

Supporting Information

Large-scale and Environmentally-friendly Synthesis of pH-responsive Oil-repellent Polymer Brush Surfaces under Ambient Conditions

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1. Materials.

(3-aminopropyl)triethoxysilane (APTES), toluene, *n*-hexane, *n*-dodecane, *n*-hexadecane, 1,4-dioxane, 2-(dimethylamino)ethyl methacrylate (DMAEMA), 2-(diethylamino)ethyl methacrylate (DEAEMA), sodium methacrylate, and ascorbic acid were purchased from Wako Chemicals Japan. Copper (II) chloride, pentamethyldiethylenetriamine, and α -bromoisobutyryl bromide (BiBB) were purchased from Sigma-Aldrich.

2. Preparation of Silane Initiator Surfaces.

Silicon (100) wafers used as the polymer brush substrate were cut into small pieces $\sim 1 \times 1 \text{ cm}^2$, before being sonicated in ethanol for 5 minutes to remove dust and grease. These small pieces were then dried in a stream of nitrogen gas before being UV-ozone cleaned for 30 minutes at 10^3 Pa . They were then placed in a large glass vial along with a smaller glass vial containing $\sim 100 \text{ }\mu\text{L}$ APTES, the large vial sealed using a screw top, and then heated to $100 \text{ }^\circ\text{C}$ for 60 minutes. This procedure functionalized the silicon surface with APTES via a condensation reaction of triethoxysilane groups with silanol groups on the silicon surface, to generate a surface terminated with amine groups. After which the silicon was removed from the glass vials while still hot, any excess APTES liquid allowed to evaporate, rinsed with toluene and blown dry. The substrates were then functionalized with the ATRP initiator BiBB by immersion in a 0.1 M solution of BiBB in 1,4-dioxane overnight, before being rinsed with 1,4-dioxane and dried. A similar procedure was used to functionalize large glass jars (1000 mL) and $30 \times 10 \text{ cm}^2$ pieces of aluminium sheets (99.9%), except glass jars were cleaned using concentrated sodium hydroxide ($\sim 0.1 \text{ M}$), and aluminium sheets by rinsing with acetone.

3. Spectroscopic Ellipsometry Measurements.

Ellipsometric measurements were carried out using a Horiba Jobin-Yvon MM-16 instrument, at an incident angle of 70° , at wavelengths $500\text{-}900 \text{ nm}$ at 2 nm intervals. In the dry state data was modeled using Cauchy layer with the constants $A = 1.49 \text{ }\mu\text{m}$, $B = 0.005 \text{ }\mu\text{m}^2$. Whereas for determination of brush layer thicknesses

under different wet conditions, a surface was placed in a sample cell with quartz windows inclined at 70°. The cell was then filled with water adjusted to a particular pH value (HCl or NaOH) and spectroscopic data collected. The obtained data was fitted using an estimated medium approximation (EMA) (Bruggeman type) model, consisting of a Cauchy material ($A=1.49\ \mu\text{m}$, $B=0.005\ \mu\text{m}^2$) and water. For study of polymer brush growth kinetics, the same substrate was repeatedly removed from the reaction solution, rinsed with water, dried and the thickness measured using ellipsometry, before being replaced back into the reaction solution. The size of the sample ($1 \times 1\ \text{cm}^2$) was sufficiently small that alignment of the ellipsometer beam on the sample measured the thickness in approximately the same location each time.

4. Contact Angle Measurements.

Advancing (θ_A) and receding (θ_R) contact angles (CAs) were measured using a CA goniometer (Kyowa, CA-V150) equipped with a liquid cell, sample holder, and either a straight needle (for dichloromethane) or hooked needle (for alkanes). Briefly, a small drop of liquid ($\sim 5\text{-}10\ \mu\text{L}$) was dispersed from a syringe needle onto the surface to be measured, and then the volume increased until the liquid/surface contact line was observed to advance across the surface. A photograph was then captured using the supplied software and the θ_A values deduced using the tangent angle algorithm. The volume of the drop was then decreased until the contact line was observed to recede, and the θ_R values measured in the same manner as before. Particular care was taken to confirm that the contact line had advanced or receded across the surface as the volume of the oil drop was changed. This issue has been highlighted in other publications.¹

5. Scanning Electron Microscopy of Polymer Brush Surfaces.

Images of the topography and side-view profiles of polymer brushes were captured using field emission scanning electron microscopy (Hitachi, S-4500). Samples were not sputter coated. To obtain side-view profiles, silicon substrates were cut through the center after deposition of the polymer brush, and images taken of the freshly cut area.

