

Supporting Information

Merging of cationic RAFT and radical RAFT polymerizations with ring-opening polymerizations for the synthesis of asymmetric ABCD type tetrablock copolymers in one-pot

Yuejia Zhu, Luoyu Gao, Zhenjiang Li*, Bo Liu, Zhihao Zhang, Haoying Tong, Yuanyuan Qu, Yusheng Quan, Xin Zou, Kai Guo*

State Key Laboratory Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, 30 Puzhu Road South, Nanjing 211816, China.

E-mail: guok@njtech.edu.cn, zjli@njtech.edu.cn; Tel: +86 25 5813 9926

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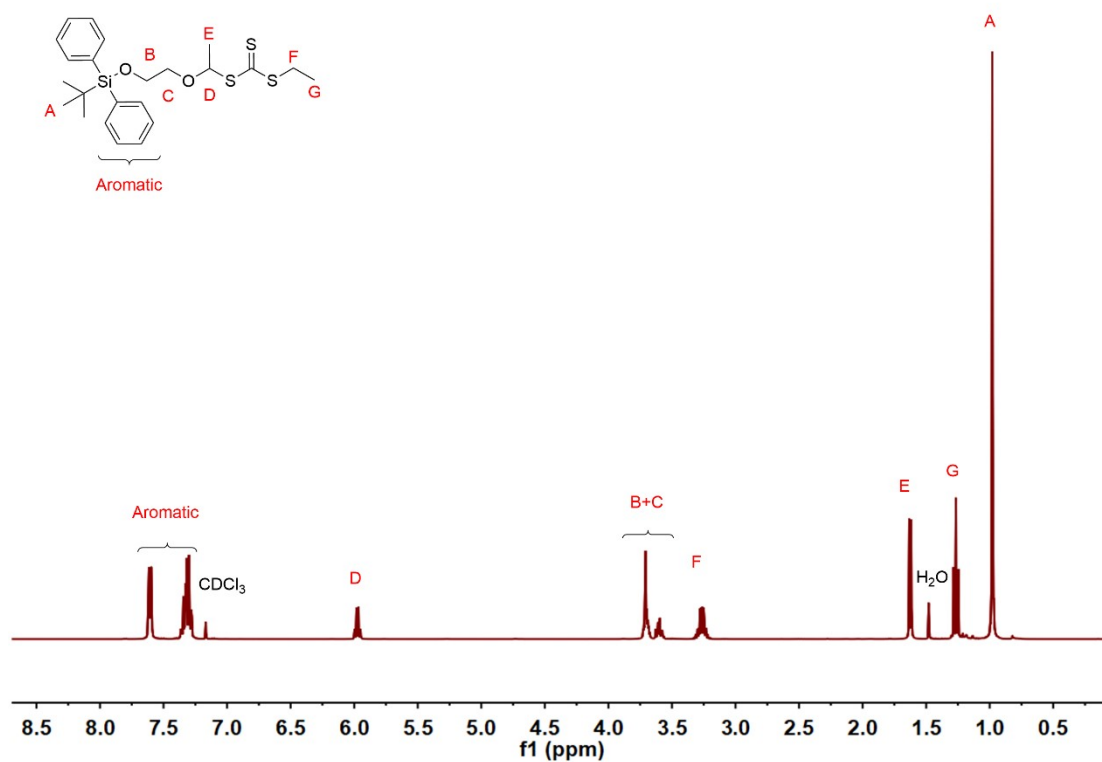


