Supporting information

Tailoring Chain Structures of L-lactide and ε-Caprolactone Copolyester Macromonomers Using *rac*-Binaphthyl-diyl Hydrogen Phosphate-Catalyzed Ring-Opening Copolymerization with Monomer Addition Strategy

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Synthesis of Homo- and Block Macromonomers (MMs)

Synthesis of Homo-MMs, LA_5-HEMA and CL_4-HEMA. Homo-MMs were synthesized with fixed molar ratios for HEMA/L-LA of 1/5 and HEMA/ε-CL of 1/4. Prior to bulk ROcoPs, reactants were heated and stirred continuously in a round-bottom flask, and the contents were purged with nitrogen gas for approximately 10 min. The flask was then sealed and lowered into a hot oil bath, and the contents were heated to the polymerization temperature prior to the addition of 0.5 mol% catalyst using a syringe. The polymerizations were conducted 1 h for LA_5-HEMA and 3 h for CL_4-HEMA under constant mechanical stirring and temperature conditions. Subsequent to copolymerizations, the flask and contents were then cooled and washed with hexane to eliminate residual reactants, and the MMs were dried at room temperature in a vacuum oven for 24 h.

Synthesis of Block MMs, LA_5-*b*-CL_4-HEMA. Block MMs were produced with a molar ratio for HEMA/ε-CL/L-LA of 1/4/5. The CL block was synthesized first. The same procedure as described above was used to obtain CL_4-HEMA. After 3 h of the polymerization, L-LA was introduced to the flask. The flask was purged again with nitrogen gas for 10 min under continuous mechanical stirring at a constant temperature. An additional 0.5 mol% $Sn(Oct)_2$ (based on L-LA) was introduced using a syringe. The polymerization was continued for an additional 1 h. The flask and contents were then cooled and washed with hexane to eliminate residual reactants, and the MMs were dried at room temperature in a vacuum oven for 24 h.

