

Supplementary Materials: Stereoselective Copolymerization of Styrene with Terpenes Catalyzed by an *Ansa*-Lanthanidocene Catalyst: Access to New Syndiotactic Polystyrene-based Materials

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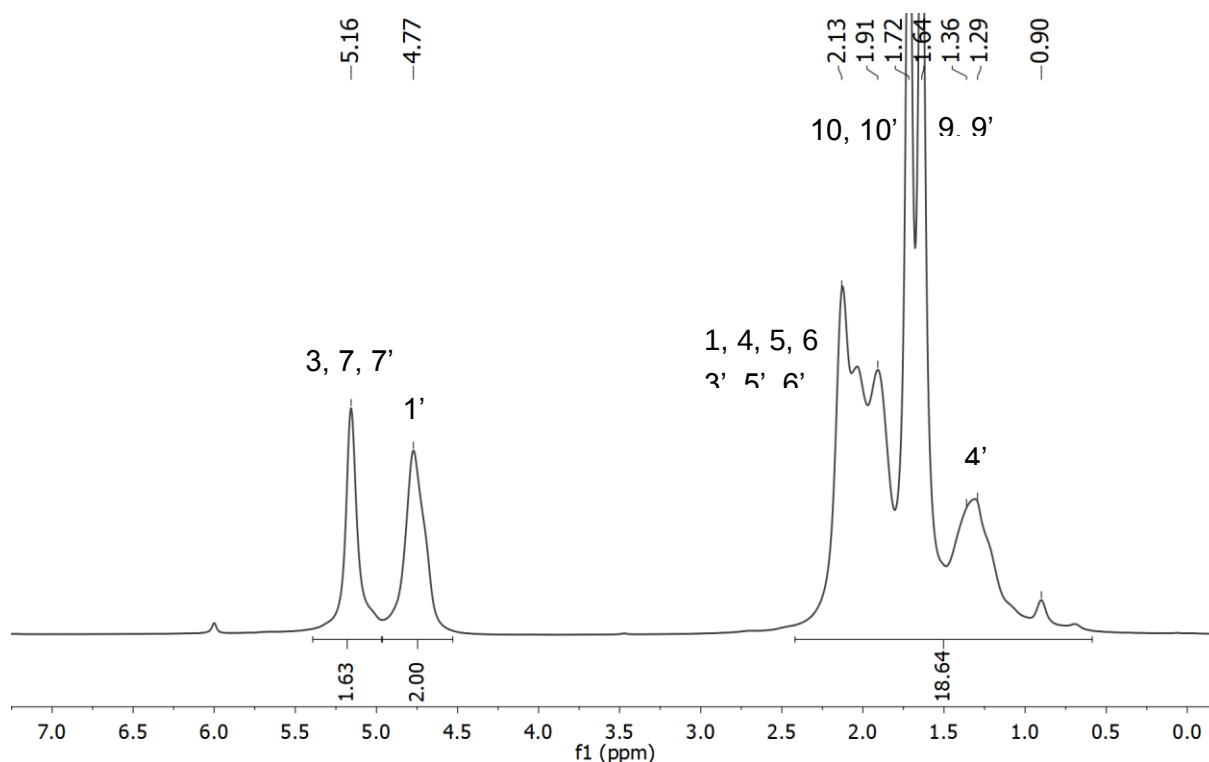


Figure S1. ^1H NMR spectrum (400 MHz, 25 °C, $\text{TCE-}d_2$) of poly(My) ($T_{\text{polym}} = 120$ °C, Table 1, entry 2).

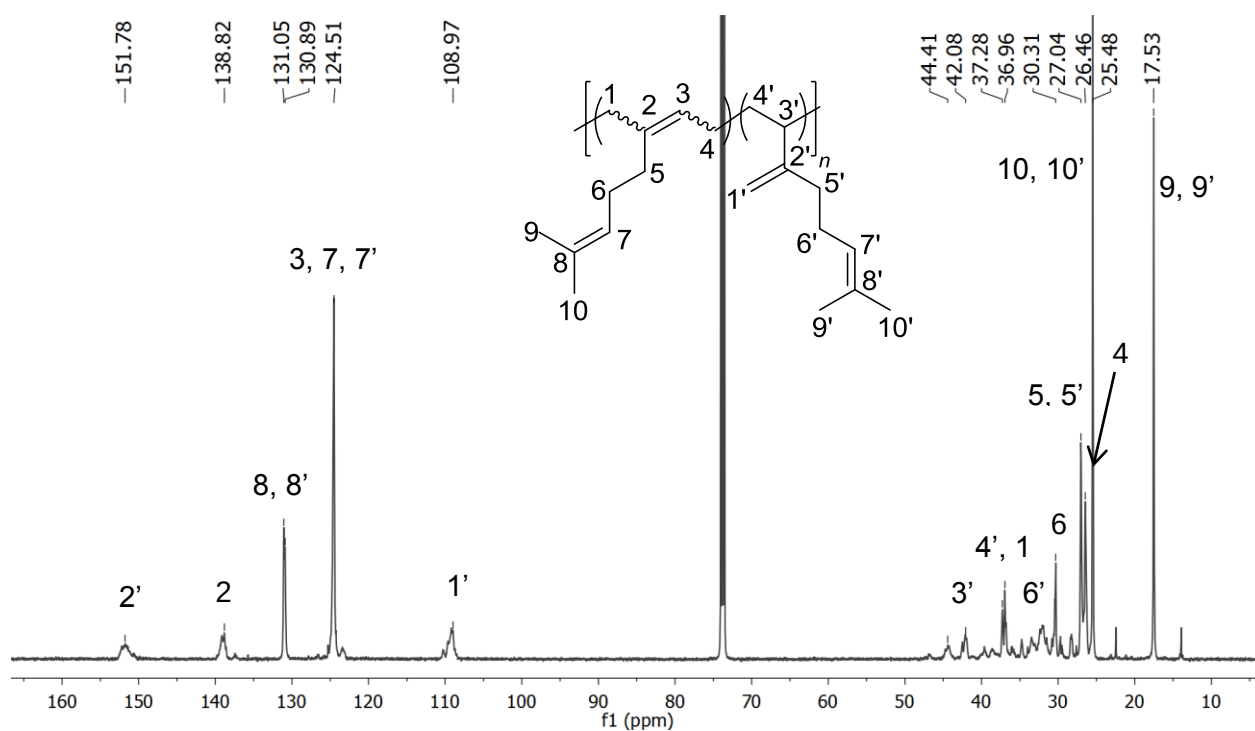


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz, 60 °C, $\text{TCE-}d_2$) of poly(My) ($T_{\text{polym}} = 60$ °C, Table 1, entry 1).

