

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263814438>

Silylative Coupling versus Metathesis— Efficient Methods for the Synthesis of Difunctionalized Double-Decker Silsesquioxane Derivatives

ARTICLE *in* CHEMISTRY - A EUROPEAN JOURNAL · JULY 2014

Impact Factor: 5.73 · DOI: 10.1002/chem.201402862

CITATIONS

2

READS

27

4 AUTHORS, INCLUDING:



Patrycja Żak

Adam Mickiewicz University

12 PUBLICATIONS 40 CITATIONS

SEE PROFILE



Beata Dudziec

Adam Mickiewicz University

25 PUBLICATIONS 131 CITATIONS

SEE PROFILE

Polyhedral Silsesquioxanes

Silylative Coupling versus Metathesis—Efficient Methods for the Synthesis of Difunctionalized Double-Decker Silsesquioxane Derivatives

Patrycja Żak,^[a] Beata Dudziec,^[a] Maciej Kubicki,^[a] and Bogdan Marciniak^{*[a, b]}

Abstract: A series of functionalized dialkenylsilsesquioxanes were obtained by efficient and highly stereoselective silylative coupling and cross-metathesis of divinylsubstituted double-decker silsesquioxanes (DDSQ-2SiVi) with substituted styrenes and other olefins. Both reactions proceed highly stereoselectively and lead to nearly quantitative formation of

E isomers. The optimized reaction conditions for styrene were adopted for successful silylative coupling polycondensation of DDSQ-2SiVi with 1,4-divinylbenzene yielding stereoregular cooligomer containing double-decker (silsesquioxyl-silylene)-vinylene-phenylene units.

Introduction

Polyhedral silsesquioxanes (POSS) are compounds of the general formula $(\text{RSiO}_{3/2})_n$. They contain well-defined nanosized molecules and have attracted widening interest due to their possible use as precursors and components of versatile inorganic/organic hybrid materials,^[1] as well as their application in optics, catalysis, and electronics.^[2] The organic functional groups (one or eight) are covalently bonded to silicon atoms and facilitate specific interactions of silsesquioxane with other particles or organic phases to which they can be connected by these groups (e.g. polymer grafting). The location of reactive functional groups on the POSS core may also play a decisive role in their further applications. The vinyl-functionalized silsesquioxanes are of particular interest as the vinyl substituents are reactive in various transformations leading to hybrid materials, for example, chromophore-POSS systems (recently well studied for OLEDs).^[3]

The group of unsaturated POSS has been extended by another new class of silsesquioxyl compounds containing rigid Si-O-Si bonds, the double-decker silsesquioxane (DDSQ).^[4] Results over the last few years have shown that development in this field of organosilicon chemistry currently follows two major trends. One—molecular—is concerned with modifica-

tions of mainly hydro- or hydroxyl-substituted double-decker silsesquioxanes by hydrolytic condensation and hydrosilylation. This results in the formation of DDSQ-based compounds of strictly defined molecular mass and structure, and which possess interesting photo, amphiphilic, and thermal properties.^[5] The other trend—macromolecular—is based on difunctionalized DDSQ (e.g. hydro, alkenyl) derivatives employed as comonomers in polymerization reactions of various nature (hydrosilylation, dehydrogenative polycondensation, or nucleophilic substitution) resulting in organic-inorganic hybrid materials with desirable chemical and physical properties (photochemical, thermal, mechanical, etc.).^[6]

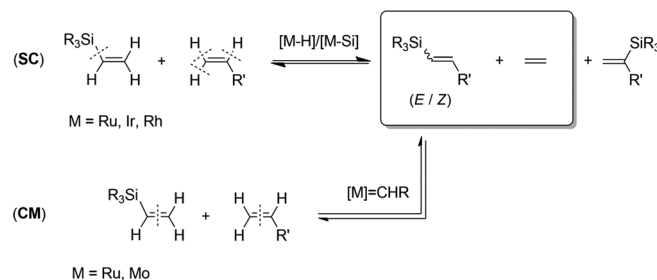
Over the last 20 years, we have developed two unique types of transition metal-catalyzed reactions, that is, silylative coupling (SC) and cross-metathesis (CM), as effective methods for synthesis of molecular and macromolecular compounds with vinylsilicon functionality.^[7] Silylative coupling occurs by cleavage of the C-H bond of the olefin and the C-Si bond of vinylsilanes. On the other hand, cross-metathesis starting with the same substrates results in a mixture of mostly the same main products, but proceeds by cleavage of the C=C bonds (Scheme 1).

There are many scientific reports on the application of the above reactions in the functionalization of mono- and octavin-

[a] Dr. P. Żak, Dr. B. Dudziec, Prof. Dr. hab. M. Kubicki, Prof. Dr. hab. B. Marciniak
Faculty of Chemistry, Department of Organometallic Chemistry
Adam Mickiewicz University in Poznań
Umultowska 89b, 61-614 Poznań (Poland)

[b] Prof. Dr. hab. B. Marciniak
Center for Advanced Technologies
Adam Mickiewicz University
Grunwaldzka 6, Poznań 60-780 (Poland)
Fax: (+48)618291508
E-mail: Bogdan.Marciniak@amu.edu.pl

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201402862>.



Scheme 1. Silylative coupling (SC) and cross-metathesis (CM) of vinylsilanes with olefins.

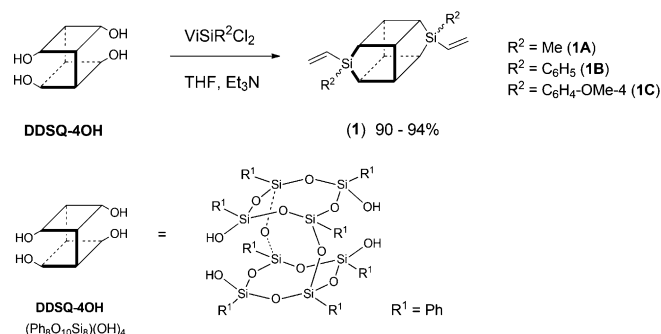
yl-substituted silsesquioxanes. Modification of vinylsilsesquioxanes by cross-metathesis has been reported by the groups of Feher,^[8] Laine,^[9] Cole-Hamilton,^[10] and ourselves.^[11] Moreover, we have demonstrated the high activity of ruthenium hydride complexes in the silylative coupling of vinyl-substituted silsesquioxanes and sphaerosilicates with styrenes and some other olefins.^[11] However, there has been no report on the use of silylative coupling and cross-metathesis for the modification of divinyl-substituted silsesquioxanes.

