The catalytic behavior of Pt- and Rh-containing polymers derived from polystyrene-polybutadiene block copolymers in hydrosilylation

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Summary

The novel Pt- and Rh-containing polymers based on polystyrene-polybutadiene block copolymers were studied in hydrosilylation of three systems of reagents: styrene/triethylsilane, 1-hexene/dimethylchlorosilane, and cyclohexanone/triethylsilane. All polymers containing Pt and Rh complexes were found to display some catalytic effect whose effectiveness for the same system of reagents is dependent on the nature of the polymeric ligand. On the other hand, the reagent nature influences even more strongly the catalytic properties of polymers. No side products of hydrosilylation was observed with Rh-containing polymer catalysts in cyclohexanone/triethylsilane system.

Introduction

Organometallic polymers and polymeric materials with metal nanoparticles can be considered as potential catalysts for many organic reactions because they might combine the advantages of both homogeneous and heterogeneous catalysts: high activity and selectivity which are related to homogeneous catalysts with processability which is inherent to heterogeneous ones [1-3]. Recently we have described the synthesis of Pd-, Rh-, and Pt-containing polymers derived from polystyrene-polybutadiene block copolymers of various structures [4]. It was found that the formation of metal complexes with macromolecule double bonds proceeds both intramolecularly and intermolecularly. The comparison of complex formation peculiarities of Pd-, Rh-, and Pt-containing polymers derived from triblock polystyrene-polybutadiene-polystyrene copolymer (SBS, Kraton) with 72 wt.-% of PB and diblock PS-PB with 15 wt.-% of PB showed that SBS with large PB block forms crosslinked polymers, while short PB block in PS-PB allows to maintain the solubility of organometallic polymers despite the intermolecular complexation. Such solubility was found to be provided by micellization in Pd-, Pt-, and Rh-containing polymers derived from PS-PB. In the present paper we report on catalytic properties of a number of Pt- and Rh-containing polymers derived from SBS, PS-PB, and PB in hydrosilylation of alkenes and ketones. Hydrosilylation of carbon-carbon multiple bonds discovered in the late 1940s has been one of the most important laboratory and industrial methods of the silicon-carbon bond formation [5,6]. The reaction is especially valuable for the attachment of organic radicals containing reactive functional groups to

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silicon, because such compounds cannot often be prepared by simple organometallic procedures.

Experimental

Materials

Triblock polystyrene-polybutadiene (SBS) (Kraton D1102, containing about 72 wt.-% of polybutadiene which consists of 91% of 1,4-units and 9% of 1,2 units, $[\eta] = 0.28$ dL/g (toluene, 20°C), received from Shell Chemical Co.). Polybutadiene (PB-1,2) prepared by anionic polymerization (University of Mainz, Germany) and containing 86% of 1,2-units, $M_n = 130000$. Polybutadiene (PB-1,4) prepared in VNIISK, Voronezh, Russia and containing 34.1% of 1,4-trans units, 56.8% of 1,4-cis units and 9.1% of 1,2 units; $M_n = 150000$. Diblock polystyrene-polybutadiene (PS-PB) prepared by anionic polymerization in Max-Plank-Institute for Colloid and Interface Research, Teltow, Germany, and containing 15 wt.-% of PB with 89% of 1,2-units; $M_n = 28570$. Zeise salt was synthesized according to ref. [7]. Other reagents were obtained commercially and used without further purification.

Hydrosilanes and cyclohexanone were received from Merck and used as received. Alkenes were purified by distillation under reduced pressure and preserved in argon in refrigerator. Benzene and toluene were purified by distillation under Na, THF was distilled under $LiAlH_4$.