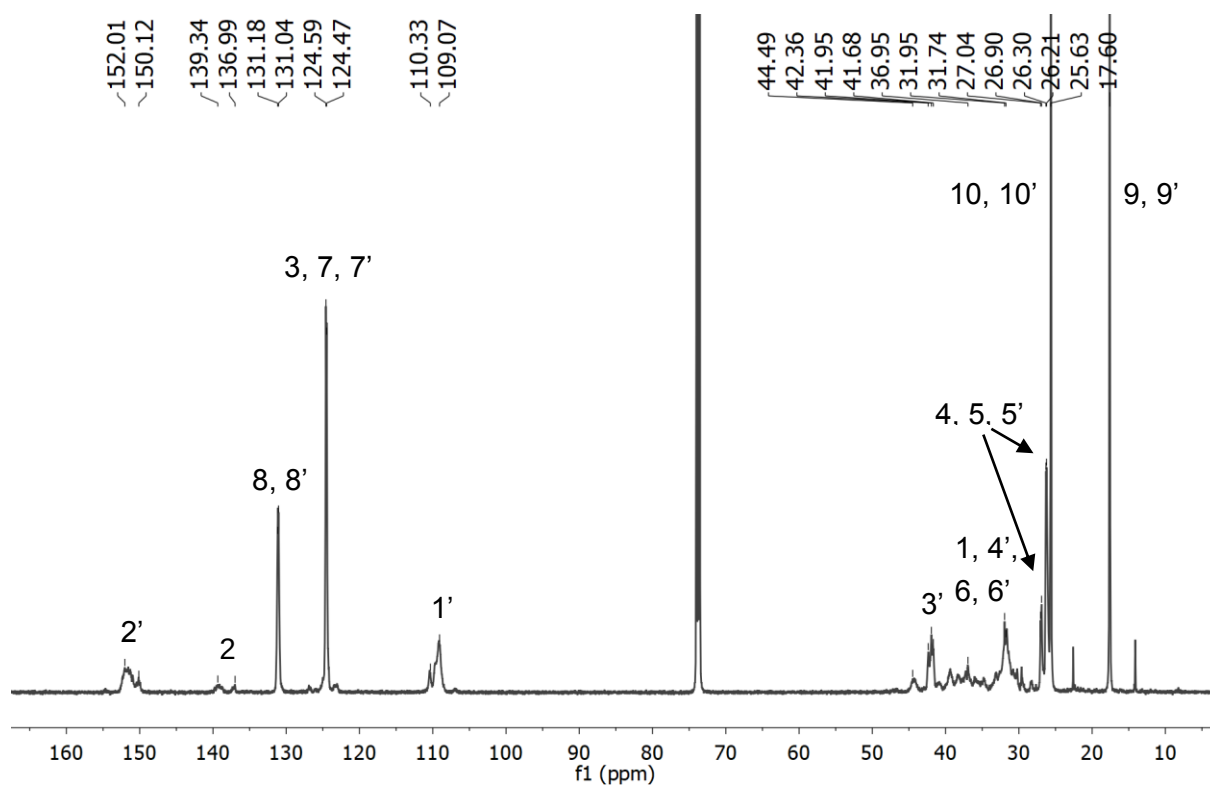


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, 25 °C, $\text{TCE-}d_2$) of poly(My) ($T_{\text{polym}} = 120$ °C, Table 1, entry 2).

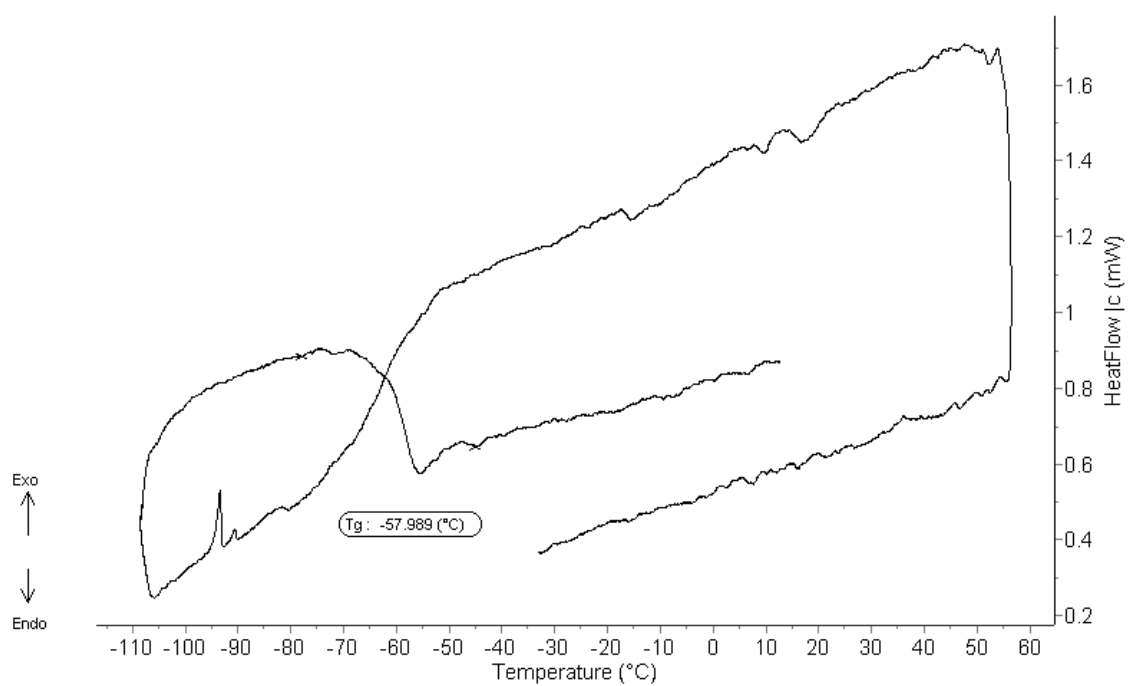


Figure S4. DSC thermogram of poly(My) (Table 1, entry 1).

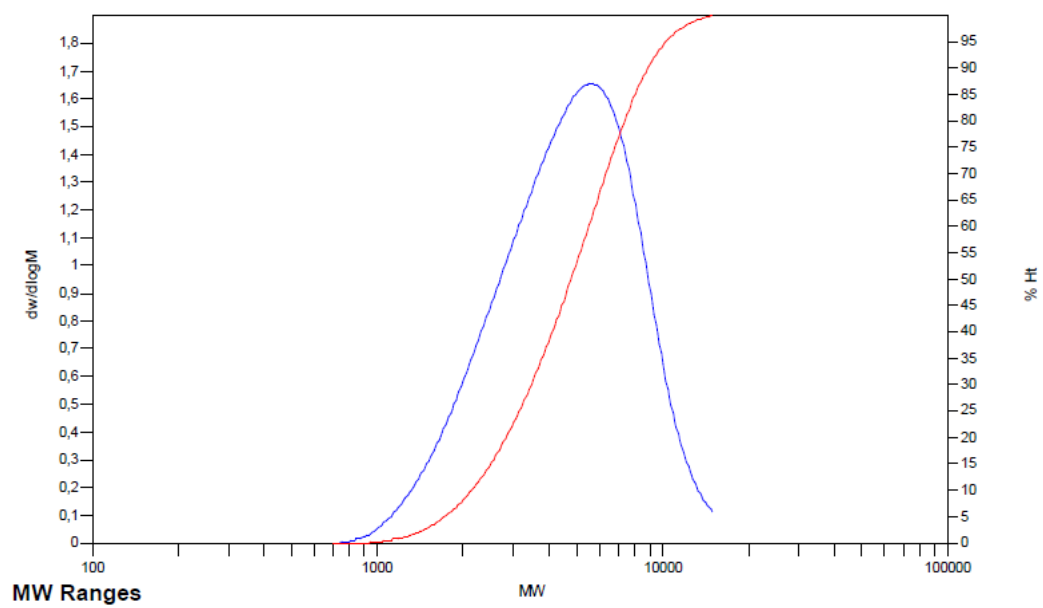


Figure S5. GPC trace of poly(Fa) (Table 1, entry 1).

