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

Summary — Hydrogenation of C=C bonds in styrene-isoprene-styrene (SIS) 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 = Cl, H, OCH_3) was investigated. All of the catalytic systems were active in these reactions. Their activity depended on the kind of the metal alkyl, the copolymer composition, reaction time, temperature and hydrogen pressure. It was established that access of catalytic species to the C=C bonds in the isoprene blocks is the most important factor in the hydrogenation efficiency. The smallest steric hindrances occur when phenoxy ligands in the catalytic systems are unsubstituted (Y = H) and styrene-isoprene diblocks (SI) are present in the SIS copolymer. Thus, the catalytic systems $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl})/\text{BuLi}$ were the most active in Kraton[®] D-1161 copolymers hydrogenation.

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

UWODORNIANIE WIĄZAŃ C=C W KOPOLIMERACH BLOKOWYCH STYREN-IZOPREN-STYREN W OBECNOŚCI UKŁADÓW KATALITYCZNYCH Z MONOCYKLOPENTADIENYLOWYMI KOMPLEKASMI TYTANU(IV)

Streszczenie — Badano uwodornienie wiązań C=C w blokowych kopolimerach styren-izopren-styren (SIS) w obecności katalitycznych układów: $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y-p})/\text{BuLi}$ i $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y-p})/\text{Et}_3\text{Al}$ (Cp = cyklopentadienyl, Bu = butyl, Et = etyl; Y = Cl, H, OCH_3). Wszystkie badane układy katalityczne były aktywne w tych reakcjach, a ich aktywność zależała od rodzaju związku metaloalkilowego, składu kopolimeru, czasu prowadzenia reakcji, temperatury i prężności wodoru. Stwierdzono, że łatwość dostępu centrów aktywnych katalizatora do wiązań C=C w blokach izoprenowych to najważniejszy czynnik wpływający na efektywność uwodornienia. Najmniejsze przeszkody steryczne występują wówczas, gdy w układzie katalitycznym ligand fenoksy jest niepodstawiony (Y = H), a w kopolimerze SIS są obecne dibloki styren-izopren. Z tych powodów układ katalityczny $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl})/\text{BuLi}$ był najbardziej aktywny w reakcji uwodornienia kopolimeru Kraton[®] D-1161.

Słowa kluczowe: kopolimer styren-izopren-styren, cyklopentadienylowe kompleksy tytanu, uwodornienie, butylołit, trietyloglin.

Hydrogenated styrene-isoprene-styrene (SEPS) block copolymers are built of styrene and ethylene/propylene blocks and are obtained by isoprene blocks hydrogenation in styrene-isoprene-styrene (SIS) block copolymers. These copolymers, in comparison to their unsaturated homologues, can give the additional advantages of increased oxidation and weather resistance, particularly higher service temperatures and increased processing stability when used as thermoset modifications [1, 2]. Isoprene blocks in SIS copolymers require relatively high

hydrogen pressure and high temperatures to be hydrogenated, because of steric hindrance of methyl groups in isoprene mers. Heterogeneous nickel or palladium catalysts are used in this hydrogenation. But they work under relatively high pressure (2–20 MPa) and high temperatures (90–200 °C) to achieve required yields [3].

To carry out this reaction under mild condition (0.4–1.0 MPa, 20–60 °C), homogeneous catalyst should be used. Among them dicyclopentadienyl titanium(IV) catalytic system *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].

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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 styrene-butadiene-styrene (SBS) or SIS obtained directly in their synthesis and to hydrogenate commercial SBS and SIS *e.g.*, Kraton® D-1101 (SBS- Shell) or Kraton® D-1111 (SIS-Shell) [5, 6].

