Macromolecules
Article
pubs.acs.org/Macromolecules

Molecular-Weight Determination of Polymer Brushes Generated by SI-ATRP on Flat Surfaces

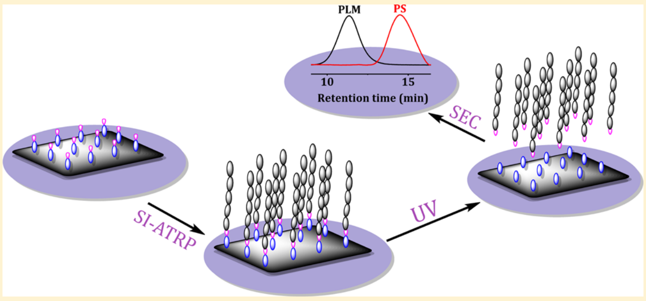
Chengjun Kang,[†] Rowena M. Crockett,[‡] and Nicholas D. Spencer*,[†]

[†]Laboratory for Surface Science and Technology, Department of Materials, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH 8093 Zurich, Switzerland

[‡]Swiss Federal Laboratories for Materials Science and Technology, Empa, Ueberlandstrasse 129, CH 8600 Duebendorf, Switzerland

S *Supporting Information*

ABSTRACT: A new type of photolabile, surface-initiated, atom-transfer radical polymerization (SI-ATRP) initiator 3-(2-bromo-2-methylpropanamido)-3-(2-nitrophenyl)propanoic acid was synthesized, and immobilized via an aminosilane linker onto a flat silicon surface. Poly(lauryl methacrylate) and polystyrene brushes were grown from the surface via SI-ATRP, and the surface-tethered polymer chains cleaved off under UV irradiation. The kinetics of the cleavage process were investigated, and an apparent effect of osmotic forces within the polymer brush could be observed. The molecular weight of the cleaved polymers could be readily determined by means of size-exclusion chromatography.



