

Preparation and Characterization of Degradation Tunable Poly(ϵ -caprolactone) Using a $\text{Sn}(\text{Oct})_2/\text{BF}_3$ Dual Catalyst

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ABSTRACT: Tailoring the degradation rate of poly(ϵ -caprolactone) (PCL) was found to be easily accomplished by the polymerization of ϵ -caprolactone using a $\text{Sn}(\text{Oct})_2/\text{BF}_3$ dual catalyst. The resulting PCL contained BF_3 , which acts as a hydrolytic degradation catalyst for PCL. The degradation rate of the polymer was controlled by the concentration of BF_3 in the polymer matrix. At lower BF_3 concentrations ($<0.002 \text{ mol dm}^{-3}$), the degradation rate was linearly proportional to the BF_3 concentration. At higher BF_3 concentra-

tions, the degradation rate rapidly increased, significantly deviating from the linear relationship between degradation rate and BF_3 concentration. The system was found to be very versatile, producing PCL with degradation rates ranging from a half-life of 0.9–46 weeks. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3733–3736, 2008

Key words: poly(ϵ -caprolactone); boron trifluoride; stannous octoate; degradation

INTRODUCTION

Biodegradable aliphatic polyesters have attracted widespread attention during the last few decades due to the increasing problems caused by nondegradable plastics to the environment. The aliphatic polyesters include polylactide (PLA), polyglycolide (PGA), and poly(ϵ -caprolactone) (PCL), poly(3-hydroxybutyrate) (PHB), and poly(butylene succinate) (PBS). They may become the substitutes of conventional commodity thermoplastics, as an answer to the increasing amount of discarded plastic waste in landfills.¹ The basic properties required of degradable polymers include a suitable degradation rate, high enough initial mechanical properties, and a balanced time course between degradation and change in strength.² The latter two properties are actually dependent on the degradation kinetics of the polymer. Therefore, tunable degradation kinetics is a desirable property for applications of these degradable polymers.

It is well known that PCL has a slow degradation rate.³ Various methods have thus been used to enhance its degradation rate. One conventional method is the block or random copolymerization of ϵ -caprolactone with other monomers such as lactide,⁴ glycolide,⁵ and sebacic anhydride.⁶ Copoly-

merization increases the degradation rate by varying the molar composition and sequence of the copolyesters so as to reduce the crystallinity of the resulting polymers. Another method is to prepare polymer blends for tailoring the degradability through the increase of hydrophilicity of the resulting polymer such as PCL blended with PLA.⁷ These methods either rely on introducing a further processing step or result in compromising the intrinsic properties of the polymer through copolymerization. An alternative approach has been designed in our lab to incorporate a degradation catalyst during the polymerization and thus avoid further processing steps to accelerate the degradation of PCL. It also becomes very easy to control the degradation rate of the polymer merely by changing the amount of degradation catalyst added to the reaction mixture.

The catalysts used for preparation of aliphatic polyesters can be roughly categorized as cationic catalysts such as a Lewis acids and coordination catalysts such as tin octoate, zinc octoate, or aluminum acetylacetonate.⁸ $\text{Sn}(\text{Oct})_2$ has received much more attention for several decades⁹ due to its high efficiency and commercial availability.¹⁰ Lewis acids received little attention due to extensive transesterification reactions during polymerization¹¹ such that a well-defined polymer with a narrow molecular weight distribution could not be prepared with such catalysts. It was noticed, however, that PCL produced using the Lewis acid BF_3 had a very fast degradation rate, which must be stabilized using KF before it can be used.^{12,13} Since $\text{Sn}(\text{Oct})_2$ is more

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efficient than BF_3 for catalyzing the polymerization of ϵ -caprolactone, a reaction mixture which contains both catalysts is expected to be predominantly catalyzed by $\text{Sn}(\text{Oct})_2$. The resultant polymer will still retain the Lewis acid which, in the presence of water will catalyze the hydrolytic degradation of the polymer. In this article, the role of the BF_3 residue for tuning degradation is explored, aiming to prove and develop this alternative approach to producing aliphatic polyesters with increased degradation rates using a $\text{Sn}(\text{Oct})_2/\text{BF}_3$ dual catalyst.

EXPERIMENTAL

Materials

ϵ -caprolactone was provided by Solvay Interox (UK). It was dried over calcium hydride (CaH_2), freshly distilled under reduced pressure just before use. $\text{Sn}(\text{Oct})_2$ (Tin(II) bis(2-ethylhexanoate)) and $\text{BF}_3\cdot\text{OMEt}_2$ were both from Sigma-Aldrich and used as received.

