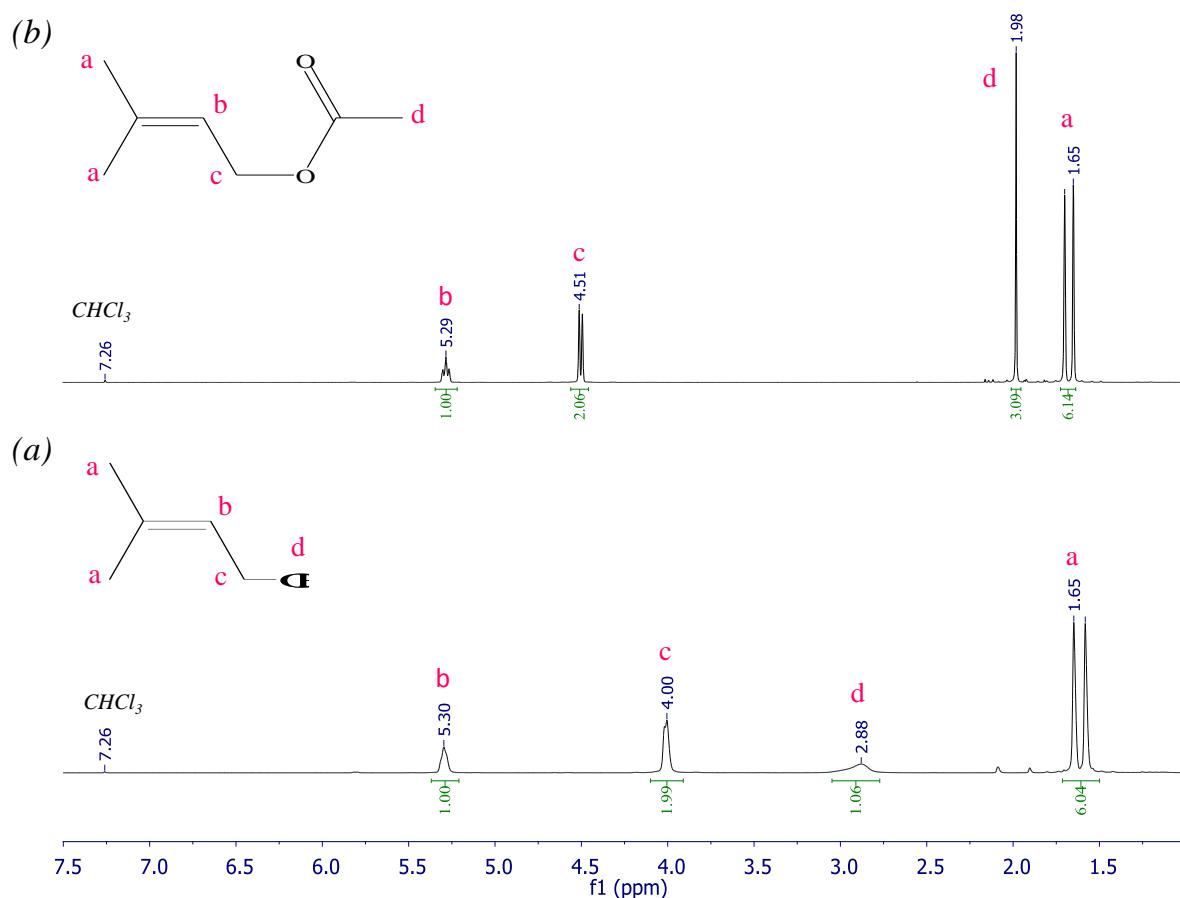


*Electronic Supplementary Information*

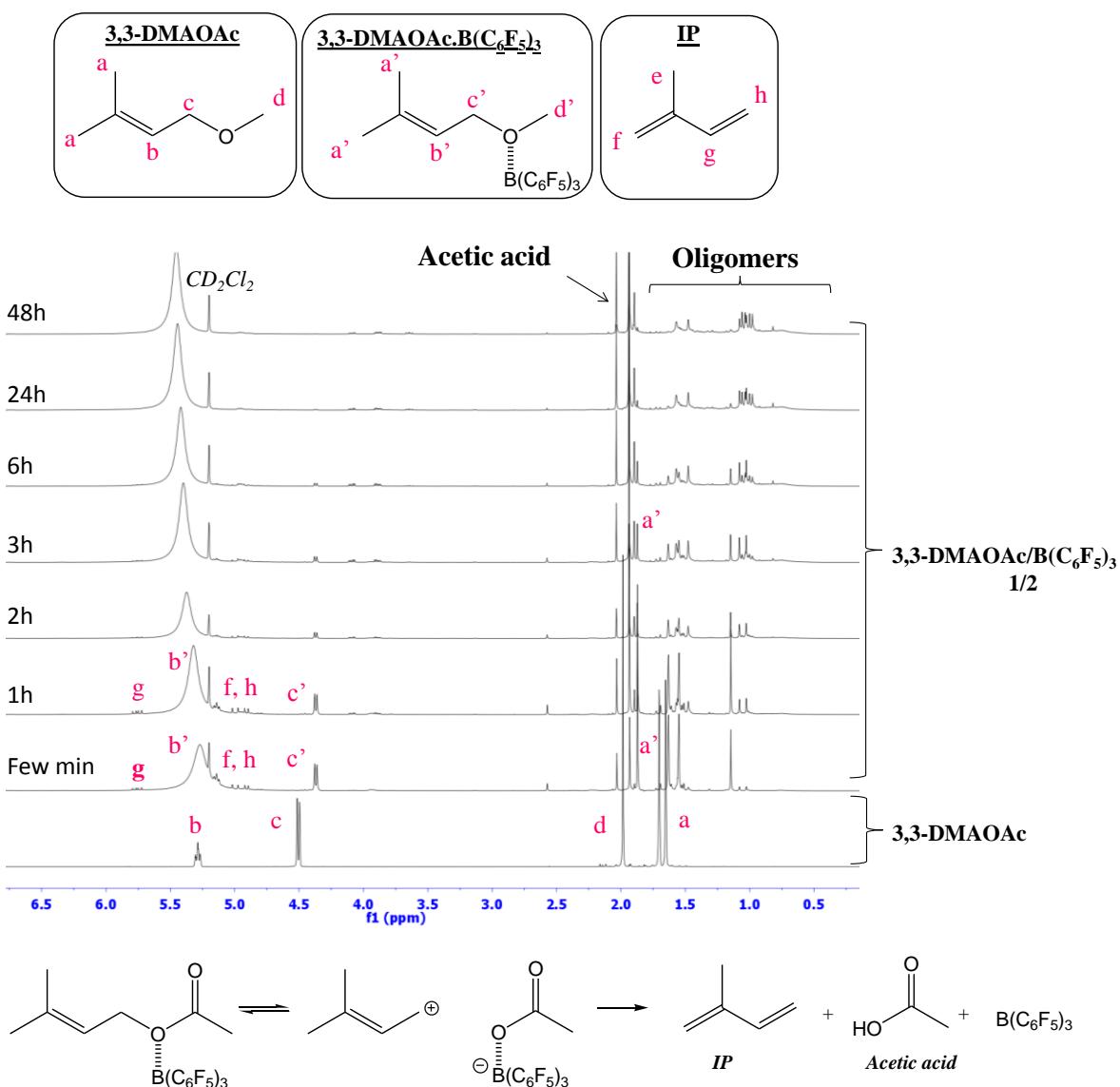
**Carbocationic polymerization of isoprene initiated by dimethylallyl derivatives associated to  $\mathbf{B}(\mathbf{C}_6\mathbf{F}_5)_3$**

