

# Copolymerization of Ethylene with Styrene Catalyzed by Scandium Catalyst

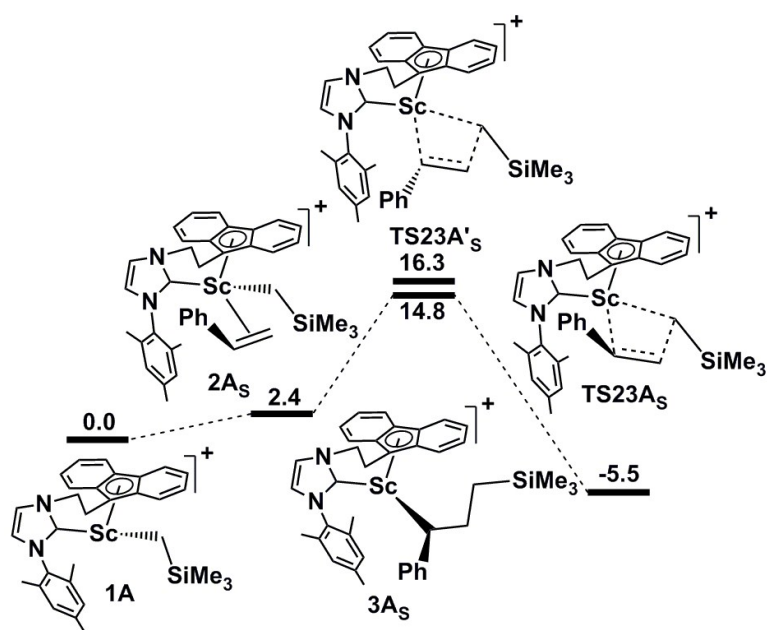
*Shihui Li<sup>†</sup>, Meiyang Wang<sup>§</sup>, and Dongmei Cui<sup>\*†</sup>*

<sup>†</sup> State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

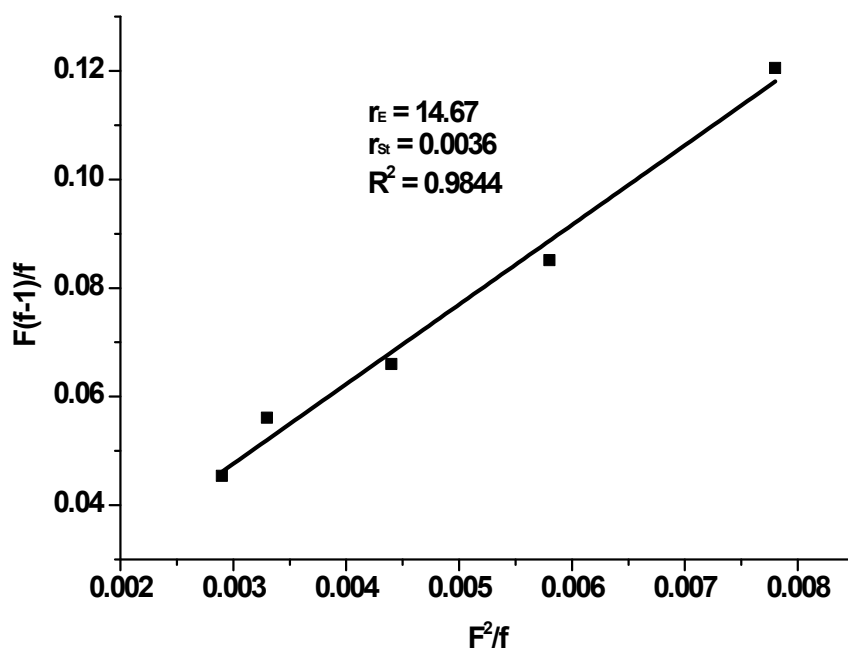
<sup>§</sup> Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, Changchun 130022, China.

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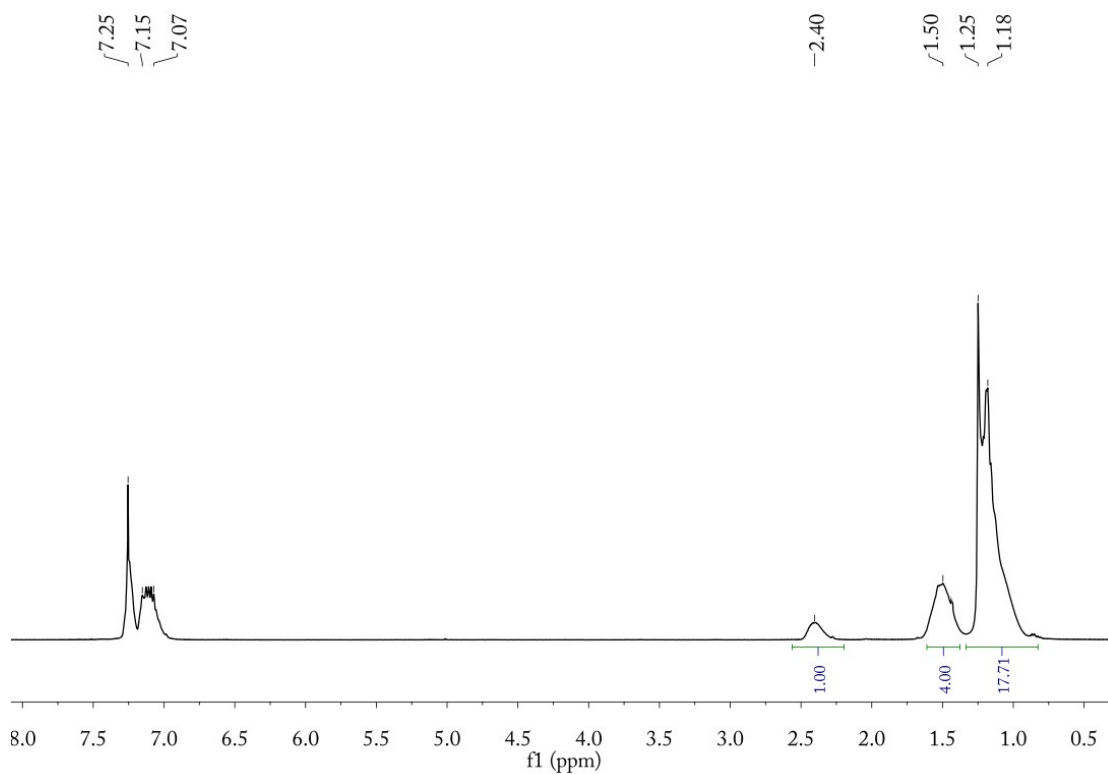
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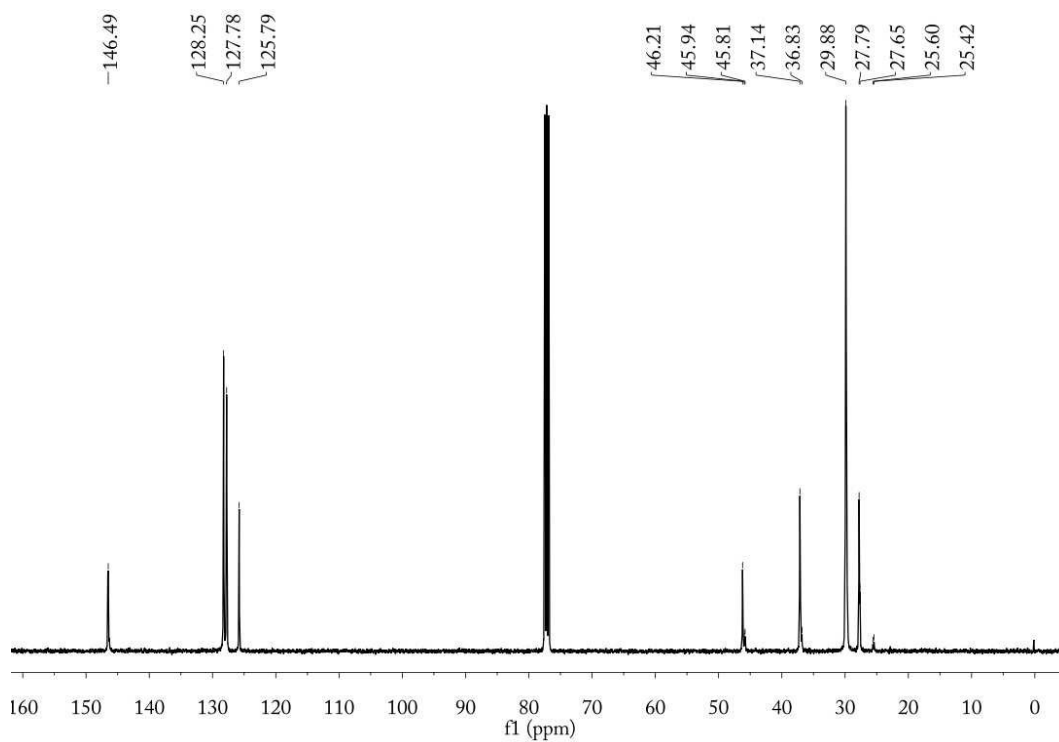
**Fig. S1.** Free energy profile (in kcal/mol) for E-St copolymerization initiated by the active species **1A**.



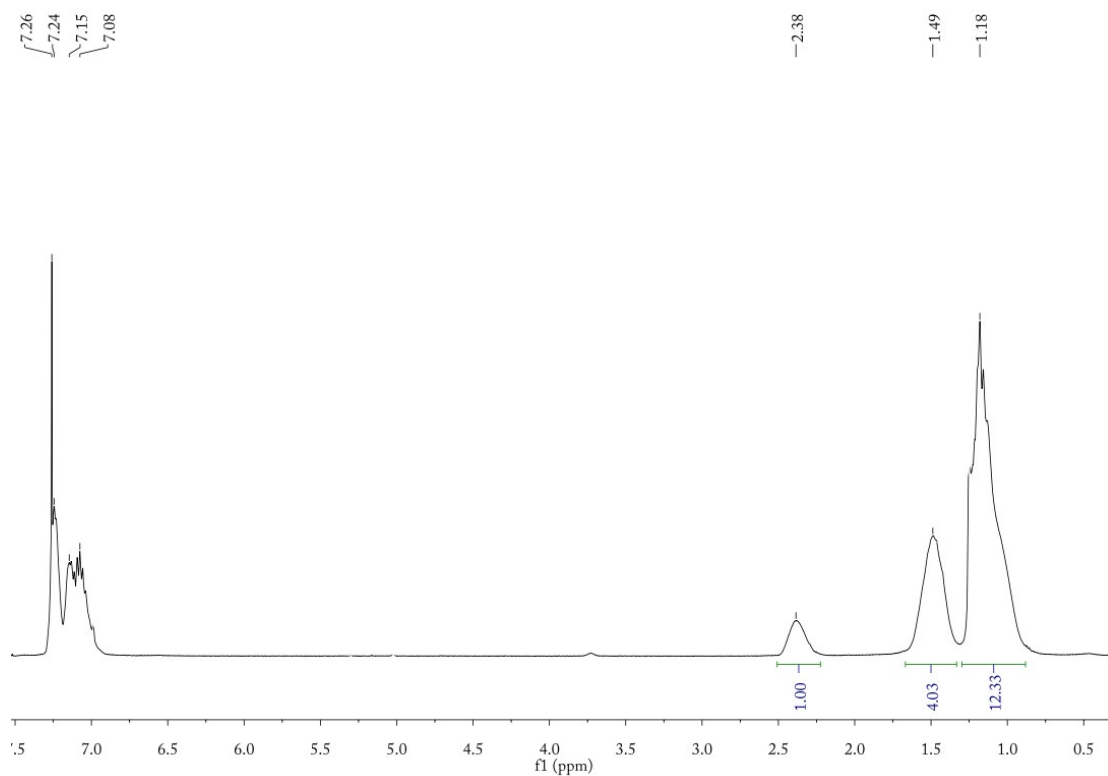
**Fig. S2.** Fineman-Ross plot for copolymerization of E/St using complex **1**.



