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Hydrogenation of polystyrene-*b*-polybutadiene-*b*-polystyrene block copolymers using a metallocene/*n*-butyllithium catalyst – the role of *n*-butyllithium

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Abstract

A metallocene catalyst system, primarily the bis(η^5-cyclopentadienyl)cobalt (Cp_2Co) combined with *n*-butyllithium (*n*-BuLi), was found to be active for the hydrogenation of polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) block copolymer. Data from the UV spectroscopy of the catalyst system indicated that one of the Cp ligand in the original Cp_2Co was substituted by the butyl group forming a CpCoBu as the major catalytic species. The kinetics of the hydrogenation reaction were studied by monitoring the extent of saturation of double bonds on the polybutadiene segment of the copolymer using FTIR spectroscopy. The temperature dependence of the hydrogenation rate was analyzed and the activation energy was determined as 14.11 kcal/mol of the double bond. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrogenation; Metallocene; Bis(η^5-cyclopentadienyl)cobalt

1. Introduction

Polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) block copolymers are an important class of the thermoplastic elastomers. Their formulating and processing flexibility have made them to be widely used in various applications [1]. However, SBS block copolymers do not have good long term heat, weather and UV stability owing to the presence of large amounts of unsaturated double bonds in their polybutadiene segments. Hydrogenation of SBS block copolymers is typically practiced in cyclohexane solution using nickel octoate and triethylaluminum catalysts. This technology requires high temperature and pressure [2–4], and has been implemented in industry for several years.

Metallocene catalysts have been of great interest to the polyolefin industry in controlling the stereoregularity of the formed polymers or copolymers [5]. These metallocene catalysts have been extensively tested for the syndiospecific polymerization of styrene [6–8], copolymerization of ethene, propene and other olefinic monomers [9–11], polymerization of diolefin monomers [12–14], or copolymerization of styrene with diolefin [15,16]. Recently, considerable studies have been found in the patent literatures on hydrogenating conjugated diolefin polymers using metallocenes as the hydrogenation catalyst. Kishimoto and Morita found that bis-(cyclopentadienyl)titanium(IV) compounds, in the presence of an alkyl lithium compound, were effective hydrogenation catalysts [17], and Chamberlain et al. claimed that a bis-(cyclopentadienyl)titanium(III) compound would also be effective as well [18]. Kishimoto and Masubuchi later discovered that the presence of alkyl lithium was not necessary when hydrogenation reaction was catalyzed by a specific titanium(IV) compound, Cp_2TiR_2, where R were any tri-substituted phenyl groups [19]. Parellada et al. provided a hydrogenation process using $Cp_2Ti(PhOR')_2$ where R' is an alkyl group [20]. Hahn and Wilson hydrogenated ethylenic unsaturations using certain monocyclopentadienyl metal compound, including Ti, Zr, Hf [21]. All these metallocene works have been concentrated on the Group IV metal complexes.

The current article describes the findings in our work exploring whether a cobaltocene catalyst would actively hydrogenate the SBS copolymer. Our studies were concentrated on the reaction kinetics and efficiency, with a determination of the activation energy for the bis(η_5-cyclopentadienyl)cobalt (Cp_2Co)/*n*-butyllithium (*n*-BuLi) catalyzed reaction. Further, efforts were also directed towards a fundamental understanding of the role of *n*-BuLi in the catalyst system. Whilst it is generally believed that the catalytic species of a metallocene/aluminoxane (MAO) system during the synthesis of polyolefins is in the

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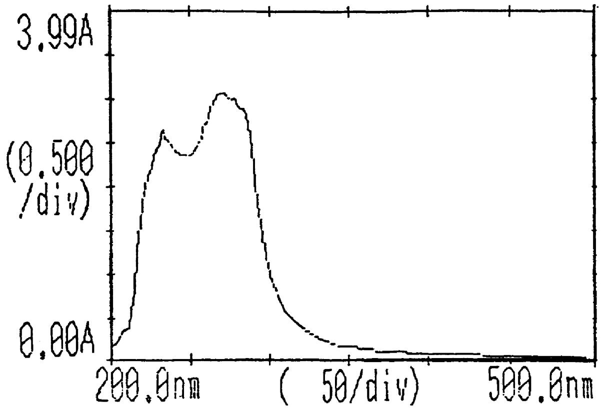


Fig. 1. UV–VIS spectrum of *n*-BuLi.

form of complex cations [16,22], there has been few studies concerning the major species of a metallocene/*n*-BuLi system during a hydrogenation reaction. In this article, our analytical data pertinent to the chemical identification of this species are presented.

2. Experimental

2.1. Materials

SBS block copolymer were obtained from Taiwan Synthetic Rubber Corp. (TSRC). This linear polymer has a molecular weight of 120 000 and a polystyrene content of 30 wt.%. The microstructure of the polybutadiene segment of the polymer comprises 43.8% 1,2 unit, 31.4% *trans*-1,4 unit, and 24.8% *cis*-1,4 unit, with a total double bonds of 13.0 mmol/g.

The cobaltocene (Cp_2Co) used for the hydrogenation and the lithium cyclopentadienide (CpLi) used as the standard for UV–VIS analysis were purchased from Aldrich. *n*-BuLi was purchased as a 15 wt.% solution in hexane from Merck. Cyclohexane solvent was obtained from TSRC and was dried with activated alumina (from Alcoa).

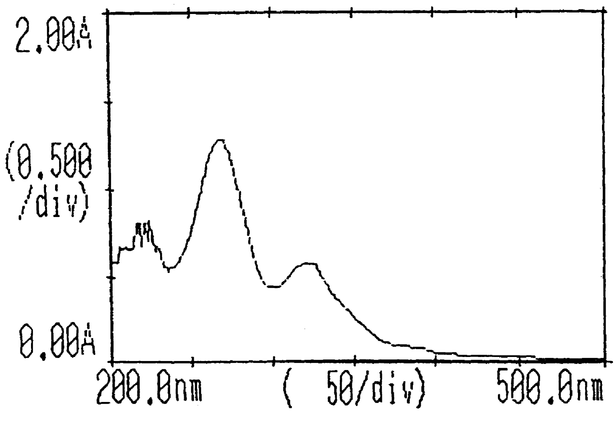


Fig. 2. UV–VIS spectrum of Cp_2Co.

