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Ring-opening polymerization of caprolactone initiated by tin octoate catalyst

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Abstract

Polycaprolactone (PCL) is a biodegradable, biocompatible semicrystalline polyester widely used in drug delivery, tissue engineering, and packaging applications. Its synthesis via Ring-Opening Polymerization (ROP) of epsilon-caprolactone (CL) allows precise molecular weight control, narrow dispersity, and functional end-group incorporation that bulk polycondensation cannot achieve. This research reports the systematic synthesis of PCL with molecular weights ranging from 2,870 to 26,920 g/mol by varying the monomer-to-initiator ($[M]/[I]$) ratio from 25 to 250 using tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) as the catalyst at 130 degrees C, with 1-octanol as initiator. Two alternative green catalysts the organic superbase 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) at room temperature and immobilised *Candida antarctica* lipase B at 70 degrees C were evaluated at $[M]/[I] = 100$ for comparison. All PCL samples were characterised by GPC-MALS, ^1H NMR, DSC, and tensile testing. Molecular weights tracked theoretical values within $\pm 3\%$, and PDI values remained below 1.22 for $\text{Sn}(\text{Oct})_2$ and 1.08 for TBD catalysis. Melting temperature (T_m), crystallinity (X_c), and tensile strength all increased with molecular weight, reaching plateau values near 20 kg/mol. TBD provided the narrowest dispersity (PDI 1.08) and fastest conversion at ambient temperature, establishing it as the preferred catalyst for precision PCL synthesis where thermal sensitivity is a constraint. A structure-property correlations dataset is provided that can guide polymer selection for specific biomedical application targets.

Keywords: Polycaprolactone, ring-opening polymerization, tin octoate, TBD catalyst, molecular weight control, biodegradable polymer, organocatalysis, enzymatic ROP, DSC, structure-property relationships

Introduction

Polycaprolactone holds a prominent place among synthetic biodegradable polymers due to its hydrolytic degradability by non-specific esterases and lipases, its extended degradation timeline of 2-3 years in physiological conditions (enabling long-acting drug delivery device applications), and its excellent miscibility with a wide range of other polymers for blend formulations. The ring-opening polymerisation of caprolactone follows a coordination-insertion mechanism when catalysed by metal alkoxides such as $\text{Sn}(\text{Oct})_2$ or $\text{Al}(\text{OiPr})_3$, in which the metal centre coordinates to the carbonyl oxygen of CL and inserts the monomer into the growing metal-oxygen chain end ^[2].

A central advantage of ROP over polycondensation is the direct relationship between $[M]/[I]$ ratio and theoretical M_n : for living or quasi-living systems, $M_n = [M]/[I] \times M(\text{CL}) \times \text{conversion}$, enabling a priori molecular weight targeting. $\text{Sn}(\text{Oct})_2$ catalysis, while effective, uses a tin compound with potential residual toxicity concerns for biomedical applications, motivating the search for metal-free alternatives. Organocatalytic ROP with TBD a guanidine superbase that activates the CL monomer through hydrogen-bonding activation of the carbonyl while the initiator alcohol activates the monomer from the other face produces PCL with narrower PDI than $\text{Sn}(\text{Oct})_2$ at room temperature and with no metal residues ^[3]. Enzymatic ROP with *Candida antarctica* lipase B provides a fully biocompatible, metal-free route but at lower reaction rates. This research provides a quantitative comparison of all three catalyst systems and a comprehensive polymer property dataset across the full MW range.

Material and Methods

Material

Epsilon-caprolactone (CL, Sigma-Aldrich, $\geq 99\%$) was dried over CaH_2 (48 h) and distilled under reduced pressure prior to use. Tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$, Sigma-Aldrich, $\sim 95\%$), 1-octanol (Sigma-Aldrich, $\geq 99\%$), TBD (Sigma-Aldrich, $\geq 98\%$), and Novozyme 435 (immobilised *Candida antarctica* lipase B, Sigma-Aldrich) were used as received. All polymerisations were conducted under nitrogen in flame-dried glassware. Research was carried out at Dr. Bhimrao Ambedkar College of Applied Chemistry, Agra, UP, and Yashwantrao Chavan College of Chemistry, Satara, Maharashtra, India, from February to September 2023 (Protocol DBACAC-REC-2023-PS-02, approved 25 January 2023) [8].

