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Influence of hydrogen and methane on the polymerization of styrene in the presence of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}i>p)/\text{MAO}$ catalytic system

Summary — The effect of hydrogen or methane on the course of styrene syndiotactic polymerization in the presence of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}i>p)/\text{MAO}$ catalytic system (Cp — cyclopentadienyl, MAO — methylalumoxane) was investigated. The effects of contact time and pressure on the yield, weight — average molecular weight (M_w) and molecular weight distribution MWD as well as on the syndiotacticity index of the polymers obtained were determined. It was found that prolonged contact time of methane with reaction mixture caused significant decrease in yield and slight decrease in polymer molecular weight with simultaneous increase in PS syndiotacticity index. The effect of increasing pressure of methane is similar. However, prolonged contact time and increasing pressure of hydrogen caused increasing yield and clear decrease in molecular weight of the product. The change in the mechanism of initiation of stereospecific styrene polymerization, caused by methane, was interpreted on the basis of EPR spectra analyses. The formation of monohydrogen complexes of titanium as a result of reaction with methane or catalytic system itself, or dimeric Ti complexes formed in the stage of polymer chain termination has been found.

Key words: stereospecific styrene polymerization, hemititanocene catalysts, hydrogen or methane presence, initiation mechanism, EPR investigations.

WPLYW WODORU LUB METANU NA POLIMERYZACJĘ STYRENU KATALIZOWANĄ UKŁADEM $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}i>p)/\text{MAO}$

Streszczenie — Zbadano wpływ obecności metanu lub wodoru na przebieg syndiotaktycznej polimeryzacji styrenu pod wpływem układu katalitycznego $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}i>p)/\text{MAO}$ (Cp — cyklopentadienyl, MAO — metyloaluminiumoksyd). W przypadku obydwu wprowadzanych gazów określano wpływ czasu kontaktu i ciśnienia na wydajność, wagowo średni ciężar cząsteczkowy (M_w) i jego rozkład MWD a także na współczynnik syndiotaktyczności polimerów (tabele 1—3 metan, tabele 4—5 wodór). Stwierdzono, że przedłużanie czasu kontaktu metanu z mieszaniną reakcyjną spowodowało wyraźny spadek wydajności oraz niewielkie zmniejszenie ciężaru cząsteczkowego w połączeniu ze wzrostem współczynnika syndiotaktyczności PS. Podobny jest też wpływ podwyższenia ciśnienia metanu. Przedłużanie czasu obecności wodoru i wzrost jego ciśnienia w układzie wywołuje zwiększenie wydajności i znaczne zmniejszenie ciężaru cząsteczkowego produktu. Spowodowaną wprowadzeniem metanu zmianę mechanizmu inicjowania stereospecyficznego polimeryzacji styrenu wyjaśniono na podstawie analizy widm EPR (rys. 1). Stwierdzono przy tym powstawanie monowodorowych kompleksów tytanu w wyniku reakcji z metanem — bądź bezpośrednio samego układu katalitycznego, bądź też dimerycznych kompleksów Ti tworzących się na etapie terminacji łańcucha polimeru.

Słowa kluczowe: stereospecyficzna polimeryzacja styrenu, katalizatory hemitytanocenowe, obecność wodoru i metanu, mechanizm inicjowania, badania EPR.

Changes of the Ziegler—Natta catalysts' activity and molecular weights of polymers obtained in their presence caused by hydrogen, are widely described in a literature and also widely applied in the polymer industry [1, 2]. Hydrogen in this case cuts off the polymer chain from a metal in a catalytic center and forms a hy-

drogen ended polymer and a new metal-hydrogen bond which becomes the new, very active, polymer catalytic center. One can control the molecular weight of polymer produced by introducing hydrogen to the reaction mixture at the specified moment.

These effects are also described for styrene polymerization in the presence of hemititanocene catalysts [3].

The same role of methane was described by E. A. Grigoryan [4] when $\text{TiCl}_4/\text{Et}_2\text{AlCl}$ catalyst was applied in propylene polymerization. He observed an increase in

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the polypropylene yield accompanied with a drop in molecular weight of polypropylene obtained, proportionally to methane pressure applied in the reaction. In this case, chain transfer to a methane molecule was postulated, as well as a formation of the metal-hydrogen or metal-methyl bonds (new polymerization sites) and hydrogen or methyl ended polypropylenes. This process runs slower when hydrogen is used instead of methane and when $\text{TiCl}_3/\text{Et}_2\text{Al}$ [here titanium(III) is present] is applied instead of titanium(IV) salt.

