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Surface-Grafted, Covalently Cross-Linked Hydrogel Brushes with Tunable Interfacial and Bulk Properties

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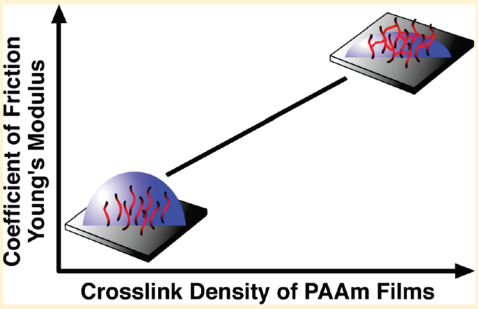
S *Supporting Information*



ABSTRACT: Tethering macromolecules to surfaces represents a versatile approach for functionalizing, protecting, and structuring both organic and inorganic materials. In this study, thin films of poly(acrylamide) (PAAm) brushes and covalently cross-linked hydrogel brushes were grown from iniferter-functionalized silicon substrates by UVLED-initiated photopolymerization and their properties subsequently studied by means of a variety of analytical methods. The employed photografting method allowed the controlled fabrication of very thick films (up to 1 μm) in an aqueous environment, over a period of less than 1 h of polymerization and in the absence of side reactions. PAAm covalently cross-linked hydrogel brushes were prepared by feeding trace amounts of the cross-linker bis(acrylamide) (up to 1.0 wt % of monomer solution) into the reaction vessel. Both bulk and interfacial properties of these polymer films were found to be strongly influenced by lateral cross-linking of the grafted polymer chains. In agreement with theoretical expectations, the decrease of polymer-brush conformational freedom with increasing cross-link density resulted in a substantial increase of film wettability with water. The swelling ratio of the hydrogel brushes, as measured by ellipsometry and atomic force microscopy (AFM), also confirmed the formation of grafted networks and was found to be directly related to the amount of cross-linker in the monomer feed. In addition, the Young's moduli and tribological properties of PAAm brushes and hydrogel brushes were tuned by adjusting the cross-linker concentration. Because of the additional constraint given by the surface tethering of each chain end, intermolecular cross-linking generated very high mechanical stresses within the brush structure. Covalently cross-linked hydrogel brushes thus displayed higher Young's moduli and coefficients of friction, when compared to the grafted polymer-brush analogues. These hydrogel brushes present an opportunity for readily tailoring physical properties, especially as they allow tuning of the physical characteristics of surfaces while maintaining the interfacial chemical composition nearly constant.

INTRODUCTION

Research activity in the synthesis of functional polymer brushes for the modification of surfaces has been growing substantially over the past decade.[1−3] The unique characteristics of these films, such as high polymer grafting density and tunable physicochemical properties, have allowed them to be extensively applied in drug-delivery systems,[4] sensors,[5] antibiofouling surfaces,[6] microfluidic devices,[7] and lubricant films.[8,9]

A novel class of hydrogel thin films is represented by surface-grafted polymer networks (polymer gels or covalently cross-linked hydrogel brushes), which possess not only some of the characteristics of polymer brushes but also tunable swelling and mechanical properties. Polymer gel brushes were previously prepared either *in situ*, by surface-initiated polymerization in the presence of cross-linker,[10] or *ex situ*, by postmodification of presynthesized polymer brushes.[11] These polymer films were subsequently employed as nanoreactors for the controlled synthesis of metal nanoparticles,[12,13] as coatings for electrophoresis[14] or to fabricate quasi-2D polymer objects.[15−17] However, none of the previous studies demonstrated a systematic influence of the degree of cross-linking on interfacial and bulk characteristics of prepared polymer gel brush films.

Hydrogel thin films, covalently grafted on surfaces with variable thicknesses and presenting tunable properties, show great promise as versatile coating materials.[18−20] The precise tailoring of interfacial, tribological, and mechanical properties of films that are otherwise chemically analogous would be a highly desirable asset in the design of novel systems for surface functionalization.

Following this fundamental objective, we report here on the fabrication and characterization of poly(acrylamide) (PAAm) covalently cross-linked hydrogel brushes. These polymer films were prepared by UVLED surface-initiated, iniferter-mediated

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photopolymerization (UVLED-SIMP) on silicon surfaces. PAAm brushes and hydrogel brushes with different properties were synthesized by varying the concentration of cross-linker in the polymerization solution. UVLED-SIMP, which was recently reported by us[21] as a modification of the well-known iniferter-based photografting method,[22,23] enabled controlled grafting of polymers exclusively from precursor-modified surfaces. The narrow UVLED emission spectrum, centered at 365 nm, which does not overlap with the monomer absorption band,[24] ensured selective activation/deactivation of the dithiocarbamate moieties immobilized on the surface and the avoidance of monomer autoinitiation in the aqueous solution.

Iniferter-based photopolymerization has already been reported as a very effective and versatile surface-initiated polymerization approach to the fabrication of polymer brushes with well-defined microarchitectures.[25] In this paper, UVLED-SIMP has been applied to acrylamide monomers, which are known to be challenging in atom transfer radical polymerization (ATRP).[26,27] UVLED-SIMP showed a quasi-living character for the polymerization of PAAm films and was performed under mild conditions and for short periods of irradiation.

The chemical composition of the synthesized PAAm films was investigated by Fourier transform infrared (FTIR) spectroscopy and confirmed a direct correlation between the amount of cross-linker in the feed and the properties of the resulting hydrogel brush layers.

The bulk and interfacial properties of the prepared films were subsequently investigated by a variety of methods, in order to determine the influence of cross-linking within the brush. Static water contact angle measurements (CA), atomic force microscopy (AFM), and ellipsometry were performed to estimate wettability, Young's modulus (E), and swelling ratio (Q), respectively, of the grafted PAAm films. Microtribometry was also employed in order to investigate the tribological properties of the films at the micrometer scale and the influence of lateral cross-linking of polymer chains on the films' lubricating behavior in an aqueous environment.

