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Synthesis of polymethylsiloxane molecular brushes

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Materials & Equipment

Commercial reagents: Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution, Sigma-Aldrich), *n*-BuLi (1.6 M solution in hexane, Acros organics), benzyl chloride (95%, Acros organics), dimethylchlorosilane (DMCS) (99.5%, ABCR), vinyldimethylchlorosilane (VDMCS) (98%, ABCR), and trimethylchlorosilane (TMHS) (99%, ABCR) were used without additional purification. Hexane, tetrahydrofuran (THF), ethanol, were pretreated according to conventional techniques [S1,S2]. Hexamethylcyclotrisiloxane (D_3) (95%, ABCR) was dried by distillation over CaH_2.

GPC measurements were carried out on a Shimadzu LC-10 high pressure chromatographic system (Japan) equipped with an SPD-10MAVP diode array detector, operating in the gel permeation chromatography mode, using THF as the eluent. The studies were performed at 40±0.1°C at a flow rate of 1.0 ml•min^{-1}, 300 × 7.8 mm column, Phenogel sorbent (Phenomenex, USA), 5 μm, pore size from 500 Å.

High-pressure chromatographic system Shimadzu LC-20 Prominence (Japan) with triple detection: refractometer, diode array detector SPD-M20A, light scattering detector Viscotek 270 for HPLC systems, operating in gel permeation chromatography mode, with THF as the eluent. The studies were carried out at a temperature of 40±0.1°C, flow rate 1.0 ml•min^{-1}, 300×7.8 mm columns, Phenogel sorbent (Phenomenex, USA), 5 μm, pore size from 50 to 106 Å.

NMR spectra were recorded on Bruker WP-250 SY instruments using tetramethylsilane as the external standard, at room temperature, using $CDCl_3$ as the solvent. Chemical shifts were determined relative to residual solvent signals. The spectra were processed using ACDLABS software.

Synthesis

*Synthesis of poly(chlorodimethylsilylethyl)methylsiloxane **3***. Dry toluene (65 ml) was added to polymethylvinylsiloxane **1** (0.8 g, 0.00918 mol), then DMCS (4.34 g, 0.05 mol) and Karstedt's catalyst (14 μl) were added in a stream of argon. The reaction time was 24 h. After removal of the excess DMCS, the content of Cl was 1.3% according to functional analysis (titration with sodium hydroxide solution). ^{1}H NMR ($CDCl_3$): δ =0.15 (m, 3H; ($\underline{CH}=C\underline{H_2}$) $Si(CH_3)$- not detected.

*Synthesis of dimethylsiloxane oligomer $LiO[SiMe_2O-]_nSiMe_2Bu$ **4***. In a dry oxygen-free medium, a solution of *n*-BuLi in hexane (0.02 mol) was added to a solution of (D_3) (20.19 g, 0.09 mol) in 60 ml of anhydrous hexane. After 2 h, dry THF (20 ml) was added, and the mixture was stirred for 6 h at room temperature. A sample of the reaction mixture terminated by VDMCS was analyzed by ^{1}H NMR ($CDCl_3$): δ=6.0 (m, 3H; $SiC\underline{H}=C\underline{H_2}$); δ=1.3 (t, $C\underline{H_2}$(Bu)), δ=0.8 (m, 3H, $C\underline{H}$3(Bu)), δ=0.56 (m, 2H; $SiC\underline{H_2}$-), δ =0.2-0.05 (90H; $SiC\underline{H_3}$).

Grafting $LiO[SiMe_2O-]_nSiMe_2Bu$ to poly(chlorodimethylsilylethyl)methylsiloxane. A solution of $LiO[SiMe_2O-]_nSiMe_2Bu$ (74 ml, 0.009 mol) in dry hexane was added to poly(chlorodimethylsilylethyl)methylsiloxane **3** (26.87 g, 30 ml) in an inert medium, and the system was stirred for 3 hours. TMCS (0.5 ml) was added to the reaction mixture. Filtration, removal of volatile products and reprecipitation of the final product from a 5% solution in hexane with ethanol have a polymethylsilsesquioxane polymer **P2** with side dimethylsiloxane chains (6.35 g, 74%). GPC (PS-standard): MMD is monomodal, Mpeak > 1,000,000 amu. ^{1}H NMR ($CDCl_3$): δ=1.3 (t, $C\underline{H_2}$(Bu)), δ=0.8 (m, 3H, $C\underline{H_3}$(Bu)), δ=0.56 (m, 2H; $SiC\underline{H_2}$-), δ =0.2-0.05 (90H; $SiC\underline{H_3}$); ^{29}Si NMR ($CDCl_3$): δ=7.21 (s, Si, $\underline{Si}(CH_3)_2Bu$), 8.3 (s, Si, $\underline{Si}(CH_3)_2CH_2$-$CH_2$-; δ=19-22 (s, Si, $\underline{Si}(CH_3)_2$).

References

[1] A. Gordon, R. Ford, *Sputnik khimika (Chemist's Companion)*, Moscow, Mir, 1976 (translated from English to Russian).

[2] W. L. F. Armarego, D. D. Perrin, *Purification of laboratory chemicals*, Oxford, Elsevier Science, 2002.