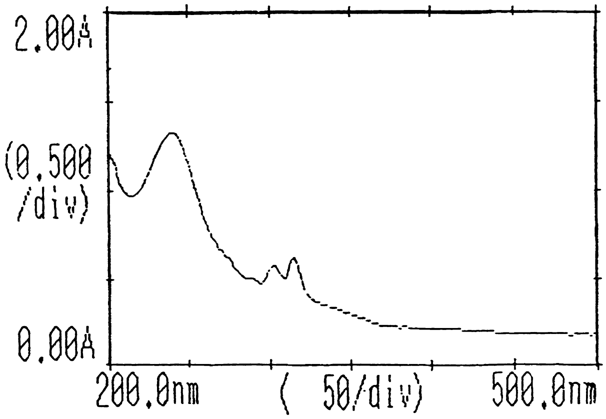


Fig. 3. UV–VIS spectrum of Cp_2Co plus *n*-BuLi.

2.2. Hydrogenation of polystyrene-b-polybutadiene-b-polystyrene

The catalyst solution was prepared in an air-free glove box. 1×10^{-3} mol of cobaltocene was dissolved into 100 ml cyclohexane in a flask. 1.1 ml of *n*-BuLi solution, calculated based on a 2 : 1 *n*-BuLi/cobaltocene mol ratio, was then added and the reaction mixture was stirred for 10 h.

The hydrogenation was performed in a 2 l mechanically stirred autoclave (made by PPI, rated to 6000 psi) at 80°C. The autoclave was filled with 330 g of the copolymer solution containing 7.3 wt.% SBS in cyclohexane solvent, and 30 ml of the catalyst solution. The hydrogen pressure was then kept constant at 25 kg/cm^2, 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.

2.3. Analysis of the polymers

The UV–VIS spectra were obtained using a Shimadzu UV-1201 spectrophotometer. The microstructures of the polymers were determined by ^{1}H-NMR spectra using Bruker AMX400 100.61 MHz spectrometer at 25°C in $CDCl_3$ at a 5% polymer concentration. The disappearance of the double bonds was evidenced by FTIR spectroscopy, and the extent of hydrogenation for each type of isomeric unit of polybutadiene was measured by a combination of ^{1}H-NMR and FTIR analyzes. The FTIR spectra were obtained on a Shimadzu FTIR-8101M instrument using a liquid N_2 cooled MCT detector. The spectral resolution was 2 cm^{-1}. The samples were prepared from cyclohexane solution as cast films on KBr plates for IR scans.

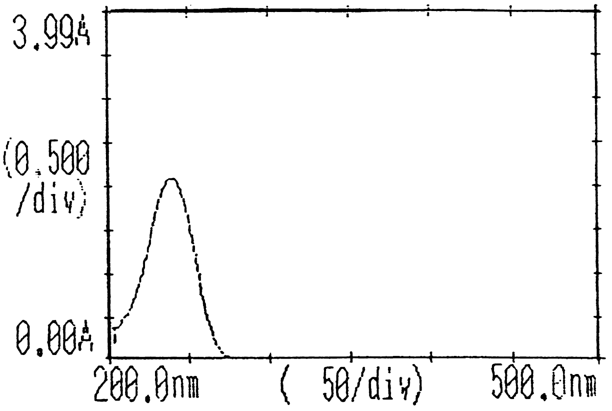


Fig. 4. UV–VIS spectrum of CpLi.

3. Results and discussion

3.1. Analysis of the catalyst system

The catalyst system used in this work was prepared, by adding *n*-BuLi to cobaltocene at a 2 : 1 mol ratio, in cyclohexane solvent as described in Section 2. Using a UV–VIS spectroscopy, the spectra of *n*-BuLi, cobaltocene and their mixture were collected and compared as shown in Figs. 1–3. The lack of any peak in between 250 and 300 nm in Fig. 3 manifested the disappearance of *n*-BuLi and Cp_2Co which would otherwise exhibit characteristic peaks as was previously shown in Figs. 1 and 2. Conversely, the new peak shown in Fig. 3 located near 240 nm indicated the generation of a new intermediate species. This location happened to be the characteristic UV–VIS location of CpLi as was observed on a pure CpLi sample in Fig. 4. As a further verification, ^{1}H-NMR spectra taken of the catalyst system and CpLi were compared. Fig. 5, taken from the catalyst system, does exhibit a characteristic CpLi peak as was shown in Fig. 6 for the pure CpLi. Consequently, it was believed that the role of *n*-BuLi in our catalyst system is to exchange alkyl for one Cp ligand with cobalt center atom (Scheme 1).

As metallocenes such as Cp_2Co are considered to have strong covalent bonding between the metal center and the Cp ligands, it seems debatable that the butyl group can be so active to undergo a nucleophilic attack on the metal center. In fact, the results from numerous late ferrocene research have shown that the coordinated Cp group tends to react with many electrophilic reagents in stead, resulting in electrophilic substitution reactions such as acylation and

