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Direct Measurement of Molecular Weight and Grafting Density by Controlled and Quantitative Degrafting of Surface-Anchored Poly(methyl methacrylate)

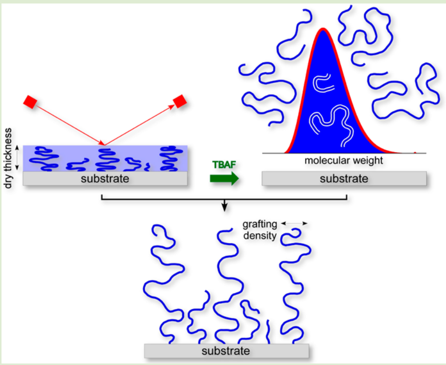
Rohan R. Patil,[†] Salomon Turgman-Cohen,[‡] Jiří Šrogl,[†] Douglas Kiserow,[†,§] and Jan Genzer*[,†]

[†]Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905, United States

[‡]Department of Chemical Engineering, Kettering University, Flint, Michigan 48504, United States

[§]US Army Research Office, Research Triangle Park, North Carolina 27709-2211, United States

Supporting Information



ABSTRACT: We report on quantitative determination of the molecular weight distribution (MWD) and grafting density (σ_P) of polymer assemblies grown by controlled radical polymerization from flat substrates as a function of polymerization time and the ratio between the inhibitor and catalyst species. Specifically, we grow poly(methyl methacrylate) (PMMA) brushes on flat silica-based surfaces by surface-initiated atom transfer radical polymerization (SI-ATRP), cleave the PMMA grafts quantitatively using tetrabutyl ammonium fluoride (TBAF), and analyze their MWD by size exclusion chromatography equipped with a high-sensitivity differential refractive index detector. The polymer growth and degrafting processes are followed by ellipsometry, X-ray photoelectron spectroscopy, and time-of-flight secondary ion mass spectrometry. The σ_P is independent of polymerization time and increases with increasing SI-ATRP inhibitor/catalyst ratio. Specifically, σ_P increases from 0.48 ± 0.06 to 0.58 ± 0.06 chains/nm^2 as the inhibitor/catalyst molar ratio increases from 0 to 0.015, respectively, providing evidence that high inhibitor/catalyst ratio offers better control of the SI-ATRP reaction, by lowering number of terminations, and leading to denser PMMA brush assemblies.

Surface-grafted polymer assemblies (SGPA) comprise polymer chains attached to a substrate by a covalent bond. The interplay between the length (i.e., molecular weight, M_n) of the grafted macromolecules and the number of polymers per unit area on the substrate (i.e., the polymer grafting density, σ_P) defines the conformation of these anchored chains. At low σ_P the grafted polymers adopt a so-called "mushroom" conformation whereby the chains remain isolated on the substrate. When σ_P is increased beyond a certain critical value, which scales with the inverse square root of the polymer size,[1] the chains enter the so-called "brush" regime and tend to extend in the direction perpendicular to the surface due to excluded volume interactions.[2,3] Literature often refers to such grafted polymer systems as polymer brushes irrespective of their grafting regime. SGPAs have been studied extensively during the past years due to their use in many potential technological applications, including (but not limited to) stimuli-responsive,[4] patterned,[5] antibiofouling,[6] ultralow friction,[7] or highly adhesive[8] surfaces. The development of controlled radical polymerization (CRP) schemes has provided a plethora of synthetic protocols for synthesizing SGPAs. The most common methods include atom transfer radical polymerization (ATRP),[9] reverse atom transfer radical polymerization (R-ATRP),[10] reversible addition−fragmentation chain transfer polymerization (RAFT),[11] or nitroxide-mediated radical polymerization (NMRP).[12]

New emerging applications demand detailed information about M_n and σ_P of the SGPAs. While σ_P is difficult (if even possible) to measure directly, it can be determined indirectly by knowing the dry polymer brush thickness (h_P) and M_n.

$$\sigma_P = \frac{h_P \rho N_A}{M_n} \tag{1}$$

where ρ is the bulk density of the polymer and N_A is Avogadro's number. While h_P can be measured accurately by ellipsometry or reflectivity, determining M_n of the macromolecules grafted to flat supports has proven challenging. Some researchers opted to synthesize free polymers in the bulk, either concurrently with growing the surface polymers or independently, and used the bulk M_n as an estimate of the molecular weight of the polymeric grafts. However, this approach may be flawed because the reaction conditions for bulk-grown polymers are not necessarily identical to those corresponding to polymerization carried out directly on the surface due to

