

Electronic Supplementary Information

Cationic Polymerization of Isoprene initiated by 2-cyclohexylidene ethanol/ $B(C_6F_5)_3$: insight into initiation and branching reactions

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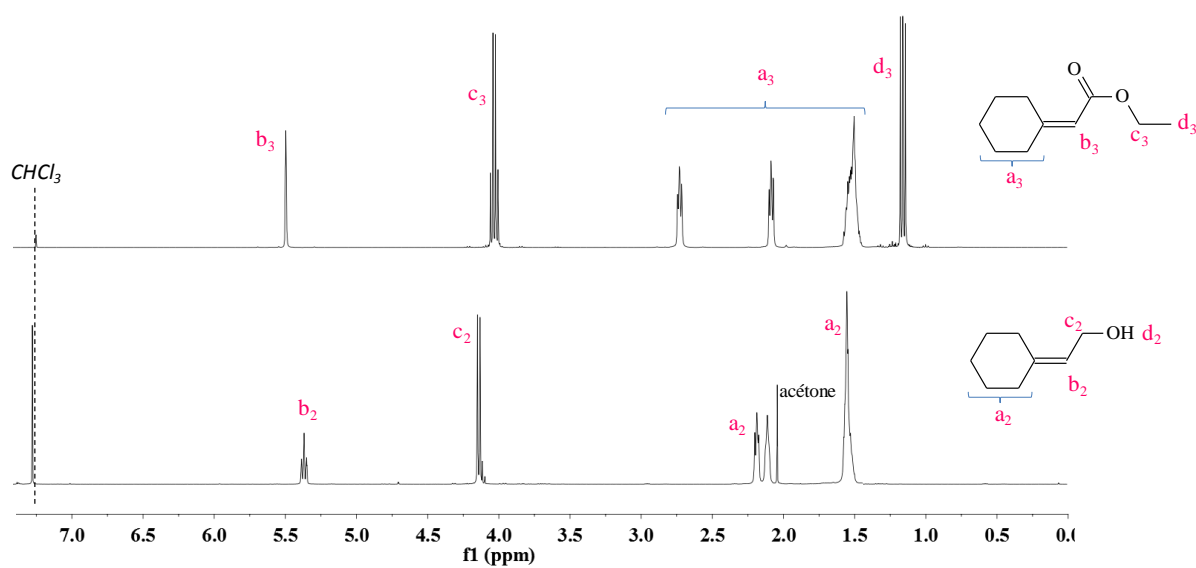


Figure S1. ^1H NMR spectra of ethylcyclohexylidene acetate and 2-cyclohexylidene ethanol.

