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Synthesis and characterization of functionalized molecular and macromolecular double-decker silsesquioxane systems†

P. Žak,^a M. Majchrzak,^a G. Wilkowski,^a B. Dudziec,^a M. Dutkiewicz^b and B. Marciniec^{*b}

Synthesis and characterization of new, molecular DDSQ-based compounds functionalized by substituted styrenes (also with heteroatoms) in a stereoselective manner is presented. Additionally, a novel class of vinylene-arylene linear copolymers with double-decker silsesquioxane fragments in the main chain is developed. These molecular and macromolecular compounds were synthesized *via* efficient and highly stereoselective silylative coupling (and copolycondensation) and cross-metathesis (and ADMET) reactions.

Introduction

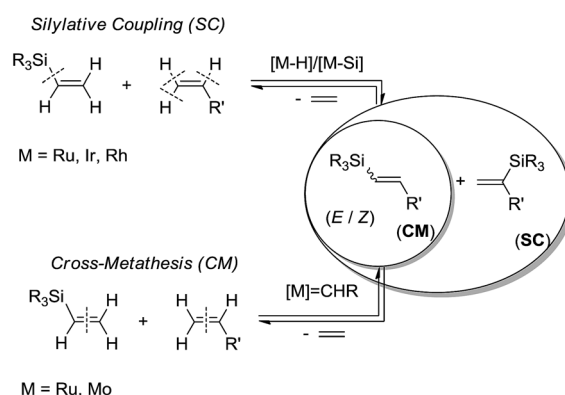
Polyhedral oligomeric silsesquioxanes (POSS) of the empirical formula $(\text{RSiO}_{1.5})_n$ with different reactive and/or inert organic coronae, have recently become the subject of growing interest in many branches of chemistry.¹ It is known that cage structure silsesquioxanes, due to their unique properties, *e.g.* the rigid inorganic SiO core with a diameter of about 1.5 nm, are often regarded as the smallest silica particles that can also influence the surface properties of functional groups attached to silicon atoms. A well-defined organization of POSS is important because of their possible use as precursors and components of versatile inorganic/organic hybrid materials that display nano-phase behavior. Not more than a decade ago, a new class of silsesquioxyl compounds containing rigid Si–O–Si bonds, *i.e.* the double-decker silsesquioxane (DDSQ), was reported by Yoshida and co-workers.² The structure of DDSQ is an open cage that includes two cyclosiloxane rings in parallel planes with 8 inert phenyl groups at the silicon atoms of each ring. These two rings are joined by oxygen bridges. Current research on that compound refers to two major trends in its development and knowledge, *i.e.* syntheses of molecular and macromolecular organosilicon compounds based on DDSQ that may exhibit interesting and desired physicochemical properties.³

The silylative coupling (SC) and cross-metathesis (CM) of olefins with vinyl-substituted organosilicon compounds have been studied and developed for the last two decades as a new, effective catalytic activation of the =C–H bond of olefins and the =C–Si bond of organosilicon compounds (Scheme 1). The

mechanisms of these reactions are diverse as they require different catalysts (mostly ruthenium hydride for SC and ruthenium-carbene for CM). However, both SC and CM proved to be effective paths for synthesis of functional vinylsilicon molecular as well as macromolecular compounds.⁴

In the previous decade, we reported both processes (SC and CM) to be complementary routes for regio- and stereoselective synthesis of functionalized vinylsilsesquioxanes and vinyl-spherosilicates.⁵ Cross-metathesis of vinylsilsesquioxanes using Grubbs catalyst was exploited by Feher,⁶ Laine,⁷ Cole-Hamilton and co-workers⁸ as well as Naka.⁹ Schrock noted the use of molybdenum catalyst for CM but in all reactions, except for styrene, a mixture of stereoisomers was obtained.⁶ On the other hand, hydrosilylation and Heck reaction were applied for vinyl-substituted POSS modification to obtain compounds of interesting photophysical properties enabling their use as sugars and peptide scaffolds.^{8a,10}

Our recent report has proved a successful use of divinyl-substituted double-decker silsesquioxanes (DDSQ-2SiVi **1A** and



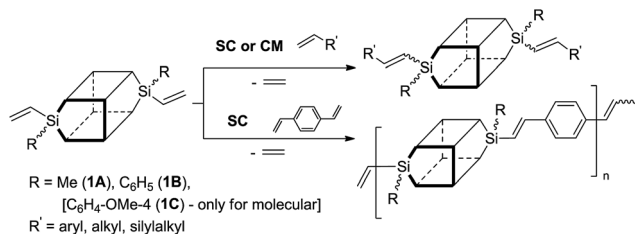
Scheme 1 Difference in regioselectivity of silylative coupling (SC) and cross-metathesis (CM) reactions of vinylsilanes with olefins.

^aDepartment of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89B, 61-614 Poznań, Poland

^bCentre for Advanced Technologies, Adam Mickiewicz University in Poznań, Umultowska 89C, 61-614 Poznań, Poland. E-mail: Bogdan.Marciniec@amu.edu.pl

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Scheme 2 Protocol using DDSQ-2SiVi for stereoselective silylative coupling (also copolycondensation) and cross-metathesis with olefins.

1B) as substrates for highly effective silylative coupling (SC) and/or cross-metathesis (CM) with olefins (Scheme 2).¹¹ The reactions led to highly stereoselective formation of *E* isomers. Preliminary studies on silylative coupling copolycondensation (SCC) of divinylbenzene (DVB) with DDSQ-2SiVi show a possibility to obtain stereoregular, linear cooligomer containing DDSQ-vinylene-phenylene units in the chain.

Here, we present a synthetic path for obtaining new, molecular DDSQ-based compounds functionalized by substituted styrenes (also with heretoatoms) in a stereoselective manner as well as a new class of vinylene-arylene copolymers with double-decker silsesquioxane in the main chain. All of the compounds were characterized *via* spectroscopic methods and their structural properties were also studied.

Experimental

Materials and methods

All reactions were carried out under argon atmosphere using standard Schlenk-line and vacuum techniques. All solvents were dried prior to use over CaH₂ and stored under argon over molecular sieves type 4 Å. Dichloromethane was additionally passed through a column with alumina and after that it was degassed by repeated freeze–pump–thaw cycles.

