



## Soluble polysiloxane-supported palladium catalysts for the Mizoroki–Heck reaction

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### ABSTRACT

Soluble polysiloxanes of various architectures (linear, star-shaped and hyperbranched), having vinyl, 2-butylthioethyl and 2-diphenylphosphinoethyl side groups have been used as supports for palladium(II) catalysts. Catalytic activity of such immobilized palladium complexes was tested in model Mizoroki–Heck reactions. The activity of the complexes in terms of yield and turnover number was comparable to that of PdCl<sub>2</sub>(PhCN)<sub>2</sub>. Polysiloxane-supported catalysts show good stability and can be reused several times. Catalysts immobilized on linear polymers show generally better stability than those immobilized on branched structures. Mercury poisoning test indicated that the true catalytic species is the supported complex. According to XPS analysis, palladium in the complexes with polysiloxanes is present as Pd(II). XRF shows however a significant metal leaching after 5–10 reaction cycles.

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### 1. Introduction

The use of polymer-supported catalysts in organic synthesis has become a common practice, especially following the rapid development of combinatorial chemistry. Soluble polymeric supports have received significant attention since they combine advantages of homogeneous catalysts (i.e., high activity) and insoluble heterogeneous catalytic systems (facile separation and reusability) [1,2]. Moreover, polymer topology as well as the ligand density may be modified over a wide range by proper design and controlled synthesis of polymer [3]. Immobilized catalysts often show also good selectivity, in some cases different from that of small molecular complexes.

In order for a polymer to be useful as a soluble support for a catalyst or reagent, the polymer should be easily available, demonstrate good chemical stability, provide appropriate functional groups for attachment of catalytic moieties, and exhibit high solubilizing power to dissolve molecular entities [1,2]. A variety of organic polymers, like polystyrene, polyethylene, poly(ethylene oxide), poly(vinylpyridine), and others, have usually been used as supports for catalysts [4–7]. The reports on the use of polysilox-

anes as catalyst supports are very scarce [8–11]. Polysiloxanes are known for their extreme flexibility, which may be advantageous, as the chain may easily adopt optimal conformation for catalytic centers to participate in the reaction. Polysiloxanes are also chemically and thermally stable and highly soluble in many organic solvents. They may also be relatively easily separated from the reaction mixture. These features make them interesting potential supports for transition metal catalysts.

Recently, we reported on the synthesis and application of linear polysiloxane with pendant thioether groups as support for palladium catalyst for the Mizoroki–Heck coupling [12]. We now extend this study to soluble polysiloxanes of various topologies, i.e., linear, star-shaped and hyperbranched, having vinyl, thioether and diphenylphosphino pendant groups, which may be used as supports for palladium catalysts for the Heck reaction. The aim of this work was to examine the activity and stability of Pd catalysts supported on polysiloxanes as a function of polymer structure and of the ligand type.

### 2. Experimental

#### 2.1. Chemicals

Toluene, methanol (POCH, analytical grade) were purified by standard methods [13]. N-methylpyrrolidone (ABCR, 99%) was purified by distillation under reduced pressure. Methyl acrylate (International Enzymes Limited, pure, stabilized with 15 ppm

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MEHQ), 1-butanethiol (Janssen Chimica, 98%) and hexamethyldisiloxane (Aldrich, pure) were used as received. Iodobenzene and bromobenzene were distilled under argon. Azobisisobutyronitrile (AIBN) (Fluca, pure) was purified by crystallization from methanol. Clarsil MO-2 was obtained by courtesy of Chemical Plant "Polish Silicones" Ltd. and used as received.  $\text{PdCl}_2(\text{PhCN})_2$  was prepared from  $\text{PdCl}_2$  (ABCR, 99.9%) and benzonitrile (ABCR, 99%) in toluene [14]. The mixture of vinylmethylcyclorosiloxanes,  $(\text{MeViSiO})_n$ ,  $n \geq 4$ , obtained by hydrolysis of  $\text{MeViSiCl}_2$  was dried by flushing nitrogen through the liquid mixture at 80 °C for 5 h. *n*-Butyllithium, 2.5 M in *n*-heptane (Aldrich) was analysed by a method described in Ref. [15]. Karstedt catalyst (PSO85, ABCR) was used as received. 1,2-Bis(dichloromethylsilyl)ethane,  $\text{Cl}_2\text{MeSiCH}_2\text{CH}_2\text{SiMeCl}_2$ , was synthesized by hydrosilylation of methylvinylchlorosilane with methylchlorosilane in the presence of the Karstedt catalyst in bulk as described in Ref. [16].

## 2.2. Analyses

**NMR spectroscopy.**  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{29}\text{Si}$  NMR spectra in  $\text{CDCl}_3$  were obtained with a Bruker 500 MHz spectrometer. Both  $^{31}\text{P}$  and  $^{29}\text{Si}$  NMR spectra were recorded with broadband proton decoupling. A heteronuclear gated decoupling with a 60 s delay or INEPT technique was used to acquire  $^{29}\text{Si}$  NMR spectra. The solid state CP MAS experiments were performed on a Bruker Avance DSX300 spectrometer equipped with a dual channel, broadband MAS probehead using  $\text{ZrO}_2$  rotors at 8 kHz rotation speed.  $^{29}\text{Si}$  resonance frequency was 59.63 MHz, spectral range 35 kHz, contact time 5 ms and pulse delay 6 s.

**IR spectroscopy.** The FTIR spectra were measured by a BIORAD spectrophotometer in an air atmosphere.

**Gas chromatography.** Gas chromatographic analysis was performed on a Hewlett Packard 5890 II apparatus equipped with a TCD detector and a HP-50+ column (30 m  $\times$  0.53 mm  $\times$  1  $\mu\text{m}$ ). Injector and detector temperature: 210 °C. Carrier gas: helium. Temperature program: the column was kept in 50 °C for 2 min, then heated to 150 °C at a rate of 5 °C/min.

**Size-exclusion chromatography (SEC).** SEC analyses were performed on an LDC Analytical refractometer IV instrument working with an RI detector and equipped with two SDV columns of the following parameters: 8 mm  $\times$  300 mm, 5  $\mu\text{m}$  particle size, with 10<sup>4</sup> Å and 100 Å pore size. Toluene was used as eluent at a flow rate of 0.7 ml/min. Molecular masses were calculated relative to polystyrene standards.

**DSC measurements.** Phase transitions of polymer (1) were studied by DSC (differential scanning calorimetry) technique using a DuPont 2000 thermal analysis system. Thermograms were taken for samples quenched rapidly from the melt upon heating at a rate of 10 °C/min. The transition temperatures were taken as corresponding to the maximum of the enthalpic peak.

Thermogravimetric analyses (TGA) were performed on a TA Instruments 2950 TGA HR analyser at a rate of 10 K/min under nitrogen.

**XPS spectra.** X-ray photoelectron spectra of all samples were acquired at room temperature using an ESCALAB-210 (VG Scientific, England) spectrometer and a non-monochromated Al K $\alpha$  ( $h\nu = 1486.6 \text{ eV}$ ) X-ray radiation source, operated at 300 W (15 kV, 20 mA). Survey scan (0–1350 eV) was acquired at pass energy of hemispherical analyser of 75 eV, with step 0.4 eV. Detail spectra in all regions were acquired at pass energy 25 eV and step 0.1 eV. The samples were attached to the sample holder and evacuated to vacuum below  $8 \times 10^{-9}$  mbar without any further treatment. Data processing was performed using Advantage Data System (Thermo Electron). Data smoothing procedure was applied and the non-linear Shirley background was subtracted. Peak synthesis by a

symmetric Gaussian–Lorentzian product function, with *L/G* ratio  $0.3 \pm 0.05$ , was used to approximate the line shapes of the fitting components. For quantification the Scofield sensitivity factors and determined transmission function of the spectrometer were used. Binding energy scale was referenced to the C 1s peak of C–Si bond of siloxane according to Beamson and Briggs data with BE = 284.38 eV [17].

