

Supramolecular Self-Assembly of Linear Oligosilsesquioxanes on Mica – AFM Surface Imaging and Hydrophilicity Studies

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Supporting Information

General Information

Materials: Triethoxyvinylsilane (Aldrich, 97%), hexamethyldisilazane (Fluka Analytical, $\geq 98\%$, GC), potassium hydroxide (Aldrich, ACS reagent, ≥ 85 , pellets), acetic acid (Aldrich, $\geq 99\%$, ReagentPlus®), magnesium sulphate (VI) MgSO_4 (Chempur, pure)] DMPA (Acros Organics, 99%), thioglycolic acid (Fisher Scientific, pure p.a.) were used as received. Solvents [ethyl acetate (Chempur, pure p.a.), hexane (Aldrich, Chromasolv® for HPLC, $\geq 97\%$, GC), n-pentane (Chempur, pure p.a), tetrahydrofuran (THF) (Chempur, pure p.a.), dichloromethane (Chempur, pure p.a.), methanol (Chempur, pure p.a.)], dioxane (Chempur, pure p.a.), toluene (Chempur, pure p.a.) were purified according to the literature procedures¹.

Muscovite mica (V-1 grade) was bought from SPI Supplies / Structure Probe, Inc. and freshly cleaved before use by removing the top layer with an adhesive tape. Glass slides coated with APTES were purchased from Aldrich (Silane-Prep Slides) and used as received, glass plates (deckgläser 100) were bought from Thermo Scientific (Menzel Gläser) and cleaned by sonication (in H_2O , MeOH and then in CH_2Cl_2) followed by blow dry in N_2 . Polished prime silicon wafers [type n, arsenic doped, orientation (100)] were obtained from Cemat Silicon S.A, cut into rectangular pieces and cleaned by MeOH clean, followed by deionised water (DI) rinse, a short immersion (30 s) in concentrated HF_{aq} , and then thoroughly washed with DI and dried in N_2 stream.

Analytic methods: Liquid state NMR (^1H , ^{13}C and ^{29}Si NMR) spectra for the precursors and condensed soluble materials were recorded in CDCl_3 , THF-d_8 or CD_3OD as a solvent on a Bruker DRX-500 MHz spectrometer, with TMS as the reference. Mass spectrometric measurements (MALDI-TOF) were performed for LPSQ-Vi using a Voyager-Elite (PerSeptive Biosystems, USA) time-of-flight instrument equipped with a pulsed N_2 laser (337 nm, 4-ns pulse width) and time-delayed extraction ion source. An accelerating voltage of 20 kV was applied. Mass spectra were recorded in the linear positive ion mode using 1,8-dihydroxy-9-anthracenone (ditranol, DT) as the matrix and LiCl as the cationization agent. Size exclusion chromatography (SEC) was performed for LPSQ-Vi using Agilent 1100 series chromatograph composed of degasser, pump, and autosampler. Two PL Gel 5 μm MIXED-C columns (7.8 x 300 mm) were used in a series (temp. 27 °C). RI (OPTILAB T-rex, Wyatt) and MALLS (DAWN HEOS, II, Wyatt, $\lambda = 682$ nm) were used as detectors. Dichloromethane was used as a mobile phase at the flow rate of 0.8 mL/min. Molecular masses were derived from a calibration curve based on polystyrene standards.

Phase transitions of polymers were studied by differential scanning calorimetry (DSC) technique (DuPont 2000 thermal analysis system). Thermograms were taken for samples (sealed in aluminium pans) quenched rapidly from the melt (room temperature) and then heated at the rate of 10 °C/min from -100 °C to 100 °C. The sample was kept at 100 °C for 3 min to destroy any thermal history. Subsequently, it was quenched to -100 °C and heated again at 10 °C/min to 100 °C.

Thermogravimetric measurements were performed using a Hi-Res TGA 2950 Thermogravimetric Analyzer (TA Instruments) in nitrogen atmosphere (heating rate 10 °C /min, resolution 3, sensitivity 3).

Dynamic Light Scattering measurements were carried at 25°C out using Nano-ZS Malvern Zetasizer. Solutions were placed in tightly covered quartz cuvettes. NOTE: DLS measurements did not give precise information about the size of objects present in solutions of LPSQ-COOH (in pure solvents and their mixtures). The records are presented to illustrate the dynamics and the difference in behavior of LPSQ-COOH in those solutions. The solutions were clear and transparent during the time of analysis and by no means contained particles that would make the sample turbid.

Synthetic procedures:

1. *Synthesis of oligo(vinylsilsesquioxanes) (LPSQ-Vi) by in situ-polycondensation of cyclic tetravinylsiloxanetetraol* ².

Solid potassium tetravinyltetracyclosiloxanolate (10.0 g, 15.6 mmol) prepared with 76% yield according to the previously described procedure³, was slowly added to a cooled (0-5°C) solution of acetic acid (4.6 ml, 63 mmol) in ethyl acetate (420 ml). Temperature of the reaction mixture was kept below 10°C during addition of cyclosiloxanolate and for another 30 minutes, once the addition was completed. Potassium acetate was filtered off and the filtrate was left for 30 minutes to warm up to room temperature. Hexamethyldisilazane (17.0 ml, 81.5 mmol) and MgSO₄ (10 g) were then added to the reaction mixture, and it was refluxed with stirring. The progress of reaction was controlled with MALDI-TOF spectrometry. The reaction was carried out to a complete condensation of silanol groups. The reaction mixture was then cooled down, MgSO₄ was filtered off, the solution was passed through a short silica plug, and all volatile parts were removed at room temperature under high vacuum. The obtained product was a viscous, colorless liquid (3.3, Y=67.5%).

¹H NMR (CDCl₃), δ [ppm]: 0.09 (s. OSiMe₃), 5.19 (m. -CH=CH₂)

¹³C NMR (CDCl₃), δ [ppm]: 1.6 (OSiMe₃), 130.2 (=CH-), 135.9 (=CH₂)

²⁹Si NMR (CDCl₃); δ [ppm]: -81.3 (H₂C=CH-SiO_{3/2}), 10.6 (OSiMe₃)

SEC in CH₂Cl₂ (RI): Mn= 1000, Mw= 1200, PDI=1.2, (MALLS): Mn=2000, Mw=3200, PDI=1.6.

2. *Synthesis of oligo[2-(carboxymethylthio)ethylsilsesquioxanes] (LPSQ-COOH) by UV initiated thiol-ene addition of thioglycolic acid to LPSQ-Vi.*

DMPA (0.25 mmol) was added to a solution of thioglycolic acid (17.6 mmol) and LPSQ-Vi (1g, 12.6 mmol Vi groups) in dry THF (15 ml), placed in a quartz vessel. The mixture was irradiated for 30 min with UV light (350 nm). Volatiles were then removed under reduced pressure and the residue was dissolved in THF (2 ml) and precipitated into n-pentane (100 ml). The purification procedure was repeated thrice. The precipitate was dried under high vacuum at room temperature to a constant weight. A viscous polymer was obtained (1.8 g, Y =83%).