The chemicals were purchased from the following sources: dichloromethane (DCM), tetrahydrofuran (THF), *n*-hexane, chloroform-*d*, dichloromethane-*d*₂, ethanol, methanol, acetone, calcium hydride, diethyl ether, tricyclohexylphosphine, 9-bromoanthracene, 1-bromonaphthalene, 2-bromothiophene, 2,5-dibromothiophene, bromopentafluorobenzene, 4-vinylphenylboronic acid, 1,4-dibromo-2,3,5,6-tetrafluorobenzene, 9,10-dibromoanthracene, 1,4-dibromonaphthalene, molecular sieves type 4 Å, copper(i) chloride and anhydrous magnesium sulfate from Aldrich, vinylmethyldichlorosilane and vinylphenyldichlorosilane from ABCR, Grubbs first generation benzylidene catalyst from Apeiron Synthesis, triethylamine and silica gel 60 from Fluka, ruthenium(III) chloride hydrate from Lancaster, tetrasilanolphenyl POSS (Ph₈O₈Si₈)(OH)₄ (DDSQ-4OH) from Hybrid Plastics. Divinyl-substituted double-decker silsesquioxanes (DDSQ-2SiVi) (**1A** and **1B**) were prepared according to the literature procedure.^{11b} All mono- and distyrylarenes were synthesized according to the literature procedure.¹² The ruthenium species [RuHCl(CO)(PCy₃)₂] was made in accordance with the procedure described in literature.¹³

Techniques and measurement

Nuclear magnetic resonance (NMR) spectroscopy. NMR spectra were recorded at 25 °C on a Bruker Ultra Shield (300 and 400 MHz) spectrometers, CDCl₃, CD₂Cl₂ were used as solvents and for internal deuterium lock. Chemical shifts are reported in ppm with reference to the residual solvents (CHCl₃, CH₂Cl₂) peaks for ¹H and ¹³C NMR and to TMS for ²⁹Si NMR.

Thin layer chromatography (TLC). TLC was conducted on plates coated with 250 mm thick silica gel and column chromatography was performed on silica gel 60 (70–230 mesh) using a mixture of *n*-hexane/DCM.

Gel permeation chromatography (GPC). GPC analyses were performed using a Waters 2414 RI detector and a set of three serially connected 7.8 × 300 mm columns (Waters Styragel HR1, HR2 and HR4). THF was used as a mobile phase at the flow rate of 0.6 mL min^{−1}; column oven temperature was 35 °C and detector temperature 40 °C. All molecular weight (*M*_n, *M*_w) and polydispersity index (PDI) values were calculated on the basis of the calibration curve using polystyrene standards (Shodex) in the range from 1.31 × 10³ to 3.64 × 10⁶ Da.

Thermal gravimetric analysis (TGA). A TA Instruments TGA Q50 analyzer was used to investigate thermal stability of the samples. The measurements were conducted in nitrogen flow of 60 mL min^{−1} from ambient temperature to 1000 °C at the heating rate of 10 °C min^{−1}. The temperature of initial degradation (*T*_d) was taken as the onset temperature of initial degradation (*T*_d) at which 5 wt% of mass loss occurs.

General procedure for the synthesis of functionalized *E,E*-vinylene-arylenesilsesquioxanes (1–8)

By cross-metathesis (CM) with olefins. An oven-dried 5 mL glass reactor equipped with a reflux condenser and magnetic stirring bar was charged under argon with divinylsilsesquioxane (**1B**) (0.1 g, 7.52 × 10^{−5} mol), olefin (1.50 × 10^{−4} mol) and dichloromethane (2 mL). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (*ca.* 45 °C). Then the first generation Grubbs' catalyst (0.0012 g, 1.50 × 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 a vacuum and cold *n*-hexane (2 mL) was added to the remaining content to form precipitate. The precipitate was filtered off and purified by column chromatography (silica gel 60/*n*-hexane : CH₂Cl₂ = 1 : 5) to remove ruthenium complexes. Evaporation of the solvent gave an analytically pure sample (white or yellow powder).

By silylative coupling (SC) with olefins. For the syntheses of molecular compounds the complex ruthenium(II)–RuHCl(CO)–(PCy₃)₂ was used as a catalyst. Toluene and dichloromethane were dried and deoxygenated and all operations were performed under argon.

System 1. A 5 mL two-necked glass reactor equipped with a reflux condenser and connected to a bubbler was charged under argon with divinylsilsesquioxane (**1A**) (0.05 g, 4.13 × 10^{−5}



mol), toluene (1 mL) and styrylarylene derivative (1.24×10^{-4} mol). The reaction mixture was heated up to 90 °C (or 110 °C for thiophene derivatives) and $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (0.0006 g, 8.26×10^{-7} mol) was added and the catalytic system was left for 24 h (except thiophene derivative for 96 h). Then the solvent was evaporated under vacuum and the crude product was dissolved in DCM (1 mL). After that, the brown solution was filtered at 'flash-system' (glass filter-SiO₂-Celite) using *n*-hexane three times (3×10 mL) to remove the excess of olefin and the final product was washed by DCM (2×10 mL). Evaporation of the solvent gave an analytically pure sample (white or yellow powder).

System 2. A 5 mL two-necked glass reactor equipped with a reflux condenser and connected to a bubbler was charged under argon with divinylsilsesquioxane (**1A**) (0.05 g, 4.13×10^{-5} mol), dichloromethane (2 mL) and styrylarylene derivative (8.26×10^{-5} mol). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (ca. 45 °C). Then the hydride ruthenium complex $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (0.0006 g, 8.26×10^{-7} mol) was added to the mixture under argon. After 5 min copper(i) chloride (0.0004 g, 4.13×10^{-6} mol) was added. The reaction mixture was heated under reflux for 24 h. Then the solvent was evaporated under vacuum and cold *n*-hexane (2 mL) was added to the remaining content to form precipitate. The precipitate was filtered off and purified by column chromatography (silica gel 60/*n*-hexane : $\text{CH}_2\text{Cl}_2 = 1 : 5$) to remove ruthenium complexes. Evaporation of the solvent gave an analytically pure sample (white or yellow powder).

Analytical data for isolated molecular compounds (1–8)

1: *trans* di[9,19-(*E*)-4-(9-anthracenyl)styrylphenyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane. ¹H NMR (400 MHz, CD_2Cl_2 , δ , ppm): 6.85 (d, $J_{\text{HH}} = 19.2$ Hz, 2H, =CH-Si), 7.05–8.61 (m, 78H, =CH-C₆H₄- and aromatic parts); ¹³C NMR (125 MHz, CD_2Cl_2 , δ , ppm): 123.36, 125.19, 125.45, 126.62, 126.97, 126.83, 127.56, 127.60, 127.65, 127.71, 127.77, 127.94, 127.99, 128.47, 129.61, 130.44 (d, $J = 4.4$ Hz), 130.71, 131.51, 134.00, 134.05, 134.11, 134.16, 137.38, 140.12, 147.53, 165.39; ²⁹Si NMR (79 MHz, CD_2Cl_2 , δ (ppm)): -44.36, -77.75, -79.21.

2: *trans* di[9,19-(*E*)-4-(1-naphthyl)styrylphenyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane. ¹H NMR (400 MHz, CD_2Cl_2 , δ , ppm): 6.75 (overlapping doublets, $J_{\text{HH}} = 19.2$ Hz, 4H, =CH-Si and =CH-C₆H₄-), 7.02–8.28 (m, 72H, aromatic parts); ¹³C NMR (125 MHz, CD_2Cl_2 , δ , ppm): 122.31, 125.40, 125.82, 126.07, 126.84 (br s), 127.54, 127.61, 127.67, 127.70, 127.95, 128.25, 130.19, 130.34, 130.46 (br s), 130.65, 131.44, 131.56, 133.85, 133.99, 134.02, 134.06, 134.08, 134.15, 134.50, 136.42, 139.75, 141.11; ²⁹Si NMR (79 MHz, CD_2Cl_2 , δ , ppm): -44.37, -77.83, -79.31.

