

# Hybrid Molecular Brushes with Chitosan Backbone: Facile Synthesis and Surface Grafting

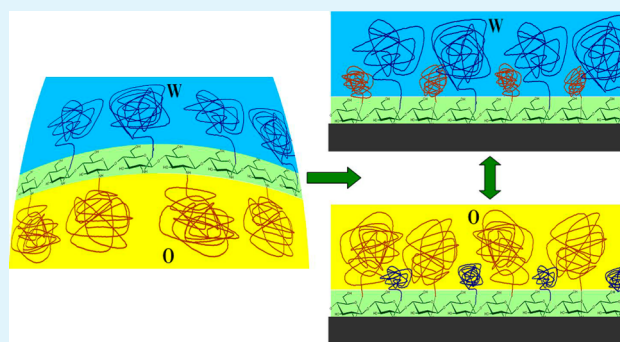
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## S Supporting Information

**ABSTRACT:** We developed a facile route toward amphiphilic hybrid molecular brushes (HMB) with chitosan backbone and concurrently grafted chains of poly(acrylamide) and polystyrene. The grafting occurs through amino groups of chitosan; no extra modification of chitosan is required. The kinetic and molecular weight characteristics of the primary molecular brush CHI-graft-PAAm are studied. The second step is grafting of PS by emulsion polymerization. The resulting HMB CHI-graft-PAAm-graft-PS form very stable emulsions. We attached the HMB on solid substrates using chitosan backbone by the “grafting to” approach. Thin films of the immobilized HMB of 3–11 nm thickness completely cover the surface. Being amphiphilic by nature, the immobilized HMB reveal the ability to adapt to the medium, which results in shifting of the hydrophobic/hydrophilic balance over a wide range.

**KEYWORDS:** molecular bottlebrush, graft copolymers, chitosan, switchable surfaces, emulsion polymerization, comb copolymers



## INTRODUCTION

Molecular brushes are macromolecular constructs composed of a polymeric backbone and side-chains. The advances in fundamental studies and application aspects of molecular brushes were the focus of several reviews.<sup>1–3</sup> A variety of approaches have been adopted to allow for the preparation of molecular brushes. The three main synthetic strategies are as follows: (1) “grafting through”, that is, polymerization of macromonomers through their terminal functionality,<sup>4–14</sup> (2) “grafting onto” synthetic route, which comprises the reaction of a polymer backbone that contains functional groups on each monomer unit and complementary end-functionalized polymers,<sup>1,15–20</sup> and (3) “grafting from” synthetic route, which begins with the preparation of a macroinitiator that has a predetermined number of initiation sites; these initiation sites are used to initiate polymerization of the side-chains.<sup>21–23</sup> Each of these synthetic methods governs different structural parameters of the resulting molecular brush. These parameters include chemical composition, degree of polymerization of the backbone, degree of polymerization of the side-chains, and grafting density.<sup>1,24</sup> For the scope of this Article, of particular interest are hybrid molecular brushes (HMB). HMB are similar to traditional molecular brushes; however, the side-chains of HMBs are composed of more than one polymer.<sup>25–27</sup> The theory and fundamental approaches of molecular brushes were developed in the late 1990s and the 2000s.

In concurrence with molecular grafting in solution, the methods of chemical modification of solid substrates with polymer chains were intensively studied. Densely grafted polymer monolayers exhibiting extended conformation are

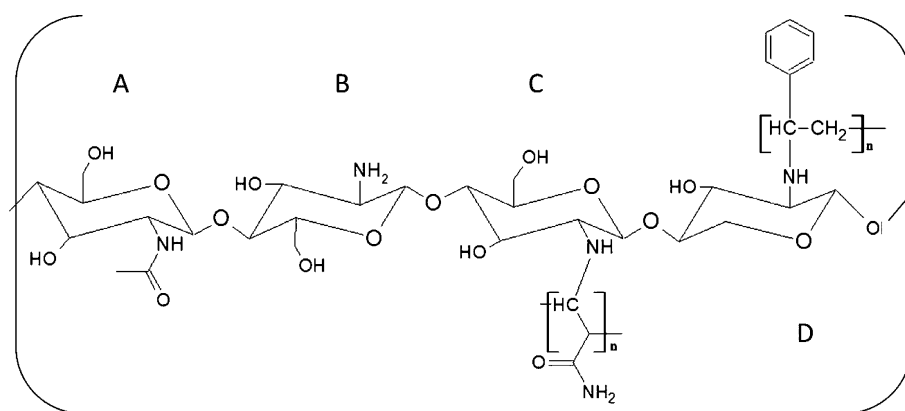
called polymer brushes. Similar to molecular brushes, there are three main approaches toward polymer brushes. The “grafting from” technique involves deposition of initiating sites on the substrates followed by radical polymerization from these sites.<sup>28</sup> A similar approach consists of the attachment of double C=C bonds, whereas the polymerization is initiated in bulk; growing radicals that reach the surface are attached by “grafting through” these bonds.<sup>29,30</sup> In the case of “grafting to”, polymers are attached to the surface, usually by “click-chemistry” reactions.<sup>31,32</sup> If two different polymers are concurrently grafted to the substrate (binary polymer brush), the system can be capable of reversible switching.<sup>33,34</sup> This occurs when one of the polymers occupies the top stratum of the brush, while another one is collapsed and hidden at the interface. Such conformational changes can be facilitated by the medium (good solvent for one polymer and nonsolvent for another), temperature, pH, etc.<sup>34–36</sup>

