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Hydrogenation of C=C bonds in styrene-butadiene-styrene block copolymers in the presence of monocyclopentadienyl titanium(IV) catalytic systems

Summary — Hydrogenation of C=C bonds in styrene-butadiene-styrene (SBS) block copolymers in the presence of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y-p})/\text{BuLi}$ and $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y-p})/\text{Et}_3\text{Al}$ catalytic systems (Cp = cyclopentadienyl, Bu = butyl, Et = ethyl, Y = NO_2 , Cl, H, CH_3 , OCH_3) was investigated. The effect of the kind of metal alkyl, Li:Ti or Al:Ti molar ratio, copolymer composition, reaction temperature and hydrogen pressure on activity of catalytic system was investigated. The best degree of hydrogenation for SBS copolymers (80–90 %), was obtained for the systems containing *p*-chlorophenoxy ligand with the most electron-acceptor properties.

Keywords: styrene-butadiene-styrene copolymer, cyclopentadienyl titanium complexes, hydrogenation, butyllithium, triethylaluminum.

UWODORNIANIE WIĄZAŃ C=C W KOPOLIMERACH BLOKOWYCH STYREN-BUTADIEN-STYREN W OBECNOŚCI UKŁADÓW KATALITYCZNYCH Z MONOCYKLOPENTADIE-NYLOWYMI KOMPLEKSAMI TYTANU(IV)

Streszczenie — Przeprowadzono uwodornianie wiązań C=C w kopolimerach blokowych styren-butadien-styren (SBS) w obecności układów katalitycznych $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y-p})/\text{BuLi}$ i $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y-p})/\text{Et}_3\text{Al}$ (Cp = cyclopentadienyl, Bu = butyl, Et = etyl, Y = NO_2 , Cl, H, CH_3 , OCH_3). Badano wpływ rodzaju związku metaloalkilowego, stosunku molowego Li:Ti lub Al:Ti, struktury kopolimeru, temperatury reakcji i ciśnienia wodoru na aktywność układu katalitycznego (tabela 1). Najwyższy stopień uwodornienia kopolimeru SBS (80–90 %) uzyskano stosując układ zawierający ligand *p*-chlorofenoksylowy, który wykazuje najsilniejsze właściwości elektro-nodonorowe (tabela 2 i 4).

Słowa kluczowe: kopolimer styren-butadien-styren, cyklopentadienylowe kompleksy tytanu, uwodornienie, butylolit, trietyloglin.

Styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) block copolymers are manufactured in living copolymerization of styrene with butadiene or styrene with isoprene initiated generally by lithium organometallic compounds. They are produced in about million metric tons/year and found the application as:

— bitumen modifiers [they significantly enhance the performance of bitumen (asphalt) used in road, runway, racetrack and roofing applications by improving life expectancy and reducing maintenance levels];

— adhesives, sealants and coatings (these copolymers can provide improved all-round performance for pressure-sensitive and contact adhesives and are used in a variety of tapes, labels, plasters, sealants, coatings and road marking paints);

— shoe sole material modifier (SBS and SIS can offer improved resilience, good low temperature flexibility and insulation, and better grip even in wet conditions);

— additives to produce materials which enhance the grip, feel, appearance and convenience of a diverse range of applications and markets products including toys, hygiene, packaging, automotive, sports and leisure, construction and molded and extruded technical goods.

The copolymers are produced in several sorts, containing various kinds of additives *i.e.*, diblock SB or SIS copolymers, and oils providing better flexibility. Presence of C=C bonds in butadiene makes them nonresistant to weather and high temperature. These bonds in SBS are hydrogenated, to allow them to be applied in these conditions. Formally, a new copolymers are obtained containing poly(ethylene/butylene) blocks. These copolymers find the same applications as mentioned above for unsaturated SBS and even more [1, 2].

Heterogeneous nickel or palladium catalysts are used in the hydrogenation. But they work under relatively high pressure and high temperatures to achieve required yields [3]. To carry out hydrogenation reaction under mild condition, homogeneous catalyst should be used.

