Electronic Supplementary Information for Chemical Communications

Room-Temperature One-Step Immobilization of Rod-like Helical Polymer onto Hydrophilic Substrates

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Synthesis of monomer and polymer

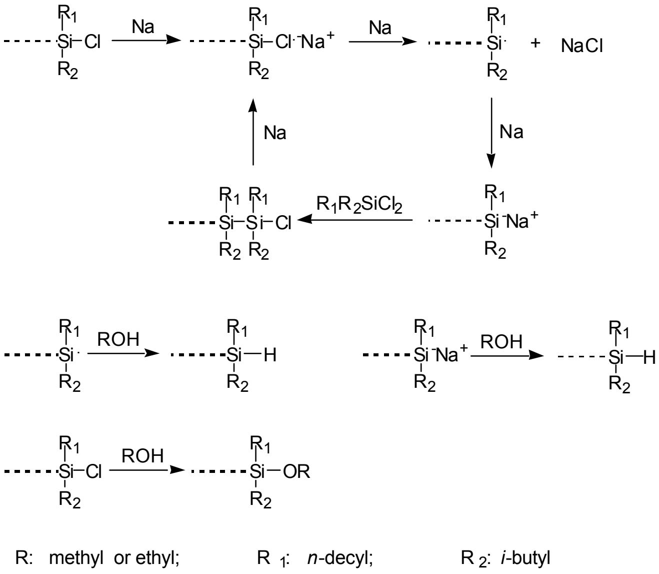
1. Synthesis of n-decyl-i-butyldichlorosilane

Magnesium turning (7.20 g, 0.30 mol) was placed to a 500 mL four-necked round flask equipped with a mechanical stir bar, a 50 mL dropping funnel, and a reflux condenser. After the flask was evacuated and charged with dry nitrogen gas for three times, 100 mL of THF and a small amount of 1,2-dibromoethane were added to the flask. After the solution was heated to reflux, 55.30 g (0.25 mol) of *n*-decyl bromide was then added dropwise under stirring over about 1 h. When the addition was complete, the reaction mixture was refluxed under stirring for further 1 h. The Grignard reagent solution obtained was then transferred to a 200 mL dropping funnel.

To another 500 mL four-necked round flask, 100 mL of anhydrous diethyl ether and 47.90 g (0.25 mol) *i*-butyltrichlorosilane were added. The freshly prepared Grignard reagent solution was added dropwise to the flask under stirring over about 1 h at room temperature. Then the reaction mixture was refluxed for 2 h. The resulting salt suspension was cooled, and the salts were removed by filtration. After the filtrate was concentrated to about 30 mL by a reduced pressure, anhydrous hexane was added to precipitate any remaining magnesium and inorganic salts in solution, and the mixture was quickly filtered under nitrogen gas to afford a clear, light brown solution. After hexane was removed by reduced pressure, a crude product was purified by a vacuum distillation. A colorless liquid was obtained. Bp: 135-138 °C / 5 mm Hg. Yield: 32.12 g (43.41%). ^{29}Si NMR ($CDCl_3$, ppm): 32.92. ^{13}C-NMR ($CDCl_3$, ppm): 14.15, 21.37, 22.49, 22.76, 24.24, 25.62, 29.22, 29.42, 29.55, 29.69, 30.47, 32.00, 32.59.

2. Synthesis of poly(n-decyl-i-butylsilane (PDBS)

A mixture of 20 mL of dry toluene, 1.53 g (66.52 mmol) of sodium, and 0.09 g (0.34 mmol) of 18-crown-6 was heated to 110 °C under nitrogen atmosphere. *n*-Decyl-*i*-butyldichlorosilane (5.00 g, 16.83 mmol) was added dropwise to the mixture under stirring for 10 min. The mixture was slowly stirred at 110 °C for 2 h. Approximately 300 mL of dry toluene was then added to reduce the solution viscosity, while continuous stirring for further 30 min. To remove inorganic salts and the residual sodium, the hot reaction mixture was processed under pressured filtration with 2.0 µm –pore size PTFE filter. To the clear filtrate, isopropanol, ethanol and/or methanol as precipitating solvents were carefully added. The white precipitates were collected by centrifugation (3000 rpm) and dried in a vacuum at 80 °C overnight. Two fractions with different M_w were used in the immobilization reactions. For the ultrahigh-M_w fraction, M_w=2.37×10^6, M_w/M_n=1.76, yield: 12.4%; for the lower-M_w (relative to the ultrahigh M_w fraction) fraction, M_w =7.86×10^5, M_w / M_n =2.12, yield: 5.8%. A very low-M_w fraction was used in the FT-IR measurement for the identification of the termini of PDBS. For this fraction, M_w=6500, M_w/M_n =1.16 Yield: 3.7%. ^{29}Si NMR ($CDCl_3$, ppm): -22.82. ^{13}C-NMR ($CDCl_3$, ppm): 14.09, 22.73, 29.47, 29.89, 32.01, 34.46.



