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Synthesis of Stereodiblock Polybutadiene Using $Cp^*Nd(BH_4)_2(thf)_2$ as a Catalyst

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Abstract: Butadiene polymerization, in both a highly *cis*- and *trans*-specific manner, was achieved by using a $Cp^*Nd(BH_4)_2(thf)_2$–Bu_2Mg system as an initiator. The *cis*-/*trans*- ratio can be tuned by the amount of trialkylaluminum-depleted modified methylaluminoxane (dMMAO). The *cis*-regularity of the polymer was much higher than those obtained by $Nd(BH_4)_3(thf)_3$. The molecular weight of *cis*-regular polymer was increased according to polymer yield, showing that there was no termination or chain transfer reaction during the polymerization. Synthesis of stereodiblock polybutadiene, which showed a high melting temperature (T_m) compared with stereodiblock polyisoprene, was also performed by the addition dMMAO during the polymerization.

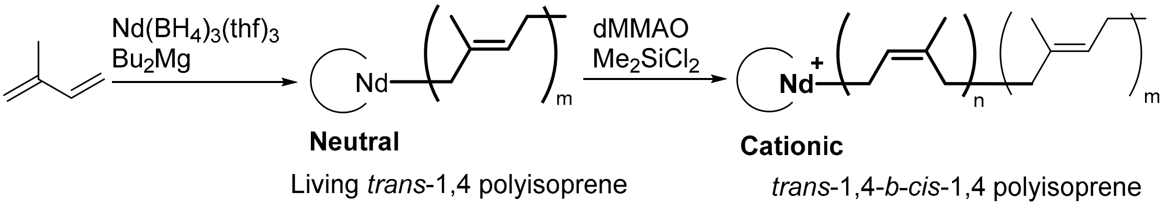
Keywords: coordination polymerization; neodymium catalyst; polyconjugated dienes; stereoblock polymer; rubber

1. Introduction

Polyconjugated dienes change their thermal and mechanical properties according to the stereoregularity. Generally, *cis*-1,4-regular polymer shows typical elastomeric property with a very low glass transition temperature (T_g) and *trans*-1,4-regular polymer has a melting point (T_m). Based on these properties, synthetic *cis*-1,4 polymer is widely applied as an alternative material to natural rubber, especially in tire industries [1]. *Trans*-1,4 polymer has great potential for shape-memory rubber and blend in *cis*-rich polymer which improves mechanical properties such as the rolling resistance of tires. Stereoblock polyconjugated dienes, which possess both *cis*- and *trans*-sequences in a single polymer chain, would be a promising material showing unique thermal and mechanical properties.

Some synthetic examples of stereoblock polymers are reported using Ni [2], Co [3,4] and Fe [5] catalysts with additional ligands, or rare-earth metal catalysts with chain transfer reagent [6]. However, these stereoblock polymers always contain atactic blocks or short stereoregular blocks consist of less than 10 repeating units. Highly stereoregular long blocks are difficult to synthesize, probably because of the difficulty of changing the stereoselectivity during the polymerization whilst keeping the living manner.

Previously, we reported the synthesis of stereodiblock polyisoprene which consists of *cis*-1,4- and *trans*-1,4-sequences using a Nd/Mg/Al combined catalyst system (Scheme 1) [7]. This is based on the idea that a simple neodymium catalyst system such as $Nd(BH_4)_3(thf)_3/Bu_2Mg$ and $(C_3H_5)NdCl_2$/methylaluminoxane (MAO) can promote *trans*- and *cis*-specific polymerization of isoprene and butadiene in a living manner, respectively (Figure 1) [8–14]. The stereospecificity is basically strongly affected by the metal charge; namely, neutral systems give *trans*-polymer and cationic systems give *cis*-polymer, and the change of the metal charge from neutral to cationic during the polymerization with Lewis acid gave stereodiblock polymer. The strategy would be applied to the other conjugated diene monomers, and as an extensive example, we attempted to synthesize stereoblock polybutadiene herein. The T_m of the polymer from the *trans*-1,4 polybutadiene block, which is an important property for the application to the thermoplastic elastomer, was significantly higher than that of stereodiblock polyisoprene.



Scheme 1. Synthesis of stereoblock polyisoprene using $Nd(BH_4)_3(thf)_3$ as a catalyst precursor. dMMAO: trialkylaluminum-depleted modified methylaluminoxane.