Figure S1. ^1H NMR spectrum (DMSO, 400 MHz) of PTRS

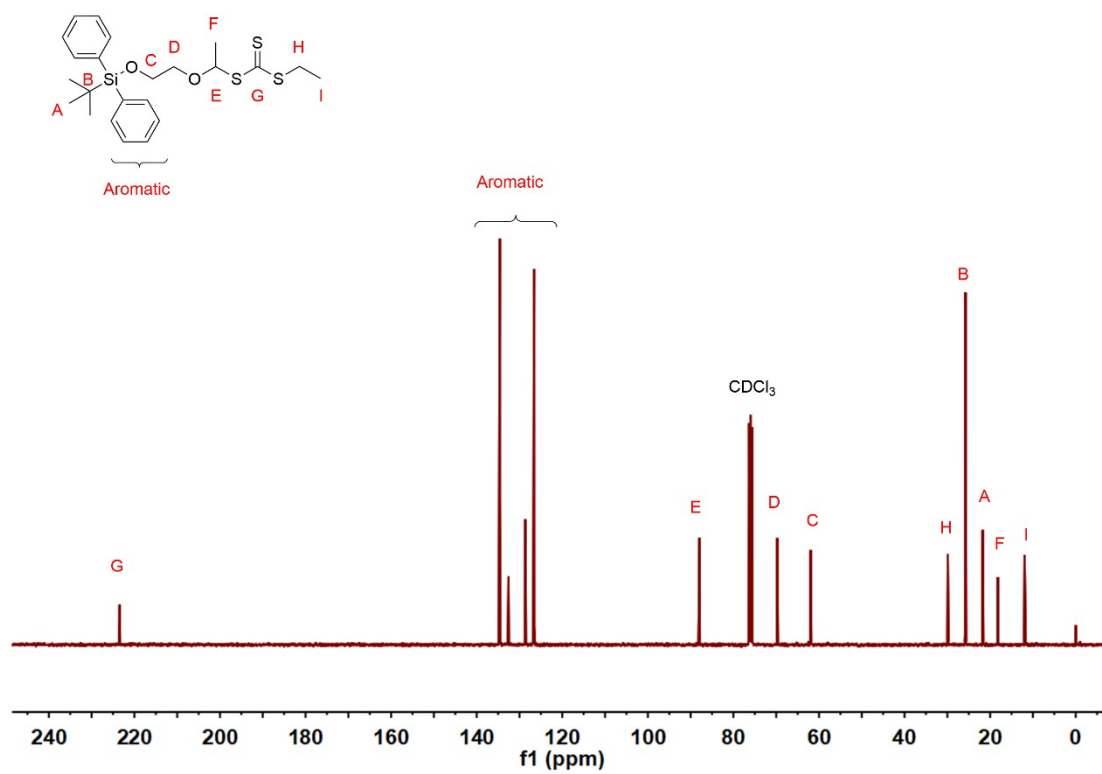


Figure S2. ¹³C NMR spectrum (DMSO, 100 MHz) of PTR A

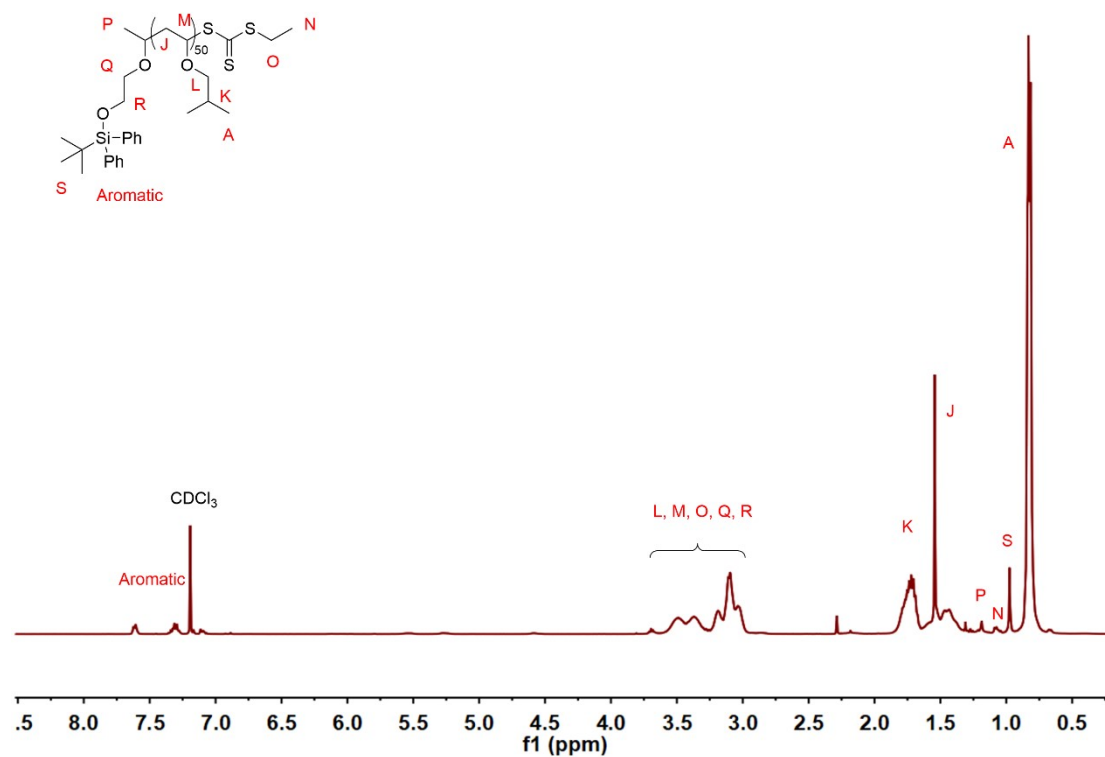


Figure S3. ¹H NMR spectrum (CDCl₃, 400 MHz) of PIBVE

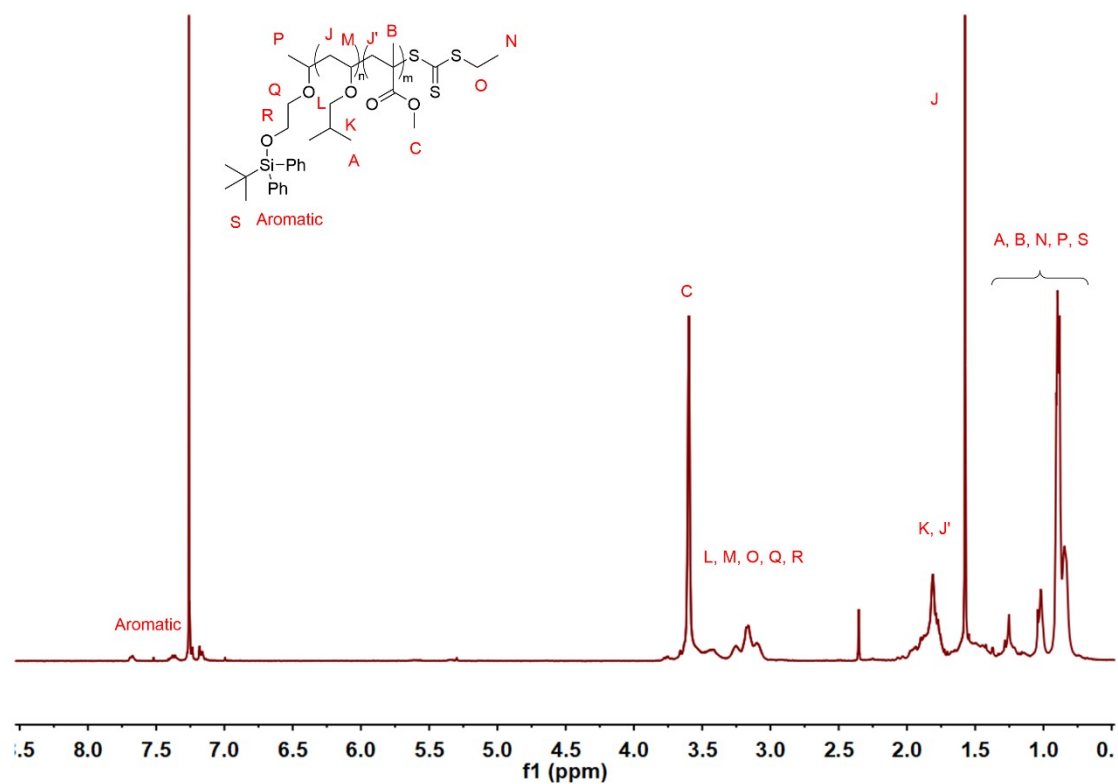


Figure S4. ^1H NMR spectrum (CDCl_3 , 400 MHz) of PIBVE-*b*-PMMA