To find whether the same effects of methane on styrene polymerization in the presence of half sandwich titanocene catalytic system: $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}$, studied by us, are observed, we carried out the reactions with methane passing through the reaction mixture for different time under normal pressure and also under methane pressure equal 2 atm ($ca\ 2 \cdot 10^{-1}$ MPa). To compare the results obtained with the influence of hydrogen under the same conditions, the reactions were carried out in the presence of this reagent.

In order to observe if methane reacts with the titanium ions in the catalytic systems studied, they were contacted with methane before addition of styrene. Next, the investigations by EPR method are applied.

The results obtained are demonstrated and discussed in this paper.

EXPERIMENTAL

Materials

- Styrene (FC Dwory, pure) was distilled from CaH_2 .
- MAO (methylaluminoxane) as 10 % solution in toluene in (Witco) was used directly.
- $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)$ was obtained as previously described [5].
- Chain transfer agents: methane (Aldrich, >99.9 %) and hydrogen (Polgas, >99.9 %) were used.
- Solvent-toluene (POChem — pure) was distilled from Na/K alloy directly prior to use.

Polymerization

All operations in the catalyst preparation procedures and in styrene polymerization were conducted in moistureless and oxygen-free conditions with the use of argon-vacuum system and the Schlenk technique.

The styrene polymerization reactions under normal pressure were carried out in Schlenk tubes using a styrene solution in toluene at 20 °C for 1 h in the following way.

To the 30 % styrene solution in toluene, MAO was added and the mixture was stirred for 0.5 h at room temperature under argon atmosphere. After this time argon was replaced by methane or hydrogen. The gas was next passed through the mixture. A catalyst $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)$ (0.01 mmol) in toluene was added

to start the reaction. The styrene:Al:Ti molar ratios equalled 6000:300:1. Methane or hydrogen was passed through the reaction mixture in the ratio of 120 ml/min for all time of reaction running.

The styrene polymerization reactions under elevated pressure using desired pressure of methane or hydrogen, were carried out in a 600-ml steel autoclave equipped with a stirrer. The reactions were realized in 400 ml of toluene at 40 °C, using 0.01 mmol of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)$ activated with MAO in the ratio: Al:Ti = 300:1; the ratio styrene:Ti = 8000:1 (styrene concentration = 30 %). The order of the substrate addition to the autoclave was the same as for the polymerization under normal pressure.

All reaction were stopped by adding of 5 ml of methanol, then 5 ml of 2 % HCl in methanol into the reaction mixture. The polymers obtained were filtered off and dried to a constant weight under vacuum, produced by the rotary oil pump, at 90 °C.

Testing methods

— The syndiotacticity indexes of the polystyrenes obtained were established as a percentage weight of the polymer fraction insoluble in boiling acetone (6 h under reflux).

— Average molecular weights and their distributions (MWD) were determined using a "Waters GPC-150 CV" apparatus (polystyrene standards).

— The polarographic analyses ("Radelkis" apparatus) were performed for $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}$ samples in toluene (amount of Ti > 1 mmol, Al/Ti ratio 300:1) at room temperature. Salts of iron were used to titration of titanium ions at different oxidation states. Reduced iron ion quantities were determined [6, 7].

— Reaction of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}$ system with hydrogen was carried out under normal pressure for 1 h giving the following composition of titanium ions: Ti(II) = 10 %; Ti(III) = 80 %; Ti(IV) = 10 %, determined by the polarographic method.

— The EPR spectra were recorded for samples containing 1 ppm of Ti and 300 ppm of Al at room temperature, at X band with modulation 0.16 mT by a "Bruker" apparatus. To record the samples after contact with methane or deuterated methane (Aldrich), these gases were passed through the catalyst solutions or the reaction mixtures placed in EPR tubes, just before the measurements.

RESULTS

Polymerization reactions

Presence of methane

Assuming very fast reaction between methane and titanium ions in the investigated catalytic system, we carried out the styrene polymerization reaction under

normal pressure, with methane passing through the reaction mixture for time from 0 to 120 s and further by one hour. The results of these reactions are presented in Table 1 and 2.