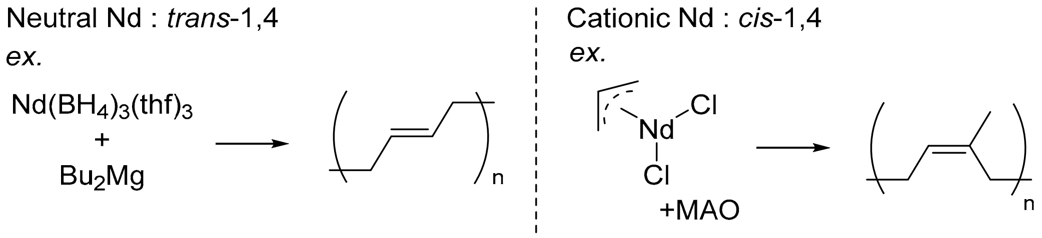


Figure 1. Examples of living butadiene/isoprene polymerization using simple neodymium catalysts. MAO: methylaluminoxane.

2. Results and Discussion

Butadiene polymerization using a combination of $Cp^*Nd(BH_4)_2(thf)_2$ and Bu_2Mg was performed in the presence of excess dMMAO (Table 1). In the previous research, $^iBu_3Al$ was an efficient chain transfer agent of borohydrido-neodymium catalyzed polymerization [15,16], and we therefore removed free trialkylaluminums from MMAO to prevent chain transfer reaction, which is a critical problem for block polymer synthesis. It is already reported that $Cp^*Nd(BH_4)_2(thf)_2$–Bu_2Mg promotes *trans*-1,4-specific polymerization of butadiene with narrow molecular weight distribution, and we successfully reproduced it (Run 1). The addition of 25 equivalents of dMMAO accelerated the reaction so that an almost quantitative amount of polymer was obtained at room temperature within an hour (Run 2). To reproduce the polymerization well, pre-activation of $Cp^*Nd(BH_4)_2(thf)_2$ with Bu_2Mg in the presence of a small amount of butadiene was required. Precipitation of the catalyst occurred without the addition of monomer, which indicated that formation of allylneodymium species was important. The molecular weight distribution was larger than the polymer obtained without dMMAO, but it is probably because of the high viscosity of the reaction mixture. The *trans*-specificity was greatly reduced according to the amount of dMMAO and finally *cis*-specificity reached 93% (Runs 2, 4, and 5), although the activity was greatly reduced with a high Al/Nd ratio. The increase of the Bu_2Mg amount slightly lowered *cis*-specificity (Runs 3 and 4). These tendencies of stereospecificity were similar with those observed in isoprene polymerization using the Nd–Mg/Al system, and use of $Cp^*Nd(BH_4)_2(thf)_2$ showed much higher *cis*-specificity and narrower molecular weight distribution than the $Nd(BH_4)_3(thf)_3$–Bu_2Mg system (Runs 4 and 6).

The ^{13}C NMR spectrum of the polymer showed four distinct signals around 130 ppm, which is assigned to stereodyad sequences (Figure 2, see also the Supplementary Materials) [17]. From the integral ratios of these four signals, the ratio of stereodyad (*tt*:*tc*:*ct*:*cc* = 17:21:22:40) was close to the calculated statistical distribution (*tt*:*tc*:*ct*:*cc* = 14:24:24:38) supposing that *trans/cis* selectivity was 38% and 62%, which was the same as the polymerization result, respectively. This result showed randomly distributed *trans* and *cis* sequences in the obtained polymer and the occurrence of interconversion between *cis*-specific and *trans*-specific active species via disproportionation (Figure 3). The increase of *cis*-specificity along with the Al/Mg ratio showed that the neutral active species with *trans*-specificity was gradually converted to a cationic *cis*-specific one by the increasing amount of dMMAO, similar to $Nd(BH_4)_3(thf)_3$-catalyzed isoprene polymerization previously reported.

Table 1. Butadiene polymerization using the $Cp^*Nd(BH_4)_2(thf)_2$–Mg/Al catalyst system.

