

Supplementary Materials

for

Ethylene/Styrene Copolymerization by $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{-4-RC}_6\text{H}_2)$ ($\text{R} = \text{H}$, SiEt_3)-MAO Catalysts: Effect of SiMe_3 group on Cp for Efficient Styrene Incorporation

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1. Crystal data and the collection parameters for analysis of (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*-Pr₂-4-RC₆H₂) [R = H (5**), SiEt₃ (**6**)].**

Table S1. Crystal data and the collection parameters for analysis of (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*-Pr₂-4-RC₆H₂) [R = H (**5**), SiEt₃ (**6**)].^a

	5	6
formula	C ₂₀ H ₃₀ Cl ₂ OSiTi	C ₂₆ H ₄₄ Cl ₂ OSi ₂ Ti
formula weight	433.30	547.56
crystal color, Habit	orange, plate	orange, plate
crystal size (mm)	0.388×0.178×0.040	0.200×0.140×0.023
crystal system	monoclinic	monoclinic
space group	<i>P</i> 1 2 ₁ / <i>n</i> 1	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	6.6649(3)	22.5185(10)
<i>b</i> (Å)	11.8405(5)	11.0402(4)
<i>c</i> (Å)	28.8139(11)	12.3590(5)
<i>α</i> (deg)		
<i>β</i> (deg)	94.699(4)	99.407(4)
<i>γ</i> (deg)		
<i>V</i> (Å ³)	2266.23(16)	3031.2(2)
<i>Z</i> value	4	4
<i>D</i> _{calcd} (g/cm ³)	1.270	1.200
<i>F</i> ₀₀₀	912	1168.0
temp (K)	123(2)	123(2)
<i>μ</i> (Mo Kα) (cm ⁻¹)	6.72	5.54
no. of reflections measured (<i>R</i> _{int})	17719	42534
	Unique: 5515 (0.0845)	Unique: 7179 (0.0651)
2 θ _{max} (deg)	56.2	55.6
no. of observations [<i>I</i> > 2.00σ(<i>I</i>)]	5515	7179
no. of variables	233	397
<i>R</i> 1 [<i>I</i> > 2.00σ(<i>I</i>)]	0.0434	0.0685,
<i>wR</i> 2 [<i>I</i> > 2.00σ(<i>I</i>)]	0.1146	0.1238
goodness of fit	1.045	1.091

^a CCDC2378274 (complex **5**), CCDC2378275 (complex **6**)

2. Selected NMR spectra of poly(ethylene-*co*-styrene)s.

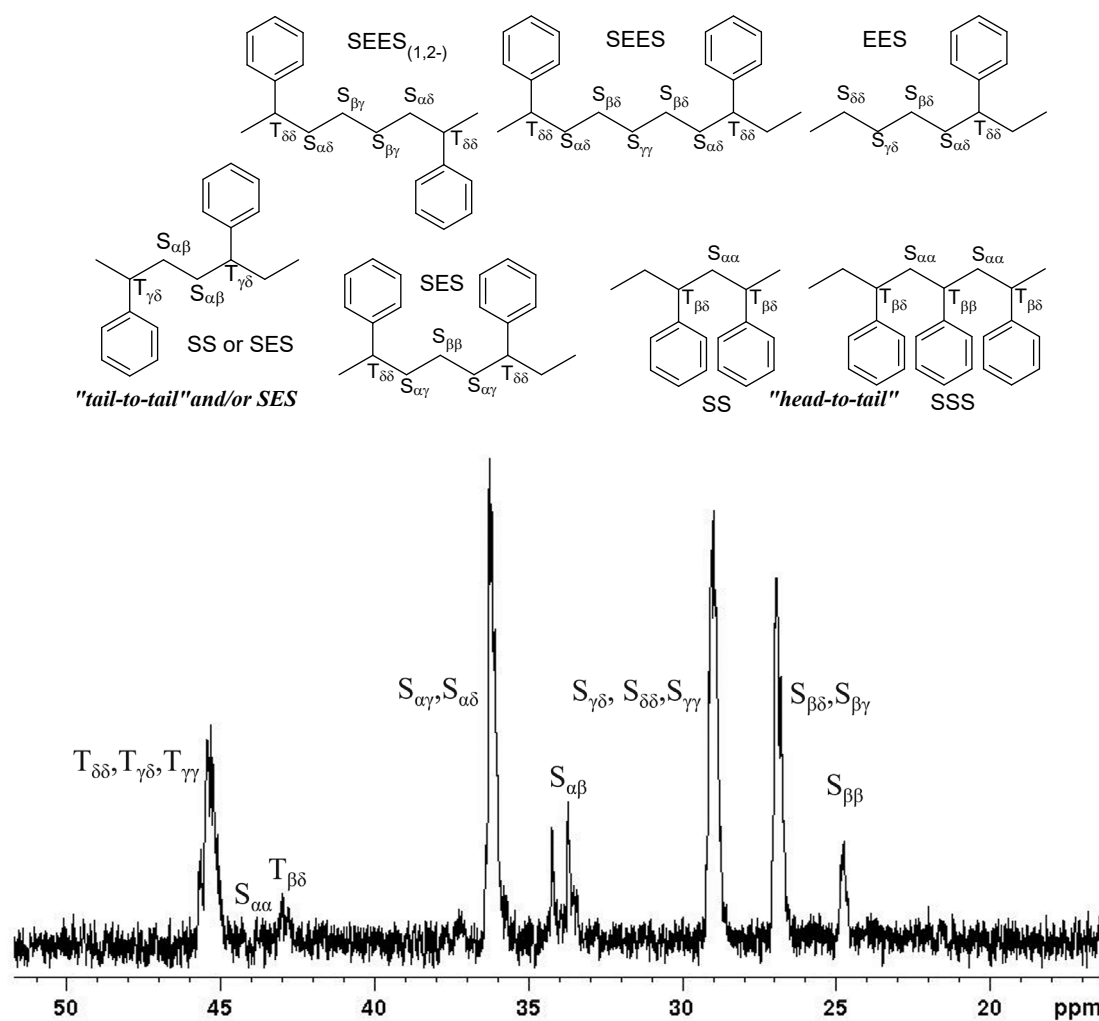


Figure S1. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane- d_2 solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by $(\text{Me}_3\text{SiC}_3\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**5**)–MAO catalyst system, styrene content 35.0 mol % (run 13).

