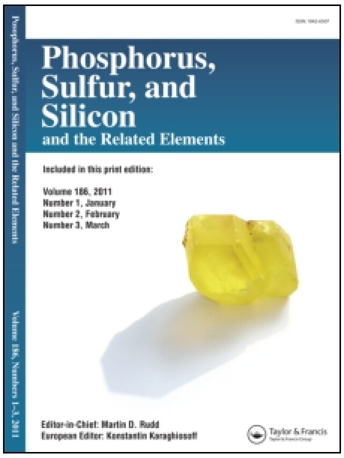

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# Soluble Alkylthiopolysiloxane-Supported Palladium Catalysts for the Heck Reaction

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# Soluble Alkylthiopolysiloxane-Supported Palladium Catalysts for the Heck Reaction

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*Soluble polysiloxanes with 2-butylthioethyl side groups have been used as support for palladium(II) catalyst. Catalytic activity of such immobilized palladium complex was tested in a model Heck reaction. The activity of the complex in terms of yield and turnover number was comparable to that of $PdCl_2(PhCN)_2$. Polysiloxane-supported catalyst shows good stability and low leaching, and its catalytic activity maintained practically unchanged through five catalytic cycles. According to XPS analysis, palladium in the complex with polysiloxane containing thioether groups appears as Pd(II).*

**Keywords** Heck reaction; palladium catalysts; polymer-supported catalysts; polysiloxanes

## INTRODUCTION

The use of polymer-supported catalysts in organic synthesis has become 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

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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(facile separation and reusability). Moreover, polymer topology as well as the ligand density may be modified over a wide range by proper design and controlled synthesis of polymer. Immobilized catalysts often show also good selectivity, in some cases different from that of small molecular complexes.

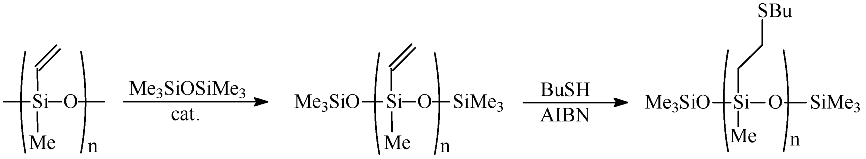
In order for a polymer to be useful as a soluble support for a catalyst or reagent, the polymer should be easily available, demonstrate good chemical stability, provide appropriate functional groups for attachment of catalytic moieties, and exhibit high solubilizing power in order to dissolve molecular entities.[1,2] A variety of organic polymers, such as polystyrene, polyethylene, poly(ethylene oxide), polyvinylpyridine, and others, have been usually applied as supports for catalysts.[3–5] The reports on the use of polysiloxanes as catalyst supports are very scarce.[6–8] 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. These features make them interesting potential supports for transition metal catalysts.

We report hereafter on the synthesis and application of polysiloxanes with pendant thioether groups as supports for a palladium catalyst, which has been tested in the Mizoroki–Heck coupling (subsequently referred to as the Heck reaction). Thiolate and thioether groups are known to effectively bind transition metals.[9,10] Palladium complexes with these ligands were successfully used as catalysts of the Heck reaction.[11,12] The use of organic polymers as supports for Heck catalysts was also reported.[13,14] However, to our knowledge, polysiloxanes with thioether groups have not yet been tested as supports for catalysts.

## RESULTS AND DISCUSSION

### Polymer Synthesis

Using the simple equilibration method of the mixture of methylvinylcyclosiloxanes in the presence of hexamethyldisiloxane as the chain regulator, the precursor polyvinylmethylsiloxane $Me_3SiO(MeViSiO)_nSiMe_3$ was prepared, which has been further modified by radical addition of *n*-butyl mercaptan (1-butanethiol) using azobisisobutyronitrile (AIBN) as initiator (Scheme 1).[15] The modification proceeds practically quantitatively; no vinyl groups remain in the product according to NMR spectroscopy. The resulting poly(2-(butylthio)ethyl)methylsiloxane was used for immobilization of palladium(II) chloride by linking to thioether side groups (Scheme 2). In this reaction, the [Pd]/[S] ratio was 1/4

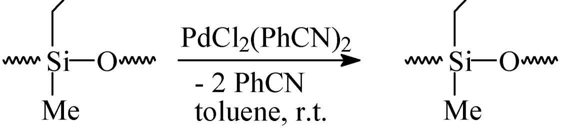


**SCHEME 1**

mol/mol. Assuming the complex involving two thioether groups coordinated to one Pd atom, half of the total amount of thioether groups should remain unbound.

