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

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ABSTRACT: Well-defined α-(cyclic carbonate), ω-hydroxyl heterotelechelic poly (D,L-lactide)s (PDLLAs) were prepared with good end-group fidelity by ring-opening polymerization (ROP) of D,L-lactide catalyzed by organo catalyst namely, N,N′ dimethyl amino pyridine (DMAP) in conjunction with a renewable, functional bio-based initiator namely glycerol 1,2-carbonate (GC) in bulk at 135 °C with 82% yield. In the case of GC/DMAP catalyzed polymerizations, the HO-PDLLA-COOH series was not observed in MALDI TOF mass analysis unlike as obtained due to transesterification reactions when catalyzed by GC/$Sn(Oct)_2$. Also, cyclic carbonate end-functional 4-arm star poly(ε-caprolactone) (PCL) was prepared via coupling of GC with $(PCL\text{-}COOH)_4$ at room temperature in the presence of N,N′-dicyclohexylcarbodiimide (DCC) and DMAP. Quantitative conversion of hydroxyl functionality in $(PCL\text{-}OH)_4$ to carboxylic acid and then to cyclic carbonate functionality was achieved with 90% yield for low molecular weight 4-arm star PCL confirmed by NMR, FT-IR, and MALDI TOF mass spectroscopy.

Keywords: Telechelics; Functional initiator; Organo catalyst; Reactive and functional polymers; Ring-opening polymerization (ROP); Poly(D,L-lactide); Poly(ε-caprolactone); Star polyesters

1. Introduction

Telechelic polymers are industrially very attractive prepolymers for making block, graft, star and cross-linked polymers with network structures [1–3]. Telechelic polymers can also be applied in coatings, as surfactants, in thermoplastic elastomers, etc. Significant contributions to the development of telechelic polymeric materials by various polymerization techniques such as anionic, cationic, group-transfer, metathesis, step-growth, ring-opening polymerization (ROP), free radical, living/controlled radical polymerizations and by chemical modification of polymer end groups continue in the literature [1–3]. ROP requires milder operating parameters to reach high molar mass polyesters derived from renewable resources, displaying controlled molecular characteristics with limited side reactions [4–15]. One of the active areas in recent developments for telechelics polymers are to design functional initiators for ROP of cyclic esters. Telechelic polyesters with specific end group were tailored to particular uses, including biodegradability. Telechelic poly(ε-caprolactone) (PCL) with biological molecule as end groups is suitable for medical and pharmaceutical applications obtained using biocompatible initiators such as amino acids [16] and carbohydrates [17]. Poly(D,L-lactide) (PDLLA) is biodegradable, atactic, linear aliphatic thermoplastic polyester useful for biomedical applications [18]. There are only few end functionalities have been published so far on telechelic PDLLAs having dicaboxylic acid [19], surface active 3,5 (di-3-(perfluorooctyl) propyloxy) benzyl [20], sugar [21] and α,ω-triethoxysilane [22] from their corresponding initiators.

The ROP of cyclic esters also provides access to an array of renewable and biodegradable star polymeric materials [23]. Star polymers offers an increased concentration of functional end groups for polymers of equal molecular weight, have improved solubility and are expected to display remarkable morphologies, rheological, dynamic, thermal and degradation properties [24]. Generally, star polymers have smaller hydrodynamic radii, smaller radii of gyration and lower internal viscosities than linear analogues of the same molecular weight [25,26]. In addition, star-shaped polymers exhibit lower melt temperatures, lower crystallization temperatures and lower degrees of crystallinity than comparable linear analogues [26]. End-functional homo star polyesters [27–34] can be utilized for making block copolymers, e.g., the COOH-terminated poly(ethylene oxide)s condensed with

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hydroxyl-terminated four-arm star PCL to obtain PCL-*b*-PEO copolymer with high coupling efficiency (97%) and in high yields (93%) [27]. Star polymers are useful in drug delivery [35], other biomedical applications [36], thermoplastics [25] and nanotechnology [37] among other applications [25].

The ROP of lactides has been accomplished [38] with a variety of metal catalysts including aluminum [39], tin [40], zinc [41], yttrium [42], $ZnOct_2$ [43], Salicylaldimine Copper(II) complex catalyst [44] and also using N-heterocyclic molecules [45]. Stannous (II) 2-ethylhexanoate [$Sn(Oct)_2$] is the most effective, versatile and commonly used catalyst for ROP of Lactides [46–48]. $Sn(Oct)_2$ is only active at elevated temperatures [49], which facilitates intermolecular and intramolecular transesterification side reactions with broadening of molecular weight distribution.

Alternative strategies using only organic compounds as polymerization catalysts have led to versatile organocatalysts amenable to a number of asymmetric transformations [50–52]. Organocatalytic methods for ROP provide a complementary (competitive in terms of rate and selectivities) approach to those mediated by metal alkoxides or enzymes [53]. Moreover, the different mechanisms of enchainment prompted by the different classes of organocatalysts provide new opportunities for the controlled synthesis of macromolecules. Waymouth and Hedrick et al. have developed several organocatalysts based on guanidine and amidine for ROP of cyclic esters such as lactides and lactones [54,55]. Hedrick et al. [56] reported first time the organocatalytic ROP of D,L-lactide using dimethyl amino pyridine (DMAP). Guillaume et al. reported [57–60] the synthesis of α-cyclobutenyl end-functionalized PLA macromonomers by organocatalyzed (DMAP or 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD)) ROP of L-lactide in presence of cis-3,4-bis (hydroxyl methyl) cyclobutene or cis-4-benzyloxymethyl-3-hydroxylmethylcyclobutene acting as an initiator and further this macromonomer was used for synthesis of polybutadiene-*g*-polylactide copolymer by ring-opening metathesis polymerization of α-cyclobutenyl functionality of polylactide. Commercially available (R,R)- and (S,S)-enantiomers of chiral thiourea-amine Takemoto's organocatalysts, squaramide derived organocatalysts and highly active organocatalysts (CN-Py-P/U4) promoted efficient control and high isoselectivity at room temperature of the ROP of racemic lactide [61–63]. Also, 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) catalyzed amide end-capped PLA reported using primary or secondary amines [64].

Polymers containing polar five-membered cyclic carbonate group have potential applications as reactive polymers [65] and useful in Li^+ ion batteries [66–69]. Use of cyclic carbonate group is attractive as, e.g., its reaction with amines [70] will yield hydroxyurethanes quantitatively without the use of hazardous isocyanates and without any by-product. The synthesis of α, ω-di(cyclic carbonate) telechelics poly(trimethylene carbonate)s [71], telechelic polyoxazoline carrying five-membered cyclic carbonate and oxazolium end groups [72] by cationic ROP of 2-methyl-2-oxazoline using glycerol carbonate tosylate as initiator and cyclic carbonate-end functional poly(methyl methacrylate) using 2-oxo-1,3-dioxolan-4-yl-(methyl-2-bromo-2-methylpropanoate) initiator via ATRP [73] are reported in the literature. We have reported [74,75] the synthesis of α-(cyclic carbonate), ω-hydroxyl telechelic PCL with controlled molecular weights and well-defined end groups using the initiator glycerol 1,2-carbonate and catalyzed by $Sn(Oct)_2$. To the best of our knowledge, there is no report on the synthesis of cyclic carbonate end-functional PDLLA and 4-arm star PCL with controlled molecular weights using ROP technique. Among lactides, we have considered PDLLA as it is amorphous in nature (T_g = 45–50 °C) and is usually consider in applications such as controlled drug release. Here in our report, the synthesis of cyclic carbonate end-functional PDLLA and 4-arm star PCL with controlled molecular weights and well-defined end groups resulted from functional and bio-based glycerol 1,2-carbonate (GC).

2. Experimental

2.1. Reagents

Stannous 2-ethyl-hexanoate (stannous octoate, ~95%), 4-(hydroxymethyl)-1,3-dioxolan-2-one (99%), N,N′ dimethyl aminopyridine (DMAP) (99%), N,N′-dicyclohexylcarbodiimide (DCC) (99%) and pentaerythritol (99%) purchased from Aldrich, St. Louis, CA, USA were used without further purification. D,L-lactide (98%, Aldrich, USA), succinic anhydride (99%, Aldrich, USA) was recrystallized twice from dry ethyl acetate. ε-Caprolactone (97%, Aldrich, USA) was dried over CaH_2 and distilled under reduced pressure. Dry triethylamine (Sonia Industries, India) was distilled over KOH. Toluene and dichloromethane purchased from Sonia Industries were dried over CaH_2 and distilled under reduced pressure.