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From them dicyclopentadienyl titanium(IV) catalytic systems *e.g.*, $\text{Cp}_2\text{TiCl}_2/\text{metal alkyl}$ [4–6] or $\text{Cp}_2\text{TiCl}_2/\text{metal hydride}$ [7, 8] are the most active. Cp_2TiR_2 (R = alkyl or aryl) complexes are also good catalysts [9]. To enhance performance of the both titanocene systems, benzoates or phenolic lithium salts are added to the reaction mixtures as co-catalysts [6]. These catalysts were applied to hydrogenate “living” forms of SBS or SIS obtained directly in their synthesis and to hydrogenate commercial SBS and SIS *e.g.*, KRATON[®] D-1101(Shell) or KRATON[®] D-1111(Shell), respectively [5, 6].

In literature are also described cobalt [10], nickel [11], rhodium [12] and ruthenium [13] homogeneous catalysts, but they are less active or more expensive than the mentioned above catalysts. Trichlorotitanium complexes of the following formula CpTiCl_3 and RTiR_3 are not active precursors [5].

We supposed that the replacement of one of the chlorine ligands in CpTiCl_3 molecule with a ligand with a phenoxy ring should lead to a new catalytic system efficiently hydrogenating the C=C bonds in SBS copolymers. Prepared this way complexes of the $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y}-p)$ formula (where Y = NO_2 , Cl, H, CH_3 and OCH_3), where phenoxy ligands differ themselves by electron-donor properties and must be activated with BuLi or Et_3Al similarly like Cp_2TiCl_2 in the mentioned earlier catalysts [4–6]. The activity of prepared catalytic systems in hydrogenation of SBS was investigated in this work.

EXPERIMENTAL

Materials

Titanium complexes [$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y}-p)$ where Y = NO_2 , Cl, H, CH_3 and OCH_3] were prepared with methods described in [14, 15].

Butyllithium (BuLi) as 1.8 M solution in hexane (Aldrich) and triethylaluminum (Et_3Al , Witco) were used as supplied.

Cyclohexane (Aldrich) was distilled from Na/K alloy just before use.

Methanol (pure, POCh, Gliwice) and toluene (pure, Chempur, Piekary Śląskie) were used as received.

Hydrogen 99.9 % (Multico) was passed through 3A molecular sieves before an inlet to an autoclave.

Commercial SBS copolymers *i.e.*, KRATON[®] D-1153 (linear, >5 % SB diblock) and KRATON[®] D-1195 (linear, 40 % vinyl, <5 % SB diblock) both manufactured by Kraton Polymers LCC were used for hydrogenation.

Catalysts preparation

To a Schlenk vessel the determined quantity of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y}-p)$ in the form 0.1 M solution in toluene and an appropriate amount of Et_3Al or 1.4 M solution of BuLi in hexane were added to assert the required Al:Ti or Li:Ti molar ratio. After 15 min of mixing the obtained

black solution was directly transferred to an autoclave for hydrogenation.

Hydrogenation reaction

SBS hydrogenations were carried out in a 600 cm³ steel autoclave equipped with a stirrer, thermocouple, manometer and operating valves. Firstly, the autoclave was dried at 90 °C under vacuum (oil pump) for 3 h, then it was filled with nitrogen and cooled down under this atmosphere to the ambient temperature. 200 cm³ of cyclohexane and 10 g of copolymer (KRATON[®] D-1153 or KRATON[®] D-1195) were added and mixed for 1 h to receive a clear solution. The solution was saturated with hydrogen and the catalyst solution was added. When temperature was increased to 50 °C and hydrogen pressure was elevated to desired values, time of the hydrogenation reaction begins to be measured. Reaction was stopped by evacuation of hydrogen excess and the reaction mixture was poured out to methanol. 2 wt. % HCl solution in methanol (36 wt. % HCl solution in water diluted to 2 wt. % with methanol) was added in the amount sufficient to dissolve the catalyst residue and to completely precipitate the polymeric product.