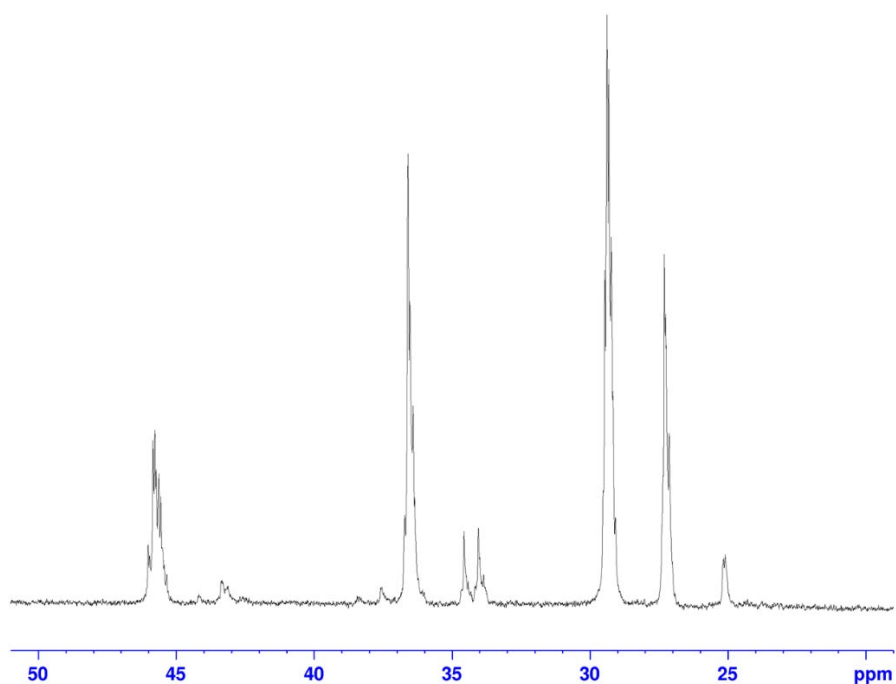


Figure S2. ¹³C NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*₂ solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by (Me₃SiC₃H₄)TiCl₂(O-2,6-*i*Pr₂C₆H₃) (**5**)–MAO catalyst system, styrene content 29.9 mol % (run 19).

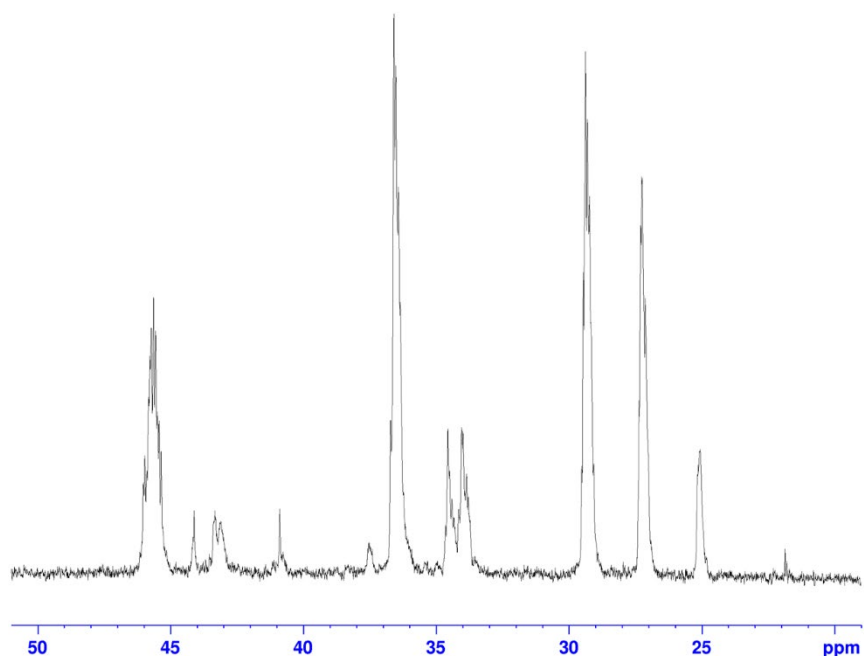


Figure S3. ¹³C NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*₂ solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by (Me₃SiC₃H₄)TiCl₂(O-2,6-*i*Pr₂C₆H₃) (**5**)–MAO catalyst system, styrene content 38.9 mol % (run 23).

