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# Synthesis of phenylene–silylene–ethylene polymers via transition metal complex catalyzed hydrosilylation polymerization

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**New phenylene–silylene–ethylene polymers have been successfully synthesized using platinum–divinylsiloxane or rhodium and iridium siloxide complex-catalysed polyhydrosilylation of divinylsubstituted carbosilanes with dihydrocarbosilanes or intermolecular hydrosilylation of new hydrovinylcarbosilane. Polycarbosilanes have been obtained with high molecular weights. They seem to be potential parent substances for future applications as preceramic and membrane materials. Copyright © 2004 John Wiley & Sons, Ltd.**

**KEYWORDS:** hydrosilylation polymerization; polycarbosilane; siloxy-rhodium and iridium complexes; Karstedt catalyst

## INTRODUCTION

Polycarbosilanes have attracted increasing attention for their applicability in new materials. Recently, these polymeric products with arylene units in the chain have been demonstrated to have specific physicochemical properties, which could be applicable in heat-resistant materials (coatings, paints or prepergs), ceramics, moulding materials, etc.[1,2–3] (EP 0661331A2). Poly(phenylene–silylene–ethylene)s also seem to be potential substrates for applications as membrane materials, because they have a relatively high gas permeability and, in contrast to commonly used polysiloxanes, they are not sensitive to hydrogen sulphide, mercaptans or thiophene, which are likely to be present in the gas streams processed. The necessary condition that has to be met for a polymer to be used as a material in the above-mentioned applications is a high average molecular weight.

Linear polycarbosilanes of general formula -[RR′Si$(CH_2)_2$]- were previously obtained by hydrosilylation polymerization of Si–H and $SiCH{=}CH_2$-containing monomers but only low-molecular-weight oligomers were obtained.[3–7] In contrast to silylene–ethylene polymers, arylene–silylene–ethylene polymers are a relatively unexplored class of materials and only a few reports have been found (EP 0661331A2).[8–15] Hydrosilylation polymerization reactions leading to arylene–silylene–alkylene polymers are usually carried out in the presence of platinum catalysts. The optimum catalysts are made from platinum supported on alumina or carbon black, platinum–vinylsiloxane complexes, platinum–olefin complexes or platinum–phosphite complexes, but in view of the catalytic activity, hexachloroplatinic acid and platinum–vinylsiloxane complexes are preferred.[8–15] Other transition metal catalysts [e.g. $RhCl(PPh_3)_3$, $RhCl_3$, $RuCl_3$, $PdCl_2 \times 2H_2O$ or $NiCl_2$] have also been tested in this process (EP 0661331A2). Although the average molecular weights of the resulting linear polymers are generally as low as several thousands, to the best of the authors' knowledge the highest molecular weight linear polycarbosilanes have been obtained by Tsumura and co-workers ($M_w = 33\,000$; EP 0661331A2). Rickle[2] was able to obtain higher molecular weight polycarbosilane as products of platinum-catalysed polyhydrosilylation reaction of dimethyldivinylsilane with 1,4-bis(dimethylsilyl)benzene in the presence of small amount of methyltrivinylsilane (cross-linking agent); however the aforementioned publication lacks complete spectroscopic and gel-permeation chromatography characterisations of the resulting polymers.

Over the last decade, several examples of monomeric and dimeric siloxy derivatives of rhodium have been synthesized, characterized spectroscopically and the structures of most of them have been determined by the X-ray method.[16–21] By analogy to the rhodium analogues, the monomeric and dimeric iridium–siloxide complexes have been recently

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synthesized and their structures have been successfully confirmed by the X-ray method.[22–23]

Our previous reports have shown that the dimeric rhodium siloxide complex $[\{\mathrm{Rh}(\mu\text{-}\mathrm{OSiMe}_3)(\mathrm{cod})\}_2]$ is an effective catalyst (even at room temperature) in the hydrosilylation of alkenes,[24] allyl ethers and allyl esters[25] with triethoxysilane as well as in the hydrosilylation of polyethers and alkenes by hydrosiloxanes.[26,27] Monomeric rhodium siloxide complexes of the general formula $[\mathrm{Rh}(\mathrm{cod})(\mathrm{PR}_3)(\mathrm{OSiR}'_3)]$, where $R = \mathrm{Ph}$ or cyclohexyl and $R' = \mathrm{Me}$, *i*-Pr or *t*-Bu, have also been found as effective catalysts of the hydrosilylation of allyl glycidyl ether by triethoxysilane.[21,28] These results have prompted us to investigate the scope of the rhodium siloxides and their iridium analogues that could be used as catalysts in the hydrosilylation polymerization reaction.

