EurJIC
European Journal of Inorganic Chemistry

ChemPubSoc Europe

SHORT COMMUNICATION

DOI:10.1002/ejic.201300283

Unprecedented Formation of *cis*- and *trans*-Di[(3-chloropropyl)isopropoxysilyl]-Bridged Double-Decker Octaphenylsilsesquioxanes

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Dedicated to Professor Dr. James W. Pavlik and Professor Dr. Yusuke Kawakami on the occasion of their retirement

Keywords: Organic–inorganic hybrid composites / Main group elements / Silanes / Silsesquioxanes

Silsesquioxane formation competing with the deprotonation of alcohol solvents in the presence of a strong base to form alkoxides is reported for the first time. Evidently, sodium isopropoxide is formed during the synthesis of the sodium salt of a double-decker octaphenylsilsesquioxane tetrasilanolate in 2-propanol as the solvent, which leads to the formation of unexpected *cis*- and *trans*-di[(3-chloropropyl)isopropoxysilyl]-bridged double-decker octaphenylsilsesquioxanes after in situ coupling with 3-chloropropyltrichlorosilane. The desired products were characterized by ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectroscopy; ESI-MS; and single-crystal X-ray diffraction.

Introduction

The sodium salt of double-decker octaphenylsilsesquioxane tetrasilanolate (**2**) is classified as one of the promising precursors of polyhedral oligomeric silsesquioxanes.[1] They have recently been coupled with dialkyldichlorosilanes[2] and alkyltrichlorosilanes[3] and later transformed into a new type of condensed polyhedral structures. Nowadays, these promising double-decker silsesquioxane monomers are considered to be novel types of carbosilane and siloxane materials that provide several specific properties such as heat resistance,[3] and they have been used in optoelectronic[4] and hybrid nanoassemblies.[5] So far, the number of available reactive double-decker silsesquioxane monomers has been limited, because isolated precursor **2** is most likely to exist in a mixture of sodium salts.[1i,2a] Therefore, the reaction progress during the formation of the sodium salt of double-decker silsesquioxanes must be investigated.

In this report, we explore the use of sodium isopropoxide (**3**) during the synthesis of **2**. After coupling **2** with 3-chloropropyltrichlorosilane, we found that **3** plays a crucial role in the formation of an isomeric mixture of unexpected products *cis*- and *trans*-di[(3-chloropropyl)isopropoxysilyl]-bridged double-decker octaphenylsilsesquioxane (**5**). For future aspects, it is noteworthy that these novel double-decker monomers could be further functionalized through nucleophilic substitution, as a method has already been proved to be efficient to obtain new silsesquioxane materials in high yield.[6]

Results and Discussion

The synthesis of **2** was first proposed by Yoshida et al. through hydrolytic condensation of phenyltrimethoxysilane in alkaline solution.[1a] Later, Woo, and Kawakami studied the conversion of the sodium salt of heptaphenylsilsesquioxane trisilanolate (**1**) into **2**.[2a] In fact, compounds **1**

