

Electronic Supplementary Information

for

Sequentially bridging anionic addition and ring-opening polymerization by cooperative organocatalysis: Well-defined block copolymers from acrylates and cyclic esters

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1. Experimental section

1.1 Chemicals

Lactide (LA) from Aldrich was recrystallized twice from ethyl acetate and then sublimed under reduced pressure. ϵ -caprolactone (ϵ -CL), δ -valerolactone (δ -VL) and β -Butyrolactone (β -BL) were purchased from Aladdin Co. And stirred with CaH_2 for 24 h, then distilled under reduced pressure. Methyl Methacrylate (MMA), Ethyl Methacrylate (EMA), Methoxymethyl Methacrylate (MEMA), Methyl Acrylate (MA), 2-(dimethylamino)ethyl Methacrylate (DMA), and N, N-Dimethylacrylamide (DMAA) from Sinopharm were distilled from CaH_2 and stored under a nitrogen atmosphere at $-20\text{ }^\circ\text{C}$. Toluene (Tol.) from Sinopharm was freshly distilled from sodium/benzophenone and stored under an argon atmosphere. 1-tert-butyl-4,4,4-tris-(dimethylamino)-2,2-bis[tris(dimethylamino) phosphoranyliden-amino]-2, 5, 5-catenadi(phosphazene) (*t*-BuP₄) from Aldrich was used as received. Benzyl alcohol (BnOH) from Aldrich were dried over sodium with a nitrogen protective atmosphere and distilled. All manipulations were performed using a standard Schlenk technique or in a nitrogen-filled Etelux Lab2000 glovebox unless otherwise mentioned.

1.2 Methods

^1H , ^{13}C , DOSY NMR spectra were recorded on a Bruker Avance III spectrometer (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) at room temperature in chloroform- d_1 (purchased from Innochem), and chemical shifts were referenced to an internal standard. DOSY NMR tests were performed at a steady temperature of $25\text{ }^\circ\text{C}$ with at least 16 gradient increments using the ledbpgp2s sequence. Gel permeation chromatography (GPC) analyses were carried out at $40\text{ }^\circ\text{C}$ and a flow rate of 1.0 mL/min , with THF as the eluent on an Agilent PL-GPC 50 instrument coupled with a refractive index (RI) detector with respect to polystyrene (PS) standards. The columns included a PLgel guard $5\mu\text{m } 50 \times 7.5\text{ mm}$ column, a PLgel mixed-B $300 \times 7.5\text{ mm}$ column and a PLgel mixed-C $300 \times 7.5\text{ mm}$ column. Samples for GPC analysis were filtered through $0.22\text{ }\mu\text{m}$ PTFE filters. The melting temperatures (T_m s) and glass transition temperatures (T_g s) of the polymer samples were measured by differential scanning calorimetry (DSC) using a TA Instruments Q2000 calorimeter equipped with an automated sampler. Analyses were performed in crimped aluminum pans under nitrogen, and data were collected with the heat/cool/heat cycle at a heating rate of $10\text{ }^\circ\text{C/min}$ from $-50\text{ }^\circ\text{C}$ to $200\text{ }^\circ\text{C}$, and processed with TA Q series software.

1.3 General procedures for catalyst optimization

A typical polymerization procedure was as follows: in an Etelux glovebox, the appropriate amount of Lewis acid (0.02 mmol, 1 equiv.), *t*-BuP₄ (0.02 mmol, 1 equiv.), BnOH (0.02 mmol, 1 equiv.) and monomers (2 mmol, 100 equiv.) were added in an oven-dried tube equipped with a magnetic stir, followed by Tol. (2 ml, 1 M). The tube was placed in the glovebox at room temperature. During polymerization, a crude aliquot was time-regularly with drawn from the system by pipette and monitored by ¹H NMR spectroscopy and GPC to determine monomer conversion and molar mass. After the defined time, the polymerization was quenched by addition of benzoic acid solution (10 mg/mL in chloroform) and dropwise precipitated into 100 mL of methanol with vigorous stirring, after which the methanol was filtrated or poured out. The resulting polymers were dried under vacuum at 40 °C. All analyses and further chemical modification were performed on crude samples.

1.4 General Procedures for homo-polymerization of acrylates and cyclic esters.

A typical polymerization procedure was as follows: in an Etelux glovebox, the reactor was charged with a predetermined amount of (thio)ureas (0.02 mmol, 1 equiv.), *t*-BuP₄ (0.02 mmol, 1 equiv., 0.8 M in *n*-Hexane), BnOH (0.02 mmol, 1 equiv.), toluene (2 ml, 1 M) in a 15 mL sealed tube. Then, the polymerization was initiated by addition of acrylates or cyclic esters via a syringe (2 mmol, 100 equiv.). After the defined time, the reaction mixture was quenched by addition of benzoic acid solution (10 mg/mL in chloroform). Then, the mixture was dropwise precipitated into 100 mL of methanol acidified by vigorous stirring, after which the methanol was filtrated or poured out. The resulting polymers were dried under vacuum at 40 °C to a constant weight.

1.5 General Procedures for block polymerization of acrylates and cyclic esters.

A typical polymerization procedure was as follows: in an Etelux glovebox the appropriate amount of TU-1 (0.02 mmol, 1 equiv.), *t*-BuP₄ (0.02 mmol 1 equiv. 0.8 M in *n*-Hexane), BnOH (0.02 mmol, 1 equiv.), Tol. (2 ml) and acrylate monomers (0.2 mmol 100 equiv.) were charged into a 15 mL Sealed tube and kept stirring for 10 min in the glovebox. After stirring for 10 min, the appropriate amounts of cyclic esters (0.2 mmol, 100 equiv.) were added. After 10 min at room temperature, the polymerization was quenched by addition of 3 mL of benzoic acid solution (10 mg/mL in chloroform). Then, the mixture was dropwise precipitated into 100 mL of methanol acidified by vigorous stirring, after which the methanol was filtrated or poured out. The resulting polymers were dried under vacuum

at 40 °C to a constant weight.

2. Optimization of catalysts and reaction condition for ROP of LA.

The general principles and recommendations for a practicable catalyst were described as follows:

(i) the selected catalyst should be effective for two different types of polymerization, which could be tested by independent polymerization experiments; (ii) growing active chains should be compatible with each discrete polymerization in the system, ensuring the formation of a copolymer rather than polymer mixtures; and (iii) there should be negligible chain transfer and chain termination side reactions in the polymerization, in which a living/controlled polymerization is highly desired.

Following the abovementioned guidelines, we attempted a series of (thio)ureas/*t*-BuP₄ to catalyze LA for selecting the best one, including 1,3-Diisopropylthiourea (TU-1), 1,3-Dicyclohexylthiourea (TU-2), 1,3-Diphenylthiourea (TU-3), 1,3-Dimethylurea(U-1), 1,3-Dicyclohexyl urea(U-2). 1,3-Diisopropylthiourea (TU-1)/*t*-BuP₄ shows the best catalytic activity among all catalysts.

Table S1 The ROP of LA catalyzed by (thio)ureas/*t*-BuP₄^a.

Entry	Monomer	Catalyst	<i>t</i> (min)	Conv. (%) ^b	<i>M</i> _{n, GPC} (kDa) ^c	<i>D</i> ^c
1	LA	<i>t</i> -BuP ₄	1	75	11.7	1.20
2	LA	<i>t</i> -BuP ₄ /TU-1	1	90	12.3	1.15
3	LA	<i>t</i> -BuP ₄ /TU-2	1	67	9.6	1.16
4	LA	<i>t</i> -BuP ₄ /TU-3	1	63	7.2	1.15
5	LA	<i>t</i> -BuP ₄ /U-1	1	65	11.5	1.16
6	LA	<i>t</i> -BuP ₄ /U-2	1	72	10.3	1.17

^a All reactions were initiated by BnOH and performed twice in toluene. the results were averaged: [initiator] = 0.02 mmol, [monomer] = 2 mmol, [monomer]/[initiator]/[catalyst] = 100/1/1. ^b Conversions were determined by analysis of the crude material by ¹H NMR spectroscopy. ^c Number-averaged molecular weight (*M*_n) and polydispersity (*D*) were determined by GPC with THF as eluents and referenced by polystyrene standards, *D* = *M*_w/*M*_n.