Analysis of the results showed a substantial influence of cross-linking on the properties of the grafted films. A stiffening of PAAm films due to intermolecular network formation was enhanced by the mechanical stress induced by the surface attachment of each polymer chain. Additionally, the reduced chain conformational freedom within hydrogel thin films—when compared to freely grafted brushes—altered the molecular behavior controlling wettability[28] and friction properties.[11,29,30]

Covalently cross-linked PAAm hydrogel brushes were shown to be versatile and chemically stable polymeric films with highly tunable properties at a nearly constant chemical composition. We believe that surface functionalization with this class of brush layer could represent a promising coating approach for independently tailoring the chemical and mechanical properties of a variety of materials.

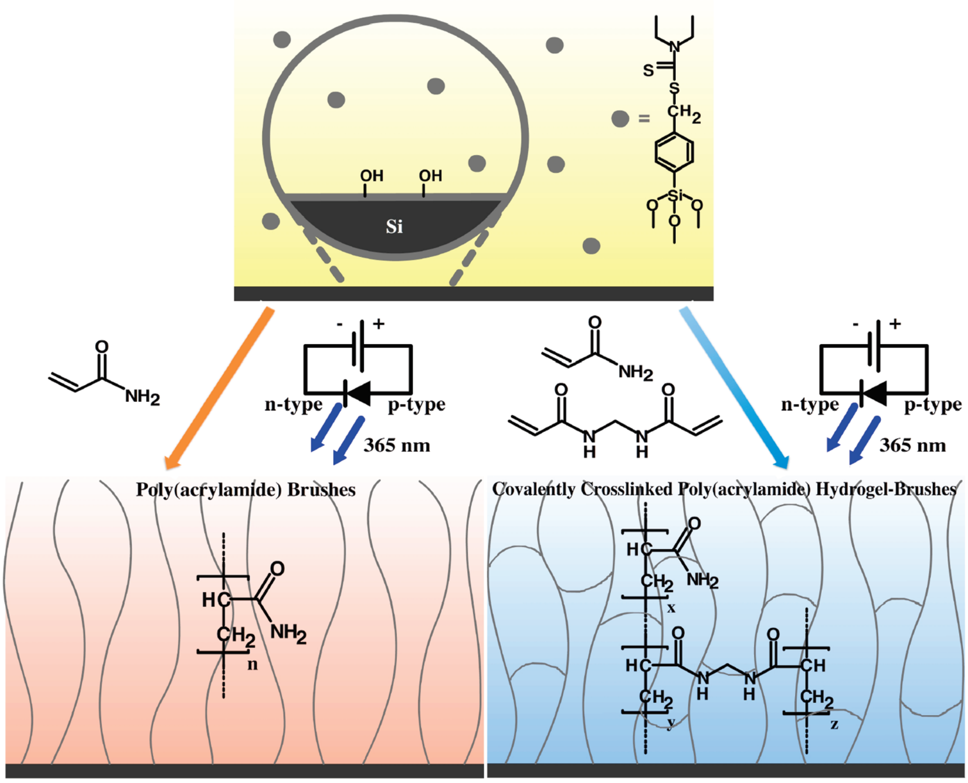
■ EXPERIMENTAL SECTION

Materials. *p*-(Chloromethyl)phenyltrimethoxysilane (ABCR, Germany), acrylamide (99+%, Acros Organics), *N*,*N*′-methylenebis(acrylamide) (>99.0%, Fluka-Chemie AG), tetrahydrofuran (99.5% extra dry, Acros, Germany), toluene (99.85%, Acros), methanol (Fluka, Switzerland), triethylamine (>99.5%, Sigma-Aldrich), sulfuric acid (95−97%, Sigma-Aldrich, Germany), and hydrogen peroxide (30 wt % in water, Merck, Germany) were used as received. Sodium *N*,*N*-diethyldithiocarbamate (97%, Fluka, Switzerland) was recrystallized from methanol. Water was deionized with a GenPure filtration system (18.2 MΩ cm, TKA, Switzerland). HEPES buffer used throughout this study was prepared by adding 1 mM 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES, BioChemika Ultra, Fluka, Switzerland) in Milli-Q water and adjusting the solution pH to 7.4.

Experimental Procedure. Polymer brushes and covalently cross-linked hydrogel brushes were synthesized by grafting polymer chains from the photoiniferter-modified surface under UVLED irradiation. The photoiniferter *N*,*N*-(diethylamino)dithiocarbamoylbenzyl(trimethoxy)silane (SBDC) was synthesized according to a previously reported route.[31] The immobilization of SBDC on the surface was performed by placing the piranha-cleaned silicon wafer (P/B ⟨100⟩, Si-Mat Silicon Wafers, Germany) into a freshly distilled toluene solution overnight with 5 mM SBDC and 2 drops of triethylamine. Piranha solution is prepared by slowly pouring 30% H_2O_2 into 70% H_2SO_4. *This solution is very corrosive, and extreme caution should be taken since it reacts violently with any organic materials.* For the synthesis of polymer brushes or hydrogel brushes, prior to the polymerization, both the acrylamide (AAm) aqueous solution (1 M) with a specific amount of cross-linker *N*,*N*′-methylenebis(acrylamide) (bisAAm) (W_{bisAAm}:W_{water} = 0, 0.1, 0.5, and 1.0) and the flask containing a SBDC-modified wafer were degassed/flushed with N_2 for 15 min, and the degassed monomer solution was then transferred to the substrate-containing flask under a nitrogen atmosphere. The polymerization was started on the SBDC-modified substrate in an aqueous environment under the irradiation of the UVLED setup, which was built in-house and incorporated a LED (NCSU033A, Nichia Corp., Japan) with a narrow emission spectrum at 365 ± 5 nm. The setup incorporated a 5 Ω resistor in series with a fan. The use of the LED guarantees polymerization exclusively on the photoiniferter-modified substrate. An optimized irradiation distance (25 mm) was determined in order to maintain a uniform exposure over the entire substrate (20 mm × 20 mm). The operating voltage and current for the UVLED were fixed at 8.5 V and 0.5 A, respectively. After the polymerization, the polymer-brush- or hydrogel-brush-bearing substrate was rinsed with copious amounts of Milli-Q water and then immersed in water for 2 days in order to remove any entangled or weakly bonded polymers from the surface before further characterization.

