# Efficiencies of Various Metallocene/Reducing Agent Catalyst Systems in the Hydrogenation of Polystyrene-*b*-Polybutadiene-*b*-Polystyrene Block Copolymers

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**ABSTRACT:** Various metallocenes, including  $bis(\eta^5$ -cyclopentadienyl)cobalt,  $bis(\eta^5$ -cyclopentadienyl)nickel, and  $bis(\eta^5$ -cyclopentadienyl)titanium dichloride, combined with various reducing agents, including *n*-butyllithium, phenyllithium, and triethylaluminum, have been evaluated for their catalytic efficiencies in the hydrogenation of polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) block copolymer. The efficiencies were determined by monitoring the extent of saturation of double bonds on the polybutadiene segment of the copolymer using FTIR and <sup>1</sup>H-NMR spectroscopy. The cobaltocene/*n*-butyllithium catalyst system was found the most active. The effects of H<sub>2</sub> pressure and the ratio of *n*-butyllithium to cobaltocene ratio on the hydrogenation efficiency were also investigated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1807–1815, 1999

**Key words:** hydrogenation; metallocene; bis( $\eta^5$ -cyclopentadienyl)cobalt; bis( $\eta^5$ -cyclopentadienyl)nickel; bis( $\eta^5$ -cyclopentadienyl)titanium dichloride; *n*-butyllithium; styrene; butadiene; block copolymer

# INTRODUCTION

Metallocene catalysts have been extensively studied by the polyolefin industry for stereospecific polymerizations such as synthesis of syndiotactic polystyrene,<sup>1-3</sup> copolymerization of ethene, propene, and other olefinic monomers,<sup>4-6</sup> polymerization of diolefin monomers,<sup>7-9</sup> or copolymerization of styrene with diolefin.<sup>10,11</sup> Recently, considerable efforts have also been directed towards using metallocene catalysts for hydrogenatingconjugated diolefin polymers. Kishimoto and Morita found that bis-(cyclopentadienyl)titanium (IV) compounds, in the presence of an alkyl lithium compound, were effective hydrogenation catalysts,<sup>12</sup> and Chamberlain et al. claimed that a bis-(cyclopentadienyl)titanium (III) compound would be effective as well.<sup>13</sup> Kishimoto and Masubuchi later discovered a specific titanium(IV) compound,  $Ti(\eta^5-C_5H_5)_2R_2$ , where R was any trisubstituted phenyl groups<sup>14</sup> that did not require the presence of an alkyl lithium. Parellada et al. provided a hydrogenation process using  $Ti(\eta^5-C_5H_5)_2(PhOR')_2$ , where R' is an alkyl group.<sup>15</sup> Hahn and Wilson hydrogenated ethylenic unsaturations using a certain monocyclopentadienyl titanium compound.<sup>16</sup> All these articles have a strong emphasis on titanocene materials.

This article describes our studies on hydrogenating polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) block copolymers using metallocene catalysts comprised of various central metals. The SBS block copolymer is a thermoplastic elastomer. Its thermoplasticity has allowed it to be widely used in

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**Figure 1** Hydrogenation efficiencies for 1,2-units of polybutadiene segment using various metallocenes with *n*-butyllithium (conditions: T = 80 °C, P = 25 kg/cm<sup>2</sup>, [polymer] = 0.073 g/g solution; *n*-BuLi/metallocene = 2).

various applications.<sup>17</sup> However, the presence of large amounts of unsaturated double bonds in its polybutadiene segment often causes poor longterm heat, weather, and UV stability.<sup>18</sup> Compared with traditional SBS hydrogenation pro-



**Figure 3** Hydrogenation efficiencies for *trans* 1,4units of polybutadiene segment using various metallocenes with *n*-butyllithium (conditions: T = 80°C, P = 25 kg/cm<sup>2</sup>, [polymer] = 0.073 g/g solution; *n*-BuLi/ metallocene = 2).

cess using nickel octoate and triethylaluminum catalysts, a metallocene catalyst offers the advantages of mild reaction temperature and pressure.<sup>18–22</sup> Because metallocene catalysts generally require a certain amount of reducing agent



**Figure 2** Hydrogenation efficiencies for *cis* 1,4-units of polybutadiene segment using various metallocenes with *n*-butyllithium (conditions: T = 80 °C, P = 25 kg/cm<sup>2</sup>, [polymer] = 0.073 g/g solution; *n*-BuLi/metallocene = 2).



