One-Shot Synthesis of Polyester Macromonomer by Enzymatic Ring-Opening Polymerization of Lactone in the Presence of Vinyl Ester

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Polyester macromonomers bearing a polymerizable methacryloyl or 10-undecenolyl group at the chain end were synthesized by the lipase-catalyzed ring-opening polymerization of 12-dodecanolide in the presence of a vinyl ester having the corresponding polymerizable group.

Polymers bearing a reactive group at the terminal such as macromonomers and telechelics are widely employed as starting materials for preparation of graft and block copolymers with well defined structures.[1] Until now, several aliphatic polyester macromonomers have been synthesized. A poly(β-butyrolactone) macromonomer having a polymerizable acryloyl group was obtained by ring-opening polymerization with tetraphenylporphinatoaluminum acrylate initiator.[2] A methacryl-type poly(ε-caprolactone) (poly(ε-CL)) macromonomer was synthesized by using diethylaluminum 2-hydroxyethyl methacrylate as initiator.[3]

There have been much interest in polymerizations catalyzed by enzymes ("enzymatic polymerizations") as new methodology of polymer syntheses.[4,5] Recently, the enzymatic polymerization has been extended to the lipase-catalyzed ring-opening polymerization of lactones.[6-11] Lipase catalysis induced the polymerization of medium size lactones (6- and 7-membered) as well as macrocyclic lactones (12-, 13-, and 16-membered) to the corresponding polyesters. Especially, the macrolides with smaller strain in ring, then showing a lower anionic polymerizability, were found to be polymerized much faster by lipase catalyst than ε-CL.[10,11] This is probably due to the stronger recognition of the macrolide by the enzyme.

Terminal functionalization of the polymer has not been achieved in the enzymatic polymerizations so far in spite of recent development of the field. This study deals with one-shot synthesis of polyester macromonomers by the lipase-catalyzed ring-opening polymerization of 12-dodecanolide (13-membered lactone, DDL) in the presence of a vinyl ester bearing a polymerizable group.

A lactone polymerization through lipase catalysis has been considered to proceed via the acyl-enzyme intermediate to give a polyester bearing a carboxylic acid at one end and a hydroxyl group at the other.[6,10] If an acyclic ester is present in this polymerization system, the hydroxyl group may be acylated to introduce the acyclic ester moiety into the polymer terminal. Recently, vinyl esters have been often utilized as acylating agent in the lipase-catalyzed transesterification with an alcohol, since the reaction proceeded irreversibly to produce the desired compound in higher yield than that using an alkyl ester.[12] Here, we have performed the enzymatic polymerization of DDL in the presence of a vinyl ester having a polymerizable group (Eq. 1). The vinyl esters used in this study were vinyl methacrylate (**1**) and vinyl 10-undecenoate (**2**).

The polymerization was carried out in bulk at 60 ℃. Lipase derived from *Pseudomonas flurorescens* (lipase PF) was used as catalyst. The polymerization results are shown in Table 1. As the feed ratio of the vinyl ester based on DDL increased, the molecular weight decreased. In using the same feed ratio of the vinyl ester, the molecular weight of the polymer obtained in the presence of **1** was larger than that from **2**.

(1)

1 : R = $CH_2=C(CH_3)$ **3** : R = $CH_2=C(CH_3)$

2 : R = $CH_2=CH(CH_2)_8$ **4** : R = $CH_2=CH(CH_2)_8$

Table 1. Synthesis of polyester macromonomer by enzymatic polymerization of DDL in the presence of vinyl ester[a]

				Macromonomer					
Entry	Vinyl Ester	$[Vinyl\ Ester]_0/[DDL]_0$	Time/h	Structure	Yield/%[b]	$Mn/x10^{-3}$[b]	Mw/Mn[b]	[Vinyl Ester]/[DDL][c]	Fc,d
1	**1**	0.075	72	**3**	98	3.7	1.8	0.034	0.57
2	**1**	0.10	72	**3**	92	3.6	1.7	0.048	0.83
3	**1**	0.125	72	**3**	79	3.3	1.7	0.077	0.95
4	**1**	0.150	72	**3**	62	2.9	1.7	0.083	>0.95
5	**2**	0.025	120	**4**	100	3.7	2.0	0.013	0.33
6	**2**	0.050	120	**4**	99	3.5	1.8	0.020	0.80
7	**2**	0.075	120	**4**	98	2.4	1.5	0.032	>0.95
8	**2**	0.10	120	**4**	37	1.9	1.5	0.051	>0.95

[a] Polymerization using lipase PF catalyst in bulk at 60 ℃. [b] Determined by GPC using polystyrene standards.
[c] Determined by ^1H NMR. [d] Functionality.