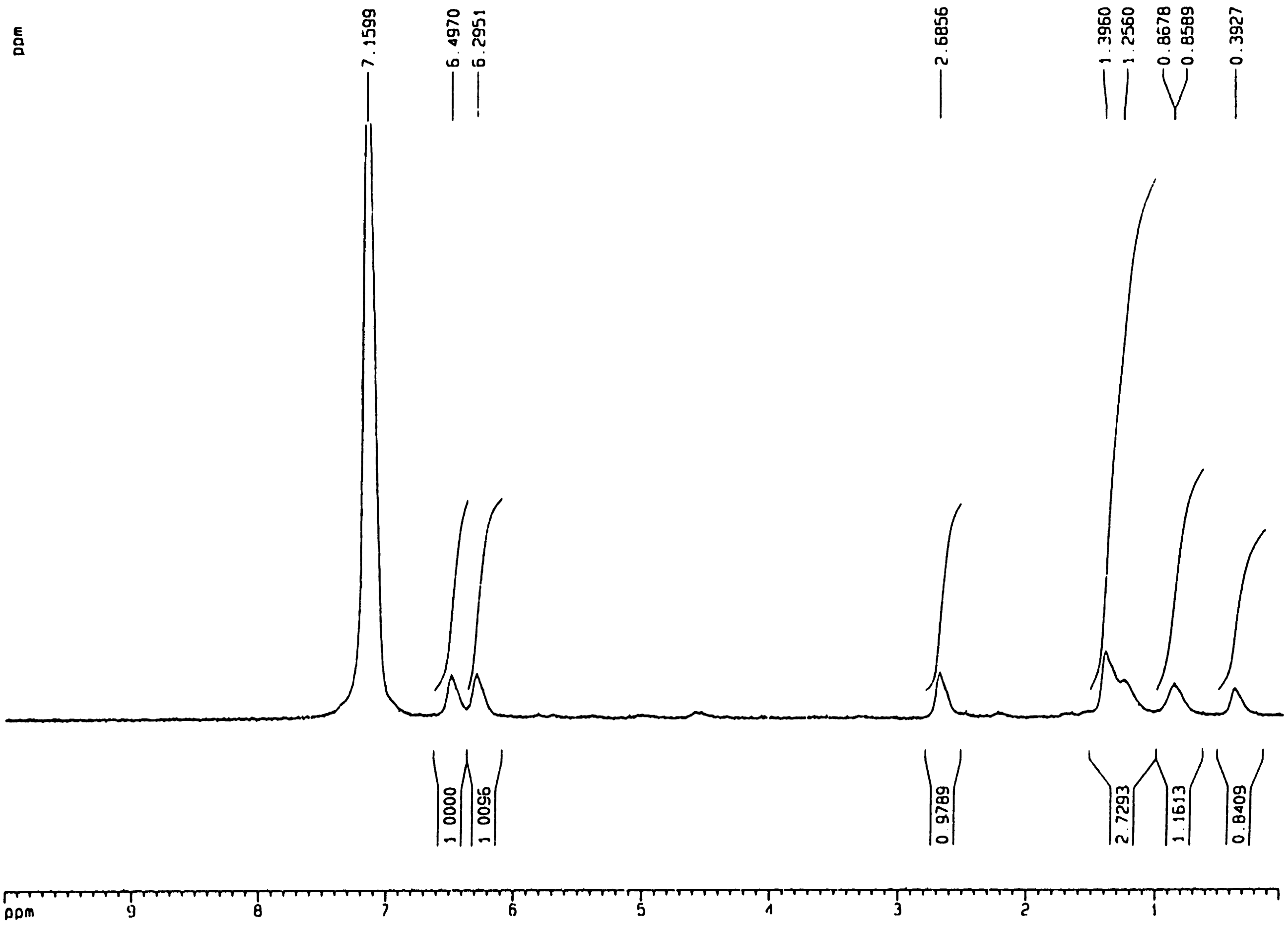


Fig. 5. ^{1}H-NMR spectrum of Cp_2Co plus *n*-BuLi.