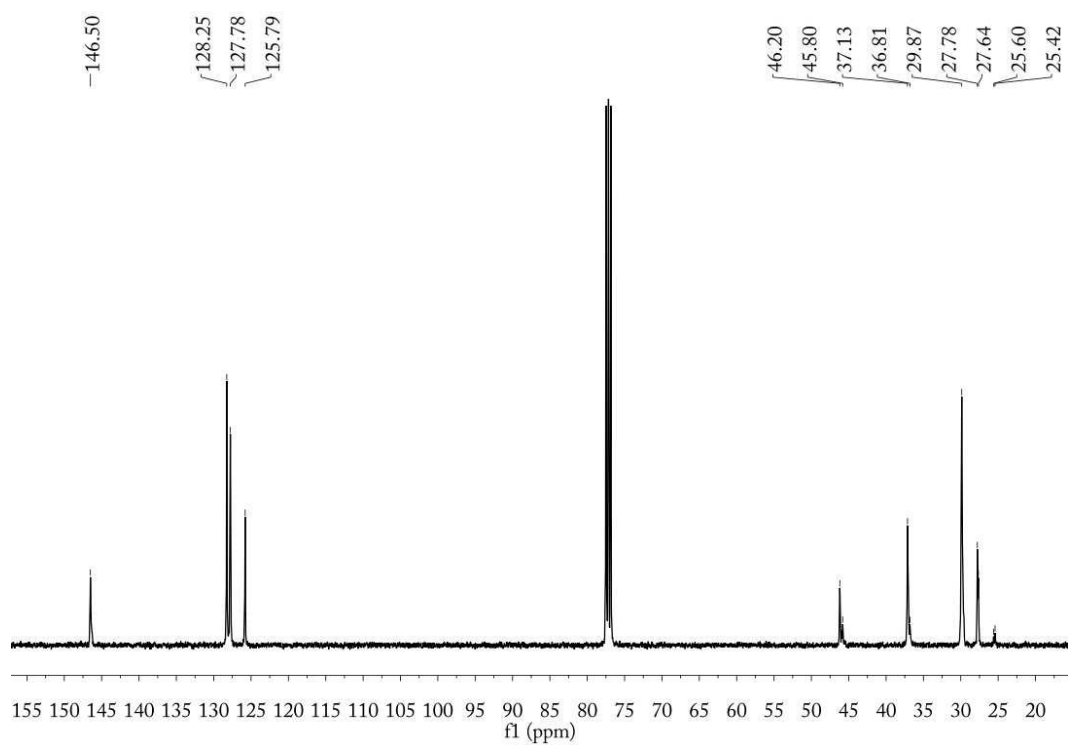
**Fig. S3.**  $^1\text{H}$  NMR spectrum of E-St copolymer with 16.1 mol% of styrene units ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 1, run 11)



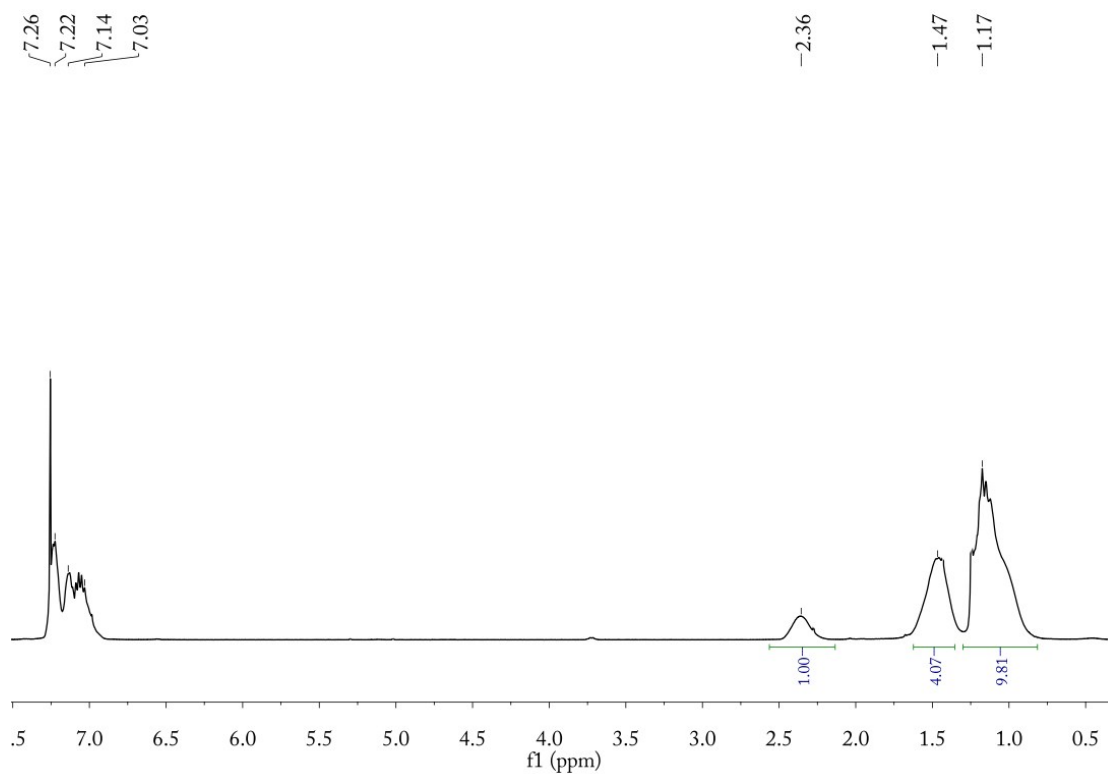
**Fig. S4.**  $^{13}\text{C}$  NMR spectrum of E-St copolymer with 16.1 mol% of styrene units ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 1, run 11)



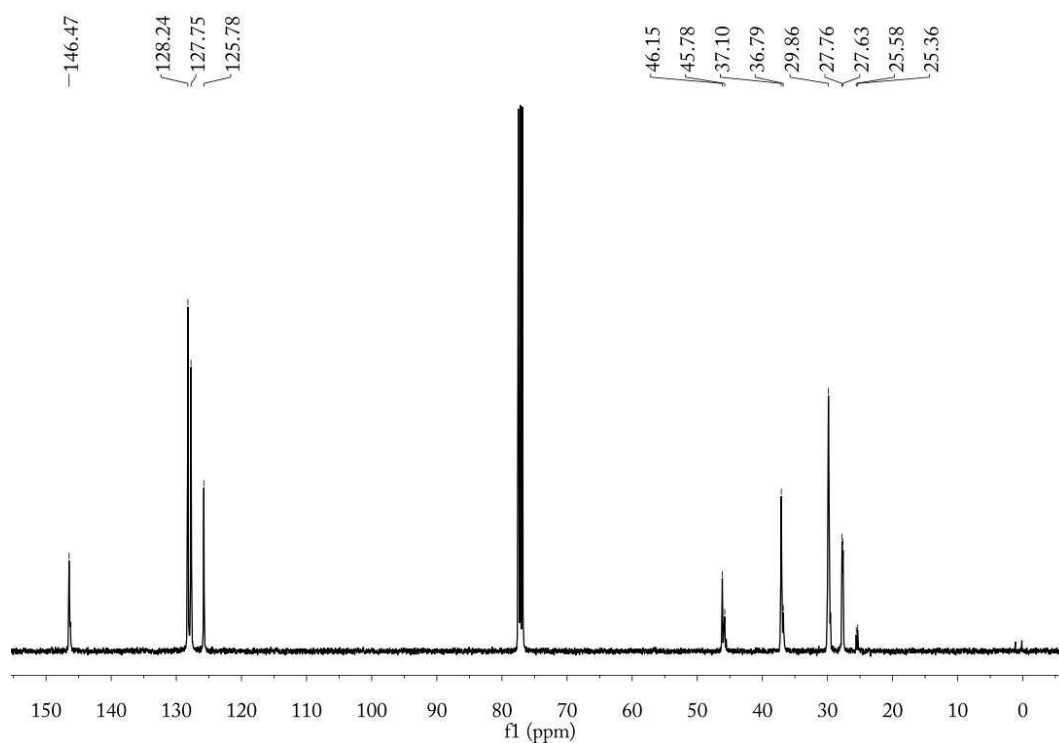
**Fig. S5.**  $^1\text{H}$  NMR spectrum of E-St copolymer with 21.8 mol% of styrene units ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 1, run 12)



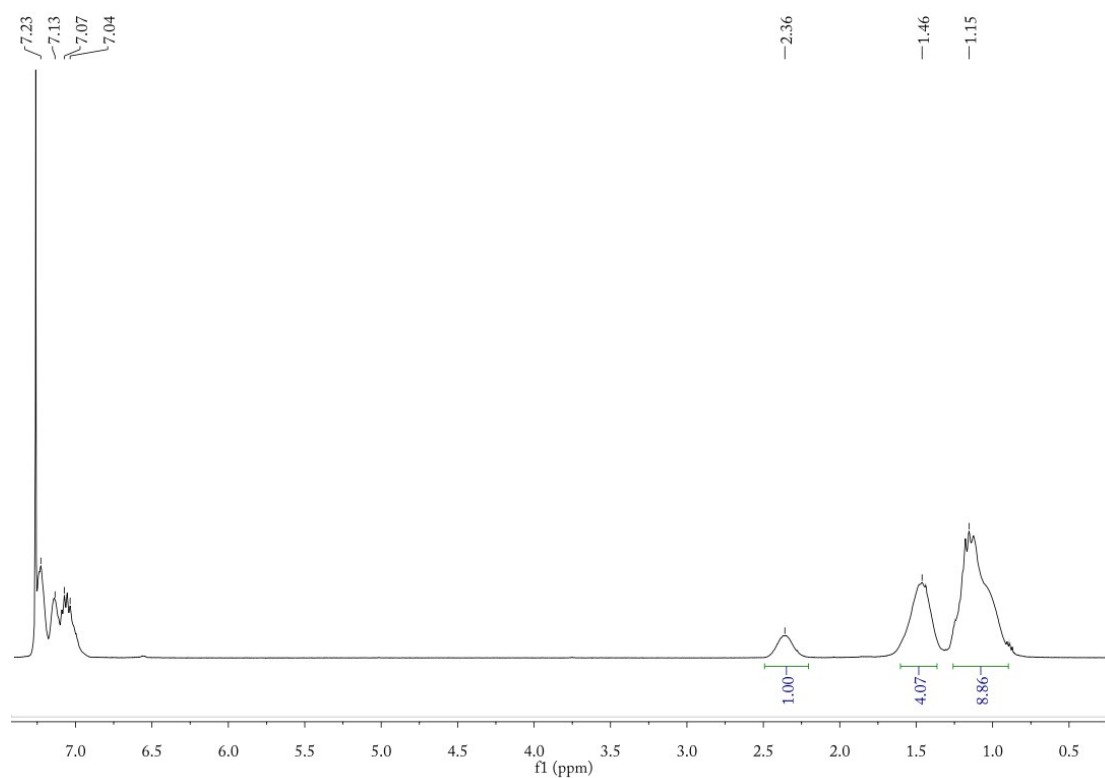
**Fig. S6.**  $^{13}\text{C}$  NMR spectrum of E-St copolymer with 21.8 mol% of styrene units ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 1, run 12)



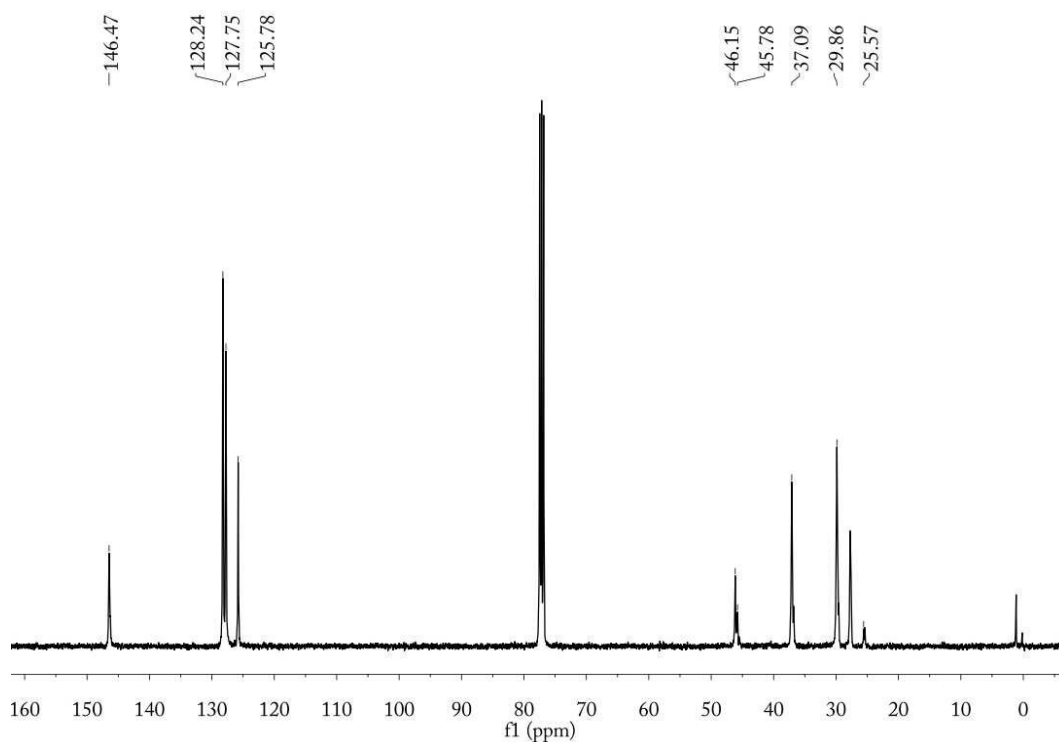
**Fig. S7.**  $^1\text{H}$  NMR spectrum of E-St copolymer with 25.2 mol% of styrene units ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 1, run 13)



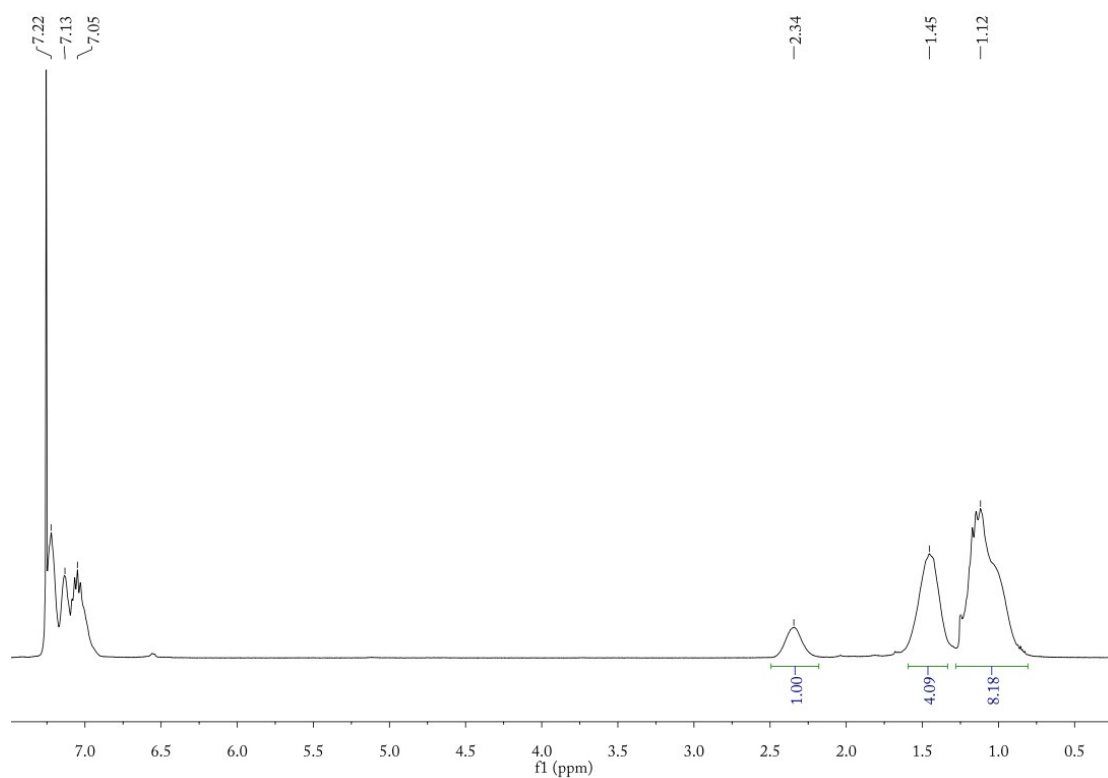
**Fig. S8.**  $^{13}\text{C}$  NMR spectrum of E-St copolymer with 25.2 mol% of styrene units ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 1, run 13)



