Polymer Chemistry

ARTICLE

Supporting information

Well-defined block copolymer synthesis *via* living cationic polymerization and nitroxide-mediated polymerization using carboxylic acid-based alkoxyamines

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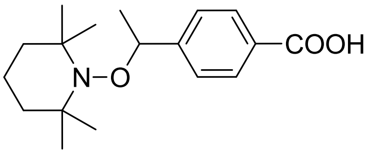
Structure	Elemental composition, [**A2**+H]$^+$	m/z_{th}	m/z_{exp}	Error (ppm)
 **A2**	$C_{18}H_{28}NO_3^+$	306.2064	306.2068 306.2068 306.2069	+ 1.3 + 1.3 + 1.6

Table S1. Accurate mass measurements of [**A2**+H]$^+$.

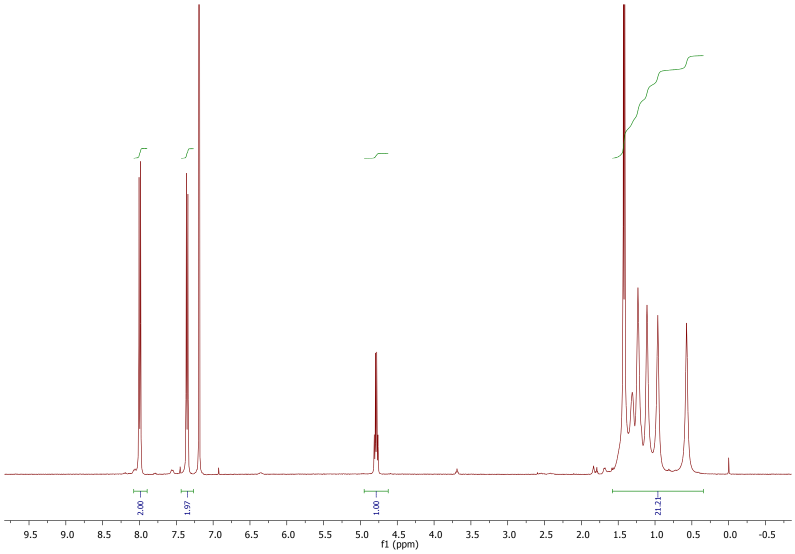


Figure S1. ^1H NMR spectrum in $CDCl_3$ of alkoxyamine **A2.**

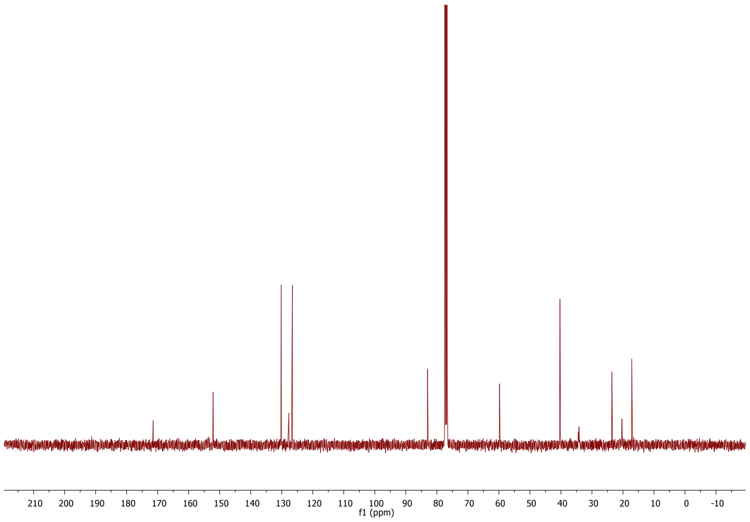


Figure S2. ^{13C} NMR spectrum in $CDCl_3$ of alkoxyamine **A2.**

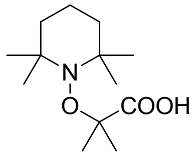
Structure	Elemental composition, [**A3**+H]$^+$	m/z_{th}	m/z_{exp}	Error (ppm)
 **A3**	$C_{13}H_{26}NO_3^+$	244.1907	244.1907 244.1908 244.1908	0 + 0.4 + 0.4

Table S2. Accurate mass measurements of [**A3**+H]$^+$.