**Atomic absorption spectrometry (AAS).** Samples were dissolved in aqua regia ( $\text{HCl}:\text{HNO}_3 = 3:1$ ) in a sealed microwave system MILESTONE 1200 MEGA. Obtained solutions were transferred to measuring flasks and diluted with deionized water. The blind sample was subjected to the same procedure. Pd content was determined by atomic absorption spectrometry using flame atomization with a SOLAAR M6 (Unicam Atomic Absorption) spectrometer at 244.8 nm.

**X-ray fluorescence (XRF) analysis.** The palladium content was determined by XRF spectroscopy using an ED-XRF (energy dispersive X-ray fluorescence) Canberra, model 1510 Spectrometer. The samples were homogenized with colloidal silica (in proportion polysiloxane– $\text{PdCl}_2$  complex/ $\text{SiO}_2 = 1:20$ ) using  $\text{MoO}_3$  as the internal standard (0.5 wt%). Obtained powder was then pressed into tablets having surface density of 0.0478 g/cm<sup>2</sup>. The tables were excited using an Am-241 source of photons at 60 keV. Pd–K and Mo–K photons were detected using a semiconductor Si(Li) detector.

## 2.3. Syntheses

**Preparation of linear polyvinylmethylsiloxane (1a).** Polyvinylmethylsiloxane **1a** was prepared by a common reaction of equilibration of the mixture of vinylmethylcyclorosiloxanes,  $(\text{MeViSiO})_n$ ,  $n \geq 4$  (28 g), in the presence of acid activated clay as catalyst, Clarsil MO-2 (ca. 3%, w/w), and hexamethyldisiloxane, HMDS (0.94 mmol), as molecular weight regulator [18]. The reaction was carried out 48 h at 70 °C. The catalyst was then removed by shaking the reaction mixture with several portions of water. Polymer was purified by twofold precipitation by adding methanol to concentrated dichloromethane solution and dried by heating under high vacuum for several hours. Colorless, transparent polymer was obtained whose molecular weight was estimated at  $M_n = 15,000$ ,  $M_w/M_n = 1.5$ , by SEC analysis and  $M_n = 22,000$  by  $^1\text{H}$  NMR spectroscopy (calculated from  $^1\text{H}$  signal ratio of the  $\text{Me}_3\text{Si}$  end-groups to the MeSi groups inside chains). The theoretically expected  $M_n$  value was 20,000, which corresponds to an average of 250 ViMeSiO units in the polymer chain. The content of vinyl groups in the polymer was calculated at 11.5 mmol/g, assuming  $M_n = 20,000$ . Glass transition temperature (DSC)  $T_g = -130$  °C.  $^1\text{H}$  NMR spectrum shows two multiplets at 5.76–5.84 and 5.90–6.04 corresponding to the vinyl groups and a singlet of methyl groups at 0.15 ppm.  $^{29}\text{Si}$  NMR spectrum shows a signal at –34.9 ppm corresponding to the ViMeSiO silicons inside the chain, in accord with earlier reports [19], and signals at –32.3 and –34.3 corresponding to the  $\text{Me}_3\text{Si}$  end group and the penultimate ViMeSiO unit, respectively.

**Synthesis of regular poly(vinylmethylsiloxane-co-dimethylsiloxane) (1b).** Regular vinylmethylsiloxane–dimethylsiloxane copolymer having vinyl groups separated by two dimethylsiloxy units was prepared by anionic ring-opening polymerization of vinylpentamethylcyclotrisiloxane ( $\text{D}_2\text{V}$ ) initiated by BuLi in THF at –10 °C as reported previously [20].  $^1\text{H}$  NMR signals of methyl protons: 0.15 ppm (s, ViMeSiO), 0.08 ppm (s,  $\text{Me}_2\text{SiO}$ ). Glass transition temperature  $T_g = -129$  °C (DSC).

**Synthesis of poly(vinylmethylsiloxane-grad-dimethylsiloxane).** Gradient copolymer of vinylmethylhexatrisiloxane ( $\text{V}_3$ ) with hexamethylcyclotrisiloxane ( $\text{D}_3$ ) was synthesized in THF using *n*-BuLi as the initiator according to previously described procedure [16].

Four-armed star polymethylvinyl-co-dimethylsiloxane (**1c**) was prepared by termination of the living poly(vinylmethylsiloxane-*grad*-dimethylsiloxane) having reactive lithium silanolate chain ends with 1,2-bis(dichloromethylsilyl)ethane,  $\text{Cl}_2\text{MeSiCH}_2\text{CH}_2\text{SiMeCl}_2$ , as described in [16]. NMR spectra were analogous to those reported in [16],  $[\text{V}]/[\text{D}] = 1.38:1$  ( $^1\text{H}$  NMR).  $M_n = 14,300$ ,  $M_w/M_n = 1.8$  (SEC) and 21,500 ( $^1\text{H}$  NMR); theoretically expected  $M_n = 20,000$ . Glass transition temperature  $T_g = -132^\circ\text{C}$  (DSC). The content of vinyl groups in the polymer was 7.1 mmol/g.

**Hyperbranched polymethylvinyl-co-dimethylsiloxane (1d).** Hyperbranched polysiloxane was prepared in two step reaction. In the first step a linear poly(vinylmethylsiloxane-*grad*-dimethylsiloxane) was prepared as described above,  $[\text{V}_3]/[\text{D}_3] = 1:1$ , theoretical  $M_n = 4000$ . The living polymer was terminated by adding bifunctional dichloromethylsilane,  $\text{MeHSiCl}_2$ , giving polysiloxane copolymer containing SiH function in the middle of each chain.  $M_n = 10,500$ ,  $M_w/M_n = 1.4$  (SEC) and 8600 ( $^1\text{H}$  NMR); theoretically expected  $M_n = 8000$ . This copolymer after purification by precipitation from  $\text{CH}_2\text{Cl}_2$  with methanol was dissolved in toluene and subjected to self-hydrosilylation by addition of the Karstedt catalyst,  $2.3 \mu\text{l}$  ( $5 \times 10^{-5}$  mol Pt per mol SiH). Hydrosilylation was carried out for 7 days at  $50^\circ\text{C}$ . Reaction progress was followed by IR and  $^1\text{H}$  NMR, by measuring the conversion of Si–H groups and the reaction was stopped as soon as the absorptions characteristic for SiH disappeared completely. Polymer was purified by precipitation with methanol from  $\text{CH}_2\text{Cl}_2$  solution.  $M_n = 59,000$ ,  $M_w/M_n = 4.4$  (SEC). The V/D ratio was 0.54:1 ( $^1\text{H}$  NMR) which corresponded to the content of vinyl groups in the polymer of 4.5 mmol/g.  $T_g = -129^\circ\text{C}$  (DSC).  $^{29}\text{Si}$  NMR 21.8 (s,  $\text{Me}_2\text{Si}$ ), 24.8 (s,  $\text{MeSiCH}_2\text{CH}_2-$ ), 34.9 (s,  $\text{MeViSi}$ ).