3: *trans* di[9,19-(*E*)-4-(2,3,4,5,6-pentafluorophenyl)styrylphenyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane. ¹H NMR (400 MHz, CD_2Cl_2 , δ , ppm): 6.73 (d, $J_{\text{HH}} = 20.0$ Hz, 2H, =CH-Si), 6.97–8.15 (m, 60H, =CH-C₆F₄ and aromatic parts); ¹³C NMR (125 MHz, CD_2Cl_2 , δ , ppm): 121.80,

124.13, 127.07, 127.59 (t, $J = 5.9$ Hz), 127.88, 127.95, 128.02, 130.26 (t, $J = 4.9$ Hz), 130.36, 130.41, 130.47, 130.67 (t, $J = 2.4$ Hz), 131.43 (t, $J = 2.1$ Hz), 133.94, 133.98, 134.02, 138.32, 147.08; ²⁹Si NMR (79 MHz, CD_2Cl_2 , δ , ppm): -44.78, -77.83, -79.33.

4: *trans* di[9,19-(*E*)-4-(2-thienyl)styrylphenyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane. ¹H NMR (400 MHz, CD_2Cl_2 , δ , ppm): 6.65 (d, $J_{\text{HH}} = 19.2$ Hz, 2H, =CH-Si), 7.05–8.28 (m, 66H, =CH-C₆H₄, C₆H₅, C₆H₄ and C₄H₃S); ¹³C NMR (125 MHz, CD_2Cl_2 , δ , ppm): 122.15, 123.32, 125.12, 125.75, 127.44, 127.50, 127.59, 127.67, 127.93, 128.15, 129.60, 130.33 (t, $J = 4.3$ Hz), 130.44 (t, $J = 3.0$ Hz), 130.63, 131.52, 134.00 (d, $J = 6.1$ Hz), 134.47, 134.51, 136.56, 143.85; ²⁹Si NMR (79 MHz, CD_2Cl_2 , δ , ppm): -44.39, -77.89, -79.34.

5: *cis* and *trans* mixture of di[9,19-(*E*)-4-(9-anthracenyl)styryl-methyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane. ¹H NMR (300 MHz, CDCl_3 , δ , ppm): 0.49 (overlapping s, 6H, -SiCH₃), 6.61 (d, 2H, $J_{\text{HH}} = 19.2$ Hz, =CH-Si), 6.95–8.08 (m, 68H, =CH-C₆H₄- and aromatic parts); ¹³C NMR (75 MHz, CDCl_3 , δ , ppm): -0.75, -0.65, 126.13, 126.24, 127.17, 127.30, 127.66, 127.74, 127.80, 128.01, 130.36, 130.49, 130.63, 130.88, 131.11, 132.00, 134.11, 134.27, 138.60, 145.63; ²⁹Si NMR (79 MHz, CDCl_3 , δ , ppm): -30.91, -78.18, -79.28, -79.46, -79.52.

6: *cis* and *trans* mixture of di[9,19-(*E*)-4-(1-naphthyl)styryl-methyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane. ¹H NMR (300 MHz, CDCl_3 , δ , ppm): 0.47 (overlapping s, 6H, -SiCH₃), 6.54 (d, 2H, $J_{\text{HH}} = 19.5$ Hz, =CH-Si), 6.88–7.94 (m, 64H, =CH-C₆H₄- and aromatic parts); ¹³C NMR (75 MHz, CDCl_3 , δ , ppm): -0.69, -0.68, 125.45, 125.88, 125.99, 126.09, 126.80, 127.57, 127.64, 127.69, 127.79, 127.91, 128.39, 130.20, 130.36, 130.41, 130.47, 130.92, 131.57, 132.05, 133.86, 134.06, 134.26, 136.62, 139.93, 140.89, 146.29; ²⁹Si NMR (79 MHz, CDCl_3 , δ , ppm): -30.13, -78.23, -79.07, -79.47, -79.86.

7: *cis* and *trans* mixture of di[9,19-(*E*)-4-(2,3,4,5,6-penta-fluorophenyl)styrylmethyl]-1,3,5,7,11,13,15,17-octaphenyl-pentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane. ¹H NMR (300 MHz, CDCl_3 , δ , ppm): 0.43 (s, 3H, -SiCH₃), 0.44 (s, 3H, -SiCH₃), 6.51 (d, 2H, $J_{\text{HH}} = 18.9$ Hz, =CH-Si), 6.86–7.61 (m, 50H, =CH-C₆F₄- and aromatic parts); ¹³C NMR (75 MHz, CDCl_3 , δ , ppm): -0.84, -0.71, 126.13, 126.24, 127.17, 127.30, 127.66, 127.74, 127.93, 128.01, 130.37, 130.49, 130.57, 130.64, 130.88, 131.11, 132.01, 134.11, 134.27, 138.59, 145.61; ²⁹Si NMR (79 MHz, CDCl_3 , δ , ppm): -30.57, -78.26, -79.18, -79.53, -79.84.

8: *cis* and *trans* mixture of di[9,19-(*E*)-4-(2-thienyl)styryl-methyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane. ¹H NMR (300 MHz, CDCl_3 , δ , ppm): 0.49 (overlapping s, 6H, -SiCH₃), 6.48 (d, 2H, $J_{\text{HH}} = 19.2$ Hz, =CH-Si), 6.98–7.66 (m, 42H, aromatic parts, 2H coming from =CH-C₆H₄- and 2H coming from -C₄H₃S-), 7.21 (d, 2H, $J_{\text{HH}} = 6.0$ Hz, -C₄H₃S-), 7.53 (d, 4H, $J_{\text{HH}} = 7.2$ Hz, -C₆H₄-), 7.70 (d, 2H, $J_{\text{HH}} = 9.0$ Hz, -C₄H₃S-), 7.74 (d, 4H, $J_{\text{HH}} = 9.0$ Hz, -C₆H₄-), 7.87 (d, 4H, $J_{\text{HH}} = 7.2$ Hz, -C₆H₄-); ¹³C NMR (75 MHz, CDCl_3 , δ , ppm): -0.62, -0.58, 123.30, 124.22, 125.12, 125.98, 127.47, 127.74, 127.97, 128.24, 130.55, 130.97, 132.10, 134.13, 134.27, 134.46, 136.87, 144.26, 146.07; ²⁹Si NMR (79 MHz, CDCl_3 , δ , ppm): -30.17, -78.25, -79.20, -79.50, -79.77.



General procedure for the synthesis of functionalized *E,E*-arylene-silsesquioxanes derivatives oligomers (9–15)

By **metathetic copolymerization (ADMET)**. A 5 mL glass reactor equipped with a reflux condenser and magnetic stirring bar was charged under argon with divinylsilsesquioxane (**1B**) (0.1 g, 7.52×10^{-5} mol), diolefin (7.52×10^{-5} mol) and dichloromethane (2 mL). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (ca. 45 °C). Then, the first generation Grubbs' catalyst (0.0012 g, 1.50×10^{-6} mol) was added to the mixture under argon. The reaction mixture was heated under reflux for 3 days. Then, the solvent was evaporated under vacuum and cold *n*-hexane (2 mL) was added to the remaining content to form precipitate. The precipitate was filtered off and purified by column chromatography (silica gel 60/*n*-hexane : CH₂Cl₂ = 1 : 5) to remove ruthenium complexes. Evaporation of the solvent gave an analytically pure sample (white or yellow powder).

