

EXPERIMENTAL

1. Thin films preparation

Solvents and reagents

Both precursors methyl-diethoxysilane $\text{HSi}(\text{CH}_3)(\text{OCH}_2\text{CH}_3)_2$ (DH) and triethoxysilane $\text{HSi}(\text{OCH}_2\text{CH}_3)_3$ (TH) were purchased from ABCR (Karlsruhe, Germany) and used as received. Water used for cleaning the substrates was obtained from a Milli-Q water purification apparatus (Millipore). Absolute ethanol for sol-gel synthesis was of synthesis grade purity. The catalyst trifluoromethanesulfonic acid $\text{CF}_3\text{SO}_3\text{H}$ (Aldrich) was dissolved in absolute ethanol (1 M). Toluene used for thin film hydrosilylation was distilled before use. The platinum-divinyltetramethyldisiloxane complex in xylene (PC072) (platinum concentration *ca.* 0.1 M assuming 2.4% Pt in xylene), also known as Karstedt's catalyst, was purchased from ABCR.

Substrate Cleaning and Activation

Silicon wafers Si(100) or microscope glass slides cut into rectangular square strips of $2 \times 2 \text{ cm}^2$ were used as substrates. To bond covalently the PMHS thin films to native oxide silica wafers (thickness $\sim 2 \text{ nm}$), or to silica glass slides, the substrates were first cleaned and activated using the previously described procedure.¹ The substrates were placed for 30 min in a hot (90°C) $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (70/30 v/v) solution ("piranha" solution) and then allowed to cool to room temperature. *Caution! Piranha solution should be handled with extreme care.* The clean substrates were then rinsed thoroughly with high-purity water, dried in a stream of dinitrogen and heated at 110°C in an oven for 20 min.

Synthesis of 5% Crosslinked PMHS

PMHS thin films of 5% crosslinking density were prepared by room temperature sol-gel polymerization of DH/TH 95:5 (mol %) sol mixtures deposited by spin-coating on freshly activated substrates using the previously described procedure^{2,3} which is summarized as

follows. Trifluoromethanesulfonic acid $\text{CF}_3\text{SO}_3\text{H}$ (1M in absolute ethanol) was used as sol-gel catalyst (0.5 mmol/mol of monomers). The mixture of monomers DH/TH was polymerized at *ca.* 4 M concentration in EtOH (molar ratio $[\text{EtOH}]/[\text{Si}] = 1$), with 0.5 equiv. water (hydrolysis ratio $h = [\text{H}_2\text{O}]/[\text{SiOEt}] = 0.5$). The resulting clear sol was allowed to age for 30 minutes with magnetic stirring before deposition by spin-coating. Subsequently, a fully crosslinked film was obtained by spin-coating the mixture under dinitrogen at 4000 rpm (spin acceleration 2000 rpm/s) the time of rotation being 30 s. The substrates with PMHS thin films were then cured at 100 °C in an oven for 10 min. The thickness of the PMHS film was about 1 μm as measured by infrared spectroscopy (see below).²

2. Synthesis of 1-allyl-1-methyl-2,3,4,5-tetraphenylsilole (1)

Solvent, reagent and analytical methods

All the reagents were purchased from Acros. Tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately before use. The ^1H , ^{13}C and ^{29}Si NMR spectra were obtained on a Bruker Advance 200 DPX spectrometer, the FT-IR spectra on a Thermo Nicolet Avatar 320 spectrometer, the UV-visible absorption spectra on a Secomam Anthelie spectrometer and the mass spectra were determined on a Waters Q-tof instrument. Elemental analyses were determined with a ThermoFinnigan Flash EA 1112 apparatus. Photoluminescence (PL) studies were made with a SPEX Fluorolog 1681 0.22 m spectrometer.

1-allyl-1-methyl-2,3,4,5-tetraphenylsilole (1)

Under dry argon, freshly cut lithium (177 mg, 25.3 mmol) shavings were added to a solution of diphenylacetylene (5 g, 28.0 mmol) in THF (25 cm^3). The mixture was stirred for 12 h at room temperature and the resulting THF solution of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene was added dropwise to a solution of allylmethyldichlorosilane (1.55 cm^3 , 10.7 mmol) in THF (120 cm^3). The mixture was stirred for 2 h at room temperature and refluxed for 5 h. After