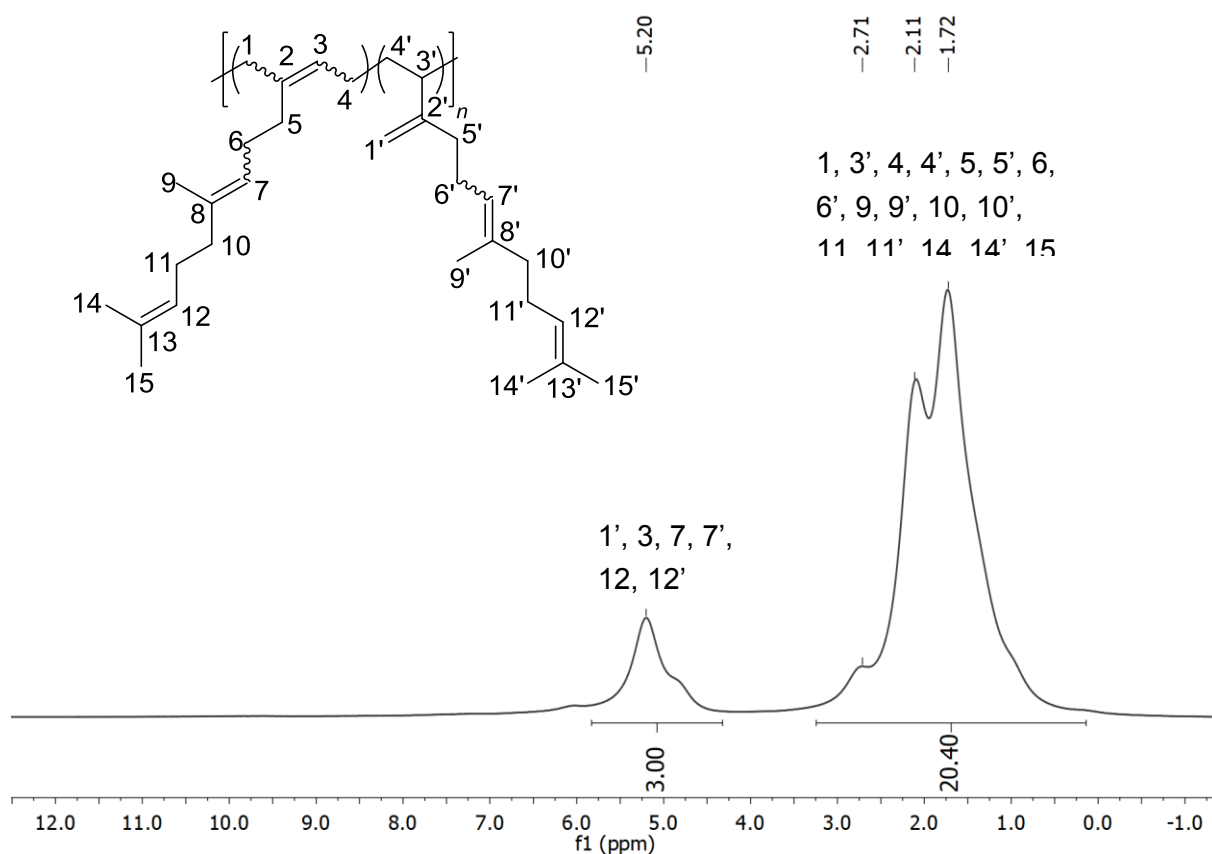


Figure S6. ^1H NMR spectrum (500 MHz, 60 °C, $\text{TCE-}d_2$) of poly(Fa) (Table 1, entry 11).

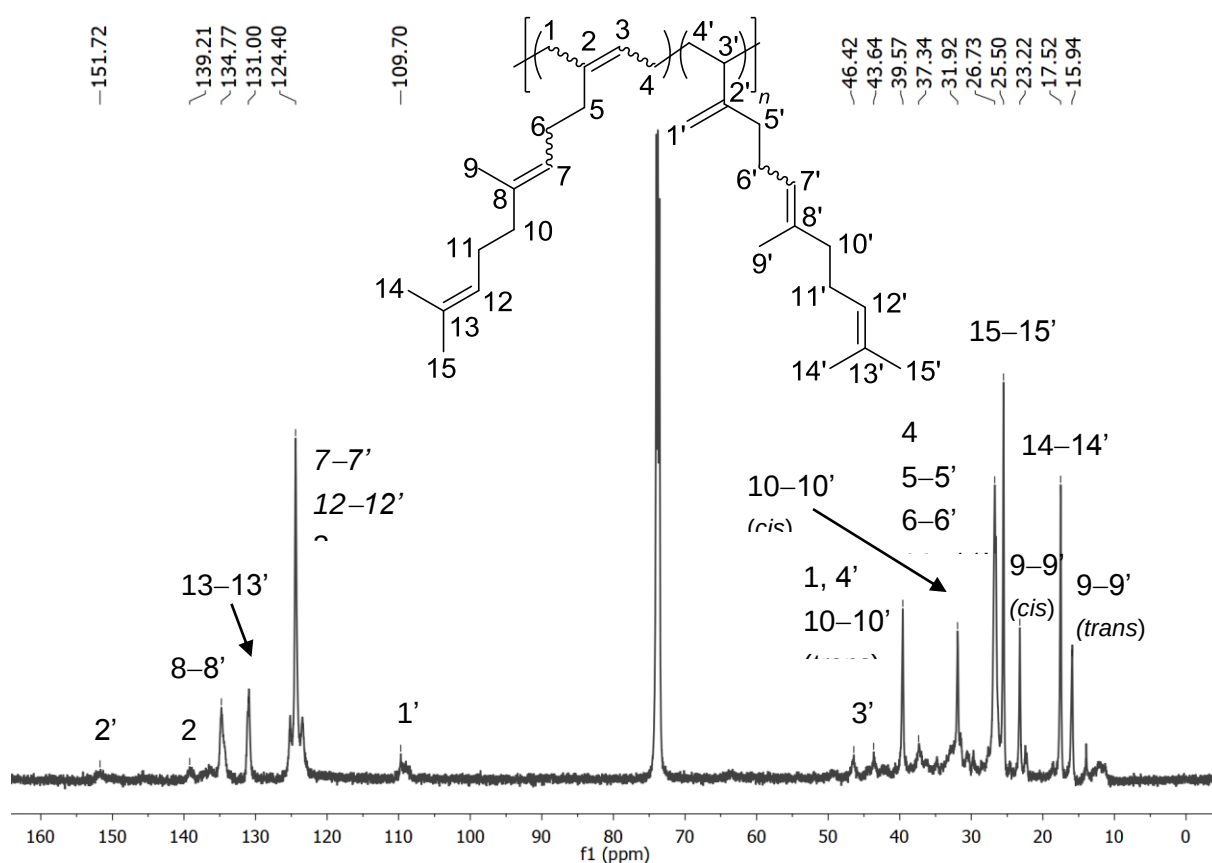
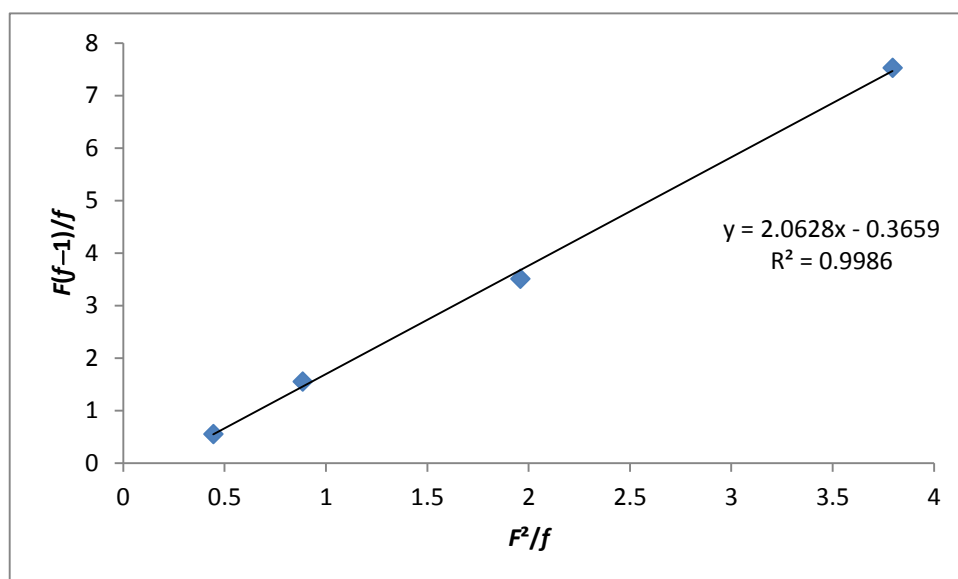
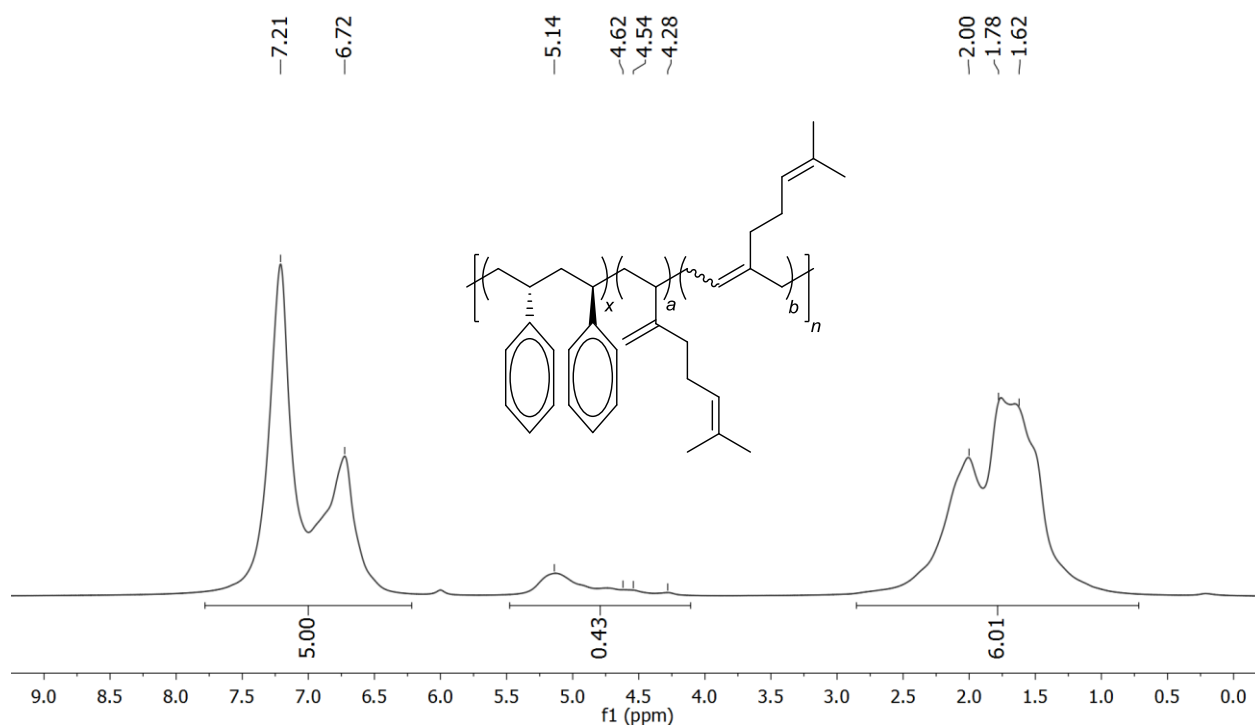


