Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Styrene-Isoprene and Styrene-1,3-Pentadiene Copolymerisation Catalyzed by Titanium [OSSO]-type Catalysts

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Figure S12. DSC curves of samples listed in Table 1: entry 2 (a), entry 3 (b), entry 4 (c), entry 5 (d), entry 6 (e).

3.3 DSC analysis of isotactic poly(styrene)-co-isoprene copolymers synthesized by 2/MAO

Figure S13. DSC curves of samples listed in Table 1: entry 8 (a), entry 10 (b), entry 11 (c), entry 12 (d), entry 13 (e).

3.4 DSC analysis of poly-1,3-pentadiene homopolymers synthesized by 1 and 2/MAO

Figure S14. DSC curves of samples listed in Table 3: entry 14 (a), entry 21 (b).

3.5 DSC analysis of isotactic poly(styrene)-co-1,3-pentadiene copolymers synthesized by 1/MAO

Figure S15. DSC curves of entries listed in Table 2: entry 15 (a), entry 16 (b), entry 17 (c), entry 18 (d), entry 19 (e), entry 20 (f).

3.6 DSC analysis of isotactic poly(styrene)-co-1,3-pentadiene copolymers synthesized by 2/MAO

Figure S16. DSC curves of samples listed in Table 2: entry 22 (a), entry 23 (b), entry 24 (c), entry 25 (d), entry 26 (e), entry 27 (f).

1. NMR ANALYSIS

1.1 NMR analysis of polyisoprene homopolymers synthesized by 1/MAO and 2/MAO

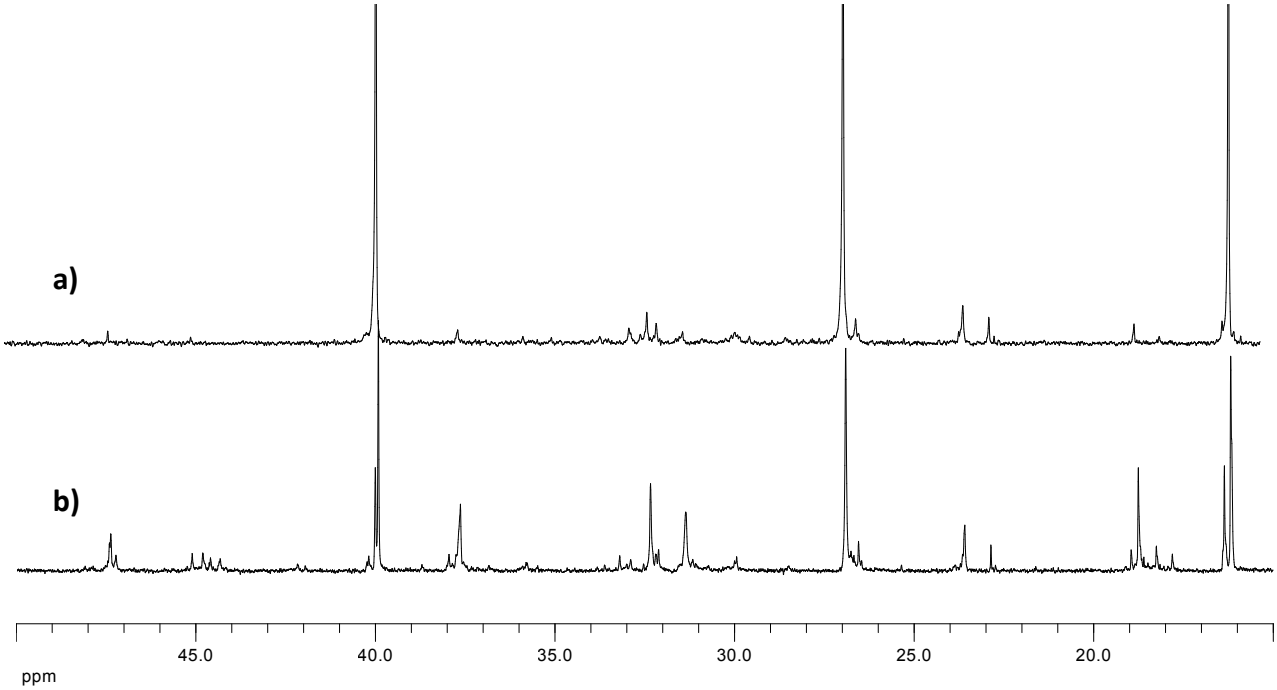

Figure S1. Aliphatic region of the ^{13}C NMR spectra ($CDCl_3$, δ in ppm) of entry 1 (a) and entry 7 (b).