2-Phenylethylsilane (containing 5% of 1-phenylethyltriethylsilane) was synthesized by hydrosilylation of styrene with triethylsilane with use of $H_2PtCl_6 \cdot 6H_2O$ as catalyst and molar ratio alkene:silane:catalyst=$1.1:1:1.5 \cdot 10^{-4}$. The yield of 2-phenylethylsilane at 30°C for 4 hours was 82% (b.p.-127-129°C/10 Torr). *n*-Hexyldimethylchlorosilane was prepared by hydrosilylation of 1-hexene with dimethylchlorosilane in the presence of $H_2PtCl_6 \cdot 6H_2O$ with the same ratio of reagents. The yield of *n*-hexyldimethylchlorosilane at 20°C for 3 hours was 96% (b.p. - 76°C/20 Torr).

Wilkinson complex $RhCl(PPh_3)_3$ was synthesized by method described in ref. [8]. Triethylsiloxycyclohexane for calibration was received according to ref. [9].

Synthesis of metal-containing polymers

The Pt-containing polymers were synthesized by the interaction of a polymer double bonds with Zeise salt. The reaction procedure is described in ref. [4]. Synthesis of Rh-containing polymers derived from PS-PB and SBS was carried out by methods described elsewhere [10]. In general, synthesis of Rh- and Pt-containing polymers was carried out as described below.

The polymer sample was placed into a Schlenk tube equipped with a Teflon stirring bar, evacuated for 15 minutes and filled with argon.The solvent (toluene) was added in argon counterflow. After dissolution of the polymer, the solution was degassed three times and the Schlenk tube filled with argon. Metal compounds were added in argon counterflow. After interaction with metal compounds, Rh- and Pt-containing PS-PB were precipitated with methanol, washed with methanol several times and dried in a vacuum-dessicator. The samples derived from SBS were precipitated with ethanol, washed with methanol and dried in a vacuum-dessicator. Polymer samples derived from PB-1,2 and PB-1,4 were precipitated with a mixture of methanol/acetone(4/1 vol.) and

then treated similarly to other polymers. Rh-containing polymers derived from RhCl$_3$ were additionally treated with methanol in a Sohzxlet extractor for two days for purification from RhCl$_3$ traces. Pt-containing polymers were washed with H$_2$O after the isolation procedure, for removing of formed KCl. The elemental analysis data on metal are given in Tables 1-3. The samples PS-PB-Rh-1 and SBS-Rh-1 were synthesized by interaction with RhCl$_3$. The PS-PB-Rh-2 and SBS-Rh-2 were prepared from [RhCl(CO)$_2$]$_2$.

Hydrosilylation procedure

Hydrosilylation was carried out in gas-sealed system consisting of a double-jacketed glass reactor containing tubes for Ar inlet and outlet, outlet for taking the probes (sealed by rubber septum) and stirring bar. The temperature was maintained and controlled by a thermostated bath. In a typical experiment, the system containing catalyst was washed with Ar and then was charged with cyclohexanone and decane (internal standard) in an Ar counterflow. Then the reaction mixture was kept for 15 minutes at room temperature and 15-20 minutes at the reaction temperature in a sealed system. After that the alkene and then the hydrosilane were injected by syringes. H$_2$PtCl$_6$·6H$_2$O was used as a 0.03 M solution in THF.
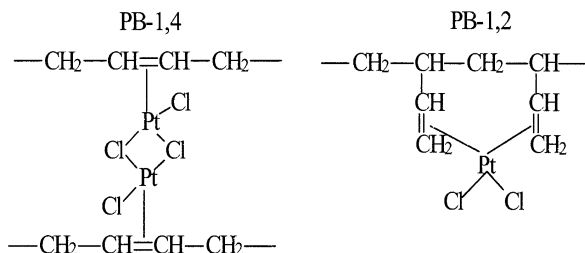
The samples withdrawal was carried out by microsyringe through a rubber septum. Identification and quantitative analysis of reaction products was done by capillary gas chromatography (quartz, ORIBOND OV-1, 25 m) with use of authentic samples. As internal standard decane was used.