This work combines two approaches, that is, molecular brushes and polymer brushes. The main idea is to prepare a HMB composed of two strongly immiscible (polar and nonpolar) polymer side-chains and permanently immobilize them via the backbone to a solid substrate. As a backbone we use chitosan (CHI), the partially deacetylated derivative of chitin (Figure 1, A units only). A molecule of CHI can be seen as a random copolymer of D-glucosamine (Figure 1, B units) and N-acetyl-D-glucosamine (Figure 1, A units, approximately

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**Figure 1.** Molecular structure of chitosan-based hybrid molecular brush. The backbone of CHI consists of two units: *N*-acetyl-*D*-glucosamine (A, approximately 15%) and *D*-glucosamine (B). Grafting of hydrophilic polyacrylamide (C) and hydrophobic polystyrene (D) results in amphiphilic HMB.

15%). CHI reveals several outstanding features: protonizable amino groups, abundant hydrogen bonds (due to the presence of the amines and hydroxyls), and a number of well-established techniques of modification with polymer chains (i.e., chemical grafting).<sup>37–41</sup> We demonstrate that HMB based on CHI with concurrently grafted polyacrylamide (PAAm) and polystyrene (PS) side-chains are suitable for surface immobilization. Moreover, dense layers of the grafted HMB reveal outstanding reversible switching from polar to nonpolar state and vice versa depending on the medium (solvent).

## EXPERIMENTAL DETAILS AND MATERIALS

**Materials.** The monomers used for our investigations were acrylamide and styrene. Acrylamide (electrophoresis grade, powder) was used without further purification (Sigma-Aldrich). Styrene (grade for analysis, stabilized) was purified using inhibitor remover (Sigma-Aldrich). Ammonium persulfate (APS) and 2,2'-azobis(isobutyronitrile) (AIBN) were used "as is" (Sigma-Aldrich). Chitosan with medium molecular weight (150 kDa according to the vendor), Brookfield viscosity of 200,000 cps, and 85% deacetylation degree (batch no.: MKBC3804) was used without further purification (Sigma-Aldrich). Toluene (ACS reagent,  $\geq 99.5\%$ ), 1,4-dioxane (anhydrous, 99.8%), chloroform (CHROMASOLV, 99.8%), methanol (anhydrous, 99%), dichloromethane (CHROMASOLV, 99.8%), hydrogen peroxide solution 30 wt % (reagent), ammonium hydroxide (35%) (ACS reagent grade, Pharmco), isopropylamine (Sigma), and glacial acetic acid 99.8% (Sigma) were used without further purification, all purchased from Sigma-Aldrich. Si wafers with a native silicon oxide layer (1.6 nm) were purchased from Addison Engineering Inc. Sample surface (silicon, glass, etc.) wafers were cut and sequentially washed with dichloromethane, methanol, and Milli-Q water in an ultrasonic bath for 10 min each. Next, wafers were placed in a mixture of Milli-Q water, ammonium hydroxide (35%), and hydrogen peroxide (30%) in a volume ratio 2:1:1 at 80 °C for 45 min. The wafers were rinsed with Milli-Q water, and blow-dried with argon. An ultrathin (2–4 nm) film of poly(glycidyl methacrylate) (PGMA) was deposited from solution by dip-coating. Mica substrates (grade V1) were purchased from Ted Pella, Inc. Mica was cleaned by Scotch tape to reveal a clean, unused layer; it was used "as is". Argon ultrahigh purity was purchased from Airgas. PGMA was polymerized from its monomer and used as an adhesive layer on Si wafers before depositions as described elsewhere.<sup>42</sup>

**Polymerization.** CHI-*graft*-PAAm was polymerized by preparing a 1% acetic acid/1% CHI aqueous solution and a solution of acrylamide (with desired concentration)/1.0% ammonium persulfate aqueous solution. These solutions were combined in a round-bottom flask in a 1:1 volume ratio. The flask was purged with argon for 5 min and sealed. The flask was then heated at 60 °C for the desired time. The

polymeric fraction was precipitated in methanol three times to remove low molecular weight components. The precipitate was dissolved in water and dried into a film; this film was soaked in 0.5% ammonium hydroxide in DI water to remove unattached PAAm. The film was finally redried in a vacuum oven.

The HMB were synthesized in a two-step procedure. The first step consists of the grafting of PAAm on CHI as described above. For all brushes, the concentration of acrylamide in the reaction mixture was 2.5%. In the second step, the solution of CHI-*graft*-PAAm in water (2.5%, "W" phase) was mixed with styrene solution in toluene ("O" phase) of the desired concentration (in the range of 5–40%), and AIBN (1.0% concentration) was used as the initiator. The phase "W"/"O" ratio was 1:1. The polymerization mixture was purged with Ar for 15 min. The emulsion formation was facilitated by 15 min of sonication and was supported by vigorous stirring during polymerization. The polymerization was performed at 60 °C for 24 h. The resulting emulsion was mixed with toluene (approximately 1:1) for extraction of ungrafted PS and low molecular weight components in a separatory funnel. The extraction was repeated five times.

