

Supporting Information

Manganese carbonyl induced reversible addition-fragmentation chain transfer (RAFT) polymerization under visible light

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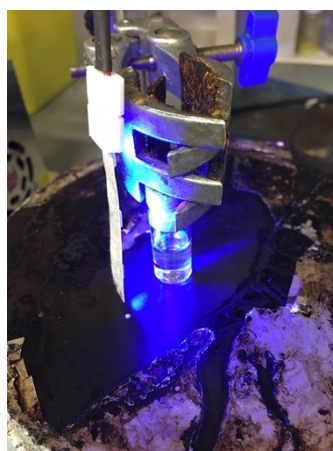


Figure S1. Photograph of the 460 nm blue LED photoreactor.

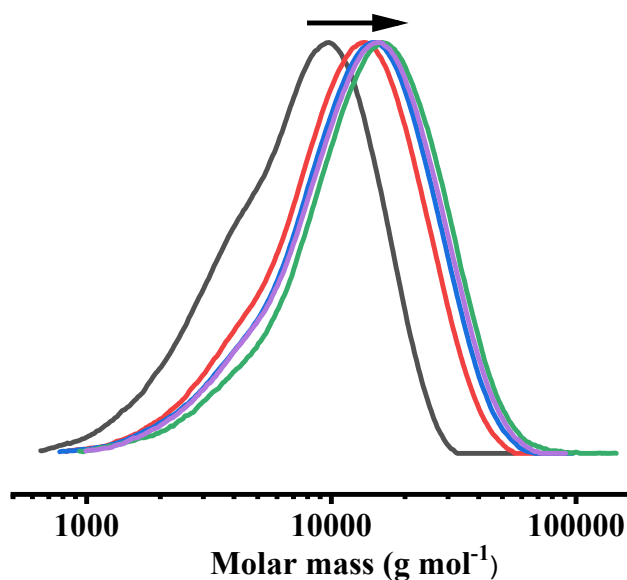


Figure S2. SEC traces for kinetic experiments of polymerization of IBVE in bulk with the molar ratio $[\text{IBVE}]_0 : [2\text{a}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 100 : 1 : 0.1 : 0.1$ at 25 °C.

Table S1. Controlled experiments for polymerization of IBVE with different conditions.

Entry	$[\text{IBVE}]_0 : [2\text{a}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0$	Time (min)	Conv.%	^a $M_{n,\text{th}}$ (g/mol)	^b $M_{n,\text{SEC}}$ (g/mol)	\bar{D}
1	100 : 1 : 0 : 0.1	5 h	-	-	-	-
2	100 : 1 : 0.1 : 0	5 h	-	-	-	-
3	100 : 0 : 0.1 : 0.1	20 min	70.8	71000	44600	1.51
^c 4	100 : 1 : 0.1 : 0.1	5 h	-	-	-	-
^d 5	100 : 1 : 0.1 : 0.1	100 min	75.7	7800	25300	1.74

a) Calculated based on conversion ($M_{n,\text{th}} = [\text{M}]_0/[\text{EBP}]_0 \times \text{conversion} \times \text{MW}_{\text{M}} + M_{\text{EBP}}$); b) Determined by SEC using polystyrene (PS) as standard in THF; c)

In the dark; d) Polymerization in the dark after 20 min irradiation of blue LED.

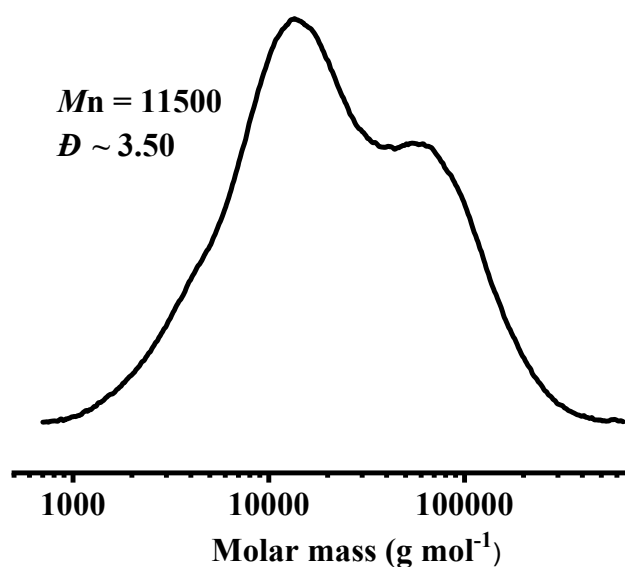


Figure S3. SEC trace for polymerization of IBVE in bulk with the molar ratio $[\text{IBVE}]_0 : [2b]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 100 : 1 : 0.1 : 0.1$ at $25\text{ }^\circ\text{C}$.

