

Ring Opening Polymerization of ϵ -Caprolactone Through Water

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Experimental section-

Materials: ϵ -Caprolactone (CL) was purchased from TCI chemicals (catalog #C0702). Isopropanol (IPA), D, L- lactide, Sn(Oct)₂ and TTIP were purchased from Sigma-Aldrich. CL was stored under nitrogen and used without further purification. The water content of a new bottle and one-year old bottle of CL were 50 ppm and 750 ppm respectively. IPA and Sn(Oct)₂ were stored under nitrogen and on molecular sieves. TTIP was stored under nitrogen and used without further purification.

Instruments: ¹H NMR spectra of the polymers were obtained on a Varian VNMRS 500 MHz spectrometer and integrated using Mestrenova 11.0.4.

Water content for solutions, reagents, and reaction mixtures was obtained using a Karl Fisher C20 instrument.

Number average molecular weights (M_n), and weight average molecular weight (M_w) were determined using gel permeation chromatography (GPC, Waters 717) equipped with a differential refractometer (Waters 410). Two Agilent PLGel 5 μ m columns (7.5 x 300 mm) with pore sizes of 10⁵ and 10³ Å in tandem were used for optimal separation of molecular weights in chloroform + 0.1% trifluoroacetic acid as a solvent. All results were relative to polystyrene standards in a range of 580 to 920,000 Daltons.

Synthesis of PCL: Bulk polymerization of CL was conducted in an oven which was preheated at 110 °C for 24 hours in order to produce consistent and reproducible results and avoid any contamination with water. The polymerization of CL with TTIP as an initiator is described as follows: In a typical synthesis of DP=100 of PCL, 5.15 g (45.12 mmol) of CL was placed in an oven dried glass vial and 21 mmol TTIP was added to CL. The molar ratio of M_o/I_o was 400 for DP=100, where M_o and I_o are corresponding to the number of moles of caprolactone, and initial number of moles of initiator respectively. The solution mixture was immediately (within 1-5 sec) placed in an oven and heated for 4 h at 110 °C. It is important to note that we tried to minimize the exposure of the solution mixture to air to reduce contamination with water as we know that TTIP is hygroscopic in nature and absorbs moisture present in air. We have seen that TTIP became precipitated out in the form of TiO₂ when we keep the solution mixture of TTIP and CL in air for more than five minutes. The final product was dissolved in chloroform and precipitated with ice-cold methanol. After

centrifugal separation, the precipitate was dried under vacuum. In the case of polymerization of PCL of DP= 25, 50, 100 the reaction time was 4 h. Whereas, the reaction time were 24 h, 48 h, and 72 h for DP= 200, 300, and 400 or 500, respectively. We have followed the same procedure for the bulk polymerization of CL with Sn(Oct)₂ except IPA was used as an initiator and the reaction was conducted with vacuum or without vacuum. In a typical synthesis of DP=100 of PCL, 46 μL of IPA and 194.82 μL of Sn(Oct)₂ were added to 5 ml of CL. The molar ratio of M_o : C_o : I_o was 100:1:1, where M_o , C_o , I_o are corresponding to the initial number of moles of monomer (CL), catalyst (Sn(Oct)₂) and initiator (IPA) respectively. Then, the solution mixture was placed in an oven and heated for 4 h at 110 °C with vacuum or without vacuum.

Synthesis of PCL-PLA block-copolymer: PCL-PLA block copolymer was successfully synthesized using TTIP as a catalyst without drying or purifying the reagents. In a typical synthesis of PCL-PLA block copolymer, 68.4 μL of TTIP was added to 5 mL of CL and the solution mixture was immediately (within 1-5 sec) placed in an oven and heated for 4 h at 110 °C. We didn't purify after the first step in order to get a "living" macroinitiator. After synthesizing the first homopolymer PCL macroinitiator, DL-lactide was added using a 50/1 molar ratio with respect to TTIP. The second stage of the synthesis was carried out at 110 °C for 20 hours. The final product was dissolved in chloroform and precipitated with ice-cold methanol. After centrifugal separation, the precipitate was dried under vacuum.

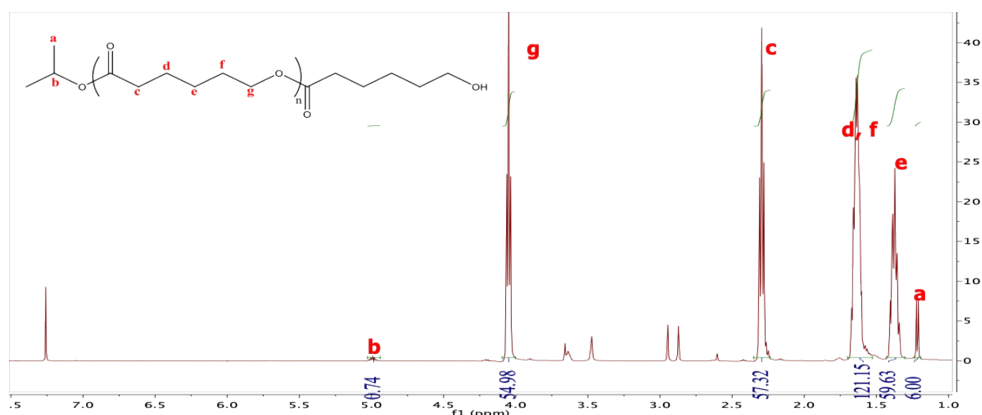


Figure S1. Typical ¹H NMR spectrum of the reaction mixture where a ratio of [IPA]: [Sn(Oct)₂]: [CL] = 1:1:25 after 4 h at 110 °C.