By **silylative coupling copolycondensation (SCC)**. For oligomers syntheses, complex ruthenium(II)–[RuHCl(CO)(PCy₃)₂] was used as a catalyst. Solvent was dried and deoxygenated and all operations were performed under argon.

System 1. A mixture of silicon monomer–divinylsilsesquioxane (**1A**) (0.05 g, 4.13×10^{-5} mol), distyrylarene (4.13×10^{-5} mol), [RuHCl(CO)(PCy₃)₂] (0.0006 g, 8.26×10^{-7} mol) and toluene (1.5 mL) was placed in a 5 mL two-necked glass reactor equipped with a magnetic stirring bar and condenser connected to a bubbler. The reaction mixture was heated at 110 °C and stirred for 72 h. The reaction progress was monitored by ¹H NMR. After the coupling process was complete, the solvent was evaporated under vacuum and dichloromethane was added. Then, the final product was purified by repeated precipitation from methanol. The polymeric material was filtered off and dried under vacuum to give an analytically pure sample (white or yellow powder).

System 2. A mixture of silicon monomer–divinylsilsesquioxane (**1A**) (0.05 g, 4.13×10^{-5} mol), distyrylarene (4.13×10^{-5} mol), and dichloromethane (2 mL) was placed in a 5 mL two-necked glass reactor equipped with a magnetic stirring bar and condenser connected to a bubbler. The reaction mixture was heated up to 45 °C and [RuHCl(CO)(PCy₃)₂] (0.0006 g, 8.26×10^{-7} mol) was added. After 5 min copper(I) chloride (0.0004 g, 4.13×10^{-6} mol) was added and the reaction mixture was heated under reflux for 3 days. The reaction progress was monitored by ¹H NMR. After the coupling process was complete, the solvent was evaporated under vacuum and cold *n*-hexane (2 mL) was added to the remaining content to form precipitate. The precipitate was filtered off and purified by column chromatography (silica gel 60/*n*-hexane : CH₂Cl₂ = 1 : 5) to remove ruthenium complexes. Evaporation of the solvent gave an analytically pure sample (white or yellow powder).

Analytical data for isolated macromolecular compounds (9–15)

9: poly[[9,19-(*E*)-4-(1-naphthyl)styrylmethyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane}s. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 0.39 (s, 3H, SiCH₃ external), 0.49 (s, 3H, SiCH₃, internal), 5.80–6.23 (dd, 3H, trace amount of

signals coming from Si–HC=CH₂ terminal), 6.62 (d, 1H, *J*_{HH} = 18.3 Hz, =CH–Si), 6.99–7.97 (m, 56H, aromatic parts and =CH–C₆H₄–); ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 0.11, 0.14, 124.45, 126.04, 126.11, 126.31, 126.95, 127.45, 128.01, 130.36, 130.48, 132.02, 132.14, 134.16, 134.35, 136.81, 138.05, 139.74, 146.32; ²⁹Si NMR (79 MHz, CDCl₃, δ, ppm): –30.19, –78.27, –79.51.

10: poly[[9,19-(*E*)-4-(1-naphthyl)styrylphenyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane}s. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 6.69 (d, 1H, *J*_{HH} = 18.7 Hz, =CH–Si), 6.98–8.27 (m, 65H, =CH–C₆H₄–, C₆H₅ and naphthalene); ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 122.71; 125.98, 126.36, 126.95, 127.46, 127.55, 127.63, 127.68, 127.75, 127.91 (br s), 129.76, 130.23, 130.32, 130.52, 130.65, 130.81, 131.74, 131.86, 134.10, 134.18, 134.23, 136.55, 139.55, 141.07, 147.71, 165.46; ²⁹Si NMR (79 MHz, CDCl₃, δ, ppm): –44.55, –77.90, –79.35.

11: poly[[9,19-(*E*)-4-(9-anthracenyl)styrylmethyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane}s. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 0.39 (s, SiCH₃ external), 0.49 (s, 3H, SiCH₃, internal), 5.92–6.23 (dd, 3H, trace amount of signals coming from Si–HC=CH₂ terminal), 6.62 (d, 1H, *J*_{HH} = 19.5 Hz, =CH–Si), 6.91–7.81 (m, 58H, aromatic part and =CH–C₆H₄–); ¹³C NMR (75 MHz, CDCl₃, δ, ppm): –0.71, 125.25, 126.89, 127.07, 129.95, 130.61, 131.61, 134.17, 134.33, 136.98, 147.90; ²⁹Si NMR (79 MHz, CDCl₃, δ, ppm): –30.46, –78.27, –78.36, –79.51.

12: poly[[9,19-(*E*)-4-(9-anthracenyl)styrylphenyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane}s. ¹H NMR (400 MHz, CD₂Cl₂, δ, ppm): 6.86 (d, 1H, *J*_{HH} = 19.2 Hz, =CH–Si), 7.03–8.74 (m, 68H, =CH–C₆H₄– and aromatic parts); ¹³C NMR (125 MHz, CD₂Cl₂, δ, ppm): 123.36, 125.15, 126.83 (t, *J* = 6.1 Hz), 127.56, 127.60, 127.65, 127.71, 127.77, 127.94, 127.99, 128.47, 129.61, 130.42, 130.47, 130.71, 131.51, 133.19, 134.00, 134.05, 134.11, 134.16, 137.38, 140.12, 147.53, 165.38; ²⁹Si NMR (79 MHz, CD₂Cl₂, δ, ppm): –44.63, –77.77, –79.25.

13: poly[[9,19-(*E*)-4-(2,3,5,6-tetrafluorophenyl)styrylmethyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane}s. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 0.39 (s, SiCH₃ external), 0.48 (s, 3H, SiCH₃, internal), 5.35 (d, 1H, *J*_{HH} = 10.5 Hz, trace amount of signals coming from >C–HC=CH₂), 5.84 (d, 1H, *J*_{HH} = 17.1 Hz, trace amount of signals coming from >C–HC=CH₂), 6.55 (d, 1H, *J*_{HH} = 19.2 Hz, =CH–Si), 6.79 (dd, 1H, trace amount of signals coming from >C–HC=CH₂), 6.88–7.76 (m, 49H, aromatic parts and 1H coming from =CH–C₆H₄–); ¹³C NMR (75 MHz, CDCl₃, δ, ppm): –1.13, –0.87, 125.95, 126.55, 127.11, 127.41, 127.76, 127.93, 128.01, 130.43, 130.51, 130.88, 132.04, 134.12, 134.26, 145.75; ²⁹Si NMR (79 MHz, CDCl₃, δ, ppm): –30.50, –78.20, –78.24, –78.95, –79.50.