Polymers were characterized by NMR spectroscopy, size-exclusion chromatography (SEC), digital scanning calorimetry (DSC), and X-ray photoelectron spectroscopy (XPS). The NMR spectra of poly(2-(butylthio)ethyl)methylsiloxane correspond well to those published previously.[15] $^1H$ and $^{29}Si$ NMR spectra of the polymer with immobilized $PdCl_2$ **1** show a similar signal pattern as its precursor, poly(2-(butylthio)ethyl)methylsiloxane. Chemical shifts of the corresponding groups are very similar (see the Experimental section), but the signals in spectra of **1** are significantly broader, which is related to the change in mobility of polymer chain segments and in relaxation times due to metal binding. Moreover, since the palladium complex was used in deficiency relative to functional groups in the polymer, approximately half of the thioether groups remain unbound, which results in more complex chain microstructure and differentiation of magnetic shielding in the siloxane units.

SEC analysis of poly(2-(butylthio)ethyl)methylsiloxane in toluene measured relative to polystyrene standards gave unreliable too low molecular weight due to difference in hydrodynamic volume between this polymer and polystyrene. On the other hand, the molecular weight estimated to ca. 43000 from $^1H$ NMR spectrum (as the ration of the



**(1)**

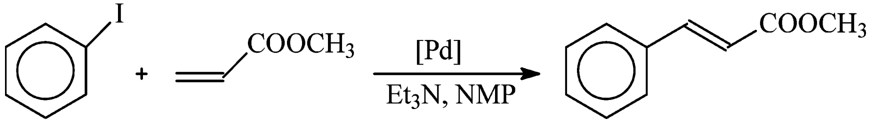
**SCHEME 2**

**TABLE I XPS Data of Poly(2-(butylthio)ethyl)methylsiloxane-$PdCl_2$ Complex 1**

| | Si 2p | O 1s | C 1s | | S 2p | Pd $3d_{5/2}$ | Cl $2p_{3/2}$ | |
|---|---|---|---|---|---|---|---|---|
| | Si-O | O-Si | C-H | C-C | S-C | Pd(II) | Cl-Pd | Cl-C |
| BE (eV) | 101.8 | 532.1 | 284.4 | 285.3 | 162.8 | 337.3 | 197.5 | 200.0 |
| atom % | 22.6 | 21.0 | 53.6 | | 2.0 | 0.12 | 0.58 | |

signal of terminal $Me_3Si$ groups to that of the MeSi groups inside the chain) agrees well with the theoretical value of 44000. DSC analysis indicates the increase of glass transition temperature of poly(2-(butylthio)ethyl)methylsiloxane upon Pd immobilization from –94.8°C to –75.7°C, which reflects partial loss of the conformational freedom of polysiloxane segments due to binding to palladium.

XPS spectrum of the freshly prepared polysiloxane-$PdCl_2$ complex **1** shows that palladium appears exclusively in the form of Pd(II) (binding energies 342.52 and 337.27 for $Pd3d_{3/2}$ and $Pd3d_{5/2}$, respectively). The observed position of $Pd3d_{5/2}$ peak at BE = 337.27 eV is close to that found for Pd(II) attached to sulfur in complexes reported by other authors (BE = 337.5 eV).[16,17] One of the binding energies observed for Cl ($Cl2p_{3/2}$, BE = 197.50 eV) is also similar to that observed in $PdCl_2$ complexes (ca. 198.0 eV). Large fraction of Cl in the surface layer is bound to C, which may be the result of secondary reactions during XPS analysis. On the other hand, a high S/Pd ratio suggests the enrichment of sulfur concentration in the vicinity of Pd. The $S2p_{3/2}$ peak of sulfur is typical for the Pd-S bonding; however many other sulfur compounds show similar BE values, which makes the identification ambiguous.[18] The surface composition is presented in Table I. The deficiency of Pd, Cl, and S at the surface compared to theoretical atomic content in the polymer **1** 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 S-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.