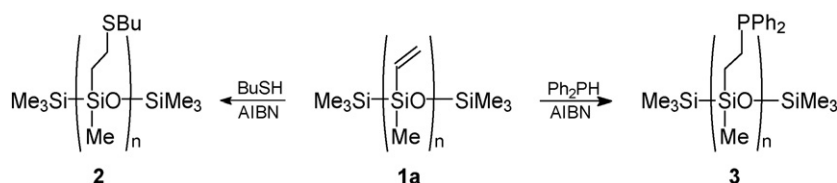
**Preparation of poly(2-(butylthio)ethyl)methylsiloxane (2).** The addition of *n*-butanethiol to polyvinylmethylsiloxane **1a** in the presence of AIBN as free-radical initiator was carried out according to the procedure described previously [12,21]. Polyvinylmethylsiloxane, 3.45 g, containing 0.040 mol of vinyl groups was mixed with 0.2 mmol of AIBN in toluene. The solution was warmed to  $60^\circ\text{C}$  and *n*-BuSH (0.049 mol) was added dropwise. The resulting poly(butylthioethyl)methylsiloxane **2** was purified by twofold precipitation with methanol from toluene and dried by heating under high vacuum for several hours. The resulting polymer had a consistence of a white rubbery resin. Conversion of vinyl groups was almost quantitative, as no vinylsilyl group signals were observed neither in  $^1\text{H}$  nor  $^{29}\text{Si}$  NMR spectra of the modified polymer. Molecular weight:  $M_n = 23,500$ ,  $M_w/M_n = 1.7$ , according to SEC analysis and  $M_n = 43,000$  according to  $^1\text{H}$  NMR spectrum (estimated from the end  $\text{Me}_3\text{Si}$  group to chain  $\text{MeSi}$  group  $^1\text{H}$  signal ratio). Theoretically expected  $M_n = 44,000$ . The content of the thioether groups in the polymer was 5.8 mmol/g. Glass transition temperature (DSC) was  $T_g = -94.8^\circ\text{C}$ .  $^1\text{H}$  NMR  $\delta$  (ppm): 2.49 (m,  $\text{SCH}_2$ ), 1.53 (m,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 1.39 (m,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 0.89 (m,  $\text{S}(\text{CH}_2)_3\text{CH}_3$ ), 0.11 (s,  $\text{Si}(\text{CH}_3)_3$ );  $^{29}\text{Si}$  NMR (INVGATE)  $\delta$  (ppm):  $-23.74$  (s,  $\text{OMe}(\text{R})\text{SiO}$ ),  $-21.38$ ,  $-21.62$  (2s,  $\text{Me}_3\text{SiO}$ );  $^{13}\text{C}$  NMR  $\delta$  (ppm): 31.66 (s,  $\text{SCH}_2$ ), 26.38, (s,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 22.09 (s,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 18.33 (s,  $\text{SiCH}_2\text{CH}_2\text{S}$ ), 13.76 (s,  $\text{S}(\text{CH}_2)_3\text{CH}_3$ ),  $-0.07$  (s,  $\text{Si}(\text{CH}_3)_3$ ).

**Preparation of poly(2-(diphenylphosphino)ethyl)methylsiloxane (3).** The addition of diphenylphosphine to polyvinylmethylsiloxane was carried out according to the procedure described previously [22].  $\text{Ph}_2\text{PH}$  (0.029 mol) was added dropwise to polyvinylmethylsiloxane **1a**, 2.51 g (0.029 mol of vinyl groups), containing 0.2 mmol of AIBN and the reaction mixture was heated to  $120^\circ\text{C}$  for 5 days. The resulting poly(diphenylphosphinoethyl)methylsiloxane **3** was purified by twofold precipitation with methanol from toluene and dried by heating under high vacuum for several hours. The resulting polymer had a consistence of a colorless rubbery resin. Conversion of vinyl groups was ca. 70%, according to  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectra. Molecular weight measured by SEC was  $M_n = 10,500$ ,  $M_w/M_n = 1.7$ . Theoretically expected  $M_n = 54,000$  (assuming 70% conversion of functional groups) and this value was used for stoichiometric calculations. The content of phosphinoethyl groups in the polymer was 3.2 mmol/g. Glass transition temperature was  $T_g = -12.8^\circ\text{C}$ , melting temperature  $T_m = 16.6^\circ\text{C}$  (DSC). The  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{29}\text{Si}$  NMR spectra were in accord with those reported earlier [22]. In the  $^{31}\text{P}$  NMR spectrum, beside the main  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{Si}$  signal ( $-9.1$  ppm), also the signal of the oxidated form,  $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_2\text{Si}$  (34.3 ppm, 3.5%) appears.

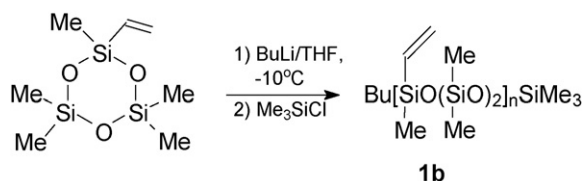
**Immobilization of palladium.** The solution of polysiloxane and palladium complex,  $\text{PdCl}_2(\text{PhCN})_2$ , ca. 0.1 mol/mol relative to the content of the functional groups in polymer, in toluene was stirred for 5 days at room temperature. The solution color faded from deep brown to pale yellow. The obtained palladium complexes with polysiloxanes were separated from solution by precipitation with methanol and then dried under vacuum. The complexes were brown, brittle solids hardly soluble in typical organic solvents at room temperature, except for the complexes with poly(butylthioethyl)methylsiloxane and poly(diphenylphosphinoethyl)methylsiloxane which were viscous syrups, soluble in toluene. Polysiloxane– $\text{PdCl}_2$  complexes were characterized by  $^{29}\text{Si}$  NMR spectroscopy, DSC, AAS, XRF and XPS. Linear polyvinylmethylsiloxane– $\text{PdCl}_2$ :  $^{29}\text{Si}$  NMR (CP MAS)  $\delta$  (ppm):  $-29.4$  (bs, free  $\text{MeViSiO}$ ),  $-56.8$  (bs,  $\text{MeViSiO-PdCl}_2$ ),  $-64.8$  (bs,  $(\text{MeViSiO})_2\text{-PdCl}_2$ ); star polyvinylmethylsiloxane– $\text{PdCl}_2$ :  $-21.5$  (s,  $\text{Me}_2\text{SiO}$  free),  $-30.4$  (s, free  $\text{MeViSiO}$ ),  $-34.4$  (s, free  $\text{MeViSiO}$ ),  $-56.9$  (s,  $\text{MeViSiO-PdCl}_2$ ),  $-66.5$  (bs,  $(\text{MeViSiO})_2\text{-PdCl}_2$ ); poly(butylthioethyl)methylsiloxane:  $^{29}\text{Si}$  NMR:  $-23.7$  (bm,  $\text{BuS}(\text{CH}_2)_2\text{MeSiO-PdCl}_2$ ),  $-21.4$ ,  $-21.7$  (2 bs, free  $\text{BuS}(\text{CH}_2)_2\text{MeSiO-}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 31.6 (s,  $\text{SCH}_2$ ), 26.3 (s,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 22.0, (s,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 18.2 (bm,  $\text{SiCH}_2\text{CH}_2\text{S}$ ), 13.7 (s,  $\text{S}(\text{CH}_2)_3\text{CH}_3$ ), 0.12 (bm,  $\text{Si}(\text{CH}_3)_3$ ); poly(diphenylphosphinoethyl)methylsiloxane:  $^{31}\text{P}$  NMR  $\delta$  (ppm):  $-9.5$  (bs, free  $\text{Ph}_2\text{PCH}_2-$ ), 21.4 (bs,  $\text{Ph}_2\text{P}(\text{CH}_2-)\text{-PdCl}_2$ ), 23.1 (bs,  $[\text{Ph}_2\text{P}(\text{CH}_2-)]_2\text{-PdCl}_2$ ), 34.0, 35.5 (bs,  $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2-)$ );  $^{29}\text{Si}$  NMR: 22.7 (bs,  $\text{Ph}_2\text{P}(-\text{PdCl}_2)\text{CH}_2\text{CH}_2\text{SiO}$ ), 34 (bs,  $\text{ViMeSiO}$ ).