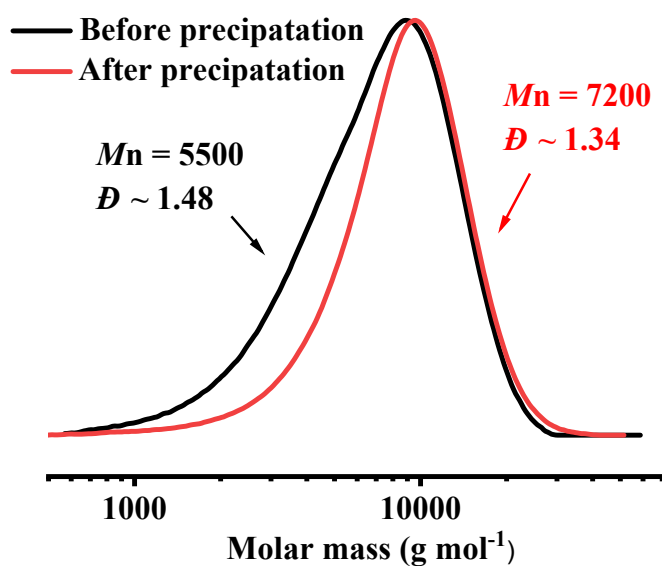


Figure S4. SEC trace for polymerization of IBVE in ethyl acetate with the molar ratio $[\text{IBVE}]_0 : [2b]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 50 : 1 : 0.1 : 0.1$ at $25\text{ }^\circ\text{C}$.

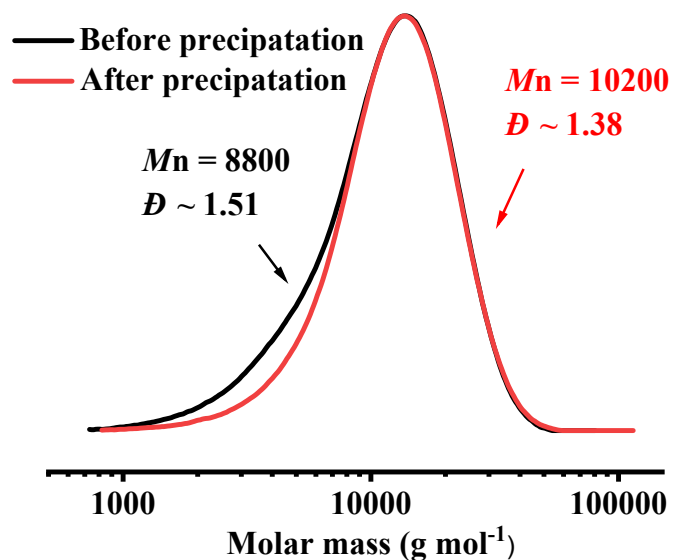


Figure S5. SEC trace for polymerization of IBVE in ethyl acetate with the molar ratio

$[\text{IBVE}]_0 : [\text{2b}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 100 : 1 : 0.1 : 0.1$ at 25 °C.

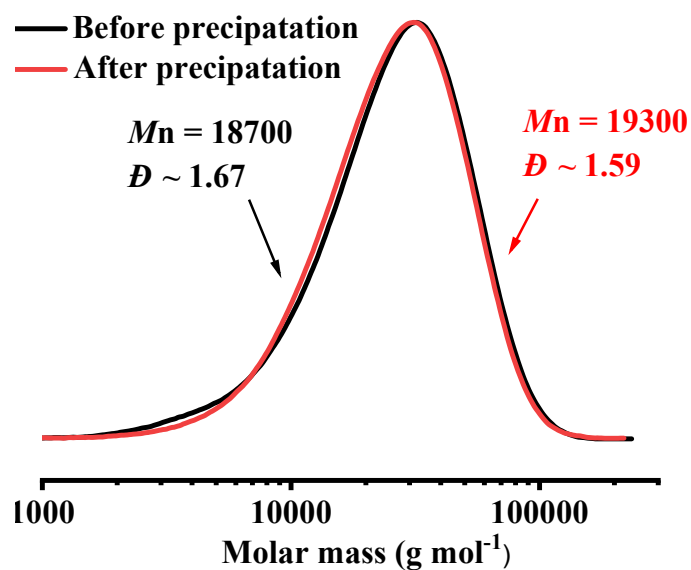


Figure S6. SEC trace for polymerization of IBVE in ethyl acetate with the molar ratio

$[\text{IBVE}]_0 : [\text{2b}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 200 : 1 : 0.1 : 0.1$ at 25 °C.

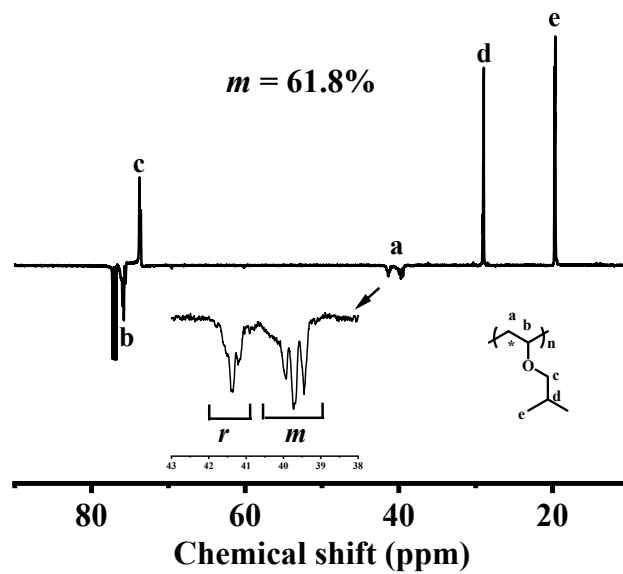


Figure S7. ^{13}C NMR spectra (in CDCl_3) of poly(IBVE) ($M_n = 8700$, $D = 1.43$) obtained with the molar ratio $[\text{IBVE}]_0 : [2\text{a}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 50 : 1 : 0.1 : 0.1$