Catalyst	Initiator	CL: Initiator: Catalyst	Time	X (%) ^a	Theoretical Molecular weight	Molecular weight (Mn) ^b	\bar{D}
Sn (Oct) ₂	IPA	25:1:1	4 hr.	99	3420	8124	1.6
Sn (Oct) ₂	IPA	50:1:1	4 hr.	95	6840	12300	1.5
Sn (Oct) ₂	IPA	100:1:1	4 hr.	95	11400	15100	1.6
Sn (Oct) ₂	IPA	200:1:1	24 hr.	99	22800	15000	1.7
Sn (Oct) ₂	IPA	300:1:1	48 hr.	99	34200	15500	1.7
Sn (Oct) ₂	IPA	400:1:1	72 hr.	95	45600	15300	1.8
Sn (Oct) ₂	IPA	500:1:1	72 hr.	95	57000	15450	1.8

Table S1. ROP of ϵ -caprolactone without vacuum by Sn(Oct)₂ at 110°C initiated by IPA where the water content is 750 ppm. ^a Determine by ¹H NMR. ^b The Mn value was calculated according to Mn = 0.56Mn (GPC), which is determined by GPC (chloroform) and is relative to polystyrene standards.

Catalyst	Initiator	CL: Initiator: Catalyst	Time	X (%) ^a	Theoretical Molecular weight	Molecular weight (Mn) ^b	\bar{D}
Sn (Oct) ₂	IPA	25:1:1	4 hr.	99	3420	8150	1.3
Sn (Oct) ₂	IPA	50:1:1	4 hr.	99	6840	12100	1.3
Sn (Oct) ₂	IPA	100:1:1	4 hr.	100	11400	15200	1.5
Sn (Oct) ₂	IPA	200:1:1	24 hr.	100	22800	24074	1.5
Sn (Oct) ₂	IPA	300:1:1	48 hr.	100	34200	32462	1.4
Sn (Oct) ₂	IPA	400:1:1	72 hr.	99	45600	32677	1.5
Sn (Oct) ₂	IPA	500:1:1	72 hr.	100	57000	31707	1.5

Table S2. ROP of ϵ -caprolactone without vacuum by Sn(Oct)₂ at 110°C initiated by isopropanol where the water content is 50 ppm. ^a Determine by ¹H NMR. ^b The Mn value was calculated according to Mn = 0.56Mn (GPC), which is determined by GPC (chloroform) and is relative to polystyrene standards.

Catalyst	Initiator	CL: Initiator: Catalyst	Time	X (%) ^a	Theoretical Molecular weight	Molecular weight (Mn) ^b	\bar{D}
Sn (Oct) ₂	IPA	25:1:1	4 hr.	99	3420	8100	1.4
Sn (Oct) ₂	IPA	50:1:1	4 hr.	99	6840	13010	1.3
Sn (Oct) ₂	IPA	100:1:1	4 hr.	99	11400	15011	1.3
Sn (Oct) ₂	IPA	200:1:1	24 hr.	99	22800	23071	1.3
Sn (Oct) ₂	IPA	300:1:1	48 hr.	100	34200	32090	1.4
Sn (Oct) ₂	IPA	400:1:1	72 hr.	100	45600	32000	1.3
Sn (Oct) ₂	IPA	500:1:1	72 hr.	100	57000	33710	1.3

Table S3. ROP of ϵ -caprolactone with vacuum by Sn(Oct)₂ at 110°C initiated by isopropanol where the water content is 750 ppm. ^a Determine by 1H NMR. ^b The Mn value was calculated according to Mn = 0.56Mn (GPC), which is determined by GPC (chloroform) and is relative to polystyrene standards.

Catalyst	Initiator	CL: Initiator: Catalyst	X (%) ^a	Theoretical Molecular weight	Molecular weight (Mn) ^b	\bar{D} (Mw/Mn)
Sn (Oct) ₂	IPA	25:1:1	100	3420	8232	1.3
Sn (Oct) ₂	IPA	50:1:1	100	6840	13272	1.2
Sn (Oct) ₂	IPA	100:1:1	99	11400	15691	1.4
Sn (Oct) ₂	IPA	200:1:1	100	22800	25070	1.5
Sn (Oct) ₂	IPA	300:1:1	99	34200	37800	1.4
Sn (Oct) ₂	IPA	400:1:1	100	45600	37805	1.4
Sn (Oct) ₂	IPA	500:1:1	100	57000	37795	1.4

Table S4. ROP of ϵ -caprolactone with vacuum by Sn(Oct)₂ at 110°C initiated by isopropanol where the water content is 50 ppm. ^a Determine by 1H NMR. ^b The Mn value was calculated according to Mn = 0.56Mn (GPC), which is determined by GPC (chloroform) and is relative to polystyrene standards.

Catalyst	CL: Initiator	Time	X (%) ^a	Theoretical Molecular weight	Molecular weight (M _n) (GPC) ^b	<i>D</i>
TTIP	25:1	4 hr.	95	3420	5800	1.4
TTIP	50:1	4 hr.	95	6840	7500	1.4
TTIP	100:1	4 hr.	90	11400	15960	1.4
TTIP	200:1	24 hr.	60	22800	-	-

Table S5. ROP of ϵ -caprolactone where the water content is 750 ppm by TTIP at 110°C without vacuum.

^a Determine by ¹H NMR. ^b The M_n value was calculated according to M_n = 0.56M_n (GPC), which is determined by GPC (chloroform) and is relative to polystyrene standards.