14: poly[[9,19-(*E*)-4-(2,3,5,6-tetrafluorophenyl)styrylphenyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane}s. ¹H NMR (400 MHz, CD₂Cl₂, δ, ppm): 6.75 (d, 1H, *J*_{HH} = 19.2 Hz, =CH–Si), 6.98–8.27 (m, 67H, =CH–C₆H₄– and aromatic parts); ¹³C NMR (125 MHz, CD₂Cl₂, δ, ppm): 123.93, 127.02, 127.61 (t, *J* = 8.6 Hz), 127.96, 130.30, 130.34, 130.37, 130.41, 130.49, 130.56, 130.67 (t, *J* = 3.7 Hz), 131.46, 134.00 (d, *J* = 7.9 Hz), 138.19, 147.21; ²⁹Si NMR (79 MHz, CD₂Cl₂, δ, ppm): –44.71, –77.81, –79.31.



15: poly{[9,19-(*E*)-4-(2-thienyl)styrylmethyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane}s. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 0.38 (s, SiCH₃ external), 0.46 (s, 3H, SiCH₃, internal), 5.86–6.25 (dd, 3H, trace amount of signals coming from Si–HC=CH₂ terminal), 6.46 (d, 1H, *J*_{H–H} = 19.2 Hz, =CH–Si), 6.85–7.80 (m, 52H, aromatic part and –Si–HC=CH–); ¹³C NMR (125 MHz, CDCl₃, δ, ppm): –1.14, –0.70, 124.21, 125.32, 125.53, 127.41, 127.62, 127.85, 128.24, 129.05, 130.42, 131.96, 134.01, 134.12, 134.22, 137.89, 145.89; ²⁹Si NMR (79 MHz, CDCl₃, δ, ppm): –30.15, –78.26, –79.41, –79.51.





Results and discussion

Taking into regard to the positive results presented in our recent paper on the possibility of using cross-metathesis reaction and silylative coupling in functionalization of divinyl-substituted double-decker silsesquioxanes, we decided to expand the palette of tested olefins to the compounds containing conjugated double bond system. The premise for this is still undiminished interest in silsesquioxanes derivatives, their limited commercial availability and consequently high prices. Therefore, it seems reasonable to perform studies aimed at optimizing and modifying this group of organosilicon compounds.

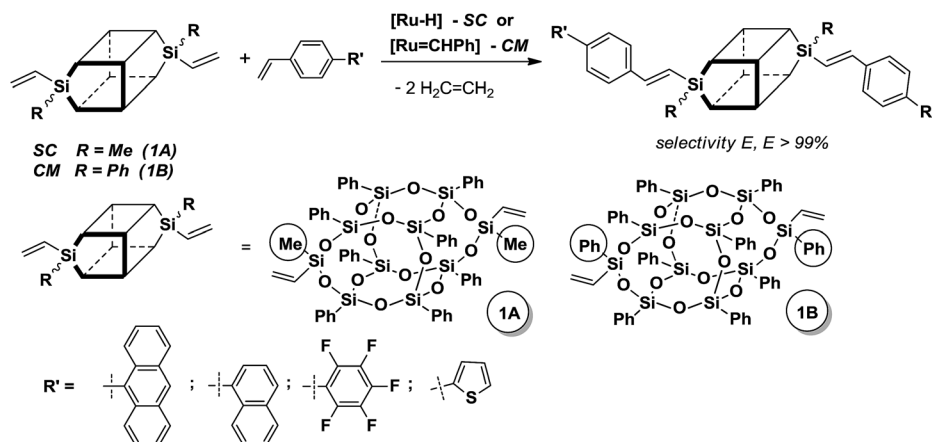
In studies presented in this paper, we focused on the functionalization of two types of double-decker silsesquioxane derivatives containing methyl (**1A**) or phenyl (**1B**) substituents located at 9 and 19 silicon atom of the core. Both substrates were prepared by a corner-capping reaction of incompletely condensed silsesquioxane **DDSQ-4OH** with vinylchloro(organo)silane. This synthetic procedure was thoroughly described in our last paper.^{11b} In view of the fact that methyl-substituted silicon derivatives are not reactive in metathetic transformation, **DDSQ-2SiVi** (**1B**) bearing phenyl substituents were applied to functionalization based on cross-metathesis reaction, while **DDSQ-2SiVi** (**1A**) with methyl groups was tested in silylative coupling reaction (Scheme 3).

Cross-metathesis of phenyl-substituted divinylsilsesquioxane (**1B**) with 1-(4-vinylphenyl)naphthalene was chosen as a model reaction for optimization studies of silsesquioxane containing two vinyl groups. Treatment of divinylsilsesquioxane (**1B**) with two equivalents of 1-(4-vinylphenyl)naphthalene in the presence of Grubbs catalyst [RuCl₂(PCy₃)₂(=CHPh)] (1% mol in relation to vinyl group of **DDSQ-2SiVi** (**1B**) in refluxing dichloromethane, resulted in its efficient transformation. Due to the large molecular mass of the silsesquioxyl substrate (**1B**), the reaction progress could not be monitored by GC. After 24 h, the reaction mixture was subjected to the ¹H NMR analysis which indicated nearly complete conversion of both substrates revealing selective formation of expected product (**2**). Similar reaction completion was observed when other 4-styryl substituted derivatives and **1B** were used as reaction partners. The results obtained were collected in Table 1. In each case, the reaction led to efficient and selective formation of *E*-isomer of the desired product. All obtained products (**1–4**) are air-stable,

Table 1 Cross-metathesis of divinyl-substituted silsesquioxanes (**1B**) with 4-styryl substituted derivatives^a

DDSQ-2SiVi	R'	Prod. no.	Isolated yield [%]	<i>E/Z</i> : <i>E/Z</i>
1B		1	88	<i>E</i> : <i>E</i>
		2	90	
		3	92	
		4	89	

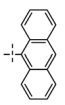



^a Reaction conditions: CH₂Cl₂, reflux, [1] : [olefin] = 1 : 2, [RuCl₂(PCy₃)₂(=CHPh)] (2 mol%), *t* = 24 h, argon.



Scheme 3 Silylative coupling and cross-metathesis of divinyl-substituted double-decker silsesquioxanes (**1A**, **1B**) with 4-styryl substituted derivatives.



Table 2 Silylative coupling of divinyl-substituted silsesquioxanes (**1A**) with 4-styryl substituted derivatives^a

DDSQ-2SiVi	R'	Prod. no.	Isolated yield [%]		E/Z : E/Z
			System 1	System 2	
1A		5	72	85	E : E
		6	81	90	
		7	86	91	
		8	62*	89	

^a Reaction conditions: system 1: toluene, 90 °C, [1] : [olefin] = 1 : 3, [RuHCl(CO)(PCy₃)₂] (2 mol%), *t* = 24 h, argon; * 110 °C, *t* = 96 h. System 2: CH₂Cl₂, 45°, [1] : [olefin] = 1 : 2, [RuHCl(CO)(PCy₃)₂] (2 mol%), [Ru] : [CuCl] = 1 : 5, *t* = 24 h, argon.

easy to handle white or yellow solids and can be purified by column chromatography.