We have found out that complexes of the $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{-Y})$ formula (where Y = Cl, H, and OCH_3) after activation with BuLi or Et_3Al form active catalytic system in SBS block copolymers hydrogenation under relatively mild conditions [10]. Y substituents are characterized by different electron donor-acceptor properties, *e.g.* Cl is an electron acceptor but OCH_3 is an electron donor. These properties caused that $\text{OC}_6\text{H}_4\text{-p}$ ligands exhibited similar properties and influenced active titanium complexes — $\text{CpTiZ}_{3-m}(\text{H})_m$ (where $m = 1, 2, 3$; Z = Cl; $\text{OC}_6\text{H}_4\text{-p}$) in the investigated catalytic systems, as it was described in our previous paper [10]. A large number of these active complexes were formed for the complexes possessing *p*-chlorophenoxy ligand [11]. In this paper we present results of the investigations on these catalytic systems activity in SIS copolymers hydrogenation.

EXPERIMENTAL

Materials

Titanium complexes [$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{-Y-p})$ where Y = Cl, H, and OCH_3] were prepared using methods described in [12, 13].

Butyllithium (BuLi) as 1.8 M solution in hexane (Aldrich) and triethylaluminum (Et_3Al , Witco) were applied as co-catalysts. Both were used as received.

Hydrogen 99.9 % (Multico) was purified by passing it through 3A molecular sieves before letting into an autoclave.

For hydrogenation two kind of commercial SIS copolymers *i.e.*, Kraton® D-1160 (linear, 0 % SI diblock) and Kraton® D-1161 (linear, 20 % SI diblock) both manufactured by Kraton Polymers LCC were chosen.

Catalysts preparation, hydrogenation reaction and methods of testing

Catalysts preparation, hydrogenation reaction and testing were performed with methods described in [10]. Difference in described methods, in comparison to the one applied here was the use of SIS copolymers instead of SBS. Therefore for SIS copolymers the degree of C=C bonds hydrogenation was determined using the signal magnitude corresponding to the unit $-(\text{CH}_3)\text{C}=\text{CH}-$ (837 cm^{-1}) [14]. In SIS copolymers only this units were hydrogenated [3].

RESULTS AND DISCUSSION

Two groups of catalytic systems, prepared by reaction of precatalysts $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{-p})$ with determined quantity of BuLi or Et_3Al , were applied to hydrogenation reactions of SIS copolymers. Y substituents in phenoxy ligands are characterized by different electron-donor properties.

The commercial precatalyst Cp_2TiCl_2 was also tested in SIS hydrogenation reaction to compare the activity of all investigated catalytic systems. Two kind of SIS copolymers were hydrogenated in various reaction conditions (reaction time, temperature and hydrogen pressure).

$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{-p})/\text{BuLi}$ system

Hydrogenation of SIS copolymers was carried out using 0.2 mmol titanium complexes with the ratio Li:Ti = 4:1 and the reaction was carried out for 3–5 h at 50 or 60 °C under initial hydrogen pressure 0.5–0.8 MPa. BuLi was commonly used to activate titanocene complexes in C=C bonds hydrogenation [3–6]. This reagent was applied in the first step of our investigations to prepare catalysts which were tested in two kind of SIS copolymers hydrogenation: Kraton® D-1160 and Kraton® D-1161, differing in SI diblock presence. The results are presented in Table 1.

In the case of Kraton® D-1160 copolymer, the $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl})/\text{BuLi}$ catalytic system exhibited relatively low activity. The hydrogenation degree was equal

Table 1. Conditions of reactions and degree of hydrogenation of Kraton® D-1160 and Kraton® D-1161 in the presence of the $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{-Y-p})$ (Y = Cl, OCH_3)/BuLi system

Titanium complex in catalytic system	Copolymer	Temperature, °C	H ₂ pressure, MPa	Time, h	Hydrogenation degree of C=C bonds, %
$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl})$	Kraton® D-1160	50	0.5	3	7
	Kraton® D-1160	50	0.8	5	15
$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{OCH}_3)$	Kraton® D-1160	50	0.8	5	10
	Kraton® D-1160	50	0.8	5	15
$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl})$	Kraton® D-1161	50	0.5	3	36
	Kraton® D-1161	60	0.8	5	74

to 7 %, when the pressure was 0.5 MPa and reaction time was 3 h and increased to 15 % when the pressure increased to 0.8 MPa and reaction time was 5 h. The commercial catalyst, Cp_2TiCl_2 , under hydrogen pressure of 0.8 MPa and reaction time 5 h exhibited the same activity. The $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{OCH}_3)$ system operating in the same conditions as $\text{CpTiCl}_2(\text{OC}_6\text{H}_5\text{-Cl})/\text{BuLi}$ (50 °C, 0.8 MPa, 5 h) was less active, giving the hydrogenation degree only 10 %.

