Articles

Synthesis and Characterization of Surface-Grafted Hyperbranched Glycomethacrylates

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ABSTRACT: Hyperbranched glycopolymers were grafted from a silicon wafer with a covalently attached initiator layer of α-bromoester fragments using self-condensing vinyl copolymerization (SCVCP) of the methacrylic AB* inimer, 2-(2-bromoisobutyryloxy)ethyl methacrylate (BIEM), and a sugar-carrying methacrylate, 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (MAIGlc), via atom transfer radical polymerization (ATRP). The film thickness and characteristic surface morphology were determined using ellipsometry and scanning force microscopy, respectively. The thickness and roughness of the resulting surfaces depend on the catalyst amount and the comonomer ratio, $\gamma = [\text{MAIGlc}]_0/[\text{BIEM}]_0$. A polymer brush of linear polyMAIGlc was also obtained in the presence of a sacrificial initiator via ATRP. Deprotection of the isopropylidene groups of the branched and linear polymer brushes resulted in hydrophilic surfaces as demonstrated by contact angle measurements. The quantitative deprotection was also confirmed by diffuse-reflectance infrared spectroscopy. X-ray photoelectron spectroscopy was further used to determine the surface chemical composition before and after deprotection.

Introduction

The surface properties of inorganic materials can be easily tailored by the preparation of ultrathin films from a variety of polymers. Polymer brushes with desired thickness grafted to or from solid substrates are very useful for a wide range of applications like protective coatings[1] to enhance the biocompatibility of materials[2] and the fabrication of electronic devices.[3] Polymer brushes can serve as smart materials, since they may collectively react to environmental stimuli such changes of the pH or ionic strength, temperature, solvent quality, or mechanical forces.[4,5] Polymer brushes have been prepared from block copolymers where one block is strongly adsorbed to the surface with the other block forming the brush layer.[6] The noncovalent nature of this method can result in low surface coverage and desorption of the brushes from the surface. To circumvent these problems, an increasing amount of interest has been devoted to the covalent attachment of the polymer chains to surfaces so-called "grafting to" approach which was limited by crowding of the chains at the surface hindering the diffusion of chain ends to surface for further attachment.[7,8] The best strategy for the synthesis of high-density and well-controlled polymeric brushes is the "grafting from" approach reported, where the functionalized initiators are covalently attached to the solid substrate, and then linear chains are grown from the surface to give the covalently attached polymer chains using free-radical polymerization.[9,10] Controlled/"living" radical polymerization has gained considerable attention in recent years and is being increasingly employed for the well-defined synthesis of polymer brushes of high grafting density.[11−19]

We have previously demonstrated a novel synthetic approach for the preparation of the hyperbranched (meth)acrylates on a planar solid substrate, in which a silicon wafer grafted with an initiator layer composed of an α-bromoester fragment was used for a self-condensing vinyl polymerization (SCVP) via atom transfer radical polyemerization (ATRP).[20,21] Here, we have adopted a similar strategy toward the one-pot synthesis of hyperbranched glycomethacrylates at the surface of a silicon wafer.

Recently, there has been an increasing attention paid to synthetic polymers with pendant saccharide moieties, so-called glycopolymers, as biological recognition agents.[22] Since carbohydrate-based monomers and polymers confer high hydrophilicity and water solubility, they are of main interest with respect to very specialized applications in biochemical and biomedical fields. Glycopolymers can serve as a model system to study the specific molecular recognition functions of saccharides and to investigate carbohydrate-based interactions.[23−26] Glycopolymers at the cell surface are involved in numerous biological functions like adhesion, cell growth regulation, cancer cell metastasis, and inflammation.[26] They have been used to understand nature's multivalent processes[27] and as well-defined models of cell surface multiantennary glycoproteins.[28] Glycodendrimers have been tested for bacterial adhesion hemagglutination assays.[29]

Here, we report on the synthesis and characterization of surface-initiated self-condensing vinyl copolymerization (SCVCP) of a methacrylic AB* initiator−monomer ("inimer") with the sugar-carrying methacrylate monomer, 3-*O*-methacryloyl-1,2:

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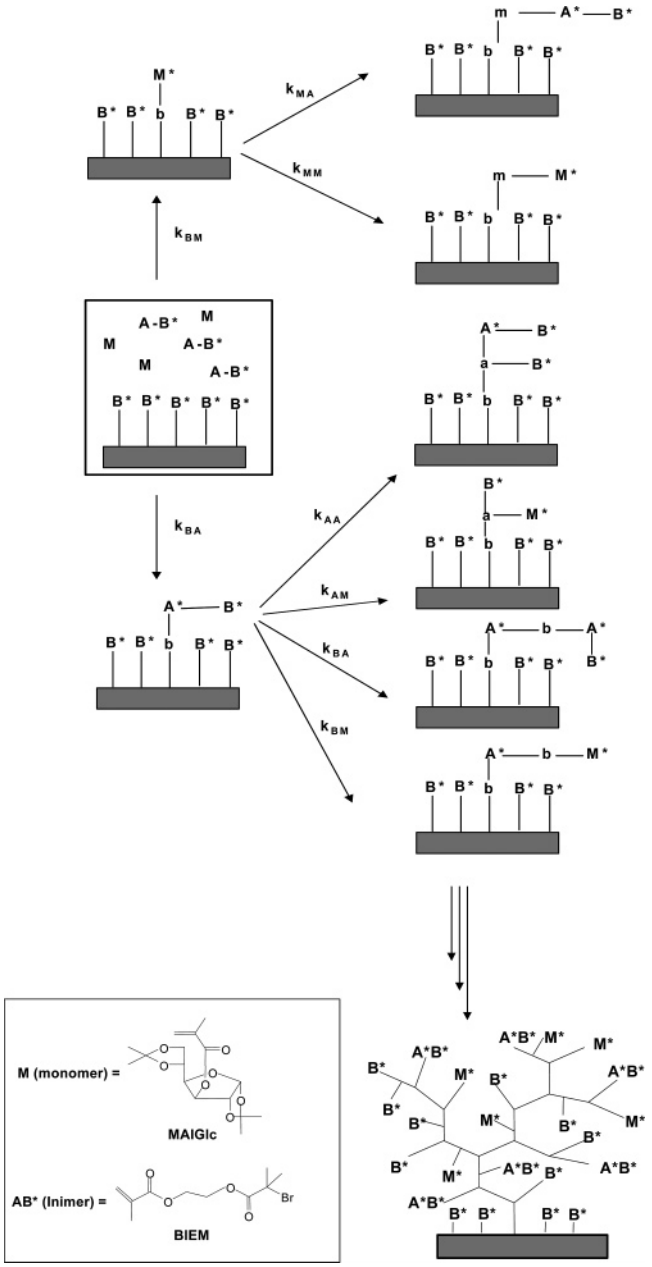
5,6-di-*O*-isopropylidene-α-D-glucofuranoside (MAIGlc), using a silicon wafer functionalized with covalently attached monolayers of initiators for ATRP to synthesize highly branched polyglycomethacrylates at the surface. Such a chemically sensitive surface with a high density of functional groups can be employed for several technological applications like chemical sensing and cellular engineering and can also be used as support materials for combinatorial chemistry. The molecular recognition abilities of these surfaces composed of glycopolymers can be conveniently estimated by measuring the strength of their interactions with appropriate proteins and are useful in the field of surface glycoengineering.[30] Hence, such interfaces can be considered as useful tools for understanding the protein−carbohydrate interactions in terms of molecular and cell recognition abilities of saccharides.

