

Large-Scale and Environmentally Friendly Synthesis of pH-Responsive Oil-Repellent Polymer Brush Surfaces under Ambient Conditions

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Supporting Information

ABSTRACT: Contrary to conventional ATRP, aqueous A(R)GET-ATRP at ambient temperature without deoxygenating reaction solutions is an extremely facile method to create polymer brushes. Using these techniques, extremely thick poly[2-(dimethylamino)ethyl methacrylate] polymer brushes can be prepared (~700 nm), or reaction solutions can be low chemical-content, consisting of 99% v/v water. Based on these techniques, we have also developed an easy and inexpensive method, referred to as “paint on”-ATRP, that directly pastes reaction solutions onto various large-scale real-life substrates open to the air. The resulting brush surfaces possess excellent oil-repellent properties, which can be activated or deactivated in response to solution pH.

KEYWORDS: poly[2-(dimethylamino)ethyl methacrylate], polymer brush, ATRP, superoleophobic, pH-responsive, large scale



Adhesion of impurities to solid surfaces from various environments (air or water) has been a major issue in practical applications. To avoid such unfavorable adhesion of impurities, extensive research has concentrated both on applying surface roughening and perfluorination using long chain ($\text{CF}_3(\text{CF}_2)_n$ ($n \geq 7$)) perfluorinated compounds (LPFCs) to create novel nonstick surfaces.^{1,2} In spite of such surfaces having exceptional liquid-repellent properties, chemical and physical effects of LPFCs on human health and the environment,³ complicated processing, and poor mechanical/optical properties of the resulting surfaces can cause great difficulties in practical applications.

More recently, trends have shifted to the development of surfaces that repel low-surface-tension liquids such as oils under water. Conventional perfluorinated surfaces,^{4,5} as well as nonperfluorinated surfaces^{6–8} have been reported that show oleophobic behavior. Among these surfaces, water-soluble polymer brush surfaces have been found to have high contact angles (CAs) with oils and low CA hysteresis (difference between the advancing (θ_A) and receding (θ_R) CAs) in water, and as such represent a new class of oil-repellent, smooth, and sustainable coatings.^{9–12} However, unfortunately, to obtain such polymer brush surfaces, complicated and expensive chemical reaction processes have been required, which limit the applicability of polymer brushes to basic research applications only.

Most notably, polymer brushes have been prepared by the specialized technique of surface-initiated atom transfer radical polymerization (ATRP). This technique typically requires high

concentrations of monomer and catalyst, use of organic solvents, elevated reaction temperatures, and the reaction to be rigorously purged of oxygen.^{13–17} Such stringent conditions make it difficult to prepare polymer brushes outside of laboratory conditions, and due to practical difficulties associated with the reaction setup (large size of airtight reaction vessel and heating apparatus), impractical for large area ($\sim 1 \text{ m}^2$) functionalization. To overcome these limitations, several improvements to conventional ATRP have been suggested. First, it has been reported that adding water to ATRP reactions significantly increases the rate of polymerization of both hydrophilic and hydrophobic monomers,^{18,19} meaning that reactions no longer need to be heated and can be carried out at ambient temperature (we hereafter refer to this method as water-accelerated ATRP). Second, activators (re)generated by electron transfer (A(R)GET) can remove the oxygen sensitivity of ATRP reactions by employing a reducing agent to regenerate oxidized catalyst,^{20,21} and has been extensively employed for the preparation of polymers in solution, but less frequently for polymer brushes.^{22–24} Using the A(R)GET technique, reaction solutions may not need to be purged of oxygen (although they normally are) and in some cases the concentration of copper catalyst can be reduced to a few parts per million (ppm).