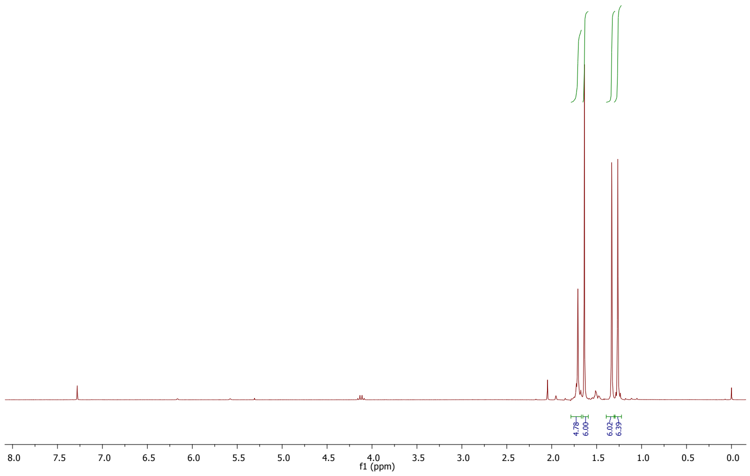


Figure S3. ^{1}H NMR spectrum in $CDCl_3$ of alkoxyamine **A3.**

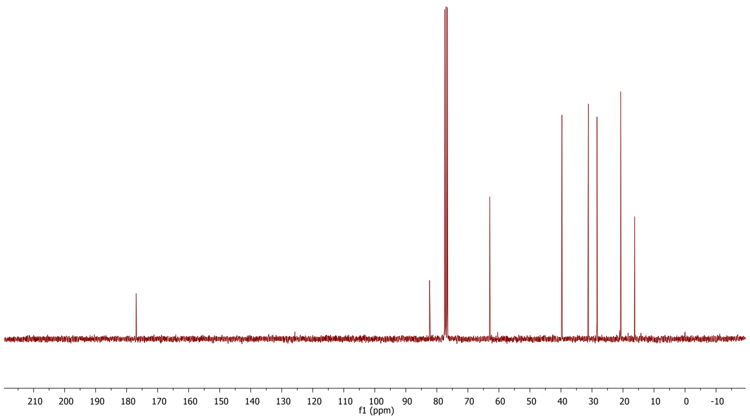


Figure S4. ^{13}C NMR spectrum in $CDCl_3$ of alkoxyamine **A3.**

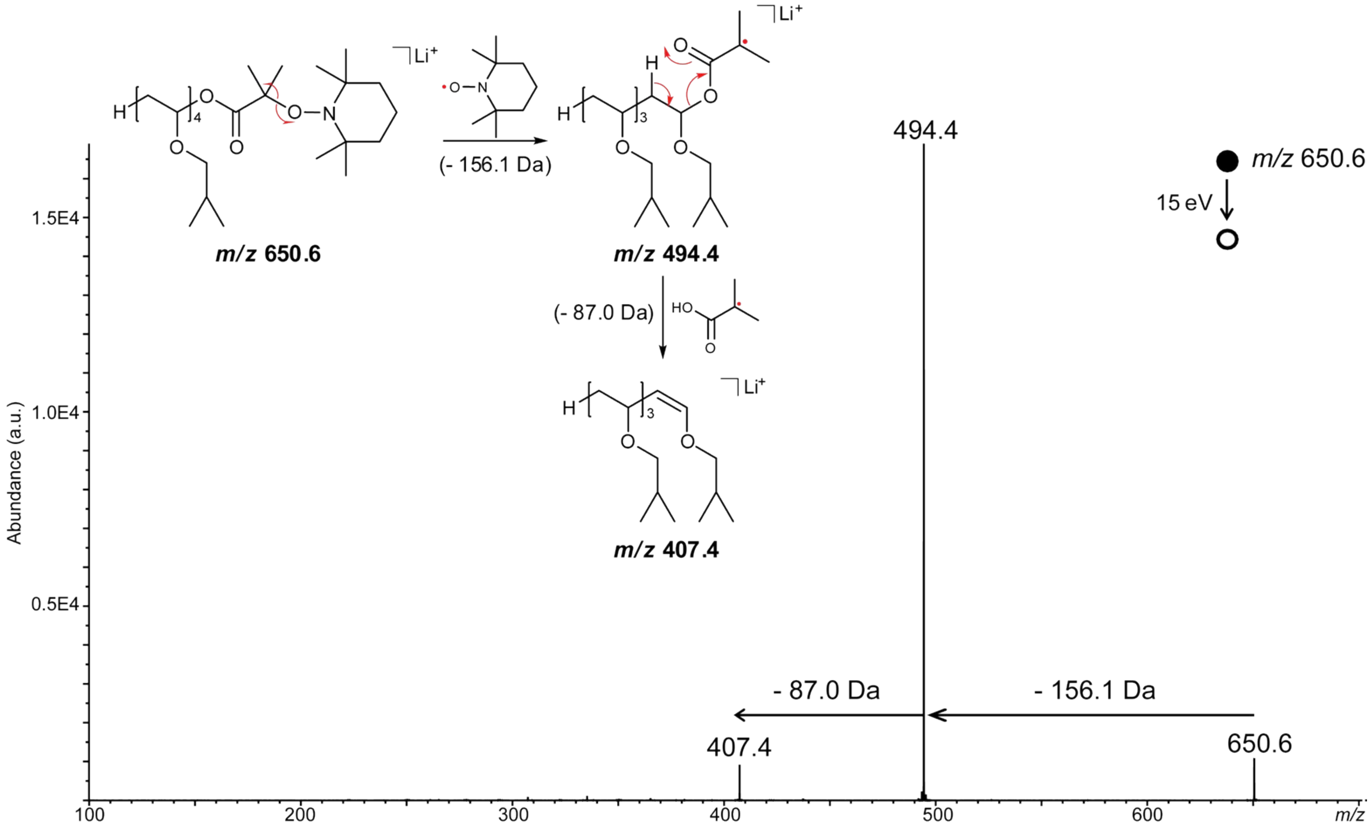


Figure S5. ESI-MS/MS spectrum of the PIBVE$_4$-TEMPO macroalkoxyamine at *m/z* 650.6, showing that the precursor ion eliminates the TEMPO radical (156.1 Da) prior to lose a 2-methyl-propanoic acid radical (87.0 Da), hence allowing the structure of the precursor ω end-group to be unambiguously characterized.

