

Coatings with Thermally Switchable Surface Energy Produced from Poly(ethylene oxide)-poly(dimethylsiloxane) Block Copolymer Films[†]

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ABSTRACT: This work explores coatings with thermally switchable wetting behavior, based on block copolymers that possess both hydrophilic and hydrophobic segments. The amphiphilic block copolymers were synthesized by coupling allyl-ended poly(ethylene oxide) (PEO) and hydride-ended poly(dimethylsiloxane) (PDMS) oligomers via a Pt catalyst. One near-symmetric diblock possessed an order-disorder transition temperature (T_{ODT}) of 64 °C. When cooled through T_{ODT} in ambient air, the PDMS domains wet the film's surface, producing a hydrophobic coating with a water contact angle (CA) = 90°.

However, when cooled in humidified air, hydrophilic PEO domains form at the surface, yielding CA = 30–40°. The coatings can be reversibly switched between the two states by reheating above T_{ODT} , in the appropriate environment, and then cooling, rapidly generating the desired room-temperature surface wettability. © 2015 Wiley Periodicals, Inc. *J. Polym. Sci., Part B: Polym. Phys.* **2015**, *00*, 000–000

KEYWORDS: block copolymer; coating; polymer surface; thermoswitchable; wettability

INTRODUCTION Materials and coatings with tunable and/or switchable properties are of broad interest and include applications in drug delivery, biosensors, and “smart” textiles.¹ Typically, these materials alter their physical conformations or properties in response to changes in external stimuli or the local environment (e.g., temperature, pH, or mechanical deformation), which act as the property “switch.” Polymers are excellent candidates for such switchable materials as simple changes in the chain length (molecular weight), composition, or architecture can lead to dramatic differences in their responses to specific stimuli.² Introducing chemical heterogeneity into the polymer chains provides a powerful design tool by which functional coatings, with tunable surface properties (e.g., wettability, adhesion), can be realized.³ Recently, great effort has been undertaken to synthesize polymeric coatings whose wetting behavior (i.e., hydrophilic vs. hydrophobic) can be manipulated. Much of this work uses heterogeneous polymer brush layers, which have been chemically grafted to an underlying substrate.^{4–6} Motornov et al. grafted mixtures of two liquid polymers, one hydrophilic and one hydrophobic, onto substrates to produce textured, hybrid brush layers whose wetting behavior switched between hydrophobic and hydrophilic states when

exposed to air and water, respectively.⁴ They attributed this responsive behavior to local rearrangements of the grafted polymers, enabled by the brush's liquid-like state, such that the chains, which produce the lowest interfacial energy present themselves at the coating's surface. Block copolymers have been employed to produce similar surfaces.^{7–11} Mori et al.⁸ and later Senshu et al.⁹ demonstrated that as-cast films (or films thermally annealed in air) of various amphiphilic block copolymers were hydrophobic, but that upon exposure to water, the hydrophobicity quickly decayed as the hydrophilic chains emerged. Upon re-annealing in air (above the glass transition temperatures, T_g , of all the blocks), the coating reverted to its hydrophobic state, although the transitions were not completely reversible, and the hydrophilic-to-hydrophobic transition was slow.

In the above approaches, the environment (air vs. water) acts as the stimulus, with the surface rearranging accordingly. However, it is often advantageous for the property “switch,” which controls surface composition to be orthogonal to changes in the use environment (i.e., to set the material's wetting behavior independently of the environment in which it is used). An example of this approach was demonstrated by Zhang et al., who synthesized linear triblock

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Additional Supporting Information may be found in the online version of this article.

copolymers, with the homopolymers of the three distinct constituent blocks covering a modest range of wettabilities (contact angles, CA, ranging from 74° to 93°). They showed that the measured CA of the film's surface could be switched over a limited range, between 89° and 96°, simply by quenching from different annealing temperatures, where different blocks presented themselves at the surface.¹¹