3. Data of homo-polymerization

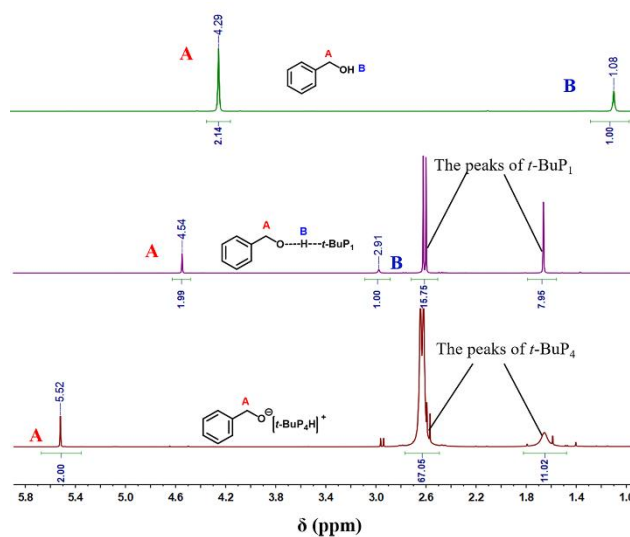


Figure S1. ^1H NMR spectra of BnOH, BnOH/*t*-BuP₁ (1/1), BnOH/*t*-BuP₄(1/1) in C_6D_6 .

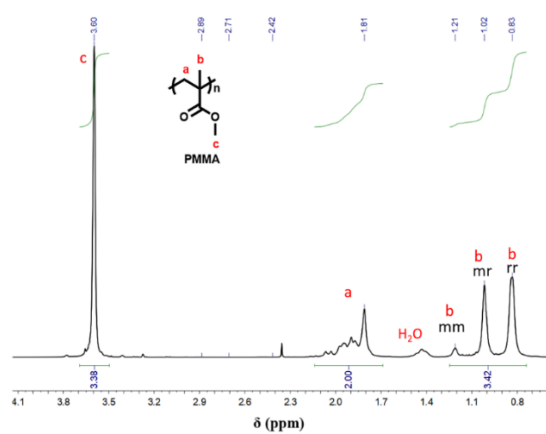


Figure S2. Representative ^1H NMR spectrum of PMMA (Table 1, entry 2).

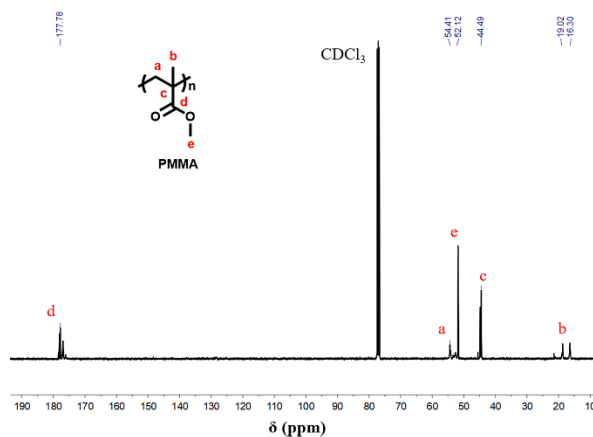


Figure S3. Representative ^{13}C NMR spectrum of PMMA (Table 1, entry 2).

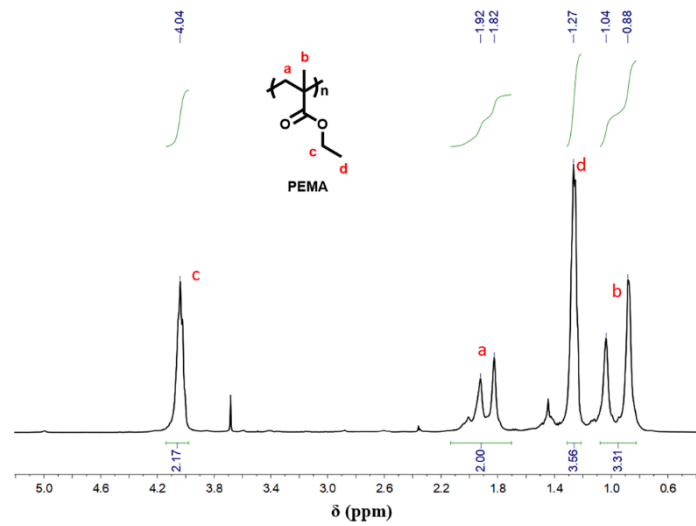


Figure S4. Representative ^1H NMR spectrum of PEMA (Table 1, entry 7).

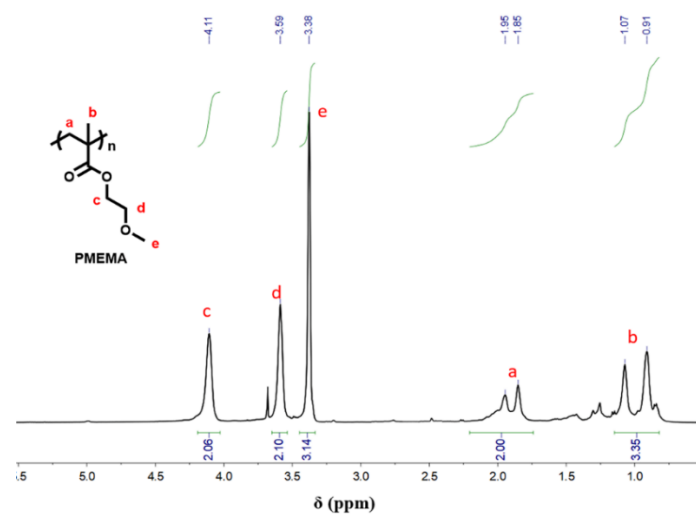


Figure S5. Representative ^1H NMR spectrum of PMEMA (Table 1, entry 8).

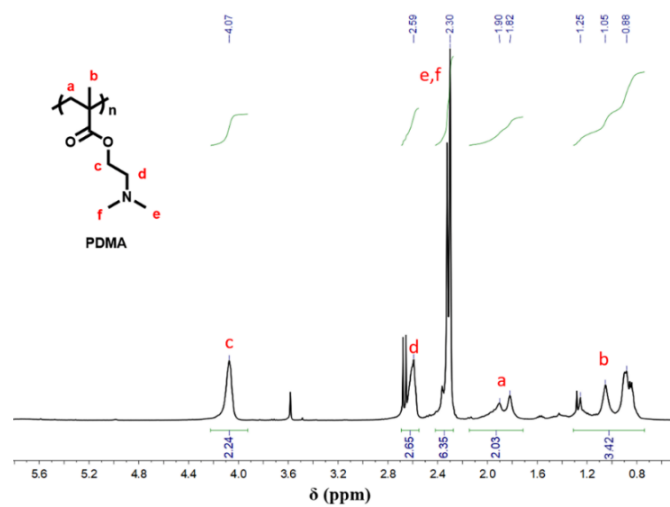


Figure S6. Representative ^1H NMR spectrum of PDMA (Table 1, entry 9).

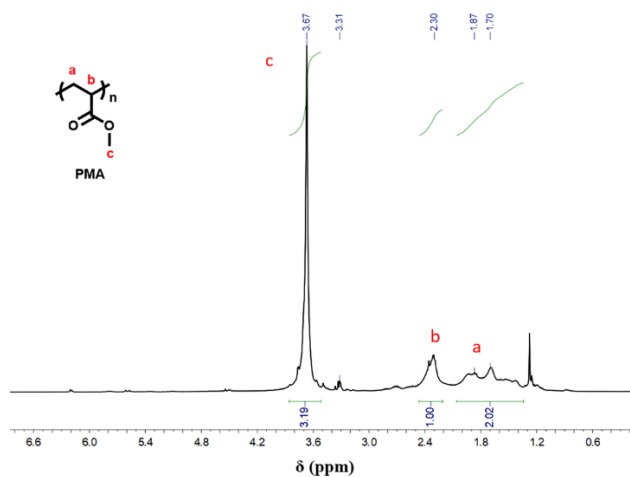


Figure S7. Representative ¹H NMR spectrum of PMA (Table 1, entry 10).