Kraton[®] D-1161 was hydrogenated using $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl})/\text{BuLi}$ system to a higher degree of 36 % (0.5 MPa, 3 h). It was much higher degree than obtained for Kraton[®] D-1160 hydrogenation in the same conditions. When the time of the reaction was longer (5 h), the reaction temperature and hydrogen pressure were higher (60 °C, 0.8 MPa), the degree increased to 74 %.

The results indicated that the presence of the SI diblock component in the investigated SIS warrants higher hydrogenation efficiency. This component is added to enhance copolymer flexibility, playing a role of plasticizer that pushed apart the SIS copolymer chains. Owing to that, the catalytic active species access easier the C=C bonds in diene blocks in the Kraton[®] D-1161 [3]. The same effect is observed in SBS block copolymers, modified and not modified by SB diblock addition [10].

$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y-p})/\text{Et}_3\text{Al}$ system

$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-p})$, $\text{CpTiCl}_2(\text{OC}_6\text{H}_5)$, $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{OCH}_3\text{-p})$ and Cp_2TiCl_2 complexes were used to prepare the catalyst systems activated with Et_3Al . They were used to establish how different electron donor-acceptor properties of the phenoxy ligands ($\text{OC}_6\text{H}_4\text{Cl-p}$ – acceptor; $\text{OC}_6\text{H}_4\text{OCH}_3\text{-p}$ – donor; OC_6H_5 – neutral), influence the catalysts performance and to compare the activity of investigated catalysts with activity of the commercial catalyst containing Cp_2TiCl_2 complex.

Kraton[®] D-1161 was applied in these investigations, because it gave better hydrogenation degree than Kraton[®] D-1160 as we described above.

Table 2. Degree of hydrogenation of C=C bonds in Kraton[®] D-1161 in the presence of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y-p})/\text{Et}_3\text{Al}$ (Y = Cl, H, OCH₃) catalytic system; reaction conditions: 0.2 mmol titanium complex, Al:Ti = 4:1, 6 h, 60 °C, 0.8 MPa of H₂

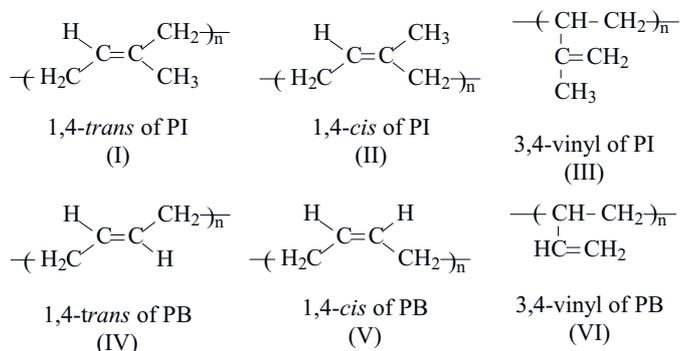
Titanium complex in catalytic system	Hydrogenation degree of C=C bonds, %
$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl})$	6.83
$\text{CpTiCl}_2(\text{OC}_6\text{H}_5)$	26.5
$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{OCH}_3)$	7.45
Cp_2TiCl_2	6.23

Hydrogenation of SIS copolymers was carried out under typical conditions using 0.2 mmol titanium com-

plexes with the ratio Al:Ti = 4:1 and the reaction was carried out for 6 h at 60 °C under H₂ pressure = 0.8 MPa. The results are presented in Table 2.

The obtained hydrogenation degree values were low (6–7 %), only for the catalytic system with complex $\text{CpTiCl}_2(\text{OC}_6\text{H}_5)$ was higher, reaching 26.5 %. These results are unexpected, since a great quantity of catalytic species should be present in the *p*-chlorophenoxy system [11]. A similar case was observed in SBS copolymers hydrogenation where the most active catalytic system was $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl})/\text{Et}_3\text{Al}$ [10].