The hydrogenated copolymer was dried at 60 °C under vacuum (oil pump) to fixed weight.

Conditions of all carried out hydrogenation reactions of copolymer with investigated catalytic system are listed in Table 1.

Methods of testing

Fourier transform infrared spectrophotometry (FT-IR) was used for determination of the degree of hydrogenation of 1,2-vinyl and 1,4-*trans* units of SBS copolymer. The spectra were recorded on SPECTRUM 2000 FT-IR (Perkin-Elmer) spectrometer. The samples were solved in boiling methylene chloride. A few drops of solutions were placed on a KBr plate and evaporated. For each spectrum, eight interferograms were collected at 4 cm⁻¹ resolution and 4000–400 cm⁻¹ wavenumber range. Since the film thickness was not measured, the degree of hydrogenation was quantified from the ratio of peak height to the internal standard.

According to the literature [16] the contents of C=C bonds in considered units was established from analytical bands as listed bellow:

- band at 909 cm⁻¹ for 1,2-vinyl units with maximum absorbance A_1 ,
- band at 970 cm⁻¹ for 1,4-*trans* units with maximum absorbance A_2 ,
- band at 1601 cm⁻¹ (internal standard) for aromatic stretching vibrations with maximum absorbance A_0 .

According to the Lambert-Beer law the absorbance ratios A_1/A_0 and A_2/A_0 are linearly related to fractions of unsaturated bonds in 1,2-vinyl and 1,4-*trans* units, respectively. The degree of hydrogenation was calculated

Table 1. Conditions of hydrogenation reactions of KRATON® D-1153 or KRATON® D-1195 carried out at temperature 50 °C using different catalytic system

Number of reaction	Type of SBS	Catalytic system	Amount of Ti, mmol	Li:Ti molar ratio	Al:Ti molar ratio	H ₂ pressure MPa	Time of reaction, h
1	KRATON® D-1153	CpTiCl ₂ (OC ₆ H ₄ NO ₂ - <i>p</i>)/Et ₃ Al	0.2	—	4:1	0.78	3
2		CpTiCl ₂ (OC ₆ H ₄ Cl- <i>p</i>)/Et ₃ Al	0.2	—	4:1	0.78	3
3		CpTiCl ₂ (OC ₆ H ₅ - <i>p</i>)/Et ₃ Al	0.2	—	4:1	0.78	3
4		CpTiCl ₂ (OC ₆ H ₄ CH ₃)/Et ₃ Al	0.2	—	4:1	0.78	3
5		CpTiCl ₂ (OC ₆ H ₄ OCH ₃ - <i>p</i>)/Et ₃ Al	0.2	—	4:1	0.78	3
6		CpTiCl ₂ (OC ₆ H ₄ Cl)/Et ₃ Al	0.2	—	2:1	0.78	3
7		CpTiCl ₂ (OC ₆ H ₄ Cl)/Et ₃ Al	0.2	—	4:1	0.78	3
8		CpTiCl ₂ (OC ₆ H ₄ Cl- <i>p</i>)/Et ₃ Al	0.2	—	8:1	0.78	3
9		CpTiCl ₂ (OC ₆ H ₄ Cl- <i>p</i>)/Et ₃ Al	0.2	—	4:1	0.78	6
10		CpTiCl ₂ (OC ₆ H ₄ Cl- <i>p</i>)/BuLi	0.2	4:1	—	0.78	3
11		CpTiCl ₂ (OC ₆ H ₄ OCH ₃ - <i>p</i>)/BuLi	0.2	4:1	—	0.78	5
12		CpTiCl ₂ /BuLi	0.2	4:1	—	0.78	5
13		CpTiCl ₂ (OC ₆ H ₄ Cl- <i>p</i>)/BuLi	0.1	4:1	—	0.49	3
14	KRATON® D-1195	CpTiCl ₂ (OC ₆ H ₄ Cl- <i>p</i>)/BuLi	0.2	4:1	—	0.78	3
15		CpTiCl ₂ (OC ₆ H ₄ Cl- <i>p</i>)/BuLi	0.1	4:1	—	0.49	2
16		CpTiCl ₂ /BuLi	0.1	4:1	—	0.49	2

by comparison of these fractions in hydrogenated and unhydrogenated samples.