6. AGET/ARGET Polymerization from Initiator Surfaces.

6-1) Production of Extremely Thick Polymer Brushes by AGET Atom Transfer Radical

Polymerization

DMAEMA (8 mL), water (7 mL), copper (II) chloride (16 mg), and pentamethyldiethylenetriamine (50 μL) were added to a glass vial (20 mL). Ascorbic acid (20 μL of 1 mg mL⁻¹ aqueous solution) was then added to this solution to initiate polymerization, and the solution stirred for ~ 2 minutes. After which an initiator substrate was inserted to the reaction solution (polished side upwards at the base of the vial) and the glass vial sealed with a PTFE screw-lid. Reaction solutions were not degassed, and glass vials contained ~ 4 mL of ambient air. Polymerizations were allowed to proceed at room temperature (23-28 °C) without stirring for the

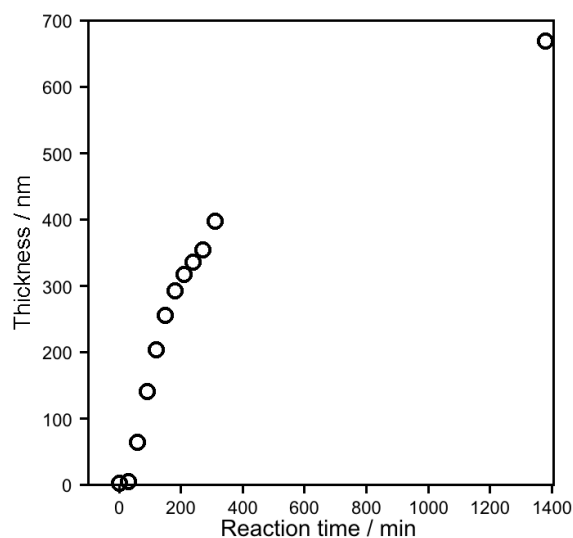


Fig. S1 Kinetics of PDMAEMA brush growth under AGET conditions.

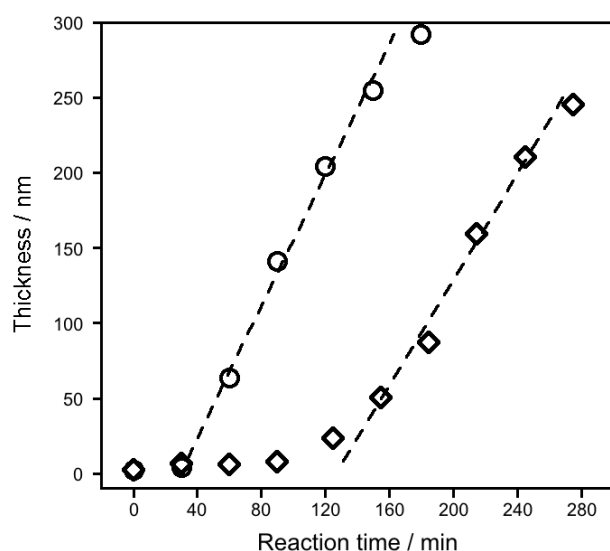


Fig. S2. Effect of catalyst concentration on polymerization kinetics. Open circles for 16 mg CuCl₂ and open diamonds for 8 mg CuCl₂.

desired amount of reaction time, before the substrates were removed from the vial and extensively rinsed with water.

As can be seen in Fig. S1, and as discussed in the text, an incubation period of around 30 minutes preceded a fast, linear increase in polymer brush thickness. The rate of brush growth was $\sim 2 \text{ nm min}^{-1}$, and reached 300 nm within 3 hours polymerization time. This linear increase in thickness suggests that a high level of control was achieved during the polymerization and that growing polymer chains retained their terminal halogen (either bromine or chlorine). Inevitably, after around 300 nm of brush growth or 200 minutes reaction time, a curvature to the plot can be observed due to the slow but continuous loss of terminal halogen

atoms, giving a decrease in the number of growing chains, and a slower rate of increase in polymer brush thickness. Nevertheless, leaving reactions to polymerize overnight led to very thick polymer brushes, although we expect that leaving polymerizations to proceed for these long periods of time leads to molecular weight distributions with a significant tail to low molecular weight.