To explain presented results in this and our previous papers [10] concerning SBS hydrogenation, all possible structures of 1,4-*trans*, 1,4-*cis* and 3,4-vinyl [formulas

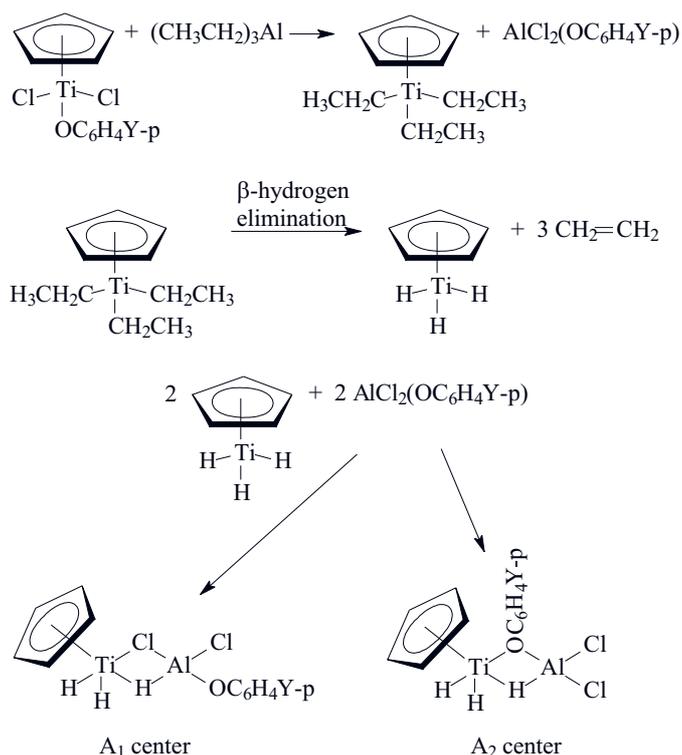


(I)–(III)], respectively, for polyisoprene (PI) blocks in SIS and 1,4-*trans*, 1,4-*cis* and 1,2-vinyl [formulas (IV)–(VI)] polybutadiene (PB) blocks in SBS, have to be taken into account.

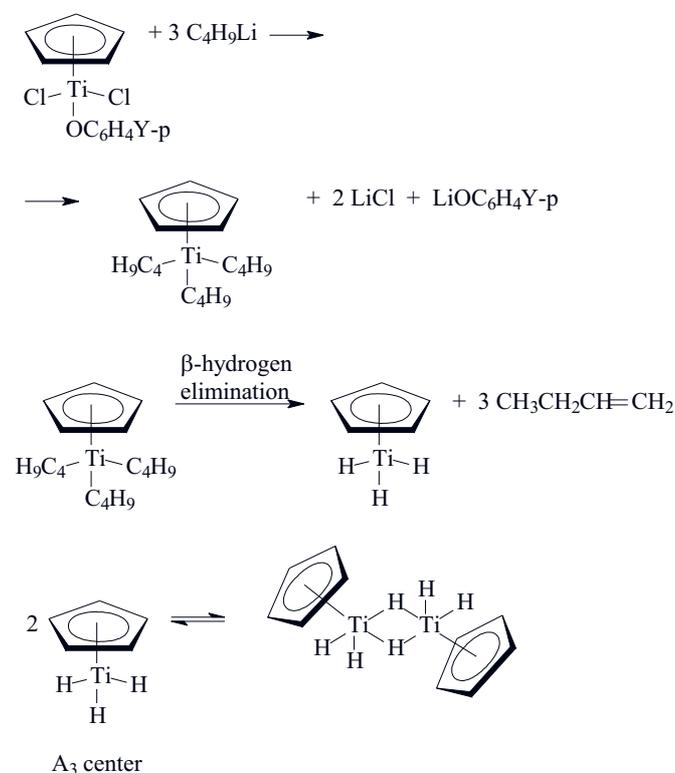
We can notice that all C=C bonds in the polyisoprene units are more sterically overcrowded. Therefore, hydrogenation of SBS copolymers runs with higher efficiency. The C=C bonds in polybutadiene should be better accessible for hydrogenation catalytic centers. In our investigations, hydrogenation of SBS copolymers in the presence of the $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-p})/\text{BuLi}$ catalytic system reached the hydrogenation degree even more than 80 % for both C=C bonds in chains and the pendant 1,2-vinyl C=C bonds [10], when hydrogenation of SIS copolymers gave at most 36 %, under the same conditions *i.e.* 50 °C, 0.5 MPa, 3 h.