Fukuda et al. reported the grafting of MAIGlc by immobilizing the initiator, 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane, on to a silicon wafer using the Langmuir−Blodgett technique and then used ATRP to obtain surface-grafted linear poly(MAIGlc)s.[15] We have recently reported the synthesis of water-soluble hyperbranched glycopolymers of sugar-carrying acrylate and methacrylate in solution by self-condensing vinyl copolymerization (SCVCP) via ATRP in the presence of CuBr/PMDETA and $(PPh_3)_2NiBr_2$ catalyst systems.[31,32] As a part of our continuous efforts to prepare glycopolymers of different architectures, involving randomly branched, star, and cylindrical brush structures,[31−34] in this work one-step self-condensing ATRP toward the synthesis of branched glycopolymer films of MAIGlc bearing a bulky side group is being reported. Here, we discuss the grafting density, surface morphology, wettability, and chemical composition of the resulting surfaces depending on the comonomer ratio, $\gamma = [\text{MAIGlc}]_0/[\text{BIEM}]_0$. Deprotection of the bulky isopropylidene groups results in hydrophilic surfaces which were further investigated by SFM, ellipsometry, and contact angle measurements. Linear poly(MAIGlc) was also grafted from the surface and characterized thoroughly.

The synthetic approach to hyperbranched glycopolymers grafted from a planar surface is shown in Scheme 1. A silicon wafer grafted with an initiator, B*, for ATRP is used for SCVCP. The inimer is denoted AB*, where A is the methacryloyl group and B* the initiating α-bromoester group of the molecule. The polymerization from the surface can be initiated in two ways (Scheme 1): (i) the addition of the active B* group of the functionalized silicon wafer to the vinyl group A of the AB* inimer forming a dimer with two active sites, A* and B*, and (ii) the addition of a B* group to the vinyl group of monomer M forming a dimer with one active site, M*. Both the initiating B* group and the newly created propagating centers A* and M* can react with any vinyl group in the system. Thus, there are three different types of active centers, A*, B*, and M*, on the silicon surface, which can react with double bonds A (inimer and macromolecules; each macromolecule contains strictly one double bond) and M (monomer). A*, B*, and M* are active radicals, and a, b, and m are respective reacted units. Simultaneously, the B* moieties of the AB* inimer in solution can add to the double bonds of another inimer or of the monomer, leading to soluble hyperbranched polymer molecules. A part of this polymer can later add to active centers of the surface-grafted polymer. However, the growth of the soluble polymers and their attachment to the surface are limited by the intramolecular attack of an active center to the vinyl group ("backbiting"). The one-pot self-condensing ATRP is versatile and can be regarded as a convenient approach toward the preparation of smart interfaces.

Scheme 1. General Route to the Synthesis of Surface-Grafted Hyperbranched Glycomethacrylates



Experimental Section

Materials. Bis(triphenylphosphine)nickel(II) bromide ($(PPh_3)_2NiBr_2$, 99%, Aldrich) and trichlorosilane (Cl_3SiH, 99.9% Fluka) were used as received. Ethyl 2-bromoisobutyrate (EBIB, 98%, Aldrich) was distilled and degassed. 3-*O*-Methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (MAIGlc) was synthesized by the reaction of 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose and methacrylic anhydride in pyridine and purified by vacuum distillation as reported by Klein et al.[35] Synthesis of a methacrylic AB* inimer, 2-(2-bromoisobutyryloxy)ethyl methacrylate (BIEM), was conducted by the reaction of 2-bromoisobutyryl bromide with 2-hydroxyethyl methacrylate in the presence of pyridine as reported previously.[21,36] The inimer was degassed by three freeze−thaw cycles. Other reagents were commercially obtained from Aldrich and used without further purification. The silicon wafers (100) used in this study were 1.2 × 1.6 cm^2 in size and were thoroughly cleaned before use as described before.[21] The preparation of the α-bromoester initiator attached to a silicon wafer was conducted by reaction of (5′-trichlorosilylpentyl) 2-bromo-2-methylpropionate with a silicon wafer as reported by Husseman et al.[16] The

trichlorosilyl α-bromoester, which has reactive species capable of bonding to the surface and a latent α-bromoester, was prepared by reaction of hex-5-enol with 2-bromoisobutyryl bromide, followed by the hydrosilylation reaction with trichlorosilane. The functionalized silicon wafers were stored at room temperature in a drybox and thereafter used for polymerizations.

