Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Metallic organophosphates catalyzed bulk ring-opening polymerizations

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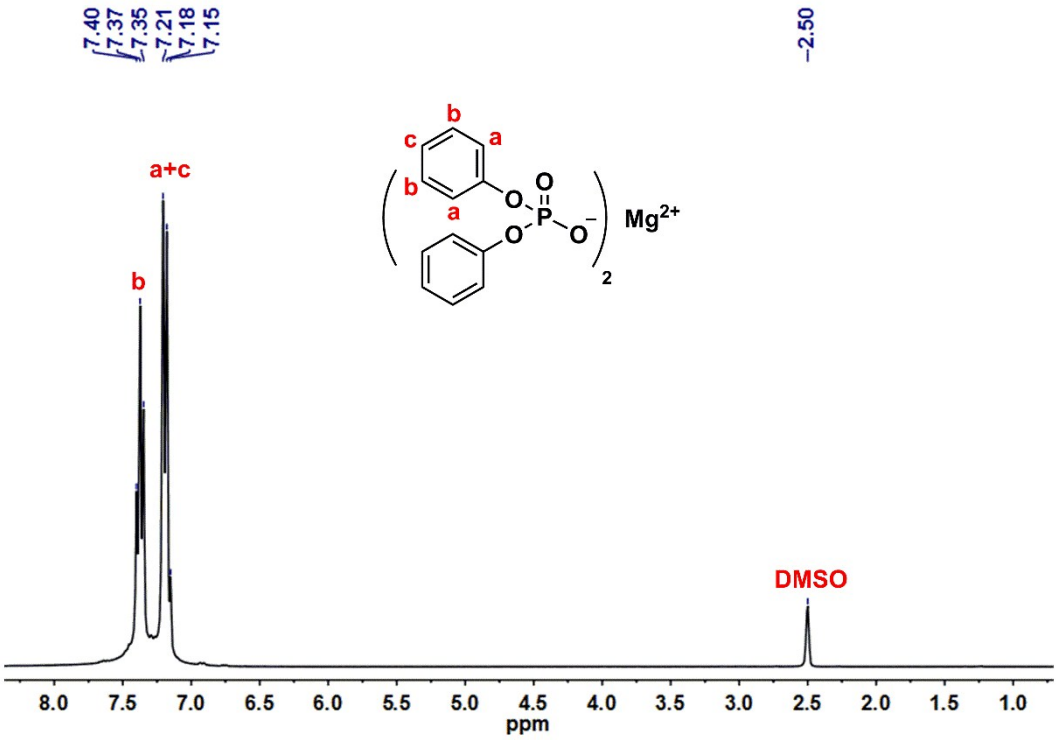


Figure S1 ^{1}H NMR spectrum of magnesium diphenyl phosphate in d_6-DMSO at room temperature.