**Figure 4** Hydrogenation efficiencies for 1,2-units of polybutadiene segment using cobaltocene with various reducing agents (conditions: T = 80 °C, P = 25 kg/cm<sup>2</sup>, [polymer] = 0.073 g/g solution; reducing agent/cobaltocene = 2).



**Figure 5** Hydrogenation efficiencies for *cis* 1,4-units of polybutadiene segment using cobaltocene with various reducing agents (conditions: T = 80°C, P = 25 kg/cm<sup>2</sup>, [polymer] = 0.073 g/g solution; reducing agent/cobaltocene = 2).

(cocatalyst) for achieving higher productivity, our metallocene catalysts were tested in the presence of various reducing agents.

# EXPERIMENTAL

A linear SBS block copolymer, having a molecular weight of 120,000 and a polystyrene content of 30



**Figure 6** Hydrogenation efficiencies for *trans* 1,4units of polybutadiene segment using cobaltocene with various reducing agents (conditions: T = 80 °C, P = 25 kg/cm<sup>2</sup>, [polymer] = 0.073 g/g solution; reducing agent/ cobaltocene = 2).

wt %, were obtained from Taiwan Synthetic Rubber Corp. (TSRC). This copolymer contains in its polybutadiene segment a total double bonds of 13.0 mmol/g, having a microstructure of 43.8% 1,2-unit, 31.4% trans 1,4-unit, and 24.8% cis 1,4unit.

Cobaltocene (bis( $\eta^5$ -cyclopentadienyl)cobalt, Co-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>), nickellocene (bis( $\eta^5$ -cyclopentadienyl)nickel, Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>), and titanocene (bis( $\eta^5$ -cyclopentadienyl)titanium dichloride, Ti( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>) used for the hydrogenation were purchased from Aldrich.



*n*-Butyllithium was purchased as a 15 wt % solution in hexane from Merck. Phenyllithium as a 17 wt % solution in cyclohexane and triethylaluminum as a 15% solution in hexane were purchased from TCI (Japan). Cyclohexane solvent was obtained from TSRC, and was dried with activated alumina (from Alcoa).

Metallocene  $(1 \times 10^{-3} \text{ mol})$  was dissolved into 100 mL of cyclohexane under an air-free environ-



**Figure 7** Effect of *n*-BuLi : cobaltocene ratio on hydrogenation efficiency for 1,2-units of polybutadiene segment (conditions: T = 80°C, P = 25 kg/cm<sup>2</sup>, [polymer] = 0.073 g/g solution).



**Figure 8** Effect of *n*-BuLi : cobaltocene ratio on hydrogenation efficiency for *cis* 1,4-units of polybutadiene segment (conditions: T = 80 °C, P = 25 kg/cm<sup>2</sup>, [polymer] = 0.073 g/g solution).

ment to make the catalyst system required for later use. An appropriate amount of reducing agent solution, calculated based on a specified reducing agent/metallocene mol ratio, was then added and the reaction mixture was stirred for 5 h.

The hydrogenation reaction was carried out in a 2-liter mechanically stirred autoclave (made by PPI, rated to 6000 psi) at 80°C. SBS copolymer solution (330 g) previously prepared at a concentration of 7.3 wt % SBS in cyclohexane solvent was first charged into the autoclave, followed by 30 mL of the catalyst solution. The hydrogen pressure was then kept constant at a specified setting, with the reaction mixture saturated with the hydrogen. Samples of the reaction mixture were taken at fixed time intervals, and were repeatedly washed with dilute sulfuric acid to remove the residual catalyst. The hydrogenated SBS copolymer was then precipitated in isopropanol and dried at 40°C in a vacuum oven.

The microstructures of the polymers were determined by <sup>1</sup>H-NMR spectra using a Bruker AMX400 100.61 MHz spectrometer at 25°C in CDCl<sub>3</sub> at a 5% polymer concentration. The disappearance of the double bonds was observed using a Shimadzu FTIR-8101M instrument with a liquid N<sub>2</sub>-cooled MCT detector. The spectral resolution was 2 cm<sup>-1</sup>, and the samples were prepared as cast films on KBr plates for IR scans. The hydrogenation efficiency for each type of isomeric unit of polybutadiene was then measured by a combination of <sup>1</sup>H-NMR and FTIR analyses.



