An Efficient Catalyst for Low Temperature Solid-phase Cyclization of Poly(*o*-hydroxyamide)

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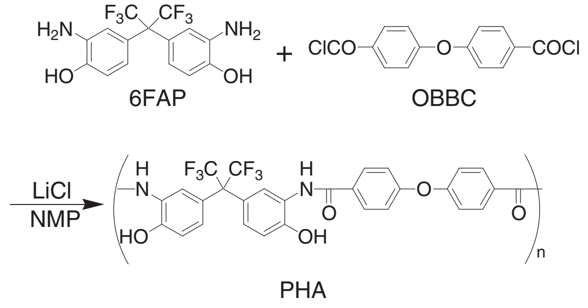
An efficient acid catalyst for the low-temperature solid-phase cyclization of poly(*o*-hydroxyamide) (PHA) has been found. Thermal cyclization of PHA into poly(benzoxazole) (PBO) proceeded quantitatively at 250 °C in 10 min in the presence of 10 wt % of a photoacitve compound, (5-propylsulfonyloxyimino-5*H*-thiophen-2-ylidene)-2-(methylphenyl)-acetonitrile (PTMA).

PBOs have been used as protection and insulation layers for very large scale integration circuits (VLSI) and multichip modules for computers owing to their high thermal stability and excellent mechanical property.[1–4] Photosensitive PBOs (PSPBOs)[5–17] have been developed to simplify the processing steps because phenolic hydroxyl groups in precursors of PBOs provide adequate solubility toward an aqueous alkaline developer. Up to now the PSPBO based on the PHA derived from 4,4′-(hexafluoroisopropylidene)bis(*o*-aminophenol) (6FAP) and 4,4′-oxybis(benzoic acid) derivatives[18,19] with a photosensitive compound is widely used, in which the image of the PSPBO is finally converted into that of PBO by thermal treatment at 350 °C. This high-temperature process is hardly applicable to the conventional electronic applications containing at least one more thermally unstable organic component. Therefore, development of novel catalysts enabling low temperature solid-phase cyclization of PHAs is required.

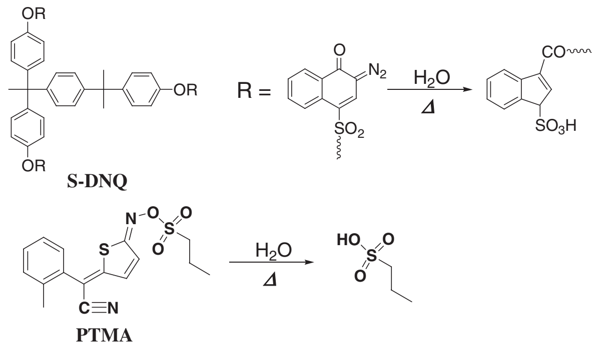
Recently, *p*-toluene sulfonic acid (*p*-TSA) and *p*-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate (NBAS) were found to be effective catalysts to lower the cyclization temperature of *O*-*tert*-butoxycarbonylated PHA (*t*-BOCPHA) derived from 6FAP with 4,4′-oxybisbenzoyl chloride (OBBC). The thermal cyclization temperature was 290 °C in the presence of NBAS, significantly lower than non-catalytic cyclization at 346 °C.[20] Process temperature below 250 °C, however, is preferable in the semiconductor manufacturing. PTMA is known to be an excellent photoacid generator with high quantum yield at 436-nm wavelength.[21] Here, we present PTMA an excellent low-temperature cyclization catalyst of PHA, where 10 wt % of PTMA is enough to complete the cyclization at 250 °C in a short time.

PHA was prepared by polycondensation of 6FAP with OBBC in 1-methyl-2-pyrrolidinone (NMP) in the presence of LiCl at 0 °C for 30 min, and room temperature for 24 h (Scheme 1).[22] The number average molecular weight (M_n) and polydispersity (M_w/M_n) of PHA were determined by GPC (in DMF at 40 °C, PSt calibration) to be 25000 and 1.6, respectively.

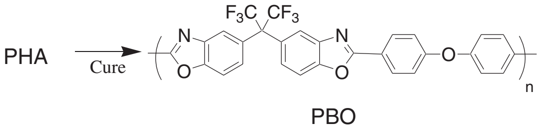
In the synthesis of thermally stable photosensitive polymers, diazonaphthoquinone (DNQ) and PTMA[23] are used as a photodissolution inhibitor and a photoacid generator, respectively, and these photoactive compounds produce strong sulfonic acids by photoirradiation or thermal treatment[24,25] (Scheme 2). Thus, these compounds would be expected to work as catalysts for low-temperature cyclization of PHA after image formations. As DNQ, we chose 1-{1,1-bis[4-(2-diazo-1-(2*H*)naphthalenone-4-sulfonyloxy) phenyl]ethyl}-4-{1-[4-(2-diazo-1(2*H*)naphthalenone-4-sulfonyloxy)phenyl]-methylethyl}benzene (S-DNQ).