Results and Discussion

Among the variety of catalysts which promote the addition of hydrosilanes to carbon-carbon multiple bonds, chloroplatinic acid has been most commonly used [6]. At the same time, it is known that olefin complexes of VIII group transition metals have extremely high activity [11]. Because of this, our research was focused on the study of the activity and selectivity of polymers containing Pt and Rh olefin complexes and on clarifying of the influence of the polymeric ligand structure on the catalytic properties in hydrosilylation.

*Structure of Pt- and Rh-containing polymers*

In our previous paper [4] we have described the synthesis of Pt-containing polymers having a polybutadiene block. It was found that in the case of PB (both containing mainly 1,2- or 1,4 units) or block copolymer (SBS) having the large PB block (72 wt.-%) with 1,4-units, polymer networks are formed due to complexation. As this takes place, different kinds of Pt complexes are formed in PB-1,4 and PB-1,2 as confirmed by far IR spectroscopy. As seen from structures presented on the left, for PB-1,4 units complexes between different macromolecules

(or different parts of one macromolecule) are formed, while for PB-1,2, double bonds located in neighboring side groups can be preferable in complexation. On the other hand, in PB-1,2 crosslinking was observed already in reaction solution that reveals the intermolecular complexation. As a result, such polymers are only swellable in organic solvents. On the other hand, diblock PS-PB containing short PB block (15 wt.-%) form soluble polymers due to micellization of PB block copolymers. The evidences of micelle formation are given in ref. [4].

The Rh-containing block copolymers behave in a similar fashion: polymers derived from PS-PB and $RhCl_3$ or $[RhCl(CO)_2]_2$ maintain the solubility, while SBS and PB derivatives provide the networks formation. The structures of Rh complexes based on $RhCl_3$ (left) and $[RhCl(CO)_2]_2$ (right) are shown below:
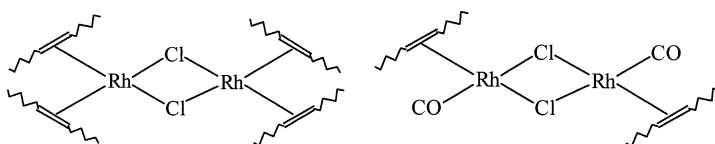
Hydrosilylation of Alkenes

The results of styrene and 1-hexene hydrosilylation with polymer catalysts and with $H_2PtCl_6 \cdot 6H_2O$ for comparison are presented in the Tables 1 and 2. The yield dependencies of hydrosilylation products on time for Pt catalysts are shown in Figures 1 and 2.

Hydrosilylation was carried out in benzene because all polymers were either swellable in this solvent or even became soluble (in most cases) after the addition of hydrosilane, though SBS-Pt, PB-1,2-Pt, and PB-1,4-Pt were only swellable in toluene after synthesis. Replacement of benzene with THF only slightly influenced the ratio of activities of $H_2PtCl_6 \cdot 6H_2O$ and polymeric catalyst (Table 1).

Table 1. Hydrosilylation in the system styrene/triethylsilane[a]

run	catalyst	metal content, wt.-%	T°C	TOF mol/min g-atom M	α-isomer amount, %	notes
1	$H_2PtCl_6 \cdot 6H_2O$		30	13.1	5.6	soluble[b]
2	PS-PB-Pt	14.77	-"-	5.2	4.8	soluble
3	SBS-Pt	16.73	-"-	25.9	5.4	soluble
4	SBS-Pt	-"-	-"-	50.6	5.3	soluble, without solvent
5	PB-1,2-Pt	23.27	-"-	6.5	5.3	swellable
6	PB-1,4-Pt	27.11	-"-	7.4	5.0	swellable
7	PS-PB-Rh-1	7.39	50	2.7	48.0	soluble
8	PS-PB-Rh-2	4.20	-"-	1.3	42.5	soluble
9	$H_2PtCl_6 \cdot 6H_2O$		30	3.1	3.6	soluble, THF
10	PS-PB-Pt	14.77	-"-	1.5	3.6	soluble, THF

[a]Molar ratio silane:1-alkene:catalyst=1:1:5·10^{-4}; TOF corresponds to maximum rate of 1 and 2- phenylethylsilanes formation; the solvent was benzene except in some cases

which are noted; for SBS-Pt the induction period is 15 min, while for other catalysts it was not observed.