Polymerization. All the polymerizations were carried out in a round-bottom flask sealed with a plastic cap in the glovebox. A representative example ($\gamma = 1$) is as follows: distilled and degassed BIEM (0.424 g, 1.52 mmol) was added to a round-bottom flask containing the functionalized silicon wafer, $Ni(PPh_3)_2Br_2$ (22.5 mg, 0.0304 mmol) and MAIGlc (0.5 g, 1.52 mmol) in ethyl acetate (50 wt % to MAIGlc). The covered flask was placed in an oil bath at 100 °C. After 1.5 h, the content was very viscous, and the polymerization was stopped by cooling. Conversion of the double bonds as detected by ^{1}H NMR of the ungrafted material was 95%. Then the mixture was dissolved in THF and was passed through an alumina column. The soluble polymer had $M_n = 8500$ and $M_w/M_n = 3.30$ (as determined by GPC/viscosity using universal calibration). Then the wafer was removed from the mixture and rinsed with THF several times followed by dichloromethane. Finally, any adsorbed polymer was removed from the wafer by Soxhlet extraction in THF for 2 days. Then the wafer was dried under nitrogen and stored at room temperature in air.

A typical experiment for homopolymerization of MAIGlc is as follows: ethyl 2-bromoisobutyrate (EBIB; 11.8 mg, 0.0609 mmol) was added to a round-bottom flask containing the functionalized silicon wafer, $Ni(PPh_3)_2Br_2$ (45.0 mg, 0.0609 mmol) and MAIGlc (2.0 g, 6.09 mmol) in ethyl acetate (50 wt % to MAIGlc). The covered flask was then placed in an oil bath at 100 °C for 1.5 h. Conversion of monomer as detected by ^{1}H NMR of the ungrafted material was 75%. The soluble polymer had $M_n = 30\,200$ and $M_w/M_n = 1.29$ (as determined by GPC/viscosity using universal calibration). The ungrafted material was removed in a manner similar to that described above for copolymerization.

Deprotection. The deprotection of the isopropylidene groups of the linear and branched poly(MAIGlc) grafts was performed by dipping the substrates in 80% formic acid for 48 h at room temperature.[15] Then they were washed several times with water and dried in a nitrogen stream. Finally, they were dried at room temperature under vacuum for 24 h.

Characterization. The polymers formed in solution were characterized by GPC using THF as eluent at a flow rate of 1.0 mL/min at room temperature. Molecular weights of the polymers were determined by the universal calibration principle[37] using the viscosity module of the PSS-WinGPC scientific V 6.1 software package. Linear PMMA standards (PSS, Mainz) were used to construct the universal calibration curve. GPC system I; column set: 5 μm PSS SDV gel, 10^3 , 10^5, and 10^6 Å, 30 cm each; detectors: Shodex RI-71 refractive index detector, Jasco Uvidec-100-III UV detector ($\lambda = 254$ nm), and Viscotek viscosity detector H 502B. The polymers bound loosely to the surface were washed with THF and passed through a neutral alumina column to remove the catalyst residues. ^{1}H NMR spectra were recorded with a Bruker AC-250 spectrometer. Topographic images of the grafted substrates were observed by scanning force microscopy (SFM), using a Digital Instruments Dimension 3100 microscope operated in Tapping Mode (free amplitude of the cantilever ≈ 30 nm, set point ratio ≈ 0.98). SFM measurements of the grafted substrates in water were performed on a Digital Instruments Nanoscope III Multimode AFM operated in tapping mode equipped with a 12 μm scanner and a liquid cell. The liquid cell was first cleaned with surfactants and then rinsed with warm water and finally with ultrapure water. Oxide sharpened tips (NanoProbes, Santa Barbara, CA) with a spring constant of 0.3 N/m were used. The average surface root-mean-square roughness (R_{rms}) of the grafted substrates was evaluated using the roughness analysis tool in the Nanoscope III software.

The thickness of the grafted layer was estimated by a Sentech 850 ellipsometer which can determine the ellipsometric angles Ψ and Δ for the whole visible range simultaneously. The measurements were typically performed in the range between 350 and 850 nm and at angles of 40°, 50°, 60°, and 70°. The refractive index of the graft layers used for the evaluation was found by spin-coating a thick layer of the corresponding soluble polymers on the silicon wafer. For the linear polymer brush, a refractive index of 1.429 was obtained. For branched polymers depending upon the comonomer ratio,γ it varied from 1.543 ($\gamma = 1$) to 1.437 ($\gamma = 10$). The thickness was evaluated on the basis of a three-layer model (silicon, oxide layer, and polymer layer). Surface coverage, Γ (mg/m^2), and grafting density, Σ (chains/nm^2), were calculated by eqs 1 and 2, respectively:

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

$$\Sigma = \Gamma N_A/M_n \tag{2}$$

where h is the layer thickness, $\rho = 1.1$ g/cm is the mass density of PMMA, N_A is Avogadro's number, and M_n is the number-average molecular weight.

To estimate the thickness of the swollen polymer layers, spectroscopic ellipsometry was performed by means of a Spectroscopic ellipsometer M-2000VI (Woollam Inc.). The angle of incidence could be set continuously in the range from 45° to 90°. The light source used was a 50-W QHT lamp. M-2000VI measured 500 wavelengths simultaneously covering the spectral range from 370 to 1700 nm. Accurate measurements over the full Δ and Ψ range could be acquired ($\Delta = 0°-360°$; $\Psi = 0°-90°$). Typical measurement times were in the range between 1 and 5 s. A cell for liquid media with deionized water was used for the measurements of the swollen layers.

Diffuse-reflectance infrared Fourier transform (DRIFT) spectra were recorded on a Bruker IFS 66V at a resolution of 2 cm^{-1}, and 256 scans were taken for all the samples. A well-cleaned bare silicon wafer was used as reference in all the cases. Contact-angle measurements were carried out in air by a sessile droplet technique on a Dataphysics, OCA 15 plus instrument (Dataphysics Instruments, GmbH, Germany). The results were evaluated using ellipse fitting.