Therefore, the aim of this work is to synthesize new polycarbosilanes containing arylene units in the backbones, via the polyhydrosilylation reaction of difunctional vinylcarbosilanes with difunctional hydrocarbosilanes or the intermolecular hydrosilylation of hydrovinylcarbosilane in the presence of dimeric and monomeric rhodium and iridium siloxide complexes and to compare their catalytic activity with that of the commonly used platinum catalysts.

## EXPERIMENTAL

### *Analytical equipment*

$^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) were recorded on a Varian XL 300 spectrometer using $\mathrm{CDCl_3}$ or $\mathrm{C_6D_6}$ as a solvent. GPC data were collected using a Gilson HPLC System equipped with UV absorbance and RI detectors with a 300 × 7.8 mm Phenogel columns, 50, 500 and $10^4$ Å (analysis conditions: mobile phase, THF; flow rate, 0.7 ml/min; temperature, ambient; injection volume, 20 $\mu$l). Molecular weights were determined by polystyrene standard calibration. Infrared spectra (KBr plates) were recorded using an FT-IR Brucker IFS-113v. Elemental analyses were carried out by Vario EL III instrument (elementar GmbH).

### *Materials*

Organosilicon chemicals—chlorodimethylsilane, chlorodi methylvinylsilane, 1,2-bis(chlorodimethylsilyl)ethane and 1,4-bis(dimethylsilyl)benzene—were received from ABCR. 1,4-Dibromobenzene, $\mathrm{LiAlH_4}$ and Karstedt catalyst (3% Pt in xylene) were purchased from Aldrich. Organic solvents were received from OBR Plock (Poland). Pentane was dried over $\mathrm{CaH_2}$, distilled under argon and stored with molecular sieves type 3A. THF, toluene and diethyl ether were dried over sodium and benzophenone and freshly distilled prior to use. The siloxide complexes, $[\{\mathrm{Rh}(\mu\text{-}\mathrm{OSiMe}_3)(\mathrm{cod})\}_2]$, $[\mathrm{Rh}(\mathrm{cod})(\mathrm{PCy}_3)(\mathrm{OSiMe}_3)]$ as well as $[\{\mathrm{Ir}(\mu\text{-}\mathrm{OSiMe}_3)(\mathrm{cod})\}_2]$ and $[\mathrm{Ir}(\mathrm{cod})(\mathrm{PCy}_3)(\mathrm{OSiMe}_3)]$, were prepared according to the previously reported procedures.[18,21–23] Vinylmagnesium bromide was synthesized via the well-known procedure. 1,4-Bis(dimethylvinylsilyl)benzene[29] and 1,2-bis(dimethylvinylsilyl) ethane[30] were synthesized according to the literature. All reactions were carried out under deoxygenated and dried argon.

### Synthesis and characterization of 1,2-bis(dimethylsilyl)ethane

To a two-necked flask equipped with a magnetic stirring bar, reflux condenser and argon bubbling tube, a portion of 8.5 g (0.223 mol) of $\mathrm{LiAlH_4}$ was introduced and slowly 100 ml of THF were dropped in. The suspension was cooled using a water bath and the solution of 20 g (0.093 mol) of 1,2-bis(chlorodimethylsilyl)ethane in 100 ml of THF was added dropwise via a syringe. The reaction mixture was stirred at 60 °C for 12 h. The product was purified by distillation to yield 10.8 g of 1,2-bis(dimethylsilyl)ethane in 79% yield as a colourless liquid.

$^1$H NMR ($\mathrm{C_6D_6}$) $\delta$ (ppm) $-0.05$ (s, 12H, $-\mathrm{SiCH_3}$), 0.58 (s, 4H, $-\mathrm{CH_2}-$), 3.84–3.88 (m, 2H, SiH). $^{13}$C NMR ($\mathrm{C_6D_6}$) $\delta$ (ppm) $-4.81$ ($-\mathrm{Si}\underline{\mathrm{C}}\mathrm{H_3}$), 7.06 ($-\underline{\mathrm{C}}\mathrm{H_2}-$).

