Organic–Inorganic Hybrid Material. I. Synthesis, Characterization, and Thermal Property of a Novel Polyhedral Cubic Silsesquioxane

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ABSTRACT: Hydrosilylation of 2-chloroethylvinyl ether by octahydridosilsesilsesquioxane catalyzed by hexachloroplatinic acid was carried out to afford a quantitative yield of **3** in its white crystals. Thermogravimetric analysis of $Si_8O_{12}(CH_2CH_2OCH_2CH_2Cl)_8$ **3** revealed that it is reasonably thermally stable. Spectroscopic data and crystal structure were used to justify the integrity, structural and molecular connectivity of the hitherto novel compound. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 907–910, 2004

Key words: hybrid materials; thermogravimetric analysis; cubic-silsesquioxane

INTRODUCTION

Polyhedral oligosilsesquioxanes (i.e., $[RSiO_{3/2}]_n$) are an interesting class of three-dimensional silsesquioxanes derived from the hydrolytic polycondensation of trifunctional organosilicon monomers (i.e., $RSiX_3$, X = Cl, OMe, OEt).[1]

The use of inorganic cage compounds as molecular building blocks for the rational design of materials is an attractive and challenging avenue for the material chemists. One example is the silicate cage compounds $(RSiO_{3/2})_n$ (R = organic or inorganic group), which are potentially a very useful class of compounds.[2–5] They were used as three-dimensional building block units for the synthesis of new materials such as precursors for ceramics and models in various fields.[3,4]

Recently, hydridosilsesquioxanes[6] (i.e., $[HSiO_{3/2}]_n$) have also attracted interest as photoresists[7] and spherosilicates.[8] In addition, an exciting structural organization of the cubic silicate species $[Si_8O_{20}]^8$ was achieved recently with various cationic surfactants.[9,10] This procedure has potential applications as highly ordered mesoporous solids, as organic–inorganic nanocomposites, and as models in the area of biomimetics.[10]

Hence, with a focus towards developing a potential photoresist material that has a lithographic action,[11] we report herein a facile synthesis, characterization, and property of a novel octasilsesquioxane, which by virtue of its terminal chlorine (—ω—C—Cl) might also be useful as a photoresist material.[12]

EXPERIMENTAL

General

Reagents used were obtained from commercial sources (e.g., Aldrich, Milwaukee, WI, and Fluka, Buchs, Switzerland) and were used without further purification. IR spectra were recorded in CH_2Cl_2, using CaF_2 optic on a Perkin–Elmer 882 spectrophotometer. The ^1H-NMR and ^{13}C-NMR were obtained on a Bruker AC 300 spectrometer. Chemical shifts are reported in δ values relative to the residual solvent resonance of $CDCl_3$ (^1H, δ 7.24; ^{13}C, δ 77.0), C_6D_6 (^1H, δ 7.15).

Low-resolution mass spectra were recorded on VG 70–250s mass spectrometer by using FAB technique. Microanalytical data were obtained with the use of a Perkin–Elmer 240C elemental analyzer. Thermal gravimetric analysis was carried out by using a Perkin–Elmer TGA-7 thermogravimetric analyzer and measurement was performed at a rate of 10°C/min under air/nitrogen.

Synthesis of octahydridosilsesquioxane (2)