2.2. Measurements

Gel permeation chromatography (GPC) was used to determine molecular weights and molecular weight distributions, M_w/M_n, of polymer samples with respect to homo polystyrene standards (Polymer Laboratory). ^1H and ^{13}C NMR spectra of the polymers were obtained on a Bruker AC-400 spectrometer using 5 mm o.d. tubes. FTIR (Thermo Scientific Nicolet 6700) was used for recording IR spectra of the polymers. End groups of polymers were analyzed by matrix-assisted laser desorption ionization (MALDI) Bruker time of flight instrument (Autoflex III Smart beam) equipped with a Nd-YAG (neodymium-doped yttrium aluminium garnet) 355 nm Solid State Laser. An accelerating voltage of 20 kV was used. Mass spectra were recorded in the reflector mode. The matrix 2,5-dihydroxybenzoic acid, was dissolved in purified THF (10 $mg\cdot mL^{-1}$) and the solution was mixed with the polymerization mixture (1 mol/L) in a 25:1 *v*/*v* ratio. Gas chromatography (GC AGILENT 7890 N or equivalent, DB-624 (30 m, 0.530 mm, 3 μm) column) was used for kinetic study.

2.3. Synthesis of α-(cyclic carbonate), ω-hydroxyl PDLLA Using DMAP/GC

All glassware and stir bar were dried at 130 °C for 24 h, fitted with septum adapter, 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, glycerol 1,2-carbonate (0.0006 mol, 0.0078 g), D,L-lactide (0.0138 mol, 2 g), DMAP catalyst (0.0013 mol, 0.162 g) were added and heated at 135 °C under Argon gas for 30 min. The polymer was then dissolved in dichloromethane and purified by precipitating into cold methanol (1.65 g, 82%) (entry 3, Table 1).

2.4. Synthesis of Hydroxyl Terminated Four-arm Star Poly(ε-caprolactone)

All glassware and stir bar were dried at 130 °C for 24 h, fitted with rubber septa and cooled under flow of dry Argon gas. To a 2-neck 25 mL round bottom flask equipped with a septum adaptor and a vacuum bend, pentaerythritol (0.000125 mol, 0.0170 g), ε-caprolactone (0.0219 mol, 2.5 g) and stannous octoate (1.1×10^{-5} mol, 0.05 mol% of CL) were added and heated at 110 °C under Argon gas for 4 h. The polymer was then dissolved in dichloromethane and precipitated in cold methanol. The white powder was dried at 60°C under vacuum and characterized (2.5 g, 99%), (entry 8, Table 3).

2.5. Synthesis of Carboxylic Acid Terminated Four-arm Star Poly(ε-caprolactone)

All glassware and stir bar were dried at 130 °C for 24 h, fitted with rubber septa and cooled under flow of dry Argon gas. To a 2-neck 25 mL round bottom flask equipped with a septum adaptor, four-arm star PCL-OH (0.001 mol, 2.5 g; M_n = 2476 g/mol, M_w/M_n = 1.18), succinic anhydride (0.0041 mol, 0.4102 g, 1.0 eq. vs. OH), triethyl amine (0.0041 mol, 0.4148 g, 1.0 eq. vs. OH), DMAP (0.0041 mol, 0.5 g, 1.0 eq. vs. OH), dry dichloromethane (10 mL) were added and the reaction was carried out at room temperature for 24 h. The reaction solution was washed with saturated $NaHCO_3$, followed by saturated NaCl solution, aqueous hydrochloric acid (5% *v*/*v*), and saturated NaCl solution. The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under vacuum yielding a viscous liquid. The polymer was then dissolved in dichloromethane and precipitated in cold methanol. The white powder was dried at 60°C under vacuum and characterized (2.64 g, 91%).

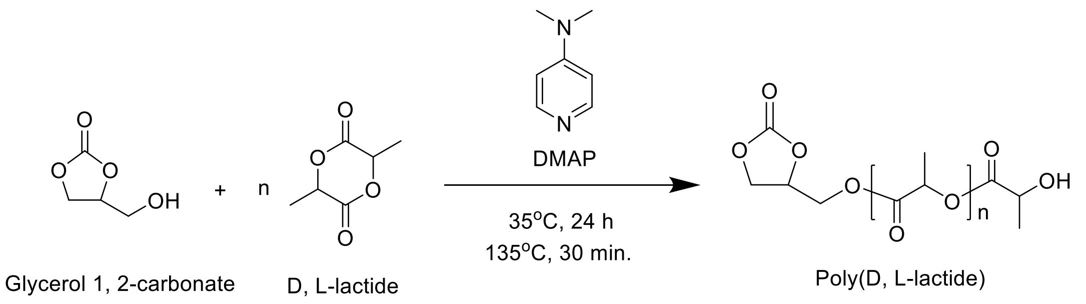
2.6. Synthesis of Cyclic Carbonate Terminated Four-arm Star Poly(ε-caprolactone)

All glassware and stir bar were dried at 130 °C for 24 h, fitted with rubber septa and cooled under flow of dry Argon gas. To a 2-neck 25 mL round bottom flask equipped with a septum adaptor, four arm star PCL-COOH (0.000342 mol, 0.8 g; M_n (^{1}H NMR) = 2344 g/mol), DCC (0.00137 mol, 0.2826 g, 1.0 eq. vs. COOH), DMAP (0.00137 mol, 0.1673 g, 1.0 eq. vs. COOH), glycerol 1,2-carbonate (0.00137 mol, 0.1617 g, 1.0 eq. vs. COOH), dry dichloromethane (10 mL) were added and the reaction was carried out at room temperature for 24 h. The reaction solution was washed with aqueous hydrochloric acid (5% *v*/*v*) followed by saturated NaCl solution. The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under vacuum yielding a viscous liquid. The polymer was then dissolved in dichloromethane and precipitated in cold methanol. The white powder was dried at 60 °C under vacuum and characterized (0.85 g, 88%).

3. Results and Discussion

3.1. Synthesis of α-(cyclic carbonate), ω-hydroxyl PDLLA using GC/DMAP Catalytic System

To find out the initiator efficiency and compatibility of glycerol 1,2-carbonate (GC) as initiator with organocatalysis, we have employed DMAP as catalyst for ROP of D,L-lactide. Scheme 1 represents the synthetic pathway for α-(cyclic carbonate), ω-hydroxyl PDLLA catalyzed by GC/DMAP at two different polymerization temperatures such as at 35 °C and at 135 °C.



Scheme 1. Synthesis of α-(cyclic carbonate), ω-hydroxyl telechelic PDLLA using GC/DMAP catalytic system.

The ^{1}H NMR spectrum (Figure 1) indicates the formation of cyclic carbonate end functional PDLLA. The peaks in the area 4.3–4.93 ppm belongs to six protons are due to the cyclic carbonate end group which are appeared at 4.93 ppm as (x) proton and 4.05–4.58 ppm belongs to α-end cyclic methylene (y), methylene (z) and hydroxyl methine (a′) of ω-end group respectively. The spectrum resembles to ^{1}H NMR spectrum of PDLLA obtained from ROP of D,L-lactide catalyzed by Sn(Oct)$_2$ (see, supporting information, Figure S1).

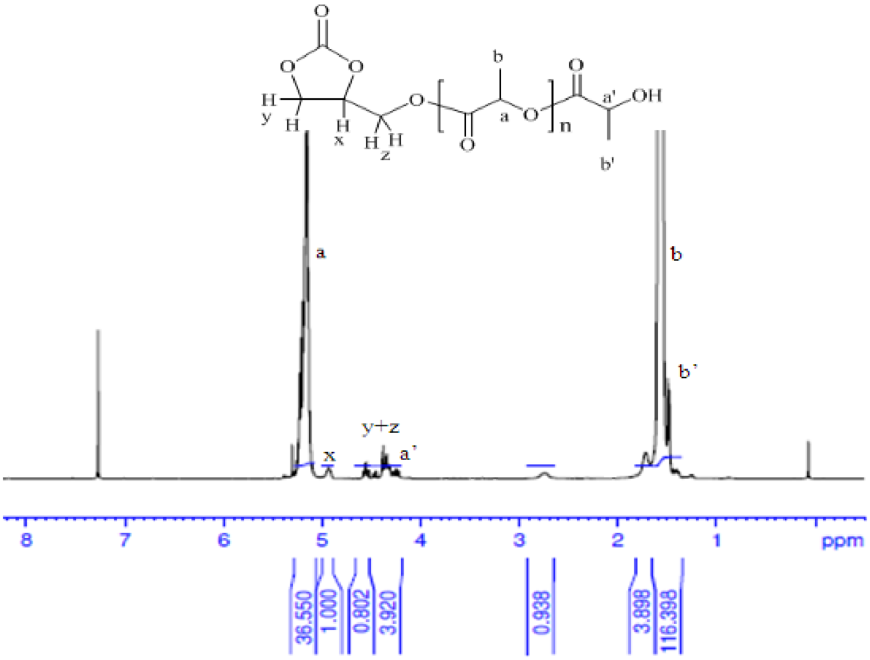


Figure 1. ^{1}H NMR spectrum of α-(cyclic carbonate), ω-hydroxyl end functional. PDLLA (M_n (NMR) = 2824 g/mol) (entry 1, Table 1), in $CDCl_3$ (400 MHz).