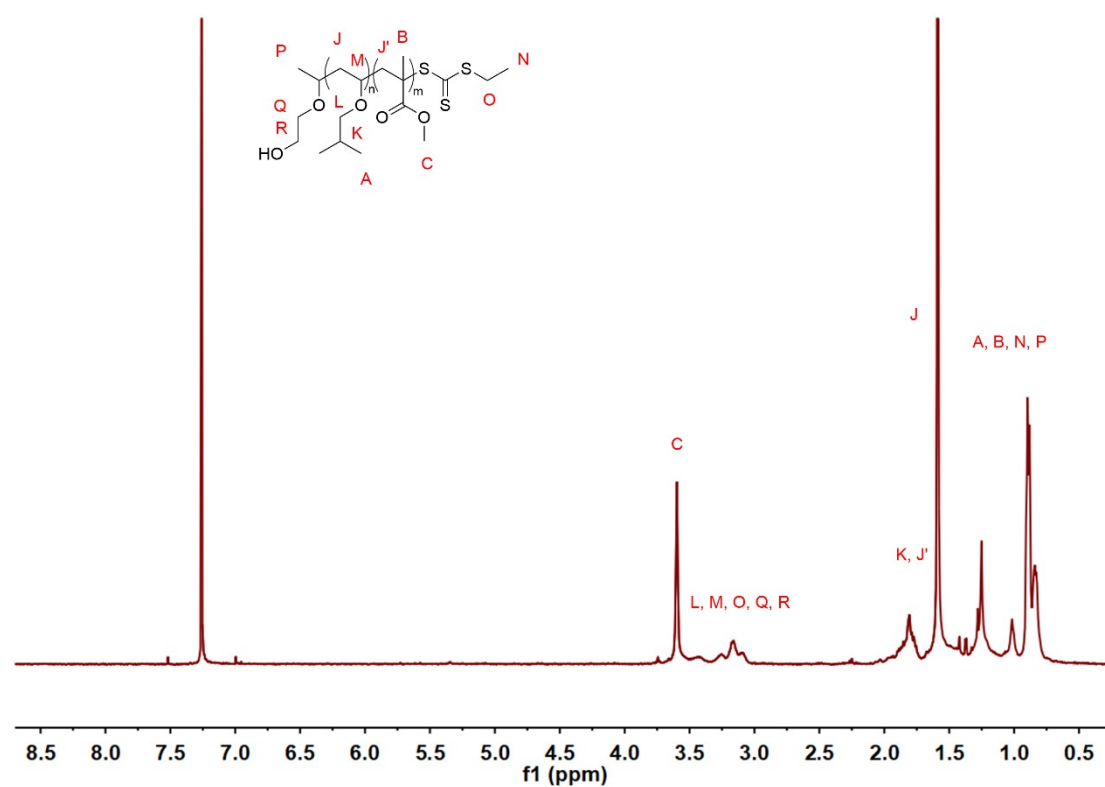


Figure S5. ^1H NMR spectrum (CDCl_3 , 400 MHz) of deprotected PIBVE-*b*-PMMA

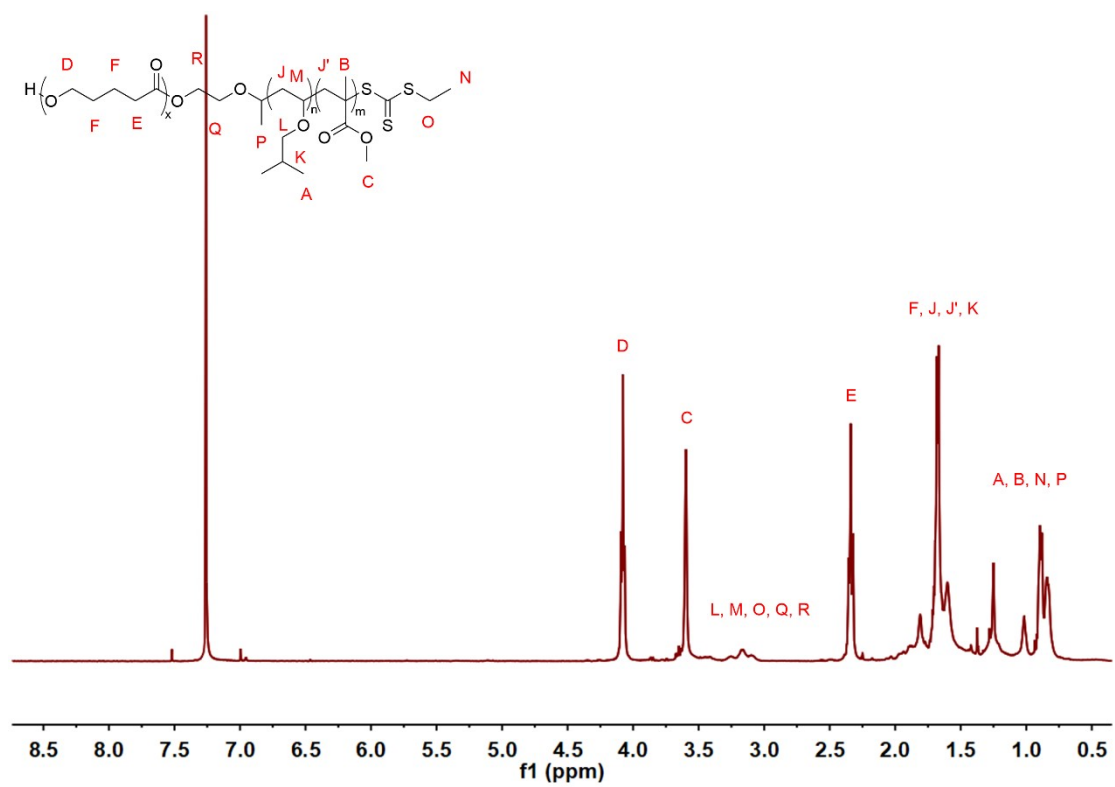


Figure S6. ^1H NMR spectrum (CDCl_3 , 400 MHz) of PIBVE-*b*-PMMA-*b*-PVL

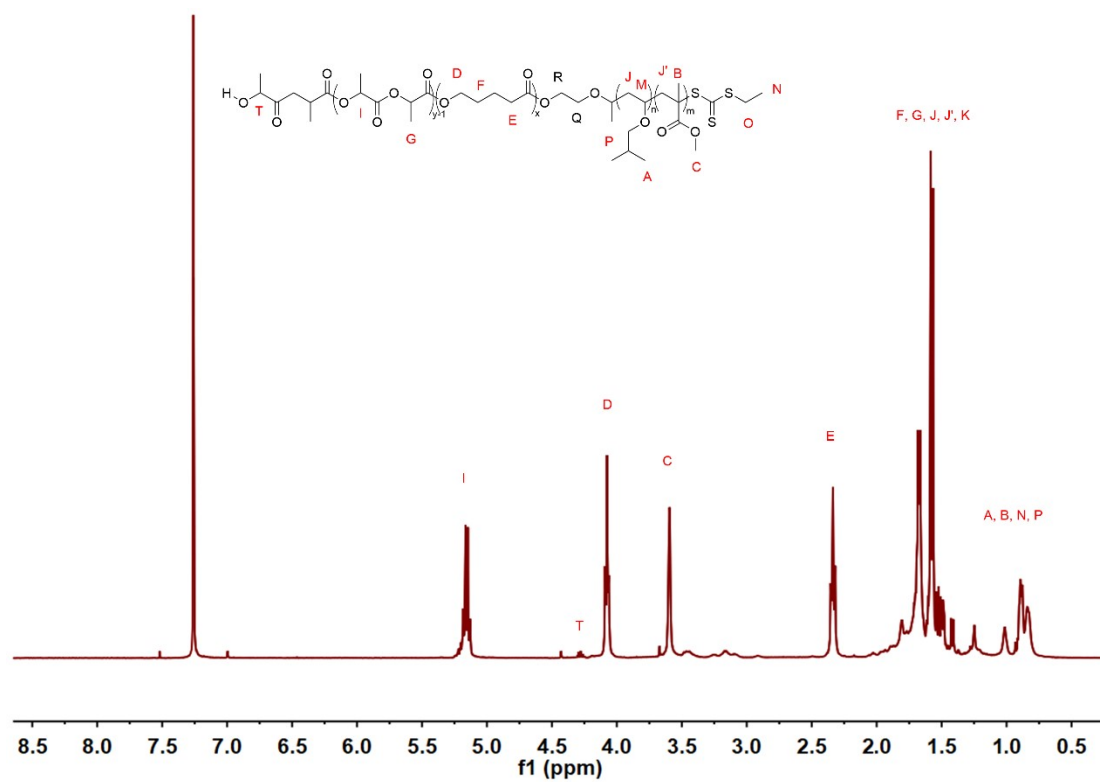


Figure S7. ^1H NMR spectrum (CDCl_3 , 400 MHz) of PIBVE-*b*-PMMA-*b*-PVL-*b*-PLLA