Combining the advantages of water-accelerated ATRP and A(R)GET, with a particularly facile monomer (2-

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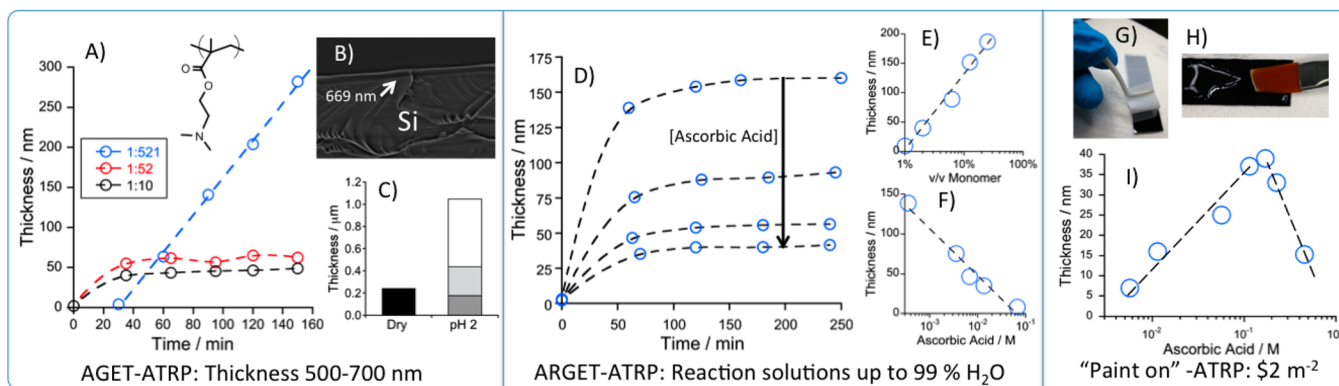


Figure 1. (A–C) pDMAEMA brushes produced using AGET-ATRP: (A) kinetics of AGET-ATRP when different amounts of ascorbic acid are used, which give the calculated Cu(I):Cu(II) ratios shown; inset, chemical structure of pDMAEMA; (B) SEM of 669 nm thick brush layer; (C) thickness of polymer brushes when submerged in acidic solutions, as modeled by three layers with increasing degrees of hydration (white, 80%; gray, 60%; and dark gray, 0% water). (D–F) Brushes produced using ARGET-ATRP: (D) kinetics of ARGET-ATRP; (E) final thickness vs monomer concentration; (F) final thickness vs ascorbic acid concentration. (G–I) Brushes produced using “Paint on”-ATRP: (G) solution to dewetting of silane initiator surfaces using adsorbent paper, as shown in (H); (I) final brush thickness vs ascorbic acid concentration.

(dimethylamino)ethyl methacrylate (DMAEMA)), we have prepared stimulus (pH)-responsive superoleophobic surfaces in a particularly easy and low-cost manner, from low chemical-content reaction solutions. In this letter, we wish to report three specific A(R)GET-ATRP formulations, which each have distinct advantages over conventional ATRP. These formulations use aqueous solutions of DMAEMA (1–50%v/v), a widely available catalyst complex (CuCl₂/pentamethyldiethylenetriamine, 25–306 ppm), and ascorbic acid (vitamin C) as a reducing agent (see details of preparation conditions and analytical methods in Supporting Information). In contrast to conventional preparations, our reported syntheses are more environmentally friendly, much easier to perform, and proceed under milder conditions (at ambient temperature), without the need for degassing of reaction solutions or using organic solvents. In addition, these surface functionalizations are advantageous, since they can also be applied to real-life substrates such as metals and glasses over large-scale areas at ambient conditions relatively inexpensively.

Our first formulation uses a moderately high catalyst concentration (306 ppm) and low concentration of reducing agent (7×10^{-6} M) (so-called AGET-ATRP conditions), to give a fast (2 nm min^{-1}) and linear increase in polymer brush thickness (Figure 1A blue data points and Figure S1). This linear increase in thickness with time indicates excellent retention of terminal halogen atoms on growing polymer chains and a well-controlled “living” polymerization. Because of the presence of dissolved oxygen, an incubation period of about 30 min preceded polymerization, during which the catalyst and reducing agent purge the reaction solution of oxygen. The formulation is unusual as the calculated ratio of copper(I) to copper(II) is extremely low (Cu(I): Cu(II) < 1:521), compared to conventional ATRP (normally Cu(I): Cu(II) > 5:1). This would normally lead to a very slow polymerization, requiring several days to grow a polymer brush of adequate thickness. We prescribe this difference to oxidation of Cu(I) to Cu(II) by residual oxygen in conventional ATRP, and by the increased rate of polymerization when water-accelerated ATRP is used. When larger amounts of reducing agent were used ($\geq 7 \times 10^{-5}$ M), poorly controlled polymerizations were observed, which resulted in smaller brush thicknesses (~ 50 nm, Figure 1A). The formulation is also unusual as it can produce very thick polymer