There are no side reactions observed with cyclic carbonate functionality and glycerol carbonate has shown high initiator efficiency towards ROP of D,L-lactide, i.e., like with Sn(Oct)$_2$ and there is no interference of GC with DMAP observed (see supporting information, Figure S1 and S2).

In Figure 2, ^{13}C NMR spectrum of α-(cyclic carbonate), ω-hydroxyl end functional PDLLA also shows evidence of a mechanism involving the ROP of D,L-lactide initiated by glycerol 1, 2-carbonate. 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 on the downfield side of peak a, was attributed to the carbonyl carbons of D,L-lactide units at the secondary hydroxyl end of the chain. The peak of C=O of cyclic carbonate (x) was observed at 154 ppm. This spectrum resembles to ^{13}C NMR spectrum of PDLLA obtained from ROP of D,L-lactide catalyzed by Sn(Oct)$_2$ (see supporting information, Figure S2). The representative GPC chromatogram of cyclic carbonate end functional PDLLA has been shown in Figure 3 (entry 1, Table 1). The polydispersities obtained from GPC are relatively narrow (1.3–1.4) and results are comparable with the data reported by Hedrick et al. [54–56].

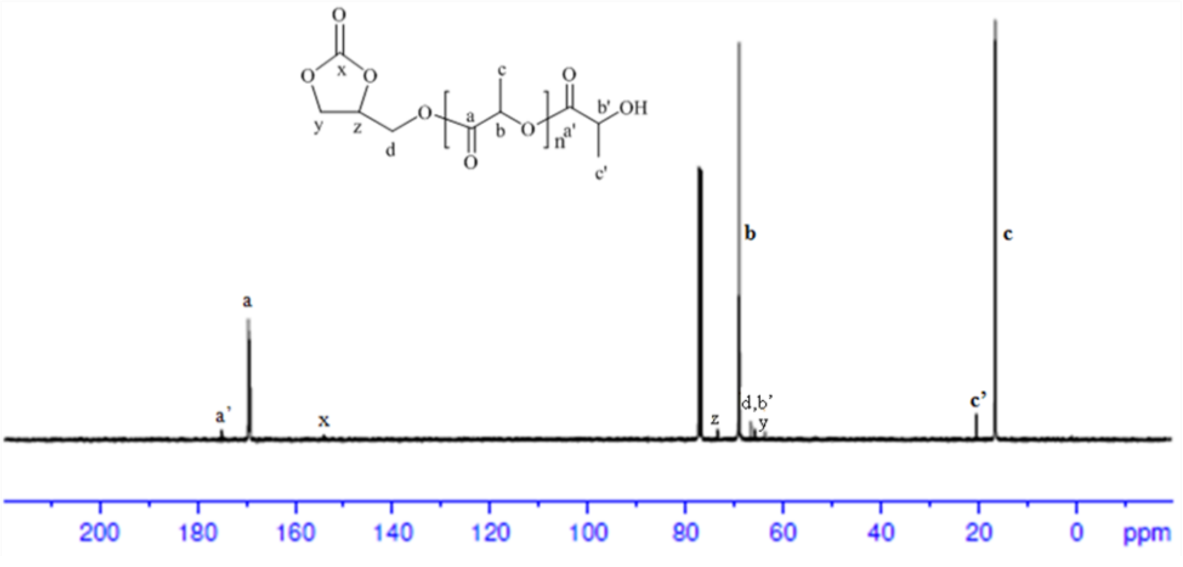


Figure 2. ^{13}C NMR spectrum of α-(cyclic carbonate), ω-hydroxyl end functional. PDLLA (entry 2, Table 1) in $CDCl_3$ (100 MHz).

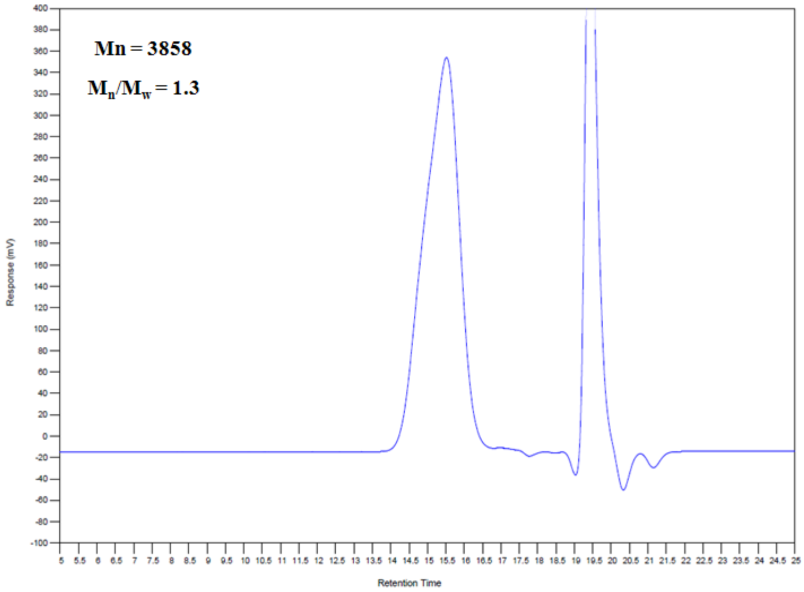


Figure 3. GPC trace of cyclic carbonate end functional PDLLA (M_n = 3858 g/mol, PDI=1.3) (entry 1, Table 1), (using RI detector).

The polymerization of D,L-lactide is carried out at 35 °C in dichloromethane using glycerol 1,2-carbonate as the initiator with 4 equivalents of DMAP relative to initiating alcohol. The two polymerizations were carried out by varying monomer to initiator ratio and the molecular weights obtained from ^{1}H NMR analysis are close to the targeted molecular weights (entry 1 and 2, Table 1). The polydispersities obtained from GPC are relatively narrow and molecular weights by GPC were determined against polystyrene standards. The yields obtained under these experimental conditions at 35°C carried out in dichloromethane are relatively good (55–82%) (Table 1).

Bulk polymerization of D,L-lactide was also investigated at 135 °C using glycerol 1,2-carbonate as initiator. At 135 °C, the catalyst also gave good molecular weight control and moderately narrow polydispersities for the ROP of D,L-lactide (Table 1). The polymerization of D,L-lactide at 35 °C gave comparatively less yields (<60%) than polymerization at 135 °C (80%). The molecular weights obtained from ^{1}H NMR analysis are correlates to the targeted molecular weights. At high temperature (135 °C) DMAP also has not shown any interference with initiator (glycerol 1,2-carbonate).

Table 1. Synthesis of cyclic carbonate end functional PDLLA-OH using GC/DMAP catalyst system in dichloromethane.

Sl. No.	D,L-lactide (mol)	Initiator (Glycerol 1,2-Carbonate) (mol)	Catalyst (DMAP) (mol)	Time (h)	Temp (ºC)	Isolated Yield (%)	M_n (Calcd.)^a (g/mol)	M_n (NMR) (g/mol)	SEC	
									M_n (g/mol)	M_w/M_n
1	0.0138	0.0006	0.0026	24	35	55	3118	2824	3858	1.3
2	0.0138	0.0005	0.0020	24	35	57	4118	3746	5165	1.3
3 *	0.0138	0.0006	0.0013	0.5	135	82	3118	3739	5229	1.4
4 *	0.0138	0.0005	0.0010	0.5	135	81	4118	4199	7603	1.4

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

Cyclic carbonate end functionalized PDLLA having molecular weights 3118 and 4118 g·mol^{-1} were synthesized at two different temperatures, i.e., at 35 °C and 135 °C. The molecular weight determined from end group analysis (^{1}H NMR) related with the targeted molecular weights and molecular weights obtained from GPC against polystyrene standards. The polydispersities obtained from GPC analysis was relatively narrow (1.3) (entry 1 and 2, Table 1) for polymerization at 35 °C and 1.4 for polymerization at 135 °C (entry 3 and 4, Table 1).