Characterization of PAAm Covalently Cross-Linked Hydrogel-Brush Thin Films. The dry thickness of the polymer brushes or hydrogel brushes was determined by a variable-angle spectroscopic ellipsometer (VASE) (M-2000F, LOT Oriel GmbH, Darmstadt, Germany) (relative humidity: 28.4%) at three different incidence angles (65°, 70°, and 75°), under the assumption that the polymer has a refractive index of 1.45. Three different spots were measured on each sample, from which the thickness was determined via the analysis of a three-layer model (software WVASE32, LOT Oriel GmbH, Darmstadt, Germany). Static water contact angles of the dried samples were measured by the sessile-drop method, employing a Ramé-Hart goniometer (Ramé-Hart Instrument Co., Model-100, Netcong, NJ) for the polymer brushes or hydrogel brushes with different dry thicknesses. FT-IR spectra were recorded on the dried samples by employing an infrared spectrometer (Bruker, IFS 66 V) equipped with a liquid-nitrogen-cooled MCT detector. Background spectra were collected by scanning a freshly cleaned bare silicon wafer (P/B ⟨100⟩, Si-Mat Silicon Wafers, Germany).

Morphologies of poly(acrylamide) brushes and hydrogel brushes in a dry state were measured by a Multimode AFM with a NanoScope IIIa controller (Veeco, Santa Barbara, CA) in Tapping Mode at room temperature (24 °C) with a silicon cantilever (Olympus, Japan), which has a resonant frequency of 300 kHz and a spring constant of 26.1 N/m. Contact-mode cantilevers (NP-S10, Veeco, Santa Barbara, CA) were used for the nanoindentation experiments in HEPES buffer, with normal spring constants in the range 0.139−0.219 N/m and tip radii of 12 ± 2 nm. The tip radius was evaluated using calibration samples (NT-MDT, Moscow, TGT01 and NanoScience Instruments, Phoenix, AZ, Scheme 1. General Scheme for Fabrication of PAAm Brushes and Covalently Cross-Linked Hydrogel Brushes



Nioprobe) and the blind estimation technique (Scanning Probe Image Processor, Image Metrology A/S, Hørsholm, Denmark). The spring constant was evaluated with the thermal-noise method (Asylum MFP-3D, Santa Barbara, CA) and with calibration tipless cantilevers (Applied Nanostructures, Santa Clara, CA). The deflection sensitivity of the optical beam-detection system was calibrated on silicon. Loads in the range of 10−50 nN and an indenter rate of 18 μm/s were used in order to measure the moduli via nanoindentation.

Tribological tests were performed by means of a microtribometer (BASALT MUST, Tetra GmbH, Germany), equipped with a stainless-steel cantilever, to which an oxidized PDMS counter surface was attached. The PDMS elastomer counter surfaces were fabricated by mixing a two-part liquid component silicone kit (Sylgard 184, Dow Corning Corp., Midland, MI) (the weight ratio of base and the curing agent of SYLGARD 184 is 10:1) according to the instruction manual of the manufacturer and molding in a commercial polystyrene culture cell plate with spherically curved wells (radius = 3 mm, 96 MicroWell Plates, NUNCLON Delta Surface, Denmark). The PDMS counter surfaces were extracted in *n*-hexane to remove unreacted monomer and afterward plasma treated for 30 s (Harrick plasma cleaner/sterilizer, Ossining, NY) immediately prior to further use. The cantilever attached to the counter surface had a normal force constant of 14.721 N/m and a tangential force constant of 14.752 N/m. The microtribological measurements of PAAm hydrogel thin films were carried out in HEPES buffer with a sliding speed of 0.1 mm/s and a stroke length of 1 mm. Friction force was acquired from the friction loops under varying loads (0.5−3.0 mN) and the coefficient of friction calculated according to the slope of the friction force−applied load plot. Each measurement was carried out over two cycles.

RESULTS AND DISCUSSION

Synthesis and Characterization of PAAm Brushes and Covalently Cross-Linked Hydrogel Brushes. PAAm brushes and covalently cross-linked hydrogel brushes were synthesized by means of UVLED-SIMP initiated by self-assembled monolayers (SAMs) of iniferter-bearing silanes on oxidized silicon surfaces (Scheme 1). Following the incubation of the silicon substrate in a 5 mM solution of (*N*,*N*-(diethylamino)dithiocarbamoylbenzyl-(trimethoxy)silane) in freshly distilled toluene for 24 h, the formation of uniform SAMs of photoiniferter was confirmed by static water contact angle measurements (CA) and ellipsometry. CA values showed an increase from less than 5°, typical for oxidized silicon substrates, to 70 ± 2° after incubation in SBDC solutions. This finding is consistent with the formation of dithiocarbamate-bearing SAMs, as has previously been reported in the literature.[31] In addition, the presence of an organic thin layer with average thickness of 1.1 ± 0.1 nm was confirmed by ellipsometry, also consistent with the formation of uniform SBDC-SAMs.

Surface-initiated, photoiniferter-mediated polymerization (SI-PIMP) has been reported as a successful approach for the controlled grafting of a wide variety of monomers at ambient temperature and in aqueous media.[23,32,33] The mild conditions required for this polymerization technique and the fast growth rates have made SI-PIMP attractive. SI-PIMP is sometimes preferable to ATRP, which has been shown to be less controllable in aqueous environments for the polymerization of acrylamide and often requires high reaction temperatures with the employment of toxic organic solvents.

In this work, acrylamide (AAm) and *N*,*N*′-methylenebis-(acrylamide) (bisAAm) mixtures were photografted from SBDC-SAMs employing a UVLED illumination setup with a narrow emission wavelength (maximum intensity at 365 nm). We recently reported the SIMP of methacrylic acid by UVLED.[21] The very narrow emission spectrum of this source assured the absence of side reactions, such as autoinitiation of the monomer,

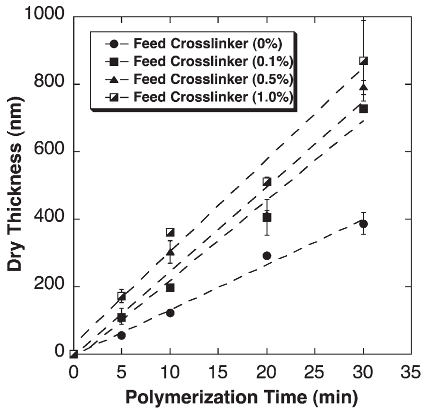


Figure 1. Growth kinetics of PAAm brushes and covalently cross-linked hydrogel brushes. Trends of polymer growth were obtained by linear least-squares fitting. Cross-linker concentration in the feed was varied from 0% to 1.0%.

