Supporting Information

Synthesis of butadiene/isoprene-styrene di-block copolymer with high *cis*-1,4 unit content based on a phosphate Ester neodymium

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1.The calculation method of micro-structure content in the copolymer PB-*b*-PS

The stereo-structures of polybutadiene (PB) segment in the copolymer PB-*b*-PS prepared by coordination polymerization include *cis*-1,4-PB, *trans*-1,4-PB and 1,2-PB. According to literature [1-5], the specific micro-structure calculation methods of PB-*b*-PS are shown in **eq**(1)-(6).

$$C_{PB}\% = \frac{(I_2 + I_1)/2}{I_3/5 + (I_2 + I_1)/2} \times 100 \qquad (1)$$

$$C_{PS}\% = \frac{I_3/5}{I_3/5 + (I_2 + I_1)/2} \times 100 \qquad (2)$$

$$C_{1,4-PB}\% = \frac{I_2}{I_1 + I_2} \times 100 \qquad (3)$$

$$C_{1,2-PB}\% = \frac{I_1}{I_1 + I_2} \times 100 \qquad (4)$$

C_{PB} and C_{PS} are the segment content of polybutadiene (PB) and polystyrene (PS) in the block copolymers PB-*b*-PS, respectively; $C_{1,4\text{-PB}}$ and $C_{1,2\text{-PB}}$ are the unit content of 1,4-PB, 1,2-PB in the PB segment; I_1 is the integration of the resonance δ = 5.05 ppm (two vinyl protons of the 1,2-Bd unit), I_2 is the integration of the resonance δ = 5.40 ppm (two vinyl protons of the 1,4-Bd unit), and I_3 is the integration of the resonance δ = 6.25-7.25 ppm (five phenyl protons of St segment), respectively, in the ^{1}H NMR spectrum of the PB-*b*-PS copolymer.

$$C_{cis-1,4-PB}\% = C_{1,4-PB} \times \frac{I_4}{I_4 + I_5} \times 100 \qquad (5)$$

$$C_{trans-1,4-PB}\% = C_{1,4-PB} \times \frac{I_5}{I_4 + I_5} \times 100 \qquad (6)$$

As shown in eq(5)-(6), $C_{1,4\text{-Bd}}$, $C_{cis\text{-}1,4\text{-PB}}$ and $C_{trans\text{-}1,4\text{-PB}}$ are the unit content of 1,4-PB, *cis*-1,4-PB and *trans*-1,4-PB in the PB segment of block copolymer PB-*b*-PS, respectively; I_4 is the integration of the resonance δ = 27.5 ppm and I_5 is the integration of the resonance δ = 32.6 ppm, respectively, in the ^{13}C NMR spectrum of the PB-*b*-PS copolymer.

A detailed calculation method of PB-*b*-PS sample (**Entry 2**, **Table 3**) prepared based on catalyst system $Nd(P_{507})_3/Al(i\text{-}Bu)_3/CHCl_3/PPh_3$ was described as a typical example. The corresponding integral data are shown in the **Fig. S1** and **Fig. S2**, the value of I_1, I_2, I_3, I_4 and I_5 are 1, 94.68, 55.06, 136.30 and 1. According to **eq** (1)-(6), it can be determined that the styrene segment content is 18.6%, and the *cis*-1,4 unit content is 98.3%, and the specific results are shown in **Table 3** and **Table 1**.

