Lipase-Catalyzed Hydrolytic Degradation of Polyurethane in Organic Solvent

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(Received March 2, 2001; CL-010178)

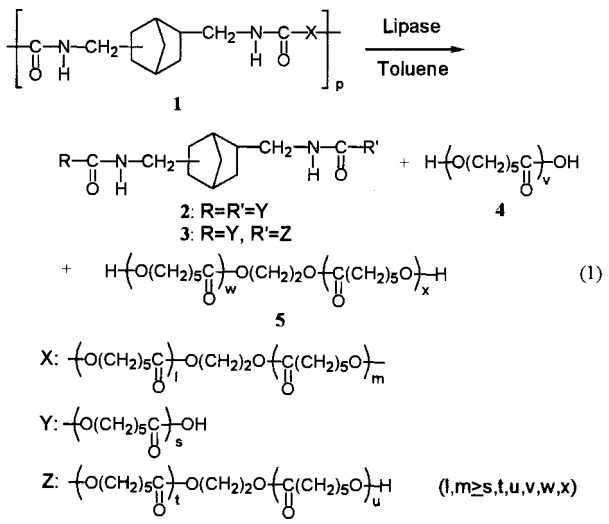
Hydrolytic degradation of polyurethane has been achieved using lipase as catalyst. The degradation of polyurethane containing an aliphatic polyester chain as soft segment rapidly took place in the presence of *Candida antarctica* lipase in toluene at 60 °C to give oligomers with molecular weight less than 500.

Since an environmental problem by plastic wastes has become a serious issue, there have been worldwide potential demands for recycling of polymeric materials.[1,2] Recycle use of thermosetting plastics is one of the most urgent subjects to be settled. However, industrial examples of chemical recycling are limited (alcoholysis of PET and PBT) and their processes normally consume much energy (high temperature and/or pressure). Therefore, development of environmentally friendly processes of chemical recycling is strongly desired. Biodegradable polymers are expected as an alternative to traditional non-biodegradable polymers.[3] These polymers are subjected to degradation by living organisms; however, their chemical recycling has not been achieved owing to difficulty of isolation of degradation products under the biodegradation conditions.

Polyurethanes are widely used for various purposes such as foams, adhesives, elastomers, paints, and fibers. Polyurethanes consist of soft and hard segments, and low molecular weight aliphatic polyesters or polyethers are used as the former. Polyurethanes containing a polyester chain of soft segment (poly(urethane-ester)s) are subjected to degradation by microorganisms,[4,5] especially by fungi. Microbial degradation of poly(urethane-ester)s is considered to take place via catalysis of esterases cleaving the ester bond of the soft segment.[5] Hitherto, several degradating enzymes were purified and their unique characteristics were reported. The enzyme derived from *Comamonas acidovorans* TB-35 possessed a secondary structure motif similar to acetylcholine esterase.[6] In addition, this enzyme had a hydrophobic surface-binding domain essential for degradation of polyurethanes, which is also observed in poly(hydroxyalkanoate) depolymerases. Recently, genes encoding an extracellular enzyme catalyzing the degradation of polyurethanes were cloned.[7–9] The amino acid sequence revealed the serine hydrolase motif, G-X-S-X-G. Some enzymes catalyzing the degradation of polyurethanes showed high amino acid sequence identical with lipases.

There has been much interest in polymer syntheses catalyzed by isolated enzymes as environmentally benign processes of plastics production under mild reaction conditions.[10–14] So far, biodegradable aliphatic polyesters have been synthesized by lipase catalyst from various monomer combinations. By selecting the reaction conditions, lipase catalysis also enabled the hydrolytic degradation of aliphatic polyesters in organic solvents to give oligomers, which were polymerized in bulk by the same catalyst.[15–17] From these data, we have first proposed a basic concept that the degradation–polymerization could be controlled by presence or absence of the solvent, providing a new methodology of plastic recycling.[15]

Despite extensive use of polyurethanes in industrial fields, chemical recycling of polyurethanes has not been achieved to our knowledge. This study deals with degradation of poly(urethane-ester) (**1**) using commercially available lipase catalysts in organic solvent to give oligomers (eq 1), which may be used as starting substrate for useful polymeric materials. Here, polyurethane (M_n=4.8 × 10^4) obtained from norbornene diisocyanate and poly(ε-caprolactone) (polyCL) glycol (M_n=2.0 × 10^3) was used as substrate. The lipase-catalyzed hydrolytic degradation was performed in toluene at 60 °C.[18] The water content of the reaction mixture was determined by Karl Fischer titrator as ca. 0.1 wt%. Poly(urethane-ester) (**1**) and degradation product were soluble in toluene. Molecular weight of the degradation product was estimated by size exclusion chromatography (SEC). The catalysts used were lipases derived from *Candida antarctica*, *Mucor miehei*, *Pseudomonas cepacia*, and *Pseudomonas fluorescens* (abbreviated to lipases CA, MM, PC, and PF, respectively). These lipase catalysts were active for both synthesis and degradation of polyesters.[14,15] Among the enzymes examined, lipases CA and MM catalyzed the degradation of polyurethane in toluene, however, no catalytic activity for the degradation was observed in lipases PC and PF.