Samira Ouardad, Alain Deffieux, Frédéric Peruch

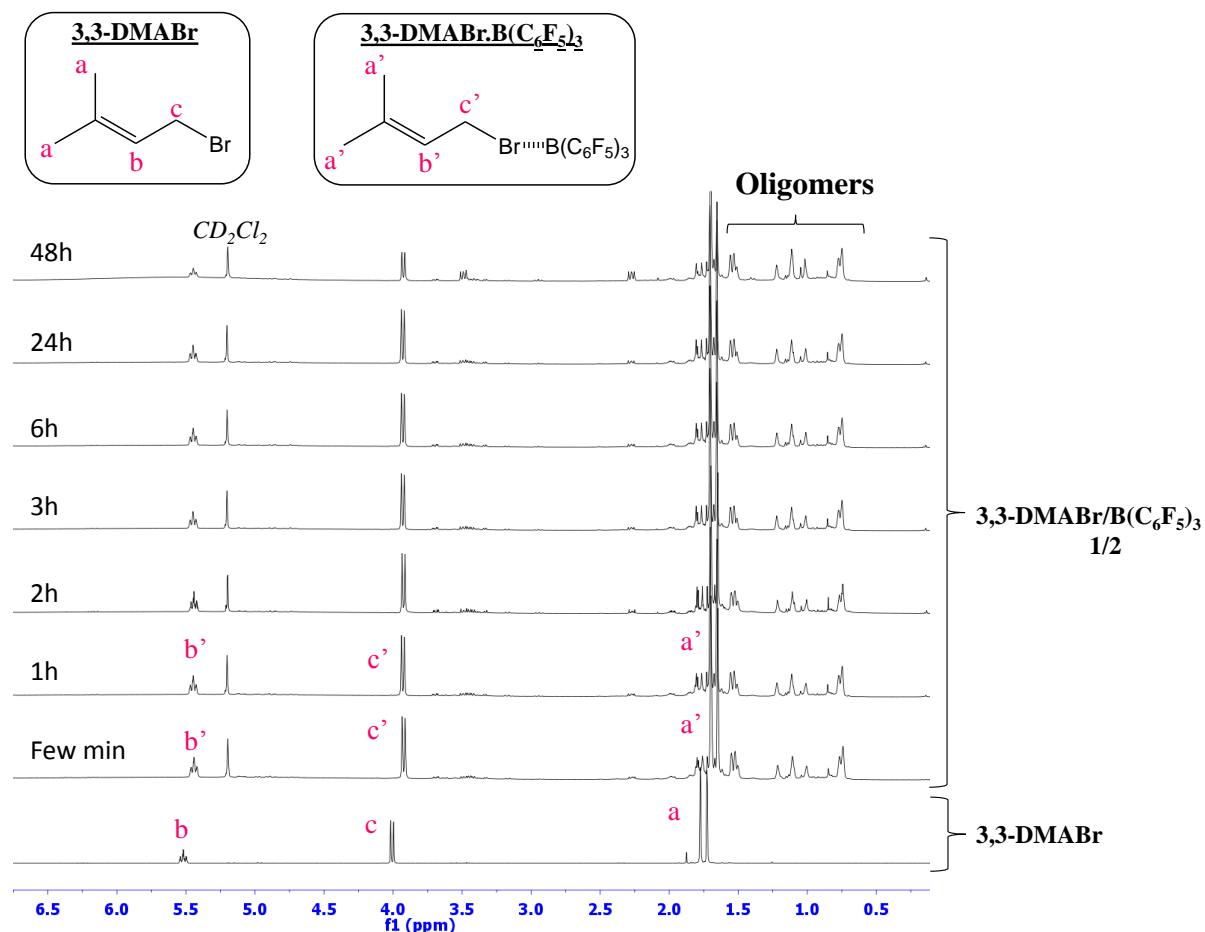
Univ. Bordeaux, LCPO, UMR 5629, F-33600 Pessac, France ; CNRS, LCPO, UMR 5629, F-33600 Pessac, France.