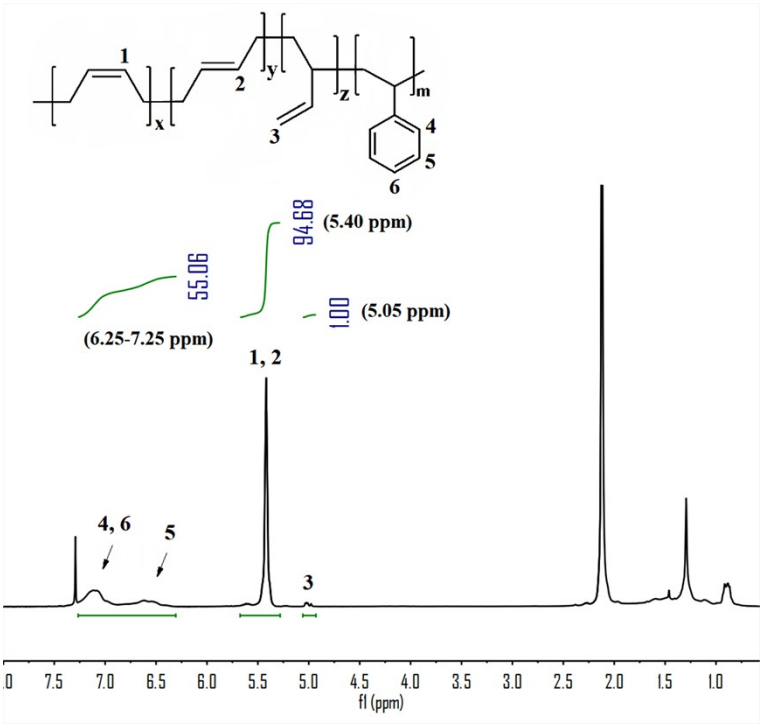

Fig. S1 Integral data in ^1H NMR spectra of the PB-*b*-PS (Entry 2, Table 3)

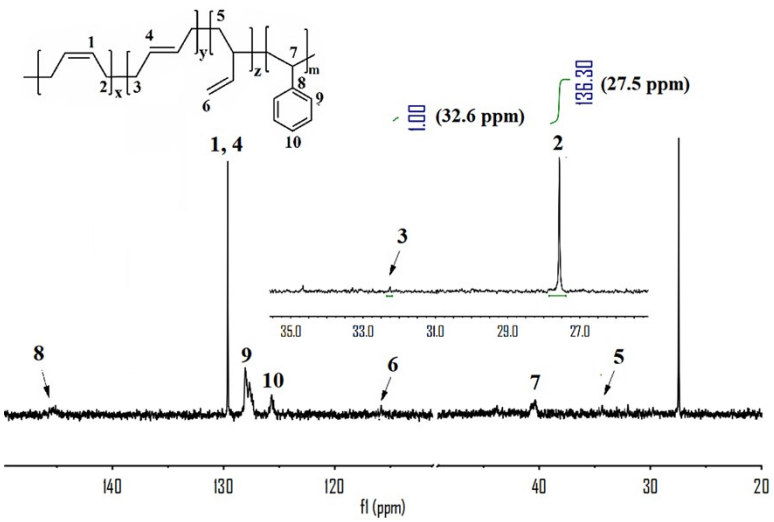

Fig. S2 Integral data in ^{13}C NMR spectra of the PB-*b*-PS (Entry 2, Table 3)

2.The calculation method of micro-structure content in the copolymer PI-b-PS

The storeo-structures of polyisoprene (PI) prepared by coordination polymerization are mainly *cis*-1,4-PI, *trans*-1,4-PI and 3,4-PI. According to literature [1-3], the specific micro-structure calculation methods of PI-*b*-PS are as shown in **eq**(7)-(10).

$$C_{PI}\% = \frac{(2I_6 + I_7)/2}{I_8/5 + (2I_6 + I_7)/2} \times 100 \qquad (7)$$

$$C_{PS}\% = \frac{I_8/5}{I_8/5 + (2I_6 + I_7)/2} \times 100 \qquad (8)$$

$$C_{1,4-PI}\% = \frac{2I_7}{I_6 + 2I_7} \times 100 \qquad (9)$$

$$C_{3,4-PI}\% = \frac{I_6}{I_6 + 2I_7} \times 100 \qquad (10)$$

C_{PI} and C_{PS} are the segment content of polyisoprene (PI) and polystyrene (PS) in the block copolymer PI-*b*-PS, respectively; $C_{1,4\text{-PI}}$ and $C_{3,4\text{-PI}}$ are the unit content of 1,4-PI, 3,4-PI in the Segment PB, respectively; I_6 is the integration of the resonance δ = 4.75 ppm (two vinyl protons of the 3,4-PI unit), I_7 is the integration of the resonance δ = 5.20 ppm (one vinyl protons of the 1,4-PI unit), and I_8 is the integration of the resonance δ = 6.25-7.25 ppm (five phenyl protons of St unit), respectively, in the ^{1}H

NMR spectrum of the PI-*b*-PS copolymer.

It can be seen from FT-IR spectrum of the PI-*b*-PS obtained via $Nd(P_{507})_3/Al(i\text{-}Bu)_3/CHCl_3/PPh_3$ catalytic system in this experiment, there is no peak at 1150 cm^{-1} and 1385 cm^{-1}, which indicates that there is almost no *trans*-1,4 unit structure in the polyisoprene segment [1,6-7], as shown in **Fig. 7**. Furthermore, there is also no obvious peak at chemical shift 18.6 ppm, 40.0 ppm and 125.3 ppm in the ^{13}C NMR of the copolymer PI-*b*-PS (as shown in **Fig. S3**), which also shows that the content of *trans*-1,4-IP structure in the block copolymer is close to Zero [1]. Therefore, in the determination about the microstructure of PI segment in this article, *cis*-1,4 and 1,4- are approximately regarded as equal [1], as shown in **eq**(11) .