**Figure 9** Effect of *n*-BuLi : cobaltocene ratio on hydrogenation efficiency for *trans* 1,4-units of polybutadiene segment (conditions: T = 80 °C, P = 25 kg/cm<sup>2</sup>, [polymer] = 0.073 g/g solution).

#### **RESULTS AND DISCUSSION**

#### Effect of the Selection of Metallocene

Various metallocene/*n*-butyllithium catalyst systems, having a 2 : 1 ratio of *n*-bytyllithium to metallocene, were used to hydrogenate the SBS block copolymer under experimental conditions of 80°C, 25 kg/cm<sup>2</sup> pressure, 7.3 wt % polymer concentration. The progress of hydrogenation was frequently monitored by FTIR at a 1-h interval. The hydrogenation efficiencies for 1,2-unit and *trans* 1,4-unit were directly determined from the FTIR spectrum. However, this was not the case for *cis* 1,4-unit, due to a significant overlapping of characteristic peaks for *cis* 1,4-unit (at 724 cm<sup>-1</sup>) and polystyrene (at 699 cm<sup>-1</sup>). This difficulty was

overcomed by a combination of FTIR and <sup>1</sup>H-NMR analyses. The total hydrogenation efficiency for all 1,4-units determined from the <sup>1</sup>H-NMR spectrum enabled us to calculate the hydrogenation efficiency for *cis* 1,4-unit knowing the efficiency for *trans* 1,4-unit from the FTIR analysis.

The results of the experiments employing cobaltocene/*n*-butyllithium, nickelocene/*n*-butyllithium, and titanocene/*n*-butyllithium as the catalyst system are shown in Figures 1, 2, and 3. In all cases, the 1,2-unit is easier to hydrogenate than 1,4unit. The higher reactivity of 1,2-unit arises from the less steric hindrance and, hence, the higher accessibility of the double bond. Furthermore, of the 1,4-unit the *cis*-isomer is hydrogenated faster than the *trans*-isomer, which can be attributed to



**Figure 10** Effect of  $H_2$  pressure on hydrogenation efficiency for 1,2-units of polybutadiene segment (conditions: T = 80°C, *n*-BuLi/cobaltocene = 2; [polymer] = 0.073 g/g solution).

the higher stability of the *trans* configuration. While the nickelocene/*n*-butyllithium catalyst system shows incomplete hydrogenation for the 1,4-units, the cobaltocene/*n*-butyllithium and the titanocene/*n*-butyllithium systems exhibit satisfactory results. The cobaltocene/*n*-butyllithium system, in particular, provides a complete hydrogenation in 5 h.

#### Effect of the Selection of Reducing Agent

The activity of cobaltocene has been evaluated in the presence of three different reducing agents, namely, *n*-butyllithium, phenyllithium, and triethylaluminum. As shown in Figures 4, 5, and 6, while no hydrogenation was observed as triethylaluminum was used as the reducing agent, both cobaltocene/*n*-butyllithium and cobaltocene/phenyllithium catalyst systems have been found to be active. The reason causing slightly lower efficiency of the latter is unknown, but could likely be ascribed to the formation of different organometallic intermediate and/or the change in the oxidation state of the central metal ion.

# Effect of the Ratio of *n*-Butyllithium to Cobaltocene

The hydrogenation of SBS polymer has been conducted using the cobaltocene/*n*-butyllithium catalyst system at various *n*-butyllithium : cobaltocene ratios. The results are shown in Figures 7, 8, and 9. An optimal ratio of *n*-butyllithium to cobaltocene was found at 1–2, regardless of the type of isomeric units. Any amount of *n*-butyllithium in excess of that ratio probably caused a complexation with the cobaltocene and, thus, decreased the activity of the catalyst.

