Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Three is company: Dual intramolecular hydrogen-bonding enabled carboxylic acid active in ring-opening polymerization

Jiaxi Xu, Jingjing Liu, Zhenjiang Li*, Xiaopei Li, Cheng Chen, Chengxu Zhao, Songquan Xu, Xianfu Pan, Jiaqi Liu and Kai Guo*

*State Key Laboratory of Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, 30 Puzhu Rd S., Nanjing 211816, China. Tel +86 25 5813 9926; Fax +86 25 5813 9935. E-mail: zjli@njtech.edu.cn; guok@njtech.edu.cn

Scheme S1. γ-Resorcylic acid (**RA**) and congener hydroxybenzoic acids (**SA,1–3**), and combinations of phenol and benzoic acid (**4** and **5**) evaluated as catalysts in the ROP of δ-valerolactone. Salicylic acid (**SA**), α-resorcylic acid (**1**), *m*-salicylic acid (**2**), *p*-salicylic acid (**3**), phenol/ benzoic acid = 1 / 1 (**4**), and phenol/ benzoic acid = 2 / 1 (**5**).

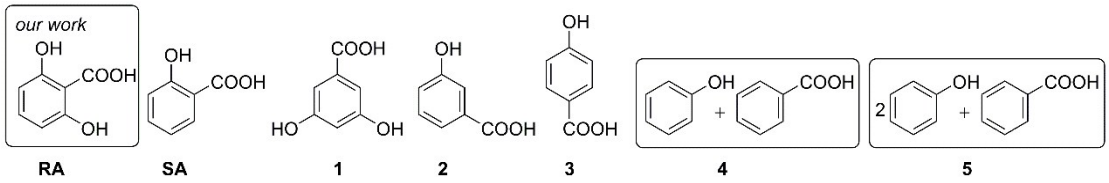


Table S1. ROP of δ-valerolactone (VL) catalyzed by several catalysts with benzyl alcohol (BnOH) as the initiator[a]

Entry	M	Catalyst	[M]/[I]	Time (h)	Conv.[b](%)	$M_{n,calcd}$ [c] (g mol^{-1})	$M_{n,NMR}$ [b] (g mol^{-1})	M_w/M_n [d]
1	VL	RA	30	24	98	3040	3310	1.08
2	VL	SA	30	24	19	670	1620	-
3	VL	1	30	-	-	-	-	-
4	VL	2	30	3 day	2	-	-	-
5	VL	3	30	3 day	1	-	-	-
6	VL	4	30	3 day	2	-	-	-
7	VL	5	30	3 day	3	-	-	-

[a] $[M]_0$ = 3.0 mol L^{-1}; room temperature. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([M]_0/[BnOH]_0)$ ×conv. ×(M_w of δ-VL) + (M_w of BnOH). [d] Determined by SEC in THF using polystyrene standards.