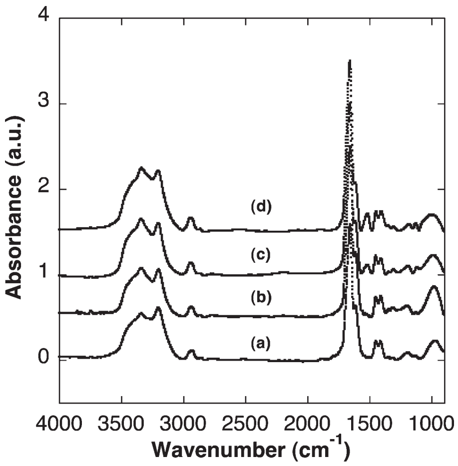


Figure 2. FT-IR spectra of dried PAAm brushes and covalently cross-linked hydrogel brushes with varying amounts of feed cross-linker: (a) PAAm-0 brushes, (b) PAAm-0.1, (c) PAAm-0.5, and (d) PAAm-1.0 hydrogel brushes. Dry thicknesses for PAAm-0, PAAm-0.1, PAAm-0.5, and PAAm-1.0 are 150, 100, 260, and 250 nm, respectively.

in the polymerization solution. This last phenomenon was recently reported to limit the maximum film thickness achievable during SIMP and caused gelation of the polymerization medium after long irradiation times. The absence of self-initiation also reduces radical recombination, and thus UVLED-SIMP shows faster film-growth rates when compared to systems employing UV sources with broader emission spectra.[34]

The film-growth rates for PAAm brushes and hydrogel brushes grafted by UVLED-SIMP were investigated by *ex situ* ellipsometry after drying. In Figure 1, the dry thickness of PAAm films is plotted as a function of irradiation time. Different bisAAm feed concentrations were used for the polymerization: 0%, 0.1%, 0.5%, and 1.0%, film samples being denoted as PAAm-0, PAAm-0.1, PAAm-0.5, and PAAm-1.0, respectively. For all feed concentrations studied, very thick films ranging from 400 to 800 nm could be obtained within 30 min of irradiation. In all cases, the film growth rates followed a linear trend while the addition of bisAAm in the feed solutions led to an increase in the polymerization rates.

Linear film-growth rates confirmed the quasi-living character of UVLED-SIMP, which has been previously observed for iniferter-mediated polymerization.[31] According to Metters et al.,[35] who studied the kinetics of SIMP in the case of methyl methacrylate, film-growth rates were proportional to the propagation rate constant, the monomer concentration, and the local concentration of surface-attached macroradicals. The linear trends observed for UVLED-SIMP of AAm/bisAAm systems thus implied negligible termination and chain-transfer reactions during the studied time period. Since the concentration of both monomer and growing radicals could be considered to be constant during polymerization, the faster film-growth kinetics upon addition of bisAAm are ascribed to a higher reactivity of the cross-linker, in comparison to acrylamide.[36]

FTIR analysis of PAAm brushes and hydrogel brushes was performed in order to determine the chemical composition of the films upon variation of AAm/bisAAm feed ratios. The FTIR spectra profiles displayed in Figure 2a−d for PAAm brushes and hydrogel brushes with 0.1, 0.5, and 1.0% of feed bisAAm were found to be very similar in all cases. The strong bands at 3338 and 3200 cm^{-1} are related to N−H asymmetric and symmetric stretching of the NH_2 repeat unit, respectively. The strong peaks originating from the amide I band after Lorentz fitting were found at 1655, 1672, and 1688 cm^{-1}, and the amide II band[37,38] was found at 1609 cm^{-1} (see Supporting Information for details).

Besides the characteristic absorption peaks of PAAm, addition of bisAAm in the feed with consequent cross-linking of the brushes was revealed by the appearance of a small absorption peak at 1520 cm^{-1}, which corresponds to the N−H bending (amide II band) of secondary amide in the cross-linker. The intensity of this peak increased with the relative concentration of bisAAm in the films. In order to estimate the cross-linker content inside the films with respect to the corresponding concentration in the feeds, the area of the 1520 cm^{-1} peak was compared to the areas of the signals between 1560 and 1760 cm^{-1}. The ratio of integral area of amide II of cross-linker to the sum of the integral area of amide I and II bands of monomer and cross-linker was used to obtain a calibration master curve, which finally allowed extrapolation of the relative content of bisAAm in the films. For each feed concentration, the corresponding bisAAm content in the brush films was thus derived (see Supporting Information for details). As expected, due to the higher reactivity of bisAAm, compared to AAm, a preferred incorporation of cross-linker in the films was found in all cases. The bisAAm content varied linearly from 0.4 to 4.8% for feed bisAAm concentrations ranging from 0.1 to 1.0%.

It could be concluded that due to the similar chemical structures of AAm and bisAAm, the degree of cross-linking of PAAm hydrogel thin films could be tuned without significantly changing the overall chemical composition.

Interfacial Properties of Covalently Cross-Linked PAAm Hydrogel Thin Films. Variation of the degree of cross-linking in surface-grafted PAAm films was expected to strongly influence the interfacial and bulk properties of the fabricated films. In order to investigate whether the lateral network of the grafted chains affected interfacial characteristics of polymer brush surfaces, AFM and static water-contact-angle (CA) analyses were performed, revealing changes in morphology and wettability, respectively, as a function of degree of cross-linking.