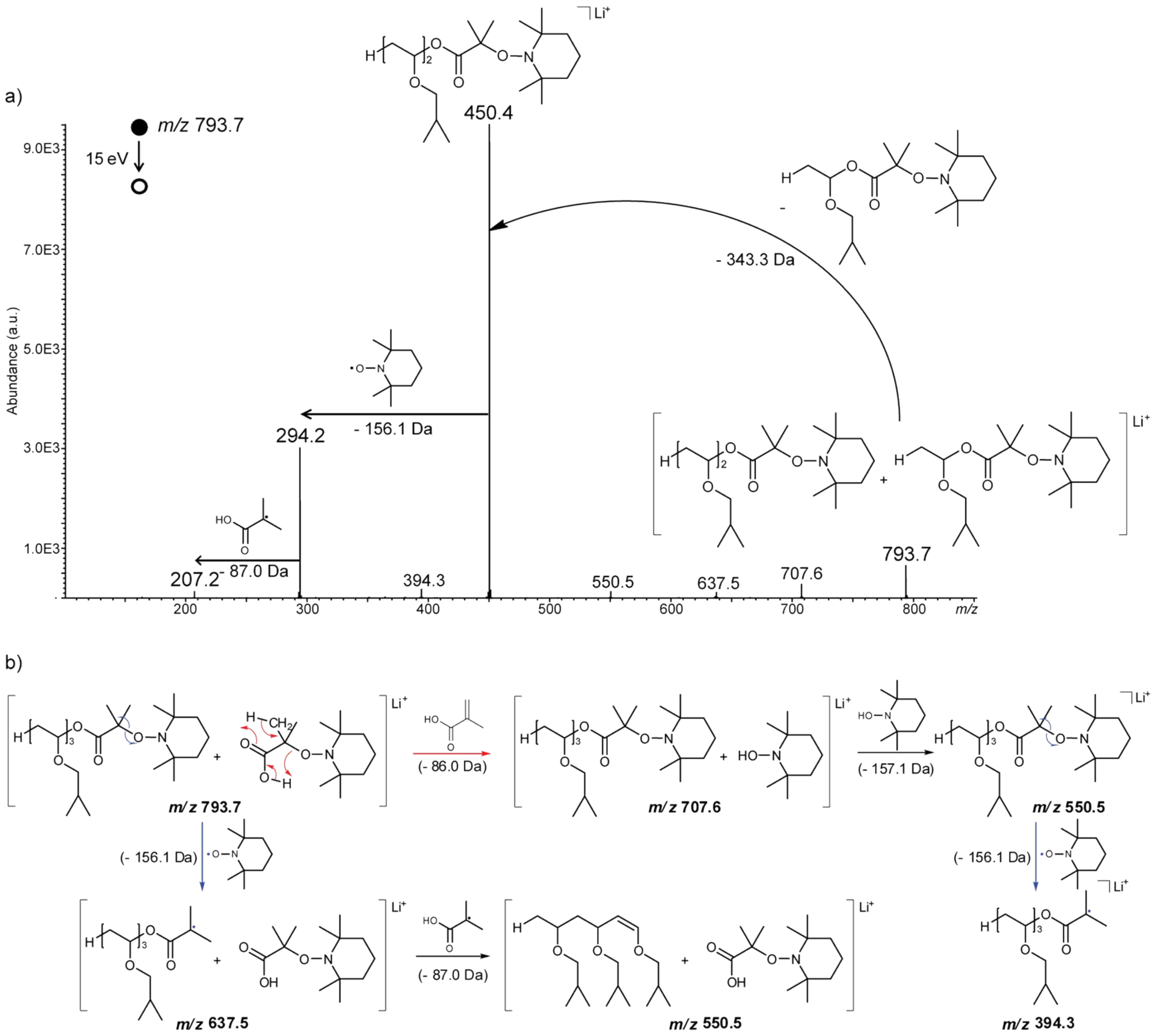


Figure S6. a) ESI-MS/MS spectrum of the *m/z* 793.7 precursor ion, allowing this species to be assigned to a non-covalent complex between PIBVE$_2$-TEMPO and PIBVE$_1$-TEMPO macroalkoxyamines. Lowest abundance fragments in this spectrum also suggested the presence of a second non-covalent complex with the same mass, which would be composed of PIBVE$_3$-TEMPO and **A3**, as detailed in the dissociation scheme shown in b).