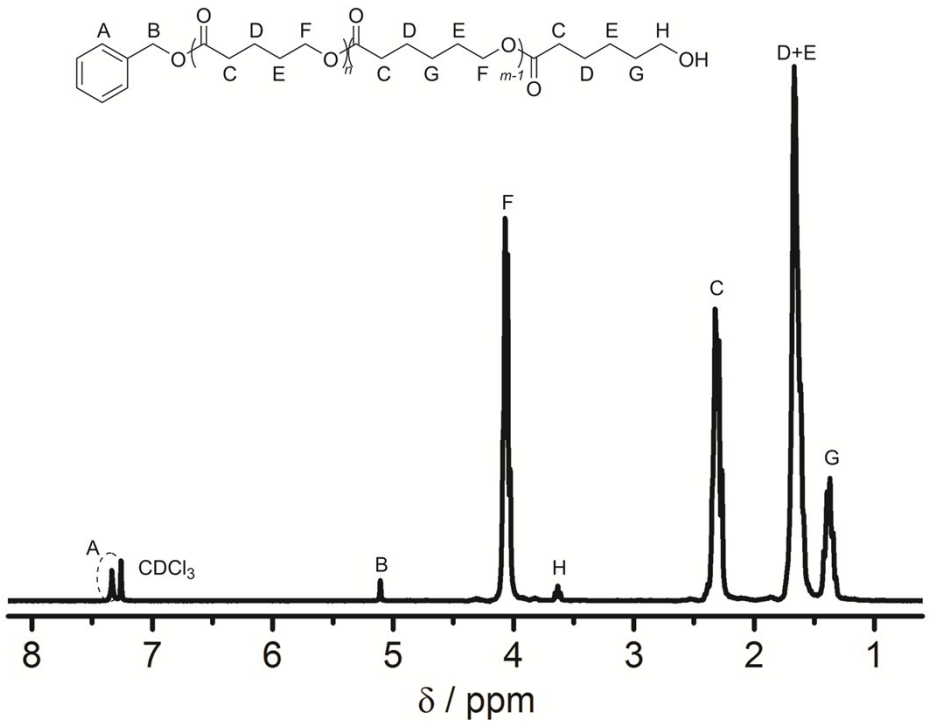


Figure S1. ^{1}H NMR spectrum of the poly(δ-valerolactones)-block-poly(ε-caprolactone).

