Electronic Supplementary Material (ESI) for Soft Matter.
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Boundary flow on high-quality densely grafted PEG brushes

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KEYWORDS. Self-assembled monolayer, polymer brush, PEG, PEO, cloud-point, interfacial slip length, boundary condition, hydrodynamic force curves, penetration length

Supporting information

We report here the details on the effect of preparation conditions on surface contamination and degradation, and on the optimisation of experimental procedures to produce high-quality, dense and reproducible PEG brushes to be used in surface force measurements.

1. Rinsing of the grafted surface

The potential for surface contamination, which is a key concern in surface force measurements, was investigated by testing the time required for rinsing away physisorbed material, and the effect of adding reducing agents in solution. As grafting above cloud point conditions is achieved in the presence of large amounts of salt, grafted samples were imaged after immersion in Milli-Q water for increasing lengths of time.

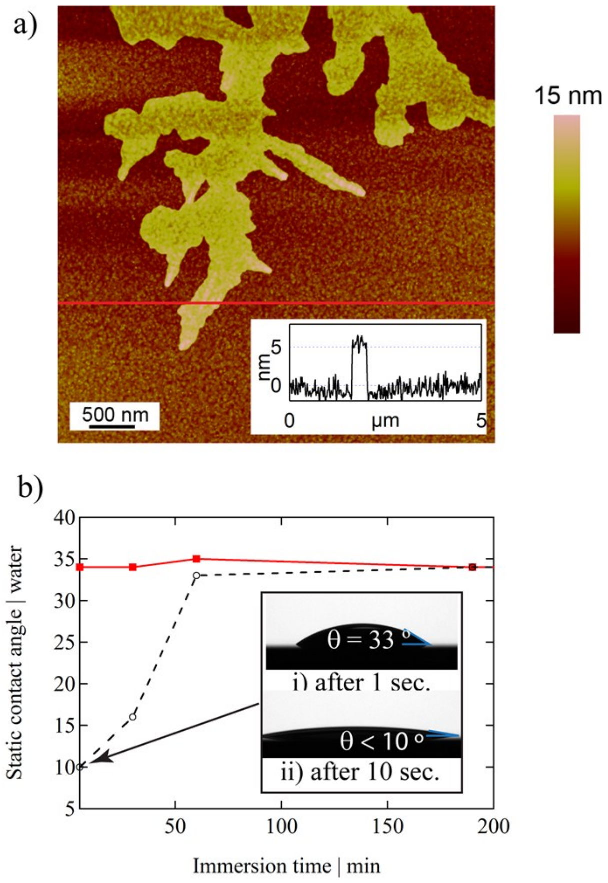


Figure S1:a) Effect of surface contamination: AFM topographical micrograph and line section of salt deposits on a CP-PEG30k sample prepared under high salt conditions (1.8 M K_2SO_4), and rinsed in water for 1 hour. b) Equilibrium contact angle (at 1 minute after deposition of the water droplet) on PEG1k (■) and PEG30k (○), on CP-grafted samples immersed in water for different times. The inset shows the initial contact angle measurement a CP-PEG30k sample before the first immersion in water, and 10 seconds after the droplet had been placed on the substrate.