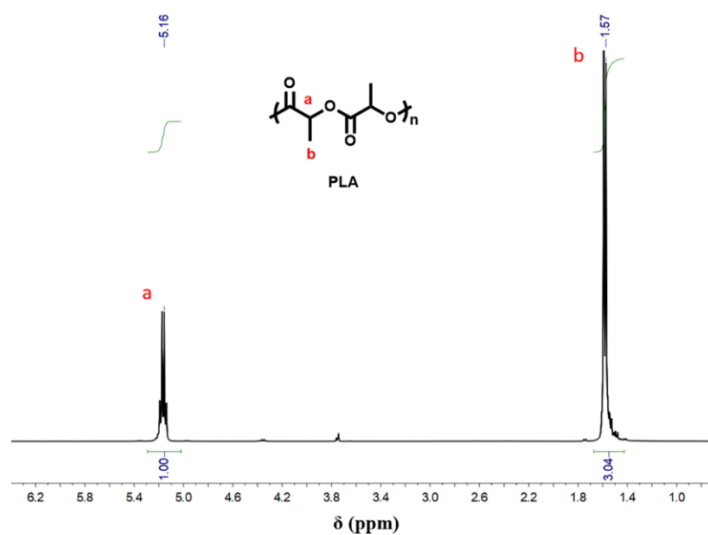


Figure S8. Representative ¹H NMR spectrum of PLA (Table 1, entry 11).

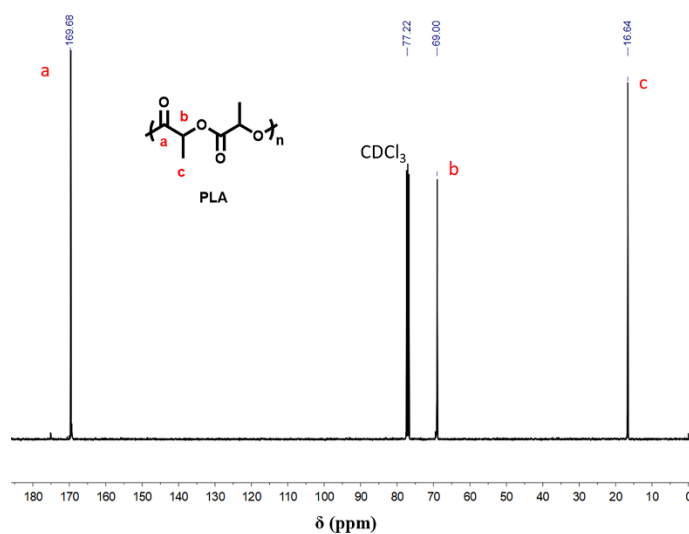


Figure S9. Representative ¹³C NMR spectrum of PLA (Table 1, entry 11).

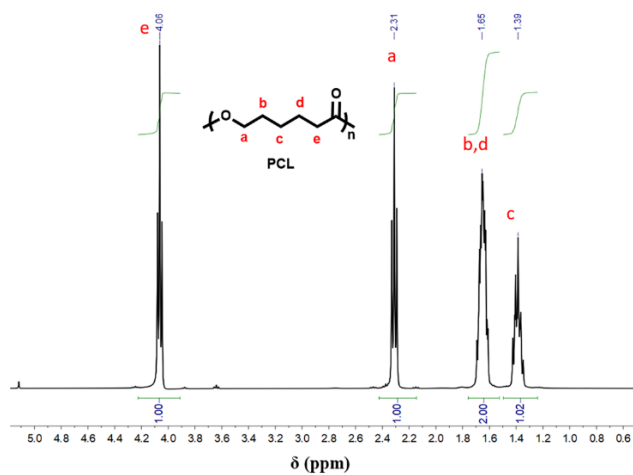


Figure S10. Representative ^1H NMR spectrum of PCL (Table 1, entry 12).

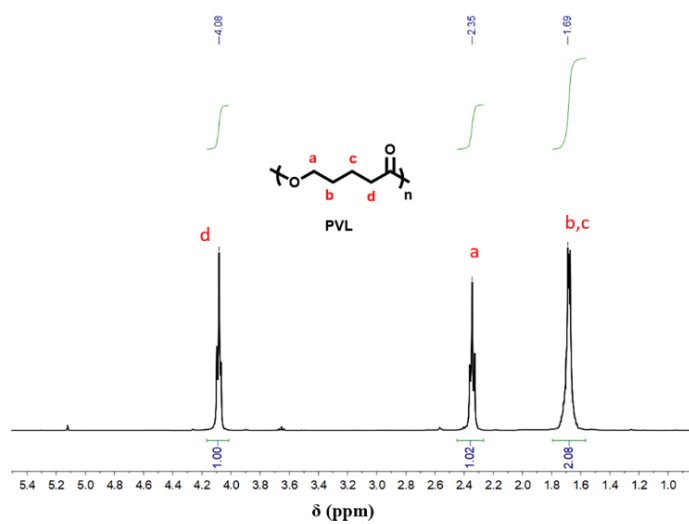


Figure S11. Representative ^1H NMR spectrum of PVL (Table 1, entry 13).

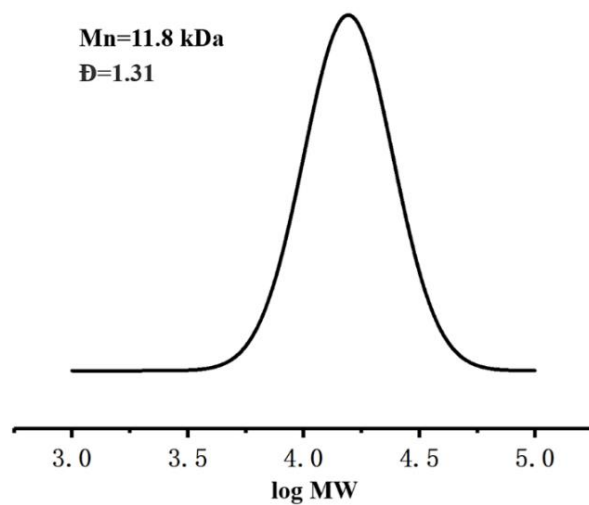


Figure S12. GPC curve of PMMA (Table 1, entry 2).

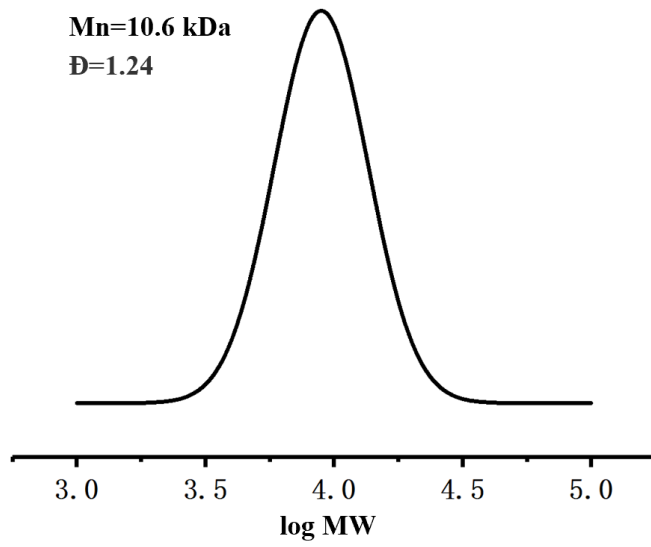


Figure S13. GPC curve of PEMA (Table 1, entry 7).

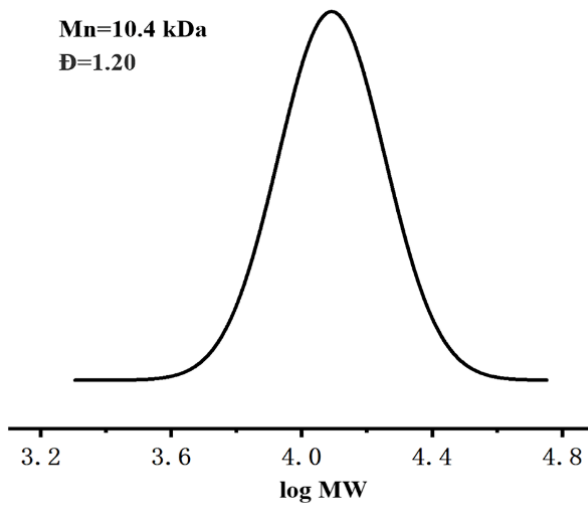


Figure S14. GPC curve of PMEMA (Table 1, entry 8).