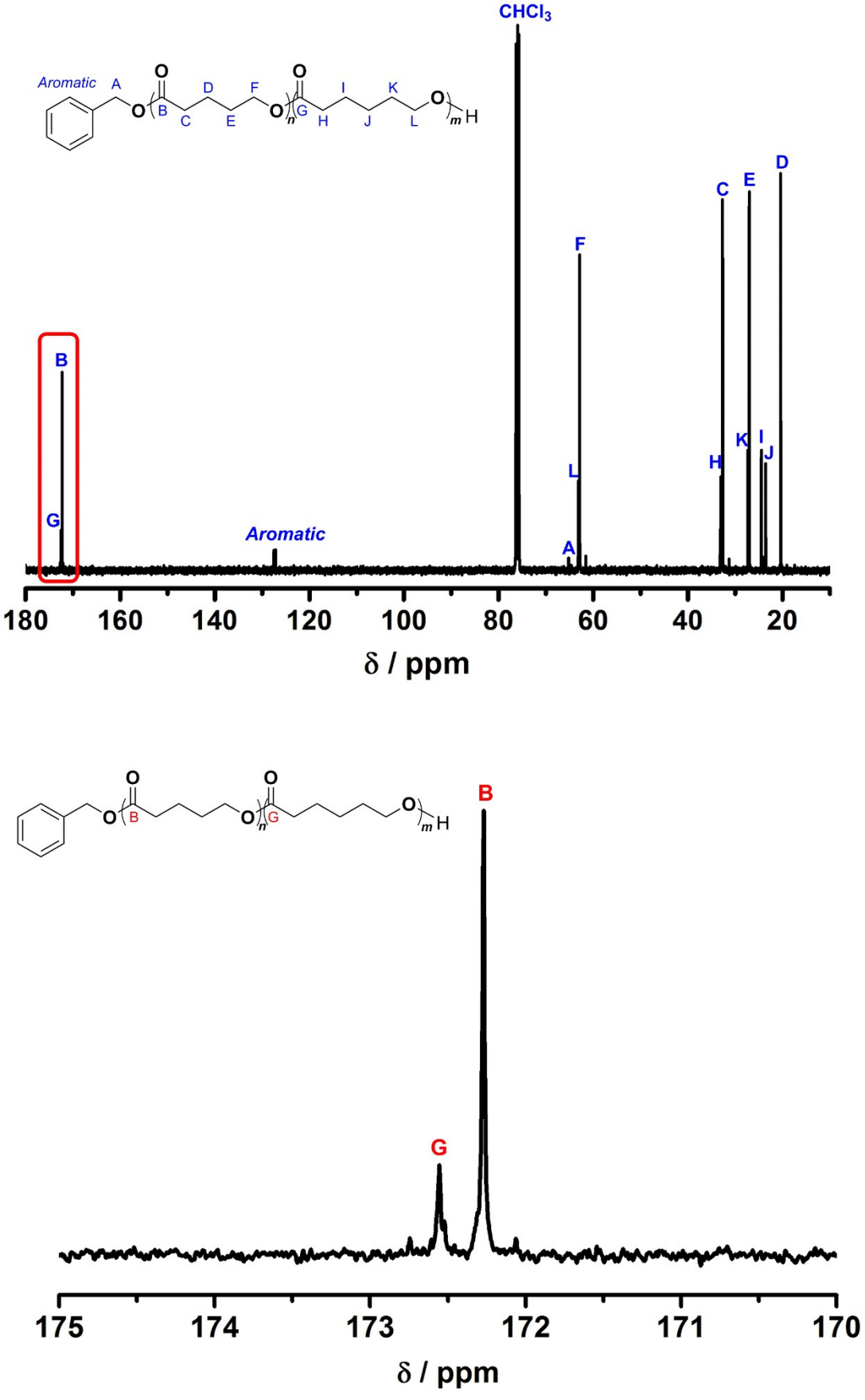


Figure S2. ^{13}C NMR spectrum of the poly(δ-valerolactones)-block-poly(ε-caprolactone).

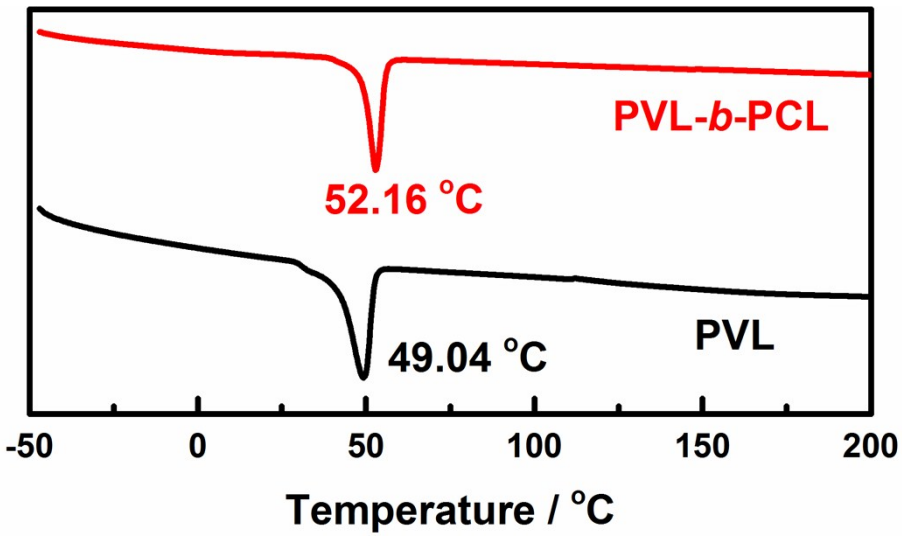


Figure S3. DSC traces of poly(δ-valerolactone) (black) and poly(δ-valerolactones)-block-poly(ε-caprolactone)(red).

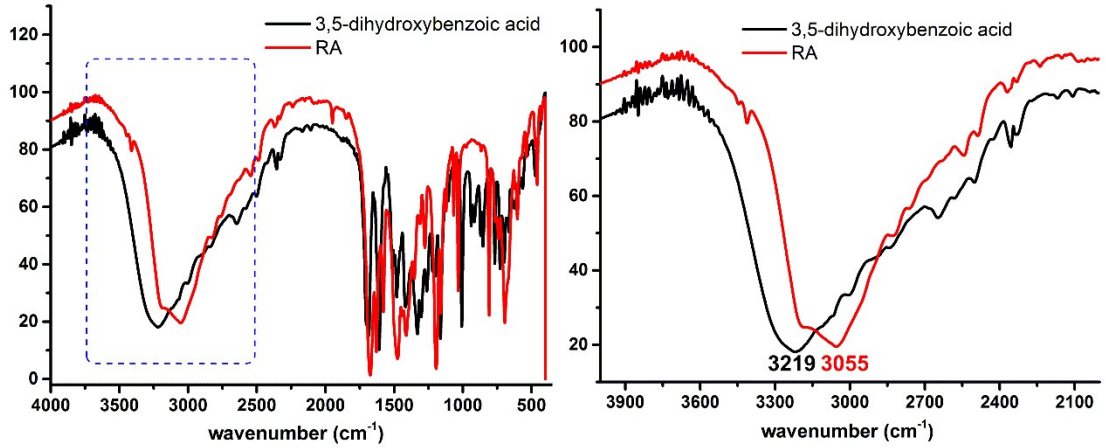


Figure S4. IR spectrum of 3,5-dihydroxybenzoic acid and RA by KBr disc.