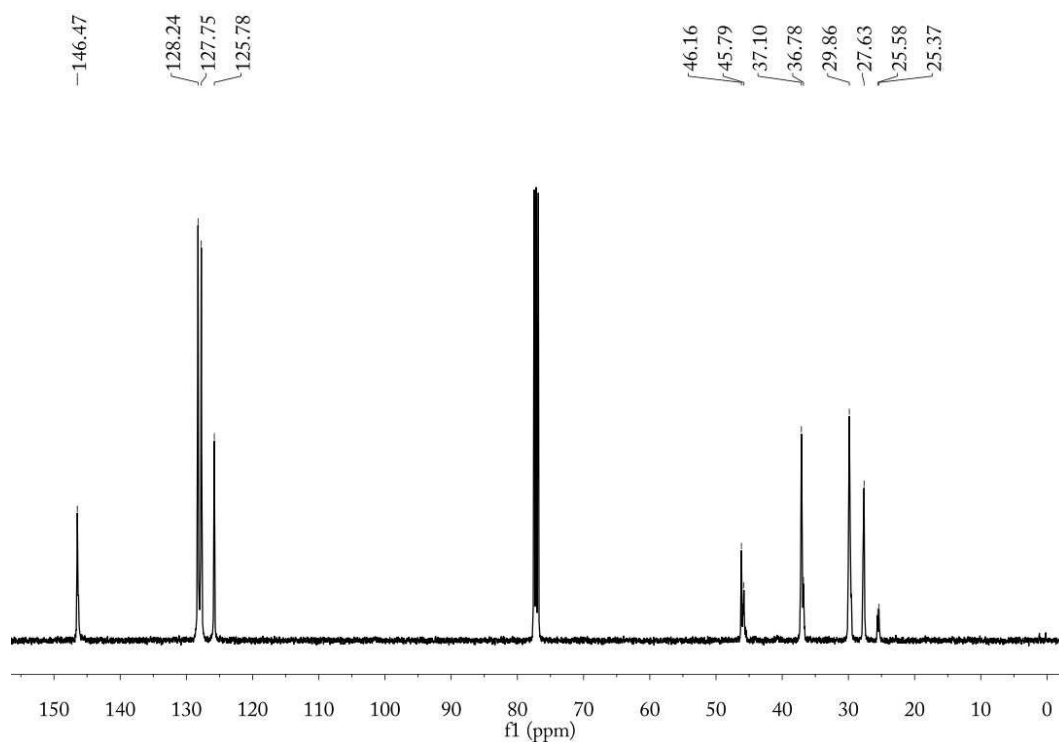
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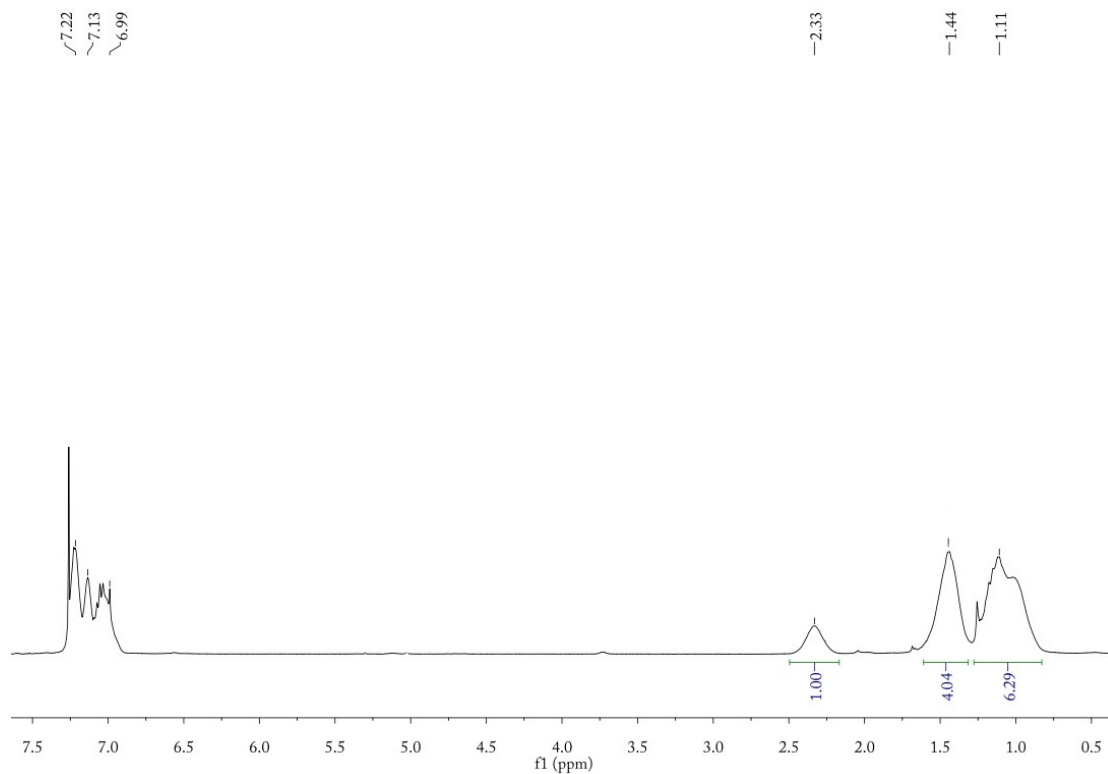
**Fig. S10.**  $^{13}\text{C}$  NMR spectrum of E-St copolymer with 26.9 mol% of styrene units ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 1, run 14)



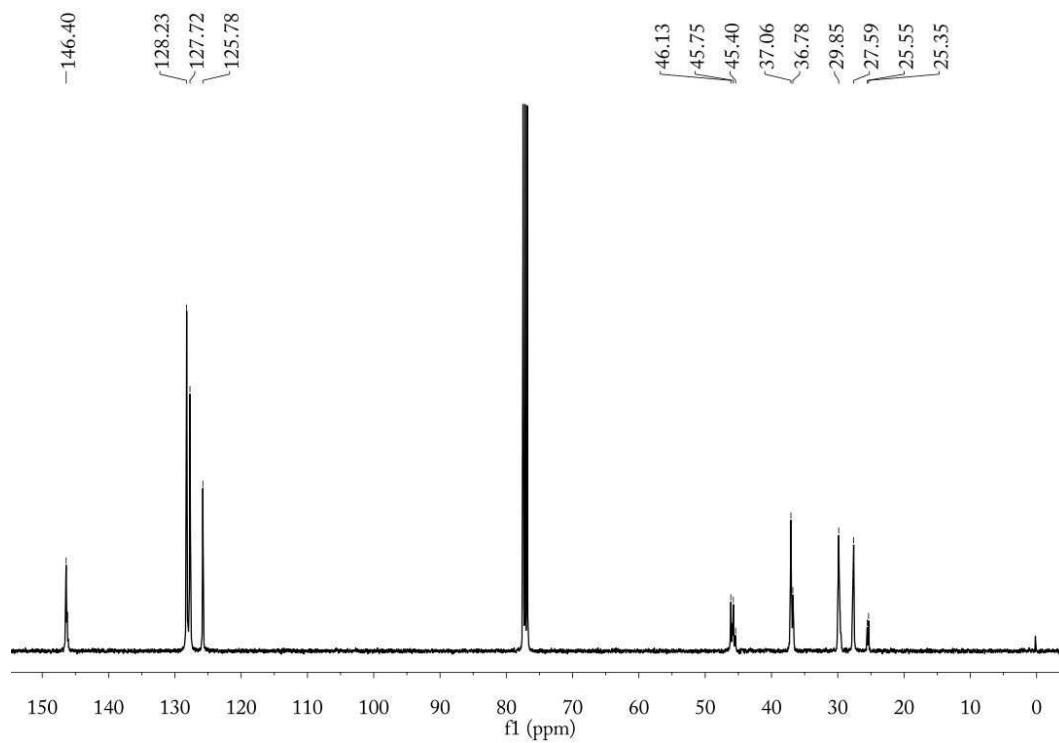
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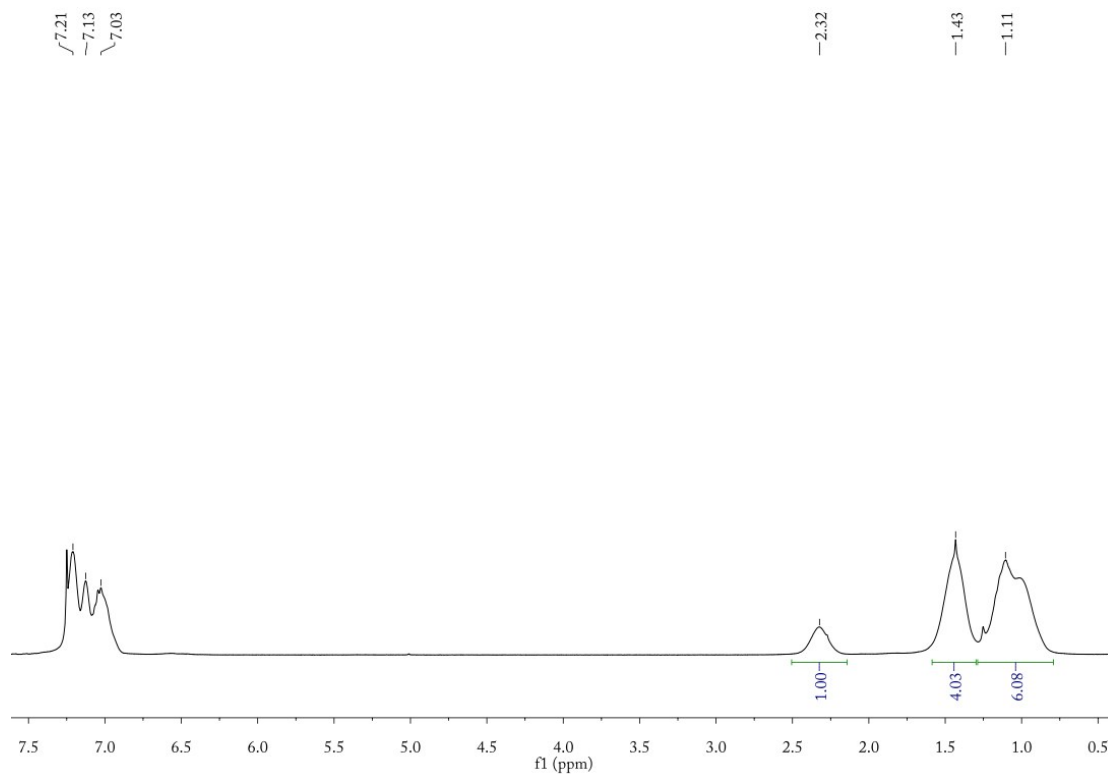


**Fig. S13.**  $^1\text{H}$  NMR spectrum of E-St copolymer with 29.3 mol% of styrene units ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 1, run 16)

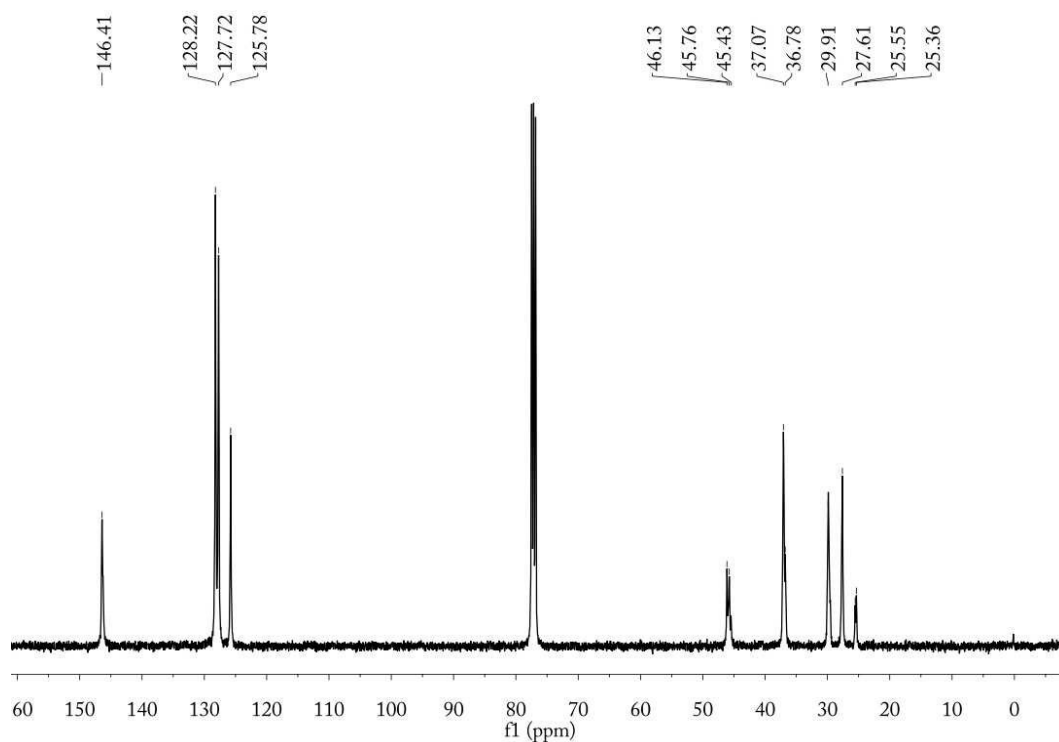


**Fig. S14.**  $^{13}\text{C}$  NMR spectrum of E-St copolymer with 29.3 mol% of styrene units ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 1, run 16)