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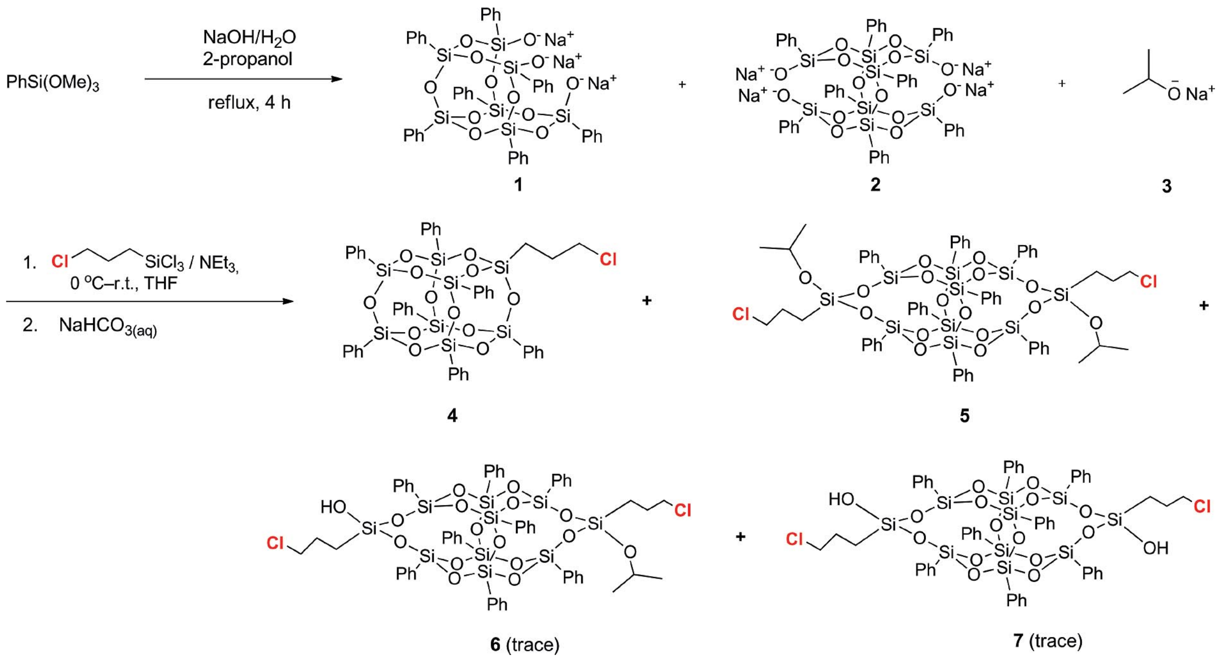
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201300283.

and **2** shown in Scheme 1 are likely found in an equilibrium mixture, which was isolated as coprecipitated sodium salts.[1i,2a] Thus, there is no direct evidence of characterization of these materials, because of their poor solubility in organic solvents. However, the original structures could only be determined qualitatively after treatment with organosilanes to obtain more-soluble materials.[2,4a] Kawakami et al. first attempted the coupling of isobutyltrichlorosilane to these precipitated mixtures of sodium salts; however, the only products found were hydrolyzable *cis*- and *trans*-di[(isobutyl)silanol]-bridged double-decker octaphenylsilsesquioxanes. The separation of the desired materials could be easily achieved by precipitation from a toluene solution, but no further analysis of the soluble products in the mother liquid was performed.[4a] In contrast, in our experiments involving the coupling of **2** with 3-chloropropyltrichlorosilane in a similar manner (Scheme 1), only 3-chloropropyl heptaphenylsilsesquioxane (**4**) could be detected and identified among the insoluble products. This result strongly confirms that not only double-decker sodium salt **2** was formed but also that T_7 sodium salt **1** exists in the precipitated mixture during double-decker formation. In addition, we further analyzed the other soluble products in the toluene solution, and our results obtained by thin-layer chromatography (CH_2Cl_2/hexane = 1:4 v/v) analysis of the mother liquid revealed the existence of three major compounds (R_f = 0.35, 0.15, 0). After purification by column chromatography to separate each pure compound, we found that the least polar (R_f = 0.35) compound was the octameric T_8 silsesquioxane of **4**, which was first isolated in 9% yield in a pure form.

Second, the major product consisted of an isomeric mixture of *cis*-**5**/*trans*-**5** in equal ratios. These compounds have an identical R_f value of 0.15. The mixture was isolated in 14% yield, and its structure was confirmed by its distinguishable $^{29}Si\{^1H\}$ NMR spectrum (Figure S7, Supporting Information). The signals at δ = –61.26, –79.08, –79.13, and –79.57 ppm are assigned to the *cis* isomer, whereas the signals at δ = –61.26, –79.08, and –79.35 ppm are assigned to the *trans* isomer. This result is also consistent with our previous report on the existence of isomeric mixtures of *cis*- and *trans*-di[(3-chloropropyl)methyl]-bridged double-decker octaphenylsilsesquioxane.[2b] Interestingly, its ^1H NMR spectrum exhibits unknown signals at δ = 4.35 and 1.09 ppm, whereas the integrated intensity of the other signals confirms the protons on eight aromatic rings and dibridging 3-chloropropyl side chains in a double-decker structure. To draw a molecular picture, mass spectrometry (ESI-MS) may give useful evidence associated with the appearance of the molecular ion at *m*/*z* = 1417.0561 (Figure S8, Supporting Information). This result strongly suggests that the double-decker backbone must be covalently attached to unexpected dibridging isopropoxysilyl substituents. Consequently, we hypothesize that this unexpected formation of **5** could actually support the presence of **3** among precipitated mixtures of **1** and **2** and could involve isopropoxide–chloride exchange during the coupling reaction with 3-chloropropyltrichlorosilane to form completely condensed double-decker silsesquioxane. Thus, such an intermediate was not suggested elsewhere, after the synthesis of **2** was known. Herein, we suggest that under strongly basic conditions, the deprotonation of any alcohol solvent to



