Electronic Supplementary Material (ESI) for Polymer Chemistry.

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

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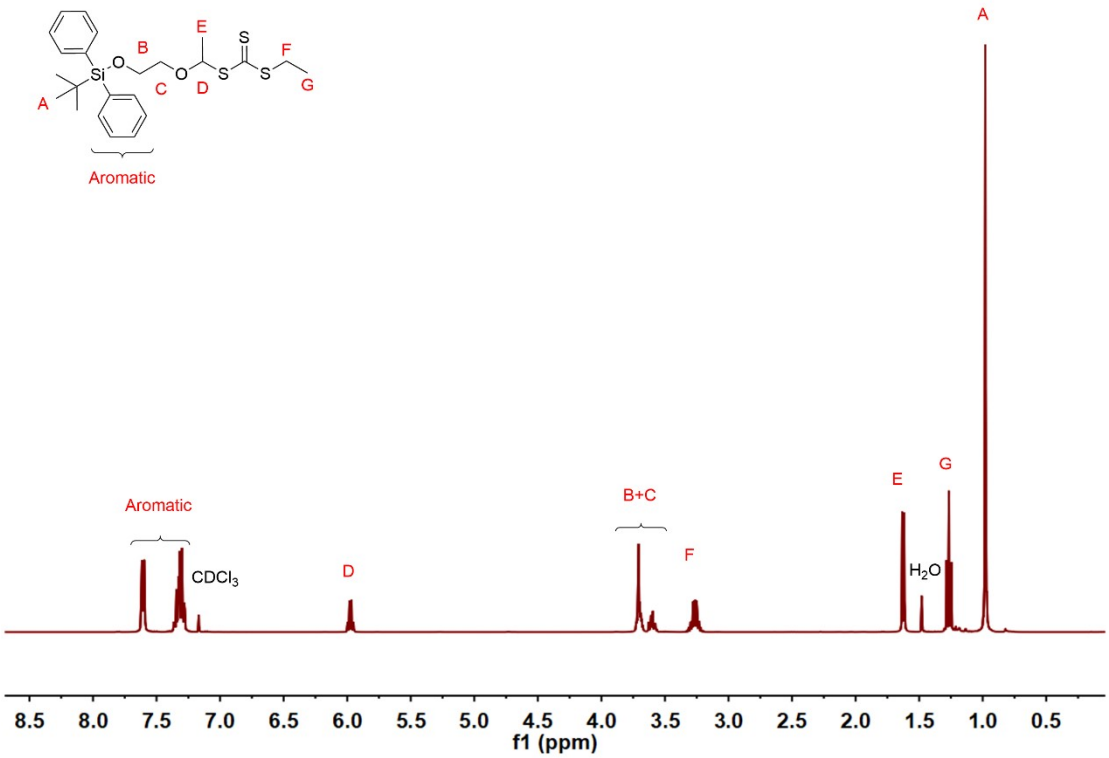