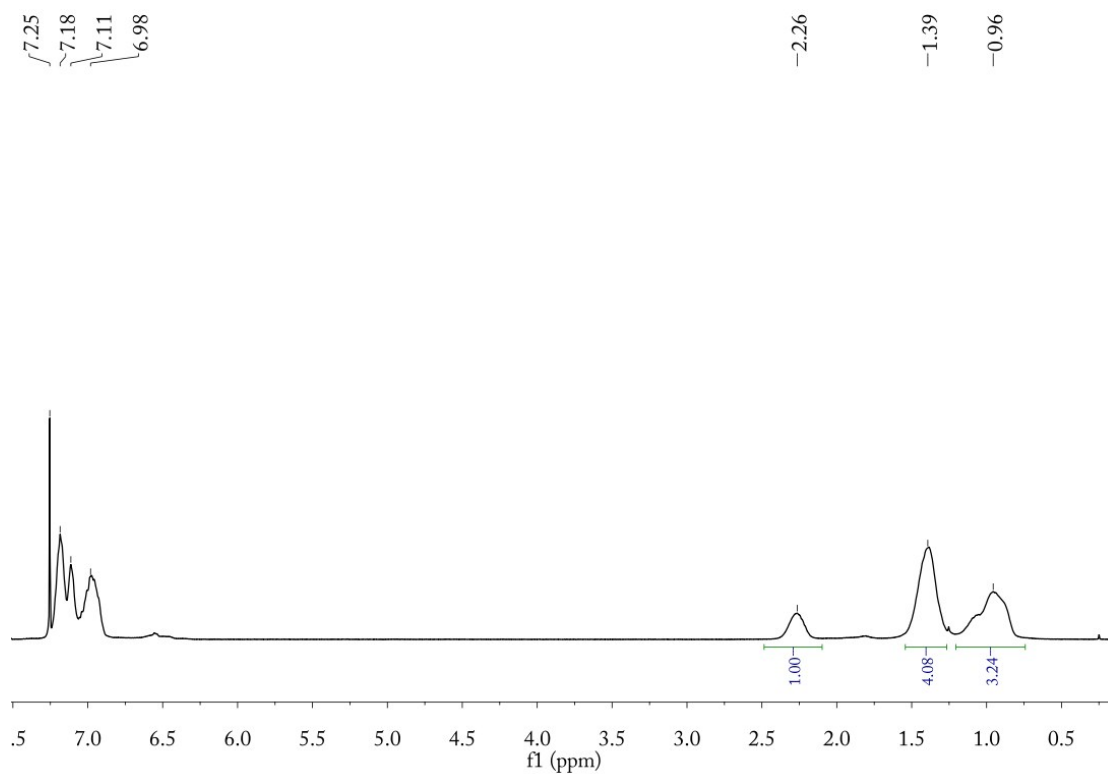




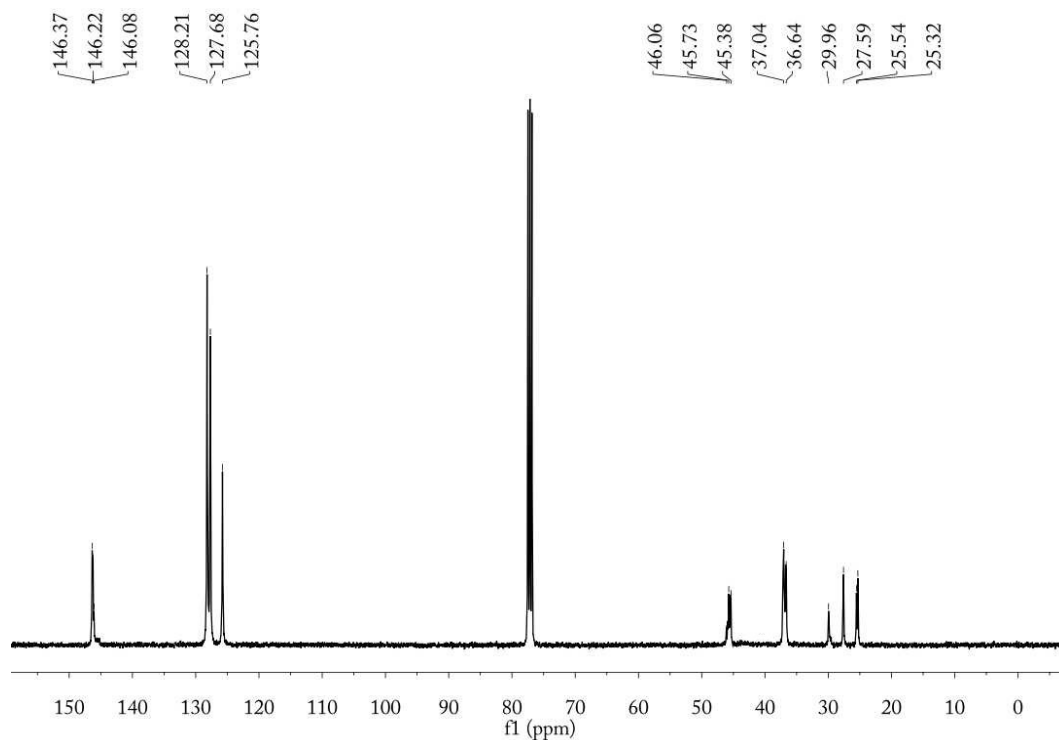
**Fig. S15.**  $^1\text{H}$  NMR spectrum of E-St copolymer with 33.1 mol% of styrene units ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 1, run 17)



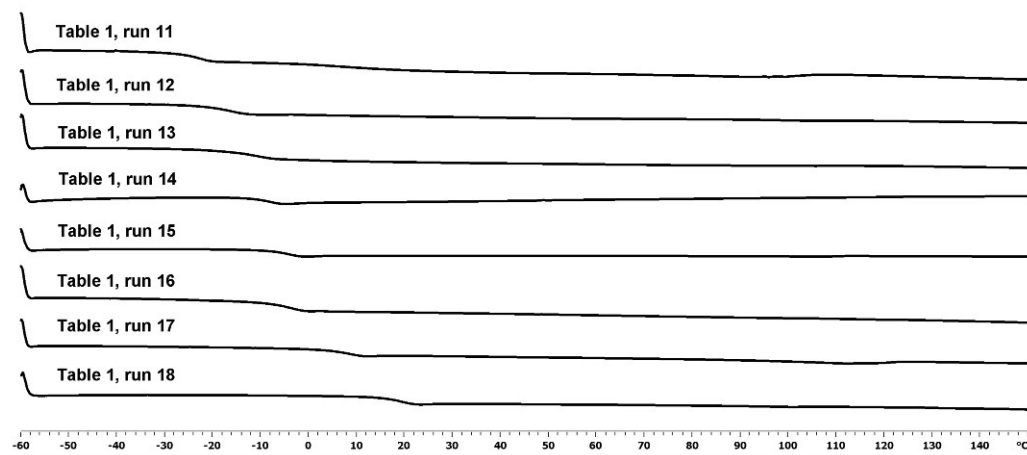
**Fig. S16.**  $^{13}\text{C}$  NMR spectrum of E-St copolymer with 33.1 mol% of styrene units ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 1, run 17)



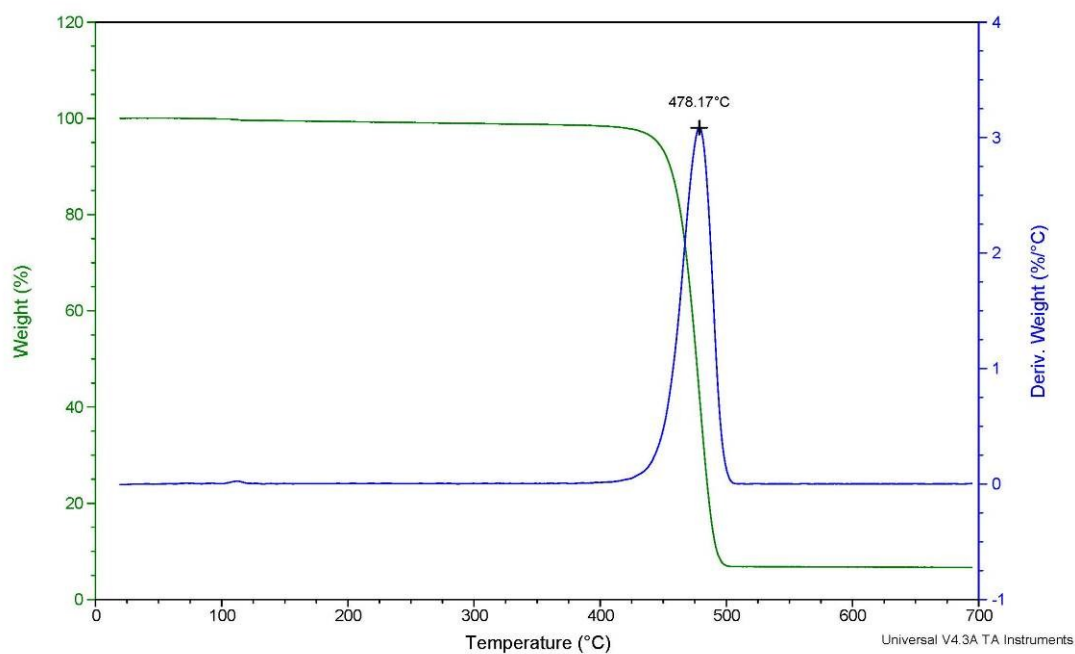
**Fig. S17.**  $^1\text{H}$  NMR spectrum of E-St copolymer with 43.2 mol% of styrene units ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 1, run 18)



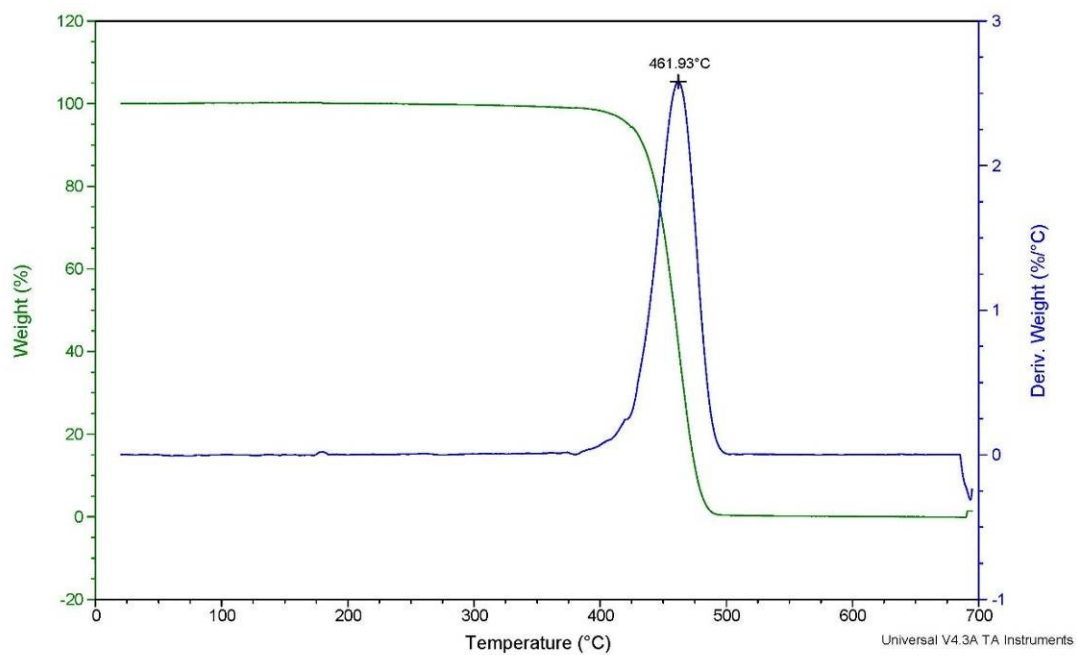
**Fig. S18.**  $^{13}\text{C}$  NMR spectrum of E-St copolymer with 43.2 mol% of styrene units ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 1, run 18)



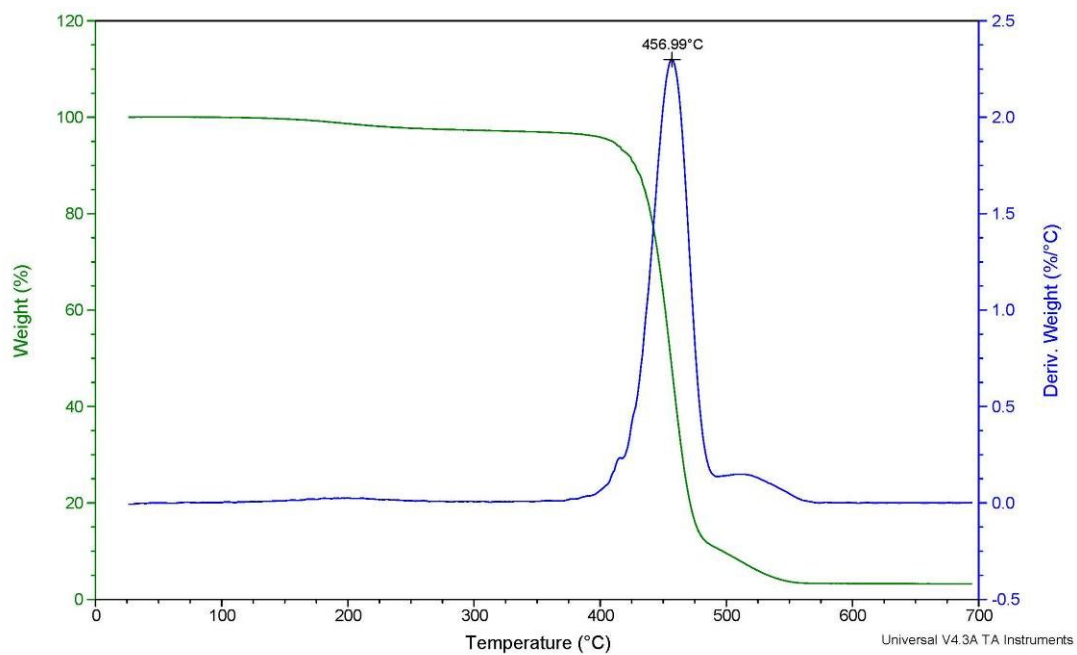
**Fig. S19.** DSC curves of E-St copolymers.