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various confinement effects, including (but not limited to) substrate curvature, chain grafting density, and complications associated with monomer delivery.[13−16] Therefore, to determine σ_P using eq 1, one has to utilize an accurate method for measuring M_n of the grafted chains. This means that all chains have to be degrafted quantitatively from the substrate, collected, and have their M_n assessed by a sensitive analytical method. Several research groups have reported on removing the grafted polymers from substrates by means of either hydrofluoric acid,[17] other acids,[18] base,[19] or using ultraviolet (UV) light.[20] However, no clear evidence was given that all polymer grafts were removed from the substrate quantitatively by employing the aforementioned protocols, which often required harsh chemicals.

In this Letter we present a simple method that facilitates quantitative degrafting of poly(methyl methacrylate) (PMMA) brushes from a silica surface using tetrabutyl ammonium fluoride (TBAF). We present the first study with experimental evidence of the effect of ATRP catalyst ratio on the σ_P of grafted polymer systems. TBAF is an ionic compound, a source of fluoride ions (F^-),[21] and is available as a solution in THF. Degrafting takes place by reaction of F^- with Si−O bonds (thus forming Si−F bonds) present exclusively at the base of the initiator and in the silica layer in the substrate. The reaction is driven thermodynamically by the formation of stable Si−F bonds (∼644 kJ/mol).[22] While here we demonstrate the degrafting method on PMMA brushes the current methodology is general and is applicable to other systems as well. The degrafted PMMA chains dissolve in THF and are analyzed using size exclusion chromatography (SEC) to obtain the full molecular weight distribution (MWD). The degrafting reaction is specific and quantitative, and conditions are mild compared to previously employed methods. As will be discussed later, this quantitative removal of all grafts from the substrate enables us to draw conclusions about the structure of the brush close to the substrate.

Figure 1 shows the stepwise characterization of the degrafting process using X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). The XPS survey spectra are shown for four substrates at different stages of the degrafting process with color corresponding to the schematic at the top. We start with the unmodified silicon substrate (black) treated with an ultraviolet ozone (UVO) lamp (184 and 254 nm). This procedure is employed to generate a large density of −OH groups on the silica (SiO_x) substrate needed to anchor chemically the polymerization initiator. A strong oxygen peak at binding energy (BE) of ∼533 eV and silicon peak at ∼99 eV are present because the top layer (∼1 nm) consists of the SiO_x layer. A monolayer of the ATRP polymerization initiator, 11-(2-bromo-2-methyl)propionyloxy undecyltrichlorosilane (eBMPUS, red), is deposited on top of the SiO_x substrate and has a thickness of 1.5 ± 0.2 nm. A characteristic bromine peak is observed at a BE of ∼70 eV. A PMMA brush layer (blue) is grown on top of the eBMPUS/SiO_x substrate using ATRP with a dry thickness measured as 184 ± 10 nm. In the XPS spectra we only detect the signals corresponding to C 1s (BE ∼ 285 eV) and O 1s from PMMA since the electron escape depth is ∼1 nm. The green spectrum corresponds to the PMMA brush incubated in 0.1 M TBAF for 6 h at 50 °C. The final thickness after PMMA degrafting was measured and found to be 0.4 ± 0.1 nm; hence, the silicon and oxygen peaks from the underlying silica are visible again, and no characteristic PMMA signals are found.