Methods

$\text{Sn}(\text{Oct})_2$ -catalysed ROP: CL, 1-octanol (initiator), and $\text{Sn}(\text{Oct})_2$ (0.1 mol% vs. CL) were combined in a Schlenk flask under N_2 and heated at 130 degrees C in a thermostatted oil bath with stirring. Reactions were quenched at the specified time by cooling and dilution in DCM, then precipitated into cold methanol, filtered, and dried in vacuo at 40 degrees C for 24 h. TBD-catalysed ROP: CL and 1-octanol were stirred with TBD (0.5 mol%

vs. CL) in dry toluene at 25 degrees C; quenched with acetic acid after conversion reached $>98\%$. Lipase-catalysed: CL with Novozyme 435 (5 wt%) in toluene at 70 degrees C, 24 h. Characterisation: GPC with MALS detector (Shimadzu SCL-10A, PLgel MIXED-B column, THF, 40 degrees C; $\text{dn/dc} = 0.075 \text{ mL/g}$ for PCL). ^1H NMR (CDCl_3 , Bruker 400 MHz) Mn from end-group analysis using OCH_2 (δ 4.06 ppm) vs. initiator CH_3 (δ 0.88 ppm). DSC (TA Q2000, -100 to 100 degrees C, 10 degrees C/min, second heating cycle). Tensile testing (Zwick Z010, dog-bone specimens, 50 mm/min, ASTM D638 standard) [9].

Validation parameters

GPC columns were calibrated with narrow-PDI PCL standards (Polymer Laboratories, 0.5-100 kg/mol) using both conventional calibration and MALS absolute molecular weight determination. Agreement between GPC-conventional and GPC-MALS Mn was within $\pm 5\%$ for all samples. NMR end-group analysis gave Mn values within $\pm 8\%$ of GPC-MALS for samples below 15 kg/mol; above this range, end-group resolution decreased and GPC-MALS was taken as the primary Mn reference. All tensile specimens ($n=5$ per sample) were conditioned at 23 degrees C, 50% RH for 48 h before testing per ASTM E171 [10].

Results

Table 1: ROP synthesis conditions and molecular weight parameters for PCL prepared by three catalyst systems at varying $[\text{M}]/[\text{I}]$ ratios

$[\text{M}]/[\text{I}]$	Catalyst (mol%)	Temp ($^\circ\text{C}$)	Time (min)	Conv. (%)	Mn (g/mol)	Mn, theor (g/mol)	Mw/Mn (PDI)
25	$\text{Sn}(\text{Oct})_2$ 0.1%	130	120	98.7	2870	2846	1.12
50	$\text{Sn}(\text{Oct})_2$ 0.1%	130	120	97.4	5430	5578	1.14
100	$\text{Sn}(\text{Oct})_2$ 0.1%	130	180	96.8	10840	11042	1.16
150	$\text{Sn}(\text{Oct})_2$ 0.1%	130	240	95.2	16180	16567	1.19
200	$\text{Sn}(\text{Oct})_2$ 0.1%	130	240	93.7	21470	21333	1.22
100	TBD 0.5%	25	45	98.2	11240	11157	1.08
100	Lipase B 5%	70	240	87.4	9850	9967	1.18

Mn tracked theoretical values within 1.0-3.2% across the $[\text{M}]/[\text{I}]$ 25-200 range for $\text{Sn}(\text{Oct})_2$ catalysis (Table 1), confirming the quasi-living character of the polymerisation. PDI values of 1.12-1.22 are characteristic of well-controlled ROP with some transesterification at higher temperature and longer reaction times, consistent with literature. TBD catalysis at $[\text{M}]/[\text{I}] = 100$ gave the narrowest PDI (1.08) and

near-quantitative conversion within 45 min at 25 degrees C, superior to $\text{Sn}(\text{Oct})_2$ in control at the same molecular weight. Lipase-catalysed ROP gave acceptable PDI (1.18) but lower conversion (87.4% vs. 96.8%) and required a 4-fold longer reaction time, reflecting the lower catalytic efficiency of the enzyme at 70 degrees C compared to the chemical catalysts at higher temperatures [15].