Herein, we focus on efficient selective procedures for the functionalization of a new type of divinyl-substituted double-decker silsesquioxane by silylative coupling and cross-metathesis with a series of olefins, for example, substituted styrenes.^[12] We also extend the silylative coupling methodology to the synthesis of novel stereoregular (silsesquioxyl-silylene)-vinylene-phenylene macromolecular compounds by the respective reaction of divinyl-substituted double-decker silsesquioxanes with 1,4-divinylbenzene.

Results and Discussion

Synthesis of divinylsubstituted double-decker silsesquioxanes (DDSQ-2SiVi)

DDSQ-2SiVi (**1A–C**) were synthesized by the hydrolytic condensation of incompletely condensed silsesquioxanes ($\text{Ph}_8\text{O}_8\text{Si}_8(\text{OH})_4$ (**DDSQ-4OH**) with vinylchloro(organo)silane ($\text{R}^2 = \text{Me}$, Ph, Ph-OMe-4) (Scheme 2). The methodology is well-

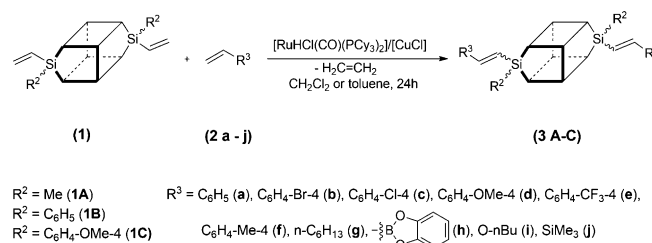


Scheme 2. Procedure for the synthesis of divinyl-substituted silsesquioxanes DDSQ-2SiVi (**1**).

documented for the synthesis of divinyl-dimethyl-substituted double-decker silsesquioxane (**1A**).^[4,13] We applied the modified procedure described earlier and synthesized new DDSQ compounds, that is, phenyl (**1B**) and 4-methoxyphenyl (**1C**) derivatives of **1**. Due to the statistical substitution of chlorosilanes, we obtained a mixture of *cis-trans* geometrical isomers taking into account the location of the R^2 and $-\text{HC}=\text{CH}_2$ groups at the Si-9 and Si-19 atoms, which is known for the DDSQ type silsesquioxanes^[14] (see the Experimental Section). All divinyl-substituted double-decker silsesquioxanes are air-stable, easy to handle, and can be synthesized on a multigram scale.

Functionalization–silylative coupling

Silylative coupling of methyl-substituted divinylsilsesquioxane (**1A**) with styrene was chosen as a model reaction for the study of the functionalization of silsesquioxanes containing two vinyl groups. Styrene was used as a reaction partner because it is highly reactive and does not isomerize under the reaction conditions.^[7] Treatment of the 1:2 mixture of **1A** and styrene in CH_2Cl_2 at 45°C with the ruthenium hydride complex $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (1 mol% in relation to the vinyl group of silsesquioxane) and copper(I) chloride (5 equiv relative to the catalyst) gave rise to slow evolution of ethane and formation of the distyryl-substituted silsesquioxane. We did not control the reaction progress by GC, due to the large molecular mass of the silsesquioxyl product, but ^1H NMR analysis of the reaction mixture performed after 18 h of the reaction course indicated nearly complete conversion of **1A** and selective formation of the silylative coupling product (**3A–a**) (Scheme 3).



Scheme 3. General procedure for synthesis of dialkenyl-substituted silsesquioxanes (**3**) by silylative coupling of DDSQ-2SiVi (**1**) with olefins (**2**).

Similar reactivity was observed when other DDSQ (**1B** and **1C**) and 4-substituted styrenes (**2b–f**) were used as reaction partners. In each case, the reaction led to efficient and selective formation of the *E*-isomer of the desired coupling product **3b–3f**. The results were obtained under the reaction conditions (catalyst concentration, presence of a co-catalyst, type of solvent, temperature, and time) optimized on the basis of a number of catalytic experiments, and are collected in Table 1. In the case of functionalization occurring by silylative coupling, particular attention was paid to detecting the possible formation of the product of undesirable styrene polymerization. The procedures presented ensure the efficient progress of silylative coupling and permit avoidance of the unwanted polystyrenes without the need for inhibitor addition. This effect was achieved thanks to the use of styrenes in the possibly lowest excess and application of mild reaction conditions (45°C). The mechanism explaining the effect of copper(I) chloride addition on the reaction course was not examined because the reasonable explanation reported in the literature for similar systems indicates that the copper salt acts as a phosphine scavenger and thus facilitates formation of catalytically active species.^[15] As indicated in Table 1, more forcing conditions (80°C , toluene and 4 mol% of catalyst) were required when vinyl alkyl ethers were tested as reaction partners. Unfortunately, in this case, the ^1H NMR spectrum of the reaction mixture revealed the formation of a mixture of stereoisomers (*E/Z* = 6/1). In our exami-

Table 1. Silylative coupling and cross-metathesis of divinyl-substituted silsesquioxanes **DDSQ-2SiVi** (**1**) with olefins (**2**).

DDSQ-2SiVi (1)	Olefin (2a–2m)	Product (3)	Silylative coupling ^[a] yield [%]	Cross- metathesis ^[b] yield [%]
1A	a	3A-a	94	–
1A	b	3A-b	96	–
1A	c	3A-c	92	–
1A	d	3A-d	94	–
1A	e	3A-e	92	–
1A	g	3A-g	91 ^[e]	–
1A	h	3A-h	0	–
1A			38 ^[c,e]	
1A	i	3A-i	80 ^[c,e]	–
1A	j	3A-j	30 ^[e]	–
1B	a	3B-a	93	94
1B	b	3B-b	91	90
1B	c	3B-c	91	89
1B	d	3B-d	99 ^[e]	99 ^[e]
1B	e	3B-e	91	95
1B	f	3B-f	93	92
1C	a	3C-a	93	88
1C	b	3C-b	92	89
1C	c	3C-c	93	93
1C	d	3C-d	99 ^[e]	99 ^[e]
1C	f	3C-f	99 ^[e]	99 ^[e]
1C	k	3C-k	–	58 ^[d,e]
1C	l	3C-l	–	60 ^[d,e]
1C	m	3C-m	–	55 ^[d,e]

