Nanolamellar triblock of poly D, L-lactide- δ-valerolactone- D, L-lactide with tuneable glass transition and crystallinity for drug delivery vesicle

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Synthesis of poly D, L-lactide

A typical procedure for synthesizing poly D, L-lactide is reported here. D, L-lactide (12.0 g, 0.083 mol), and 1, 6-hexanediol (12.39 mg, 0.1049 mmol) were added in a 25 mL round bottom flask equipped with a Teflon – coated magnetic stirrer under nitrogen atmosphere. The sealed reaction vessel was then placed in an oil bath and heated up to 90 °C followed by addition of Sn(Oct$_2$) (0.043 g, 0.1049 mmol). The reaction mixture was then heated to 140 °C for 12 hrs. After cooling, the solid reaction product was dissolved in dichloromethane and precipitated in excess methanol. The solvent was removed under reduced pressure at room temperature for 2 days. This sample was designated as L1. Time of reaction was varied from 4 hrs to 12 hrs. The initiator concentration i.e.$[M]_0/[I]_0$ ratio was varied from 333 to 793 when $[M]_0/[cat]_0$ ranging between 793 to 2000.Table S1 furnishes details about the conditions imposed for synthesizing L1, L2, L3 and L4. The product was characterized by FTIR, ^{1}H NMR, ^{13}C NMR and GPC. ^{1}H NMR (CDCl$_3$): δ 7.29 (s, 4H), 5.2 (m, 141H), 3.77 (t, 4H), 1.6 (m, 434H). ^{13}C NMR (CDCl$_3$): δ169.6, 72.46, 69.42, 66.72, 20.45, 16.73, 15.78.

Characterization of poly D, L-lactide

The bulk ring opening polymerization technique has been adopted for the synthesis of poly D, L-lactide homopolymer using tin 2-ethyl hexanoate as catalyst and1, 6- hexane diol as initiator at 140 °C for 12 hrs. A series of four polymerizations have been investigated by varying the monomer to initiator ratio from 333 to 793, where the catalyst to monomer ratio has also been varied from 793 to 2000. An aliquot of the cooled reaction mixture was thoroughly analyzed by ^{1}H NMR, ^{13}C NMR, GPC.

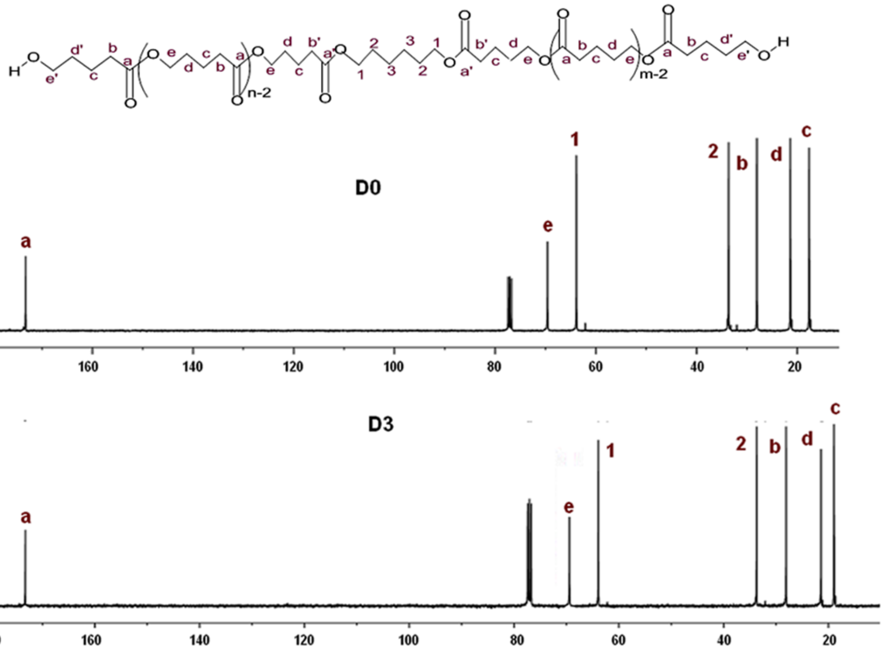

Fig. S1 ^{13}C NMR spectra of homopolymers D0 and D3.