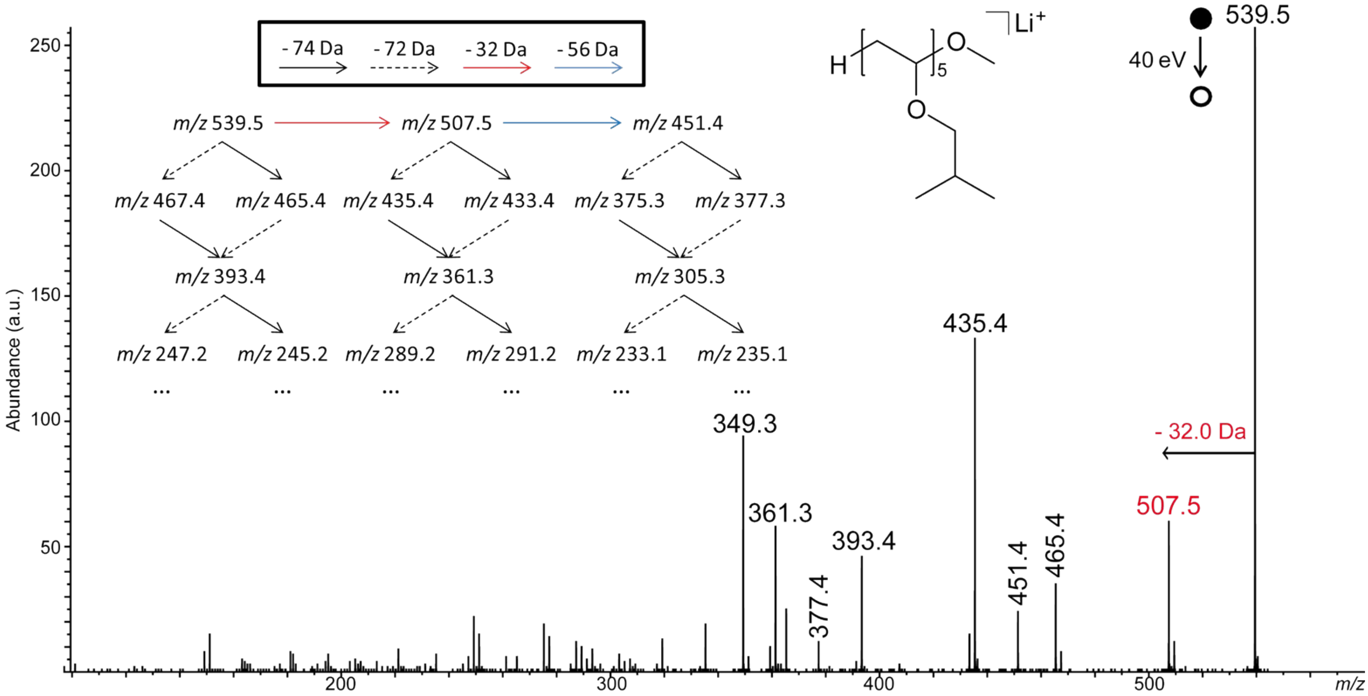


Figure S7. ESI-MS/MS spectrum of the *m/z* 539.5 precursor ion, proposed to be a PIBVE 5-mer holding OCH_3 as the ω end-group, as evidenced by the loss a 32 Da neutral from the precursor ion. As the *m/z* 539.5 is a lithiated molecule, mass calculation indicates that the α end-group should be H. Additional fragments in the MS/MS spectrum could be explained by successive dissociation reactions occurring in the pendant groups (as described by the dissociation scheme in the inset) and consisting of the elimination of i) a 74 Da neutral, assigned to $(CH_3)_2CH\text{-}CH_2\text{-}OH$, ii) a 72 Da neutral, assigned to $(CH_3)_2CHCH{=}O$, and iii) a 56 Da neutral, assigned to $CH_2{=}CH\text{-}CH_3$.