Scheme 1. Synthetic approach to the formation of *cis*- and *trans*-di[(3-chloropropyl)isopropoxysilyl]-bridged double-decker octaphenylsilsesquioxane (**5**).

form alkoxides competes with the formation of silsesquioxane materials, and researchers should be aware of this fact.

Further attempts to separate each pure isomer from the *cis*-**5**/*trans*-**5** mixture by recrystallization in THF/hexane (1:1) successfully provided colorless crystals of pure *trans*-**5**. In Figure 1, the perspective view of *trans*-**5** obtained by single-crystal X-ray diffraction analysis is displayed, and its crystalline data and structural refinement parameters are summarized in Tables S1 and S2 (Supporting Information).

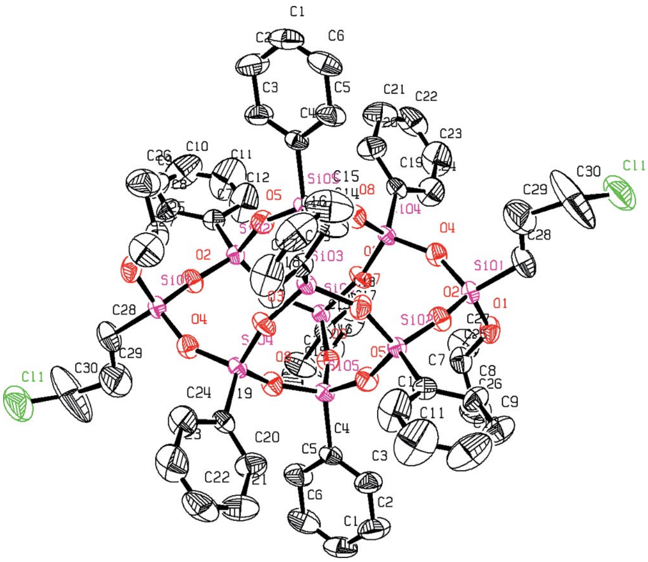


Figure 1. Thermal ellipsoid plot of *trans*-**5** at the 30% probability level; hydrogen atoms are omitted for clarity.

Other double-decker products were obtained in trace amounts (<5% yield) from fractions obtained at a later stage during purification by column chromatography. Partially hydrolyzed di(3-chloropropyl)[(isopropoxysilyl)silanol]-bridged double-decker octaphenylsilsesquioxane (**6**) could be isolated by gradient elution [R_f = 0.31, CH_2Cl_2/hexane (2:3)]. Its NMR spectra (Figures S17–S19, Supporting Information) also confirm that one side of the bridging double-decker is already hydrolyzed to a silanol group, whereas the other still remains alkylated. Moreover, completely hydrolyzed di[(3-chloropropyl)silanol]-bridged double-decker octaphenylsilsesquioxane (**7**) was also collected in a trace amount (R_f = 0.50, CH_2Cl_2). In fact, this isolated fraction was found to be insoluble in chloroform, dichloromethane, and THF but showed good solubility in DMSO. However, the majority of the peaks in the $^{29}Si\{^1H\}$ NMR spectrum (Figure S23, Supporting Information) in [D$_6$]DMSO can be attributed to the *trans* isomer. We suggest that most of *cis*-**7**/*trans*-**7** is possibly excluded as an insoluble material as a result of its poor solubility in common organic solvents. Unlikely, hydrolyzable *cis*- and *trans*-di[(isobutyl)silanol]-bridged double-decker octaphenylsilsesquioxanes could be considered to be more soluble in organic solvents because of the hydrophobic incorporation of the isobutyl groups into the double-decker structure.[4a] These hydrolytic products can be possibly formed after quenching with an aqueous solution under acid–base conditions.

