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Lipase-Catalyzed Polymerization of Divinyl Adipate with Glycols to Polyesters

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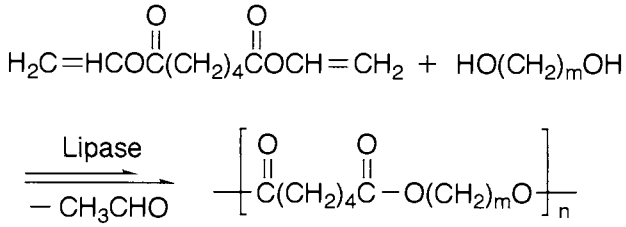
Enzymatic polymerization of divinyl adipate with four glycols was carried out catalyzed by three kinds of lipase. The polymerization with 1,4-butanediol by *Pseudomonas fluorescens* lipase in *i*-propyl ether at 45 °C for 48 h produced a corresponding polyester with molecular weight of 6700 in 50% yield. With ethylene glycol, 1,6-hexanediol or 1,10-decanediol as a glycol, the corresponding polyester was also obtained, however, its molecular weight decreased, compared with that of 1,4-butanediol.

Enzymatic polymerizations have received much attention as a new methodology for polymer synthesis.[1,2] Recently, we have reported two new types of the enzymatic polymerization involving ring-opening of monomers by lipase catalyst, e.g., the ring-opening polymerization[3] and copolymerization[4] of lactones, and the poly(ring-opening-addition-condensation) of a cyclic acid anhydride with a glycol.[5] These reactions afforded polyesters under mild conditions.

Syntheses of esters by lipase catalyst have been extensively investigated to prepare chiral compounds.[6,7] Transesterifications using lipase catalyst are often very slow owing to the reversible nature of the reactions. Recently, an irreversible procedure for the lipase-catalyzed acylation using enol esters as acylating agent has been developed, where a leaving group, an unsaturated alcohol, tautomerizes to a ketone or aldehyde.[8] In these cases, the reaction with the enol ester proceeds much faster to produce the desired compound in higher yields, in comparison with the alkyl ester. On the other hand, a bis(enol ester) has not been employed as a monomer for the polyester synthesis. The present study deals with synthesis of aliphatic polyesters by lipase-catalyzed polymerization of a bis(enol ester), divinyl adipate, with glycols under mild conditions.



The enzymatic polymerization of divinyl adipate with a glycol was performed in *i*-propyl ether.[9] At first, three lipases with different origin were used as catalysts for the polymerization with 1,4-butanediol at 45 °C. Among the lipases examined, lipase derived from *Pseudomonas fluorescens* (lipase P) was active for the polymerization (entry 4 in Table 1). In our previous studies on polyester syntheses by lipase catalyst, lipase P also exhibited excellent catalytic properties.[3-5] On the other hand, lipases from *Candida cylindracea* and porcine pancreas (lipase B and PPL, respectively) did not show catalytic activity toward the polymerization. In the polymerization without the enzyme, both monomers were recovered unchanged (entry 6), indicating that the polymerization proceeds by enzyme catalysis. The homopolymerization of divinyl adipate with the lipase catalyst was not observed. In comparison with conventional polycondensation reactions, the present enzymatic polymerization proceeded under milder conditions to produce aliphatic polyesters.

Table 1. Enzymatic polymerization of divinyl adipate with glycols[a]

	Polymerization			Polymer		
Entry	Glycol	Catalyst	Temp /°C	Yield/%[b]	M_n[c]	M_w/M_n[c]
1	Ethylene glycol	Lipase P	45	35[d]	2000	1.9
2	1,4-Butanediol	Lipase P	35	38	3700	1.6
3	1,4-Butanediol	Lipase B	45	0	-----	---
4	1,4-Butanediol	Lipase P	45	50	6700	1.9
5	1,4-Butanediol	PPL	45	0	-----	---
6	1,4-Butanediol	-----	45	0	-----	---
7	1,4-Butanediol	Lipase P	55	54	5500	2.4
8	1,6-Hexanediol	Lipase P	45	50	5900	2.3
9	1,10-Decanediol	Lipase P	45	45	2700	1.8

a) Polymerization in *i*-propyl ether for 48 h. b) Methanol insoluble part. c) By GPC. d) Diethyl ether insoluble part.

The polymer structure was confirmed by ^{1}H and ^{13}C NMR spectroscopies.[10] Figure 1 shows the effect of the polymerization time on the yield and the molecular weight of the polymer in using 1,4-butanediol. The

yield of the polymer insoluble in methanol increased to 50% with increasing the reaction time until 48 h, afterwhile the yield was constant.[11] The molecular weight of the polymer was almost the same during the polymerization. These phenomena were different from those of conventional polycondensations. This may be because the resulting polymer precipitated during the polymerization due to the low solubility of the polymer in the solvent. After 48 h, the both monomers disappeared and the methanol-soluble part was composed of mainly oligoesters of molecular weight less than 1000.