$FeCl_3$ (anhydrous, 50 g) was taken in a round-bottomed flask, and concentrated aqueous HCl (20 mL) was added followed by CH_3OH (40 mL). Hexane (350 mL) was added and the mixture was stirred. A solution of $HSiCl_3$ (20 mL, 0.2 mol) in hexane (150 mL) was added dropwise over a period of 9 h. After an additional 30 min of stirring, the upper hexane layer was transferred to another round-bottomed flask along with a suspended yellow solid. K_2CO_3 (14 g) and $CaCl_2$ (10 g) were added to the flask and the contents were stirred overnight. The mixture was filtered, and
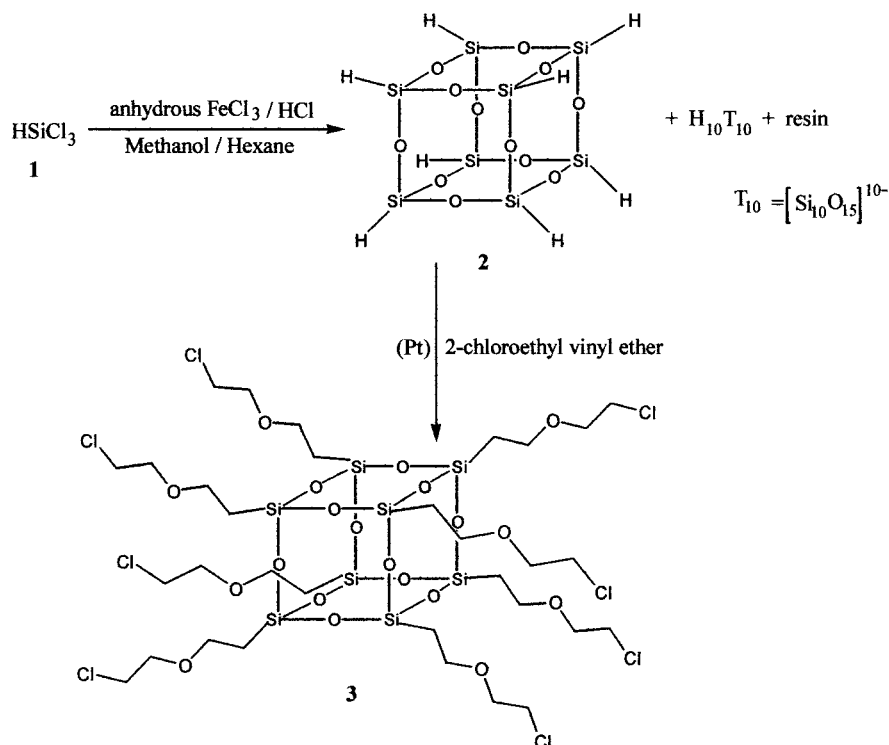
Scheme 1 Synthetic pathway of a novel compound **3.**

the filtrate volume was reduced by evaporation until it was about 20 mL. ^{1}H-NMR (C_6D_6) showed that these crystals were a mixture of H_8–T_8 and H_{10}–T_{10} with singlet at δ 4.19 and 4.23, respectively. H_{10}–T_{10} was eliminated by further washings of the mixture with hexane to give a yield of **2** as 17.5%. **2:** ^{1}H-NMR (C_6D_6): δ 4.19 (s, 8H). MS (FAB): 425.4 (M^+).

Hydrosilylation reaction of 2 with 2-chloroethylvinylether

2-Chloroethylvinylether (2.0 mL, 1.9×10^{-2} mol) was added to a 5.0-mL flask containing H_8–T_8 (0.25 g, 5.7×10^{-4} mol). Eight drops of 0.1 M H_2PtCl_6 in i-PrOH were added and the mixture was heated at reflux overnight before vacuum removal of excess reactant to give off-white microcrystals which were washed with hexane to give {Cl(CH$_2$)$_2$O(CH$_2$)$_2$}$_8$-T$_8$ **3.**

Yield = 98%. **3:** ^{1}H-NMR (CHCl$_3$): δ 1.06 (t, SiCH$_2$, 2H); 3.55–3.67 (m, CH$_2$OCH$_2$CH$_2$Cl, 6H). ^{13}C-NMR (CDCl$_3$): δ 13.99, 42.94, 66.65, and 70.38 (all CH$_2$). IR (CH$_2$Cl$_2$): 3685.2 (C—H), 1449.0 (Si—CH$_2$—), 1118.3 (Si—O—Si) cm^{-1} MS (FAB): 1275.1 (M^+, parent ion). Elem. Anal. Calcd. for $C_{32}H_{64}O_{20}Si_8Cl_8$: C, 30.01%; H, 4.98%; Found: C, 29.75%; H, 4.91%.

RESULTS AND DISCUSSION

The complete synthesis of compound **3** was accomplished in a high yield by the reaction of octahydrido-silsesquioxane **2** with an excess of 2-chloroethylvinyl ether in the presence of H_2PtCl_6 H_2O as catalyst. The reaction pathway adopted for the synthesis of **3** is represented in Scheme 1.

The first step involves a sol–gel reaction of HSiCl$_3$ **1** under a water-starved condition by using FeCl$_3$/HCl to give mixtures of silsesquioxanes (i.e., T_8 and T_{10}) as originally developed by Agaskar.[13] The mechanism was considered to be hydrolytic polycondensation,[13–15] which forms the basis for most sol–gel reactions to date.