1.2 NMR analysis of isotactic poly(styrene)-co-isoprene copolymers synthesized by 1/MAO

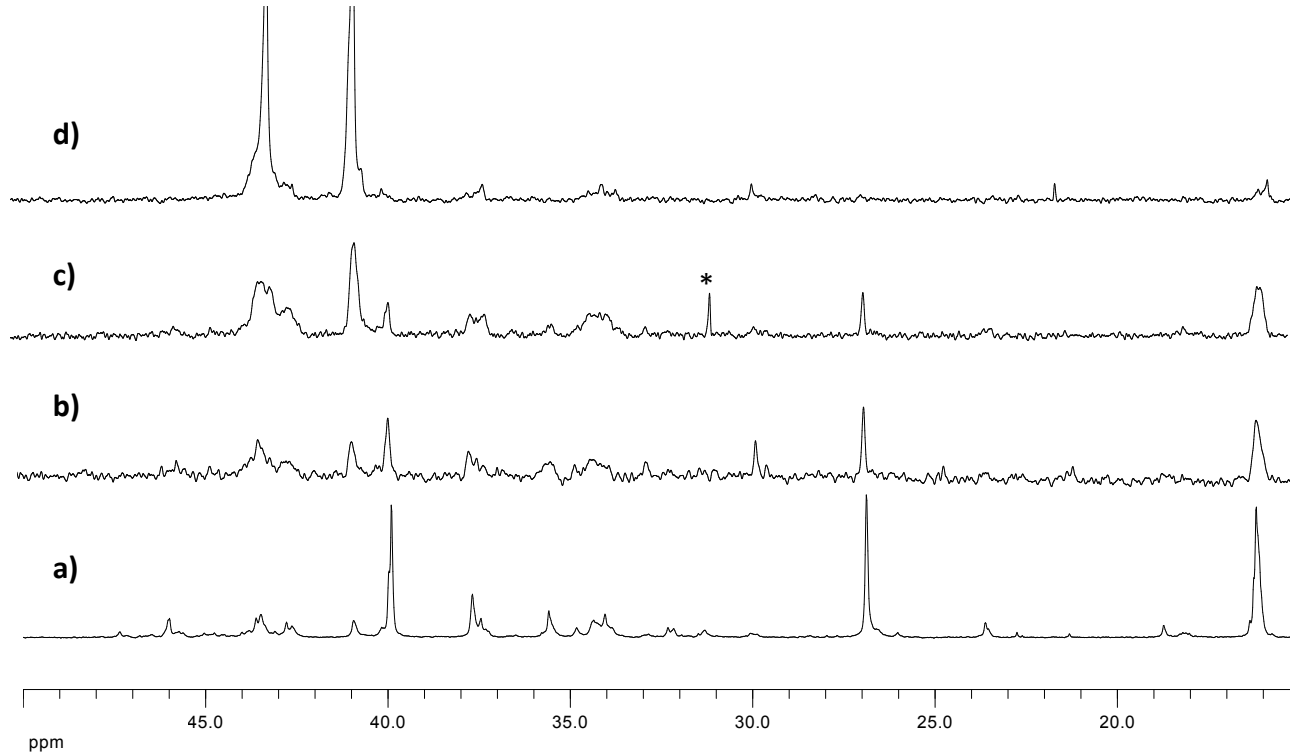

Figure S2. Aliphatic region of the ^{13}C NMR spectra ($CDCl_3$, δ in ppm) of samples: entry 2 (a, $x_s = 0.33$), entry 4 (b, $x_s = 0.77$) , entry 5 (c, $x_s = 0.86$), entry 6 (d, $x_s = 0.98$) of table 1. Peak marked with * is due to acetone impurity.

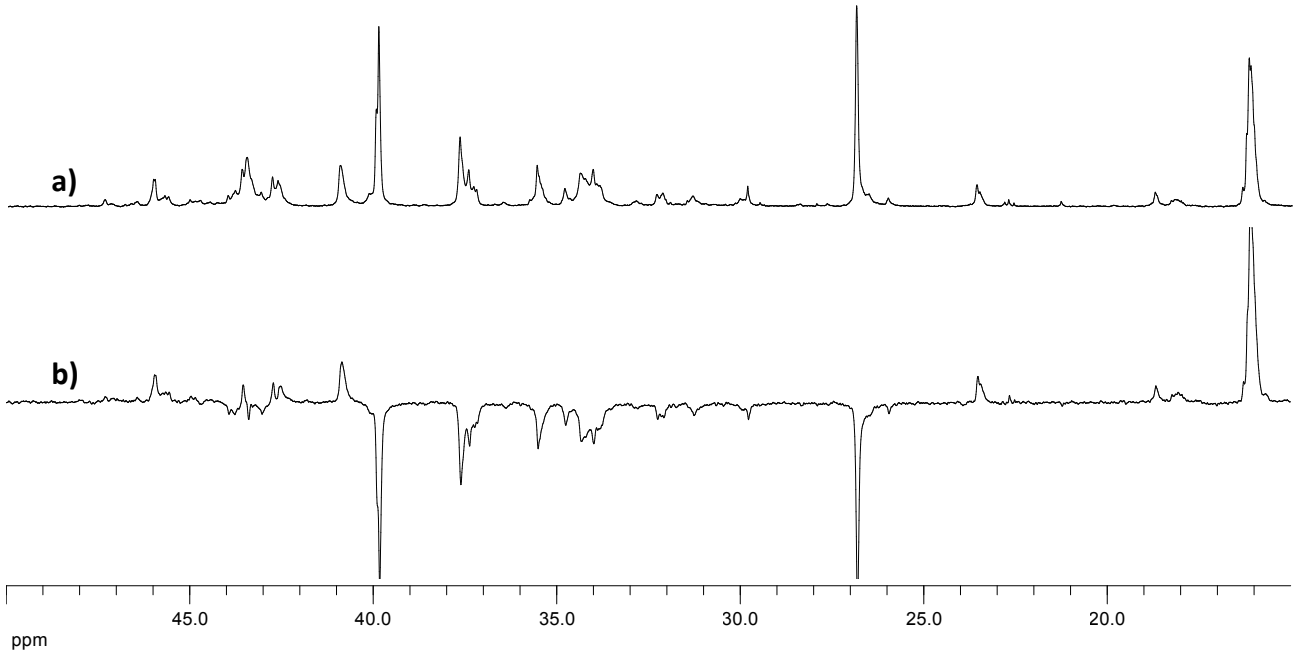

Figure S3. Aliphatic region of ^{13}C NMR spectrum ($CDCl_3$, δ in ppm)(a) and DEPT 135 (b) of entry 3 (x_s=0.40).

