Supplementary Information

Synthesis and Characterization of Cyclic Carbonate End-Functional Linear and Star Polyesters *via* Ring Opening Polymerization

S1. Synthesis of α-(cyclic carbonate), ω-hydroxyl telechelic PDLLA using $Sn(Oct)_2$/glycerol 1,2-carbonate

All glassware and stir bar were dried at 130°C for 24 h, fitted with rubber septa, and cooled under a flow of dry Argon gas. To a 2-neck 25 mL round bottom flask equipped with a septum adapter and a reflux condenser were added glycerol 1, 2-carbonate (0.0002 mol, 0.0236 g), D, L- Lactide (0.0173 mol, 2.5 g), stannous octoate catalyst (8.65×10^{-6} mol, 0.05 mol% of D, L-lactide) and 5 mL of toluene and heated at 110°C under Argon gas for 14 h. Toluene was then removed under reduced pressure. The polymer was dissolved in dichloromethane and purified by precipitating into cold methanol (2.1 g, 83 %) (entry 5, **Table S1**).

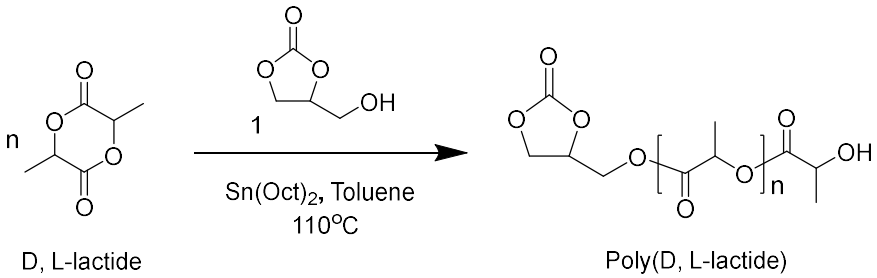
S2. Kinetics of ROP of D, L-Lactide using glycerol 1, 2-carbonate/$Sn(Oct)_2$ monitored by GC

All glassware and stir bar were dried at 130°C for 24 h, fitted with rubber septa, and cooled under a flow of dry Argon gas. To a 2-neck 25 mL round bottom flask equipped with a septum adapter and a reflux condenser were added glycerol 1, 2-carbonate (0.0016 mol, 0.1889 g), D, L-lactide (0.0346 mol, 5 g), stannous octoate catalyst (1.734×10^{-5} mol, 0.05 mol% of D, L-lactide), 10 mL of toluene and heated at 110°C under Argon gas for 1 h. The sample pick outs have been taken for

every 10 minutes interval of time over the period of 1 h and analyzed by GC. After removing of toluene, the polymer was then dissolved in dichloromethane and purified by precipitating into cold methanol and analyzed by GPC.

S1.1. Synthesis of α-(cyclic carbonate), ω-hydroxyl telechelic PDLLA using GC/Sn(Oct)$_2$

In the presence of an alcohol, Sn(Oct)$_2$ is one of the best catalyst in the synthesis of PDLLA due to control of molecular weight and an appropriate route for the end-functionalization [1, 2, 3, 4]. The synthesis of α-(cyclic carbonate), ω-hydroxyl heterotelichelic PDLLA is depicted in **Scheme S1**, involves ROP of D, L-lactide using functional biobased initiator namely glycerol 1, 2-carbonate (**1**) in the presence of stannous octoate catalyst in toluene at 110^{o}C for 14 h. The polymerization is also carried out in bulk at 140^{o}C (entry 1, **Table S1**) but the broader molecular weight distribution (M_n/M_w = 1.6) is observed due to increased transesterification side reactions at high temperature [5, 6, 7].



Scheme S1. Synthesis of α-(cyclic carbonate), ω-hydroxyl telechelic PDLLA using GC\Sn(Oct)$_2$ in toluene at 110^{o}C

^{1}H NMR spectrum clearly shows that the formation of cyclic carbonate end functional PDLLA. The peaks in the area of 4.3-4.9 ppm belong to five protons of cyclic carbonate end group. The

molecular weight of the polymer obtained by ^{1}H NMR (e.g. **Figure S1**, M_n = 982 g/mol) are close to theoretical (1127 g/mol) as well as with molecular weight analyzed by GPC (M_n = 1469 g/mol) (entry 1, **Table S1**) against homo-polystyrene standards.