Figure S1. ^{1}H NMR spectrum (DMSO, 400 MHz) of PTRA

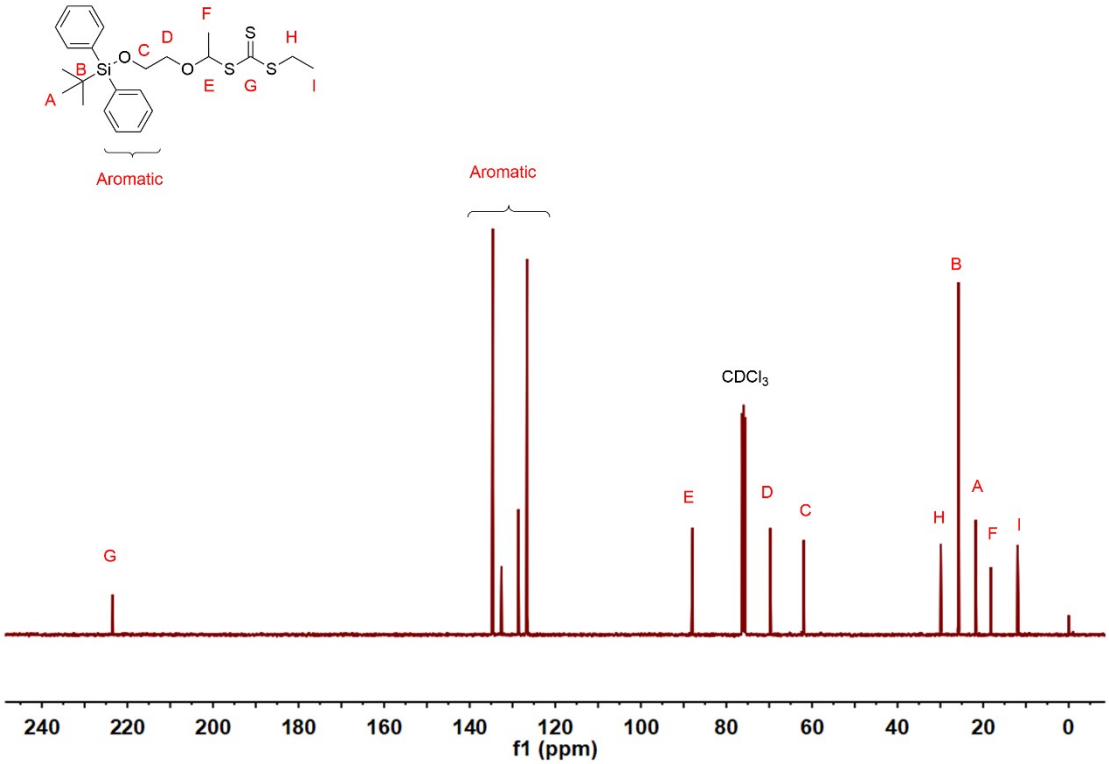


Figure S2. ^{13}C NMR spectrum (DMSO, 100 MHz) of PTRA

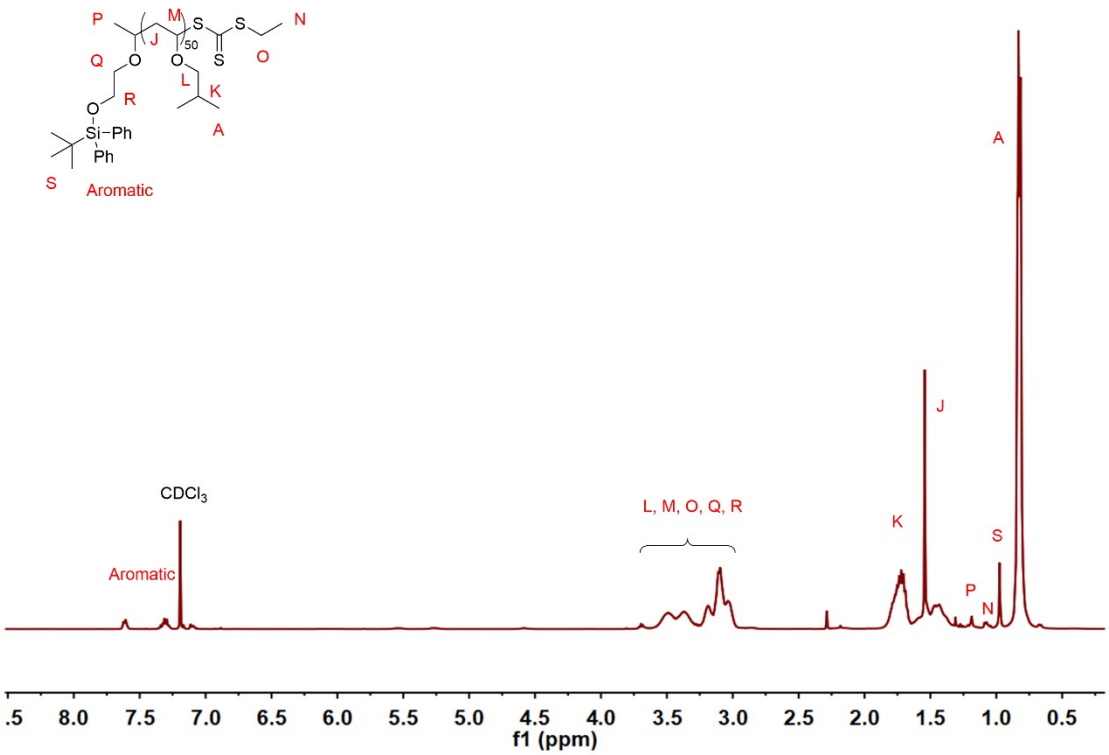


Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of PIBVE

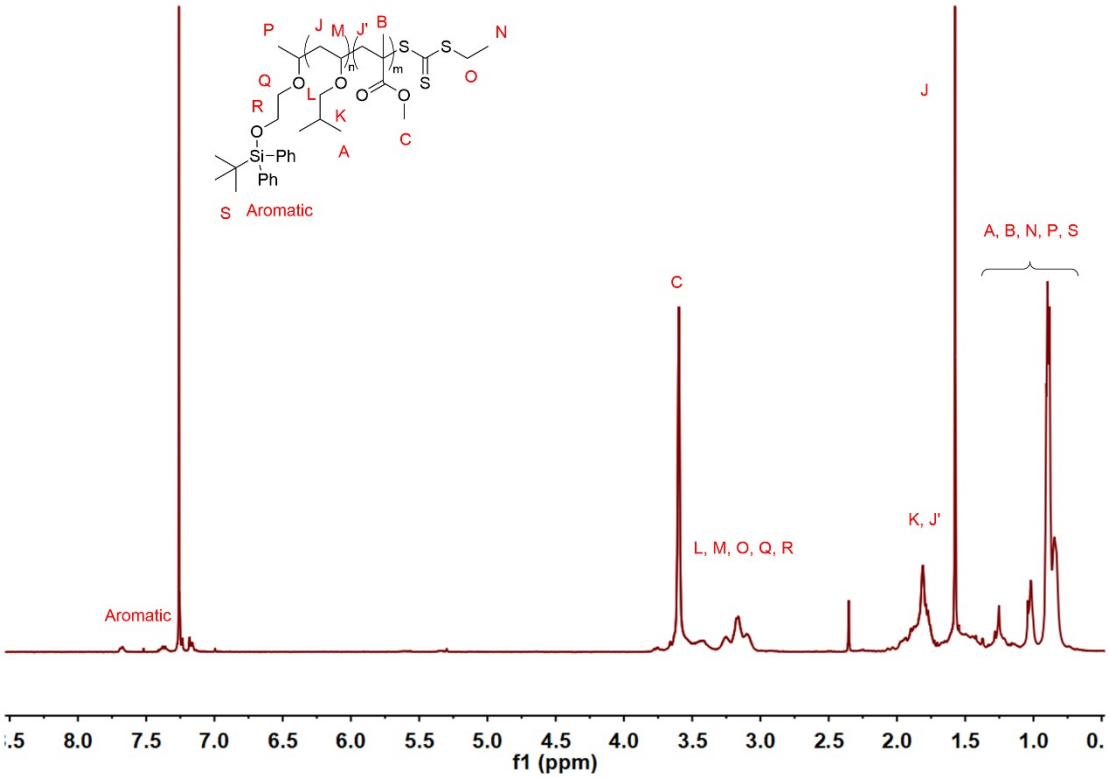


Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of PIBVE-*b*-PMMA

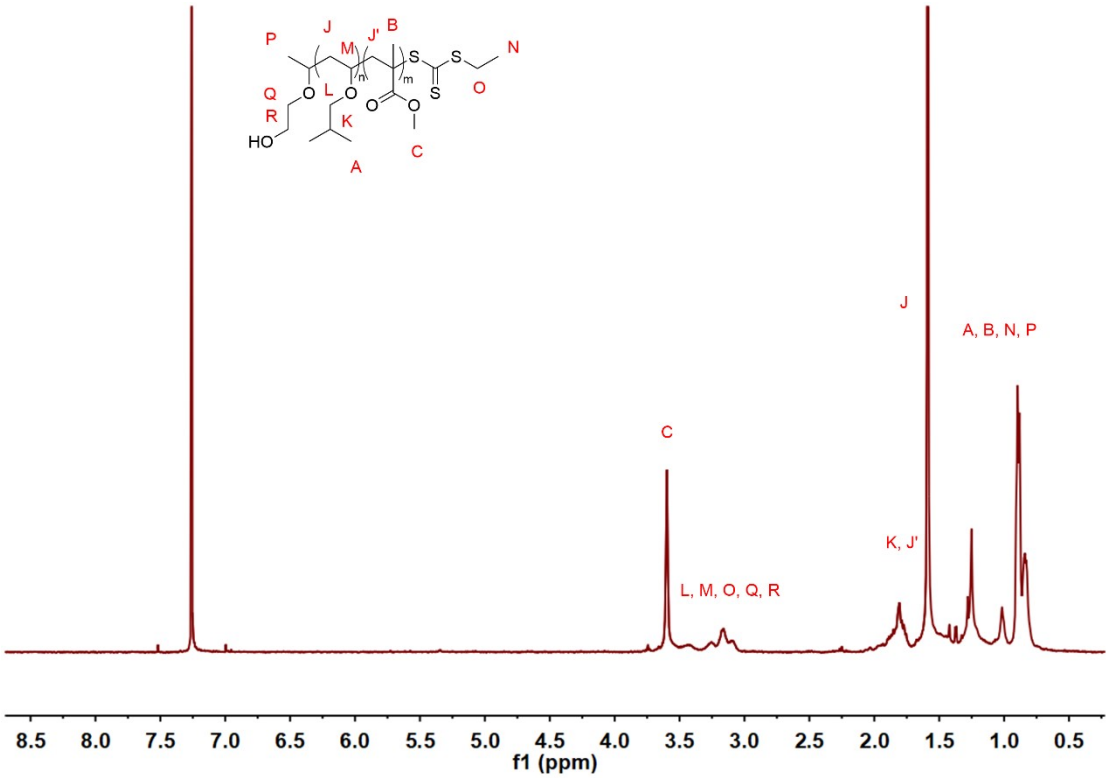


Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of deprotected PIBVE-*b*-PMMA