1.3 NMR analysis of isotactic poly(styrene)-co-isoprene copolymers synthesized by 2/MAO

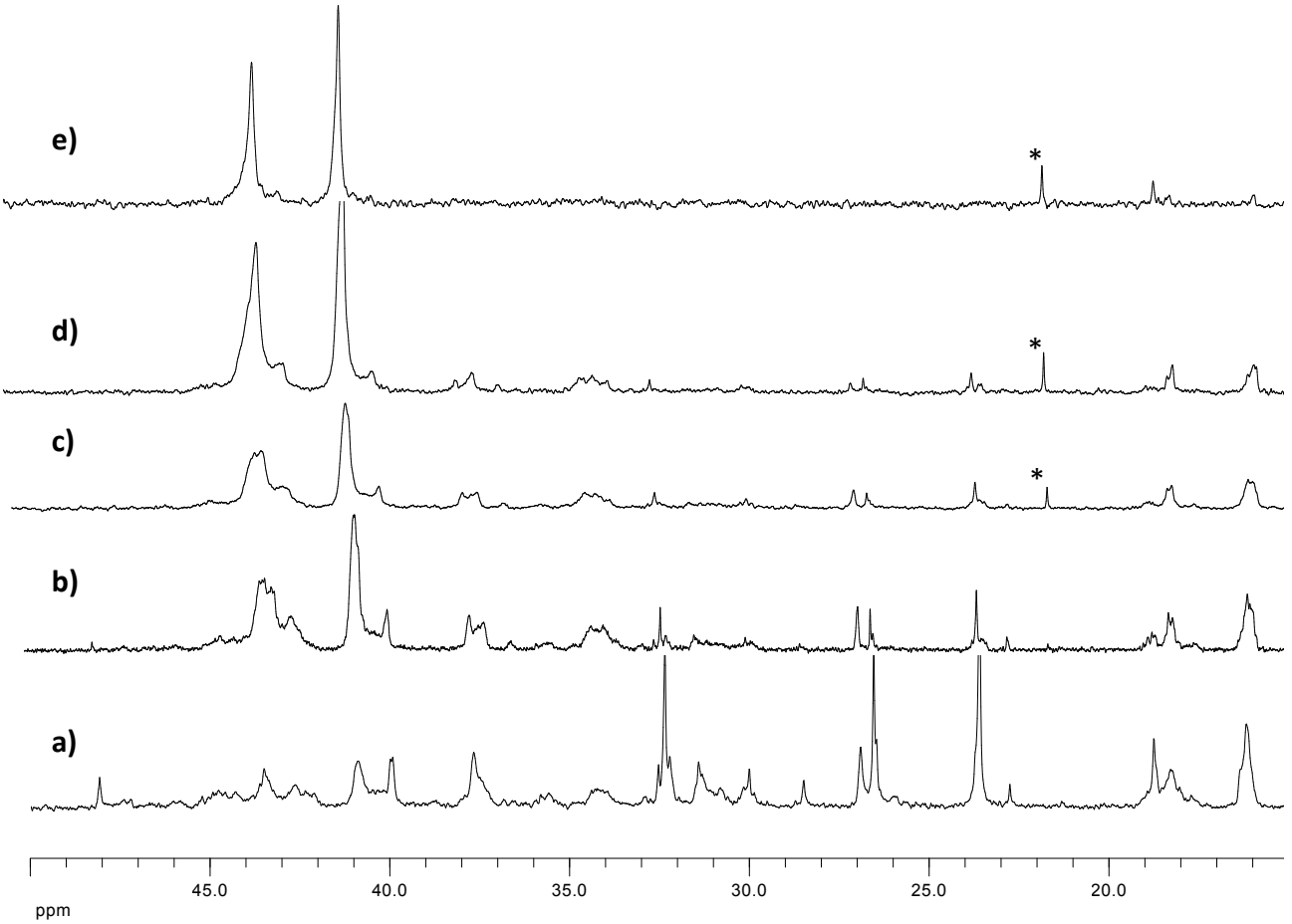

Figure S4. Aliphatic region of the ^{13}C NMR spectra ($CDCl_3$, δ in ppm) of samples: entry 8 (a, x_s = 0.27), entry 10 (b, x_s = 0.66) , entry 11 (c, x_s = 0.75), entry 12 (d, x_s = 0.92), entry 13 (e, x_s = 0.97) of table 1.Peaks marked with * are due to toluene impurity.