**Deposition.** For spin-coating depositions, one droplet of polymer solution or emulsion was placed on the substrate so that the entire surface was covered. The droplet was allowed to sit on the substrate for approximately 1 min before spinning at 3200 rpm. For immersion deposition, a silicon wafer was immersed in a vial containing the polymer solution or emulsion. The pH of the emulsion was adjusted by addition of either acetic acid (pH 3.0) or  $\text{NH}_4\text{OH}$  (pH 9.0) when required; the neutral solutions (pH 6.1) were used by default. The wafer remained immersed in the vial for 40 min. The wafer was then removed from the vial and rinsed with DI water for approximately 2 min and acidic water for approximately 2 min. The wafer was finally dried with argon.

**Characterization.** The GPC analysis was performed using a PerkinElmer series 200 and a 785A UV/vis detector set at 210 or 190 nm. The column for aqueous solvents was A4000 by Malvern Instruments. The analysis was done with a flow rate of 1.0 mL/min at 40 °C, and the sample sizes were 40  $\mu\text{L}$ . The GPC system was calibrated against five dextran standards (Sigma-Aldrich) in the range of 1000–670 000 g/mol. The morphology of immobilized molecular brushes and immobilized HMB was investigated with an atomic force microscope (AFM). The instrument used was an Innova (Veeco), tapping mode, cantilever Tap 190-G (Budget Sensors). The AFM images were treated and analyzed using WSxM software.<sup>43</sup> The thickness of the polymer films was measured by a manual null ellipsometer. The instrument was designed and constructed at USciences. The refractive index of the polymer layer was set at 1.50, and the incident angle was  $70^\circ \pm 0.05^\circ$ . FTIR measurements were performed using a Thermo Nicolet Avatar 370 spectrometer. Contact angle measurements were taken using a custom-made setup in regime of sessile droplet.

## ■ SYNTHESIS OF MOLECULAR BRUSHES

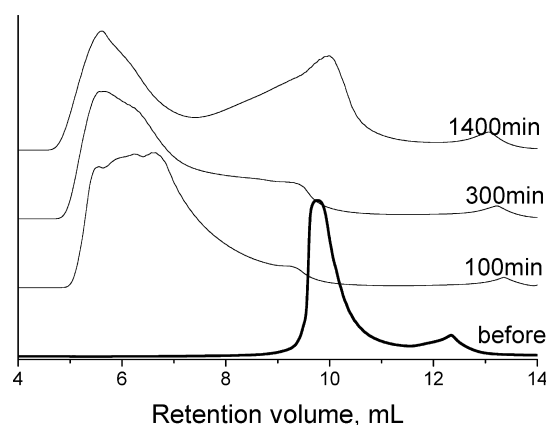
In the classic “grafting from” and “grafting onto” approaches, the key part is modification of the backbone to introduce the functions that facilitate further grafting. Recent discoveries suggest that grafting of polymer chains to CHI occurs directly if radical polymerization is initiated by a persulfate initiator, for example, APS. It makes the grafting process versatile and inexpensive. The mechanism of grafting was proposed by Wang et al.<sup>44</sup> The sulfate radical anion  $\text{SO}_4^{\bullet-}$  extracts a hydrogen from an amino group of chitosan resulting in a  $\text{RNH}^{\bullet}$  radical. The CHI chain serves as a macroinitiator, and the molecular brush is formed according to the “grafting from” mechanism. Syntheses of several graft-copolymers of CHI with polyacrylates and polyvinyls side-chains have been reported.<sup>24</sup>

Our primary side-chain polymer grafted to CHI backbone was PAAm. Successful modification of CHI with PAAm was apparent by the solubility of the product, CHI-*graft*-PAAm. Neat CHI is only soluble in acidic conditions. However, upon polymerization of acrylamide (2.5% w/v monomer concentration) in the presence of CHI, the product is fully soluble in acidic (pH 2.5), neutral (pH 7.0), and basic (pH 12.5) conditions as achieved by additions of concentrated  $\text{NH}_4\text{OH}$ . The fact that no precipitation of the polymerization mixture that initially contained CHI was observed meant that CHI fully converted to CHI-*graft*-PAAm. More evidence of grafting is provided in the Supporting Information (GPC, Raman spectroscopy). When dried, the resulting film of CHI-*graft*-PAAm only swells in water until sonication is applied. We used this property of dried films to extract ungrafted PAAm and low molecular weight components (monomer, initiator). The process of drying/swelling was repeated until the mass of the film was constant. The film was weighted, and grafting yield was estimated according to ref 24. We found that 0.100 g of CHI retained up to 0.140 g of grafted PAAm (total mass 0.240 g of the dried film found). The results reveal a relatively high PAAm yield of 55% (0.250 g of AAm in polymerization mixture initially) and 140% grafting yield.

Gel permeation chromatography (GPC) experiments targeted two aims: evidence for the formation of CHI-*graft*-PAAm brush through an obvious increase in the molecular weight and optimization of the grafting process. The results of the polymerization kinetics measured by GPC are shown in Figure 2 as compared to neat CHI. Formation of a high molecular weight fraction (approximately 300 K g/mol) in a relatively short polymerization time of 1.5 h is clear evidence of multiple grafting of PAAm side-chains. Longer polymerization time results in further increase of the molecular weight of CHI-*graft*-PAAm. Some accumulation of the homopolymer PAAm concurs the grafting to CHI backbone. First appearing as a shoulder, it becomes more evident after 5 h of polymerization (a peak at 9.5 mL of the retention volume, 5000–10 000 g/mol) and even more overwhelming after 24 h. We assume that the molecular weight of the grafted side-chains and free homopolymer is the same. Taking an average molecular weight  $MW_{\text{graft}}$  of CHI-*graft*-PAAm of about 560 K g/mol and  $MW_{\text{homo}}$  of the side-chains of about 15K g/mol (5 h run), simple calculations give about 30 grafted PAAm chains  $N_{\text{PAAm}}$ :

$$N_{\text{PAAm}} = (MW_{\text{graft}} - MW_{\text{CHI}})/MW_{\text{homo}}$$

where  $MW_{\text{CHI}}$  is the averaged MW of CHI, subtracted from MW of CHI-*graft*-PAAm.