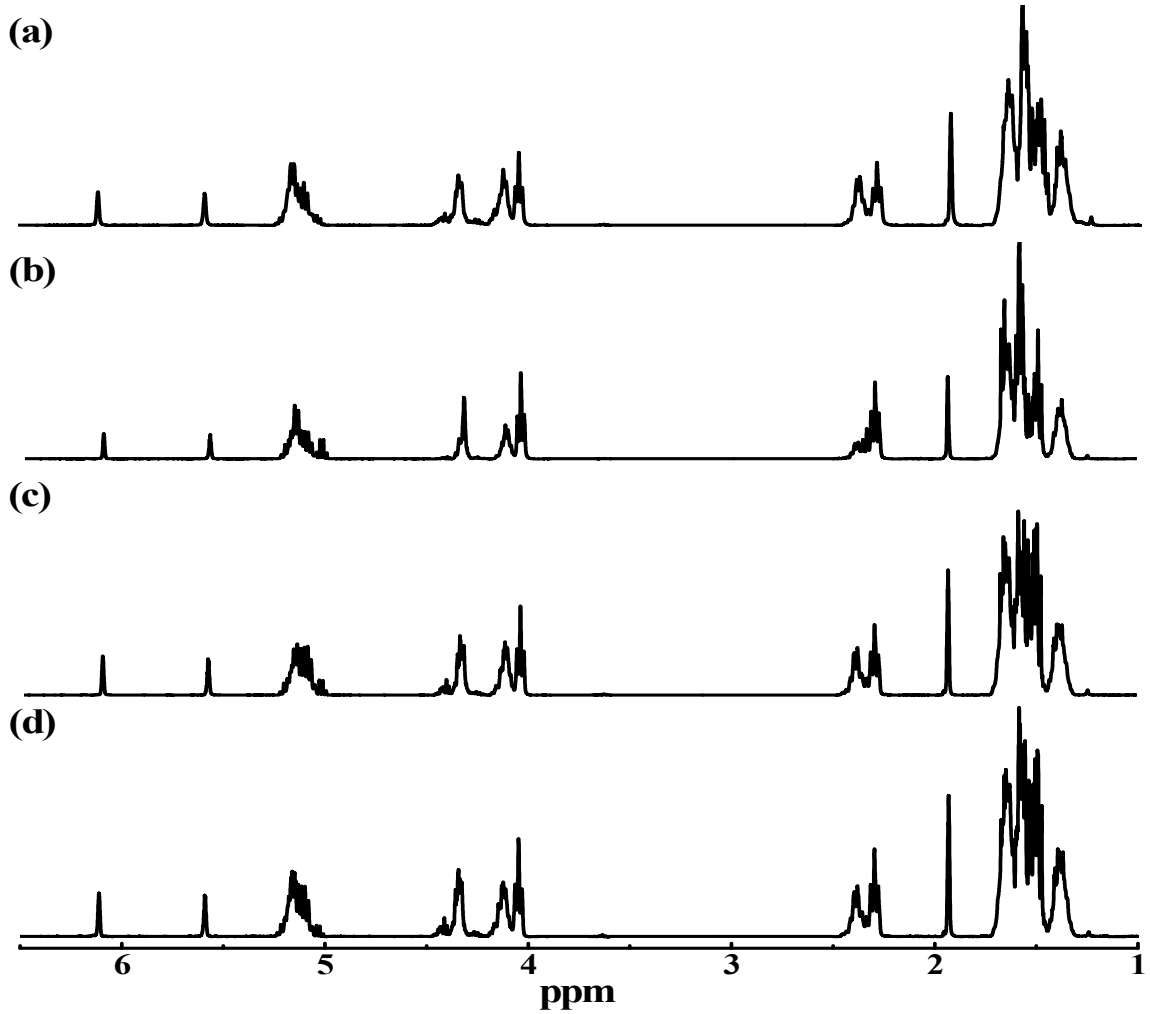


Figure S1. ^{1}H NMR spectra for MMs synthesized in Runs (a) B8: $Sn(Oct)_2$, Batch; (b) B5: *rac*-BNPH, Batch; (c) SB1: *rac*-BNPH, Semibatch with v_{CL} = 0.0468 mol/h; and (d) SB2: *rac*-BNPH, Semibatch with v_{CL} = 0.0187 mol/h.

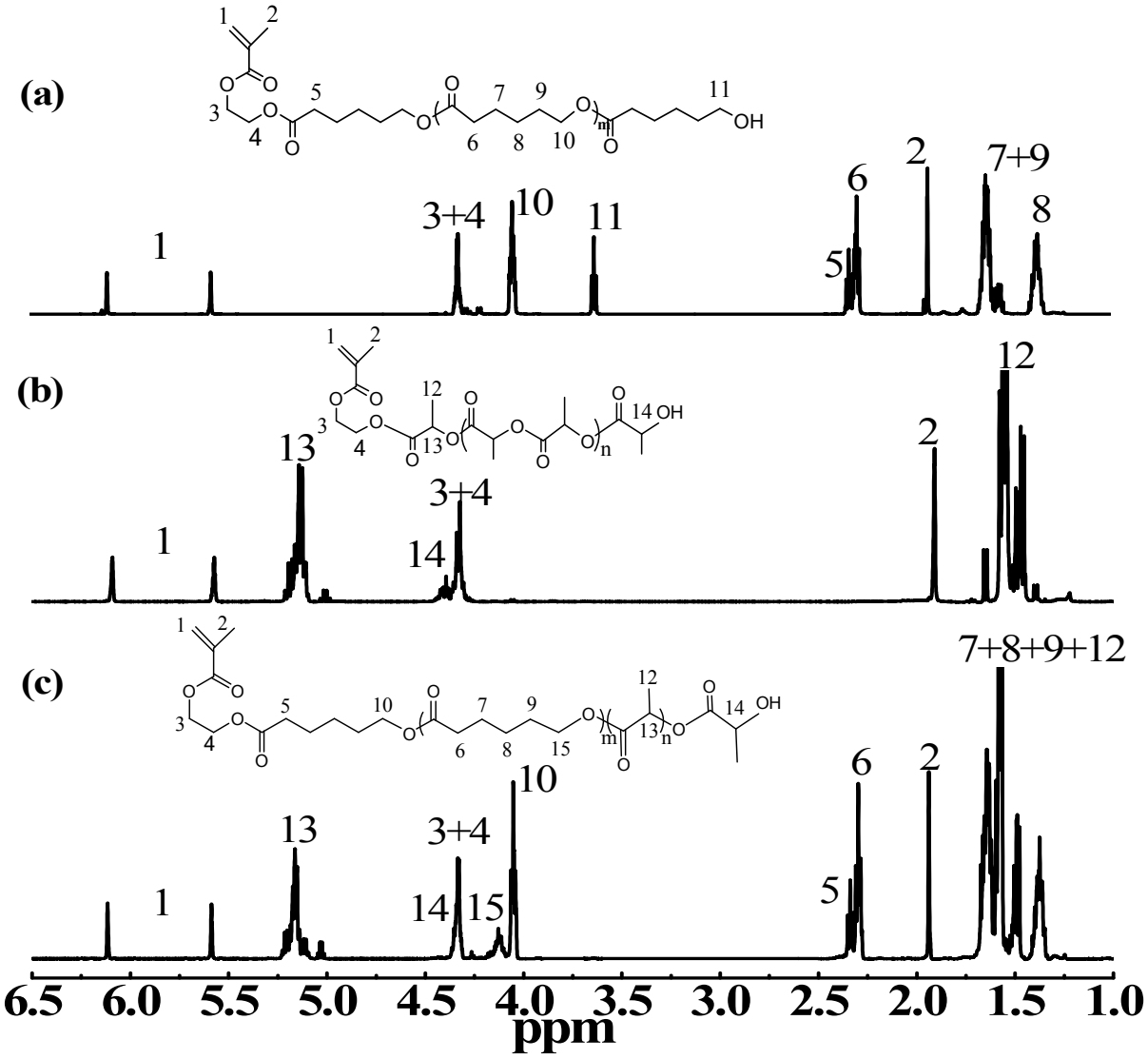
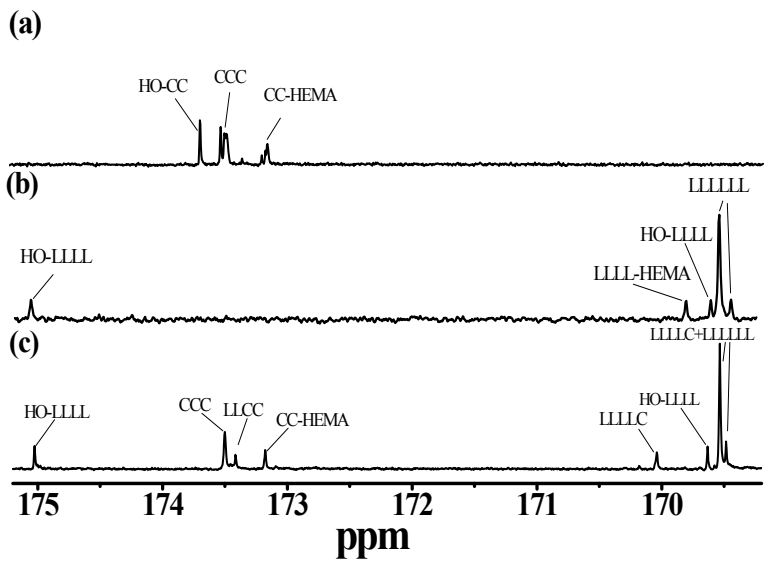