being allowed to cool to room temperature, the mixture was filtered and the crude product was purified on a silica gel column using pentane/dichloromethane (8:2 by volume) as eluent. Product **1** (2.6 g) was isolated in 55% yield (based on allylmethyltrichlorosilane) as a yellow-white solid: mp 120-121 °C. ¹H-NMR (200MHz, CDCl₃) δ [ppm] 7.07 (m, 6H), 6.95 (m, 10H), 6.79 (m, 4H), 5.72 (m, 1H), 4.85 (m, 2H, *J* = 8 Hz, *J* = 17 Hz), 1.99 (d, 2H, *J* = 8 Hz, SiCH₂), 0.55 (s, 3H, SiCH₃); ¹³C-NMR (200MHz, CDCl₃) δ [ppm] 155.5, 140.7, 140.2, 139.2, 133.6, 130.5, 129.5, 128.4, 127.9, 126.7, 126.0, 114.5, 21.3, -5.4; ²⁹Si NMR (200MHz, CDCl₃) δ [ppm] 7.0; IR (KBr), $\bar{\nu}$ (cm⁻¹): 3047, 2872, 1621, 698. UV (CH₂Cl₂) λ_{max} 365 nm; ε_{max} 5394 dm³ mol⁻¹ cm⁻¹. m/z 441 [(M+1)]. Anal. Calcd for C₃₂H₂₈Si: 87.22 %C, 6.51 %H; found: 87.33 %C, 6.51 %H.

3. Hydrosilylation with the silole compound

In a typical preparation, two samples grafted with a PMHS thin film (~1 μm) were placed in the presence of air in a 10 mM solution of the silole **1** (24 mg; 0.055 mmol) and Karstedt's catalyst (4 μL) in toluene (25 cm³). After the reaction mixture had been stirred for 18h at 60°C, the samples were removed, rinsed with toluene (twice) and chloroform (once) to remove any physisorbed material, and dried under a stream of dinitrogen.

4. Characterization of PMHS Thin Films

Infrared spectra of the PMHS layer were recorded on a Nexus FTIR spectrometer with the use of unmodified silicon wafer substrates as the background in the 400–4000 cm⁻¹ range. The thickness (*e*) of the virgin PMHS thin films deposited on the glass or wafer substrate by spin-coating was measured by infrared spectroscopy from the absorbance of the Si–H peaks at *ca.* 2167 cm⁻¹: $A_{2167} = \alpha_{SiH} e$ where α_{SiH} (0.27 μm⁻¹) is the calibrated absorption coefficient.² A mean thickness of 1.23 ± 0.05 μm was found for 4 spin-coated samples.

To quantify the *SiH* conversion after hydrosilylation of the PMHS thin films, the disappearance of the strong Si–H stretching bands $\nu(\text{SiH})$ of both DH and TH subunits was studied by measuring the total integrated absorbances in the 2100–2300 cm^{-1} region of the reacted and unreacted samples. The SiH residual percentage (% *SiH*) of *ca.* 15-17 % is calculated by dividing the integrated absorbance of the reacted samples with that measured before reaction (same sample).

Following PMHS hydrosilylation with the silole compound **1**, the percentage of PMHS functionalization (% *SiC*) of *ca.* 7-8 % can be measured with good sensitivity from the strong absorption of the methylene group, $\nu_{\text{as}}(\text{CH}_2)$ antisymmetric stretching, in the 2935–2915 cm^{-1} region for alkanes.⁴ For this calculation, the $\nu_{\text{as}}(\text{CH}_2)$ absorption was previously calibrated for alkyl-functionalized PMHS thin films ($\sim 1 \mu\text{m}$) prepared by hydrosilylation with 1-alkenes $\text{CH}_2=\text{CH}(\text{CH}_2)_{n-2}\text{CH}_3$ of various lengths ($n = 5$ to 17).^{2,3} Following reaction of the SiH groups, the normalized absorbance ratio $A_{\text{CH}_2}/A_{\text{SiH}}$ increases with the number of methylene groups (n) in the hydrocarbon chain $\text{Si}(\text{CH}_2)_n\text{CH}_3$ as follows:

$$\frac{A_{\text{CH}_2}}{A_{\text{SiH}}} = 0.284n \times \text{SiC}$$

where *SiC* = 100% for complete addition of the alkene molecules to the SiH bonds as well as for the functionalization of the PMHS network with short alkyl sides chains.

In the case of the silole functionalized PMHS, the above equations were applied assuming the number of methylene groups is $n = 3$; A_{CH_2} of the reacted silole samples was measured from the peak at *ca.* 2922 cm^{-1} ; A_{SiH} was measured before the hydrosilylation reaction at *ca.* 2167 in the corresponding unreacted samples (virgin PMHS).

References

1. T. Thami, B. Bresson and C. Fretigny, *J. Appl. Polym. Sci.*, 2007, **104**, 1504-1516.

2. T. Thami, G. Nasr, H. Bestal, A. V. D. Lee and B. Bresson, *Journal of Polymer Science Part A: Polymer Chemistry*, 2008, **46**, 3546-3562.
3. G. Nasr, H. Bestal, M. Barboiu, B. Bresson and T. Thami, *J. Appl. Polym. Sci.*, 2009, **111**, 2785-2797.
4. D. Lin-Vien, N. B. Colthup, W. G. Fateley and J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, Boston, 1991.