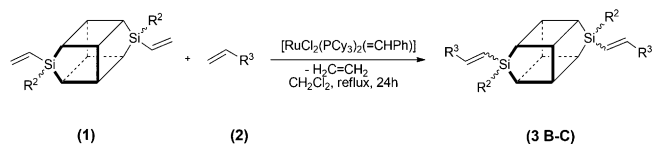
[a] Silylative coupling: CH₂Cl₂, reflux, argon, [1]:[2] = 1:2, [RuHCl(CO)(PCy₃)₂]/CuCl, [RuHCl(CO)(PCy₃)₂] (2 mol %), [Ru]:[Cu] = 1:5, 24 h. [b] Cross-metathesis: CH₂Cl₂, reflux, argon, [1]:[2] = 1:2, [RuCl₂(PCy₃)₂(=CHPh)] (2 mol %), 24 h. [c] Toluene, 80 °C, [RuHCl(CO)(PCy₃)₂] (4 mol %). [d] [RuCl₂(PCy₃)₂(=CHPh)] (4 mol %). [e] Not isolated. Conversion was determined by GC analysis on the basis of solvent as a standard.

nations, we did not apply silylative coupling for the modification of divinylsilsesquioxanes with allyl derivatives. As we previously reported, silylative coupling of allyl derivatives in the presence of ruthenium hydride complexes is always accompanied by isomerization (migration of the C=C double bond and *cis–trans* isomerization) leading to a mixture of products. As isomerization cannot be avoided, the silylative coupling of isomerizing olefins has no synthetic potential.

Functionalization–cross-metathesis

An analogous procedure was performed with the Grubbs catalyst (**I**) used instead of the catalytic system [RuHCl(CO)(PCy₃)₂]/CuCl. Reactions of divinylsilsesquioxane (**1B** and **1C**) with substituted styrenes (**2a–2f**), performed under the same conditions as those used for the corresponding **SC**, led to high conversions of substrates and evolution of ethylene (Scheme 4).

A divinyl-substituted double-decker silsesquioxane containing a methyl group located at Si-9 and Si-19 atoms (**1A**) proved to be inactive in metathetic transformation, which was expected in the context of our earlier reports indicating the inactivity of vinylmethylsilanes in cross-metathesis reactions. All results are presented in Table 1. In all cross-metathesis experiments performed, no competitive olefin *homometathesis* was observed. This selectivity was achieved thanks to the proper



R² = C₆H₅ (**1B**) R³ = C₆H₅ (**a**), C₆H₄-Br-4 (**b**), C₆H₄-Cl-4 (**c**), C₆H₄-OMe-4 (**d**), C₆H₄-CF₃-4 (**e**),
R² = C₆H₄-OMe-4 (**1C**) C₆H₄-Me-4 (**f**), CH₂SiMe₃ (**k**), CH₂C₆H₅ (**l**), CH₂OH (**m**)

Scheme 4. General procedure for synthesis of dialkenyl-substituted silsesquioxanes (**3**) by cross-metathesis of **DDSQ-2SiVi** (**1**) with olefins (**2**).

choice of the catalyst. The optimum catalyst used in the cross-metathesis reactions studied was the first-generation Grubbs' catalyst (**I**), which was a consequence of its low activity in the process of *homometathesis* of the olefins studied, in particular styrenes, under the conditions of the process. Effective metathesis transformation was observed also when silsesquioxane was treated with olefins in the presence of the second-generation Grubbs' catalyst (**II**) but the product of the cross-metathesis was accompanied by considerable amounts of those of olefin *homometathesis*. Divinylsilsesquioxane **1C** was tested also in the reaction with selected allyl derivatives in the presence of first-generation Grubbs' catalyst (**I**). As indicated in Table 1, incomplete conversion was observed even when 2 mol % of a ruthenium alkylidene catalyst in relation to the vinyl group of silsesquioxanes was used. However, ¹H NMR spectroscopic analysis of the post-reaction mixture demonstrated the exclusive formation of *E*-isomers and no isomerization of the expected product was observed. Reactions of **DDSQ** with vinyl ethers were not tested in the presence of a ruthenium alkylidene catalyst. It was demonstrated earlier that, under the conditions used, instead of metathesis, silylative coupling takes place, which is catalyzed by ruthenium hydride complexes formed by thermal decomposition of ruthenium alkoxybenzylidene complexes.^[16]

X-ray analysis of selected dialkenylsilsesquioxanes

Molecular compounds **3A-b**, **3A-j**, and **3B-e** proved to be solids and gave crystals amenable to X-ray crystal structure determination. Figures 1–3 show the perspective views of the three molecules. The molecules **3B-e** (Figure 2) and **3A-j** (Figure 3) have exact *Ci* symmetry, as they occupy the special position on the inversion center in the space groups *P*2₁/*c* and *P*1̄, respectively. Molecule **3A-b** (Figure 1) is also quite regular but it lacks the exact symmetry. The Si–O 'cage' is indeed almost perfectly centrosymmetric (the pseudo-center of inversion lies at 0,0.5,0.31), but the disposition of substituents—in particular the bromophenyl one—significantly deviates from this symmetry. In all three compounds the Si₁₀O₁₄ systems are very similar—Figure 4 shows the overlap of these fragments. The geometrical parameters of the complexes are typical, and similar to those described by us earlier:^[11] narrow distribution of Si–O and Si–C bond lengths, and relatively wide range of Si–O–Si angles (132.6°–168.1°), without clear relation to the position of the O atom.

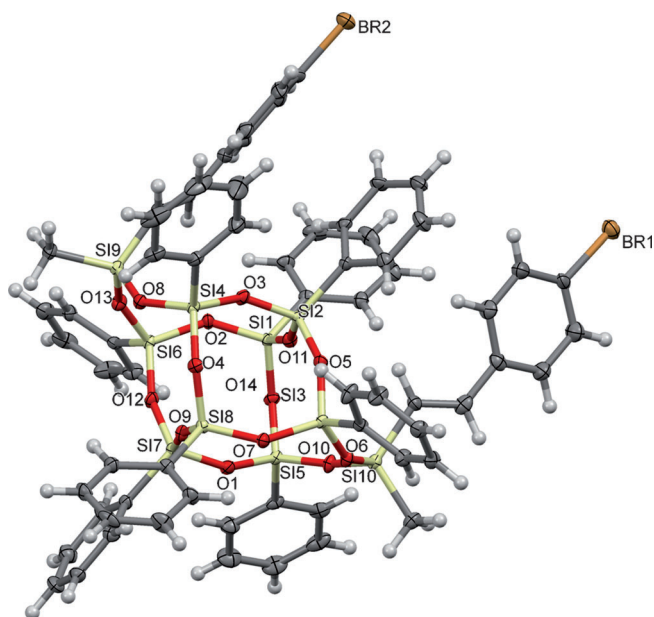


Figure 1. Perspective view of the molecule **1** (**3A-b**); ellipsoids are shown at the 33% probability level, hydrogen atoms are represented by spheres of arbitrary radii. Some geometrical data: $\langle \text{Si-O} \rangle$ 1.617(9) Å, O-Si-O range 138.9–166.4°, $\langle \text{Si-C} \rangle$ 1.844(10) Å.