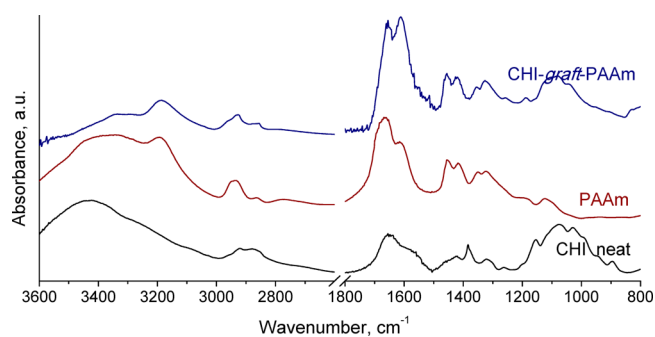


**Figure 2.** Evolution of polymerization mixture traced by GPC. A strong peak of ungrafted CHI at 9.75 mL (“before”) gives way to a broad peak at approximately 6 mL. Significant accumulation of ungrafted homopolymer PAAm (9–10 mL) occurs after 5 h and becomes overwhelming after approximately 24 h.

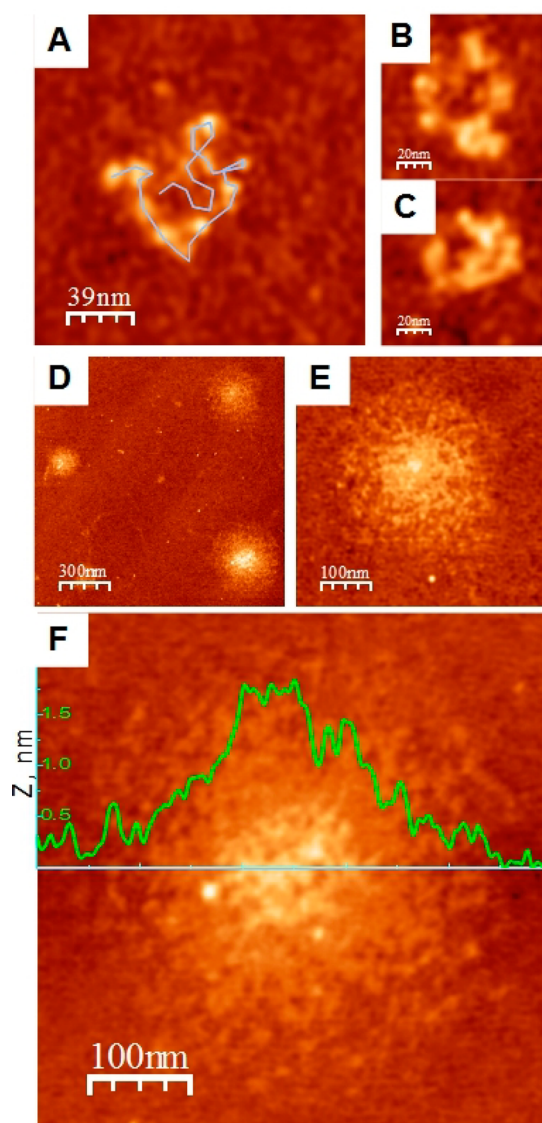
According to the vendor,  $MW_{\text{CHI}}$  is 150 K g/mol. This number deviates significantly from the results of our GPC, which is due to the polyelectrolyte nature of CHI.<sup>45,46</sup> Another possible reason is free radical degradation of CHI by persulfate initiator.<sup>47</sup> The GPC of ungrafted CHI is shown in Figure 2. The distinct peak at retention volume of 9.75 mL associated with ungrafted CHI completely disappears after 1 h, indicating that grafting is fairly efficient. The GPC of CHI-*graft*-PAAm obtained with various concentrations of AAm are presented in the Supporting Information.

Both CHI and PAAm contain many of the same or similar chemical groups: carbonyls, amides, and alkyls. This makes the rational FTIR analysis of CHI-*graft*-PAAm a challenge. Yet, direct comparison of the IR spectra of neat CHI, homopolymer PAAm, and CHI-*graft*-PAAm infers successful grafting of PAAm with the large fraction of the latter. The presence of CHI is obvious by a broad bump ( $900\text{--}1200\text{ cm}^{-1}$ ) in the fingerprint region characteristic for CHI and alteration of the relative intensities of the PAAm peaks at  $1612\text{ cm}^{-1}$  ( $\text{NH}_2$  deformation) and  $1661\text{ cm}^{-1}$  (amide adjacent carbonyl group stretch) (Figure 3).