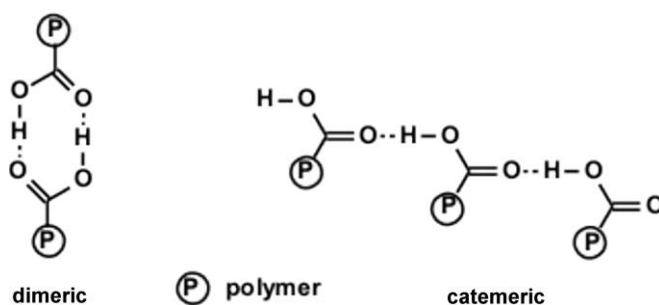
¹H NMR (THF-d₈), δ [ppm]: 0.17 (s. OSiMe₃), 1.08 (m. SiCH₂), 2.79 (CH₂S), 3.20 (m. SCH₂), 8.30 (COOH)

¹³C NMR (CD₃OD), δ [ppm]: -0.5 (OSiMe₃), 11.4 (SiCH₂), 25.3 (CH₂S), 31.6 (SCH₂), 170.9 (COOH)

²⁹Si NMR (CD₃OD); δ [ppm]: -70.4 (-CH₂-SiO_{3/2}), 10.9 (OSiMe₃)

Literature:

- 1 W. L. F. Armarego and Ch. L. L. Chai in "Purification of laboratory chemicals", 5th edition, Elsevier Science, 2003
- 2 A. Kowalewska and M. Nowacka, *Silicon*, 2014, (accepted DOI 10.1007/s12633-014-9209-z
- 3 O. I. Shchegolikhina, Yu. A. Pozdnyakova, A. A. Chetverikov, A. S. Peregudov, M. I. Buzin and E. V. Matukhina, *Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 83.



Scheme ESI-1. Cyclic dimeric and linear catemeric structures as possible binding arrangements for hydrogen bonding in LPSQ-COOH.

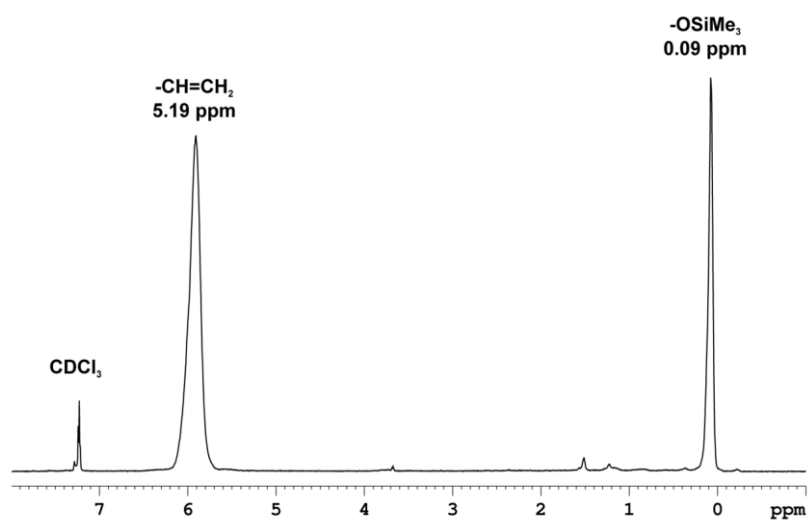


Figure ESI-1. ^1H NMR of LPSQ-Vi.

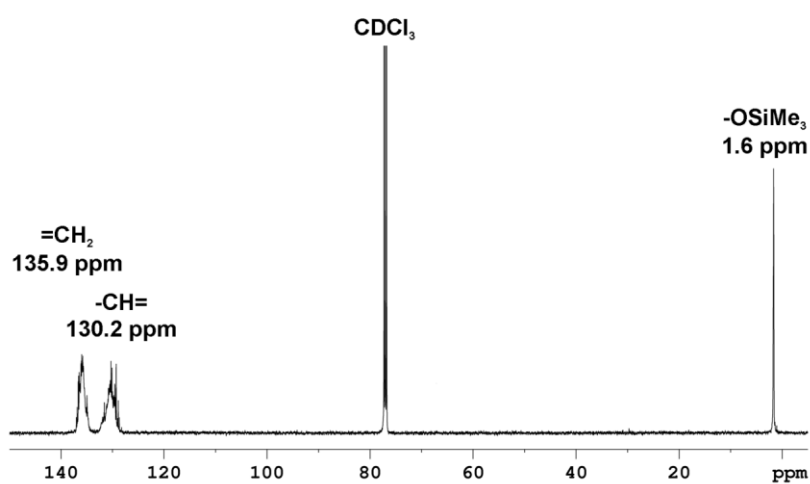


Figure ESI-2. ^{13}C NMR of LPSQ-Vi.

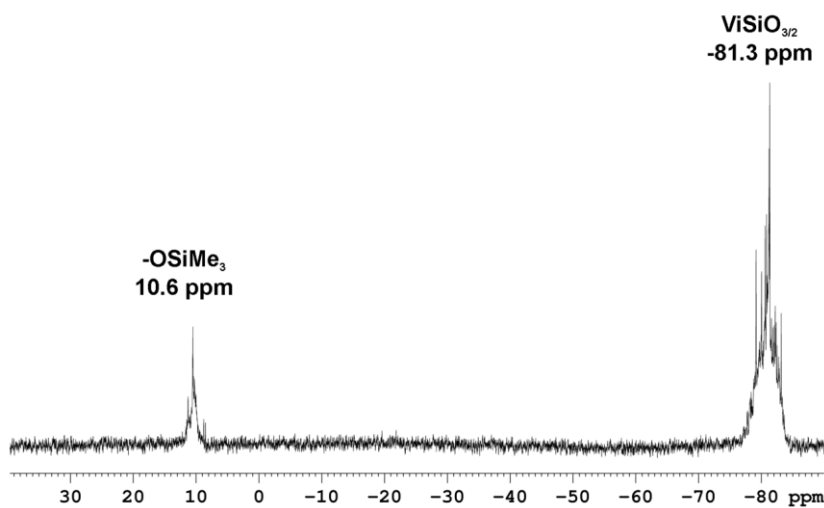


Figure ESI-3. ^{29}Si NMR of LPSQ-Vi.