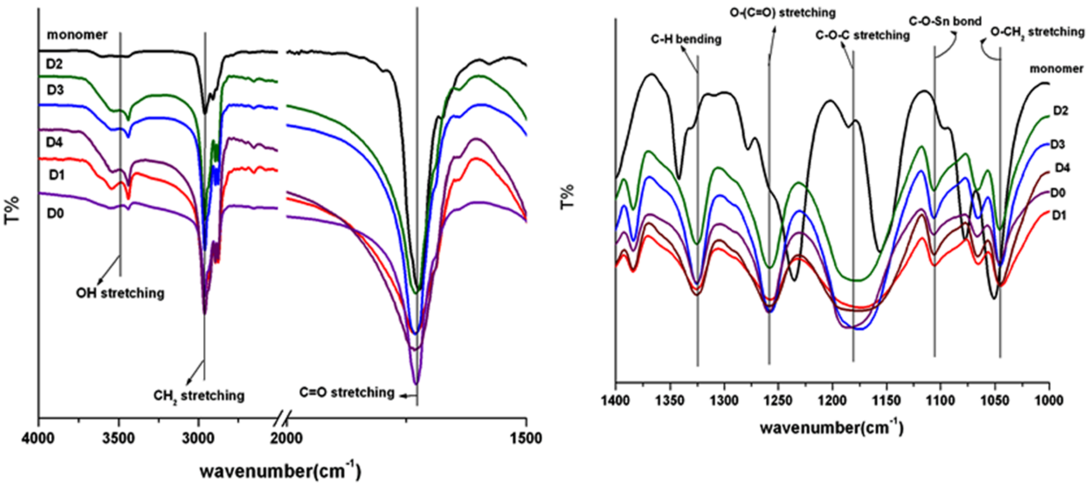

Fig. S2 FTIR spectra of δ–valerolactone monomer and homopolymers D0, D1, D2, D3 and D4.

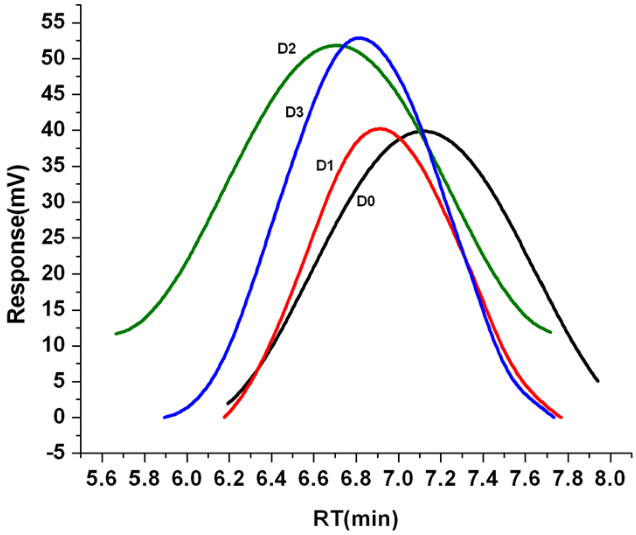

Fig. S3 SEC traces of homopolymers D0, D1, D2 and D3.