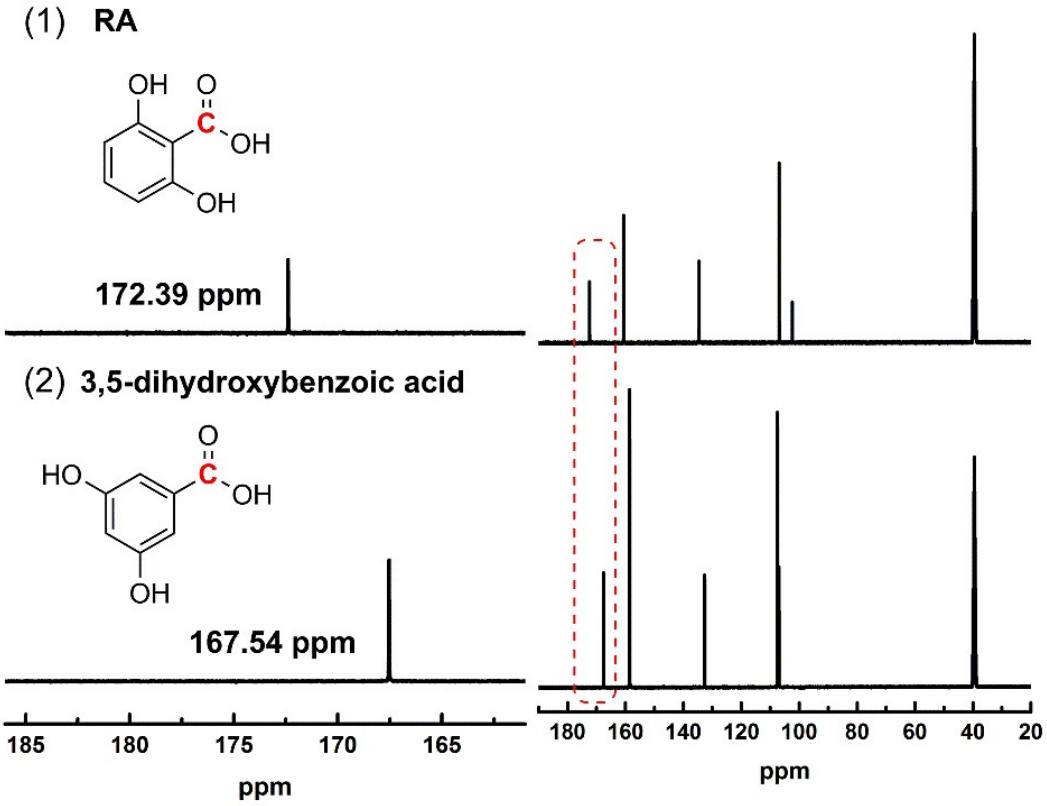


Figure S5. ^{13}C NMR spectrum of 3,5-dihydroxybenzoic acid and RA in DMSO-d_6.