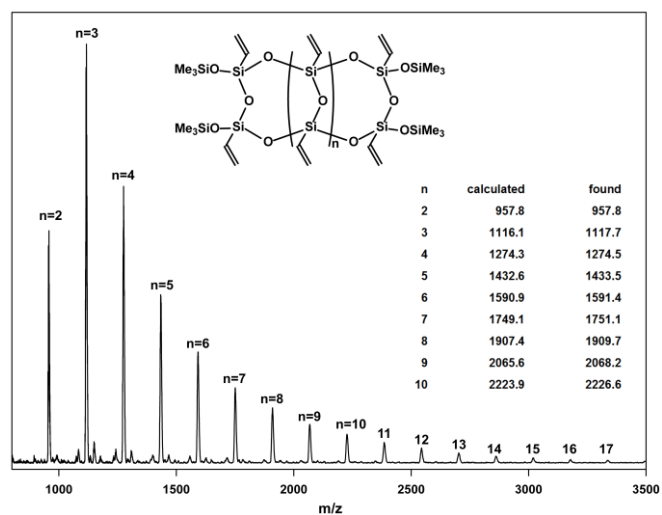


Figure ESI-4. MALDI of LPSQ-Vi (matrix: ditranol, Li^+)

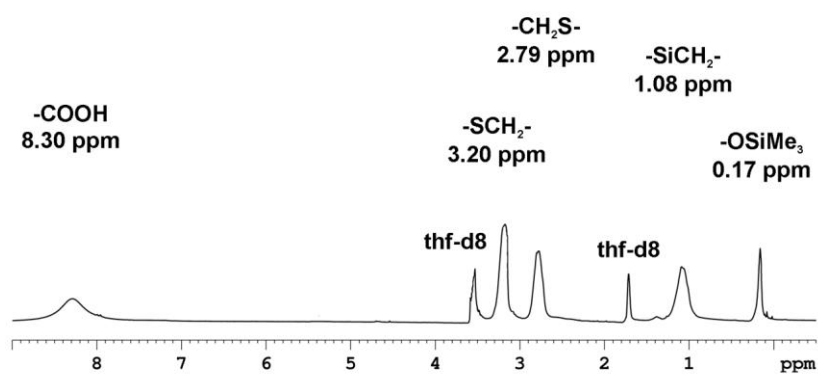


Figure ESI-5. ^1H NMR of LPSQ-COOH.

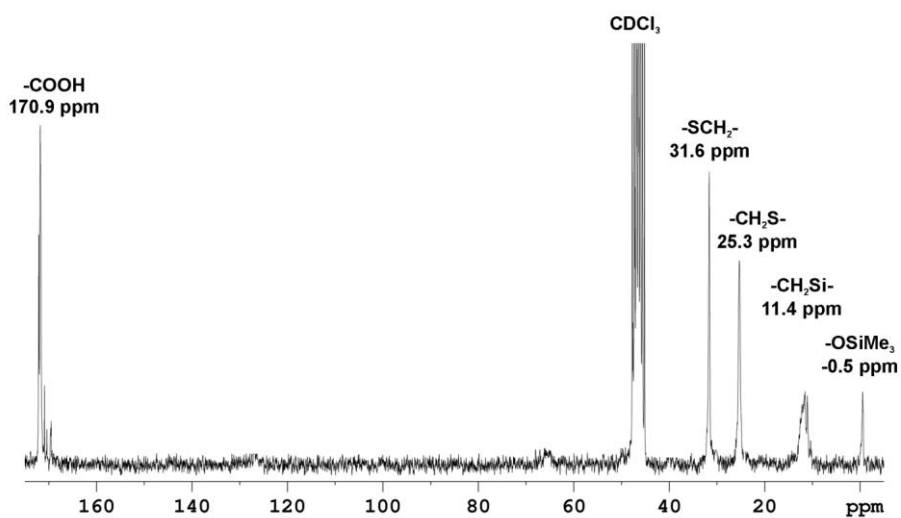


Figure ESI-6. ^{13}C NMR of LPSQ-COOH.

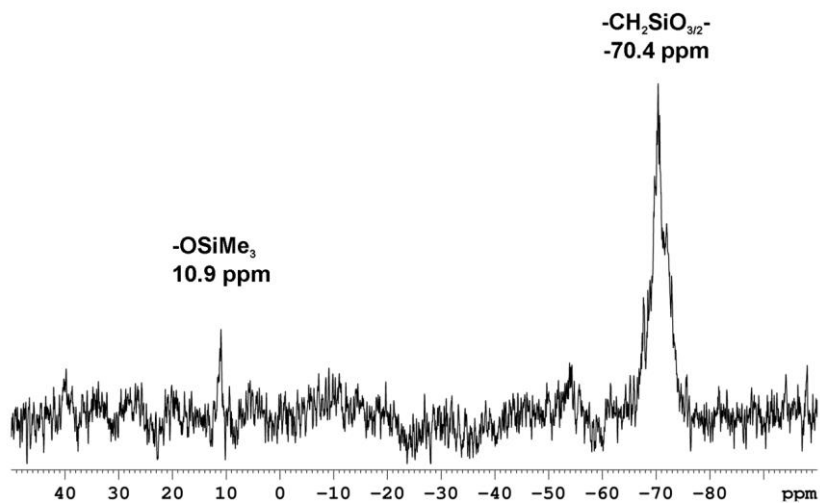


Figure ESI-7. ^{29}Si NMR of LPSQ-COOH.

Table ESI-1. Vibrational Mode Assignments of LPSQ-COOH.

Peak (cm^{-1})	assignment
3500-2700	ν OH
2600-2400	$\nu(\text{s,as})$ CH
1707	ν C=O
1421	δ OH in-plane
1409	$\delta(\text{as})$ CH_3
1286	ν C-O
1254	$\delta(\text{s})$ $\text{Si}(\text{CH}_3)_3$
1190	δ $\text{Si}(\text{CH}_2)$
1116	$\nu(\text{as})$ SiOSi
1060	$\nu(\text{s})$ SiOSi
937	ν OH out-of-plane

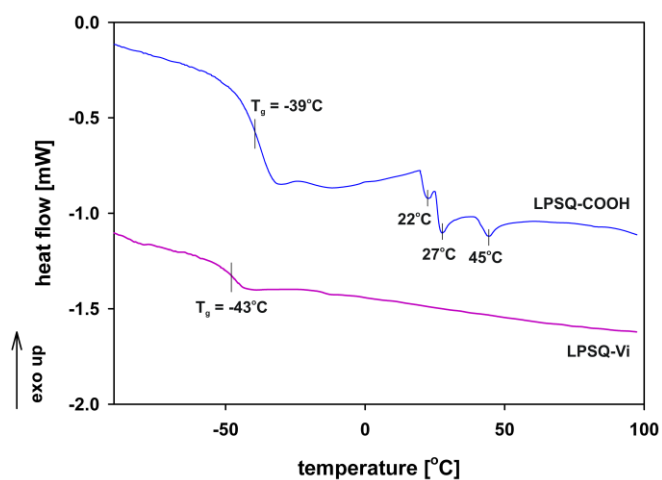


Figure ESI-8. DSC traces of LPSQ-COOH and LPSQ-Vi ($10^\circ\text{C}/\text{min}$, second run).