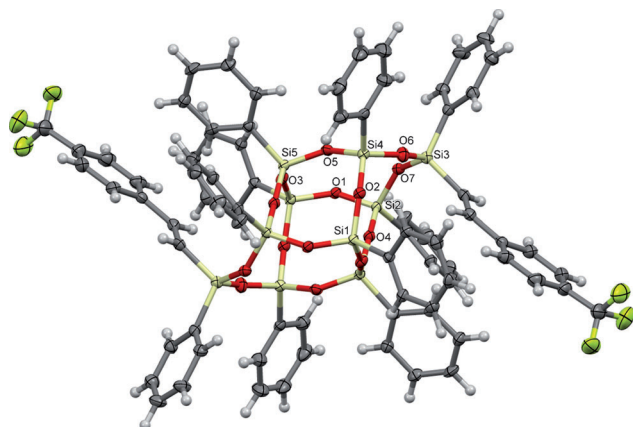


Figure 2. Perspective view of the molecule **2** (**3B-e**); ellipsoids are shown at the 33% probability level, hydrogen atoms are represented by spheres of arbitrary radii. The unlabelled part of the molecule is related to the labelled one by the symmetry operation $2-x, 1-y, 1-z$. Some geometrical data: $\langle \text{Si-O} \rangle$ 1.614(9) Å, O-Si-O range 133.9–164.0°, $\langle \text{Si-C} \rangle$ 1.841(8) Å.

Interestingly, the orientation of the substituents shows significant differences. In the symmetrical **3B-e** and **3A-j** compounds, the improper torsion angle C(vinyl)-Si...Si-C(vinyl), due to the symmetry, is 180° in accordance with the structure proposed for **3A-b** in Scheme 3. However in the compound **3A-b** the same angle is -2.3° , which suggests the *cis*-like (and not *trans*) disposition. It may be a result of obtaining a mixture of both conformers, of which only one is able to form single crystals. This might also explain the trouble associated with growing single crystals of appropriate quality. In the crystal structures there are no C-H...O type interactions with H...O separations shorter than 2.65 Å. Therefore, the only specific in-

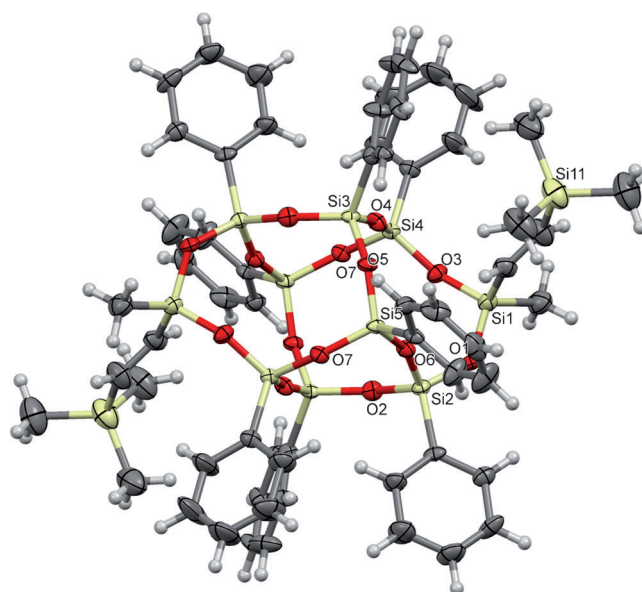


Figure 3. Perspective view of the molecule **3** (**3A-j**); ellipsoids are shown at the 33% probability level, hydrogen atoms are represented by spheres of arbitrary radii. The unlabelled part of the molecule is related to the labelled one by the symmetry operation $1-x, 1-y, 2-z$. Some geometrical data: $\langle \text{Si-O} \rangle$ 1.618(9) Å, O-Si-O range 132.6–168.1°, $\langle \text{Si-C} \rangle$, excluding Si11 1.844(11) Å, with Si11 1.853(14) Å.

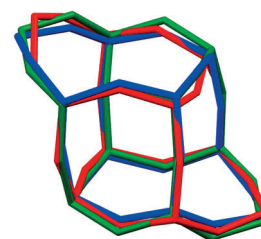


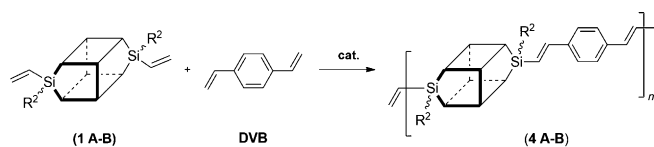
Figure 4. Comparison of the conformations of $\text{Si}_{10}\text{O}_{14}$ fragments of three molecules.

teractions are weak C-H... π ones ($\text{H}\cdots$ centroid separations 2.8–3.0 Å, C-H...centroid angles 141–152°). Only in Figure 1 is one of the Br atoms (Br2) involved in an almost linear halogen bond of C-Br...O type (Br...O 3.335(7) Å, C-Br...O 174.9(4)°).

Synthesis of macromolecular compounds

Positive results of silylative coupling (**SC**) of DDSQ-2SiVi (**1**) with styrene (yielding the distyryl-substituted derivative of double-decker silsesquioxane (**3A-a**)), prompted us to perform preliminary tests for **SC** of **1** with 1,4-divinylbenzene (**DVB**) to explore its utility towards the synthesis of hybrid materials (Scheme 5).