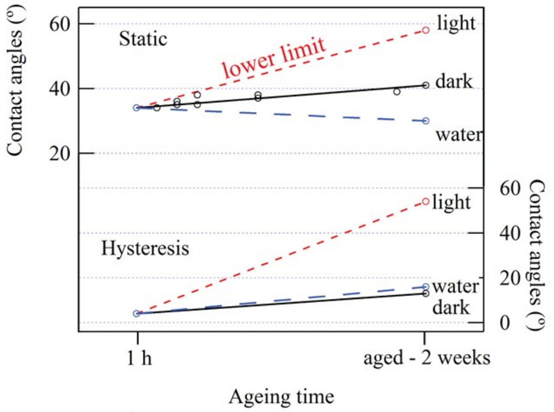
In **Figure S1(a)**, the AFM micrograph of a CP-PEG30k surface, freshly-prepared and only rinsed for 1 hour, shows large dendritic patches, that are about 5 nm high over the polymer brush, as seen in the inset. Similar aggregates were observed on all prepared CP-PEG30k surfaces, including with grafting time longer than 4 hours. Immersion in water for increasing lengths of time after grafting reduced the density and the width of the patches (height remained constant and around 5 nm), and finally they were no longer observable by AFM after immersion in water for more than 4 hours. These aggregates are most probably a mix of salt deposits and physisorbed polymers, entangled with the polymer brush, and they are particularly stable, resisting simple rinsing, due to the collapse of the polymer chains occurring during the CP-grafting. The formation of dendritic patches was not observed on CP-PEG1k surfaces following brief rinsing, probably due to the shorter length of the polymer chains.

The wetting properties of the surfaces were characterised as a means to establish the success and the extent of surface grafting, the removal of salt deposits, and the stability of the grafted brushes over time. The contact angle of water on the plasma-cleaned gold substrate was very low (< 10º), as typical of a clean gold surface. Upon application of the brush the surface wettability clearly changed, attesting that the chemistry of the surface had been modified. The equilibrium contact angle of water was measured to be 33º ± 1º for both systems, significantly higher than that of clean gold. The value of contact angle hysteresis was low for both brush systems: 2º for PEG1k and 7º for PEG30k (advancing 34º and receding 27º). In the case of the CP-PEG1k surface, the value of the equilibrium contact angle remained constant at 33°, immediately after grafting, brief rinsing in water, and immersion in water for 10 minutes (Figure S1(b)). On the other hand, on the CP-PEG30k surface the spreading of the water droplet occurred in two steps: as soon as the droplet was deposited, the equilibrium contact angle was close to 35º, but within 10 seconds the water drop suddenly spread onto the surface, giving rise to a contact angle of less than 10º, as depicted in the inset in **Figure S1(b)**. The contact angle value on the CP-PEG30k surface stabilised at 33° only after immersion times longer than 2 hours. This immersion time (around 200 minutes) was the same immersion time required to remove deposits of salt and physisorbed polymer on the surface of CP-PEG30k from the AFM micrographs (**Figure S1(a)**), which being highly hydrophilic, provide a ‘channel’ for spreading on the surface.

2. Aging of the grafted surface

The stability of the polymer brushes was tested over time, by storing the PEG surfaces in different environmental conditions: they were stored for 2 weeks either “in the dark” (samples stored in a sample box wrapped in aluminium foil, with no light exposure), “in ambient light” (samples stored in a transparent plastic box on a bench in the lab), and “under water” (samples stored immersed in Milli-Q water, which reduces UV exposure and oxygen). Several CP-PEG1k and CP-PEG30k surfaces, grafted under the same conditions (grafting time 2 hours, followed by immersion in Milli-Q water for 1 and 4 hours, for CP-PEG1k and CP-PEG30k respectively, prior to contact angle measurements and storage) all exhibited an equilibrium contact angle of 33° shortly after preparation. Then the surfaces were stored either in the dark, in ambient light, or under water, for two weeks, and the contacts angle measured again as summarized in **Figure S2(a) and (b).**

a) CP-PEG1k



b) CP-PEG30k

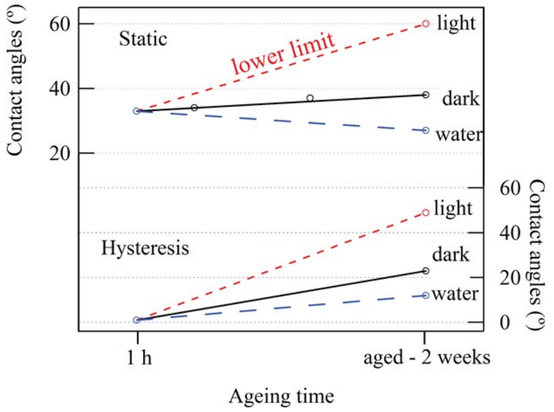


Figure S2: Equilibrium contact angle and contact angle hysteresis for a) CP-PEG1k, and b) CP-PEG30k surfaces, measured for freshly prepared samples and for samples aged 2 weeks in various conditions: in ambient light (red circles), in the dark (black circles) and under water (blue circles). The lines are guide to the eye.

