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Velcro-Mimicking Surface Based on Polymer Loop Brushes

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Experimental details

Synthesis of telechelic poly(ε-caprolactone) with hydroxyl terminal groups (HO-PCL$_{56}$-OH). To a Schlenk flask 1.545 g of CL (13.5 mmol), 56.8 mg of (5-methoxy-1,3-phenylene)dimethanol (0.34 mmol) and 14 mg of tin(II) 2-ethylhexanoate (0.034 mmol) were added. The flask was degassed and refilled with N_2 5 times before brought to 110 ^{o}C for polymerization. The reaction was stopped after 24 hr and the solid was dissolved in dichloromethane and precipitated in cold methanol. The polymer appeared as white powder was collected by filtration and stored under vacuum at room temperature for 24 hrs before characterizations and further reactions (yield: 90%).

Synthesis of telechelic poly(ε-caprolactone) with alkoxysilane terminal groups ($(H_5C_2O)_3$Si-PCL$_{56}$-Si$(OC_2H_5)_3$). 100 mg of HO-PCL$_{56}$-OH was dissolved in 10 mL anhydrous dichloromethane. To this solution 0.5 mL of 3-(triethoxysilyl)propyl isocyanate and 0.6 mg of dibutyltin dilaurate was added. The reaction was allowed to proceed at room temperature for 12 hr. After the reaction was stopped, the solution was concentrated using rotary evaporator and precipitated into cold methanol. $(H_5C_2O)_3Si\text{-}PCL_{56}\text{-}Si(OC_2H_5)_3$ was collected via filtration and stored under vacuum at room temperature for at least 24 hr before characterizations and further reactions (yield: 78%). Characterization results of the chemical structures are summarized in Figure S1.

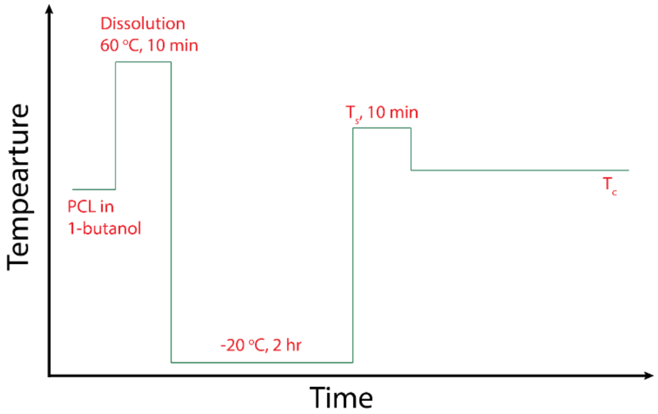
Solution crystallization of $(H_5C_2O)_3Si\text{-}PCL_{56}\text{-}Si(OC_2H_5)_3$ with polymer chains fold five times perpendicular to the lamellae. $(H_5C_2O)_3Si\text{-}PCL_{56}\text{-}Si(OC_2H_5)_3$ single crystals (PSCs) with controlled lamellar thickness were grown from dilute solution in 1-butanol (0.03 wt.%) using self-seeding method illustrated in Scheme S1. The seeding temperature (T_s) was set at 41.5 ^oC, and the crystallization temperature (T_c) was 5 ^oC. The crystallization process was carried out for 12 hr until most of the crystals sedimented at the bottom of the vial. These crystal precipitates were separated from solution and redispersed in fresh 1-butanol and stored at 5 ^oC for characterizations and further reactions.

Polymer loop brushes (PLBs) formation on glass substrates. PLBs on glass substrates were templated from $(H_5C_2O)_3Si\text{-}PCL_{56}\text{-}Si(OC_2H_5)_3$ PSCs. Before crystal immobilization, the glass substrates were cleaned using hot piranha solution and dried using dry nitrogen. $(H_5C_2O)_3Si\text{-}PCL_{56}\text{-}Si(OC_2H_5)_3$ single crystals were then spincoated or dropcasted onto clean glass substrates from suspension in 1-butanol. After the solvent was dried, the coated glass was put into a closed chamber, in which 200 μL ammonia was added as catalyst for the chemical reaction between exposed alkoxysilane groups on lamellar surface with siloxyl groups on glass substrates. The immobilization process was performed at room temperature for 20 min, and the unbounded polymers were removed by sonication of glass slides in acetone for 10 min. The morphology and properties of polymer brushes were then characterized by atomic force microscopy (AFM), as described in the following section.

