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

Tomohito Ogura and Mitsuru Ueda*

Department of Organic & Polymeric Materials, Graduate School of Science & Engineering, Tokyo Institute of Technology, 2-12-1-H120, O-okayama, Meguro-ku, Tokyo, Japan 152-8552

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Recently, photosensitive poly(benzoxazole)s (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 spacings, and very thin insulation, insulating materials with lower dielectric constants are required for high speed and frequency multilayer printed circuit boards.[1−4]

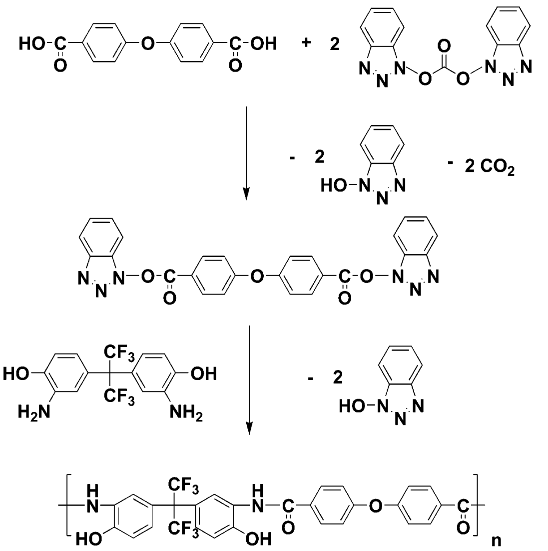
The most promising PSPBO is composed of a poly(benzoxazole) (PBO) precursor, poly(*o*-hydroxyamide) (PHA), and a diazonaphthoquinone sensitizer. The phenolic hydroxyl groups of PHA are desirable as base-soluble functional groups for aqueous alkaline developable photosensitive resists. Furthermore, the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

Scheme 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]

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.

Scheme 1. Synthetic Route of PHA



Scheme 2. Preparation of *p*-Nitrophenylbenzoate

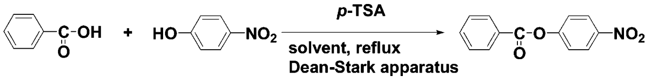


Table 1. Preparation of *p*-Nitrophenylbenzoate from Benzoic Acid and *p*-Nitrophenol[a]

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.

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).

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). The results are summarized in Table 1.

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

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 3). The results are summarized in Table 2.

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.

Synthesis of PHA. 1-Hydroxybenzotriazole (HOBt) catalyzes the polycondensation of di(*p*-nitrophenyl isophthalate) with

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* To whom all the correspondence should be addressed. E-mail: mueda@polymer.titech.ac.jp.

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Scheme 3. Preparation of 4,4′-Oxybis(*p*-nitrophenylbenzoate), 1

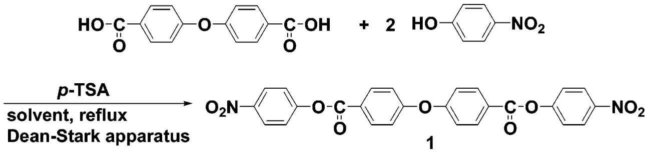

Table 2. Preparation of 1 from 4,4′-Oxybis(benzoic acid) and *p*-Nitrophenol[a]

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.

Scheme 4. Preparation of Poly(*o*-hydroxyamide)

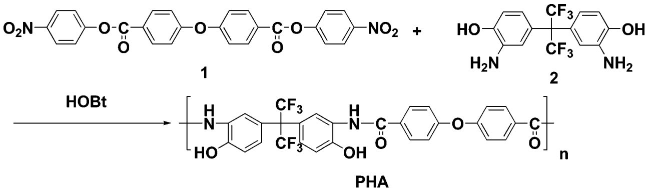

Table 3. Preparation of Poly(*o*-hydroxyamide) from 1 and 2[a]

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).

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 4).

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.

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.

Supporting Information Available: Experimental procedures and characterization for *p*-nitrophenylbenzoate, 4,4′-oxybis(*p*-nitrophenylbenzoate) (**1**), and poly(*o*-hydroxyamide). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) SEC measurements are crude estimations.

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