(1)

Degradation results are summarized in Table 1. Both enzymes afforded the oligomer with molecular weight less than 500. A smaller amount of lipase CA was sufficient for the degradation than that of lipase MM, showing the higher catalytic activity of lipase CA toward the degradation. In the higher loading of polyurethane, the molecular weight of the degradation product became larger. In the degradation without the enzyme (control experiment), polyurethane was recovered unchanged, indicating

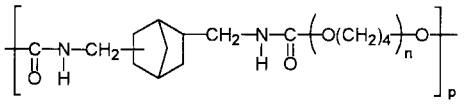
Table 1. Lipase-catalyzed degradation of polyurethane (**1**)[a]

Entry	**1** /mg	Catalyst	Time /h	Conv.[b] /%	M_n[b] /×10^{-3}
1	50	Lipase CA	24	100	0.47
2	100	Lipase CA	24	89	1.6[c]
3	100	Lipase CA	120	100	1.5
4	200	Lipase CA	24	100	14
5	50	Lipase MM	24	66	1.1[c]
6[d]	50	Lipase MM	24	100	0.41

[a]Degradation of **1** using lipase catalyst (20 mg) in toluene (10 mL) at 60 °C for 24 h. [b]Determined by SEC using THF eluent. [c]Data of oligomeric part. [d]Lipase MM amount = 100 mg.

that the present degradation proceeded via the lipase catalysis.

The structure of the degradation product was analyzed by matrix-assisted laser desorption/ionization–time of flight mass (MALDI–TOF MS) and NMR spectroscopies. In the MALDI-TOF MS spectrum, there were mainly four sets of two peaks cationized with H^+ and Na^+ in regular peak-to-peak distance (114) (Figure 1). These peaks could be ascribed to two types of urethane-containing oligoCLs (**2** and **3**) and two linear oligoCLs (**4** and **5**). In the ^{13}C NMR chart (not shown), a strong peak at δ 63.0 ascribed to α-methylene carbon of hydroxy group newly appeared and intensity of a peak at δ 64.0 due to α-methylene carbon of ester group dramatically decreased. On the other hand, intensity of a peak at δ 157.0 due to carbonyl carbon of urethane group hardly changed after the degradation. These data strongly support the formation of **2–5** by the enzymatic degradation of **1**. Furthermore, polyurethane having a poly(tetramethylene oxide) chain as soft segment (**6**) was not subjected to the lipase-catalyzed degradation in toluene. These data suggest that the ester moiety in **1** was cleaved by lipase catalyst in the enzymatic degradation, yielding oligomers **2–5**. The polymerization of the degradation product by lipase CA is currently investigated.



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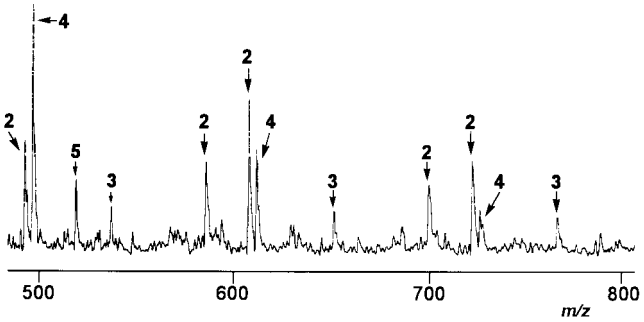

Figure 1. MALDI-TOF MS spectrum of degradation products from **1** (entry 2)

In conclusion, commercially available lipases catalyzed the hydrolytic degradation of poly(urethane-ester) **1** in toluene, yielding the oligomer with molecular weight less than 500. The present study will expand the scope on enzymatic chemical recycling to various polyester-based materials. Furthermore, the enzymatic chemical recycling is an environmentally highly benign process, giving a good example to achieve "green polymer chemistry".[19] Further investigations on enzymatic recycling of useful polymers containing biodegradable polymer chains are under way in our laboratory.

This work was supported by a Grant-in-Aid for Exploratory Research (No. 12875180) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and by Program for Promotion of Basic Research Activities for Innovative Bioscience. We acknowledge the gift of lipases from Novozymes Japan Ltd. and Amano Pharmaceutical Co.

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18 A typical run was as follows (entry 1). A mixture of 50 mg of polyurethane, 20 mg of lipase CA, and 10 mL of toluene was placed in the dried test tube. The mixture was kept at 60 °C under gentle stirring. After 24 h, the solvent was removed under reduced pressure. Tetrahydrofuran (5 mL) was added to the residue and the part of the organic solution was separated by filtration. The filtrate was used for SEC analysis.
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