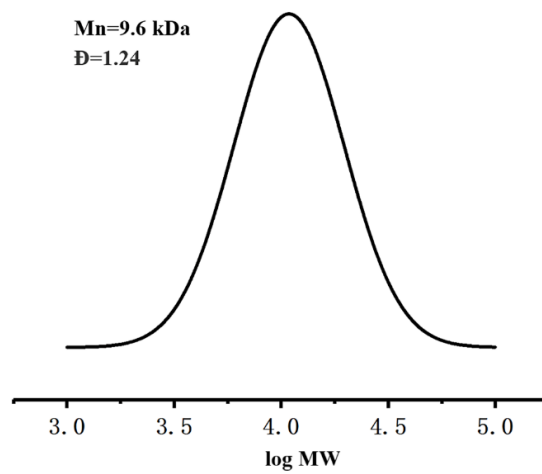


Figure S15. GPC curve of PDMA (Table 1, entry 9).

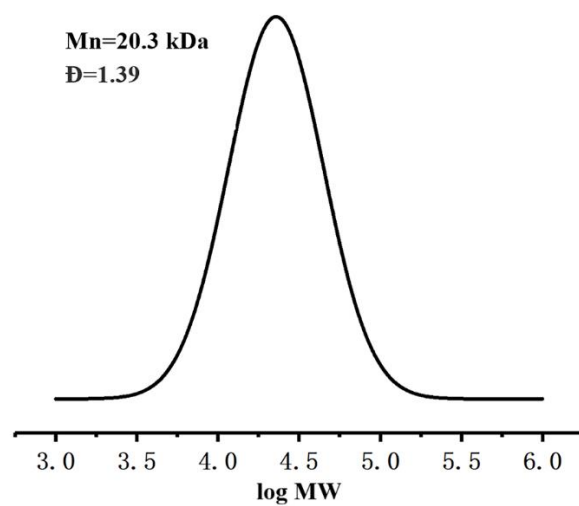


Figure S16. GPC curve of PMA (Table 1, entry 10).

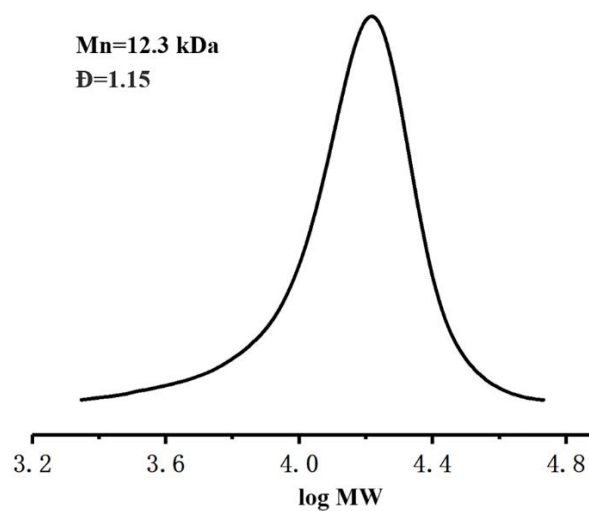


Figure S17. GPC curve of PLA (Table 1, entry 11).

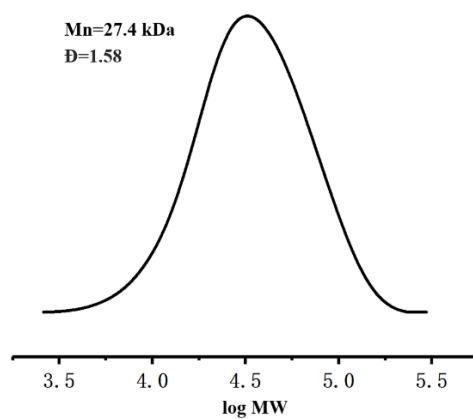


Figure S18. GPC curve of PCL (Table 1, entry 12).

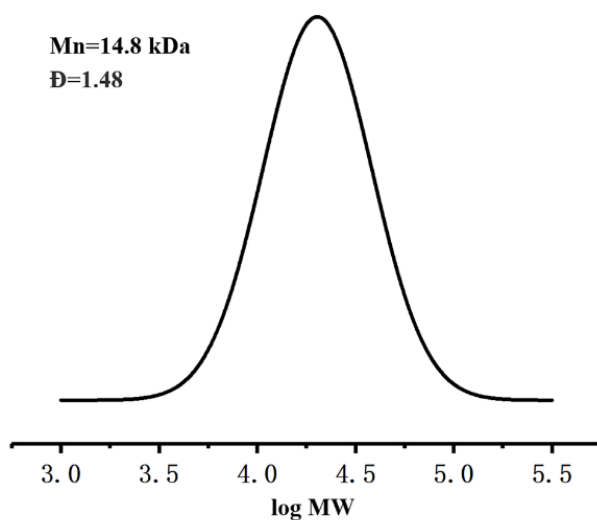


Figure S19. GPC curve of PVL (Table 1, entry 13).

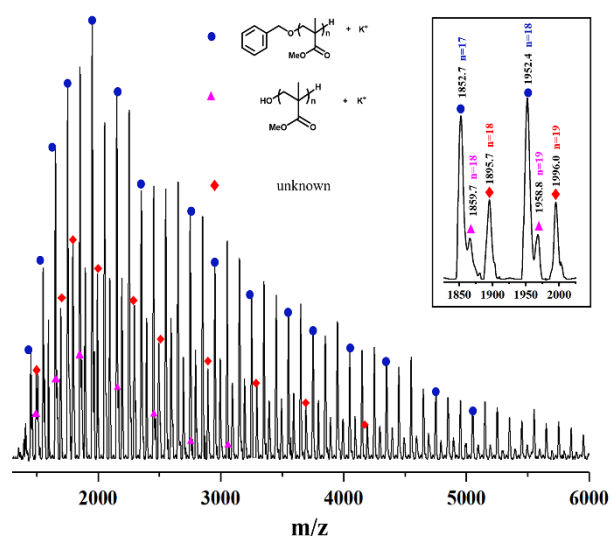


Figure S20. MALDI-TOF spectrum of PMMA with *t*-BuP₄/TU-1.

4. Data of block polymerization

Table S2 The block polymerization of MMA with TU-1/*t*-BuP₄.^a

Entry	Monomer	MMA/ <i>t</i> -BuP ₄ /TU-1	<i>t</i> (min)	Conv. (%) ^b	<i>M</i> _{n,GPC} (kDa) ^c	<i>D</i> ^c
1 ^d	MMA	100/1/1	10	97	10.6	1.28
2 ^d	MMA	100/1/1	10	98	10.2	1.27
3 ^d	MMA	100//1/1	10	>99	11.4	1.29
4 ^d	MMA	50/1/1	10	>99	7.5	1.20
5 ^d	MMA	150/1/1	10	92	14.1	1.32
6 ^e	MMA	100/1/1	15	>99	15.6	1.39
7 ^f	MMA	100/1/1	15	94	10.3	1.32

^a All reactions were performed twice in toluene, and the results were averaged: [initiator] = 0.02 mmol, [monomer] = 2 mmol. ^b Conversions were determined by analysis of the crude material by ¹H NMR spectroscopy. ^c Number-averaged molecular weight (*M*_n) and polydispersity (*D*) were determined by GPC with THF as eluents and referenced by polystyrene standards, $D = M_w/M_n$. ^d Initiator = benzoic alcohol. ^e Initiator = terephthalyl alcohol. ^f Initiator = trimethylolpropane

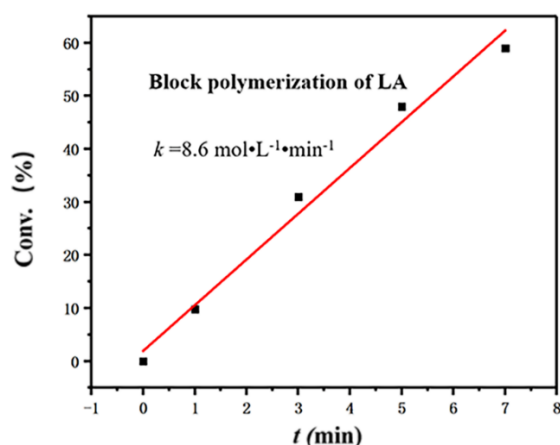


Figure S21. Kinetic plot for block polymerization of LA([TU-1]/[*t*-BuP₄]/[BnOH]/[LA] = 1:1:1:100).