The polycondensation reaction between the methyl derivative of DDSQ-2SiVi (**1A**) and **DVB** was performed in refluxed CH_2Cl_2 and post reaction ^1H NMR spectra showed the disappearance of the signals of vinyl groups (both **1A** and **DVB**) and a new resonance line, a doublet at $\delta=6.39$ ppm with a coupling constant of $J_{\text{H-H}}=19.2$ Hz proving the formation of



R² = Me (1A)
R² = C₆H₅ (1B)

cat. = [RuHCl(CO)(PCy₃)₂]/[CuCl], CH₂Cl₂, reflux, 18–72h

Scheme 5. General procedure for synthesis of stereoregular (oligo)polymer with double-decker silsesquioxanes as a spacer (**4A** and **4B**) by silylative coupling of **DDSQ-2SiVi** (**1A** and **1B**) with **DVB**.

a *trans*-substituted vinylene group. The GPC analysis performed in THF revealed four oligomeric fractions of **4A** of molecular weight $M_w = 9510 \text{ g mol}^{-1}$ of the longest linear chain and a polydispersity index (PDI) of 1.335. Analogous results were obtained for the phenyl derivative of **DDSQ-2SiVi** (**1B**). To analyze the effect of the reaction time on its effectiveness, that is on polymer formation, a similar test for the silylative coupling of **1A** and **DVB** was performed for 72 h. Increasing the reaction time resulted in an increase in molecular weight of **4A-2** to $M_w = 34974 \text{ g mol}^{-1}$ (Figure 5). Application of the

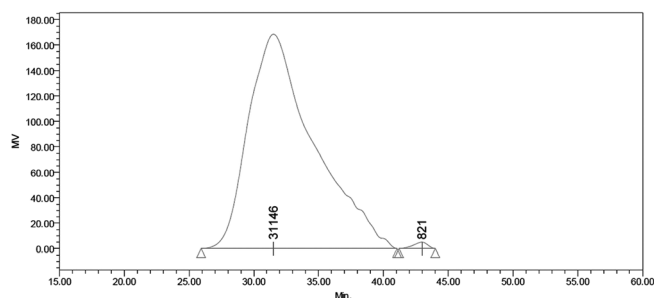


Figure 5. Gel permeation chromatogram of **4A-2**.

[RuHCl(CO)(PCy₃)₂]/[CuCl] system as a catalyst for the copolycondensation of **1A** and **1B** with **DVB** confirmed the possibility of synthesizing exclusively linear oligomers **4A** and **4B** containing *trans*-vinylene bonds between (silsesquioxyl-silylene)-phenylene units.

The new oligomeric products obtained were purified by twice repeated precipitation from MeOH or hexane at room temperature. Both polymeric materials are solids with good solubility in common organic solvents such as THF, CHCl₃, and CH₂Cl₂. All parameters of the oligomers, that is, M_n , M_w and PDI are summarized in Table 2.

These preliminary tests for the synthesis of a new class of stereoregular (oligo)polymers with double-decker silsesquioxanes embedded in the linear structure of products **4A** and **4B** are the first performed by a ruthenium-catalyzed process. The *trans*-stereochemistry of the HC=CH bonds is resolved and was confirmed on the basis of the J_{H-H} coupling constant of 19.2 Hz for the vinylene protons from the ¹H NMR spectra (for detailed ¹H, ¹³C, ²⁹Si NMR spectra see the Supporting Information).

Table 2. Results of silylative coupling polycondensation for (silsesquioxyl-silylene)-vinylene-phenylene (oligo)polymers.

Product	Fraction	$M_w^{[a]}$	$M_n^{[a]}$	PDI ^[a]	$\eta^{[b]}$
4A	1	9510	7125	1.335	5
4A	2	2822	2793	1.010	5
4A	3	1883	1857	1.014	5
4A	4	946	919	1.029	5
4A-2	1	34974	13309	2.628	10
4A-2	2	875	856	1.023	10
4B	1	8493	6358	1.336	4
4B	2	2503	2476	1.011	4
4B	3	1664	1639	1.015	4
4B	4	840	819	1.025	4

[a] The weight-average (M_w), number-average (M_n), and PDI were determined by GPC using polystyrene standards (in THF) as reference.
[b] Number of mers obtained by GPC.

Conclusion

Divinyl-substituted double-decker silsesquioxanes undergo efficient functionalization by silylative coupling and cross-metathesis with styrenes and selected vinyl and allyl derivatives in the presence of ruthenium complexes. Respective products have been obtained with high yields and selectivities. The reactions with styrenes give exclusively the *E* isomer. From the synthetic point of view, along with silylative coupling, cross-metathesis provides efficient and complementary synthetic routes leading to functionalized double-decker dialkenyl-silsesquioxanes of great practical importance. Preliminary tests of copolycondensation of divinyl-substituted silsesquioxanes with 1,4-divinylbenzene by silylative coupling turned out to be very promising and resulted in the synthesis of novel stereoregular *trans*-silsesquioxyl-silylene-vinylene-phenylene molecular derivatives. The oligomers are exclusively linear with low molecular weight. The methodology presented in this article opens up a possibility to obtain a new class of *trans*-unsaturated (oligo)polymers with a silsesquioxyl-silylene spacer. The focus is now to develop new, promising materials with interesting optoelectronic and thermal properties on the basis of the results obtained.

Experimental Section

General methods and chemicals

All syntheses and catalytic tests were carried out under dry argon. ¹H and ¹³C NMR spectra were recorded on a Varian 400 operating at 402.6 and 101.2 MHz, respectively. ³¹P NMR spectra were recorded on a Mercury 300 operating at 121.5 MHz. ²⁹Si NMR spectra were recorded on a Varian Avance 600 operating at 119.203 MHz. Mass spectrometry analyses were performed by using a Synapt G2-S mass spectrometer (Waters) equipped with the Electrospray ion source and quadrupole-time-of-flight mass analyzer. Acetonitrile was used as a solvent. Measurements were performed in positive-ion mode with the desolvation gas flow 200 L h⁻¹ and capillary voltage set to 5000 V with the flow rate

20 $\mu\text{L min}^{-1}$. GC analyses were carried out on a Varian CP-3800 (column: Rtx-5 30 m I.D. 0.53 mm) equipped with TCD.

Thin layer chromatography (TLC) was recorded on plates coated with 250 μm thick silica gel and column chromatography was performed on silica gel 60 (70–230 mesh) using hexane/dichloromethane. Gel permeation chromatography (GPC) analysis was performed by using an Waters Alliance 2695 system equipped with a Waters 2414 RI detector and the set of three serially connected 7.8 \times 300 mm columns (Waters Styragel HR1, HR2 and HR4). THF was used as mobile phase with a flow rate of 0.60 mL min^{-1} ; column oven temperature 35 $^{\circ}\text{C}$ and detector temperature 40 $^{\circ}\text{C}$. All molecular weight (M_n , M_w) and polydispersity index (PDI) values were determined by a polystyrene Shodex standards calibration curve in a range from 1.31×10^3 to 3.64×10^6 Da.