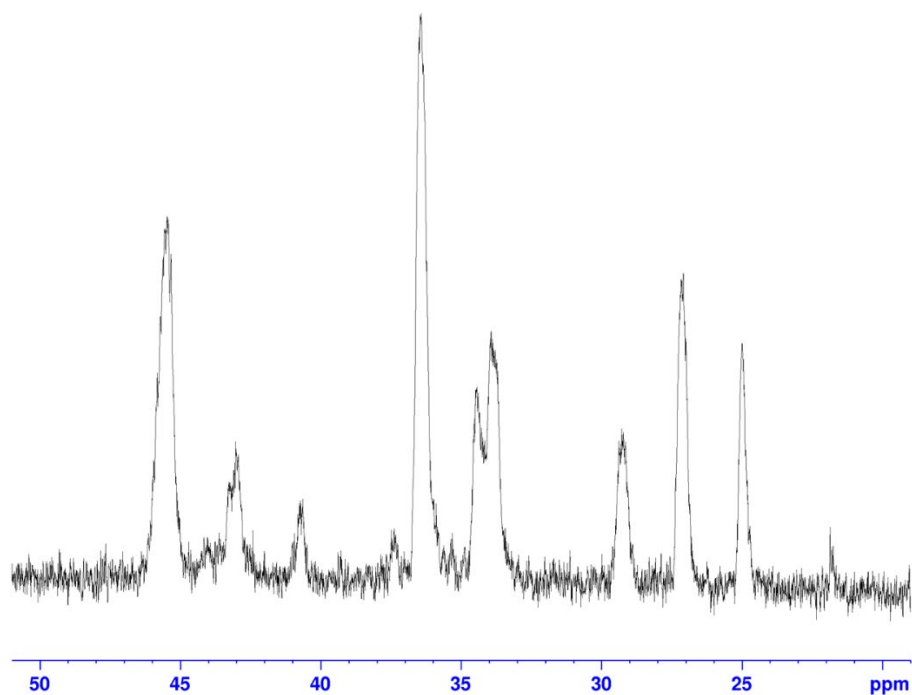


Figure S4. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane- d_2 solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by $(\text{Me}_3\text{SiC}_3\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**5**)–MAO catalyst system, styrene content 54.2 mol % (run 15).

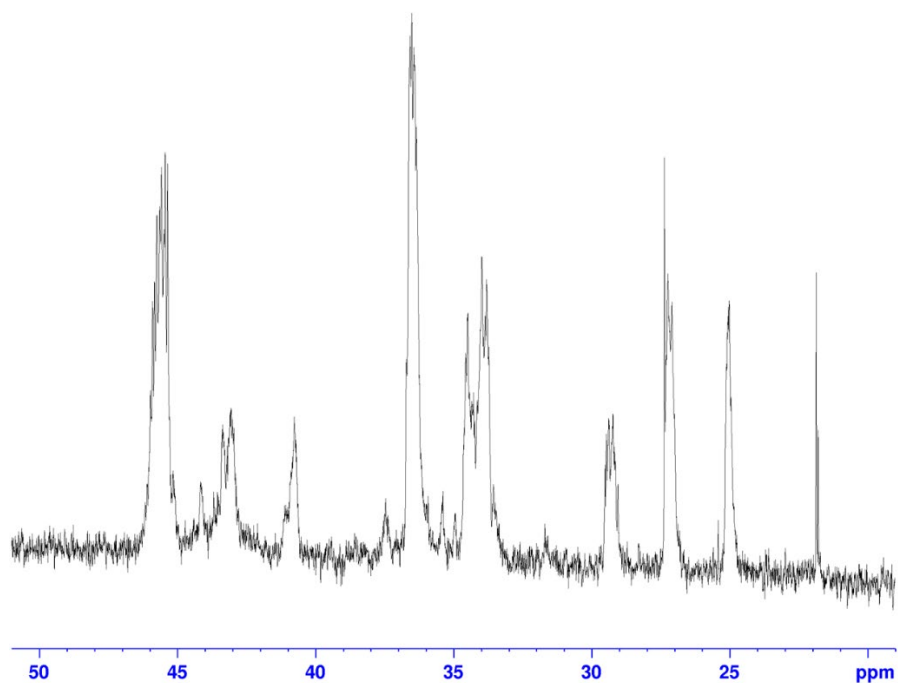


Figure S5. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane- d_2 solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by $(\text{Me}_3\text{SiC}_3\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**5**)–MAO catalyst system, styrene content 56.5 mol % (run 27).

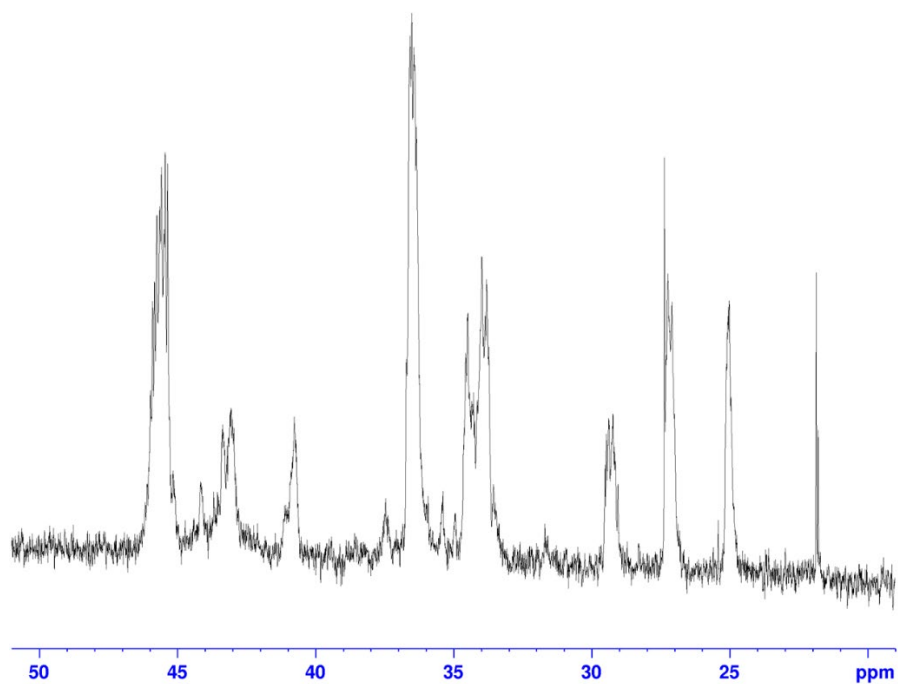


Figure S6. ¹³C NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*₂ solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*-Pr₂-4-SiEt₃C₆H₂) (**6**)-MAO catalyst system, styrene content 36.6 mol % (run 16).