brushes. For example, within 2 h the polymer brush thickness reached of over 200 nm, and leaving reactions to polymerize overnight resulted in extremely thick brush layers. The greatest thickness achieved was 669 nm (as shown in Figure 1B), and we frequently obtained brush layers over 600 nm. When these samples are submerged in acidic water (pH 2), they are protonated and formed thick diffuse layers swollen by water. A dry brush of 236 nm was found to swell to over $1 \mu\text{m}$ thick, and formed a gradient from 100% pDMAEMA close to the silicon substrate to $\sim 100\%$ water $1 \mu\text{m}$ above the substrate (Figure 1C).²⁵

Polymer brush surfaces prepared by this well-controlled AGET-ATRP reaction are among the thickest polymer brushes ever reported,^{26,27} and yet because of the oxygen insensitivity, and ambient reaction temperature of the AGET-ATRP protocol, are extremely easy to prepare. Furthermore, typical polymer brushes are thin (less than 100 nm thick), whereas to enhance mechanical durability and lifespan, commercially available functional coatings are micrometers to millimeters thick.²⁸ Our proposed AGET-ATRP protocol bridges this difference in thickness, while being significantly easier to perform than conventional ATRP.

Although the above preparation method is extremely facile, and costs have been reduced by using less catalyst and water as the solvent (from $\sim \$1,668$ to $\$756 \text{ m}^{-2}$), it is still too expensive to be industrially applicable. We performed a rough cost analysis to identify areas where potential savings could be made (Tables S1–S5 in the Supporting Information). As shown in Figure 2, catalyst contributes to the cost under AGET-ATRP conditions, but the majority of the cost is due to monomer, which in conventional ATRP is typically $\sim 50\%$ v/v. Using this high concentration of monomer means that functionalization of surfaces must occur in well ventilated areas (fume hood), is environmentally damaging, and a major source of cost-inefficiency. Whereas pDMAEMA has been determined to be food-contact-safe by the Food and Drug Administration,²⁹ monomers such as DMAEMA are toxic and a burden on the environment, and so it is desirable to minimize the amounts used to generate polymer brushes. Unlike in solution ATRP, this high concentration can be significantly reduced in surface initiated ATRP, as very little of the monomer is converted to polymer ($\sim 0.003\%$, see the Supporting Information).

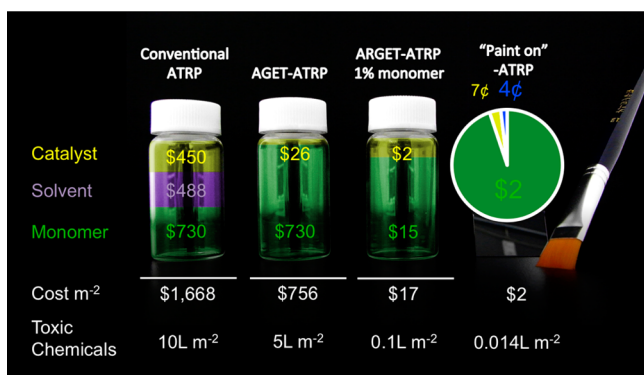


Figure 2. Costs of polymer brushes created using conventional ATRP, AGET-ATRP, ARGET-ATRP and “paint on”-ATRP. Green indicates cost of monomer, purple cost of organic solvent, yellow cost of catalyst, and blue cost of ascorbic acid. The total cost per square meter is shown at the bottom, along with the amount of toxic chemicals used.

