

## **Supporting information**

### **Controlled Radical Polymerization of Myrcene in Bulk: Mapping the Effect of Conditions on the System.**

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*Synthesis of 2-ethylsulfanyltiocarbonylsulfanyl-propionic acid ethyl ester CTA.*

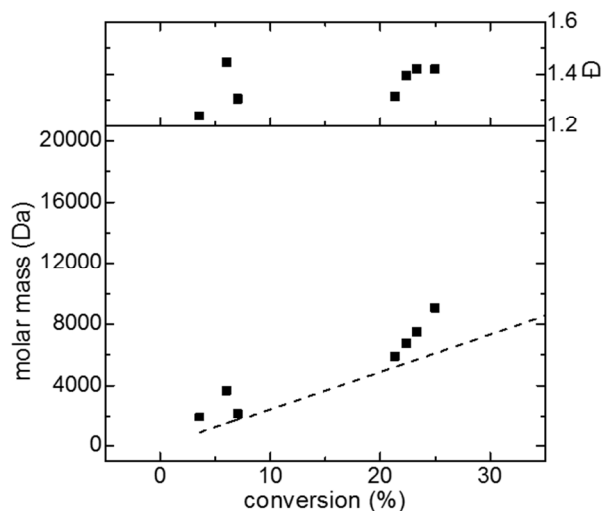
30 mL abs. toluene, KOH (0.025 g, 0.43 mmol), 1,1'-thiocarbonyl diimidazole (1.80 g, 9.60 mmol) were placed into a three neck round bottom flask, under N<sub>2</sub>. Then 2-mercaptopropionate (1.32 mL, 1.36 g, 9.60 mmol) was dropwise added to the solution. The mixture was heated to 60 °C for 6 h and stirred overnight at room temperature. In the next step ethanethiol (0.70 mL, 0.75 g, 9.60 mmol) was added also dropwise, heated to 60 °C for 6 h and stirred overnight at room temperature. The mixture was filtered, and concentrated by rotavap. The product was purified by silica gel column chromatography (eluent: hexane/EtOAc (5%)), concentrated by rotavap to give the CTA as a yellow oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.25-1.29 (t, 3H), 1.33-1.37 (t, 3H), 1.58-1.60 (d, 3H), 3.33-3.39 (q, 2H), 4.16-4.21 (q, 2H), 4.77-4.83 (q, 1H)

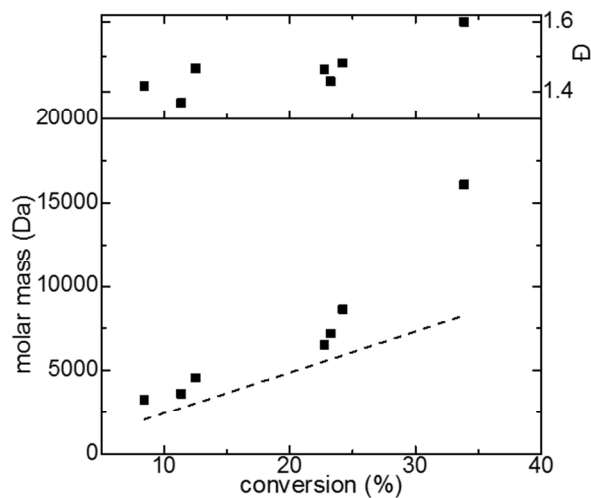
*Synthesis of S-1-Dodecyl-S'-( $\alpha,\alpha'$ -dimethyl- $\alpha''$ -acetic acid)trithiocarbonate CTA.*

48 mL (0.20 mol) Dodecanethiol, 122 mL acetone and 3.6 mL (0.008 mol) Aliquot 336 were placed into a two-neck round bottom flask, under N<sub>2</sub>. 11 mL (0.21 mol) 50 wt.% NaOH solution was added dropwise while the temperature kept under 10 °C. After one hour, 12.1 mL (0.20 mol) CS<sub>2</sub> dissolved in 26 mL acetone was slowly added to the solution at room temperature. Afterwards, 24.2 mL (0.30 mol) chloroform was syringed into the solution, and after 30 mins, 52.5 mL (1 mol) 50 wt.% NaOH solution was dropwise added. The reaction was stirred overnight at room temperature. First, 300 mL distilled water and then 50 mL cc. HCl was carefully added to the solution. The product was filtered, washed with water and recrystallized from *n*-hexane.

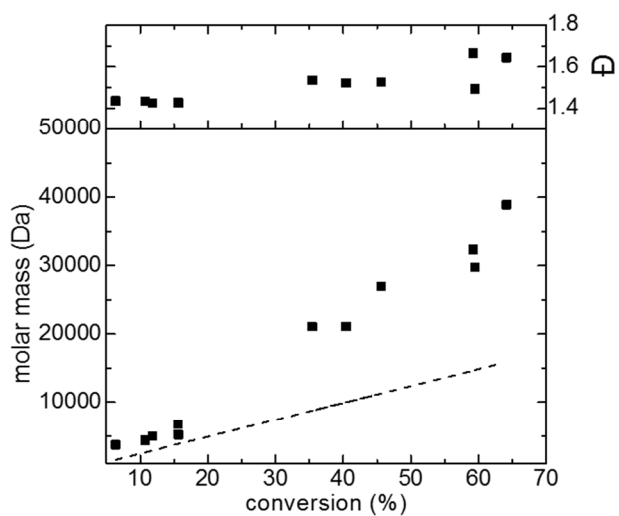
$^1\text{H}$  NMR ( $\text{d}_6\text{-DMSO}$ ): 0.84- 0.87 (t, 3H), 1.24-1.33 (m, 20H), 1.62 (s, 6H), 3.28- 3.31 (t, 2H), 12.9 (s, 1H).