In this work, we demonstrate an alternate approach for producing polymer coatings with thermally switchable surface energies, using amphiphilic block copolymers with a modest order-disorder transition temperature, T_{ODT} which acts as the property switch. Above T_{ODT} a block copolymer film exists as a disordered, homogeneous melt, but upon cooling to ambient temperature, the T_{ODT} is crossed, causing the polymer melt to self-assemble into a periodic nanostructure.¹² The block, which wets the polymer-air interface, can be controlled by manipulating the humidity of the film's environment while annealing (above T_{ODT}) and during the subsequent cooling step (i.e., when cooled in dry air the hydrophobic block presents itself at the surface; when cooled in humid air the hydrophilic block wets). Ideally, crossing the T_{ODT} should "lock in" the film's morphology, and therefore wetting behavior, though chain mobility below T_{ODT} may require that the film be cooled further to achieve an effective "lock." The coating can be repeatedly reprocessed simply by reheating and cooling through the film's T_{ODT} , thus erasing its previously "set" wetting behavior (see Fig. 1 for a schematic of the proposed switching process). This approach should enable fast and reversible switching. It could even be employed to achieve patterned control of the wetting behavior via a resistive heating array incorporated into the substrate,¹³ which would make these coatings of interest for electronically reconfigurable printing plates compatible with digital-direct and digital-offset lithography.¹⁴

We explore a route towards such coatings based on block copolymers of poly(ethylene oxide) (PEO) and poly(dimethylsiloxane) (PDMS). PEO and PDMS serve as model hydrophilic and hydrophobic polymers, respectively, that are widely available and whose properties have been extensively studied. Recently, PEO-PDMS block copolymers have been examined as vehicles for hydrophobic drug delivery¹⁵ and have been incorporated into comb-like brushes (similar to those described above) to create coatings with adaptive adhesive properties.^{16,17} In addition, the bulk¹⁸ and solution¹⁹ phase behavior of PEO-PDMS block copolymers has been previously investigated. Due to the strong chemical incompatibility between the blocks,^{18,20} these materials will microphase-separate even at very low molecular weights. Therefore, PEO-PDMS block copolymers are strong candidate materials for the present application: accessible T_{ODT} (<100 °C) at low molecular weight (and therefore low melt viscosity, enabling fast "switching" kinetics), and the desired hydrophilic/hydrophobic character.

Two block copolymers, PEO_{1.2}-PDMS_{1.3} (a waxy solid at room temperature; the subscripts indicate the block molecu-

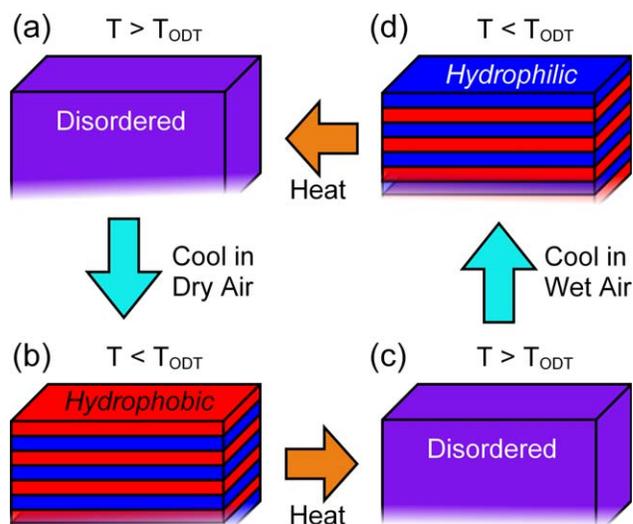


FIGURE 1 Schematic illustrating the concept of thermally switchable coatings enabled by block copolymer self-assembly. (a) At sufficiently high temperatures, the block copolymer coating is in a disordered, homogeneous state (purple). (b) Upon cooling below T_{ODT} in ambient air, the block copolymer microphase-separates, yielding alternating lamellae with the hydrophobic block (red) wetting the air interface. (c) This pattern can be erased upon reheating above T_{ODT} and then (d) reset with the hydrophilic block (blue) exposed at the surface upon cooling below T_{ODT} in humid air.