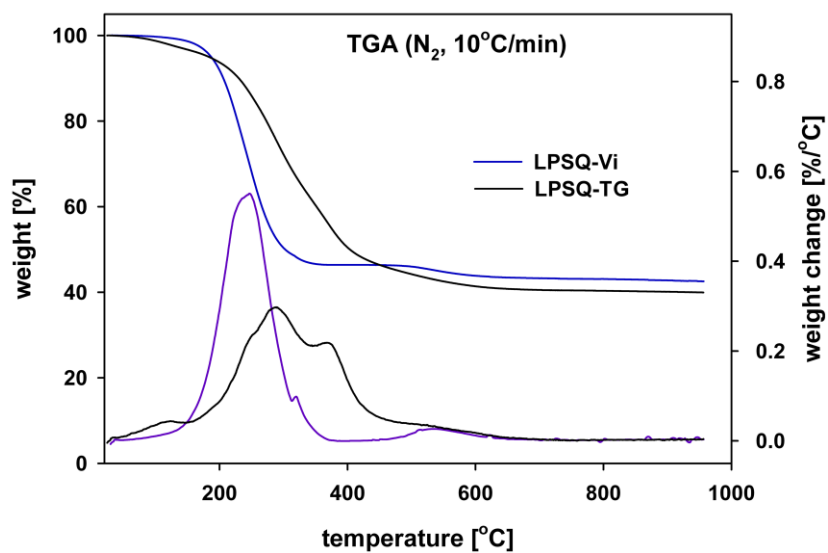


Figure ESI-9. TGA of LPSQ-Vi and LPSQ-TG (N_2 , $10^\circ\text{C}/\text{min}$).

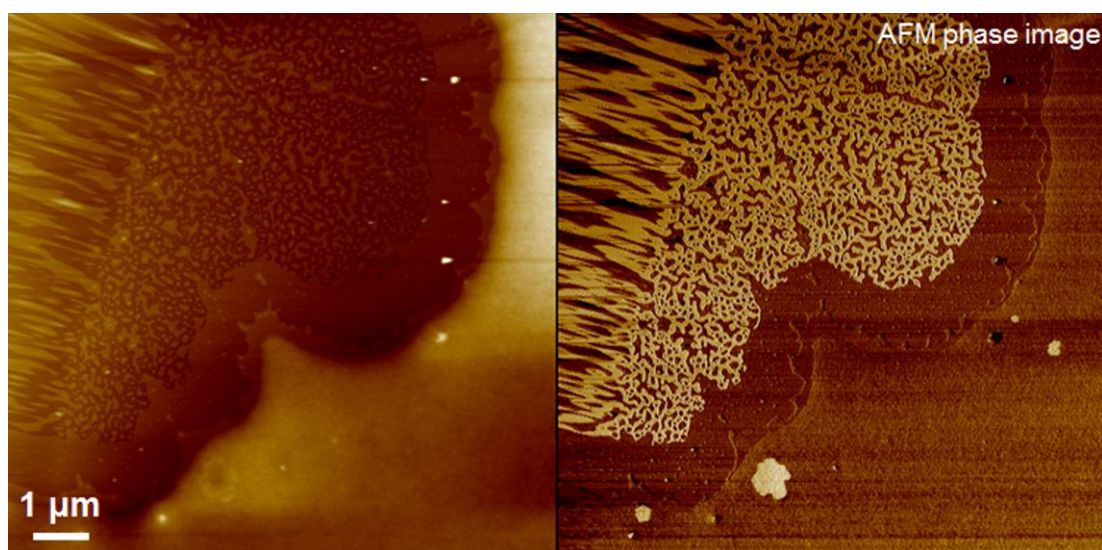


Figure ESI-10. AFM height/phase image of LPSQ-COOH dip coated from 0.045%wt solution in THF (24°C , $t_i=5$ s) onto muscovite mica (enlarged scan area).

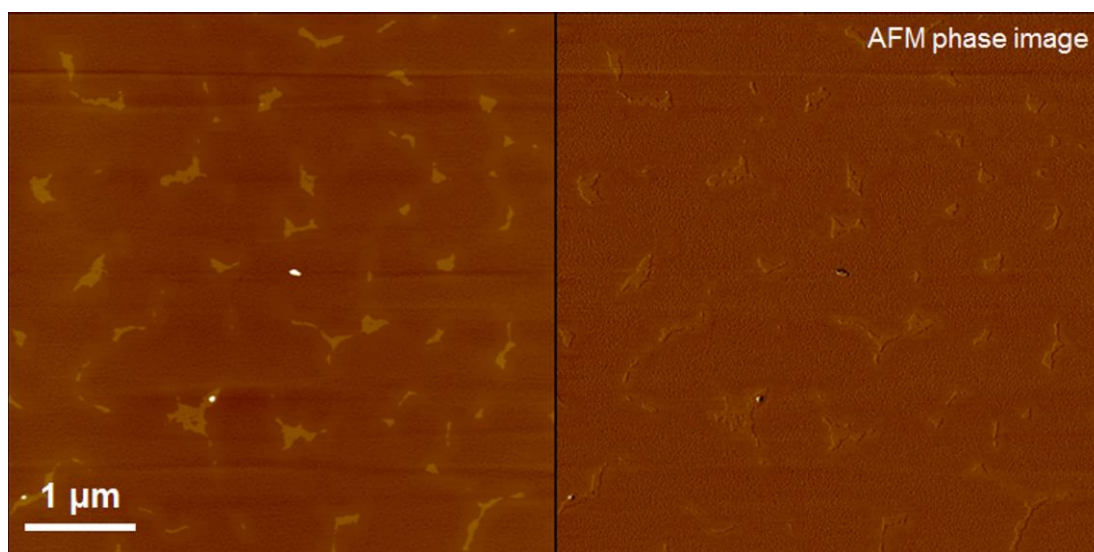


Figure ESI-11. AFM height/phase image of LPSQ-COOH film dip coated on muscovite mica (0.0022%wt in THF, $t_i=5$ s) (enlarged scan area).

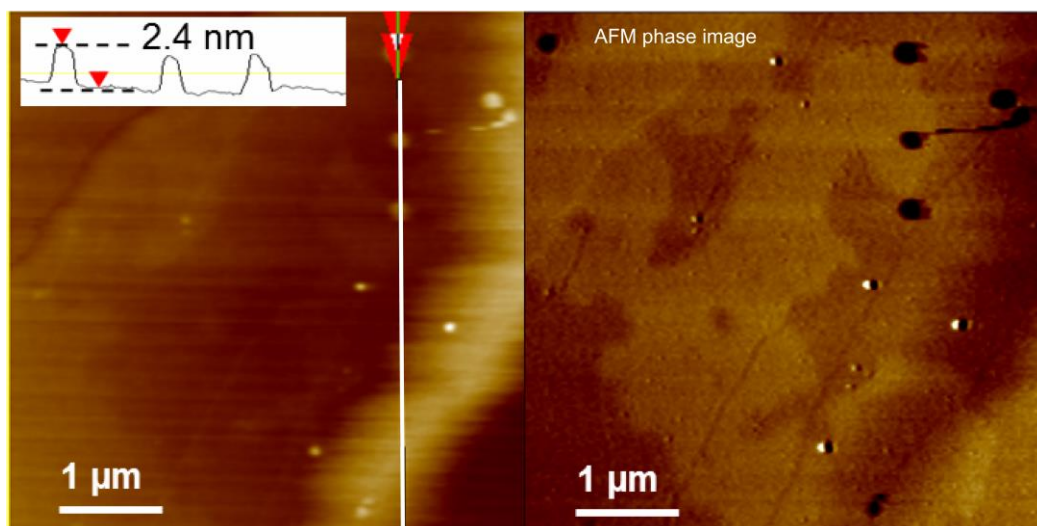


Figure ESI-12. AFM topographic height/phase image and the corresponding surface profile of LPSQ-Vi dip coated from 0.051%wt solution in THF (24°C, $t_i=5$ s) onto muscovite mica (v.d.=2.4 nm).