Syntheses of end-functionalized poly(δ-valerolactone)

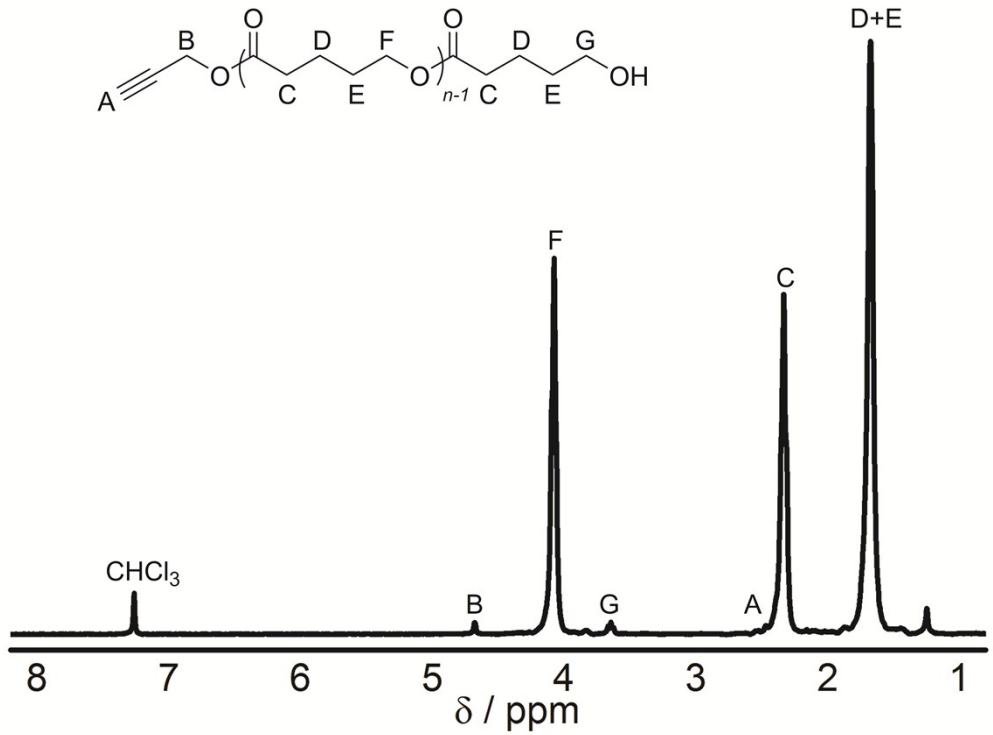


Figure S6. ^{1}H NMR spectrum of end-functionalized PVL initiated from propargyl alcohol in $CDCl_3$