X-ray photoelectron spectra (XPS) were measured using a Perkin-Elmer PHI 5600 ESCA spectrometer with a monochromatic Mg K X-ray source ($E_{exc} = 1253.6$ eV). The survey spectra (0−1000 eV) were recorded at an analyzer pass energy of 187.85 eV (step width, 800 meV; step time, 20 ms). For detailed spectra, the step width of 25 meV and step time of 100 ms were used. All the spectra were recorded at a takeoff angle of 45°.

Results and Discussion

Synthesis of Surface-Grafted Hyperbranched Glycopolymers. We have previously reported the synthesis and extensive characterization of silicon wafers with surface-functionalized initiators containing an α-bromoester group capable of initiating self-condensing ATRP of AB* inimers.[21] In this study, we have adopted a similar procedure for the functionalization of the silicon wafer toward the synthesis of hyperbranched glycopolymers using SCVCP via ATRP. The conditions for the copolymerizations were adjusted to yield polymers quantitatively (conversion of double bonds as determined by ^{1}H NMR was >90% in all cases). For the synthesis of the surface-grafted hyperbranched glycopolymers with characteristic structure and properties, it is important to adjust the comonomer-to-catalyst ratio, $\mu = ([MAIGlc]_0 + [BIEM]_0)/[(PPh_3)_2NiBr_2]_0$, and the comonomer ratio, $\gamma = [MAIGlc]_0/[BIEM]_0$, because these two parameters affect significantly the degree of branching, molecular weights, and polydispersity of the branched polymers obtained by SCVCP. The influence of comonomer ratio γ is discussed. The effect of the comonomer-to-catalyst ratio, μ, on the thickness, morphology, and grafting density of the grafted polymers is described in the Supporting Information (see also Table 1).

Table 1. Synthesis and Characterization of Surface-Grafted Highly Branched and Linear Glycomethacrylates and Properties of Soluble Polymers[a]

γ[b]	μ[d]	$M_{n,GPC/VISCO}$[e]	M_w/M_n[e]	mean film thickness[f] (nm)	mean roughness[g] (nm)	surface coverage,[h] Γ (mg/m^2)	grafting density,[i] Σ (chains/nm^2)	DB_{theo}[j]	contact angle[k] (deg)
1	100	8 500	3.30	3.0	2.08	3.30	0.23	0.49	
1	200	9 400	3.23	6.7	3.58	7.37	0.47	0.49	80.3
5	200	10 500	2.92	6.5	3.15	7.15	0.41	0.29	73.4
10	200	28 000	1.51	6.0	2.12	6.60	0.14	0.09	67.7
∞[c]		30 200	1.29	12.0	1.79	13.20	0.26	0	78.0

[a] Copolymerization at 100 °C with $(PPh_3)_2NiBr_2$ in the presence of ethyl acetate (50 wt % to MAIGlc). Almost full conversion was reached after 1.5−3 h. [b] $\gamma = [MAIGlc]_0/[BIEM]_0$. [c] Homopolymerization of MAIGlc (50 wt % to ethyl acetate) with ethyl 2-bromoisobutyrate (equimolar to catalyst) as a controlling initiator at 100 °C with $(PPh_3)_2NiBr_2$. [d] $\mu = ([MAIGlc]_0 + [BIEM]_0)/[(PPh_3)_2NiBr_2]_0$. [e] As determined by GPC/viscosity measurement of the polymers formed in solution. [f] Determined by ellipsometry. [g] Determined by SFM. [h] According to eq 1. [i] According to eq 2. [j] Theoretical degree of branching. [k] Obtained by sessile drop method using ellipse fitting.

Surface Topography. The surface topography of the grafted hyperbranched glycopolymers obtained after Soxhlet extraction in THF for 2 days was investigated using tapping mode SFM. Three to four scans were taken at different spots on the sample. Table 1 represents the properties of the soluble as well as grafted polymers obtained. When the copolymerization was carried out with BIEM inimer and MAIGlc monomer at $\mu = 200$ and comonomer ratio $\gamma = [MAIGlc]_0/[BIEM]_0 = 1$ at 100 °C, a viscous polymer was obtained after 1.5 h. The soluble polymer had $M_n = 9400$ and $M_w/M_n = 3.23$ as determined by GPC/viscosity using universal calibration. Theoretical calculations have shown that the molecular weights and molecular weight distributions of the surface-grafted hyperbranched polymers formed by SCVCP are comparable to those formed in the solution.[38] However, we cannot exclude that a hyperbranched polymer molecule formed in solution attaches with its double bond to one of the active centers of a polymer molecule bound to the surface, increasing its molecular weight. This effect is limited by the disappearance of double bonds due to the intramolecular cyclization reaction. Consequently, the molecular weights of the polymers formed in solution can be regarded as lower limits of those formed on the surface, and we do not believe that the difference is extreme.

To clarify the influence of the comonomer ratio, γ, on the grafting behavior, SCVCP of BIEM and MAIGlc was carried out at different comonomer ratios, $\gamma = 1$, 5, and 10, keeping the comonomer-to-catalyst ratio at a constant value of $\mu = 200$. Table 1 summarizes the results of the soluble and grafted polymers obtained by SCVCP. As can be seen from Table 1, the absolute molecular weights of the soluble polymers increase with the increasing comonomer ratio, γ, which confirms earlier reports on SCVCP.[32,39,40] The mean thickness of the resulting polymer films after Soxhlet extraction has a slight dependency only on the comonomer ratio; at $\gamma = 1$ it is 6.7 nm whereas at $\gamma = 10$ is 6.0 nm. As can be seen from Figure 1a,b, protrusions are irregularly distributed throughout the copolymer surface. The roughness of the resulting copolymer surfaces also decreases with the increasing comonomer ratio. The copolymer surface at $\gamma = 1$ (Figure 1a) has smaller but more protrusions when compared to the surface at $\gamma = 10$ (Figure 1b). The increase in the size in the case of $\gamma = 10$ can be due to the accumulation of a higher number of polymer chains. This can also be explained on the basis of the fact that with the increase in the comonomer ratio, γ, the degree of branching, DB, decreases. This implies that the copolymer surface at $\gamma = 10$ has a higher radius of gyration, R_g, and thus shows larger protrusions. Since $R_g \sim DB^{-1/4}M^{0.4}$,[41] this effect cannot be very large but can still contribute to some extent to the increase in the size of the protrusion compared to the copolymer surface at $\gamma = 1$. Thus, the decrease in the number of protrusions can be either due to the overlap with the neighboring protrusions or due to a lower efficiency of the initiating sites on the surface.