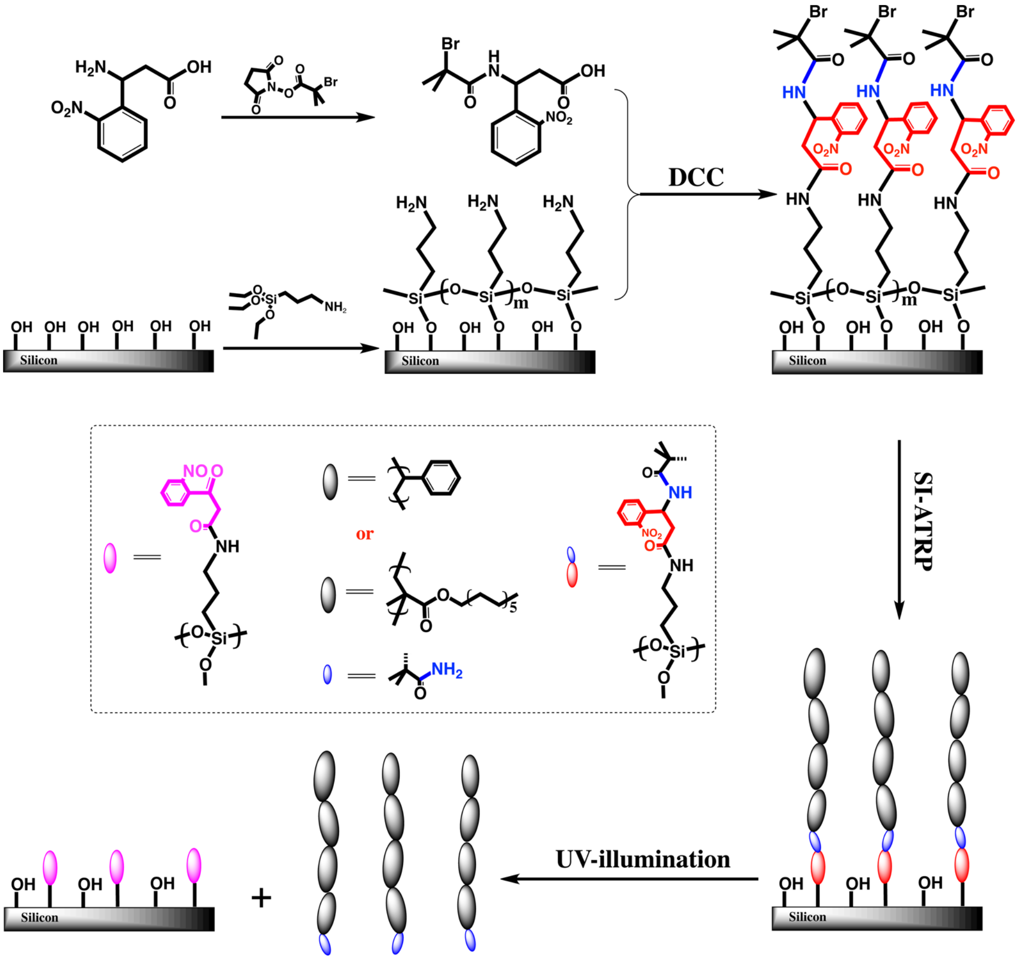
■ INTRODUCTION

The chemical and physical properties of materials have frequently been tailored by coating with densely grafted polymer chains, composed of homo- or copolymers with one end attached to the substrate. These surface-tethered polymer chains stretch out to form brush-like structures in good solvents,[1] in order to minimize chain−chain interactions. Polymer brushes can be fabricated by grafting from the substrates through surface-initiated controlled radical polymerization (SI-CRP) techniques,[2] such as surface-initiated atom-transfer radical polymerization (SI-ATRP),[3] surface-initiated reversible addition−fragmentation chain-transfer polymerization (SI-RAFT),[4] and surface-initiated nitroxide-mediated polymerization (SI-NMP).[5] Compared to "grafting to" methods, these techniques allow much more flexibility in designing the architecture of polymer brushes and can lead to a much higher chain-grafting density. SI-ATRP, first reported by Huang and Wirth in 1997,[3] is the most frequently used controlled radical polymerization method because it is chemically versatile, compatible with a large variety of monomers, tolerant to a relatively high concentration of impurities, including oxygen, and the commercial availability of most of the components necessary for ATRP synthesis.

Substrates modified with polymer brushes have been extensively used in a variety of applications, such as responsive surfaces,[6] nonfouling surfaces,[7] cell-adhesive surfaces,[8] and low-friction surfaces.[9] However, the characterization of polymer brushes tethered to surfaces remains challenging, as crucial properties including the grafting density, molecular weight, and polydispersity index (PDI) of surface-tethered polymer brushes have been difficult to determine. One possible way to determine these parameters is to cleave polymer brushes from the substrates and measure them directly via size-exclusion chromatography (SEC). Several publications have reported, for example, the cleaving of poly(styrene) (PS) from silica nanoparticles by dissolving the silica substrates in selectively corrosive media,[10−12] such as hydrofluoric acid, or the growth of polymer brushes from substrates initiated by an acid-labile linker that could be cleaved off with, for example, *p*-toluenesulfonic acid.[13] The inherent curvature of nanoparticle substrates can potentially lead to significant differences in the polymer-growth kinetics compared to brushes formed on planar surfaces. Furthermore, these methods cannot be applied to corrosion-resistant substrates or to HF-sensitive polymers. Moreover, intricate separation procedures are involved, introducing the risk of incorporating impurities in the small amounts of polymers harvested. Since analyzing polymers from flat substrates is more challenging, because a much smaller amount of polymer is generated than on nanoparticles, the determination of molecular weight and PDI of surface-tethered polymers has often been carried out on polymers grown simultaneously in the bulk solution while the polymer grows on the surface.[14] This approach relies on the assumption that the polymers generated in solution and on the surface have the same molecular weight and PDI. Experimental data suggest that this is not always the case,[5,13] and the assumption has been convincingly challenged by numerical simulations.[15] Compared to acidic or basic cleavage techniques, the photocleavage

Received: September 20, 2013
Revised: November 25, 2013

Scheme 1. Schematic of the Growth and UV-Induced Cleavage of ATRP-Generated Polymers from an Oxidized Silicon Surface



technique is a mild, clean, and easily controlled procedure. Photolabile linkers have been frequently used in the biomedical field,[16] particularly in drug discovery and development,[17] and controlled cell, peptide, and protein delivery.[18−20]

We report an efficient photochemical method for cleaving polymer brushes from planar silicon substrates. We have utilized this approach to facilitate characterization of the molecular weight and PDI of the surface-grown polymers by means of SEC. To this end, an *o*-nitrobenzyl type[21] photocleavable ATRP initiator, 3-(2-bromo-2-methylpropanamido)-3-(2-nitrophenyl)propanoic acid (BMNP) (Scheme 1), has been developed.

■ EXPERIMENTAL SECTION

Materials. 3-Amino-3-(2-nitrophenyl)propanoic acid (98%, ABCR-Chemicals, Germany), lauryl methacrylate (96%, Acros Organics Belgium), styrene (99%, Sigma-Aldrich, Germany), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam, 97%, Sigma-Aldrich, Germany), anisole (99%, Sigma-Aldrich, Germany), 4,4′-dinonyl-2,2′-bipyridine (97%, Sigma-Aldrich, Germany), *n*-nonane (99%, ABCR-Chemicals, Germany), *N*,*N*-dimethylformamide (DMF, 99.8%, anhydrous, Acros, Germany), *N*,*N*′-dicyclohexylcarbodiimide, (DCC, 99%, Sigma-Aldrich, Germany), 2-bromo-2-methylpropanoyl bromide (98%, Sigma-Aldrich, Germany), tetrahydrofuran (THF, 99.7%, Alfa-Aesar, Germany), triethylamine (NEt_3, 99.5%, Sigma-Aldrich, Germany), copper(II) bromide (99.9%, Sigma-Aldrich, Germany), copper(I) bromide (CuBr, 99.9%, Sigma-Aldrich, Germany), (3-aminopropyl)triethoxysilane (APTES, 98%, Sigma-Aldrich, Germany), and ethyl 2-bromoisobutyrate (EBiB, 98%, ABCR-Chemicals, Germany) were used as received. All solvents were purchased from Sigma-Aldrich and used as received.