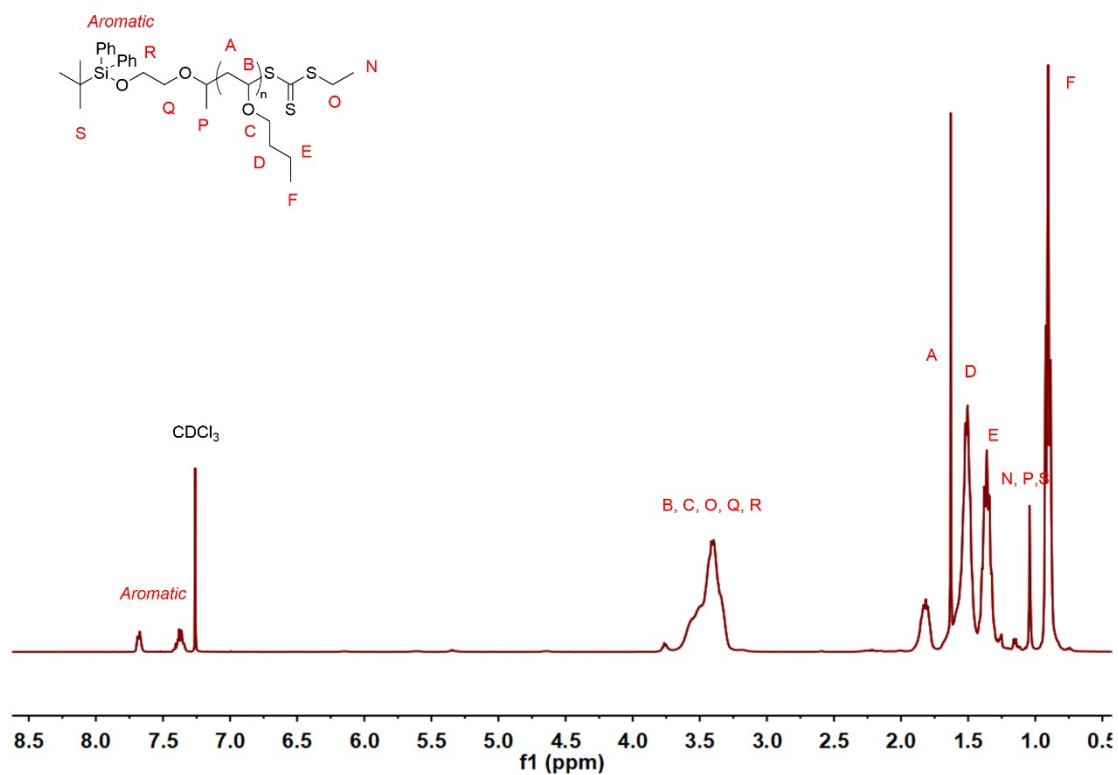


Figure S8. ^1H NMR spectrum (CDCl_3 , 400 MHz) of PBVE

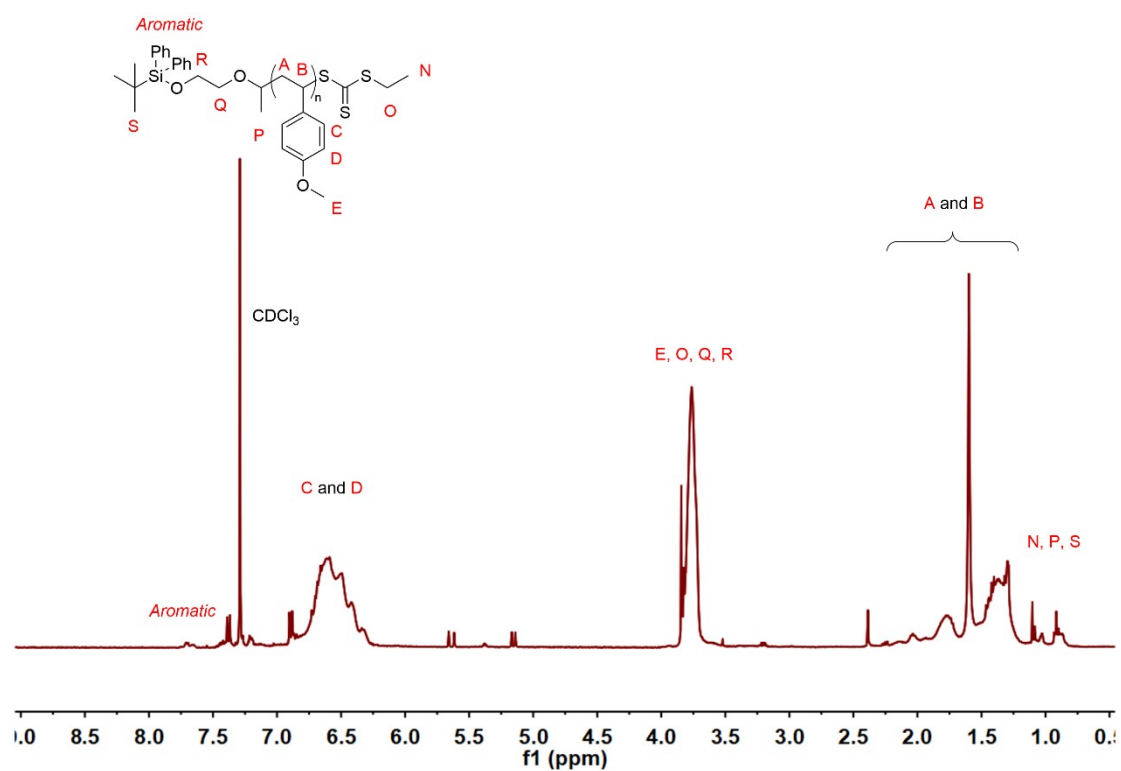


Figure S9. ^1H NMR spectrum (CDCl_3 , 400 MHz) of poly(4-methoxystyrene)

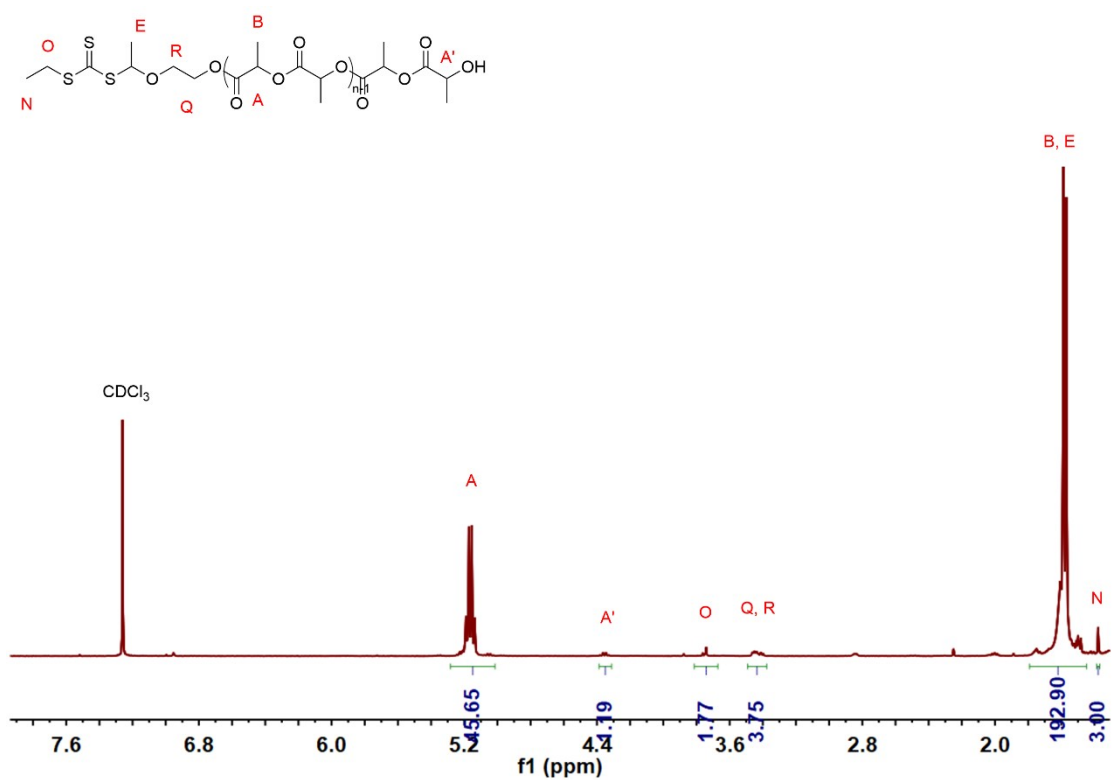


Figure S10. ^1H NMR spectrum (CDCl_3 , 400 MHz) of PLA.

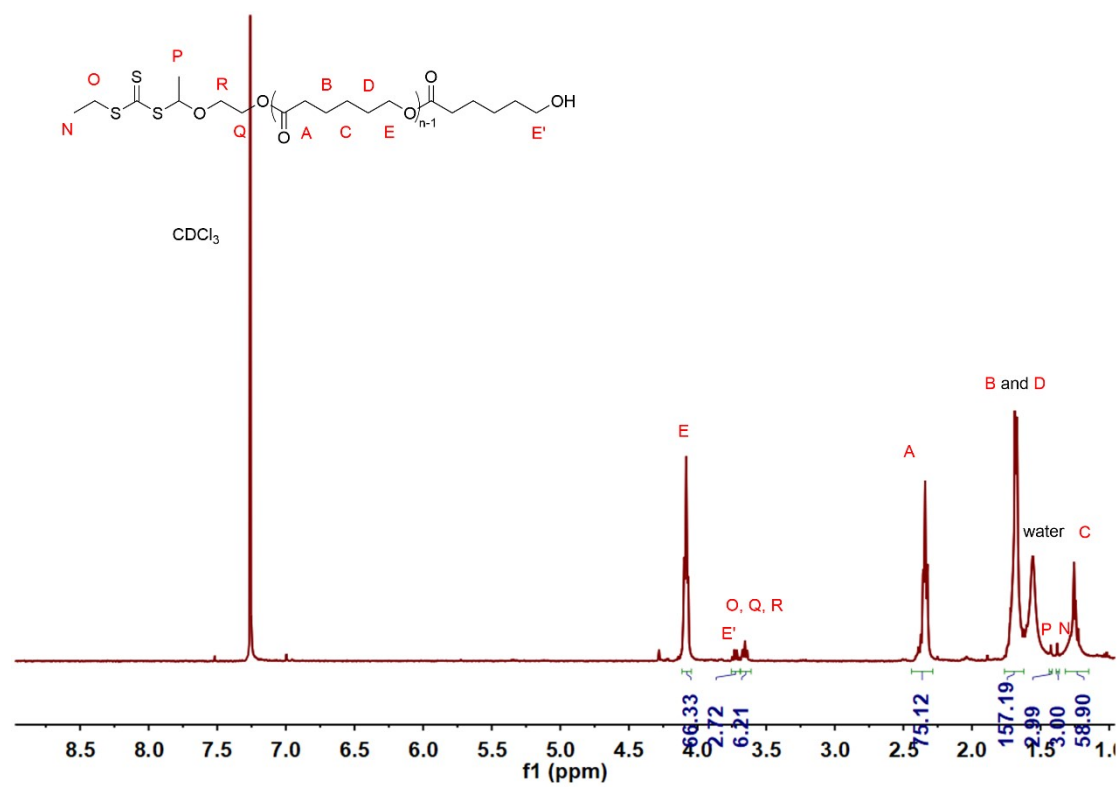


Figure S11. ^1H NMR spectrum (CDCl_3 , 400 MHz) of PCL.

