## **Supporting Information**

## Contents

- 1. <sup>13</sup>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. <sup>13</sup>C NMR spectra of poly(IBVE) obtained at various reaction conditions



**Figure S2.** <sup>13</sup>C NMR spectra of poly(IBVE) in CDCl<sub>3</sub> showing relative integrations amounting to  $\sim$ 94% m (Table 1, Entry 1).



**Figure S3a.** <sup>13</sup>C NMR spectra of poly(IBVE) in CDCl<sub>3</sub> showing relative integrations amounting to 98% m (Table 1, Entry 2).



**Figure S3b.** <sup>13</sup>C NMR spectra of poly(IBVE) in CDCl<sub>3</sub> showing relative integrations amounting to 98% 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.** <sup>13</sup>C NMR spectra of poly(IBVE) in CDCl<sub>3</sub> showing relative integrations amounting to  $\sim$ 94% m (Table 1, Entry 3)



Figure S5. <sup>13</sup>C NMR spectra of poly(IBVE) in CDCl<sub>3</sub> showing relative integrations amounting to  $\sim$ 79% m (Table 1, Entry 4)



Figure S6. <sup>13</sup>C NMR spectra of poly(IBVE) in CDCl<sub>3</sub> showing relative integrations amounting to  $\sim$ 91% m (Table 1, Entry 5)



Figure S7. <sup>13</sup>C NMR spectra of poly(IBVE) in CDCl<sub>3</sub> showing relative integrations amounting to  $\sim$ 88% m (Table 1, Entry 6)



**Figure S8.** <sup>13</sup>C NMR spectra of poly(IBVE) in CDCl<sub>3</sub> showing relative integrations amounting to  $\sim$ 88% m (Table 1, Entry 7)



Figure S9. <sup>13</sup>C NMR spectra of poly(IBVE) in CDCl<sub>3</sub> showing relative integrations amounting to  $\sim$ 85% m (Table 1, Entry 8).



Figure S10a. <sup>13</sup>C NMR spectra of poly(IBVE) in CDCl<sub>3</sub> showing relative integrations amounting to  $\sim$ 90% m (Table 1, Entry 9).



**Figure S10b.** <sup>13</sup>C NMR spectra of poly(IBVE) in CDCl<sub>3</sub> showing relative integrations amounting to  $\sim$ 90% 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%.





**Figure S11.** DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of 10 °C/min (Table 1, Entry 1).



Figure S12. DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of 10 °C/min (Table 1, Entry 2).



Figure S13. DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of 10 °C/min (Table 1, Entry 3).



**Figure S14.** DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of 10 °C/min (Table 1, Entry 4).



**Figure S15.** DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of 10 °C/min (Table 1, Entry 5).



**Figure S16.** DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of 10 °C/min (Table 1, Entry 6).



**Figure S17.** DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of 10 °C/min (Table 1, Entry 7).



**Figure S18.** DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of 10 °C/min (Table 1, Entry 8).



Figure S19. DSC curve for poly(IBVE) during the second heating cycle at a temperature ramp rate of 10 °C/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).