Synthesis of 3-(2-Bromo-2-methylpropanamido)-3-(2-nitrophenyl)propanoic Acid (BMNP). 12.0 mL of triethylamine (NEt_3) was added to a suspension of active ester 2,5-dioxopyrrolidine-1-yl 2-bromo-2-methylpropanoate (DBMP) (11.0 g, 41.6 mmol), and 3-amino-3-(2-nitrophenyl)propanoic acid (ANPA) (7.3 g, 34.7 mmol) in 80 mL of DMSO over 15 min with gentle stirring, after which a clear brown solution was obtained. After the mixture had reacted for 24 h, DMSO was removed under reduced pressure to yield a semisolid, which was dissolved in a mixture of 250 mL of H_2O and 19.2 mL of NEt_3 (pH ≈ 9.0). Next, ethyl acetate (EtOAc, 180 mL) was added under vigorous stirring, and the aqueous layer was separated, acidified with 12 N HCl to pH ≈ 2.0, and extracted with EtOAc (3 × 250 mL). The organic layers were combined and washed with 1 N HCl (1 × 160), H_2O (2 × 160), dried over $MgSO_4$, and then filtered and concentrated under vacuum to give 11.2 g of a light yellow solid (yield, 89%). ^{1}H NMR (300 MHz, *d*-DMSO): δ (ppm) 7.55−8.03 (m, 4H), 5.28 (m, 1H), 2.62−2.97 (m, 2H), 2.05 (s, 6H). ^{13}C NMR (300 MHz, *d*-DMSO): δ (ppm) 171.68, 170.66, 148.59, 137.39, 129.05, 128.89, 124.48, 120.12, 60.29, 46.84, 39.15, 31.28. Elemental analysis: calcd: C 43.47%, H 4.21%, N 7.80%. Found: C 43.63%, H 4.26%, N 7.76%.

If not specified otherwise, all experiments described in this paper were carried out under the exclusion of light.

Fabrication of APTES-Modified Silicon Surfaces. Silicon wafers (P/B(100), Si-Mat Silicon Wafers, Germany) were cut to size, sonicated three times (10 min each) in 2-isopropanol, dried with nitrogen gas, and then cleaned in a UV-ozone cleaner (UV/Ozone ProCleaner and ProCleaner Plus, BioForce, Ames, IA) for 30 min. The cleaned wafers were immediately placed into an oven at 150 °C for 0.5

h and subsequently put into a desiccator with one drop of (3-aminopropyl)trimethoxysilane (APTES) at the bottom. The desiccator was evacuated with a vacuum pump for 1 h, after which the pump was valved off and the desiccator pressure held constant for another 1.5 h (i.e., at the vapor pressure of the APTES). Finally, APTES-modified silicon wafers were sonicated in toluene (3 × 10 min) and dried with nitrogen gas.

Fabrication of BMNP-Modified Silicon Surfaces. In a typical procedure, BMNP (0.6 g, 1.6 mmol) and DCC (1.7 g, 8 mmol) were dissolved in 40 mL of DMF over 5 min to yield a clear, light-brown solution, into which the freshly prepared APTES-modified silicon wafer (2.5 × 4 cm^2) was transferred under a nitrogen atmosphere. After 48 h, the wafer was removed and rinsed by DMF three times, followed by sonication in toluene for 5 min to remove physisorbed BMNP.

SI-ATRP of Lauryl Methacrylate. All polymerization reactions were carried out in a Schlenk line under a nitrogen atmosphere. In a typical experiment, dNbpy (1.9 mmol, 0.8 g) and $CuBr_2/(dNbpy)_2$ complexes (0.05 mmol) in 550 μL of DMF were first dissolved in lauryl methacrylate (50 mL, 0.17 mol), after which the solution underwent three freeze−pump−thaw circles (10 min each) to remove the dissolved oxygen. Then the mixture was transferred to another flask containing CuBr (0.95 mmol, 0.14 g). After stirring for 30 min at room temperature, 75 μL of EBiB/monomer solution (0.1% v/v) was added to the clear dark solution, and the mixture was immediately transferred to freshly prepared, initiator-modified samples. Polymerization was carried out at 110 °C for various lengths of time (see Results and Discussion), and subsequently the reaction was quenched by precipitation in methanol, the wafer being subsequently sonicated in toluene to remove physisorbed polymers.

SI-ATRP of Styrene. In a typical procedure, dNbpy (0.008 mmol, 3.2 mg) and Me_4cyclam (0.08 mmol, 10.4 mg) were first dissolved in a 10 mL mixture of styrene, DMF, and anisole (v:v:v = 3:1:1), after which the solution underwent three freeze−pump−thaw circles (10 min each) to remove the dissolved oxygen, before being transferred to another flask containing CuBr (0.04 mmol, 6.0 mg) and $CuBr_2$ (0.004 mmol, 1.0 mg). After stirring for 30 min at 50 °C, 1.5 μL of EBiB was added to yield a clear, light-green solution, into which the freshly prepared initiator-modified samples were immediately transferred. Polymerization was carried out at 90 °C for various lengths of time (see Results and Discussion). The polymerization solution was quenched by precipitation with methanol, the wafer being subsequently sonicated in toluene to remove physisorbed polymers.

Cleavage and Collection of Polymer Brushes from Silicon Surfaces. In order to remove impurities from the brush-covered surfaces, all substrates were extracted in chloroform for 24−48 h before cleaving off the polymer brushes. In a typical procedure, a PLM-modified silicon wafer was immersed in 3 mL of nonane in a glass dish, which was illuminated under a UV lamp (254 nm) for various lengths of time (see Results and Discussion). Each sample was fixed at a distance of 2.5 cm away from the UV light source, which had a measured intensity of 1.5 mW/cm^2. PLM cleaved from silicon surfaces was gathered by removing the nonane under reduced pressure at room temperature. The cleavage of PS from substrates involved the same cleaving procedures as above, except that THF was used as the solvent instead of nonane.