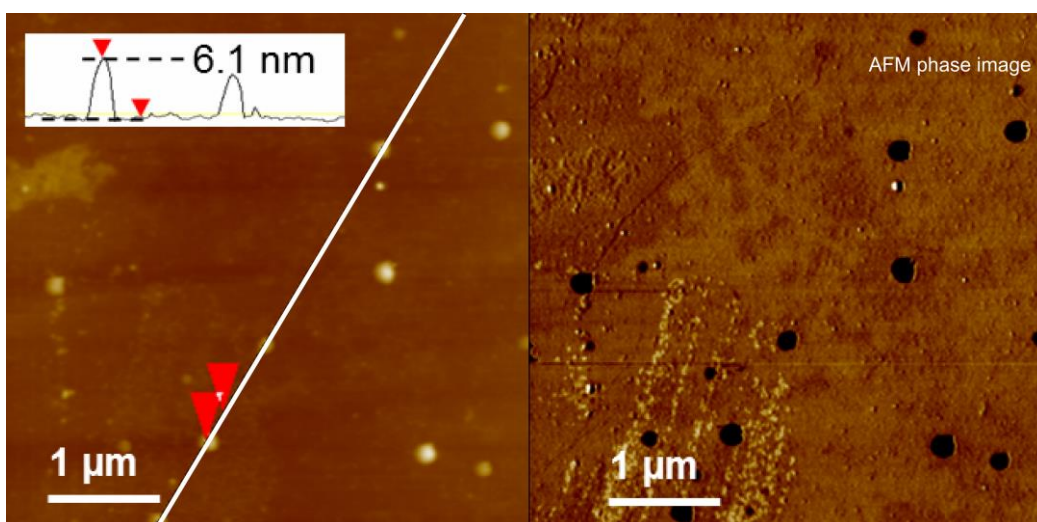


Figure ESI-13. AFM topographic height/phase image and the corresponding surface profile of LPSQ-Vi dip coated from 0.051%wt solution in THF (24°C, $t_i=30$ min) onto muscovite mica.

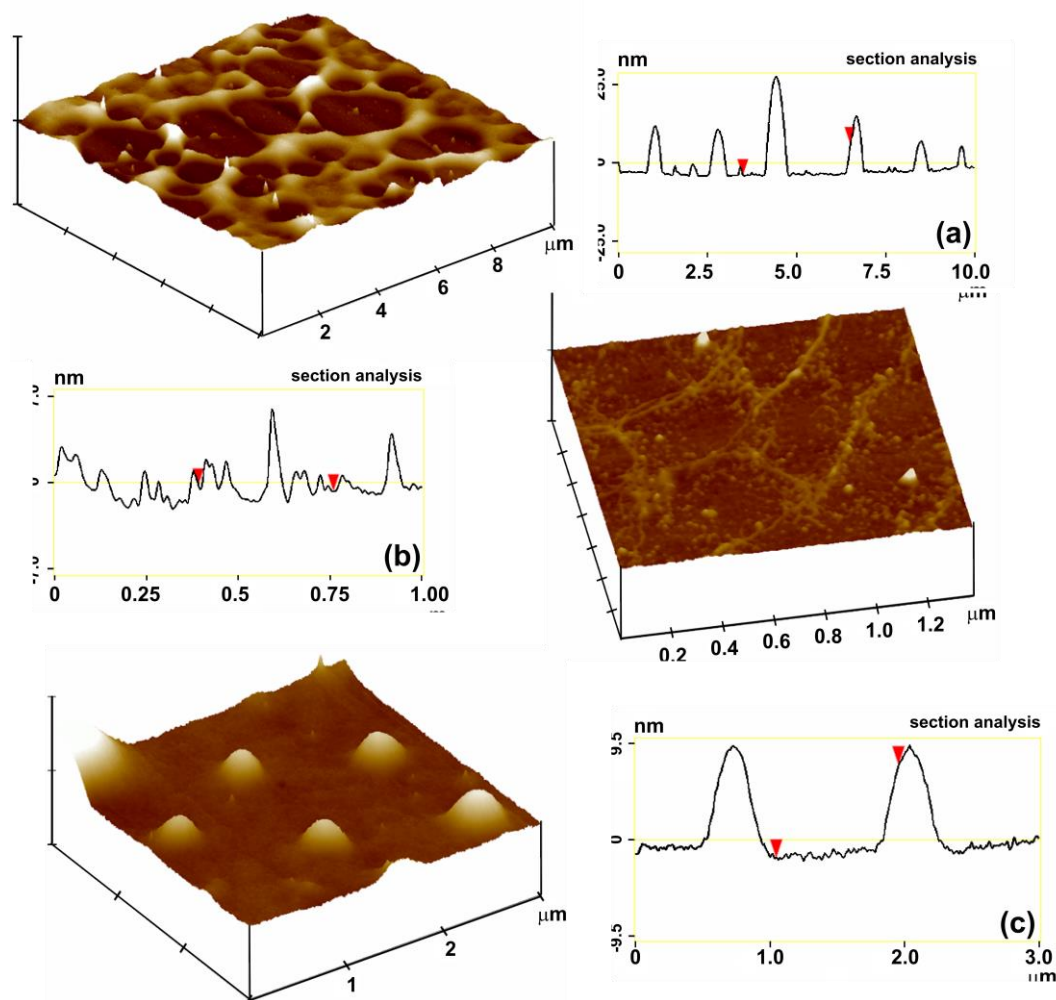


Figure ESI-14. Structure of LPSQ-COOH deposits dip-coated on a) APTES-silanized glass ($t_i=5s$), b) HF-treated silicon wafer ($t_i=5s$), c) glass ($t_i=4$ days, slow evaporation), (AFM height images and corresponding surface profiles, 0.044%wt solution in THF).