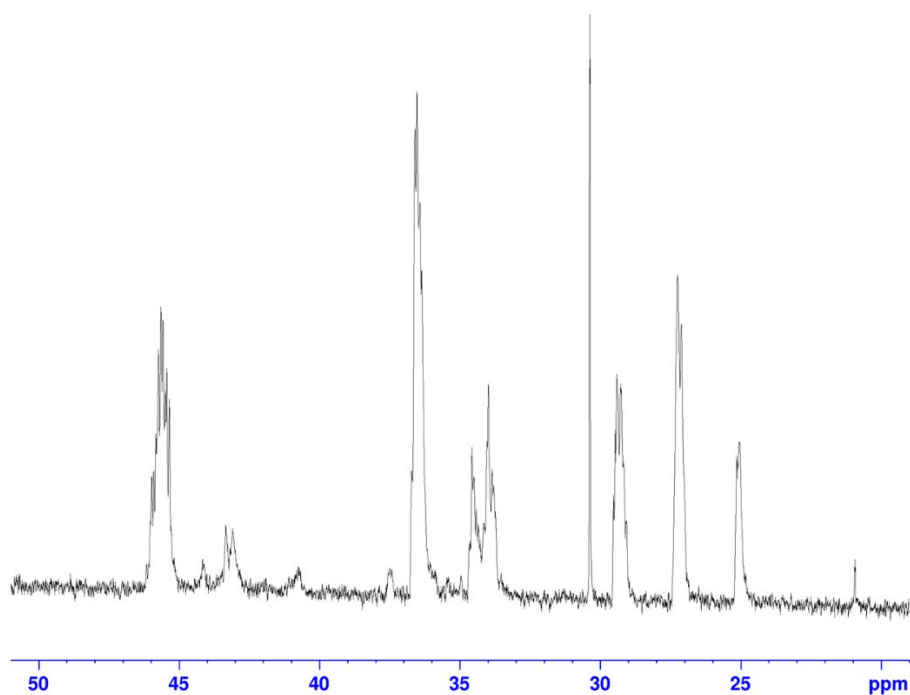


Figure S7. ¹³C NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*₂ solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*-Pr₂-4-SiEt₃C₆H₂) (**6**)-MAO catalyst system, styrene content 44.9 mol % (run 17).

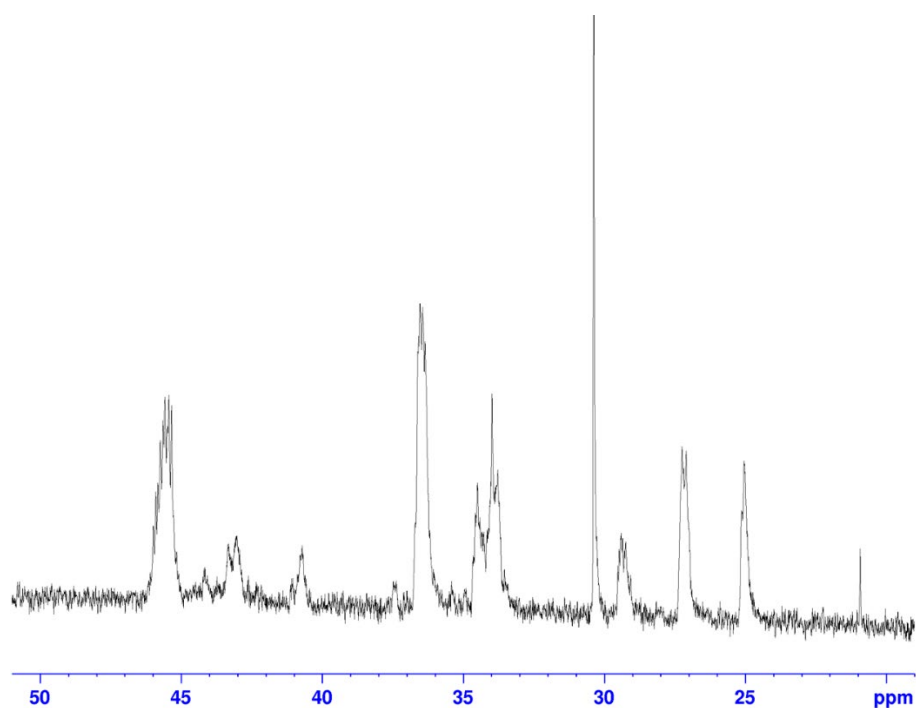


Figure S8. ¹³C NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*₂ solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*-Pr₂-4-SiEt₃C₆H₂) (**6**)–MAO catalyst system, styrene content 55.6 mol % (run 18).