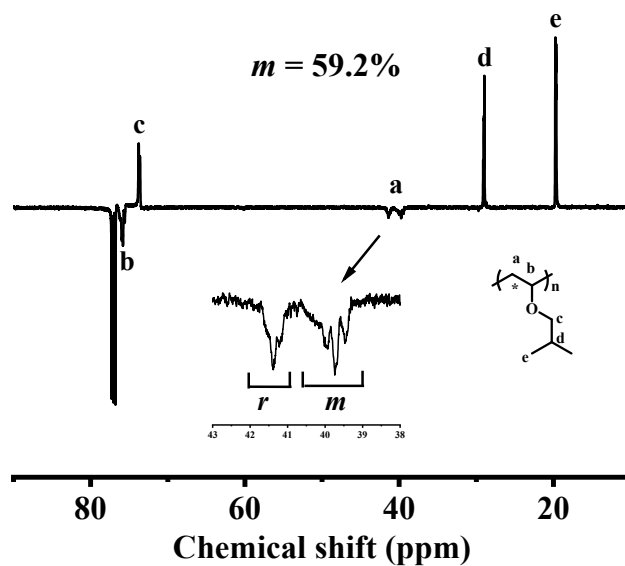


Figure S8. ¹³C NMR spectra (in CDCl₃) of poly(IBVE) ($M_n = 8300$, $D = 1.27$)

obtained with the molar ratio [IBVE]₀ : [2b]₀ : [EBP]₀ : [Mn₂(CO)₁₀]₀ = 50 : 1 : 0.1 :

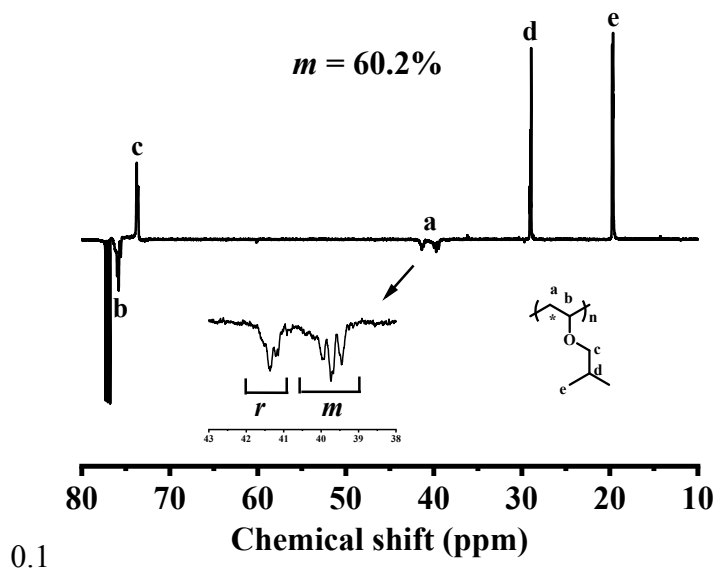


Figure S9. ¹³C NMR spectra (in CDCl₃) of poly(IBVE) ($M_n = 5400$, $D = 1.11$)

obtained with the molar ratio [IBVE]₀ : [2c]₀ : [EBP]₀ : [Mn₂(CO)₁₀]₀ = 50 : 1 : 1 :

0.1.