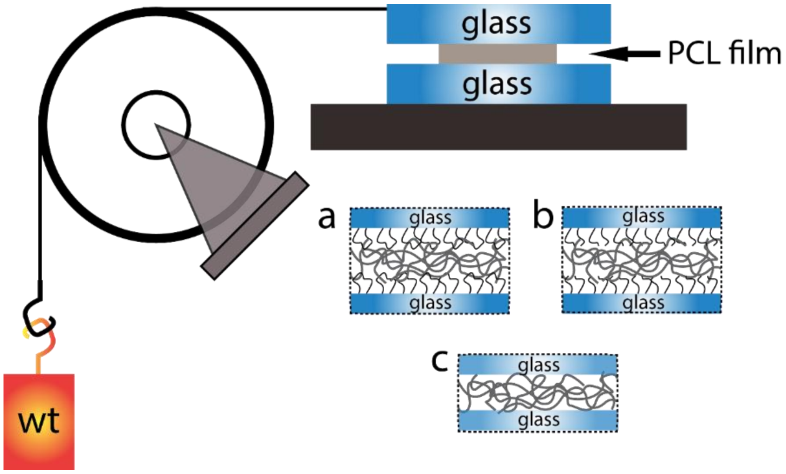
Single-tethered polymer brushes (STPBs) on glass slides from mono-functionalized PCL_{28}-$Si(OC_2H_5)_3$. Mono-hydroxyl terminated PCL (PCL_{28}-OH) was synthesized using (4-methoxyphenyl)methanol as initiator for the polymerization of CL. Typically, 1.545 g of CL (13.5 mmol), 103.6 mg of (4-methoxyphenyl)methanol (0.75 mmol) and 30.4 mg of tin(II) 2-ethylhexanoate (0.075 mmol) were added into a Schlenk flask. The solution was degassed and refilled with N_2 for three times before it was brought to 110 ^{o}C for polymerization. The reaction was stopped after 18 hr, and the solid was dissolved in dichloromethane. PCL_{28}-OH was obtained by precipitation of the solution into cold methanol followed by filtration. The white solid was collected and dried under vacuum at room temperature for following reaction (yield: 85%). Characterization results of the chemical structure are summarized in Figure S2.

Mono-alkoxysilane terminated PCL (PCL_{28}-$Si(OC_2H_5)_3$) was synthesized by reacting PCL_{28}-OH with 3-(triethoxysilyl)propyl isocyanate using the aforementioned method. After obtaining the pure polymer, it was crystallized in dilute 1-butanol solution (0.03 wt.%) following self-seeding method (Scheme S1) where T_s was set to 40.5 ^{o}C and T_c was fixed at 5 ^{o}C. The PSCs of PCL_{28}-$Si(OC_2H_5)_3$ were purified by separating the sediment from clean solution followed by redispersion of the precipitated crystals. The immobilization of PCL_{28}-$Si(OC_2H_5)_3$ PSCs on clean glass slides was performed using the exact same procedure as the immobilization of telechelic PCL PSCs. After polymer chains were successfully bounded to the substrates, the glass slides were washed by sonication in acetone for 10 min, and the PCL STPBs coated surface was immediately used for AFM studies.

Fabrication of PCL grafted AFM probe. Functionalization of triangular silicon nitride (Si_3N_4) probes with spring constant around 0.27 N/m (BudgetSensors, Sofia, Bulgaria) using PCL_{380}-OH was performed following published method.[1] Typically, as received probes were firstly cleaned using hot piranha solution to remove organic contaminant, then the tips were modified by immersing in a 2 mL solution of 2-aminoethanol hydrochloride in dry dimethylsulfoxide (DMSO) (5.7 M) with 4 Å molecular sieves for 16 hr. After that, the cantilevers were rinsed with dry DMSO, transferred into a 0.04 M p-phenylene-diisocyanate solution in dry DMSO and left to react for 20 min. The cantilevers were rinsed again with dry DMSO and transferred to the final solution of 1.5 mg/mL PCL_{380}-OH in dry DMSO and left for 2 hr at 50 ^{o}C. After that the cantilevers were rinsed subsequently with dry DMSO, dichloromethane and ethanol, dried under nitrogen, and stored in a gel pack until use.



Scheme S1. Temperature profile of self-seeding method for the preparation of polymer single crystals.



Scheme S2. Illustration of the shear adhesion measurement device. PCL film prepared from PCL with MW ~ 80k g/mol is sandwiched between two bare glass slides or functionalized glass slides with identical grafted polymer brushes. (a), (b) & (c) illustrate the interactions at film/glass interfaces between loop brushes and PCL chains (a), STPBs and PCL chains (b), and bare glass surface with PCL chains (c). The images are not drawn to scale.