Surface coating with LPSQ-COOH – comparison of substrate material:

It was found that LPSQ-COOH does not form ordered nanolayers on bare glass or hydrophobic surfaces (HF-treated silicon and APTES silanized glass). Polymeric coatings broke into polygonal structures (Figure ESI-14) characteristic for dewetting on hydrophobic surfaces. APTES glass plates were covered with a thick layer (10-25 nm) of LPSQ-COOH riddled by cylindrical holes (Figure ESI-14a). The material seems to be partly anchored onto the surface (possibly due to formation of ionic structures – $(CH_2)_3NH_3^+COO^-$) but is not organized. The film formed on a silicon wafer is very thin and forms fine rims surrounding empty cells, contacting each other and decayed into droplets (Figure ESI-14b). The presence of such interconnected ‘cellular’ structures on a hydrophobic surface is surprising. Separate droplets, as those observed in the case of LPSQ-Vi coated on mica, should rather be formed. The chemical structure of LPSQ-COOH and formation of intermolecular hydrogen bonding can account for the durability of fine filaments. A certain affinity of LPSQ-COOH to silica can be observed on clean glass plates. Thin separated spikes of about 3 nm can be seen on the glass surface after short immersion, but on prolonged contact (4 days) and concentration increase, the spikes grow and become wider (Figure ESI-14c). At this stage the surface of glass was completely covered with the polymer.

Dynamic light scattering measurements (DLS) studies of LPSQ-COOH behaviour in solutions:

We have studied the size of objects that could possibly be found on agglomeration of LPSQ-COOH in solutions. Figure ESI-15 shows that no defined agglomerates of LPSQ-COOH can be detected in solutions in THF of different concentration. The coloured profiles correspond to each record taken during a particular measurement. The time span between measurements was 10 minutes. We have not observed any increasing or decreasing trend in the size of scattering object with time. It means that the dissolved system is dynamic and no coagulation takes place. Addition of toluene to the solution in THF did not change this trend (Figure ESI 16 A and B). The situation is different in less polar dioxane. LPSQ-COOH dissolves well in this solvent but DLS studies indicated the presence of defined objects (Figure ESI-16 F). The population is composed of small (about 10 a.u. in Figure ESI-16) and larger objects (increment of about 10x). Apparently, the polymer tends to form discrete micelles (solution is stable for 30 hours) that finally sediment with time (>48 h). Addition of toluene to the solution in dioxane did not change the general trend (Figure ESI-16 C, D, E). It can be also observed that addition of smaller amounts of toluene caused formation of smaller secondary micelles.

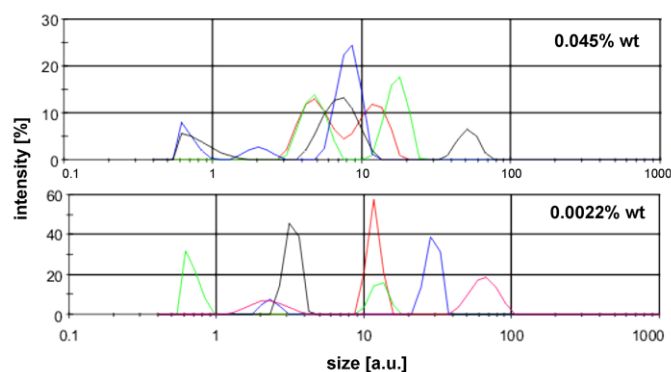


Figure ESI-15. DLS records taken for samples of LPSQ-COOH dissolved in THF at a given concentration.

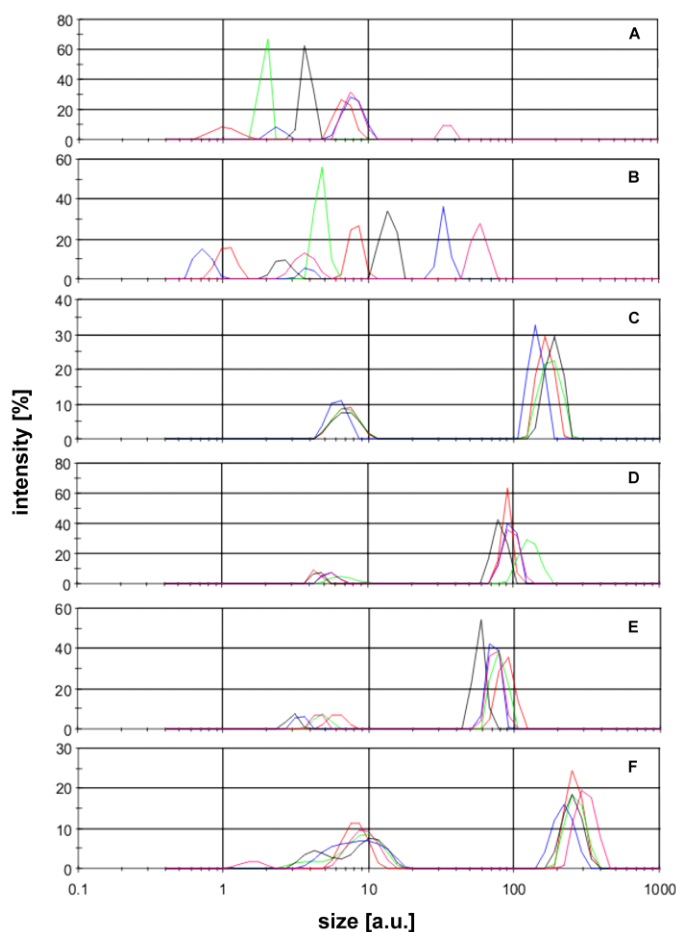


Figure ESI-16. DLS records taken for samples of LPSQ-COOH dissolved (0.06% wt) in A) THF, B) THF/toluene (2:1 v/v), C) dioxane/toluene (2:1 v/v), D) dioxane/toluene (4:1 v/v), E) dioxane/toluene (9:1 v/v), F) dioxane.

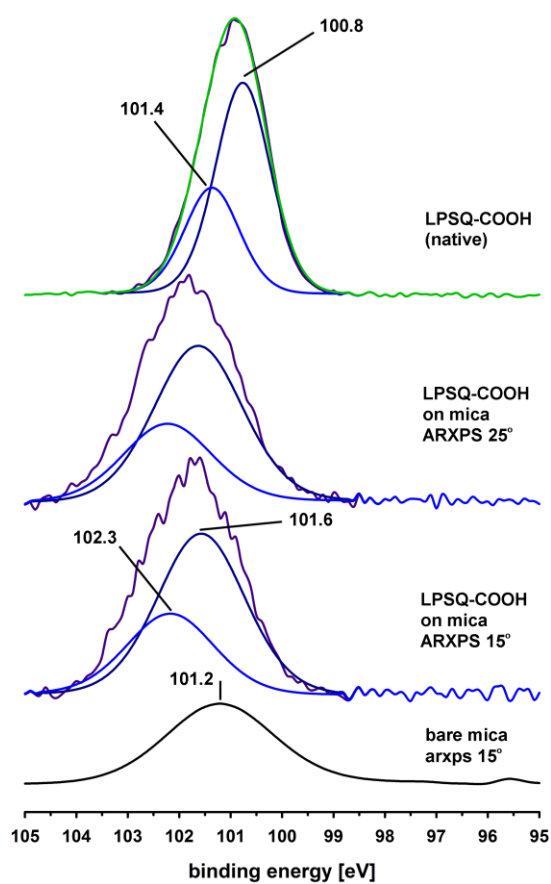


Figure ESI-17. XPS Si2p peak deconvolution in native and adsorbed LPSQ-COOH compared to air-cleaved mica.