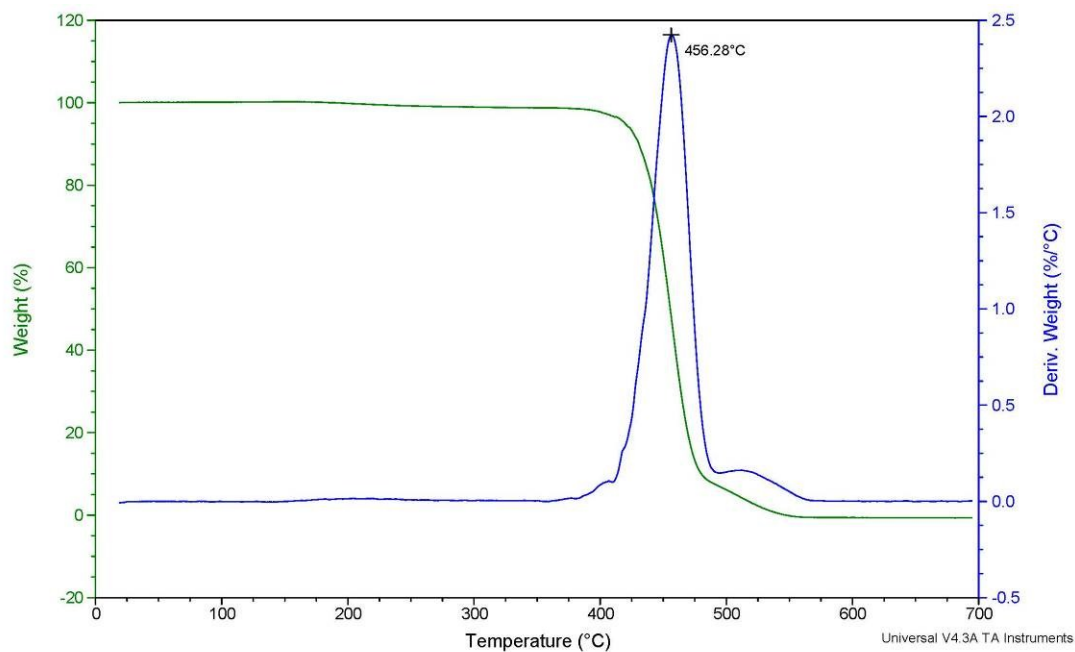
**Fig. S20.** TGA curve of polyethylene (Table 1, run 1)



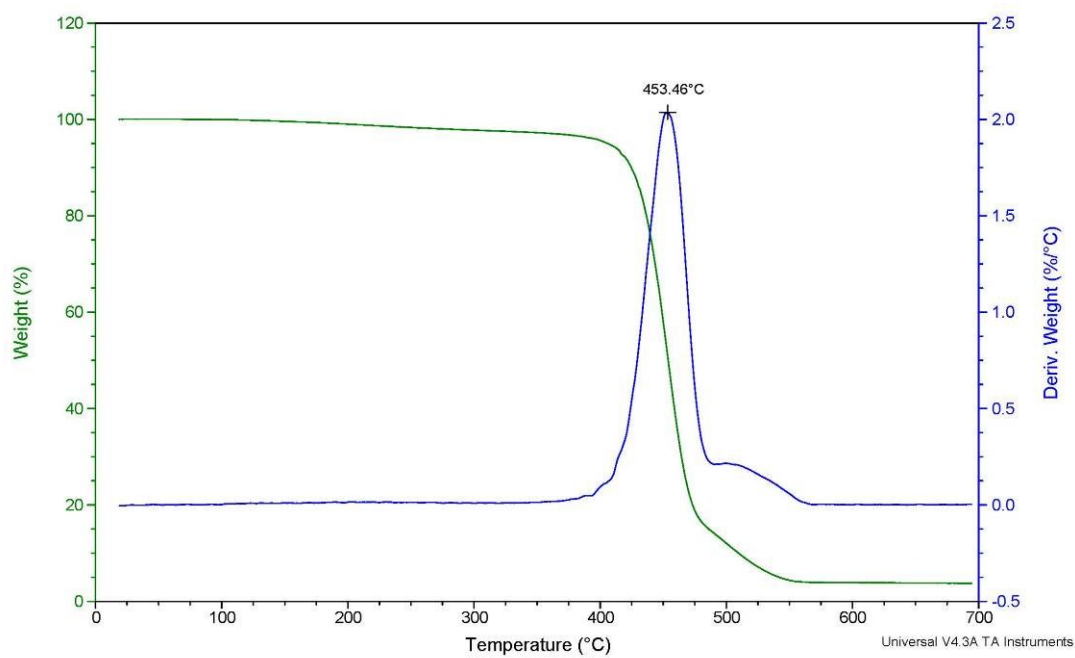
**Fig. S21.** TGA curve of E-St copolymer with 16.1 mol% of styrene units (Table 1, run 11).



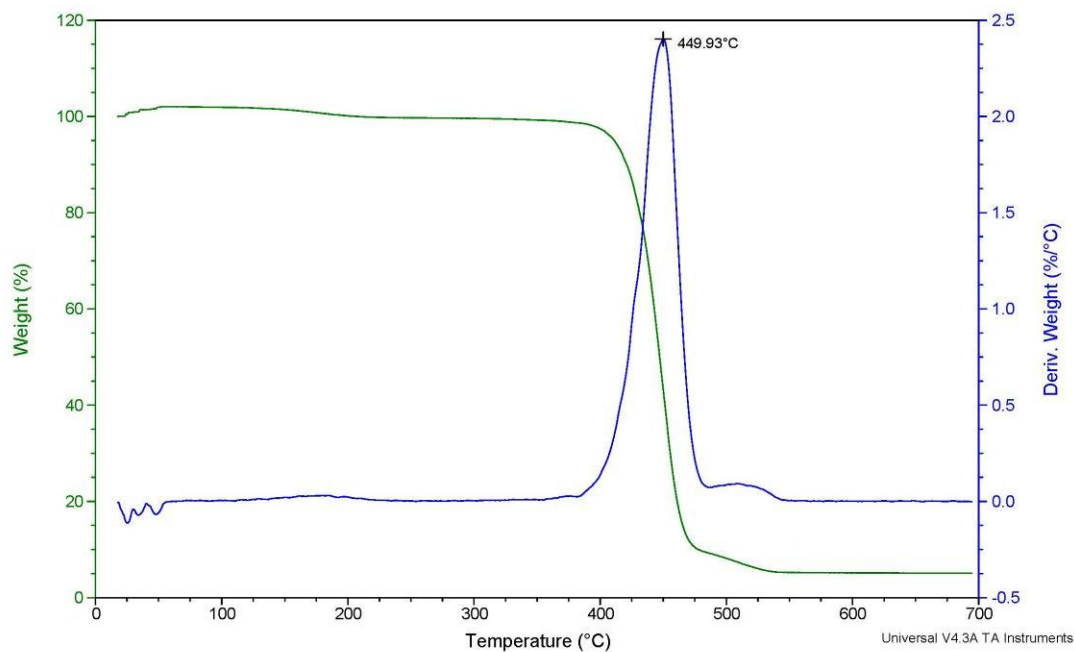
**Fig. S22.** TGA curve of E-St copolymer with 21.8 mol% of styrene units (Table 1, run 12)



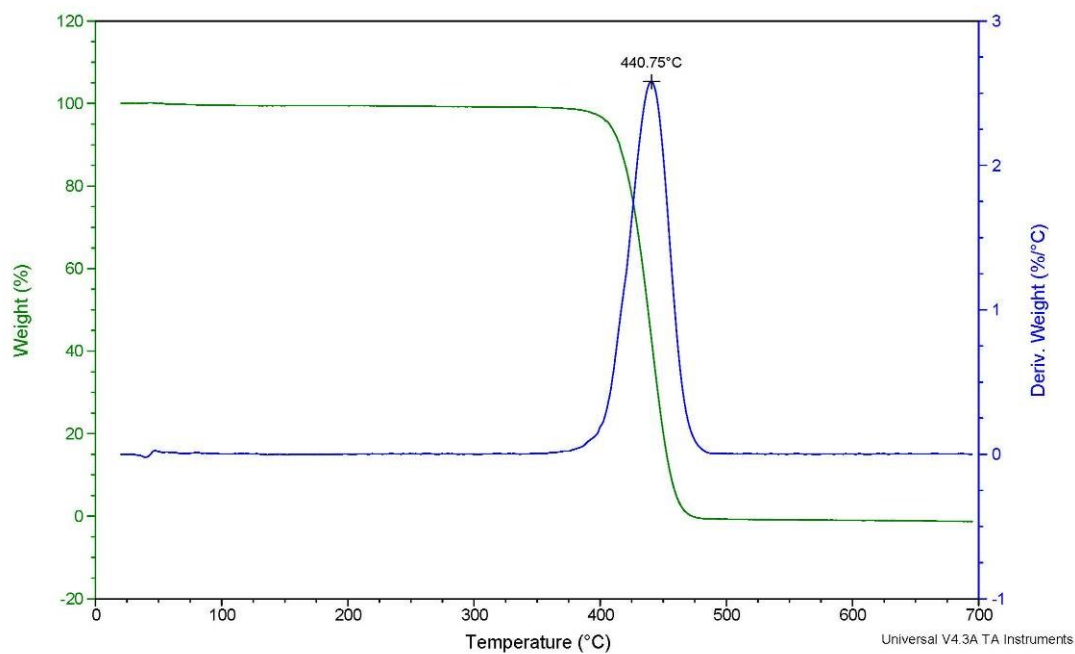
**Fig. S23.** TGA curve of E-St copolymer with 25.2 mol% of styrene units (Table 1, run 13)



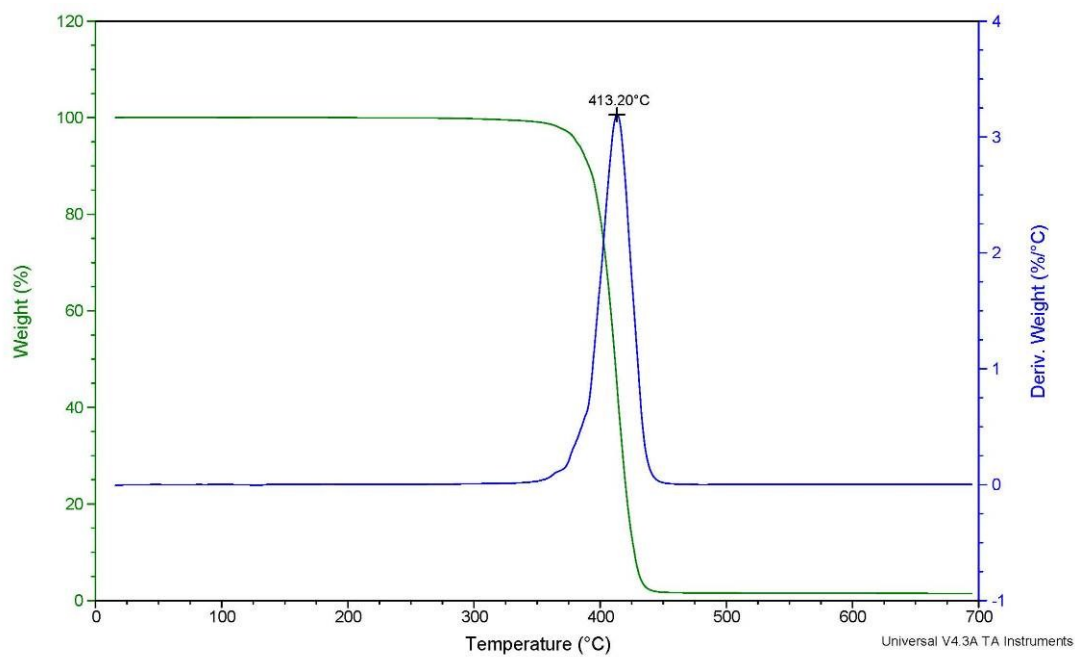
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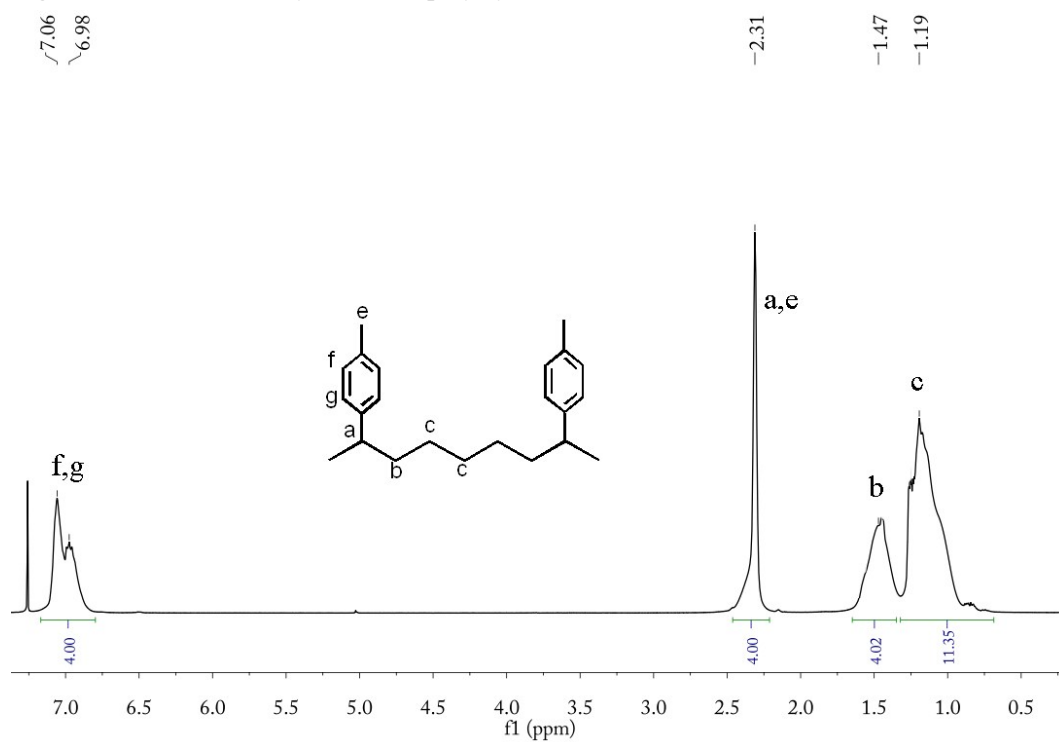
**Fig. S25.** TGA curve of E-St copolymer with 25.2 mol% of styrene units (Table 1, run 17)



