

Study of Polybenzoxazole Precursors for Low Temperature Curing

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1. Introduction

Photodefinable polybenzoxazoles (PD-PBOs) are attracting positive-tone materials in silicon technology process integration such as insulating and buffer coating, because of their excellent electrical, thermal and mechanical properties, which are comparable to polyimides (PIs) [1]. For these applications, insoluble PBOs are formed through cyclization of soluble PBO precursors, namely poly (*o*-hydroxyamide)s (PHAs), by thermal treatment at much more than 300 °C. This high-temperature process is hardly applicable to novel organic devices such as gate dielectric layers [2] or insulation layers [3], because these devices requires much less than 300 °C curing temperature to obtain the satisfactory results. In PIs application, there are several approaches to reduce the imidization temperature including the introduction of flexible structure [4].

Herein, we focused on the PHAs containing flexible structure. We synthesized the PHAs and then evaluated cyclization degree and the photolithographic properties for positive-tone low temperature curing material.

2. Method

PHAs were prepared from several dicarboxylic acids and bis (*o*-aminophenol)s (BAPs) by acid chlorination method. The diazonaphthoquinone (DNQ) as a photoacid generator and N-methyl-2-pyrrolidone (NMP) as a solvent were

used as purchased.

A solution of a PHA was spin-coated on a silicon wafer, which was then soft-baked on a hot plate at around 120 °C for 3 min to give a thin film whose thickness was adjusted to about 15 μm. The resulting film was cured at 200 °C for 1 h under a nitrogen atmosphere. The cyclization percentage was estimated by infrared (IR) spectroscopy (Shimadzu FTIR-8300).

Each photopolymer solution was prepared by dissolving 90-wt% of PHA, 10-wt% of DNQ and other additives such as adhesion promoter in NMP. Then the solution was spin-coated on silicon wafer, soft-baked on a hot plate, and exposed to the radiation of an *i*-line stepper. The puddle method with 2.38% aqueous TMAH as the developer was applied for the development.

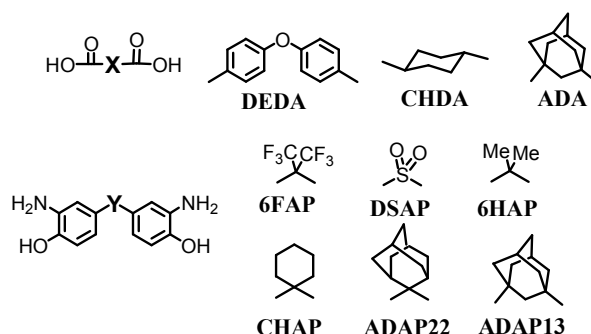


Figure 1. Structure of monomers used.

3. Results and Discussion

3.1. Thermal Cyclization of PBO precursors

To investigate the relationship between cyclization ability of PHAs and their chemical structures, we synthesized several PHAs that were derived from BAPs and aromatic or alicyclic dicarboxylic acid (see Figure 1). Molecular weight (M_w) of these PHAs were 5,700-21,600. Herein, we introduce Percentage of rigid chain length (PRCL) that expresses rigidity parameter of a polymer chain [5], since chemical structures of PHA could be converted into numerical value. The PRCL of PHAs are defined by the following equation.

$$\text{PRCL} = L_{\text{rigid}}/L_{\text{total}} \times 100 \quad (1)$$

Where, L_{rigid} is the length of a rigid part in a monomer unit, and L_{total} is the length of the whole of the unit. In this study, the amide part as a common structural unit is omitted for calculating PRCL for simplification. The evaluation of cyclization of PHAs was estimated by IR spectroscopy of the PHA films cured at 200 °C for 1 h on silicon wafers.

The cyclization percentage of films cured at 200 °C is plotted as a function of calculated PRCLs of PHAs as shown in Figure 2. We found that the cyclization percentage of cured film increase relatively with decreasing the PRCL. Among the structure of monomer examined, PHAs derived from CHAP, ADAP22, AdAP13, CHDA and ADA (PRCL \leq 63%) showed high cyclization percentage, which are over 50%. These results suggest that the PHAs having alicyclic structure showed higher cyclization ability.

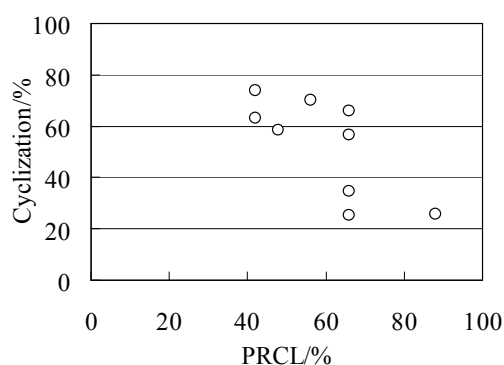
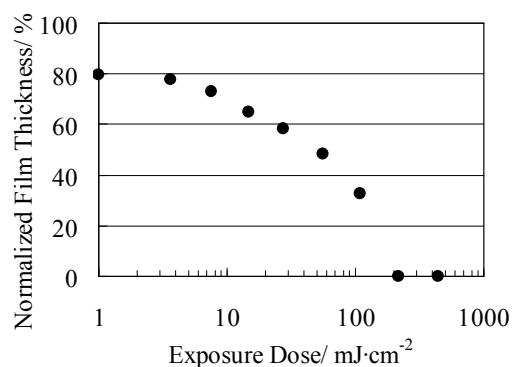


Figure 2. PRCL of PBO precursors versus cyclization percentage of films cured at 200 °C.

3.2. Photolithography

On the basis of the above survey, the PHAs

derived from promising monomer were subjected to the photolithographic study. The photopolymer solution consisting of DNQ was evaluated on a 12- μ m-thick prebaked film. Its sensitivity curve is shown in Figure 3. The sensitivity (D_0 : dose to clear) was around 200 mJ/cm^2 along with 80% film retention after 2.38% aqueous TMAH development; moreover, 3- μ m trench can be resolved. The aliphatic backbone structure is known to be high transparency.



Therefore, it will be concluded that this high performance is resulted from the high transparency of PHA afforded by the alicyclic structure adapted. Figure 3. Sensitivity curve of the photodefinable PBO for 12- μ m-thick prebaked.

4. Conclusion

Various PBO precursors have been examined by comparing structures and their cyclization ability to reduce curing temperature. We found that the PHAs containing alicyclic structure in BAP part or dicarbocyclic acid part showed high cyclization percentage at the cured temperature of 200 °C. In addition, high sensitivity and fine resolution of patterns were obtained from the DNQ positive system. The incorporation of alicyclic structure was advantageous to PD-PBOs, because it was effective lower the curing temperature and higher the photolithographic properties.

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