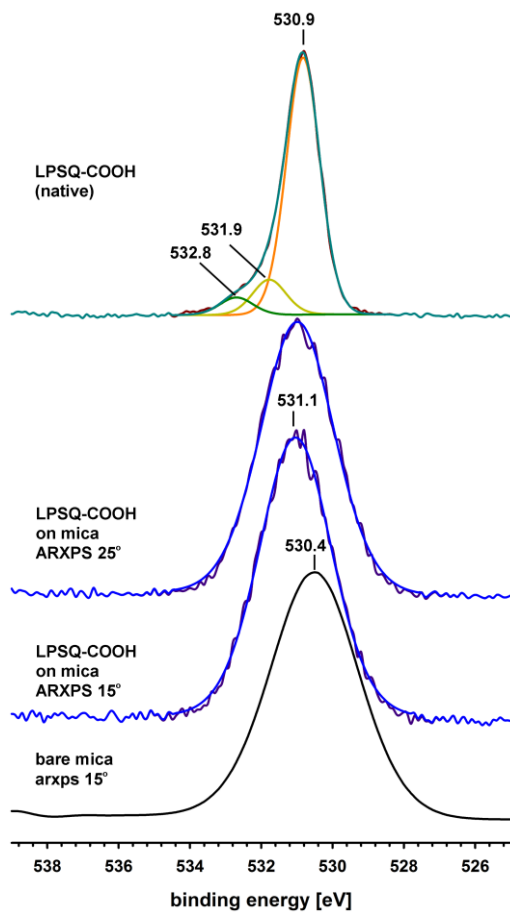


Figure ESI-18. XPS O1s peak deconvolution in native and adsorbed LPSQ-COOH compared to air-cleaved mica.

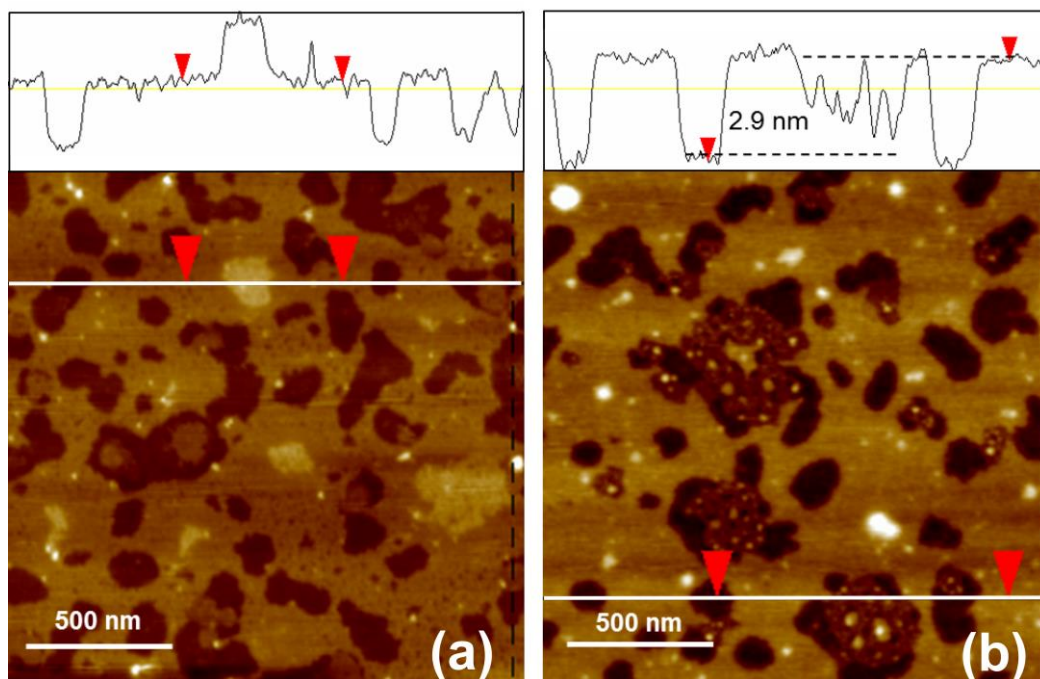


Figure ESI-19. AFM images of LPSQ-COOH spin coated from the solution in THF (0.06% wt) onto mica, and the corresponding surface roughness profiles recorded a) directly after coating b) after 2 months at room temperature.

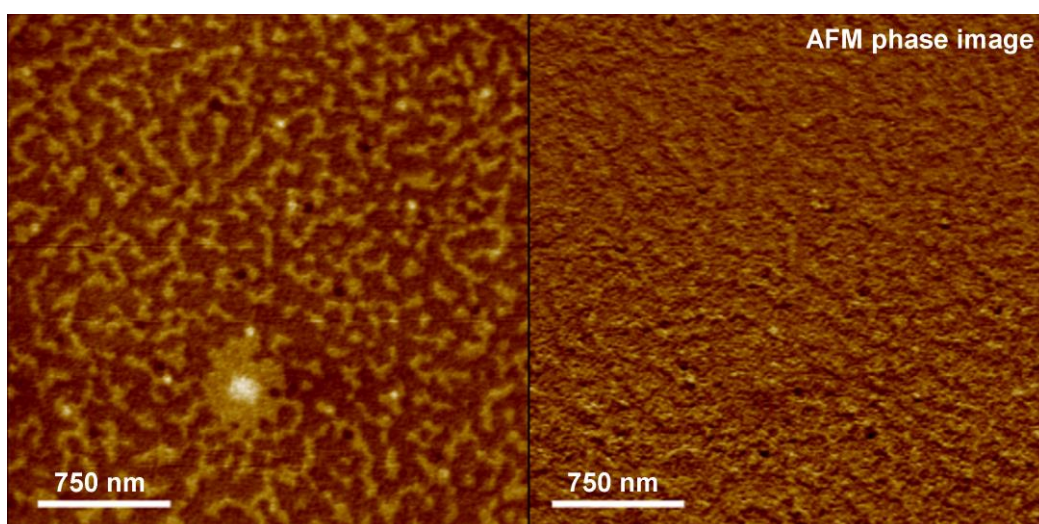


Figure ESI-20. AFM height/phase image of LPSQ-COOH spin coated from 0.06%wt solution in toluene/dioxane (1:2 v/v) (a large-scale scan).