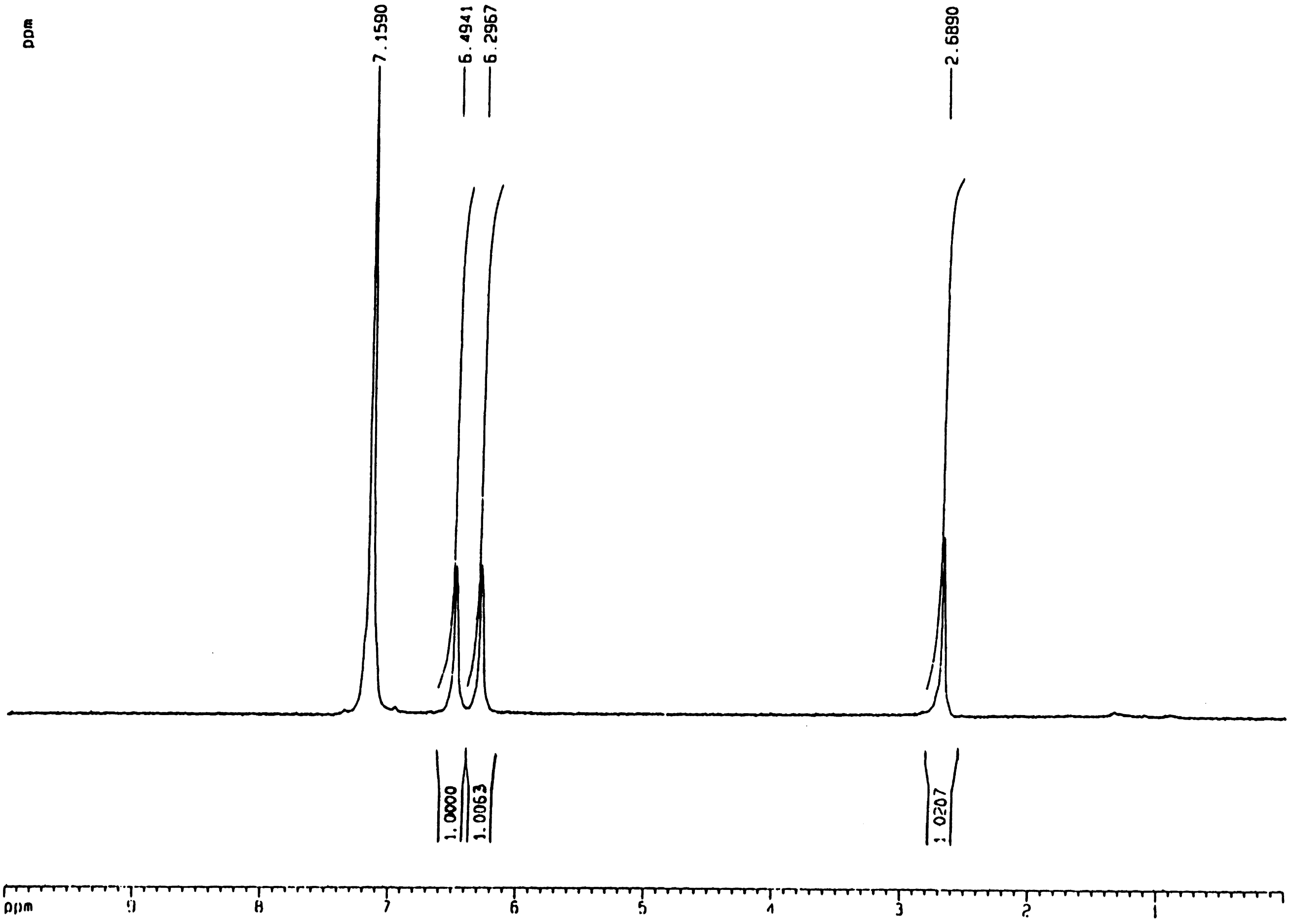


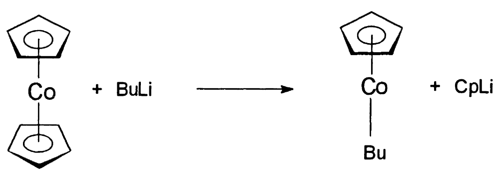
Fig. 6. ^{1}H-NMR spectrum of CpLi.

metallation. Therefore, it is questionable that whether the new species generated in our catalyst system is, rather than the CpLi, actually lithio derivatives formed via a lithiation reaction (Scheme 2).

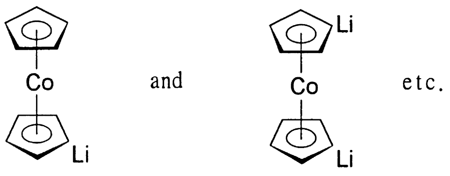
However, the lithium–carbon bond in these lithio derivatives is different from that in the CpLi. The former is a monohapto σ bond, in which case the Cp contributes one electron to the bond, whilst the latter is a pentahapto bond between the lithium metal and the π-orbitals of the Cp, in which case the Cp donates five electrons (although both bonds may be essentially ionic) (Scheme 3).

In a ^{1}H-NMR spectrum the carbon–lithium bonds in lithios would destroy the symmetry, i.e., the chemical shift equivalence, and entail multiple peaks rather than a single peak. As our UV and ^{1}H-NMR spectra indicate that our catalyst system contains only a species having a signal peak identical to that of CpLi, it is reasonable to claim that the nucleophilic attack on the metal is the dominating reaction, rather than the electrophilic substitution on the Cp ring. Unlike ferrocene, our cobaltocene is paramagnetic and does not have as good a thermal stability as ferrocene (which has 18-electron valence orbitals). Therefore, dissociation of the rings from the metal atom might become easier.

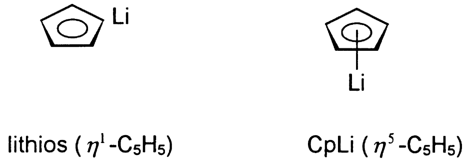
Owing to the complex nature of the metallocene catalyst and the lack of sample standards, exact steps of the hydrogenation reaction are not precisely known. However, it is very likely that, after the alkylation of the cobalt as mentioned in Scheme 1, a hydrogenolysis of the thus formed metal–alkyl bond occurs to yield a metal hydride [23,24]. Changes in the oxidation state of the metal are also possible, resulting in other highly reactive intermediate species and/or dimeric compounds [25,26].



Scheme 1.



Scheme 2.



Scheme 3.

3.2. Hydrogenation efficiency

The prepared cobaltocene/*n*-BuLi catalyst solution, having a 2 : 1 ratio of *n*-BuLi to cobaltocene, was then used to hydrogenate the SBS block copolymer. Under experimental conditions of 80°C, 25 kg/cm^2 pressure, 7.3 wt.% polymer concentration, the progress of hydrogenation was frequently monitored by FTIR at an 1 h interval. The FTIR spectra are shown in Fig. 7. The decreases in the unsaturated 1,2-, *cis*-1,4, and *trans*-1,4 isomeric units in the polybutadiene segment of the SBS copolymer can be clearly seen from the diminishing peaks located at 911, 724, and 967 cm^{-1}, respectively. While the degree of hydrogenation for 1,2-unit and *trans*-1,4 unit could be determined directly from the FTIR spectrum, the degree of hydrogenation for *cis*-1,4 unit could not. This was because of a significant overlapping of characteristic peaks for *cis*-1,4 unit (at 724 cm^{-1}) and polystyrene (at 699 cm^{-1}). In order to quantitatively determine the degree of hydrogenation for *cis*-1,4 unit, an additional ^{1}H-NMR analysis was needed. Although the degrees of hydrogenation for *cis*-1,4 and *trans*-1,4 polybutadiene units were difficult to separate in a ^{1}H-NMR spectrum, the degree of hydrogenation for the total 1,4-polybutadiene units could be determined. As the fractions of *cis*-1,4 and *trans*-1,4 polybutadiene units for the copolymer feed was previously determined, the degree of hydrogenation of *cis*-1,4 polybutadiene could be back calculated from the following equation:

$$X_{1,4} = F_{cis-1,4}X_{cis-1,4} + F_{trans-1,4}X_{trans-1,4}.$$

The calculated results shown in Fig. 8 clearly indicates that the double bonds of the polybutadiene segment in the SBS copolymer were hydrogenated nearly to completion.

3.3. Effect of temperature on hydrogenation efficiency

The hydrogenation reaction were conducted several times, each time at a different reaction temperature. The hydrogenation efficiency for 1,2-polybutadiene, *cis*-1,4 polybutadiene, and *trans*-1,4 polybutadiene are shown in Figs. 9–11, respectively. Hydrogenation at a higher temperature exhibited a faster reaction rate and led to a higher efficiency. To ensure a complete hydrogenation, a reaction temperature higher than 80°C was needed. The ultimate hydrogenation efficiencies of the three isomeric units of polybutadiene are summarized in Table 1, indicating that the efficiency decreases in the order 1,2-unit > *cis*-1,4 unit > *trans*-1,4 unit. The double bond in the 1,2-unit has less steric hindrance, and therefore is easier to hydrogenate. The double bond in the *trans*-1,4 unit is the most difficult to hydrogenate probably because of a higher stability of the *trans* configuration.