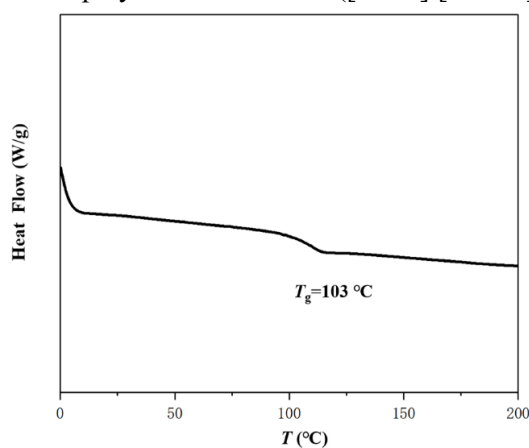


Figure S22. DSC thermogram of PMMA (Table 1, entry 2).

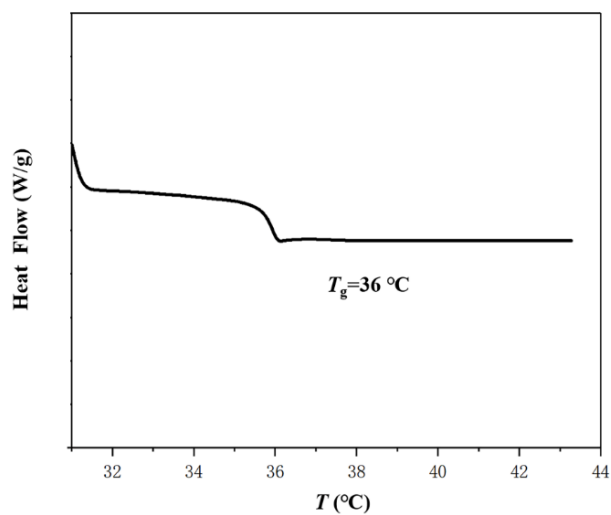


Figure S23. DSC thermogram of PLA (Table 1, entry 11).

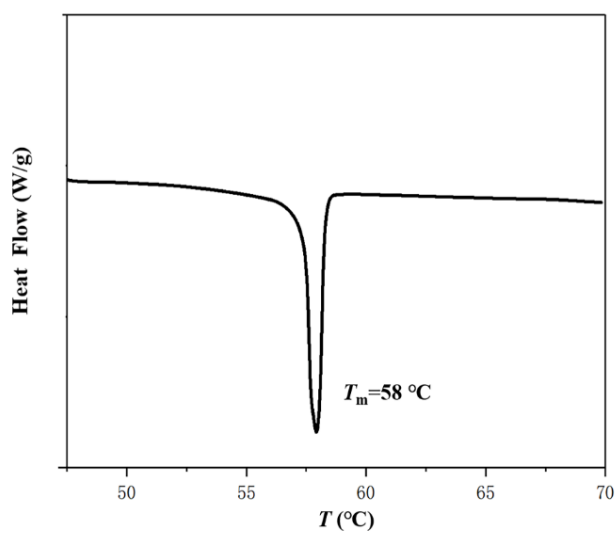


Figure S24. DSC thermogram of PCL (Table 1, entry 12).

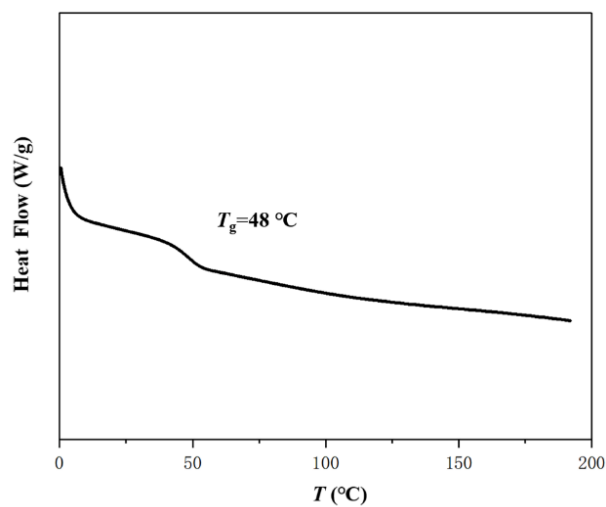


Figure S25. DSC thermogram of PMMA-*b*-PLA (Table 2, entry 1).

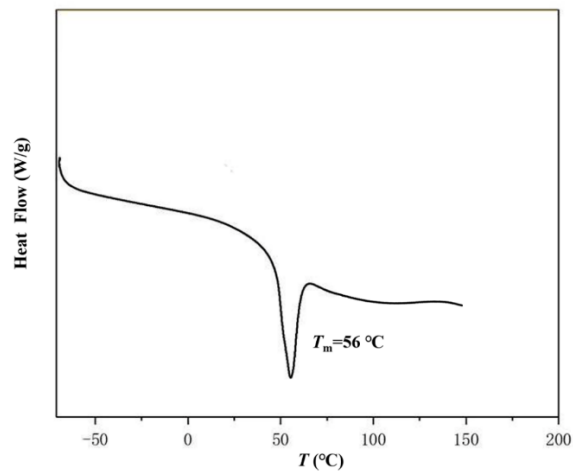


Figure S26. DSC thermogram of PMMA-*b*-PCL (Table 3, entry 5).

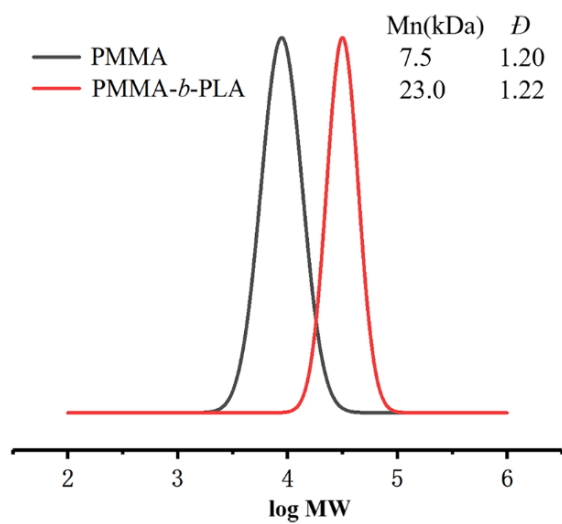


Figure S27. GPC curves of PMMA and PMMA-*b*-PLA (Table 2, entry 2).

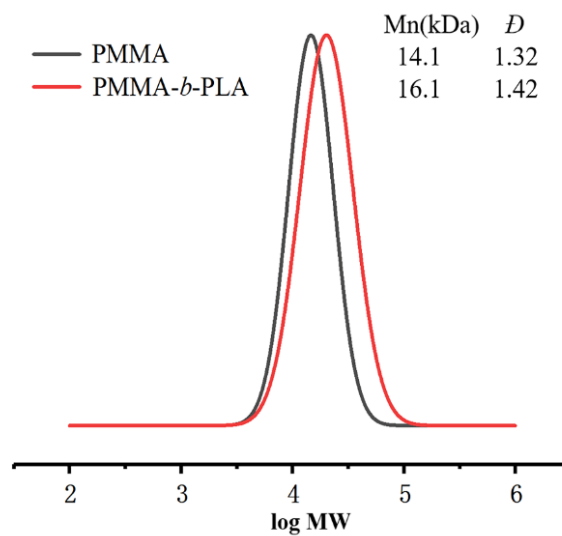


Figure S28. GPC curves of PMMA and PMMA-*b*-PLA (Table 2, entry 3).