The chemicals were obtained from the following sources: vinyltrichlorosilane, vinylmethylchlorosilane, vinylphenyldichlorosilane and vinyltrimethylsilane from ABCR, diethyl ether, tetrahydrofuran, dichloromethane, acetone, *n*-pentane, ethanol, $[\text{D}_2]$ dichloromethane, $[\text{D}_6]$ benzene, $[\text{D}]$ chloroform, decane, dodecane, styrene, 4-chlorostyrene, 4-bromostyrene, 4-methoxystyrene, 4-methylstyrene, 4-(trifluoromethyl)styrene, 2-methoxyethanol, allylbenzene, *n*-butyl vinyl ether, allyltrimethylsilane, 1-hexene, tricyclohexylphosphine, formaldehyde, catecholborane, copper(I) chloride, allyl alcohol, methyltriphenylphosphane iodide, potassium *tert*-butoxide, terephthalic aldehyde, anthracene, magnesium, calcium hydride, molecular sieves, and anhydrous magnesium sulfate from Aldrich, triethylamine and silica gel 60 from Fluka, Grubbs first-generation benzylidene catalyst from Apeiron Synthesis, ruthenium(III) chloride hydrate from Lancaster, tetrasilanolphenyl POSS from Hybrid Plastics,^[17] toluene and *n*-hexane from Chempur. $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ was prepared according to the literature procedure.^[18] Divinylbenzene (DVB) was prepared according to the literature procedure.^[19] All solvents were dried prior to use over CaH_2 and stored under argon over molecular sieves type 4 Å. CH_2Cl_2 was additionally passed through a column with alumina and after that it was degassed by repeated freeze-pump-thaw cycles.

Synthesis and characterization of DDSQ-2SiVi (1)

Synthesis of 1A: A two-necked, 500 mL flask equipped with a reflux condenser and connected to gas and vacuum line was charged under argon with tetrasilanolphenyl POSS (DDSQ-4OH) (3 g, 2.8×10^{-3} mol), THF (300 mL), and triethylamine (1.6 mL, 1.12×10^{-2} mol). The mixture was cooled down in an ice bath to 0 $^{\circ}\text{C}$ and ViSiMeCl_2 (0.73 mL, 5.6×10^{-3} mol) was quickly added in one portion, which resulted in the formation of a white precipitate. The suspension was stirred for 24 h at room temperature and filtered on a glass frit. The precipitate was washed with THF (3 \times 50 mL). The filtrate, reduced to 100 mL in volume, was extracted three times with 30 mL of water to remove residues of ammonium salt. The organic phase was dried with MgSO_4 . Evaporation gave the analytically pure product as a white powder; yield: 3.04 g (90%). Spectroscopic data: ^1H NMR (400 MHz, CDCl_3 , 25 $^{\circ}\text{C}$): δ = 0.36 (s, 6H, CH_3), 5.88 (dd, $J_{\text{H-H}} = 20.0$, 4.0 Hz, 1H), 5.95 (dd, $J_{\text{H-H}} = 15.1$, 4.0 Hz, 1H), 6.11 (dd, $J_{\text{H-H}} = 20.0$, 15.1 Hz, 1H), 7.1–7.72 ppm (m, 40H, Ph); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^{\circ}\text{C}$): δ = −1.17, 127.6 (t, $J = 4.8$ Hz), 127.76, 130.33 (d, $J = 3.8$ Hz), 130.99 (t, $J = 3.2$ Hz), 131.92, 133.95, 134.06, 134.42, 135.19 ppm; ^{29}Si NMR (99 MHz, CDCl_3 , 25 $^{\circ}\text{C}$): δ = −31.41 (s, 2Si), −78.36 (s, 4Si), −79.53 ppm (s, 4Si); MS (FD): m/z (%): 1227.09 (90), 1228.10 (100), 1229.10 (88), 1230.09 (51), 1231.109 (25); HRMS (FD): calcd for $\text{C}_{54}\text{H}_{52}\text{O}_{14}\text{Si}_{10}\text{Na}$: 1227.0947; found: 1227.0942; elemental analysis calcd (%) for $\text{C}_{54}\text{H}_{52}\text{O}_{14}\text{Si}_{10}$: C: 53.79, H: 4.35; found: C: 53.46, H: 4.31

Synthesis of 1B: Compound 1B was synthesized according to the procedure described for 1A. Isolated yield 3.47 g, 93%; white solid. Spectroscopic data: ^1H NMR (400 MHz, CDCl_3 , 25 $^{\circ}\text{C}$): δ = 5.96 (dd, $J_{\text{H-H}} = 20.2$, 3.9 Hz, 1H), 5.98 (dd, $J_{\text{H-H}} = 20.2$, 3.8 Hz, 1H), 6.11 (dd, $J_{\text{H-H}} = 14.9$, 3.8 Hz, 1H), 6.12 (dd, $J_{\text{H-H}} = 14.9$, 3.8 Hz, 1H), 6.30 (dd, $J_{\text{H-H}} = 20.2$, 14.9 Hz, 1H), 6.31 (dd, $J_{\text{H-H}} = 20.2$, 14.9 Hz, 1H) (overlapping dd, 1H, *cis* and *trans* mixture), 7.05–7.7 ppm (m, 48H, Ph); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^{\circ}\text{C}$): δ = 127.46 (t, $J = 13.9$ Hz), 127.76, 130.09 (d, $J = 3.6$ Hz), 130.22, 130.35 (d, $J = 5.4$ Hz), 130.66, 130.91, 131.61, 133.47, 133.98, 134.03, 134.05, 134.09, 134.32, 136.11 ppm; ^{29}Si NMR (99 MHz, CDCl_3 , 25 $^{\circ}\text{C}$): δ = −45.89 (*cis*, *trans*), −78.12 (*cis*, *trans*), −79.14 (*cis*), −79.43 (*trans*), −79.69 ppm (*cis*); MS (FD): m/z (%): 1351.13 (79), 1352.13 (100), 1353.13 (88), 1354.13 (52), 1355.13 (27), 1356.13 (13); HRMS (FD): calcd for $\text{C}_{64}\text{H}_{56}\text{O}_{14}\text{Si}_{10}\text{Na}$: 1351.1260; found: 1351.1262; elemental analysis calcd (%) for $\text{C}_{64}\text{H}_{56}\text{O}_{14}\text{Si}_{10}$: C: 57.80, H: 4.24; found: C: 57.14, H: 4.31