Single molecules of CHI-*graft*-PAAm were successfully visualized by means of AFM. Figure 4A–C shows molecules of the molecular brush deposited on mica substrate from a diluted solution at pH 3.0. A “necklace” of about 250–350 nm long with 10–20 “beads” is clearly seen on each image. We interpret them as elongated CHI backbones with grafted



**Figure 3.** FTIR spectrum of CHI-*graft*-2.5% PAAm. The spectra of neat CHI and homopolymer PAAm are provided for comparison.



**Figure 4.** AFM images (topography, tapping mode) of CHI-graft-PAAm single molecules deposited on mica at pH 3.0 (A–C, different locations are shown to demonstrate consistency) reveal “necklace” conformation; the same polymer deposited at pH 9.0 (D–F) shows molecules in “spider” conformation. (F) Typical profile (green). The scale bar is shown in the bottom left corner of each image.

“beads” of PAAm side-chains. At low pH values, the backbone is charged and thus exists in an extended conformation due to Coulombic repulsion.<sup>48</sup> In contrast, deposition from solution at pH 10.0 (same sample) shows a different conformation. The backbones of CHI collapse into dense coils of 30–50 nm in diameter due to hydrogen bonds characteristic of CHI. The periphery of each is filled up with chains of grafted PAAm.

### ■ GRAFTING OF HYDROPHOBIC SIDE-CHAINS

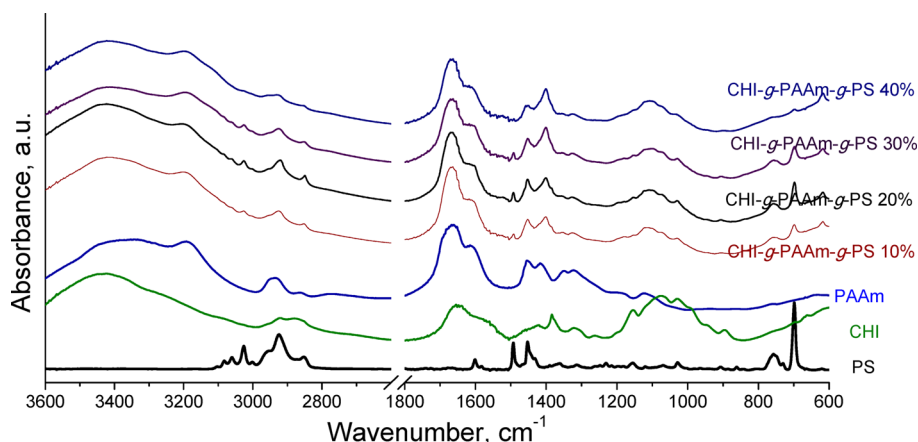
As expected, grafting of PAAm side-chains significantly improves the solubility of the graft copolymer in aqueous solutions. Yet, it is still insoluble in the solvents suitable for grafting of hydrophobic chains. On the other hand, CHI-graft-PAAm reveals strong emulsifier properties. Therefore, we have run grafting of styrene using emulsion polymerization. A similar approach has been successfully used by N. Preda and M. Enculescu for grafting of PS, poly(methyl methacrylate), and

poly(glycidyl methacrylate) to CHI backbone.<sup>49</sup> In our work, we grafted PS side-chains to CHI-graft-PAAm as a secondary hydrophobic graft. We have varied the concentration of styrene in the range of 10–40% while maintaining a constant concentration of CHI-graft-PAAm and O/W phase ratio of the emulsion (1:1). The resulting emulsion contains CHI-graft-PAAm-graft-PS, which is very stable. It shows no signs of separation or degradation after 2 years of bench storage at standard conditions. It is apparent that a significant fraction of PS formed during emulsion polymerization is ungrafted; that is, homopolymerization of PS within the oil droplets competes with grafting onto CHI. Together with unreacted styrene, ungrafted PS separates in the oil (toluene) phase. The presence of ungrafted PS has been revealed by precipitation of PS from the oil phase with methanol. A triple extraction with toluene allows for complete removal of the monomer and ungrafted PS as probed by precipitation of the oil phase into methanol. The DLS characteristics of some HMB emulsions are presented in the Supporting Information. The amphiphilic HMB can be dried in the form of films or flakes. It can also be redispersed in water for further manipulations.

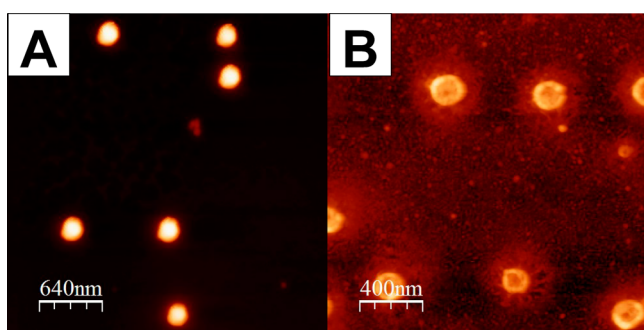
FTIR has been used to confirm successful polymerization of our HMBs. The spectra (Figure 5) reveal that CHI is successfully modified by both PAAm and PS. Successful modification is evident by the appearance of peaks corresponding to both PS and PAAm on the spectra of the HMBs. A strong peak at  $698\text{ cm}^{-1}$  corresponds to aromatic bending in PS; a series of three peaks appearing between  $1400$  and  $1500\text{ cm}^{-1}$  correspond to alkyl chain of both PS ( $1453\text{ cm}^{-1}$ ,  $1493\text{ cm}^{-1}$ ) and PAAm ( $1405\text{ cm}^{-1}$ ,  $1451\text{ cm}^{-1}$ ); peaks appearing between  $2850$  and  $3030\text{ cm}^{-1}$  correspond to the aromatic stretch in PS. The presence of PAAm chains is evident as a broad peak (N–H sym stretch) at  $3195\text{ cm}^{-1}$ , a peak at  $2940\text{ cm}^{-1}$  (alkyl chain stretch), a strong increase in intensity of the peaks at  $1612\text{ cm}^{-1}$  ( $\text{NH}_2$  deformation) and  $1661\text{ cm}^{-1}$  (amide adjacent carbonyl group stretch), and two peaks of medium intensity at  $1415\text{ cm}^{-1}$  (a C–N stretch) and at  $1455\text{ cm}^{-1}$ . Characteristic peaks of both PAAm and PS were present on the FTIR spectra of the HMBs and strongly suggested that CHI was successfully modified by both side-chains (Figure 5).