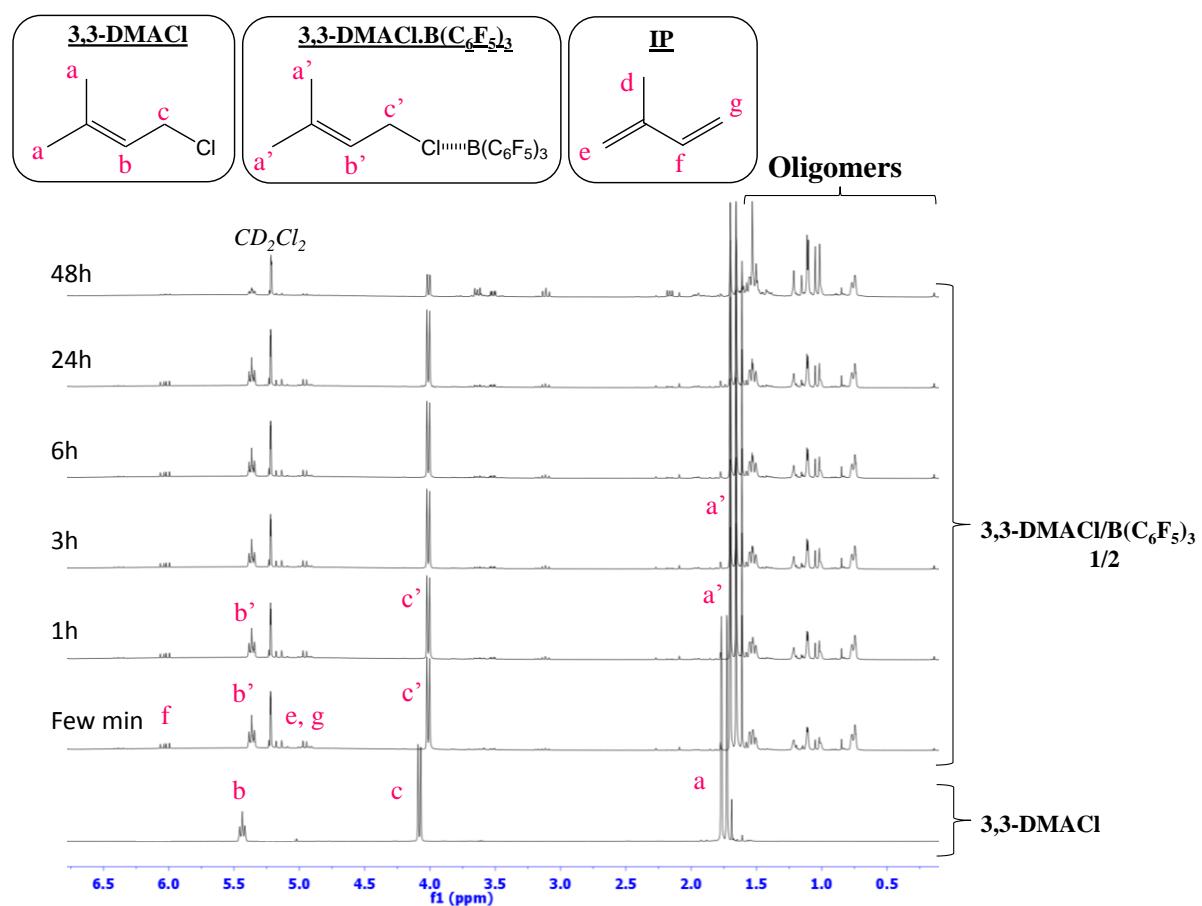
**Figure S1.**  $^1\text{H}$  NMR spectra of 3,3-DMAOH (a) and 3,3-DMAOAc (b)



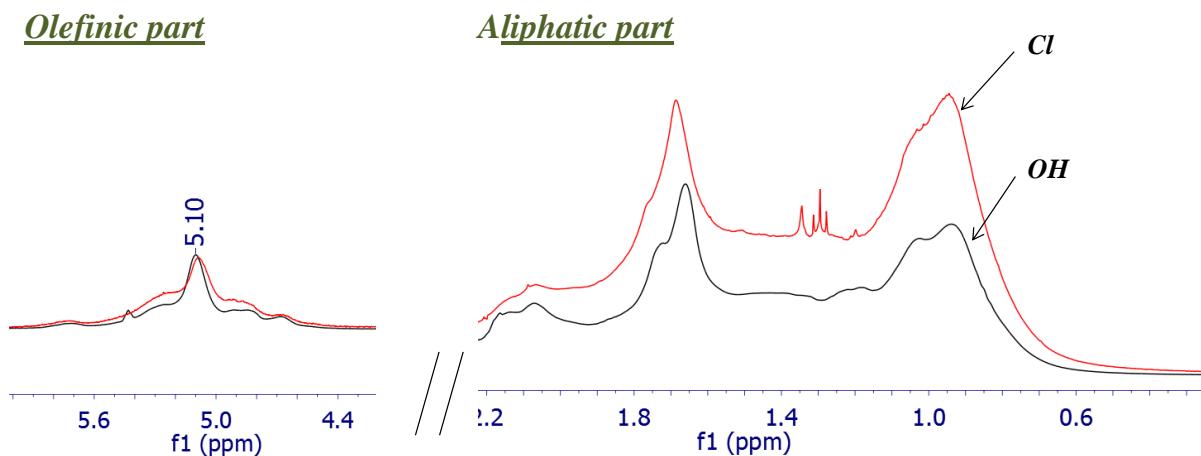
**Figure S2.**  $^1\text{H}$  NMR spectra of 3,3-DMAOAc/ $\text{B}(\text{C}_6\text{F}_5)_3$  at ratio 1/2 over time in  $\text{CD}_2\text{Cl}_2$  at 20°C.