On the basis of this rationale, our second formulation uses less catalyst (25–54 ppm), lower monomer concentrations (down to 1% v/v), and an excess of reducing agent (3×10^{-4} to 7×10^{-2} M) (so-called ARGET conditions). As shown in Figure 1D, this gives curved thickness vs time plots, indicating a poorly controlled polymerization. As with AGET-ATRP, adding less ascorbic acid gave thicker polymer brushes, presumably due to a slower more controlled ATRP reaction (Figure 1F). But even at the lowest ascorbic acid concentrations, reaction kinetics suggest that the polymerization is poorly controlled (Figure 1D). Nevertheless, pDMAEMA brushes were produced with thicknesses up to ~ 160 nm (at 50% v/v monomer) at ambient temperature without the need to degas the reaction solution. Thickest polymer brushes were produced at the highest monomer concentration (50% v/v). However, surprisingly, even at very low monomer concentrations, polymer brushes could be produced. For example, at 2% monomer 98% v/v water, a thickness of 39 nm could be achieved, or at 1% monomer 99% v/v water an 11 nm thick brush (Figure 1E). As far as we are aware, preparation of polymer brushes at these low monomer concentrations has never been reported before. Lowering the monomer concentration gives a significant reduction in the cost of brush coatings (they can be produced for as little as $\$17 \text{ m}^{-2}$). As the reaction solution can be up to 99% v/v water with 25 ppm copper catalyst, it is much more environmentally friendly than conventional preparations. In addition, as aqueous ARGET-ATRP at ambient temperature is used, our process is very facile. To illustrate this point, we functionalized a large jar (1.3 L) using this facile low chemical-content reaction to yield a pH-responsive superoleophobic surface at a cost of only $\$2$ (see Figure S3 in the Supporting Information), whereas conventional ATRP would have cost $\$217$ to perform the same reaction, and would be difficult to perform because of the oxygen sensitivity.

Considering practical applications of these types of coatings, submersion in a reaction solution is often inconvenient for surface functionalization of large areas. Painting or spraying onto target surfaces would be desirable for industrial applications. With the oxygen tolerance and low chemical content of the methods described so far, we wondered if A(R)GET-ATRP reaction solutions could be painted or sprayed onto surfaces to grow polymer brushes. This would allow easy functionalization of many practical substrates, and

render them superoleophobic. This leads to our third reported formulation, which consists of the ARGET-ATRP polymerization described above, applied to surfaces in thin layers by a simple painting process. Using this “paint on”-ATRP method allows the amount of reaction solution to be reduced from $\sim 10 \text{ L m}^{-2}$ down to 0.28 L m^{-2} , giving significant savings and a reduction in toxic chemicals used by 99.9% (from 10 L of 50% monomer 50% organic solvent, to 0.28 L of 5% monomer in water).

Preliminary experiments showed that drops of reaction solution could be placed on initiator surfaces left open to the air, and that polymer brushes of up to ~ 100 nm thickness grown. But, initiator surfaces painted with reaction solutions often dewetted due to their moderate hydrophobicity (Figure 1H). To overcome this problem, we placed a piece of adsorbent paper (Whatman filter paper, paper thickness = 0.2 mm) on top of initiator surfaces wet with a few drops of reaction solution (Figure 1G). This allowed surface initiated polymerization and prevented dewetting of the surface. We also note that there are many different initiator surfaces from which polymer chains can be grown, and that perhaps some of these are more hydrophilic.^{30–32}