Relatively low yields of the SBS and SIS hydrogenations were obtained in the presence of the catalytic systems modified with Et_3Al . It suggests better accessibility of created hydrogenation catalytic centers to the C=C bonds in the block SBS and SIS copolymers, in the case of the BuLi modified catalysts.

It is well known that reaction of alkylaluminum compounds with transition metal chlorides occurs with formation of alkyl transition metal derivatives as it is presented in Scheme A. They can transform by β -hydrogen elimination to the hydride complexes and chloroaluminum compounds as side products. They couple the hydride complexes *via* relatively stable Al-Cl-M_t bridges



Scheme A. Formation of the hydrogenation catalytic centers in the catalytic systems with Et_3Al



Scheme B. Formation of the hydrogenation catalytic centers in the catalytic systems with BuLi

(M_t — transition metal). And these complexes should be considered as hydrogenation active centers [15, 16].

In the case of changing the alkylaluminum compounds into alkyl lithium compounds, metal hydride compounds and LiCl as the side product are formed, as it can be seen in Scheme B. On the contrary to alkyl aluminum compounds, LiCl does not create complexes with hydride titanium derivatives, but separates from the reaction mixture [17]. In this case titanium hydride complexes can form dinuclear titanium complexes where the titanium ions are connected with a relatively weak dihydrogen bridge. These complexes can dissociate to monohydride titanium species, forming hydrogenation catalytically active centers [11, 18].

In the investigated catalytic systems consisting of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y-p})$ complexes excess amount of Et_3Al or BuLi ($\text{Li}:\text{Ti} = 4$ or $\text{Al}:\text{Ti} = 4$) were used to assert completely alkylation of the titanium complexes. The formation of the hydrogenation active centers is shown in Schemes A and B. A_1 and A_2 structures correspond to the Ti-Al system and A_3 structure to the Ti-Li system. The A_3 center is less bulky than A_1 and A_2 , it accesses the $\text{C}=\text{C}$ bonds in the SBS and particularly in SIS copolymers in an easier way.

The bulkiness of A_1 and A_2 centers depends on the size of phenoxy ligands. From all investigated $\text{OC}_6\text{H}_4\text{Y}$ ligands OC_6H_5 is the smallest and thanks to that the catalytic center possessing this ligand exhibits the highest efficiency. This effect in the SIS hydrogenation is stronger than the electron-donor phenoxy ligand impact. In the case of SBS hydrogenation, the electron-donor phenoxy ligand impact strongly differentiated the investigated catalysts activity.

The presence of the diblock components, which play a role of plasticizer, warrants in both cases better accessibility of catalytic centers to the $\text{C}=\text{C}$ bonds in the investigated copolymers. They separate the copolymer chains, as we mentioned above, and simplify the catalytic species attainment to the $\text{C}=\text{C}$ bonds.

CONCLUSIONS

Steric effects play the main role in SIS hydrogenation. The most significant factors are:

- the presence of SI component in SIS copolymers,
- the use of lithiumalkyl co-catalyst,
- bulkiness of phenoxy ligand in the investigated pre-catalysts.

These factors help catalyst active species to access the $\text{C}=\text{C}$ bonds in the isoprene blocks in highly efficient way.

The $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y-p})/\text{BuLi}$ and $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Y-p})/\text{Et}_3\text{Al}$ catalytic systems exhibit similar efficiency in SIS block copolymers hydrogenation as the commercial systems containing Cp_2TiCl_2 pre-catalyst, respectively.

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