#### 2.4. Kinetic studies

Iodobenzene (0.28 ml, 2.5 mmol), methyl acrylate (0.23 ml, 2.5 mmol)/butyl acrylate (0.36 ml, 2.5 mmol)/acrylonitrile (0.16 ml, 2.5 mmol) and triethylamine (0.32 ml, 2.5 mmol) were mixed with 1 ml of *N*-methylpyrrolidone (NMP). The liquid mixture was placed in a 15 ml autoclave and then ca. 0.05 g of polysiloxane– $\text{PdCl}_2$  com-



Scheme 1.



Scheme 2.

plex containing ca. 0.03 mmol Pd was added. The reaction mixture was heated to 80 °C while vigorously agitating with a magnetic stirrer. The reaction was monitored at certain time intervals by gas chromatography using toluene as the internal standard. Conversion was determined based on the amount of iodobenzene consumed. After 2 h the reaction mixture was cooled down and the catalyst was precipitated by addition of methanol, filtered and rinsed with methanol. The remainder was dried at 90 °C under vacuum for 3 h before reuse.

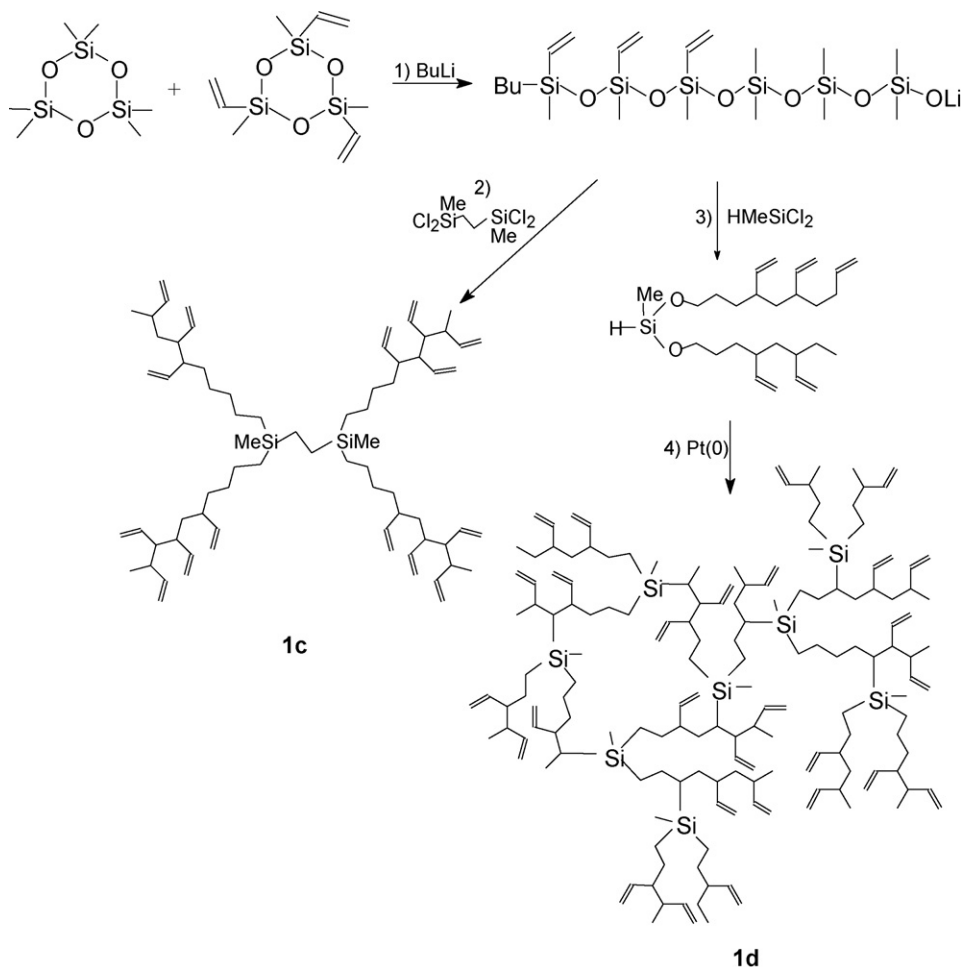
The kinetic studies of the reaction of bromobenzene with styrene were performed analogously, using 0.26 ml (2.5 mmol) of PhBr and 0.29 ml (2.5 mmol) of styrene. The amounts of NMP, Et<sub>3</sub>N and catalyst were the same as in the reaction of iodobenzene with methyl acrylate. The reaction was carried out for 3 h at 120 °C.

### 3. Results and discussion

#### 3.1. Polymer synthesis

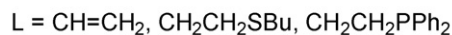
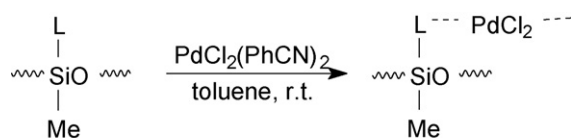
The well known equilibration method of the mixture of methylvinylcyclosiloxanes and hexamethyldisiloxane as the chain regulator in the presence of a solid acid catalyst [18], linear polyvinylmethylsiloxane Me<sub>3</sub>SiO(MeViSiO)<sub>n</sub>SiMe<sub>3</sub> was prepared, which has been used as the catalyst support by itself or has been further modified in the reaction with *n*-butyl mercaptan (1-butanethiol) [21] or diphenylphosphine [22] in the presence of AIBN as the free-radical initiator (Scheme 1). The addition of thiol proceeds practically quantitatively; no vinyl groups remain in the product according to NMR spectroscopy. Modification by diphenylphosphine proceeds in a 70% yield (NMR). Molecular weight for this polymer measured by SEC was unfortunately unreliable due to the difference in hydrodynamic volume of this copolymer compared to polystyrenes used as standards. It was also not possible to estimate the *M<sub>n</sub>* from <sup>1</sup>H NMR, because the end group signals were invisible. Thus, the theoretical *M<sub>n</sub>* of 54,000 was assumed in stoichiometric calculations.

An influence of the density of ligands on the activity of the supported catalysts was checked by comparing the activity of the catalyst immobilized on **1a** with that of the catalyst immobilized on the polysiloxane having the vinyl group at each third silicon atom in the chain. Such a regular vinylmethylsiloxane–dimethylsiloxane copolymer was synthesized by controlled anionic ring-opening



Scheme 3.





Scheme 4.

polymerization of vinylpentamethylcyclotrisiloxane ( $\text{D}_2\text{V}$ ) at  $-10^\circ\text{C}$  (Scheme 2). Since the silicon substituted by the vinyl group is more electrophilic the nucleophilic attack of the silanolate anion is preferentially directed to this silicon in the ring. Polymerization at this temperature proceeds with high regioselectivity up to 80% as confirmed by  $^{29}\text{Si}$  NMR [20].

Star-shaped and hyperbranched polysiloxanes **1c** and **1d** were used in comparison to **1a** in order to examine the influence of polymer architecture (linear vs. highly branched) on the activity of the supported catalysts. They were synthesized in a multistep reaction. In the first step, linear copolymers of gradient composition of vinyl units along the chain were obtained by simultaneous copolymerization of hexamethylcyclotrisiloxane with 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane initiated by BuLi (Scheme 3, route 1) [16]. Due to much different reactivities of both monomers the obtained copolymers had high density of vinyl groups at the beginning of each chain and a high density of dimethyl units close to the active silanolate chain end, which, upon termination, resulted in copolymers which had high content of ligand groups in the outer part of the macromolecule. The obtained polymers with a living chain ends were terminated by 1,2-bis(dichloromethylsilyl)ethane to give four-arm star copolymer or with methylchlorosilane to give a linear polymer with an SiH function in the middle of each chain (Scheme 3, routes 2 and 3). The latter polymer was then a subject of self-hydrosilylation by addition of the Karstedt catalyst,  $\text{Pt}_2\{[(\text{CH}_2=\text{CH})\text{Me}_2\text{Si}]_2\text{O}\}_3$ , giving hyperbranched polymer of irregular structure (Scheme 3, route 4).