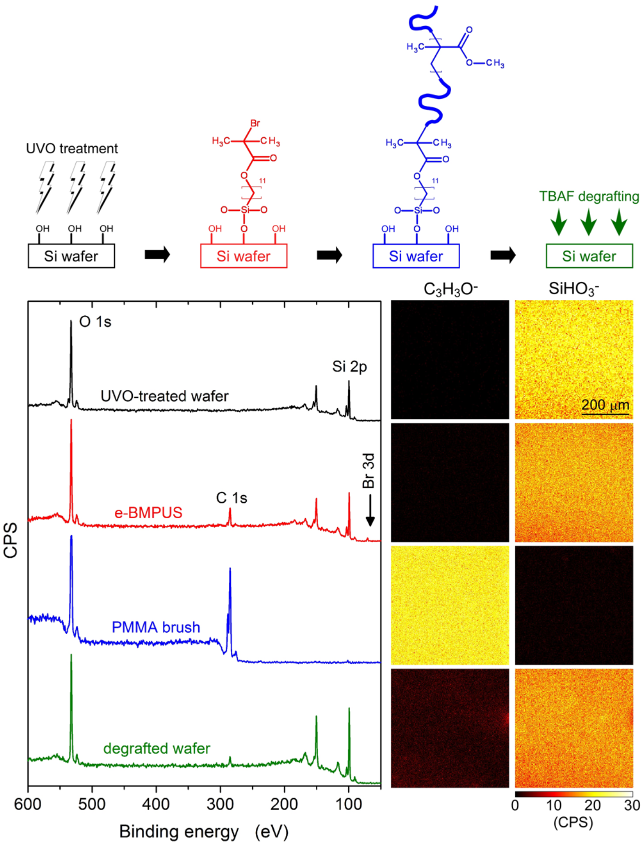

Figure 1. (top) Schematic showing the processing steps leading to the formation of PMMA brushes on flat surfaces and their degrafting using TBAF solutions. (bottom) The chemical composition of the surface of the silicon wafer and the individual processes as monitored by XPS. The images on the right depict scans from TOF-SIMS collected at m/z equal to 55.02 and 76.97, which correspond to $C_3H_3O^-$ and $SiHO_3^-$ ions, respectively. The color scale depicts the counts/second and ranges from 0 (black) to 30 (white).

The information obtained from XPS is further confirmed by TOF-SIMS that is sensitive to the uppermost monolayer present on the substrate. The TOF-SIMS scans shown in Figure 1 for PMMA ($C_3H_3O^-$) and silica ($SiHO_3^-$) ions confirm the growth and quantitative removal of the PMMA layer by TBAF (see Supporting Information).

We grew PMMA brushes from silica substrates (size: 4.2 cm × 4.2 cm) using ATRP at four different inhibitor/activator ratios (i.e., $Cu^{(II)}/Cu^{(I)}$). This size was chosen to produce a sufficient amount of PMMA for SEC analysis. As demonstrated by the data in the Supporting Information, the polymer concentration has to be >0.1 mg/mL to obtain meaningful SEC curves using our differential refractive index (DRI) detector. The polymerization time was varied from 6 to 24 h to obtain brushes with increasing M_n. After synthesizing the grafted PMMA by surface-initiated (SI) ATRP, the dry thickness was measured using ellipsometry, and the polymer was degrafted by incubating the sample in 25 mL of 0.04 M TBAF in THF at 50 °C for 24 h. The polymer chains were then dissolved in THF solution, which was collected and evaporated under reduced pressure to the volume ∼1 mL. The resulting solution was passed through the SEC to obtain the MWD using a high-sensitivity DRI detector. Figure 2 shows dry thickness (h_P, a), number-average molecular weight (M_n, b), and polydispersity index (PDI, c) of the degrafted PMMA for four different $Cu^{(II)}$/

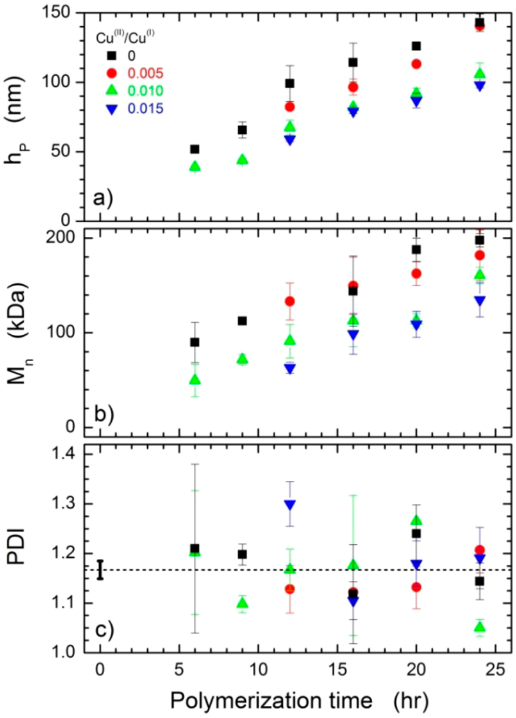

Figure 2. Dry thickness of the PMMA brush (top), number-average molecular weight after TBAF degrafting of PMMA chains (middle), and the corresponding polydispersity index (bottom) as a function of MMA polymerization time at four concentrations of $Cu^{(II)}/Cu^{(I)}$ in the ATRP solution. The dashed lines in the bottom plot depict the average values of PDI; the error bars correspond to the standard deviation.