The cyclic carbonate end functional PDLLA obtained from GC/DMAP catalyzed polymerization also analyzed by MALDI TOF MS. A set of peaks with difference in mass of ($\Delta m/z$ = 144 Da, two repeat units of D,L-lactide) was observed unlike PDLLA obtained catalyzed by GC/Sn(Oct)$_2$. Figure 4 shows the MALDI TOF mass spectrum of α-(cyclic carbonate), α-hydroxyl end functional PDLLA in which Na$^+$ and K$^+$ adducts are detected apart from other series in various proportions. Similarly, MALDI analysis shows less number of side reactions in case of PDLLA at 35 °C. Representative mass difference between calculated and observed series from MALDI spectrum has been given in Table 2. We have not observed HO-PDLLA-COOH series unlike PDLLA obtained catalyzed by GC/Sn(Oct)$_2$ (see Supporting Information, Figure S7).

Table 2. Observed series in MALDI TOF mass spectrum of α-(cyclic carbonate), ω-hydroxyl end functional PDLLA using GC/DMAP as catalyst.

n = 13	144.13 (D,L-lactide)	118.09 (GC)	22.99 (Na)	M_n (theory) = 2014.76	M_n (MALDI)$^@$ = 2013.58	Δ = 1.10
n = 13	144.13 (D,L-lactide)	118.09 (GC)	39.10 (K)	M_n (theory) = 2030.88	M_n (MALDI) = 2030.55	Δ = 0.33

@: $[M_n + Na]^+$ (MALDI) = [144.13 (D,L-lactide) × n (DP)] + 118.09 (GC) + 22.99 (Na^+)/39.10 (K^+).

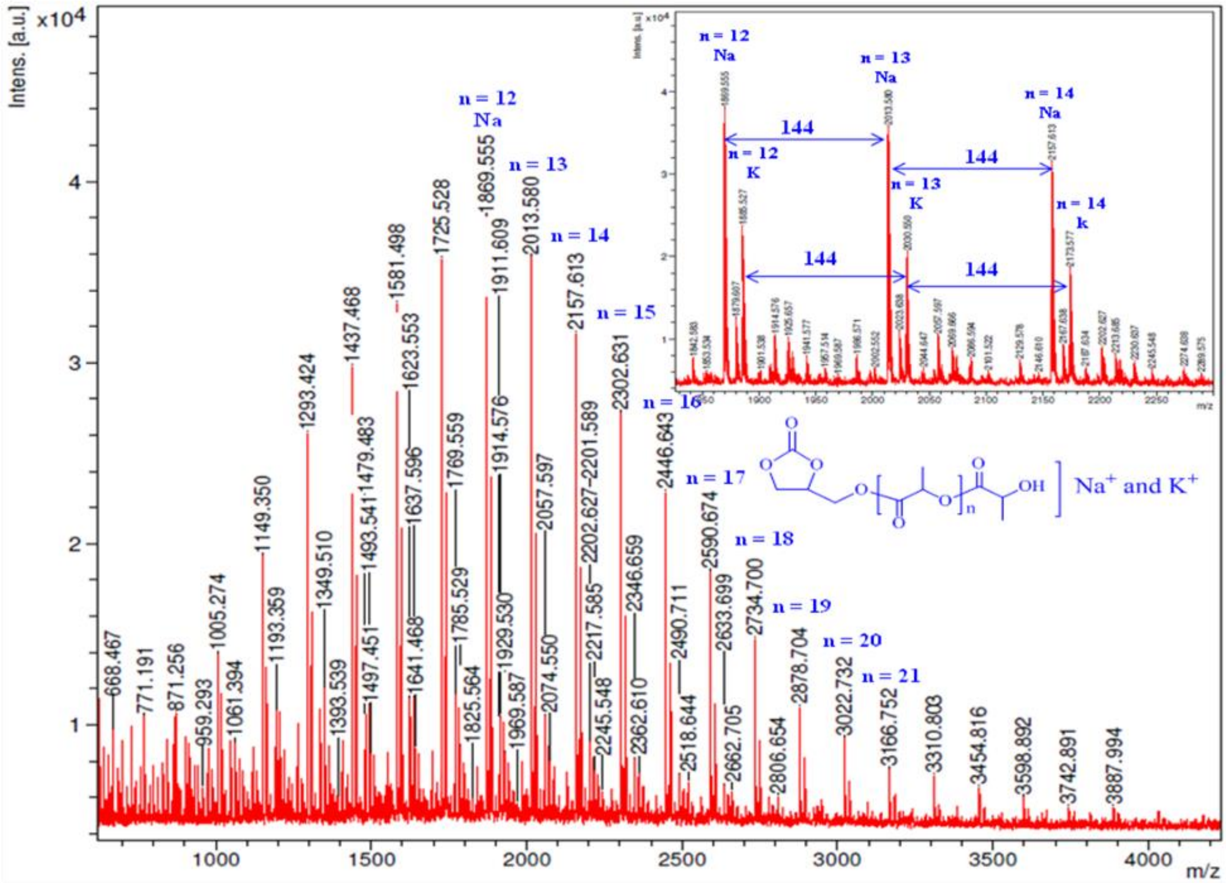
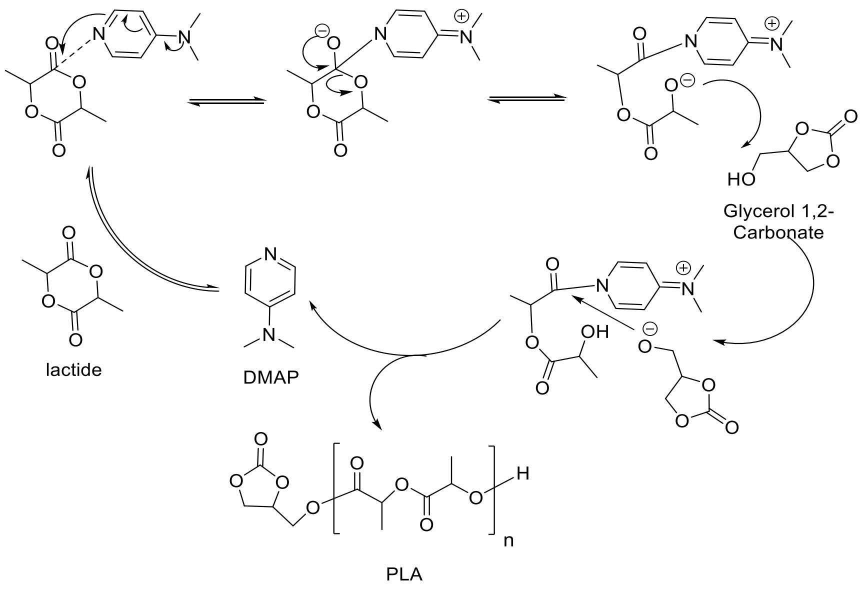


Figure 4. MALDI TOF mass spectrum of α-(cyclic carbonate), ω-hydroxyl end functional PDLLA (entry 2, Table 1). $[M_n + Na]^+$ (MALDI) = [144.13 (PDLLA repeat unit) × n (DP)] + 118.09 (GC) + 22.99 (Na^+), (Δ = 1.1).

ROP of D,L-lactide using GC/DMAP catalytic system was proposed to occur through a monomer-activated mechanism as shown in Scheme 2, but an alcohol-activated mechanism (chain-end activation) cannot be ruled out. The monomer-activated mechanism is proposed to occur by nucleophilic attack by DMAP on the monomer to generate an alkoxide/acyl pyridinium zwitterion. Subsequent proton transfer from the initiating or propagating alcohol, followed by acylation of the resultant alkoxide, generates the hydroxyl-terminated ring-opened monomer [53].

Polymerization proceeded by reaction of the ω-hydroxyl group with the next DMAP-lactide intermediate. NMR spectroscopy (Figures 1 and 2) confirms the α-chain end of the PDLLA bears the ester from the initiating alcohol and ω-chain end bears a hydroxyl group. DMAP is effective for the ROP of lactide in the presence of either a primary or a secondary alcohol. The resulting propagating species, a secondary alcohol, however, is only active towards the lactide monomer and not the polymer chain, minimizing undesirable transesterification reactions.



Scheme 2. Proposed monomer-activated mechanism for the ROP of lactide using GC/DMAP catalytic system.