Platinum-catalyzed hydrosilylation of $H_8Si_8O_{12}$ **2** provides a variety of functionalized silsesquioxanes.[16–18] However, in most cases the products are mixtures of isomers as a consequence of α and β addition to the alkene. For the present study, β addition could be suppressed by using excess of 2-chloroethylvinyl ether such that treatment of **2** with reactant affords a high yield of **3,** which crystallizes spontaneously from solution as colorless crystals. The slow and total evaporation of the mother liquor of **3** in ether solution results in the formation of a single crystal whose Oakridge thermal ellipsoid program (ORTEP) plot is shown in Figure 1.

The X-ray crystal structure of **3** reveals that the molecule is required crystallographically to possess a center of symmetry. The linear arms, except that extending from Si3, are virtually all-*trans* in conformation with *ω*–C—Cl. The arm extending from Si2 has a kind of disorder in the terminal region; the a common feature in the X-ray structure of silsesquioxanes. On
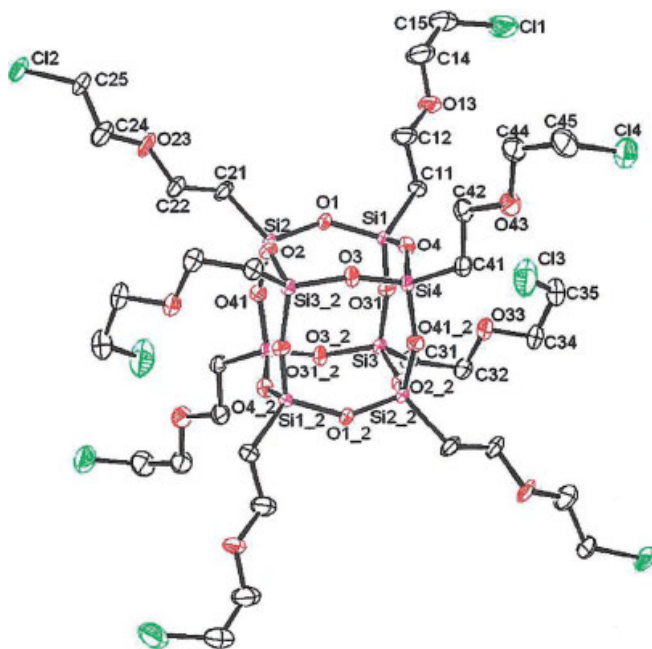
Figure 1 ORTEP Plot of **3.**

the average, R-factor < 0.10, and the core Si—O bond length $= 1.616 \pm 0.007$ Å, and the core $\angle$O—Si—O bond angle $= 149.03 \pm 4.2°$. These values conform with most reported[19] silsesquioxanes core.

Molecular structure of **3** with H-atoms, C25′, and Cl2′ omitted for clarity. Selected bond lengths: Sil-O1 1.627(3), Sil-O4 1.616(4), Sil-O31 1.605(3), Si2-O1 1.614(3), Si2-O2 1.608(4), Si2-O41 1.618(3), Si3-O2 1.613(3), Si3-O3 1.631(3), Si3-O31 1.605(3), Si4- O3 1.621(3), Si4-O4 1.619(4), Si4-O41 1.614(3) Å; Sil-C11 1.842(5), Si2-C21 1.846(5), Si3-C31 1.841(5), Si4-C41 1.837(5) Å; bond angles: O1-Sil-O4 108.42(19), O1-Sil-O31 108.79(18), O1-Sil-C11 109.01(20), O4-Sil-O31 109.52(18), O4-Sil-C11 111.64(23), O31-Sil-C11 109.42(23), O1-Si2-O2 109.50(18), O1-Si2-O41 108.45(18), O1-Si2-C21 107.96(20), O2-Si2-O41 108.83(18), O2-Si2-C21 109.98(23), O41-Si2-C21 112.09(24), O2-Si3-O3 108.32(18), O2-Si3-O31 109.44(19), O2-Si3-C31 110.53(21), O3-Si3-O31 107.69(18), O3-Si3-C31 108.74(21), O31-Si3-C31 112.01(21), O3-Si4-O4 108.45(18), O3-Si4-O41 109.97(18), O3-Si4-C41 109.67(22), O4-Si4-O41 110.14(20), O4-Si4-C41 111.28(22), O41-Si4-C41 107.33(21) °; consecutive torsion angles: Sil-C11-C12-O13- -C14-C15-C11 −175.6°, −177.2°, −179.1°, −49.8°; Si2-C21-C22-O23-C24-C25-C12 176.7°, −174.1°, 159.0°, 155.0°; Si3-C31-C32-O33-C34-C35-C13 −52.4°, 169.6°, 178.5°, 62.8°; Si4-C41-C42-O43-C44-C45-C14 178.9°, 177.3°, −179.7°, 63.8°.