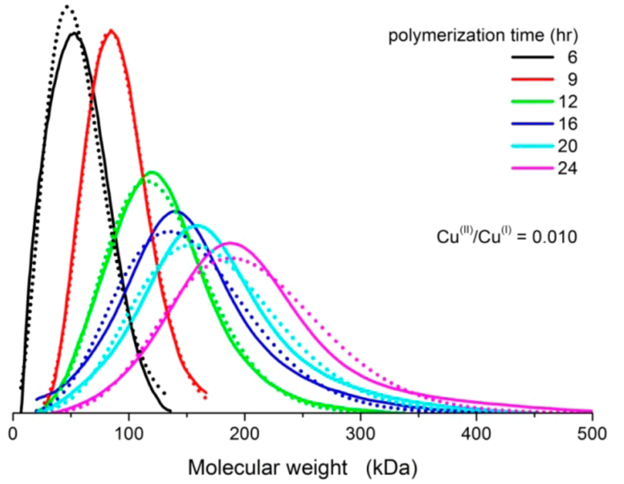

Figure 3. Solid lines denote elution curves (DRI signal) obtained from PMMA chains degrafted from silica substrate via TBAF. The PMMA brushes were grown via ATRP ($Cu^{(II)}/Cu^{(I)}$ = 0.010) for various polymerization times (see legend). Dotted lines represent the best fits to the experimental data using the ATRP model (see Supporting Information for details).

$Cu^{(I)}$ ratios plotted as a function of polymerization time. A linear increase in the h_P and M_n is observed, which is in agreement with previous SI-ATRP studies involving a large excess of bulk monomer and relatively low monomer conversion. As expected, h_P and M_n increase with decreasing $Cu^{(II)}/Cu^{(I)}$, which corresponds to faster ATRP reactions with less control of the MWD. In contrast, the PDI does not exhibit any distinct trend with regard to polymerization time or the $Cu^{(II)}/Cu^{(I)}$ ratio; the PDI values vary between 1.05 and 1.35 with an average at 1.167. While the measured PDI of the grafted polymers is higher than that for bulk polymer grown under identical polymerization conditions (which is usually <1.2), the PDI values are relatively low indicating that SI polymerization proceeded at reasonably "living" conditions. The higher PDI in SGPAs is due to confinement caused by crowding of the chains on the surface,[14] which broadens the MWD. This is further exacerbated by the presence of poor solvent (i.e., PMMA is not very soluble in methanol).[15,24−26]

Figure 3 depicts representative SEC eluograms of degrafted PMMA brushes made by using $Cu^{(II)}/Cu^{(I)}$ = 0.01 (solid lines). As expected, with increasing polymerization time the elution curves broaden and shift to higher M_n. The dotted lines in Figure 3 represent best fits to the experimental data using the model of Mastan et al.[27] While Mastan et al. developed the model to describe ATRP in continuous stirred tank reactors with no termination, the approach is applicable in our setup because we work with a large excess of monomer and run the reaction to low monomer conversions (i.e., monomer concentration around the brush does not change). In a subsequent paper,[23] we provide an in-depth analysis of the experimental MWDs using six different MWD models and demonstrate that the MWDs of PMMA brushes grown from flat substrate at various $Cu^{(II)}/Cu^{(I)}$ ratios can all be described by the aforementioned model as well as other models employed in characterizing controlled radical polymerization.

