficient of thermal expansion (CTE) was chosen as a base polymer to be modified [3,4]. The alkali-solubility of the PAA could be precisely controlled by copolymerization using the imide-containing fluorinated diamines with a minor fraction, as a result, fine positive-tone patterns could be formed without sacrificing the original low-K and low-CTE characteristics. We have also developed a fluorene-containing tetracarboxylic dianhydride (Fig.2) for the same purpose. The partial use of this monomer for copolymerization also showed a well-controlled solubility in TMAH while maintaining the excellent properties.

Our approach was extended to applying high-modulus, low-CTE, and low-water absorption poly(ester imide)s (PEsIs) to buffer-coating films on the basis of an expectation that even the PEsI precursors (PEsAAs) should have somewhat controlled solubility in TMAH for obtaining fine positive-tone patterns. The results

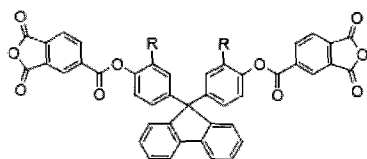


Fig.2 Structure of fluorine-containing tetracarboxylic dianhydride used in our previous work.

revealed that a combination of DNQ and PEsAA derived from an ester-containing tetracarboxylic dianhydride and 2,2'-bis(trifluoromethyl)benzidine

(TFMB) allowed to form fine positive-tone patterns and the thermally cured film attained target properties (tensile modulus > 5GPa, CTE < 25 ppm/K, and water absorption $W_A < 1.0\%$) [5].

However, as far as the 2.38 wt% TMAH aqueous solution is chosen as a fixed developer, it is expected that polybenzoxazole (PBO) precursor, i.e., polyhydroxyamide (PHA) systems are more advantageous than PAA systems for higher resolution patterning since the former possesses phenolic OH groups as in novolac resins and they completely disappear upon thermal cyclization toward PBOs. However, the polymerization processes of PHAs are rather complex compared to those of PAAs in which no catalyst and no activation of the monomers are needed.

In the present work, we propose a novel positive-type photosensitive polyimide system which possesses the easiness of polymerization like PAA systems and fine patternability as in PBO precursor systems. The feature of the present system is that the polymer contains hydroxyamide groups in the main chains which can be completely transformed to benzoxazole units upon heating after positive-tone pattern formation.

2. Experimental Section

2.1. Materials.

A hydroxyamide-containing tetracarboxylic dianhydride (Fig.3) was synthesized as follows: 10 mmol of bis(3-amino-4-hydroxyphenyl)sulfone (BAPS, supplied from Nippon Kayaku) was dissolved in dry acetone containing propylene oxide as an acid acceptor in a double cap-sealed flask. To this solution, trimellitic anhydride chloride (TA, 22 mmol) dissolved in dry acetone was slowly added using a syringe at 0°C then stirred 3 h. The product precipitated was collected

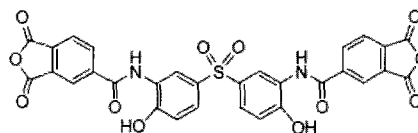


Fig.3 Structure of hydroxyamide-containing tetracarboxylic dianhydride used in this work.

by filtration and washed with toluene and hexane then vacuum-dried at 40°C for 12 h. This procedure suppressed esterification between the hydroxyl groups in BAPS and the carbonyl chloride group in TA and allowed almost quantitative amidation. The structure of the product (Fig.3) was confirmed from the infrared

and $^1\text{H-NMR}$ spectra.