Polysiloxanes were characterized by  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectroscopy (phosphino-functionalized polysiloxane also by  $^{31}\text{P}$  NMR), size-exclusion chromatography (SEC) and digital scanning calorimetry (DSC). NMR spectra of functional polysiloxanes correspond well to those published previously [16,19,21,22].

### 3.2. Immobilization of palladium

The resulting polysiloxanes were used for immobilization of palladium(II) chloride by linking to vinyl, thioether or phosphinyl side groups (Scheme 4). In most cases, the  $[\text{Pd}]/[\text{L}]$  ratio was about 0.1 mol/mol. Assuming that the complex involves two ligands coordinated to one Pd atom, 80% of the total amount of functional groups should remain unbound.

In the case of polysiloxanes with thio- and phosphino-based ligands complete discoloration of the solution was observed after a few minutes. In the case of vinyl polysiloxanes solutions were yellow even after 5 days indicating that some amount of  $\text{PdCl}_2(\text{PhCN})_2$  remained in equilibrium with a polymer complex. In all cases the theoretical content of Pd was calculated assuming quantitative immobilization of palladium. The metal content was measured by atomic absorption spectroscopy (AAS) and by X-ray photoelectron spectroscopy (XPS). Unfortunately, the AAS measurements proved quite inaccurate when the Pd content was below 10 wt% and might serve as a rough estimation of the metal content only. The results of analysis are collected in Table 1.

For linear PMVS we have measured the maximum catalyst capacity. The maximum Pd content measured by XRF was 28.8 wt% which corresponds to the  $[\text{Pd}]/[\text{Vi}]$  ratio of 0.416 mol/mol. This amount of palladium binds 83% of vinyl groups assuming the  $\text{L}_2\text{PdCl}_2$  stoichiometry of the complex. Thus, less than 20% of vinyl groups remain unbound, probably for steric reasons.

Vinyl polysiloxane-supported Pd complexes (**1a-d**)-Pd were characterized by solid state CP MAS  $^{29}\text{Si}$  NMR spectroscopy, digital scanning calorimetry (DSC) and X-ray photoelectron spectroscopy (XPS). Due to poor solubility in typical solvents at room temperature, size-exclusion chromatography (SEC) of these complexes was impossible. On the other hand, the complexes of palladium with thioether- and phosphino-substituted polysiloxanes (**2-Pd** and **3-Pd**, respectively) were sufficiently soluble to perform the NMR measurements in solution and SEC analysis. Unfortunately, SEC analysis of butylthioethyl- and diphenylphosphinoethylpolysiloxane-PdCl<sub>2</sub> complexes gave molecular weights of 10,000 and 23,000, respectively, which were unrealistically low compared to theoretical values. Taking into account that polysiloxanes do not depolymerize upon free-radical induced hydrosulfination and hydrophosphination [21,22] we may conclude that SEC is not a reliable method for analysis of these polymeric complexes, due to difference in hydrodynamic volume between siloxane copolymers and polystyrene standards which were used as the reference. On the other hand, the molecular weights estimated from  $^1\text{H}$  NMR spectra (as the ratio of the signal intensity of the terminal  $\text{Me}_3\text{Si}$  groups to that of the  $\text{MeSi}$  groups inside the chain) agree quite well with the theoretical values. The general change in the NMR spectra upon immobilization of palladium is a significant line broadening, which is related to the change in the mobility of polymer chain segments and in the relaxation times due to metal binding.  $^{29}\text{Si}$  chemical shifts of silicons having vinyl groups bound to metal are strongly shifted to higher field, i.e.,  $-56$  and  $-64$  ppm, compared to  $-34$  ppm for the free  $\text{ViMeSi}$  signals. Two signals correspond probably to different structures of palladium complexes (structures **I** and **II**, respectively) [23,24]. Analogously, two signals are observed in  $^{31}\text{P}$  NMR of the phosphinoethylsiloxane-PdCl<sub>2</sub> complex at 21.4 and 23.3 ppm as it was found before for the other polymer-supported palladium-phosphine complexes [25]. Chemical shifts of the signals of Si substituted by thioethyl and phosphinoethyl groups

**Table 1**  
Palladium content in the polysiloxane-PdCl<sub>2</sub> complexes according to AAS and XRF in weight %.

Polymer <sup>a</sup>	Funct. groups [mmol/g]	Pd [mmol/g]	Pd theor.	AAS (fresh)	AAS (after reaction)	XRF (fresh)	XRF (after <i>n</i> reaction cycles) <sup>b</sup>
Linear PMVS ( <b>1a</b> )	11.5	0.785	8.36	8.68	6.06	10.07 (±0.2)	5.48 (±0.11)
Linear PMVS ( <b>1a</b> )	11.5	3.73	39.67	29.99	n/a	28.8 (±0.6)	n/a
Regular PMVS ( <b>1b</b> )	3.6	1.504	16.00	14.69	11.14	n/a	n/a
4-Arm star PMVS ( <b>1c</b> )	7.1	0.627	6.67	3.9	n/a	n/a	n/a
Hyperbranched PMVS ( <b>1d</b> )	4.5	0.537	5.71	1.13	1.61	6.27 (±0.13)	4.76 (±0.12)
Linear PME <sup>SBu</sup> S ( <b>2</b> )	5.8	0.563	6.00	3.5	3.6	5.89 (±0.12)	2.42 (±0.06)
Linear PME <sup>PPh<sub>2</sub></sup> S ( <b>3</b> )	3.2	0.705	7.50	11.42	n/a	10.01 (±0.2)	1.40 (±0.035)

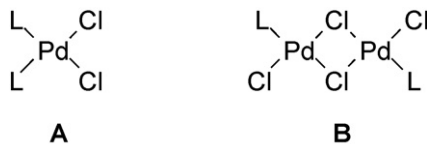
<sup>a</sup> M – methyl, E – ethyl, V – vinyl.

<sup>b</sup> *n* means the maximum number of cycles performed for each catalyst; see Table 3.

**Table 2**  
Binding energies (BE, in eV) and the shares (in %) of individual XPS peak components.

	Si 2p		Pd 3d <sub>5/2</sub>		Pd 3d <sub>5/2</sub>		Pd 3d <sub>5/2</sub>		S 2p		P 2p <sub>3/2</sub>		Cl 2p <sub>3/2</sub>		Cl 2p <sub>3/2</sub>		C 1s		C 1s	
	BE [eV]	at%	BE [eV]	at%	BE [eV]	at%	BE [eV]	at%	BE [eV]	at%	BE [eV]	at%	BE [eV]	at%	BE [eV]	at%	BE [eV]	at%	BE [eV]	at%
<b>1a-Pd</b>	102.04	21.53	337.03	5.40	335.19	0.14	198.23	7.32	163.27	2.00	131.20	2.00	199.91	1.81	284.38	15.23	284.7	37.37		
<b>1d-Pd</b>	102.04	24.41	337.94	0.30	336.77	0.30	197.98	0.30					200.80	0.34	284.38	11.96				
<b>2-Pd</b>	102.21	18.55	337.61	0.13			197.95	0.11					200.44	0.47	284.38	9.95				
<b>3-Pd</b>	102.25	20.21	337.98	0.34	336.55	0.16	198.11	0.86					200.55	0.47						

change insignificantly upon complexation.