Characterization. The chemical structure of BMNP was determined using a ^{1}H NMR Bruker Avance 300 spectrometer, the signal of DMSO-d_6 (^{1}H 2.54 ppm) being used as internal standard for the determination of chemical shift. The dry thicknesses of APTES and the surfaces modified with polymer brushes were measured with a variable-angle spectroscopic ellipsometer (VASE, M-2000F, LOT Oriel GmbH, Darmstadt, Germany) at an incident angle of 70°, using a three-layer model (software WVASE32, LOT Oriel GmbH, Darmstadt, Germany), each sample being measured at three different spots. Morphologies of APTES-modified silicon surfaces were determined at room temperature in TappingMode using a Multimode AFM with a NanoScope IIIa controller (Veeco, Santa Barbara, CA) equipped with a silicon cantilever (Olympus, Japan), with resonant frequency 300 kHz and a spring constant of 26.1 N/m. MTR-IR spectra of dried samples were recorded on a Bruker infrared spectrometer (IFS 66 V), equipped with a liquid-nitrogen-cooled detector. Before measuring the samples, background spectra were obtained by using freshly cleaned bare silicon wafers (P/B (100), Si-Mat Silicon wafers, Germany). UV−vis measurements of photocleavable initiators were performed on a V-660 spectrometer (JASCO, Japan), the measurement range being 400−170 nm and the scanning speed 100 nm/min. Analytical SEC measurements were carried out on a Viscotek SEC-system equipped with a pump, a degasser (SEC max VE2001), a detector module (Viscotek 302 TDA), a UV detector (Viscotek 2500, λ = 254 nm), and two columns (PLGel Mix-B, PLGel Mix-C), using chloroform as eluent (flow rate 1.0 mL/min). The molecular weights of samples were calibrated by universal calibration with polystyrene as standards in the range of M_p 1480−4 340 000.

■ RESULTS AND DISCUSSION

Synthesis of Photocleavable SI-ATRP Initiator BNMP. The photocleavable moiety 2-nitrobenzyl has previously been shown to be a relatively stable linker, yet can be efficiently cleaved under UV-irradiation.[22,23] This moiety was employed in the design of the photocleavable ATRP initiator BMNP, which was synthesized by reacting 2,5-dioxopyrrolidine-1-yl 2-bromo-2-methylpropanoate (DBMP)[24] with 3-amino-3-(2-nitrophenyl)propanoic acid (ANPA) in DMSO at room temperature in the presence of triethylamine (NEt_3) (Scheme 1). The successful synthesis of BMNP was confirmed by ^{1}H NMR, ^{13}C NMR, and elemental analysis. The strong absorption peak in the UV−vis spectrum of BMNP in THF (see Supporting Information for details) at 256 nm indicates the possibility of cleavage of BMNP at this wavelength.

Tethering BMNP onto Silicon Substrate. In order to immobilize BMNP onto the surface of a silicon wafer, surface modification was required to provide covalently bound amine groups. Aminosilanes have been widely used for modifying silicon-based surfaces due to their bifunctional nature, and (3-aminopropyl)triethoxysilane (APTES) is the most frequently used of these. However, the polymerization of APTES in solution is difficult to avoid.[25,26] Thus, vapor-phase deposition of the APTES was carried out in order to generate a monolayer.[27] By controlling the deposition time, it was possible to obtain an ATPES coating with a thickness of 0.5 ± 0.1 nm and with a static water contact angle of 59 ± 2°. The formation of a monolayer of APTES and the absence of APTES polymers on the silicon substrate were confirmed by the smooth surface morphology observed with atomic force microscopy (AFM) (see Supporting Information for details).

BMNP was then tethered to the amine groups on the silicon surface by amino-dehydroxylation. The successfully reaction of BMNP with APTES was confirmed with ellipsometry—the thickness of the organic film on the silicon substrate increased to 0.8 ± 0.1 nm. Furthermore, following the reaction with BMNP, the multiple-transmission−reflection infrared (MTR-IR)[28] spectrum showed an additional absorption peak at 1663 cm^{-1}, assigned to the amide bond (see Supporting Information for details).

Growing Polymer Brushes from Silicon Surfaces. SI-ATRP was carried out according to the procedure previously reported by Bielecki et al.,[29] with minor modifications. A kinetic study with ellipsometry showed an approximately linear increase in dry polymer film thickness with reaction time, suggesting that the polymer chains were growing from the surface in a controlled manner (see Supporting Information for details). MTR-IR measurements after polymer growth showed a strong absorption peak at 1730 cm^{-1} (top spectrum of Figure

1), which was assigned to the ester groups of PLM. The surface morphology of the silicon substrate coated with polymer brushes was also characterized by AFM (see Supporting Information for details).

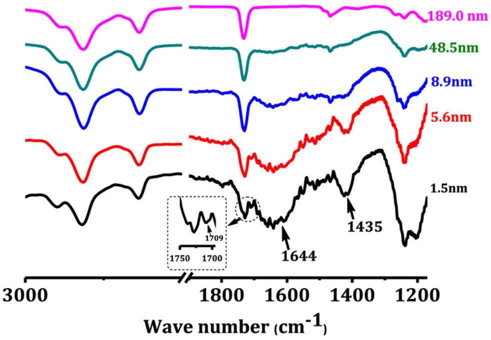


Figure 1. MTR-IR spectrum of a PLM-functionalized silicon substrate as the polymer thickness (measured dry) is reduced by UV-induced cleavage from the surface. Top spectrum represents the surface prior to irradiation. Spectra are normalized to the C−H stretch at 2929 cm^{-1}.