Prior to PAA polymerization, tetracarboxylic dianhydrides are usually heated at elevated temperatures such as 150–200°C to ensure complete cyclization of a partially hydrolyzed anhydride portion. However, such heat treatment was not applied to the present dianhydride to avoid unfavorable partial transformation of the hydroxyamide groups to oxazole rings. Even heat treatment in vacuum at lower temperatures such as 100°C caused unknown reactions as suggested

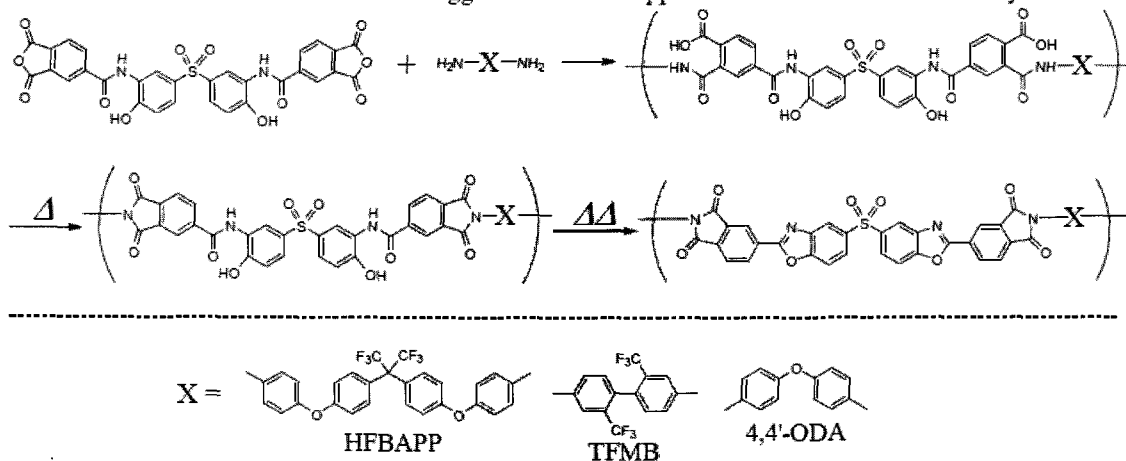


Fig.4 Synthetic routes of PHA-AAs, PHAIs, and PBOIs.

from a significant change in the infrared spectrum.

Fig.4 shows the reaction schemes of the polymerization of hydroxyamide-containing poly(amic acids) (PHA-AAs), its imidization, and cyclodehydration to form poly(benzoxazole imide)s (PBOIs). PHA-AAs were polymerized as follows unless stated otherwise: the equimolar amount of TA-BAPS dianhydride powder was gradually added into the NMP solution of diamines (HFBAPP, TFMB, and 4,4'-ODA) at room temperature with stirring for a prolonged period until the reaction mixture turned to a viscous and clear solution.

The PHA-AAs obtained were heated in solution at 160°C for 3 h in a nitrogen flow to ensure imidization. No precipitation occurred in this procedure, indicating that the hydroxyamide-containing PIs formed, PHAIs, are highly soluble in NMP. The PHAI was precipitated into a large amount of water and collected by filtration then vacuum-dried at 80°C for 12 h. The $^1\text{H-NMR}$ spectra of the polymers in dimethylsulfoxide- d_6 showed that imidization was completed with practically no decrease in the phenolic OH proton.

The reduced viscosities of the PHAIs obtained

are shown later.

The PHAI powder was re-dissolved in NMP at a concentration of 20 wt %, then doctor-bladed on a glass substrate to form ca. 20 μm thick films and then dried at 80°C for 2 h in an air-convection oven. The PHAI films were heated at 300°C for 1 h in vacuum to form poly(benzoxazole imide)s (PBOIs) as fixed on a glass substrate. The transmission mode FT-IR spectra of the thermally cured thin films (4–5 μm thick) showed complete disappearance of the amide carbonyl stretching

bands peaking at 1663 (amide-I) and 1531 cm^{-1} (amide-II), suggesting that the hydroxyamide groups was completely transformed to benzoxazole ring. The films cured on a substrate were removed from the substrate and successively annealed at established temperatures to eliminate residual stress in the films. The PBOI films obtained were all high-quality and completely clear. No cracks were observed for all PBOI films examined in this study on a 180° folding test, showing good flexibility.

For the formation of positive-tone patterns, DNQ (NT-200, Toyo Gosei, Fig. 5) was dissolved into the solutions of solubility-modified PHAI. The DNQ-containing PHAI films (DNQ = 30 wt %) cast at 60°C/2h were pre-baked at 100°C/10min then irradiated on a high-pressure mercury lamp (Harison Toshiba Lighting, Toscore 251) through a photo-mask, and finally developed by a TMAH aqueous solution (2.38 wt%) containing 2-propanol.