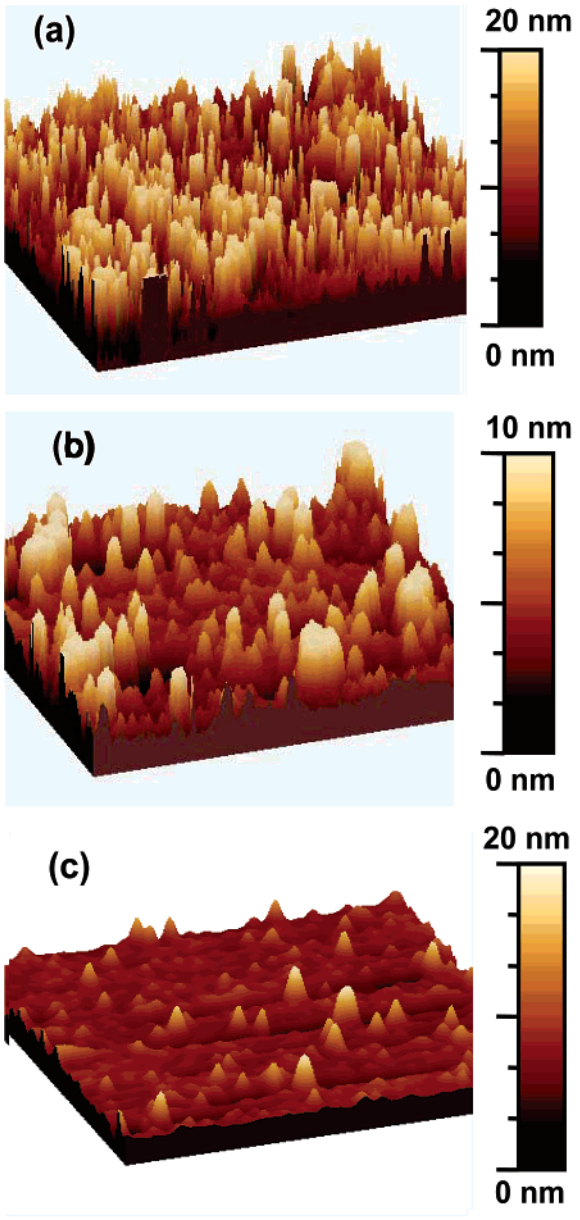


Figure 1. Three-dimensional height images of the grafted polymers obtained from SCVCP of BIEM and MAIGlc at $\mu = 200$ and (a) $\gamma = 1$, (b) $\gamma = 10$, and (c) $\gamma = \infty$ (homopolymerization of MAIGlc). The *X*, *Y* scale is 5 μm.

A lower efficiency of the initiating sites can be the result of the bulkiness of the monomer MAIGlc used in this study. With

the increase in the comonomer ratio, the monomer content of MAIGlc increases in the system, and this can lead to enhanced steric crowding, resulting in the decrease of the grafting density as can be seen from Table 1. These grafting densities must be seen as the upper limits since the M_n values used for their calculation were obtained for the soluble polymer and are regarded as lower limits of the values of the grafted polymers. We have reported a grafting density of 0.39 chains/nm^2 for highly branched PMMA obtained by SCVCP of BIEM and MMA at a comonomer ratio $\gamma = 10$ under similar conditions using the same silicon-functionalized initiator whereas in this study, a grafting density of 0.14 chains/nm^2 is obtained for branched poly(MAIGlc) at $\gamma = 10$, indicating the strong influence of the bulkiness and geometry of the monomer MAIGlc used here. The grafting density decreases drastically from 0.47 to 0.14 chains/nm^2 depending upon the comonomer ratio, which again indicates that with the increase in the content of MAIGlc in the system the grafting density decreases due to the enhanced steric crowding. Another possible explanation is that the rigidity of the glycomonomer in the copolymer with high MAIGlc content is related to the apparent decrease in the grafting density. The significant impact of the bulkiness of the monomer MAIGlc in reducing the initiating efficiency has already being observed in the case of glycocylindrical brushes and glycostars.[33,34]

The homopolymerization of MAIGlc was performed from a functionalized silicon wafer using EBIB as a controlling ("sacrificial") initiator at a $[MAIGlc]_0$:$[EBIB]_0$:$[(PPh_3)_2NiBr_2]_0$ ratio of 100:1:1 at 100 °C. After 1.5 h, the monomer conversion (as determined by ^{1}H NMR) was 75%, resulting in a viscous polymer. The linear poly(MAIGlc) has $M_n = 30\,200$ ($DP_{n,exp} \approx 80$) and $M_w/M_n = 1.29$ (as determined by GPC/viscosity using universal calibration), which is fairly in agreement with $M_{n,calcd} = 24\,600$. In living polymerizations of conventional monomers from surface-grafted initiators, the molecular weight and molecular weight distribution of the grafted polymers are generally assumed to be almost equal to that of polymer initiated by added soluble initiators.[16,42] The added "sacrificial" initiator (EBIB) maintains the ATRP equilibrium between active and dormant chain ends by the generation of sufficient concentration of persistent radicals (deactivators) leading to a controlled polymerization.[12,16] The film thickness obtained after Soxhlet extraction for 2 days is 12.5 nm as determined by ellipsometry. This value is in between the diameter of a random coil ($2R_g \approx 2 \times 0.25$ nm $\times$ DP$^{1/2} \approx 5$ nm) and that of a fully extended chain ($L_c = 0.25$ nm $\times$ $DP_n \approx 20$ nm), indicating a brushlike structure below the maximum brush density ($\Sigma_{max} = 0.7$ chains/nm^2 for linear PMMA brushes as reported by Fukuda et al.[13]). The film thickness should be around L_c if the backbone of the polymer was fully extended. In our study the measured thickness is much less than the expected value which indicates that the polymer film does not consist of fully extended chains. Such observations have already been reported in the literature; even if the measured thickness increases with the reaction time, there are certain discrepancies between the calculated and observed values.[19] The SFM height image (Figure 1c) of this surface-grafted poly(MAIGlc) revealed a relatively uniform and smooth surface with a mean roughness of 1.79 nm. The grafting density of the polymer brushes obtained by homopolymerization of MAIGlc is found to be 0.26 chains/nm^2, which is higher than the value of 0.1 chain/nm^2 as obtained by Fukuda et al. for the synthesis linear poly(MAIGlc) brushes by Cu-based ATRP from a silicon surface functionalized with 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane.[15]