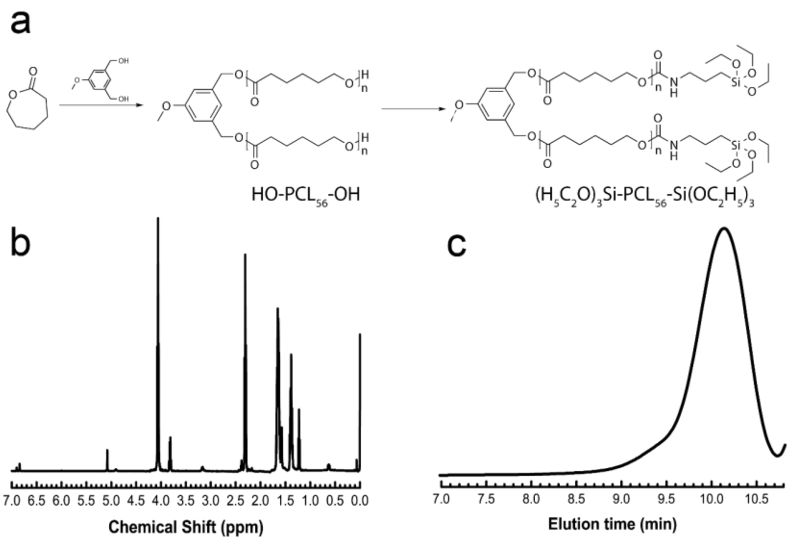


Figure S1. (a). Synthetic route of $(H_5C_2O)_3Si\text{-}PCL_{56}\text{-}Si(OC_2H_5)_3$; (b) ^1H Nuclear Magnetic Resonance (NMR) spectrum of as-synthesized $(H_5C_2O)_3Si\text{-}PCL_{56}\text{-}Si(OC_2H_5)_3$; (c) Gel permeation chromatography (GPC) curves of $(H_5C_2O)_3Si\text{-}PCL_{56}\text{-}Si(OC_2H_5)_3$.

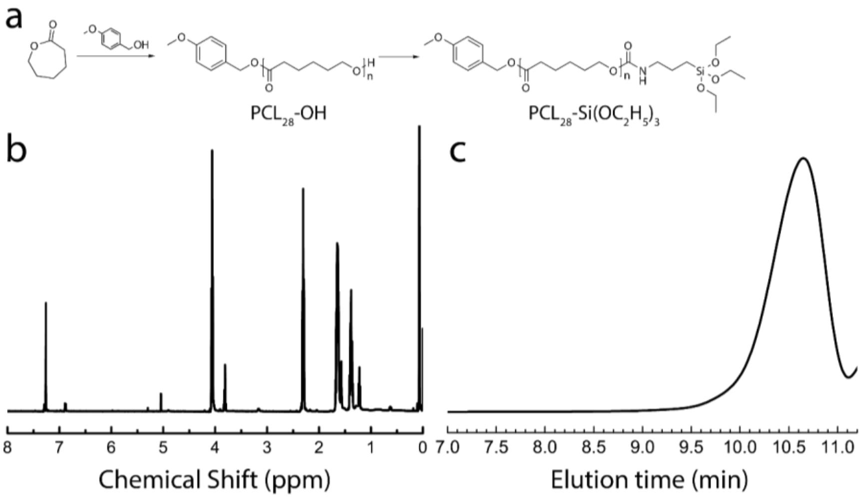


Figure S2. (a). Synthetic route of PCL$_{28}$-Si(OC$_2$H$_5$)$_3$; (b) ^{1}H Nuclear Magnetic Resonance (NMR) spectrum of as-synthesized PCL$_{28}$-Si(OC$_2$H$_5$)$_3$; (c) Gel permeation chromatography (GPC) curves of PCL$_{28}$-Si(OC$_2$H$_5$)$_3$.