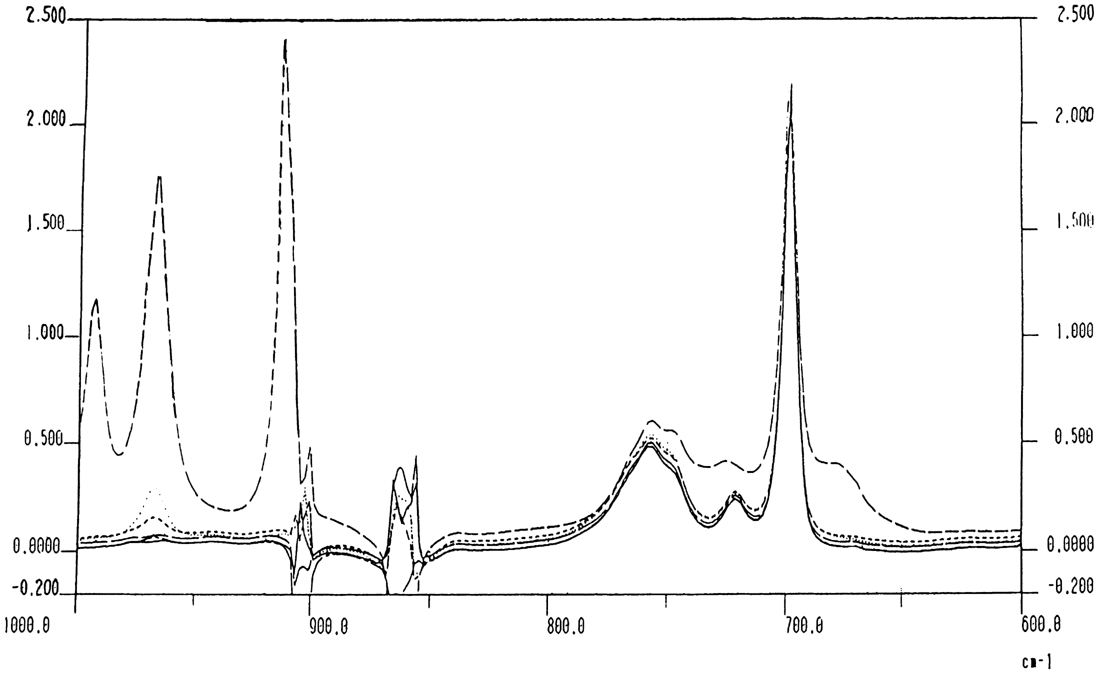


Fig. 7. FTIR spectra of the reaction mixture at various reaction times under conditions: $T = 80$°C, $P = 25$ kg/cm^2, [polymer] = 0.073 g/g solution; *n*-BuLi/cobaltocene = 2, (from top to bottom: 0–5 h).

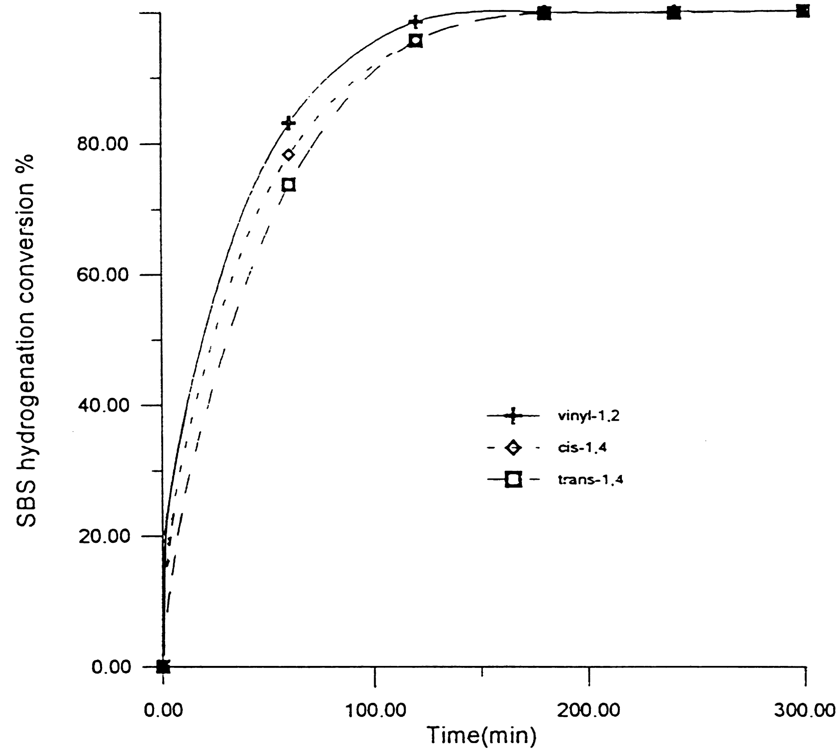


Fig. 8. Hydrogenation efficiencies for various isomeric units of polybutadiene (conditions: $T = 80°C$, $P = 25$ kg/cm^2, [polymer] = 0.073 g/g solution; **n**-BuLi/cobaltocene = 2).