3.2. Synthesis of Cyclic Carbonate End-functional 4-arm Star PCL

The another purpose of this research is to synthesize and characterize a new class of four-arm star PCL biodegradable polymer having cyclic carbonate end functionality which can be explored as a precursor for new block copolymers, with amine terminated polymers. The synthesis involved three basic steps. First, low molecular weight hydroxyl-functionalized 4-arm star PCL (PCL-OH)$_4$ will be synthesized by ROP of ε-CL. Secondly, functionalization of hydroxyl-terminated prepolymer will be carried out with succinic anhydride to get carboxylic acid terminated four-arm star PCL (PCL-COOH)$_4$. Finally, cyclic carbonate end functional four-arm star-shaped PCL will be prepared via coupling of glycerol 1,2-carbonate with (PCL-COOH)$_4$ and end group functionality is determined by NMR, FTIR and MALDI TOF MS.

3.2.1. Synthesis of Hydroxyl Terminated Four-arm Star Poly(ε-caprolactone)

In the 1st step, four-arm star-shaped PCL's (Scheme 3) with terminal hydroxyl groups were prepared via the controlled ROP of ε-caprolactone in bulk using tin octoate (Sn(Oct)$_2$) as a catalyst and pentaerythritol as a tetrafunctional initiator at 110 °C for 4 h. The results, summarized in Table 3, are mostly in good agreement with the theoretical values, indicating good control over polymerization and the preparation of a well-defined four-arm star architecture. Four-arm star PCL having molecular weight range from 2600 to 27,000 g·mol^{-1} were synthesized by varying monomer to initiator ratios. The polymers obtained with narrow polydispersities (1.12–1.28) and shows characteristic living nature of polymerization. The molecular weight determined from end group analysis (^{1}H NMR) coincide fairly well with the targeted molecular weights depending on ε-CL/pentaerythritol and molecular weights obtained from GPC were higher as measured against to homo polystyrene standards using THF as eluent.

Maglio et al. [27] reported the mole fraction of 4-arm, 3-arm, and linear macromolecules formed in various ratios. Their ^{1}H NMR spectrum reveled that a small fraction (15–22%) of hydroxyl groups of pentaerythritol was not involved in the initiation step. This behavior, also reported by Lang and Chu [76] and Turunen et al. [77], most likely occurred because of steric hindrance caused by adjacent growing chains, which reduces the accessibility of monomer to the unreacted -OH groups. However, Lang et al. [76] also found 29–7% residual hydroxyls groups of pentaerythritol depending on low molecular weight to high molecular weight 4-arm star PCL (they determined the molar ratio of PCL arm end group -CH$_2$OH/the residual hydroxyl group -CH$_2$OH of pentaerythritol according to its ^{1}H-NMR spectra). We found this ratio as 7.6 (entry 6, Table 3). It is possible that one, two, or even three hydroxyl groups of pentaerythritol in 4-arm star PCL-OH may remain unreacted [76] over such a wide range of the feed molar ratio of the CL to OH. Lang and Chu [76] observed 4-arm star PCL-OH with all four possible structures of four-, three-, two-, and one-arm (PCL-OHs) for molar ratio of CL/OH = 5/1. When the feed molar ratio of CL/OH increased to 20:1 (entry 6, Table 3), more than three hydroxyls in pentaerythritol took part in the reaction with ε-CL to produce mainly three and four-arm PCL-OH. The number of arms of the star-shaped PCL was determined from ^{13}C NMR spectrum [77].

3.2.2. Synthesis of Carboxylic Acid Terminated Four-arm Star Poly(ε-caprolactone)

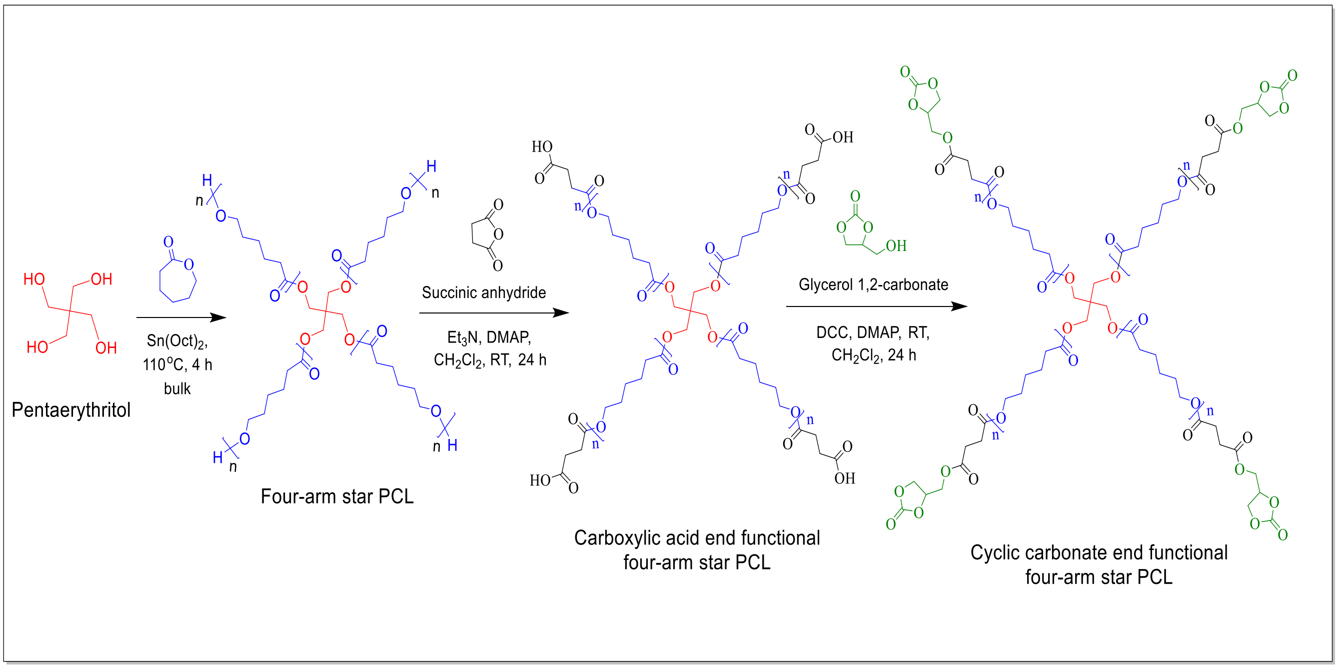
In this study, the carboxylic acid end functional four-arm star PCL was obtained in high yield without any side reactions [71,78,79]. To facilitate characterization, we used low molecular weight four-arm star PCL-OH (each arm M$_n$ (calcd.) = 500 g/mol, Table 3, entry 1) for modifying hydroxyl groups to carboxylic acid by reacting with succinic anhydride. The carboxylic end functional PCL (CAEFPCL) was prepared by the reaction between hydroxyl end-functionality of PCL-OH and succinic anhydride, at room temperature for 24 h, in CH_2Cl_2 catalyzed by DMAP and Et_3N. The appearance of the small H_f peak (3.66 ppm) in Figure 5 indicated the terminal hydroxyl groups were not completely reacted with succinic anhydride.

The new signal at 2.66 ppm can be assigned to the methylene proton (H_h, $-2CH_2$-of succinic group). The methylene group in the PCL-OH shifted from 3.66 ppm in the 4-arm star PCL-OH to 4.1 ppm in the 4-arm star PCL-COOH (it is merged with 'g', 'e' $-CH_2-COO$). As this polymer is not precipitated in earlier step as well as in this present step, unreacted ε-CL peaks at 4.25, 1.85 and 1.75 ppm are observed. So when functionalization of the hydroxyl-terminated 4-arm star PCL was carried out with succinic anhydride, the hydroxyl groups were substituted with very high carboxylic acid end groups in 91% yield. Molecular weight of carboxylic acid end functional 4-arm star PCL calculated by ^1H NMR as M_n (NMR) = 2344 g/mol.

Table 3. Synthesis of four-arm star PCL-OH in bulk at 110°C for 4 h [a].

Sl. No.	**DP of 4-arm star**	**Isolated yield (%)**	**M_n [b] (Calcd.) g/mol**	**M_n (^1H NMR) g/mol**	**SEC**	
					M_n	**PDI**
1	20	89	2419	2574	2476	1.18
2	80	81	9267	7145	10356	1.12
3	100	85	11550	10540	15841	1.12
4	60	94	6985	6065	8662	1.13
5	120	95	13833	9530	22034	1.16
6	20	90	2419	2586	2978	1.22
7	140	95	16116	15889	20089	1.24
8	175	99	20111	27073	20855	1.27

a: catalyst ($Sn(Oct)_2$) used is 0.05 mol% of ε-caprolactone.
b: DP of 4-arm star PCL × 114.14 + 136.15 (Pentaerythritol).



Scheme 3. Synthetic route for cyclic carbonate end functional four-arm star PCL.