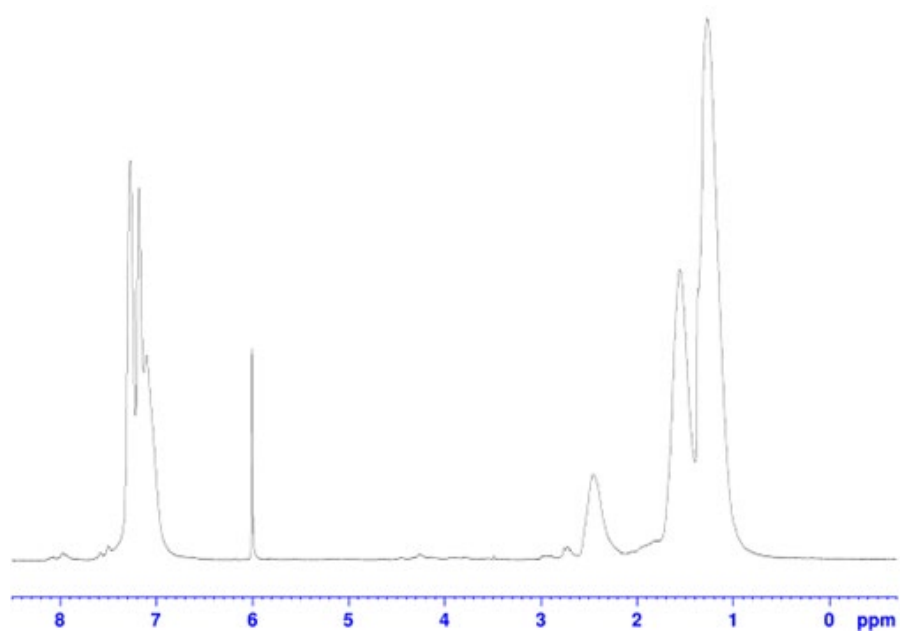


Figure S9. ¹H NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*₂ solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*-Pr₂C₆H₃) (**5**)–MAO catalyst system, styrene content 29.9 mol % (run 19).

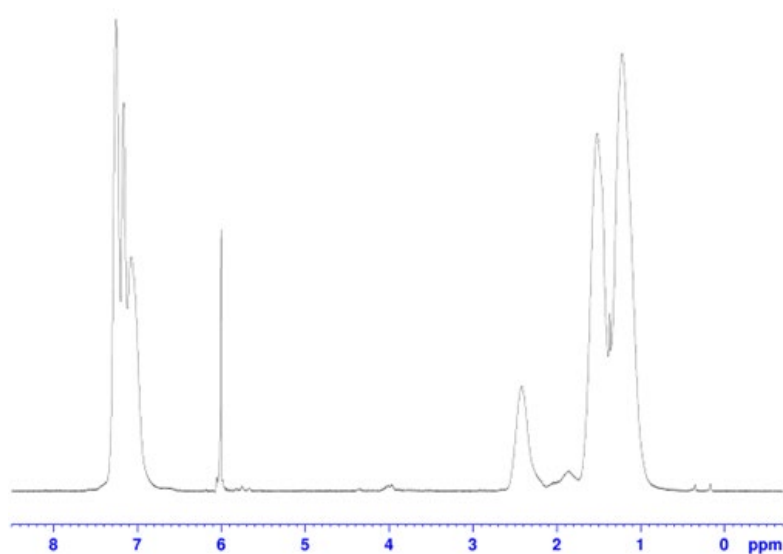


Figure S10. ¹H NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*₂ solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*-Pr₂C₆H₃) (**5**)–MAO catalyst system, styrene content 35.0 mol % (run 13).

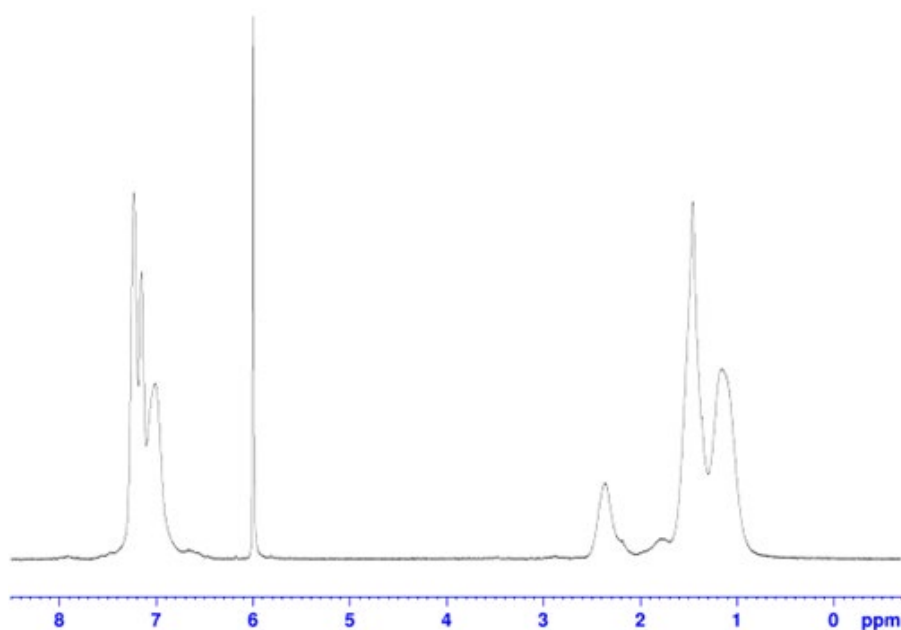


Figure S11. ¹H NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*₂ solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*-Pr₂C₆H₃) (**5**)–MAO catalyst system, styrene content 41.0 mol % (run 21).