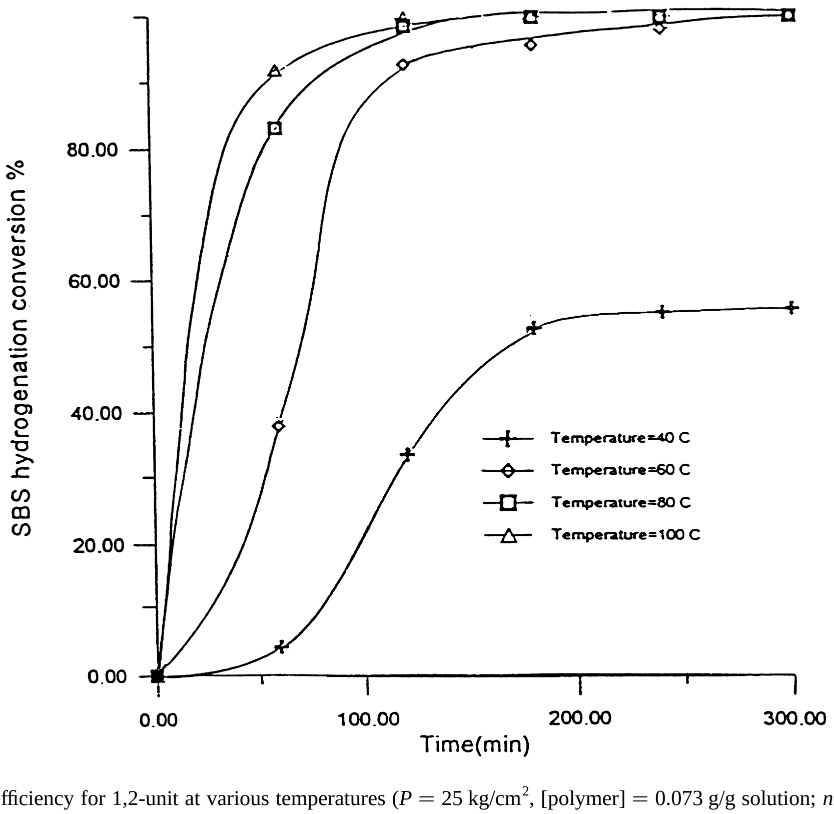


Fig. 9. Hydrogenation efficiency for 1,2-unit at various temperatures ($P = 25$ kg/cm^2, [polymer] = 0.073 g/g solution; *n*-BuLi/cobaltocene = 2).

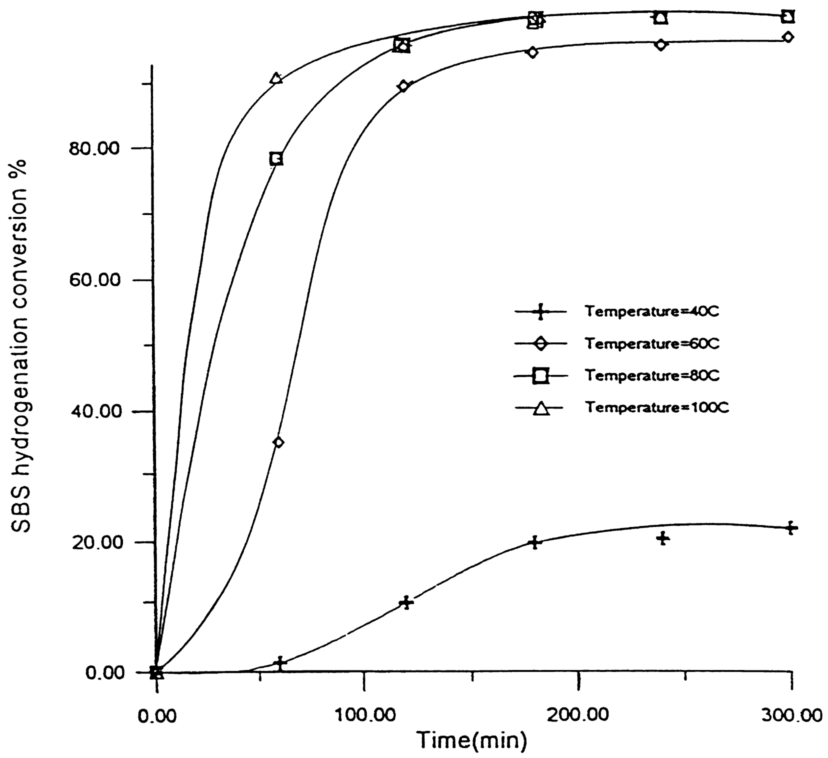


Fig. 10. Hydrogenation efficiency for *cis*-1,4 unit at various temperatures ($P = 25$ kg/cm^2, [polymer] = 0.073 g/g solution; *n*-BuLi/cobaltocene = 2).

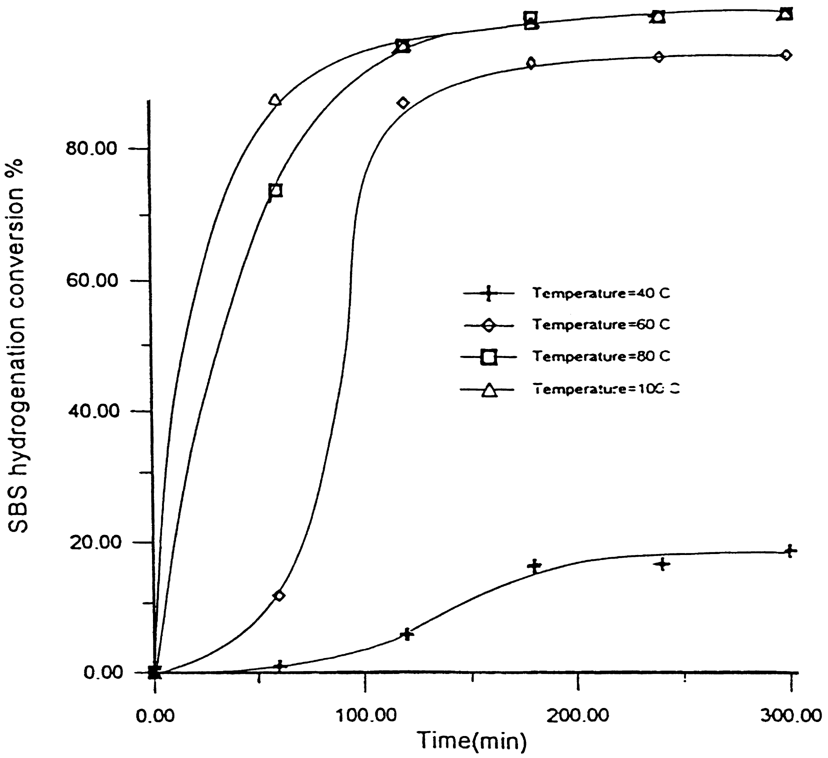


Fig. 11. Hydrogenation efficiency for *trans*-1,4 unit at various temperatures ($P = 25$ kg/cm^2, [polymer] = 0.073 g/g solution; *n*-BuLi/cobaltocene = 2).