Crystal data of **3:** $C_{32}H_{64}Cl_8O_{20}Si_8$, FW 1277.16; Triclinic P −1, a, 8.9592(13); b, 12.4123(19); c, 13.1479(12) Å; α, 99.719(11); β, 95.264(11); γ, 84.052(12)°; V = 1429.2(3) Å³; Z = 1; F(000) 664; D_{calc}, 1.477 g/cm³; λ, 0.7107 ›; μ, 0.63 mm⁻¹; 2θ max, 50.0°; Nonius CAD4

data; $-10 < h < 10$, $0 < k < 14$; $-15 < l < 15$; crystal size, 0.21 × 0.24 × 0.40 mm; transmission factors 0.483–0.868; T = 298 K; no. of refined atoms, 36; no. of calculated atoms, 32; no. of refined parameters, 325; no. of unique reflections, 5038; no. of observed reflections, 3618 [$I > 2.0\sigma(I)$]; $R = 0.076$; $R_w = 0.106$; Goodness of fit = 1.76; $(\Delta/\sigma)_{max} = 0.0001$; $(D\text{-map})_{max} = 1.050$ e/Å³; minimizing function = $\Sigma(w\|F_o| − |F_c\|^2)$; weighting scheme = counting statistics plus a weight modifier 0.05.

Final fractional coordinates of non-H atoms are given in Table I.

Characterization of **3** was further accomplished by ¹H, ¹³C, IR, mass, and elemental analyses. The reaction, which was monitored by ¹H-NMR spectroscopy, indicated a total disappearance of resonance at δ4.19, and the emergence of appropriate peaks due to the expected compound **3.** As well, there are good ¹³C,

TABLE I
Final Fractional Coordinates of Nonhydrogen Atoms of 3

Atom	x	y	z	Biso
Si1	0.62559(15)	0.55395(10)	0.83948(9)	2.75(5)
Si2	0.54165(15)	0.32253(9)	0.85134(8)	2.69(5)
Si3	0.76642(14)	0.57978(10)	1.07048(9)	2.65(5)
Si4	0.31717(15)	0.65225(10)	0.91708(9)	2.94(6)
C11	0.8684(5)	0.6944(3)	0.3933(2)	15.18(28)
C12	0.3547(3)	−0.2486(2)	0.5220(2)	5.88(10)ᵃ
C12′	0.4982(35)	−0.2238(21)	0.5585(16)	23.21(55)ᵇ
C13	0.5945(3)	0.8754(2)	0.9093(2)	9.43(14)
C14	−0.0278(3)	1.0540(2)	0.6430(2)	7.91(12)
O1	0.6027(4)	0.4237(2)	0.8097(2)	3.3(1)
O2	0.3644(4)	0.3476(3)	0.8654(2)	3.4(1)
O3	0.2236(4)	0.5452(2)	0.9043(2)	3.4(1)
O4	0.4618(4)	0.6213(3)	0.8490(3)	3.7(2)
O13	0.7809(6)	0.5792(4)	0.5633(3)	6.2(2)
O23	0.5092(5)	0.0252(3)	0.6659(3)	5.3(2)
O31	0.7224(4)	0.5747(3)	0.9488(2)	3.5(1)
O33	0.8732(5)	0.7939(3)	1.0333(3)	5.0(2)
O41	0.6289(4)	0.3105(3)	0.9627(2)	3.8(1)
O43	0.0332(5)	0.8462(3)	0.7482(3)	5.1(2)
C11	0.7280(7)	0.5949(4)	0.7390(4)	4.1(2)
C12	0.6865(9)	0.5476(6)	0.6314(4)	6.4(4)
C14	0.7394(13)	0.5396(8)	0.4599(5)	9.2(5)
C15	0.8292(14)	0.5664(8)	0.3883(5)	9.8(6)
C21	0.5759(7)	0.1981(4)	0.7546(4)	4.3(2)
C22	0.4720(7)	0.1114(4)	0.7477(4)	4.5(2)
C24	0.4097(9)	−0.0567(6)	0.6452(6)	6.6(4)
C25	0.4088(36)	−0.1219(18)	0.5472(18)	8.0(15)ᶜ
C25′	0.4817(19)	−0.1436(17)	0.5698(17)	4.7(8)ᵈ
C31	0.9494(6)	0.6353(4)	1.1099(4)	3.6(2)
C32	0.9440(7)	0.7597(5)	1.1236(4)	4.5(3)
C34	0.8382(8)	0.9090(5)	1.0440(5)	5.5(3)
C35	0.7683(10)	0.9363(5)	0.9444(6)	6.6(4)
C41	0.1949(6)	0.7672(4)	0.8748(4)	3.8(2)
C42	0.1258(7)	0.7495(4)	0.7657(4)	4.4(2)
C44	−0.0294(8)	0.8350(5)	0.6441(5)	5.7(3)
C45	−0.1230(8)	0.9358(6)	0.6285(5)	6.3(3)