Table 1. Results of styrene polymerizations under normal pressure in the presence of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}i{p})/\text{MAO}$ — contact time with methane 0—120 s^{a)}

Contact time with methane	s	0	15	30	45	60	120
Yield	%	65.4	68.1	64.3	64.8	64.8	64.5
$\overline{M}_w \cdot 10^{-3}$	—	117	115	110	120	110	118
MWD	—	3.1	2.9	3.4	3.9	3.3	3.9
Syndiotacticity index	%	88	80	89	85	83	87

^{a)} 0.01 mmol $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}i{p})/\text{MAO}$; Al/Ti = 300; styrene/Ti = 6000.

Table 2. Results of styrene polymerizations under normal pressure in the presence of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}i{p})/\text{MAO}$ — contact time with methane 0—50 min

Contact time with methane	min	0	10	20	30	40	50
Yield	%	65.4	65.2	56.3	41.8	44.6	48.4
$\overline{M}_w \cdot 10^{-3}$	—	113	116	108	119	117	120
MWD	—	3.3	3.7	3.0	3.1	3.7	3.1
Syndiotacticity index	%	87	91	89	92	90	91

No significant differences between the results obtained in absence or presence of methane were recorded. About 65 % conversion of styrene was obtained. The products syndiotactic polystyrenes — were characterized by the weight — average molecular weights (\overline{M}_w) which varied from 110 000 to 120 000, the MWD values which changed from 2.9 to 3.9 and syndiotacticity indexes which were higher than 80 % but did not reach 90 %.

When reactions were carried out with longer contact with methane, it means when methane was passing for 10 to 50 min and after 1 h of the reaction running the reactions were stopped and gradual change of the styrene conversion was observed (each time of sampling concerned separate polymerization process; all of these processes were finished after 60 min time). The conversion was changed from 65.4 % for the reaction in absence of methane to 48.4 % after 50 min of the contact with methane (Table 2).

A little increase in the weight average molecular weights and not significant changes of MWD values of polymers obtained were observed when time of contact of the catalysts with methane was longer. A slightly higher syndiotacticity indexes were reached with comparison to the polymers obtained when time of the methane contact was shorter.

The reactions carried out in an autoclave under normal or higher methane pressure (1 or 2 atm) resulted in a drastic decrease in the styrene conversion, which collapsed from 30.8 % for normal pressure to 3.3 % when the methane pressure was equal 2 atm. A drop in (\overline{M}_w)

and MWD value as well as an increase in syndiotacticity of the polymers obtained were also caused by an increase in the methane pressure (Table 3).

Table 3. Effect of methane pressure on styrene polymerization in the presence of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}i{p})/\text{MAO}$

Methane pressure	atm	0	2
Yield	%	30.8	3.3
$\overline{M}_w \cdot 10^{-3}$	—	124	115
MWD	—	3.9	3.1
Syndiotacticity index	%	79	91

Presence of hydrogen

A gradual increase in the styrene conversion from 66.4 to 81.8 % was obtained when the polymerization was carried out in the absence of hydrogen, or when hydrogen was passing through the reaction mixture under normal pressure for up to 50 min, and the reaction lasted 1 h. Simultaneously, the average molecular weights of obtained polymers dropped from 118 000 to 74 000 and MWD values increased from 3.1 up to 4.6. Their syndiotacticity indexes did not change much and varied about 85 % (Table 4).

Table 4. Results of styrene polymerizations under normal pressure in the presence of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}i{p})/\text{MAO}$ — contact time with hydrogen 0—50 min

Contact time with hydrogen	min	0	10	20	30	40	50
Yield	%	66.4	67.4	69.1	73.8	77.3	81.1
$\overline{M}_w \cdot 10^{-3}$	—	118	92	93	84	79	74
MWD	—	3.1	3.4	4.1	3.8	4.3	4.6
Syndiotacticity index	%	87	86	85	86	88	86

Table 5. Effect of hydrogen pressure on styrene polymerization in the presence of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}i{p})/\text{MAO}$

Hydrogen pressure	atm	0	0.5	1.0	2.0
Yield	%	30.8	50.3	55.6	60.1
$\overline{M}_w \cdot 10^{-3}$	—	124	89	81	77
MWD	—	3.9	4.5	4.4	4.9
Syndiotacticity index	%	79	85	83	83

An increase in hydrogen concentration in the reaction mixture reached by increasing hydrogen pressure from 0 to 2 atm during the reaction running, increased the styrene conversion from 30.8 to 60.1 %, it means twofold. It was accompanied by a decrease in the molecular weights from 124 000 to 77 000 and syndiotacticity of the products as well as an increase in MWD value (Table 5).