1.4 NMR analysis of poly-1,3-pentadiene homopolymers synthesized by 1/MAO and 2/MAO

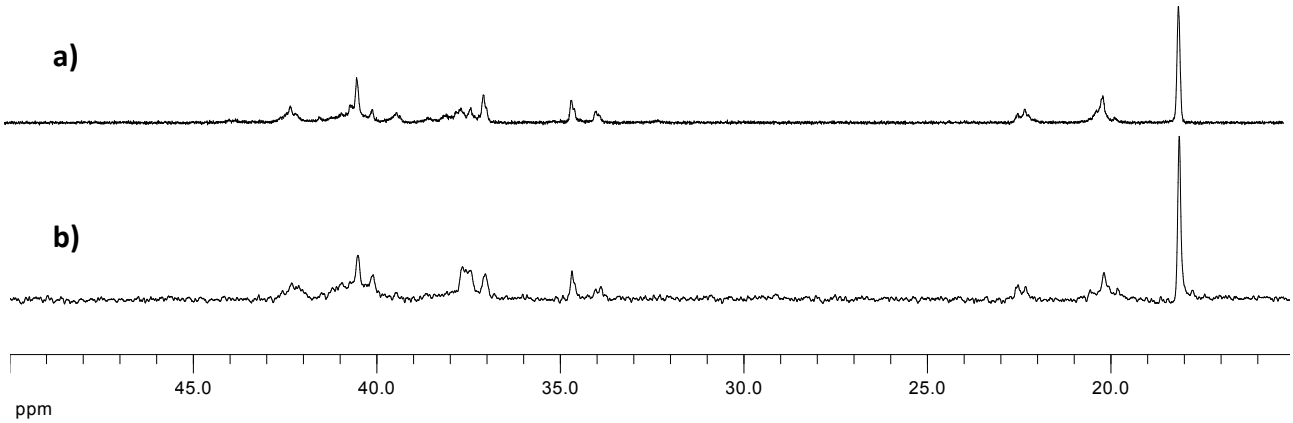

Figure S5. Aliphatic region of the ^{13}C NMR spectra ($CDCl_3$, δ in ppm) of entry 14 (a) and entry 21 (b).

1.5 NMR analysis of isotactic poly(styrene)-co-1,3-pentadiene copolymers synthesized by 1/MAO

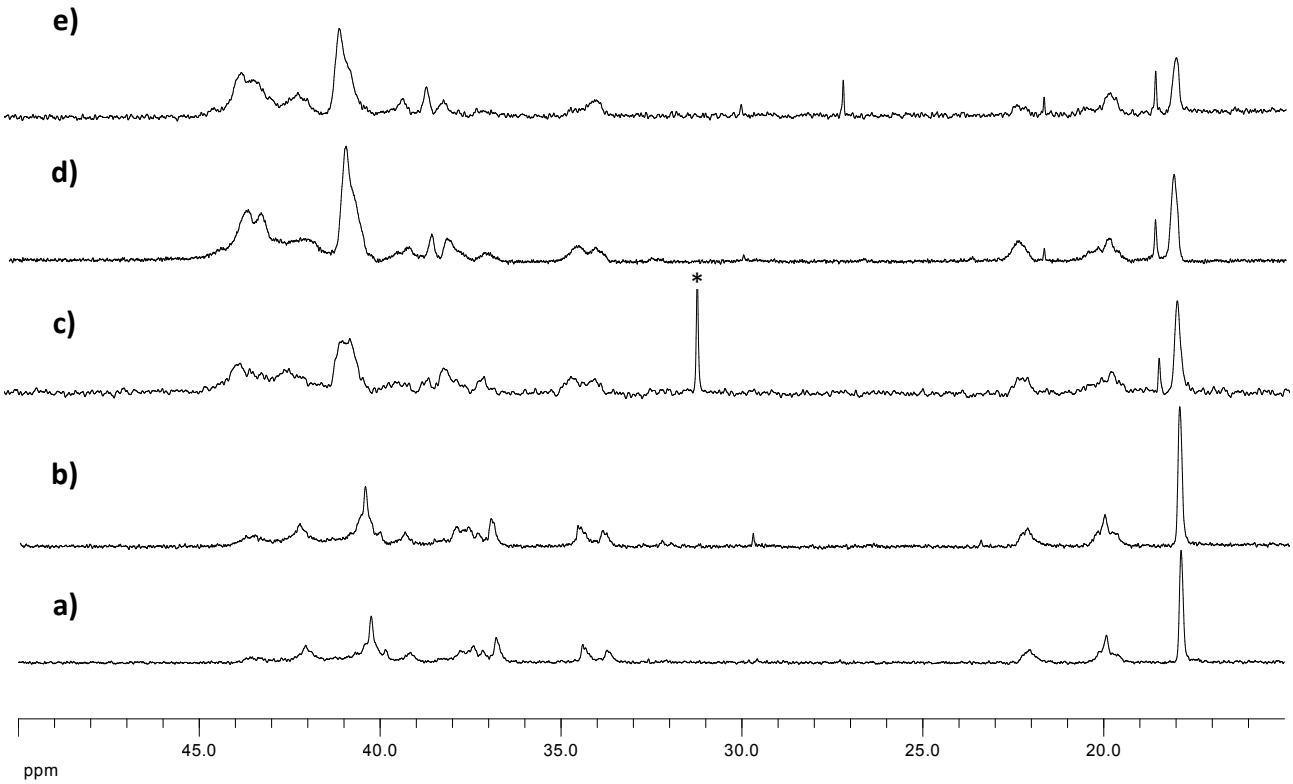

Figure S6. Aliphatic region of the ^{13}C NMR ($CDCl_3$, δ in ppm) spectra of samples: entry 16 (a, $x_s = 0.39$), entry 17 (b, $x_s = 0.52$), entry 18 (c, $x_s = 0.60$), entry 19 (d, $x_s = 0.71$), entry 20 (e, $x_s = 0.80$) of table 2.Peak marked with * is due to acetone impurity.