### Synthesis and characterization of 1-(dimethylsilyl)-4-[{2-(dimethylvinylsilyl)ethyl}dimethylsilyl] benzene

#### *Synthesis of 1-bromo-4-(dimethylsilyl)benzene*

A solution of 20 g (0.085 mol) of 1,4-dibromobenzene in 150 ml dry THF was introduced into a two-necked, 500 ml round-bottomed flask equipped with a magnetic stirring bar, rubber septum cap and argon bubbling tube and then it was treated at −78 °C with a solution of 35.6 ml (0.089 mol) of *n*-BuLi added dropwise. After 1 h, a 19.5 ml (0.178 mol) of chlorodimethylsilane was added. The reaction was stirred at −78 °C for 1 h and then for 18 h at room temperature. After the substrate disappearance was confirmed by GC, 50 ml of pentane were added, then the resulting salt was filtered off and the volatiles were removed in an evaporator. Distillation under reduced pressure (40–45 °C/0.5 mmHg) afforded 14.57 g of 1-bromo-4-(dimethylsilyl)benzene in 80% yield as a colourless liquid.

$^1$H NMR ($\mathrm{CDCl_3}$) $\delta$ (ppm): 0.34–0.36 (m, 6H, $-\mathrm{SiCH_3}$), 4.41–4.43 (m, 1H, $-$SiH), 7.37–7.52 (m, 4H, Ph). $^{13}$C NMR ($\mathrm{CDCl_3}$) $\delta$ (ppm): $-1.81$ ($-\mathrm{Si}\underline{\mathrm{C}}\mathrm{H_3}$), 123.98, 130.98, 135.56, 136.17 (Ph).

#### *Synthesis of 1-bromo-4-[{2-(chlorodimethylsilyl) ethyl}dimethylsilyl]benzene*

Into a Schlenk tube, under argon, were placed 7 ml (0.05 mol) of chlorodimethylvinylsilane and 50 $\mu$l ($4.6 \times 10^{-6}$ mol) of Karstedt catalyst (3% Pt solution in xylene). Then 10 g (0.046 mol) of 1-bromo-4-(dimethylsilyl)benzene were added dropwise and the reaction mixture was stirred over 2 h at room temperature. The excess of chlorosilane was removed in vacuum. Distillation under reduced pressure (80–85 °C/0.5 mmHg) afforded 14.97 g of product in 96% yield as a colourless liquid.

$^1$H NMR ($CDCl_3$) $\delta$ (ppm): 0.29 [d, 6H, $-Si(CH_3)_2Cl$], 0.41 [d, 6H, $-Si(CH_3)_2-$], 0.72–0.76 (m, 4H, $-CH_2-$), 7.36–7.52 (m, 4H, Ph). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): −3.71 [$-Si(CH_3)_2-$], 0.92 [$-Si(CH_3)_2Cl$], 6.99 [$-Si(CH_3)_2\underline{C}H_2CH_2Si(CH_3)_2Cl$], 11.34 [$-Si(CH_3)_2CH_2\underline{C}H_2Si(CH_3)_2Cl$], 123.73, 130.92, 135.20, 137.50 (Ph).

### *Synthesis of 1-bromo-4-[{2-(dimethylvinylsilyl) ethyl}dimethylsilyl]benzene*

A solution of 10 g (0.029 mol) of $BrC_6H_4Si(CH_3)_2CH_2CH_2Si(CH_3)_2Cl$ in 100 ml dry THF was introduced into a two-necked, 250 ml round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, rubber septum cap and argon bubbling tube. Then 0.044 mol of vinylmagnesium bromide in dry THF was added dropwise. The reaction mixture was refluxed under argon for 2 h. The excess Grignard reagent was quenched by adding 5 ml of water and the mixture was extracted from pentane–$H_2O$. The ethereal phase was dried over $MgSO_4$ and filtered, the volatiles removed in an evaporator and the mixture was passed through a silica gel column (eluent, pentane). After isolation by distillation under reduced pressure (110–113 °C/0.5 mmHg), 6.23 g of the product was afforded in 64% yield as a colourless liquid.