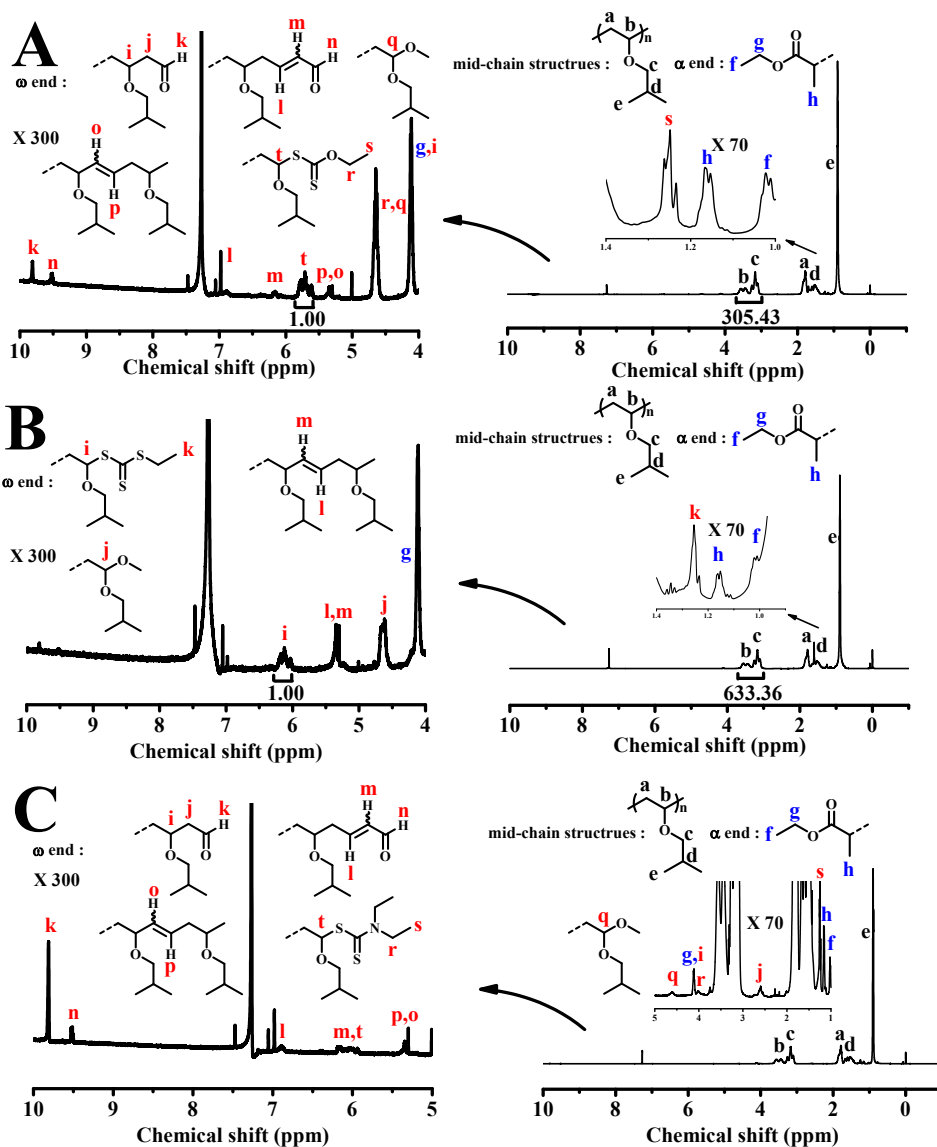


Figure S10. ^1H NMR spectra (in CDCl_3) of (A) poly(IBVE) ($M_n = 8700$, $D = 1.43$) obtained with the molar ratio $[\text{IBVE}]_0 : [2a]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 50 : 1 : 0.1 : 0.1$; (B) poly(IBVE) ($M_n = 8300$, $D = 1.27$) obtained with the molar ratio $[\text{IBVE}]_0 : [2b]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 50 : 1 : 0.1 : 0.1$; (C) poly(IBVE) ($M_n = 5400$, $D = 1.11$) obtained with the molar ratio $[\text{IBVE}]_0 : [2c]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 50 : 1 : 1 : 0.1$.

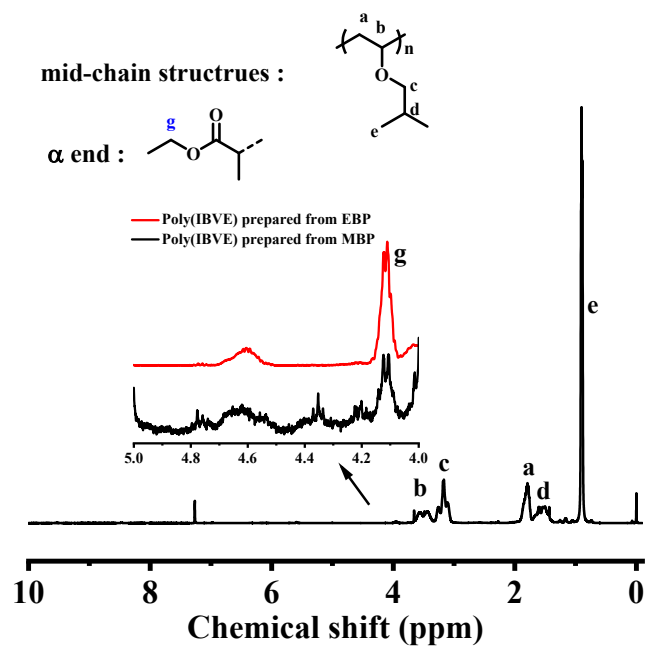


Figure S11. ^1H NMR spectra (in CDCl_3) of poly(IBVE) ($M_n = 5400$, $D = 1.11$)

obtained with the molar ratio $[\text{IBVE}]_0 : [2c]_0 : [\text{MBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 50 : 1 : 1 :$

0.1.

1.11) obtained with the molar ratio $[\text{IBVE}]_0 : [2\text{c}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 50 : 1 : 1 : 0.1$.