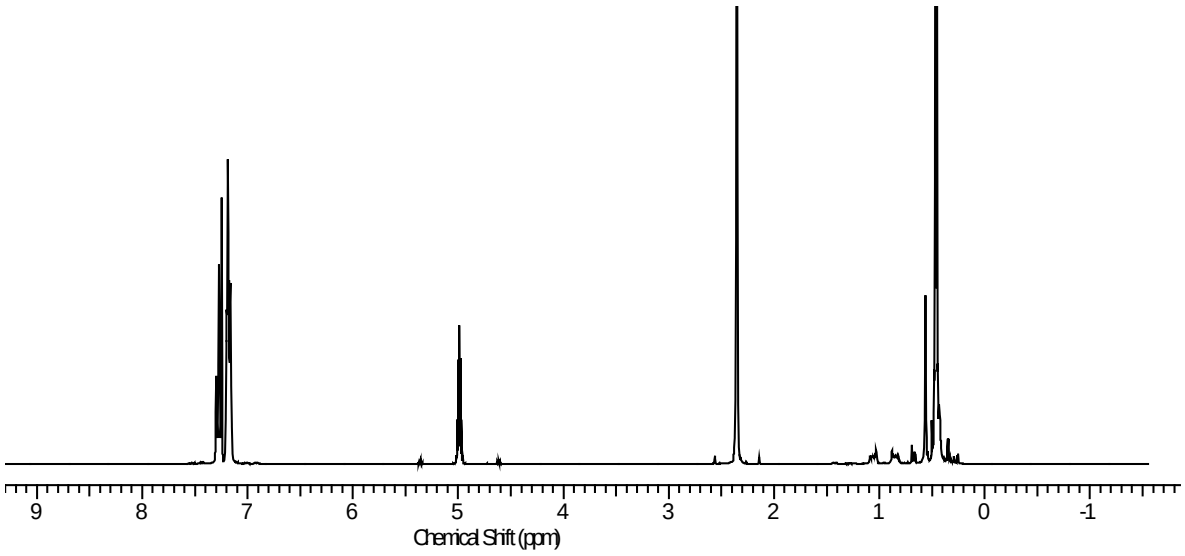

Figure S1 *^{1}H NMR spectrum of poly(dimethylchlorosilylethyl)methylsiloxane*

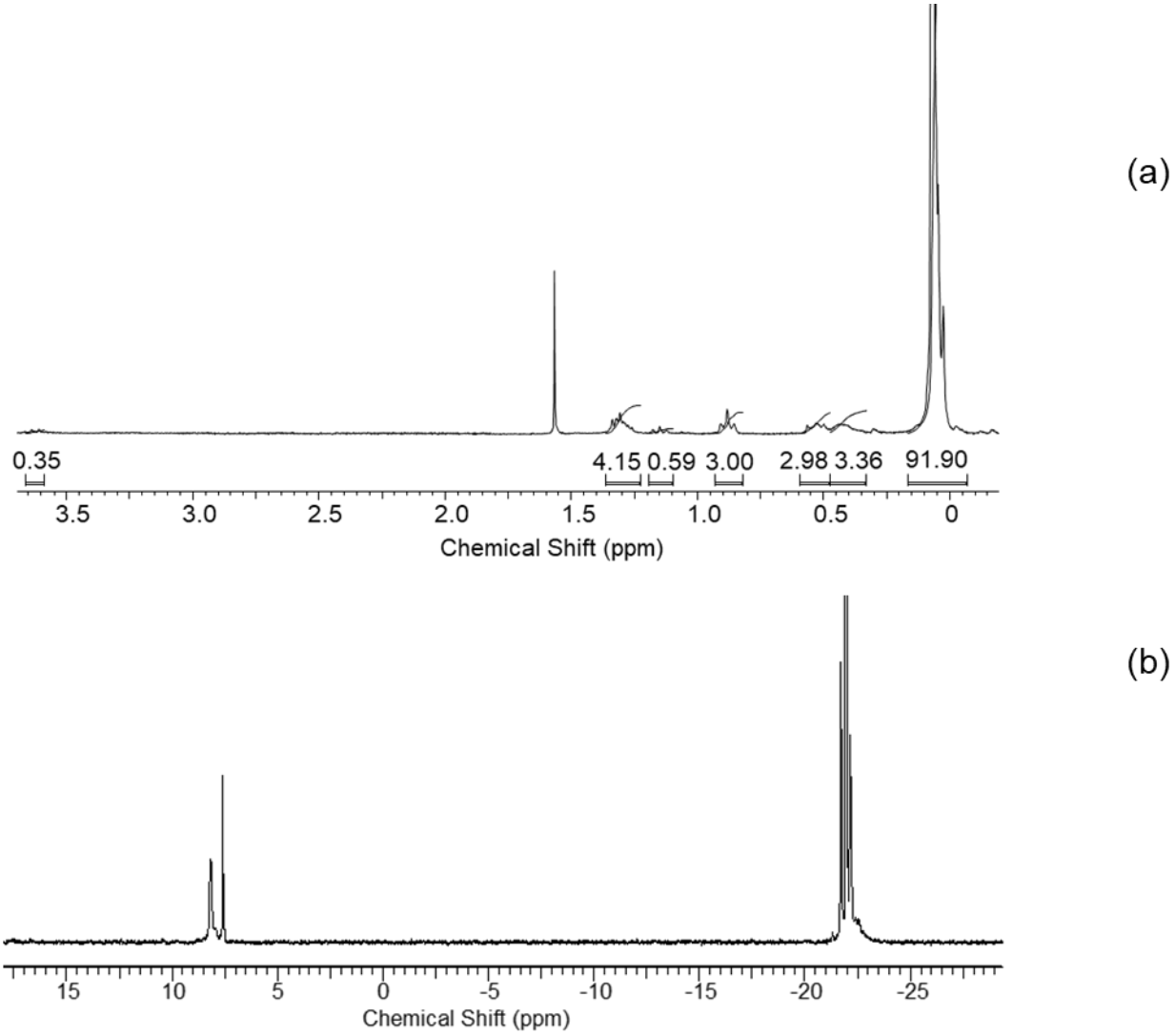

Figure S2 *(a) ^{1}H NMR and (b) ^{29}Si NMR spectra of comb-like polydimethylsiloxane*