**SCHEME 3**

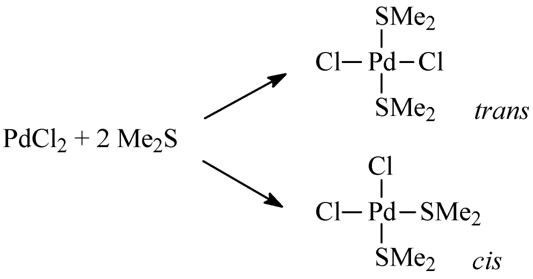
**TABLE II Heck Arylation of Methyl Acrylate with Iodobenzene Catalyzed by the Poly(2-(butylthio)ethyl)methylsiloxane-$PdCl_2$ Complex 1 and by $PdCl_2(PhCN)_2$**

| Catalyst | Cycle | [Pd]/[PhI] (%mol) | T (°C) | Time (h) | Conversion (%) | TON |
|---|---|---|---|---|---|---|
| 1 | 1 | 1.16 | 80 | 1 | 88 | 75 |
| 1 | 2 | 1.16 | 80 | 1 | 89 | 76 |
| 1 | 3 | 1.16 | 80 | 1 | 84 | 72 |
| 1 | 4 | 1.16 | 80 | 1 | 89 | 77 |
| 1 | 5 | 1.16 | 80 | 1 | 86 | 74 |
| $PdCl_2(PhCN)_2$ | 1 | 1.60 | 80 | 1 | 86 | 53 |

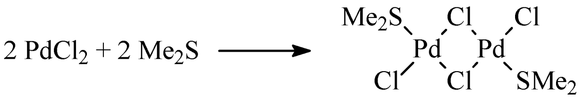
## Catalytic Study

The obtained supported catalyst (**1**) was tested for its activity and stability in a model Heck reaction of methyl acrylate with iodobenzene (Scheme 3). This catalyst system is not sensitive to oxygen and moisture, and the reaction can be carried out in air, with no change in activity. The catalyst activity was compared to the homogeneous $PdCl_2(PhCN)_2$ complex measuring maximum conversion of iodobenzene and the rate of the reaction (time when the maximum conversion is reached). Since only one product, methyl *trans*-cinnamate, was detected by GC, we assumed 100% reaction selectivity.

The activity of polysiloxane-palladium(II) complex **1** in terms of maximum conversion of substrates and of turnover number (TON) is comparable to that of the homogeneous $PdCl_2(PhCN)_2$ complex (Table II). Moreover, TON does not change after five catalytic cycles. However, the homogeneous complex reacts faster than **1**, giving a maximum conversion of iodobenzene after ca. 10 min. In the case of polymer-supported catalyst **1**, maximum conversion is reached after 20 min, and the reaction slows down after each cycle of reaction. Thus, in the fifth catalytic



**SCHEME 4**



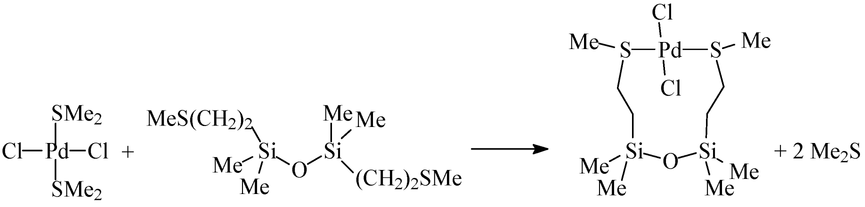
**SCHEME 5**

cycle, the time needed to achieve maximum conversion of iodobenzene was ca. 40 min. This points to partial deactivation of the catalyst due to some changes in the structure of the complex. According to atomic absorption spectroscopy (AAS) measurements, palladium content in polysiloxane-$PdCl_2$ complex **1** does not change significantly upon the reaction. AAS data showed the Pd content of 3.5 w% in the complex before the reaction and 3.6 w% after five catalytic cycles. These values are lower than the theoretical palladium loading of 6 w%. The Pd content of 5.9 w% determined by X-ray fluorescence spectroscopy (XRF) was very close to the theoretical value. Thus, the AAS analysis probably involves a systematic error. Nevertheless, almost identical values for the Pd content before and after five reaction cycles suggest that the metal leaching is negligible.

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. Since the precipitation was not quantitative, some loss of the catalyst occurred after each run.