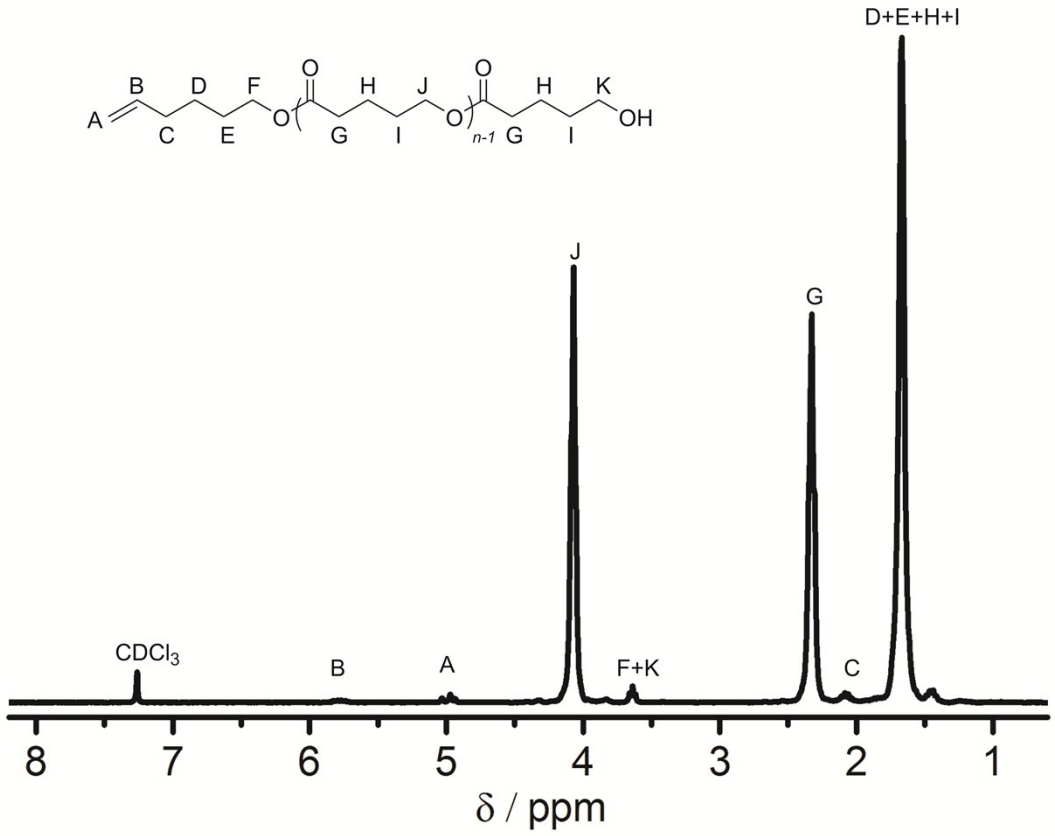


Figure S7. ^{1}H NMR spectrum of end-functionalized PVL initiated from 5-hexen-1-ol in $CDCl_3$

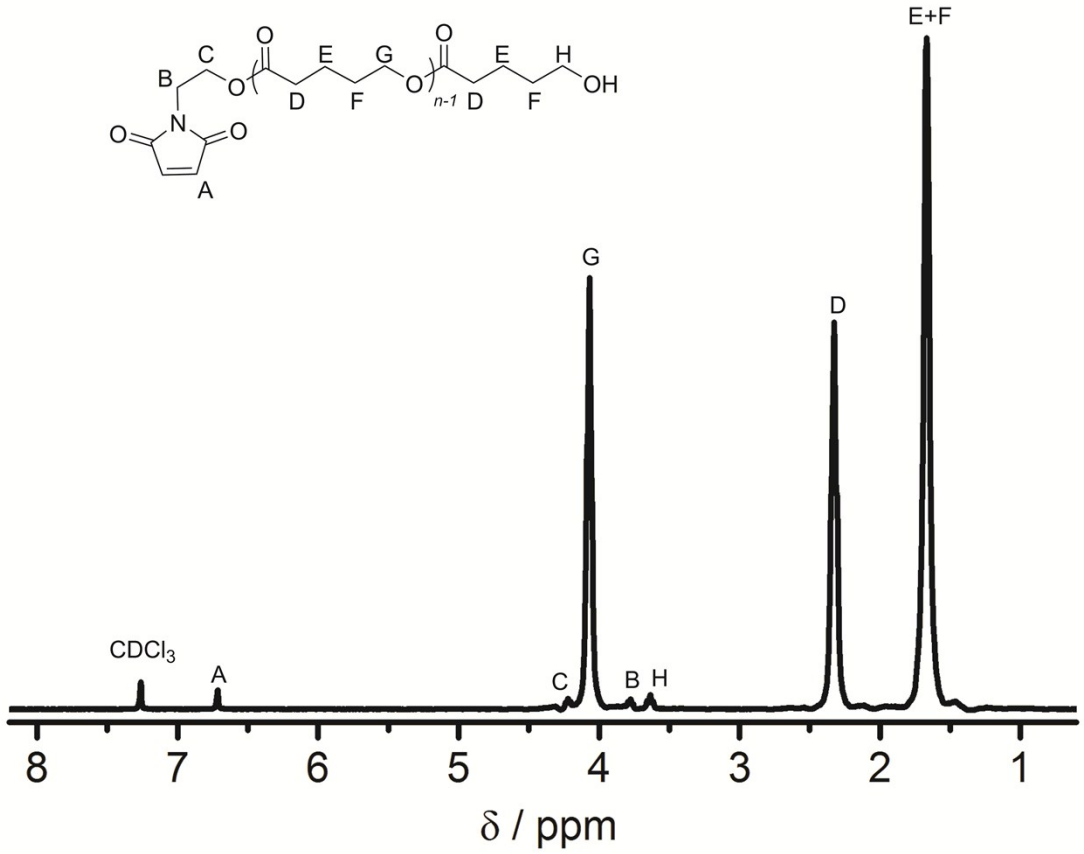


Figure S8. ^{1}H NMR spectrum of end-functionalized PVL initiated from N-(2-hydroxyethyl) maleimide in $CDCl_3$