1.6 NMR analysis of isotactic poly(styrene)-co-1,3-pentadiene copolymers synthesized by 2/MAO

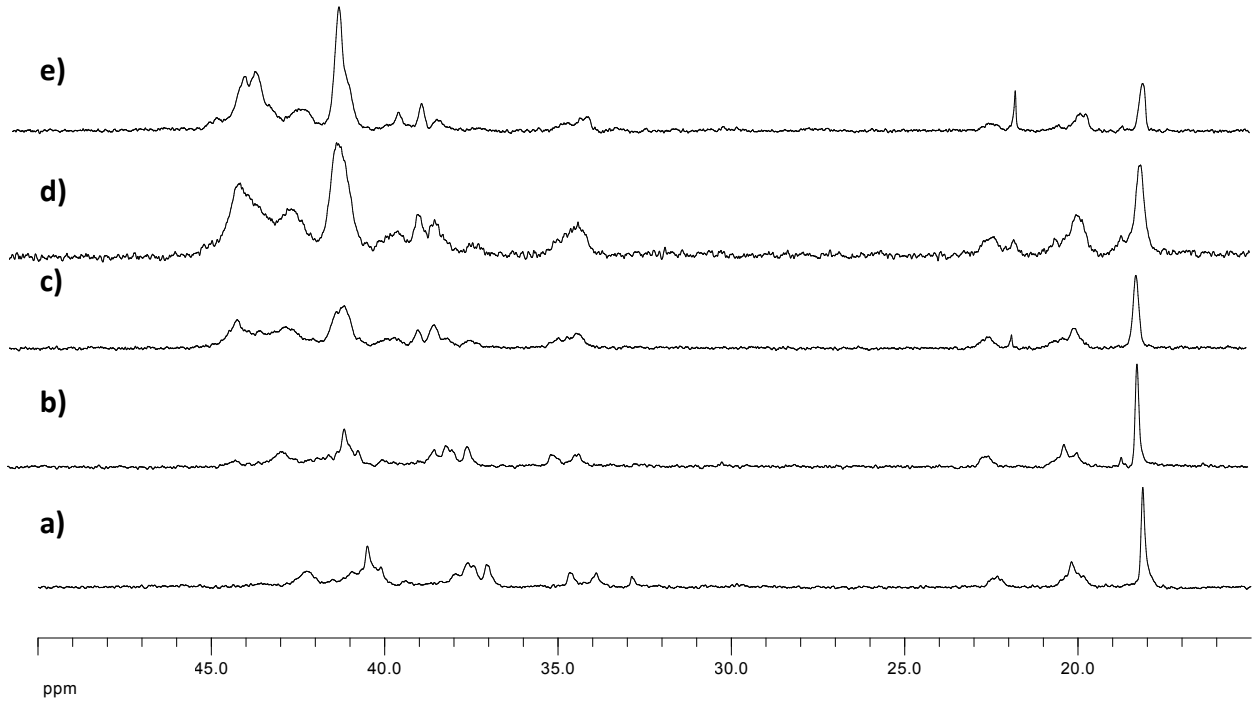

Figure S7. Aliphatic region of the ^{13}C NMR ($CDCl_3$, δ in ppm) spectra of samples: entry 22 (a, x_s = 0.08), entry 24 (b, x_s = 0.27), entry 25 (c, x_s = 0.63), entry 26 (d, x_s = 0.74), entry 27 (e, x_s = 0.85) of table 2.

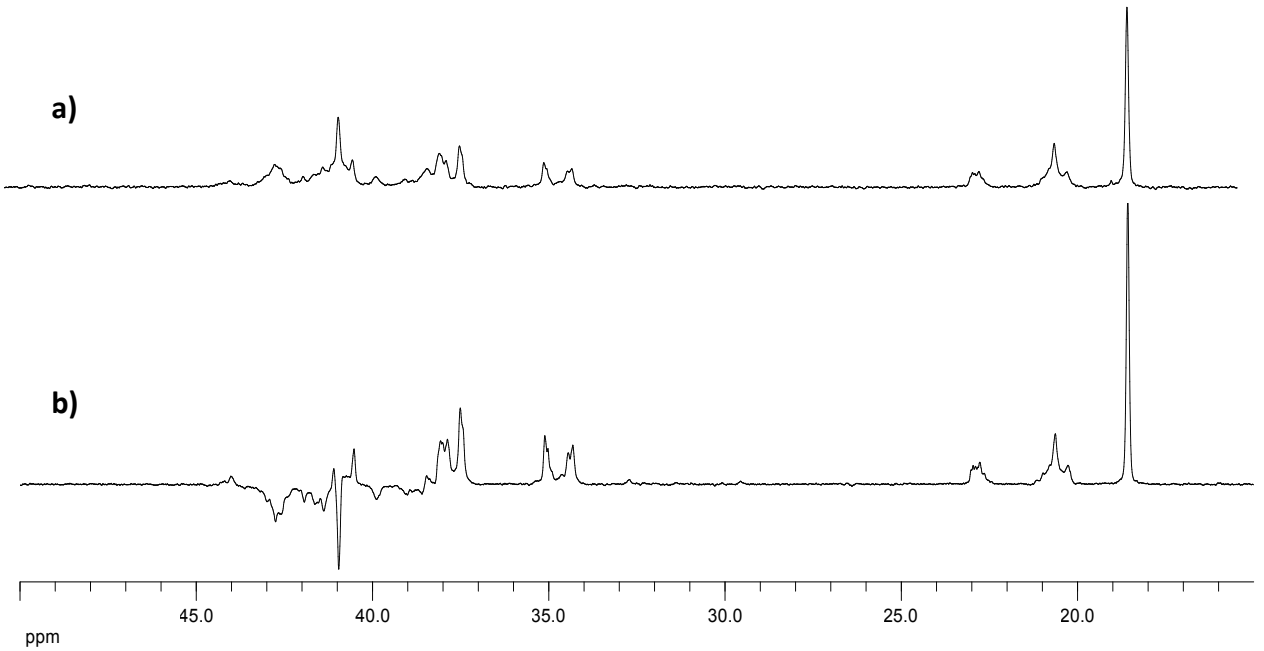

Figure S8. Aliphatic region of ^{13}C NMR spectrum ($CDCl_3$, δ in ppm)(a) and DEPT 135 (b) of entry 23 (x_s=0.13).