Run	Nd (μmol)	Al/Mg (mol/mol)	Time (h)	Yield (%)	M_n [a] ($\times 10^4$)	M_w/M_n [a]	*trans*:*cis*:vinyl [b] (mol %)
1 [c]	25	0	1	20	0.8	1.3	93:3:4
2	25	25	1	85	8.2	1.5	34:61:5
3 [d]	25	25	0.5	70	7.9	1.7	15:81:4
4	25	50	1	84	10.2	1.7	13:84:3
5	25	100	12	28	2.7	1.7	6:92:2
6 [e]	50	25	1.5	93	5.2	2.5	59:38:3

[a] Determined by GPC (gel permiation chromatography) calibrated with PS standard. [b] Determined by ^1H and ^{13}C NMR. [c] Performed at 40 °C. [d] 4 equivalents of Bu_2Mg was used. [e] $Nd(BH_4)_3(thf)_3$ was used instead of $Cp^*Nd(BH_4)_2(thf)_2$.

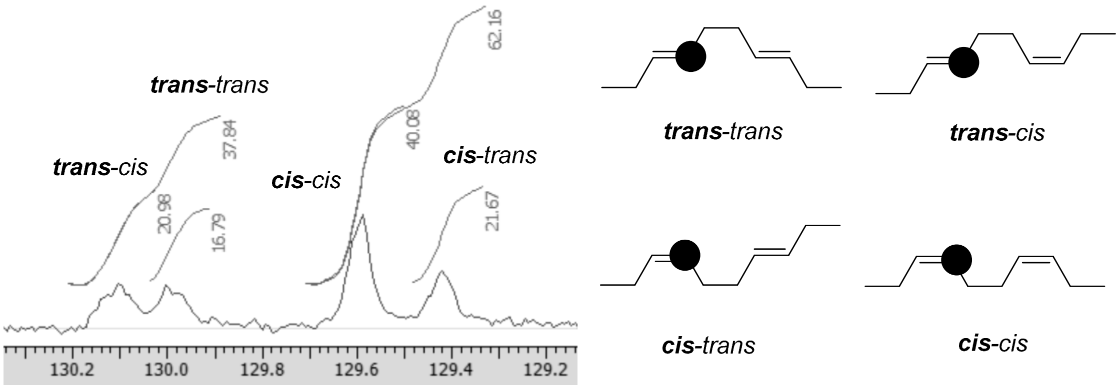


Figure 2. ^{13}C NMR spectrum of polybutadiene (Table 1, Run 2, 125 MHz, in $CDCl_3$).

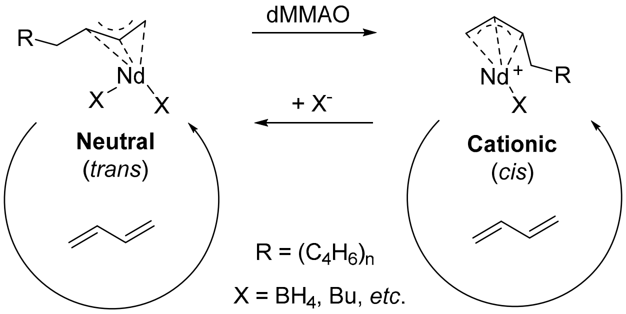
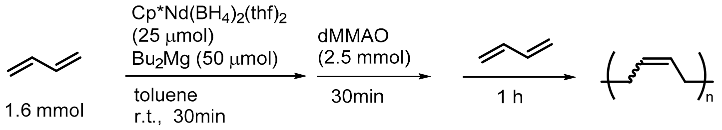


Figure 3. Plausible mechanism of stereospecificity change of butadiene polymerization at low dMMAO concentration.

Next, the relationship between the initial butadiene feed and molecular weight of the polymer was investigated (Table 2). Each run did not reach full conversion because of the high viscosity of the reaction mixture at the end of the polymerization and gave relatively broad molecular weight distribution. However, a constant *N* value, which is the number of polymer chains per Nd catalyst, showed that the molecular weight of the polybutadiene was linearly increased according to the amount of consumed monomer. These results indicated that no chain transfer reaction exists during the polymerization, which is a critical problem for synthesizing the block polymer.

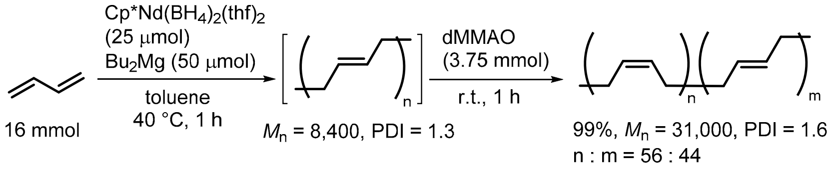
Table 2. Effect of initial monomer feed on the molecular weight in the butadiene polymerization using the Cp*Nd(BH_4)$_2$(thf)$_2$–Mg/Al catalyst system.