$$C_{cis-1,4-PI}\% = C_{1,4-PI}\% = \frac{2I_7}{I_6 + 2I_7} \times 100 \qquad (11)$$

A detailed calculation method of PI-*b*-PS sample (**Entry 2**, **Table 5**) prepared based on catalyst system $Nd(P_{507})_3/Al(i\text{-}Bu)_3/CHCl_3/PPh_3$ was described as a typical example. The corresponding integral data are shown in the **Fig. S4** , the value of I_6, I_7 and I_8 are 1, 25.86 and 29.60. According to **eq** (7)-(11), it can be concluded that the styrene segment content is 18.3%, and the *cis*-1,4 unit content is 98.1%, the specific results are shown in **Table 4** and **Table 5**.

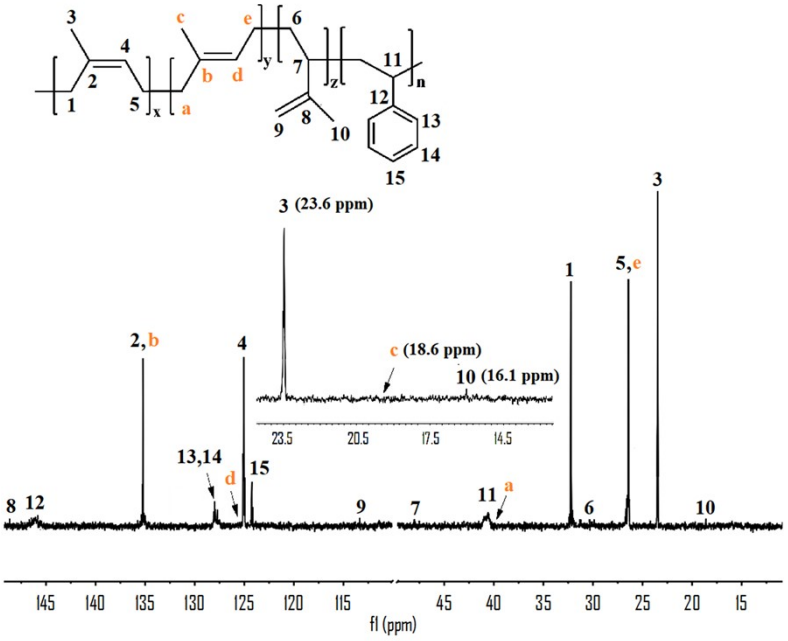

Fig. S3 ^{13}C NMR spectra of the PI-*b*-PS (Entry 2, Table 5)

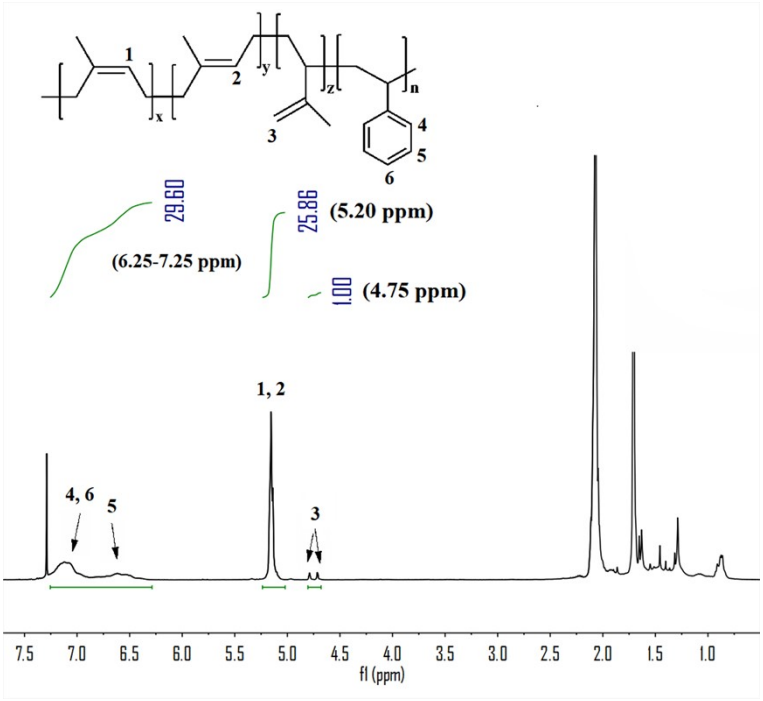

Fig. S4 Integral data in ^{1}H NMR spectra of the PI-*b*-PS (Entry 2, Table 5)

Reference

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