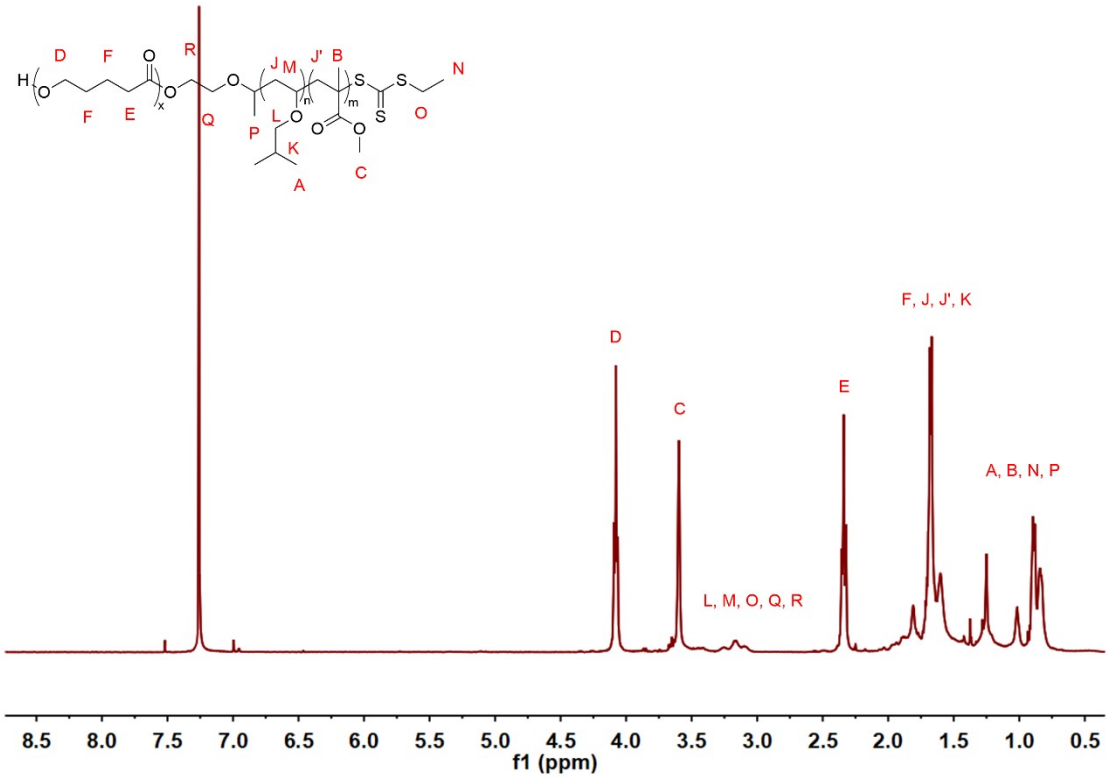


Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of PIBVE-*b*-PMMA-*b*-PVL

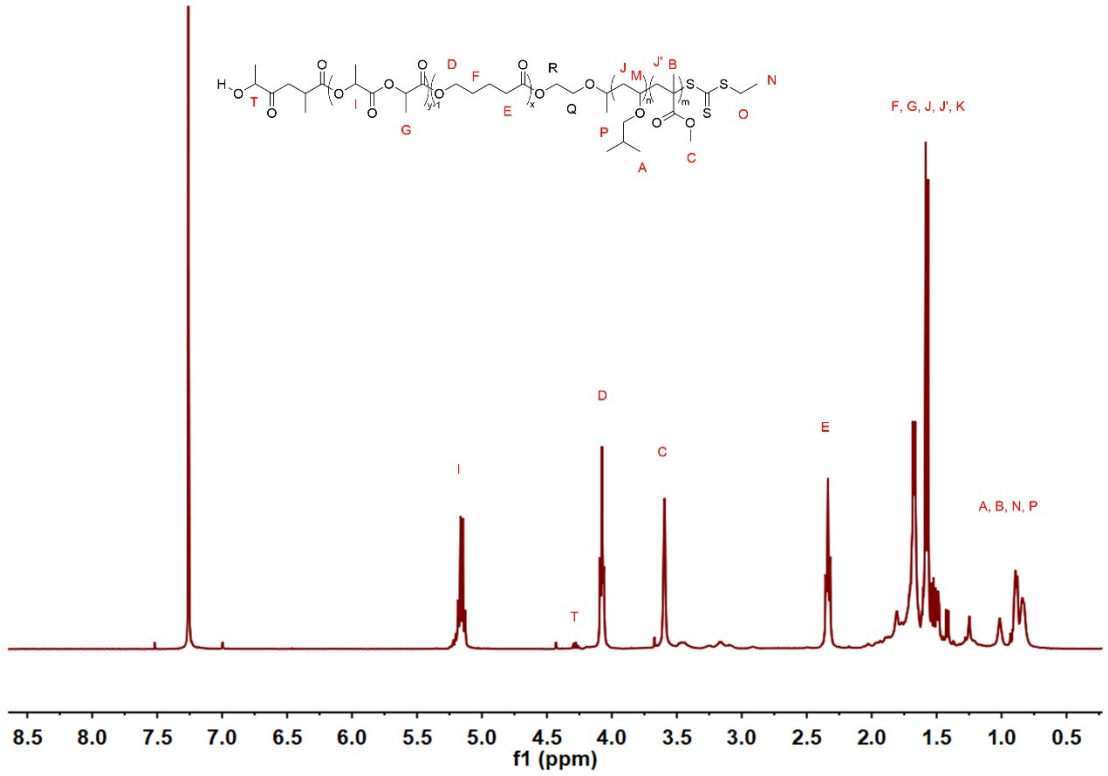


Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of PIBVE-*b*-PMMA-*b*-PVL-*b*-PLLA

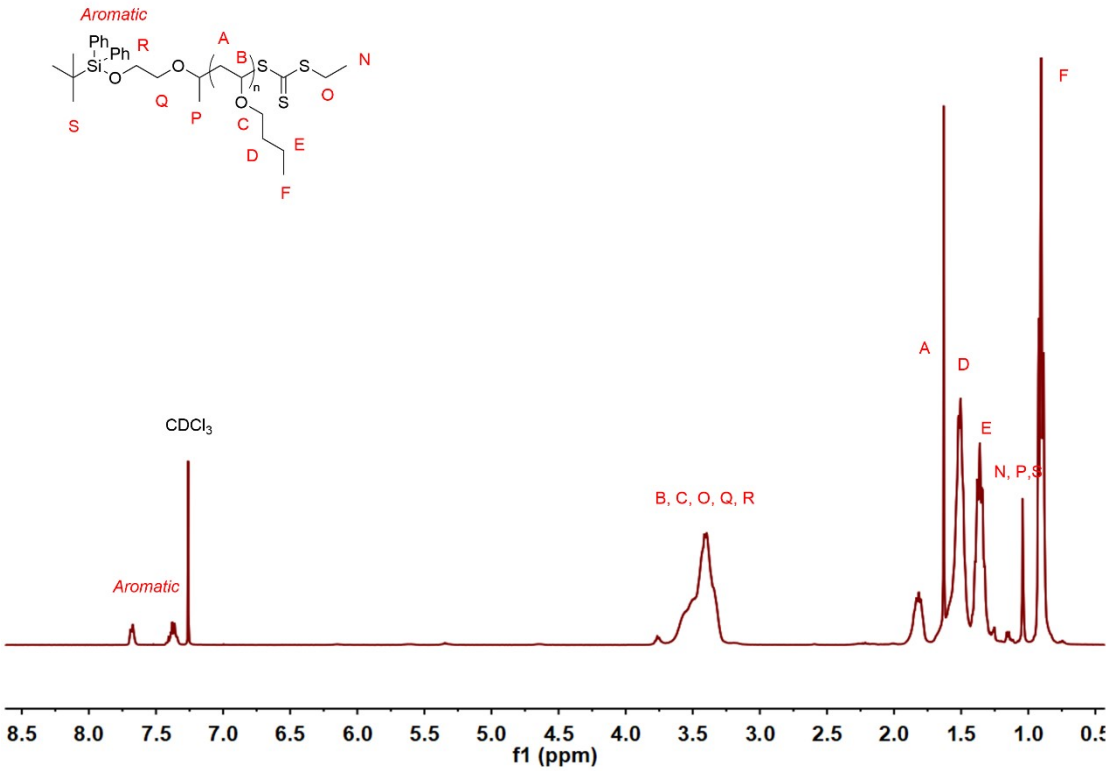


Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of PBVE

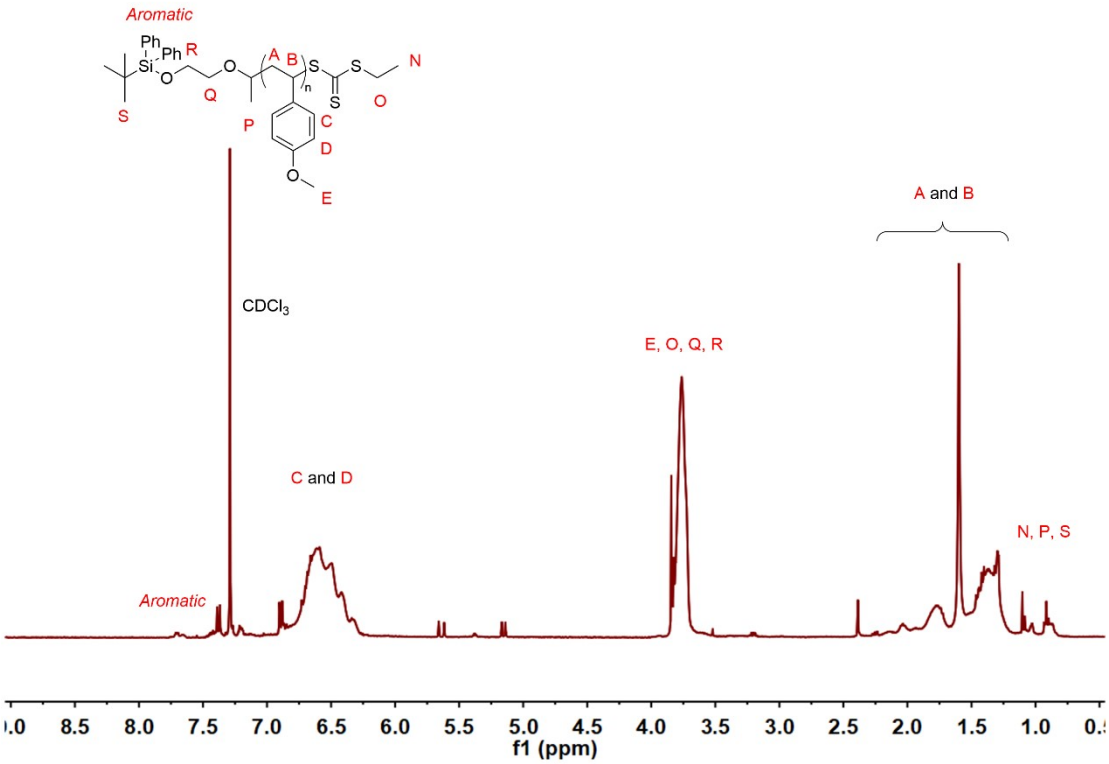


Figure S9. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of poly(4-methoxystyrene)