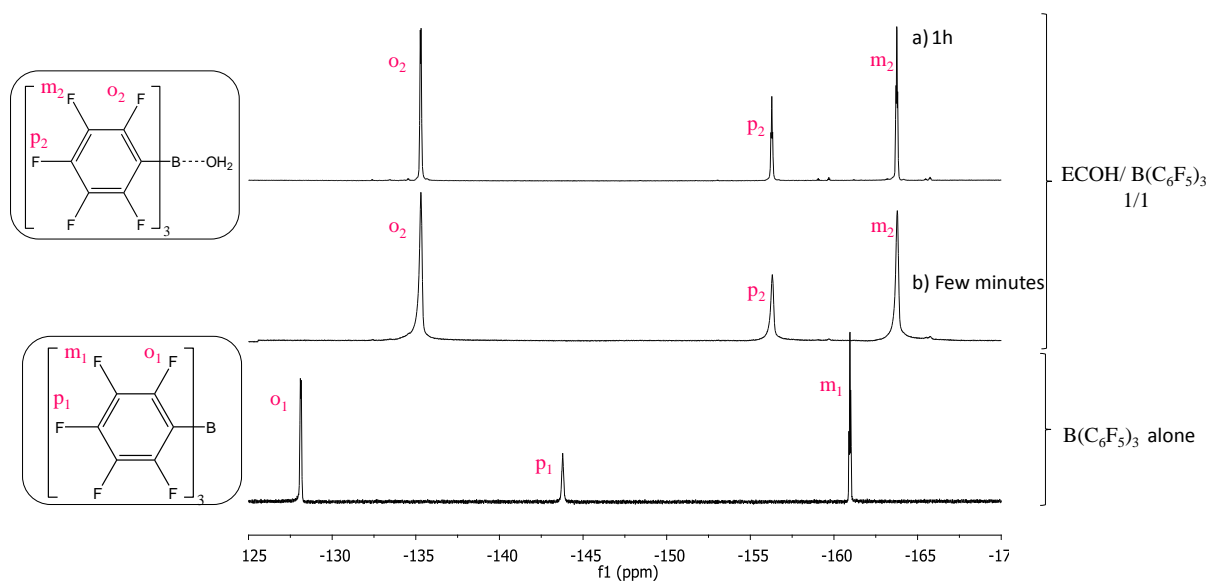


Figure S2. ^{19}F NMR spectra measured at different time for the ionization study of ECOH by $\text{B}(\text{C}_6\text{F}_5)_3$ (1/1) in CD_2Cl_2 .

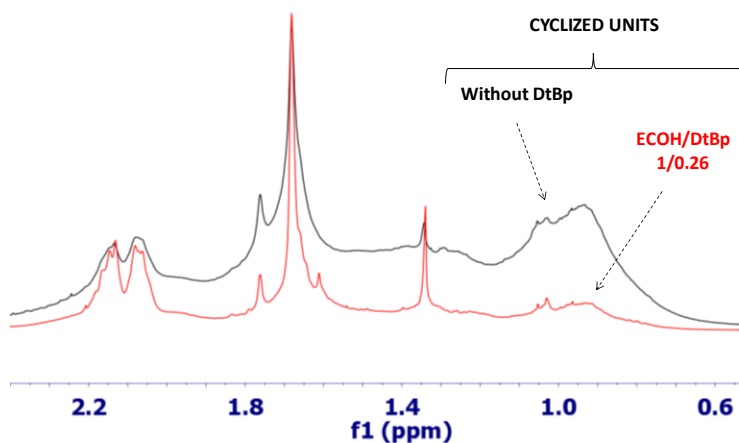


Figure S3. ^1H NMR spectra (0-2 ppm region) of oligoisoprenes obtained without and with $d^t\text{BP}$.