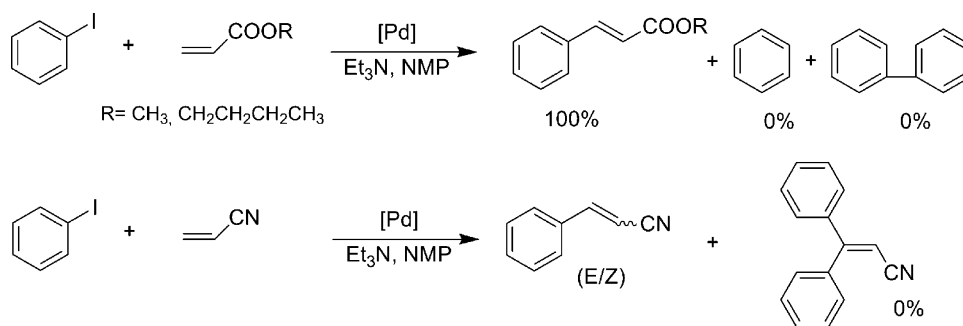
DSC analysis indicates the increase in glass transition temperature of siloxane copolymers upon Pd immobilization by ca. 10–90 °C, depending on the Pd content, which reflects a partial loss of the conformational freedom of polysiloxane segments due to complexation with palladium.

In order to examine the thermal stability of polysiloxanes in the presence of palladium, we have performed thermogravimetric analyses (TGA) of the three representative linear polysiloxanes complexed with PdCl<sub>2</sub>: linear polymethylvinylsiloxane, polymethyl(butylthioethyl)siloxane and polymethyl(diphenylphosphinoethyl)siloxane. In all cases the presence of palladium deteriorates the stability of polysiloxanes to some extent. Slight decomposition starts at about 150 °C but up to 300 °C the samples revealed a weight loss of only ca. 8%. A most serious weight loss occurs at ca. 390 °C, while the corresponding unmodified polysiloxanes decompose at a temperature of 400–500 °C. Interestingly, the most unstable system is the thioethylpolysiloxane–PdCl<sub>2</sub> complex, which decomposes at 390 °C losing 70% of its initial weight. Nevertheless, all catalysts may be considered perfectly stable up to temperature of 150 °C, below which many reactions are carried out.

XPS spectra of the freshly prepared vinyl-(**1a-Pd** and **1d-Pd**) butylthioethyl-(**2-Pd**) and diphenylphosphinoethyl-(**3-Pd**) polysiloxane–PdCl<sub>2</sub> complexes show that palladium appears dominantly in the form of Pd(II) (binding energies from 337.03 eV in **1a-Pd** to 337.98 eV in **3-Pd** for Pd3d<sub>5/2</sub>). The observed positions of the Pd3d<sub>5/2</sub> peaks are close to that found for Pd(II) reported by other authors (BE = 337.5 eV) [26–29]. Some minor fractions of Pd(0) are observed in **1d-Pd** and **3-Pd**. Such complexes are easily formed in the presence of phosphine ligands [29]. Their formation in the case of hyperbranched polysiloxane with vinyl groups is rather surprising. This may point to partial oxidation of Pd-nanoparticles specifically trapped in the complex structure of the hyperbranched polymer to PdO (BE = 336.3 eV [30]). In **1a-Pd** and **3-Pd** minor fractions of Pd<sup>δ+</sup> nanoclusters are also observed. It has been shown that polysiloxane chains might stabilize such catalytically active Pd-nanoparticles [31]. Binding energies observed for Cl, S, P and Si are in accord with earlier data and support the identification (Table 2) [30]. The deficiency of Pd and Cl at the surface compared to the theoretical atomic content in the polysiloxane–Pd complexes may be explained by the known tendency of flexible polysiloxane chains to migrate to the interface, due to their low surface tension. Thus, the polar L–Pd–Cl groupings in the solid state may be mostly hidden in the bulk. This is different from the situation in solution, where dynamic equilibrium leads to averaging of the conformational states.

### 3.3. Catalytic study

The activity and stability of the supported catalysts were tested in model Mizoroki–Heck reaction of methyl acrylate with iodobenzene in N-methylpyrrolidone (NMP) in the presence of Et<sub>3</sub>N (Scheme 5). This catalyst system seems rather insensitive to oxygen and moisture. Kinetics of the reaction was followed by GC, by withdrawing samples at certain time intervals. Thioalkyl- and phosphinyl-polysiloxane-supported palladium catalysts showed good solubility in the reaction mixture. The evaluated NMP solubility limit of **2-Pd** and **3-Pd** were about 4 g/l at 40 °C and 30 g/l at 25 °C, respectively. The solubility of catalyst supported on



Scheme 5.

polysiloxanes with pendant vinyl groups in the reaction medium was generally worse than that of the other catalysts. At room temperature we have observed swelling of the catalyst. At higher temperature the solubility should increase or the catalyst may act as a suspension of gel particles, penetrated by solvent and reagents. After the reaction, the catalyst was separated from the reaction mixture by precipitation with methanol at room temperature. The catalyst was then washed with methanol, dried and reused. Some loss of the catalyst was observed during the separation procedure, depending on solubility of the particular catalytic system. Therefore, the kinetic runs were repeated until the catalyst was completely lost. The activity of the polysiloxane-PdCl<sub>2</sub> catalysts was compared to the homogeneous PdCl<sub>2</sub>(PhCN)<sub>2</sub> complex by measuring maximum conversion of iodobenzene and the rate of the reaction (time when the maximum conversion is reached). Methyl *trans*-cinnamate was the only product observed in GC, indicating nearly 100% selectivity of the reaction. No polymerization of acrylate takes place as no polymer was detected by SEC analysis of the reaction products.

The activity of polysiloxane-PdCl<sub>2</sub> complexes in terms of maximum conversion of substrates is comparable to that of the homogeneous PdCl<sub>2</sub>(PhCN)<sub>2</sub> complex (Table 3). The low molecular complex is more active than polymer-supported ones giving a maximum conversion of iodobenzene after ca. 10 min (Figs. 1 and 2). In the case of polymer-supported catalysts, maximum conversion in the first cycle was reached after 20 min and the reaction slowed down after each cycle of reaction. For example, in the 5th kinetic run the time needed to achieve maximum conversion of iodobenzene using butylthioethylpolysiloxane-supported catalyst was ca. 40 min. This points to partial deactivation of the catalyst due to Pd leaching and possibly to some changes in the structure of the complex [32,33]. XRF data confirmed that the Pd content in the complexes drops down after a few reaction cycles (Table 1). The XRF analysis of the reaction solution after separation of the catalyst shows the trace of palladium, also proving that some leaching occurs during the reaction.

Table 3

Conversion of iodobenzene after 1 h in all catalytic runs and turnover frequency (TOF, mol product/mol of Pd/h) in the reaction with methyl acrylate.

Cycle	conversion [%]						
	1a-Pd <sup>a</sup>	1b-Pd <sup>a</sup>	1c-Pd <sup>a</sup>	1d-Pd	2-Pd	3-Pd	PdCl <sub>2</sub> (PhCN) <sub>2</sub>
1 (TOF)	99 (32)	87 (15)	84 (34)	85 (79)	88 (156)	86 (122)	86 (213)
2	93	84	79	85	89	90	
3	92	74	85	40	84	87	
4	82	85	81	29	89	83	
5	95	70	81	14	86	80	
6	93	86	68	14			
7	89	76	53	10			
8	91	70		8			
9	94						
10	79						
11	85						

<sup>a</sup> Conversion after 2 h.