[b] Here and in other tables it is indicated whether a catalyst is soluble or swellable in reaction mixture.

As may be seen from Figures 1 and 2, all polymers containing Pt and Rh display some catalytic effect. The value of this catalytic effect for the same system of reagents is dependent on the nature of polymeric ligand, though such an influence can be clearly explained by the difference in solubility of polymers or by variance in a degree of complexation. At the same time, in different systems of reagents the catalytic properties of organometallic polymers are completely different.

Table 2. Hydrosilylation in the system 1-hexene/dimethylchlorosilane[a].

run	catalyst	metal content, wt. %	T°C	TOF mol/min g-atom M	α-isomer amount, %	notes
11	$H_2PtCl_6 \cdot 6H_2O$		20	11.9	0	soluble[b]
12	PS-PB-Pt	14.77	-"-	2.7	0	soluble
13	SBS-Pt	16.73	-"-	2.1	0	swellable
14	PB-1,2-Pt	23.27	-"-	3.6	0	swellable
15	PB-1,4-Pt	27.11	-"-	5.8	0	soluble
16	PS-PB-Rh-1	7.39	25	0.6	12.0	soluble
17	PS-PB-Rh-2	4.20	-"-	0.3	17.0	soluble

[a]Molar ratio silane:1-alkene:catalyst=1:1:5·10⁻⁴; TOF corresponds to a maximum rate of n-hexyldimethylchlorosilane formation; the solvent was benzene; the induction period of 200 min was observed solely for $H_2PtCl_6 \cdot 6H_2O$.
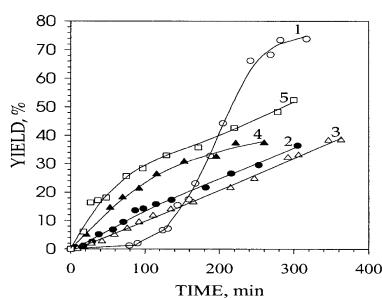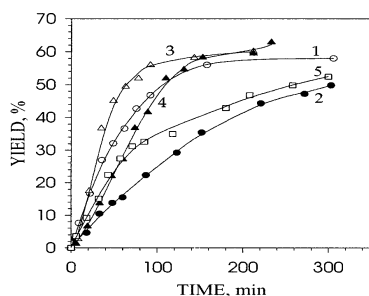

Fig. 1 (left). The yield dependence of 1- and 2-phenylethyltriethylsilane on time with the following catalysts: $H_2PtCl_6 \cdot 6H_2O$ (1); PS-PB-Pt (2); SBS-Pt (3); PB-1,2-Pt (4); PB-1,4-Pt (5).

Fig. 2 (right). The yield dependencies of n-hexyldimethylchlorosilane on time with the following catalysts: $H_2PtCl_6 \cdot 6H_2O$ (1); PS-PB-Pt (2); SBS-Pt (3); PB-1,2-Pt (4); PB-1,4-Pt (5).

Among other things, SBS-Pt (Table 1, run 3) as a system of styrene/triethylsilane (I) seemed to be more active than $H_2PtCl_6 \cdot 6H_2O$ almost by a factor of 2. Alternatively, in the

system of 1-hexene/dimethylchlorosilane (II) (Table 2, run 13) the activity of SBS-Pt turned out to be low. As this takes place, in system I this catalyst becomes soluble after the injection of silane in a few minutes, but in the system II the same catalyst was only swellable. We suggest that dissolution of SBS-Pt in reagents I has a chemical nature, that is the decomposition of intermolecular π-bonds formed by Pt complexes. Those facts show that complexes immobilized on polymers react with hydrosilylation substrates forming intermediate species.

