Supporting Information

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

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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$_3$, $\delta$ 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$_3$, $\delta$ in ppm) of samples: entry 2 (a, $x_s = 0.02$), entry 4 (b, $x_s = 0.05$), entry 5 (c, $x_s = 0.1$), entry 6 (d, $x_s = 0.5$) of table 1.

Figure S3. Aliphatic region of $^{13}$C NMR spectrum (CDCl$_3$, $\delta$ in ppm)(a) and DEPT 135 (b) of entry 3 ($x_s$=0.03).

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$_3$, $\delta$ in ppm) of samples: entry 8 (a, $x_s = 0.02$), entry 10 (b, $x_s = 0.05$), entry 11 (c, $x_s = 0.1$), entry 12 (d, $x_s = 0.2$), entry 13 (e, $x_s = 0.5$) of table 1.

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$_3$, $\delta$ 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$_3$, $\delta$ in ppm) spectra of samples: entry 16 (a, $x_s = 0.03$), entry 17 (b, $x_s = 0.1$), entry 18 (c, $x_s = 0.3$), entry 19 (d, $x_s = 0.5$), entry 20 (e, $x_s = 0.7$) of table 2.

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$_3$, $\delta$ in ppm) spectra of samples: entry 22 (a, $x_s = 0.02$), entry 24 (b, $x_s = 0.1$), entry 25 (c, $x_s = 0.3$), entry 26 (d, $x_s = 0.5$), entry 27 (e, $x_s = 0.7$) of table 2.

Figure S8. Aliphatic region of $^{13}$C NMR spectrum (CDCl$_3$, $\delta$ in ppm)(a) and DEPT 135 (b) of entry 23 ($x_s$=0.03).

Figure S9. Aliphatic region of $^{13}$C NMR spectrum (CDCl$_3$, $\delta$ in ppm)(a) and DEPT 135 (b) of entry 25 ($x_s$=0.3).

Figure S10. Aliphatic region of $^{13}$C NMR spectrum (CDCl$_3$, $\delta$ in ppm)(a) and DEPT 135 (b) of entry 26 ($x_s$=0.5).

2. EVALUATION OF THE AVERAGE STYRENE BLOCK LENGTH

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

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

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 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](image1)

*Figure S1.* Aliphatic region of the $^{13}$C NMR spectra (CDCl$_3$, $\delta$ 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](image2)

*Figure S2.* Aliphatic region of the $^{13}$C NMR spectra (CDCl$_3$, $\delta$ 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.
1.3 NMR analysis of isotactic poly(styrene)-co-isoprene copolymers synthesized by 2/MAO

Figure S3. Aliphatic region of $^{13}$C NMR spectrum (CDCl$_3$, $\delta$ in ppm)(a) and DEPT 135 (b) of entry 3 ($x_s$=0.40).

Figure S4. Aliphatic region of the $^{13}$C NMR spectra (CDCl$_3$, $\delta$ 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$_3$, $\delta$ 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$_3$, $\delta$ in ppm)(a) and DEPT 135 (b) of entry 23 ($x_s=0.13$).
**Figure S9.** Aliphatic region of $^{13}$C NMR spectrum (CDCl$_3$, $\delta$ in ppm) (a) and DEPT 135 (b) of entry 25 ($x_s=0.63$).

**Figure S10.** Aliphatic region of $^{13}$C NMR spectrum (CDCl$_3$, $\delta$ 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

\[ n_s = \frac{SSS + ISS + SSI + ISI}{ISI + \frac{1}{2}(ISS + SSI)} \]

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

\[ \approx \frac{(SSS) + (CSS + VSS + TSS) + (CSS + VSS + TSS) + (CSS + VSS + TSS) + (CSS + VSS + TSS)}{(CSS + VSS + TSS) + (CSS + VSS + TSS) + (CSS + VSS + TSS) + (CSS + VSS + TSS) + (CSS + VSS + TSS)} \]

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

\[ n_s = \frac{SSS + DSS + SSD + DSD}{DSD + \frac{1}{2}(DSS + SSD)} \]

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

\[ \approx \frac{(SSS) + (VSS + TSS) + (VSS + TSS) + (VSS + TSS)}{(VSS + TSS) + \frac{1}{2}[(VSS + TSS) + (VSS + TSS)]} \]
3. DSC ANALYSIS

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

![DSC curves of samples listed in Table 1: entry 1 (a), entry 7 (b).](image1)

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

![DSC curves of samples listed in Table 1: entry 2 (a), entry 3 (b), entry 4 (c), entry 5 (d), entry 6 (e).](image2)

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

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

*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

![DSC curves of samples listed in Table 3: entry 14 (a), entry 21 (b).](image)

*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](image1.png)

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](image2.png)

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).