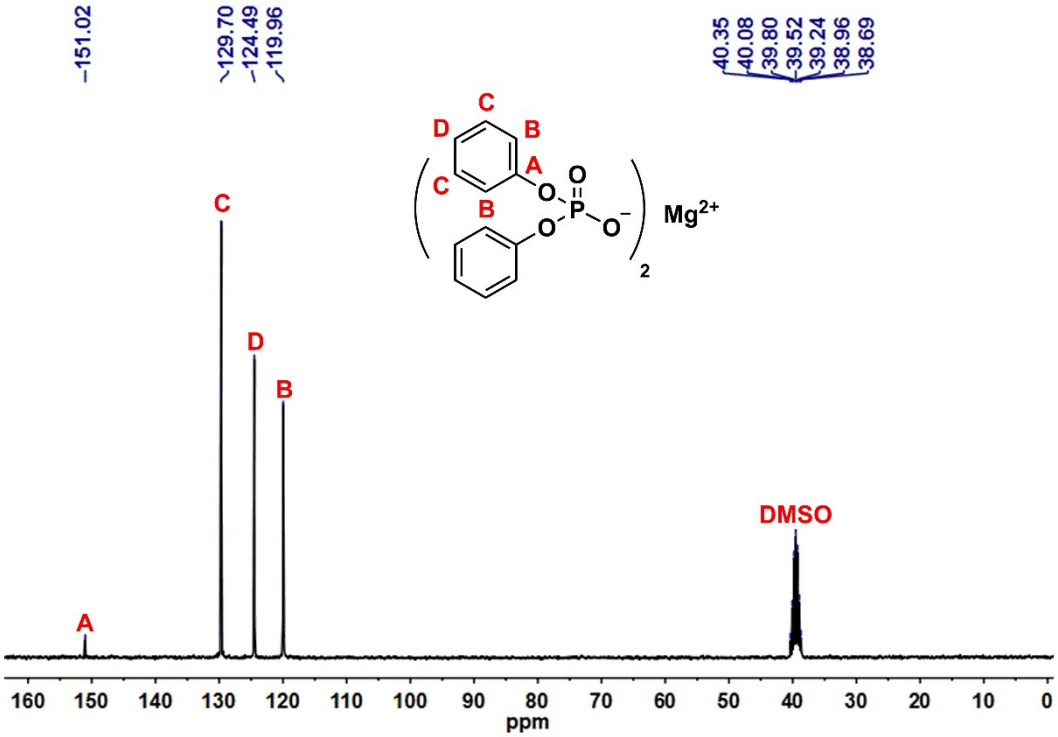


Figure S2 ^{13}C NMR spectrum of magnesium diphenyl phosphate in d_6-DMSO at room temperature.

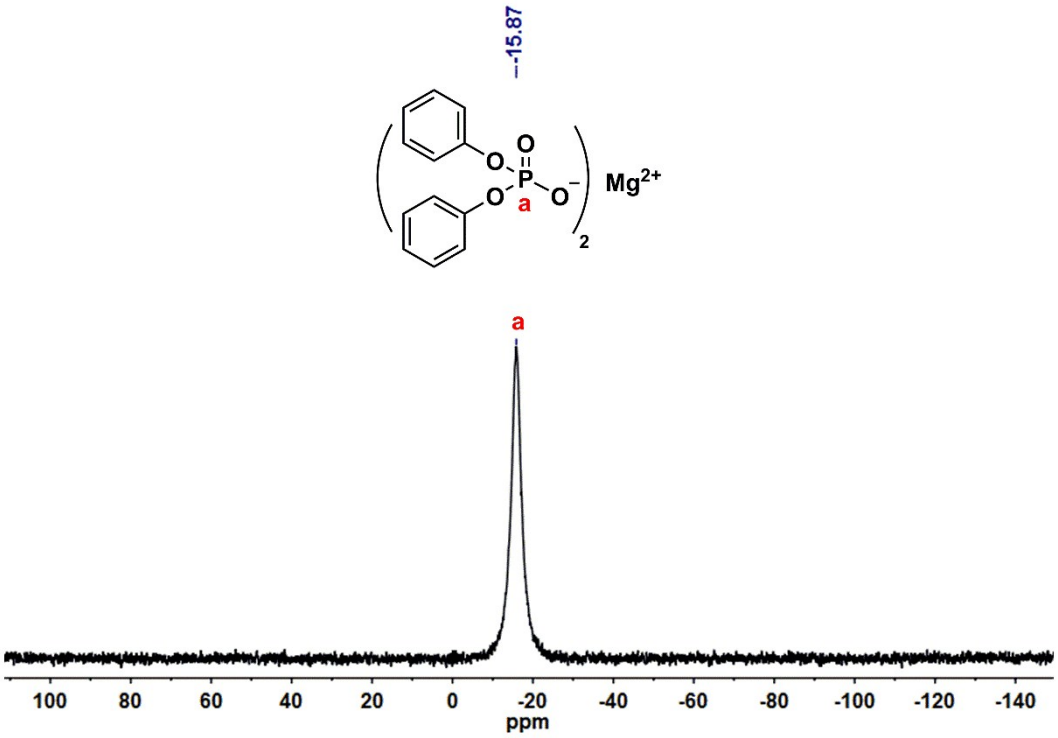


Figure S3 ^{31}P NMR spectrum of magnesium diphenyl phosphate in d_6-DMSO at room temperature.

Table S1 Bulk ring-opening polymerization of trimethylene carbonate with various ratios of [I]/[C] [a].

Entry	$[I]_0/[C]_0$	Time (h)	Conv. [b] (%)	$M_{n,theo}$ [c] (kg mol^{-1})	$M_{n,NMR}$ [b] (kg mol^{-1})	$M_{n,SEC}$ [d] (kg mol^{-1})	M_w/M_n [d]
1	1/0	18	0	–	–	–	–
2	1/0.25	18	36	1.24	1.55	1.62	1.22
3	1/0.5	18	63	2.06	2.26	2.38	1.18
4	1/0.75	18	82	2.65	2.95	3.30	1.17
5	1/1	18	96	3.07	3.27	3.56	1.17

[a] Using MgDP as catalyst and PPA as initiator; keeping $[M]_0/[I]_0$ = 30; polymerizations were conducted at 60 °C. [b] Determined by ^{1}H NMR spectroscopy in $CDCl_3$. [c] Calculated from ($[TMC]_0/[PPA]_0$) × conv. × (M_w of TMC) + (M_w of PPA). [d] Determined by SEC in THF using PSt standards.