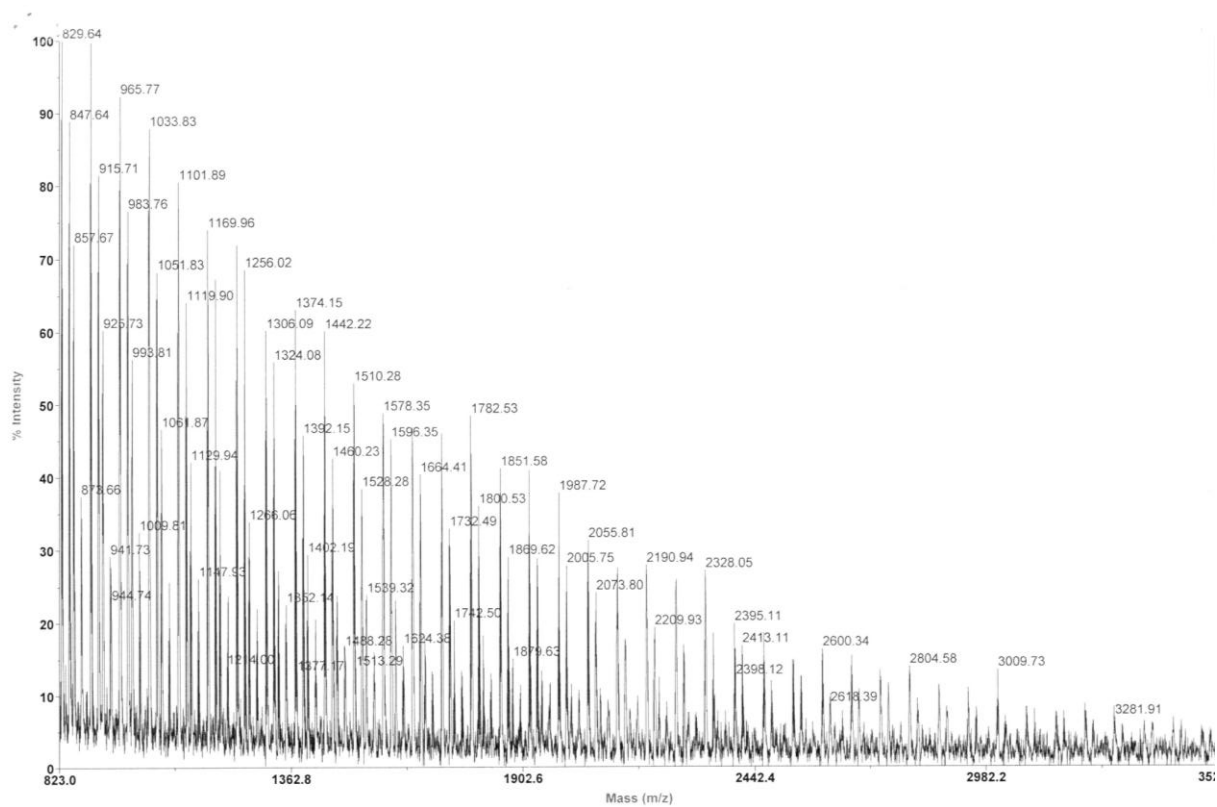


Figure S4. Maldi-ToF spectrum of run 1 in Table 3

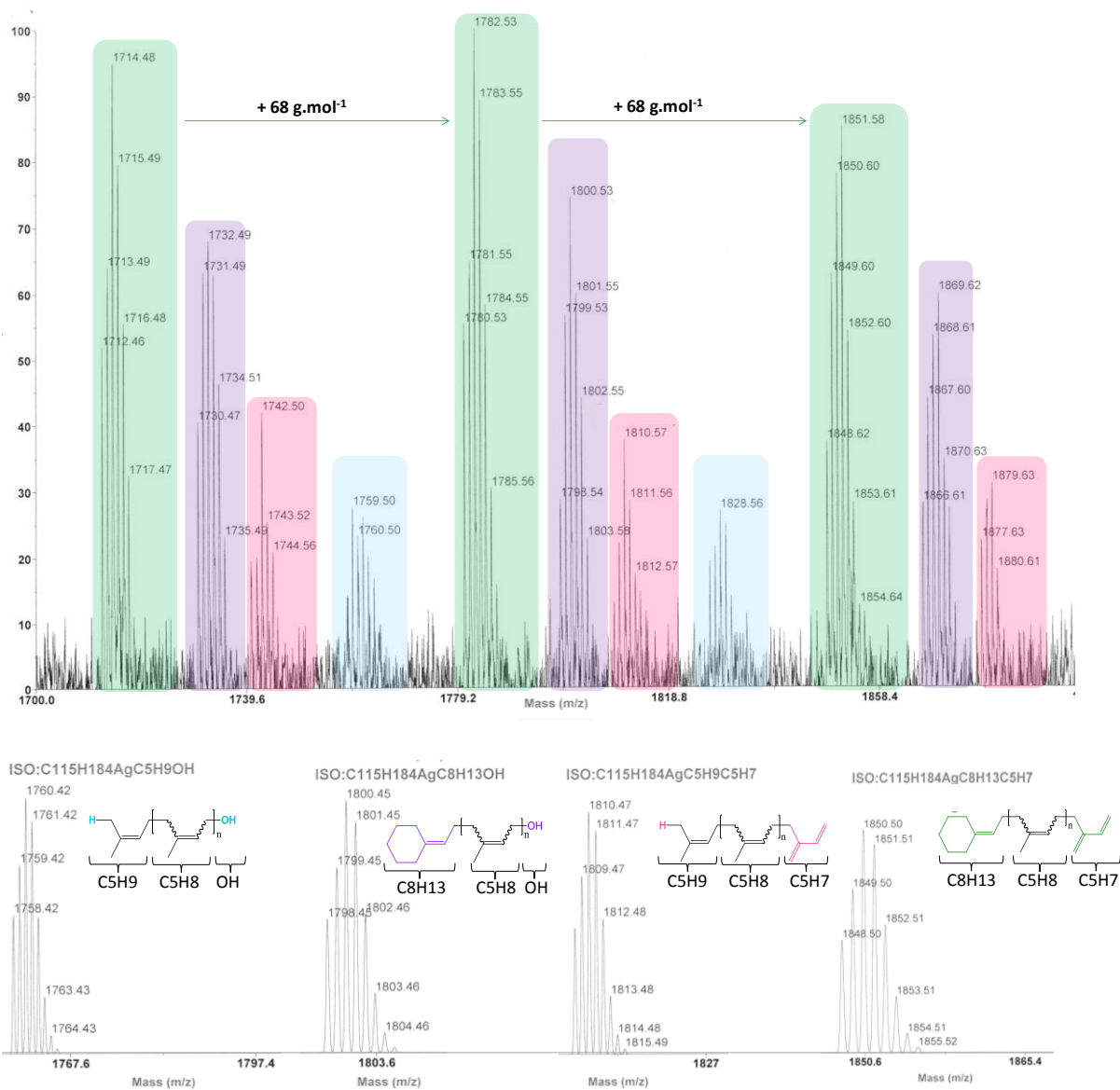


Figure S5. Simulations of Maldi-Tof spectrum compared to experimental results for polyisoprene chains bearing different chain-ends.

n	nC ₅ H ₈ AgC ₈ H ₁₃ C ₈ H ₁₃ C ₅ H ₇ C ₅ H ₇	nC ₅ H ₈ AgC ₈ H ₁₃ C ₈ H ₁₃ C ₅ H ₇ OH	nC ₅ H ₈ gC ₈ H ₁₃ C ₈ H ₁₃ OH
19	1752,27	1702,22	1652,17
20	1820,27	1770,22	1720,17
21	1888,28	1838,23	1788,17
22	1956,28	1906,23	1856,18