lar weights in kg/mol) and PEO_{0.5}-PDMS_{1.3} (liquid at room temperature), were synthesized by coupling of hydride-ended PDMS_{1.3} and allyl-ended PEO_{1.2} or PEO_{0.5} oligomers using a Pt catalyst (chromatographs of PEO_{1.2}-PDMS_{1.3} and its constituent homopolymers are shown in Fig. S3 in the Supporting Information; absolute molecular weights were determined by end-group analysis, see Supporting Information Figs. S1 and S2). The bulk phase behavior of the two PEO-PDMS block copolymers was assessed via one-dimensional small-angle X-ray scattering (SAXS). At room temperature, PEO_{0.5}-PDMS_{1.3} showed no peak in the SAXS pattern, indicating that it forms a disordered melt. However, PEO_{1.2}-PDMS_{1.3} displayed two peaks at room temperature: a broad peak centered around $q' = 0.5 \text{ nm}^{-1}$ and a relatively narrow peak at $q^* = 0.82 \text{ nm}^{-1}$ (see Fig. S4 in the Supporting Information). Upon heating to 50 °C, the peak at q' completely vanishes, indicating that this peak corresponds to scattering from semicrystalline material (differential scanning calorimetry shows that the melting temperature for the precursor PEO_{1.2} oligomer is ~35 °C, see Fig. S6 in the Supporting Information). Upon heating to 64 °C, the q^* peak broadens and drops in intensity [see Fig. 2(a,b)], indicating $T_{ODT} = 64 \pm 2$ °C. Below T_{ODT} , PEO_{1.2}-PDMS_{1.3} is microphase-separated with a characteristic domain spacing $d = 7.7 \text{ nm}$ (where $d = 2\pi/q^*$); given the near-symmetric composition of the copolymer (volume fraction $\phi_{PEO} = 0.43$ at 70 °C, based on homopolymer densities²¹), the microdomains are likely

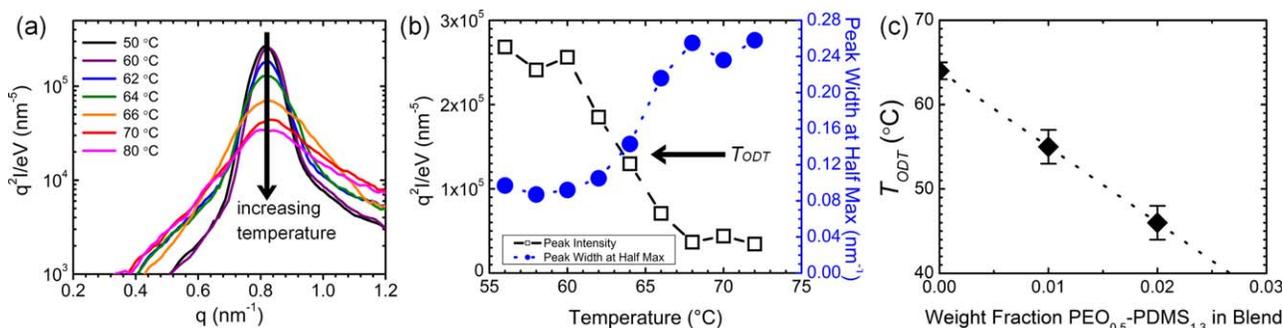


FIGURE 2 Plots showing the phase behavior of PEO_{1.2}-PDMS_{1.3} as probed via small-angle x-ray scattering (SAXS). (a) SAXS patterns as a function of temperature reveal a transition from an ordered structure (with a domain spacing of 7.7 nm) to a disordered melt. (b) T_{ODT} is determined as the temperature at which there is a sharp decrease in peak intensity (open squares) and a corresponding increase in the peak width at half the maximum intensity (blue circles); $T_{ODT} = 64 \pm 2$ °C. (c) T_{ODT} can be tuned via blending with a modest fraction of PEO_{0.5}-PDMS_{1.3}.

alternating lamellae, although no higher-order peaks were observed in the SAXS pattern. The value of T_{ODT} can also be continuously tuned by blending small amounts of PEO_{0.5}-PDMS_{1.3} into PEO_{1.2}-PDMS_{1.3} [see Fig. 2(c)]; the blends were produced simply by codissolving the polymers and casting from toluene. Since $\phi_{PEO} < 0.5$ in PEO_{1.2}-PDMS_{1.3}, and is even smaller in PEO_{0.5}-PDMS_{1.3} ($\phi_{PEO} = 0.23$), small additions of PEO_{0.5}-PDMS_{1.3} depress T_{ODT} significantly.

To set the surface to be either hydrophobic or hydrophilic, the films are annealed above T_{ODT} in either ambient or humidified air, respectively. After cooling to room temperature, the films are allowed to rest, in ambient air, for 10 min and then their static water CA values are measured. Films of the precursor PEO_{1.2} and PDMS_{1.3} oligomers had CA values of $35 \pm 6^\circ$ and $98 \pm 2^\circ$, respectively (\pm indicates one standard deviation in the values measured for 3 or more separately prepared samples), comparable to literature values.^{22,23} PEO_{1.2}-PDMS_{1.3} films prepared in ambient air possessed a CA = $91 \pm 2^\circ$ [see Fig. 3(a)], while films prepared in humidified air displayed CA = $36 \pm 5^\circ$. This result is consistent with our proposed scheme in Figure 1, where PDMS domains form at the surface upon cooling through T_{ODT} in ambient air, while PEO domains cover the surface when cooling through T_{ODT} in humidified air, even after removal from the humid environment. To test the reversibility of the film surface energy upon cycling, a hydrophobically prepared film was reannealed under humidified conditions and its CA measured to be $35 \pm 6^\circ$ [see Fig. 3(b), \pm indicates one standard deviation in the values measured on 3 or more spots along the same sample]; this shows that the initial hydrophobicity of the coating has been completely erased and that the wetting behavior can be easily reset. This switching behavior was demonstrated over multiple cycles [see Fig. 3(c,d)]; the film showed no degradation of the hydrophobic/philic properties over the range investigated.