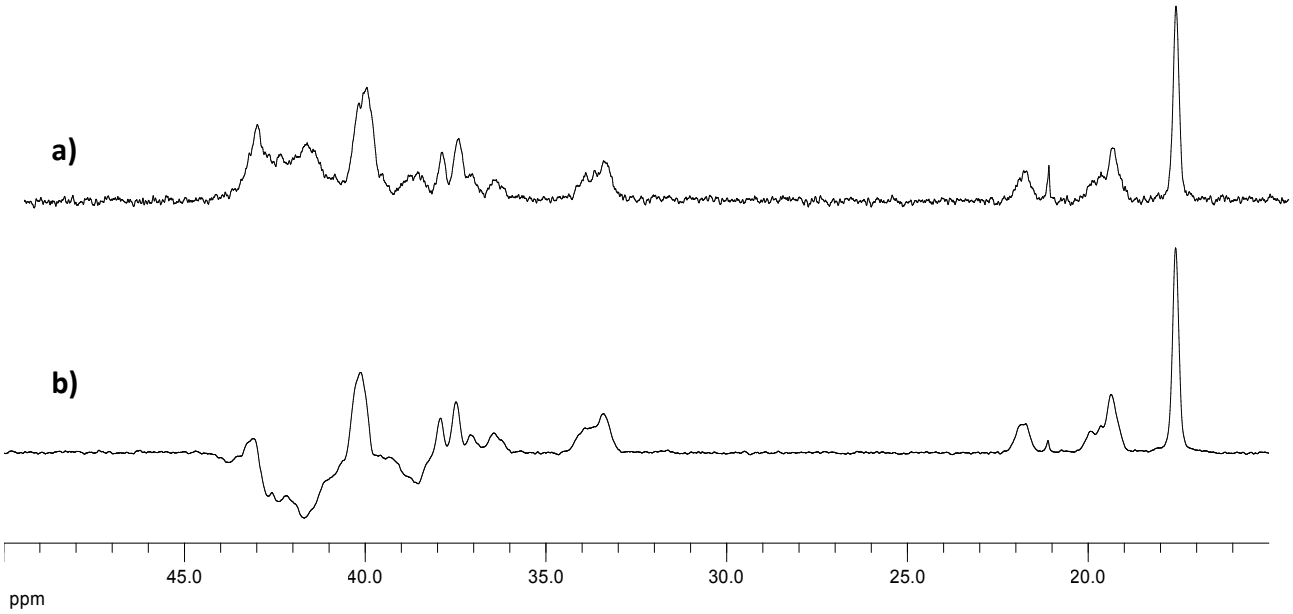

Figure S9. Aliphatic region of ^{13}C NMR spectrum ($CDCl_3$, δ in ppm) (a) and DEPT 135 (b) of entry 25 (x_s=0.63).

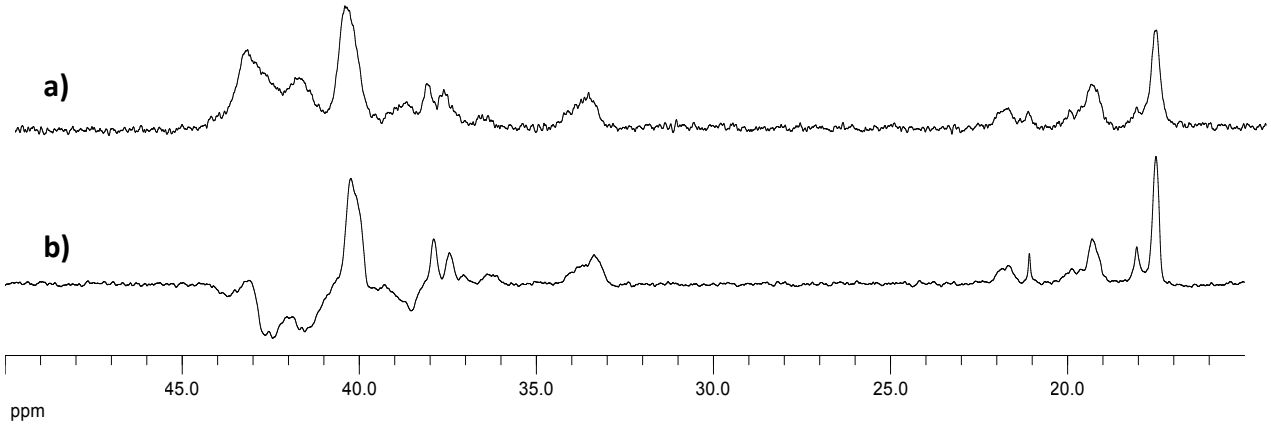

Figure S10. Aliphatic region of ^{13}C NMR spectrum ($CDCl_3$, δ in ppm)(a) and DEPT 135 (b) of entry 26 (x_s=0.74).