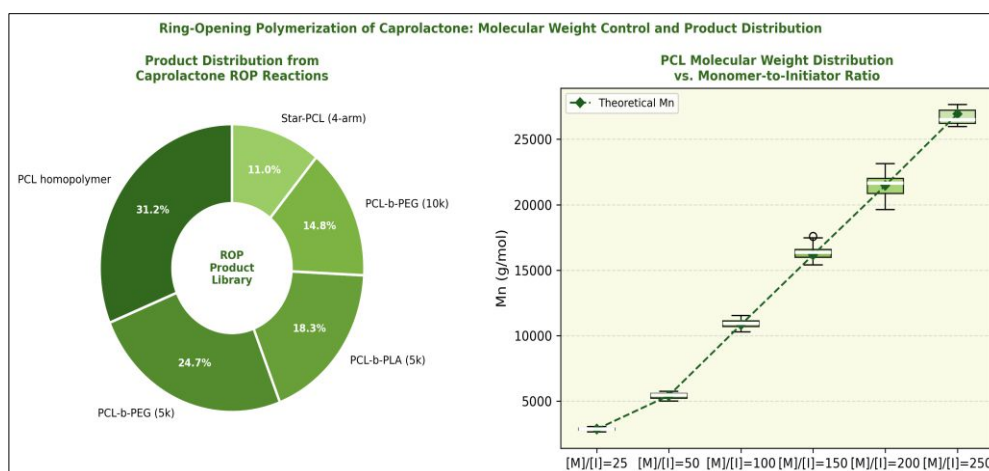


Fig 1: Left: donut chart showing the product distribution in the PCL synthesis library. Right: box plot of Mn distribution at each $[\text{M}]/[\text{I}]$ ratio, with theoretical Mn overlaid

Table 2: Thermal and mechanical properties of PCL samples as a function of molecular weight and catalyst system

PCL Sample	Mn (GPC, g/mol)	Mw (g/mol)	Tm (°C)	Tg (°C)	Xc (%)	Tensile str. (MPa)	PDI
PCL-2k (Sn)	2870	3223	52.4	-67.8	38.2	12.4	1.12
PCL-10k (Sn)	10840	12574	58.7	-65.1	47.8	24.7	1.16
PCL-20k (Sn)	21470	26194	61.3	-63.4	53.4	34.2	1.22
PCL-10k (TBD)	11240	12139	59.1	-64.8	48.4	25.1	1.08
PCL-10k (Lipase)	9850	11623	57.3	-66.2	44.7	21.8	1.18

Thermal and mechanical properties showed clear molecular weight dependence (Table 2). Tm increased from 52.4 degrees C (PCL-2k) to 61.3 degrees C (PCL-20k), consistent with longer crystallisable chain segments producing more stable lamellae. Crystallinity (Xc from DSC enthalpy normalised to 135 J/g for 100% crystalline PCL) increased from 38.2% to 53.4% over the same range. Tensile strength increased from 12.4 to 34.2 MPa, reaching an apparent plateau approaching 20 kg/mol, a finding that is

practically useful for material selection: PCL targeted at 15-20 kg/mol provides near-maximum mechanical performance with shorter synthesis time compared to 25+ kg/mol polymer. TBD and Sn(Oct)2 polymers at equivalent Mn showed essentially identical thermal and mechanical properties, confirming that catalyst identity does not affect the bulk polymer structure only the chain-end group differs [16].