The concentrations of copper catalyst in this reported synthesis is $\sim 1/4$ of that typically used in conventional ATRP. We investigated if this concentration of catalyst could be reduced further, as shown in Fig. S2. As can be seen, reducing the concentration of catalyst by half significantly increased the incubation period from around 30 minutes to ~ 120 minutes. This is because lower concentrations of catalyst are slower to purge the reaction solution of oxygen. Whereas when 16 mg of catalyst was used and brush growth started sharply at around 30 minutes, when 8 mg of catalyst was used, an increasing rate of polymerization is observed up to around 200 minutes. This is due to the rate of ATRP being proportional to the relative ratios of Cu(I) and Cu(II). For example, at 80 minutes a small amount of Cu(I) is present, resulting in a slow increase in brush thickness, whereas this amount of Cu(I) is larger at 120 minutes and brush growth is faster. By around 200 minutes, all of the oxygen has been removed from the reaction solution, and from now onwards the concentration of Cu(I) remains at its highest level and constant. Due to the increasing length of incubation periods when using smaller concentrations of catalyst, and because the catalyst is not a significant in the cost of the reaction, lower concentrations of catalyst were not explored.

6-2) Production of Polymer Brushes using ARGET-ATRP and Low Concentrations of Monomer

Under ARGET conditions the concentration of catalyst was reduced from 16 mg to 2.8 mg, and the amount of added ascorbic acid was increased from 0.02 mg to 1-190 mg, such that under ARGET conditions the ratio of ascorbic acid to Cu(II) was approximately equal to or greater than 1. A typical experimental protocol was: DMAEMA (0.15-8 mL), water (7-15 mL), copper (II) chloride (2.8 mg), and pentamethyldiethylenetriamine (5 μ L) were added to a glass vial (20 mL). Ascorbic acid (1-190 mg in aqueous solution) was then added to this solution to initiate polymerization, and the solution stirred for ~ 2 minutes. After which an initiator substrate was inserted to the reaction solution (polished side upwards at the base of the vial) and the glass vial sealed with a PTFE screw-lid. Reaction solutions were not degassed, and glass vials contained ~ 4 mL of ambient air. Polymerizations were allowed to proceed at room temperature (23-28 $^{\circ}$ C) without stirring for the desired amount of reaction time, before the substrates were removed from the vial and extensively rinsed with water.

Study of polymerization kinetics, as shown in Fig. 1D, gave a fast increase in brush thickness which then quickly decreased over time. This is consistent with a poorly controlled ATRP reaction, during which terminal halogen atoms (chlorine or bromine) are lost from growing polymer chains resulting in termination of polymer chain growth. Consistent with this hypothesis, we immersed polymer brushes created by long ARGET reaction times back into a fresh ARGET reaction solution, and observed no further increase in brush thickness, as the vast majority of terminal halogen atoms had been lost from growing chains.

We also studied how the concentration of the reducing agent ascorbic acid affected brush growth, and found that lower concentrations of reducing agent gave thicker polymer brushes. This is again consistent with a poorly controlled ATRP reaction, as using a lower concentration of reducing agent results in the slower generation of Cu(I), and a lower concentration of polymeric radicals at any one time. With a lower concentration of polymeric radicals, growing polymers are less likely to terminate by combination. In contrast to AGET conditions, we didn't observe any incubation period for ARGET polymerization, probably due to the faster rate at which Cu(II) is reduced to Cu(I) by the high concentrations of ascorbic acid. And in contrast to well-controlled conventional ATRP reactions where brush thickness is a function of reaction time, in our reported ARGET synthesis polymer brush thickness can be controlled through the concentration of ascorbic acid.

To reduce the cost of these polymer brush surfaces, we investigated if the major cost in polymer brush ATRP reactions – monomer – could be decreased to smaller concentrations. As discussed in the text, and shown in Fig. 1E, reducing monomer concentration resulted in a decrease in polymer brush thickness, but even at concentrations as low as 1 % v/v, polymer brushes could be produced with a thickness of 11 nm. We used this low-chemical content ARGET-ATRP reaction to functionalize large glass jars and render them superoleophobic at low pH, as shown in Fig. S3 top. As can be seen, at pH 2 hexane dyed blue does not adhere to the surface and the jar is relatively oil-free, but at pH 10 the surface of the jar is fouled by oil.