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz, 60 °C, $\text{TCE-}d_2$) of poly(Fa) (Table 1, entry 11).**Figure S8.** Fineman-Ross plot for the copolymerizations of styrene and myrcene with $1/(n\text{Bu})_2\text{Mg}$ at 60 °C and least-square best-fit line ($F = [\text{St}]/[\text{My}]$ in feed, $f = [\text{St}]/[\text{My}]$ in copolymer).**Figure S9.** Typical ^1H NMR spectrum (500 MHz, 60 °C, $\text{TCE-}d_2$) of poly(S-co-My) (Table 1, entry 8).

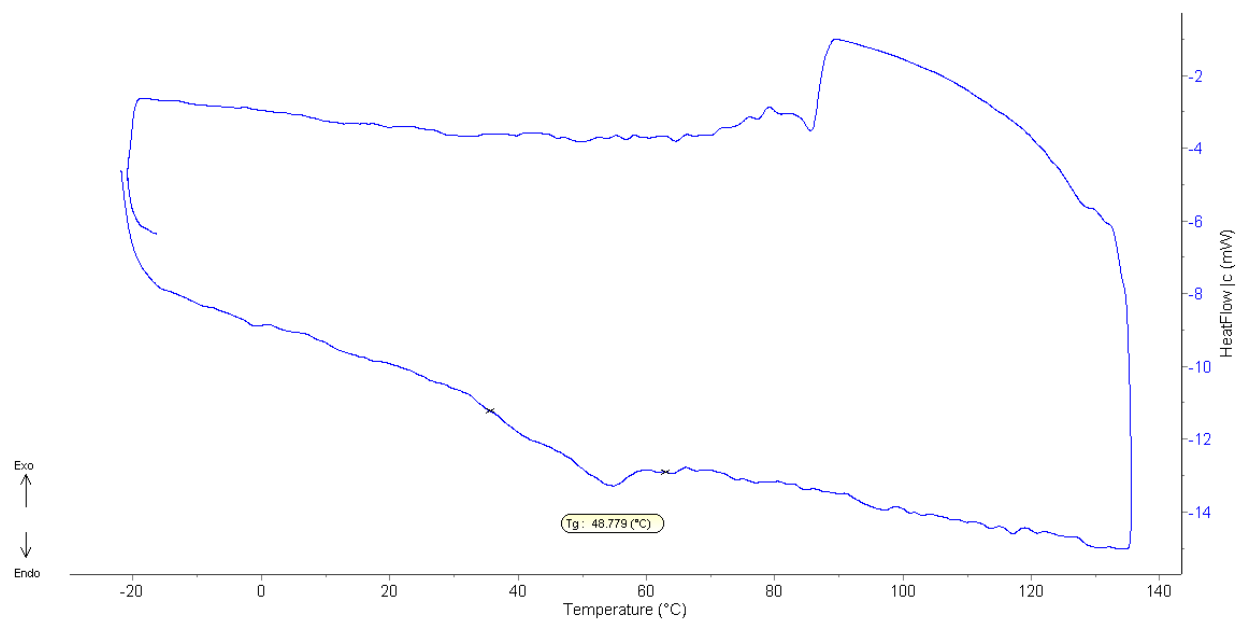


Figure S10. DSC thermogram of poly(S-co-My) (Table 1, entry 8).