In the case of “paint on”-ATRP, an optimum concentration of reducing agent (ascorbic acid) was 0.2 M (Figure 1I, ARGET conditions), whereas, when the reaction was carried out in solution, using less reducing agent gave thicker polymer brushes (Figure 1F). This difference is due to diffusion of oxygen from the air into the reaction solution close to the initiator surface, oxidizing the catalyst and preventing polymerization. As the rate of diffusion is proportional to the thickness of reaction solution squared, this process only dominates when the reaction solution layer is thin. Using this optimum amount of reducing agent and 50% v/v monomer, polymer brushes up to 40 nm in thickness can be grown by painting the reaction solution onto initiator surfaces left open to air at ambient temperature. The amount of monomer in these reaction solutions can also be reduced to lower costs and environmental burden, and polymer brushes of acceptable thickness be grown (≥ 10 nm). Although we were only able to decrease the monomer concentration to 5% v/v when in a thin layer, as a higher concentration of reducing agent must be added, giving a less controlled reaction. Even so, because the low concentration of monomer and small volumes of reaction solution ($\sim 0.28 \text{ L m}^{-2}$), polymer brushes can be prepared in a simple, easy fashion, for as little as $\$2 \text{ m}^{-2}$. This corresponds to a decrease in cost of nearly three orders of magnitude compared to conventional ATRP ($\$1,668 \text{ m}^{-2}$), and a decrease in toxic chemicals by 99.9%. By using much smaller volumes of reaction solution, the calculated yield of the reaction is increased 150-fold to around 0.5%. Using a “paint on” methodology also increases the practical applicability of the surface coatings to real-life surfaces. For example, a $30 \times 10 \text{ cm}^2$ piece of aluminum was functionalized using our “paint on”-ATRP, which ellipsometry confirmed to yield a surface initiated pDMAEMA brush (see Figure S3 in the Supporting Information). Functionalization of this moderately large-scale substrate using conventional ATRP would be very difficult, if not impossible, because of the oxygen sensitivity and high costs of reactions.

We confirmed pDMAEMA brushes created using these three different protocols have excellent underwater oleophobic properties. As shown in Figure 3, when pDMAEMA surfaces are ionized due to protonation of tertiary amine groups at low

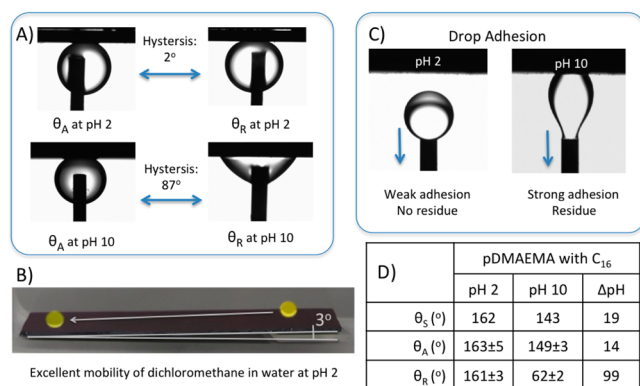


Figure 3. Underwater wetting behavior of pDMAEMA brush surfaces prepared by ARGET-ATRP. (A) CA hysteresis of *n*-hexadecane (C₁₆) at high and low pH. (B) Drops of dichloromethane slide along coated surfaces at small angles of incline. (C) C₁₆ drop adhesion. At pH 2 C₁₆ drops are easily detached from the surface and leave no residue, whereas at pH 10 they are strongly adhered. (D) Table of typical θ_S, θ_A, and θ_R values at high and low pH.

pH, the surface becomes superoleophobic, having large dynamic CAs with oils (in the present case, *n*-hexadecane dynamic CAs (θ_A/θ_R) were 163°/161°). Combination of these high dynamic CAs and negligible CA hysteresis (~2°) results in excellent nonstick behavior and high mobility of oil drops on the surface. We found that drops of dichloromethane are able to slide across the surface at angles of incline of only 3° (Figure 3B and Movie S1 in the Supporting Information), and that *n*-hexadecane drops can easily detach from the surface without leaving residue (Figure 3C). Polymer brushes created by poorly controlled ARGET-ATRP or “paint on”-ATRP polymerizations had identical underwater superoleophobic properties to those produced by well-controlled AGET-ATRP polymerizations. Thus, the surfaces produced from low chemical-content reaction solutions and an inexpensive manner make excellent oleophobic surfaces when submerged in water. As mentioned before, we attribute these excellent dewetting properties to hydration of the polymer brush with water (Figure 1C), which leads to a very hydrophilic (oleophobic) composite layer when underwater. This superoleophobicity can be activated or deactivated by protonation/deprotonation of tertiary amine groups via solution pH (Figure 3A, C, and D). At high pH, the polymer brush is no longer ionized and is less hydrated. Consequently, oil drops tend to strongly adhere because of the more oleophilic nature of the surface, resulting in the increased CA hysteresis.