Cleavage of Polymer Brushes from Silicon Substrates. Before cleaving the polymer brushes from the substrates, the silicon wafers were extracted in Soxhlet sets for 24−48 h with chloroform, in order to remove surface-attached impurities, such as adsorbed polymers generated by the free initiator. The cleaving processes were carried out by exposing poly(lauryl methacrylate) (PLM)-modified substrates, both dry and under nonane, in which PLM dissolves, to UV irradiation with a wavelength of 254 nm. The cleavage reaction is shown in Scheme 2.

The progress of the cleavage reaction was monitored by determining the change in thickness (measured dry) of the polymer films on the substrates (Figure 2). Cleavage of PLM was also monitored by MTR-IR. As the polymer brushes were cleaved from the surface, new absorption peaks at 1709 and 1435 cm^{-1} appeared, which could be assigned to ketone and nitroso groups, respectively,[30] both of these being present in the photolysis products of BMNP[17] (Figure 1). The entire process was also repeated, for comparison purposes, for the synthesis of polystyrene (PS) brushes.

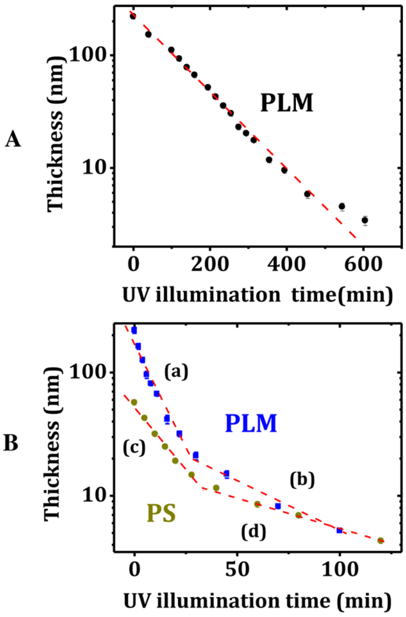
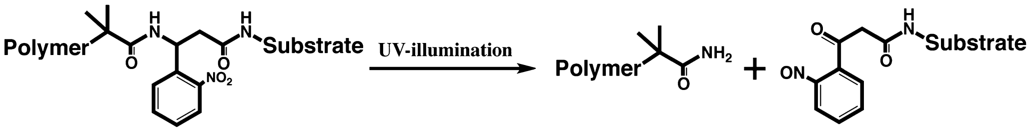


Figure 2. Kinetics of cleavage by UV irradiation (A) from the PLM modified substrates in dry state and (B) from the PLM-modified substrates immersed in nonane and the PS-modified substrates under THF. Dashed lines are intended as a guide to the eye. (a)−(d) indicate linear regions of the kinetic plot, referred to in detail in the text.

As can be seen from Figure 2, when dry, polymer-coated substrates were directly exposed to UV light, it took over 10 h to achieve a 95% reduction of total polymer film thickness. The cleavage kinetics exhibited first-order behavior, as indicated by the logarithmic decrease in film thickness with UV-illumination time (Figure 2A). When PLM was removed with UV under nonane, much faster cleavage was observed. A sharp decrease in film thickness from 219.6 ± 11.8 to 21.0 ± 1.5 nm over the first 30 min was followed by a slower reduction, with the thickness being reduced by more than 99% over 2 h. The cleavage kinetics appeared to be composed of two distinct first-order processes, which were connected by a turning point at a dry polymer thickness of approximately 20 nm (Figure 2B). This phenomenon could possibly be explained by the brush−mushroom transition as the reaction proceeds; however, the UV-exposure used to obtain polymer for SEC measurements involved was restricted to short periods of time to avoid decomposition of the PLM or PS. The length of the polymers at the turning point in the reaction rate was, therefore, not determined. In the initial stage at high coverage (Figure 2B(a), slope $k = 0.044$), the relatively higher grafting density resulted in a brush configuration, with strong repulsion forces between the solvated, surface-tethered polymer chains leading to high osmotic pressure and facilitating the photocleavage process by the faster "ejection" of cleaved chains. The crowding in the brush state presumably lowered the energy of the transition state, accelerating the cleaving reaction by about 15-fold, compared to the collapsed conformation of dry polymer chains on substrates (Figure 2A, slope $k = 0.003$). As the grafting density decreased, due to the cleavage reaction, the solvated, surface-tethered polymers formed the mushroom-like conformation (Figure 2 B(b), slope $k = 0.008$), and the rate of cleavage under solvated conditions was thus reduced to only about 2 times greater than that of the polymer chains under dry conditions. The osmotically accelerated detachment of polymer brushes from substrates has been previously observed by Paripovic et al.,[31] who investigated the influence of SI-ATRP initiator chemical structures on the detachment of anchored polymer brushes, when incubated in deionized water and cell-culture medium. It was proposed that those reactions involved

Scheme 2. Schematic of the Cleavage Reaction of Polymer Brushes Tethered on Substrates under UV Illumination



the breakage of the Si−O bond that connects the brush and substrate[32] due to steric-crowding-induced tension along the polymer backbone. This mechanism is consistent with two further reports showing that noncovalent interfacial interactions can result in the breakage of a covalent bond.[33,34]

Aromatic groups strongly absorb UV-light and may therefore block its penetration through the polymer film, preventing the cleavage process. To examine this possibility, poly(styrene) (PS) was generated on the surface and then removed following the same cleaving procedure as for PLM, in THF rather than in nonane. The transition in cleavage rate observed for PLM was also observed for PS. The cleavage kinetics exhibited a slower rate compared to PLM, which may have been due to the partial absorption of UV-light by PS chains (Figure 2B(c) slope k = 0.023, Figure 2B(d) slope k = 0.005). The thickness of the PS coating decreased from 57 ± 2.7 to 6.9 ± 0.5 nm within 30 min and was reduced by 95% within 2 h (Figure 2B).