Despite this demonstration that the wetting behavior of these materials can be easily set and reversibly switched, the wetting behaviors observed were only transiently stable at

room temperature. When exposed to water, the CA values of the hydrophobically prepared films decayed from $\approx 90^\circ$ to $\approx 40 - 60^\circ$ over the course of minutes (see Fig. 4), due to rearrangement of the polymer chains at the surface induced by the sessile water droplet. This rapid rearrangement to a hydrophilic state is consistent with previously examined amphiphilic block copolymer films.^{8,9} Mori et al. observed that as-cast films of low- T_g block copolymers showed an immediate (within a few seconds) reduction in their CA when exposed to water; annealing the films created somewhat more stable coatings, but even these lost their hydrophobicity within minutes.⁸ The rearrangement times of our materials seem consistent with the latter preparation, whose increased stability (compared to the as-cast films) can be

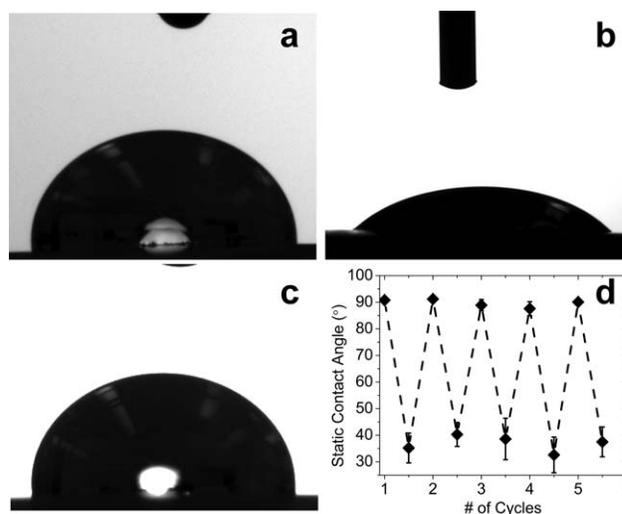


FIGURE 3 Images of a water droplet on a Si wafer coated with PEO_{1.2}-PDMS_{1.3}. (a) Film annealed at 80 °C and cooled to room temperature in ambient air; CA = 91°. (b) Film then reannealed at 80 °C and cooled in humidified air; CA = 39°. (c) Film annealed again at 80 °C and cooled in ambient air, thus illustrating the full reversibility of the process; CA = 90°. (d) CA values through several “switching” cycles.