Polymer synthesis

A series of PCL samples containing different concentrations of BF_3 was prepared as follows. 80 cm^3 of freshly distilled ϵ -caprolactone was put into a 200-cm^3 three neck, round-bottomed flask with a magnetic stirrer under the blanket of dry nitrogen, and then a predetermined amount of $\text{Sn}(\text{Oct})_2$ was added to the ϵ -caprolactone to prepare a reaction mixture of $\text{Sn}(\text{Oct})_2/\epsilon$ -caprolactone = 1/1000 (molar ratio). After thoroughly mixing, 5 cm^3 of the reaction mixture was removed from the reaction mixture and then injected into a 2-cm^3 reaction vial under the protection of dry nitrogen, and the reaction vials were sealed immediately after injection. A predetermined amount of $\text{BF}_3\cdot\text{O}(\text{CH}_3)_2$ was then added to the remaining mixture (75 cm^3) to prepare a reaction mixture with a higher concentration of BF_3 . After thoroughly mixing, 5 cm^3 was removed from the reaction mixture and injected into another 2-cm^3 glass vial. Reaction mixtures containing higher BF_3 concentrations were prepared in a similar manner and injected into the reaction vials. The reaction vials were then placed in a 110°C oven to polymerize the ϵ -caprolactone. After allowing 24 h for reaction, the glass vials were removed from the oven. The reaction vials were broken, after cooling down, to remove the samples. This yielded a series of PCL cylinder sample with a diameter of 6 mm containing different BF_3 concentrations for degradation testing.

Degradation test

At least ten 0.5-mm thick disks were cut from each PCL cylinder sample using a microtome. Each set of

disks were randomized and immersed in 30 cm^3 of double distilled water in a test tube. These samples were placed in an oven at $(37 \pm 1)^\circ\text{C}$ for the degradation test. The water in the tubes was replaced every week. At appropriate time intervals, one disk was removed from each tube and their molecular weights were measured using GPC after drying in a vacuum oven overnight at 37°C .

Characterization

Gel permeation chromatography (GPC) experiments were performed to determine molecular weights of the degraded polymer samples. The Polymer Labs GPC system consisted of two $5\text{ }\mu\text{m}$ PLgel columns and a guard column, a refractive index (RI) detector. Chloroform (HPLC grade) was used as the mobile phase at a flow rate of $1\text{ cm}^3/\text{min}$ at 35°C , and polystyrene standards (Polymer Labs PS2 narrow standard) were used to calibrate the system. The PCL sample was dissolved into 5 cm^3 chloroform to obtain a solution of about 0.2% (wt). About 1.2 cm^3 was filtered through a $0.45\text{-}\mu\text{m}$ Nylon filter and transferred into a 2-cm^3 sample vial for GPC analysis. The molecular weight thus measured represented the molecular weight of the whole sample. According to the manufacturer of the GPC, for each measurement, there was a maximum of 5% relative error.

RESULTS AND DISCUSSION

A series of PCL samples containing various amounts of BF_3 were prepared as described in the experimental section. Their weight average molecular weights (M_w) and number average molecular weights (M_n) were measured using GPC, as listed in Table I together with their polydispersities (M_w/M_n). When the BF_3 concentration was below $0.0012\text{ mol dm}^{-3}$, molecular weights and molecular weight distribution were not affected significantly. However, M_n decreased and the molecular weight distribution increased at higher BF_3 concentrations. The presence of BF_3 may cause back-biting degradation during polymerization, leading to

TABLE I
Molecular Weights and Molecular Weight Distributions of the As-Prepared PCL Samples Containing Various BF_3 Concentrations

BF_3 concentration (mol/dm^3)	M_w (kg mol^{-1})	M_n (kg mol^{-1})	M_w/M_n
0	224.24	150.50	1.49
0.00027	218.75	148.81	1.47
0.00059	199.71	136.80	1.46
0.00085	202.66	133.33	1.52
0.0012	179.86	113.12	1.59
0.0019	168.32	110.01	1.53
0.0032	157.99	89.77	1.76