Table S2 Bulk ring-opening polymerization of *δ*-valerolactone using magnesium diphenyl phosphate as catalyst and 3-phenyl-1-propnal as initiator [a].

Entry	Monomer	Catalyst	$[M]_0/[I]_0$	Time (h)	Conv. [b] (%)	$M_{n,theo}$ [c] (kg mol^{-1})	$M_{n,NMR}$ [b] (kg mol^{-1})	$M_{n,SEC}$ [d] (kg mol^{-1})	M_w/M_n [d]
1	*δ*-VL	MgDP	30	20	97	3.10	3.30	3.90	1.27
2	*δ*-VL	MgDP	60	38	96	6.00	6.20	6.70	1.26
3	*δ*-VL	MgDP	90	66	94	8.70	9.00	9.20	1.23
4	*δ*-VL	MgDP	120	82	92	11.2	11.6	12.0	1.23

[a] Keeping $[I]_0/[C]_0 = 1$; polymerizations were conducted at 90 °C. [b] Determined by ^{1}H NMR spectroscopy in $CDCl_3$. [c] Calculated from $([\delta\text{-VL}]_0/[PPA]_0) \times$ conv. $\times$ (M_w of *δ*-VL) + (M_w of PPA). [d] Determined by SEC in THF using PSt standards.

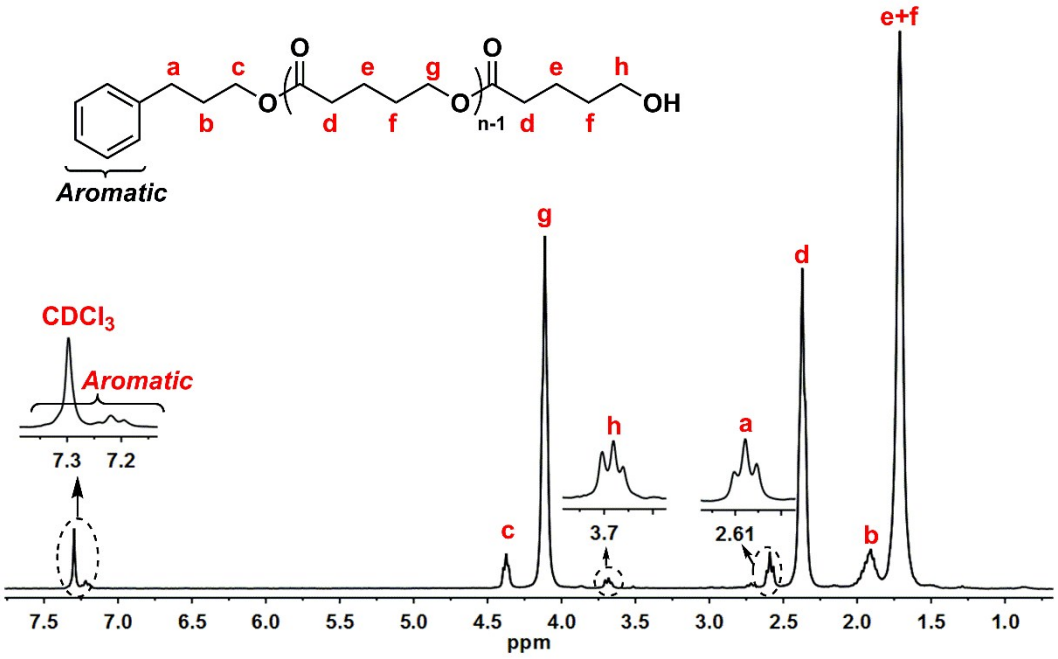
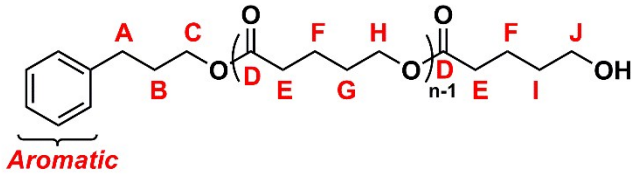


Figure S4 ^{1}H NMR spectrum of poly(*δ*-valerolactone) in $CDCl_3$ at room temperature.