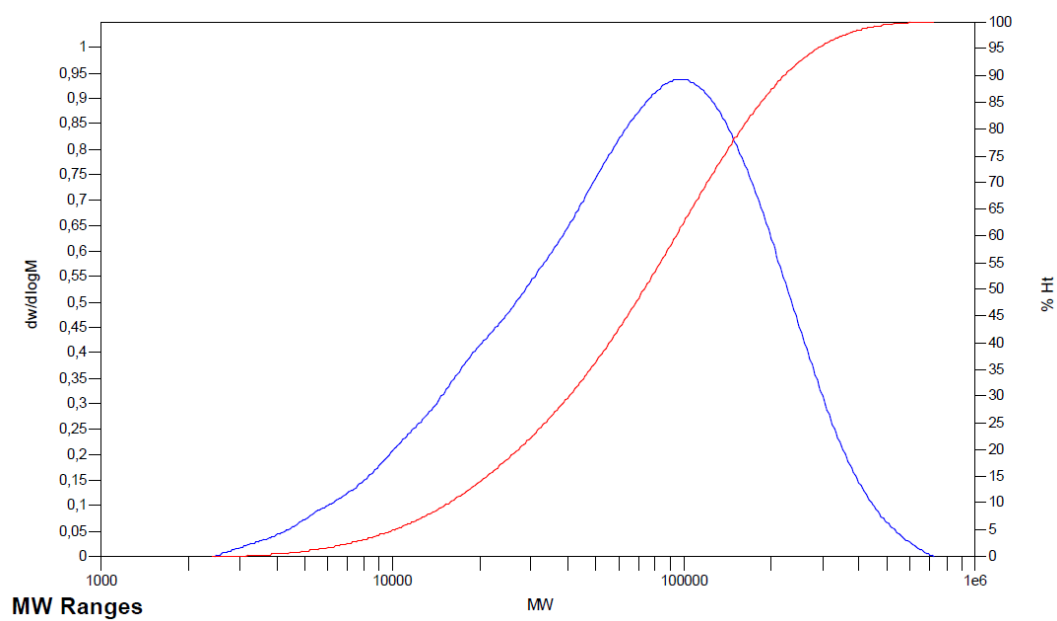


Figure S11. GPC trace of poly(S-co-My) (Table 1, Entry 8).

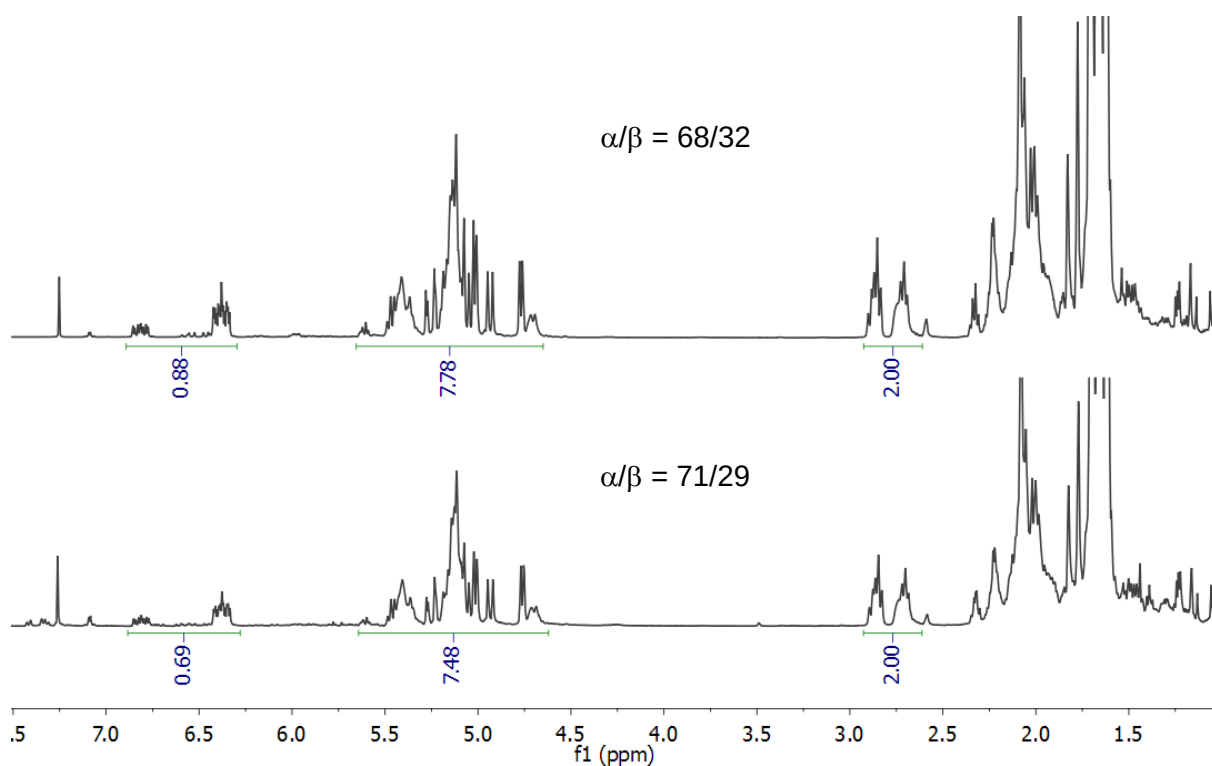


Figure S12. ^1H NMR spectra (400 MHz, 25 °C, CDCl_3) of farnesene: before styrene-farnesene copolymerization (top), after styrene-farnesene copolymerization (bottom) (Table 1, entry 4).

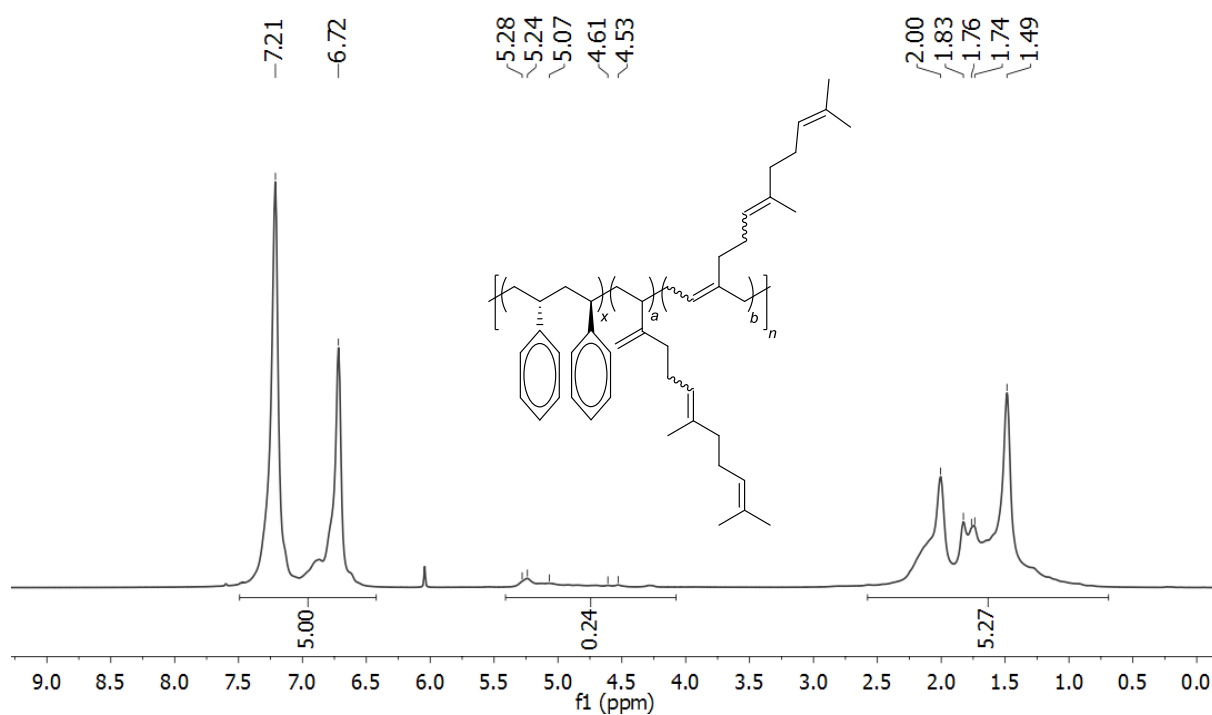


Figure S13. Typical ^1H NMR spectrum (500 MHz, 60 °C, $\text{TCE-}d_2$) of poly(S-co-Fa) (Table 1, entry 17).