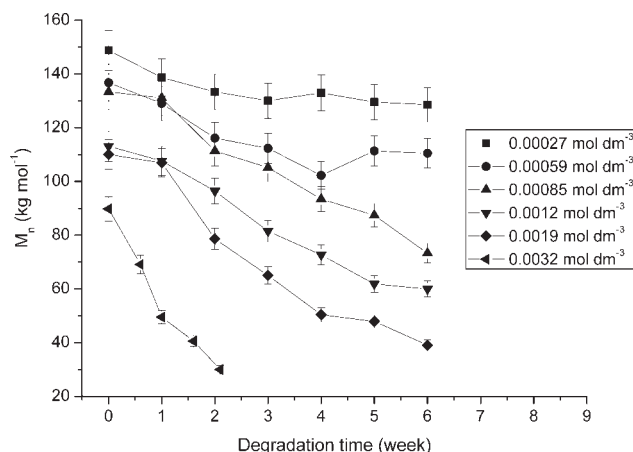


Figure 1 Molecular weight (M_n) change with degradation time for PCL containing various concentrations of BF_3 . The degradation test was performed in double distilled water at 37°C .

the decrease of number average molecular weight and the increase of the polydispersity.¹²

The polymer samples were degraded in double distilled water at 37°C . Figure 1 shows the change in M_n of the PCL samples with degradation time over a period of six weeks. As can be seen, M_n decreased steadily with degradation time. The more BF_3 in the sample, the faster the M_n decreased. The system was found to be very versatile, producing PCL with degradation rates ranging from a half-life of 0.9 weeks ($\text{BF}_3 = 0.032 \text{ mol dm}^{-3}$) to 46 weeks ($\text{BF}_3 = 0.00027 \text{ mol dm}^{-3}$). The sample which contained $0.0032 \text{ mol dm}^{-3}$ of BF_3 began to break into small particles after 2 weeks. The molecular weight was not measured for this sample after 2 weeks considering that some of the low molecular weight part may diffuse into the water with the breaking of the sample. Within the duration of the degradation test, polymer samples containing no BF_3 did not change significantly. The self degradation of PCL can thus be ignored. This is consistent with the results obtained by other researchers.¹⁴ Since $\text{Sn}(\text{Oct})_2$ concentration was the same in all the samples, the higher degradation rate resulted from the existence of BF_3 .

The degradation of PCL in water is due to the hydrolytic cleavage of the ester bonds in the polymer. The hydrolysis of one ester bond produces one carboxylic acid group and one hydroxyl group. The rate of appearance of carboxylic acid group can thus be used to express the rate of degradation. The degradation rate is likely to be related to water, ester and BF_3 concentration, which can be expressed by the form of eq. (1).

$$\frac{dC_{\text{COOH}}}{dt} = kC_{\text{BF}_3}C_{\text{ester}}C_{\text{H}_2\text{O}} \quad (1)$$

where k is the degradation rate constant, and C_{COOH} , C_{BF_3} , C_{ester} , $C_{\text{H}_2\text{O}}$ represents the concentrations of

carboxylic acid end groups, BF_3 , ester bonds (within the polymer chain), and water in the polymer matrix respectively. When the extent of chain cleavage is small, both $C_{\text{H}_2\text{O}}$ and C_{ester} can be assumed to be constant. BF_3 concentration can also be assumed to be constant when there is a small extent of chain cleavage (earlier work showed that there was no appreciable leaching of BF_3 from PCL immersed in DDW at 37°C ¹³). Whenever a new carboxylic acid group is generated, there will appear a new polymer molecule during degradation, yielding eq. (2).

$$\Delta C_{\text{COOH}} = \frac{\rho}{M_n} - \frac{\rho}{M_n^0} \quad (2)$$

where M_n is the number average molecular weight of the sample at time t , M_n^0 is the initial number average molecular weight, and ρ is the density of PCL. Substitution of eq. (2) into eq. (1) and integrating this equation yields

$$\frac{1}{M_n} = k_d t + \frac{1}{M_n^0} \quad (3)$$

where $k_d = kC_{\text{BF}_3}C_{\text{ester}}C_{\text{H}_2\text{O}}/\rho$. Therefore, one would expect plots of $1/M_n$ versus degradation time to be linear if there is no weight loss during degradation. $1/M_n$ versus degradation time was plotted in Figure 2. The data points for each concentration of BF_3 were regressed using a linear relationship. $1/M_n$ showed a good linear relationship with degradation time across the range of BF_3 concentrations investigated, indicating first order kinetics. It can also be seen that the gradient for the fitted line increases with increasing BF_3 concentration.