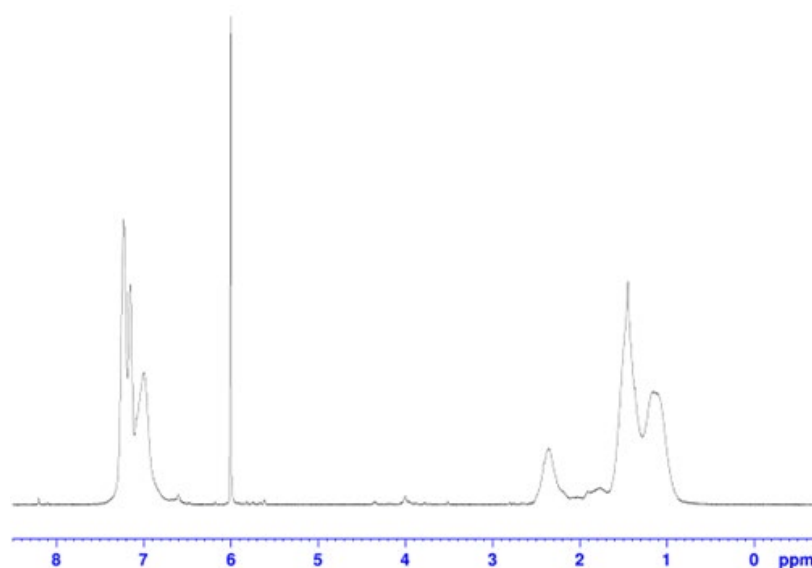


Figure S12. ¹H NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*₂ solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*-Pr₂C₆H₃) (**5**)–MAO catalyst system, styrene content 50.0 mol % (run 26).

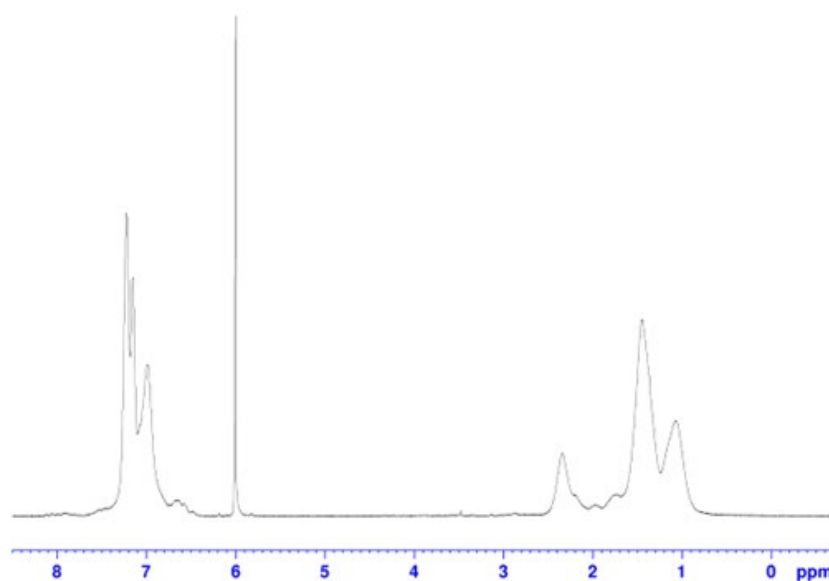


Figure S13. ¹H NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*₂ solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*-Pr₂C₆H₃) (**5**)–MAO catalyst system, styrene content 54.3 mol % (run 22).

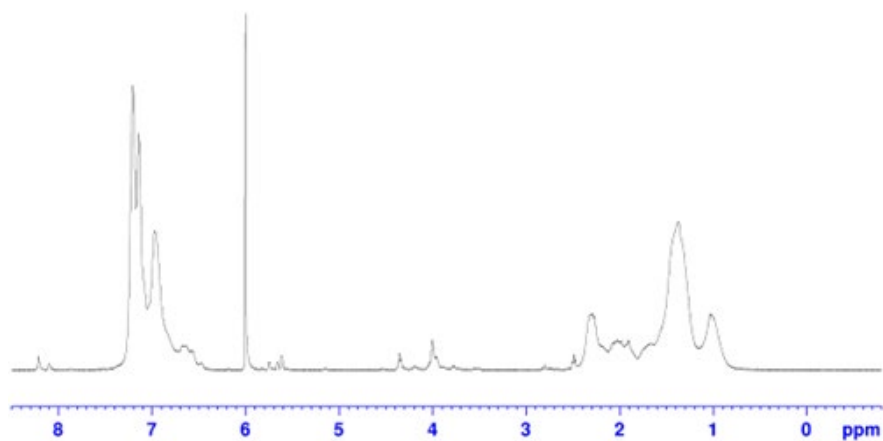


Figure S14. ^1H NMR spectrum (in 1,1,2,2-tetrachloroethane- d_2 solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**5**)–MAO catalyst system, styrene content 63.6 mol % (run 29).