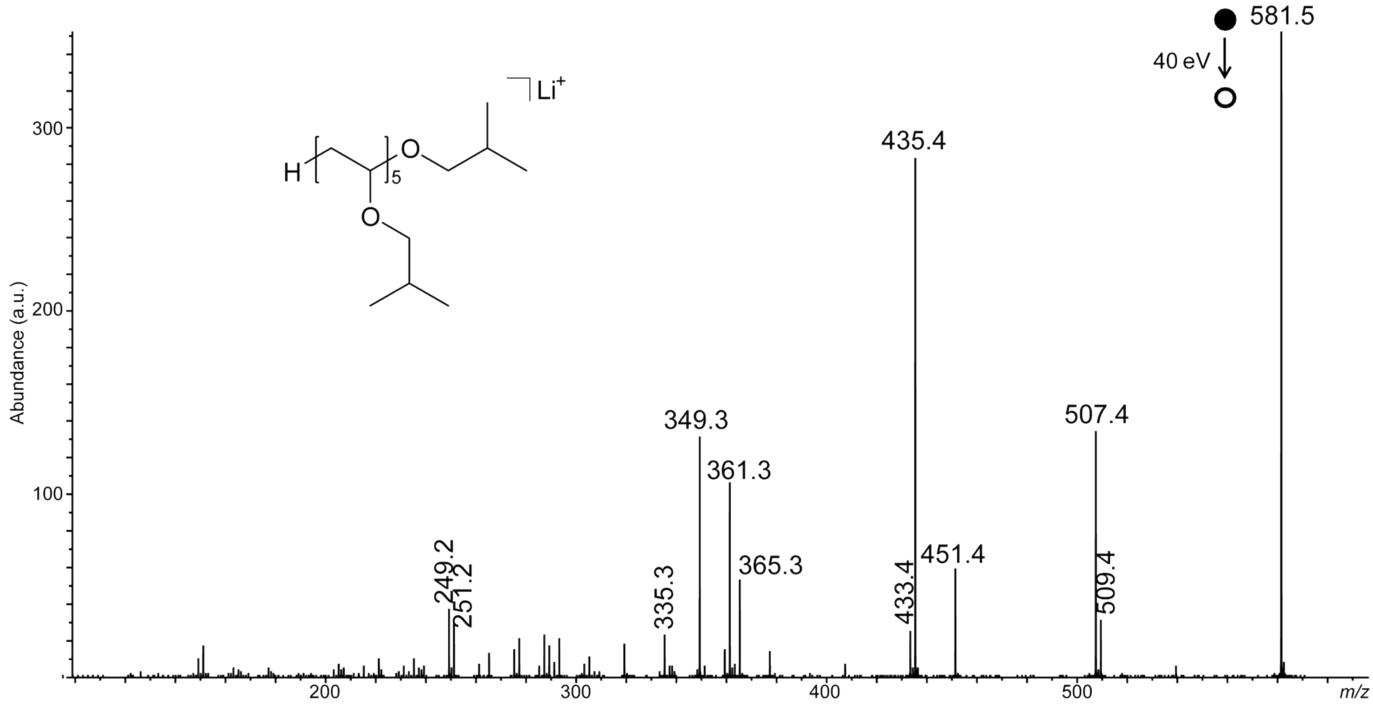


Figure S8. ESI-MS/MS spectrum of the *m/z* 581.5 precursor ion, proposed to be a PIBVE 5-mer holding OCH$_2$–C(CH$_3$)$_2$ as the ω end-group. This MS/MS spectrum does not show any specific reactions but the successive releases, from the pendant groups, of i) (CH$_3$)$_2$CH-CH$_2$-OH (74 Da), ii) (CH$_3$)$_2$CHCH=O (72 Da), and iii) CH$_2$=CH-CH$_3$ (56 Da) previously described in Figure S7.