Surface Composition. X-ray photoelectron spectroscopy (XPS) was employed to determine the composition of the branched and linear glycopolymer brushes. The survey scan spectra of the branched copolymer surfaces at $\gamma = 1$, 5 and the linear polymer brush are shown in Figure S-2 (Supporting Information). The survey scan spectrum of the branched copolymer surface at $\gamma = 1$ shows the presence of three elements: oxygen (533 eV), carbon (285 eV), and silicon (150 and 99 eV). Additionally, the bromine peaks assigned to Br_{3d} (70 eV), $Br_{3p1/2}$ (184 eV), and Br_{3s} (278 eV) are also visible. But there are still silicon peaks indicating that the thickness of the layer is smaller than the photoelectron escape depth of about 11 nm.[43] These results are quite comparable to the thickness and surface topography observed by SFM. The atomic composition (45% C and 42% O) of this branched copolymer brush is fairly in agreement with the calculated value (51% C), indicating the successful formation of the branched polymer on the surface. Since the branched copolymer surface at $\gamma = 1$ has a higher degree of branching and thus more end groups, this results in enhancement and enrichment of bromine groups at the surface, which is also clearly confirmed by XPS.

Figure S-2b,c of the Supporting Information depicts that the spectra of the branched copolymer at $\gamma = 5$, and the linear polymer brush shows again C, O, and Si peaks, but in the case of the linear polymer brush, the signal for Si is very weak since the thickness is comparatively higher. For the copolymer surface at $\gamma = 5$, the bromine peak is seen additionally, but the intensity is not as high as in the case of $\gamma = 1$, owing to its lower degree of branching. In the case of the linear polymer brush obtained by ATRP, there is no significant peak for bromine. Such observations were also reported for branched poly(*tert*-butyl acrylate)s where a significant difference in the Br content at the surfaces of the branched and linear polymers was confirmed by XPS.[21]

Deprotection of MAIGlc to MAGlc Units. The deprotection of the isopropylidene groups on the grafted substrates was performed by treatment with 80% formic acid for 48 h at room temperature.[15,32] The thickness of the graft layer after deprotection for a branched copolymer surface at $\gamma = 10$ decreased from 6.0 to 4.6 nm, whereas for the linear polymer brush it decreased from 12 to 11 nm, respectively. The slight decrease in the thickness after deprotection could be due to the decrease in the volume of the polymer, associated with the removal of the bulky isopropylidene groups which may be partially compensated by hydration.

The surface topography of the deprotected brushes was again visualized using SFM. Figure 2 depicts the SFM images obtained for the brush with $\gamma = 10$ and for the linear polymer brush. In the case of $\gamma = 10$, the protrusions are randomly distributed throughout, and the roughness is 1.59 nm (corresponding to 34% of thickness), which is much smaller in *absolute* terms than before hydrolysis (2.12 nm, 38% of thickness) but has the same *relative* value. In the case of the linear polymer brush, the surface roughness is 1.50 (13.5% of thickness), which is comparable to that before hydrolysis (1.79, corresponding to 14% of thickness).

To investigate the swelling behavior of the grafted polymer layers in water after deprotection, ellipsometry measurements in water using a cell for liquid media was performed. As can be seen from Table 2, for the branched copolymer surface at $\gamma = 10$, the thickness of the polymer film increased from 4.6 nm (dry state) to 29.9 nm under water, indicating a significant amount of swelling. In the case of the linear brush, the thickness increased from 11 nm (dry state) to 19 nm (close to its contour