In the next experiments, silylative coupling of methyl-substituted divinylsilsesquioxane (**1A**) with 4-styryl substituted derivatives was performed. A series of catalytic tests aimed at optimizing the reaction systems for efficient and selective synthesis of dialkenyl-substituted derivatives (**5–8**) was carried out. Optimization involved selection of a suitable solvent, ratios of reactants, concentration of catalyst used, reaction temperature and time as well as determination of possible influence of cocatalyst on the reaction course. According to obtained results of performed tests, effective functionalization of **1A** based on silylative coupling may be conducted in two ways concerning different reaction conditions. The first reaction was carried out in toluene at 90 °C or 110 °C under constant flow of argon in the presence of ruthenium(II) hydride complex [RuHCl(CO)(PCy₃)₂] used at 2 mol% (1% mol in relation to vinyl group of DDSQ-2SiVi (**1A**)). Similar effect can be achieved by introducing

a cocatalyst to the reaction system which is copper(I) chloride. The addition of the afore-mentioned salt helps to reduce the reaction temperature to 45 °C and change the solvent from toluene to methylene chloride. The results obtained are collected in Table 2.

The mechanism explaining the effect of copper(I) chloride addition on the reaction course was not examined. A reasonable explanation reported in literature for similar systems indicates that copper salt acts as a phosphine scavenger and thus facilitates the formation of catalytically active species.^{14,15} Both reaction systems were tested using different 4-styryl substituted derivatives and in each case complete conversion of silsesquioxyl substrate **1A** was achieved.

The results presented in Table 2 show that irrespective of the type of olefin used, all reactions are stereoselective and lead exclusively to the product of *E* geometry of the resulting substituted vinylene bond (¹H NMR data along with the high values of *J*_{HH} coupling constant are to confirm this). The reactions performed with copper chloride(I) allow the preparation of the desired products under mild reaction conditions. However, it is necessary to isolate the 4-styryl substituted derivatives of **1A** from the reaction mixtures on chromatographic columns. This necessity follows mainly from poor solubility of the copper salt used in the solvent that precipitates silsesquioxyl products (methanol, acetone, *n*-hexane). Furthermore, these systems may be applied only in the case of olefins soluble in refluxing methylene chloride. Applying harsh conditions, *i.e.* toluene, 90 °C or 110 °C, promotes (or increases) the homogeneity of the system as with increasing temperature the solubility of most styryl derivatives also increases. Therefore, these systems can be advantageously used for substrates that cause solubility problems. Both developed reaction systems are characterized by high stereoselectivity and selection of appropriate conditions for functionalization largely depend on the type olefins used.

Synthesis of macromolecular compounds with DDSQ embedded in the linear chain – ADMET and silylative coupling copolycondensation

Positive results obtained for the functionalization of divinylsilsesquioxanes *via* cross-metathesis and silylative coupling with

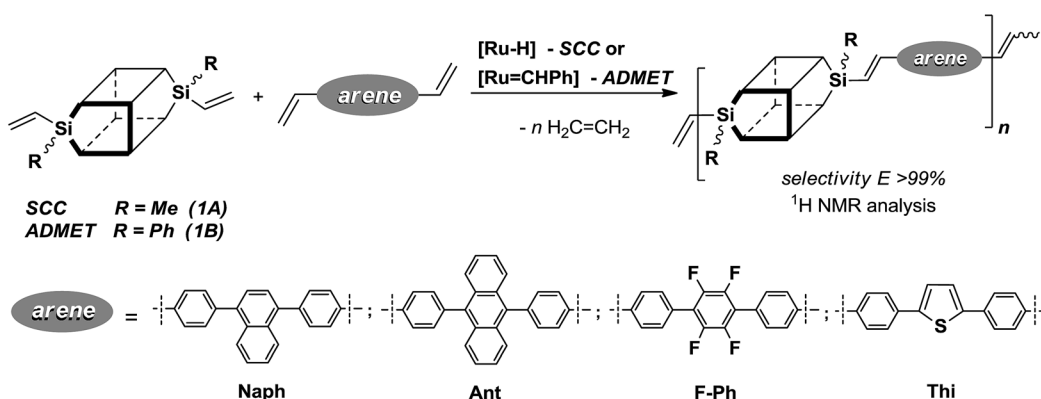
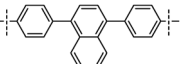
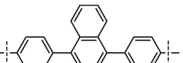
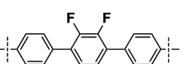
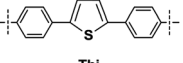
**Scheme 4** Silylative coupling copolycondensation (SCC) and metathetic copolymerisation (ADMET) of divinyl-substituted double-decker silsesquioxanes (**1A**, **1B**) with diolefins.

Table 3 Silylative coupling copolycondensation and ADMET of divinyl-substituted silsesquioxanes DDSQ-2SiVi (1A, 1B) with diolefins^a

DDSQ-2SiVi	R'	Prod. no.	SCC isolated yield [%]		ADMET isolated yield [%]
			System 1	System 2	
1A		9	93	89	—
1B		10	—	—	90
	Naph				
1A		11	90	86	—
1B		12	—	—	85
	Ant				
1A		13	91	85	—
1B		14	—	—	93
	F-Ph				
1A		15	80	0	—
1B		16	—	—	0
	Thi				

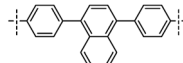
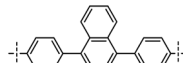
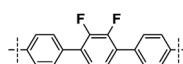
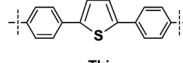
^a Reaction condition: SCC reaction: system 1: toluene, 110 °C; [1] : [diolefin] = 1 : 1; RuHCl(CO)(PCy₃)₂ (2 mol%), *t* = 72 h, argon; system 2: CH₂Cl₂, 45 °C, [1] : [diolefin] = 1 : 1, [RuHCl(CO)(PCy₃)₂] (2 mol%), [Ru] : [CuCl] = 1 : 5, *t* = 72 h, argon. ADMET reaction: CH₂Cl₂, reflux, argon, [1] : [diolefin] = 1 : 1, [RuCl₂(PCy₃)₂(=CHPh)] (2 mol%), *t* = 72 h.

a series of *para*-substituted styrenes with highly π -conjugated substituents prompted us to extend the range of olefins to diolefins. According to literature processes, we synthesized a number of distyrylarenes, which were then subjected to SCC and ADMET copolymerization with DDSQ-2SiVi. The overview of this processes is presented in Scheme 4.