As Figure 1 indicates, the yield of the target product in benzene does not exceed 60%. The limiting value of yield was found to depend on the amount of solvent: the higher the concentration of the reagents, the higher the limiting value of the yield. In the absence of a solvent the yield reached almost 100%. So, even the presence of such non-coordinating solvent as benzene diminishes the rate of hydrosilylation.

The activity of SBS-Pt in the styrene/triethylsilane system without solvent exhibit the best result (Table 1, run 4, TOF=50.6 mol/min g-atom Pt, 30°C). It is close to the activity of the low molecular bis(olefin)complex cis-PtC1$_2$(PhCH=CH$_2$)$_2$. The magnitude of TOF for which calculated according to the data of ref. [11], is about 28 mol/min g-atom Pt at room temperature for the same reactants.

Both reactant systems studied did not display the induction period in the hydrosilylation though with H$_2$PtCl$_6$·6H$_2$O for system II the induction period was about 200 min (Figure 2). It is speculated that the presence of an induction period can be explained by the reduction of Pt(IV) to Pt(II) and the formation of π-olefin complexes with Pt(II). Just these π-olefin complexes are the active species in hydrosilylation [12]. The absence of an induction period for Pt-containing polymers with π-olefin Pt complexes is the evidence for such a supposition. On the other hand, the solubilization of crosslinked polymers derived from SBS and PB and lack of strong differences in catalytic activity among various polymers rather testify that catalytic species are formed during the reaction. In some cases in system II we also observed the reverse effect when activity decreased with progress of time. We suppose that the fact observed is related to the decomposition of more active polymer π-olefin Pt complexes and the formation of complexes with 1-hexene as a ligand.

Rh catalysts displayed a low activity and particularly low selectivity. Besides, in the reactants system I, in addition to a notable amount of α-addition product, the formation probably of β-(triethylsilyl)-trans-styrene [13] and ethylbenzene was also observed. By GC the amount of β-adduct was nearly the same as the quantity of α-adduct in the case of PS-PB-Rh-1 and twice as much for the PS-PB-Rh-2.

*Hydrosilylation of Carbonyl Compounds*

The catalytic hydrosilylation of carbonyl compounds is a rather new and unique way of reduction of aldehydes and ketones because the resulting silyl ethers can be easily hydrolyzed. The fast development of this method became possible after the discovery of Wilkinson's catalyst: RhCl(PPh3)3 [14]. Later, the number of compounds which can be catalysts for such reactions constantly grew [15].

The results of the hydrosilylation of cyclohexene by triethylsilane with polymer catalysts are presented in Table 3. In this case, the solubilization of crosslinked polymers (SBS-Rh-1 and SBS-Rh-2) was not observed. One can see that a number of catalysts synthesized (runs 18, 19, 21) have a higher catalytic activity than Wilkinson complex. We suppose that the cause of the higher activity of polymeric π-olefin complexes lies in

less σ-donor and more π-acceptor ability of olefin ligands as compared to phosphine ones [16]. A similar behavior was also observed for olefinic complexes of Pt which catalytic activity in hydrosilylation of alkenes exceeds the activity of phosphine Pt complexes.

At the same time, during the reaction, presumably a partial decomposition of the bis-π-olefin Rh complexes proceeds and new complexes form which, in fact, catalyze the reaction. A first hint of that is an induction period in this reaction which was observed in most of the experiments. Besides that after the isolation of the complexes from reaction medium (run 20), the catalyst is completely inactive for reuse.