$^1$H NMR ($CDCl_3$) $\delta$ (ppm): 0.08 (s, 6H, $-Si(C\underline{H}_3)_2CH{=}CH_2$), 0.28 (s, 6H, $-Si(CH_3)_2-$), 0.45–0.51 (m, 2H, $-Si(CH_3)_2CH_2C\underline{H}_2Si(CH_3)_2CH{=}CH_2$), 0.64–0.70 (m, 2H, $-Si(CH_3)_2C\underline{H}_2CH_2Si(CH_3)_2CH{=}CH_2$) 5.68 (dd, 1H, $C\underline{H}_2{=}CH$), 5.99 (dd, 1H, $C\underline{H}_2{=}CH$), 6.15 (dd, 1H, $CH_2{=}C\underline{H}$), 7.36–7.53 (m, 4H, Ph). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): −3.99 ($-Si(CH_3)_2-$), −3.66 ($-Si(C\underline{H}_3)_2CH{=}CH_2$), 7.40 ($-Si(CH_3)_2\underline{C}H_2CH_2Si(CH_3)_2CH{=}CH_2$), 7.63 ($-Si(CH_3)_2CH_2\underline{C}H_2Si(CH_3)_2CH{=}CH_2$), 123.55, 130.83, 138.19, 135.23 (Ph), 131.72 ($\underline{C}H_2{=}CH$), 138.76 ($CH_2{=}\underline{C}H$).

### *Synthesis of 1-(dimethylsilyl)-4-[{2-(dimethylvinylsilyl)ethyl} dimethylsilyl]benzene*

A solution containing 5 g (0.015 mol) of $BrC_6H_4Si(CH_3)_2CH_2CH_2Si(CH_3)_2CH{=}CH_2$ and 3.3 ml (0.030 mol) of chlorodimethylsilane in 10 ml of dry THF was added dropwise to a suspension of magnesium turnings (0.73 g, 0.030 mol) in dry THF. After the addition was finished, the reaction mixture was stirred under reflux for 2 h. Then THF was evaporated under vacuum and 20 ml of hexane were added. After evaporation of organic solvents the resulting salt was filtered off and the residue was distilled under reduced pressure (100–102 °C/0.5 mmHg). After isolation 2.62 g of the product were obtained in 56% yield as a colourless liquid.

$^1$H NMR ($CDCl_3$) $\delta$ (ppm): 0.07 [s, 6H, $-Si(C\underline{H}_3)_2CH{=}CH_2$], 0.27 [s, 6H, $-Si(C\underline{H}_3)_2-$], 0.36–0.38 [d, 6H, $-Si(C\underline{H}_3)_2H$], 0.47–0.53 [m, 2H, $-Si(CH_3)_2CH_2C\underline{H}_2Si(CH_3)_2CH{=}CH_2$], 0.65–0.71 [m, 2H, $-Si(CH_3)_2C\underline{H}_2CH_2Si(CH_3)_2CH{=}CH_2$], 4.43–4.46 [m, 1H $-Si(CH_3)_2\underline{H}$] 5.69 (dd, 1H, $C\underline{H}_2{=}CH$), 5.97 (dd, 1H, $C\underline{H}_2{=}CH$), 6.14 (dd, 1H, $CH_2{=}C\underline{H}$), 7.51–7.58 (m, 4H, Ph). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): −3.84 [$-Si(\underline{C}H_3)_2H$], −3.71 [$-Si(\underline{C}H_3)_2-$], −3.51 [$-Si(C\underline{H}_3)_2CH{=}CH_2$], 7.59 [$-Si(CH_3)_2CH_2\underline{C}H_2Si(CH_3)_2CH{=}CH_2$], 7.76 [$-Si(CH_3)_2\underline{C}H_2CH_2Si(CH_3)_2CH{=}CH_2$], 131.52 ($\underline{C}H_2{=}CH$), 133.14, 132.95, 137.77, 140.48 (Ph), 138.82 ($CH_2{=}\underline{C}H$).

## Typical procedure of the synthesis of polycarbosilane 1

The monomers were degassed and distilled prior to polymerization. In a typical reaction 0.50 g ($2.0 \times 10^{-3}$ mol) of 1,4-bis(dimethylvinylsilyl)benzene, 0.292 g ($2.0 \times 10^{-3}$ mol) of 1,2-bis(dimethylsilyl)ethane and 4 ml of dry toluene [or respectively 0.5 g ($2.5 \times 10^{-3}$ mol) of 1,2-bis(dimethylvinylsilyl)ethane, 0.485 g ($2.5 \times 10^{-3}$ mol) of 1,4-bis(dimethylsilyl) benzene and 4 ml of dry toluene] were combined with the catalyst and placed in a 25 ml, two-necked, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser and argon bubbling tube. The typically used monomer-to-catalyst ratio was $1:1:10^{-5}$ (for Pt-catalyst) or $1:1:10^{-3}$ (for Rh and Ir catalysts). The reaction mixture was heated at 110 °C under argon flow for 24 h. After completion of the reaction, the resultant polymers were isolated and purified by repeated precipitation from methanol to afford a white powder of polycarbosilane 1.