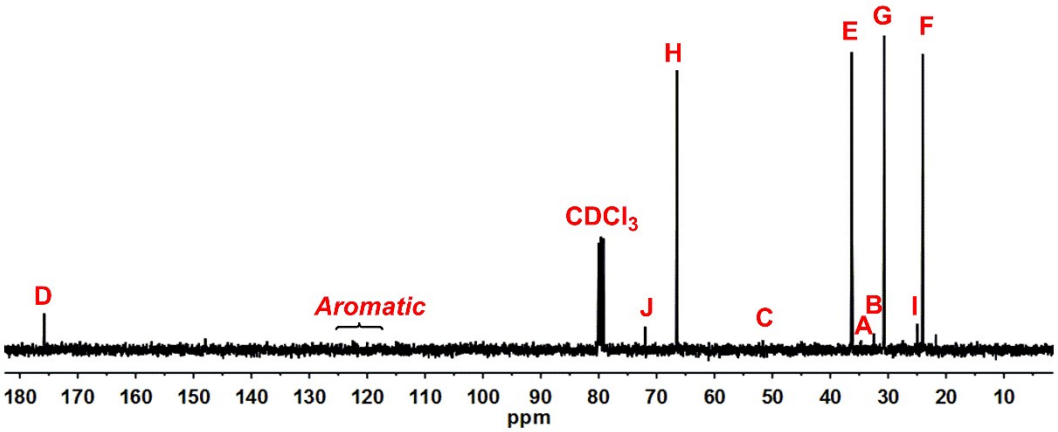
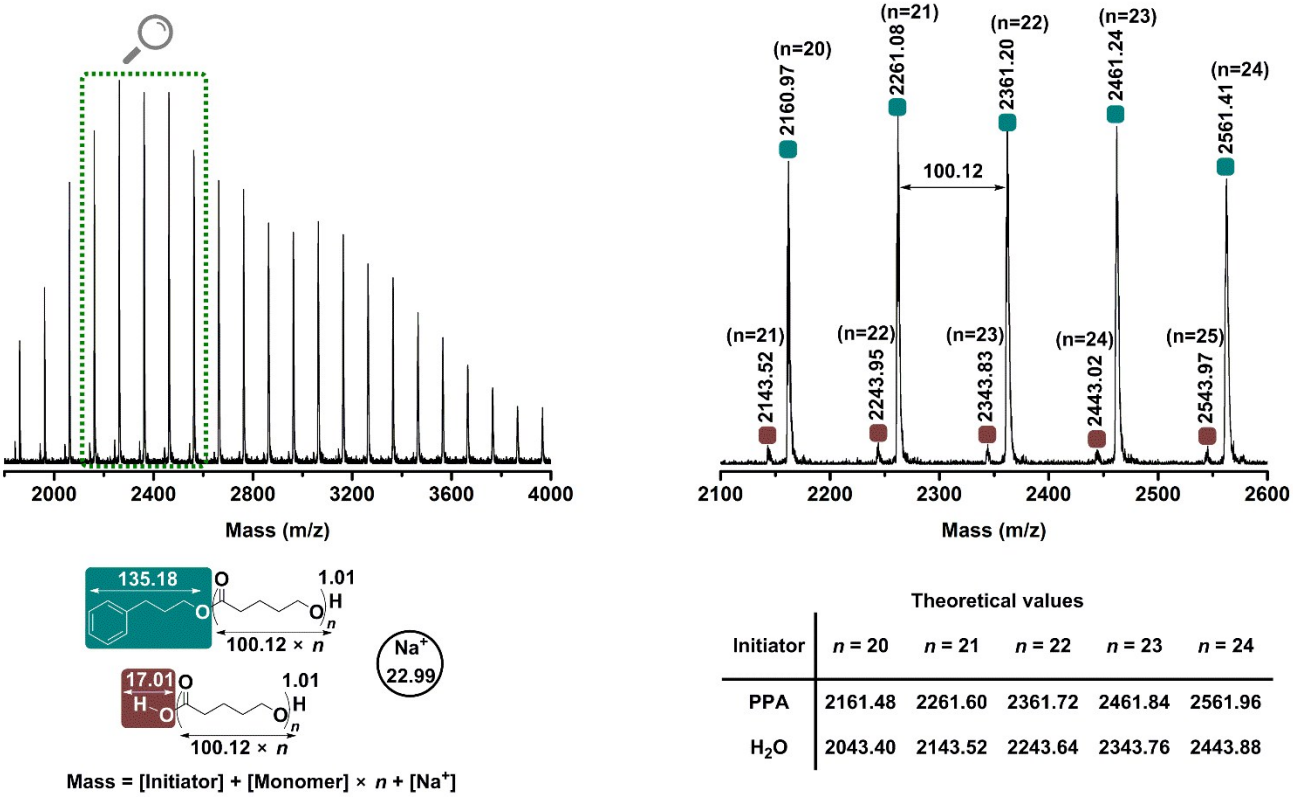


Figure S5 ^{13}C NMR spectrum of the poly(δ-valerolactone) in $CDCl_3$ at room temperature.