Table 3. Hydrosilylation of cyclohexanone:

$$c\text{-}C_6H_{10}\!\!=\!\!O \;+\; HSiEt_3 \longrightarrow c\text{-}C_6H_{11}OSiEt_3$$
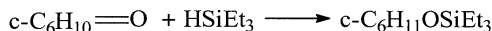
run	catalyst[a]	metal content, %	induction period, min	TOF[b] mol/min g-atom Rh(Pt)	yield for 3 h, %	solubility of catalyst[c]
17	RhCl(PPh$_3$)$_3$	-	0	73	70.1	sol
18	PS-PB-Rh-1	7.39	8	120	99.0	sol
19	PS-PB-Rh-2	4.20	10	180	99.1	sol
20	PS-PB-Rh-2[d]	4.20	0	0	0	sol
21	SBS-Rh-1	12.52	10	150	94.6	swel
22	SBS-Rh-2	16.51	8	69	50.3	swel
23	PS-PB-Pt	14.77	-	0	0	sol

[a] Molar ratio c-C$_6$H$_{10}$O/HSiEt$_3$/catalyst = 1/1/3·10^{-4}; T=40°C;
[b] TOF corresponds to maximum rate of silyl ether formation;
[c] Solubility of catalyst: sol=soluble, swel=swellable;
[d] Reuse of catalyst after isolation from reaction medium.

It should be noted that in all cases when the catalyst was not soluble but only swellable in the reaction medium (runs 21 and 22) the deactivation of the catalysts and the emergence of the second step on the kinetic curves were observed (Fig. 3). Moreover, the maximum yield of silyl ether (for 3 hours, table 3) is proportional to the initial activity (TOF) of the catalyst (Fig. 4). The latter indicates that the life time of highly active catalytic species is the same for 2 cases (about 70 minutes).
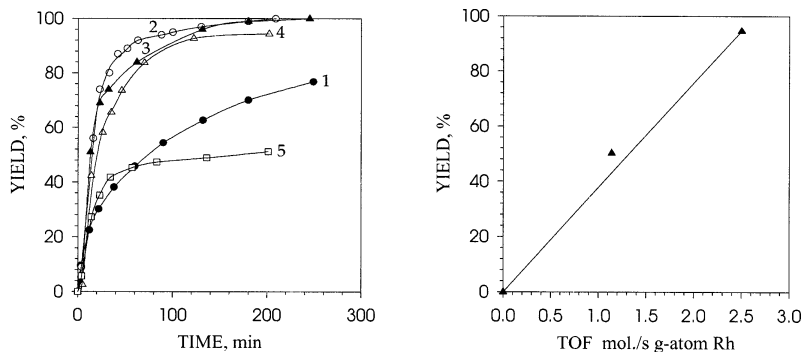
Fig. 3 (left). The yield dependencies of triethylsiloxycyclohexane on time with various catalysts: RhCl(PPh$_3$)$_3$ (1), PS-PB-Rh-1 (2), PS-PB-Rh-2 (3), SBS-Rh-1 (4), SBS-Rh-2 (5). Molar ratio of reagents: c-C6H$_{10}$O/HSiEt$_3$/catalyst = 1/1/3·10^{-4}; T = 40°C.

Fig. 4 (right). The yield dependence of triethylsiloxycyclohexane on TOF for catalysts 21 and 22 (table 3).

   In the case of soluble catalysts (runs 18, 19) the similar behavior was not found. This phenomenon can be associated with the fact during the reaction bis-olefin polymer ligands can be replaced with other ligands (for instance, ketones). If a polymer is in solution, such a substitution can be reversible and does not lead to a change of activity. If the polymer is not soluble, the migration of Rh(I) in bulk solution (due to the substitution of the polymer ligands), which volume significantly exceeds the volume of swollen polymer, results in the situation when the reverse interaction of the metal with the olefin ligands becomes less probable. This is reflected in the kinetics of hydrosilylation. The Pt analog of very active PS-PB-Rh-2 displayed no activity. In all cases no side products of hydrosilylation were observed.

Acknowledgments

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