In **Figure S2**, ^{13}C NMR spectrum of α-(cyclic carbonate), ω-hydroxyl end functional PDLLA macromonomer shows evidence of a mechanism involving the ROP of D, L-lactide initiated by glycerol 1, 2-carbonate (**1**). In the carbonyl carbon region of the spectrum are three peaks designated **a, a'** and **x**. The largest (**a**) at 169.5 ppm was attributed to the ester carbonyl carbons derived from internal D, L-lactide repeat units that are adjacent to other D, L-lactide units. Peak **a'**, distinct as a shoulder on the downfield side of peak **a**, was attributed to the carbonyl carbon of D, L-lactide units at the hydroxyl end of the chain. The peak of C=O of cyclic carbonate end group (**x**) was observed at 154 ppm. The $Sn(Oct)_2$ is used as initiator/catalyst to promote the ROP of six-membered [8] cyclic carbonate bearing pendent allyl ether group in bulk at 120^{o}C. Here, we report that the $Sn(Oct)_2$ catalyst is not interfered with five membered cyclic carbonate end group as evident from NMR analysis. It was reported [9] that propylene carbonate cannot be polymerized significantly even at 140^{o}C within few days. Rokicki and Kowalczyk reported [10] transesterification reaction in the presence of tin catalysts at very high temperature, i.e. 175-180 ^{o}C. Therefore, under our experimental conditions (110^{o}C), these side reactions are insignificant.

The size exclusion chromatographic (SEC) analysis (**Figure S3**) of α-cyclic carbonate heterotelichelic PDLLA macromonomer (entry 4, **Table S1**) showed the monomodal and narrow molecular weight distribution (M_n= 7446 g/mol; M_w/M_n = 1.1). The molecular weight distributions were narrow also indicating living/controlled polymerization of D, L-lactide at 110°C.

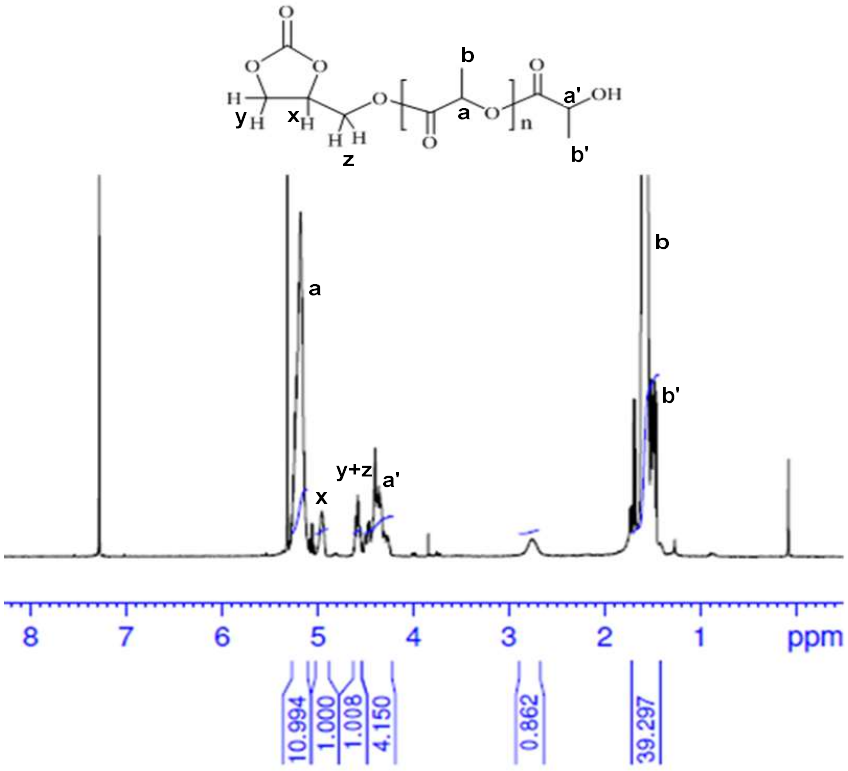


Figure S1. ^{1}H NMR spectrum of α-(cyclic carbonate), ω-hydroxyl telechelic PDLLA (M_n (NMR) = 982 g/mol) (entry 1, **Table S1**) in $CDCl_3$ (400 MHz)