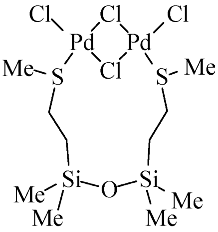
## Quantum Chemical Calculations

In order to get a deeper insight into the nature of these complexes, we have performed calculations of the structures and binding energies for model complexes $PdCl_2(SMe_2)_2$ and $PdCl_2((MeSCH_2CH_2Si)_2O)$. Thus, the enthalpy of formation of *trans*-$PdCl_2(SMe_2)_2$ from $PdCl_2$ and $Me_2S$ is –73.5 kcal/mol (–69.7 kcal/mol after BSSE correction, which gives the Pd-S bond formation enthalpy of –34.9 kcal/mol). *Cis*-$PdCl_2(SMe_2)_2$ is



2

**SCHEME 6**



**3**

**SCHEME 7**

by 6.4 kcal/mol less stable (Scheme 4). Both types of structural isomers are known.[19,20]

Sulfur complexed $PdCl_2$ may also form dimeric structures (Scheme 5).[19] The enthalpy of its formation according to Scheme 5 was calculated to $\Delta$ H = –121.7 kcal/mol. Since two Pd-Cl and two Pd-S bonds are formed in this reaction, the enthalpy of formation of one Pd-Cl and one Pd-S bonds equals 60.9 kcal/mol, which is by ca. 9 kcal/mol less than the enthalpy of formation of the two Pd-S bonds according to Scheme 4. Thus, in the presence of an excess of thioether groups, the formation of the dimer seems less probable.

To model the interactions of metal with a polysiloxane chain, we have calculated the enthalpy of ligand exchange between $PdCl_2(SMe_2)_2$ and disiloxane containing methylthioethyl groups (Scheme 6). The reaction is energetically favorable, $\Delta$ H = –4.2 kcal/mol (–37.0 kcal/Pd-S bond). This means that there is no significant ring strain nor steric hindrance in complex **2**, and the Pd complexation by polysiloxane is expected to proceed smoothly. Formation of the "dimeric" complex **3** (Scheme 7), in a reaction analogous to that shown in Scheme 5, is again less favorable than formation of the "monomeric" complex **2** shown in Scheme 6. The difference in enthalpy of formation of one Pd-Cl and one Pd-S bonds in **3** and enthalpy of formation the two Pd-S bonds in **2** is ca. 10 kcal/mol.

Good solubility of the polymer–palladium complex indicates that the Pd-S interactions are mostly intramolecular. Intermolecular coordination would lead to cross-linking and to a decrease in solubility of the polysiloxane-$PdCl_2$ complex.

## CONCLUSIONS

Soluble linear polysiloxanes with pendant butylthioethyl groups have been used as support for the palladium(II) ($PdCl_2$) catalyst. Catalytic activity of such immobilized palladium complex **1** was tested in the model Heck arylation of methyl acrylate by iodobenzene. Polysiloxanes with thioether groups are interesting and effective supports for catalysts of the Heck C-C coupling. The activity of the polysiloxane-Pd catalyst **1** was comparable to that of $PdCl_2(PhCN)_2$. Complex **1** also shows fair stability and small leaching, since its activity and palladium content (measured by atomic absorption spectrometry) were maintained at the same level through five catalytic cycles. The disadvantage of this polysiloxane-$PdCl_2$ complex is a relatively good solubility in many organic solvents, which causes some loss of the catalyst during the precipitation procedure.

## EXPERIMENTAL

### Chemicals

Toluene and methanol (POCh, analytical grade) were purified by standard methods.[21] N-methylpyrrolidone (ABCR, 99%) was purified by distillation under reduced pressure. Hexamethyldisiloxane (Aldrich, pure) was used as received. Iodobenzene was purified by distillation under argon. Methyl acrylate (International Enzymes Limited, pure, stabilized with 15 ppm MEHQ) and 1-butanethiol (Janssen Chimica, 98%) were used as received. AIBN (Fluca, pure) was purified by crystallization from methanol. Clarsil MO-2 was obtained by courtesy of the chemical plant Polish Silicones Ltd. and used as received. $PdCl_2(PhCN)_2$ was prepared from $PdCl_2$ (ABCR, 99.9%) and benzonitrile (ABCR, 99%).[22] The mixture of vinylmethylcyclosiloxanes, $(MeViSiO)_n$, $n \geq 4$, obtained by hydrolysis of $MeViSiCl_2$, was dried by flushing nitrogen through the liquid mixture at 80°C for 5 h.

### NMR Spectroscopy

$^1H$, $^{13}C$, and $^{29}Si$ NMR spectra in $CDCl_3$ were obtained with Bruker 500 MHz spectrometer. $^{13}C$ spectra were obtained with broadband proton decoupling. A heteronuclear gated decoupling with a 60-sec delay or INEPT technique was used to acquire $^{29}Si$ NMR spectra.