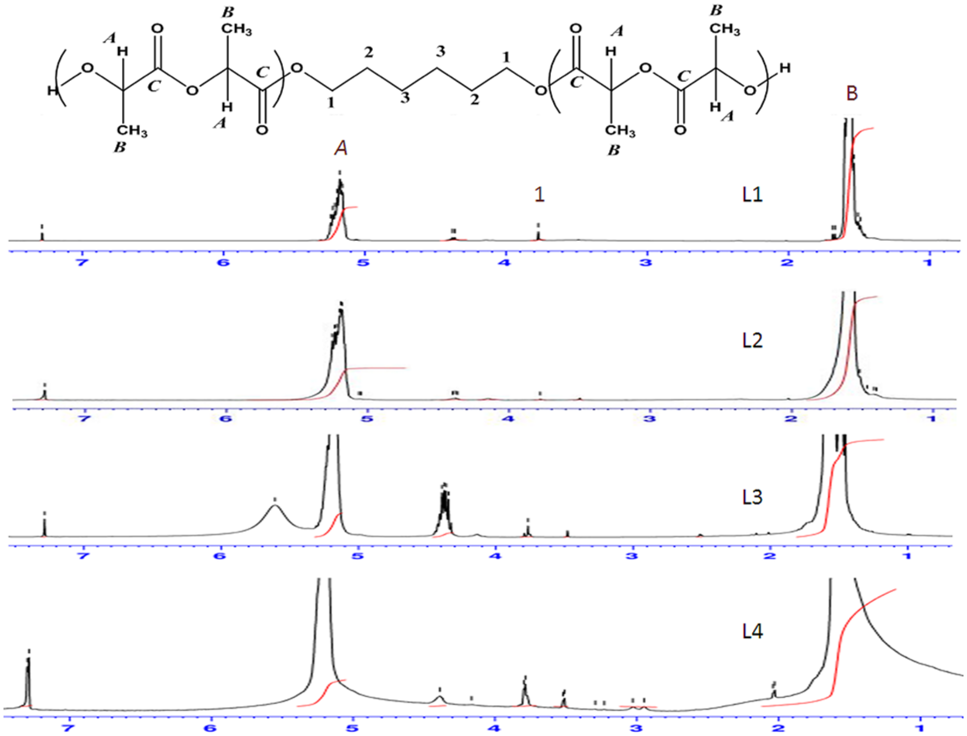

Fig. S4 ^{1}H NMR spectra of poly D, L-lactide homopolymers L1, L2, L3 and L4.