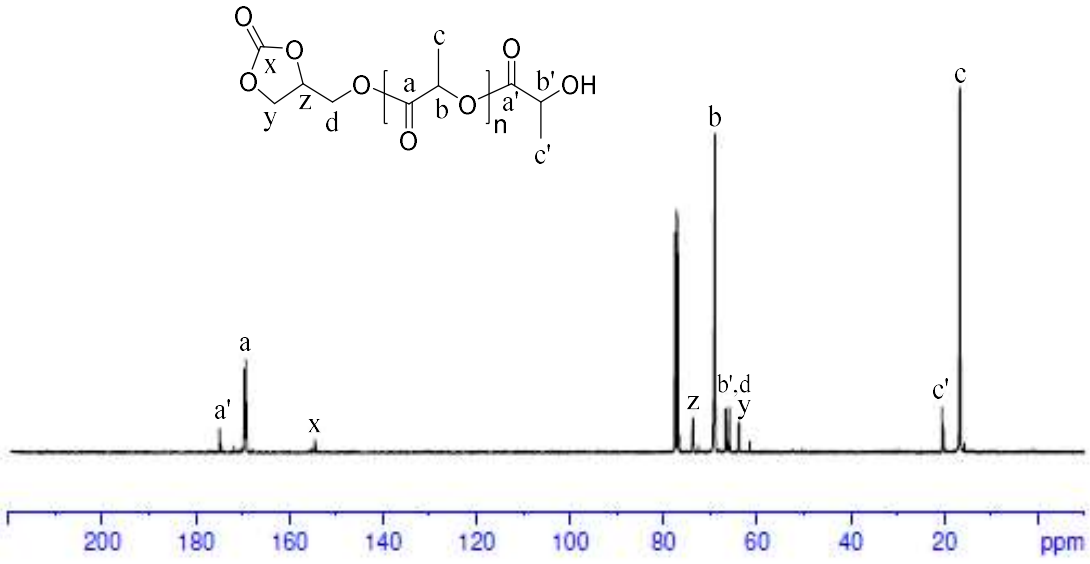


Figure S2. ^{13}C NMR spectrum of α-(cyclic carbonate), ω-hydroxyl end functional PDLLA macromonomer (M_n (NMR) = 982 g/mol) (entry 1, **Table S1**) in $CDCl_3$ (400 MHz)

Table S1. Synthesis of cyclic carbonate end functional PDLLA macromonomer using $Sn(Oct)_2$/GC catalyst system in toluene at 110°C for 14 h[@]

Sl. No.	$[M_o]/[I_o]$	Isolated Yield (%)	M_n (Calcd.)[a] (g/mol)	M_n (NMR) (g/mol)	SEC	
					M_n (g/mol)	M_w/M_n
1*	7:1	95	1127	982	1469	1.6
2	35:1	90	5163	3789	6062	1.2
3	57:1	85	8334	6466	5060	1.2
4	69:1	86	10063	9034	7446	1.1
5	86.5:1	83	12585	11326	11859	1.2

@: $Sn(Oct)_2$ = 0.05 mol% of D, L-lactide

a: DP of PDLLA x 2 (72.065) + 118.09 (Glycerol 1, 2-Carbonate)

*: in bulk at 140°C

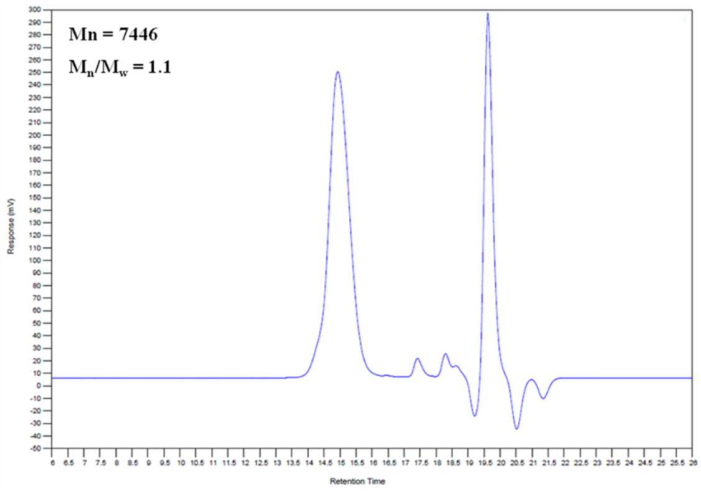


Figure S3. GPC trace of cyclic carbonate end functional PDLLA macromonomer (M_n = 7446 g/mol, PDI=1.1) (entry 4, **Table S1**) (using RI detector)