6-3) “Paint-on” -ATRP

Our initial attempts to apply reaction solutions to surfaces in thin layers with a paintbrush used the ARGET protocol described above. Using this protocol we found that the reaction solution spread easily over the surface of the silicon wafer surface, but often after a few seconds dewet from parts of the surface. Where the reaction liquid continued to wet the surface, brush thicknesses of up to ~100 nm were measured via ellipsometry. Whereas in areas that dewet, thicknesses were less than 2 nm. To overcome these problems of dewetting, we tried several ideas as potential solutions. First, poly(vinyl alcohol) (up to 10 % v/v) was added to the reaction solution to increase the viscosity, and to form an air-tight film skin at the top of the reaction solution. This variation of the procedure gave moderate improvements in preventing dewetting, but due to the increased viscosity of the reaction solution, was detrimental to the final polymer brush thickness. Second, the initiator surface was wet with reaction solution and then a piece of adsorbent paper was placed on top. This prevented dewetting of the surface, and allowed growth of polymer brushes.

As discussed in the text, the optimum concentration of ascorbic acid was found to be 0.2 M when the reaction solution was applied to the surface using the “paint-on” method. This optimum results from two processes: lower concentrations of ascorbic acid give slower, more controlled polymerizations resulting in greater thicknesses, whereas high concentrations of ascorbic acid generate Cu(I) for longer periods of time before being used up, allowing longer polymerization times. Under conditions where Cu(I) is slowly oxidized to Cu(II), as when the initiator surface is submerged in reaction solution, lower concentrations of ascorbic acid give more controlled ATRP reactions which result in large brush thicknesses. Whereas when Cu(I) is oxidized

quickly, as when a thin layer of reaction solution is applied to the surface, brush thickness is independent of the degree of control and only depends on the reaction time. Using a concentration of ascorbic acid which is moderately high (0.2 M) allows for a degree of control which enables moderate retention of terminal halogen atoms for the duration of the polymerization. Using a lower concentration results in a well-controlled polymerization which doesn't have sufficiently long reaction time to grow to large thickness. And high concentrations of ascorbic acid result in polymerizations where terminal halogen atoms are lost before the end of the reaction time, resulting in thin polymer brushes.

Following optimization of the concentration of ascorbic acid, we reduced the concentration of monomer. This reduced the final thickness of our obtained polymer brushes but we found that at concentrations as low as 5 % polymer brushes of >10 nm thickness could be grown. As stated in the text, we were unable to reduce the concentration as much as in the solution polymerization described in the previous section, as the high concentration of ascorbic acid gives a less controlled ATRP reaction, resulting in smaller final brush thicknesses. Our final protocol for "paint-on" polymer brushes was: DMAEMA (0.75 mL), water (14.25 mL), copper (II) chloride (2.8 mg), and pentamethyldiethylenetriamine (5 μ L) were added to a glass vial (20 mL). Ascorbic acid (20 mg) was then added to this solution to initiate polymerization, and the solution stirred for ~2 minutes. Then a few drops of this solution was applied to a silicon initiator surface and a piece of adsorbent paper (Whatman filter paper 4A) placed on top. Polymerizations were allowed to proceed at room temperature (23-28 $^{\circ}$ C) for 90 minutes before being rinsed with water. Using this protocol we were able to functionalize large aluminum sheets (30 x 10 cm²) relatively easily, as shown in Fig. S3 bottom. Ellipsometry confirmed growth of pDMAEMA brush on the surface, although in this case the thickness appeared to be larger than when on silicon (30-40 nm compared to 11 nm).