UV light with a wavelength of 256 nm leads to the scission of polymer chains and therefore to a reduction in polymer film thickness, even in the absence of a photocleavable linker, potentially confounding the measurements of cleavage kinetics. To explore this possibility, the nonoptically sensitive initiator 2-bromo-2-methylpropanoic acid (BMPA) was immobilized on silicon substrates by reacting DBMP directly with amino groups on APTES-modified substrates. PLM brushes were then generated and subsequently illuminated with UV light, as described for the photocleavable initiator. Figure 3 shows the reduction in dry film thickness as measured by ellipsometry against illumination time. The rate of reduction in thickness for the BMPA-initiated polymer brushes was far lower than that of the polymer brushes initiated by BNMP. For example, the thickness of BMPA-initiated polymer brushes decreased from 201.8 to 195.7 nm in the first 20 min, while during the same time period the thickness of BNMP-initiated brushes reduced from 219.6 to 31.8 nm. Thus, for similar thicknesses, UV-light-induced polymer-chain decomposition contributes only approximately 4% to total thickness reduction.

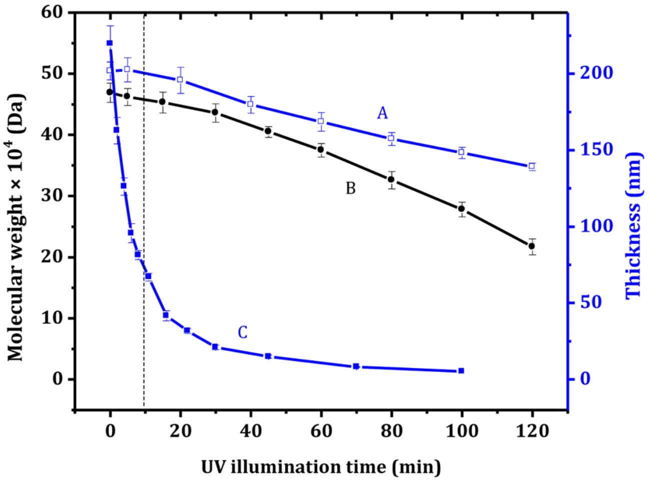


Figure 3. (A) Kinetics of UV-decomposition of polymer brushes that had been grown from the nonphotocleavable BMPA, (B) UV-induced molecular weight reduction of free PLM in nonane solution, and (C) UV-cleavage of polymer brushes initiated by the photocleavable initiator, BNMP. The vertical line indicates the maximum UV-exposure time after which polymers were harvested from the surface prior to SEC analysis in order to minimize polymer decomposition.

Furthermore, in order to quantitatively determine the reduction of PLM molecular weight due to UV-induced polymer chain decomposition, PLM (M_w = 4.69 × 10^5 Da) was dissolved in nonane (1.0 mg/mL) and illuminated under the same conditions as those of polymer brushes on the modified substrate. As can be seen from Figure 3, the total molecular weight of free PLM was reduced by about 40% after 2 h UV illumination. However, during the first 20 min, the reduction of molecular weight could not be significantly distinguished by SEC. Therefore, in order to avoid the influence of UV-induced decomposition, the polymer brushes attached to modified substrates were exposed to UV for a maximum of 10 min (see dotted line in Figure 3), 2 min being most frequently used for substrates with a polymer film thickness above 100 nm.

SEC Measurement of Cleaved Polymers. Polymerizations to produce PLM were carried out for three different lengths of time, each being carried out three times, in order to determine the total experimental error (A, B, and C series). Cleaved chains from samples with approximately 210 nm (PLM-A series), 120 nm (PLM-B series), or 60 nm (PLM-C series) dry thickness of tethered polymers were collected by removing the solvent under reduced pressure at room temperature and then redissolving in 0.2 mL of chloroform prior to characterization by SEC. For a planar substrate with an area of 20 cm^2 and a reduction in dry polymer film thickness of 50 nm, the concentration of polymer in 0.2 mL of chloroform was approximately 0.5 mg/mL. As PS yielded a strong signal in the UV-detector in SEC, this could be detected at a lower concentration than PLM (Figure 4).

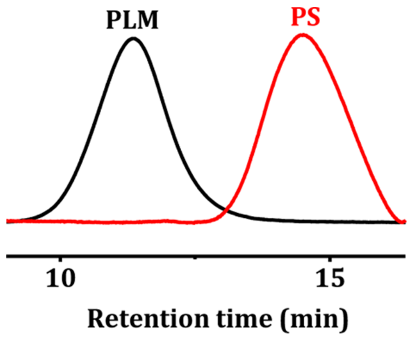


Figure 4. Typical SEC traces of PLM and PS.

Detailed information about the molecular weight of the polymer brushes is presented in Table 1.