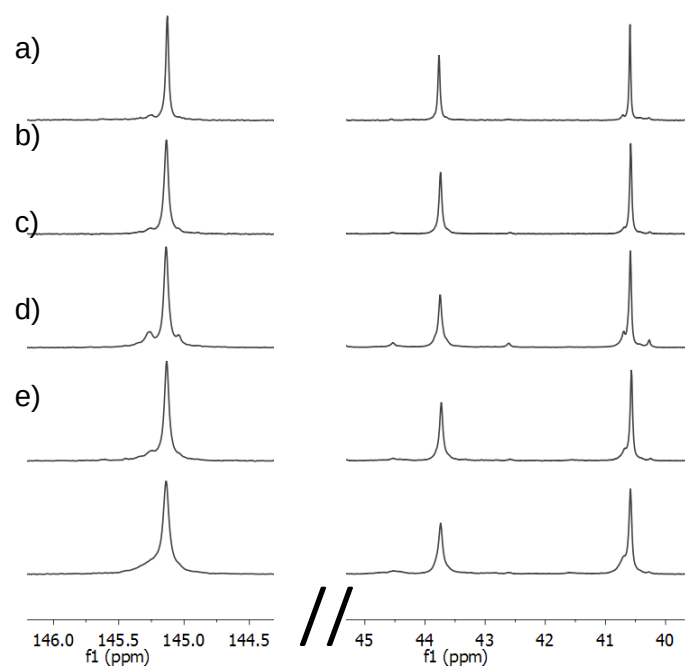


Figure S14. Stack-plot of detailed regions (left, *ipso*; right: methylene carbon) of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (125 MHz, $\text{TCE-}d_2$, 60 °C) of poly(S-*co*-Fa) copolymers (Table 1): a) pure sPS (Table 1, entry 3), b) 2.5 mol% of farnesene (entry 13), c) 3.4 mol% of farnesene (entry 14), d) 4.7 mol% of farnesene (entry 16), e) 9.8 mol% of farnesene (entry 17).

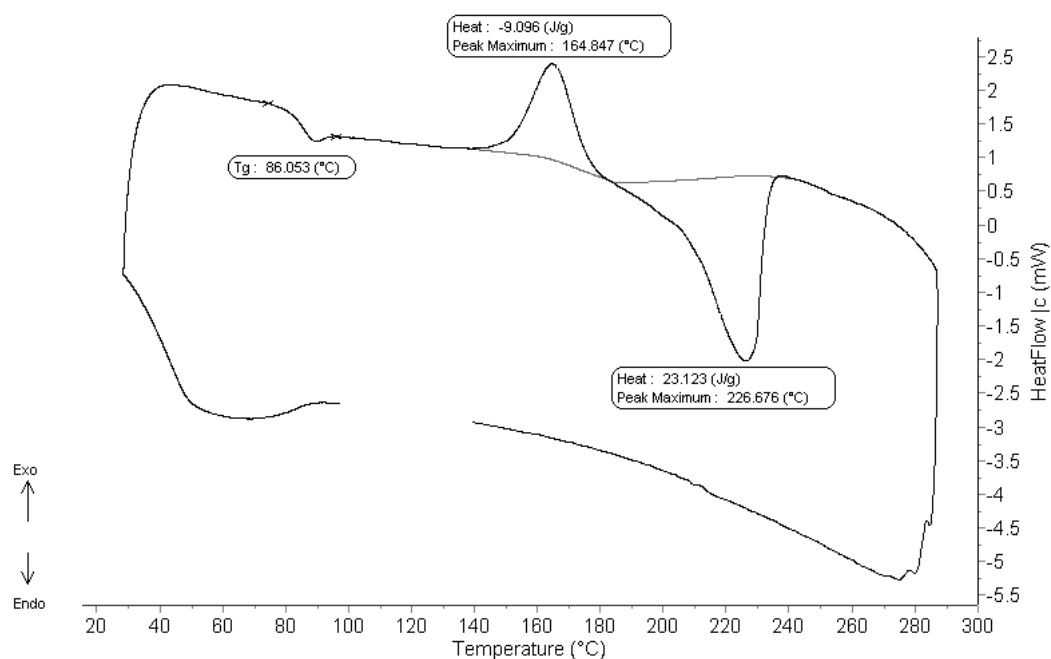


Figure S15. DSC thermogram of poly(S-*co*-Fa) (Table 1, entry 14).

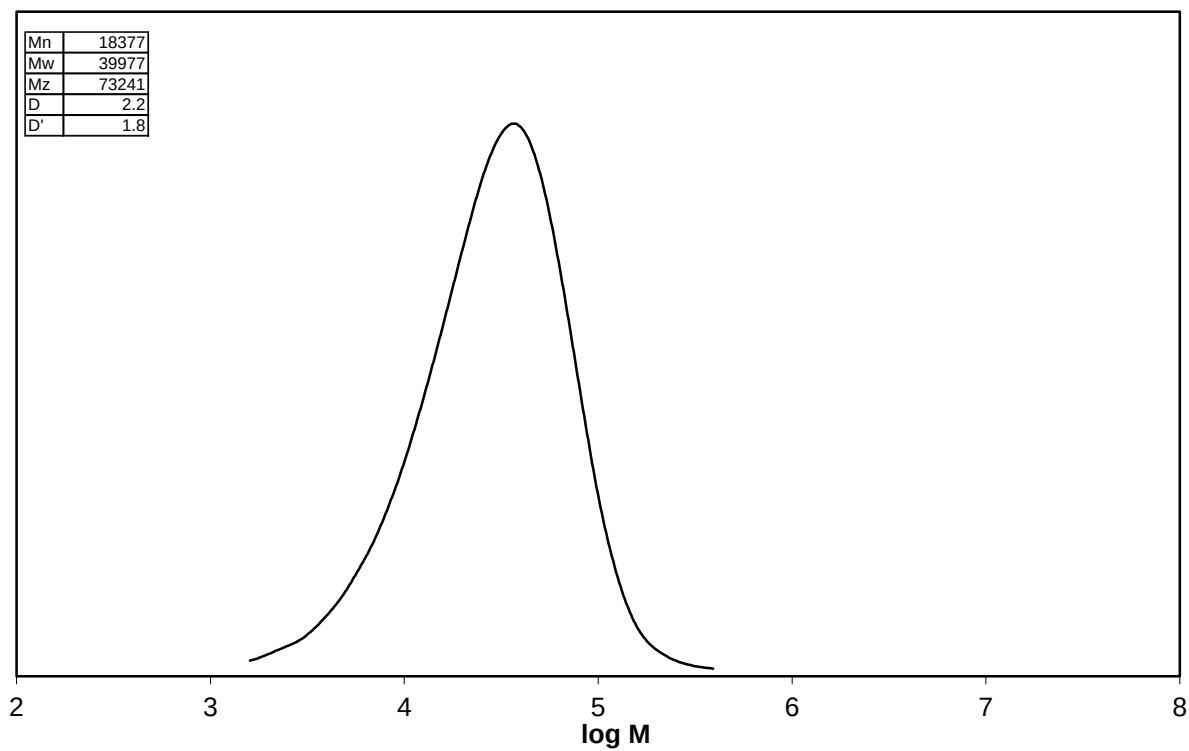


Figure S16. GPC trace of poly(S-co-Fa) (Table 1, entry 14).