After 2 weeks of storage, the value of the equilibrium contact angle on samples exposed to ambient light was more than twice as high as the value of the freshly grafted samples, changing from 33° to above 60° in both PEG1k and PEG30k systems. The contact angle hysteresis also changed drastically, increasing from around 0° to around 60° in both systems over two weeks of storage to ambient light. Several other samples exposed to slightly different light conditions (for example long sessions of AFM imaging) exhibited equilibrium contact angle values systematically higher to that depicted in **Figure S2(b)** (data not shown). The values of contact angle and hysteresis for samples stored in the dark and under water showed a smaller increase or no variation after two weeks. Contact angle values measured on similar samples stored in dark conditions for intermediate aging times are in good agreement with the trends depicted in **Figures S2(b) and (c)**.

The dramatic change in equilibrium contact angle and contact angle hysteresis of the PEG30k and PEG1k surfaces exposed to ambient light over time is a sign of degradation of the thiol-gold bond due to UV and oxygen exposure. Previously, alkanethiolates in self-assembled monolayers on gold have been observed to oxidize in air, in the dark, to form the corresponding sulfinates and sulfonates, which desorb from the surface. [1-2] Here clearly the effect is slower when stored in the dark or under water. The increase in hysteresis could indicate the degradation of the brush in patches, so that the contact line becomes pinned upon retraction of the droplet during the measurement of the receding contact angle. XPS data (not shown) for the aged samples were not significantly different from those of freshly grafted PEG brushes, so the oxidation of the thiol-gold bonds could not be confirmed by XPS. Nonetheless, the substantial and reproducible change in contact angle over time demonstrated that the chemical properties of the surfaces were modified after storage in a laboratory environment, and that keeping the PEG surfaces away from all light (stored in a dark) or with reduced UV and oxygen (by immersing in a UV-adsorbing medium such as water) largely preserves the quality of the PEG layer.

3. Grafting with TCEP reducing agent

Upon adding the 3 molar equivalents of reducing agent tris(2-carboxyethyl)phosphine (TCEP) to the thiol PEG30k grafting solution, as this is commonly used in combination with thiol. [3], QCM experiments showed evidence of a loss of mass

Figure S3(a). After a first negative frequency jump induced by the injection of the grafting solution, a steady increase of frequency in the 7th harmonic was observed, as the grafting solution was flowing over the gold sensor (between 1000 s and 4000 s). After rinsing with water (t = 5000 s), the final frequency shift measured was positive, indicating that some mass was removed from the surface.