The surface coverage Γ (mg/m^2), grafting density Σ (chain/nm^2), and mean distance between polymer chains D (nm) were calculated. The surface coverage Γ (mg/m^2) can be calculated from the dry thickness of polymer brushes h (nm) by means of eq 1:[13]

$$\Gamma = \rho \times h \tag{1}$$

where ρ (1.05 g/cm^3) and ρ (0.897 g/cm^3)[35] are the densities of polystyrene and poly(lauryl methacrylate), respectively. The grafting density Σ (chains/nm^2) can be determined from eq 2:

$$\Sigma = \Gamma N_A \times 10^{-21}/M_n = (6.023\Gamma \times 100)/M_n \tag{2}$$

where N_A is Avogadro's number and M_n (g/mol) is the number-average molecular weight of the grafted polymer. The

Table 1. SEC Data with Calculated Grafting Density and Mean Chain−Chain Spacing of Polymers Cleaved from Surface[a]

polymer brushes	dry thickness (nm)	$M_n \times 10^5$ (Da)	$M_w \times 10^5$ (Da)	PDI	grafting density (chains/nm^2)	mean chain−chain spacing (nm)
PLM-A-1	217.1 ± 3.5	6.3	11.9	1.9	0.19	2.5
PLM-A-2	215.0 ± 2.6	7.6	15.9	2.1	0.15	2.8
PLM-A-3	220.3 ± 5.2	9.0	18.0	2.0	0.13	3.0
PLM-B-1	120.5 ± 6.3	4.6	7.8	1.7	0.14	2.9
PLM-B-2	125.4 ± 4.4	4.2	6.7	1.6	0.17	2.6
PLM-B-3	118.7 ± 6.4	4.5	7.6	1.7	0.14	2.9
PLM-C-1	57.8 ± 4.9	2.1	3.4	1.6	0.15	2.8
PLM-C-2	55.1 ± 3.4	1.9	2.9	1.5	0.16	2.7
PLM-C-3	60.1 ± 4.7	2.6	4.2	1.6	0.13	3.0
PS-A	41.5 ± 1.2	0.5	0.8	1.6	0.50	1.5
PS-B	47.1 ± 1.9	0.7	1.3	1.9	0.44	1.6

[a] Thickness results are averages of three measurements at different locations on the sample.

distance between grafting sites was obtained with eq 3, assuming that the packing is hexagonal.

$$D = \sqrt{\frac{2}{\sum \times \sqrt{3}}} \tag{3}$$

The results of the calculation of grafting density and average grafting site distance are shown in Table 1. From Table 1, it can be seen that the grafting density did not change significantly as the thickness of the polymer brushes increased from approximately 60 to 210 nm. This indicates that the number of growing chains remained constant and negligible chain termination occurred during the polymerization process, which is consistent with the approximately linear polymerization kinetics (see Supporting Information for details). The PLM brushes are separated by an average distance of about 2.8 nm, which is much larger than PS chain average distance 1.6 nm (Table 1). This difference could be attributed to the longer side chains of PLM compared to PS, which lead to greater steric repulsion.

The molecular weight of PLM was also estimated from the ellipsometric thickness, assuming a swelling ratio of 10 to 15 in nonane.[28] This yields for PLM-A-1, for example, an average height of 2173−3260 nm for the solvated polymer brush. Taking a repeat distance of 0.295 nm per monomer and assuming, for the purposes of establishing a lower limit of M_w, that the brush is completely stretched, this yields an average molecular weight of (1.9−2.8) × 10^6, which is consistent with the values of M_w measured by SEC and slightly higher than the values of M_n (Table 1).

CONCLUSION

It could be shown that the cleavage of polymer brushes from planar silicon surfaces by means of UV-irradiation of a photocleavable SI-ATRP initiator is a convenient method for harvesting grafted polymer chains for molecular weight and polydispersity analysis. This approach allowed 99% of the polymer brushes on the silicon surface to be cleaved off within 2 h. The cleavage kinetics of polymer brushes exhibited linear first-order behavior, composed of two distinct regions that may correspond to a transition in the polymer conformation from “brush” to “mushroom” regimes. Cleaved polymers were collected by removing the solvent under vacuum and analyzing by SEC. The polymer chain grafting density as well as average chain distance remained almost constant, within experimental error, during the polymerization process, which indicates that the number of growing chains remained constant during polymerization. Finally, the much lower grafting density for PLM than for PS could be attributed to the longer side chains of PLM, which result in significant steric interactions that act to separate neighboring chains.

ASSOCIATED CONTENT

Supporting Information

Detailed information about the AFM images of APTES- and PLM-modified silicon surfaces, growing kinetics of polymer brushes, MTR-IR spectra of silane- and initiator-modified surfaces, and UV−vis spectra of initiator in THF. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Fax +41 44 633 10 27; Tel +41 44 632 58 50; e-mail nspencer@ethz.ch (N.D.S).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors express their gratitude to Dr. Thomas Schweizer (ETH Zurich, Switzerland) for his help with the SEC measurements. Funding from the ETH Research Commission is gratefully acknowledged.

REFERENCES

(1) Gennes, D. P. G. *Macromolecules* **1980**, *13*, 1069−1075.

(2) Barbey, R.; Lavanant, L.; Paripovic, D.; Schüwer, N.; Sugnaux, C.; Tugulu, S.; Klok, H. A. *Chem. Rev.* **2009**, *109*, 5437−5527.