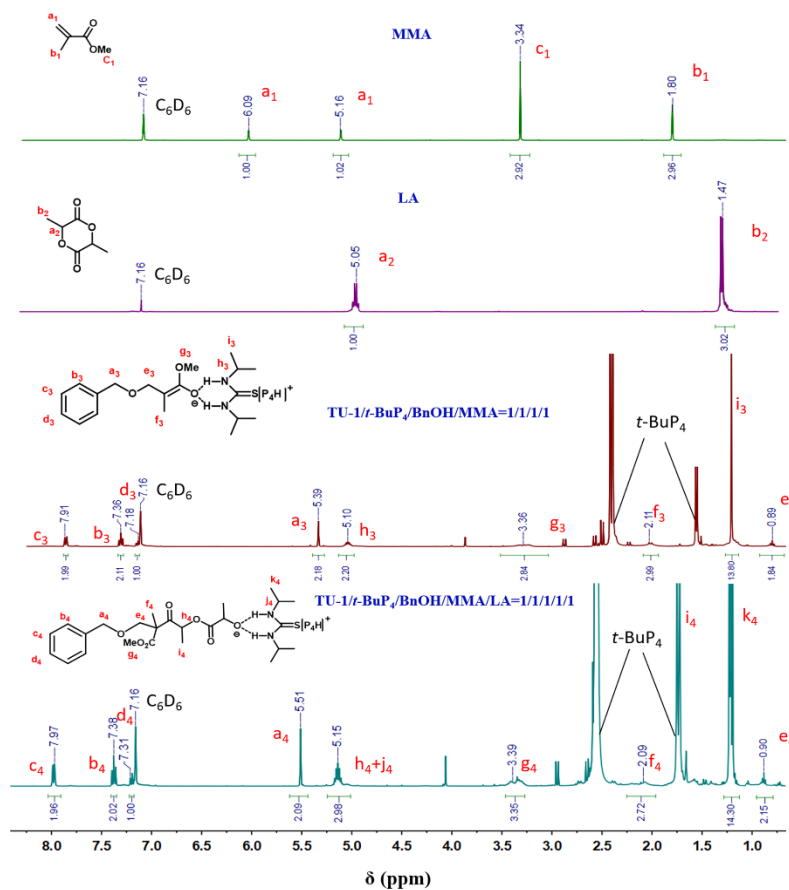


Figure S29. ^1H NMR spectra of MMA, LA, TU-1/*t*-BuP₄/BnOH/MMA (1/1/1/1), TU-1/*t*-BuP₄/BnOH/MMA/LA (1/1/1/1) in C₆D₆.

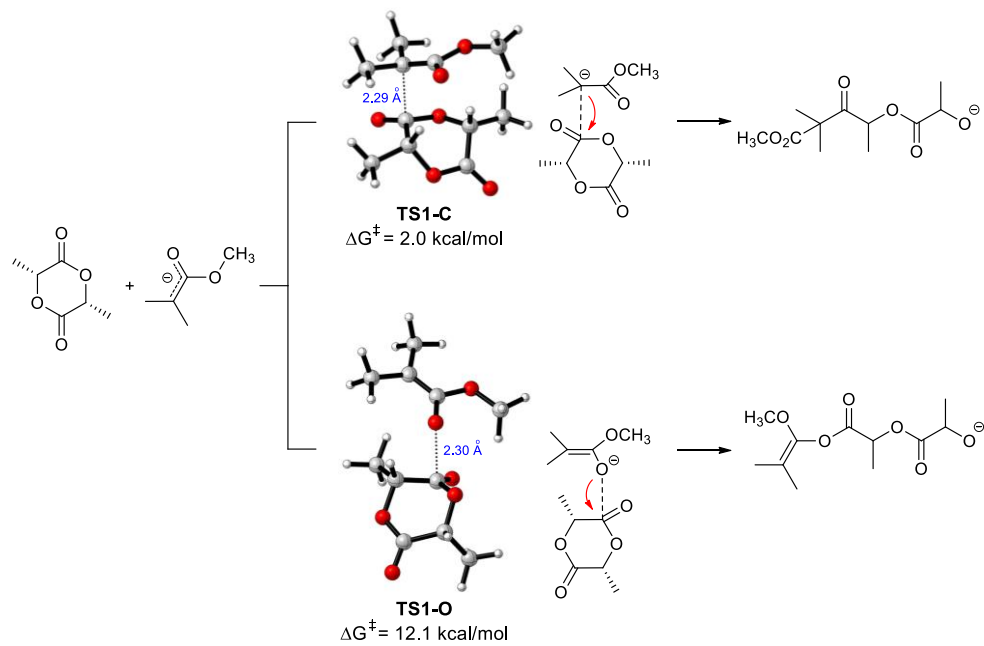


Figure S30. density functional theory (DFT) calculations of the reaction of enolate with LA.

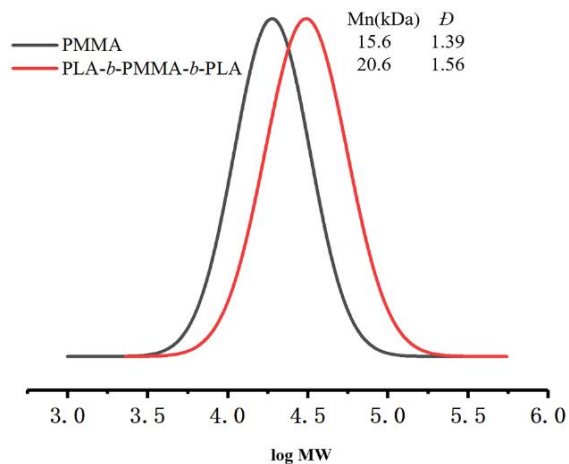


Figure S31. GPC curves of PMMA and the triblock copolymer of MMA and LA (Table 2, entry 6).

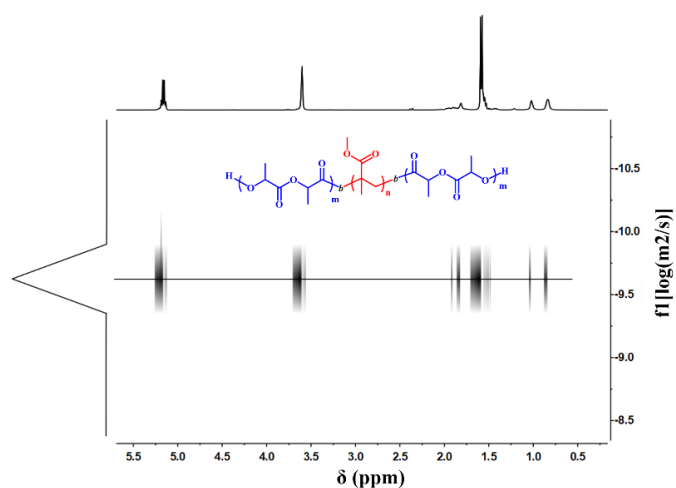


Figure S32. The DOSY NMR spectrum of the BAB-type triblock copolymer of MMA and LA (Table 2, entry 6).

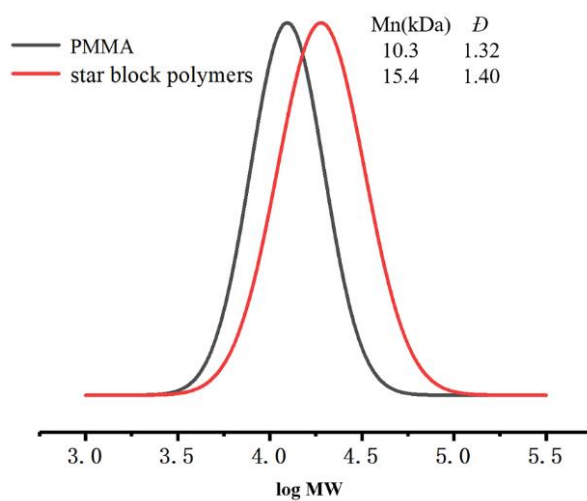


Figure S33. GPC curves of PMMA and the star block copolymer of MMA and LA (Table 2, entry 7).

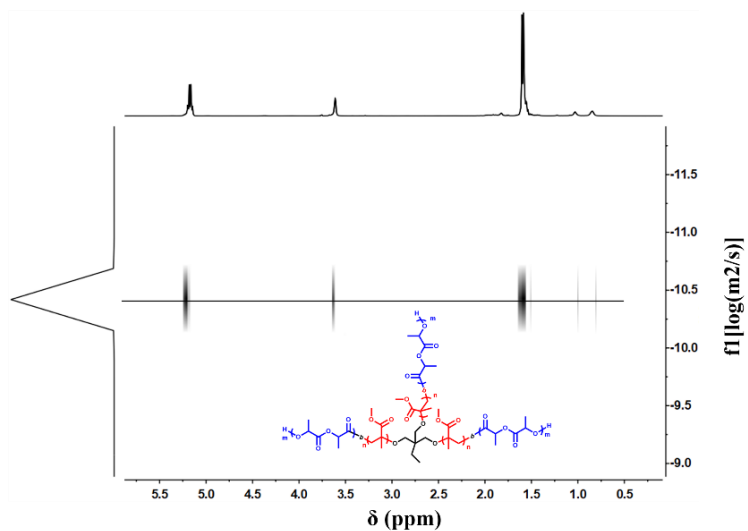


Figure S34. The DOSY NMR spectrum of the star block copolymer of MMA and LA (Table 2, entry 7).