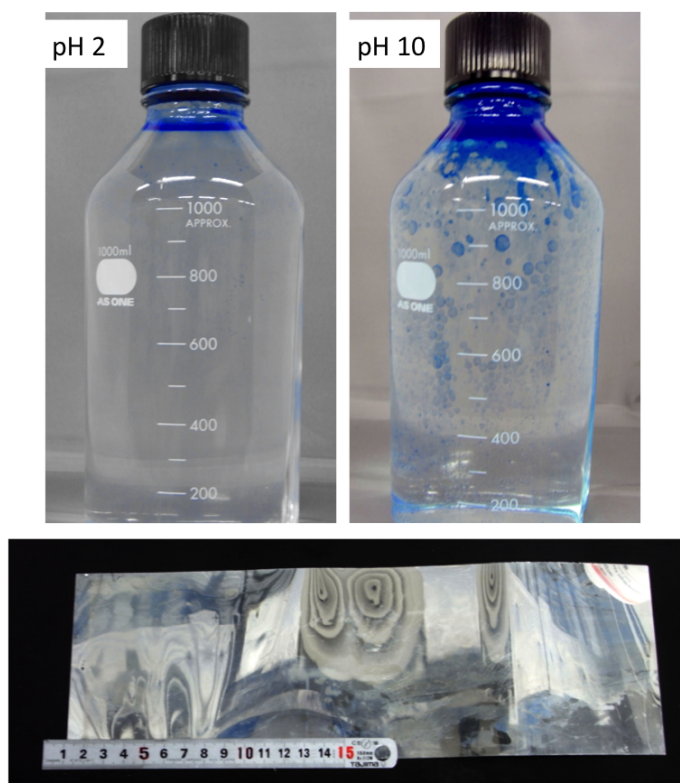


Fig. S3. Functionalization of large real life substrates. Top – 1.3 L glass jar functionalized by low-chemical content ARGET-ATRP. Jars contain water adjusted to either pH 2 or pH 10 and *n*-hexane containing blue dye. At pH 2 the surface of the jar is superoleophobic, whereas at pH 10 oil drops adhere to the surface. Bottom – a 30 x 10 cm² aluminum sheet functionalized using “Paint on”-ATRP.

7. Costs of Preparing pDMAEMA Brush Surfaces.

Many different methods of preparing pDMAEMA brush surfaces via surface initiated ATRP have been reported, but typically, protocols use 50% v/v monomer, 50 % v/v solvent, ligand, $\sim 1 \times 10^{-2}$ M Cu(I), and $0 - 1 \times 10^{-3}$ M Cu(II). A selection of example protocols are given in the references. Commonly used solvents include alcohols,² dimethylformamide (DMF),³ dimethyl sulfoxide (DMSO),⁴ and acetone.⁵ Less frequently, water is reported as a solvent.⁶ The reaction solution is then heated to an elevated temperature ($\sim 35-100$ °C).

Table S1. Unit prices of chemicals required for polymer brush synthesis. Prices are per litre for liquids and per gram for solids. Taken from Sigma-Aldrich October 2013.

Isopropanol	\$97.60
DMF	\$85.40
DMSO	\$85.40
Acetone	\$79.40
Water	\$0.00
Ascorbic acid	\$0.11
Cu(I) (Cl or Br)	\$6.40
Cu(II) (Cl or Br)	\$1.06
Pentamethyldiethylenetriamine	\$223.00
2-(Dimethylamino)ethyl methacrylate	\$146.00

Using the costs listed in Table S1, the cost of a conventional ATRP reaction which uses the conditions listed above or similar can be calculated:

Table S2. Cost of polymer brushes prepared by a typical conventional ATRP reaction. Assuming that the depth of the reaction solution covering the initiator surface is 1 cm.

Solvent	$5 \text{ dm}^3 \times \$97.60 \text{ per dm}^3$	=	\$488
Monomer	$5 \text{ dm}^3 \times \$146 \text{ per dm}^3$	=	\$730
Cu(I)	$50\text{g} \times \$6.40 \text{ per g}$	=	\$320
Ligand	$0.6 \text{ dm}^3 \times \223 per dm^3	=	\$130
Total		=	\$1,668 m⁻²

Table S3. Cost of polymer brushes prepared by the AGET protocol described above. Assuming that the depth of the reaction solution covering the initiator surface is 1 cm.

Solvent	5 dm ³ x \$0 per dm ³	=	\$0
Monomer	5 dm ³ x \$146 per dm ³	=	\$730
Cu(II)	17.5g x \$1.06 per g	=	\$18.55
Ligand	30ml x \$223 per dm ³	=	\$7.00
Ascorbic acid	0.01g x \$0.11 per g	=	\$0.00
Total		=	\$756 m⁻²

Table S4. Cost of polymer brushes prepared by the 1% v/v ARGET protocol described above. Assuming that the depth of the reaction solution covering the initiator surface is 1cm.