### Analyses

#### *Gas Chromatography*

Gas chromatography analysis was performed on Hewlett Packard 5890 II apparatus equipped with a TCD detector and a HP-50+ column (30 m × 0.53 mm × 1 $\mu$ m). Injector and detector temperature: 210°C.

The carrier gas was helium. Temperature program: The column was kept at 50°C for 2 min, then heated to 150°C at a rate of 10°C/min.

### Size Exclusion Chromatography (SEC)

SEC analyses were performed on an LDC Analytical refractoMonitor IV instrument working with RI detector and equipped with two columns SDV 8 × 300, 5 $\mu$ m particle size, with $10^4$ 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.

### Differential Scanning Calorimetry (DSC) Measurements

Phase transitions of polymer (**1**) were studied by DSC 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.

### X-Ray Photoelectron Spectra (XPS)

XPS of all samples were acquired at room temperature using ESCALAB-210 (VG Scientific, England) spectrometer and non-monochromated Al K$\alpha$ (h$\nu$ = 1486.6 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 analyzer 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 sample holder and evacuated to vacuum below $8 \times 10^{-9}$ mbar without any further treatment. Data processing was performed using Avantage Data System (Thermo Electron). After data smoothing, a nonlinear Shirley background has been subtracted. Peak synthesis by symmetric Gaussian–Lorentzian product function, with L/G ratio 0.3 ± 0.05, were 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 C1s peak of C-Si bond of siloxane according to Beamson and Briggs data with BE=284.38 eV.[23]

### Atomic Absorption Spectrometry (AAS)

Samples were dissolved in aqua regia ($HCl:HNO_3 = 3:1$) 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 the SOLAAR M6 (Unicam Atomic Absorption) spectrometer at 244.8 nm.

### *X-Ray Fluorescence (XRF) Analysis*

Palladium content was determined by XRF spectroscopy using the ED-XRF (energy dispersive X-ray fluorescence) Canberra, model 1510 spectrometer. The samples were homogenized with colloidal silica (in proportion $\mathbf{1}/SiO_2 = 1:20$) using $MoO_3$ as the internal standard (0.5 w%). Obtained powder was then pressed into tablets having surface density of 0.0478 g/cm$^2$. The tablets were excited using the Am-241 source of photons at 60 keV. Pd-K and Mo-K photons were detected using semiconductor Si(Li) detector.

### *Computational Studies*

All calculations were performed using the Gaussian03 program.[24] Geometry optimizations were carried out at the B3LYP level of theory using the 6-31G* basis set for H, C, O, Cl, S, Si, and P and the effective core potential (ECP) basis set LANL2DZ for Pd. All equilibrium structures were identified by the frequency calculations. Thermal corrections to enthalpies were scaled by 0.96. BSSE corrections were computed using the counterpoise method as implemented in Gaussian03. Single point energies were computed using the 6-311+G(2d,p) basis set for all atoms except Pd, for which the LANL2DZ basis set incremented by four sets of 4f polarization functions was applied.[25]

## Synthesis

### *Preparation of Polyvinylmethylsiloxane*

Polylvinylmethysiloxane was prepared by a common reaction of equilibration of the mixture of vinylmethylcyclosiloxanes, $(MeViSiO)_n$, n $\geq$ 4 (28 g), in the presence of acid-activated clay catalyst, Clarsil MO-2 (ca. 3 % w/w), and hexamethyldisiloxane (HMDS), 0.94 mmol, as the molecular weight regulator.[26] 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, the molecular weight of which was estimated to $M_n = 15000$, MWD = 1.5, by SEC analysis and $M_n = 22000$ by $^1H$ NMR spectroscopy (as calculated from the end $Me_3Si$ group to chain MeSi group $^1H$ signal ratio). The theoretically expected $M_n$ value was 20000.

The content of vinyl groups in the polymer was 0.0116 mol/g. Glass transition temperature (DSC) was $T_g = -130°C$.