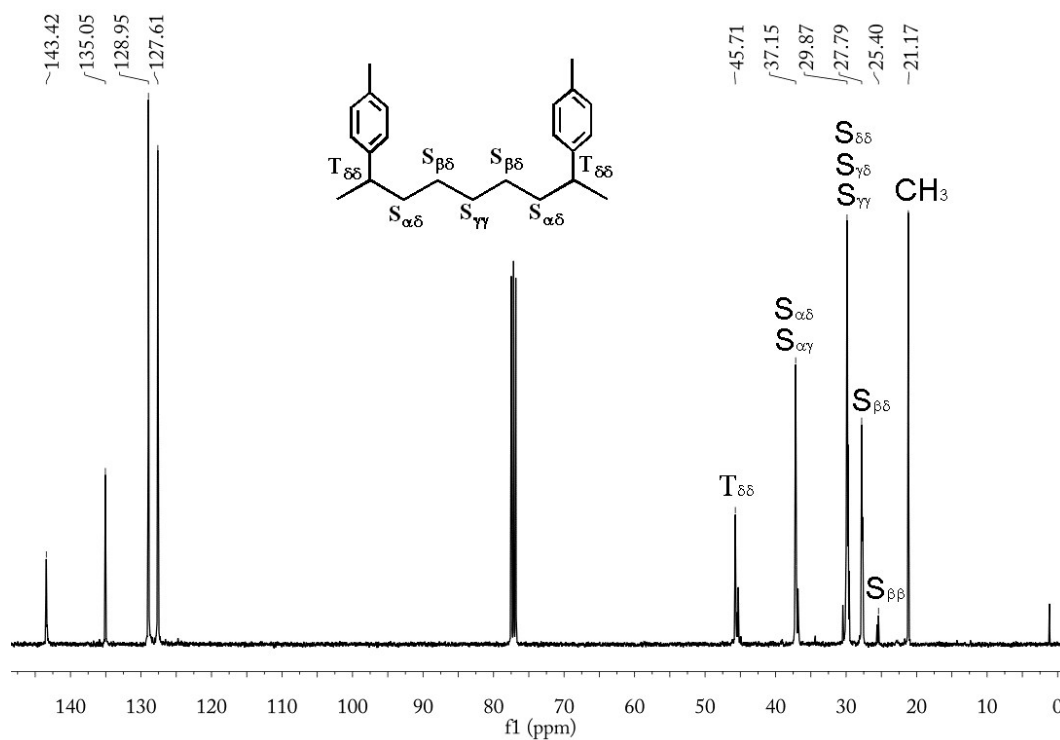
**Fig. S26.** TGA curve of E-St copolymer with 43.2 mol% of styrene units (Table 1, run 18)



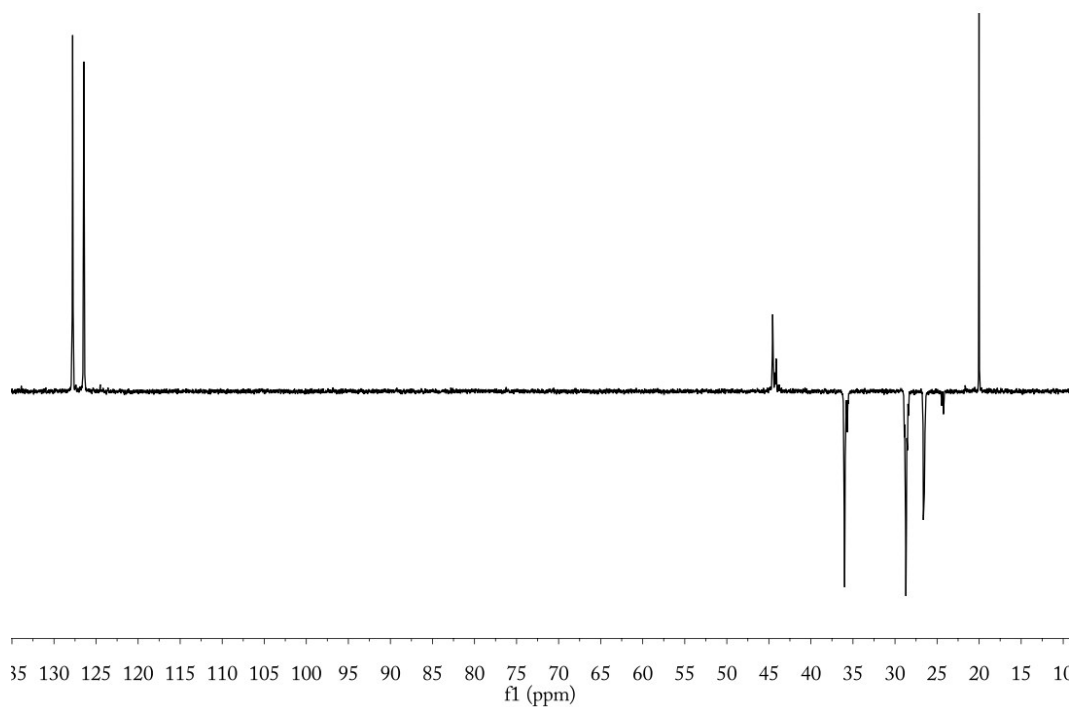
**Fig. S27.** TGA curve of syndiotactic polystyrene



**Fig. S28.** <sup>1</sup>H NMR spectrum of ethylene-4-methylstyrene copolymer (CDCl<sub>3</sub>, 25 °C) (Table 2, run 1)

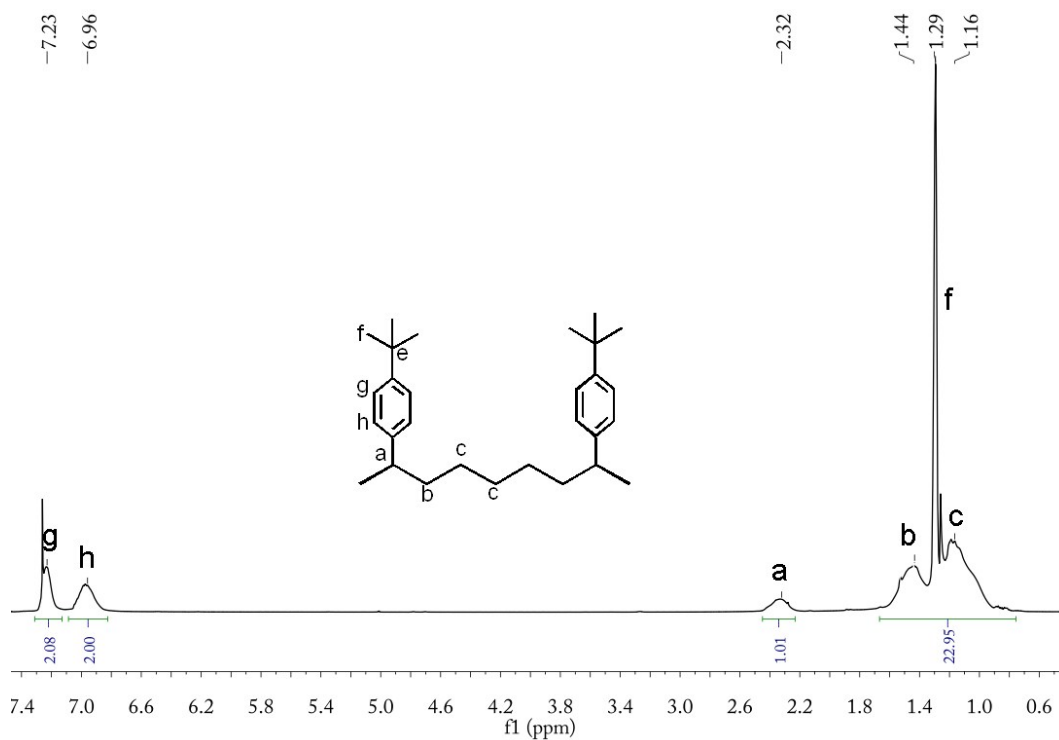


**Fig. S29.**  $^{13}\text{C}$  NMR spectrum of ethylene-4-methylstyrene copolymer ( $\text{CDCl}_3$ , 25 °C) (Table 2, run 1)