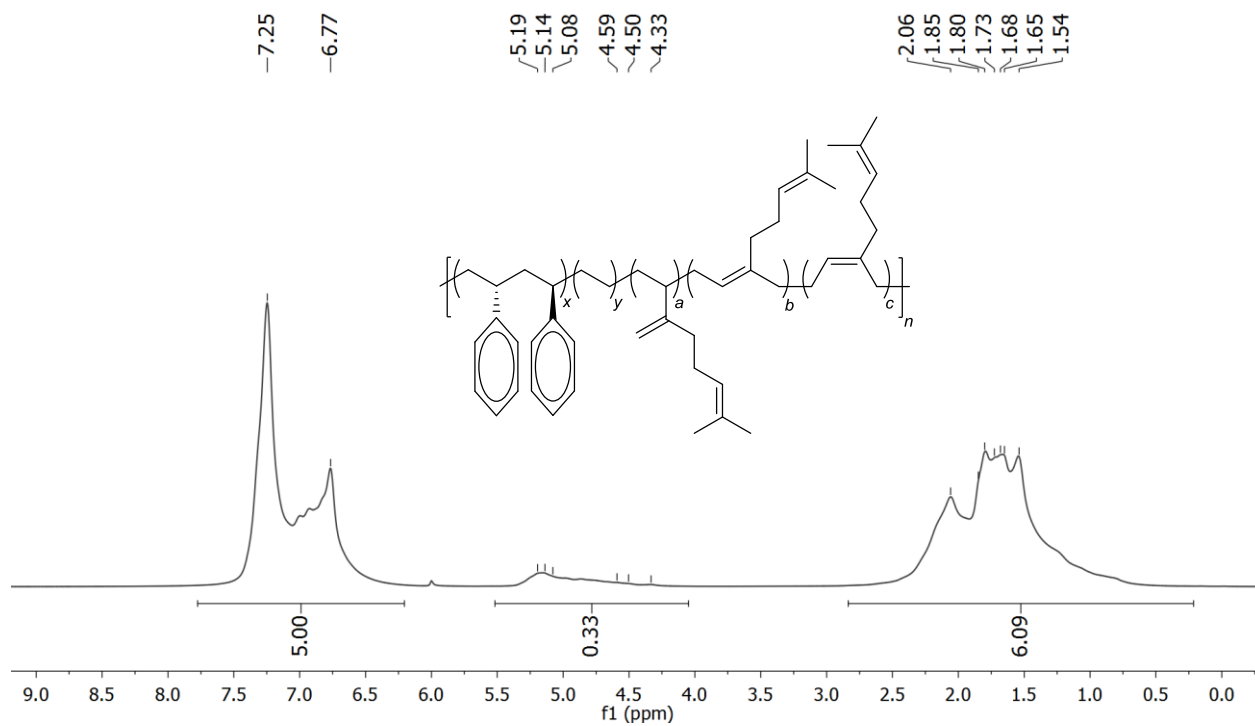


Figure S17. Typical ¹H NMR spectrum (500 MHz, 60 °C, TCE-d₂) of poly(S-co-E-co-My) (Table 2, entry 3).

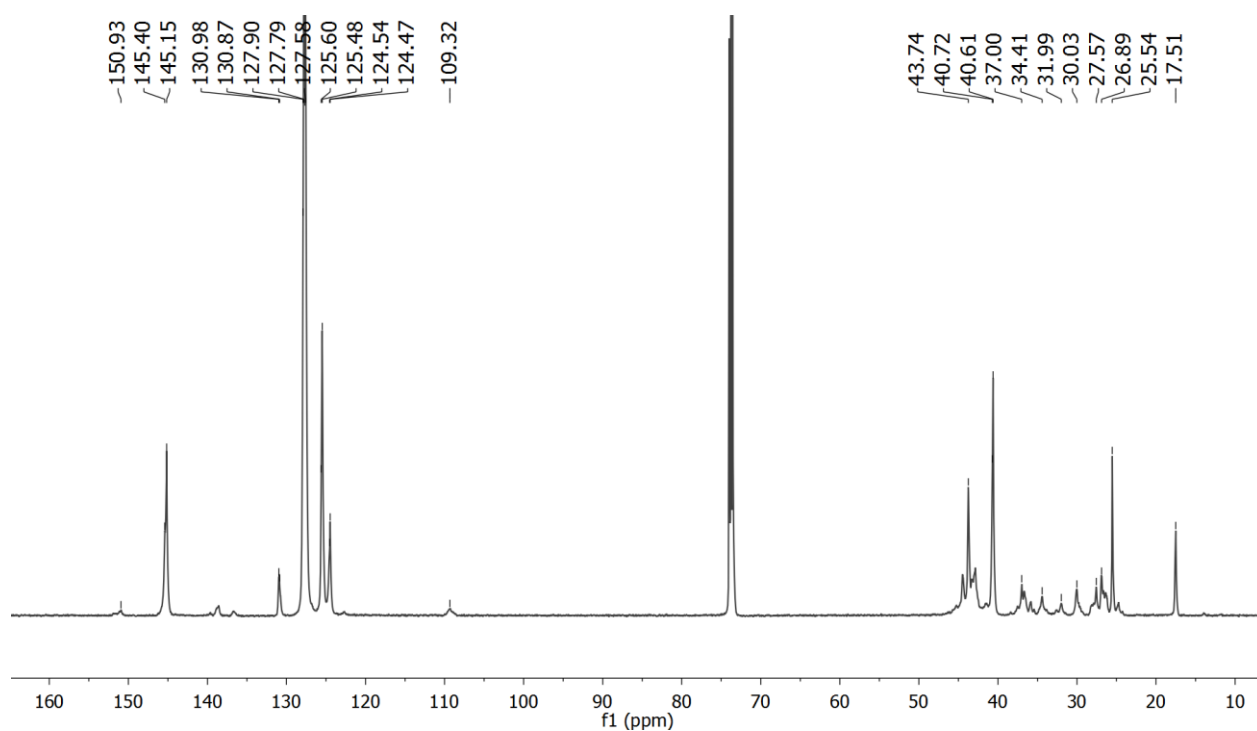


Figure S18. Typical $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz, 60 °C, $\text{TCE-}d_2$) of poly(S-co-E-co-My) (Table 2, entry 3).