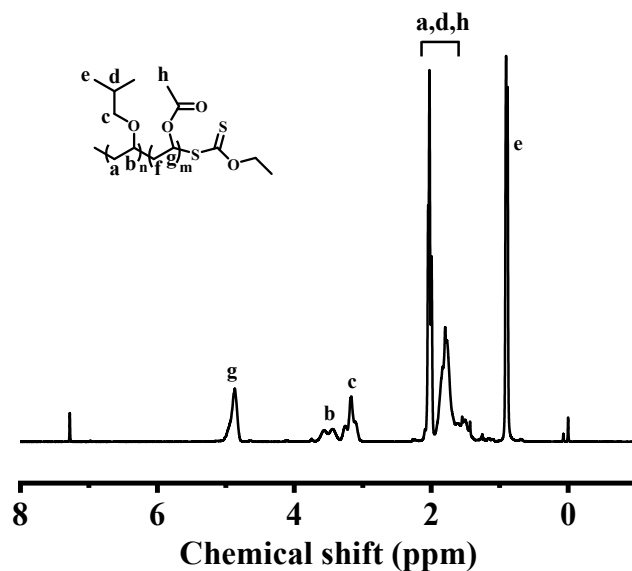


Figure S13. ¹H NMR spectra (in CDCl₃) of poly(isobutyl vinyl ether)-*b*-poly(vinyl acetate)

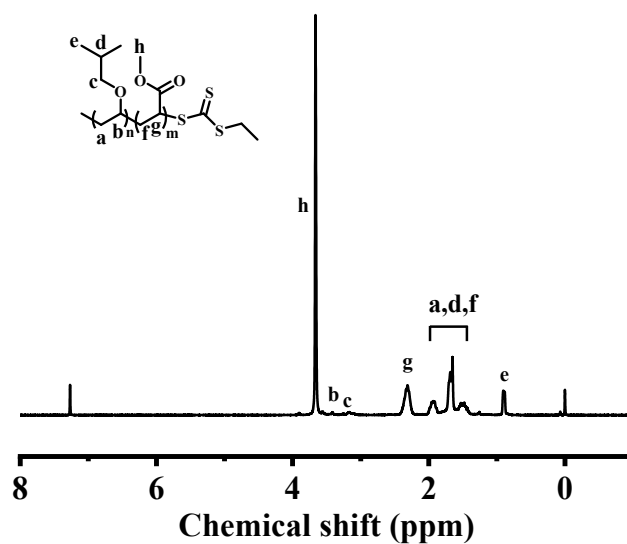


Figure S14. ¹H NMR spectra (in CDCl₃) of poly(isobutyl vinyl ether)-*b*-poly(methyl acrylate)

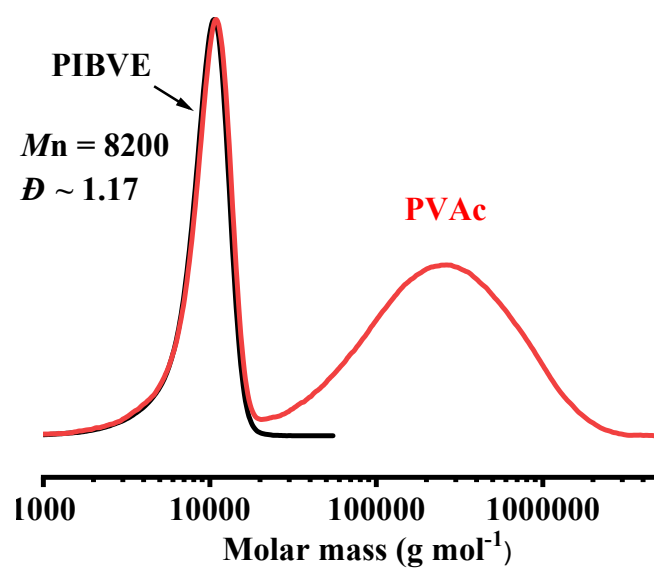


Figure S15. SEC traces of chain extension experiments using 2c derived poly(IBVE)s as macroRAFT agent with VAc

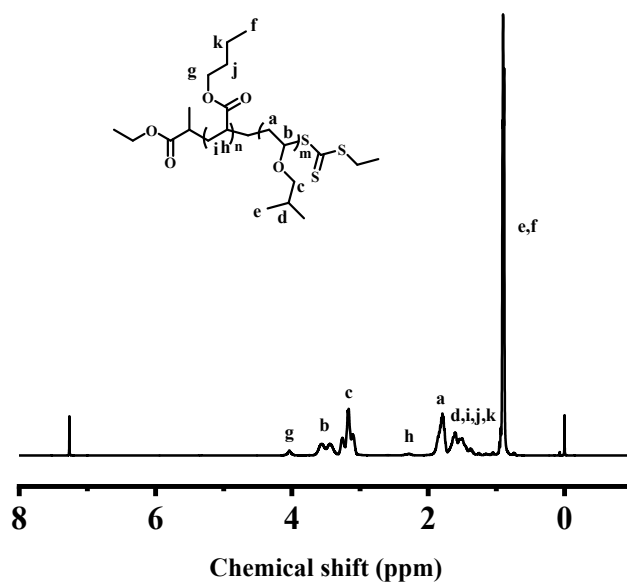


Figure S16. ^1H NMR spectra (in CDCl_3) of poly(butyl acrylate)-*b*-poly(isobutyl vinyl ether)