	Theoretical values				
Initiator	n = 20	n = 21	n = 22	n = 23	n = 24
PPA	2161.48	2261.60	2361.72	2461.84	2561.96
H_2O	2043.40	2143.52	2243.64	2343.76	2443.88

Figure S6 MALDI-TOF MS spectrum of poly(δ-valerolactone) ([δ-VL]$_0$/[MgDP]$_0$/[PPA]$_0$ = 30/1/1, 90 ˚C, conversion = 97%, $M_{n,\,NMR}$ = 3.10 kg mol^{-1}, M_w/M_n = 1.27)

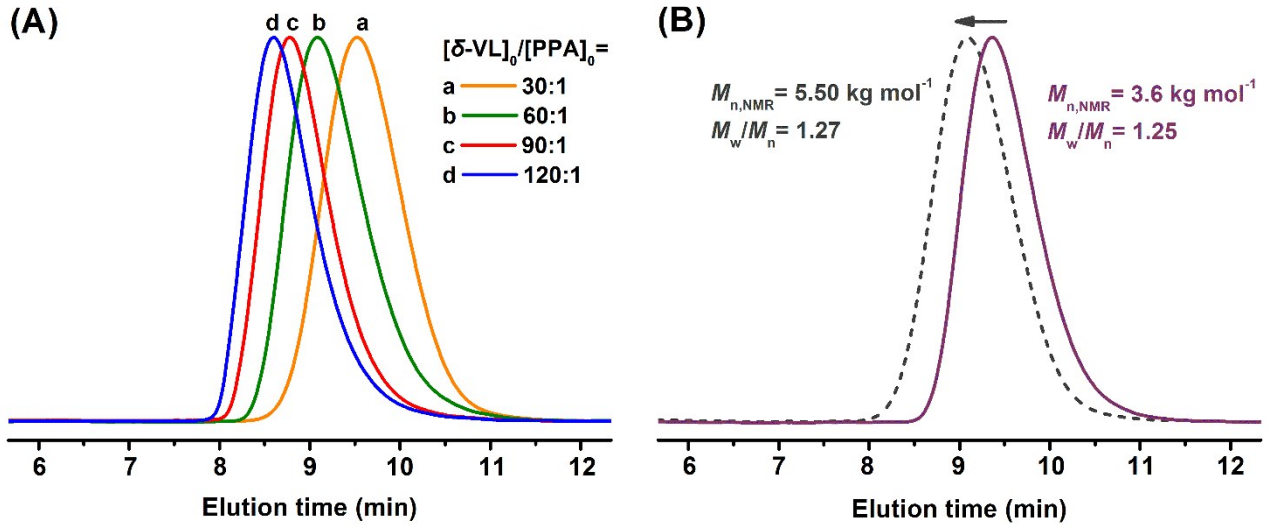


Figure S7 (A) SEC traces of poly(*δ*-valerolactone)s with various monomer/initiator ratios; (B) SEC traces of first poly(*δ*-valerolactone) sequence (solid line) and post polymerization (dash line). (Eluent = THF; flow rate = 0.7 mL min^{-1})