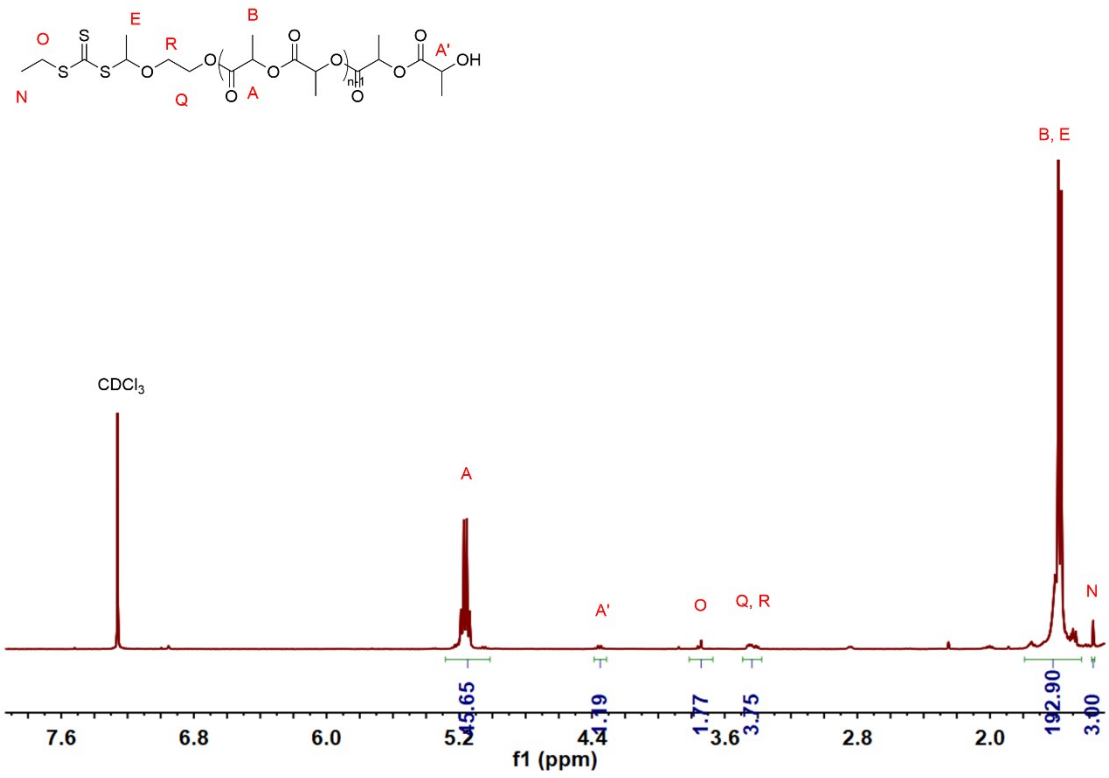


Figure S10. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of PLA.

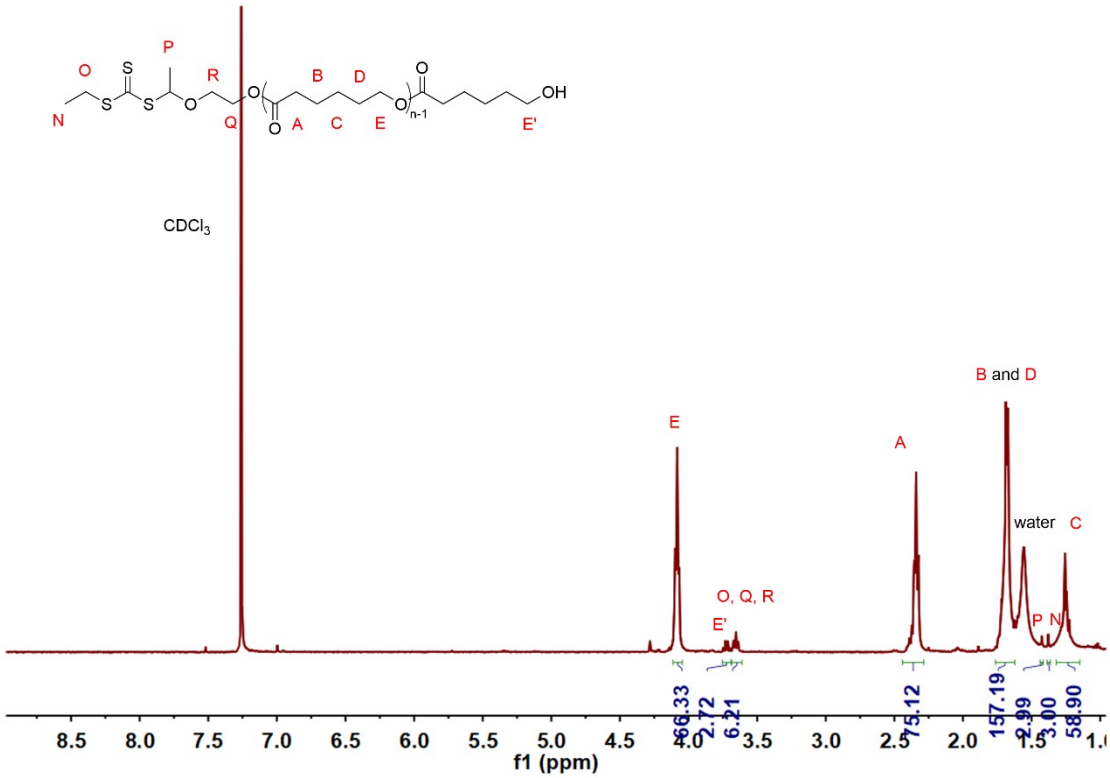


Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of PCL.

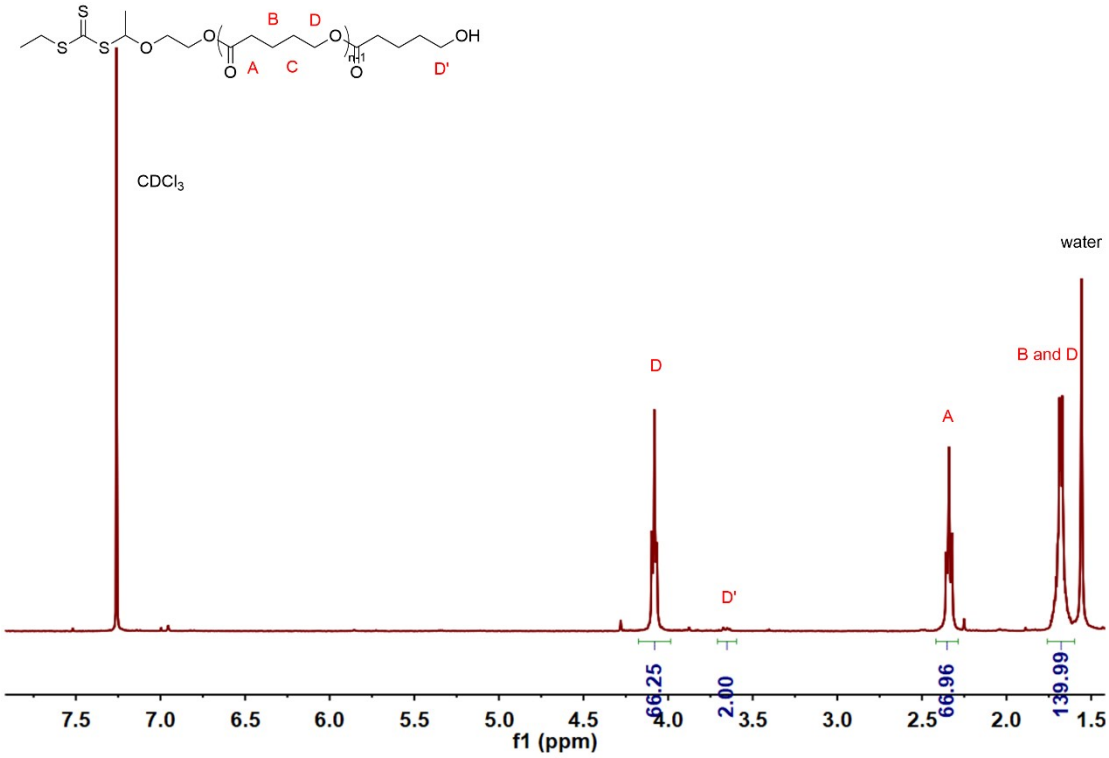


Figure S12. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of PVL.