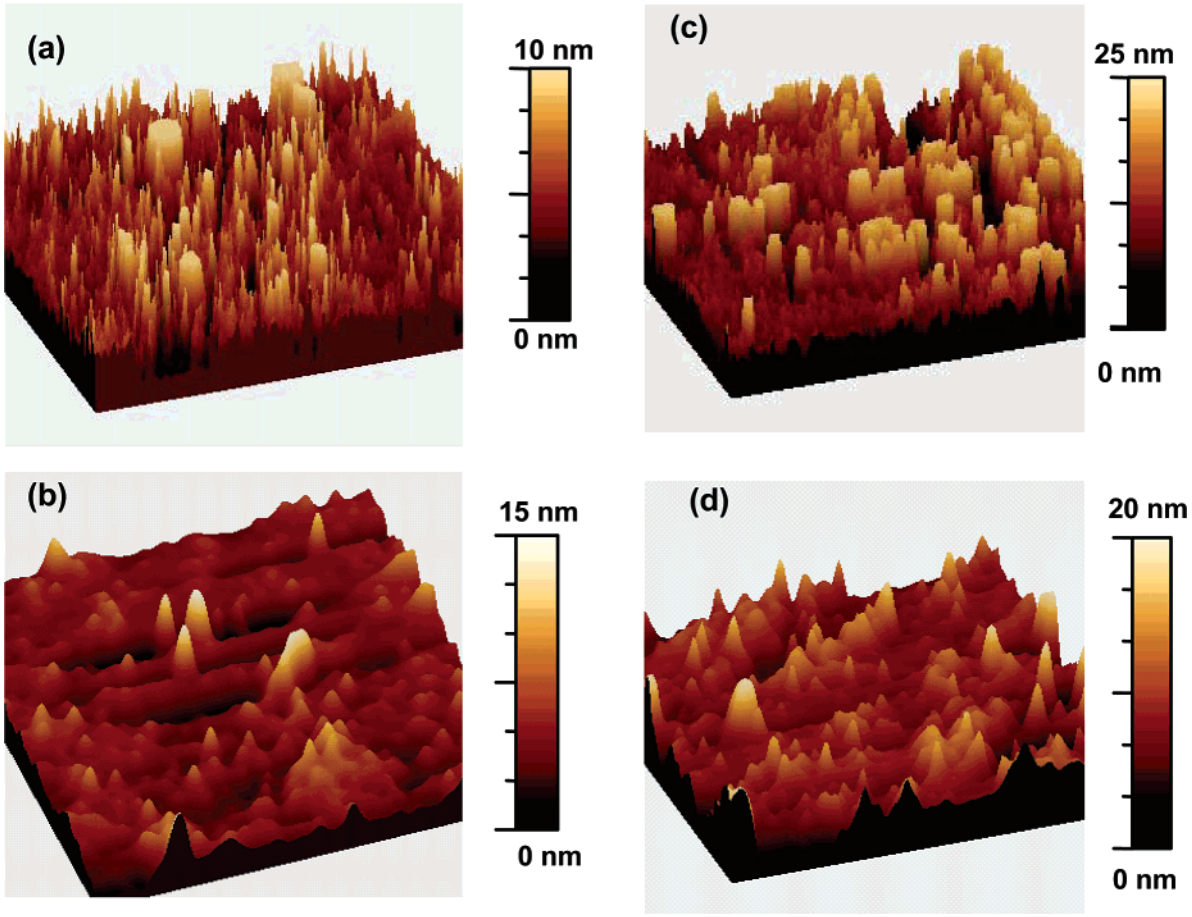


Figure 2. Three-dimensional height images of the grafted polymers obtained after deprotection in the dry state (a, b) and under water (c, d): (a, c) branched copolymer surface at $\gamma = 10$; (b, d) linear polymer brush. The *X*, *Y* scale is 5 μm.

Table 2. Characterization of Surface-Grafted Highly Branched and Linear Glycomethacrylates Obtained after Deprotection

γ^a	$M_{n,calcd}$	mean film thickness[c] (nm)	mean film thickness[d] (nm)	mean roughness[e] (nm)	surface coverage,[f] Γ (mg/m^2)	grafting density,[g] Σ (chains/nm^2)	contact angle[h] (deg)
1	8 100[b]	5.0			5.5	0.40	58
10	21 700[b]	4.6	29.9	1.59	5.1	0.14	49
∞	21 000	11.0	19.0	1.50	12.1	0.34	39

[a] $\gamma = [MAIGlc]_0/[BIEM]_0$. [b] $M_{n,calcd} = M_{n,GPC-VISCO}$ of poly(MAIGlc) $\times$ $(m_{MAIGlc}\gamma + m_{BIEM})/(m_{MAIGlc}\gamma + m_{BIEM})$. [c] As determined by ellipsometry. [d] As determined by ellipsometry under water. [e] As determined by SFM. [f] According to eq 1. [g] According to eq 2. [h] Obtained by sessile drop method using ellipse fitting.

length, $L_c = 20$ nm) under water, indicating that the chains are almost completely stretched.

Preliminary measurements were performed using SFM in water. The SFM image in water of the deprotected copolymer surface at $\gamma = 10$ showed a significant increase in the height of the protrusions, which are broader than in the dry state as can be seen from Figure 2c, and the roughness also increased from 1.59 to 4.61 nm, indicating the swelling of the polymer layer in water. In the case of the linear polymer brush (Figure 2d) compared to that in dry state, the roughness increased from 1.50 to 2.40 nm. These results indicate that in the case of the linear polymer brush the chains are more stretched than the branched copolymer surface in the dry state so the extent of swelling in water is not that significant compared to the branched copolymer surface.

To ensure quantitative deprotection, diffuse-reflectance infrared Fourier transform (DRIFT) spectra were measured on the grafted wafers. Figure 3a,b represents DRIFT spectra for the grafted linear polymer brushes after and before deprotection. Before deprotection, the absorption bands due to the isopropylidene groups are observed at 1450 and 1380 cm^{-1} assigned to the C−H asymmetric and symmetric deformation modes, respectively, as indicated by arrows in Figure 3b. The C−O stretching band of the isopropylidene group is overlapping with the SiO_2 layer, which is also detected in the region between 1200 and 1000 cm^{-1}. After the deprotection, these bands disappear, and a strong absorption band around 3500 cm^{-1} is observed due to the hydroxyl group formed by the deprotection. The decrease in the intensity of the carbonyl group after deprotection can be due to the decrease in the film thickness. The DRIFT spectrum of the deprotected branched copolymer surface at $\gamma = 10$ is shown in Figure S-3 (Supporting Information). The intensities of the hydroxyl and carbonyl peaks are very weak owing to its very low thickness (4.6 nm). Nevertheless, the absence of the peaks attributed to the isopropylidene groups and presence of the hydroxyl groups around 3500 cm^{-1} are clearly visible, indicating the successful deprotection.