2.2. Measurements

The inherent viscosities (η_{red}) of PHA-AAs and PHAIs were measured at 0.5 wt% in NMP at 30°C

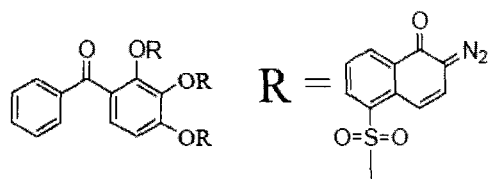


Fig.5 Structure of DNQ used.

using an Ostwald viscometer. η_{red} can be regarded as inherent viscosity (η_{inh}).

The CTEs of the PBOI specimens (10 mm long, 5 mm wide, and typically 20 μm thick) were measured at a heating rate of 5°C/min as an average within 100–200°C for the film plane direction on a thermomechanical analyzer (Bruker-AXS TMA 4010) with a load (0.5 g per film thickness in μm) in a nitrogen flow. In this case, the data were collected from the second heating run up to 120°C to eliminate the adsorbed water since the first run occasionally shows an abnormal TMA curve. Storage modulus (E') and loss energy (E'') were measured as a function of temperature to determine T_g from a peak temperature of the E'' curve using the same instrument at a heating rate of 5°C/min with a sinusoidal load frequency of 0.1 Hz in a nitrogen atmosphere.

Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability of PBOI films at a heating rate of 10°C/min in nitrogen and air. The 5 % weight loss temperatures (T_d^5) were compared.

The in-plane (n_{in}) and out-of-plane (n_{out}) refractive indices of PBOI films were measured at D-line (589 nm) on an Abbe refractometer (Atago 4T) equipped with a polarizer using a contact liquid (sulfur-saturated methylene iodide $n_D = 1.78$ –1.80, depending on the sulfur concentration) and a test piece ($n_D = 1.92$). The average refractive index was calculated from the relation: $n_{av} = (2n_{in} + n_{out}) / 3$.

The dielectric constant was estimated from the relation: $\epsilon_{cal} = 1.1 n_{av}^2$ [2,3].

The transparency of the modified PHAI films was evaluated from the transmittance (T %) at 435 and 365 nm (g- and i-lines of high-pressure mercury lamp) and the cut off wavelength where transmittance is 0.5 %.

The dissolution rates were measured from the thickness changes monitored on a Filmetrics F-20 thin-film analyzer. The photosensitivity and the γ value were determined on the basis of the plots of normalized thickness as a function of exposure dose.

3. Results and Discussion

3.1. Molecular Design

The present system possesses both the features of PI and PBO systems: PHAIs can be readily polymerized from hydroxyamide-containing tetracarboxylic dianhydride and diamines as in the conventional PAA polymerization, in addition, the hydroxyamide groups can be completely converted to benzoxazole units via thermal cyclodehydration after the patterning process. The easiness of polymerization also means that the chain structures of the present systems can be readily modified by copolymerization using a variety of commercially available diamines and dianhydrides. As mentioned above, the hydroxyamide-containing tetracarboxylic dianhydride could be synthesized from trimellitic anhydride and bis(o-aminophenols). In this work, we chose a sulfone-containing bis(o-amino phenol), BAPS, for the synthesis of hydroxyamide-containing dianhydride monomer since the incorporation of the $-\text{SO}_2-$ groups into polymer backbones is in general very effective for enhancing both T_g and solubility. We have previously illustrated that a combination of BAPS and 1,4-cyclohexane dicarboxylic acid led to a colorless PBO film possessing both a high T_g at 294°C and excellent solubility in common organic solvents such as NMP [6].