## *Preparation of Poly(2-(butylthio)ethyl)methylsiloxane*

The addition of n-butyl thiol to polylvinylmethysiloxane was carried out according to the procedure described previously.[15] The reaction was performed in dried toluene solution containing 1:1 (v/v) of the polymer for 5 h at 60°C. Polyvinylmethylsiloxane (3.45 g) containing 0.04 mol of vinyl groups was mixed with 0.2 mmol of AIBN. The solution was warmed to 60°C, and *n*-BuSH (0.049 mol) was added dropwise. The resulting poly(butylthioethyl)methylsiloxane was purified by twofold precipitation with methanol from toluene and dried by heating under high vacuum for several hours. The resulting polymer had a consistency of a yellow rubbery resin. Conversion of vinyl groups was almost quantitative, since no vinylsilyl group signals were observed either in $^1H$ or in the $^{29}Si$ NMR spectra of the modified polymer. Molecular weight: $M_n = 23500$, MWD = 1.7, according to SEC analysis and $M_n = 43000$ according to $^1H$ NMR (estimated from the end $Me_3Si$ group to chain MeSi group $^1H$ signal ratio). Theoretical $M_n$ was 44000. Glass transition temperature (DSC) was $T_g = -94.8$ °C. ($^1H$ NMR ($CDCl_3$)$\delta$ (ppm): 2.49 (m, $SC\underline{H}_2$), 1.53 (m, $SCH_2C\underline{H}_2CH_2$), 1.39 (m, $SCH_2CH_2C\underline{H}_2$), 0.89 (m, $S(CH_2)_3C\underline{H}_3$), 0.11 (s, $Si(C\underline{H}_3)_3$); $^{29}Si$ NMR (INVGATE, $CDCl_3$)$\delta$ (ppm): -23.74 (s, $OMe(R)\underline{Si}O$), 21.38, 21.62 (2 s, $Me_3\underline{Si}O$); $^{13}C$ NMR ($CDCl_3$) $\delta$ (ppm): 31.66 (s, $S\underline{C}H_2$), 26.38, (s, $SCH_2\underline{C}H_2CH_2$), 22.09 (s, $SCH_2CH_2\underline{C}H_2$), 18.33 (s, $Si\underline{C}H_2CH_2S$), 13.76 (s, $S(CH_2)_3\underline{C}H_3$), 0.07 (s, $Si(\underline{C}H_3)_3$).

## *Immobilization of Palladium*

The mixture of poly(2-(butylthio)ethyl)methylsiloxane and palladium complex [$PdCl_2(PhCN)_2$, 0.25% mol/mol relative to the content of the functional groups in polymer] in toluene was mixed and stirred for 72 h at room temperature. The obtained palladium complex with polysiloxane was separated by precipitation with methanol and dried under vacuum. The resulting complex had a consistency of yellow viscous syrup. It was characterized by $^1H$ and $^{29}Si$ NMR spectroscopy, DSC, AAS, and XRF. Glass transition temperature (DSC) was $T_g = -75.7°C$. Palladium content was measured to 3.5 w% (AAS) and 5.9 ± 0.12 w% (XRF). $^1H$ NMR ($CDCl_3$) $\delta$ (ppm): 2.52 (m, $SC\underline{H}_2$), 1.55 (m, $SCH_2C\underline{H}_2CH_2$), 1.41 (m, $SCH_2CH_2C\underline{H}_2$), 0.91 (m, $S(CH_2)_3C\underline{H}_3$), 0.13 (s, $SiC\underline{H}_3$); $^{29}Si$ NMR (INEPT, $CDCl_3$) $\delta$ (ppm): –23.69 (bm, $OMe(R)\underline{Si}O$-), –21.36, –21.65 (2 bs, $Me_3\underline{Si}O$); $^{13}C$ NMR ($CDCl_3$) $\delta$ (ppm): 31.56 (s,

$S\underline{C}H_2$), 26.28 (s, $SCH_2\underline{C}H_2CH_2$), 22.02, (s, $SCH_2CH_2\underline{C}H_2$), 18.23 (bm, $Si\underline{C}H_2CH_2S$), 13.69 (s, $S(CH_2)_3\underline{C}H_3$), 0.12 (bm, $Si(\underline{C}H_3)_3$).

## Kinetic Studies

Iodobenzene (0.28 mL), methyl acrylate (0.23 mL), and triethylamine (0.32 mL) were mixed with 1 mL N-methylpyrrolidone (NMP). The liquid mixture was put into the autoclave (15 mL volume), and then ca. 0.05 g of poly(2-(butylthio)ethyl)methylsiloxane-$PdCl_2$ complex **1** was added. The reaction mixture was heated to 80°C while vigorously agitating with 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. Methyl *trans*-cinnamate was the only product observed in GC, thus we concluded that the reaction proceeds with 100% selectivity. After 2 h, the reaction mixture was cooled down, and the catalyst was precipitated by the addition of methanol, filtrated, and rinsed with methanol. The remainder was dried at 90°C under vacuum for 3 h before reuse.

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