Run	Bd Total (mmol)	Bd/Nd (mol/mol)	Yield (%)	M_n [a] ($\times 10^4$)	PDI [a]	*Trans*:*Cis*:Vinyl [b] (mol %)	*N* [c]
7	8	320	98	4.9	1.9	14:83:3	0.35
8	16	640	84	10.2	1.7	13:84:3	0.28
9	32	1280	73	16.0	1.7	20:76:4	0.32

[a] Determined by GPC; calibrated with PS standard. [b] Determined by ^{1}H and ^{13}C NMR. [c] Number of polymer chains per Nd calculated from M_n and yield. Bd: butadiene.

Synthesis of stereodiblock polybutadiene was performed by the addition of dMMAO during *trans*-specific polymerization using the Cp*Nd(BH_4)$_2$(thf)$_2$–Bu_2Mg system (Scheme 2). The *cis/trans* ratio was not proportional to the molecular weight, probably because the generation of *cis*-specific active species is slow, but the stereodiblock polymer with a narrow molecular weight distribution was obtained. The whole GPC trace of the *trans*-prepolymer was shifted to a higher molecular weight region in the stereodiblock polymer, indicating high block efficiency (Figure 4). The *trans–trans* and *cis–cis* stereodyad ratio calculated from the ^{13}C NMR spectrum was much higher than the ratio of the others (Figure 5). Moreover, the polymer was not soluble in Et_2O, showing that there was no *cis*-polybutadiene included in the obtained polymer. The difference of T_m and T_g of the polymer measured by DSC (T_m = 50 °C, T_g = −103 °C, Figure 6) was broader than that of stereodiblock polyisoprene [7] (T_m = 32 °C, T_g = −67 °C), showing potential as a building block for the thermoplastic elastomer.



Scheme 2. Synthesis of stereoblock polybutadiene using Cp*Nd(BH_4)$_2$(thf)$_2$ (Run 10).

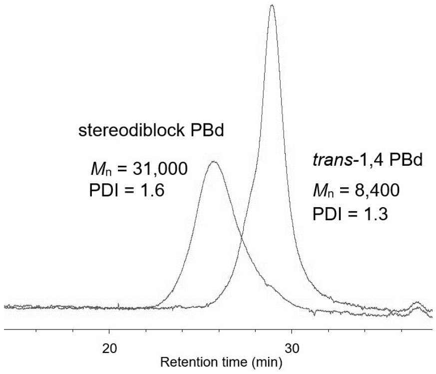


Figure 4. GPC traces of *trans*-1,4 prepolymer and stereodiblock polymer synthesized in Run 10.

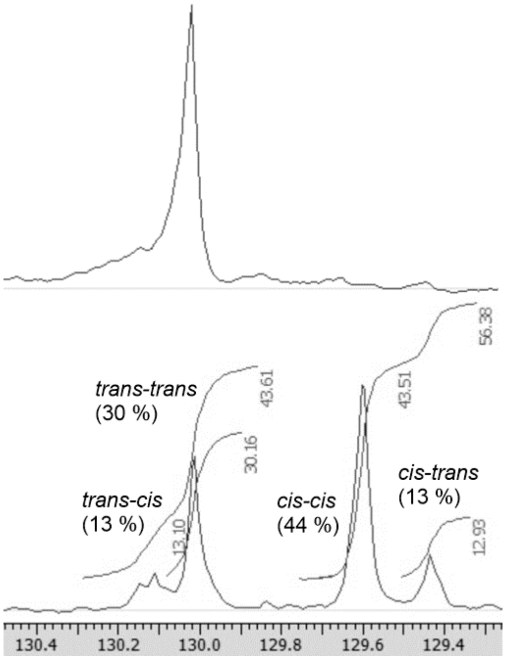


Figure 5. ^{13}C NMR spectrum (125 MHz, in $CDCl_3$) of *trans*-1,4 prepolymer (**above**) and stereodiblock polybutadiene synthesized in Scheme 2 (**below**).