Synthesis of 1C: Compound 1C was synthesized according to the procedure described for 1A. Isolated yield 3.67 g, 94%; white solid. Spectroscopic data: ^1H NMR (400 MHz, CDCl_3 , 25 $^{\circ}\text{C}$): δ = 3.61–3.62 (overlapping s, 6H, OCH_3 , *cis* and *trans* mixture), 5.85 (dd, $J_{\text{H-H}} = 20.3$, 2.0 Hz, 1H), 5.98 (dd, $J_{\text{H-H}} = 14.7$, 2.8 Hz, 1H), 6.23–6.12 (m, 1H), 6.64–7.64 ppm (m, 48H, Ph); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^{\circ}\text{C}$): δ = 54.86, 54.88, 113.53 (d, $J = 1.8$), 125.46, 127.43 (t, $J = 19.9$ Hz), 127.78, 130.24 (t, $J = 11.3$ Hz), 130.38, 130.75, 130.97, 131.74, 133.85, 134.00, 134.12, 135.72, 135.84, 161.22, 161.23 ppm; ^{29}Si NMR (99 MHz, CDCl_3 , 25 $^{\circ}\text{C}$): δ = −45.09 (*cis*, *trans*), −78.11 (*cis*, *trans*), −79.15 (*cis*), −79.44 (*trans*), −79.70 ppm (*cis*); MS (FD): m/z (%): 1411.15 (78), 1412.15 (100), 1413.15 (88), 1414.15 (53), 1415.15 (28); HRMS (FD): calcd for $\text{C}_{66}\text{H}_{60}\text{O}_{16}\text{Si}_{10}\text{Na}$: 1411.1472; found: 1411.1458; elemental analysis calcd (%) for $\text{C}_{66}\text{H}_{60}\text{O}_{16}\text{Si}_{10}$: C: 57.03, H: 4.35; found: C: 57.44, H: 4.38

General procedure for catalytic tests

Silylative coupling: The oven-dried 5 mL glass reactor equipped with a condenser and magnetic stirring bar was charged under argon with divinylsilsesquioxane (2.49×10^{-5} mol), CH_2Cl_2 (2 mL), internal standard (decane or dodecane, 20 μL), and olefin (4.98×10^{-5} mol). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (ca. 45 $^{\circ}\text{C}$). Then the hydride ruthenium complex $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (0.0004 g, 4.98×10^{-7} mol) was added to the mixture under argon. After 5 min, copper(I) chloride (0.0002 g, 2.49×10^{-6} mol) was added. The reaction mixture was heated under reflux for 24 h. Conversion of the substrate was monitored by gas chromatography. Reaction yields were calculated on the basis of the ^1H NMR spectra of the reaction mixture.

Cross-metathesis: The oven-dried 5 mL glass reactor equipped with a condenser and magnetic stirring bar was charged under argon with divinylsilsesquioxane (2.49×10^{-5} mol), CH_2Cl_2 (2 mL), internal standard (decane or dodecane, 20 μL), and olefin (4.98×10^{-5} mol). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (ca. 45 $^{\circ}\text{C}$). Then the ruthenium benzylidene complex (0.0004 g, 4.98×10^{-7} mol) was added to the mixture under argon. The reaction mixture was heated under reflux for 24 h. Conversion of the substrate was monitored by gas chromatography. Reaction yields were calculated on the basis of the ^1H NMR spectra of the reaction mixture.

General procedure for synthesis of functionalized dialkenylsilsesquioxanes (3A–3C)

By silylative coupling with olefins: A 5 mL glass reactor equipped with a reflux condenser and connected to argon/vacuum line was

charged under argon with divinylsilsequioxane (8.29×10^{-5} mol), CH_2Cl_2 (3 mL), and olefin (1.66×10^{-4} mol). The mixture was warmed to 45°C in an oil bath and $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (0.0012 g, 1.66×10^{-6} mol) was added to the mixture under argon. After 5 min, copper(I) chloride (0.0008 g, 8.29×10^{-6} mol) was added. The reaction mixture was heated under reflux for 24 h. Then the solvent was evaporated under vacuum and cold hexane (2 mL) was added to the residue to form a colorless precipitate. The precipitate was filtered off and purified by column chromatography (silica gel 60/hexane: $\text{CH}_2\text{Cl}_2 = 1:5$) to remove ruthenium complexes. Evaporation of the solvent gave an analytically pure sample (white powder).

By cross-metathesis with olefins: A 5 mL glass reactor equipped with a reflux condenser and connected to an argon/vacuum line was charged under argon with divinylsilsequioxane (8.29×10^{-5} mol), CH_2Cl_2 (3 mL), and olefin (1.66×10^{-4} mol). The mixture was warmed to 45°C in an oil bath, and then first-generation Grubbs' catalyst (0.0014 g, 1.66×10^{-6} mol) was added to the mixture under argon. The reaction mixture was heated under reflux for 24 h. Then the solvent was evaporated under vacuum and cold hexane (2 mL) was added to the remaining content to form a colorless precipitate. The precipitate was filtered off and purified by column chromatography (silica gel 60/hexane: $\text{CH}_2\text{Cl}_2 = 1:5$) to remove ruthenium complexes. Evaporation of the solvent gave an analytically pure sample (white powder).

General procedure for silylative coupling copolycondensation

The syntheses were performed under argon using $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ as a catalyst. Reagents and solvent were dried and deoxygenated. A mixture of monomer **1A** or **1B** (1.5×10^{-4} mol), **DVB** (1.5×10^{-4} mol), complex $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (3.07×10^{-6} mol), copper(I) chloride (1.5×10^{-5} mol), and CH_2Cl_2 (1.5 mL) was placed in a 5 mL glass mini-reactor equipped with a magnetic stirring bar and condenser connected to a bubbler. The reaction mixture was stirred and heated at 45°C under an argon flow for 18–72 h. After the reaction was complete, the excess of solvent was evaporated under vacuum. The resulting polymer was dissolved in THF, isolated, and purified by repeated precipitation from methanol. The final polymeric material was filtered off and dried under vacuum for 15 min.

Crystallography

For crystal data, data collection, and structure refinement see the Supporting Information. CCDC-971972 (**3A-b**), CCDC-971973 (**3B-e**), and CCDC-992188 (**3A-j**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Acknowledgements

The authors gratefully acknowledge the financial support from the National Science Centre (Poland) (MAESTRO Project No. 2011/02A/ST5/00472 and SONATA Project No 2012/05/D/ST5/03348).