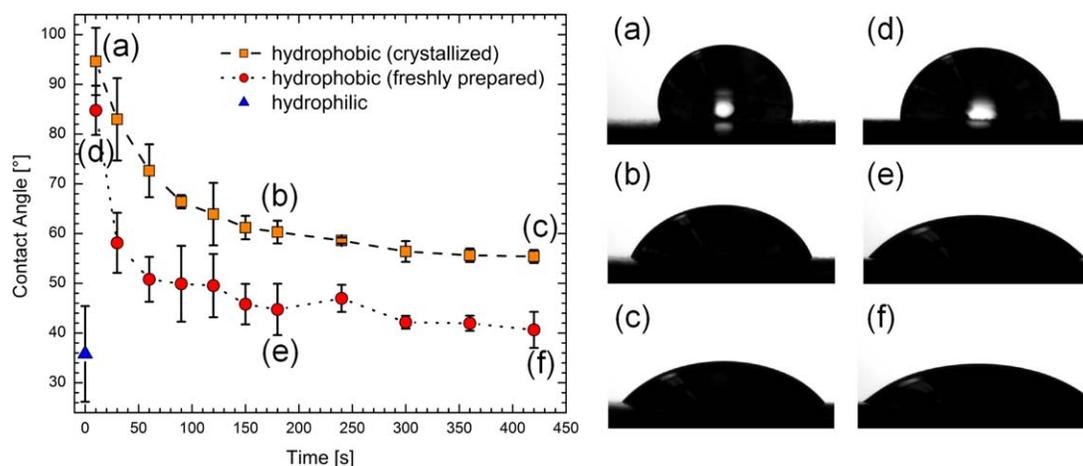


FIGURE 4 Plot showing water CA as a function of time for a hydrophobic film cooled to and held at room temperature (red circles), and one cooled to $-10\text{ }^{\circ}\text{C}$ for 15 min and reheated to room temperature (orange squares). Also shown for reference is a hydrophilic film (blue triangle), which shows no change in CA over time. (a–f) Representative images showing the evolution of CA with time for both hydrophobic film preparations, corresponding time points are indicated on main figure.

attributed to the greater degree of ordering (and therefore enrichment of hydrophobic blocks at the surface). In addition, similar to the findings of Mori et al.,⁸ we observe that the converse rearrangement, from hydrophilic back to a hydrophobic state (by simply allowing the film to rest for a prolonged time in ambient air) is much slower; after ~ 1 day, the CA for PEO_{1.2}-PDMS_{1.3} increases by only $\sim 5\text{--}10^{\circ}$.

Interestingly, the rate and terminal value of the CA decay were dependent on the films' thermal history. Films which were "freshly prepared", as described above, lost their hydrophobicity more quickly, and after ~ 5 min displayed CA values consistent with the hydrophilically prepared films. Films which were allowed to sit overnight at room temperature, or which were more deeply cooled (placed in a $-10\text{ }^{\circ}\text{C}$ freezer for 15 min), did not show as rapid a CA reduction, nor did the CA decay to as low a value. The primary difference between these film preparations is the degree of crystallinity present in the PEO block. Freshly prepared films possess no detectable crystallinity; however, given sufficient time, or subambient cooling, the PEO blocks crystallize (the presence of PEO crystals was confirmed via wide-angle X-ray scattering, see Fig. S5 in the Supporting Information). These crystals likely act as physical crosslinks, which retard the chain rearrangements; however, they cannot eliminate them completely, given PEO's solubility in water. To gain further insight into the crystallization kinetics of PEO_{1.2}-PDMS_{1.3}, isothermal crystallization experiments were performed via differential scanning calorimetry (DSC, see Fig. S6 in the Supporting Information). A freshly prepared sample held at room temperature possesses no detectable PEO crystallinity during the first 10 min, but subsequently crystallizes, saturating to $\sim 15\%$ overall crystallinity after 2 h. A film cooled to $-10\text{ }^{\circ}\text{C}$, however, immediately crystallizes (<1 min) to a level comparable to the film held at room temperature for 2 h or more. Thus, chain rearrangement at room tempera-

ture can be slowed during the initial "setting" process by cooling from above T_{ODT} to $-10\text{ }^{\circ}\text{C}$ to induce crystallization, followed by reheating to room temperature.

We have shown that coatings with thermally switchable wetting properties (hydrophobic vs. hydrophilic) can be achieved using low molecular weight PEO-PDMS block copolymers, readily synthesized via coupling of commercially available end-functionalized oligomers. Heating above the polymer's T_{ODT} erases the material's nanostructure, and subsequent cooling in the presence of dry or wet air creates a hydrophobic or hydrophilic surface, respectively. Static CA measurements demonstrated the efficacy and complete reversibility of the method. The primary limitation of this material is the residual chain mobility present at ambient conditions, which allows the domains to reorganize within minutes when exposed to water, causing the initial hydrophobic character to decay; these rearrangements can be retarded, but not eliminated, by crystallization of the PEO block. While this study has demonstrated proof of concept, practical application of such materials would be better enabled if the wetting behavior could be more effectively "locked in." One approach would be to employ at least one glass-forming block, with $T_{\text{room}} < T_g < T_{\text{ODT}}$; upon cooling, the block copolymer will first order and then vitrify, more effectively preserving the film structure, although even this may not completely eliminate rearrangement.⁸ A good candidate material for the hydrophobic block might be a high- T_g polysiloxane (e.g., poly(diphenylsiloxane), $T_g = 40\text{ }^{\circ}\text{C}$ ²⁴), whose similar chemistry to PDMS would make it compatible with the synthetic approach employed here.