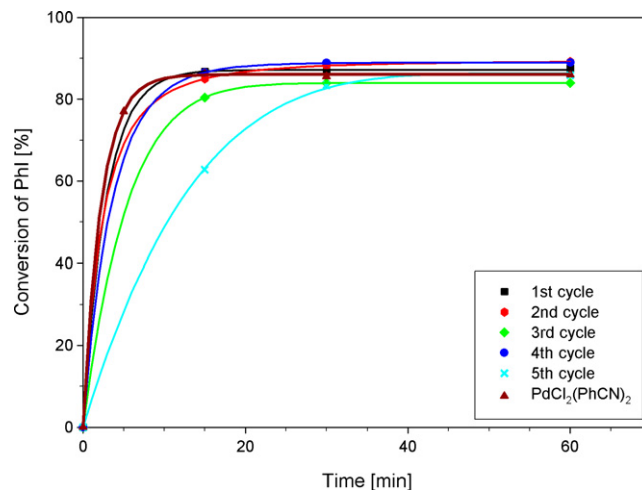
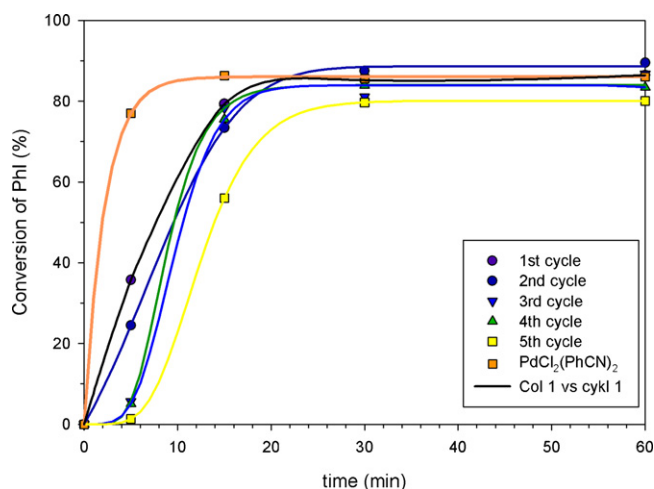


Fig. 1. Kinetics of the reaction of iodobenzene with methyl acrylate catalyzed by poly(butylthioethyl)methylsiloxane-PdCl<sub>2</sub> complex (5 reaction cycles); kinetics of the reaction catalyzed by PdCl<sub>2</sub>(PhCN)<sub>2</sub> is shown for reference.

Precipitation of the polymer-attached catalyst with methanol may be applied to recover the catalyst from the reaction mixture, and the catalyst can be reused in subsequent catalytic runs. However, the precipitation was not quantitative and some catalyst was lost after each run. The loss of the catalyst is the reason why only five cycles were performed with thioether and phosphino polysiloxane complexes.

To rule out the possibility of catalysis by microparticles (colloids or nanoclusters) of zero-valent palladium formed from leached and reduced Pd(II) precursor, a mercury poisoning experiment was carried out by adding mercury to the reaction mixture before the catalytic test. The mercury poisoning of metal(0) particles, by amalgamating the metal or adsorbing on the metal surface, is a widely used test for the heterogeneity/homogeneity of catalysis



**Fig. 2.** Kinetics of the reaction of iodobenzene with methyl acrylate catalyzed by poly(diphenylphosphinoethyl)methylsiloxane–PdCl<sub>2</sub> complex (5 reaction cycles); kinetics of the reaction catalyzed by PdCl<sub>2</sub>(PhCN)<sub>2</sub> is shown for reference.

[34]. It is known that trace amounts of leached metal particles or soluble palladium complex can be very catalytically active [35]. Polysiloxane-supported palladium catalyst vigorously stirred with large excess of mercury for 24 h prior reaction, shows almost the same catalytic activity for Mizoroki–Heck reaction as before poisoning. As additional evidence for the identity of the true catalyst, mercury poisoning test for reaction catalyzed by homogeneous precatalyst complex, PdCl<sub>2</sub>(PhCN)<sub>2</sub>, was performed. In this case, addition of Hg(0) to the homogeneous reaction solution completely suppressed the catalytic activity, indicating that molecular species detached from support is not the catalytically active site. Thus, poisoning results suggest that catalysis is not associated with leached precursor complexes or in situ formed palladium nanoclusters but rather with polysiloxane immobilized Pd(II) species.

Comparison of the activities of palladium supported on vinyl polysiloxanes leads to conclusion that the most active and stable catalyst is Pd supported on linear polymethylvinylsiloxane having vinyl groups at each siloxane unit in the chain (**1a-Pd**). The regular polymethylvinyl-co-dimethylsiloxane having a vinyl group at each third silicon atom in the chain (**1b-Pd**) is much less stable and its activity decreases significantly with the increasing number of reaction cycles. Probably, low density of ligands causes weaker binding of the metal and its more extensive leaching. On the other hand, branched polysiloxanes **1c-Pd** and **1d-Pd** are also less effective catalysts and their activity decreases with the increasing number of repeating cycles. Deactivation is particularly noticeable for the hyperbranched polymer, **1d-Pd**. The reason for lower activity of the catalysts supported on highly branched polymers may be similar to that reported for dendrimer-supported catalysts [36]. A part of PdCl<sub>2</sub> is immobilized on ligands located in the inner part of the macromolecule where the steric congestion makes the access of reagents more difficult. Moreover, part of the catalyst may be complexed by the ligands from two different branches which probably makes the metal unavailable to reagents. While the content of metal located in the outer part of molecule is leached out, the complex loses its activity rapidly. This may explain why, despite of the fact that the palladium content in the hyperbranched polymer **1d-Pd** is still high after 8 cycles, the catalytic activity of the complex is low.

To confirm that vinyl groups of polysiloxanes **1a-d** did not undergo reduction under the reaction conditions the IR spectra of catalysts before and after five reaction cycles were taken. The vinyl absorption peaks (1405–1420 cm<sup>-1</sup>, 1590–1620 cm<sup>-1</sup>, 2950–3050 cm<sup>-1</sup>) at IR spectra (not presented here) of catalysts after reaction remained practically unchanged compared to the

**Table 4**

Conversion of iodobenzene after 5 h (in %) and turnover frequency (TOF, mol product/mol of Pd/h) in the reactions with butyl acrylate and acrylonitrile.

	Cycle	Conversion [%]			
		1a-Pd	2-Pd	3-Pd	PdCl <sub>2</sub> (PhCN) <sub>2</sub>
Butyl acrylate	1	86	98	100	95
	(TOF)	(94)	(47)	(129)	(157)
	6	82	96	95	
Acrylonitrile	1	99 (19.5/80.5) <sup>a</sup>			88 (18.8/81.2) <sup>a</sup>
	(TOF)	(65)			(120)
	6	93 (19.4/80.6) <sup>a</sup>			

<sup>a</sup> Values in parentheses indicate the *Z/E* isomer ratio (%).



**Scheme 6.**

spectrum of the fresh catalyst. This proved that pendant vinyl groups of polysiloxane supports are stable after prolonged use of the catalysts.

Catalysts having thioether and phosphine ligands show high activity, which is maintained through five repeating runs (Figs. 1 and 2). However, due to high solubility the separation procedure was not effective and after 5 cycles all the catalyst was lost. In terms of the turnover frequency (TOF) per 1 h, measured for the first reaction cycle, catalysts immobilized on thioether and phosphine ligands, **2-Pd** and **3-Pd** show the highest activity. The TOF values for the catalysts immobilized on vinyl groups are considerably smaller.