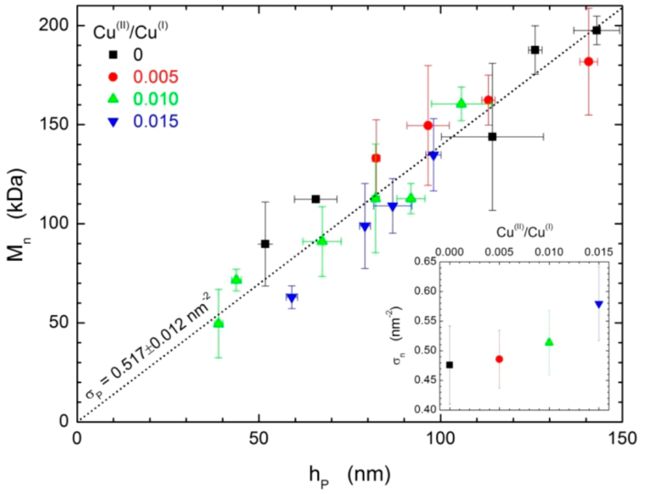

Figure 4. Number-average molecular weight plotted as a function of the dry PMMA brush thickness at four different catalyst ratios, i.e., $Cu^{(II)}/Cu^{(I)}$, in the ATRP solution for MMA polymerization. The inset depicts the dependence of the brush grafting density, σ_P, on the $Cu^{(II)}/Cu^{(I)}$ ratio.

Because the $Cu^{(II)}/Cu^{(I)}$ ratio affects the rate of ATRP and the PDI of polymers grown in bulk, one would expect similar effects to take place in SI-ATRP. In Figure 4 we plot the dependence of M_n on h_P using the data from Figure 2. The data follow a line that passes through the origin. Using eq 1 we determine $\sigma_P \approx 0.517 \pm 0.012$ chains/nm^2. The data demonstrate that σ_P is independent of the MWD, which is expected, as documented in the Supporting Information. A close inspection of the data in the inset to Figure 4 reveals, however, that σ_P increases slightly with increasing the $Cu^{(II)}/Cu^{(I)}$ ratio. We reconcile this observation as follows. Due to fast

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initiation in ATRP, most initiators present on the substrate are activated nearly instantaneously.[28] Moreover, the application of Br-based initiators and Cl-based transition metal ions results in high activation rates.[29] At low $Cu^{(II)}/Cu^{(I)}$ ratios, the brushes grow rapidly and lead to early terminations, which result in the production of short chains located close to the substrate. These chains, when degrafted, are too short and are present in small quantities, which are below the detection limit of the DRI detector. Thus, the measured MWDs are skewed toward higher values of M_n, which, in turn, produce lower σ_P (cf. eq 1). With increasing the $Cu^{(II)}/Cu^{(I)}$ ratio the polymerization proceeds more slowly and more controllably, leading to longer chains that do not terminate instantaneously; those chains may be long enough and be populated in high enough densities so that they can be detected by the SEC. This set of events results in the detection of a more accurate MWD, which provides higher values of σ_P relative to those measured at low $Cu^{(II)}/Cu^{(I)}$ ratios.[30] The major finding is that early terminations in SGPAs occur at lower level of ATRP control, i.e., at low $Cu^{(II)}/Cu^{(I)}$, which leads to higher chain termination and subsequently lower σ_P.

In conclusion, we have established direct measurement of MWDs for grafted PMMA chains on flat silicon substrates. The polymer grafting density (0.517 ± 0.012 chains/nm^2) determined from h_P and M_n measured for degrafted polymers has been found to be independent of the graft PDI. The detected dependence of σ_P on the $Cu^{(II)}/Cu^{(I)}$ ratio is reconciled by considering that the ATRP reaction carried out at low $Cu^{(II)}/Cu^{(I)}$ is less controlled and thus leads to a larger number of early polymer terminations. Increasing the $Cu^{(II)}/Cu^{(I)}$ ratio results in more controlled reactions featuring fewer terminations. Those conclusions could only be reached by considering that all chains got removed from the substrate quantitatively. We documented the latter in our experiments.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, determination of mildness of TBAF, sensitivity of the SEC, molecular weight distribution modeling, and fitting. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jan_genzer@ncsu.edu.

Notes

The authors declare no competing financial interest.

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(30) One may argue that the observed behavior can be attributed to sequential initiation. However, this is unlikely. First, the polymerization proceeds initially very rapidly. Even if additional chains were activated after the polymerization commences, delivery of monomers to a newly activated center will be hindered by the fact that the present PMMA chains are not completely swollen in the methanol environment. Moreover, even if new chains are activated, their growth will be hindered by confinement due to both the presence of long growing chains as well as their limited swelling.