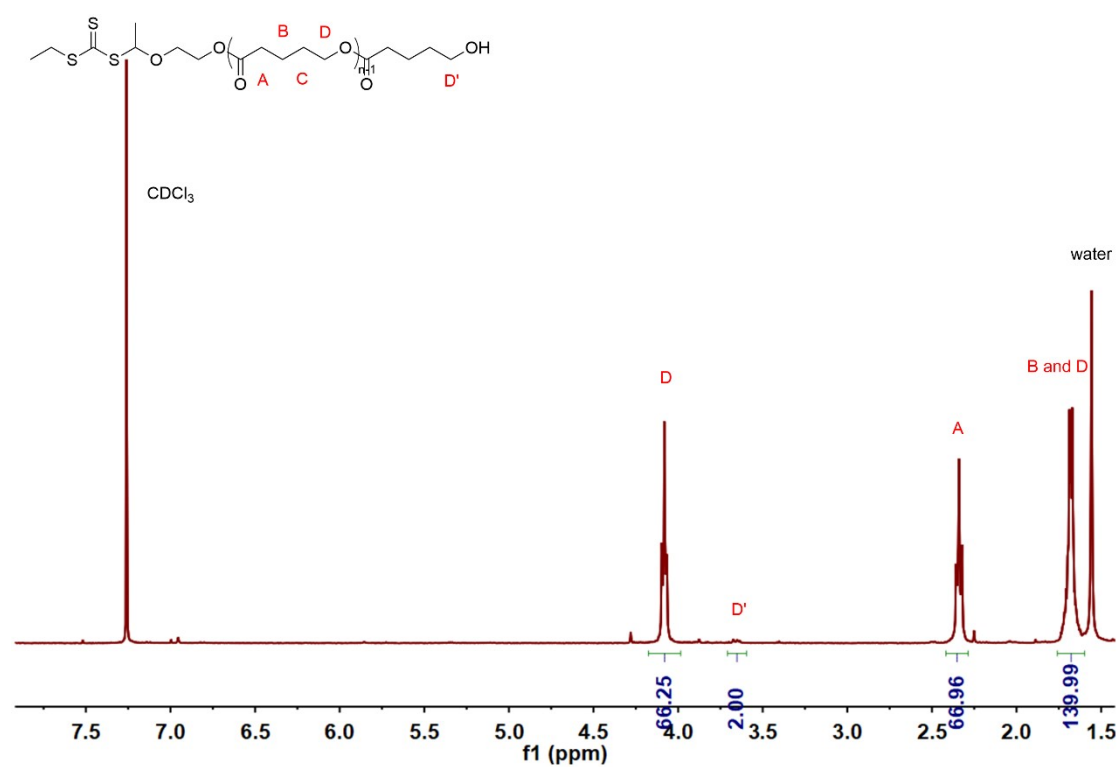


Figure S12. ^1H NMR spectrum (CDCl₃, 400 MHz) of PVL.

Cationic RAFT → Deprotection → ROP

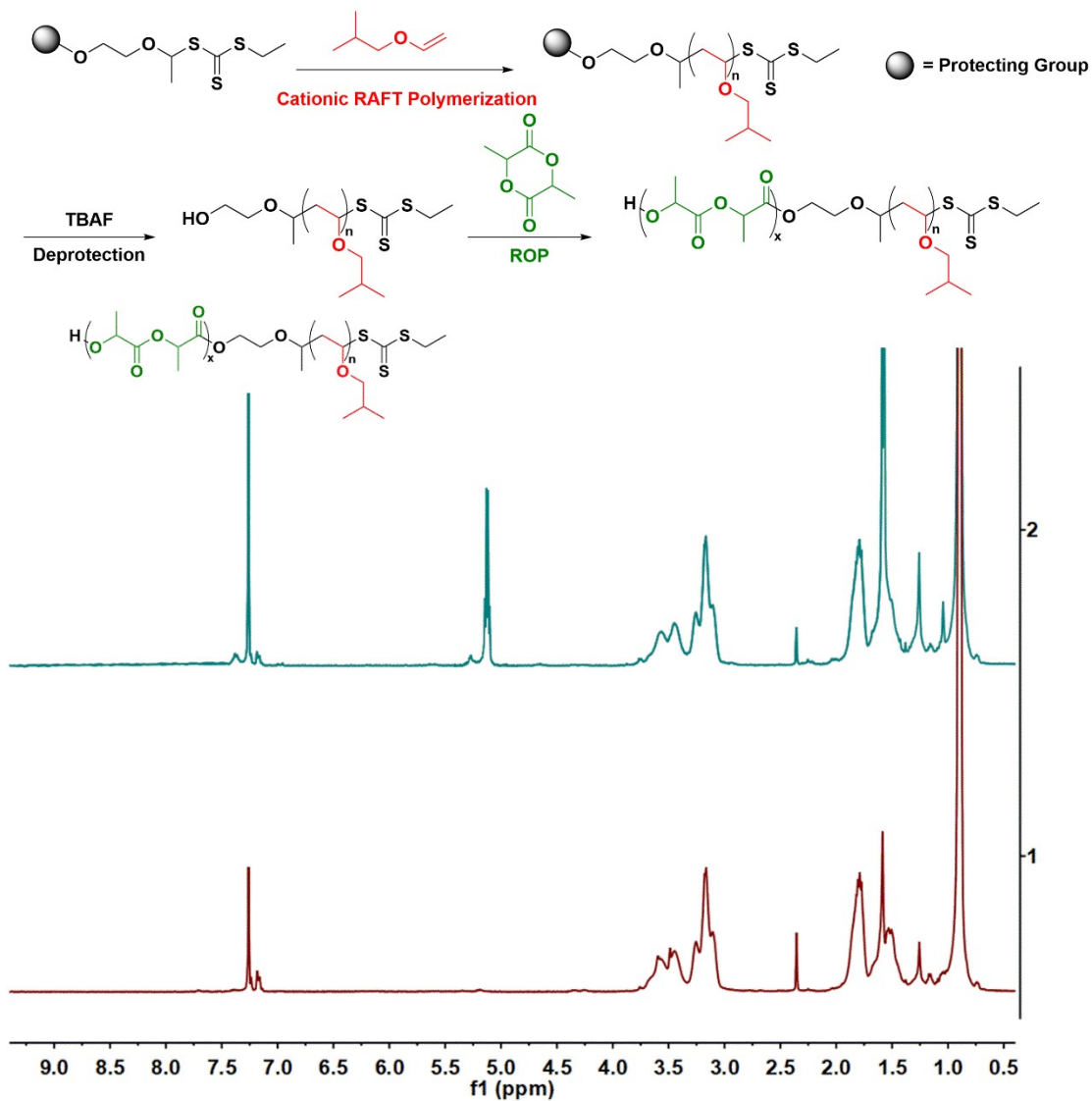


Figure S13. Merging of cationic RAFT polymerization and ring-opening polymerization for preparing PIBVE-*b*-PLLA

