Convenient Synthesis of Poly(butylene succinate) Catalyzed by Distannoxane

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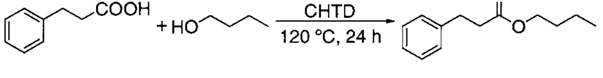
A convenient method for the synthesis of poly(butylene succinate) (**1**) of high molecular weight has been developed. This polyester was prepared readily by the distannoxane-catalyzed polycondensation of succinic acid (**2**) with 1,4-butanediol (**3**) in decalin at 190 °C under azeotropic condition. The polycondensation proceeded in decalin-melted polymer two-phase, giving **1** with the number average molecular weight of 150000.

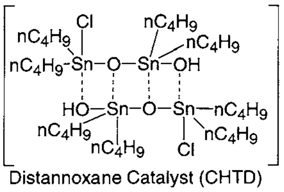
Aliphatic polyesters are currently receiving considerable attention for their applications in biodegradable fibers, film, bottles, and injection-molded products.[1] Most of aliphatic polyesters for the commercial uses are prepared from cyclic esters and biosynthesis.[2,3] Recently, much attention has been paid to the synthesis of aliphatic polyesters from aliphatic dicarboxylic acid and diols. However, it was very difficult to prepare aliphatic polyesters with high molecular weights because of low thermal and hydrolytic stability. Thus, high molecular weight polymers are prepared by the polymerization of chain extender, such as diisocyanates or diphenyl carbonates, with hydroxy terminated prepolymers from diacids and diols.[4,5] Quite recently, new methods using a direct polycondensation of **2** with diols in solvents and in bulk under high vacuum have been developed to obtain aliphatic polyesters with high molecular weights.[6,7] However, these methods still require a high vacuum system. Thus, more simple method would be expected to develop.

Otera et al. reported that distannoxane catalysts were very effective for esterfication of carboxylic acids with alcohols,[8] and applied successfully these catalysts for the synthesis of poly(L-lactic acid).[9] These findings prompted us to develop a new synthetic method for aliphatic polyesters having high molecular weights by a direct polyesterfication of aliphatic dicarboxylic acids with diols.

In this paper, we report the successful synthesis of high molecular weight **1** from **2** and **3** in the presence of 1-chloro-3-hydroxy-1,1,3,3-tetrabutyldistannoxane catalyst (**4**) under atmospheric pressure.

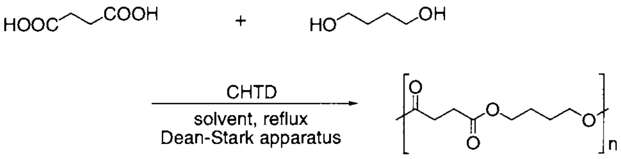
Before attempting the polymer synthesis, we first studied the catalytic effects of **4** on the reaction of equimolar amounts of 3-phenylpropionic acid and 1-butanol in bulk (Scheme 1). Because, the reported esterification of carboxylic acids in the presence of the distannoxane catalyst was carried out using a large excess of alcohols.[8] The reaction proceeded slow at 100 °C but gave a quantitative yield of the 3-phenylpropionic butyl ester after 24 h.





Distannoxane Catalyst (CHTD)

On the basis of the model reaction, the distannoxane-catalyzed polyesterification of **2** and **3** was investigated. In the distannoxane-catalyzed esterification, it is reported that the reverse reaction (hydrolysis) cannot occur, and removal of the formed water is unnecessary.[8] Thus, direct polycondensation was carried out in bulk in the presence of **4** (1 mol%) at 120 °C under nitrogen atmosphere. This polymerization produced **1** with a number average molecular weight (Mn) of 4000 (relative to polystyrene standard), which means the water concentration is about 0.2 mol% when an equilibrium constant for the polyesterification is 4. The polyesterification catalyzed by distannoxane gave **1** without removing the water. The molecular weight of polymer obtained, however, was not enough to make films and fibers. The water concentration must be lowered to achieve a high degree of polymerization. Then, water was removed by a slow flow of nitrogen at 120 °C. This method was somewhat effective to improve the Mn of **1** (Mn = 9000). Driving an equilibrium constant toward polyester can be carried out more efficiently with azeotropic distillation. Therefore, a mixture of equimolar amounts of each monomer and the catalyst (0.01 or 1 mol%) in solvent was refluxed in a Dean-Stark apparatus (Scheme 2). A typical polymerization was carried out as follows. A mixture of **2** (20.0 mmol, 2.362 g) and **3** (20.0 mmol, 1.802 g) in the presence of **4** (0.01 or 1 mol%) was placed in a 50 cm^3 round-bottom flask equipped with Dean-Stark apparatus and a condenser. The mixture was stirred at 120 °C for 1 h, and then the solvent was added. The mixture was refluxed for 24 or 72 h. After the polymerization, the mixture was cooled to room temperature, the solvent was removed by decantation. The polymer was dissolved in 20 cm^3 of chloroform and the resulting solution was poured into a large amount of hexane. The polymer was obtained almost quantitatively. These results are summarized in Table 1.



When *p*-chlorotoluene (Run 1) was used for the solvent, the polymerization proceeded in homogeneous state. On the other hand, the polymerization in nonane (Run 2) proceeded in

Table 1. Distannoxane-catalyzed polyesterification of succinic acid and 1,4-butanediol in a Dean-Stark apparatus[a]

Run No.	**4** mol%	Solvent	Temp. °C	Time h	Mn[b]	PD[c]
1	1	*p*-chlorotoluene	162	24	3800	3.2
2	1	nonane	151	24	16000	1.9
3	1	decalin	190	24	33000	2.2
4	0.01	decalin	190	24	70000	1.9
5	0.01	decalin	190	72	147000	1.8

[a]Reaction condition: 20.0 mmol of monomers (succinic acid and 1,4-butanediol), 30 cm^3 of solvent. [b]Measured by GPC in chloroform based on standard polystyrene. [c]PD is Mw/Mn.

two phase, that is, a solvent-melted polymer phase, which means nonane does not dissolve the polymer. In the latter case, higher molecular weight polyester, **1** was produced. This two-phase system is very effective for keeping the concentration of reactants high. Finally, the polymerization (Run 5) was conducted in the presence of 0.01 mol% of **4** in decalin at 190 °C for 72 h, giving a very high molecular weight of **1** (Mn = 147000). For the comparison of the catalytic activity of **4**, the polymerizations in the presence of Sn and $SnCl_2$ catalysts that gave high molecular weights of poly(lactic acid) by direct polycondensation of lactic acid [10] were carried out under the same condition described above (cat. 0.01 mol%, 190 °C, 72 h), and producing **1** with the number average molecular weights of 47000 and 51000, respectively.

The structure of the polymer was identified as the expected **1** by IR, ^1H-, and ^{13}C-NMR spectroscopies.

In summary, we have shown that **1** with a very high molecular weight is readily prepared by the distannoxane-catalyzed polycondensation of **2** with **3** in decalin under azeotropic condition. Since this preparation method is simple and gives quantitatively aliphatic polyester of high molecular weight, it is generally superior to conventional methods for the synthesis of aliphatic polyester.

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