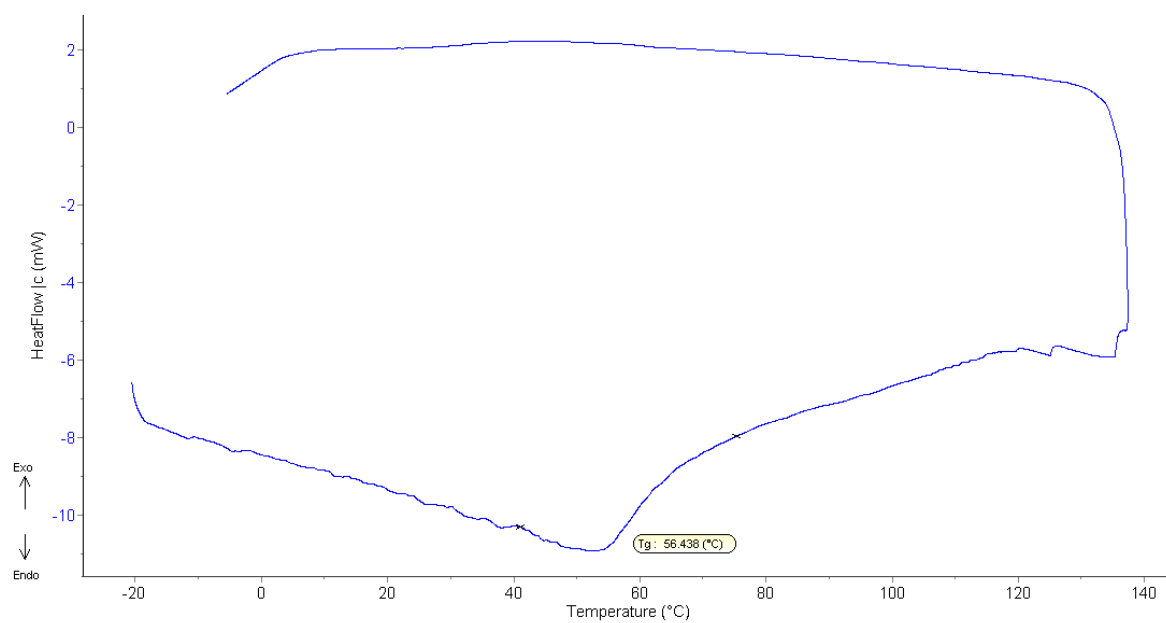


Figure S19. DSC thermogram of poly(S-co-E-co-My) (Table 2, entry 3).

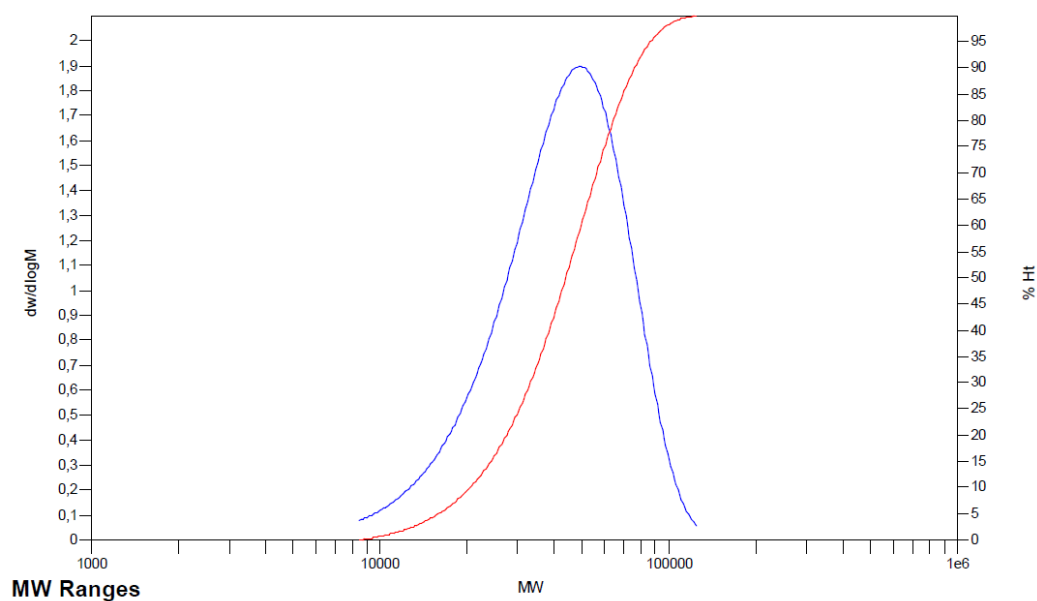


Figure S20. GPC trace of poly(S-co-E-co-My) (Table 2, entry 3).

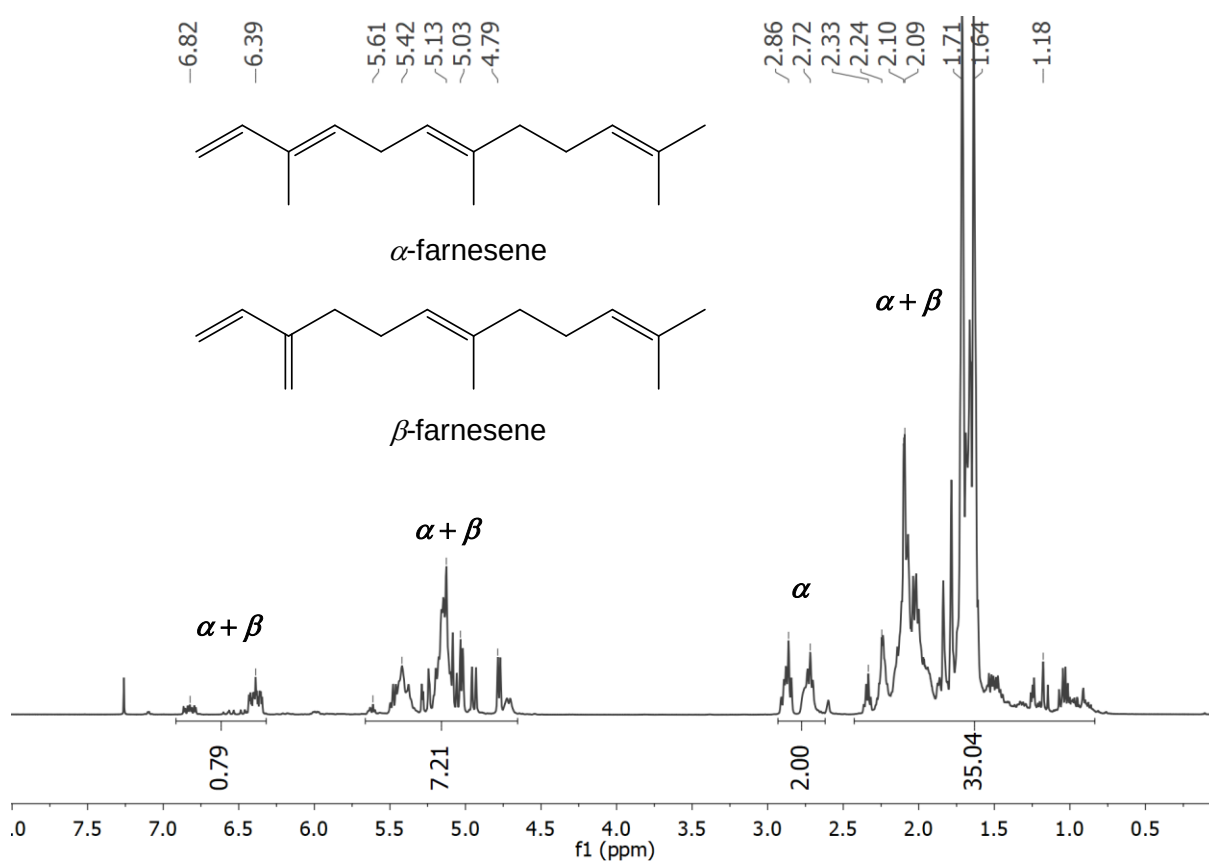


Figure S21. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of farnesene as a mixture of α - and β - isomers.