Finally, we further applied these protocols to prepare a limited number of other pH-responsive polymer brush surfaces, but unfortunately, none of these were as unique as pDMAEMA brush surfaces (see Table S6 in the Supporting Information). For example, a similar AGET-ATRP polymerization using sodium methacrylate produced a thickness of only 151 nm compared to 669 nm with DMAEMA (see Figure S3 in the Supporting Information), and an A(R)GET-ATRP polymerization using 1% v/v monomer gave a thickness of only 3 nm. ATRP of acidic monomers can be more difficult due to protonation of the catalyst complex, or displacement of the ligand.^{33,34} Poly(sodium methacrylate) brush surfaces also did not show clearly switchable oleophobicity in response to pH, because changes in dynamic CAs at different pH values were much smaller than those of other polymer brush surfaces. Although poly[2-(diethylamino)ethyl methacrylate] brush

surfaces showed a larger change in dynamic CAs in response to pH, they possessed moderately high CA hysteresis at pH 2 (8°). Thus, we could not achieve superoleophobicity like pDMAEMA brush surfaces. In addition, the monomer is water-immiscible and requires organic solvents to prepare (see Supporting Information). Although only a limited study, this highlights the unique facile preparation of pDMAEMA brushes showing underwater superoleophobicity, which can be tuned in response to solution pH.

In summary, we have highlighted the pH-responsive superoleophobicity of pDMAEMA brush surfaces, which gives excellent oil drop mobility and low adhesion underwater. It may be thought that to generate such surfaces with superior properties, complicated and expensive methods are required. However, as we have shown here, our preparation methods can be facile, low-cost, and applicable to large-scale real-life substrates. Notably, polymerizations can: (i) be performed under mild conditions such as in aqueous solution at ambient temperature, without the need to rigorously purge reaction solutions of oxygen; (ii) produce extremely thick brush layers up to ~700 nm thick; (iii) use monomer concentrations as low as 1% v/v; (iv) be applied to surfaces in thin layers through a painting method; and (v) be vastly less expensive and use less toxic chemicals than when conventional ATRP is used. Through these practical advantages, we are able to significantly simplify polymer brush preparation, and simultaneously reduce the preparation cost by almost three orders of magnitude. The environmental impact of the synthesis is also reduced with a reduction in toxic chemicals by 99.9%. We hope these advances will help provide a facile and inexpensive route toward the fabrication of commercially available polymer brushes showing superoleophobic properties underwater.

■ ASSOCIATED CONTENT

Supporting Information

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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■ REFERENCES

- (1) Li, X.-M.; Reinhoudt, D.; Crego-Calama, M. What Do We Need for a Superhydrophobic Surface? A Review on the Recent Progress in the Preparation of Superhydrophobic Surfaces. *Chem. Soc. Rev.* **2007**, *36*, 1350–1368.
- (2) Roach, P.; Shirtcliffe, N. J.; Newton, M. I. Progress in Superhydrophobic Surface Development. *Soft Matter* **2008**, *4*, 224–240.
- (3) Wang, Z. Y.; Cousins, I. T.; Scherlinger, M.; Hungerbühler, K. Fluorinated Alternatives to Long-Chain Perfluoroalkyl Carboxylic Acids (PFCAS), Perfluoroalkane Sulfonic Acids (PFSAS) and Their Potential Precursors. *Environ. Int.* **2013**, *60*, 242–248.