3.2.3. Synthesis of Cyclic Carbonate Terminated Four-arm Star Poly(ε-caprolactone)

The esterification of carboxylic acid end functional four-arm star PCL with glycerol 1,2-carbonate was carried out in the presence of DMAP and DCC, at room temperature, for 24 h, in CH_2Cl_2 to prepare the cyclic carbonate end functional 4-arm star PCL (CCEFPCL) in 88% yield. The ^1H NMR spectrum of four-arm star CCEFPCL is illustrated in Figure 6. The signal corresponding to the methine proton (z) in the cyclic carbonate was observed at 4.94 and the methylene proton (j, y) in cyclic carbonate appeared at 4.57–4.34 ppm.

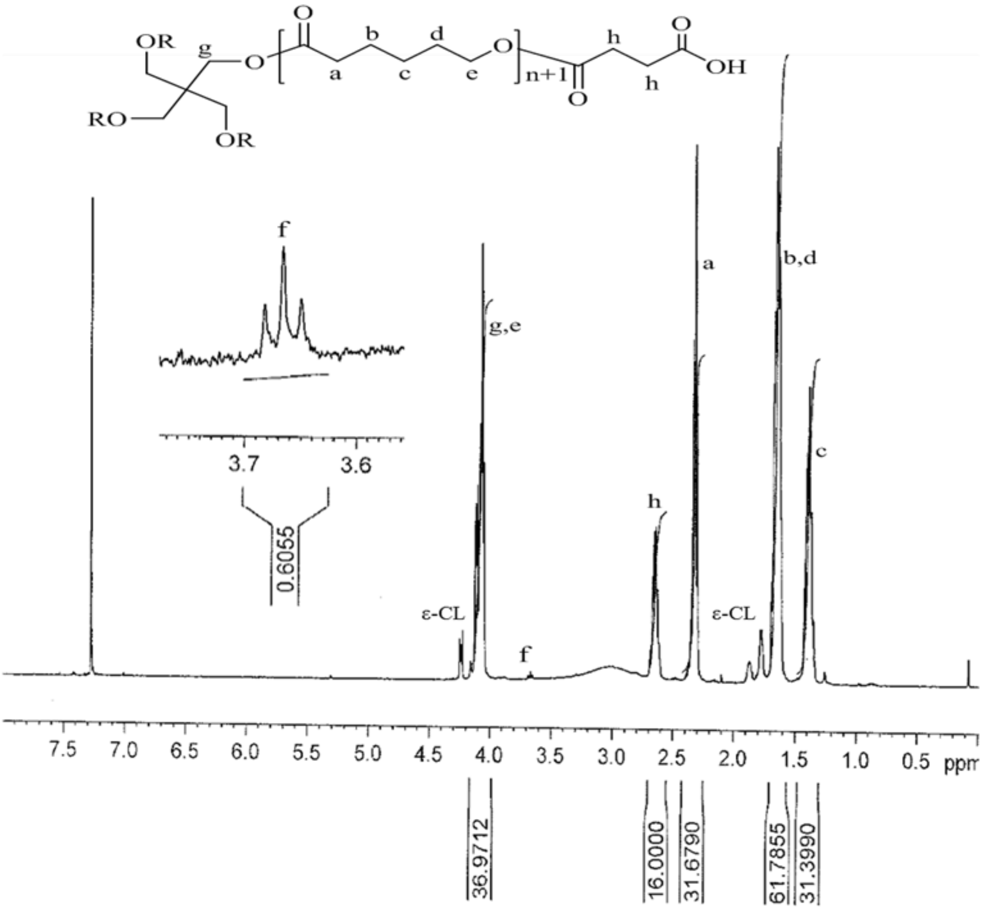


Figure 5. ^{1}H NMR spectrum of carboxylic acid end functional four-arm star PCL. (M_n (NMR) = 2344 g/mol) in $CDCl_3$ (400 MHz).

Residual hydroxyl groups of pentaerythritol will react with succinic anhydride to result in carboxylic acid end groups which in turn reacts with glycerol 1,2-carbonate to yield cyclic carbonate end groups. The residual hydroxyl groups of pentaerythritol in 4-arm star PCL-OH (3.51–3.62 ppm) disappeared due to its possible reaction with electrophile. Molecular weight of cyclic carbonate end functional 4-arm star PCL calculated by ^{1}H NMR as M_n (NMR) = 3327 g/mol (Figure 6).

The ^{13}C NMR (Figure 7) spectrum of four-arm star CCEFPCL showed the cyclic C=O and the methine carbon peak of cyclic carbonate at 154.39 ppm and 73.7 ppm, respectively and two methylene carbons j and y appeared at 66 ppm and 63.2 respectively. The additional peaks at 63.4 and 65.6 may arise due to cyclic carbonate end functional group attached as a result of presence of residual hydroxyl groups of pentaerythritol. The peak at 173.6 ppm and 172.9 ppm are corresponds to the ester carbonyl carbon (k) of PCL unit and ester carbonyl carbon (k′) connected to pentaerythritol respectively.

Also, the ester carbonyl carbon (k″) connected to succinic group unit and ester carbonyl carbon (k‴) connected to glycerol carbonate unit appeared at 172.2 and 171.8 ppm respectively apart from residuals of these peaks (of pentaerythritol) may be appeared at 171.6 and 171.5 ppm. There are two type of close ‘q’ peaks present (close to 42 ppm) indicating once again more than three hydroxyls in pentaerythritol took part in the reaction with ε-CL to produce mainly three and four-arm CCEFPCL. Thus ^{13}C NMR shows the clear evidence of presence of cyclic carbonate end group.

Figure 8 shows FTIR overlay of four-arm star CCEFPCL over four-arm star PCL-OH and it confirms the presence of cyclic carbonate end group in PCL. The absorption band of carbonyl group of cyclic carbonate was observed at 1810 cm^{-1} and there was almost no absorption band in the region 3200–3500 cm^{-1}. All the observations from NMR and FTIR confirmed the formation of the cyclic carbonate terminated four-arm star PCL. Molecular weight of CCEFPCL (M_n = 4282; M_w/M_n = 1.1) measured by GPC (Figure 9) was against homo PS standards. The difference of molecular weight (though narrow molecular weight distribution is retained) by GPC compared to M_n by ^{1}H NMR (M_n(NMR) = 3327 g/mol) after functionalization could be explained by the change in the polymer hydrodynamic volume in the SCE analysis [80] compared with homo PS standards.

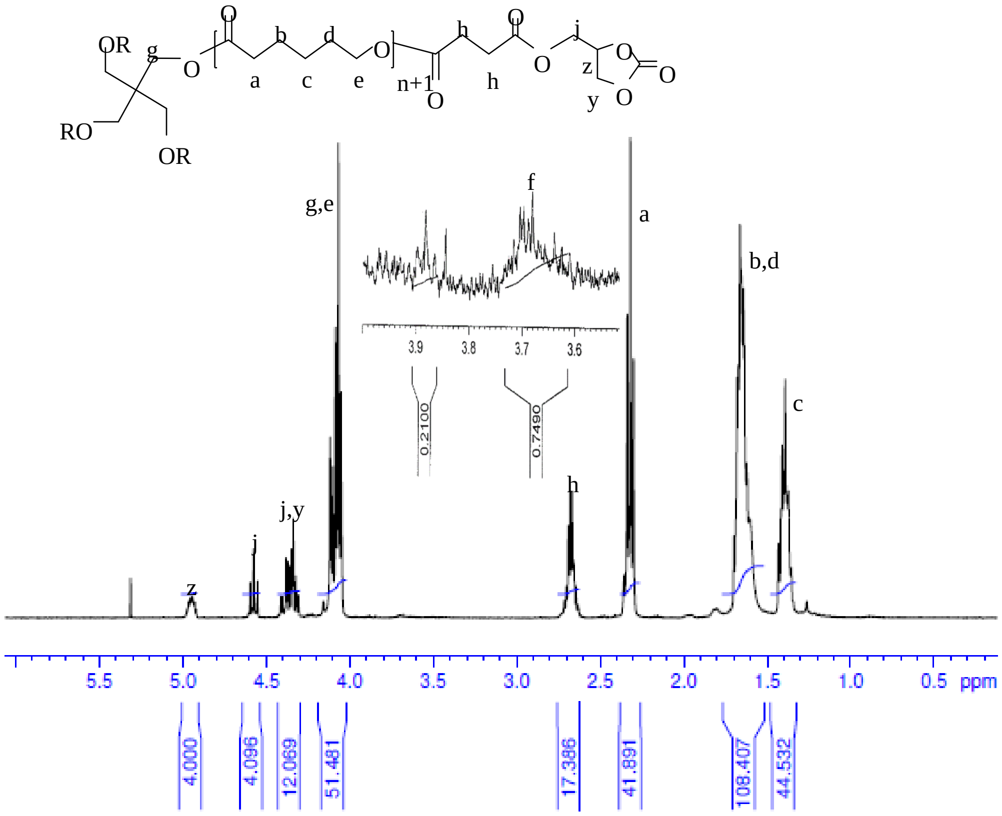


Figure 6. ^{1}H NMR spectrum of four-arm star CCEFPCL (M_n (NMR) = 3327 g/mol) in $CDCl_3$ (400 MHz).