Some of the catalysts were additionally tested in the Mizoroki–Heck arylation of butyl acrylate and acrylonitrile with iodobenzene. As shown in Table 4, the activity of **1a-Pd**, **2-Pd**, **3-Pd** catalysts in terms of maximum conversion of substrate and of TOF is also comparable, or even better, to that of the homogeneous Pd complex precatalyst. Interestingly, in the reaction of acrylonitrile, the ratio of (*E*) to (*Z*) isomers of cinnamitrile formed over supported Pd catalysts was almost the same as for the homogeneous counterpart. Further, for all tested catalysts formation of byproduct 1-cyano-2,2-diphenylethene was not observed.

Since iodobenzene is known to be very reactive in Mizoroki–Heck coupling reactions, we have also examined the activity of polysiloxane–PdCl<sub>2</sub> complexes in the reaction of less reactive bromobenzene with styrene (Scheme 6). In this case the activity of the catalysts was rather poor. After 3 h at 120 °C conversion of bromobenzene was 4%, 3% and 32% for **1a-Pd**, **2-Pd** and **3-Pd**, respectively. Thus, only the phosphino-substituted catalyst **3-Pd** showed the activity comparable to that of PdCl<sub>2</sub>(PhCN)<sub>2</sub> (26% conversion after 3 h).

#### 4. Conclusions

Soluble polysiloxanes with pendant vinyl, butylthioethyl and diphenylphosphinoethyl groups have been used as supports for palladium(II) (PdCl<sub>2</sub>) catalyst. Vinyl-containing polysiloxanes have different macromolecular topologies to examine the effect of macromolecular structure on the stability and activity of the supported catalysts. Catalytic activity of such immobilized palladium complexes was tested in the model Mizoroki–Heck arylations of methyl acrylate, butyl acrylate, and acrylonitrile by iodobenzene and of styrene by bromobenzene. The activity of the polysiloxane–Pd catalysts was comparable to that of PdCl<sub>2</sub>(PhCN)<sub>2</sub> and maintained through 5–10 reaction cycles. Comparison of



catalysts supported on polysiloxanes of different structures and different ligand densities in the polymer chain shows that (i) polymers with higher density of ligands bind metal more effectively; (ii) catalysts immobilized on linear polymers are more stable than those immobilized on branched structures. Particularly interesting seem the polysiloxanes with pendant thioether and phosphino ligands. However, they are very well soluble in organic solvents, which causes some loss of the catalyst during the separation procedure. All polysiloxane-supported catalysts show a considerable palladium leaching from the support as shown by XRF. Mercury poisoning test showed that polysiloxane–palladium complexes are true active catalysts of the reaction.

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### References

- [1] D.E. Bergbreiter, *Chem. Rev.* 102 (2002) 3345–3384.
- [2] T.J. Dickerson, N.N. Reed, K.D. Janda, *Chem. Rev.* 102 (2002) 3325–3344.
- [3] J. Jagur-Grodzinski (Ed.), *Living and Controlled Polymerization: Synthesis, Characterization and Properties of the Respective Polymers and Copolymers*, Nova Publishers, New York, 2006.
- [4] J.E. Mark, N.M. Bikales, C.G. Overberger, G. Menges (Eds.), *Encyclopedia of Polymer Science and Engineering*, Wiley, New York, 1985.
- [5] M.R. Buchmeiser (Ed.), *Polymeric Materials in Organic Synthesis*, Wiley-VCH, Weinheim, 2003.
- [6] Y. Uozumi, *Recent Progress in Polymeric Palladium Catalysts for Organic Synthesis*, Springer-Verlag, Berlin, 2004, pp. 77–112.
- [7] A.M. Trzeciak, J.J. Ziółkowski, *Coord. Chem. Rev.* 251 (2007) 1281–1293.
- [8] M.O. Farrell, C.H. van Dyke, L.J. Boucher, S.J. Metlin, *J. Organomet. Chem.* 172 (1979) 367–376.
- [9] F. Keller, H. Weinmann, V. Schurig, *Chem. Ber.* 130 (1997) 879–885.
- [10] T. Arai, H.T. Ban, T. Uozumi, K. Soga, *J. Polym. Sci. A: Polym. Chem.* 36 (1998) 421–428.
- [11] S. Laue, L. Greiner, J. Woltinger, A. Liese, *Adv. Synth. Catal.* 343 (2001) 711–720.
- [12] M. Cypriak, P. Pospiech, K. Strzelec, J.W. Sobczak, *Phosphorus, Sulfur, and Silicon and Rel. Elem.* 184 (2009) 1586–1598.
- [13] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, New York, 1966.
- [14] F.R. Hartley, *The Chemistry of Platinum and Palladium; with Particular Reference to Complexes of the Elements*, Applied Science Publishers Ltd., London, 1973.
- [15] C.L. Frye, R.M. Salinger, F.W.G. Fearon, J.M. Klosowski, T. De Young, *J. Org. Chem.* 35 (1970) 1308–1314.
- [16] J. Chojnowski, M. Cypriak, W. Fortuniak, M. Ścibiorek, K. Różga-Wijas, *Macromolecules* 36 (2003) 3890–3897.
- [17] G. Beamson, D. Briggs, *High Resolution XPS of Organic Polymers. The Scienta ESCA300 Database*, John Wiley & Sons, Chichester, 1992.
- [18] W. Noll, *The Chemistry and Technology of Silicones*, Academic Press, New York, 1968.
- [19] M. Ziemelis, J.C. Saam, *Macromolecules* 22 (1989) 2111–2116.
- [20] J. Chojnowski, M. Cypriak, W. Fortuniak, K. Różga-Wijas, M. Ścibiorek, *Polymer* 43 (2002) 1993–2001.
- [21] K. Różga-Wijas, J. Chojnowski, T. Zundel, S. Boileau, *Macromolecules* 29 (1996) 2711–2720.
- [22] J. Chojnowski, K. Różga, *J. Inorg. Organomet. Polym.* 2 (1992) 297–317.
- [23] C. Andersson, R. Larsson, *J. Catal.* 81 (1983) 179–193.
- [24] C. Andersson, R. Larsson, *J. Catal.* 81 (1983) 194–203.
- [25] H. Danjo, D. Tanaka, T. Hayashi, Y. Uozumi, *Tetrahedron* 55 (1999) 14341–14352.
- [26] P. Brant, L.S. Benner, A.L. Balch, *Inorg. Chem.* 18 (1979) 3422–3427.
- [27] M.Z. Cai, Q.H. Xu, J.W. Jiang, *J. Mol. Catal. A* 260 (2006) 190–196.
- [28] M. Cai, H. Zhao, Y. Huang, *J. Mol. Catal. A* 238 (2005) 41–45.
- [29] B. Chen, D. Wang, H. Liu, *Polym. Commun.* (1985) 48–55.
- [30] NIST X-ray Photoelectron Spectroscopy Database, v. 3.5, 2008. <http://srdata.nist.gov/xps/>.
- [31] B.P.S. Chauhan, J.S. Rathore, T. Bando, *J. Am. Chem. Soc.* 126 (2004) 8493–8500.
- [32] N.T.S. Phan, M. Van Der Sluys, C.W. Jones, *Adv. Synth. Catal.* 348 (2006) 609–679.
- [33] I. Pryjomska-Ray, A. Gniewek, A.M. Trzeciak, J.J. Ziolkowski, W. Tylus, *Topics Catal.* 40 (2006) 173–184.
- [34] J.A. Widegren, R.G. Finke, *J. Mol. Catal. A* 198 (2003) 317–341.
- [35] J.M. Richardson, C.W. Jones, *J. Catal.* 251 (2007) 80–93.
- [36] P.P. Zwemi, H. Alper, *Adv. Synth. Catal.* 346 (2004) 849–854.