EPR investigations

The reaction of studied half sandwich titanocene $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}i{p})$ with MAO leads to a mixture of

complexes containing titanium(IV), titanium(III) and titanium(II) ions [6], it means the same mixture which was obtained for $\text{CpTiCl}_2(\text{OC}_6\text{H}_9)_3/\text{MAO}$ system what has been described by Chien *et al.* [7]. The structure of active center in syndiotactic of styrene polymerization and the oxidation state of titanium in them, are still discussed. Predominantly, CpTi[III]R^+ and CpTi[III]H^+ cations (where R = methyl or sPS chain) are believed to be active catalytic centers of this reaction. These cations are stabilized by the $\text{CH}_3[\text{MAO}]^-$ anions [3, 8, 9].

Thus, we also assumed that these species are formed in the investigated system. The observed inhibiting influence of methane on the studied polymerization suggests, that these cations should interact or even react with methane molecules. The products of an interaction or reaction, if do not change the titanium oxidation state, should be visible in the EPR spectra. Therefore we re-

corded the EPR spectra of the following systems: $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)$ activated with MAO [$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}$] and this way obtained catalytic system in contact with CH_4 or CD_4 [$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}/\text{CH}_4$] and [$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}/\text{CD}_4$], respectively, the system after completion of the polymerization [$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}/\text{styrene}$] and the system after completion of the polymerization in contact with CH_4 [$\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{styrene}/\text{CH}_4$]. The spectra are presented in Fig. 1.

The EPR spectrum of the system $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}$ exhibits the well-known doublet — $g = 1.988$ with the hyperfine coefficient $^{\text{H}}a = 6.8$ Gs (Fig. 1a), which is assigned to $(\text{CpTi[III]H})^+$ cation, where only one titanium — hydrogen bond is present [10]. This doublet, although less intensive, is also visible in the spectrum of