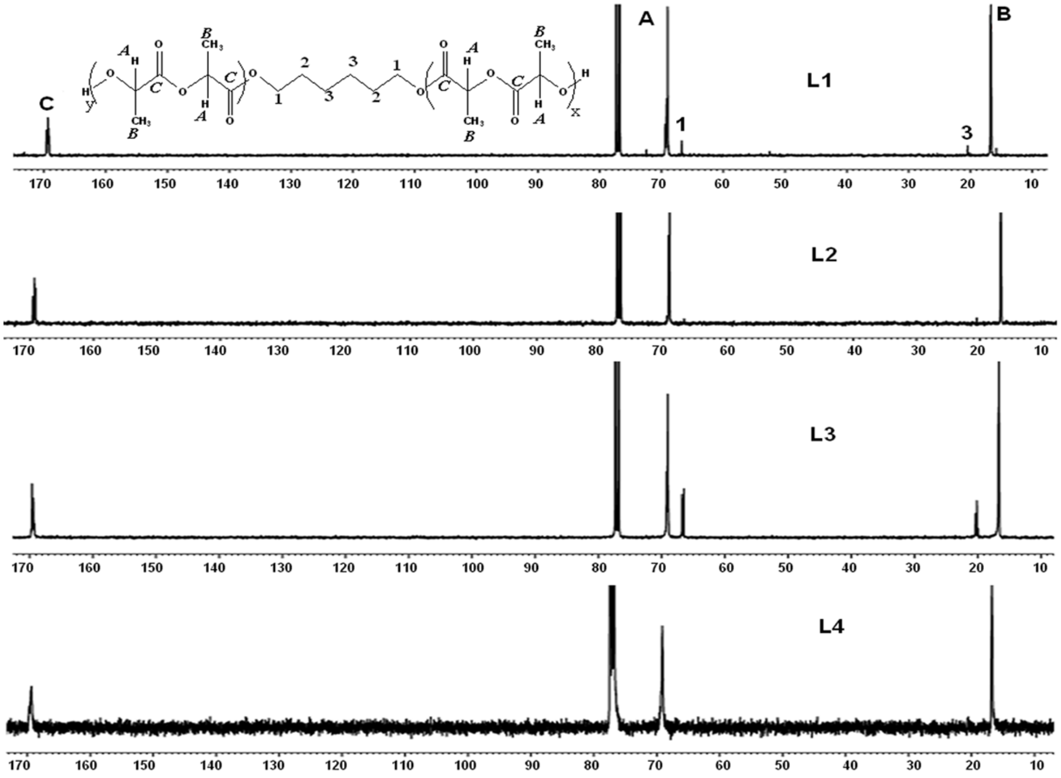

Fig. S5 ^{13}CNMR spectra of poly D, L-lactide homopolymers L1, L2, L3 and L4.

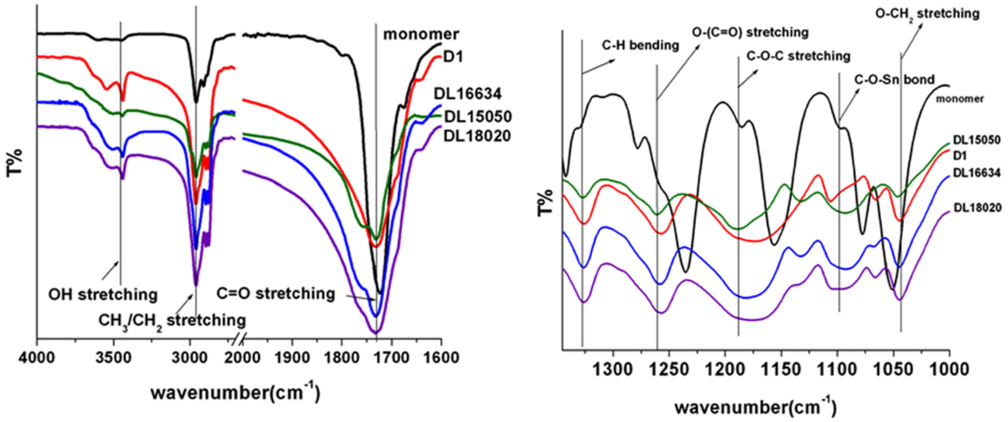

Fig. S6 FTIR spectra of δ–valerolactone monomer, homopolymers D1 and copolymers DL15050, DL16634 and DL18020.

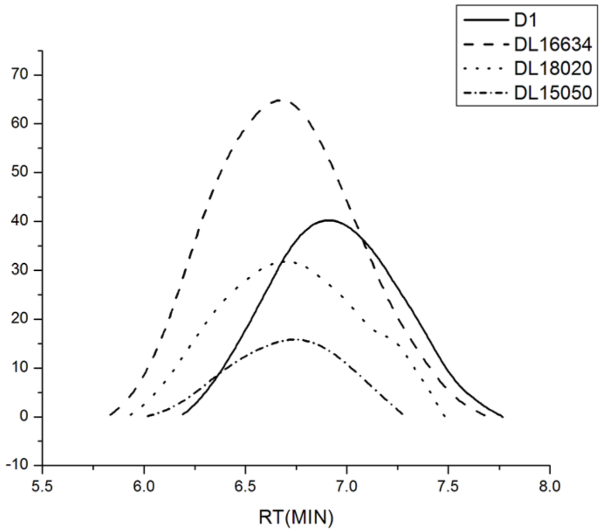

Fig. S7 SEC traces of copolymers DL15050, DL16634, DL18020 and homopolymer D1.