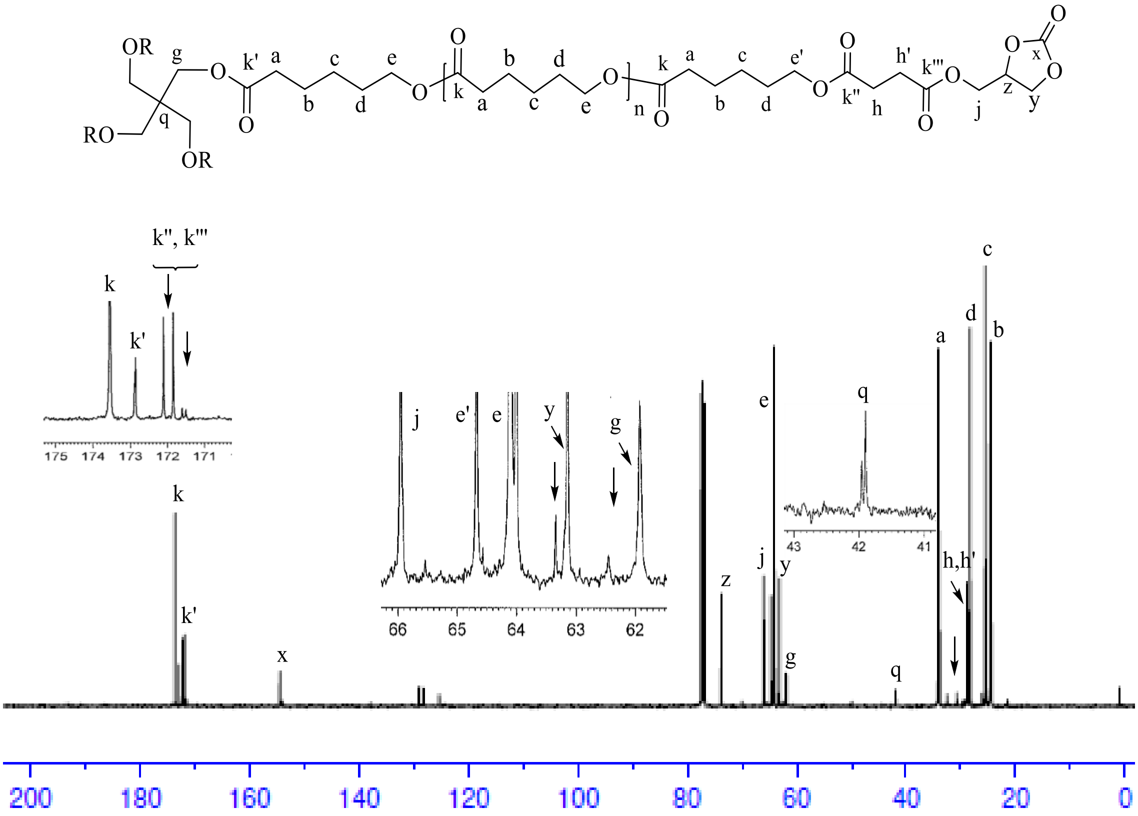


Figure 7. ^{13}C NMR spectrum of four-arm star CCEFPCL (M_n (NMR) = 3327 g/mol) in $CDCl_3$ (100 MHz).

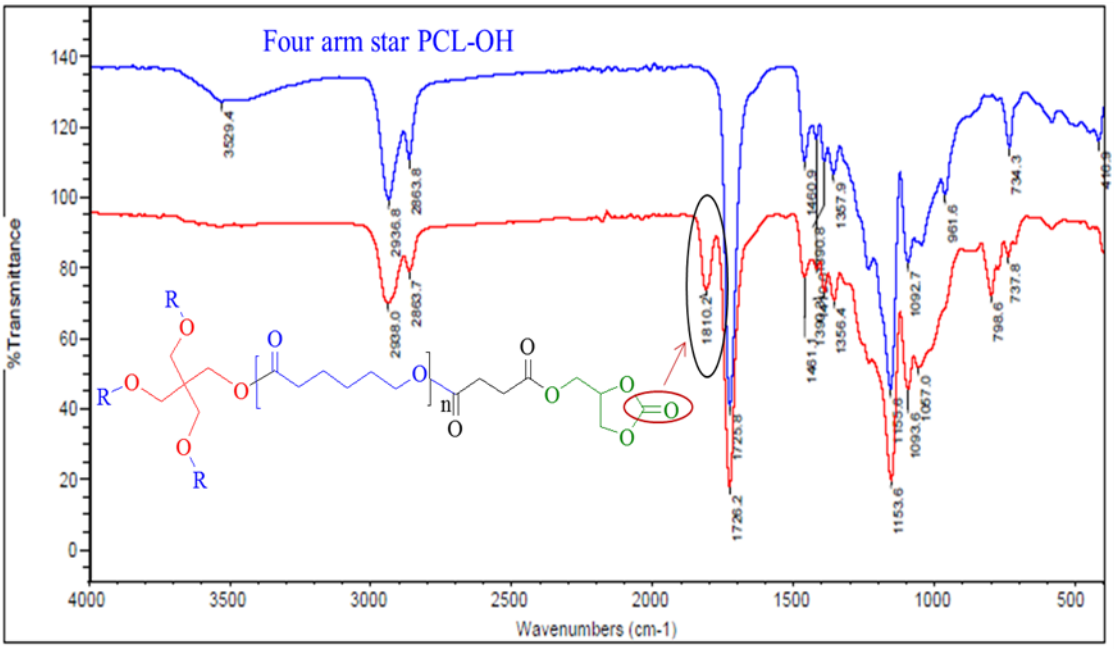


Figure 8. IR overlay of four-arm star CCEFPCL (M_n (NMR) = 3327 g/mol) with 4-arm star PCL-OH (M_n (NMR) = 2574 g/mol).

The MALDI-TOF mass spectra provided additional strong evidence for almost quantitative conversion to the cyclic carbonate end group, as the previously described hydroxyl resonances were almost completely lost, and a new set of resonances, dominated by the unique cyclic carbonate functionality were observed in reflector mode. Figure 10 shows typical MALDI-TOF mass spectrum of cyclic carbonate end functional four-arm star PCL. The MALDI-TOF mass spectrum comprises two major series of peaks along with other series. The most prominent series of peaks is characterized by a mass increment of 114 Da, which is equal to the mass of the repeating unit in the PCL arm (Figure 10). First major series is expected for four-arm star PCL terminated with a cyclic carbonate and detected as the Na^+ adduct ($\Delta = 0.58$).

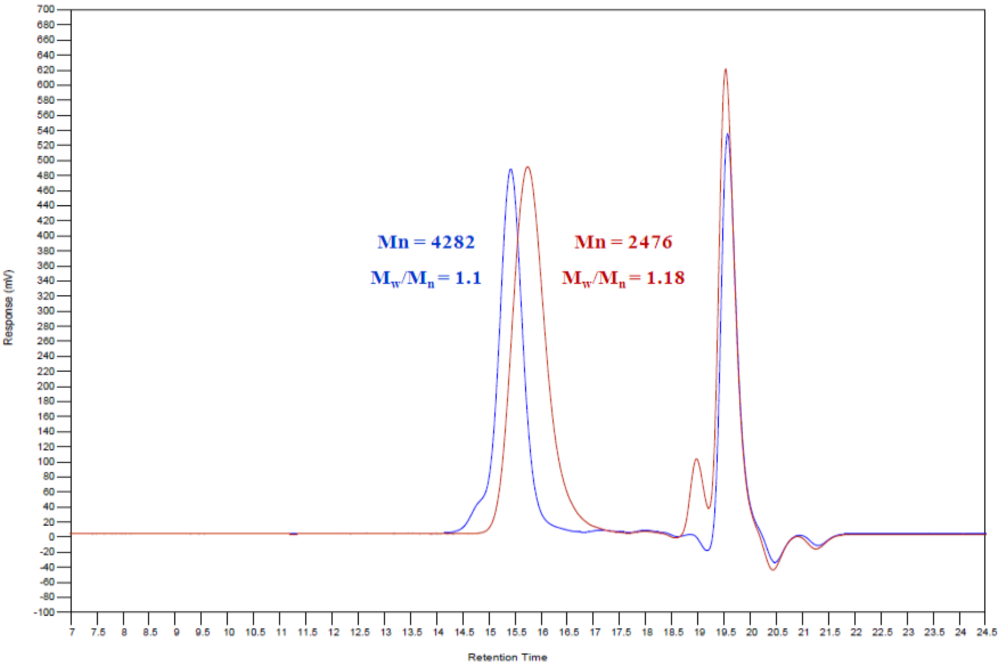


Figure 9. GPC overlay of four-arm star CCEFPCL (M_n(NMR) = 3327 g/mol) with PCL-OH (M_n(NMR) = 2574) (using RI detector, against narrow PS standard).