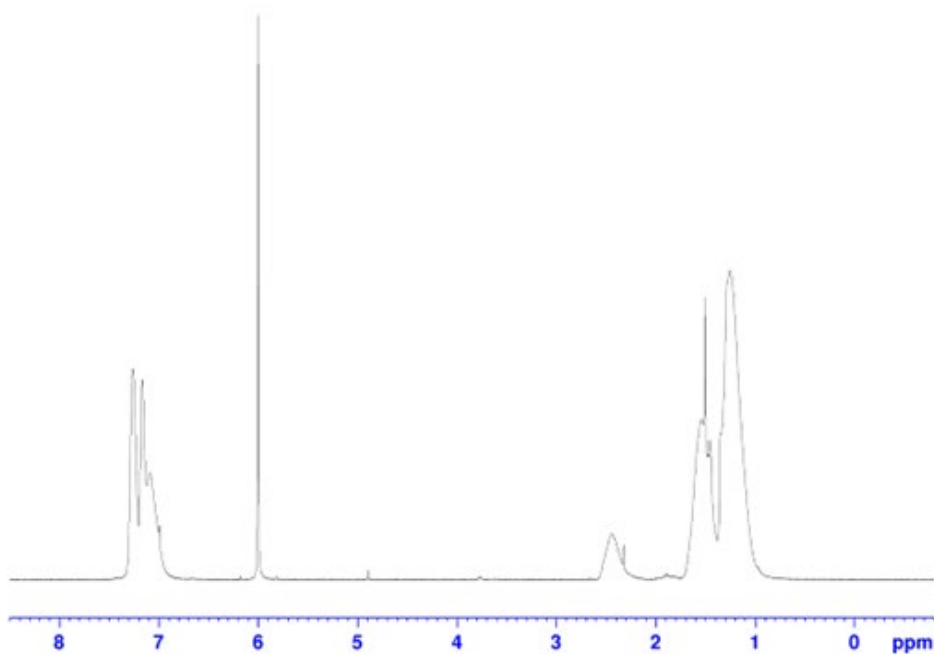


Figure S15. ^1H NMR spectrum (in 1,1,2,2-tetrachloroethane- d_2 solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{-4-SiEt}_3\text{C}_6\text{H}_2)$ (**6**)–MAO catalyst system, styrene content 27.2 mol % (run 30).

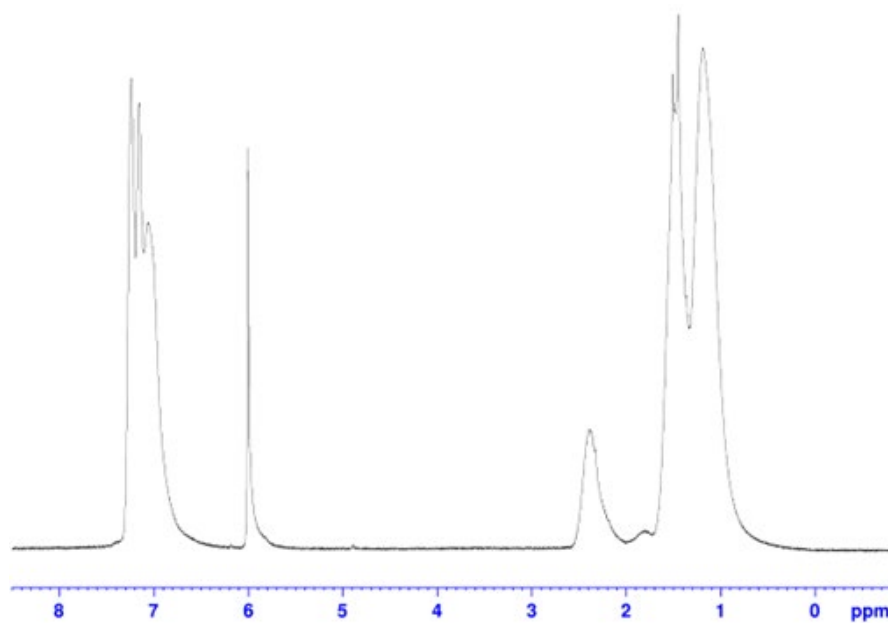


Figure S16. ¹H NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*₂ solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*-Pr₂-4-SiEt₃C₆H₂) (**6**)–MAO catalyst system, styrene content 36.6 mol % (run 16).

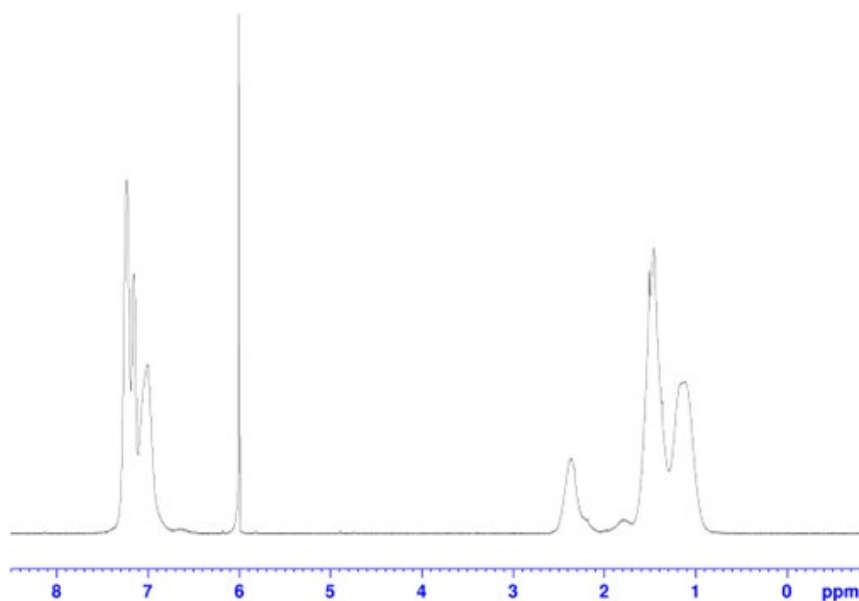


Figure S17. ¹H NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*₂ solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*-Pr₂-4-SiEt₃C₆H₂) (**6**)–MAO catalyst system, styrene content 44.9 mol % (run 17).