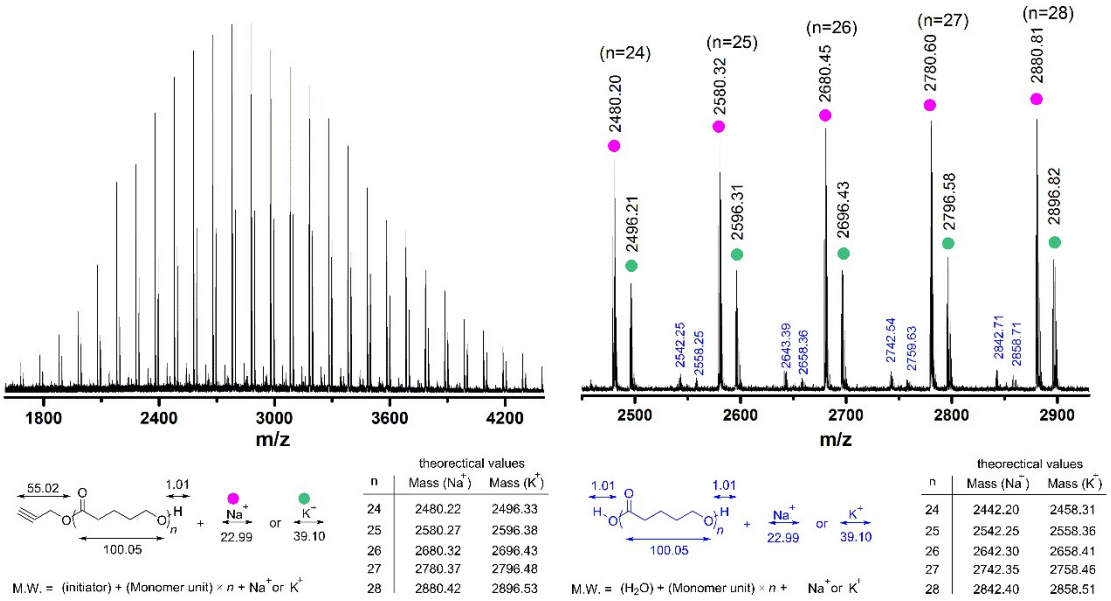


Figure S9. MALDI-ToF MS spectrum of the obtained PVL ($[VL]_0$/ $[propargyl\ alcohol]_0$/ $[RA]_0$ = 50/ 1/ 1, CH_2Cl_2, rt, $[VL]_0$ = 1.0 mol L^{-1}).