If k_d is used to represent degradation rate, the relationship between degradation rate and BF_3 concentration can be obtained by plotting the slopes in

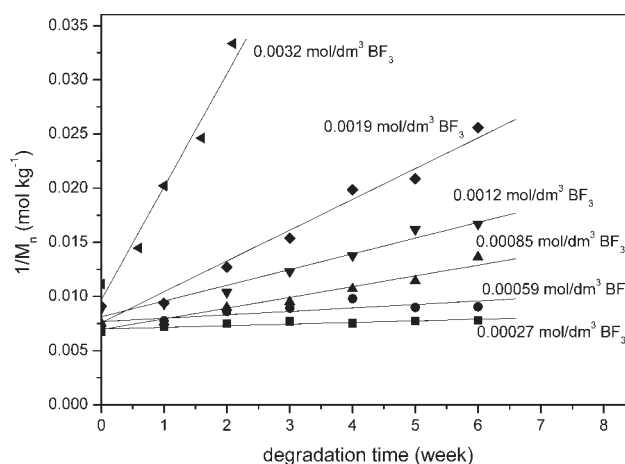


Figure 2 Reciprocal number average molecular weight ($1/M_n$) versus degradation time (data derived from Fig. 1).

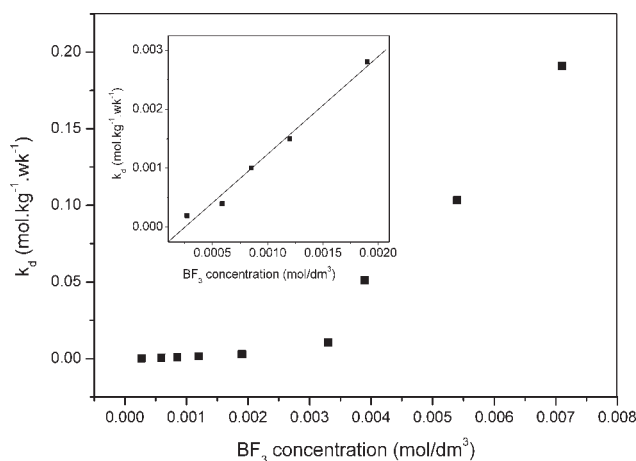


Figure 3 Degradation rate constant (k_d) for the PCL samples versus BF_3 concentration. k_d is defined as in eq. (3).

Figure 2 and the corresponding BF_3 concentrations, as shown in Figure 3. At lower BF_3 concentrations, k_d increased with the increase of BF_3 concentration with an approximately linear relationship (which can be seen clearly in the insert of Fig. 3). However, k_d increased much more rapidly for higher BF_3 concentrations, which also appears to have a linear relationship, but with a steeper gradient. The linear relationship between k_d and BF_3 concentration is given in eqs. (4) and (5) using least square regression, where R is the residue of linear regression.

$$k_d = 1.65C_{\text{BF}_3} - 0.00041 \quad (C_{\text{BF}_3} < 0.002 \text{ mol dm}^{-3}) \quad (R^2 = 0.99) \quad (4)$$

$$k_d = 45.68C_{\text{BF}_3} - 0.41 \quad (C_{\text{BF}_3} \geq 0.002 \text{ mol dm}^{-3}) \quad (R^2 = 0.99) \quad (5)$$

It is well known that BF_3 is a strong Lewis acid. The carbonyl oxygen in PCL forms a complex with BF_3 . This makes the carbonyl carbon more electrophilic. The water that diffuses into the sample then attacks the carbonyl carbon acting as a nucleophile, leading to the dissociation of the ester bond. The BF_3 in the polymer matrix may also react with diffused water first to release a proton, which then catalyzes the hydrolysis as a protonic acid. At higher concentrations

of BF_3 , both mechanisms may operate. Another factor to be taken into account is the large amount of carboxylic acid produced due to the catalytic hydrolysis of the ester bond when BF_3 concentration is higher.

It can be seen that BF_3 is an effective degradation tuning agent for the degradation of poly(ϵ -caprolactone). The wide spectrum of degradability of PCL containing BF_3 can be applied to the production of agriculture mulch films and packaging materials when blending with other renewable materials such as starch. The methodology may also be useful for tuning the degradation of other polyesters.

CONCLUSIONS

The results of the present work illustrate that the degradation rate of PCL can be easily tuned by the concentrations of BF_3 in PCL matrix without the need for using complicated chemistry for copolymerization with other monomers or blending with other polymers using specialist equipment and process. The more BF_3 in the polymer matrix, the higher is the degradation. The degradation rate and BF_3 concentration has a linear relationship as given in eqs. (4) and (5).

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