Radical RAFT → Deprotection → ROP

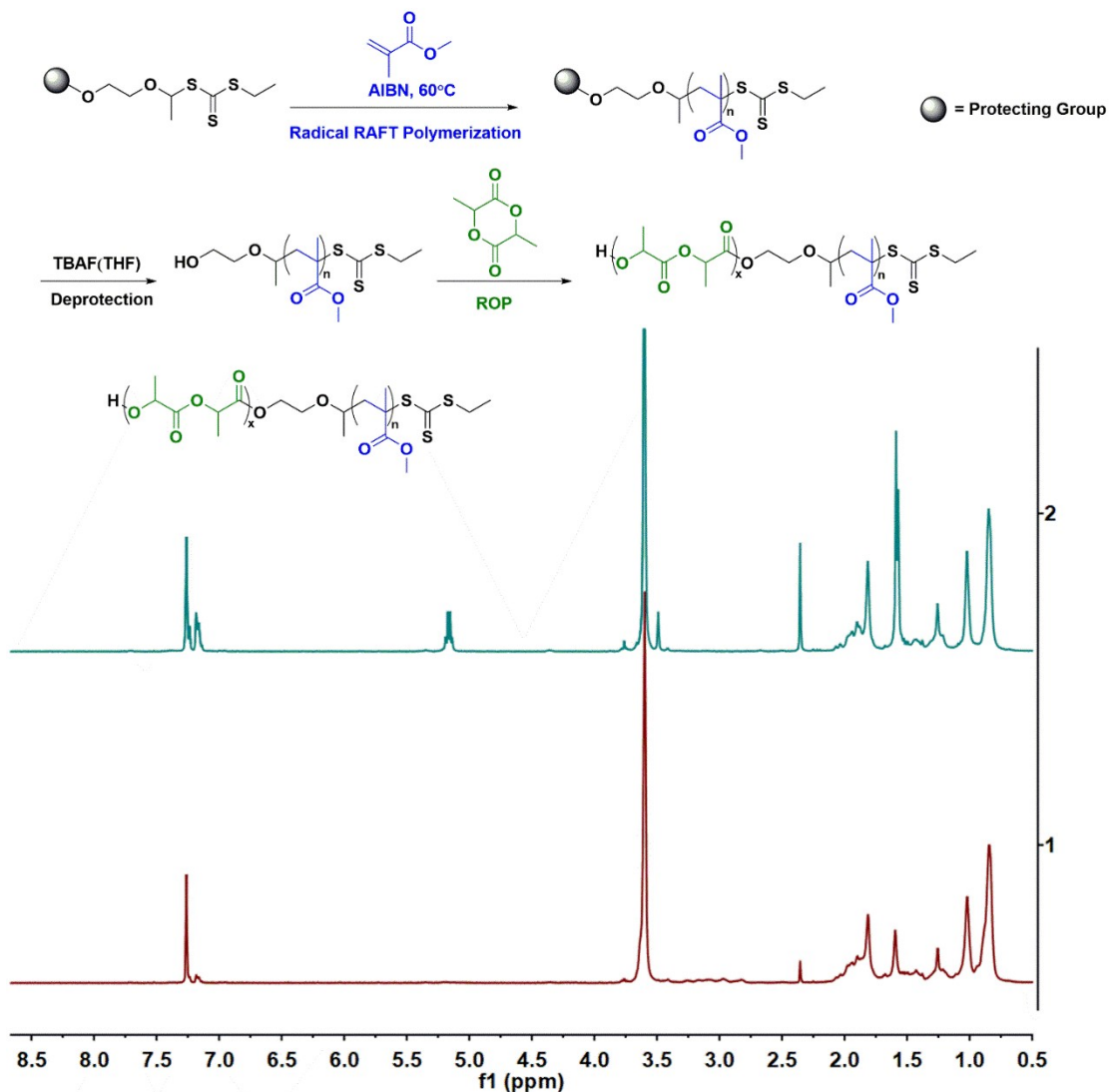


Figure S14. Merging of radical RAFT polymerization ($M_{n,NMR} = 3.4$, $\mathcal{D} = 1.17$) and ring-opening polymerization for preparing PMMA-*b*-PLLA ($M_{n,NMR} = 7.9$, $\mathcal{D} = 1.24$)