The reaction conditions and results for synthesis of cyclic carbonate-terminated PDLLA macromonomer are summarized in **Table S1**. Polymerization reactions were carried out in bulk (entry 1, **Table S1**) as well as in toluene (entry 2-5, **Table S1**). The reactions were carried out with different ratio of $[M_o]/[I_o]$ and the conversions were determined by gravimetric analysis. The molecular weight determined from end group analysis (^{1}H NMR) coincided well with the targeted molecular weights and molecular weights obtained from GPC against polystyrene standards. These cyclic carbonate end functional PDLLA are useful as potential precursors for the preparation of block, and star block copolymers.

Kinetic studies of ROP of D, L-lactide using glycerol 1, 2-carbonate as the initiator with [D, L-lactide]:[GC]:[$Sn(Oct)_2$] = [21.63:1:0.01] in toluene at 110°C was carried out. The linear relationship between $\ln[M]_o/[M_t]$ vs time (where M_o and M_t are initial and actual monomer concentration) indicated constant concentration of active species during polymerization (**Figure S4**). The linearity of plot of molecular weight (Mn, GPC) and narrow polydispersity index (1.3-1.19) vs monomer conversion also demonstrated controlled polymerization behavior (**Figure S5**). Similarly, all the aliquots were analyzed by GPC to determine molecular weights. The GPC chromatogram (**Figure S6**) of all the aliquots clearly shows that the growing molecular weights up to 50th min and there is very little increase in molecular weight at 60th min sample. At the same time there is decrease in D, L-lactide concentration which clearly seen from peaks adjacent to the polymer peak in the overlay.

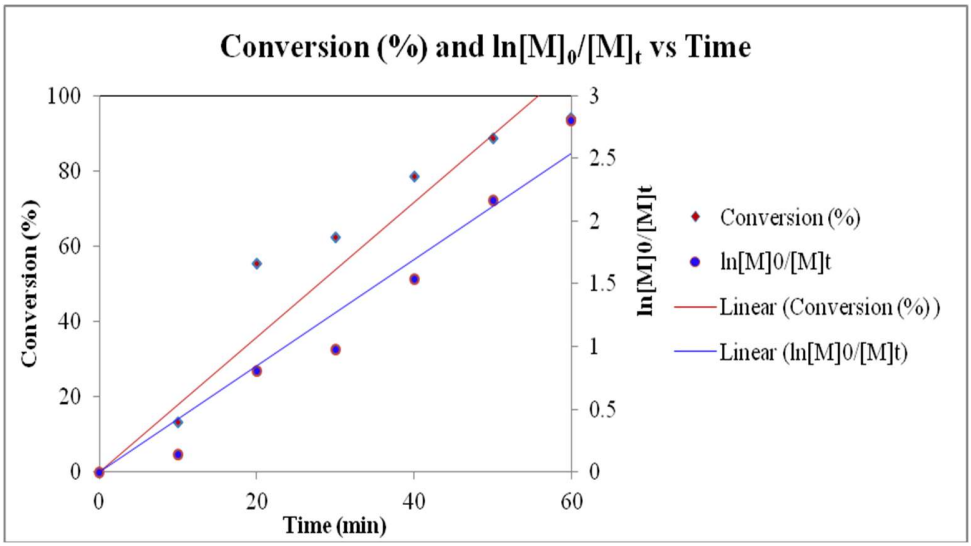


Figure S4. Conversion (%) and $\ln[M]_o/[M]_t$ as functions of time (min) ([D, L-lactide]: [GC]:[$Sn(Oct)_2$] = [21.63:1:0.01])