Scheme 1. A proposed mechanism for the formation of Si-H and/or Si-OR end groups in the Wurtz-type polysilane synthesis and the subsequent precipitating process of polysilane with ethanol or methanol.

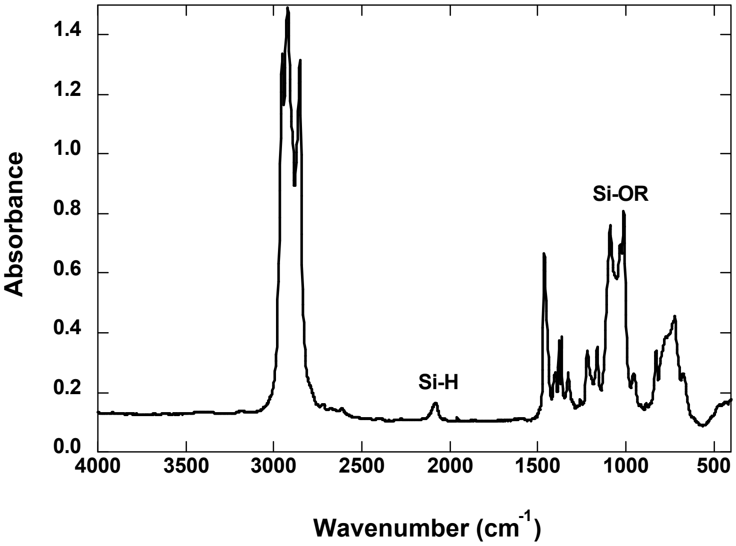


Figure 1. FT-IR absorption spectrum of PDBS (M_w=6500, M_w/M_n= 1.16) (resolution: 4 cm^{-1}, thin film onto KBr casting from isooctane solution).

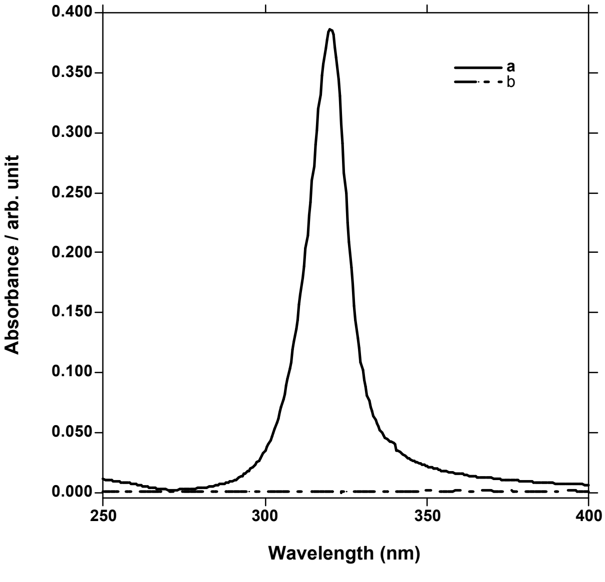


Figure 2 UV spectra of (a) spin-coated PDBS (M_w = 7.86×10^5, M_w/M_n = 2.12) on quartz from 0.01 M PDBS in *iso*-octane solution; (b) after washing of the sample with good solvent, *n*-hexane, exactly in the same way as

used for grafted samples.

The results indicate that adsorbed PDBS chains could be completely removed in the way described in the text.

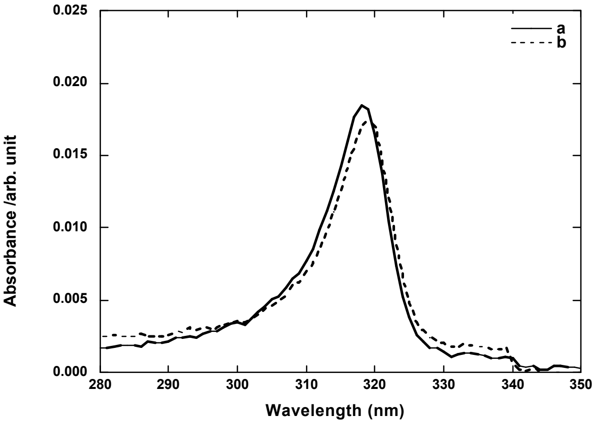


Figure 3. UV spectra of end-grafted PDBS (a) after repeatedly rinsed and immersed in *n*-hexane in the way described in the main text; (b) the same sample which was used in Fig. 3a was then immersed in fresh *n*-hexane for overnight and washed with the good solvent.

The intensity of UV absorbance in Figure 3b is a little smaller than that in 3b. This little difference may result from degradation of end-grafted PDBS in UV measurement, which resulted in decrease in absorption intensity, because polysilanes are sensitive to light.