23	2024,28	1974,23	1924,18
24	2092,29	2042,24	1992,18
25	2160,29	2110,24	2060,19
26	2228,30	2178,24	2128,19

Table S1. Theoretical Maldi-ToF molar masses of branched polyisoprenes obtained by intermolecular branching (chains bearing 2 cyclohexylene moieties), molar masses highlighted in grey are the expected ones for the zoom in Figure S5.

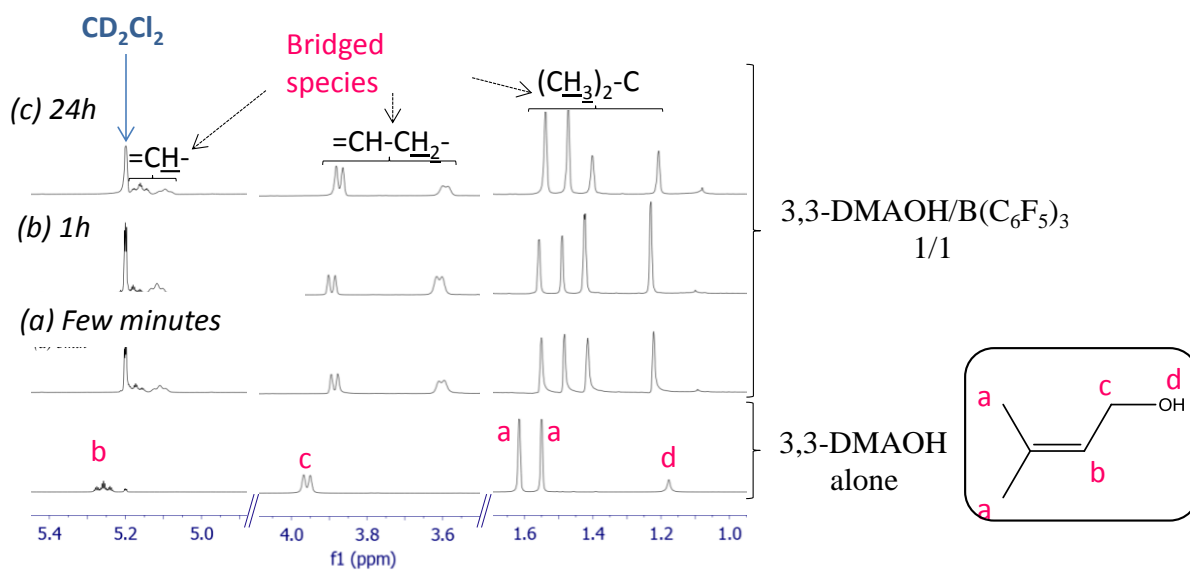


Figure S6. ¹H NMR spectra of 3,3-DMAOH/B(C₆F₅)₃ (1/1) system for different reaction time in CD₂Cl₂ at – 40°C.