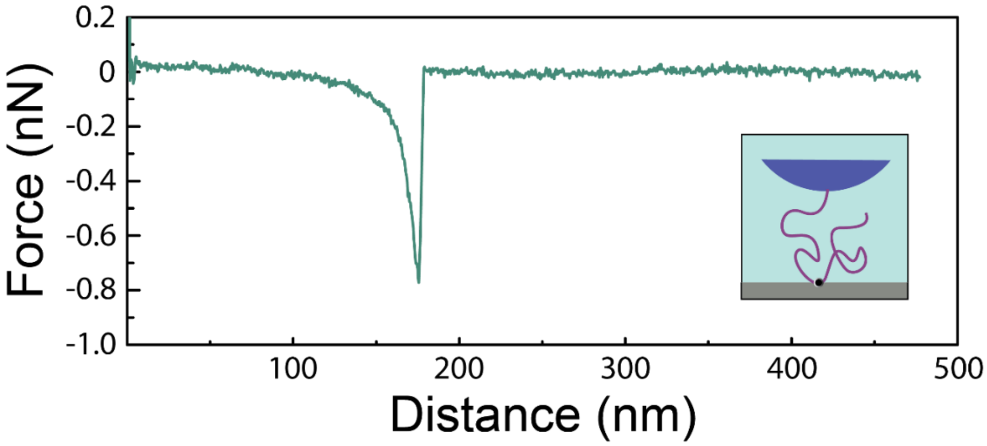


Figure S3. The retraction portion of a force-distance (F-D) curve of a functional AFM probe on mica surface. The F-D curve demonstrates extension and rupture of adsorbed polymer chain on mica, and the unique curve shape is due to typical entropic elasticity of polymeric linker in this system. The single peak observed in the F-D curve confirms that only one polymer chain was grafted per AFM probe, which is due to the high molar mass of the attached polymer on the probe and the small tip surface area. The inset illustrates the physical interaction between polymer chain and substrate.

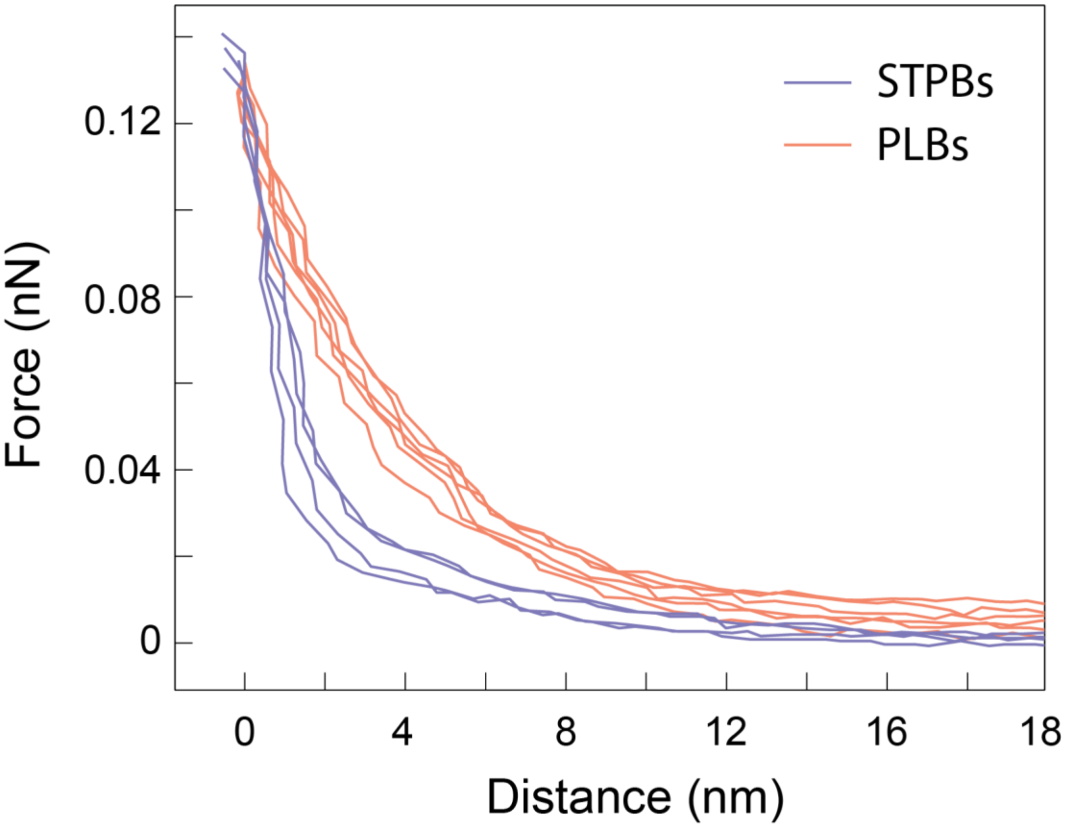


Figure S4. The approaching portion of representative force-distance (F-D) curves of a functional AFM probe on glass surfaces functionalized with single-tethered polymer brushes (STPBs) and polymer loop brushes (PLBs).

Reference

1. E. Spruijt, S. A. van den Berg, M. A. C. Stuart and J. van der Gucht, *ACS Nano*, 2012, **6**, 5297-5303.