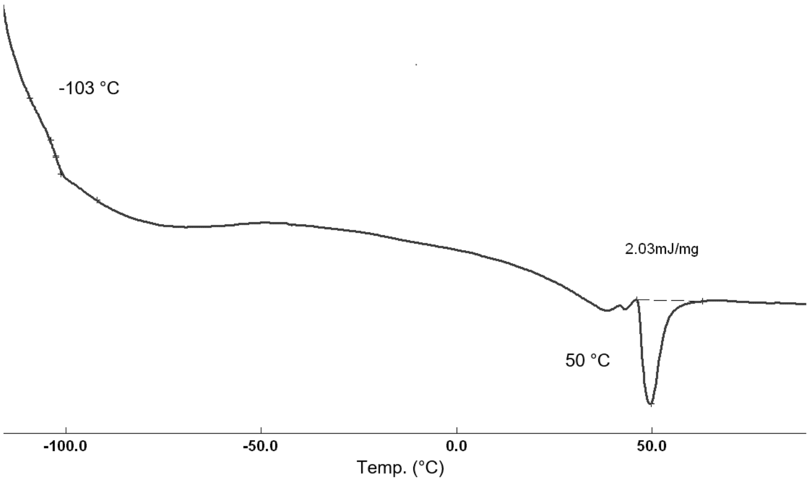


Figure 6. Differential scanning calorimetry (DSC) trace of stereoblock polybutadiene synthesized in Run 10.

3. Experimental Section

3.1. General

All manipulations were performed under an atmosphere of nitrogen using standard Schlenk line techniques. Trialkylaluminum-depleted MMAO (dMMAO) was prepared by the treatment of modified methylaluminoxane (MMAO), which was generously donated by Tosoh-Finechem Co. (Shunan, Japan), with SiO_2 according to the literature [18]. Dry toluene was purchased from Kanto Chemical Co. Inc. (Tokyo, Japan), and a trace of residual water was removed by reaction with sodium metal. Butadiene solution in toluene were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan) and used as received. $Nd(BH_4)_3(thf)_3$ and $Cp^*Nd(BH_4)_2(thf)_2$ was prepared according to the literature and used immediately after the preparation [19]. Other materials were used without further purifications.

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in chloroform-*d* on a Varian 500 NMR spectrometer. The obtained spectra were referenced to the signal of residual protonated solvent [^{1}H: $\delta = 7.26$ ppm] or the signal of solvent [^{13}C: $\delta = 77.16$ ppm]. Molecular weights of polymers were determined by Tosoh HLC-8320 gel permiation chromatography (GPC) system (Tokyo, Japan), calibrated with polystyrene standard ($T = 40$ °C; eluent: THF). T_g, T_m and melting enthalpy (ΔH_m) of the polymer were measured by differential scanning calorimetry (DSC) analyses performed by a SII EXSTAR6000 system (Tokyo, Japan).

3.2. Polymerization Procedure

3.2.1. Butadiene Polymerization Using the Cp*Nd(BH_4)$_2$(thf)$_2$–Bu_2Mg/dMMAO System

To a 20 mL Schlenk flask, Cp*Nd(BH_4)$_2$(thf)$_2$ (11 mg, 25 μmol) was charged and dissolved into butadiene solution in toluene (0.50 mL, containing 1.6 mmol butadiene). To this light blue solution, Bu_2Mg in heptane (50 μL, 1.0 M, 50 μmol) was added and the resulting yellow-green solution was stirred at room temperature for 30 min. dMMAO solution in toluene (1.10 mL, 1.25 mmol) was added to the solution and further stirred at room temperature for 30 min. To the resulting light-yellow solution, butadiene in toluene (3.2 M, 4.5 mL, 14.4 mmol) was added to start the polymerization. After stirring at room temperature for 30 min, the reaction mixture was poured into acidic methanol containing 2% of hydrochloric acid and the precipitated solid was recovered. The polymer was dried under vacuum overnight until constant weight. An amount of 735 mg (85%) of colorless viscous polymer was obtained.

3.2.2. Synthesis of Stereoblock Polybutadiene Using Cp*Nd(BH_4)$_2$(thf)$_2$ as a Catalyst

To a 20 mL Schlenk flask, Cp*Nd(BH_4)$_2$(thf)$_2$ (11 mg, 25 μmol), butadiene solution in toluene (3.2 M, 5.0 mL, 16 mmol) and Bu_2Mg in heptane (50 μmol, 1.0 M, 50 μL) was charged and stirred for 1 h at 40 °C. The resulting mixture was cooled to room temperature and a toluene solution of dMMAO (3.75 mL, 3.75 mmol) was added. The mixture was further stirred for 1 h and poured into acidic methanol containing 2% of hydrochloric acid. The polymer was recovered and dried under vacuum overnight until constant weight. An amount of 862 mg (99%) of colorless polymer was obtained.