Surface morphologies of PAAm brushes and covalently cross-linked hydrogel-brushes with varying amounts of cross-linking were determined by tapping-mode AFM in the dry state. PAAm brush surfaces showed a uniformly smooth morphology and

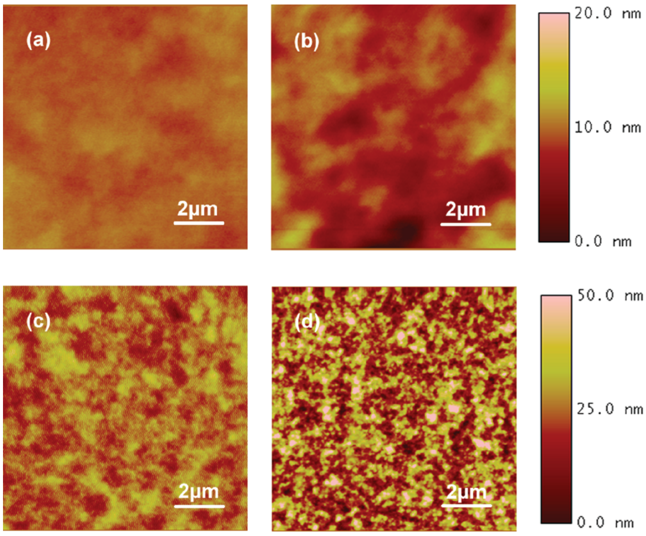


Figure 3. AFM images of dried PAAm brushes and covalently cross-linked hydrogel brushes with varying amounts of feed cross-linker: (a) PAAm-0 brushes, (b) PAAm-0.1, (c) PAAm-0.5, and (d) PAAm-1.0 hydrogel brushes. (a) and (b) share the same height scale bar (0−20 nm); (c) and (d) share the same height scale bar (0−50 nm).

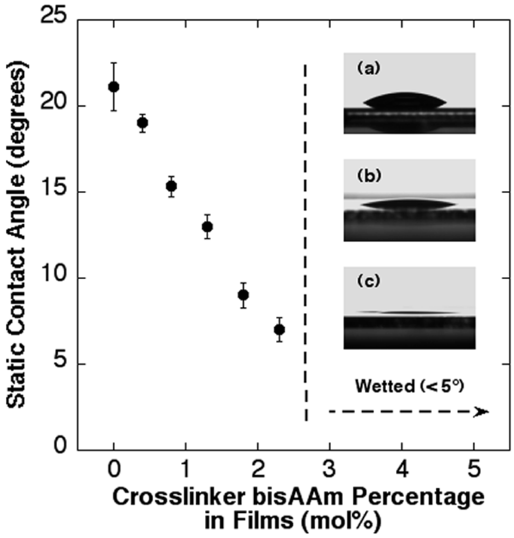


Figure 4. Static contact angles of dried PAAm brushes and covalently cross-linked hydrogel brushes with varying amounts of feed cross-linker. Sessile drops on three different surfaces shown in inset: (a) PAAm brushes, dry thickness: 128 nm with 0% feed cross-linker; (b) PAAm hydrogel brushes, dry thickness: 181.9 nm with 0.3% feed cross-linker; (c) PAAm hydrogel brushes, dry thickness: 146.1 nm with 1.0% feed cross-linker.

presented an average rms roughness of 0.4 nm (calculated over an area of 5 μm × 5 μm, Figure 3a). The addition of cross-linker led to a clear roughening of the dry film surface, presumably due to spatial variations in cross-linking density during polymerization, leading to clustering of the growing chains. Similar clustering effects have been observed upon cross-linking in cast films.[39] The roughness of PAAm-0.1 brush films reached 0.7 nm while in the cases of PAAm-0.5 and PAAm-1.0, values of rms roughness of 3.2 and 5.7 nm, respectively, were found.

In addition to the effects on the surface morphology, the increase of cross-linking also strongly affected the wettability of the resulting polymer films. Surfaces modified with polymer brushes usually show finite contact angle values even when wetted by good solvents. This phenomenon has been reported as being due to a "bridging effect" of the grafted polymer chains at the solvent−vapor interface, which generates partial wetting and nonzero surface pressure.[28] The lateral cross-linking of surface-grafted chains is assumed to strongly hinder chain conformational freedom, thus inhibiting the bridging effect and causing an increase in wettability. To the best of our knowledge, this study experimentally shows, for the first time, the removal of the "bridging effect" by covalent cross-linking of polymer brushes.

By varying the cross-linker concentration in the feed from 0.1 to 1.0% (Figure 4) and monitoring the CA values of the PAAm hydrogel-brush films formed, the breaking of the "bridging effect" could be studied. Un-cross-linked PAAm brushes showed a CA of 22°,[26,27] while addition of cross-linker led to a continuous decrease of CA which, for a bisAAm concentration in the feed of >0.6%, reached below 5°. Thus, "bridging effects" by grafted polymer chains were found to be completely absent above a certain bisAAm content in the films (∼2.8 mol %) and the hydrogel-brush surfaces showed greatly increased wettability compared to freely grafted brush films. For bisAAm feed concentrations in the range 0−0.6%, the surface wettability was precisely tunable as a function of the degree of cross-linking (and thus conformational freedom of brushes) in the prepared films.

It is well-known that the wetting of solid surfaces is influenced by the roughness;[40] however, in this study the significant decrease of the contact angle upon cross-linking cannot be attributed to the small increase of surface roughness (0.4−5.7 nm) according to the predictions of the Wenzel equation (see Supporting Information for details).

Mechanical and Swelling Properties of Covalently Cross-Linked PAAm Hydrogel Thin Films. In order to study how the mechanical and swelling properties of PAAm brushes and covalently cross-linked hydrogel brushes were influenced by the lateral cross-linking of grafted chains, an AFM-based nanoindentation technique was employed.[41,42] As shown in Figure 5, PAAm brush films with different amounts of cross-linker in the feed were indented by an AFM tip, and the characteristic load−penetration depth profiles recorded for all samples, while immersed in buffer solution. PAAm brushes and hydrogel brushes presenting similar dry thicknesses (around 35 nm, as measured by ellipsometry) showed markedly different load−penetration curves, due to the different degrees of swelling for films with different levels of cross-linking. From these profiles, the hydrated thicknesses of PAAm films could be measured as a depth difference between tip−brush contact point (the distance at which the measured force first rises above the baseline) and the region where the underlying substrate was sensed upon further compression (as indicted by a the pronounced increase of the slope of the applied load against penetration depth, since the AFM tip cannot indent the stiff silicon substrate). Since the dry films were shown in independent measurements to possess elastic moduli of ∼10 GPa, the compressed (dehydrated) films may have been too stiff to be indented at large penetration depths, thus leading to an underestimate of the true film thickness and an underestimate of the swelling ratio (see below). PAAm brushes presented a hydrated thickness of 880 nm, while hydrogel brushes, as expected, showed lower values of 300, 190, and 90 nm in the case of PAAm-0.1, PAAm-0.5, and PAAm-1.0, respectively.