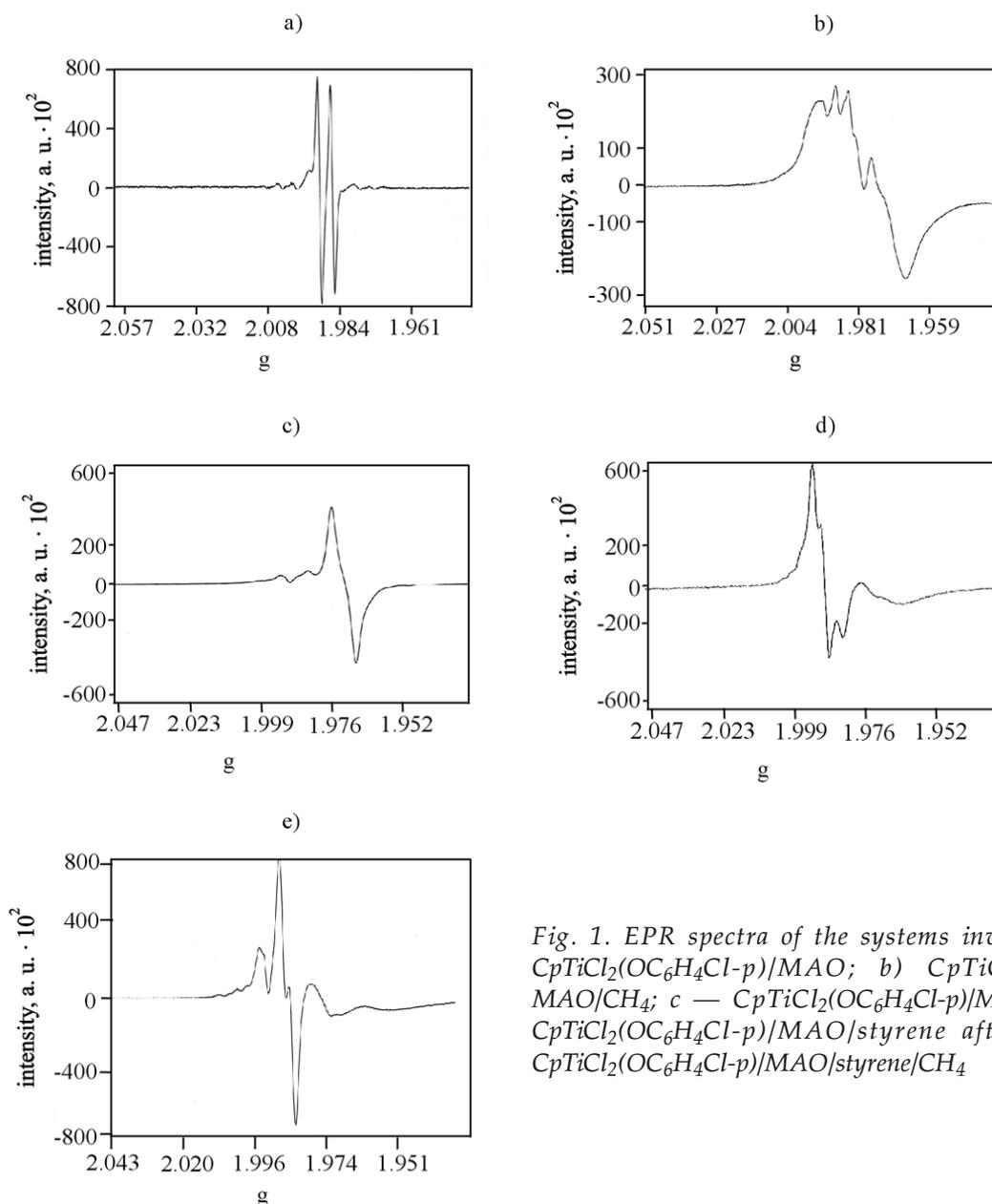


Fig. 1. EPR spectra of the systems investigated: a — $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}$; b — $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}/\text{CH}_4$; c — $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}/\text{CD}_4$; d — $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}/\text{styrene}$ after 24 h; e — $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}/\text{styrene}/\text{CH}_4$

the system $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}/\text{CH}_4$ (Fig. 1b). It is located on broad line derived probably from titanium(III) complexes being so close each other that the spin-spin interaction widens their spectrum [11]. Beside the mentioned doublet, one can see the other doublet shifted relatively to the higher field, located on the slope of the broad signal. It is $^{\text{H}}a$ value equal 8.5 Gs and $g = 1.979$. These doublets disappeared in the spectrum of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}/\text{CD}_4$ system and only irregular singlet with $g_0 = 1.976$ and relatively small two wide signals in the lower field are present (Fig. 1c). It proves that hydride ligands responsible for the recorded doublets are now replaced by D or CD_3 . The same phenomenon was described by F. Gauvin *et al.* [12] for cyclopentadienyl titanium complexes investigated by them.

The EPR spectrum of the investigated catalytic system, taken when the polymerization is completed, shows the described earlier [6] triplet with the g value = 1.994 and $^{\text{H}}a = 7$ Gs, which is assigned to a titanium dimeric complex where titanium ions are bonded by the μ^1, μ^1 dihydridobridge (Fig. 1d). When methane was added to this complex, the triplet signal disappeared, but a new EPR signal occurred. It is shifted to the higher field and consists of a broad signal with a marked doublet with $g_0 = 1.982$ and $^{\text{H}}a = 5.4$ Gs (Fig. 1e).

DISCUSSION

Influence of methane on investigated catalytic system

An influence of methane on the yield increase and a decrease in molecular weights of polypropylenes obtained in the presence of $\text{TiCl}_4/\text{Et}_2\text{AlCl}$, described by Grigoryan and coworkers [4] was related, by the authors, to methylation of the titanium-carbon bond from the end of growing polymer chain according to the reaction (1).

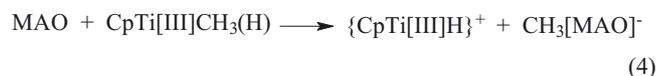
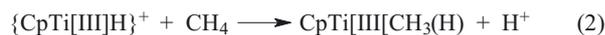


This way, interrupted propagation of the polymer chain results in the chain shortening, and the new Ti-CH_3 bond, well known olefin propagation center, initiates a new polymer chain growth. The reaction of propagation, in its first step is usually very fast, and thanks to that, the mentioned higher polypropylene yield could be observed.

In the case of the investigated $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-}p)/\text{MAO}$ catalytic system, this effect is not the same at all. A decrease in M_w and MWD values of syndiotactic polystyrenes obtained in the reaction carried out when concentration of methane was relatively high — it means under 2 atm pressure of methane (Table 3) — can suggest that the methylation reaction also runs now, too. However, the observed drop in the catalytic system activity

when methane concentration in the reaction mixture was relatively high, suggests that this reaction does not occur, what probably happens, methane reacts with catalytic active titanium species deactivating them reversibly. If this deactivation was irreversible, sPS yield drop should be seen even at relatively low concentration of methane in the reaction mixture.