RESULTS AND DISCUSSION

Two catalytic systems prepared by reaction of CpTiCl₂(OC₆H₄Y-*p*) with a determined quantity of Et₃Al or BuLi were investigated. SBS copolymers were hydrogenated to different degree according to electron-donor properties of Y substituents and the hydrogenation reaction conditions: copolymer structure, the Li(Al):Ti molar ratio hydrogen pressure.

CpTiCl₂(OC₆H₄Y-*p*)/Et₃Al catalytic systems

To establish influence of the Y-substituents on the activity of investigated catalysts in the hydrogenation of C=C bonds in SBS copolymers, the reactions of KRATON® D-1153 were carried out in the presence of the CpTiCl₂(OC₆H₄Y-*p*)/Et₃Al system under preliminary assumed standard conditions described in [5] *i.e.*, 0.2 mmol of Ti, molar ratio Al:Ti = 4:1, temp. 50 °C, H₂ pressure 0.78 MPa and time 3 h (reactions 1–5 in Table 1).

In Table 2 the degree of hydrogenation of C=C bonds in 1,4-*trans* units and 1,2-vinyl units are collected.

The first group of catalytic systems labeled with Y = NO₂ and OCH₃ (reactions 1 and 5 in Table 2), hydrogenate only C=C bonds in 1,2-vinyl units with the yield ~15 %. The catalytic activity of these systems is low. The second group labeled with Y = Cl, H and CH₃ (reactions 2, 3, and 4, respectively) is more active and hydrogenate C=C bonds in both kind of units. The C=C bonds in 1,2-vinyl units were hydrogenated in the presence of the se-

cond group of catalysts with the yields from 30.4 % for the system with the most electron-donor properties ligand *i.e.* *p*-methylophenoxy, up to 33.5 % for the system with the least electron-donor properties ligand *i.e.* *p*-chlorophenoxy. Greater differences of the yields were observed in the case of hydrogenation of C=C bonds of 1,4-*trans* units. The most active catalytic system with *p*-chlorophenoxy ligand hydrogenated them with the yield 60.6 %, whereas the least active catalyst with a *p*-methylphenoxy ligand with the yield only 0.3 %.

Table 2. Degree of hydrogenation of C=C bonds in 1,4-*trans* and 1,2-vinyl units of KRATON® D-1153 in the presence of the CpTiCl₂(OC₆H₄Y-*p*)/Et₃Al catalytic system and other conditions specified according to number of reaction in Table 1

Number of reaction	Hydrogenation degree of C=C bonds in units, %	
	1,4- <i>trans</i>	1,2-vinyl
1	—	16.9
2	60.6	33.5
3	7.4	33.3
4	0.3	30.4
5	—	14.8

The most active in standard conditions CpTiCl₂(OC₆H₄Cl-*p*)/Et₃Al system was chosen for investigation of the effect of Al:Ti molar ratio on the catalytic activity. Results of these studies are listed in Table 3.

The obtained total degree of hydrogenation indicates that the amount of Et₃Al asserted by the ratio Al:Ti = 4:1 is optimal (reactions 7 and 9 in Table 3). It is probably a re-

sult of creation of the biggest amount of active catalytic sites. Increase in the Al:Ti molar ratio results in the increase of hydrogenation yield of C=C bonds in 1,2-vinyl units (reaction 8). For 1,4-*trans* units the catalytic systems with the ratio Al:Ti = 4:1 are optimal for hydrogenation. These results indicate the presence of two kinds of active hydrogenation centers of different selectivity. The first seems to be responsible for 1,2-vinyl units hydrogenation, the second for 1,4-*trans* units hydrogenation.