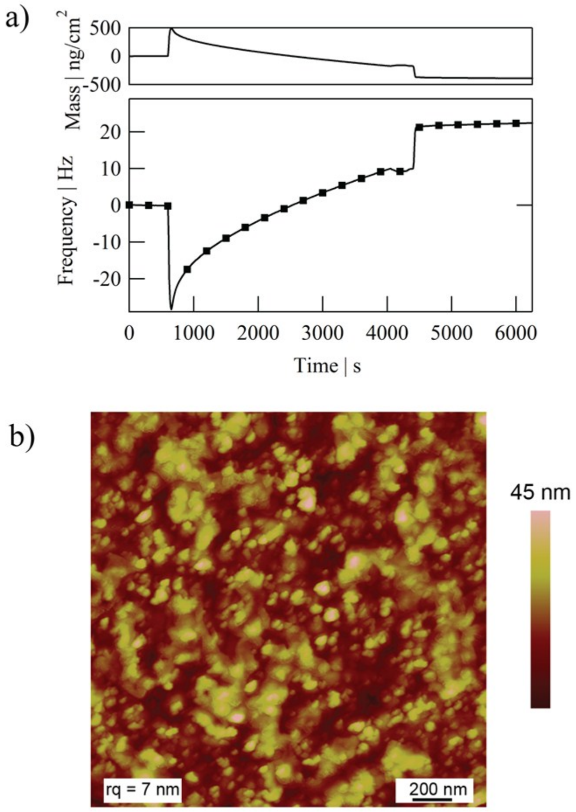


Figure S3 : a) Frequency signal of the 7th harmonic during a QCM experiment on a gold-coated sensor grafted with a PEG30k solution containing 3 molar equivalent of TCEP..b) AFM micrograph of a gold substrate grafted with a PEG30k solution, which has been roughened by the addition of 3 molar equivalent of the reducing agent TCEP.

Tapping mode AFM images shown in Figure S3b show that, after immersion in a grafting solution containing TCEP, the RMS roughness r_q of the CP-PEG30k was increased, to around 7 nm, with a large r_{max} value, of at least 50 nm. AFM data, and

QCM data reported in the following, suggest that the use of TCEP increased the surface roughness because it etched away the surface of the gold substrate.

AFM imaging

The roughness of the bare gold substrate was measured from AFM micrograph using the QNM mode. The vertical scale bar is 7 nm.

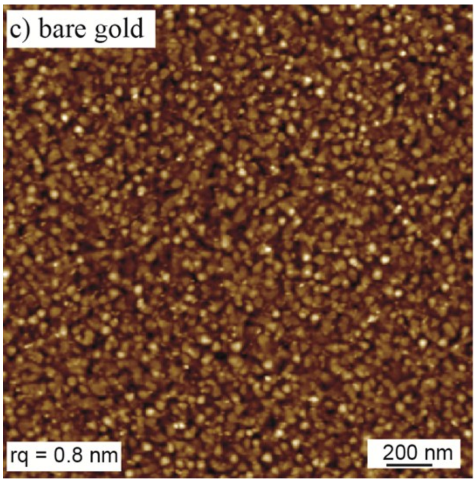


Figure S4: AFM topography image of the bare gold substrate. The root mean square roughness is 0.8 nm.

XPS analysis

The XPS data in **Table S1** show the atomic percentages of various elements (O1s, C1s, S2p, Au4f) present on the surface of brush samples that have aged a few days. The presence of Au 4f signals demonstrate that the total thickness of both CP-PEG1k and CP-PEG30k brush systems is lower than the thickness of the sampling depth of XPS, which is of the order of < 10 nm. This was expected as the measurement is performed under vacuum in a state where the polymer chains are more collapsed than in air. The thicknesses of the film in ultra high vacuum were calculated at $t_{\text{CP-PEG1k}} = 3.72 \pm 0.04$ nm and $t_{\text{CP-PEG30k}} = 6.54 \pm 0.21$ nm, using a standard XPS overlayer algorithm. [4] Both values confirm that the grafting densities are high enough (see Table 2) and that polymer brushes are grafted onto the substrates. However, the thickness of short/low molecular weight SAM is often overestimated with XPS as the signal is dominated by hydrocarbon which are presumably adventitious, as observed in the high resolution C 1s spectra (data not shown); this would explain why the thickness of CP-PEG1k is high with respect to the size of a polymer coil (r_g(PEG1k) = 0.54 nm).

Sample	O 1s (%)	C 1s (%)	S 2p (%)	Au 4f (%)	S/C
CP-PEG1k	24.85	25.53	3.09	39.42	0.12
CP-PEG30k	25.14	53.10	1.28	19.62	0.02

Table S1: Atomic composition obtained by XPS analysis of CP-PEG1k and CP-PEG30k brush systems on gold.

XPS analysis confirmed the etching of gold upon exposure to TCEP, as Si and Cr signals, both elements associated with the Cr-coated glass substrate present below the gold layer, were detected (data not shown). No clear evidence of degradation of the CP-PEG SAMs with aging time (14 days in dark and light conditions) was observed with XPS.

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