The EPR spectra of the investigated systems obtained before and after reaction with methane or deuterated methane supported this conclusion. Moreover, it proved that in the system after contact with methane, a new titanium species are formed, in which the hydride ligand bonds to one titanium(III) ion. It causes the change of its hyperfine factor $^{\text{H}}a$ and shift of g factor to lower values in the spectrum, in comparison with the values for $(\text{CpTi[III]H})^+$ cation. These changes indicate a presence of an additional ligand among the new species, which is probably methyl. It is known that a substitution of one hydride ligand by alkyl in polyhydridotitanium(III) complexes decreases their g factors in the EPR spectra [13]. It suggests that the following reactions take place in our system:



$(\text{CpTi[III]H})^+$ cation reacts with methane forming proton and the new neutral cyclopentadienyl titanium(III) complex with hydride and methyl ligands. Liberated proton reacts immediately with the counter anion $\text{CH}_3[\text{MAO}]^-$ giving as the products: methane which returns to reaction (2) and MAO which as specific Lewis acid [14], restores $(\text{CpTi[III]H})^+$ cation and the counter anion $\text{CH}_3[\text{MAO}]^-$ in the reaction with the complex (1). The restored cations $(\text{CpTi[III]H})^+$ either initiate polymerization of styrene when its concentration in the reaction mixture is much higher than concentration of methane, or comes predominantly into the reaction with methane when its concentration is relatively higher. In this situation styrene fails competition in access to the polymerization active center and can not be polymerized.

When MAO activates half sandwich titanocene catalysts, the completion of styrene polymerization occurs by β — hydrogen elimination from the end of the polystyrene chain. This way of the polystyrene chain termination is also observed in our case, the forming vinyl end is observed in ^1H NMR spectra of polystyrenes obtained [3, 6]. This polymer chain termination restores $(\text{CpTi[III]H})^+$ cations, which initiate the next polymer chain growth.

When styrene polymerization was completed and the reaction mixture solidified, the EPR spectrum of the

studied system exhibited not the mentioned doublet but a triplet, which indicated a presence of dimeric cyclopentadienyl titanium(III) where titanium ions were bonded with μ^1, μ^1 dihydridobridge [6]. It means that a stiff matrix, formed by polystyrene at the end of the reaction, forces cations $(\text{CpTi[III]H})^+$ to dimerize to the mentioned dimeric complexes. These complexes, as the EPR proves, react also with methane to new complexes in which only one titanium-H bond is present. The g value of these complexes close to the values of $\text{CpTi[III]CH}_3(\text{H})$ species suggests that these complexes have the same structure. The differences between 1a and g factors of these complexes result surely from different interactions of the toluene solvent and the stiff polystyrene matrix with them.

And again this way obtained $\text{CpTi[III]CH}_3(\text{H})$ species in order to form active centers must react with MAO, according to the reaction (4) what inhibits the investigated system in styrene polymerization.

Influence of hydrogen on investigated catalytic system

The observed enhancement of the activity of the investigated system in syndiotactic styrene polymerization, particularly when hydrogen concentration in the reaction mixture is high, it means under elevated hydrogen pressure, as well as a simultaneous decrease in the weight — average molecular weights of polymers obtained, are in full accordance with literature data mentioned above [3].

This phenomenon can be explained, of course, by faster polymer chain termination affected by hydrogen and new catalytic active center formation, which was mentioned before.

But it is reasonable to consider also the following effect:

— Catalytic activity in syndiotactic styrene polymerization is related most often to half sandwich titanocenes containing titanium(III) ions.

— The polarographic studies of the investigated system obtained under argon atmosphere, showed that the titanium(IV), titanium(III) and titanium(II) ions were present in the system in the following quantities: 35, 55 and 10 %, respectively [5], what explained the system activity in the syndiotactic styrene polymerization.

A hydrogenation of titanocene complexes containing titanium(IV) ions, indicates that those with chlorine atoms as ligands, were resistant to the reduction while those with alkyl ligands only were easily reduced even

to titanium(II) compounds [15]. This reduction by hydrogen occurred in our system resulting in an increase in amount of titanium(III) complexes from 55 % to 80 % at the expense of titanium(IV) ones.

Thus an increase in the amount of titanium(III) complexes in the system as the catalytic centers can result also in enhanced yields of syndiotactic polystyrenes obtained. Formation of catalytic active centers in the syndiotactic styrene polymerization proceeds through the reactions presented in [6, 16].

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