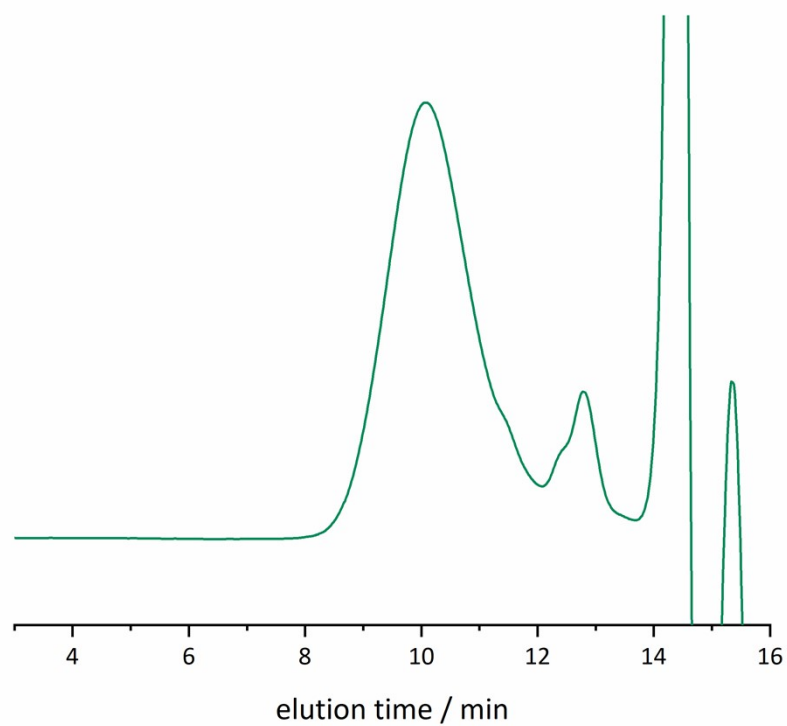


Figure S15. SEC traces of PIBVE

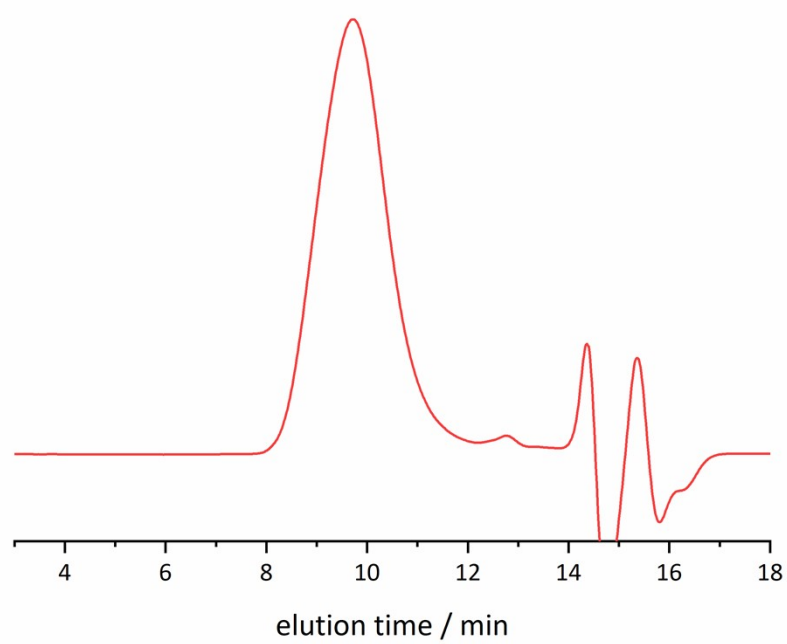


Figure S16. SEC traces of PIBVE-*b*-PMMA

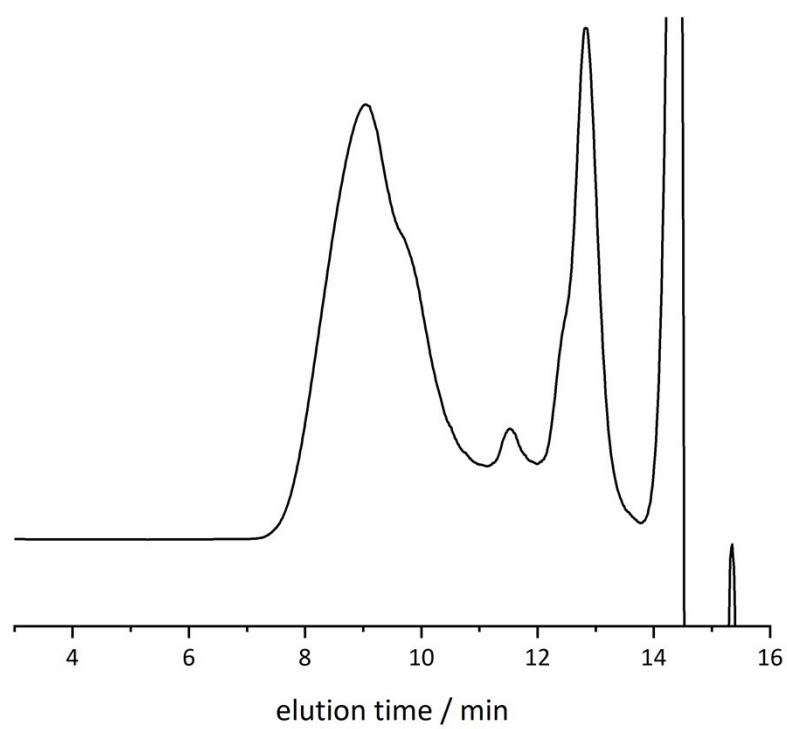


Figure S17. SEC traces of PIBVE-*b*-PMMA-*b*-PVL

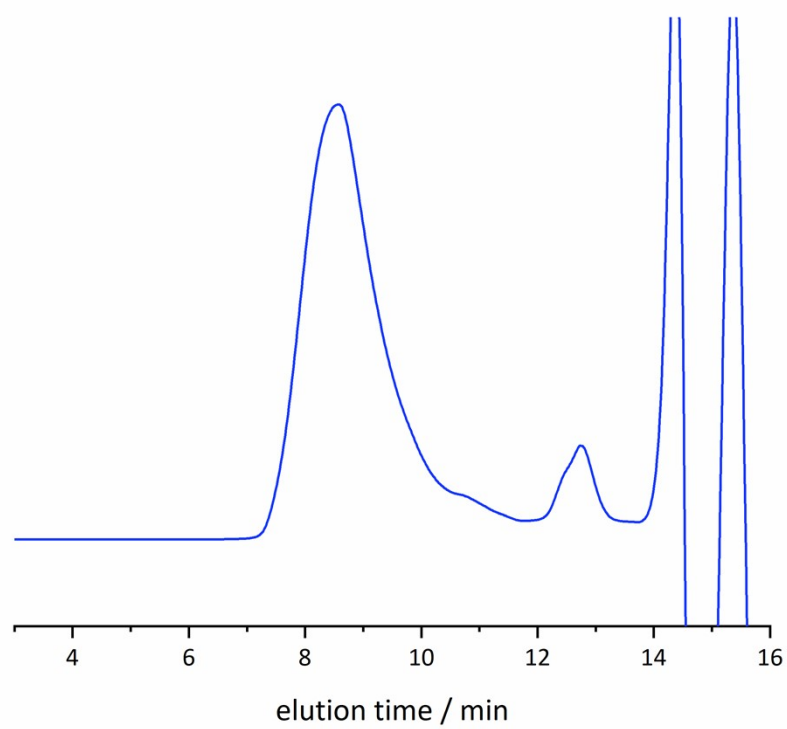


Figure S18. SEC traces of PIBVE-*b*-PMMA-*b*-PVL-*b*-PLA

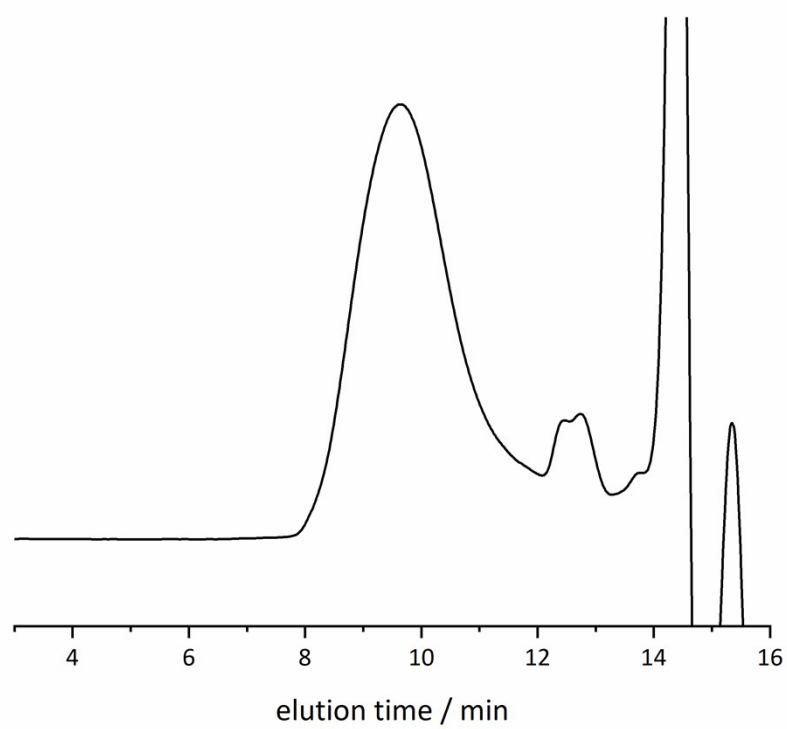


Figure S19. SEC traces of PIBVE-*b*-PLA

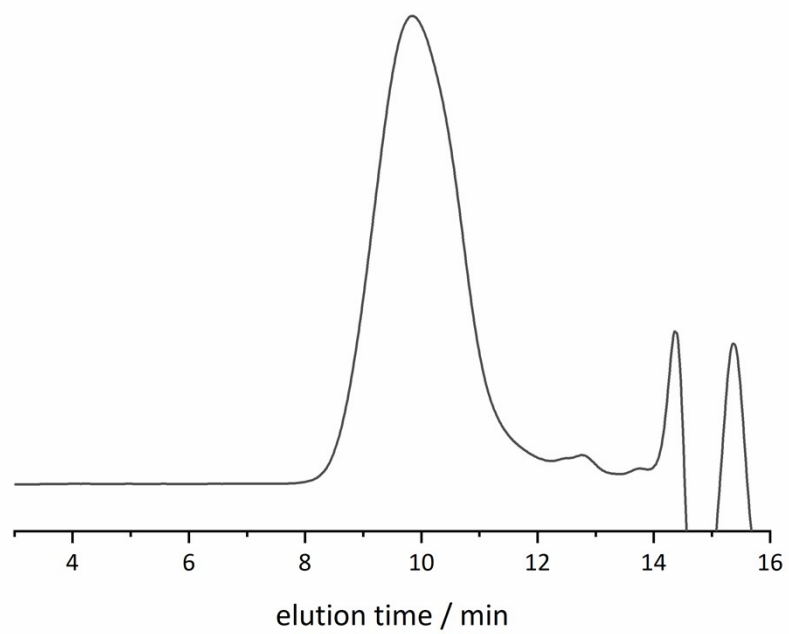


Figure S20. SEC traces of PMMA-*b*-PLA

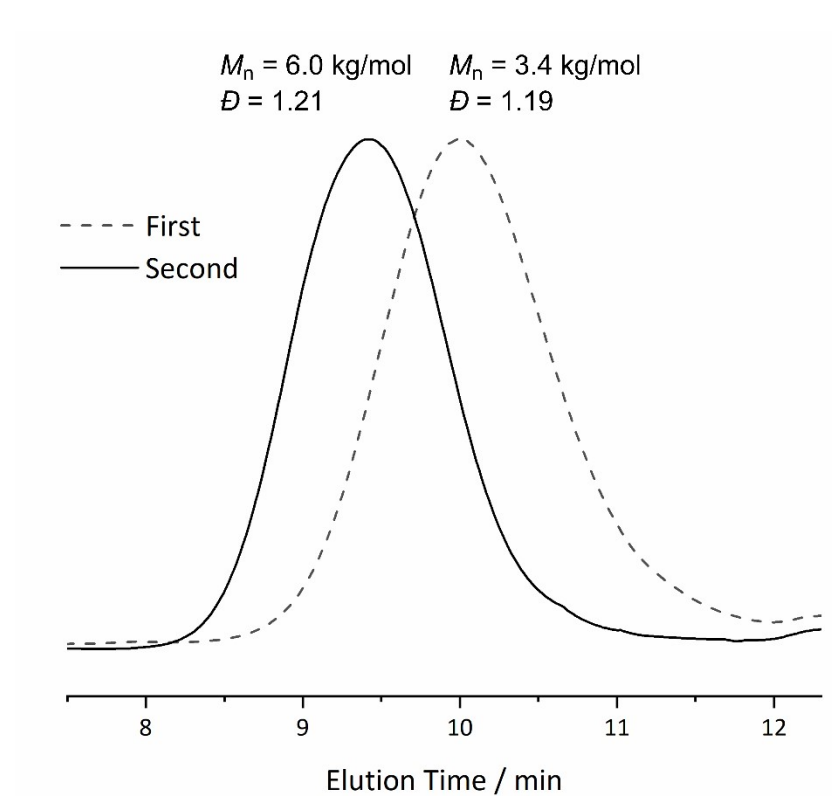


Figure S21. SEC traces of first polylactide and post-polymerization (dashed and solid line respectively) (eluent, THF; flow rate, 0.7 ml min⁻¹).