The second series of the peaks also from four-arm star PCL terminated with a cyclic carbonate group, but corresponds to the K^+ adduct ($\Delta = 0.71$) (Table 4). The complexity of spectrum (in terms of more peaks) could be attributed to presence of different fractions of four-arm, three-arm, and possible transesterification side products [6,14,15] arising from first step due to use of transesterification catalyst $Sn(Oct)_2$, at high temperature. These cyclic carbonate terminated four-arm star PCL has scope in synthesizing four-arm star PCL di-block copolymers by reacting it with amine terminated polymers via coupling chemistry.

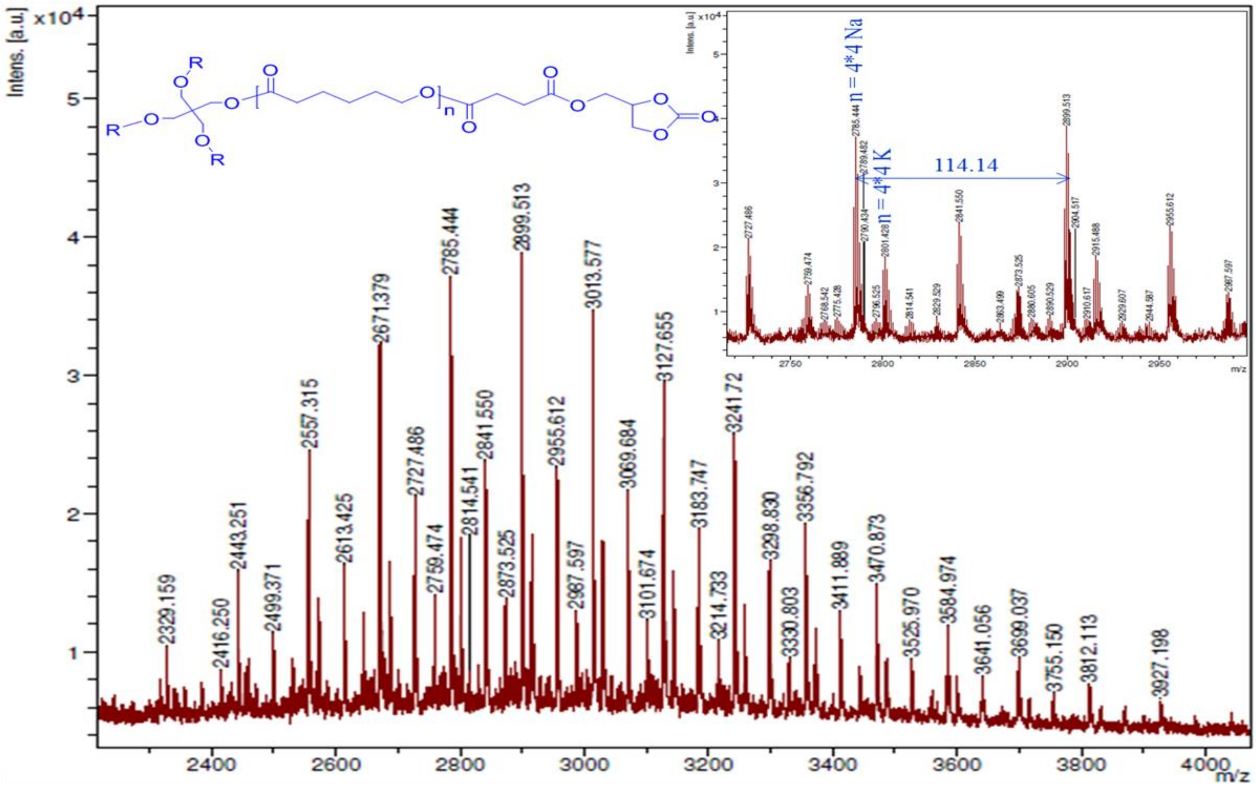


Figure 10. MALDI TOF mass spectrum of four arm star CCEFPCL (Matrix: 2,5-Dihydroxybenzoic acid) [M_n + Na]$^+$ (MALDI) = [114.14 (CL) × n (DP)] × 4 +136.15 (pentaerythritol) + 4 × 118.09 (glycerol 1, 2-carbonate) + 4×100.07 (succinc anhydride) − 72 (4 × H_2O) + for Na^+(22.99) (Δ = 0.58); for K^+ (39.10) (Δ = 0.71).

Table 4. Observed series in MALDI TOF mass spectrum of cyclic carbonate end functional four-arm star PCL.

n = 4×4	114.14 (CL)	100.07 (SA)	118.09 (GC)	136.15 (pentaerythritol)	22.99 (Na)	M_n (theory) = 2786.02	M_n (MALDI)$^@$ = 2785.44	Δ = 0.58
n = 4×4	114.14 (CL)	100.07 (SA)	118.09 (GC)	136.15 (pentaerythritol)	39.10 (K)	M_n (theory) = 2802.13	M_n (MALDI) = 2801.42	Δ = 0.71

Matrix: 2, 5-Dihydroxybenzoic acid.
@: [M_n + Na]$^+$ (MALDI) = [114.14 (CL) × n (DP)] ×4 + 136.15 (pentaerythritol) + 4 ×100.07 (succinc anhydride) + 4 × 118.09 (glycerol 1,2-carbonate) − 72 (4 × H_2O) + for Na^+ (22.99) (Δ = 0.58); for K^+ (39.10) (Δ = 0.71).

4. Conclusions

In summary, we have synthesized well-defined cyclic carbonate end-functional PDLLA and 4-arm star PCL with good end-group fidelity by ROP. Molecular weights were well-controlled with relatively narrow polydispersities by adjusting the monomer to initiator molar ratios. In view of green chemistry and biodegradability, the biomass (glycerol) origin of glycerol 1,2-carbonate, and the polymers made here, makes our strategy a more environmentally friendly process. In comparison with more traditional tin-based catalyst (Sn(Oct)$_2$), the DMAP catalyst was considerably more active and allowed low polymerization temperatures with good control of the molecular weight and relatively narrow polydispersities. Also, Sn(Oct)$_2$ and DMAP catalysts were not interfered with fivemembered cyclic carbonate end group as evident from NMR analysis. Moreover, MALDI TOF mass analysis data shows very less number of transesterification reactions during polymerization at 110 °C with Sn(Oct)$_2$ catalyst. In case of GC/DMAP catalyzed polymerizations, we have not observed HO-PDLLA-COOH series unlike PDLLA obtained catalyzed by GC/Sn(Oct)$_2$. Potential uses of this cyclic carbonate end-functional PDLLA as a macromonomer in the synthesis of poly(ether carbonates)-graft-poly(D,L-lactide) and in the synthesis of various four-arm star PCL di-block copolymers will be explored by reacting terminal cyclic carbonate 4-arm star PCL with an amine terminated polymers. Five-membered cyclic carbonate end group reaction with 2-phenylethylamine enables the hydroxy urethane ends functional PDLLA without the use of the relatively more hazardous isocyanates and without any by-product. Work is in progress in our laboratory to synthesize new block copolymers and ABA multiblock copolymers from these asymmetric telechelic PDLLAs and will be reported separately.

Supplementary Materials

The following supporting information can be found at: https://www.sciepublish.com/article/pii/67.

Author Contributions

Conceptualization, R.G.; Methodology, R.M.P.; Software, R.G.; Validation, R.G.; Formal Analysis R.M.P. and R.G.; Investigation, R.M.P.; Resources, S.G.; Data Curation, R.G.; Writing—Original Draft Preparation, R.M.P.; Writing-Review & Editing, R.G. and S.G.; Visualization, R.M.P.; Supervision, R.G.; Project Administration, S.G.; Funding Acquisition, S.G.

Ethics Statement

Not applicable.

Informed Consent Statement

Not applicable.

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Declaration of Competing Interest

The authors declare no conflict of interest.

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