- (4) Zhang, G.; Zhang, X.; Huang, Y.; Su, Z. A Surface Exhibiting Superoleophobicity Both in Air and in Seawater. *ACS Appl. Mater. Interfaces* **2013**, *5*, 6400–6403.
- (5) Jin, M.; Li, S.; Wang, J.; Xue, Z.; Liao, M.; Wang, S. Underwater Superoleophilicity to Superoleophobicity: Role of Trapped Air. *Chem. Commun.* **2012**, *48*, 11745–11747.
- (6) Liu, M.; Wang, S.; Wei, Z.; Song, Y.; Jiang, L. Bioinspired Design of a Superoleophobic and Low Adhesive Water/Solid Interface. *Adv. Mater.* **2009**, *21*, 665.
- (7) Xu, L.-P.; Zhao, J.; Su, B.; Liu, X.; Peng, J.; Liu, Y.; Liu, H.; Yang, G.; Jiang, L.; Wen, Y.; Zhang, X.; Wang, S. An Ion-Induced Low-Oil-Adhesion Organic/Inorganic Hybrid Film for Stable Superoleophobicity in Seawater. *Adv. Mater.* **2013**, *25*, 606–611.
- (8) Liu, M.; Liu, X.; Ding, C.; Wei, Z.; Zhu, Y.; Jiang, L. Reversible Underwater Switching between Superoleophobicity and Superoleophilicity on Conducting Polymer Nanotube Arrays. *Soft Matter* **2011**, *7*, 4163–4165.
- (9) Cheng, Q.; Li, M.; Yang, F.; Liu, M.; Li, L.; Wang, S.; Jiang, L. An Underwater pH-Responsive Superoleophobic Surface with Reversibly Switchable Oil-Adhesion. *Soft Matter* **2012**, *8*, 6740–6743.
- (10) Tan, K. Y.; Hughes, T. L.; Nagl, M.; Huck, W. T. S. Nonfouling Capture-Release Substrates Based on Polymer Brushes for Separation of Water-Dispersed Oil Droplets. *ACS Appl. Mater. Interfaces* **2012**, *4*, 6403–6409.
- (11) Kobayashi, M.; Terayama, Y.; Yamaguchi, H.; Terada, M.; Murakami, D.; Ishihara, K.; Takahara, A. Wettability and Antifouling Behavior on the Surfaces of Superhydrophilic Polymer Brushes. *Langmuir* **2012**, *28*, 7212–7222.
- (12) Chen, L.; Liu, M.; Lin, L.; Zhang, T.; Ma, J.; Song, Y.; Jiang, L. Thermal-Responsive Hydrogel Surface: Tunable Wettability and Adhesion to Oil at the Water/Solid Interface. *Soft Matter* **2010**, *6*, 2708–2712.
- (13) Barbey, R.; Lavanant, L.; Paripovic, D.; Schuewer, N.; Sugnaux, C.; Tugulu, S.; Klok, H.-A. Polymer Brushes Via Surface-Initiated Controlled Radical Polymerization: Synthesis, Characterization, Properties, and Applications. *Chem. Rev.* **2009**, *109*, 5437–5527.
- (14) Edmondson, S.; Osborne, V. L.; Huck, W. T. S. Polymer Brushes Via Surface-Initiated Polymerizations. *Chem. Soc. Rev.* **2004**, *33*, 14–22.
- (15) Xu, F. J.; Cai, Q. J.; Kang, E. T.; Neoh, K. G. Surface-Initiated Atom Transfer Radical Polymerization from Halogen-Terminated Si(111) (Si-X, X = Cl, Br) Surfaces for the Preparation of Well-Defined Polymer-Si Hybrids. *Langmuir* **2005**, *21*, 3221–3225.
- (16) Lattuada, M.; Hatton, T. A. Functionalization of Monodisperse Magnetic Nanoparticles. *Langmuir* **2007**, *23*, 2158–2168.
- (17) Xu, F. J.; Cai, Q. J.; Kang, E. T.; Neoh, K. G. Covalent Graft Polymerization and Block Copolymerization Initiated by the Chlorinated SiO₂ (SiO₂-Cl) Moieties of Glass and Oriented Single Crystal Silicon Surfaces. *Macromolecules* **2005**, *38*, 1051–1054.
- (18) Jones, D. M.; Huck, W. T. S. Controlled Surface-Initiated Polymerizations in Aqueous Media. *Adv. Mater.* **2001**, *13*, 1256–1259.