Conclusions

The discovery of sodium isopropoxide (**3**) during the formation of the sodium salt of double-decker octaphenylsilsesquioxane (**1**) by coincidence of the deprotonation of 2-propanol as the solvent under strongly basic conditions has been reported for the first time. Thus, **3** plays a crucial role in an isopropoxide–chloride exchange reaction during the coupling of **1** with slightly sterically hindered 3-chloropropyltrichlorosilane, which directly leads to the formation of unexpected *cis*- and *trans*-di[(3-chloropropyl)isopropoxysilyl]-bridged double-decker octaphenylsilsesquioxane (**5**). Finally, the authors believe that the use of these novel monomers in polymerization and functionalization through nucleophilic substitution reactions to obtain various functional materials should be considered in the near future.

Experimental Sections

Materials and Methods: Phenyltrimethoxysilane and 3-chloropropyltrichlorosilane were obtained from Tokyo Chemical Industry Co., Ltd., and used without additional purification. 2-Propanol and THF were purchased from B&J Company. THF was further dried with sodium metal and distilled under anhydrous conditions. Fourier-transform NMR spectra were obtained by using Bruker-AV 300 for ^1H (300 MHz) and Bruker-AV 500 high-resolution NMR spectrometers for ^1H (500 MHz), $^{13}C\{^1H\}$ (125 MHz), and $^{29}Si\{^1H\}$ (99 MHz). The chemical shifts are reported in δ units (parts per million) relative to $SiMe_4$ (TMS), and the residual solvents peaks ($CHCl_3$) were used for reference. High-resolution mass spectrometry was performed by using a Micromass VQ-TOF 2.

X-ray Structural Determination: Crystalline *trans*-**5** suitable for X-ray structural analysis was obtained by recrystallization in THF/hexane. X-ray data were collected with a Bruker SMART APEX II CCD area-detector diffractometer with a Mo-K_α radiation source (λ = 0.7107 Å) at 296 K. The crystal structures were solved by direct methods with SHELXS-97.[7] The full-matrix least-squares procedures by using SHELXL-97 on F^2 anisotropic for all non-hydrogen atoms was used to refine the crystal structures. Hydrogen atoms were placed in their calculated positions and refined following the riding model.

CCDC-912558 (for *trans*-**5**) contains 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.

Synthesis of the Sodium Salt of Heptaphenylsilsesquioxane Trisilanolate (1), the Tetrasodium Salt of Double-Decker Octaphenylsilsesquioxane (2), and Sodium Isopropoxide (3): Phenyltrimethoxysilane (50 mL, 47.6 g, 0.27 mol) was added dropwise to a solution 2-propanol (260 mL), deionized water (5.5 mL, 0.31 mol), and sodium hydroxide (7.12 g, 0.18 mol) at room temperature for 15 min. The reaction mixture was heated at reflux for 4 h to obtain a milky-white precipitate. The suspension solution was cooled down at room temperature and left overnight. It was subsequently filtered and washed with 2-propanol and dried at 60 °C for 5 h under vacuum to obtain a completely dry white powder mixture of sodium salts **1**, **2**, and **3** (22.15 g).