## Characterization of polycarbosilane 1

$^1$H NMR ($CDCl_3$) $\delta$ (ppm): −0.06 [s, $-Si(C\underline{H}_3)_2CH_2CH_2Si(CH_3)_2C_6H_4-$], 0.26 [s, $-Si(CH_3)_2CH_2CH_2Si(C\underline{H}_3)_2C_6H_4-$], 0.33–0.46 [m, $-Si(CH_3)_2C\underline{H}_2CH_2Si(CH_3)_2-$ and $-Si(CH_3)_2C\underline{H}_2CH_2Si(CH_3)_2C_6H_4-$], 0.60–0.68 [m, $-Si(CH_3)_2CH_2C\underline{H}_2Si(CH_3)_2C_6H_4-$], 7.48–7.52 (m, Ph). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): −4.29 [$-Si(\underline{C}H_3)_2CH_2CH_2Si(CH_3)_2C_6H_4-$], −3.48 [$-Si(CH_3)_2CH_2CH_2Si(\underline{C}H_3)_2C_6H_4-$], 6.71 [$-Si(CH_3)_2C\underline{H}_2CH_2Si(CH_3)_2-$], 6.83 [$-Si(CH_3)_2\underline{C}H_2CH_2Si(CH_3)_2C_6H_4-$], 7.80 [$-Si(CH_3)_2CH_2\underline{C}H_2Si(CH_3)_2C_6H_4-$], 132.77, 132.86, 132.93, 139.98 (Ph). **IR** $\nu$ (KBr cm$^{-1}$): 3050, 2952, 2901, 1404, 1379, 1248, 1133, 1058, 1045, 832, 815, 799, 770, 705. Anal. calcd for $(C_{20}H_{40}Si_4)_n$: C, 61.14; H, 10.26. Found: C, 60.28; H, 10.09.

## Typical procedure of the synthesis of polycarbosilane 2

The monomer **1** was degassed and distilled prior to polymerization. In a typical reaction 0.5 g ($1.63 \times 10^{-3}$ mol) of 1-(dimethylsilyl)-4-[{2-(dimethylvinylsilyl)ethyl}dimethylsilyl]benzene and 3.3 ml of dry toluene (0.5 M solution) were combined with the catalyst and placed in a 25 ml, two-necked, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser and argon bubbling tube. The typically used monomer to catalyst ratio was $1:10^{-5}$ (for Pt-catalyst) or $1:10^{-3}$ (for Rh and Ir catalysts). The reaction mixture was heated at 110 °C under argon flow for 24 h. After completion of the reaction, the resultant polymers were isolated and purified by repeated precipitation from methanol to afford a fair-yellow powder of polycarbosilane 2.

## Characterization of polycarbosilane 2

$^1$H NMR ($CDCl_3$) $\delta$ (ppm): −0.08 [s, $-Si(C\underline{H}_3)_2CH_2CH_2Si(CH_3)_2C_6H_4-$], 0.24 [s, $-Si(CH_3)_2CH_2CH_2Si(C\underline{H}_3)_2C_6H_4-$], 0.33–0.45 [m, $-Si(CH_3)_2C\underline{H}_2CH_2Si(CH_3)_2C_6H_4-$], 0.57–0.63

[m, $-Si(CH_3)_2CH_2C\underline{H}_2Si(CH_3)_2C_6H_4-$], 7.46–7.49 (m, Ph). $^{13}C$ NMR ($CDCl_3$) $\delta$ (ppm): −4.32 [$-Si(\underline{C}H_3)_2CH_2CH_2Si(CH_3)_2C_6H_4-$], −3.44 [$-Si(CH_3)_2CH_2CH_2Si(\underline{C}H_3)_2C_6H_4-$], 6.79 [$-Si(CH_3)_2\underline{C}H_2CH_2Si(CH_3)_2C_6H_4-$], 7.77 [$-Si(CH_3)_2CH_2\underline{C}H_2Si(CH_3)_2C_6H_4-$], 132.76, 139.74, 139.95 (Ph). **IR** $\nu$ (KBr $cm^{-1}$): 3049, 2962, 2902, 1405, 1379, 1261, 1134, 1094, 1055, 1021, 800, 731, 704. Anal. calcd for $(C_{16}H_{30}Si_3)_n$: C, 62.56; H, 9.86. Found: C, 60.52; H, 9.62.