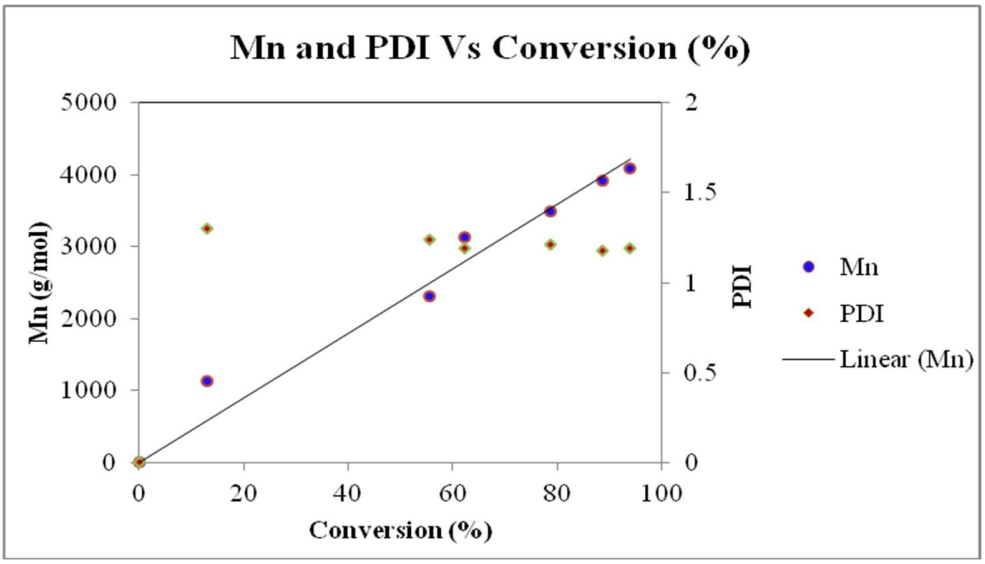


Figure S5. Molecular weight (Mn) and polydispersity (PDI) as functions of conversion (%) ([D, L-lactide]:[GC]:[$Sn(Oct)_2$] = [21.63:1:0.01])

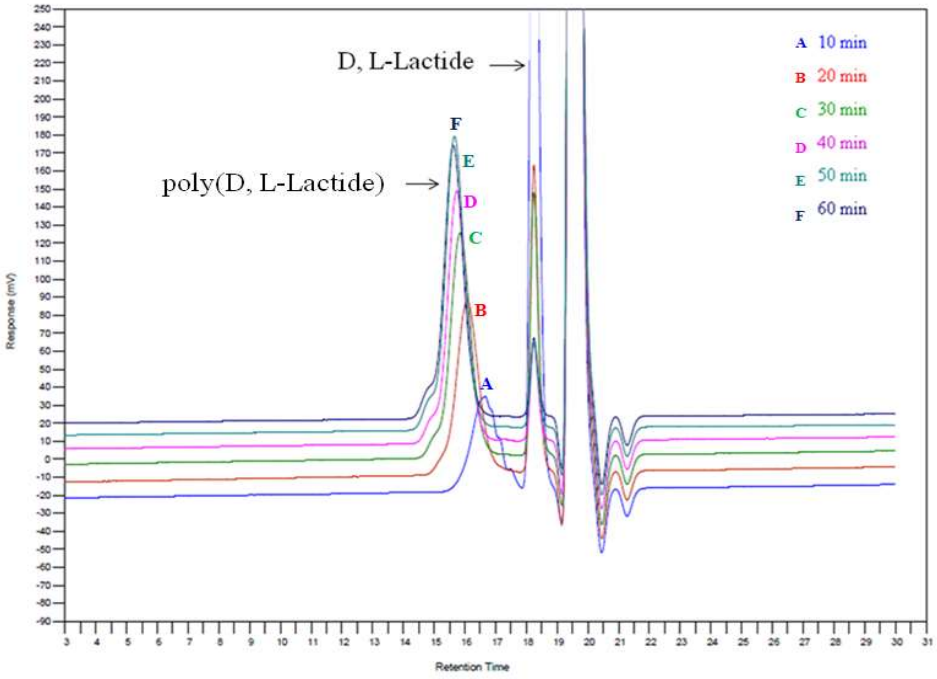


Figure S6. Kinetic study of PDLLA macromonomer via GPC (using RI detector) with time, ([D, L-lactide]:[GC]:[$Sn(Oct)_2$] = [21.63:1:0.01])