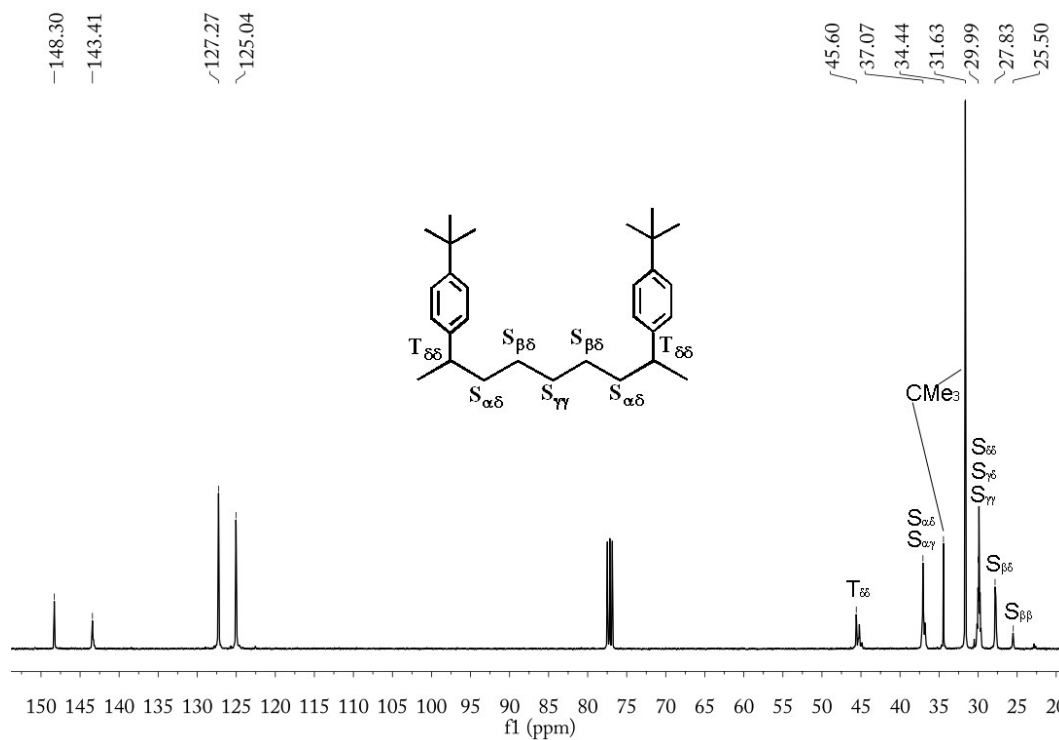


**Fig. S30.** DEPT $^{135}$  spectrum of ethylene-4-methylstyrene copolymer ( $\text{CDCl}_3$ , 25 °C) (Table 2, run 1)

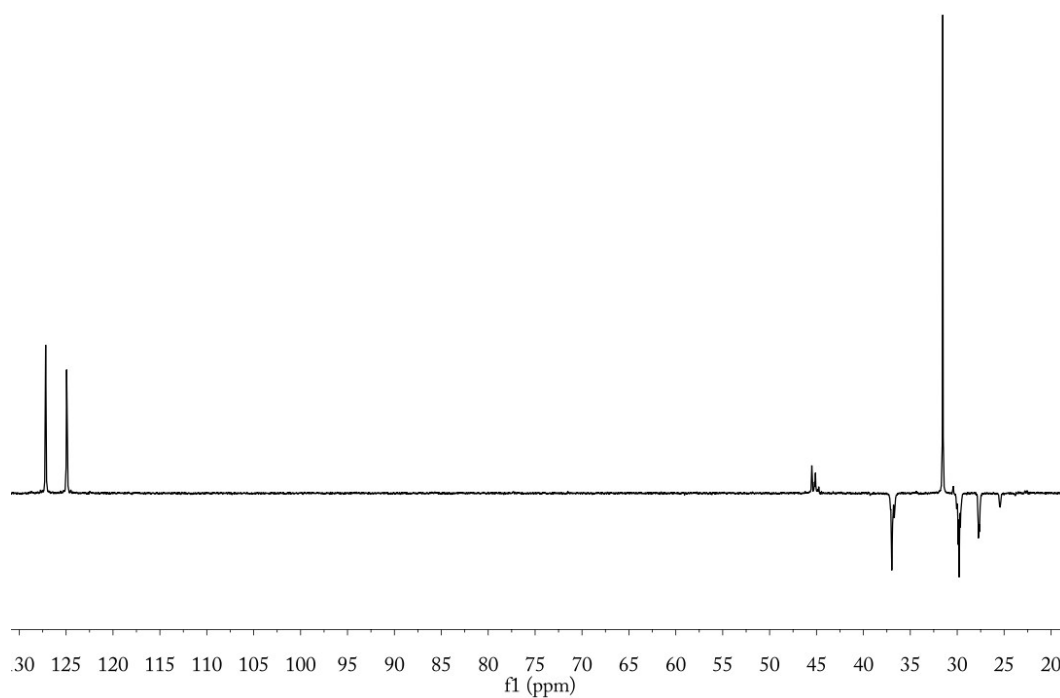




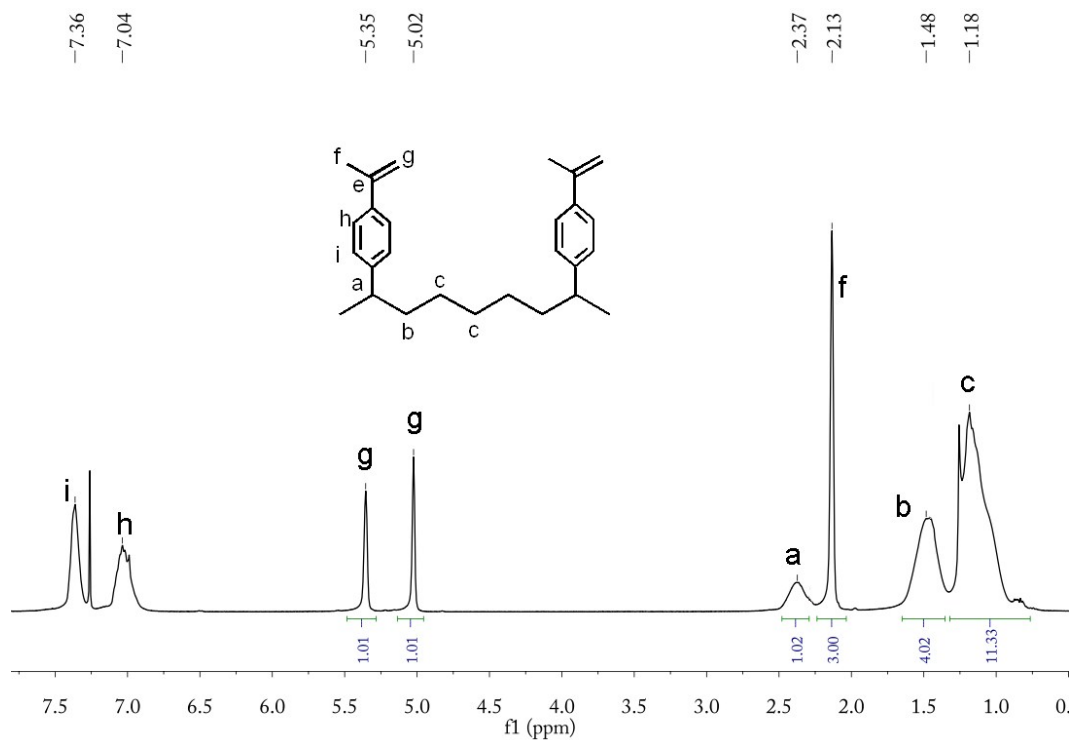
**Fig. S31.** <sup>1</sup>H NMR spectrum of ethylene-4-*tert*-butylstyrene copolymer (CDCl<sub>3</sub>, 25 °C) (Table 2, run 2)



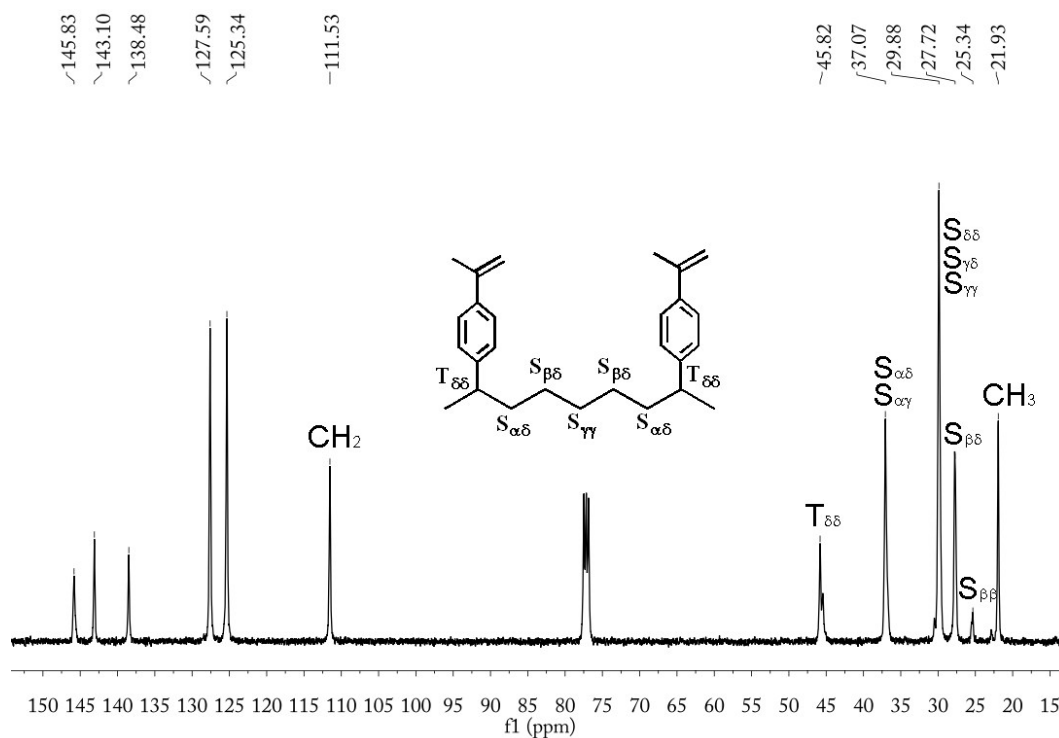
**Fig. S32.** <sup>13</sup>C NMR spectrum of ethylene-4-*tert*-butylstyrene copolymer (CDCl<sub>3</sub>, 25 °C) (Table 2, run 2)



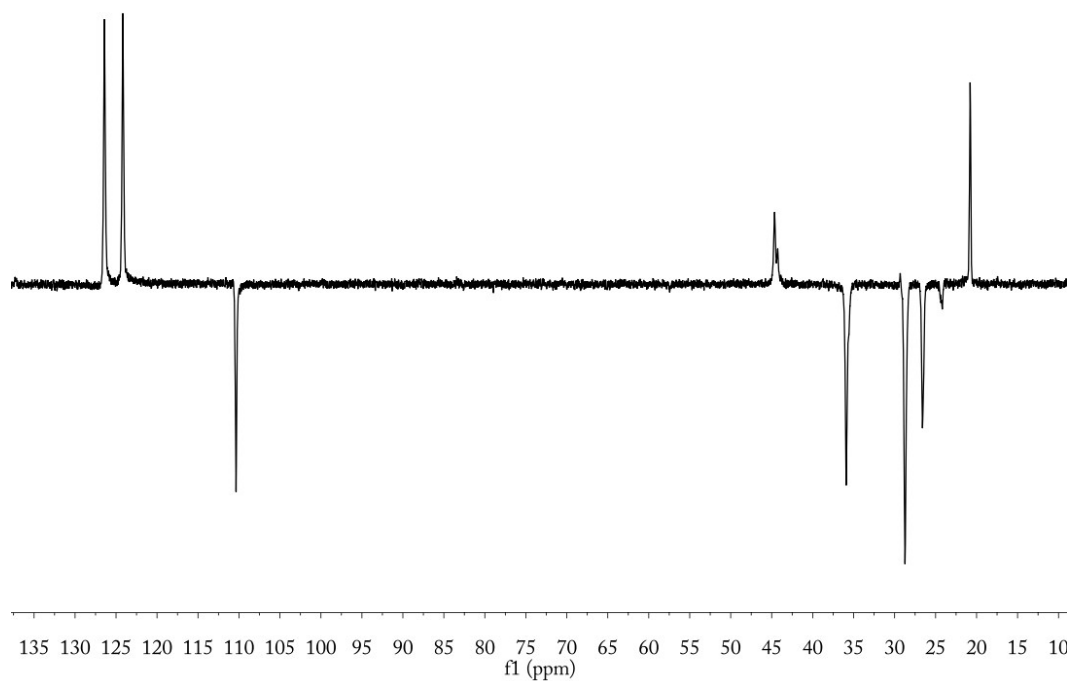
**Fig. S33.** Dept<sup>135</sup> spectrum of ethylene-4-*tert*-butylstyrene copolymer (CDCl<sub>3</sub>, 25 °C) (Table 2, run 2)



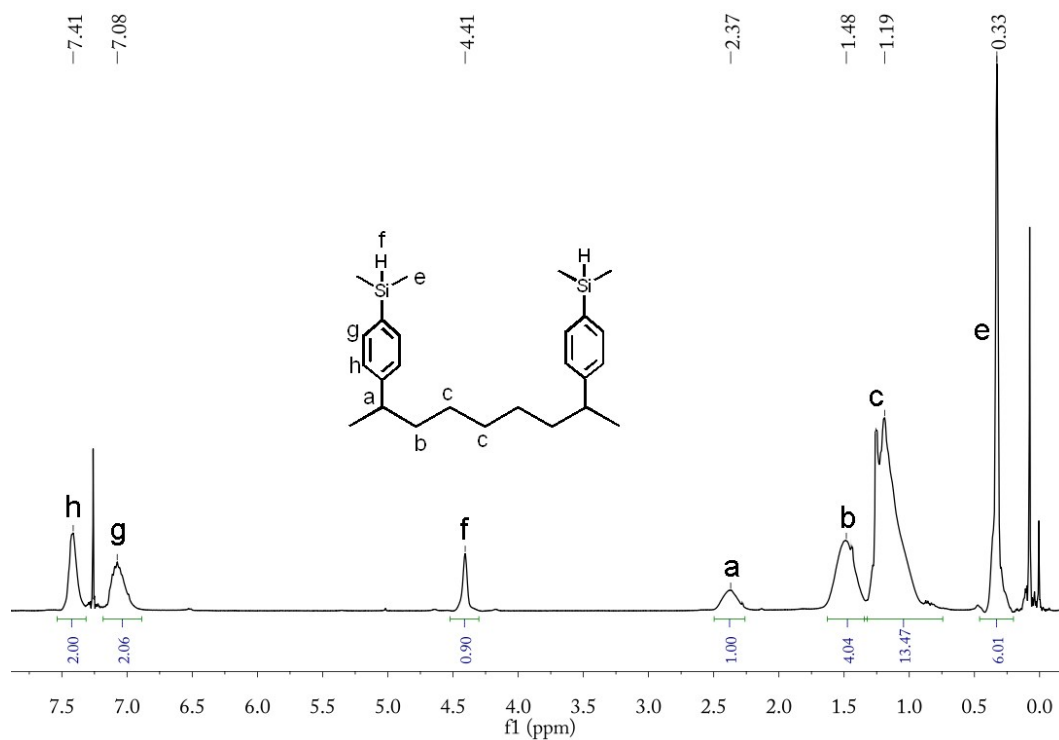
**Fig. S34.** <sup>1</sup>H NMR spectrum of ethylene-4-isopropenylstyrene copolymer (CDCl<sub>3</sub>, 25 °C) (Table 2, run 3)



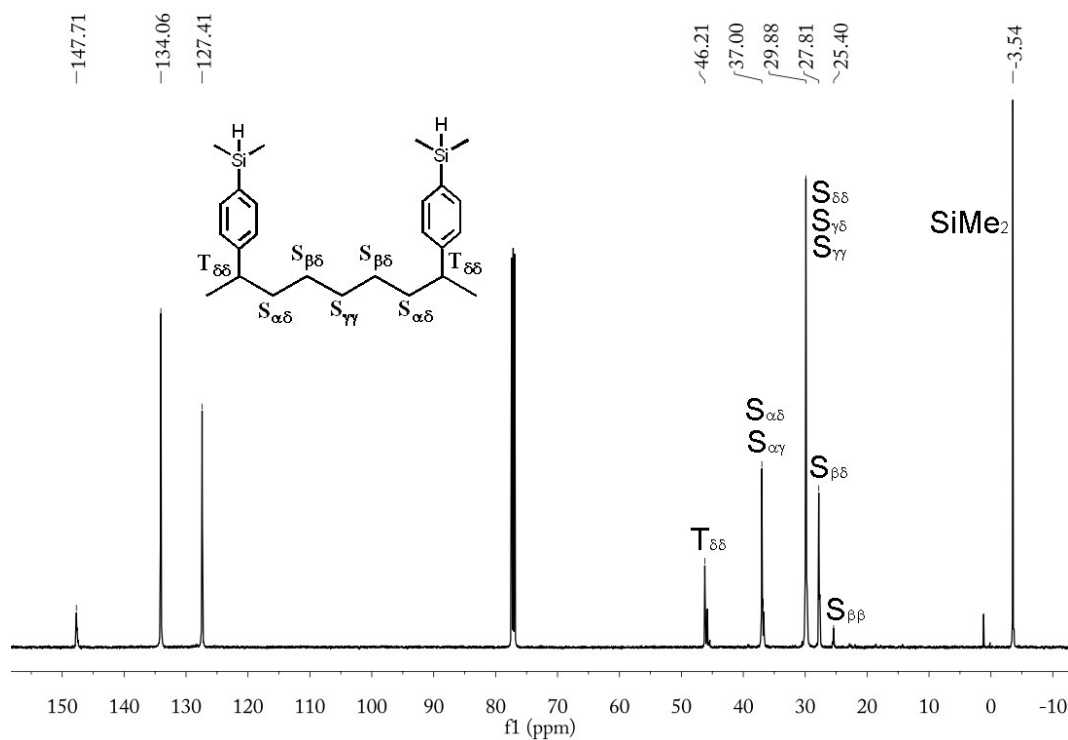
**Fig. S35.**  $^{13}\text{C}$  NMR spectrum of ethylene-4-isopropenylstyrene copolymer ( $\text{CDCl}_3$ , 25 °C) (Table 2, run 3)