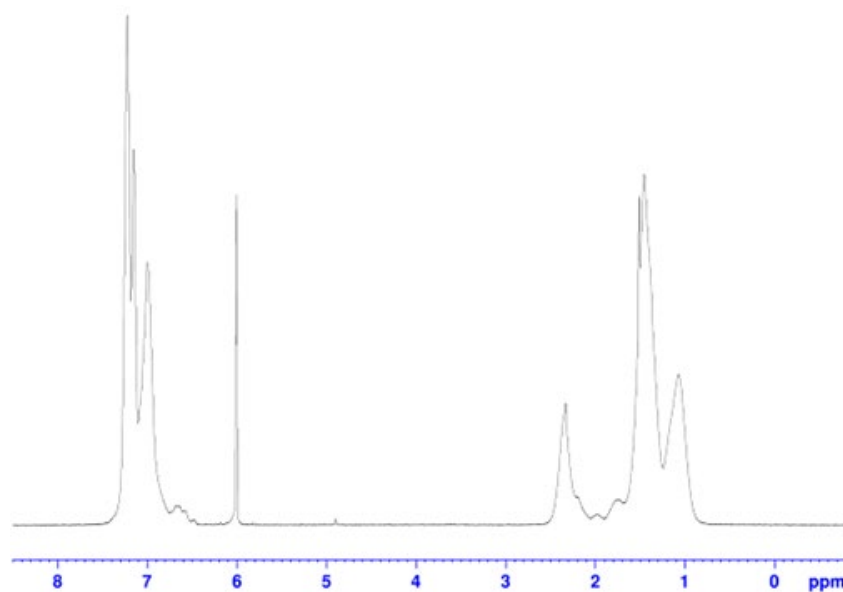


Figure S18. ^1H NMR spectrum (in 1,1,2,2-tetrachloroethane- d_2 solution at 110 °C) for poly(ethylene-*co*-styrene) prepared by $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{-4-SiEt}_3\text{C}_6\text{H}_2)$ (**6**)–MAO catalyst system, styrene content 55.6 mol % (run 18).

3. Selected DSC thermogram in the resultant poly(ethylene-*co*-styrene)s.

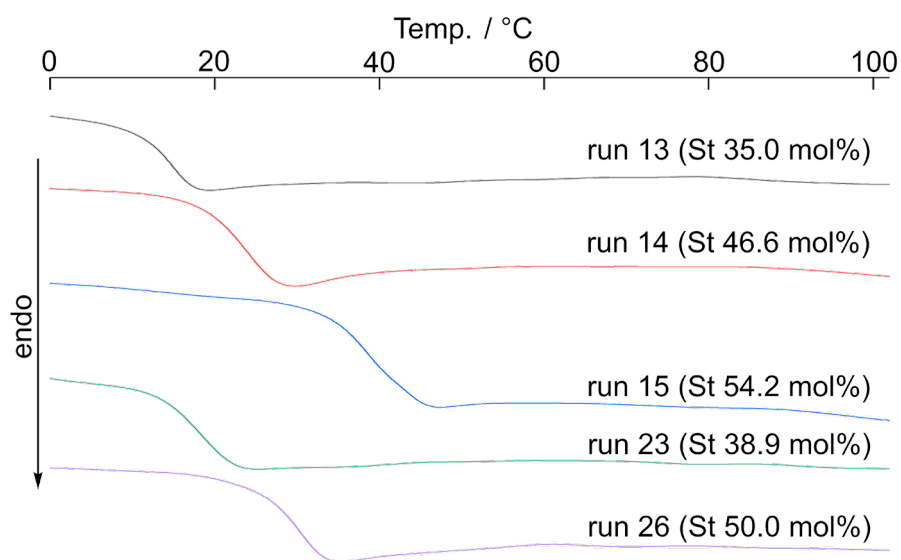


Figure S19. Selected DSC thermograms in the resultant poly(ethylene-*co*-styrene)s prepared by $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**5**)–MAO catalyst system.

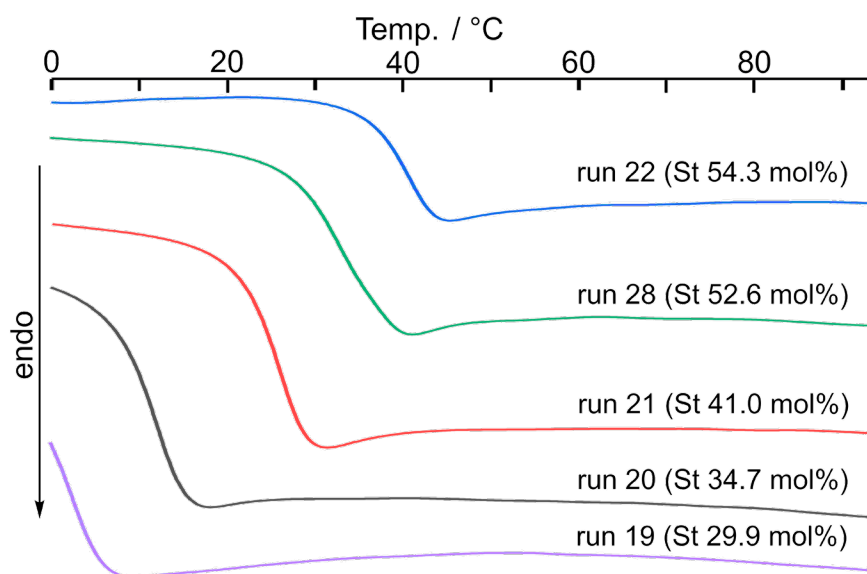


Figure S20. Selected DSC thermograms in the resultant poly(ethylene-*co*-styrene)s prepared by $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**5**)–MAO catalyst system.