Noteworthy, the highest fraction of PS chains in HMB corresponds to a moderate level of styrene in polymerization emulsion of about 20–30% of styrene monomer added as evident from the specific PS bands at  $3027$ ,  $1493$ , and  $698\text{ cm}^{-1}$  (result of 5% styrene polymerization is comparable with 40%, the spectrum is not shown here). We associate this observation with the interfacial aspects of emulsion polymerization. In particular, it may depend on the size of the droplets. This is the subject of a separate study, and the results are to be published elsewhere.

The AFM analysis of the HMB dispersions reveals spherical droplets of about 100 nm scale size. Deposited on mica by spin-coating from diluted (approximately 1:10 ratio) dispersions, the droplets are fairly uniform in size and circular in shape (Figure 6A). For example, the statistical analysis of over 200 droplets obtained by deposition of CHI-graft-PAAm-graft-PS25% gives an average height of the features of 120 nm with the standard deviation of 12 nm. The lateral dimensions of these features are very close (130 nm); within the accuracy of lateral size detection (tip broadening effect), we therefore define the particles as spherical. A short time exposure of the same mica sample to toluene (less than a minute) results in a “deflation” of the spheres (Figure 6B). The spheres are uniformly converted



**Figure 5.** FTIR spectra of four different HMB prepared by polymerization of 10%, 20%, 30%, and 40% styrene in toluene in the presence of 2.5% solution of CHI-graft-PAAm, W/O ratio 1:1. The spectra of homopolymers CHI, PAAm, and PS are provided for comparison.



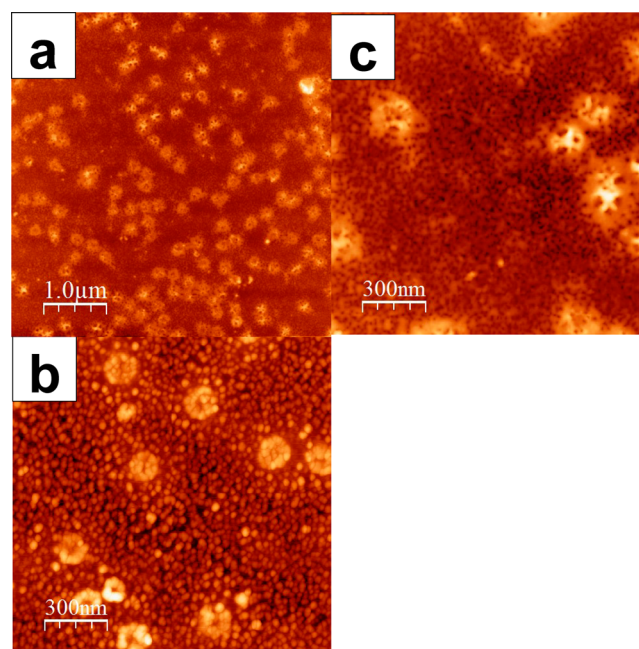
**Figure 6.** AFM images of the emulsion of CHI-graft-PAAm-graft-PS25% deposited on mica: (A) as deposited,  $3.2 \times 3.2 \mu\text{m}$ , vertical scale 140 nm; (B) “deflated” upon rinse with toluene,  $2 \times 2 \mu\text{m}$ , vertical scale 40 nm.

into doughnut-like circular features of 10–20 nm thickness in the center valley and 25–40 nm tall walls; the diameter is approximately 140–150 nm. Apparently, toluene extracts ungrafted PS from the interior while the droplet shells remain on the surface. Such “deflation” has allowed us to reveal the “hairy” outer shell of the “doughnuts”. We associate these projections with PAAm chains grafted to CHI the same as in the case of CHI-graft-PAAm (compare with features in Figure 4D,E).

### ■ HMB FILMS AND SURFACE GRAFTING

The dense (up to a monolayer and thicker) depositions of droplets of HMB emulsions can be prepared by spin-coating of undiluted emulsions on Si wafers and mica samples. Some examples are presented in the Supporting Information, Figure S3. Both spin-casting and dip-coating result in thick featureless films of about 100 nm or thicker. The dried films can be redispersed in hot water (60 °C and above) or sonication. However, if wafers are modified with a thin layer of PGMA, a substantial amount of HMB remains immobilized on the surface. This is achieved due to covalent bonding between glycidyl groups of PGMA and amines of CHI. “Grafting to” approach using PGMA multisite anchoring has been suggested by I. Luzinov et al.<sup>42</sup> and explored in our recent studies.<sup>50</sup> In the case of HMB, the method is robust and facile. The thickness of grafted HMB layers varied in the range of 3–11 nm depending on the pH of emulsion deposited and PS content.