Table 1
Hydrogenation efficiencies at various temperatures (under a constant H_2 pressure of 25 kg/cm^2)

	40°C	60°C	80°C	100°C
1,2-unit	55.6%	100%	100%	100%
Cis-1,4 unit	22.1%	96.9%	100%	100%
Trans-1,4	18.6%	93.7%	100%	100%

3.4. Effect of H_2 pressure on hydrogenation efficiency

Our experimental data showed that the efficiencies were equally high for hydrogenation taken place under a constant H_2 pressure of either 15 or 25 kg/cm^2. However, no hydrogenation reaction occurred when the experiment was conducted under a 10 kg/cm^2 pressure. Apparently the H_2 pressure was too low to start the alkyl exchange. However, an increase in the pressure to 40 kg/cm^2 significantly decreased the efficiency. This surprising results were observed for all three isomeric units, as reported in Table 2. As late transition metals do not readily lose Cp ligands to hydrogenation [27], the decrease in hydrogenation efficiency can be attributed to the formation of dimeric compounds [25,26]. The thus formed dimeric species tended to precipitate as blackish residues which often required multiple acid washes to be removed from the polymer solution.

3.5. Effect of n-butyllithium/cobaltocene ratio on hydrogenation efficiency

n-BuLi, functioning as an alkylating agent, played an important role in the hydrogenation reaction of SBS copolymers. The highest hydrogenation efficiency was achieved when employing a catalyst system made from *n*-BuLi and cobaltocene at a ratio of 1–2, as shown in Table 3, regardless of the type of the isomeric units. An insufficient amount of *n*-BuLi failed to activate the cobaltocene thus resulting in a low hydrogenation efficiency. However, an excessive amount of *n*-BuLi would likely have caused a complexation with the cobaltocene and rendered the catalyst ineffective.

3.6. Activation energy of the hydrogenation reaction

The hydrogenation reaction occurred homogeneously in the cyclohexane solvent. The rate of reaction in the entire system, based on a second-order reaction mechanism, could be expressed as:

$$-\frac{d[=]}{\mathrm{d}t} = k[=][H_2],$$

where k is the rate constant, and [=] and [H_2] are the concentrations of unsaturated double bonds and dissolved hydrogen in the cyclohexane solvent, respectively. The temperature dependence of the rate of hydrogenation (in terms of activation energy) was determined by conducting experiments under a constant, high H_2 pressure, with vigorous mixing. Therefore, [H_2]was assumed to be in equilibrium with the gaseous pressure and remained constant during the reaction. Consequently, the reaction could be viewed as a pseudo-first-order reaction

$$-\frac{d[=]}{\mathrm{d}t} = k_a[=],$$

where k_a is the apparent rate constant in the cyclohexane phase. After integration, this equation is further expressed in terms of the conversion of unsaturated double bonds (extent of hydrogenation), x

$$\ln\frac{1}{1-x} = k_a t,$$

where t is the reaction time. The results are summarized in Fig. 12 showing a linear relationship between ln(1)/(1 − x) and t. The apparent rate constant at each temperature was then readily determined from the slope of the corresponding curve. The calculated rate constants are shown in Table 4.

The activation energy of the hydrogenation reaction, $_E$, was determined from the Arrhenius forms of those rate constants:

$$k_a = Ae^{-E/RT}.$$

After rearranging, this equation could be expressed as:

$$\ln k_a = \ln A - \frac{E}{R}\frac{1}{T}.$$

As shown in Fig. 13, the activation energy could be determined from the slope of the ln k_a vs. 1/T curve. The resulting activation energy was determined as 14.11 kcal/mol of the double bond.

Table 2
Hydrogenation efficiencies at various pressures (under a constant temperature of 80°C)

	10 kg/cm^2	15 kg/cm^2	25 kg/cm^2	40 kg/cm^2
1,2 unit	0%	100%	100%	99.2%
Cis-1,4 unit	0%	100%	100%	79.2%
Trans-1,4 unit	0%	100%	100%	63.5%

Table 3
Hydrogenation efficiencies at various *n*-BuLi/cobaltocene ratios

	0	0.5	1	2	4	8	16
1,2-unit	0%	82.1%	100%	100%	99.5%	79.0%	0%
Cis-1,4	0%	44.3%	98.5%	100%	93.5%	41.5%	0%
trans-1,4	0%	37.3%	98.0%	100%	92.2%	33.3%	0%