2. EVALUATION OF THE AVERAGE STYRENE BLOCK LENGTH

2.1 Average styrene block lengths for isotactic poly(styrene)-co-isoprene copolymers synthesized by 1 and 2/MAO

$$n_s = \frac{SSS + ISS + SSI + ISI}{ISI + {}^{1}\!/_{2}(ISS + SSI)}$$

$$= \frac{(SSS) + (CSS + VSS + TSS) + (SSC + SSV + SST) + (CSC + VSV + CST + CSV + VSC + VST + TST)}{(CSC + VSV + CST + CSV + VSC + VST + TST) + {}^{1}\!/_{2}[(CSS + VSS + TSS) + (SSC + SSV + SST)]}$$

$$\approx \frac{(SS_1S + SS_2S) + (CS_1S + CS_2S + TS_2S) + (SS_1C + SS_2T + SST_1 + SS_1T) + (C_4SC + CS_2C +}{(C_4SC + CS_2C + CS_1C + VS_1V + VS_1C' + TS_2T + TS_1T + TST_1) + {}^{1}\!/_{2}[(CS_1S + CS_2S -}$$

2.2 Average styrene block lengths for isotactic poly(styrene)-co-1,3-pentadiene copolymers synthesized by 1/MAO and 2/MAO

$$n_s = \frac{SSS + DSS + SSD + DSD}{DSD + {}^{1}\!/_{2}(DSS + SSD)}$$

$$= \frac{(SSS) + (VSS + TSS) + (SSV + SST) + (VSV + VST + TST)}{(VSV + VST + TST) + {}^{1}\!/_{2}[(VSS + TSS) + (SSV + SST)]}$$

$$\approx \frac{(SS_1S + SS_2S) + (T_4SS) + (SS_1T + SS_2T) + (TS_4T)}{TS_4T + {}^{1}\!/_{2}[(T_4SS) + (SS_1T + SS_2T)]}$$

3. DSC ANALYSIS

3.1 DSC analysis of polyisoprene homopolymers synthesized by 1 and 2/MAO

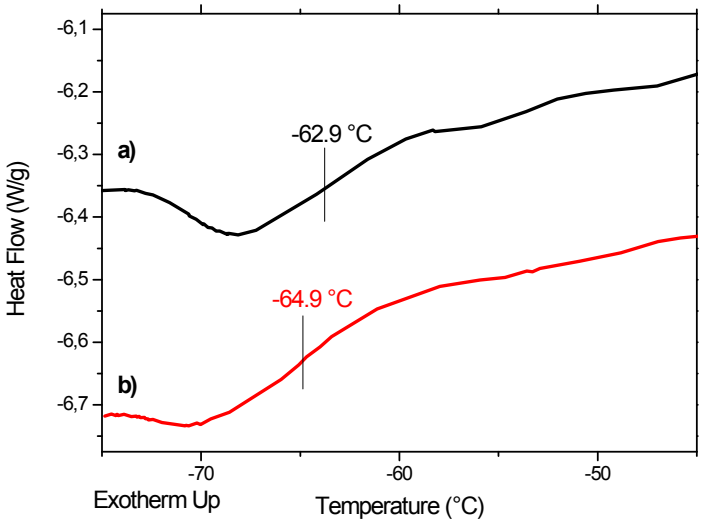

Figure S11. DSC curves of samples listed in Table 1: entry 1 (a), entry 7 (b).

3.2 DSC analysis of isotactic poly(styrene)-co-isoprene copolymers synthesized by 1/MAO

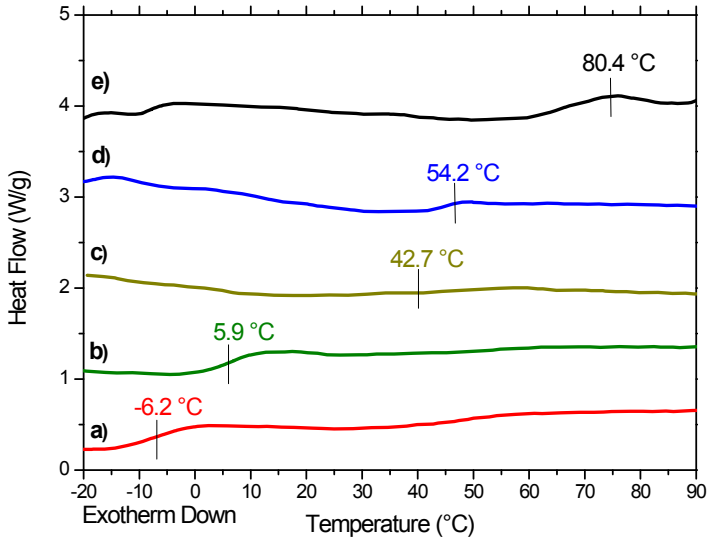

Figure S12. DSC curves of samples listed in Table 1: entry 2 (a), entry 3 (b), entry 4 (c), entry 5 (d), entry 6 (e).