The morphology of grafted HMB is reminiscent of the emulsion. Small circular features (of approximately 100 nm diameter and approximately 10 nm tall) are clearly seen on AFM images of immobilized HMB (film upon exposure to toluene, Figure 7a). We associate them with “deflated” droplets



**Figure 7.** Texture of the immobilized HMB CHI-graft-PAAm-graft-PS 25% as revealed by AFM:  $5 \times 5 \mu\text{m}$  after toluene (a),  $1.5 \times 1.5 \mu\text{m}$  after water (b), and  $1.5 \times 1.5 \mu\text{m}$  after toluene (c).

of HMB emulsions. Yet, the majority of the surface (at least 90% of the area, according to our estimation) represents area rug-like morphology typical for classic polymer brushes (Figure 7b, immobilized HMB upon exposure to water). The dots of the hydrophilic component of the HMB (i.e., PAAm grafts) reach 5 nm in height and are uniformly distributed over the surface. The rms roughness (measured on  $1 \times 1 \mu\text{m}^2$ , AFM digital resolution  $512 \times 512$ ) is 2.3 nm. The contact angle (CA) measurements of grafted HMBs after immersion in water reveal the hydrophilic nature of the surface and vary in the range of 29–32° for different pH values of CHI-graft-PAAm-graft-PS 25% emulsion (Table 1). The exposure of immobilized

**Table 1. Surface Characteristics of Immobilized HMBs: Thickness (Not Including PGMA Anchor Layer), and Contact Angles after Immersion in Water ( $CA_{\text{water}}$ ) and Toluene ( $CA_{\text{tol}}$ ), Measured with Accuracy of  $1^\circ$**

HMB <sup>a</sup>	pH	thickness, nm	$CA_{\text{water}}$ , deg	$CA_{\text{tol}}$ , deg
CHI-graft-PAAm-graft-PS 10%	3.0	2.4 ± 0.4	48	62
	6.1	4.8 ± 0.6	37	78
	9.0	13.7 ± 0.9	48	91
CHI-graft-PAAm-graft-PS 20%	3.0	2.7 ± 0.5	32	65
	6.1	3.5 ± 0.7	21	65
	9.0	2.4 ± 0.6	22	69
CHI-graft-PAAm-graft-PS 25%	3.0	8.8 ± 0.5	29	78
	6.1	11.0 ± 0.5	30	80
	9.0	11.0 ± 0.6	32	87
CHI-graft-PAAm-graft-PS 30%	3.0	3.5 ± 0.4	25	66
	6.1	3.7 ± 0.4	30	65
	9.0	3.0 ± 0.7	26	45

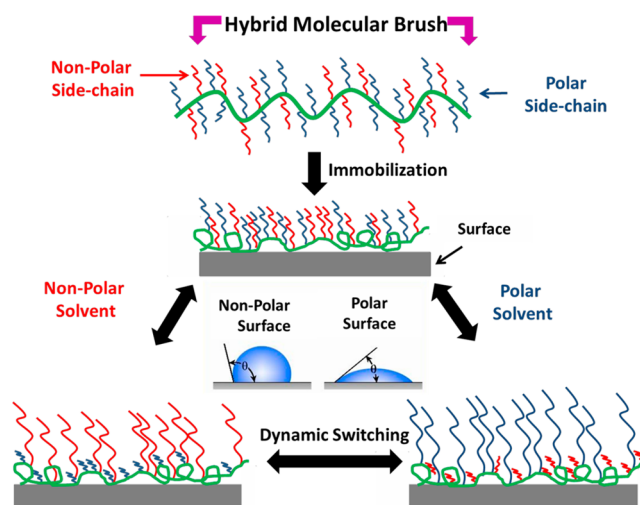
<sup>a</sup>The percentile in the HMB code corresponds to the concentration of styrene monomer used in the polymerization.

HMBs to toluene results in switching of the surface to hydrophobic state (CAs in the range of 78–87° for different pH of depositions, CHI-graft-PAAm-graft-PS 25%). The AFM reveals the associated morphology changes in texture: the toluene-exposed samples (Figure 7c) demonstrate wells of about 4 nm depth. The chemical composition of the top layer therefore is dominated by grafted PS chains. The roughness is substantially decreased down to 1.0 nm (rms roughness, measurement conditions identical to those of Figure 7b).

## DISCUSSIONS

The phenomenon of surface response has been extensively explored. In the classic approach, polymer chains of two polymers A and B are attached to the surface concurrently. When exposed to a selective solvent good for a polymer A, its chains swell and occupy the surface. Meanwhile, the polymer B collapses and remains hindered. Therefore, the surface properties are commanded by polymer A. The switching is reversible and generally requires two steps: exposure to a nonselective solvent good for both polymers (both A and B chains relaxed) followed by exposure to a selective solvent good for B. A variety of systems have been designed with responses in hydrophobic/hydrophilic balance, adhesion, mechanical properties, etc. The essential element required for both classic synthesis and switching is a nonselective solvent good for both polymers. This condition sufficiently restricts the choice of the polymer pair. There are a large number of polymer pairs that are attractive to create switchable surfaces with high contrast, yet there is no common good solvent for them. One such pair is polar PAAm and nonpolar PS. Once combined in HMB, they can be chemically immobilized on the substrate surface, revealing high contrast in hydrophobic/hydrophilic balance (Figure 8).