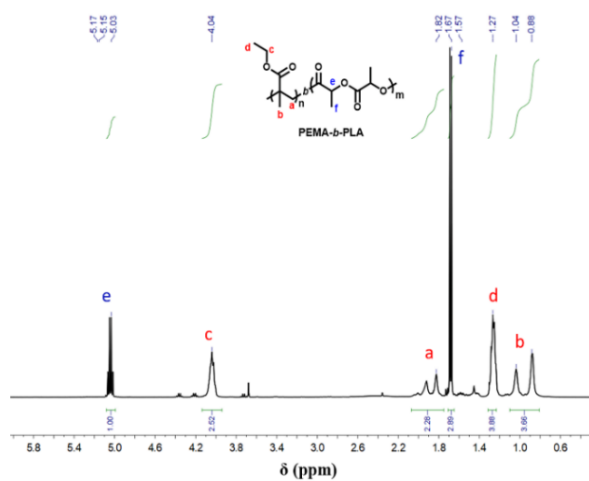


Figure S35. ^1H NMR spectrum of PEMA-*b*-PLA (Table 3, entry 1)

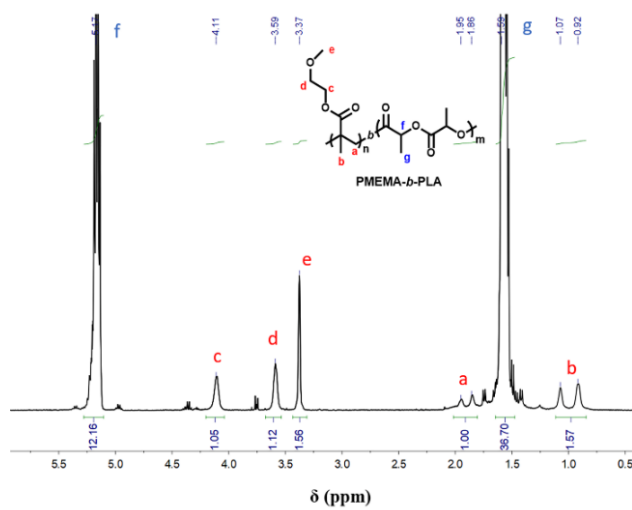


Figure S36. ^1H NMR spectrum of PMEMA-*b*-PLA (Table 3, entry 2).

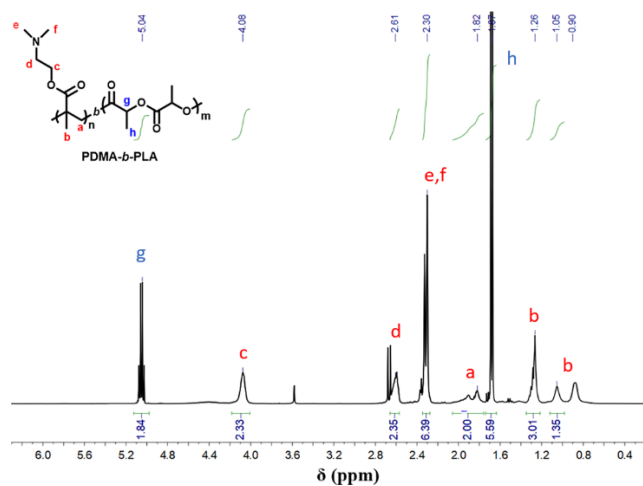


Figure S37. ¹H NMR spectrum of PDMA-*b*-PLA (Table 3, entry 3).

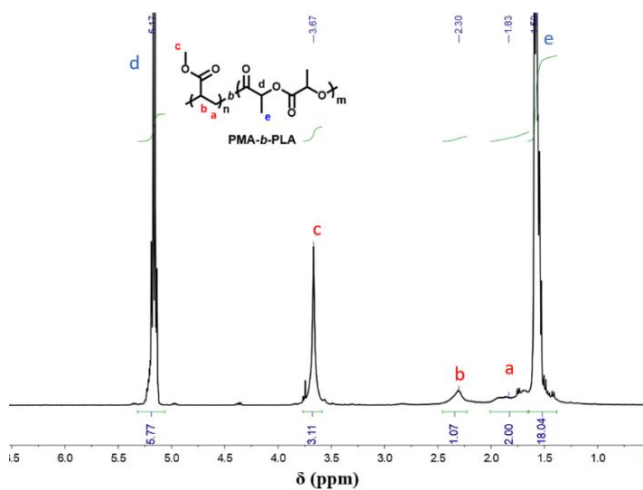


Figure S38. ¹H NMR spectrum of PMA-*b*-PLA (Table 3, entry 4).

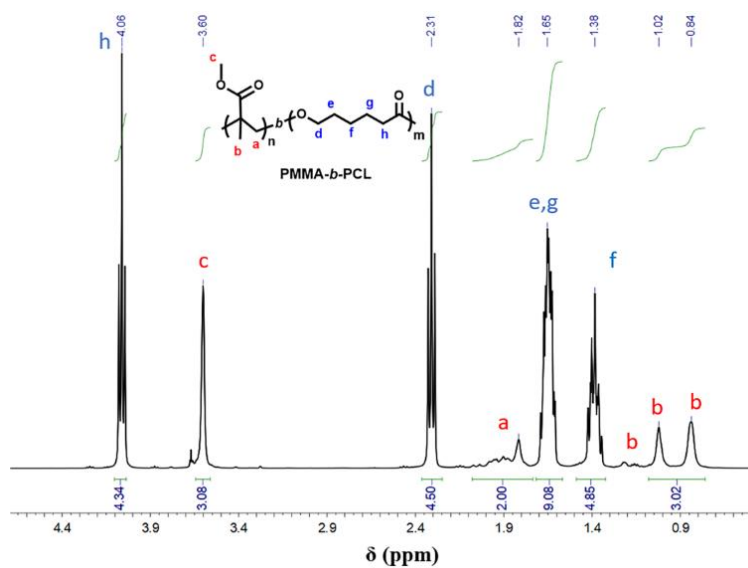


Figure S39. ¹H NMR spectrum of PMMA-*b*-PCL (Table 3, entry 5).

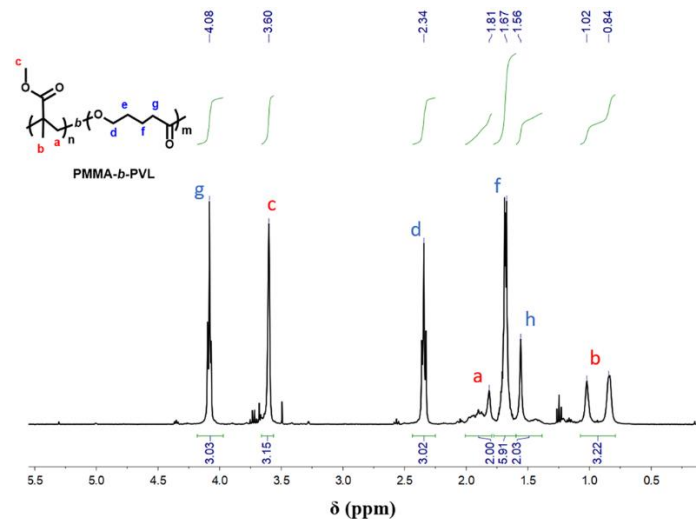


Figure S40. ^1H NMR spectrum of PMMA-*b*-PVL (Table 3, entry 6).