(3) Huang, X.; Wirth, M. J. *Anal. Chem.* **1997**, *69*, 4577−4580.

(4) Baum, M.; Brittain, W. J. *Macromolecules* **2002**, *35*, 610−615.

(5) Husseman, M.; Malmström, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424−1431.

(6) Chen, J. K.; Hsieh, C. Y.; Huang, C.-F.; Li, P. M.; Kuo, S. W.; Chang, F. C. *Macromolecules* **2008**, *41*, 8729−8736.

(7) Li, L.; Chen, S.; Zheng, J.; Ratner, B. D.; Jiang, S. *J. Phys. Chem. B* **2005**, *109*, 2934−2941.

(8) Petrie, T. A.; Raynor, J. E.; Reyes, C. D.; Burns, K. L.; Collard, D. M.; García, A. J. *Biomaterials* **2008**, *29*, 2849−2857.

(9) Kobayashi, M.; Terayama, Y.; Hosaka, N.; Kaido, M.; Suzuki, A.; Yamada, N.; Torikai, N.; Ishihara, K.; Takahara, A. *Soft Matter* **2007**, *3*, 740−746.

(10) Pasetto, P.; Blas, H.; Audouin, F.; Boissière, C.; Sanchez, C.; Save, M.; Charleux, B. *Macromolecules* **2009**, *42*, 5983−5995.

(11) Kruk, M.; Dufour, B.; Celer, E. B.; Kowalewski, T.; Jaroniec, M.; Matyjaszewski, K. *Macromolecules* **2008**, *41*, 8584−8591.

(12) Xiang, P.; Petrie, K.; Kontopoulou, M.; Ye, Z.; Subramanian, R. *Polym. Chem.* **2013**, *4*, 1381−1395.

(13) Koylu, D.; Carter, K. R. *Macromolecules* **2009**, *42*, 8655−8660.

(14) Feng, W.; Brash, J.; Zhu, S. *Biomaterials* **2006**, *27*, 847−855.

(15) Turgman, C. S.; Genzer, J. *J. Am. Chem. Soc.* **2011**, *133*, 17567−17569.

(16) Yu, H.; Li, J.; Wu, D.; Qiu, Z.; Zhang, Y. *Chem. Soc. Rev.* **2010**, *39*, 464−473.

(17) Dormán, G.; Prestwich, G. D. *Trends Biotechnol.* **2000**, *18*, 64−77.

(18) Parker, L. L.; Brueggemeier, S. B.; Rhee, W. J.; Wu, D.; Kent, S. B. H.; Kron, S. J.; Palecek, S. P. *Analyst* **2006**, *131*, 1097−1104.

(19) Yan, F.; Chen, L.; Tang, Q.; Wang, R. *Bioconjugate Chem.* **2004**, *15*, 1030−1036.

(20) Wirkner, M.; Alonso, J. M.; Maus, V.; Salierno, M.; Lee, T. T.; García, A. J.; Campo, D. A. *Adv. Mater.* **2011**, *23*, 3907−3910.

(21) Brown, B. B.; Wagner, D. S.; Geysen, H. M. *Mol. Diversity* **1995**, *1*, 4−12.

(22) Li, Z.; Bai, X.; Ruparel, H.; Kim, S.; Turro, N. J.; Ju, J. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 414−419.

(23) Kim, S.; Shi, S.; Bonome, T.; Ulz, M. E.; Edwards, J. R.; Fodstad, H.; Russo, J. J.; Ju, J. *Anal. Biochem.* **2003**, *316*, 251−258.

(24) Lecolley, F. O.; Tao, L.; Mantovani, G.; Durkin, I.; Lautru, S.; Haddleton, D. M. *Chem. Commun.* **2004**, 2026−2027.

(25) Howarter, J. A.; Youngblood, J. P. *Langmuir* **2006**, *22*, 11142−11147.

(26) Zhu, M.; Lerum, M. Z.; Chen, W. *Langmuir* **2011**, *28*, 416−423.

(27) Jönsson, U.; Olofsson, G.; Malmqvist, M.; Rönnberg, I. *Thin Solid Films* **1985**, *124*, 117−123.

(28) Liu, H. B.; Venkataraman, N. V.; Spencer, N. D.; Textor, M.; Xiao, S. J. *ChemPhysChem* **2008**, *9*, 1979−1981.

(29) Bielecki, R. M.; Benetti, E. M.; Kumar, D.; Spencer, N. D. *Tribol Lett.* **2012**, *45*, 477−487.

(30) Bradley, G. M.; Strauss, H. L. *J. Phys. Chem.* **1975**, *79*, 1953−1957.

(31) Paripovic, D.; Klok, H. A. *Macromol. Chem. Phys.* **2011**, *212*, 950−958.

(32) Onclin, S.; Ravoo, B. J.; Reinhoudt, D. N. *Angew. Chem., Int. Ed.* **2005**, *44*, 6282−6304.

(33) Sheiko, S. S.; Sun, F. C.; Randall, A.; Shirvanyants, D.; Rubinstein, M.; Lee, H. I.; Matyjaszewski, K. *Nature* **2006**, *440*, 191−194.

(34) Deng, Y.; Zhu, X. Y. *J. Am. Chem. Soc.* **2007**, *129*, 7557−7561.

(35) Zhao, J.; Xiao, C.; Xu, N.; Ma, X. *Polym. Bull.* **2012**, *69*, 733−746.