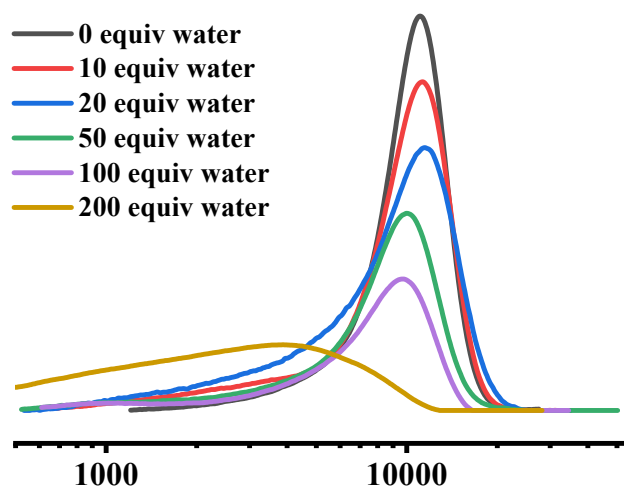


Figure S17. SEC traces of the cationic RAFT polymerization in the presence of water with the molar ratio $[\text{IBVE}]_0 : [2\text{c}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 100 : 1 : 1 : 0.1$

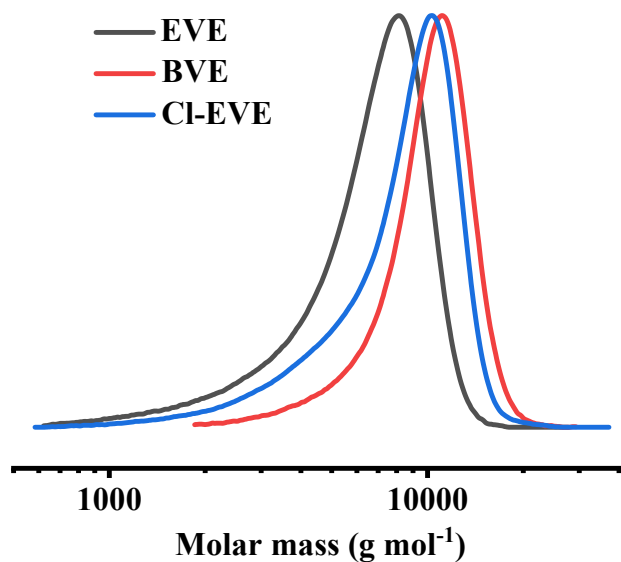


Figure S18. SEC trace for cationic RAFT polymerization of different monomers with the molar ratio $[\text{Monomer}]_0 : [2\text{c}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 100 : 1 : 1 : 0.1$ under blue LED at 25 °C.