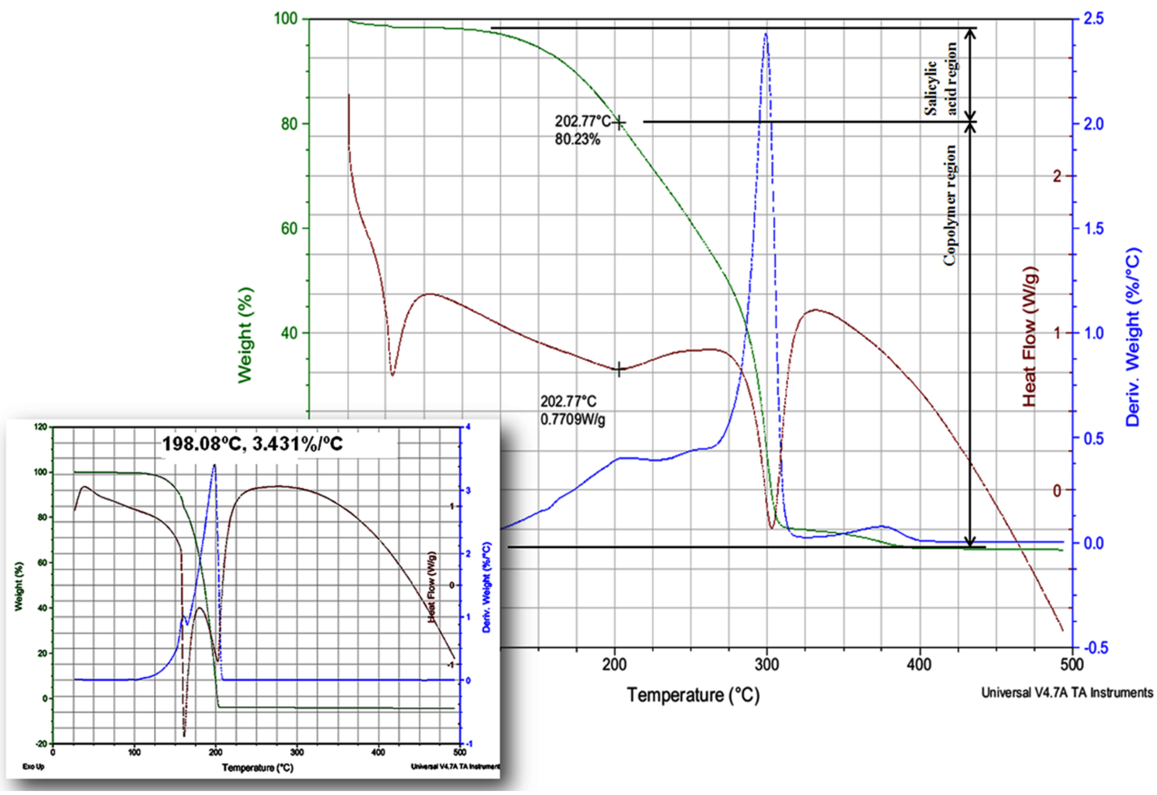

Fig. S8 Thermogravimetric analysis showing salicylic acid degradation around 198 ºC (inset) and a hump around 202 ºC in salicylic acid loaded microsphere due to degradation of salicylic acid observed in heat flow curve and derivative weight curve.

Table S1 % Conversion, M_n and PDI determination for homo poly D,L-lactide

	CONDITION	$[M]_0/[I]_0$	$[M]_0/[cat]_0$	% conversion	M_n(SEC) Dalton	M_n(NMR)g/mol	PDI
L1	140 °C, 12 hrs	793	793	80.0	16,270	10140	1.37
L2	140 °C, 6 hrs	333	793	80.4	17200	10100	1.16
L3	140 °C, 6 hrs	333	2000	82.0	16,890	17300	1.20
L4	140 °C, 6 hrs	793	793	84.0	11900	10730	1.42