Table 3. Degree of hydrogenation of C=C bonds in 1,4-*trans* and 1,2-vinyl units of KRATON® D-1153 in the presence of the CpTiCl₂(OC₆H₄Cl-*p*)/Et₃Al (catalytic system and other conditions specified according to number of reaction in Table 1)

Number of reaction	Hydrogenation degree of C=C bonds in units, %	
	1,4- <i>trans</i>	1,2-vinyl
6	13.0	29.7
7	60.6	33.5
8	32.8	44.3
9	68.4	46.6

It surely concerns the whole investigated CpTiCl₂(OC₆H₄Y-*p*)/Et₃Al system where the substituted phenoxy ligands probably decided on the number and kind of formed active sites.

The increase in the hydrogenation degree when the reaction was carried out longer than the standard 3 h *i.e.* 6 h (reaction 9), proved that the prepared hydrogenation active sites are relatively stable.

CpTiCl₂(OC₆H₄Y-*p*)/BuLi catalytic systems

Buthyllithium is also used to activate titanocene complexes in C=C bonds hydrogenation [3–6]. This agent was applied to prepare catalysts which were tested in more kinds of SBS and SIS copolymers hydrogenation.

Results obtained from hydrogenation of KRATON® D-1153 in the presence of the CpTiCl₂(OC₆H₄Y-*p*)/BuLi (Y = Cl, OCH₃) together with Cp₂TiCl₂/BuLi catalytic system, are presented in Table 4.

Table 4. Degree of hydrogenation of C=C bonds in 1,4-*trans* and 1,2-vinyl units of KRATON® D-1153 in the presence of the CpTiCl₂(OC₆H₄Y-*p*)/BuLi (Y = Cl, OCH₃) (catalytic system and other conditions specified according to number of reaction in Table 1)

Number of reaction	Hydrogenation degree of C=C bonds in units, %	
	1,4- <i>trans</i>	1,2-vinyl
10	80	90
11	30	50
12	65	88
13	70	85

Similarly like in the system activated by Et₃Al, the system with BuLi and prepared using titanium complexes with the least electron-donor properties *p*-chlorophenoxy ligand (reaction 10 in Table 4), was the most efficient in the hydrogenation. It was even more active than the commercial one prepared using Cp₂TiCl₂ (reaction 12). CpTiCl₂(OC₆H₄Cl-*p*)/BuLi system hydrogenated 80 % of C=C bonds in 1,4-*trans* and 90 % in 1,2-vinyl units of polybutadiene blocks. Hydrogenation carried out under lower hydrogen pressure, shorter time and using half amount of the catalyst (reaction 13), gave the yield of hydrogenation degree only a little lower than for standard conditions.

But on the contrary to the system activated with Et₃Al, the systems activated with BuLi hydrogenated 1,2-vinyl units more effectively than 1,4-*trans* units.

Hydrogenation of other kind of SBS copolymer containing higher fraction of 1,2-vinyl polybutadiene units *i.e.* KRATON® D-1195 using CpTiCl₂(OC₆H₄Cl-*p*)/BuLi was also investigated. Corresponding results are presented in Table 5. Obtained for KRATON® D-1195 (reaction 14 in Table 5) hydrogenation degree of C=C bonds in 1,4-*trans* and 1,2-vinyl units is similar (30 % and 88 %, respectively) as for hydrogenation of KRATON® D-1153 in the same conditions.