Yet, the problem of the common solvent should be solved for switching of the immobilized HMB with two strongly immiscible polymer grafts. If a sample with nonpolar polymer on top (PS) is placed directly into polar solvent (water, nonsolvent for PS), the top layer remains on top due to limited mobility of the chains, thus screening hydrophilic chains (PAAm). A similar scenario takes place when we attempt to switch a sample vice versa from the polar state (PAAm on top)



**Figure 8.** Scenario of dynamic switching of an immobilized HMB.

to the nonpolar by a selective solvent good for PS, for example, toluene. The switching may require a very long time if it occurs at all. We overcame this problem by introduction of a common “non-solvent” or a common poor solvent. In the case of our HMBs with grafts of PS and PAAm, we successfully use methanol. In the hydrophobic state, the chains of PS form a top layer. Upon short time exposure to methanol, the chains collapse into an array of condensed coils and coexist with PAAm coils. This conformation is ambivalent and enables either PAAm or PS to occupy the top stratum of the responsive surface.

The presence of two strongly immiscible polymers in HMB unavoidably prohibits solubility of HMBs. However, the form of emulsion allows for easy immobilization of the HMB onto a surface. Chitosan backbone plays a key role in one-step “grafting to” immobilization as opposed to the classic schematic of step-by-step grafting. The result is a facile and very consistent method of surface modification with switchable properties in a wide range.

Another important aspect to be discussed here is the advantages of the general concept of immobilization of amphiphilic copolymer versus the classic approach of step-by-step tethering (either by “grafting from” or by “grafting to”) of polymer chains of different nature concurrently to the solid substrate. Several attempts of grafting of amphiphilic copolymers have been reported recently. V. V. Tsukruk et al. have explored a Y-shape approach.<sup>51</sup> They immobilized a block copolymer of PS and poly(acrylic acid) by grafting its junction group to a functional stem-like segment. The results of Auger electron spectroscopy, micromechanic measurements, and microtribology experiments have proved successful grafting of the Y-shaped brush and switching of the surface composition. However, the CA measurements showed rather a moderate switching in the range of 54–73° at most. These results imply an incomplete switching of the Y-shape construct. A similar approach was explored by S. Minko et al. when a triblock copolymer of PS, poly(2-vinylpyridine), and poly(ethylene oxide) was grafted to the nanoparticles by the middle (PVP) block.<sup>52</sup> The nanoparticles showed an aggregation/dispersion response to the medium. Again, no substantial switch in contact angles was reported for this system.

Very recently, a method of synthesis of and surface modification by another HMB was designed by R. Verduzco

et al.<sup>27</sup> The molecular brush containing both PS and poly(ethylene glycol) was synthesized using a “grafting through” ring-opening metathesis polymerization approach. The reconstruction of the layers and changes in surface chemistry as response to the medium (methanol and cyclohexane as selective solvents for PEG and PS correspondingly) were demonstrated by XPS; again, the CA results revealed a rather minor response of 11° (46.8–58.3°) or less. The authors explained such a modest response by the reduced flexibility of PS chains.

The HMB based on “grafting from” CHI described in the present study shows high consistency and easiness in synthesis, convenient immobilization, and good response to the medium. We associate such high responsive performance with the grafting architecture of the hybrid molecular brush and correct choice of the polymer pair. The effect of common nonsolvent on the surface reconstruction is still not clear and is the subject of our current studies.

We anticipate that HMB may find many applications in different fields. First, the emulsions of HMB combine high stability and functionality of the CHI backbone. This combination of properties may be used for nanoscale size scaffolding, microgel modification, surfactant-free emulsion polymerization, etc. On the other hand, HMB deposited on surface of nanoparticles may serve as the basis for Pickering emulsions due to the amphiphilic character of the HMB. However, its highest potential lies in the modification of planar surfaces. The immobilization of HMB allows for the control of the surface properties, such as surface tension, wettability, and adhesion. One can foresee broad application of HMB for antifouling surfaces, adhesives, anticorrosion films, and other fields.

## CONCLUSION

A series of HMBs with various amounts of PAAm and PS grafted to the chitosan backbone was synthesized by a two-step process. A “grafting from” approach was employed to introduce the hydrophilic polymer, PAAm, to the molecular brush of CHI-graft-PAAm. The hydrophobic polymer (PS) was attached using emulsion polymerization where CHI-graft-PAAm served both as a surfactant and as the grafting substrate. Very stable emulsions were obtained and characterized by DLS and AFM (upon deposition). The deposition of HMB films onto substrates modified by glycidyl groups resulted in immobilized films of HMBs; amino groups of CHI backbone were used for chemical binding. Such films demonstrate strong ability to adapt to both polar and nonpolar mediums, resulting in shifting of the hydrophobic/hydrophilic balance over a wide range.

## ASSOCIATED CONTENT

### Supporting Information

GPC of CHI-graft-PAAm prepared with different concentrations of the monomer; fragments of Raman spectra of neat CHI and CHI-graft-PAAm basic solution; DLS of HMB CHI-graft-PAAm-graft-PS 25% emulsion; and AFM images of several depositions of the same HMB. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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