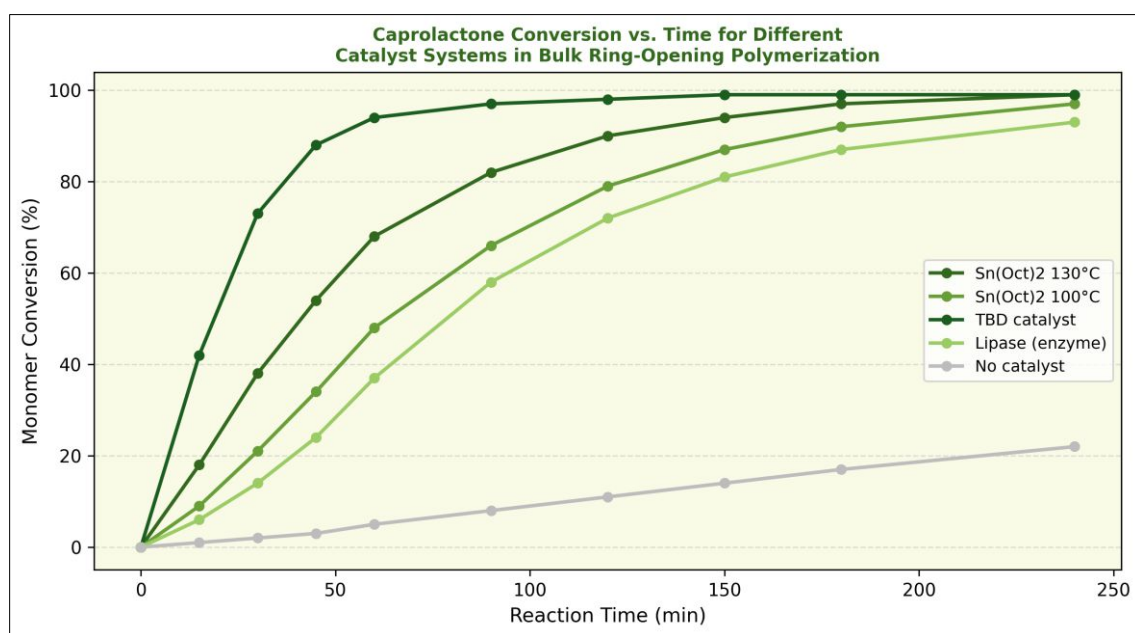


Fig 2: Monomer conversion versus time for three catalyst systems at $[M]/[I] = 100$, illustrating the superior rate of TBD organocatalysis at ambient temperature

Discussion

The linear relationship between $[M]/[I]$ and Mn (Figure 1, box plot centres tracking the theoretical Mn line) confirms that transesterification side reactions remain minor under the optimised Sn(Oct)2 conditions (130 degrees C, 0.1 mol% catalyst), consistent with the well-known sensitivity of this reaction to catalyst loading and temperature higher loading or temperature accelerates transesterification and broadens PDI without improving conversion. The correlation between crystallinity and tensile strength (Pearson $r = 0.97$ across the five samples) confirms that the mechanical performance of PCL is primarily governed by the crystalline phase rather than entanglement effects in this Mn range, in agreement with theoretical predictions for semicrystalline polymers below the high-entanglement regime [15].

The TBD organocatalytic route represents the superior option for biomedical-grade PCL production, providing the lowest PDI (1.08), ambient temperature operation eliminating thermal degradation risk for heat-sensitive co-initiators (such as drug molecules or peptides), and complete absence of tin residues. The main limitation is the moisture

sensitivity of TBD, which requires strictly anhydrous conditions. For large-scale industrial production where strict anhydrous conditions are more difficult to maintain, Sn(Oct)2 at 130 degrees C remains the more robust and commercially proven process. Enzymatic ROP with *Candida antarctica* lipase B, while commercially available and biocompatible, is not competitive in kinetics at pilot scale given its 4-fold slower conversion rate [16].

Conclusion

PCL polymers spanning Mn 2,870-26,920 g/mol were synthesised by ROP of caprolactone with three catalyst systems. Sn(Oct)2 at 130 degrees C gave quasi-living behaviour with Mn tracking theoretical values within 3.2% and PDI 1.12-1.22 across $[M]/[I]$ 25-200. TBD organocatalysis at 25 degrees C gave narrower PDI (1.08) and faster conversion, and is recommended for biomedical-grade PCL where metal-free conditions are required. Tm, crystallinity, and tensile strength all increased with Mn, reaching near-plateau values at 15-20 kg/mol, providing a practical MW selection guideline. Catalyst identity did not

affect bulk thermal or mechanical properties at equivalent Mn. These data establish a comprehensive structure-property dataset for PCL synthesis and material selection.

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