Another attempt has been done for positive-tone patterning; a bis(o-aminophenol) as a diamine component was reacted with a dianhydride to polymerize a soluble OH-pendant PI [7]. Its typical main chain structure is shown in Fig.6. However, in this system, the OH groups can

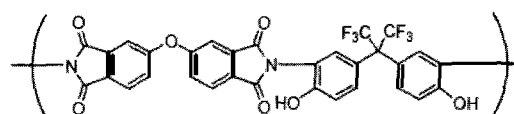


Fig.6 A typical structure of a conventional phenolic OH-pendant soluble polyimide.

not be eliminated upon thermal treatment after the patterning process, thus the remaining OH groups negatively contribute to water absorption in contrast to our systems.

3.2. Properties of PBOI films

Table 1 summarizes the properties of PBOI films and the transparency of PHAI films with different diamine components. The molecular weights (inherent viscosities) of the PHAIs ranged 0.48 to 0.74 dL/g, which were high enough to

form flexible PHAI/DNQ films. Even when flexible HFBAPP was used as a diamine, its PBOI film exhibited a high T_g at 298°C. The use of 4,4'-ODA enhanced the T_g up to 323°C. The results are probably attributed to combined effect of the imide and sulfone groups in the structures which both cause strong intermolecular interaction. These PBOI films also showed excellent thermo-oxidative stability as suggested from their high 5% weight loss temperatures in air approximate to 500°C owing to the absence of aliphatic groups in the structures. The PBOIs examined in this work possessed common CTE values ranging 49–55 ppm/K. This is due to bent chain structures at $-SO_2-$ and the ether linkages, which are disadvantageous for in-plane chain orientation induced by thermal cyclization [8]. The very low values of birefringence ($\Delta n < 0.002$) observed in these films reflect the poor extents of in-plane orientation. Low CTE characteristics (< 20 ppm/K) are limited to PI [9–11], PEI [12,13], and PBO [14] systems possessing stiff/linear chain structures. The PBOI films using fluorinated diamines (HFBAPP and TFMB) showed a low extent of water absorption (< 1.0 %) but PBOI film from 4,4'-ODA did not.

Higher-modulus buffer-coating films are, if available, more convenient since thinner films can be used to protect chips and passivation layers from mechanical stress. We have previously developed a high modulus photosensitive PEI system exceeding 5 GPa [5]. However, the present PBOI systems showed common values of tensile modulus ranging 2.85 to 3.22 GPa. The results are based on the poor in-plane orientation (almost three-dimensionally random orientation). The PBOI films were sufficiently flexible as suggested from the elongation at break (E_b) of about 10 %.

The optical transparency was also evaluated for the PHAI films (ca. 10 μm thick) since the transmittance of the films directly influences the sensitivity. The transmittances at 435 nm (g-line)

were high enough for all the films, however, the films were not transparent at 365 nm (i-line). This is attributed to intra- and intermolecular charge-transfer interaction [15]. An approach to improve the transparency at 365 nm is in progress.

3.3. Positive-tone patterning

The PHAI(HFBAPP)/DNQ film showed almost no dissolution in 2.38 wt% TMAH. This is probably due to the hydrophobicity of the trifluoromethyl groups in the structure. Similar

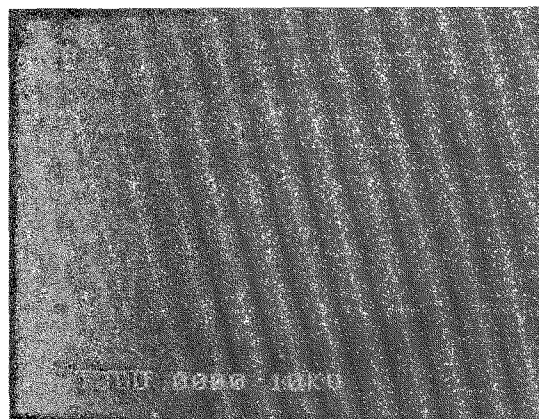


Fig.7 SEM photograph (X 200) of positive-type pattern of PBOI copolymer (4,4'-ODA75/HFBAPP 25) as formed by development using a 2.38 wt% TMAH aq. containing 2-propanol (10wt%) at 23°C for 25 sec. A scale bar represents 100 μm .