Solvent	9.9 dm ³ x \$0 per dm ³	=	\$0
Monomer	0.1 dm ³ x \$146 per dm ³	=	\$14.60
Cu(II)	1.75g x \$1.06 per g	=	\$1.86
Ligand	3μl x \$223 per dm ³	=	\$0.70
Ascorbic acid	0.63g x \$0.11 per g	=	\$0.07
Total		=	\$17.23 m⁻²

Table S5. Cost of polymer brushes prepared by the “paint-on” protocol described above using 5 % v/v monomer and 0.2 M ascorbic acid. Assuming that 1ml of reaction solution is spread over 36 cm².

Solvent	0.26 dm ³ x \$0 per dm ³	=	\$0
Monomer	0.01 dm ³ x \$146 per dm ³	=	\$2.03
Cu(II)	0.05g x \$1.06 per g	=	\$0.05
Ligand	0.08μl x \$223 per dm ³	=	\$0.02
Ascorbic acid	0.35g x \$0.11 per g	=	\$0.04
Total		=	\$2.14 m⁻²

8. Comparison of PDMAEMA Brush Surfaces to Other pH-Responsive Brush Surfaces.

8-1) AGET Polymerization of Sodium Methacrylate

The AGET polymerization procedure of DMAEMA was used to prepare poly(sodium methacrylate) (pSMA) brush surfaces. Sodium methacrylate (3 g), water (4.6 mL), copper (II) chloride (8 mg), and pentamethyldiethylenetriamine (25 μL) were added to a glass vial (20 mL). Ascorbic acid (10 μL of 1 mg mL^{-1} aqueous solution) was then added to this solution to initiate polymerization, and the solution stirred for ~ 2 minutes. After which an initiator substrate was inserted to the reaction solution (polished side upwards at the base of the vial) and the glass vial sealed with a PTFE screw-lid. The reaction solution was not degassed, and glass vials contained ~ 14 mL of ambient air. Polymerizations were allowed to proceed at room temperature (23-28 $^{\circ}\text{C}$) without stirring for the desired amount of reaction time, before the substrates were removed from the vial and extensively rinsed with water.

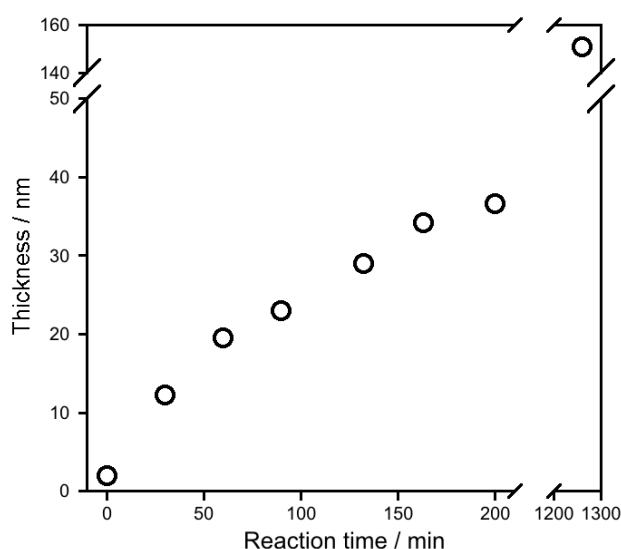


Fig. S4. Polymerization kinetics of sodium methacrylate under AGET conditions.

As can be seen from Fig. S4, AGET-ATRP of sodium methacrylate did not yield polymer brushes with unusually large thickness like when the monomer DMAEMA is used. From the curvature of the increase in polymer brush thickness it appears as though the reaction is poorly controlled, and that terminal halogen atoms are lost over time, resulting in the smaller thickness. It is known that acidic monomers such as methacrylic acid can deactivate ATRP catalysts by protonation of the ligand. For this reason, the neutralized sodium salt of methacrylic acid is often used instead, which gives much better results. Although, carboxylic acid groups can strongly coordinate to the metal center, displace the ligand and alter the redox potential of the catalyst, which may explain the smaller thickness of this reaction.