Synthesis of *cis*- and *trans*-Di[(3-chloropropyl)isopropoxysilyl]-Bridged Double-Decker Octaphenylsilsesquioxane (5): Under a dry argon atmosphere, a mixture of anhydrous THF (260 mL), sodium salts **1**, **2**, and **3** (25.81 g), and triethylamine (9.29 mL, 66.81 mmol) was cooled down to 0 °C in an ice bath. 3-Chloropropyltrichlorosilane (14.16 g, 10.49 mL, 66.81 mmol) was added dropwise over 10 min. After warming to room temperature overnight (12 h), the mixture was then cooled down to 0 °C again before the addition of a saturated $NaHCO_3$ solution (60 mL) to neutralize and dissolve any inorganic materials. CH_2Cl_2 (3×50 mL) was added to extract the desired products. The combined organic layer was separated, washed repeatedly with water until it became neutral, washed with brine, and dried with anhydrous sodium sulfate. Evaporation of the solvent gave a crude product, which was further dissolved in toluene (200 mL) to form a suspension. To fully precipitate the insoluble materials, the solution mixture was left in a refrigerator overnight, at which point it separated into two phases: insoluble white solid (A) and mother liquid solution (A). The insoluble solid (A, 4.41 g) was collected by filtration and further dissolved in THF to yield a solution containing some insoluble materials, which were further removed by filtration. An equivalent volume of ethyl acetate was added to the remaining clear solution, which was then placed at room temperature until the complete formation of cubic-like T_8 crystal **4** (0.40 g, 0.39 mmol, 9%). Evaporation of the mother liquid solution (A) yielded a white solid (24.06 g), which was then analyzed by thin-layer chromatography (CH_2Cl_2/hexane = 1:4 v/v). The analysis clearly showed three separate spots at $R_f = 0.35$ and 0.15 along with a broad baseline ($R_f = 0.10$–0). Crude product (7.13 g) was purified by conventional column chromatography (gradient system CH_2Cl_2/hexane = 1:4, 1:3, 3:7, 2:3, 1:1, and pure CH_2Cl_2) to give an additional product of pure **4** ($R_f = 0.35$; 0.66 g, 0.64 mmol, 9%) and an isomeric mixture of *cis*-**5**/*trans*-**5** ($R_f = 0.15$; 1.00 g, 0.72 mmol, 14%). Further recrystallization of *cis*-**5**/*trans*-**5** in THF/hexane (1:1 v/v) yielded colorless crystals of only pure *trans*-**5**, and evaporation of the remaining solution gave a majority of *cis*-**5**. Thus, **6** [$R_f = 0.30$, CH_2Cl_2/hexane (2:3)] and *trans*-**7** ($R_f = 0.50$, CH_2Cl_2) were isolated in only trace amounts (<5% yield). Data for **4**: ^1H NMR (300 MHz, $CDCl_3$): δ = 7.77–7.72 (m, 14 H), 7.50–7.34 (m, 21 H), 3.52 (t, J = 6.6 Hz, 2 H), 1.98 (quint., J = 6.6 Hz, 2 H), 0.99 (t, J = 8.2 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, TMS): δ = 134.18, 134.13, 130.84, 130.79, 130.21, 130.12, 127.92, 127.87, 47.11, 26.25, 9.48 ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$, TMS): δ = –65.61, –78.23, –78.56 ppm. HRMS (ESI): calcd. for $C_{45}H_{41}ClO_{12}Si_8$ $[M + K]^+$ 