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Tetrabutyl Titanate-Controlled Polymerization of ε-Caprolactone at Ambient Temperature

Jun-Bing Fan, Ke Yang, Hu-Qiang Yi, Ting Fu, Ming-Xing Xia, Xiao-Bo Xu*, Ming-Qiang Zhu*

Biomedical Engineering Center, State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha, Hunan 410082, P.R.China.

MATERIALS

ε-Caprolactone (ε-CL) (Sigma-Aldrich, USA) was purified by drying over calcium hydride (CaH_2) and distilling under reduced pressure. Tetrabutyl titanate(TBT), Dichloromethane (DCM) and anhydrous ether (from Beijing Chemical Reagent Ltd., China) were used as received without further purification. Tetrahydrofuran (THF) (from Beijing Chemical Reagent Ltd., China) was distilled under reduced pressure before use.

CHARACTERIZATION

The molecule weights of TBT-PCL polymers were determined by ^1H NMR (Varian INOVA400 spectrometer) with $CDCl_3$ as solvent with 0.03 v/v% tetramethylsilane (TMS) as an internal standard, and Gel Permeation Chromatography (GPC) (PL50 apparatus equipped with two PLgel 5um MIXED-C columns, 300×7.5mm and one PLgel 5um Guard column, 50×7.5mm) at 40□. Tetrahydrofuran was served as eluent at flow rate of 1.0mL/min. Polystyrene standard was used for calibration.

1. Synthesis of TBT-PCL polymer

The synthesis of TBT-PCL polymers were carried out with a ring-opening polymerization of ε-CL in presence of TBT, where TBT served as initiator. Briefly, the polymerization

reaction was initiated by adding a certain amount of TBT into ε-CL. After the solution was stirred for 4 ~ 24 h at 10℃ ~ 40℃, the crude product was dissolved with methylene chloride and precipitated in anhydrous ether, and then dried under vacuum at room temperature until constant weight. The obtained polymers were analyzed by ^{1}H NMR and GPC for monomer conversion and molecular weight of the polymer formed. The monomer conversion was calculated from the integration values of the ^{1}H NMR spectra for monomer and polymer peaks. ^{1}H NMR ($CDCl_3$, 400 MHz):δ4.06 (s, 2H, e), 3.65 (s, 2H, a), 2.31 (s, 2H, d), 1.65(s, 4H, b), 1.38 (s, 2H, c), 0.94 (s, 3H, f).

2. Hydrolysis kinetics of the TBT-PCL

Polymerization reaction for M/I=800 were employed to investigate the hydrolysis kinetics of the TBT-PCL polymers. Briefly, TBT (0.05 mmol) was added into ε-CL (40 mmol). After the solution was stirred for 24 h at 40℃, the crude product was dissolved with methylene chloride, and then divided into three parts. Three portions were precipitated in (a) anhydrous ether; (b) the mixed solution of enthanol/H_2O =2/1; (c) ethyl ether containing 0.1v/v% HCl. Finally, the as-obtained polymers were dried under vacuum at room temperature until constant weight for GPC analysis. The obtained TBT-PCL polymers were labeled Polymer-X where the X was corresponded to the number of TBT-PCL polymers from **Table S1**.

3. Chain extension and cross propagation of $Ti(OPCL)_4$ as macroinitiator

Tetra-branch star-shape $Ti(OPCL)_4$ as an isolated macroinitiator to form a new star-shape or star-shape block copolymer by chain extension of ε-CL monomer or cross propagation using a fresh batch of lactide (LA). In a typical synthesis, ε-CL (25 mmol) was injected into a 10 mL flask containing TBT (0.5 mmol). After the solution was stirred for 1 h at 40℃, three portions of crude product were taken out. One portion was purified for GPC analysis, the other two portions were injected into fresh ε-CL (10 mmol) and LA

(10 mmol) in THF, respectively. The mixtures were then stirred for 24 h at 60℃, the product was dissolved with methylene chloride and precipitated in anhydrous ether, and dried under vacuum at room temperature until constant weight for GPC analysis.

Table S1 GPC trace of the hydrolysis kinetics of the TBT-PCL

Polymer	$M_{n,GPC}$[b] (g/mol)	M_w/M_n[c]	precipitant
Polymer-1	45000	1.41	anhydrous ether
Polymer-2	43000	1.45	enthanol/H_2O =2/1
Polymer-3	16000	1.56	ethyl ether containing 0.1 % HCl

Table S2 Chain extension and cross propagation of $Ti(OPCL)_4$ as macroinitiator

Polymer	$M_{n,GPC}$[c] (g/mol)	M_w/M_n[d]
Original $Ti(OPCL)_4$	3000	1.3
$Ti(OPCL)_4$ after chain extension	10000	1.4
$Ti(O\text{-}PLA\text{-}b\text{-}PCL)_4$ after cross propagation	10000	1.4

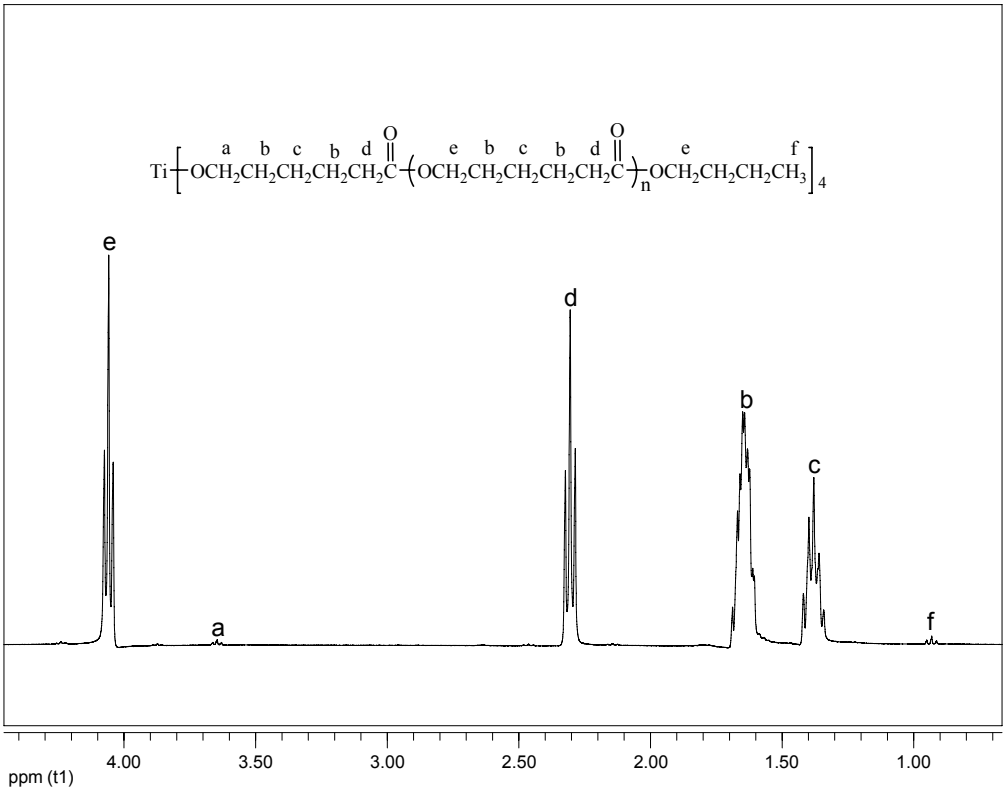

Fig S1 ^{1}H NMR spectrum of the living PCL in presence of TBT