3.3 DSC analysis of isotactic poly(styrene)-co-isoprene copolymers synthesized by 2/MAO

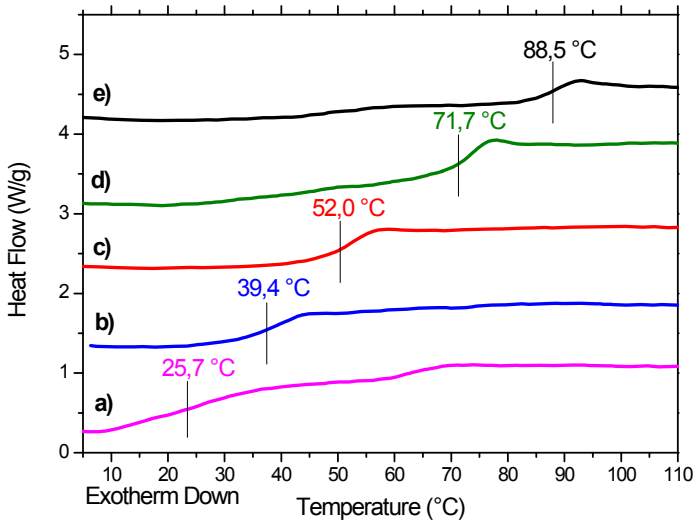

Figure S13. DSC curves of samples listed in Table 1: entry 8 (a), entry 10 (b), entry 11 (c), entry 12 (d), entry 13 (e).

3.4 DSC analysis of poly-1,3-pentadiene homopolymers synthesized by 1 and 2/MAO

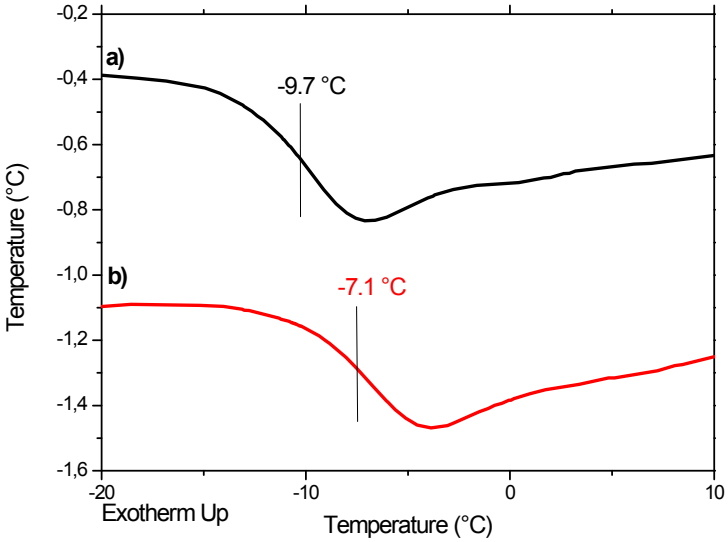

Figure S14. DSC curves of samples listed in Table 3: entry 14 (a), entry 21 (b).

3.5 DSC analysis of isotactic poly(styrene)-co-1,3-pentadiene copolymers synthesized by 1/MAO

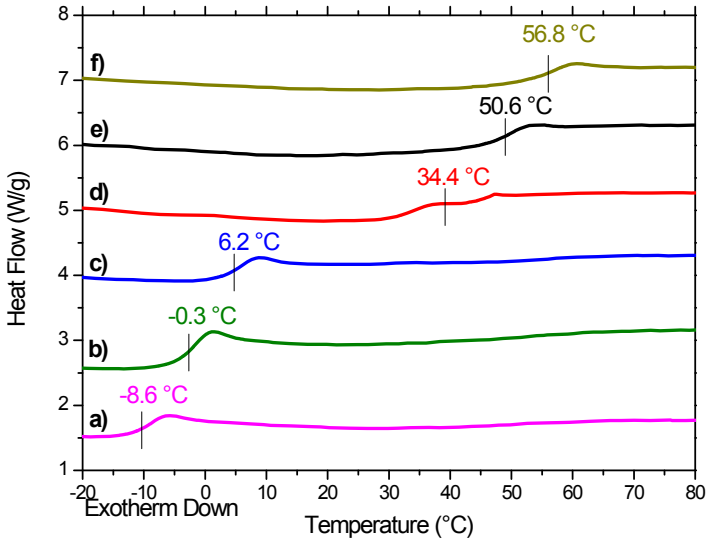

Figure S15. DSC curves of entries listed in Table 3: entry 15 (a), entry 16 (b), entry 17 (c), entry 18 (d), entry 19 (e), entry 20 (f).

3.6 DSC analysis of isotactic poly(styrene)-co-1,3-pentadiene copolymers synthesized by 2/MAO

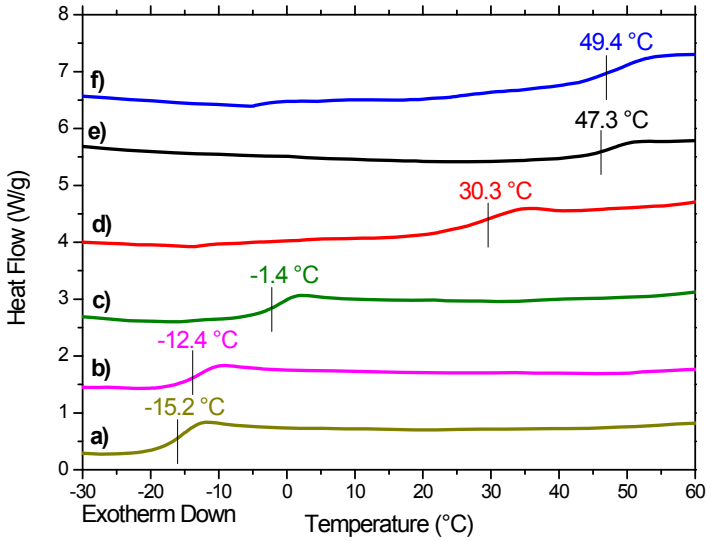

Figure S16. DSC curves of samples listed in Table 3: entry 22 (a), entry 23 (b), entry 24 (c), entry 25 (d), entry 26 (e), entry 27 (f).