Table 4
Calculated rate constants at various reaction temperatures

	323°K	333°K	343°K	353°K
k_a(min^{-1})	0.029257	0.046177	0.11867	0.17010

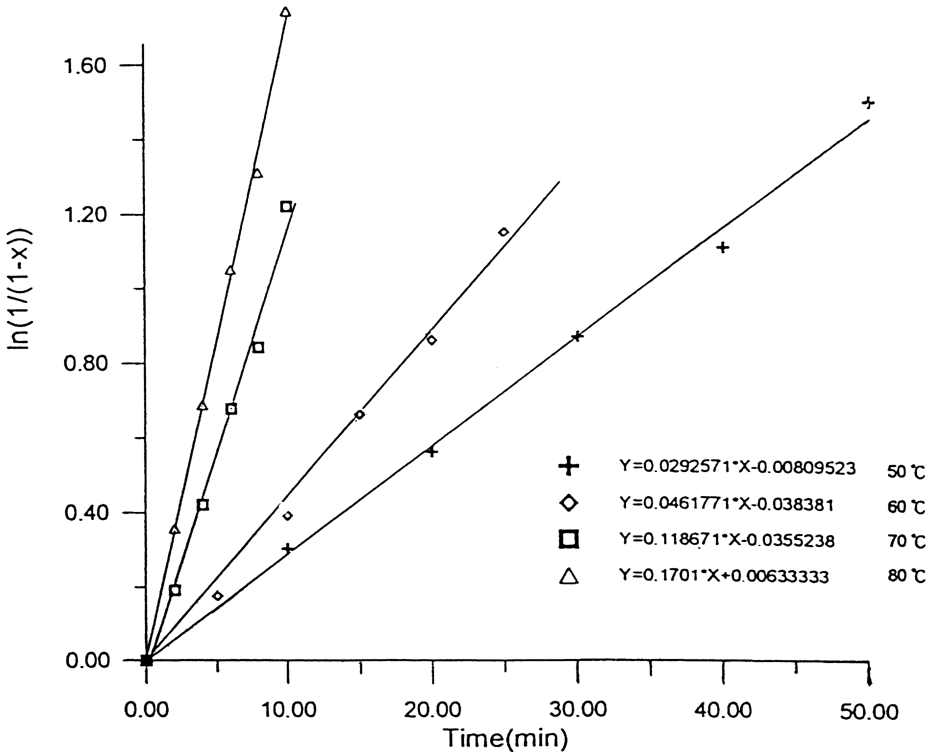


Fig. 12. ln(1)/(1-x) vs. t at various experimental temperatures.

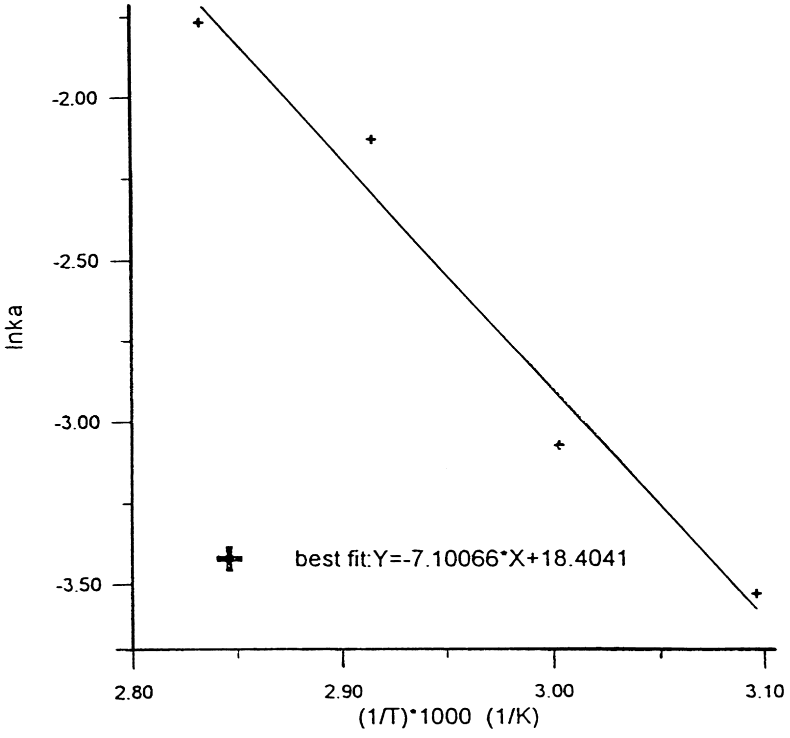


Fig. 13. lnk_a vs. $1/T$.

Table 5
Comparison between Cp_2TiCl_2/*n*-BuLi and Cp_2Co/*n*-BuLi systems

	Cp_2TiCl_2/*n*-BuLi [17]	Cp_2Co/*n*-BuLi
Metallocene loading	1.0×10^{-5} mol/g polymer	1.2×10^{-5} mol/g polymer
Molal ratio of (*n*-Buli)/(metallocene)	4	2
Reaction temperature	50°C	80°C
Reaction pressure	5 kg/cm^2	25 kg/cm^2
Reaction time	2 h	2 and 3 h
Degree of hydrogenation	95%–100%	95%–100%

3.7. Comparison of the Hydrogenation capability between cobaltocene and titanocene dichloride

Kishimoto et al. had previously patented (assigned to Asahi Chemical Co., Japan) bis-(cyclopentadienyl)titanium(IV) compounds, Cp_2TiR_2, either with or without the presence of an alkyl lithium compound, as effective hydrogenation catalysts [17,19]. Their experimental conditions and hydrogenation efficiencies (using Cp_2TiCl_2/*n*-BuLi system) are compared with ours (using Cp_2Co/*n*-BuLi system) in Table 5. The comparison indicates that using a higher molal ratio of *n*-BuLi to Cp_2TiCl_2, their system has catalyzed the hydrogenation reaction at milder conditions. While Cp_2TiCl_2 and Cp_2Co are two different types of matallocene catalyst, both have required a similar catalyst loading and achieved a quantitative degree of hydrogenation.

4. Conclusions

A catalyst system consisting of Cp_2Co and *n*-BuLi at a 1 : 2 mol ratio, was found to be active for the hydrogenation of SBS block copolymer. The major catalytic species of this catalyst system appeared to be the CpCoBu after one of the Cp ligand in the original Cp_2Co was substituted. The hydrogenation efficiencies for the three isomeric units of polybutadiene decreased in the order 1,2-unit $>$ *cis*-1,4 unit $>$ *trans*-1,4 unit, and a reaction temperature higher than 80°C was needed in order to achieve complete hydrogenation. While it was advantageous to increase the H_2 pressure, an overpressure of hydrogen caused an adverse effect on the hydrogenation efficiency. The highest hydrogenation efficiency was achieved when employing a catalyst system made from an 1–2 *n*-BuLi/cobaltocene ratio. The kinetics of the hydrogenation reaction were studied by monitoring the extent of saturation of double bonds and the temperature dependence of the hydrogenation rate was analyzed. The activation energy was determined as 14.11 kcal/mol of double bonds.

Acknowledgements

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