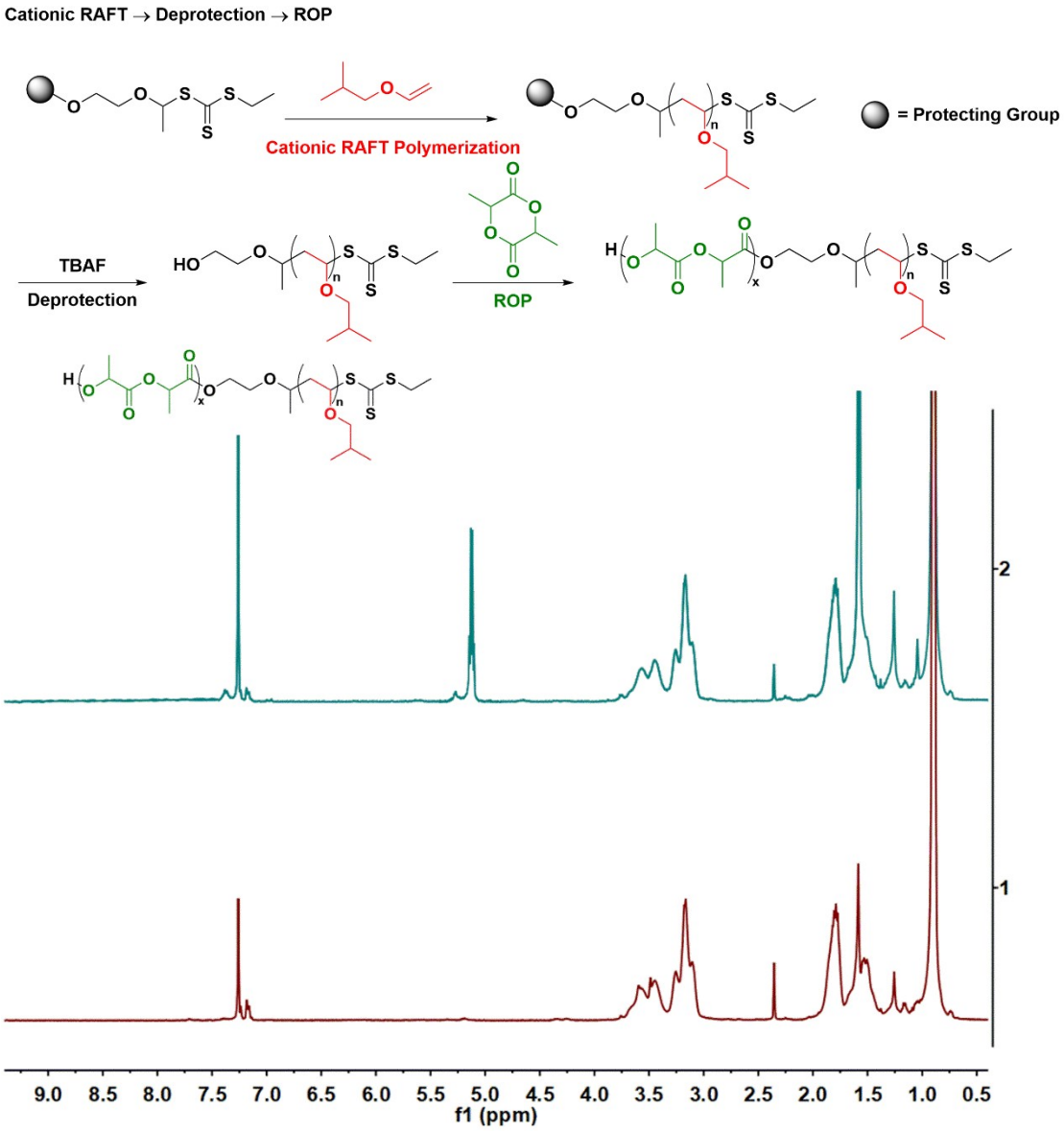


Figure S13. Merging of cationic RAFT polymerization and ring-opening polymerization for preparing PIBVE-*b*-PLLA

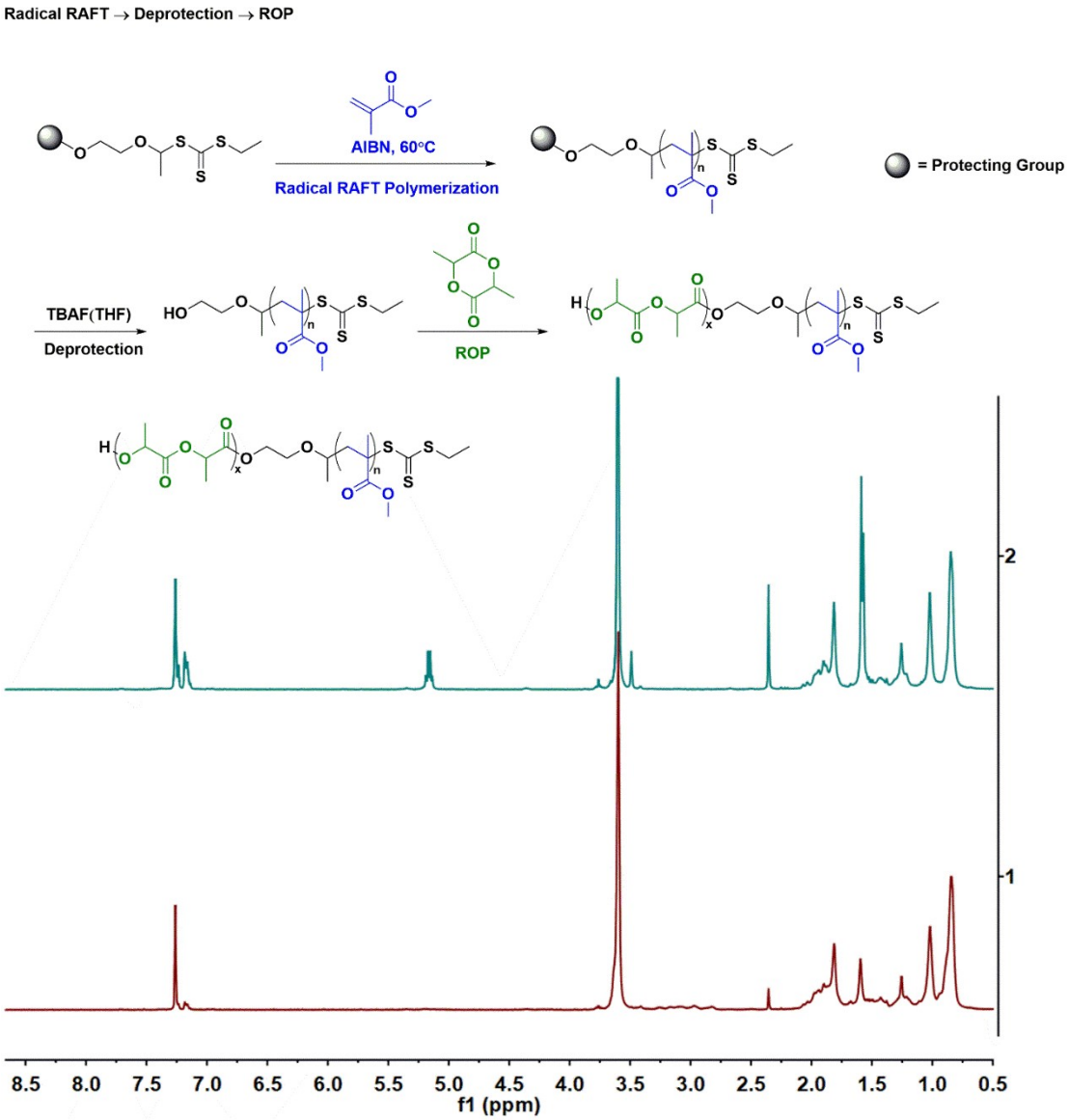


Figure S14. Merging of radical RAFT polymerization ($M_{n,NMR}$ = 3.4, $Đ$ = 1.17) and ring-opening polymerization for preparing PMMA-*b*-PLLA ($M_{n,NMR}$ = 7.9, $Đ$ = 1.24)