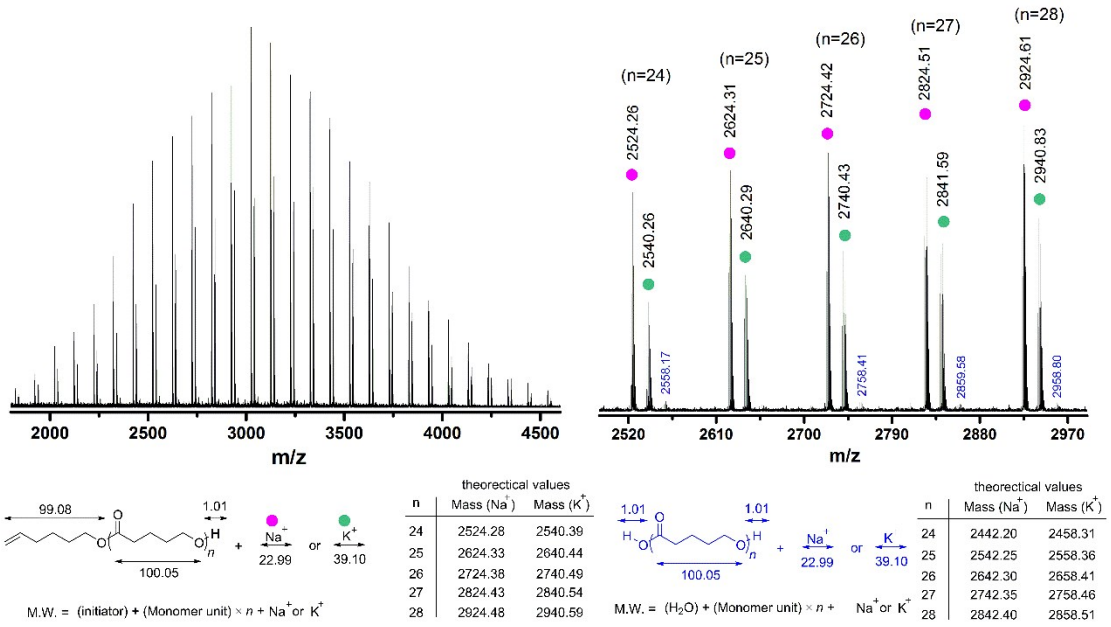
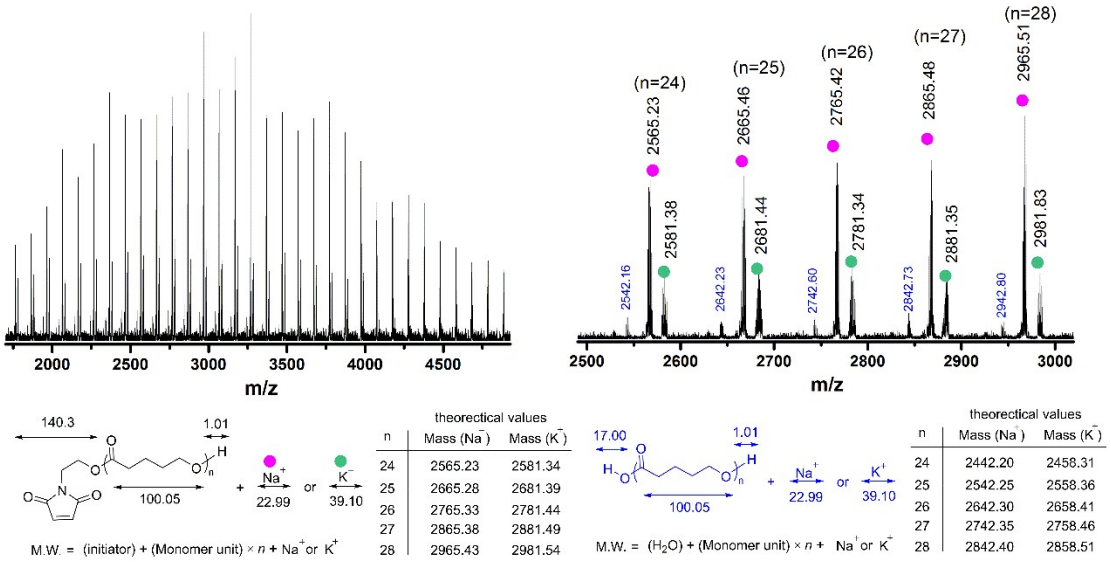


Figure S10. MALDI-ToF MS spectrum of the obtained PVL ($[VL]_0$/ $[5\text{-hexen-1-ol}]_0$/ $[RA]_0$ = 50/ 1/ 1, CH_2Cl_2, rt, $[VL]_0$ = 1.0 mol L^{-1}).



n	theorectical values Mass (Na^+)	Mass (K^+)
24	2565.23	2581.34
25	2665.28	2681.39
26	2765.33	2781.44
27	2865.38	2881.49
28	2965.43	2981.54

n	theorectical values Mass (Na^+)	Mass (K^+)
24	2442.20	2458.31
25	2542.25	2558.36
26	2642.30	2658.41
27	2742.35	2758.46
28	2842.40	2858.51

Figure S11. MALDI-ToF MS spectrum of the obtained PVL ($[VL]_0$/ [N-(2-hydroxyethyl) maleimide]$_0$/ $[RA]_0$ = 50/ 1/ 1, CH_2Cl_2, rt, $[VL]_0$ = 1.0 mol L^{-1}).