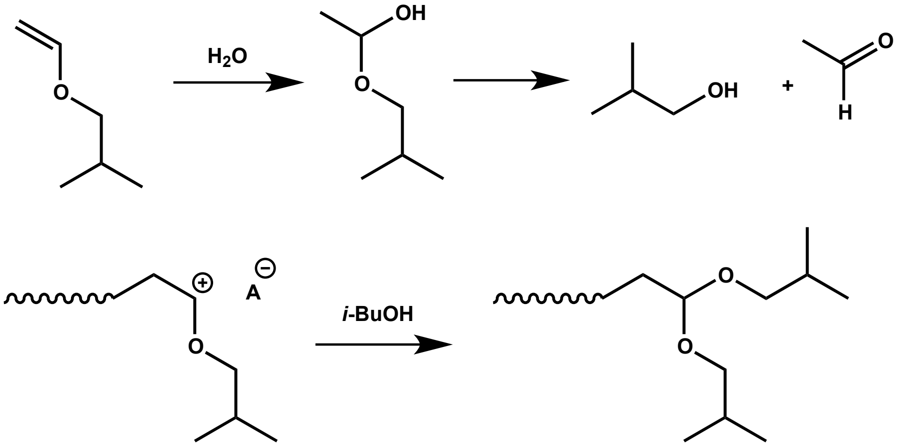


Figure S9. Side reactions with formation of iso-butanol producing by the presence of water during the polymerization of IBVE and the formation of PIBVE with ω-end −OiBu specie.

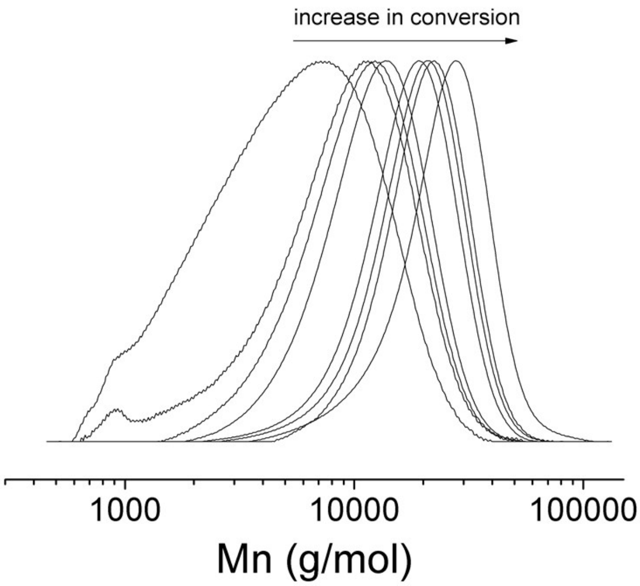


Figure S10. Evolution of SEC traces of PIBVE with time for the CLP of IBVE using **A3** as dual initiator.