Figure S2. ^{1}H NMR spectra for L-LA and ε-CL homo-MMs and their block MMs synthesized using HEMA as the initiator and $Sn(Oct)_2$ as the catalyst. Shown are spectra for (a) CL_4-HEMA, (b) LA_5-HEMA and (c) LA_5-*b*-CL_4-HEMA.



Chemical Shift (ppm)	Sequence
175.05	HO-LLLL
173.75	HO-CC
173.54	CCC
173.46	LLCC
173.22	CC-HEMA
170.09	LLLLC
169.81	LLLL-HEMA
169.60	HO-LLLL
169.58	LLLLLL

Figure S3. ^{13}C NMR spectra of L-LA and ε-CL homo-MMs and a diblock MM of ε-CL and L-LA synthesized using HEMA as initiator and $Sn(Oct)_2$ as the catalyst. Shown are spectra for (a) CL_4-HEMA, (b) LA_5-HEMA, and (c) LA_5-*b*-CL_4-HEMA. Also shown are the triad assignments.

Table S1. Chemical shift assignments of carbonyl carbon sequences in MMs

Sequence	**Chemical Shift (ppm)**
CCC	173.54
LLCC	173.46
CCLL	172.90
LLCLL	172.80
CLLLL	170.30
CLLC	170.22-170.30
LLLLC	170.09
LLLLLL	169.70-169.50
CLCC	173.49
LLCLC+CLCLC	172.75-172.72
CLC	170.83
CLLLC	169.65

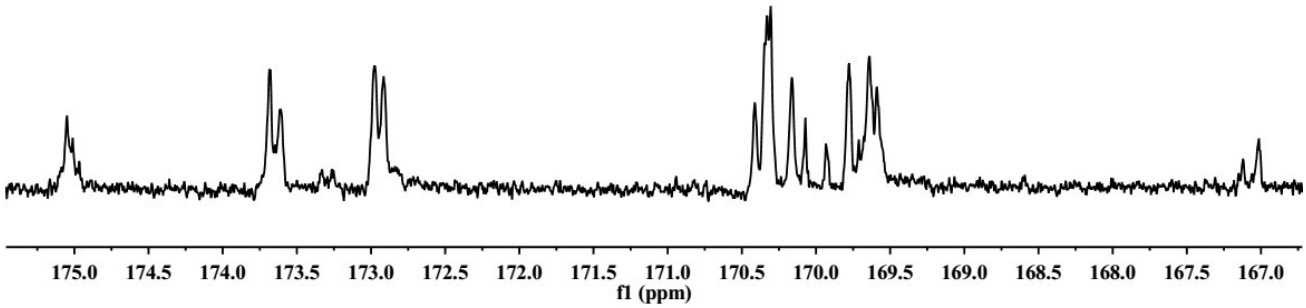


Figure S4. Carbonyl carbon region in ^{13}C NMR spectrum for MM synthesized in Run SB1 acquired at 150 MHz.

Table S2. The ^{13}C NMR spin-lattice relaxation times (T_1) acquired at 150 MHz. for carbonyl carbons in MMs synthesized in Run SB1. (Determined using the T_1 Mode Analysis Method of Agilent Technologies DD2.)

Index	**Sequences**	**T_1/s**
1	HO-L	5.529
2	CCC	3.628
3	CCLL	2.306
4	CLLC	2.884
5	LLLLC	2.576
6	CL-HEMA	4.703
7	LL-HEMA	3.489
8	CLLLL	2.059
9	LLLLLL	2.209
10	HEMA	12.62