The polymerization at different temperatures has been performed (entries 2,4, and 7). The yield of the polymer obtained at 35 °C was lower than that at 45 or 55 °C. The polymer of the highest molecular weight was obtained by the polymerization at 45 °C. These results indicate that 45 °C is the most suitable as the polymerization temperature. Table 1 shows the results of the polymerization using four glycols. For all glycols examined, the corresponding polyester was obtained with the lipase P catalyst. The reaction mixture from ethylene glycol was soluble in methanol, and hence, the polymer was isolated by reprecipitation using chloroform (good solvent) and diethyl ether (poor solvent). The yield and the molecular weight were lower than those from 1,4-butanediol. In the polymerization with 1,6-hexanediol or 1,10-decanediol, the polymer yield was almost the same as that with 1,4-butanediol. The molecular weight, on the other hand, decreased to some extent in both cases.

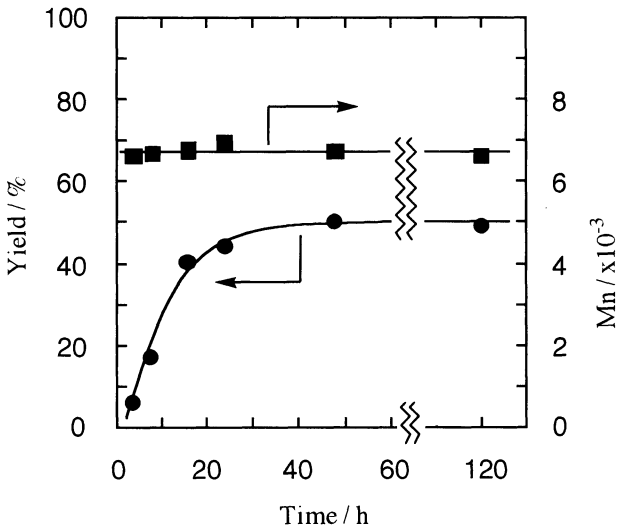


Fig. 1. Time versus polymer yield and molecular weight in the polymerization of divinyl adipate with 1,4-butanediol using lipase P catalyst.

For comparison, the enzymatic polymerization of adipic acid or diethyl adipate instead of divinyl adipate with 1,4-butanediol was carried out using lipase P catalyst in *i*-propyl ether for 48 h. The polymerization of adipic acid did not enzymatically proceed at all. In the polymerization of diethyl adipate, only 20% of the monomers was reacted to produce methanol-soluble oligomers (molecular weight < 1000) and no polymer formation was observed under the similar reaction conditions. These data indicate that the bis(enol ester) monomer was very reactive toward the lipase catalyst to produce the aliphatic polyester.

In conclusion, the enzymatic polymerization of divinyl adipate with a glycol using lipase P produced the polyester. The use of the bis(enol ester) afforded the polyester under milder conditions than those for a

dicarboxylic acid or its ester derivative. Further investigations on the effects of various polymerization parameters are now in progress.

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9) A typical run was as follows (entry 4). A mixture of 0.40 g (2.0 mmol) of divinyl adipate, 0.18 g (2.0 mmol) of 1,4-butanediol, and 0.20 g of lipase P in 10 mL of *i*-propyl ether was placed in a test tube. The mixture was heated at 45 °C for 48 h with shaking (150 shaking movements per min). 20mL of chloroform was added to the reaction mixture and the insoluble part was removed by filtration. The solvent was evaporated under reduced pressure. The residue was dissolved in 2 mL of chloroform and the solution was poured into a large amount of methanol to precipitate white powders. The polymeric material was isolated by filtration and dried in vacuo to give 0.23 g of the polymer (50% yield).

10) ^{1}H NMR (entry 4 in Table 1, $CDCl_3$, δ in ppm): 1.7 (8H, $CH_2CH_2CH_2CH_2$, br); 2.2 (4H, $CH_2CH_2C{=}O$, br); 4.1 (4H, CH_2CH_2O, br). ^{13}C NMR ($CDCl_3$, δ in ppm): 24.2, 25.1 ($CH_2CH_2CH_2CH_2$); 33.8 ($CH_2CH_2C{=}O$); 63.8 (CH_2CH_2O); 173.2 ($CH_2C(=O)O$).

11) Before the reprecipitation procedure, the residue (chloroform soluble part) showing the molecular weight of 1500 was obtained in 98% yield in the polymerization with butanediol at 45 °C for 48 h.

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