ᵃ C12: occupancy factor = 0.75.
ᵇ C12′: occupancy factor = 0.25.
ᶜ C25: occupancy factor = 0.50.
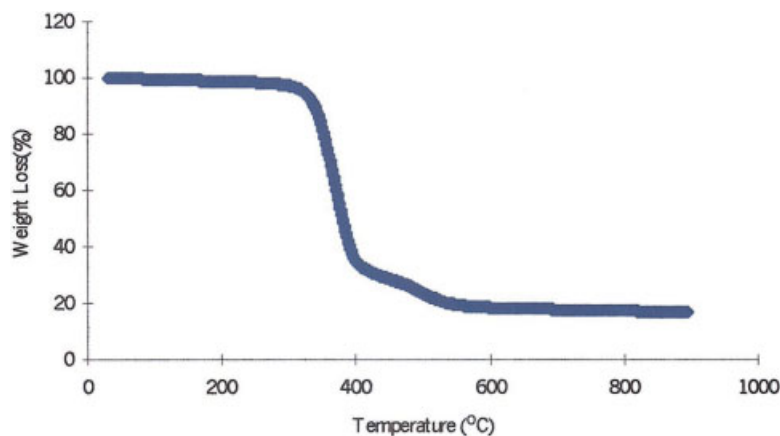ᵈ C25′: occupancy factor = 0.50.

Figure 2   Thermogravimetric analysis of **3** (% weight loss versus temperature).

mass, and elemental analyses data to justify the integrity and molecular connectivity of the new compound.

The generally accepted hydrosilylation reaction mechanism based on fundamental transition metal reactions includes oxidative addition of Si—H bond on Pt olefin coordination, migratory 1,2-insertion of hydride, and reductive elimination (i.e, the Chalk–Harod mechanism).[20] High yield, and a very broad absorption (1118 cm^{-1}) on the IR corresponding to Si—O—Si, is evidence that hydrosilylation proceeded under retention[21] (i.e., retention of $[Si_8O_{12}]^8$ cage).

Thermal stability of **3** was evaluated thermogravimetrically in air/nitrogen at the rate 10°C/min. It is evident in Figure 2 that **3** is reasonably stable, and experiencing precipitous weight loss above 350°C. The multistep weight loss could be attributed to its ether linkages.

CONCLUSION

A straightforward procedure was developed for the synthesis of etheric chlorine-terminated silsesquioxane, a novel compound that is reasonably thermally stable. However, the presence of terminal halogens in the compound suggests practical application as photoresist and lithographic material. Literature reviews[11,12] on related polysiloxanes with such terminal halogen have found application as useful lithographic material.

This result also represents important progress in the development of silsesquioxanes as models for functionalized silica.

Overall, an inorganic cubic system was converted into a new organic–inorganic hybrid material, which hopefully would combine advantageous properties of disparate components into singular material.

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