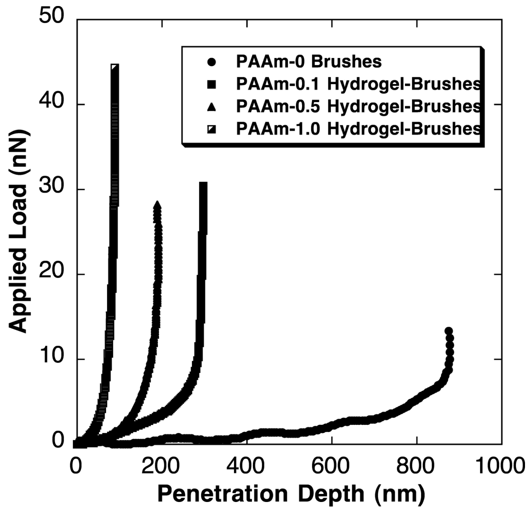


Figure 5. Applied load versus penetration depth curves for PAAm brushes and covalently cross-linked hydrogel brushes in HEPES buffer with varying amounts of feed cross-linker. Dry thicknesses for PAAm brushes and hydrogel brushes with 0.1%, 0.5%, and 1.0% feed cross-linker are 33.9, 38.9, 44.5, and 30.8 nm, respectively.

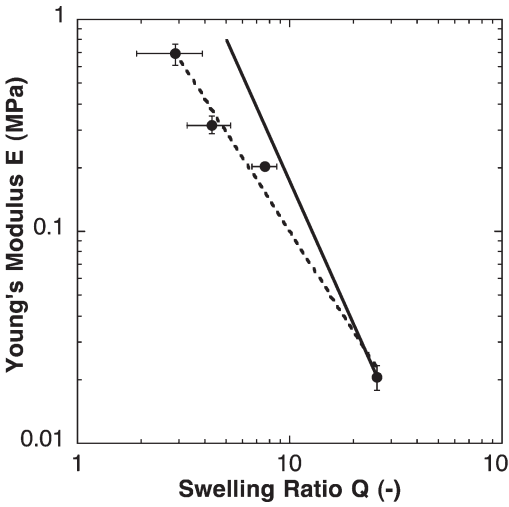


Figure 6. Young's modulus versus swelling ratio for PAAm brushes and covalently cross-linked hydrogel brushes with varying amounts of feed cross-linker. Dashed line denotes $E \propto Q^{-1.57}$ (1D swelling); solid line denotes $E \propto Q^{-2.25}$ (3D swelling); dry thicknesses for PAAm brushes and hydrogel brushes with 0.1%, 0.5%, and 1.0% feed cross-linker are 33.9, 38.9, 44.5, and 30.8 nm, respectively.

Because of the confinement of surface-attached polymer networks, the effective swelling of the films could be considered as being mainly perpendicular to the surface[43,44] and has previously been observed to be larger than the monodimensional swelling of bulk networks at constant cross-linking density.[43] We define the swelling ratio as:

$$Q = V_{\mathrm{sw}}/V_{\mathrm{dry}} = d_{\mathrm{sw}}/d_{\mathrm{dry}} \tag{1}$$

where V_{sw} and V_{dry} are swollen and original volume of unconstrained hydrogel; d_{sw} and d_{dry} are wet and dry thickness of PAAm hydrogel thin films, respectively, measured by AFM and ellipsometry.

PAAm brushes were thus shown to swell profusely when immersed in a good solvent ($Q = 25.9 \pm 1.0$). The lateral cross-linking of the hydrogel brushes effectively decreased the hydration of PAAm films, as previously reported by the groups of Rühe and Hilt.[44,45] The presence of even a small degree of cross-linking, e.g. for PAAm-0.1, led to a 70% decrease in the swelling ratio of the PAAm brushes ($Q = 7.7 \pm 1.0$). Further addition of cross-linker turned the films into rather rigid structures, which were far less capable of incorporating water into their structures. PAAm-0.5 and PAAm-1.0 showed very low values of Q: 4.3 ± 1.0 and 2.9 ± 1.0, respectively.

The Young's moduli (E) of PAAm brushes and hydrogel brushes were evaluated according to Sneddon's model[42] from the region of the force curves corresponding to penetration depths smaller than 10 nm, in order to avoid substrate effects. The values of E are reported in Figure 6, where they are correlated with the corresponding swelling ratios Q of the films. In general, the elastic moduli of PAAm brush and hydrogel-brush films were found to lie within the range 20−700 kPa, comparable with reported moduli for bulk PAAm hydrogels.[46−48]

The Young's moduli for the different brush films could be precisely tuned by varying the amount of cross-linker in the formed films. While PAAm brushes behaved as very compliant films mainly constituted of water, a considerable stiffening of the PAAm hydrogel brushes was observed upon increasing the concentration of bisAAm in the feed.

In the case of isotropic bulk polymeric networks, different Young's moduli have been obtained by varying the equilibrium polymer volume fraction when immersed in a good solvent. According to de Gennes and Candau,[49,50] Young's modulus E and the swelling ratio Q (the reciprocal of the equilibrium polymer volume fraction) scale with an exponent equal to −2.25. However, in contrast to this 3D swelling, the anisotropic 1D swelling of the covalently cross-linked PAAm thin films in this study shows a scaling exponent of −1.57 (Figure 6). It should also be borne in mind that for the un-cross-linked brushes the point of contact is difficult to detect precisely, while for the PAAm hydrogel brushes with a high degree of cross-linking the compressed hydrogel brushes may have become dehydrated, resulting in such a substantial stiffening that the soft AFM cantilevers used could not indent the film completely.

Microtribological Properties of Covalently Cross-Linked PAAm Hydrogel Thin Films. In view of their different physical and morphological properties, PAAm brushes and hydrogel brushes are expected to display different tribological characteristics as the degree of cross-linking is changed. Thus, in order to investigate the influence of cross-linking on the frictional properties of PAAm films, microtribological tests were performed.[51,52]

Microtribological measurements were carried out in aqueous buffer by operating a microtribometer setup with a hydrophilic, oxidized poly(dimethylsiloxane) (Ox-PDMS) spherical counter surface[53] glued to a cantilever with known normal and tangential force constants. The coefficients of friction for PAAm brushes and hydrogel brushes were thus obtained by sliding the cantilever in contact with the films' surfaces at normal loads ranging from 0.5 to 3.0 mN. As shown in Figure 7, the friction coefficient of PAAm hydrogel brushes sliding against a hydrophilic counter surface increased dramatically upon increasing the degree of cross-linking in the films.