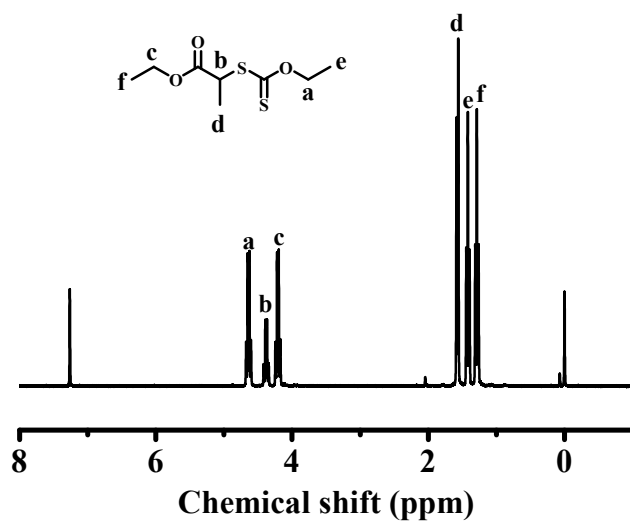


Figure S19. ¹H NMR spectra (in CDCl₃) of 2a

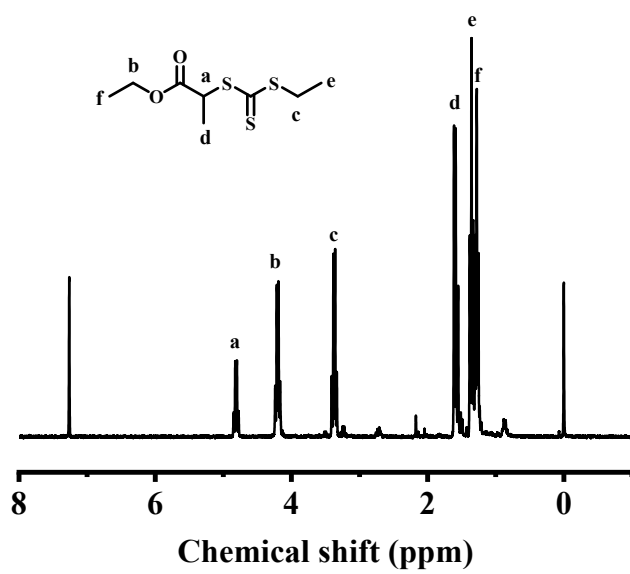


Figure S20. ¹H NMR spectra (in CDCl₃) of 2b

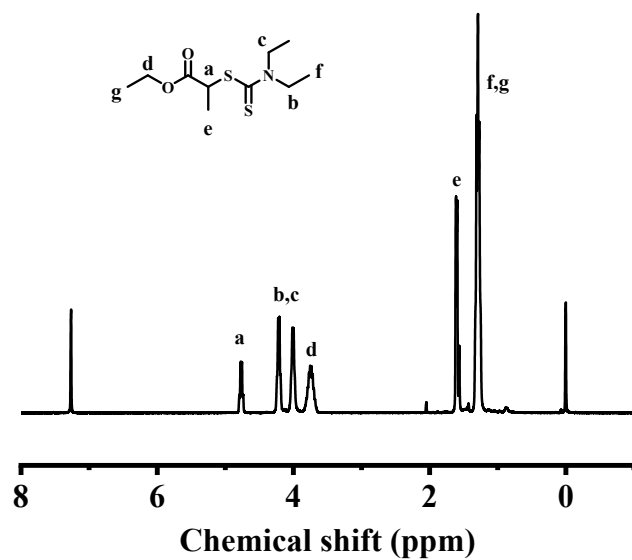


Figure S21. ¹H NMR spectra (in CDCl₃) of 2c

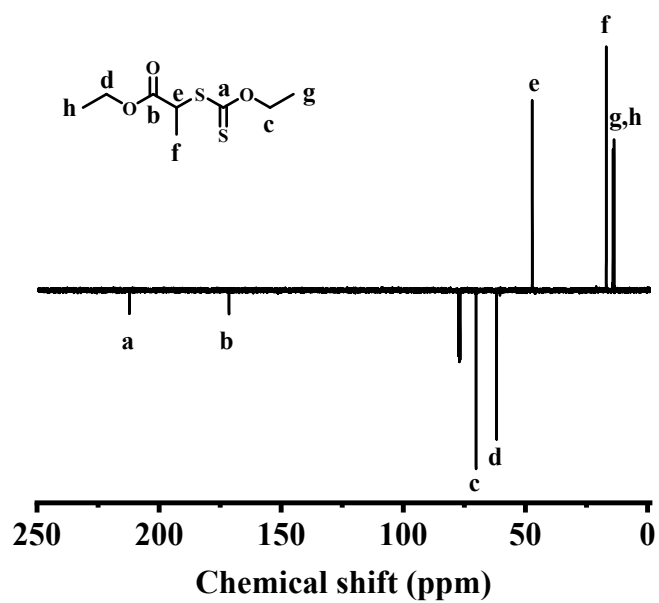


Figure S22. ¹³C NMR spectra (in CDCl₃) of 2a

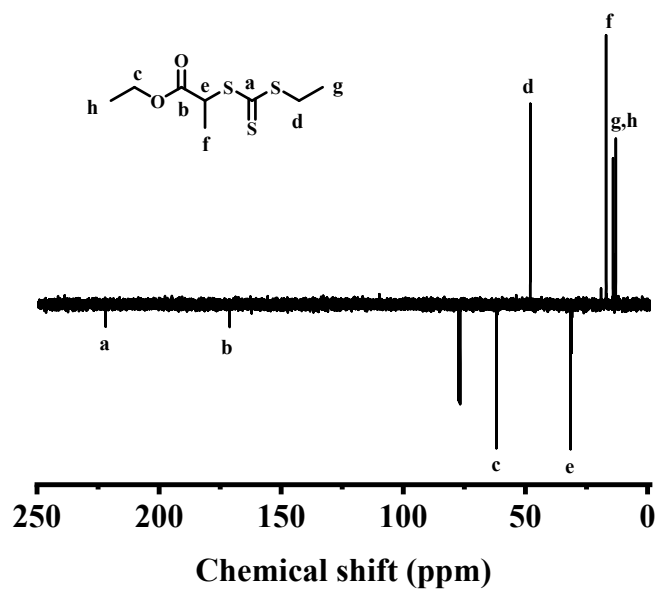


Figure S23. ¹³C NMR spectra (in CDCl₃) of 2b

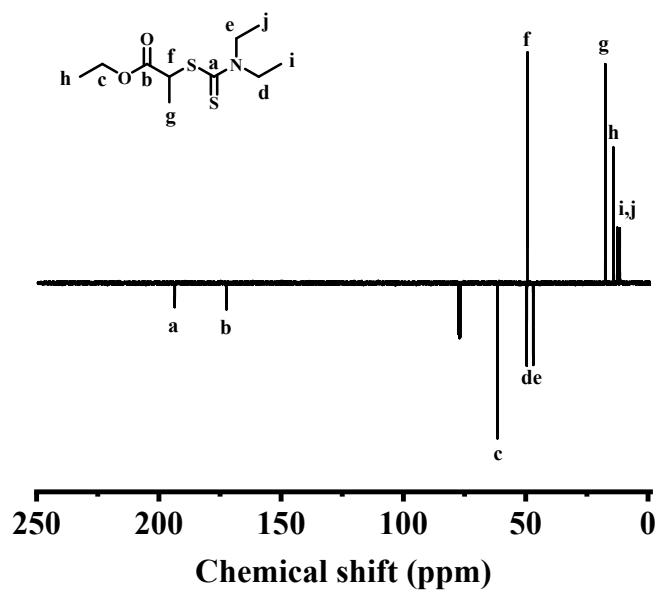


Figure S24. ¹³C NMR spectra (in CDCl₃) of 2c

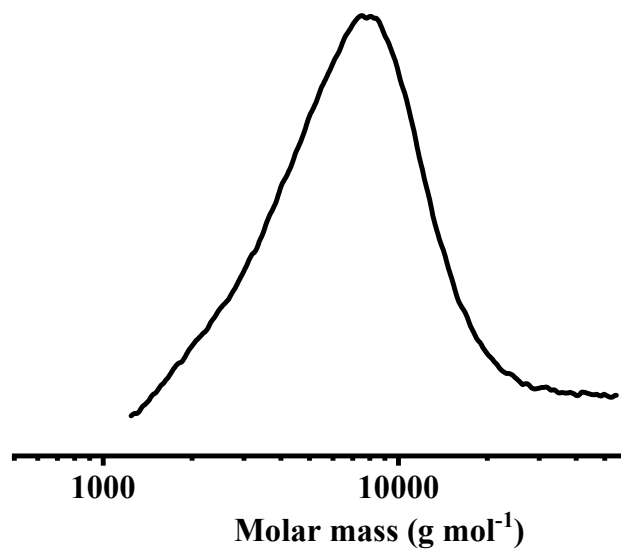