Table 5. Degree of hydrogenation of C=C bonds in 1,4-*trans* and 1,2-vinyl units of KRATON® D-1195 in the presence of the CpTiCl₂(OC₆H₄Cl-*p*)/BuLi (catalytic system and other conditions specified according to number of reaction in Table 1)

Number of reaction	Hydrogenation degree of C=C bonds in units, %	
	1,4- <i>trans</i>	1,2-vinyl
14	80	88
15	33	37
16	35	38

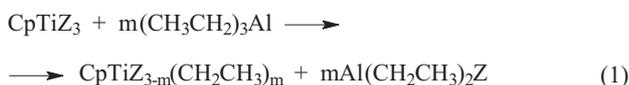
It can be seen that hydrogenation under lower hydrogen pressure and for a shorter time, using half of the standard amount of the catalyst (reaction 15) give yields about 2.5 times lower. The commercial catalyst (reaction 16) presents similar activity.

Explanation of the catalytic systems activity

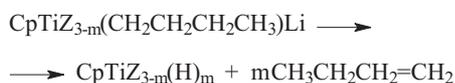
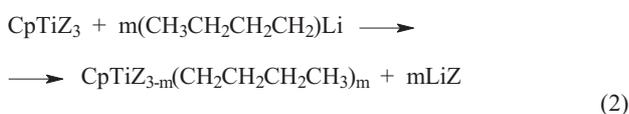
For catalytic systems activated by both BuLi and Et₃Al complexes CpTiCl₂(OC₆H₄Cl-*p*) was the most active in SBS hydrogenation. Among the investigated catalytic systems, those activated with BuLi are a little bit more active than those activated with Et₃Al (compare reactions 2 and 10 or reactions 5 and 11).

Catalytic systems activated with BuLi hydrogenate C=C bonds in 1,2-vinyl units with higher efficiency than in 1,4-*trans* units. While in the cases of systems activated with Et₃Al different activity for 1,2-vinyl and 1,4-*trans*

units was stated. To explain the described catalysts properties, mechanism of hydrogenation titanocene catalysts formation should be considered [17]. According to this mechanism the active centers are prepared *via* formation of titanocene hydrides *e.g.* Cp₂Ti H₂ described by Bercaw and Brintzinger [18, 19] as intermediates, the following reactions could be expected in the investigated systems:



where: $m = 1, 2$ or 3 ; $Z = \text{Cl}, \text{OC}_6\text{H}_4\text{Y-}p$



Further transformations of such obtained titanium(IV) complexes yield titanium(III) and even titanium(II) compounds. Polarographic measurements of such systems proved that acceptor phenoxy ligands prevent reduction of titanium(IV) ions in CpTiCl₂(OC₆H₄Y-*p*) complexes to lower oxidation titanium ions [20]. These data, related to the obtained results showing that titanium complexes with the strongest acceptor *p*-chlorophenoxy ligands formed the most active catalysts, suggest that formation of cyclopentadienyl titanium(IV) hydrides is a crucial factor deciding on activity of the investigated catalysts.

Beside cyclopentadienyltitanium hydride species, chlorodiethylaluminium, phenoxydiethylaluminium and phenoxytitanium are formed in these reactions, respectively. Just formed phenoxytitanium compounds, as mentioned above [6], can act as cocatalysts, and they are probably responsible for relatively higher activity of the BuLi activated systems.

Our results indicated also, that presence of diblock components in the investigated SBS copolymers asserts higher hydrogenation efficiency. Since this additives are added to enhance copolymers flexibility, probably this effect helps catalytic active species to access the C=C bonds in diene blocks in the investigated copolymers.

Our results showed, that investigated CpTiCl₂(OC₆H₄Y-*p*) and described in literature Cp₂TiCl₂ [4–6] complexes after modification with lithium and aluminum alkyls, give SBS active hydrogenation catalysts, while CpTiCl₃ was not active [5]. It is known that dicyclopentadienyl metal complexes can be dissolved

very well in polymers *e.g.*: Cp₂Fe in polyurethanes [21] and Cp₂Co in SBS [10]. Thanks to that they exhibit required high activity in solid fuels combustion or SBS hydrogenation, respectively. The same effect should act in the investigated systems, when phenoxy ligands play the role of Cp ring asserting demanded solubility. The third chlorine ligand in the CpTiCl₃ molecule, does not play this role.

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