The range of contact pressures in the microtribological studies (22.3−40.5 kPa) was too small to produce any wear track that could be discerned by optical microscopy. Thus, it is believed that the dramatic increase in the coefficient of friction is mainly due to

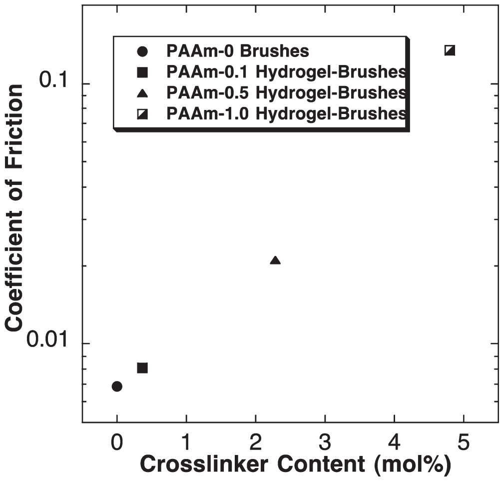


Figure 7. Coefficient of friction of PAAm brushes and covalently cross-linked hydrogel brushes with varying amount feed cross-linker measured by microtribometry against an oxidized PDMS countersurface in HEPES buffer with a sliding speed of 0.1 mm/s and a stroke length of 1 mm. Friction forces were acquired from the friction loops under varying loads (0.5−3.0 mN). Dry thicknesses of PAAm-0, PAAm-0.1, PAAm-0.5, and PAAm-1.0 are 238, 265, 208, and 155 nm, respectively.

the changes in the structure of the thin films upon cross-linking, rather than dissipative processes associated with wear.

We also expect the microtribological properties of PAAm films to be related to the extent to which mobile, brush-forming polymer chains are present in the outermost layer of the films. As the degree of cross-linking increases, the chains are less available for the formation of the highly hydrated brush architecture that has been widely reported to facilitate sliding.[8,9] The decrease in free surface chain concentration has already been discussed above in the context of the wettability results. The degree of swelling is also related to the presence of the brush-forming, free chains: The PAAm-0 brush films presented a swelling ratio value of $Q = 25.9$, which corresponds to 96.1% of water inside a completely brushlike structure. The increase of cross-linking for PAAm-0.1, PAAm-0.5, and PAAm-1.0 films led to a decrease in the water content inside the hydrogel thin layers (water content: 87.0%, 76.7%, and 65.5%, respectively). As the brush formation became less pronounced upon cross-linking, brush-induced lubrication was hindered, leading to an increase of friction coefficient. A similar contrast in macroscopic lubrication behavior for gels with and without brush termination has been reported by Gong.[29,30]

■ CONCLUSIONS

Poly(acrylamide) (PAAm) brushes and covalently cross-linked hydrogel brushes with various amounts of cross-linker were successfully synthesized by UVLED surface-initiated in-iferter-mediated photopolymerization (UVLED-SIMP) from SAMs of photoiniferter immobilized on oxidized silicon surfaces. The employment of a UVLED guaranteed that photopolymerization occurs exclusively at the photoiniferter-modified surfaces. Addition of cross-linker dramatically increased both the film-growth rate and the dry roughness without significantly altering the chemical composition of the hydrogel thin films. Lateral cross-linking of the PAAm brushes was demonstrated to strongly determine the interfacial properties of the fabricated films to an extent that was directly related to the amount of cross-linker in the monomer feed. A marked increase in wettability for hydrogel brushes was attributed to the lateral networking of grafted polymer chains, which eliminated their “bridging effect” at the solvent−vapor interface.

The bulk properties of the PAAm brush films could also be tailored by varying the amount of cross-linker in the feed. Young’s moduli and swelling ratios of the PAAm hydrogel thin films, measured by AFM, varied from the typical values for profusely swollen and compliant brushes to values characteristic of “stiff” bulk gels, as the lateral cross-links were introduced. Finally, microscale tribological measurements demonstrated that frictional properties of PAAm films were modified by the addition of cross-linker. PAAm brushes behaved as highly effective lubricating films when immersed in an aqueous environment. In contrast, hydrogel brushes showed an increase in the coefficient of friction with increasing amounts of cross-links due to the progressive elimination of the lubricious brush structure coupled with the reduction of the water content of the films.

In conclusion, a fine control over wettability, water content, and mechanical and tribological properties of PAAm hydrogel brushes was demonstrated. A relatively straightforward fabrication method based on UVLED-SIMP provides an attractive polymeric platform displaying the advantages of a polymer brush layer together with the versatility of bulk gel materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed description on the integration of the IR bands, calibration of cross-linking degrees, the influence of surface roughness on the contact angle and microtribology of PAAm films. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Milner, S. T. *Science* **1991**, *251*, 905.

(2) Advincula, R. C.; Brittain, W. J.; Caster, K. C.; Rühe, J. *Polymer Brushes: Synthesis, Characterization, Applications*; Wiley-VCH: Weinheim, Germany, 2004.

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

(4) Motornov, M.; Tam, T. K.; Pita, M.; Tokarev, I.; Katz, E.; Minko, S. *Nanotechnology* **2009**, *20*, 434006.

(5) Fries, K.; Samanta, S.; Orski, S.; Locklin, J. *Chem. Commun.* **2008**, 6288.

(6) Ma, H.; Hyun, J.; Stiller, P.; Chilkoti, A. *Adv. Mater.* **2004**, *16*, 338.

(7) Ionov, L.; Houbenov, N.; Sidorenko, A.; Stamm, M.; Minko, S. *Adv. Funct. Mater.* **2006**, *16*, 1153.

(8) Chen, M.; Briscoe, W. H.; Armes, S. P.; Klein, J. *Science* **2009**, *323*, 1698.

(9) Lee, S.; Spencer, N. D. *Science* **2008**, *319*, 575.

(10) Huang, W. X.; Baker, G. L.; Bruening, M. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 1510.