As a result of a series of catalytic tests, successful procedures that ensure the efficiency of both reactions were developed. They allow avoidance of generation of the undesirable polyarenes without the need for any inhibitor addition. Analogously,

as in the synthesis of the molecular products, for the studies on metathetic copolymerization (ADMET), phenyl-substituted silsesquioxane (1B) was applied exclusively whereas in the silylative coupling copolycondensation double-decker silsesquioxane derivative with methyl group at 9 and 19 silicon atom (1A) was used. After optimization of the reaction conditions, a series of copolymers of stereoregular DDSQ-silylene-vinylene-arylene units was obtained (Table 3). As indicated in Table 3, metathetic transformation failed to give cooligomer containing sulfur atom in its structure (16). This may be associated with the

Table 4 Results of GPC analysis of oligomers obtained

DDSQ-2SiVi	R'	Prod. no.	<i>M</i> _n	<i>M</i> _w	PDI	Purity%
1A		9	5200	7300	1.4	100
1B		10	9100	13 600	1.5	91
	Naph					
1A		11	6000	8900	1.5	100
1B		12	13 000	29 200	2.2	95
	Ant					
1A		13	5400	6000	1.1	46
1B		14	18 300	46 100	2.5	98
	F-Ph					
1A		15	5200	11 000	2.1	61
1B		16	—	—	—	—
	Thi					



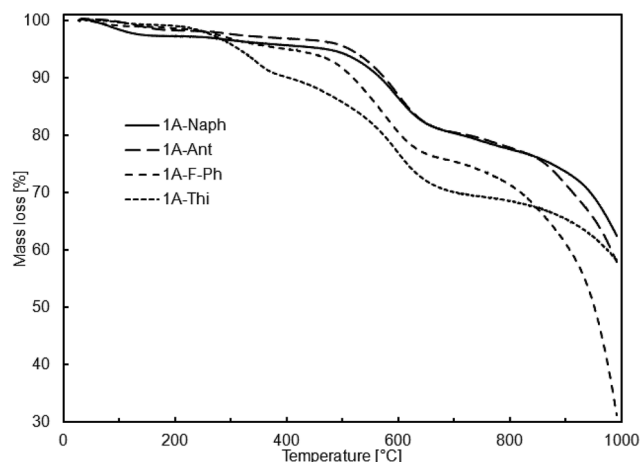


Fig. 1 TGA curves of obtained cooligomers via SCC.

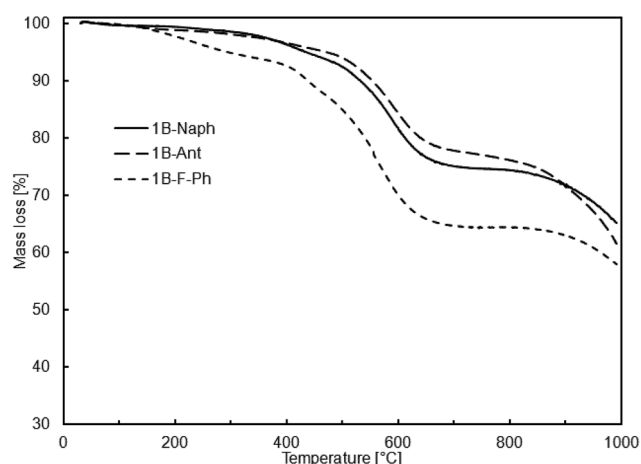


Fig. 2 TGA curves of obtained cooligomers via ADMET copolymerization.

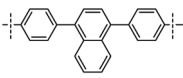
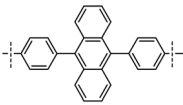
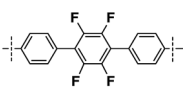
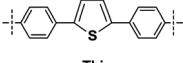
lack of solubility of the distyrylthiophene (Thi) used in refluxing methylene chloride. There was also no reaction progress observed when increasing the amount of the solvent used or when twofold load of alkylidene catalyst was used. To the best of our knowledge, no experiments with Grubbs I generation catalyst have been conducted at high temperatures because of its thermal degradation and *in situ* formation of ruthenium hydride species that catalyze silylative coupling process.¹⁶ Co-oligomer containing thiophene derivative was synthesized only by SCC in the high temperature system ensuring the solubility of the diolefin used.

The new oligomeric products obtained were purified by twice repeated precipitation in methanol or *n*-hexane. Products obtained in the presence of catalytic systems containing copper chloride(I) required further purification on column chromatography with silica gel because the co-catalyst also was not soluble in the precipitant solvent. All oligomeric materials are white or yellow solids and show good solubility in common organic solvents, *e.g.* THF, CHCl_3 and CH_2Cl_2 . They were analyzed by spectroscopic methods.

Subsequently, all prepared samples were analyzed by gel permeation chromatography. They were also subjected to thermogravimetric analysis to evaluate the effect of the comonomers used and the type of catalytic process on their molecular weights, molecular weight distribution and thermal stability. GPC results obtained for cooligomers synthesized *via* silylative coupling copolycondensation (SCC) and ADMET copolymerization processes are summarized in Table 4.

On the basis of the data obtained, it can be noted that ADMET process led to formation of products of relatively higher molecular weights (M_n and M_w) and higher PDI values except for co-oligomer containing thiophene derivative. These results are in good agreement with those in the few available papers concerning the synthesis of similar linear polymers with a DDSQ

Table 5 Thermal properties of obtained cooligomers

DDSQ-2SiVi	R'	Prod. no.	Temp. of mass loss [°C]		Residue at 1000 °C [%]
			5%	10%	
1A		9	464	567	62
1B		10	431	531	65
	Naph				
1A		11	512	575	58
1B		12	467	553	62
	Ant				
1A		13	398	518	31
1B		14	291	437	58
	F-Ph				
1A		15	314	403	58
1B		16	—	—	—
	Thi				



spacer and π -conjugated arenes. Kakimoto *et al.* obtained analogous systems with M_n weight in the range of 11 900 to 29 100, and M_w/M_n values of 2.9–4.9.^{3e}

According to the thermogravimetric studies, all prepared cooligomers show relatively high thermal stability (Fig. 1 and 2).

It is worth noting that there is relatively good correlation between the sample thermal stability and its purity or more precisely, the content of higher molecular weight fraction. It may be an explanation why the samples obtained *via* SCC process are more thermally stable despite their relatively lower molecular weights in comparison to the samples obtained *via* ADMET copolymerization (Tables 4 and 5).

So far, there has been scarce information on similar oligomeric systems with DDSQ fragments. However, among those rare examples in literature, high temperatures of 10% mass loss, reaching over 550 °C, are characteristic of DDSQ copolymers irrespective of the comonomer or catalytic process used.^{3h} This effect may be also attributed to the general tendency of the high thermal stability of POSS compounds heaving phenyl groups.^{3e}

Conclusions

Recent years have shown that the concept of synthesis of molecular and macromolecular organosilicon compounds based on DDSQ led to two major trends in their development. Molecular derivatives based on a DDSQ core are a class of compounds that may be synthesized using, among others, stoichiometric types of modifications, *i.e.* a condensation of tetrasilanolphenyl POSS (DDSQ-4OH) with alkoxy- or chlorosilanes. On the other hand, difunctional DDSQ compounds with reactive groups, *e.g.* a Si–H or Si–HC=CH₂ bond, are ideal substrates for further catalytic modifications. We described divinyl-substituted double-decker silsesquioxanes that undergo efficient functionalization *via* cross-metathesis and silylative coupling reactions with a series of *para*-substituted styrenes that possess highly π -conjugated substituents. For all styrene derivatives tested, both reactions proceeded effectively and with high stereoselectivity leading to exclusive formation of *E* isomer. A divinyl-substituted double-decker silsesquioxane containing a methyl group located at Si-9 and Si-19 atoms (**1A**) was inactive in metathetic transformation, but this result was expected in the context of our earlier reports.¹⁷ Cross-metathesis and silylative coupling silylative are convenient and complementary synthetic routes leading to functionalization of vinyl-substituted silicon derivatives. However, the choice of the optimum catalytic method depends on the specific character of the reaction system. The other synthetic path for DDSQ applications is to try to embed them into the main chain of the polymeric system. We proved that both, SCC and ADMET reactions may be used for the stereoselective synthesis of a new class of vinylene-arylene copolymers containing DDSQ in the main chain. New copolymeric material was characterized in terms of molecular weights, PDI as well as thermal analysis. TG analysis has proved the high level of thermal resistance of the obtained systems, reaching over 550 °C, that is in close correlation with DDSQ copolymers.