Scheme 1. Synthesis of PHA.



Scheme 2. Acid generation from S-DNQ and PTMA.



Scheme 3. Transformation of PHA into PBO.

These compounds were added to a solution of PHA in γ-butyrolactone and the mixture was stirred at room temperature for 1 h. The solution was spin-cast on a silicon wafer, and baked at 120 °C for 5 min, resulting in 2–3-µm thick films. The reference PBO film was prepared by heating a PHA film at 250, 300, and 350 °C, respectively for 1 h under nitrogen (Scheme 3).

The degree of cyclization was determined assuming the absorptions at 1051 (C–O stretch of benzoxazole) and 1250 cm^{-1} (C–O stretch of phenyl ether) had no influence by the catalyst and solvent.

Figure 1 shows the change in the IR spectra of the PHA film

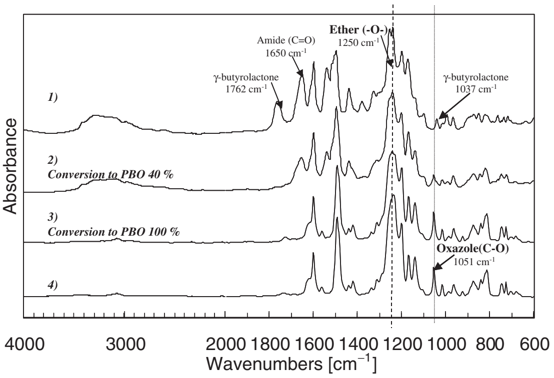


Figure 1. IR spectra of 1) PHA film after spin-cast. 2) PHA film containing 10 wt % PTMA baked at 200 °C for 10 min. 3) PHA film containing 10 wt % PTMA baked at 250 °C. 4) reference PBO film.

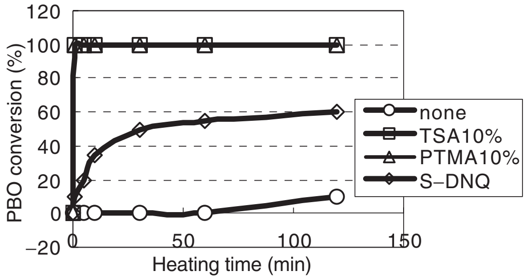


Figure 2. Dependence of cyclization on curing time at 250 °C.

containing 10 wt % PTMA upon heating at various temperatures for 10 min and the reference PBO film. The degree of cyclization in the presence of PTMA is 40% at 200 °C, and accelerated at 250 °C, reaching 100% in 10 min.

The progress of cyclization at 250 °C in various catalysts including *p*-TSA, S-DNQ, and PTMA is shown in Figure 2. The cyclization is completed in a few minutes in the presence of *p*-TSA and PTMA. On the other hand, S-DNQ accelerates the cyclization comparing the absence of catalyst, but the degree of cyclization is around 60% even after 2 h. This phenomenon may be explained by thermal cross-linking of decomposed products derived from S-DNQ, which inhibits the diffusion of sulfonic acid moieties (Figure 2).

The cyclization process involves several interrelated elemental reactions, and dynamic changing physical properties such as diffusion rate, chain mobility, solvation, and acidity. Thus, it is very difficult to predict the proper acid-catalyzed cyclization mechanism. In this work, sulfonic acids would accelerate the attack of a phenolic hydroxyl group on an amide carbonyl unit through protonation on the oxygen of the amide group.

In summary, we have found that the photoacid generator PTMA accelerates the thermal cyclization of PHA films at low temperature. This method not only will provide a potentially efficient route for the low-temperature solid-phase cyclization of PHA, but also will be very useful for the PSPBO process.

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25 To ensure the thermal acid generation from PTMA, 0.143 mmol of PTMA was placed in a glass sample-tube and heated at 180 °C for 5 min. After cooling the solid to 25 °C, 0.143 mmol of triphenylmethane was added as an internal standard (IS). The yield of propanesulfonic acid was determined to be 85% from the integration ratio of a methine proton at 5.55 ppm of IS and β-protons of propanesulfonic acid at 1.85 ppm in the ^{1}H NMR spectrum (CDCl$_3$).

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