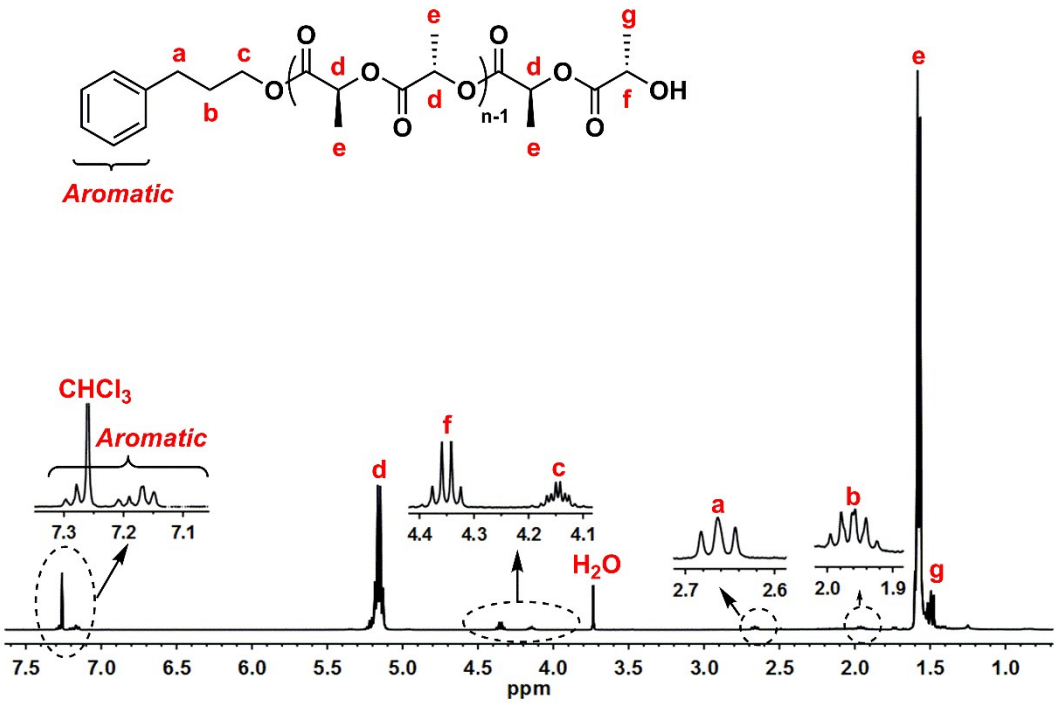


Figure S8 ^{1}H NMR spectrum of the polylactide in $CDCl_3$ at room temperature.

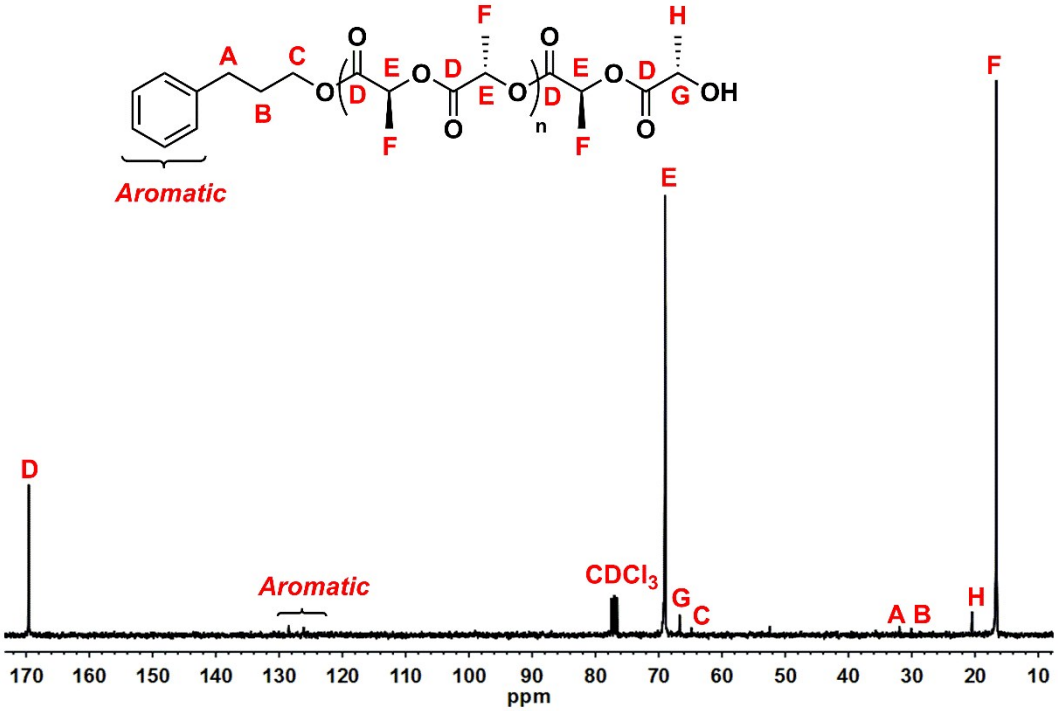
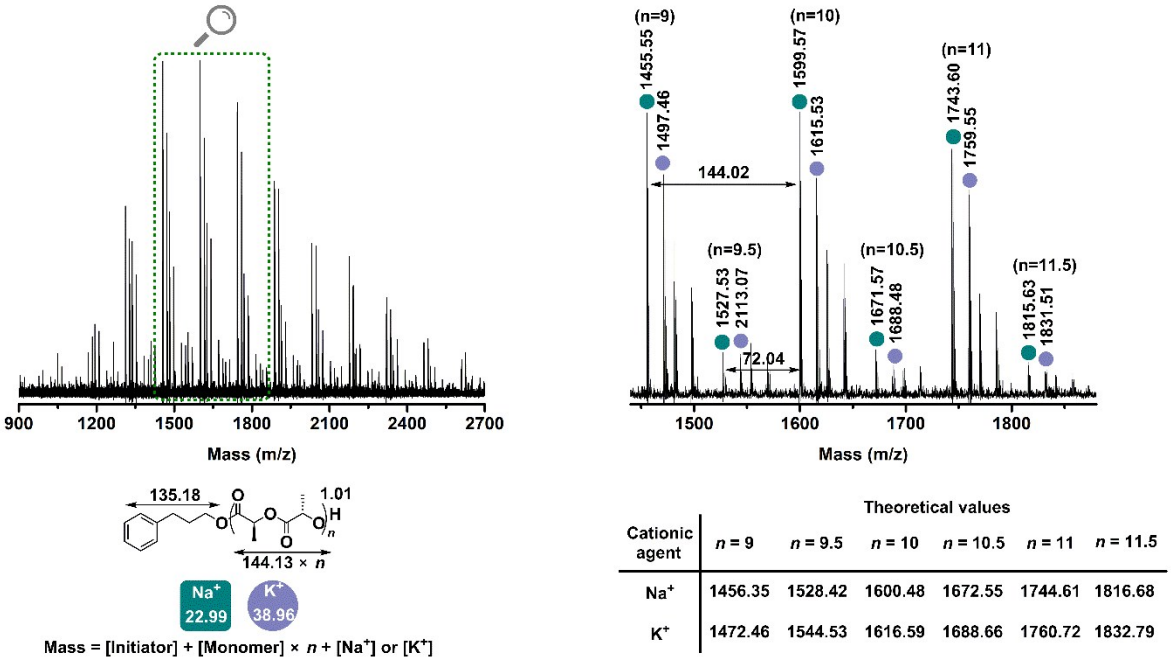