EXPERIMENTAL

Low molecular weight PEO-PDMS block copolymers were synthesized via Pt-catalyzed hydrosilylation coupling of end-functionalized oligomers.²⁵ All of the polymers used in this

study were monofunctional, thus their coupling yielded diblocks. α,ω -allyl,methyl-ended PEO oligomers were generously provided by Clariant. The two PEO oligomers used in this study (AM1100 and AM450, hereafter denoted PEO_{1,2} and PEO_{0,5}) were measured to have number-average molecular weights, M_n , of 1170 and 460 g/mol, and dispersities, \mathcal{D} , of 1.09 and 1.25, respectively. Monohydride-ended PDMS was purchased from Gelest (MCR-H11, hereafter PDMS_{1,3}) with measured $M_n = 1320$ g/mol and $\mathcal{D} = 1.19$. M_n was determined by end group analysis, via ^1H NMR spectroscopy in CDCl_3 using a Bruker AVANCE (see Supporting Information for details). \mathcal{D} was measured using size exclusion chromatography (SEC). PEO and the diblock copolymer were run in tetrahydrofuran (THF) using a Waters 515 HPLC pump, two 30 cm Agilent PLgel Mixed-C columns operating at 35 °C, and a Wyatt OptiLab T-rEX (differential refractive index) detector operating at 658 nm and 25 °C, while PDMS was run in toluene using a Waters 590 HPLC pump, two PLgel Mixed-C 30 cm columns, and a Waters 410 Differential Refractometer, all operating at 40 °C. Both systems' elution times were calibrated using a series of narrow-distribution polystyrene standards of known molecular weight for the calculation of \mathcal{D} . PEO and PDMS were run on separate systems due to the very small refractive index increments for PEO in toluene, and PDMS in THF.

The hydrosilylation coupling reaction was catalyzed using a homogeneous organoplatinum Karstedt's catalyst purchased from United Chemical Technologies (PC072, 2 wt % platinum-divinyltetramethyl disiloxane complex in xylene).^{26,27} To synthesize the diblocks, PEO and PDMS were dissolved in toluene (ACS grade, purchased from EMD) at ~ 20 wt % solids; the PEO was added at $\sim 30\%$ stoichiometric excess to ensure that all of the hydride end groups reacted to completion. The catalyst was added at a 1:5,000 molar ratio of Pt-complex to silane (Si—H) groups.^{25,28} The reaction proceeded overnight at room temperature and its completion was confirmed via ^1H NMR (when the Si—H peak, ~ 4.5 – 4.7 ppm, became undetectable). The excess unreacted PEO was removed via repeated washing (3–5 times) of the reaction mixture with water; the PEO homopolymer is preferentially extracted into the dense aqueous phase, while the diblock creates a water-toluene emulsion. Once the unreacted PEO becomes undetectable (by SEC), the purified block copolymer is collected by removing the solvents from the emulsion (first under flowing N_2 , then under vacuum).

SAXS experiments were performed using CuK_α radiation from a PANalytical PW3030 generator with long-fine-focus Cu tube, a slit-collimated Anton Paar compact Kratky camera, an MBraun OED-50M position sensitive detector, and a home-built hot-stage.²⁹ Data were corrected for empty beam scattering, sample thickness and transmittance, compared to a polyethylene standard for absolute intensity, and desmeared.²⁹

Films of PEO_{1,2}-PDMS_{1,3} were prepared both by drop-casting concentrated solutions of the polymer (~ 20 wt % in toluene) and by simple melting at 100 °C onto Si wafers (Silicon-

Quest, with native oxide, liberally rinsed with toluene prior to use). Both methods yielded relatively thick films (~ 40 – 80 μm , assessed by cross-sectional optical microscopy); such thick samples prevent the polymer from dewetting and eliminate any influence of the substrate on the film's surface morphology. To control the wetting behavior of these films, the samples were placed on a hot plate and heated to 80 °C (well above the polymer's T_{ODT}) and held for 15 min. To prepare a hydrophobic surface, the film was cooled in ambient air to room temperature (~ 19 °C) at ~ 10 °C/min; annealing and cooling the film under vacuum also produces hydrophobicity. For a hydrophilic coating, the film is similarly annealed at 80 °C for 15 min and cooled to room temperature, but in a humidified atmosphere. The saturated water vapor environment is produced by placing a small reservoir of liquid water onto the hot plate adjacent to the film and covering both with an inverted crystallization dish (effectively a "bell jar" style solvent vapor anneal³⁰).

CA values were measured using a Ramé-Hart CA goniometer, model 500-F1 (with a water droplet mass of ~ 2.5 mg; the CA value was determined using the circle method in the Ramé-Hart software).

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