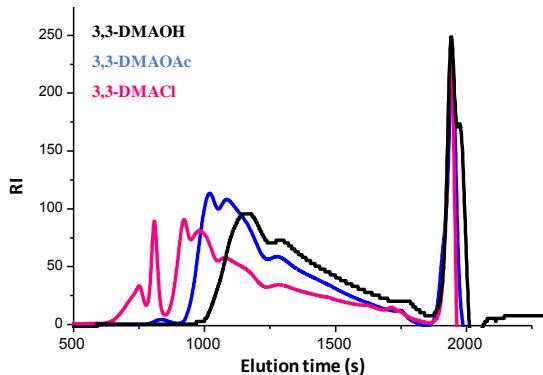
**Figure S3.**  $^1\text{H}$  NMR spectra of 3,3-DMABr/ $\text{B}(\text{C}_6\text{F}_5)_3$  at ratio 1/2 over time in  $\text{CD}_2\text{Cl}_2$  at 20°C.



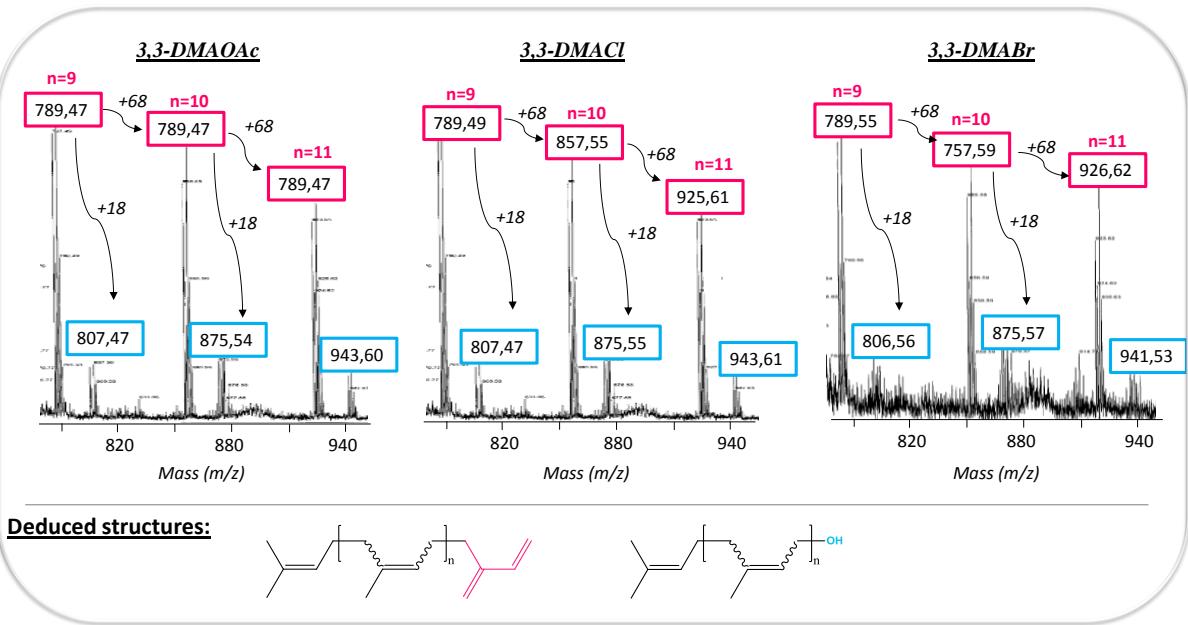
**Figure S4.** <sup>1</sup>H NMR spectra of 3,3-DMACl/ $B(C_6F_5)_3$  at ratio 1/2 over time in  $CD_2Cl_2$  at 20°C.



**Figure S5.** <sup>1</sup>H NMR spectra superimposition of PIs obtained with the system IP/3,3-DMA/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> /DtBp 75/1/2/0 in CH<sub>2</sub>Cl<sub>2</sub> at 20 °C (case X = OH, Cl). Normalization based on the olefinic peaks characteristic of a *trans*-1,4 unit at 5.1 ppm.



**Figure S6.** SEC chromatograms of PIPs obtained in presence of IP/3,3-DMA/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in 75/1/2 proportions in CH<sub>2</sub>Cl<sub>2</sub> at 20°C (PIPs obtained with 3,3-DMABr were insoluble in THF).



**Figure S7.** Zoom of Maldi-TOF spectrum of polyisoprenes obtained with IP/3,3-DMA<sub>x</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/d<sup>t</sup>BP (75/1/2/0.26) in dichloromethane at 20°C (ionized by Ag).