Figure S9 ^{13}C NMR spectrum of polylactide in $CDCl_3$ at room temperature.



Cationic agent	Theoretical values					
	n = 9	*n* = 9.5	*n* = 10	*n* = 10.5	*n* = 11	*n* = 11.5
Na^+	1456.35	1528.42	1600.48	1672.55	1744.61	1816.68
K^+	1472.46	1544.53	1616.59	1688.66	1760.72	1832.79

Figure S10 MALDI-TOF MS spectrum of polylactide ($[LA]_0/[MgDP]_0/[PPA]_0$ = 30/1/1, 140 ˚C, conversion = 97%, $M_{n,\,NMR}$ = 4.62 kg mol^{-1}, M_w/M_n = 1.43)

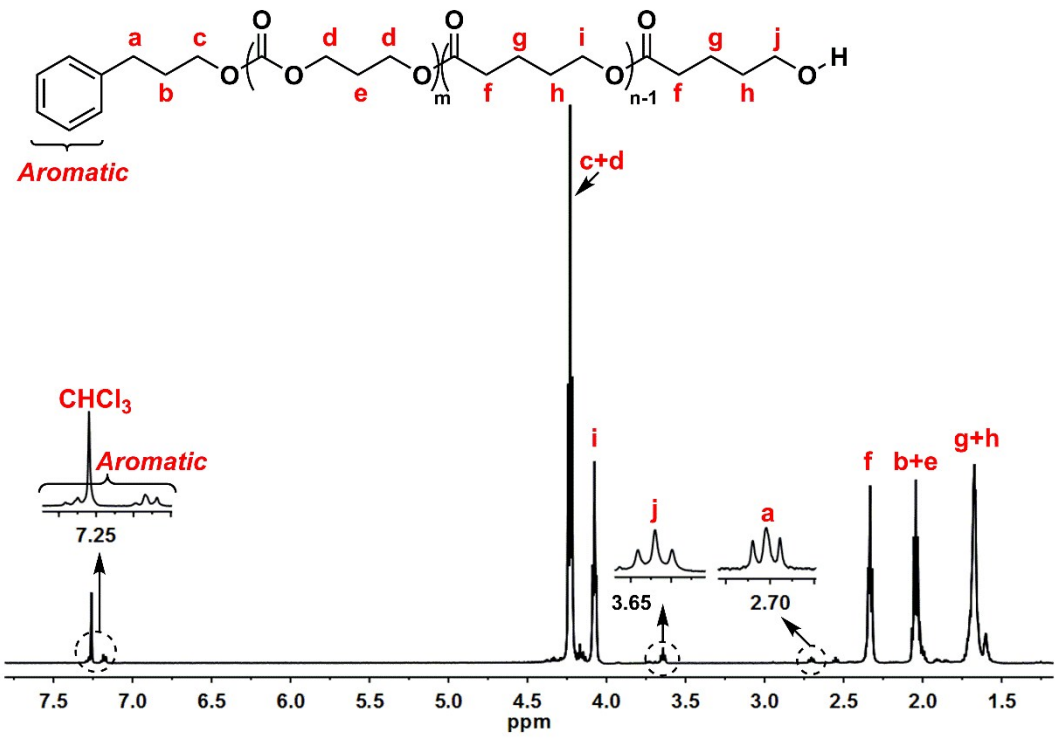


Figure S11 ^{1}H NMR spectrum of the obtaine poly(trimethylene carbonate)-*block*-poly(*δ*-valerolactone) in $CDCl_3$ at room temperature.

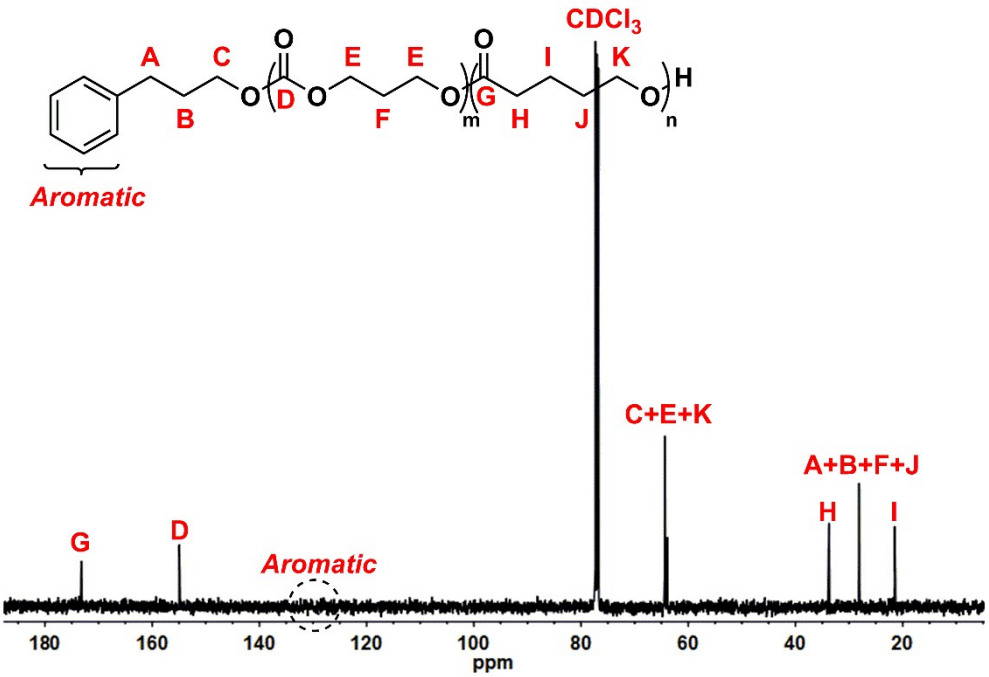


Figure S12 ^{13}C NMR spectrum of poly(trimethylene carbonate)-*block*-poly(*δ*-valerolactone) in $CDCl_3$ at room temperature

Table S3 Turnover frequency (TOF) of different catalysts in the ROP of TMC

$$\mathrm{TOF}\ (\mathrm{h}^{-1}) = \frac{[\mathrm{M}]_0 \times \text{ conv.}}{[\mathrm{Cat.}]_0 \times \text{ polymerization time (h)}}$$

Catalyst	TOF (h^{-1})	Conditions
MgDP	1.58	$[M]_0/[I]_0/[C]_0$=30/1/1, 60 °C, in bulk
DPP[1]	48.94	$[M]_0/[I]_0/[C]_0$=25/1/0.05, 80 °C, in bulk

Reference

1. T. Saito, Y. Aizawa, K. Tajima, T. Isono and T. Satoh, *Polym. Chem.*, 2015, **6**, 4374-4384.