(11) Loveless, D. M.; Abu-Lail, N. I.; Kaholek, M.; Zauscher, S.; Craig, S. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 7812.

(12) Benetti, E. M.; Sui, X. F.; Zapotoczny, S.; Vancso, G. J. *Adv. Funct. Mater.* **2010**, *20*, 939.

(13) Wang, J. Y.; Chen, W.; Liu, A. H.; Lu, G.; Zhang, G.; Zhang, J. H.; Yang, B. *J. Am. Chem. Soc.* **2002**, *124*, 13358.

(14) Huang, X. Y.; Doneski, L. J.; Wirth, M. J. *Anal. Chem.* **1998**, *70*, 4023.

(15) Edmondson, S.; Huck, W. T. S. *Adv. Mater.* **2004**, *16*, 1327.

(16) Edmondson, S.; Frieda, K.; Comrie, J. E.; Onck, P. R.; Huck, W. T. S. *Adv. Mater.* **2006**, *18*, 724.

(17) Comrie, J. E.; Huck, W. T. S. *Langmuir* **2007**, *23*, 1569.

(18) Cohen Stuart, M. A.; Huck, W. T. S.; Genzer, J.; Müller, M.; Ober, C.; Stamm, M.; Sukhorukov, G. B.; Szleifer, I.; Tsukruk, V. V.; Urban, M.; Winnik, F.; Zauscher, S.; Luzinov, I.; Minko, S. *Nature Mater.* **2010**, *9*, 101.

(19) Tokarev, I.; Minko, S. *Adv. Mater.* **2009**, *21*, 241.

(20) Tokarev, I.; Minko, S. *Soft Matter* **2009**, *5*, 511.

(21) Heeb, R. E.; Bielecki, R. M.; Lee, S.; Spencer, N. D. *Macromolecules* **2009**, *42*, 9124.

(22) Otsu, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2121.

(23) Rahane, S. B.; Floyd, J. A.; Metters, A. T.; Kilbey, S. M., II *Adv. Funct. Mater.* **2008**, *18*, 1232.

(24) Skelly, N. E.; Husser, E. R. *Anal. Chem.* **1978**, *50*, 1959.

(25) Matsuda, T. *Adv. Polym. Sci.* **2006**, *197*, 67.

(26) Cringus-Fundeanu, I.; Luijten, J.; van der Mei, H. C.; Busscher, H. J.; Schouten, A. J. *Langmuir* **2007**, *23*, 5120.

(27) Cringus-Fundeanu, I.; van der Mei, H. C.; Schouten, A. J.; Busscher, H. J. *Colloids Surf., B* **2008**, *64*, 297.

(28) Cohen Stuart, M. A.; de Vos, W. M.; Leermakers, F. A. M. *Langmuir* **2006**, *22*, 1722.

(29) Gong, J. P.; Kurokawa, T.; Narita, T.; Kagata, G.; Osada, Y.; Nishimura, G.; Kinjo, M. *J. Am. Chem. Soc.* **2001**, *123*, 5582.

(30) Gong, J. P. *Soft Matter* **2006**, *2*, 544.

(31) de Boer, B.; Simon, H. K.; Werts, M. P. L.; van der Vegte, E. W.; Hadziioannou, G. *Macromolecules* **2000**, *33*, 349.

(32) Nakayama, Y.; Matsuda, T. *Macromolecules* **1996**, *29*, 8622.

(33) Nakayama, Y.; Matsuda, T. *Macromolecules* **1999**, *32*, 5405.

(34) Benetti, E. M.; Reimhult, E.; Bruin, J. de.; Zapotoczny, S.; Textor, M.; Vancso, G. J. *Macromolecules* **2009**, *42*, 1640.

(35) Rahane, S. B.; Kilbey, S. M., II.; Metters, A. T. *Macromolecules* **2005**, *38*, 8202.

(36) Baselga, J.; Llorente, M. A.; Hernández-Fuentes, I.; Piérola, I. F. *Eur. Polym. J.* **1989**, *25*, 477.

(37) Lu, X. L.; Mi, Y. L. *Macromolecules* **2005**, *38*, 839.

(38) Schweitzer-Stenner, R. *Vib. Spectrosc.* **2006**, *42*, 98.

(39) Krzeminski, M.; Molinari, M.; Troyon, M.; Coqueret, X. *Macromolecules* **2010**, *43*, 8121.

(40) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988.

(41) Oliver, W. C.; Pharr, G. M. *J. Mater. Res.* **1992**, *7*, 1564.

(42) Tranchida, D.; Kiflie, Z.; Acierno, S.; Piccarolo, S. *Meas. Sci. Technol.* **2009**, *20*, 095702.

(43) Junk, M. J. N.; Berger, R.; Jonas, U. *Langmuir* **2010**, *26*, 7262.

(44) Toomey, R.; Freidank, D.; Rühe, J. *Macromolecules* **2004**, *37*, 882.

(45) Chirra, H. D.; Zach Hilt, J. *Langmuir* **2010**, *26*, 11249.

(46) Matzelle, T. R.; Geuskens, G.; Kruse, N. *Macromolecules* **2003**, *36*, 2926.

(47) Constantinides, G.; Ilke Kalcioglu, Z.; McFarland, M.; Smith, J. F.; Van Vliet, K. J. *J. Biomech.* **2008**, *41*, 3285.

(48) Jacot, J. G.; Dianis, S.; Schnall, J.; Wong, J. Y. *J. Biomed. Mater. Res.* **2006**, *79A*, 485.

(49) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(50) Candau, S.; Bastide, J.; Delsanti, M. *Adv. Polym. Sci.* **1982**, *44*, 27.

(51) LeMieux, M. C.; Julthongpiput, D.; Bergman, K. N.; Cuong, P. D.; Ahn, H.; Lin, Y.; Tsukruk, V. V. *Langmuir* **2004**, *20*, 10046.

(52) LeMieux, M. C.; Lin, Y.; Cuong, P. D.; Ahn, H.; Zubarev, E. R.; Tsukruk, V. V. *Adv. Funct. Mater.* **2005**, *15*, 1529.

(53) Efimenko, K.; Wallace, W. E.; Genzer, J. *J. Colloid Interface Sci.* **2002**, *254*, 306.