## RESULTS AND DISCUSSION

The polycarbosilane **1** was synthesized using two different routes: by polyaddition of 1,2-bis(dimethylsilyl)ethane with 1,4-bis(dimethylvinylsilyl)benzene (reaction **I**) or by polyaddition of 1,4-bis(dimethylsilyl)benzene with 1,2-bis(dimethylvinylsilyl)ethane (reaction **II**) occurring in the presence of platinum, rhodium and iridium complexes, according to Scheme 1.

The polyhydrosilylation reactions were proceeded in toluene, which was selected as the reaction solvent because it is a good solvent for the catalysts used and has favourably high boiling point. Table 1 summarizes the molecular weights and PDI of the polycarbosilanes **1** synthesized via reaction of 1,2-bis(dimethylsilyl)ethane with 1,4-bis(dimethylvinylsilyl)benzene (reaction **I**).

The use of a platinum–divinylsiloxane catalyst (Karstedt catalyst) in this reaction led to a polymer with $M_w = 14\,100$. Two rhodium siloxides, $[\{Rh(\mu\text{-}OSiMe_3)(cod)\}_2]$ and $[Rh(OSiMe_3)(cod)(PCy_3)]$, and two iridium analogues, $[\{Ir(\mu\text{-}OSiMe_3)(cod)\}_2]$ and $[Ir(OSiMe_3)(cod)(PCy_3)]$, were also found to be effective catalysts of the process. The use of dimeric and monomeric rhodium siloxide complexes gave the possibility of synthesizing polycarbosilanes with higher molecular weight of about $M_w = 16\,400–20\,200$.

Unfortunately, siloxy iridium complexes showed less catalytic activity in the hydrosilylation polymerization of 1,4-bis(dimethylvinylsilyl)benzene by 1,2-bis(dimethylsilyl)ethane than the corresponding rhodium siloxides. The reactions proceeded quantitatively and homogeneously at 110 °C.

The second possible way of synthesizing polycarbosilane **1** was the reaction between 1,4-bis(dimethylsilyl)benzene and 1,2-bis(dimethylvinylsilyl)ethane (reaction **II**) in the presence of platinum, rhodium and iridium complexes. The experimental procedure of the polyhydrosilylation reaction **II** was the same as that described above for the hydrosilylation polymerization of 1,4-bis(dimethylvinylsilyl)benzene and 1,2-bis(dimethylsilyl)ethane. The results are shown in Table 2.

It can be seen from these data that molecular weights of the resulting polycarbosilanes are mostly lower and PDI, Polydispersity index ($M_w/M_n$) higher than the corresponding values of the polycarbosilanes obtained in the reaction **I**. Despite quite satisfactory results in the presence of the Karstedt catalyst, this particular method did not seem to be a useful reaction for synthesis of polycarbosilanes.

Phenylene–silylene–ethylene polymers can be also synthesized via intermolecular hydrosilylation of the monomers containing both the Si–H bond and the $SiCH{=}CH_2$ group

**Table 1.** Molecular weights and polydispersity indexes of polycarbosilanes **1** obtained via reaction **I**

| Catalyst | $M_w$ | $M_w/M_n$ | Yield (%) |
|---|---|---|---|
| $[Pt_2\{(CH_2{=}CHSiMe_2)_2O\}_3]$ | 14 100 | 1.88 | 88 |
| $[\{Rh(\mu\text{-}OSiMe_3)(cod)\}_2]$ | 20 200 | 2.04 | 95 |
| $[Rh(OSiMe_3)(PCy_3)(cod)]$ | 16 400 | 2.26 | 82 |
| $[\{Ir(\mu\text{-}OSiMe_3)(cod)\}_2]$ | 10 500 | 1.93 | 90 |
| $[Ir(OSiMe_3)(PCy_3)(cod)]$ | 14 000 | 2.10 | 74 |

Reaction conditions: toluene, 110 °C, 24 h.
$[HSi\,L]:[CH_2{=}CHSi\,L]:[cat.] = 1:1:10^{-5}$ (for Pt catalyst) or $1:1:10^{-3}$ (for Rh and Ir catalysts).