1071.0100; found 1070.9490. Data for *cis*-**5**/*trans*-**5** (1:1): ^1H NMR (500 MHz, $CDCl_3$): δ = 7.53–7.11 (m, 40 H), 4.35 (oct., J = 6.2 Hz, 2 H), 3.37 (t, J = 6.8 Hz, 4 H), 1.86 (quint., J = 8.1 Hz, 4 H), 1.09 (d, J = 6.3 Hz, 12 H), 0.82 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, TMS): δ = 134.19, 134.15, 134.01, 133.98, 133.94, 131.41, 130.61, 130.56, 130.49, 127.90, 127.76, 127.69, 127.62, 65.73, 47.18, 26.52, 25.43, 10.35 ppm. $^{29}Si\{^1H\}$ NMR [99 MHz, $CDCl_3$, TMS, $Cr(acac)_3$]: δ = –61.26, –79.08, –79.13, –79.57 (*cis*-**5**; relative intensity ratio 1:2:1:1), –61.26, –79.08, –79.35 (*trans*-**5**; relative intensity ratio 1:2:2) ppm. HRMS (ESI): calcd. for $C_{60}H_{66}Cl_2O_{16}Si_{10}$ $[M + Na]^+$ 1417.1300; found 1417.0561. Data for *trans*-**5**: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.57–7.18 (m, 40 H), 4.40 (oct., J = 6.1 Hz, 2 H), 3.41 (t, J = 6.8 Hz, 4 H), 1.90 (m, 4 H), 1.12 (d, J = 6.1 Hz, 12 H), 0.85 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, TMS): δ = 134.03, 133.99, 131.49, 130.69, 130.57, 130.50, 127.91, 127.71, 65.76, 47.16, 26.58, 25.46, 10.41 ppm. $^{29}Si\{^1H\}$ NMR [99 MHz, $CDCl_3$, TMS, $Cr(acac)_3$]: δ = –61.28, –79.11, –79.37 ppm. HRMS (ESI): calcd. for $C_{60}H_{66}Cl_2O_{16}Si_{10}$ $[M + Na]^+$ 1417.1300; found 1417.1489. Data for *cis*-**5**: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.56–7.18 (m, 40 H), 4.39 (oct., J = 6.1 Hz, 2 H), 3.41 (t, J = 6.8 Hz, 4 H), 1.90 (m, 4 H), 1.12 (d, J = 6.2 Hz, 12 H), 0.85 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, TMS): δ = 134.91, 134.83, 132.30, 131.45, 128.78, 128.66, 128.51, 66.61, 48.09, 27.41, 26.32, 11.24 ppm. $^{29}Si\{^1H\}$ NMR [99 MHz, $CDCl_3$, TMS, $Cr(acac)_3$]: δ = –61.28, –79.08, –79.34, –79.57 ppm. HRMS (ESI): calcd. for $C_{60}H_{66}Cl_2O_{16}Si_{10}$ $[M + Na]^+$ 1417.1300; found 1417.1271. Data for **6**: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.58–7.20 (m, 40 H), 4.40 (oct., J = 6.1 Hz, 1 H), 3.42 (m, 4 H), 1.89 (m, 4 H), 1.13 (d, J = 8.7 Hz, 6 H), 0.94 (m, 2 H), 0.86 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, TMS): δ = 134.01, 133.96, 133.89, 131.32, 131.11, 130.64, 130.56, 130.43, 127.91, 127.89, 127.73, 127.69, 65.71, 47.18, 26.48, 26.35, 25.40, 10.30 ppm. $^{29}Si\{^1H\}$ NMR [99 MHz, $CDCl_3$, TMS, $Cr(acac)_3$]: δ = –56.49, –61.20, –78.62, –79.00, –79.10, –79.31 ppm. HRMS (ESI): calcd. for $C_{57}H_{60}Cl_2O_{16}Si_{10}$ $[M + Na]^+$ 1375.0800; found 1375.0634. Data for *trans*-**7**: ^1H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.18 (m, 40 H), 3.40 (t, J = 6.5 Hz, 4 H), 2.74 (br., 2 H), 1.90 (m, 4 H), 0.93 (t, J = 8.5 Hz, 4 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, TMS): δ = 134.01, 133.89, 131.08, 130.59, 130.36, 127.91, 127.74, 47.17, 26.34, 10.29 ppm. $^{29}Si\{^1H\}$ NMR [99 MHz, $[D_6]$DMSO, TMS, $Cr(acac)_3$]: δ = –58.11, –78.96, –79.25 ppm. HRMS (ESI): calcd. for $C_{54}H_{54}Cl_2O_{16}Si_{10}$ $[M + Na]^+$ 1332.04; found 1331.9689.