#### Effect of H<sub>2</sub> Pressure on Hydrogenation Efficiency

The hydrogenation of SBS has been carried out using cobaltocene/*n*-butyllithium catalyst system under four different  $H_2$  pressures, 10, 15, 25, and 40 kg/cm<sup>2</sup>. Data in Figures 10, 11, and 12 show that there is no significant difference in efficiencies for hydrogenation taken place under a constant H<sub>2</sub> pressure of either 15 kg/cm<sup>2</sup> or 25 kg/ cm<sup>2</sup>. However, a 10 kg/cm<sup>2</sup> H<sub>2</sub> pressure was too low to start the reaction. On the other hand, it is surprising to note that an increase in the pressure to 40 kg/cm<sup>2</sup> significantly decreased the hydrogenation efficiency for all three isomeric units. Without any further information, it is speculated that an overpressure of hydrogen was likely to cause an undesirable reaction converting the catalytic cobaltocene into the inert cobalt hydride, thus resulting in a decrease in hydrogenation efficiency.

# Effect of Hydrogenation on the Molecular Weight of SBS

Because diene polymers are prone to a chain scission and/or crosslinking during their reactions,



Figure 11 Effect of  $H_2$  pressure on hydrogenation efficiency for *cis* 1,4-units of polybutadiene segment (conditions: T = 80°C, *n*-BuLi/cobaltocene = 2; [polymer] = 0.073 g/g solution).



**Figure 12** Effect of  $H_2$  pressure on hydrogenation efficiency for *trans* 1,4-units of polybutadiene segment (conditions: T = 80°C, *n*-BuLi/cobaltocene = 2; [polymer] = 0.073 g/g solution).

the molecular weight of our SBS copolymer, after being hydrogenated for 5 h under a condition of  $80^{\circ}$ C, P = 25 kg/cm<sup>2</sup>, *n*-BuLi/cobaltocene = 2, and [polymer] = 0.073 g/g solution, was compared with its original value. The comparison was done using a Waters gel permeation chromatography (GPC) equipped with a Waters 410 differential refractive index (RI) detector. The GPC was operated using three Waters Styragel columns (HR 3, HR 4, and HR 5) at a flow rate of 1 mL/min, with a sample concentration of 0.1% in THF solvent. As shown in Figure 13, the GPC chromatograms are nearly identical, thus indicating an insignificant polymer degradation upon hydrogenation.

The complexity of the coordination catalysis and the lack of reference standards made it ex-

tremely difficult to investigate the exact steps of the catalytic mechanism. Nevertheless, because it now seems to be well established that the catalytic mechanism of metallocene dichloride in the presence of methyl aluminoxane (MAO) comprises an alkylation of the metal and a hydrogenolysis of the metal-alkyl bond,<sup>23-26</sup> it is likely bis( $\eta^5$ -cyclopentadienyl)metal hydride or ( $\eta^5$ -cyclopentadienyl)metal hydride will form in our system. In fact, highly reactive species, such as Cp<sub>2</sub>TiH and Cp<sub>2</sub>Ti, had been postulated in earlier titanocene studies<sup>27</sup> to exist as reaction intermediates forming a dimeric compound,  $\mu$ -( $\eta^5$  :  $\eta^5$ fulvalene)-di-µ-hydrido-bis(cyclopentadienyltitanium).28,22 Existence of other intermediate species and a possible change in the oxidation state of



**Figure 13** GPC chromatograms of the SBS copolymer: (A) before hydrogenation, (B) 5 h hydrogenation at *n*-BuLi/cobaltocene = 2, T = 80 °C, P = 25 kg/cm<sup>2</sup>, [polymer] = 0.073 g/g solution.

the metal are also likely. However, the nature of these intermediate species in the hydrogenation reaction is not precisely known, and their roles in the reaction mechanism remain speculative.

# **CONCLUSIONS**

Catalyst systems consisting of a metallocene and a reducing agent at a 1:2 mol ratio have been

evaluated for their efficiencies in the hydrogenation of SBS block copolymers. The metallocenes evaluated include  $bis(\eta^5$ -cyclopentadienyl)cobalt,  $bis(\eta^5$ -cyclopentadienyl)nickel, and  $bis(\eta^5$ -cyclopentadienyl)titanium dichloride, and the reducing agents include *n*-butyllithium, phenyllithium, and triethylaluminum. The  $bis(\eta^5$ -cyclopentadienyl)cobalt paired with *n*-butyllithium rendered the highest hydrogenation efficiencies for all types of isomeric butadiene units. An optimal H<sub>2</sub> pressure exists, as does an optimal reducing agent : metallocene ratio.

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