behavior was also observed for the system prepared from another fluorinated diamine, TFMB. On the other hand, the PHAI(4,4'-ODA)/DNQ film was rapidly dissolved in the same developer thereby it was difficult to form fine patterns. Then copolymerization was carried out using 4,4'-ODA (75 mol%) and HFBAPP (25 mol%) to control the dissolution rates. **Fig.7** shows a SEM photograph of positive-tone pattern for the cured copolymer/DNQ system. UV-irradiation through photo-mask from an unfiltered high-pressure mercury lamp (ca. 3000 mJ/cm^2) allowed the formation of a fine positive-type pattern with L&S

Table 1 Properties of PBOI films (20 μm thick) and transparency of PHAI films (10 μm thick) prepared from different diamines.

Diamine	η_{inh} (dL/g)	T_g (°C)	CTE (ppm/K)	$T_d^5 N_2$ (°C)	T_d^5 air (°C)	$T\%_{435}$ (%)	Cut-off (nm)	W_A (%)	E_b (%)	Modulus (GPa)
HFBAPP	0.74	298	54.4	515	500	52.5	387	0.89	9.9	2.85
TFMB	0.48	310	52.0	500	494	78.3	371	0.69	6.5	3.22
4,4'-ODA	0.48	323	49.6	497	494	75.2	369	2.81	10.4	3.12

= 20 μm using a 2.38 wt% TMAH aqueous solution containing 2-propanol (10 wt%).

3.4. A new approach for obtaining highly transparent PHAI films

In order to improve drastically the PHAI film transparency at 365 nm (i-line), we synthesized novel hydroxyamide-containing cycloaliphatic tetracarboxylic dianhydrides from hydrogenated trimellitic anhydride with bis(o-aminophenols) as shown in Fig.8. PHAIs were polymerized from these novel tetracarboxylic dianhydrides with several common diamines according to the procedures mentioned above. The PHAI films (10 μm thick) were highly transparent at 365 nm (transmittance > 70 % at 365 nm). In addition, the PHAI films could be cured to poly(benzoxazole imide) (PBOI) even at a much lower temperature such as 260 °C than in conventional PHA systems. The PBOI film properties and photo-patternability will be also discussed in this report.

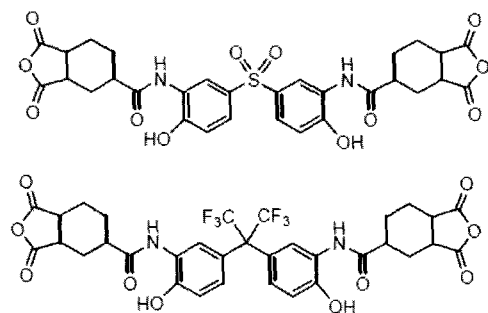


Fig.8 Structure of novel hydroxyamide-containing tetracarboxylic dianhydrides derived from hydrogenated trimellitic anhydride with bis(o-aminophenol)s.

4. Conclusions

We developed a new type of positive-working soluble PI system bearing phenolic OH groups, namely, poly(hydroxyamide imide)s (PHAIs). In contrast to conventional OH pendant soluble PI systems, thermal curing of the present PHAI films at 300 °C led to complete disappearance of the OH groups via cyclodehydration of the hydroxyamide groups to form poly(benzoxazole imide)s (PBOIs). The PBOI films displayed high T_g 's ranging 298–323 °C. The use of fluorinated diamines caused much lower water absorption. The PHAI films were highly transparent at 435 nm but not at 365 nm. This is a problem to be solved for high sensitivity patterning at i-line. The alkali-solubility

of the PHAI films was controlled by copolymerization using 4,4'-ODA and HFBAPP. Photo-irradiation of the copolymer/DNQ film at g-line allowed the formation of a file positive-type pattern by development using a 2.38 wt% TMAH containing 2-propanol. This work was also extended to highly transparent PHAI systems. For this purpose, novel hydroxylamide-containing tetracarboxylic dianhydrides were synthesized from hydrogenated trimellitic anhydride with bis(o-aminophenols) in this work. The PHAI films possessed $T > 70\%$ at 365 nm and lower temperature curing ability.

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