## Supporting Information

## Contents

1. ${ }^{13} \mathrm{C}$ NMR spectra of poly(IBVE) obtained under various reaction conditions
2. DSC data of poly(IBVE) obtained under various reaction conditions
3. GPC results of poly(IBVE) obtained under various reaction conditions


Figure S1. Continuous flow through process (left) for the cationic polymerization of IBVE. Actual experimental setup (right)

1. ${ }^{13} \mathrm{C}$ NMR spectra of poly(IBVE) obtained at various reaction conditions


Figure S2. ${ }^{13} \mathrm{C}$ NMR spectra of poly(IBVE) in $\mathrm{CDCl}_{3}$ showing relative integrations amounting to $\sim 94 \% \mathrm{~m}$ (Table 1, Entry 1).


Figure S3a. ${ }^{13} \mathrm{C}$ NMR spectra of poly(IBVE) in $\mathrm{CDCl}_{3}$ showing relative integrations amounting to $98 \% \mathrm{~m}$ (Table 1, Entry 2).


Figure S3b. ${ }^{13} \mathrm{C}$ NMR spectra of poly(IBVE) in $\mathrm{CDCl}_{3}$ showing relative integrations amounting to $98 \% \mathrm{~m}$ (Table 1, Entry 2). Fitted peaks (blue), peak sum (magenta) and peak residual (red) are shown overlaid on the original spectrum (black). Triad mm $\%$ value is $84 \%$.


Figure S4. ${ }^{13} \mathrm{C}$ NMR spectra of poly(IBVE) in $\mathrm{CDCl}_{3}$ showing relative integrations amounting to $\sim 94 \% \mathrm{~m}$ (Table 1, Entry 3)


Figure S5. ${ }^{13} \mathrm{C}$ NMR spectra of poly(IBVE) in $\mathrm{CDCl}_{3}$ showing relative integrations amounting to $\sim 79 \% \mathrm{~m}$ (Table 1, Entry 4)


Figure S6. ${ }^{13} \mathrm{C}$ NMR spectra of poly(IBVE) in $\mathrm{CDCl}_{3}$ showing relative integrations amounting to $\sim 91 \% \mathrm{~m}$ (Table 1, Entry 5)


Figure S7. ${ }^{13} \mathrm{C}$ NMR spectra of poly(IBVE) in $\mathrm{CDCl}_{3}$ showing relative integrations amounting to $\sim 88 \% \mathrm{~m}$ (Table 1, Entry 6 )


Figure S8. ${ }^{13} \mathrm{C}$ NMR spectra of poly(IBVE) in $\mathrm{CDCl}_{3}$ showing relative integrations amounting to $\sim 88 \% \mathrm{~m}$ (Table 1, Entry 7)


Figure S9. ${ }^{13} \mathrm{C}$ NMR spectra of poly(IBVE) in $\mathrm{CDCl}_{3}$ showing relative integrations amounting to $\sim 85 \% \mathrm{~m}$ (Table 1, Entry 8 ).


Figure S10a. ${ }^{13} \mathrm{C}$ NMR spectra of poly(IBVE) in $\mathrm{CDCl}_{3}$ showing relative integrations amounting to $\sim 90 \% \mathrm{~m}$ (Table 1, Entry 9).


Figure S10b. ${ }^{13} \mathrm{C}$ NMR spectra of poly(IBVE) in $\mathrm{CDCl}_{3}$ showing relative integrations amounting to $\sim 90 \% \mathrm{~m}$ (Table 1, Entry 9). Fitted peaks (blue), peak sum (magenta) and peak residual (red) are shown overlaid on the original spectrum (black). Triad mm\% value is $80 \%$.

## 2. DSC data of poly(IBVE) obtained at various reaction conditions



Figure S11. DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of $10^{\circ} \mathrm{C} / \mathrm{min}$ (Table 1, Entry 1).


Figure S12. DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of $10^{\circ} \mathrm{C} / \mathrm{min}$ (Table 1, Entry 2).


Figure S13. DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of $10^{\circ} \mathrm{C} / \mathrm{min}$ (Table 1, Entry 3).


Figure S14. DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of $10^{\circ} \mathrm{C} / \mathrm{min}$ (Table 1, Entry 4).


Figure S15. DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of $10^{\circ} \mathrm{C} / \mathrm{min}$ (Table 1, Entry 5).


Figure S16. DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of $10^{\circ} \mathrm{C} / \mathrm{min}$ (Table 1, Entry 6).


Figure S17. DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of $10^{\circ} \mathrm{C} / \mathrm{min}$ (Table 1, Entry 7).


Figure S18. DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of $10^{\circ} \mathrm{C} / \mathrm{min}$ (Table 1, Entry 8).


Figure S19. DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of $10^{\circ} \mathrm{C} / \mathrm{min}$ (Table 1, Entry 9).

3 GPC results of poly(IBVE) obtained at various reaction conditions


Figure S20. GPC trace of isotactic poly(BVE) (Table 1, Entry 1).


Figure S21. GPC trace of isotactic poly(BVE) (Table 1, Entry 2).


Figure S22. GPC trace of isotactic poly(BVE) (Table 1, Entry 3).


Figure S23. GPC trace of isotactic poly(BVE) (Table 1, Entry 4).


Figure S24. GPC trace of isotactic poly(BVE) (Table 1, Entry 5).


Figure S25. GPC trace of isotactic poly(BVE) (Table 1, Entry 6).


Figure S26. GPC trace of isotactic poly(BVE) (Table 1, Entry 7).


Figure S27. GPC trace of isotactic poly(BVE) (Table 1, Entry 8).


Figure S28. GPC trace of isotactic poly(BVE) (Table 1, Entry 9).