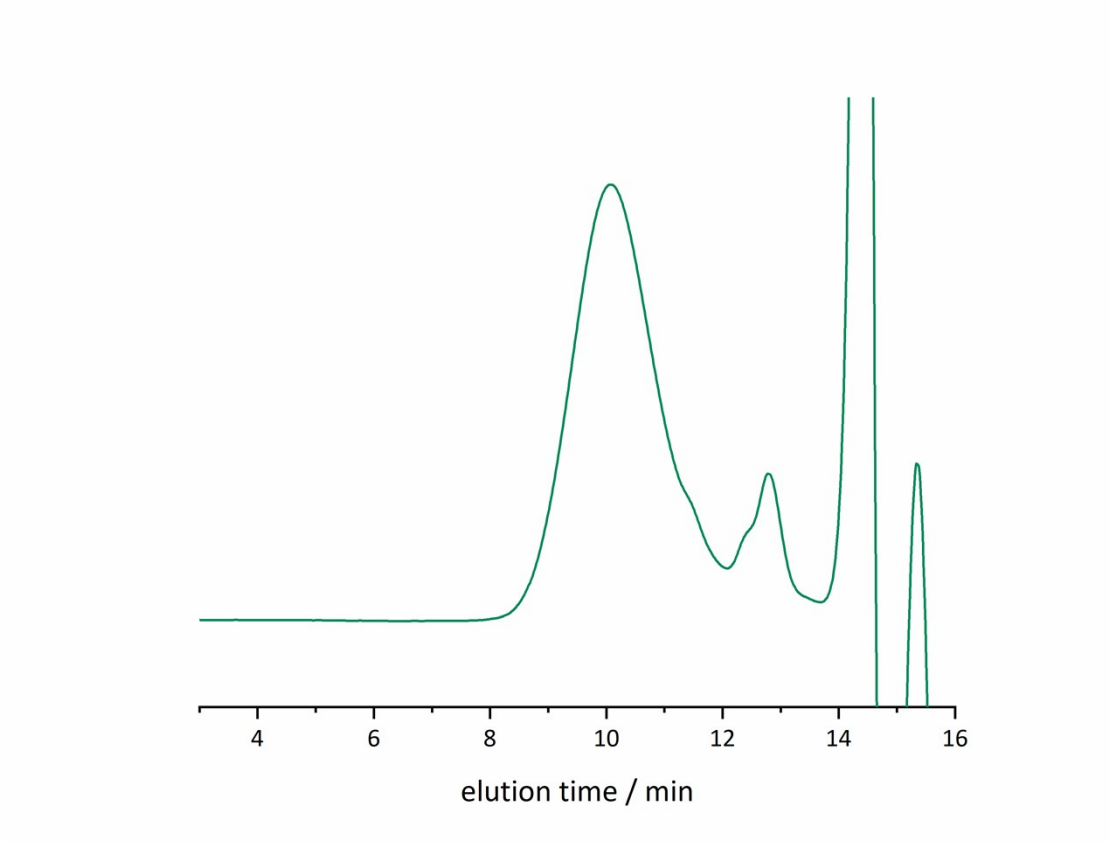


Figure S15. SEC traces of PIBVE

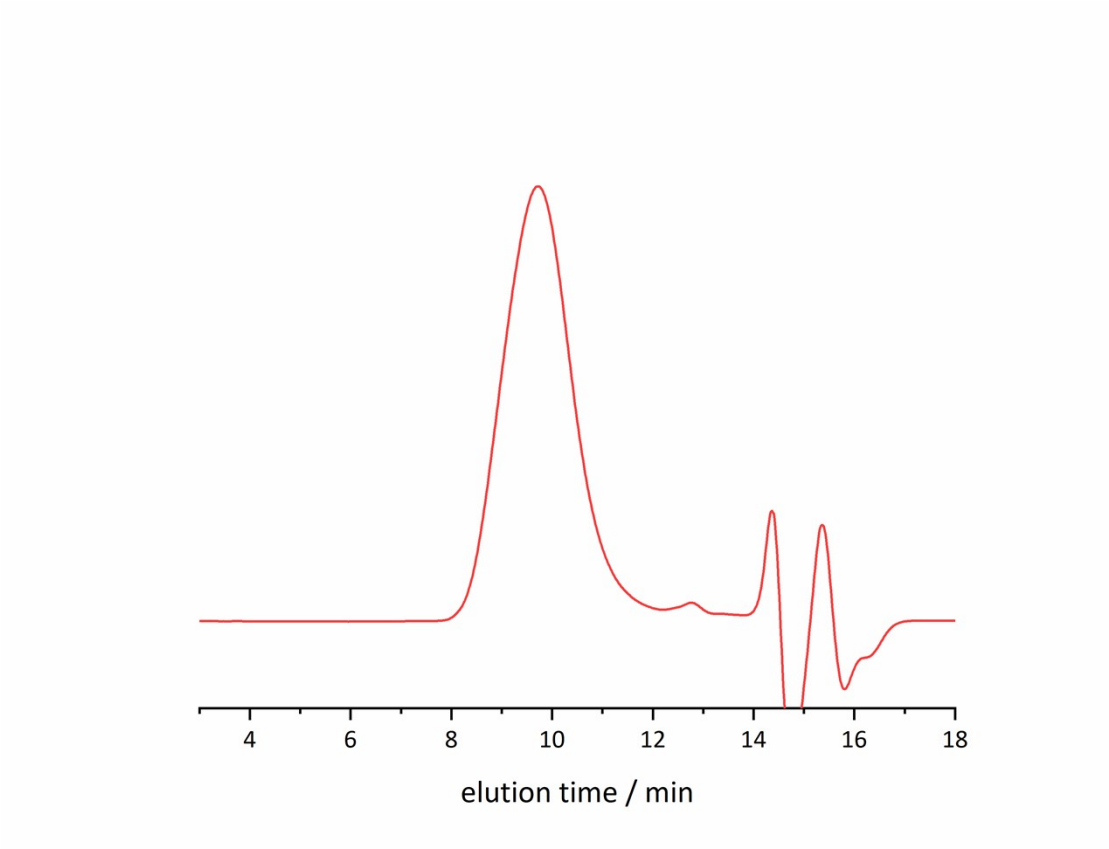


Figure S16. SEC traces of PIBVE-*b*-PMMA

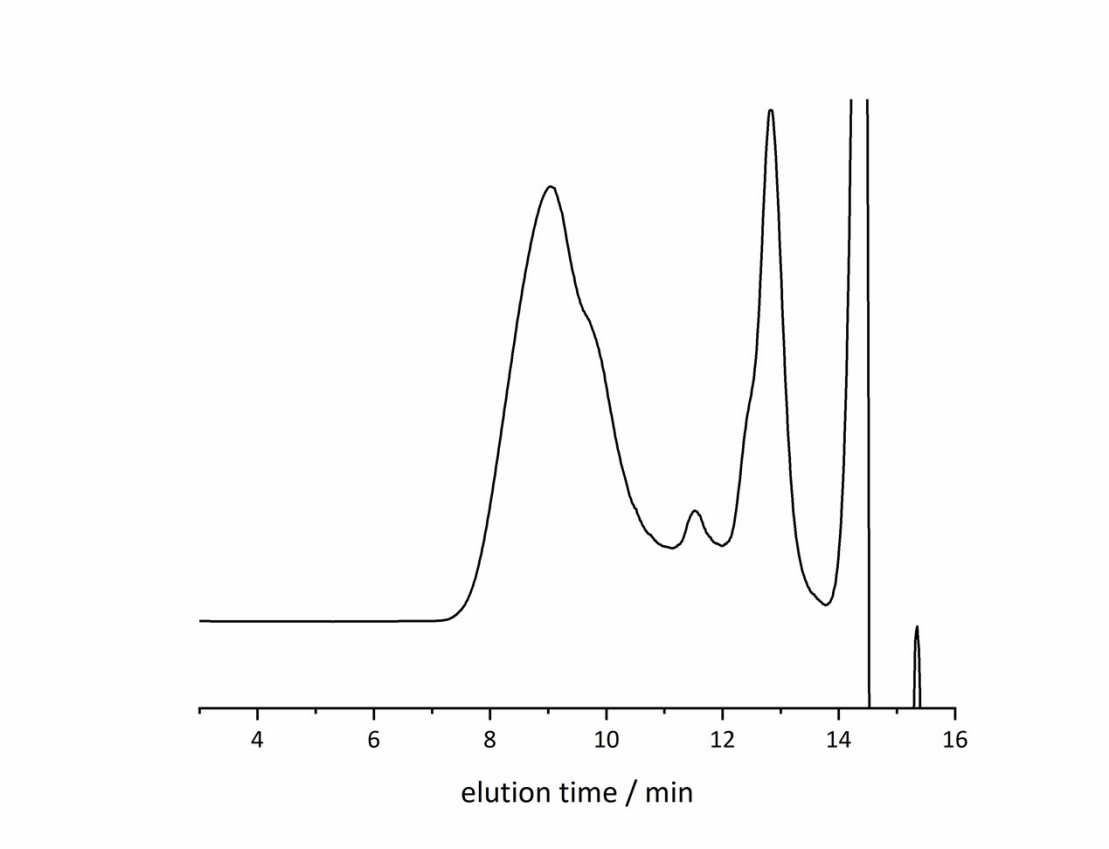


Figure S17. SEC traces of PIBVE-*b*-PMMA-*b*-PVL

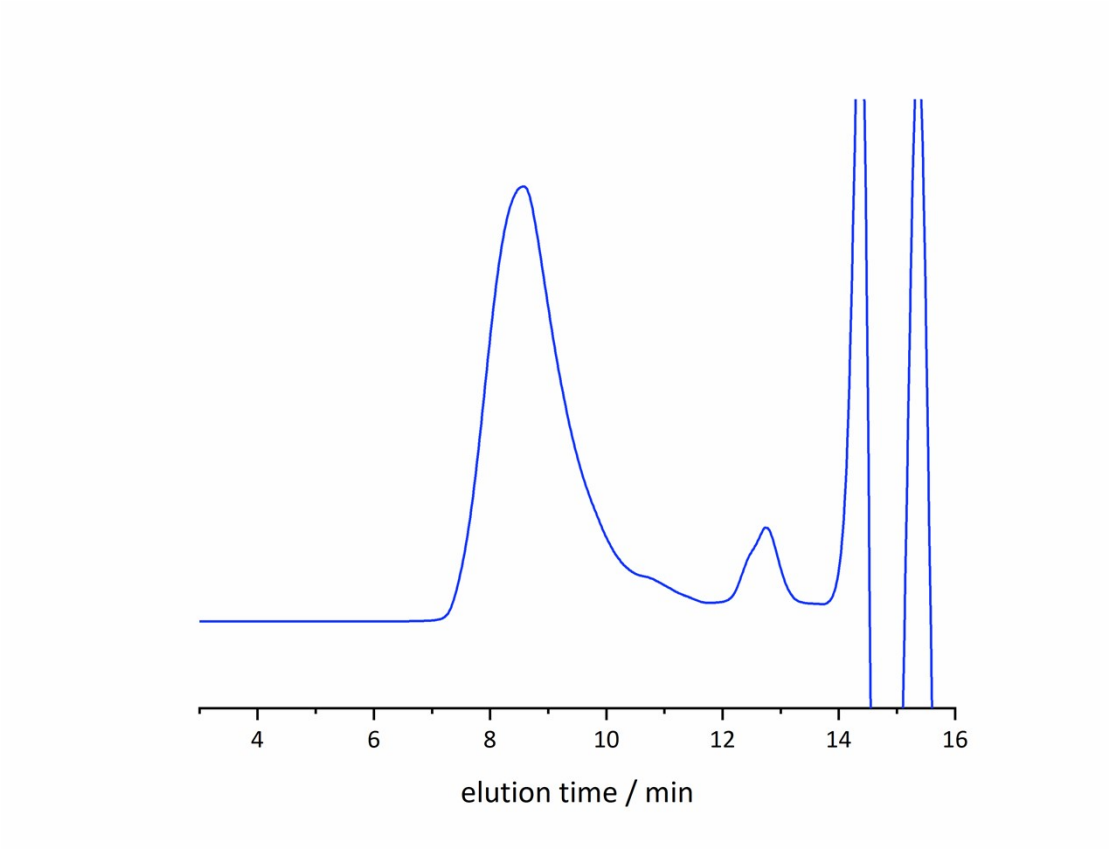


Figure S18. SEC traces of PIBVE-*b*-PMMA-*b*-PVL-*b*-PLA

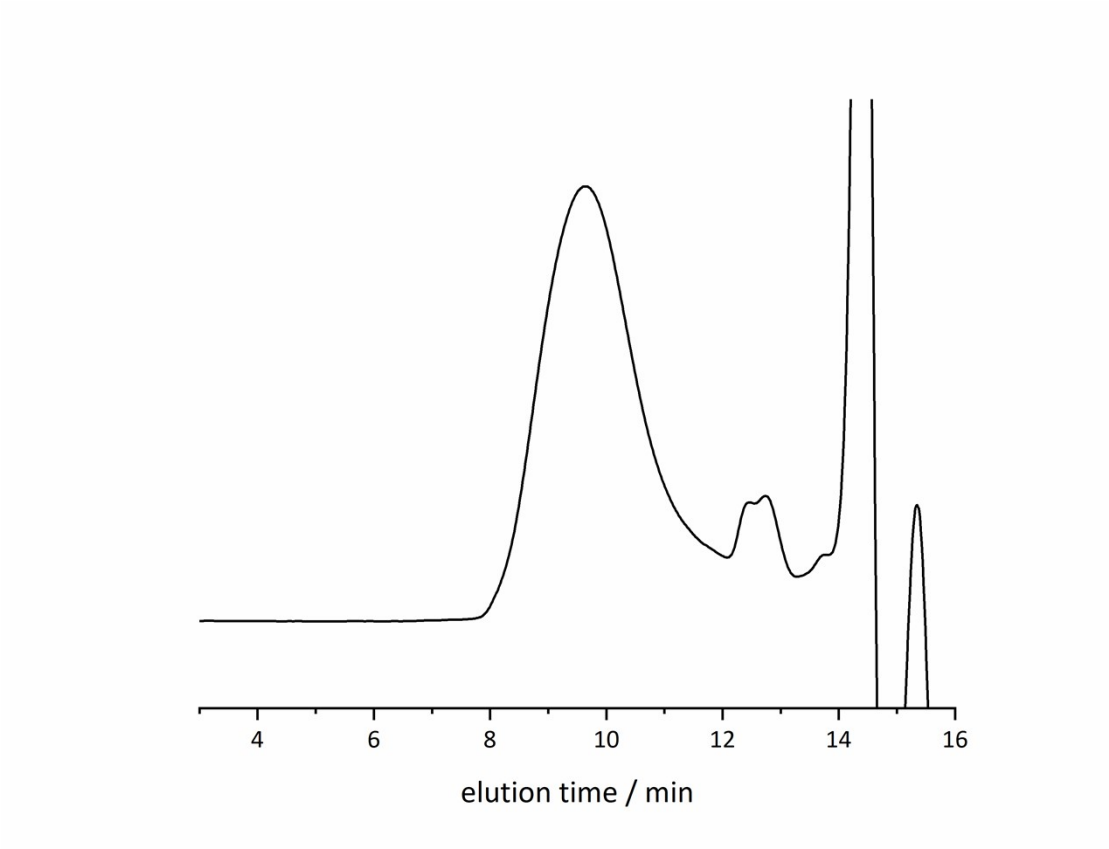


Figure S19. SEC traces of PIBVE-*b*-PLA

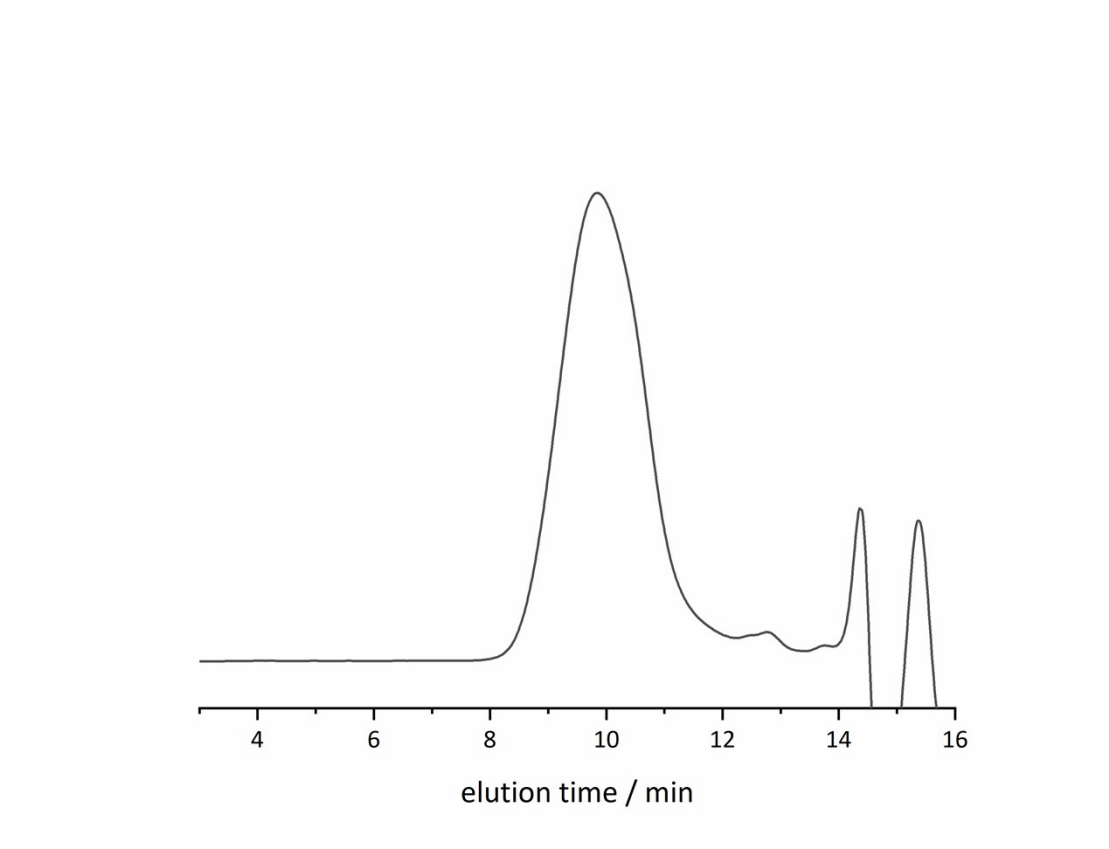


Figure S20. SEC traces of PMMA-*b*-PLA

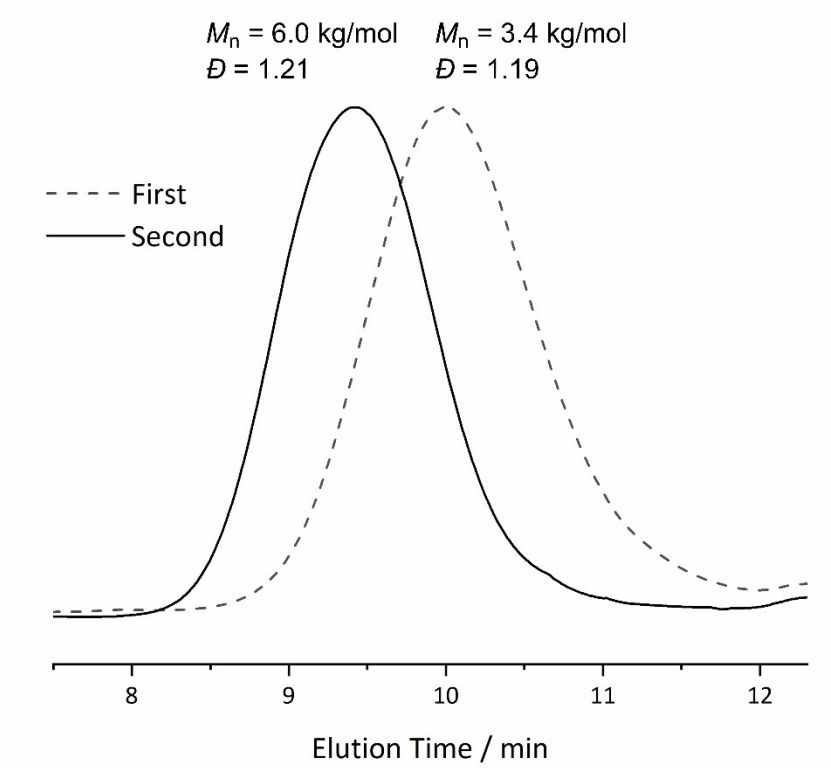