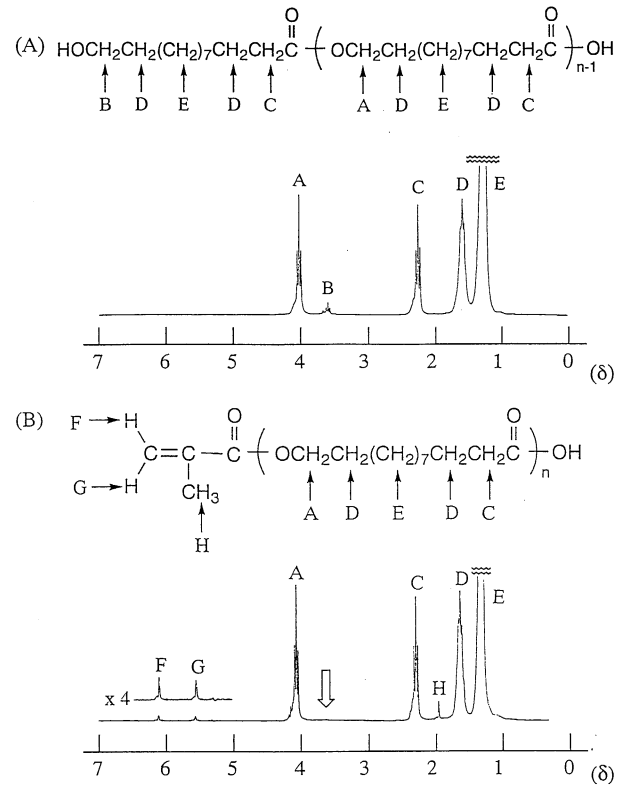

Figure 1. ^{1}H NMR spectra of (A) polyDDL obtained in the absence of vinyl ester and (B) macromonomer **3** (entry 3).

Figure 1(A) shows ^{1}H NMR chart of the polymer produced by the lipase-catalyzed polymerization of DDL in the absence of the vinyl ester. A small triplet peak at δ 3.6 (peak B) is ascribed to the α-methylene protons of the terminal hydroxyl group. On the other hand, this triplet peak almost disappeared in the chart (Figure 1(B)) of the polymer obtained in the presence of **1** (entry 3) and three characteristic peaks due to the methacryloyl group appeared at δ 6.1, 5.6, and 1.9 (peaks F, G, and H). These results indicate that the polymerizable methacryloyl group was almost quantitatively introduced at the terminal of **3**. Peaks around δ 0.9 due to the methyl protons of polymethacrylate were not observed, indicating that the methacryloyl group was not polymerized under the present reaction conditions.

The ratio of the introduced polymerizable group into the terminal (functionality) was determined from that of the integrated area between peak B and the peak due to the polymerizable group. The functionality value increased with increasing the feed ratio of the vinyl ester on DDL. The quantitative introduction of the polymerizable group in **3** was achieved in the feed ratio of **1** more than 0.125, on the other hand, a decreased amount of **2** was necessary to produce macromonomer **4** bearing a 10-undecenoyl group quantitatively at the polymer end. In all cases, the ratio of the polymerizable group and polyDDL unit was smaller than the feed ratio between the vinyl ester and DDL, suggesting that the vinyl ester was partly used for the introduction of the polymerizable group. ^{1}H NMR and GPC analyses exhibited no reaction of the terminal alkenyl group during the polymerization of DDL.

The present macromonomer formation may be explained by considering the following reactions as the principle reaction pathway. In our previous paper, the lipase-catalyzed polymerization is assumed to proceed via monomer-activated mechanism.[10] The key step is the formation of the acyl-enzyme intermediate from the monomer and lipase. The propagation is a nucleophilic attack of the terminal hydroxyl group in the polymer onto the acyl carbon of the intermediate. The catalyst is also reacted with the vinyl ester to give the acyl-lipase intermediate, which is subjected to the reaction with the polymer to give the macromonomer. The resulting macromonomer has no hydroxyl group, and hence, can not be reacted with the intermediate anymore. Therefore, the vinyl ester is considered to act as terminator.

In conclusion, the polyester macromonomer bearing polymerizable methacryloyl or 10-undecenoyl group at the chain end was synthesized by the lipase-catalyzed ring-opening polymerization of DDL in the presence of the vinyl ester having the corresponding polymerizable group. The macromonomer was obtained by a convenient, one-shot procedure. The present system can be applied to the synthesis of the telechelics having a carboxylic acid group at both ends by the addition of divinyl sebacate in the reaction mixture.[13] Further studies concerning the polymerization of lactones in the presence of various vinyl ester compounds are now under way in our laboratory.

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