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Hydroxyl-functionalized alkyl-terminated silsesquioxanes as surface modificators of friction geomodifiers

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Experimental

IR spectra in the 4000-400 cm^{-1} region were recorded on a Spectrum 1000BX-11 (Perkin-Elmer) instrument in KBr pellets. NMR spectra were recorded in $CDCl_3$ using a Bruker Avance AV-400 spectrometer and tetramethylsilane as a standard.

Trichlorosilane, H_2PtCl_6, magnesium, iodomethane, 1-bromobutane, 1-bormoheptane and 1-bromohexadecane (Sigma-Aldrich) were used as purchased. Diethyl ether was distilled over sodium metal. Grignard reagents were prepared routinely in diethyl ether. All syntheses of Grignard reagents and dendrimers were carried out in an argon atmosphere.

Octavinylsilsesquioxane **1** was obtained by a procedure similar to that [1]. Trichlorovinylsilane (80.75 g, 0.5 mol) was added under vigorous stirring to 95% ethanol (680 ml). The reagent ratio was ν(silane) : ν(H_2O) : ν(EtOH) = 1 : 3 : 11. The mixture was stirred at 50 °C for 4 h and at 6 °C for 72 h. The precipitate was recrystallized twice from acetone. The yield of **1** was 7.32 g (18.5%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): 6.13-5.88 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm, δ): 137.19, 128.87; ^{29}Si NMR (80 MHz, $CDCl_3$, ppm, δ): -79.78; FT-IR (KBr, ν, cm^{-1}): 3068, 3028, 2988, 2962, 1604, 1410, 1276, 1112, 1006, 972, 780, 584, 464; ESI-MS (m/z): 654.93 $[M + Na]^+$, calc. for $C_{16}H_{24}O_{12}Si_8$ is 631.94; Elemental Analysis data: Calc. C, 30.36; H, 3.82; Si, 35.49; Expt. C, 30.22; H, 3.91; Si, 35.43.

Octakis(2-trichlorosilylethyl)silsesquioxane **2** was prepared as described [2].

Hydroxy-functionalized alkyl-terminated silsesquioxanes 4a-c. In a 100 ml autoclave, to a suspension of compound **2** (1.06 g, 0.617 mmol) diethyl ether (20 ml) was added a solution of the corresponding Grignard reagent (1 M, 25 ml, 25 mmol) and heated at 120 °C for 6 h. The reaction mixture was then poured with stirring into a solution of NH_4Cl (2.67 g, 0.05 mol) in water (50 ml), the organic layer was separated, extracted with diethyl ether and dried over sodium sulfate. The solution was evaporated to a minimum volume and purified by gel

permeation chromatography on a styrene-divinylbenzene gel with toluene as the eluent. The target fraction was evaporated to the required volume. The yields of the compounds were determined after evaporation of the solvent under reduced pressure: 1.24 g (86%) for **4a**, 2.11 g (66%) for **4b** and 3.03 g (76%) for **4c**.

Methyl-functionalized alkyl-terminated silsesquioxanes 5a-c. In a 100 ml autoclave to a suspension of compound **2** (1.06 g, 0.617 mmol) in diethyl ether (20 ml) was added the corresponding Grignard reagent (1 M, 25 ml, 25 mmol) and heated 120 °C for 6 h. The autoclave was cooled, opened, and excess of methylmagnesium iodide (1 M, 15 ml, 15 mmol) was added. The autoclave was sealed again, and heating was continued for more 3 h at 120 °C. The reaction mixture was then poured with stirring into a solution of NH_4Cl (2.67 g, 0.05 mol) in water (50 ml), the organic layer was separated, extracted with diethyl ether and dried over sodium sulfate. The solution was evaporated to a minimum volume and purified by gel permeation chromatography on a styrene-divinylbenzene gel with toluene as the eluent collecting the fraction in the range of the following molecular weights: 1900-2300 for **5a** (1.20 g, 85%), 2800-3200 for **5b** (2.08 g, 64%) and 5000 for **5c** (2.99 g, 74%).