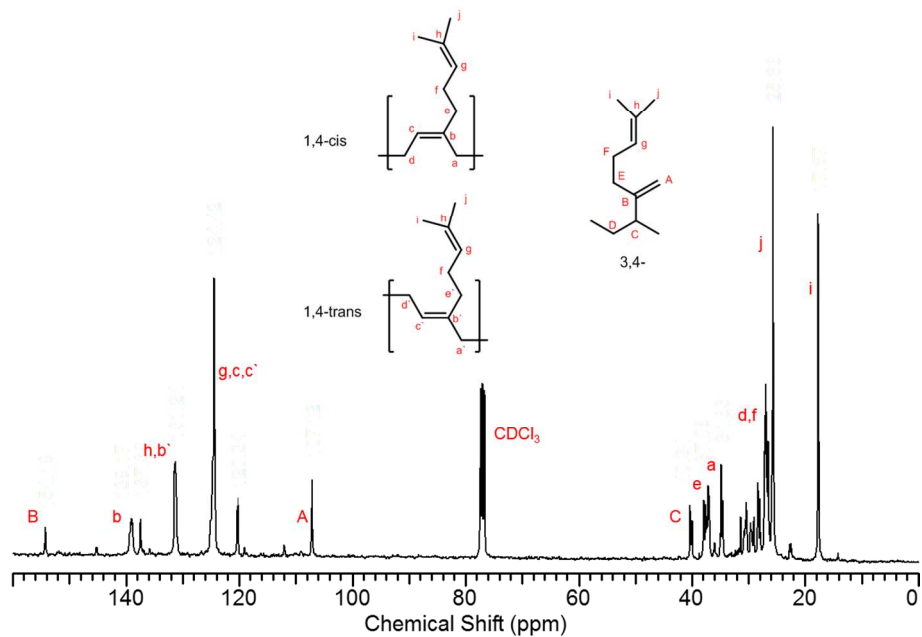
**Figure S1.** Evolution of molar masses (■) and Đ (●) with conversion for the bulk RAFT polymerization of myrcene using the initiator/CTA system AIBN/DATC at 90 °C. The theoretical molar masses (dashed lines) are also included.



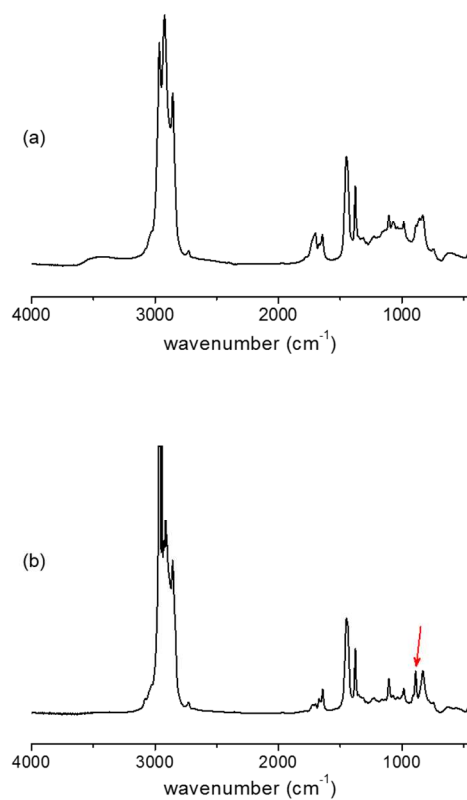
**Figure S2.** Evolution of molar masses (■) and Đ (●) with conversion for the bulk RAFT polymerization of myrcene using the initiator/CTA system DBPO/DATC at 90 °C. The theoretical molar masses (dashed lines) are also included.



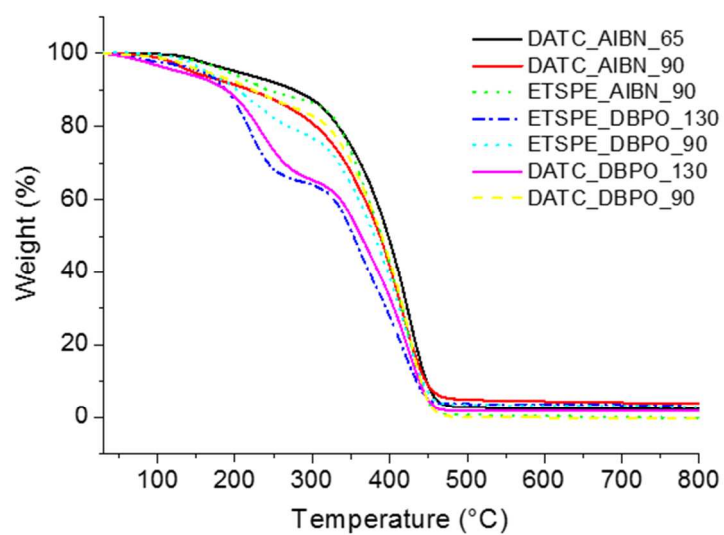
**Figure S3.** Evolution of molar masses (■) and  $\bar{D}$  (●) with conversion for the bulk RAFT polymerization of myrcene using the initiator/CTA system DBPO/DATC at 130 °C. The theoretical molar masses (dashed lines) are also included.



**Figure S4.** 100 MHz  $^{13}\text{C}$  NMR spectrum of polymyrcene at 65 % monomer conversion, using DATC/DBPO CTA-initiator system at 130 °C in  $\text{CDCl}_3$ .



**Figure S5.** FT-IR spectra of polymyrce using (a) AIBN/DATC at 65 °C at 13 % monomer conversion, and DBPO/DATC at 130 °C 59 % monomer conversion.



**Figure S6.** TGA thermograms of the polymyrce samples of this work.