Figure S25. UV absorption at 309 nm for SEC detection of poly(IBVE) ($M_n = 8700$, $D = 1.43$) obtained with the molar ratio $[\text{IBVE}]_0 : [2\text{a}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 50 : 1 : 0.1 : 0.1$

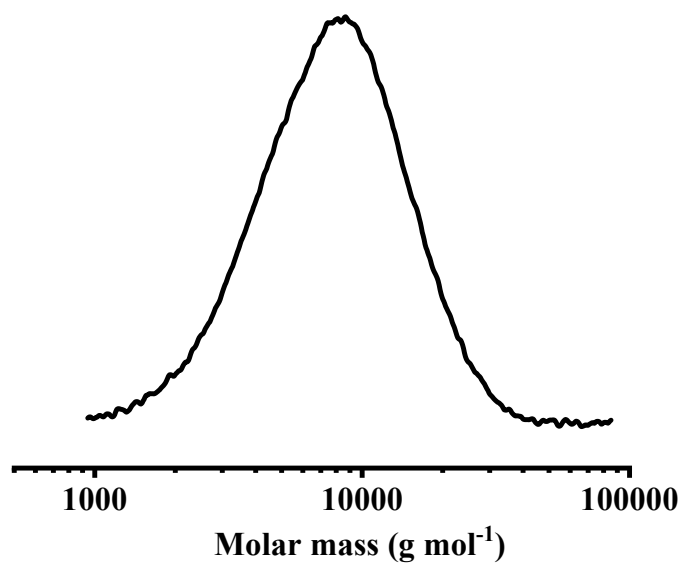


Figure S26. UV absorption at 309 nm for SEC detection of poly(IBVE) ($M_n = 8300$, $D = 1.27$) obtained with the molar ratio $[\text{IBVE}]_0 : [2\text{b}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 50 : 1 : 0.1 : 0.1$

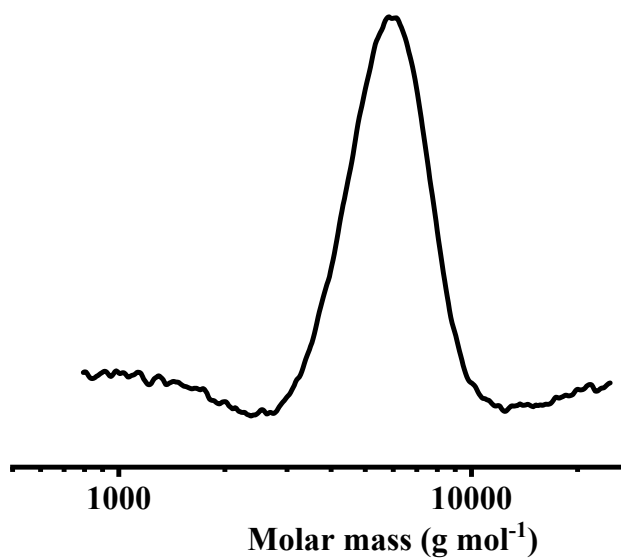


Figure S27. UV absorption at 309 nm for SEC detection of poly(IBVE) ($M_n = 5400$, $D = 1.11$) obtained with the molar ratio $[\text{IBVE}]_0 : [2c]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 50 : 1 : 1 : 0.1$.