**Table 2.** Molecular weights and polydispersity indexes of polycarbosilanes **1** obtained via reaction **II**

| Catalyst | $M_w$ | $M_w/M_n$ | Yield (%) |
|---|---|---|---|
| $[Pt_2\{(CH_2{=}CHSiMe_2)_2O\}_3]$ | 16 800 | 1.63 | 66 |
| $[\{Rh(\mu\text{-}OSiMe_3)(cod)\}_2]$ | 6 200 | 2.32 | 78 |
| $[Rh(OSiMe_3)(PCy_3)(cod)]$ | 8 300 | 2.87 | 77 |
| $[\{Ir(\mu\text{-}OSiMe_3)(cod)\}_2]$ | 4 100 | 1.96 | 83 |

Reaction conditions: toluene, 110 °C, 24 h.
$[HSi\,L]:[CH_2{=}CHSi\,L]:[cat.] = 1:1:10^{-5}$ (for Pt catalyst) or $1:1:10^{-3}$ (for Rh and Ir catalysts).

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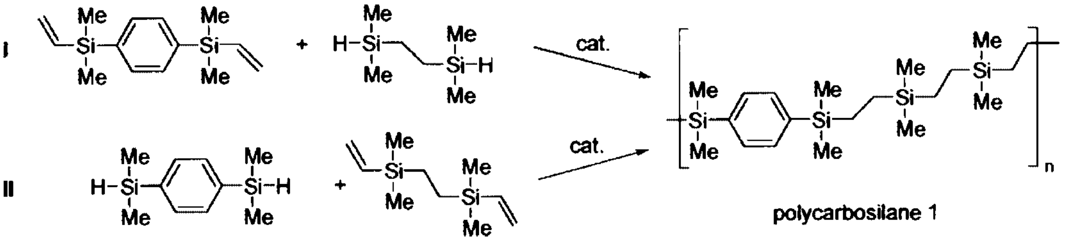

**Scheme 1.** Synthesis of polycarbosilane **1**.

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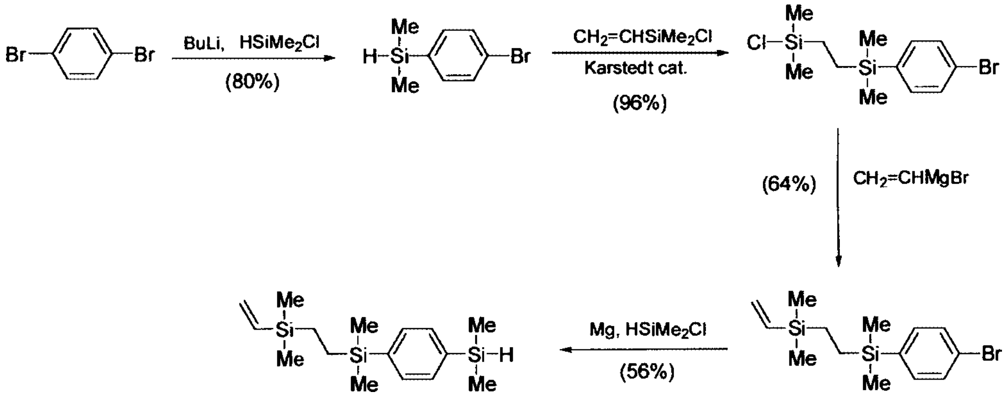

**Scheme 2.** Synthesis of 1-(dimethylsilyl)-4-[{2-(dimethylvinylsilyl)ethyl}dimethylsilyl]benzene.

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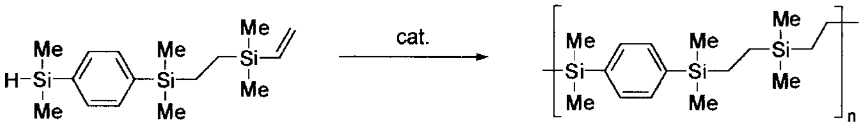

polycarbosilane 2

**Scheme 3.** Synthesis of polycarbosilane **2**.

in the molecule. The original four-step synthetic protocol for synthesis of the new organosilicon monomer applied in this reaction is presented in Scheme 2.