The presence of cyclic carbonate end group on PDLLA macromonomer was also confirmed by MALDI TOF MS (**Figure S7**). A set of peaks with difference in mass of ($\Delta m/z$ = 72.065 Da), which corresponds to mass of lactide repeating unit was observed and each envelope corresponds to the different ω-(cyclic carbonate), α-hydroxyl end functional PDLLA species with Na^+ and K^+ adducts. Also, MALDI TOF analysis shows small amounts of HO-PLA-COOH (Na^+ series), which attributed due to H_2O initiated ROP of D, L-lactide. H_2O was practically not observed at beginning of the polymerization, which has formed along with octoate end functional PDLLA as a result of esterification reaction of -OH end functional PDLA with octoate group of tin octoate [11, 12, 13, 14]. These side reactions are characteristics of ROP of cyclic esters using $Sn(Oct)_2$ at high

temperatures. Representative mass difference between calculated and observed series from MALDI spectrum has been given in **Table S2**.

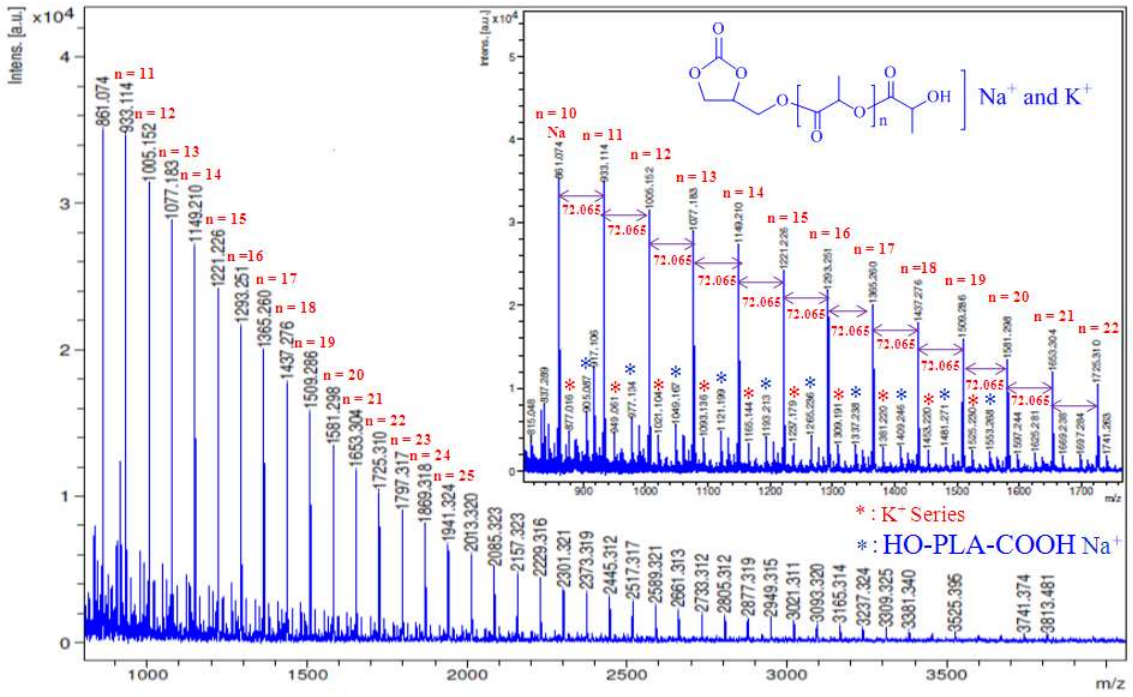


Figure S7. MALDI TOF spectrum of ω-(cyclic carbonate), α-hydroxyl end functional PDLLA macromonomer (entry 1, **Table S1**) $[M_n + Na]^+$ (MALDI) = [72.065 (PDLLA repeat unit) × n (DP)] + 118.09 (GC) + 22.99 (Na^+), (Δ = 0.65)

Table S2. Observed series in MALDI TOF spectrum of α-(cyclic carbonate), ω-hydroxyl end functional PDLLA macromonomer using $Sn(Oct)_2$ as catalyst

n = 10	72.065 (D,L-Lactide)	118.09 (GC)	22.99 (Na)	M_n (theory) = 861.73	M_n (MALDI)@ = 861.074	Δ = 0.65
n = 10	72.065 (D,L-Lactide)	118.09 (GC)	39.10 (K)	M_n (theory) = 877.84	M_n (MALDI) = 877.016	Δ = 0.82