Figure S21. SEC traces of first polylactide and post-polymerization (dashed and solid line respectively) (eluent, THF; flow rate, 0.7 ml min^{-1}).

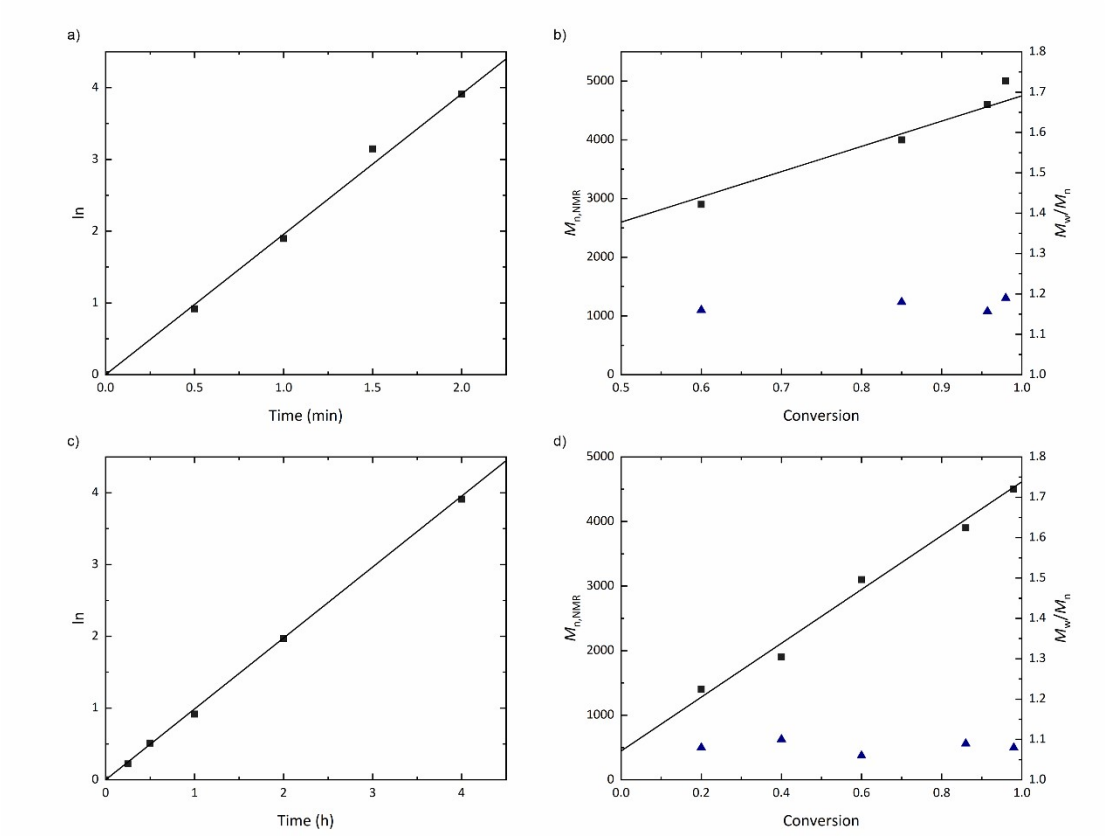


Figure S22 (a) The semi-logarithmic kinetics plot for poly(isobutyl vinyl ether) (PIBVE) ($[IBVE]_0/[RAFT\ agent]_0$ = 40/1, toluene, -40 °C). (c) The semi-logarithmic kinetics plot for polylactide (PLA) ($[LA]_0/[deprotected\ RAFT\ agent]_0$ = 30/1, toluene, room temperature). (b, d) Plots of molecular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