- (19) Kizhakkedathu, J. N.; Norris-Jones, R.; Brooks, D. E. Synthesis of Well-Defined Environmentally Responsive Polymer Brushes by Aqueous ATRP. *Macromolecules* **2004**, *37*, 734–743.
- (20) Min, K.; Gao, H.; Matyjaszewski, K. Use of Ascorbic Acid as Reducing Agent for Synthesis of Well-Defined Polymers by Arget ATRP. *Macromolecules* **2007**, *40*, 1789–1791.
- (21) Dong, H.; Matyjaszewski, K. ARGET ATRP of 2-(Dimethylamino)Ethyl Methacrylate as an Intrinsic Reducing Agent. *Macromolecules* **2008**, *41*, 6868–6870.
- (22) Simakova, A.; Averick, S. E.; Konkolewicz, D.; Matyjaszewski, K. Aqueous Arget ATRP. *Macromolecules* **2012**, *45*, 6371–6379.
- (23) Cheesman, B. T.; Smith, E. G.; Murdoch, T. J.; Guibert, C.; Webber, G. B.; Edmondson, S.; Wanless, E. J. Polyelectrolyte Brush pH-Response at the Silica-Aqueous Solution Interface: A Kinetic and Equilibrium Investigation. *Phys. Chem. Chem. Phys.* **2013**, *15*, 14502–14510.
- (24) Matyjaszewski, K.; Dong, H.; Jakubowski, W.; Pietrasik, J.; Kusumo, A. Grafting from Surfaces for "Everyone": ARGET ATRP in the Presence of Air. *Langmuir* **2007**, *23*, 4528–4531.
- (25) We were unable to generate exact fits to ellipsometric data from our thickest polymer brushes (669nm) when swollen in acidic water, but qualitative fits suggest that the thickness is ~4000nm.
- (26) Edmondson, S.; Nguyen, N. T.; Lewis, A. L.; Armes, S. P. Co-Nonsolvency Effects for Surface-Initiated Poly(2-(Methacryloyloxy)-Ethyl Phosphorylcholine) Brushes in Alcohol/Water Mixtures. *Langmuir* **2010**, *26*, 7216–7226.
- (27) Huang, W. X.; Kim, J. B.; Bruening, M. L.; Baker, G. L. Functionalization of Surfaces by Water-Accelerated Atom-Transfer Radical Polymerization of Hydroxyethyl Methacrylate and Subsequent Derivatization. *Macromolecules* **2002**, *35*, 1175–1179.
- (28) Wang, D.; Bierwagen, G. R. Sol-Gel Coatings on Metals for Corrosion Protection. *Prog. Org. Coat.* **2009**, *64*, 327–338.
- (29) Code of Federal Regulations Title 21:21CFR 117.1010.
- (30) Bocheng, Z.; Edmondson, S. Polydopamine-Melanin Initiators for Surface-Initiated ATRP. *Polymer* **2011**, *52*, 2141–2149.
- (31) Edmondson, S.; Armes, S. P. Synthesis of Surface-Initiated Polymer Brushes Using Macro-Initiators. *Polym. Int.* **2009**, *58*, 307–316.
- (32) Edmondson, S.; Vo, C. D.; Armes, S. P.; Unali, G. F.; Weir, M. P. Layer-by-Layer Deposition of Polyelectrolyte Macroinitiators for Enhanced Initiator Density in Surface-Initiated ATRP. *Langmuir* **2008**, *24*, 7208–7215.
- (33) Tugulu, S.; Barbey, R.; Harms, M.; Fricke, M.; Volkmer, D.; Rossi, A.; Klok, H.-A. Synthesis of Poly(Methacrylic Acid) Brushes Via Surface-Initiated Atom Transfer Radical Polymerization of Sodium Methacrylate and Their Use as Substrates for the Mineralization of Calcium Carbonate. *Macromolecules* **2007**, *40*, 168–177.
- (34) Wang, X. S.; Jackson, R. A.; Armes, S. P. Facile Synthesis of Acidic Copolymers Via Atom Transfer Radical Polymerization in Aqueous Media at Ambient Temperature. *Macromolecules* **2000**, *33*, 255–257.