@: $[M_n + Na]^+$ (MALDI) = [72.065 (D, L-lactide) × n (DP)] + 118.09 (GC) + 22.99 (Na^+)/39.10 (K^+)

References

1. Jamie, M. M., Adam, D. S., Storey, R. F. Synthesis and characterization of A–B–A triblock copolymers derived from chloro-telechelic poly(L-lactide): combining ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP). Polymer, **2005**, 46, 3628-3638.
2. Wiggins, J. S., Mohammad, K. H., Kenneth, A. M., Storey, R. F. Hydrolytic degradation of poly(D, L-lactide) as a function of end group: Carboxylic acid vs. hydroxyl. Polymer, **2006**, 47, 1960-1969.
3. Hutchings, L. R., Narrainen, A. P., Eggleston, S. M., Clarke, N., Thompson, R. L. Surface-active fluorocarbon end-functionalized polylactides. Polymer**, 2006,** 47, 8116-8122.
4. Vuorinen, S., Antikainen, O., Lahcini, M., Repo, T., Yliruusi, J., Heinamaki J. Sugar End-Capped Poly-D, L-lactides as Excipients in Oral Sustained Release Tablets. AAPS Pharm. Sci. Tech., **2009**, 10, 566-573.
5. Dubois, P., Jacobs, C., Jérôme, R., Teyssié, P. Macromolecular engineering of polylactones and polylactides. 4. Mechanism and kinetics of lactide homopolymerization by aluminum isopropoxide. Macromolecules **1991**, 24, 2266-2270.
6. Kricheldorf, H. R., Kreiser-Saunders, I. Polylactones, 19[†]. Anionic polymerization of L-lactide in solution. Makromol. Chem. **1990**, 191, 1057-1066.
7. Penczek, S., Duda, A., Szymanski, R. Intra- and intermolecular chain transfer to macromolecules with chain scission. The case of cyclic esters. Macromol. Symp. **1998**, 132, 441-449.
8. He, F., Wang, Y. P., Liu, G., Jia, H. L., Feng, J., Zhuo, R. X Synthesis, characterization and ring-opening polymerization of a novel six-membered cyclic carbonate bearing pendent allyl ether group. Polymer **2008**, 49, 1185-1190.
9. Soga, K., Hosoda, S., Tazuke, Y., Ikeda, S. Polymerization of propylene carbonate J. Polym. Sci. Part A: Polym. Chem. **1977**, 15, 219-229.
10. Rokicki, G., Kowalczyk, T. Synthesis of oligocarbonate diols and their characterization by MALDI-TOF spectrometry. Polymer, **2000**, 41, 9013-9031.

11. Patil, R. M., Hong, H., Chai, C. L. L., Satyanarayana, G., Gnaneshwar, R. Synthesis of α-(cyclic carbonate), ω-hydroxyl-telechelic poly (ε-caprolactone). Polym. Prepr. (Am Chem Soc Div Polym Chem) **2012**, 53, 165-66.
12. Patil, R. M., Hong, H., Chai, C. L. L., Anil, A. G. Satyanarayana, G., Gnaneshwar, R. Synthesis and characterization of α-(cyclic carbonate), ω-hydroxyl/itaconic acid asymmetric telechelic poly(ε-caprolactone). Polym. Bull. **2015**, 72, 2489-2501.
13. Libiszowski, J., Kowalski, A., Duda, A., Penczek, S. Kinetics and mechanism of cyclic esters polymerization initiated with covalent metal carboxylates, 5†. End-group studies in the model ε-caprolactone and L, L-dilactide/Tin(II) and zinc octoate/butyl alcohol systems. Macromol. Chem. Phys. **2002**, 203, 1694-1701.
14. Kowalski, A., Duda, A., Penczek, S. Mechanism of Cyclic Ester Polymerization Initiated with Tin(II) Octoate. 2.† Macromolecules Fitted with Tin(II) Alkoxide Species Observed Directly in MALDI-TOF Spectra. Macromolecules **2000**, 33, 689-695.