3.2.3. Determination of Stereoregularity of Polybutadiene

The ratio of 1,4- and 1,2-unit was calculated from ^{1}H NMR spectra according to the following equation [17]:

$$R_{1,2}(\%) = 200 I_{\text{ter}} / (2 I_{\text{int}} + I_{\text{ter}})$$

where $R_{1,2}$ represents the ratio of 1,2-unit, I_{int} represents the integral ratio of internal olefinic protons observed at 5.4 ppm, and I_{ter} represents the integral ratio of terminal vinyl protons observed at 5.0 ppm. The ratio of *trans*-1,4 and *cis*-1,4 unit was calculated from the integral ratio of the signals at 27.4 (*cis*-1,4) and 32.7 ppm (*trans*-1,4) on ^{13}C NMR spectra.

4. Conclusions

Stereodiblock polybutadiene was successfully synthesized by using Cp*Nd(BH_4)$_2$(thf)$_2$ as a catalyst. Unlike the previously reported synthesis of stereodiblock polyisoprene using Nd(BH_4)$_3$(thf)$_3$, there was no need to add a chloride source such as ^{t}BuCl and Me_2SiCl_2. The obtained stereodiblock polybutadiene showed high T_m compared with the corresponding stereodiblock polyisoprene. This result showed the great potential of stereoblock polydienes for application to the thermoplastic elastomer.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/7/10/284/s1. Figure S1. ^{1}H NMR spectrum of polybutadiene obtained in Table 1, Run 1 (500 MHz, in $CDCl_3$), Figure S2. ^{13}C NMR spectrum of polybutadiene obtained in Table 1, Run 1 (125 MHz, in $CDCl_3$), Figure S3. ^{1}H NMR spectrum of polybutadiene obtained in Table 1, Run 2 (500 MHz, in $CDCl_3$), Figure S4. ^{13}C NMR spectrum of polybutadiene obtained in Table 1, Run 2 (125 MHz, in $CDCl_3$), Figure S5. ^1H NMR spectrum of polybutadiene obtained in Table 1, Run 3 (500 MHz, in $CDCl_3$), Figure S6. ^{13}C NMR spectrum of polybutadiene obtained in Table 1, Run 3 (125 MHz, in $CDCl_3$), Figure S7. ^1H NMR spectrum of polybutadiene obtained in Table 1, Run 4 (500 MHz, in $CDCl_3$), Figure S8. ^{13}C NMR spectrum of polybutadiene obtained in Table 1, Run 4 (125 MHz, in $CDCl_3$), Figure S9. ^1H NMR spectrum of polybutadiene obtained in Table 1, Run 5 (500 MHz, in $CDCl_3$), Figure S10. ^{13}C NMR spectrum of polybutadiene obtained in Table 1, Run 5 (125 MHz, in $CDCl_3$), Figure S11. ^1H NMR spectrum of polybutadiene obtained in Table 1, Run 6 (500 MHz, in $CDCl_3$), Figure S12. ^{13}C NMR spectrum of polybutadiene obtained in Table 1, Run 6 (125 MHz, in $CDCl_3$), Figure S13. ^1H NMR spectrum of polybutadiene obtained in Table 2, Run 7 (500 MHz, in $CDCl_3$), Figure S14. ^{13}C NMR spectrum of polybutadiene obtained in Table 2, Run 7 (125 MHz, in $CDCl_3$), Figure S15. ^1H NMR spectrum of polybutadiene obtained in Table 2, Run 9 (500 MHz, in $CDCl_3$), Figure S16. ^{13}C NMR spectrum of polybutadiene obtained in Table 2, Run 3 (125 MHz, in $CDCl_3$), Figure S17. ^1H NMR spectrum of stereoblock polybutadiene (500 MHz, in $CDCl_3$), Figure S18. ^{13}C NMR spectrum of stereoblock polybutadiene (125 MHz, in $CDCl_3$).

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Conflicts of Interest: The authors declare no conflict of interest.

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