8-2) ARGET-ATRP of 2-(Diethylamino)ethyl methacrylate

To investigate the wetting properties of different pH-responsive polymer brush surfaces, DEAEMA was polymerized (pDEAEMA) under ARGET conditions. As the monomer is more hydrophobic than the related monomer DMAEMA, it is water immiscible and so the ARGET protocol above was modified to use a mixture of ethanol and water as follows: DEAEMA (8 mL), water (3 mL), ethanol (4 mL), copper (II) chloride (2.8 mg), and pentamethyldiethylenetriamine (5 μ L) were added to a glass vial (20 mL). Ascorbic acid (1 mg in aqueous solution) was then added to this solution to initiate polymerization, and the solution stirred for ~2 minutes. After which an initiator substrate was inserted to the reaction solution (polished side upwards at the base of the vial) and the glass vial sealed with a PTFE screw-lid. The reaction solution was not degassed, and glass vials contained ~4 mL of ambient air. Polymerizations were allowed to proceed at room temperature (23-28 °C) without stirring for the desired amount of reaction time, before the substrates were removed from the vial and extensively rinsed with ethanol.

8-3) Wetting Behavior and Comparison to pDMAEMA

Table S6. Wetting behavior of different polymer brush surfaces with *n*-hexadecane (C₁₆) when submerged in water adjusted to either pH 2 or 10 using HCl/NaOH. Δ pH refers to the change in either θ_A or θ_R with pH. CA hysteresis is calculated as $\theta_A - \theta_R$.

	pDMAEMA				pSMA				pDEAEMA		
	pH 2	pH 10	Δ pH		pH 2	pH 10	Δ pH		pH 2	pH 10	Δ pH
θ_A (°)	163 \pm 5	149 \pm 3	14		153 \pm 3	152 \pm 5	1		158 \pm 5	134 \pm 7	24
θ_R (°)	161 \pm 3	62 \pm 2	99		144 \pm 6	151 \pm 5	7		150 \pm 4	36 \pm 4	114
CA Hysteresis (°)	2	87			9	1			8	98	

To investigate if pDMAEMA brush surfaces are unique in their ease of preparation and excellent wetting properties, we investigated a limited number of other common pH-responsive polymers. As discussed in the text, sodium methacrylate could be polymerized using a similar method to pDMAEMA, but didn't yield as great thicknesses under AGET conditions, and couldn't be produced at as low monomer concentrations.

In our present case, CA hysteresis played a key role in determining final oil dewetting properties, namely whether the surface is oil-repellent or oil-adhesive. The former state should have high dynamic CAs (150-160°) and low CA hysteresis (1~2°) to give excellent mobility of oil drops on the surface and low adhesion of oil drops. Conversely, the latter state should have lower CAs (30~150°) and more CA hysteresis (8~100°) to allow oil drops to adhere to the surface and be immobilized. Only pDMAEMA brush surfaces satisfy these criteria, having large dynamic CAs with low CA hysteresis at pH 2 (163°/161°/2° respectively), and smaller dynamic CAs with increased CA hysteresis at pH 10 (149°/62°/87° respectively). In the case of poly(sodium methacrylate) brush surfaces, the changes in dynamic CAs were much smaller than those of other polymer brushes with changing solution pH. Thus, they didn't show clearly switchable oleophobicity in response to pH. A more hydrophobic polymer brush of pDMAEMA is pDEAEMA, which also showed a greater change

in dynamic CAs with changing solution pH. But this polymer brush surfaces had moderately high CA hysteresis at pH 2 (8°), preventing oil drops from sliding across the surface. This means that pDEAEMA brush surfaces are not superoleophobic like pDMAEMA brush surfaces. Again, due to hydrophobicity of DMAEMA monomer, it is water-immiscible and requires an organic solvent for the polymerization. Although investigation of other monomers was limited, we believe that pDMAEMA brush surfaces are fairly unique, in that they are easily prepared using water as a solvent at room temperature, and their superoleophobicity can be switched on/off via solution pH.

9. Yield of Polymerization Reactions.

Conventional ATRP uses >1 mL of reaction solution, per square centimeter of polymer brush surface created, and the monomer concentration is typically 50 %, which normally gives a polymer brush <100 nm thick. Calculations based on these numbers gives a yield of <0.003 %. Our reported “paint-on” protocol uses much less reaction solution (0.028 mL cm⁻²) and a lower concentration of monomer (5 % v/v) to give a polymer brush which is ~10 nm thick. Calculation of the yield based on these numbers gives 0.45 %.

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