This method seems to be more efficient for the synthesis of high-molecular-weight polycarbosilanes, because the structure of the monomer guarantees an exact 1 : 1 stoichiometry of the Si–H bond to the vinyl group, which is difficult to achieve using two difunctional monomers. The replacement of 1,4-bis(dimethylvinylsilyl)benzene and 1,2-bis(dimethylsilyl)ethane by 1-(dimethylsilyl)-4-[{2-(dimethylvinylsilyl)ethyl}dimethylsilyl]benzene and its intermolecular hydrosilylation led to polycarbosilane **2**, whose structure is similar to that of polycarbosilane **1**. This reaction produced a polycarbosilane of the analogous structure to that of the one obtained by Rickle,[2] but in this case the reaction was carried out without a cross-linking agent Scheme 3.

The experimental procedure of the intermolecular hydrosilylation reaction was fully analogous to that described above for the hydrosilylation polymerization of divinylsubstituted carbosilanes and dihydrocarbosilanes. Table 3 summarizes the molecular weights and PDI of the polycarbosilanes **2** synthesized via polyhydrosilylation reaction of 1-(dimethylsilyl)-4-[{2-(dimethylvinylsilyl)ethyl}dimethylsilyl]benzene.

The best results were achieved in the presence of dimeric rhodium siloxide catalyst. In this reaction, polycarbosilane **2** with molecular weights as high as $M_w = 102\,000$ was obtained (in comparison to the reaction with platinum catalyst, $M_w = 14\,000$), but unfortunately, this high-molecular-weight fraction did not exceed 60% of the whole polymeric product. Apart from these, polymers with lower molecular weights ($M_w = 2000–14\,000$) were also formed. The GPC chromatogram of polycarbosilane **2** obtained in the presence of $[\{Rh(\mu\text{-}OSiMe_3)(cod)\}_2]$ showed a multimodal distribution of the molecular weight with three peaks ranging from 102 000 to 2100. Although, the rhodium- and iridium-catalysed polyhydrosilylation proceeded with a catalyst concentration higher than that of the platinum catalyst ($10^{-5}$ for Pt catalyst and $10^{-3}$ for Rh and Ir catalysts), these catalytic systems seem to be more useful for synthesis of high-molecular weights polymers, which can be applied to preceramic and membrane materials.

**Table 3.** Molecular weights and polydispersity indexes of polycarbosilanes **2**

| Catalyst | $M_w$ | $M_w/M_n$ | Yield (%) |
|---|---|---|---|
| $[Pt_2\{(CH_2{=}CHSiMe_2)_2O\}_3]$ | 14 000 | 1.77 | 73 |
| $[\{Rh(\mu\text{-}OSiMe_3)(cod)\}_2]$ | 102 000 (14 000, 2100) | — | 84 |
| $[Rh(OSiMe_3)(PCy_3)(cod)]$ | 28 400 | 2.19 | 92 |
| $[\{Ir(\mu\text{-}OSiMe_3)(cod)\}_2]$ | 8500 | 2.33 | 76 |
| $[Ir(OSiMe_3)(PCy_3)(cod)]$ | 6300 | — | 69 |

Reaction conditions: toluene, 110 °C, 24 h.
[monomer]:[cat.] = $1 : 10^{-5}$ (for Pt catalyst) or $1 : 10^{-3}$ (for Rh and Ir catalysts).

## CONCLUSION

Application of platinum–divinylsiloxane complex and dimeric and monomeric rhodium and iridium siloxide complexes of the general formula $[\{M(\mu\text{-}OSiMe_3)(cod)\}_2]$ and $[M(OSiMe_3)(cod)(PCy_3)]$ ($M = Rh$, Ir) as catalytic systems in the hydrosilylation polymerization of 1,4-bis(dimethylvinylsilyl)benzene with 1,2-bis(dimethylsilyl)ethane or 1,2-bis(dimethylvinylsilyl)ethane with 1,4-bis(dimethylsilyl)benzene and intermolecular hydrosilylation of 1-(dimethylsilyl)-4-[{2-(dimethylvinylsilyl)ethyl}dimethylsilyl]benzene led to linear poly(phenylene–silylene–ethylene)s. The most favourable synthetic procedures seem to be the hydrosilylation polymerization in the presence of dimeric rhodium siloxide complex, $[\{Rh(\mu\text{-}OSiMe_3)(cod)\}_2]$.

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