Supporting Information (see footnote on the first page of this article): ^1H NMR, $^{13}C\{^1H\}$ NMR, and $^{29}Si\{^1H\}$ NMR spectra; HRMS (ESI) spectra; characterization data for **4**–**7** including crystallographic data for *trans*-**5**.

Acknowledgments

This research was financially supported by the Thailand Research Fund (MRG5580011), the Office of the Higher Education Commission, Center of Excellence for Innovation in Chemistry (PERCH-CIC), and the Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand through its program of Center of Excellence Network. The authors are very thankful to Assoc. Prof. Dr. Nongnuj Muangsin for a discussion of the single-crystal X-ray analysis.

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[1] a) K. Yoshida, K. Ito, H. Oikawa, M. Yamahiro, Y. Morimoto, K. Ohguma, K. Watanabe, N. Ootake, *United States Patent Application* **2004**, 20040068074; b) F. J. Feher, T. A. Budzichowki, *Organometallics* **1991**, *10*, 2526; c) A. R. Bassindale, M. Pourny, P. G. Taylor, M. B. Hursthouse, M. E. Light, *Angew. Chem.* **2003**, *115*, 3612; *Angew. Chem. Int. Ed.* **2003**, *42*, 3488; d) B. Marciniec, M. Dutkiewicz, H. Maciejewski, M. Kubicki, *Organometallics* **2008**, *27*, 793; e) H. Liu, S. Kondo, R. Tanaka, H. Oku, M. Unno, *J. Organomet. Chem.* **2008**, *693*, 1301; f) V. Ervithayasuporn, J. Abe, X. Wang, T. Matsushima, H. Murata, Y. Kawakami, *Tetrahedron* **2010**, *66*, 9348; g) V. Ervithayasuporn, X. Wang, B. Gacal, B. N. Gacal, Y. Yagci, Y. Kawakami, *J. Organomet. Chem.* **2011**, *696*, 2193; h) X. Wang, V. Ervithayasuporn, Y. Zhang, Y. Kawakami, *Chem. Commun.* **2011**, *47*, 1282; i) Y. Kawakami, *React. Funct. Polym.* **2007**, *67*, 1137; j) K. Yoshida, T. Hattori, N. Ootake, R. Tanaka, H. Matsumoto, in: *Silicon Based Polymers: Advances in Synthesis and Supramolecular Organization* (Eds.: F. Ganachaud, S. Boileau, B. Boury), Springer, Berlin, **2008**, p. 205–211; k) R. M. Laine, M. F. Roll, *Macromolecules* **2011**, *44*, 1073.

[2] a) D. W. Lee, Y. Kawakami, *Polym. J.* **2007**, *39*, 230; b) V. Ervithayasuporn, X. Wang, Y. Kawakami, *Chem. Commun.* **2009**, 5130.

[3] a) M. Seino, T. Hayakawa, Y. Ishida, M. Kakimoto, *Macromolecules* **2006**, *39*, 3473; b) S. Wu, T. Hayakawa, R. Kikuchi, S. J. Grunzinger, M. Kakimoto, *Macromolecules* **2007**, *40*, 5698; c) S. Wu, T. Hayakawa, M. Kakimoto, H. Oikiawa, *Macromolecules* **2008**, *41*, 3481; d) B. Seurer, V. Vij, T. Haddad, J. M.

Mabry, A. Lee, *Macromolecules* **2010**, *43*, 9337; e) L. Wang, C. Zhang, S. Zheng, *J. Mater. Chem.* **2011**, *21*, 19344.

[4] a) M. A. Hoque, Y. Kakihana, S. Shinke, Y. Kawakami, *Macromolecules* **2009**, *42*, 3309; b) M. Kohri, J. Matsui, A. Watanabe, T. Miyashita, *Chem. Lett.* **2010**, *39*, 1162.

[5] a) A. C. Kucuk, J. Matsui, T. Miyashita, *J. Colloid Interface Sci.* **2011**, *355*, 106; b) J. Espinas, J. D. A. Pelletier, E. Abou-Hamad, L. Emsley, J.-M. Basset, *Organometallics* **2012**, *31*, 7610.

[6] a) U. Dittmar, B. J. Hendan, U. Flrke, H. C. Marsmann, *J. Organomet. Chem.* **1995**, *489*, 185; b) M. Dutkiewicz, H. Maciejewski, B. Marciniec, *Synthesis* **2009**, *12*, 2019; c) V. Ervithayasuporn, T. Tomeechai, N. Takeda, M. Unno, A. Chaiyanurakkul, T. Osotchan, *Organometallics* **2011**, *30*, 4475; d) T. Jaroentomeechai, P. Yingsukkamol, C. Phurat, E. Somsook, T. Osotchan, V. Ervithayasuporn, *Inorg. Chem.* **2012**, *51*, 12266.

[7] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

Received: February 28, 2013