Substance 5a. ^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): -0.06 (s, 15H, Si-C$\underline{H}_3$), 0.5-0.61 (m, 67H, Si-C$\underline{H}_2$), 0.86-0.91 (t, 62H, C$\underline{H}_3$-CH_2), 1.25-1.36 (m, 77H, C$\underline{H}_{2(alkyl)}$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, δ): -3.95 (C$\underline{H}_3$-Si); 3.82, 4.59 (Si-C$\underline{H}_2$-C$\underline{H}_2$-Si); 12.65-14.37 (C$\underline{H}_3$-CH_2); 25.34-35.05 (C$\underline{H}_{2(alkyl)}$). ^{29}Si NMR (80 MHz, $CDCl_3$, ppm, δ): -65.96, -65.80 ($\underline{Si}O_{1,5}$); 4.59, 5.19 ($\underline{Si}Alk_2CH_3$); 16.73 ($\underline{Si}Alk_3$). IR (KBr, ν, cm^{-1}): 473, 542, 635, 1123, 1256, 1410, 1464, 2874, 2924, 2959. Elemental Analysis data (%): calc. for $C_{97}H_{218}O_{12}Si_{16}$ C 57.50, H 10.84, Si 22.18; expt. C 57.34, H 10.99, Si 21.91.

Substance 5b. ^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): -0.06 (s, 15H, Si-C$\underline{H}_3$), 0.5-0.59 (m, 67H, Si-C$\underline{H}_2$), 0.86-0.90 (t, 66H, C$\underline{H}_3$-CH_2), 1.26-1.30 (m, 210H, C$\underline{H}_{2(alkyl)}$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, δ): -3.94 (C$\underline{H}_3$-Si); 3.84-4.66 (Si-C$\underline{H}_2$-C$\underline{H}_2$-Si); 12.95-14.71 (C$\underline{H}_3$-CH_2); 22.67-33.77 (C$\underline{H}_{2(alkyl)}$). ^{29}Si NMR (80 MHz, $CDCl_3$, ppm, δ): -65.98, -65.82 ($\underline{Si}O_{1,5}$); 4.53 ($\underline{Si}Alk_2CH_3$); 16.61 ($\underline{Si}Alk_3$). IR (KBr, ν, cm^{-1}): 471, 540, 723, 775, 841, 885, 1124, 1254, 1379, 1408, 1464, 2854, 2924, 2957. Elemental Analysis data (%): calc. for $C_{154}H_{332}O_{12}Si_{16}$ C 65.46, H 11.84, Si 15.90; expt. C 65.33, H 11.78, Si 15.65.

Substance 5c. ^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): -0.06 (s, 13H, Si-C$\underline{H}_3$), 0.5-0.58 (m, 70H, Si-C$\underline{H}_2$), 0.86-0.90 (t, 63H, C$\underline{H}_3$-CH_2), 1.20-1.35 (m, 572H, C$\underline{H}_{2(alkyl)}$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, δ): -3.89 (C$\underline{H}_3$-Si); 3.83-4.70 (Si-C$\underline{H}_2$-C$\underline{H}_2$-Si); 13.01-14.79 (C$\underline{H}_3$-CH_2); 22.72-33.84 (C$\underline{H}_{2(alkyl)}$). ^{29}Si NMR (80 MHz, $CDCl_3$, ppm, δ): -65.98 ($\underline{Si}O_{1,5}$); 4.53 ($\underline{Si}Alk_2CH_3$); 16.60 ($\underline{Si}Alk_3$). IR (KBr, ν, cm^{-1}): 473, 721, 787, 854, 1126, 1254, 1468, 2851, 2920, 2957.

Elemental Analysis data (%): calc. for $C_{325}H_{674}O_{12}Si_{16}$ C 74.66, H 12.90, Si 8.58; expt. C 75.02, H 13.13, Si 8.17.

References

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