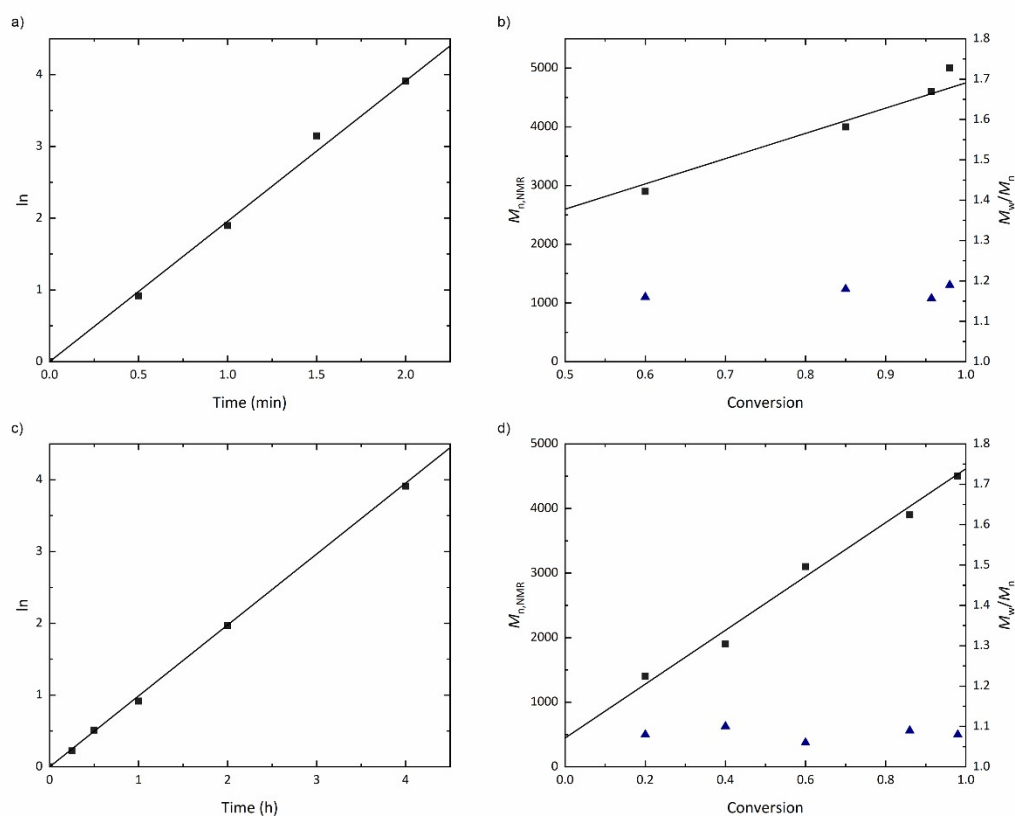


Figure S22 (a) The semi-logarithmic kinetics plot for poly(isobutyl vinyl ether) (PIBVE) ($[IBVE]_0/[RAFT\ agent]_0 = 40/1$, toluene, $-40\ ^\circ C$). (c) The semi-logarithmic kinetics plot for polylactide (PLA) ($[LA]_0/[deprotected\ RAFT\ agent]_0 = 30/1$, toluene, room temperature). (b, d) Plots of molecular weight ($M_{n,NMR}$) and dispersities ($\bar{D}$) versus the monomer conversion.

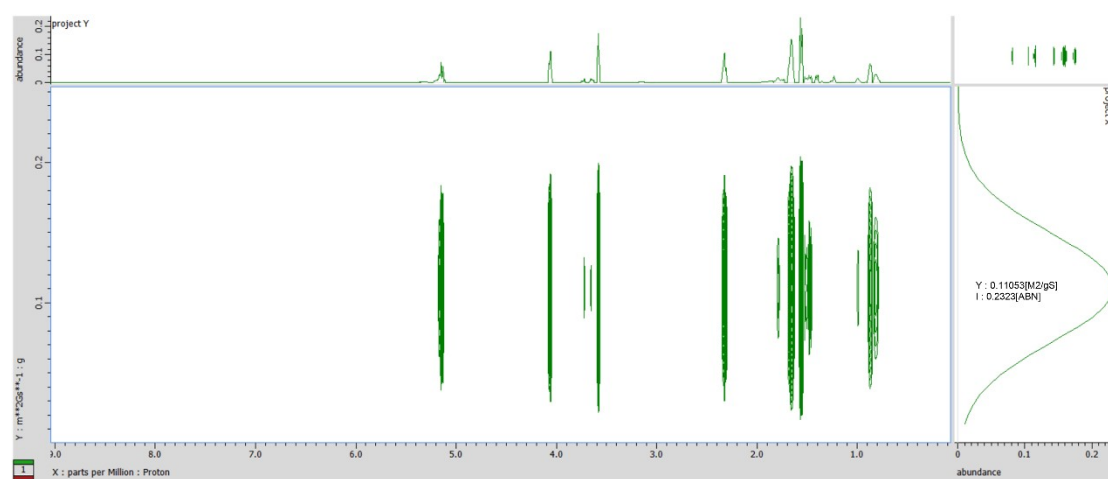
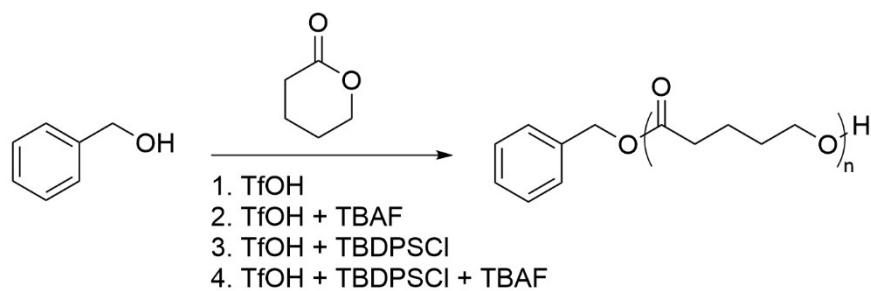


Figure S23. DOSY NMR spectrum (CDCl_3) of PIBVE-*b*-PMMA-*b*-PVL-*b*-PLLA.

Table S1. The effect of TABF and chlorosilane on the ROPs^a



Entry	Additives	$[M]_0/[I]_0/[C]_0/[A]_0$	Conv. ^b (%)	$M_{n,th}^c$ (kg mol ⁻¹)	$M_{n,NMR}^b$ (kg mol ⁻¹)	$M_{n,GPC}^d$ (kg mol ⁻¹)	$\bar{D}^d$
1	-	30/1/1/0	95	3.0	3.1	2.9	1.14
2	TBAF	30/1/2/1	96	3.0	2.8	2.5	1.16
3	TBDPSCI	30/1/1/1	96	3.0	3.0	2.9	1.09
4	TBAF and TBDPSCI	30/1/2/1/1	96	3.0	3.0	2.9	1.15

^a Reaction conditions: benzylalcohol (I, 1 equiv), VL (M, 30 equiv), 4 hours; ring-opening polymerizations processed in toluene at room temperature. ^b Determined by ¹H NMR in CDCl₃. ^c Calculated from $([M]_0/[I]_0) \times \text{conv.} \times (M_w \text{ of M}) + (M_w \text{ of I})$. Theoretical molecular weight (full conversions) of PVL is about 3.1 kg mol⁻¹. ^d Determined by GPC in THF using PSt Standards and correction factors.