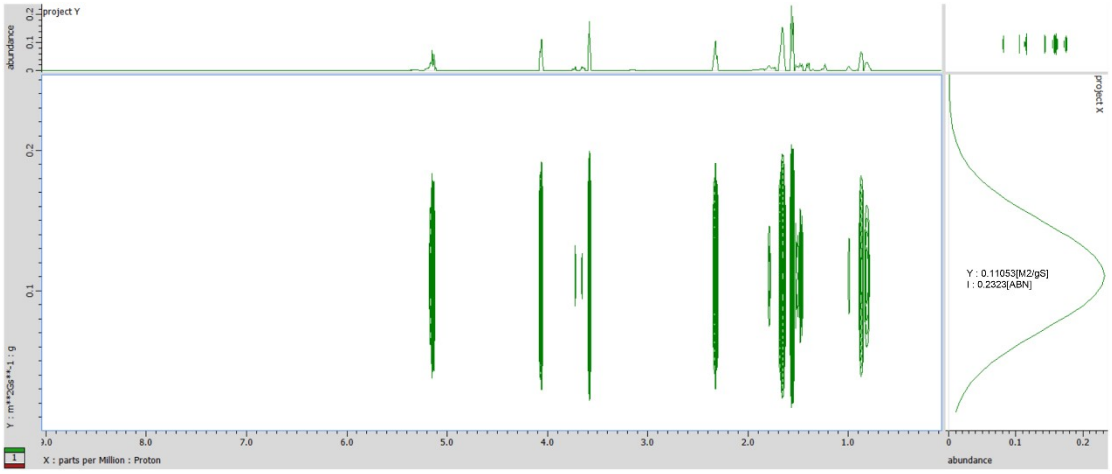
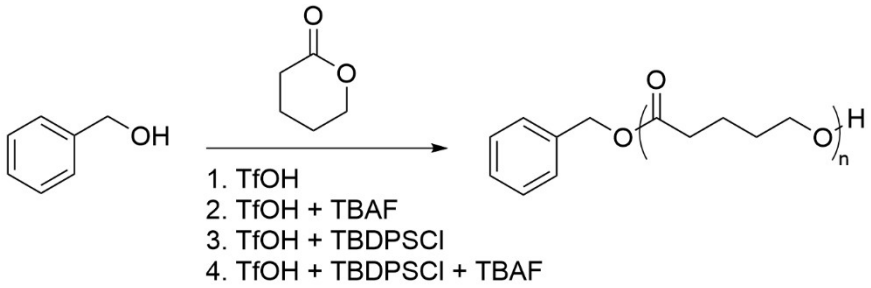


Figure S23. DOSY NMR spectrum ($CDCl_3$) of PIBVE-*b*-PMMA-*b*-PVL-*b*-PLLA.

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})	$Đ$[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	TBDPSCl	30/1/1/1	96	3.0	3.0	2.9	1.09
4	TBAF and TBDPSCl	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 ^{1}H NMR in $CDCl_3$. [c] Calculated from $([M]_0/[I]_0) \times$ conv. $\times$ (M_W of M) + (M_W 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.