Keywords: C–H activation • double-decker silsesquioxanes • homogeneous catalysis • metathesis • silylative coupling

- [1] a) D. B. Cordes, P. D. Lickiss, F. Rataboul, *Chem. Rev.* **2010**, *110*, 2081–2173; b) S. Yamaguchi, K. Tamao in *Silicon-containing polymers* (Eds.: R. G. Jones, W. Ando, J. Chojnowski), Kluwer, **2000**, ch. 17; c) F. Wang, X. Lub, Ch. He, *J. Mater. Chem.* **2011**, *21*, 2775–2782.
- [2] a) R. Duchateau, *Chem. Rev.* **2002**, *102*, 3525–3542; b) M. Y. Lo, C. G. Zhen, M. Lauters, G. E. Jabbour, A. Sellinger, *J. Am. Chem. Soc.* **2007**, *129*, 5808–5809; c) H. Dodiuk, P. F. Rios, A. Dotan, S. Kenig, *Polym. Adv. Technol.* **2007**, *18*, 746–750; d) G. R. Pan, J. E. Mark, D. W. Schaefer, *Polym. Sci. Part B: Polym. Phys.* **2003**, *41*, 3314–3323.
- [3] a) J. D. Froehlich, R. Young, T. Nakamura, Y. Ohmori, S. Li, A. Mochizuki, *Chem. Mater.* **2007**, *19*, 4991–4997; b) K. I. Chan, P. Sonar, A. Sellinger, *J. Mater. Chem.* **2009**, *19*, 9103–9120.
- [4] N. Ootake, K. Yoshida, K. Watanabe, Y. Yamaryo US 8 173 758 (B2).
- [5] a) C. A. Kucuk, J. Matsui, T. Miyashita, *Thin Solid Films* **2013**, *534*, 577–583; b) A. C. Kucuk, J. Matsui, T. Miyashita, *J. of Colloid and Interface Sci.* **2011**, *355*, 106–114; c) M. Kohri, J. Matsui, A. Watanabe, T. Miyashita, *Chem. Lett.* **2010**, *39*, 1162–1163; d) B. Seurer, V. Vij, T. Haddad, J. M. Mabry, A. Lee, *Macromolecules* **2010**, *43*, 9337–9347; J. Espinas, J. D. A. Pelletier, E. A. Hamad, L. Emsley, J.-M. Basset, *Organometallics* **2012**, *31*, 7610–7617.
- [6] a) M. Seino, T. Hayakawa, Y. Ishida, M. Kakimoto, K. Watanabe, H. Oikawa, *Macromolecules* **2006**, *39*, 3473–3475; b) S. Wu, T. Hayakawa, R. Kikuchi, S. J. Grunzinger, M. Kakimoto, *Macromolecules* **2007**, *40*, 5698–5705; c) L. Wang, Ch. Zhang, S. Zheng, *J. Mater. Chem.* **2011**, *21*, 19344–19352; d) K. Wei, L. Wang, S. Zheng, *J. Polym. Sci. Part A* **2013**, *51*, 4221–4232; e) W. Zhang, J. Xu, X. Li, G. Song, J. Mu, *J. Polym. Sci. Part A* **2014**, *52*, 780–788.
- [7] For a review see: a) B. Marciniak, C. Pietraszuk in *Handbook of Metathesis*, Vol. 2 (Ed.: R. H. Grubbs), Wiley-VCH, Weinheim, **2003**, p. 463; b) B. Marciniak, C. Pietraszuk, *Curr. Org. Chem.* **2003**, *7*, 691–735; c) B. Marciniak, *Coord. Chem. Rev.* **2005**, *249*, 2374–2390; d) B. Marciniak, C. Pietraszuk in *Green Metathesis Chemistry. Great Challenges in Synthesis Catalysis and Nanotechnology*, (Eds.: V. Dragutan, A. Demonceau, I. Dragutan, E. S. Finkelshtein), Springer, Berlin, **2010**, p. 157.
- [8] F. J. Feher, D. Soulvong, A. G. Eklund, K. D. Wydham, *Chem. Commun.* **1997**, 1185–1186.
- [9] S. Sulaiman, A. Bhaskar, J. Zhang, R. Guda, T. Goodson III, R. M. Laine, *Chem. Mater.* **2008**, *20*, 5563–5573.
- [10] a) G. Cheng, N. R. Vautravers, R. E. Morris, D. J. Cole-Hamilton, *Org. Biomol. Chem.* **2008**, *6*, 4662–4667; b) N. R. Vautravers, P. Andre, A. M. Z. Slavin, D. J. Cole-Hamilton, *Org. Biomol. Chem.* **2009**, *7*, 717–724; c) N. R. Vautravers, P. Andre, D. J. Cole-Hamilton, *J. Mater. Chem.* **2009**, *19*, 4545–4550.
- [11] a) Y. Itami, B. Marciniak, M. Kubicki, *Chem. Eur. J.* **2004**, *10*, 1239–1248; b) J. Waehner, B. Marciniak, P. Pawluc, *Eur. J. Inorg. Chem.* **2007**, 2975–2980; c) P. Žak, C. Pietraszuk, B. Marciniak, G. Spolnik, W. Danikiewicz, *Adv. Synth. Catal.* **2009**, *351*, 2675–2682; d) P. Žak, B. Marciniak, M. Majchrzak, C. Pietraszuk, *J. Organomet. Chem.* **2011**, *696*, 887–891.
- [12] P. Žak, B. Dudziec, B. Marciniak Pol. Pat. Appl. P.407444, **2014**.
- [13] R. M. Laine, M. F. Roll, *Macromolecules* **2011**, *44*, 1073–1109.
- [14] a) M. D. Hoque, Y. Kakihana, S. Shinke, Y. Kawakami, *Macromolecules* **2009**, *42*, 3309–3315; b) V. Ervithayasuporn, X. Wang, Y. Kawakami, *Chem. Commun.* **2009**, 5130–5132; c) V. Ervithayasuporn, R. Sodkhomkhum, T. Teerawatananond, Ch. Phurat, P. Phinyocheep, E. Somsook, T. Osotchan, *Eur. J. Inorg. Chem.* **2013**, 3292–3296.
- [15] E. L. Dias, S. T. Nguyen, R. H. Grubbs, *J. Am. Chem. Soc.* **1997**, *119*, 3887–3897.
- [16] B. Marciniak, M. Kujawa, C. Pietraszuk, *Organometallics* **2000**, *19*, 1677–1681.
- [17] Vinylsilsesquioxanes purchased from Hybrid Plastics Inc. and used as received do not undergo silylative coupling. Successful reactivity was achieved by preliminary purification by extraction from the pentane solution of the reagent with water followed by drying of the organic phase with magnesium sulfate and solvent evaporation.
- [18] J. Levison, S. D. Robinson, *J. Chem. Soc. A* **1970**, 2947.
- [19] M. Ludwiczak, M. Majchrzak, B. Marciniak, M. Kubicki, *J. Organomet. Chem.* **2011**, *696*, 1456–1464.

Received: March 31, 2014