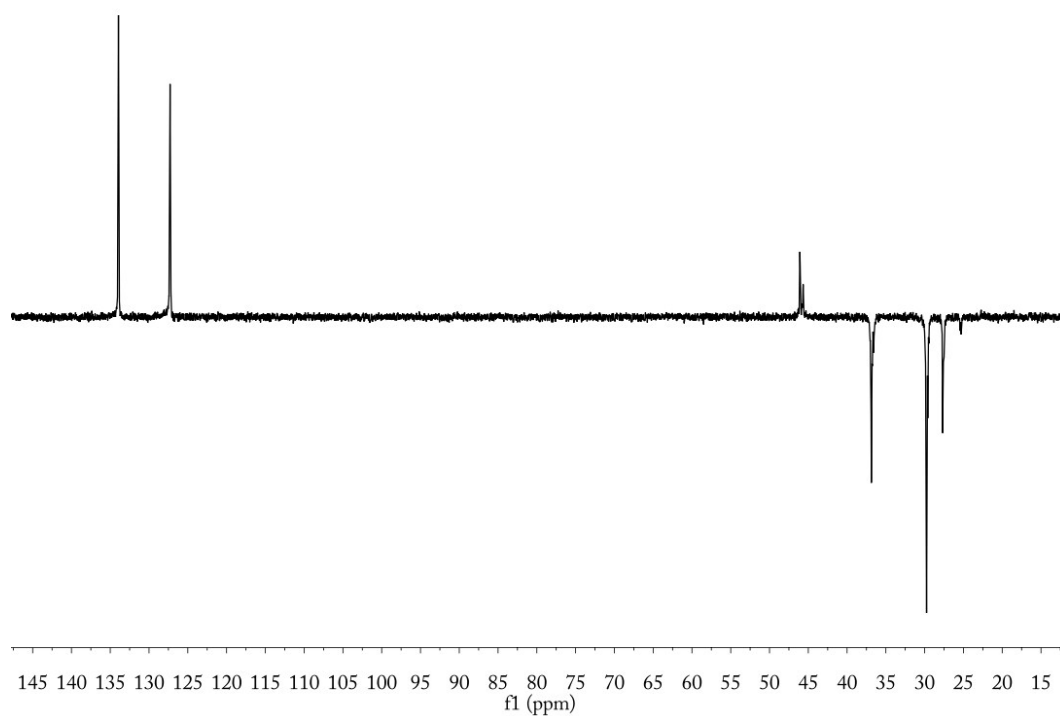
**Fig. S36.**  $\text{DEPT}^{135}$  spectrum of ethylene-4-isopropenylstyrene copolymer ( $\text{CDCl}_3$ , 25 °C) (Table 2, run 3)



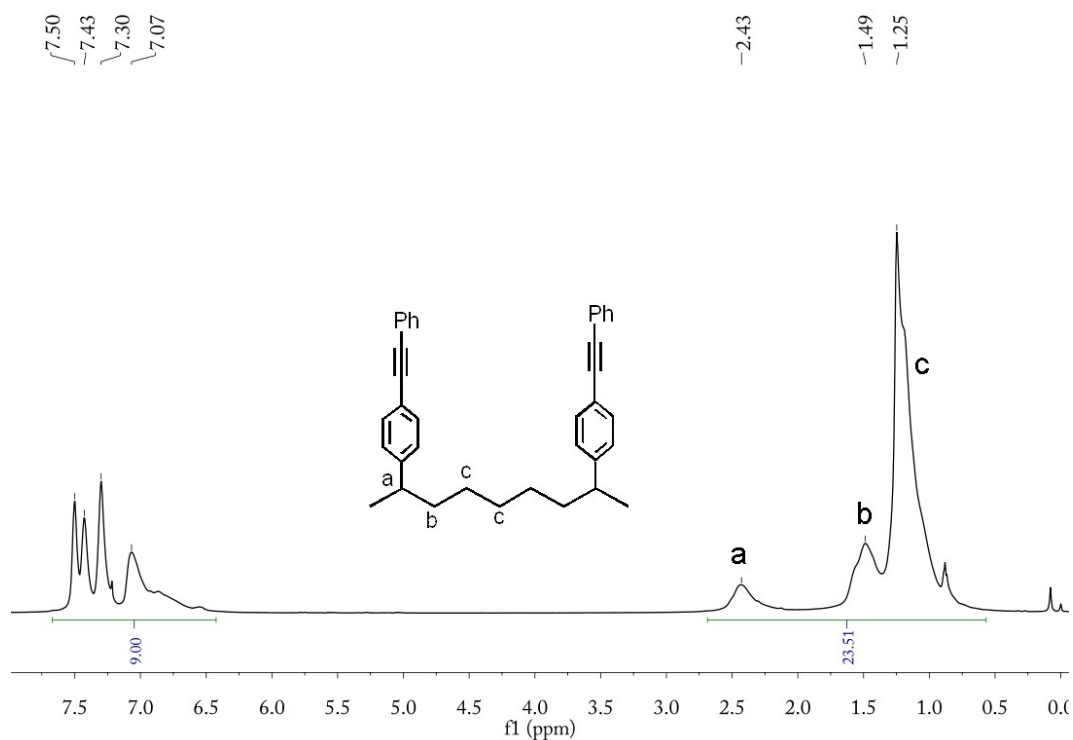
**Fig. S37.** <sup>1</sup>H NMR spectrum of ethylene-4-vinylphenyl dimethylsilane copolymer (CDCl<sub>3</sub>, 25 °C) (Table 2, run 4)



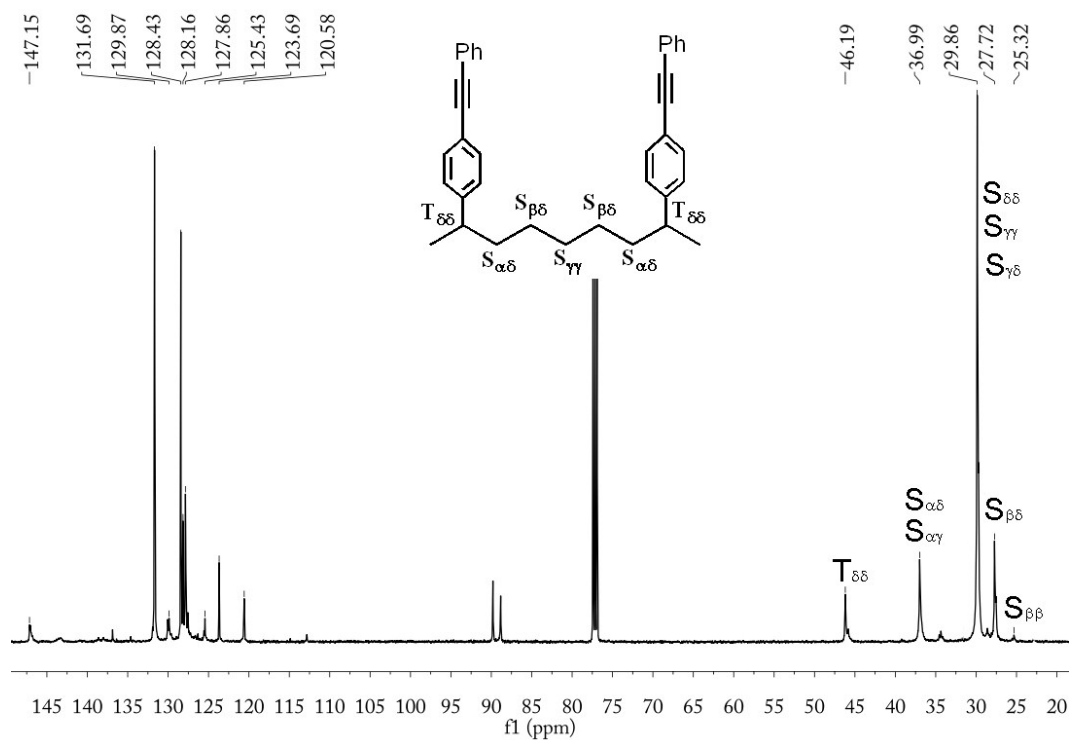
**Fig. S38.** <sup>13</sup>C NMR spectrum of ethylene-4-vinylphenyl dimethylsilane copolymer (CDCl<sub>3</sub>, 25 °C) (Table 2, run 4)



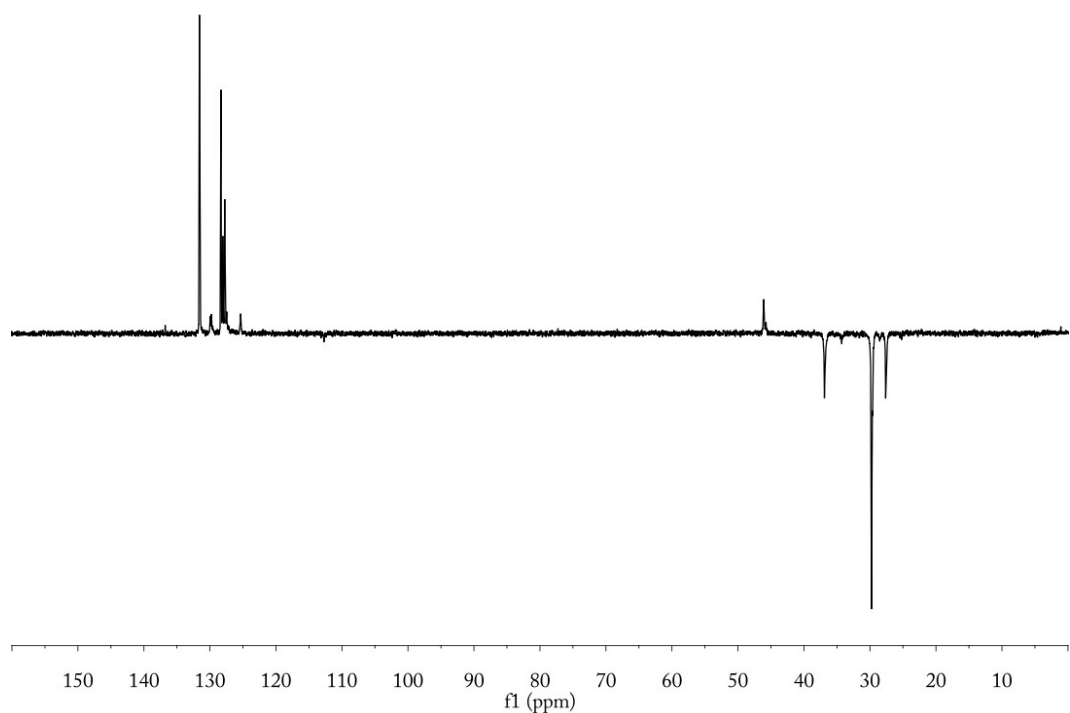
**Fig. S39.** Dept<sup>135</sup> spectrum of ethylene-4-vinylphenyl dimethylsilane copolymer (CDCl<sub>3</sub>, 25 °C) (Table 2, run 4)



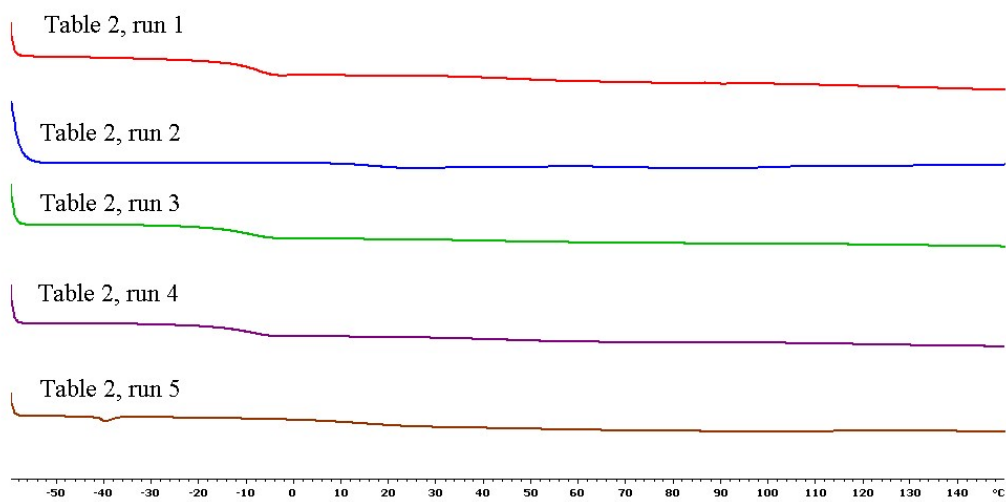
**Fig. S40.** <sup>1</sup>H NMR spectrum of ethylene-4-phenylethynylstyrene copolymer (CDCl<sub>3</sub>, 25 °C) (Table 2, run 6)



**Fig. S41.**  $^1\text{H}$  NMR spectrum of ethylene-4-phenylethynylstyrene copolymer ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 2, run 6)



**Fig. S42.**  $^1\text{H}$  NMR spectrum of ethylene-4-phenylethynylstyrene copolymer ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) (Table 2, run 6)



**Fig. S43.** DSC curves of E-St derivatives copolymers.