The deprotected substrates were further investigated by XPS in order to determine the surface composition of the resulting

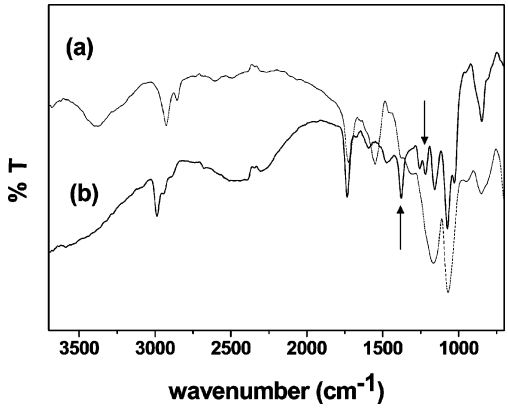


Figure 3. Diffuse-reflectance infrared Fourier transform (DRIFT) spectra of surface-grafted (a) linear poly(MAIGlc) brush after deprotection and (b) linear poly(MAIGlc) brush.

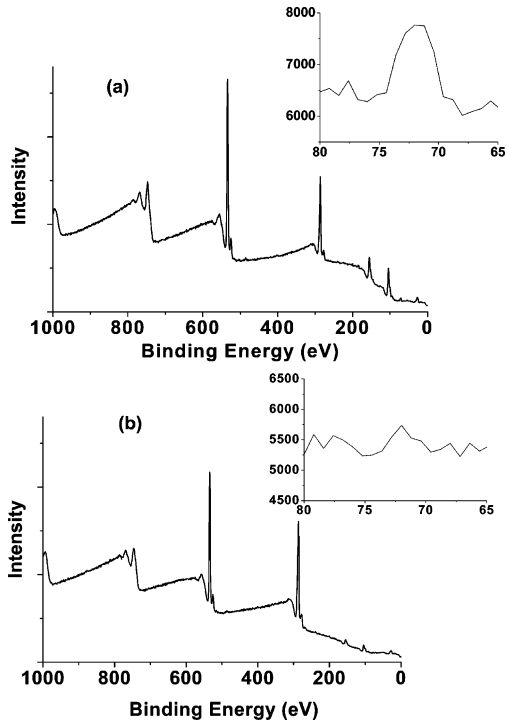


Figure 4. XPS survey spectra of the grafted polymers obtained after deprotection of (a) branched copolymer brush at γ = $[MAIGlc]_0$:$[BIEM]_0$ = 10 and (b) linear poly(MAIGlc) brush. Insets: region associated with the peak derived from bromine.

surfaces. Figure 4a depicts the XPS survey spectrum of the deprotected branched copolymer surface at γ = 10. Three elements—oxygen (533 eV), carbon (285 eV), and silicon (150 and 99 eV)—are clearly seen, similar to the spectrum before hydrolysis. The bromine peaks assigned to Br_{3d} (70 eV), $Br_{3p1/2}$ (184 eV), and Br_{3s} (278 eV) are also visible, which shows that a sufficient amount of α-bromoester groups remains, which can be further modified or used to initiate "hyperstars". The atomic composition (48% C and 38% O) is in good agreement with the calculated values (47.0% C and 42.7% O) of the deprotected branched copolymer surface, indicating the successful deprotection of the isopropylidene groups at the surface.

Figure 4b depicts the XPS survey spectrum of deprotected linear poly(MAIGlc) brush. Atomic compositions of 74% C and 25% O (calcd: O, 28%) are obtained for the linear poly(MAIGlc) brush before deprotection, whereas after deprotection the compositions are 67.8% and 31.5% (calcd: O, 33%), which clearly indicates that after deprotection there is an increase in the oxygen content at the surface due to the presence of the hydroxyl groups and decrease in the carbon content.

Tuning the Surface Properties. Tables 1 and 2 show the water contact angles of a series of copolymer surfaces obtained by SCVCP and the linear polymer brush obtained via ATRP before and after deprotection of the isopropylidene groups. The copolymer surface of thickness 6.7 nm at γ = 1 and μ = 200 shows a contact angle of 80.3°. This indicates that the copolymer surface is hydrophobic, and the hydrophobicity decreases with the increase in the comonomer ratio, γ, which could be attributed to the decrease in the roughness and grafting density with the increase in the comonomer ratio. The linear polymer brush with relatively thick and uniform layer of 12.0 nm shows a contact angle of 78°. These hydrophobic surfaces were transformed into hydrophilic surfaces via deprotection of the isopropylidene groups and further confirmed by contact angle measurements.

As can be seen from Table 2, the deprotected branched copolymer surfaces at γ = 1 and γ = 10 have contact angles of 58° and 49°, respectively, and for the linear polymer brush the angle is 39°. The contact angles of the branched copolymer surfaces (γ = 1 and 10) are higher due to the presence of the hydrophobic inimer units as compared to the linear poly(MAIGlc) brush. The significant decrease in the contact angles compared to those before deprotection confirms that the substrates are completely hydrophilic due to the presence of hydroxyl groups at the surface. These results indicate the versatility of this approach to prepare surfaces of desired properties and the ease in employing SCVCP via ATRP to achieve this goal. The grafting density of the branched and linear polymer brushes after hydrolysis (Table 2) is comparable to that before deprotection (Table 1), indicating that no significant degrafting occurred during the course of hydrolysis.

Conclusions

We present the facile one-pot self-condensing ATRP for the synthesis of surface-grafted hyperbranched glycopolymers. The randomly branched copolymer surfaces possess characteristic architecture, topography, and surface tuning properties. The grafted hyperbranched films are rougher than the linear polymer brushes made for comparison. A significant difference in Br content between linear and branched polymers brushes, as observed by XPS, demonstrates the feasibility to control and modify the surface chemical functionality. Deprotection of the bulky isopropylidene groups results in hydrophilic surfaces, and the successful deprotection was confirmed by DRIFT, XPS, and contact angle measurements. There are significant differences in the wettability between the randomly branched and linear polymer brushes. Because of the α-bromoeseter terminal units, such surfaces can be further modified and employed for understanding carbohydrate−protein interactions and as models for understanding complicated nature's multivalent processes.

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Supporting Information Available: Effect of comonomer-to-catalyst ratio, μ, on film thickness and grafting density (Figures S-1, S-2 and S-3). This material is available free of charge via the Internet at http://pubs.acs.org.

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