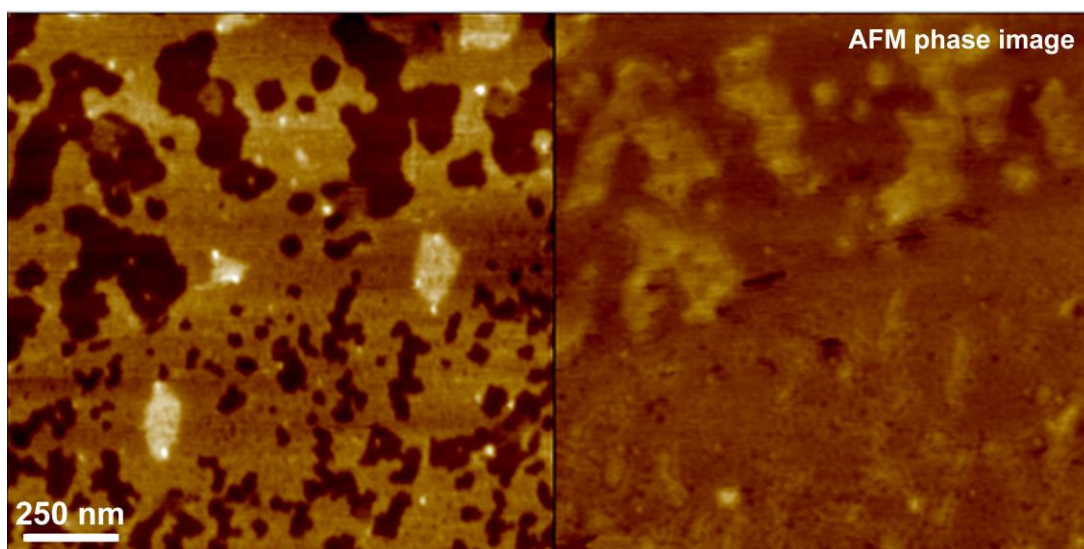


Figure ESI-21. AFM height/phase image of LPSQ-COOH spin coated from 0.06%wt solution in THF (a large-scale scan).

Table ESI-2. Contact angles of reference liquid drops on the studied surfaces.

entry	sample	method	water			glycerol		
			static	advancing	receding	static	advancing	receding
-	bare mica	-	19.2 ± 2.7	15.7 ± 0.9	14.3 ± 2.3	45.7 ± 5.8	36.2 ± 4.1	16.5 ± 3.6
I	LPSQ-Vi on mica	slit cast	106.3 ± 1.9	105.9 ± 3.4	84.8 ± 4.7	87.5 ± 1.6	89.5 ± 0.8	70.0 ± 1.4
II	LPSQ-COOH on mica	slit cast	71.7 ± 2.0	75.9 ± 2.0	37.4 ± 4.8	87.1 ± 3.4	83.8 ± 3.0	48.2 ± 3.5
III	LPSQ-COOH on mica	dip coated	18.2 ± 2.7	13.1 ± 3.8	-	61.7 ± 2.3	61.3 ± 4.1	22.4 ± 2.6

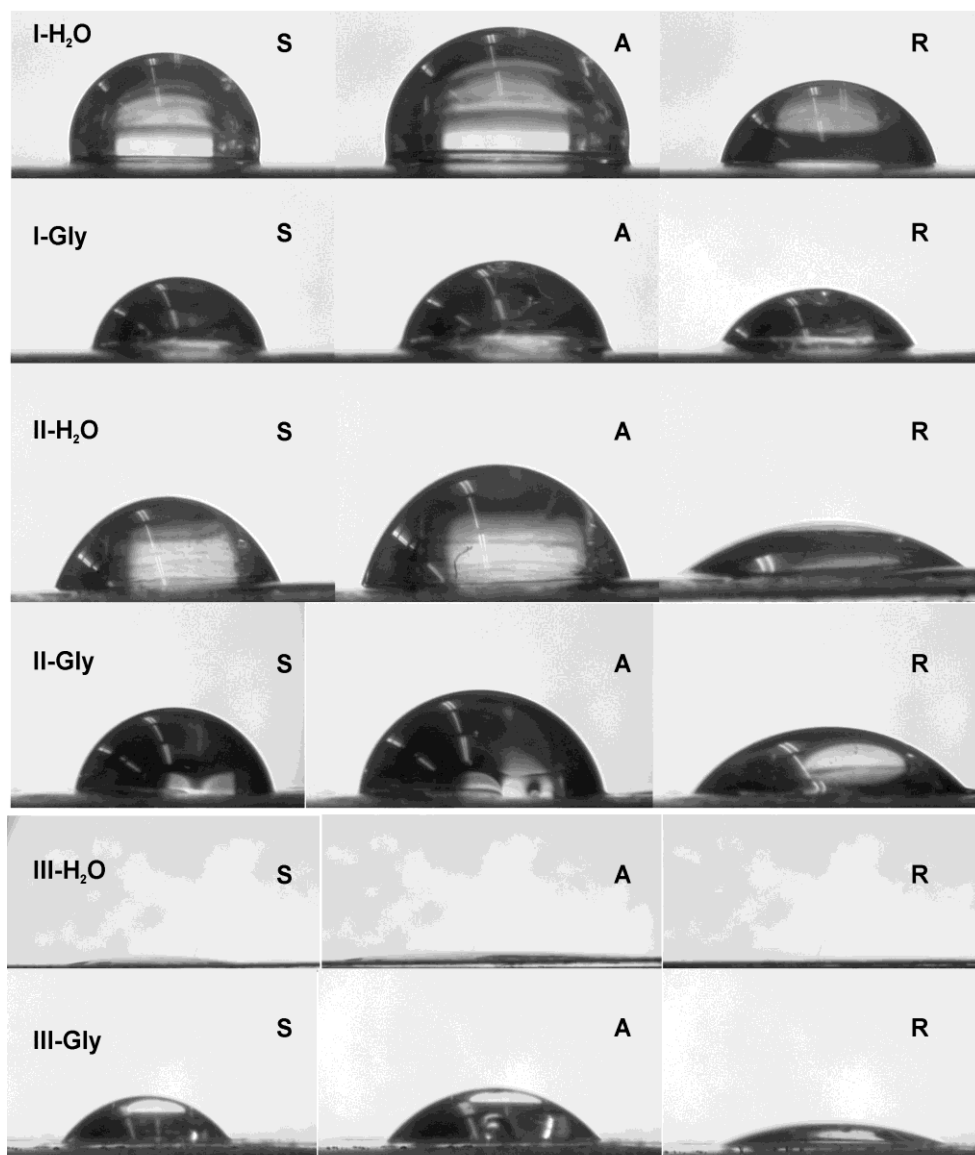


Figure ESI-22. Differences in the shape of droplets (S – stationary, A – advancing, R – receding) of reference liquids [water and glycerine (Gly)] on surfaces (Table ESI-2) prepared using slit-coater (I and II) and by dip-coating (III).