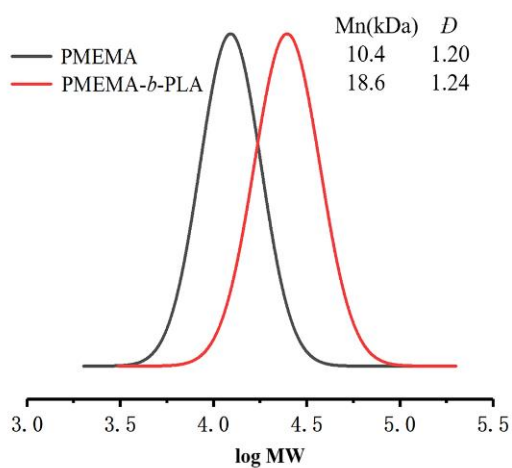


Figure S41. GPC curves of PMEMA and PMEMA-*b*-PLA (Table 3, entry 2).

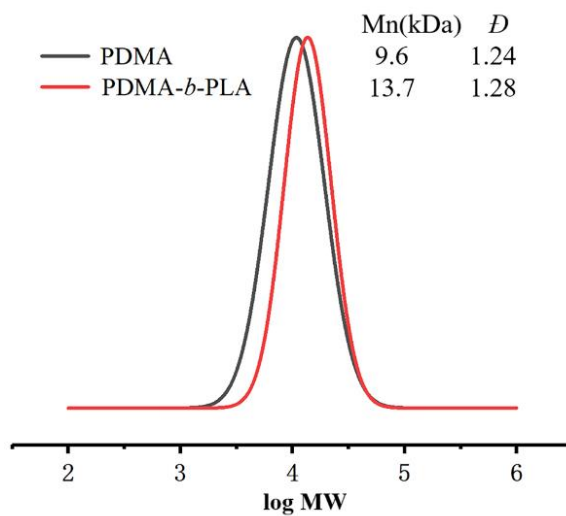


Figure S42. GPC curves of PDMA and PDMA-*b*-PLA (Table 3, entry 3).

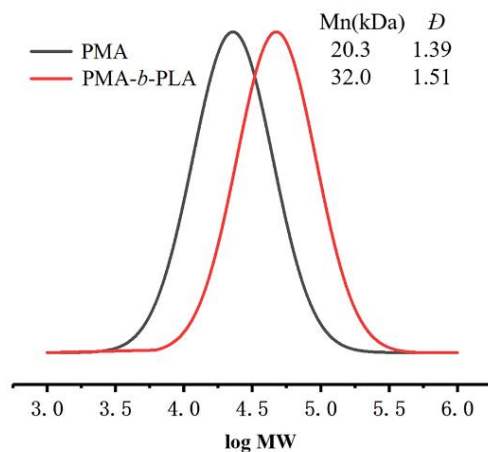


Figure S43. GPC curves of PMA and PMA-*b*-PLA (Table 3, entry 4).

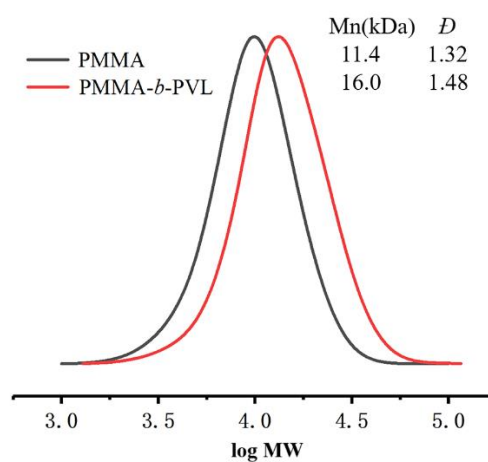


Figure S44. GPC curves of PMMA and PMMA-*b*-PVL (Table 3, entry 6).

5. Cartesian coordinates for model reactions

Substrate

C	-1.247032	-0.469675	0.440791
C	1.247029	0.469657	0.440828
H	-1.130694	-0.464624	1.534906
H	1.130684	0.464586	1.534941
O	0.258002	1.343788	-0.121816
O	-0.258000	-1.343787	-0.121864
C	1.031338	-0.955687	-0.060451
O	1.918571	-1.692977	-0.381569
C	-1.031335	0.955675	-0.060471
O	-1.918569	1.693012	-0.381474
C	-2.608602	-1.000452	0.055626
H	-3.382354	-0.353421	0.469536

H	-2.730770	-2.014791	0.437404
H	-2.707912	-1.008107	-1.031082
C	2.608600	1.000443	0.055682
H	3.382350	0.353399	0.469577
H	2.730769	2.014772	0.437488
H	2.707915	1.008128	-1.031025

Nucleophile

C	-1.067217	0.102320	0.000146
C	0.234635	-0.352279	0.000022
C	-2.173638	-0.904625	0.000029
H	-1.745796	-1.911125	0.002357
H	-2.843120	-0.818508	0.878465
H	-2.840640	-0.821763	-0.880636
C	-1.456250	1.547018	-0.000078
H	-2.070340	1.826981	-0.878751
H	-2.071943	1.826534	0.877595
H	-0.576186	2.194192	0.000830
O	0.686872	-1.520616	-0.000101
O	1.203565	0.706548	0.000014
C	2.522015	0.244968	-0.000009
H	3.166715	1.132891	-0.001000
H	2.750669	-0.369592	0.880309
H	2.749874	-0.371472	-0.879129

TS1-C

C	-0.895484	-1.317625	-0.665293
C	-1.160742	1.056561	0.372759
O	-0.678125	0.101490	1.305521
O	-2.254248	-0.783242	-0.690682
C	-2.414896	0.476167	-0.261432
O	-3.473037	1.046702	-0.370646
C	-0.310959	-1.124820	0.750978
O	-0.140143	-2.066667	1.512130
C	1.843549	-0.600684	0.197215
C	1.729081	0.517258	-0.657174
C	2.246897	-1.898812	-0.450065
H	1.913938	-1.941603	-1.492128
H	3.341149	-2.038013	-0.450243
H	1.817305	-2.743312	0.107038
C	2.332160	-0.431262	1.609168
H	1.943242	-1.257352	2.218564
H	3.432169	-0.449932	1.679887
H	1.978957	0.504878	2.046053

O	1.480050	0.535292	-1.874192
O	1.809685	1.746794	0.012671
C	1.608820	2.871258	-0.809004
H	0.569960	2.947925	-1.159388
H	1.844170	3.745527	-0.196277
H	2.249872	2.842492	-1.694597
C	-1.405046	2.356552	1.099643
H	-0.453599	2.713593	1.500095
H	-1.822101	3.097164	0.414063
H	-2.113122	2.200614	1.916637
C	-1.029853	-2.783053	-1.008645
H	-1.576869	-3.294343	-0.214819
H	-1.557825	-2.891973	-1.959385
H	-0.040600	-3.233628	-1.089663
H	-0.433509	1.206010	-0.434335
H	-0.307766	-0.780248	-1.418829

TS1-O

C	-0.742188	-1.121327	0.075581
C	-2.823652	0.689328	-0.601855
H	-0.377047	-1.278542	-0.937424
H	-3.196366	0.846131	-1.619379
O	-1.453213	1.054063	-0.607950
O	-2.135872	-1.580093	0.129462
C	-3.120381	-0.781957	-0.275107
O	-4.258045	-1.185770	-0.338145
C	-0.732994	0.366586	0.356131
O	-0.413974	0.883355	1.394204
C	0.038993	-1.895884	1.102629
H	1.071715	-1.532449	1.084799
H	0.016796	-2.963885	0.873538
H	-0.384138	-1.722212	2.094836
C	-3.601163	1.570931	0.375752
H	-4.658231	1.299408	0.370488
H	-3.479874	2.616769	0.087151
H	-3.194966	1.445580	1.383137
C	3.154299	-0.672681	-0.191655
C	2.275795	0.365775	-0.376516
C	2.860037	-2.010414	-0.801841
H	1.914186	-1.976293	-1.350380
H	2.791010	-2.824139	-0.058242
H	3.646330	-2.321799	-1.511835
C	4.481900	-0.519393	0.488220
H	5.329007	-0.697274	-0.198696

H	4.611537	-1.244273	1.309747
H	4.598475	0.481459	0.907293
O	1.146562	0.345854	-0.969512
O	2.697770	1.597922	0.145120
C	1.838333	2.678496	-0.129779
H	1.610585	2.753775	-1.198472
H	2.371568	3.577783	0.197453
H	0.889706	2.600539	0.411195