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Notes and references

- (a) D. B. Cordes, P. D. Lickiss and F. Rataboul, *Chem. Rev.*, 2010, **110**, 2081; (b) D. B. Cordes and P. D. Lickiss, in *Applications of Polyhedral Oligomeric Silsesquioxanes, Advances in Silicon Science 3*, ed. C. Hartmann-Thompson, Springer, 2011.
- (a) Y. Morimoto, K. Watanabe, N. Ootake, J. Inagaki, K. Yoshida and K. Ohguma, EP 1 428 795 (A1), 2004; US 7 169 873 (B2), 2007; US 7 449 539 (B2), 2008; (b) K. Yoshida, *Polymer Preprints Japan*, 2003, **52**, 316; (c) N. Ootake and K. Yoshida, *US pat.*, 2006/0155091(A1), 2006.
- (a) A. C. Kucuk, J. Matsui and T. Miyashita, *Thin Solid Films*, 2013, **534**, 577; (b) B. Seurer, V. Vij, T. Haddad, J. M. Mabry and A. Lee, *Macromolecules*, 2010, **43**, 9337; (c) M. Kohri, J. Matsui, A. Watanabe and T. Miyashita, *Chem. Lett.*, 2010, **39**, 1162; (d) J. Espinas, J. D. A. Pelletier, E. Abou-Hamad, L. Emsley and J.-M. A. Basset, *Organometallics*, 2012, **31**, 7610; (e) M. Seino, T. Hayakawa, Y. Ishida, M. Kakimoto, K. Watanabe and H. Oikawa, *Macromolecules*, 2006, **39**, 3473; (f) K. Yoshida, T. Hattori, N. Ootake, R. Tanaka and H. Matsumoto, Silsesquioxane-based polymers: synthesis of phenyl silsesquioxanes with double-decker structure and their polymers, in *Silicon Based Polymers. Advances in Synthesis and Supramolecular Organization*, ed. F. Ganachaud, S. Boileau and B. Boury, Springer, London-New York, 2008, p. 205; (g) S. Wu, T. Hayakawa, M. Kakimoto and H. Oikawa, *Macromolecules*, 2008, **41**, 3481; (h) M. Miyasaka, Y. Fujiwara, H. Kudo and T. Nishikubo, *Polym. J.*, 2010, **42**, 799; (i) K. Wei, L. Wang and S. Zheng, *Polym. Chem.*, 2013, **4**, 1491; (j) K. Wei, L. Wang and S. Zheng, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 4221; (k) W. Zhang, J. Xu, X. Li, G. Song and J. Mu, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **52**, 780; (l) K. Wei, L. Wang, L. Li and S. Zheng, *Polym. Chem.*, 2015, **6**, 256; (m) B. Dudziec and B. Marciniak, *Curr. Org. Chem.*, 2015, DOI: 10.2174/1385272820666151228193728.
- (a) B. Marciniak, *Coord. Chem. Rev.*, 2005, **249**, 2374; (b) B. Marciniak, *Acc. Chem. Res.*, 2007, **40**, 943; (c) B. Marciniak and C. Pietraszuk, in *Green Metathesis Chemistry. Great Challenges in Synthesis Catalysis and Nanotechnology*, ed. V. Dragutan, A. Demonceau, I. Dragutan and E. S. Finkelshtein, Springer, Berlin, 2010, p. 157; (d) C. Pietraszuk, P. Pawluć and B. Marciniak, in *Handbook on Metathesis*, R. Grubbs and D. J. O'Leary, 2015, vol. 2, 9, pp. 583–631.
- (a) Y. Itami, B. Marciniak and M. Kubicki, *Chem.–Eur. J.*, 2004, **10**, 1239; (b) J. Waehner, B. Marciniak and P. Pawluć, *Eur. J. Inorg. Chem.*, 2007, 2975; (c) P. Żak, C. Pietraszuk, B. Marciniak, G. Spolnik and W. Danikiewicz, *Adv. Synth.*



- Catal.*, 2009, **351**, 2675; (d) P. Żak, B. Marciniak, M. Majchrzak and C. Pietraszuk, *J. Organomet. Chem.*, 2011, **696**, 887.
- 6 F. J. Feher, D. Soulivong, A. G. Eklund and K. D. Wydham, *Chem. Commun.*, 1997, 1185.
- 7 S. Sulaiman, A. Bhaskar, J. Zhang, R. Guda, T. Goodson III and R. M. Laine, *Chem. Mater.*, 2008, **20**, 5563.
- 8 (a) G. Cheng, N. R. Vautravers, R. E. Morris and D. J. Cole-Hamilton, *Org. Biomol. Chem.*, 2008, **6**, 4662; (b) N. R. Vautravers, P. Andre, A. M. Z. Slavin and D. J. Cole-Hamilton, *Org. Biomol. Chem.*, 2009, **7**, 717; (c) N. R. Vautravers, P. Andre and D. J. Cole-Hamilton, *J. Mater. Chem.*, 2009, **19**, 4545.
- 9 H. Araki and K. Naka, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 4170.
- 10 M. Lo Conte, S. Staderini, A. Chambery, N. Berthet, P. Dumy, O. Renaudet, A. Marra and A. Dondoni, *Org. Biomol. Chem.*, 2012, **10**, 3269.
- 11 (a) P. Żak, B. Dudziec and B. Marciniak, US Appl. US 14,640,618, EP 15461513.2, 2015; (b) P. Żak, B. Dudziec, M. Kubicki and B. Marciniak, *Chem.-Eur. J.*, 2014, **20**, 9387.
- 12 (a) M. Majchrzak, S. Kostera, M. Kubicki and I. Kownacki, *Dalton Trans.*, 2013, **42**, 15535; (b) M. Majchrzak, M. Hybsz, S. Kostera, M. Kubicki and B. Marciniak, *Tetrahedron Lett.*, 2014, **55**, 3055.
- 13 C. S. Yi, D. W. Lee and Y. Chen, *Organometallics*, 1999, **18**, 2043.
- 14 P. Żak, M. Kubicki, B. Marciniak, S. Rogalski, C. Pietraszuk and D. Frąckowiak, *Dalton Trans.*, 2014, **43**, 7911.
- 15 E. L. Dias, S. T. Nguyen and R. H. Grubbs, *J. Am. Chem. Soc.*, 1997, **119**, 3887.
- 16 B. Schmidt, *Eur. J. Org. Chem.*, 2004, 1865.
- 17 C. Pietraszuk and H. Fischer, *Chem. Commun.*, 2000, 2463.

