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# Contact angle hysteresis: a different view and a trivial recipe for low hysteresis hydrophobic surfaces

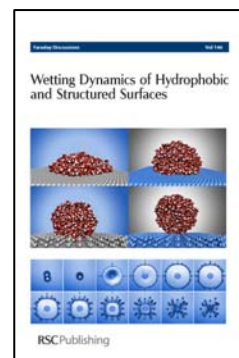
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# Contact angle hysteresis: a different view and a trivial recipe for low hysteresis hydrophobic surfaces

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Received 27th November 2009, Accepted 22nd January 2010

DOI: 10.1039/b925045j

Contact angle hysteresis is addressed from two perspectives. The first is an analysis of the events that occur during motion of droplets on superhydrophobic surfaces. Hysteresis is discussed in terms of receding contact line pinning and the tensile failure of capillary bridges. The sign of the curvature of the solid surface is implicated as playing a key role. The second is the report of a new method to prepare smooth low hysteresis surfaces. The thermal treatment of oxygen plasma-cleaned silicon wafers with trimethylsilyl-terminated linear poly(dimethylsiloxane) (PDMS - commercial silicone oils) in disposable glass vessels is described. This treatment renders silicon/silica surfaces that contain covalently attached PDMS chains. The grafted layers of nanometre scale thickness are liquid-like (rotationally dynamic at room temperature), decrease activation barriers for contact line motion and minimize water contact angle hysteresis. This simple method requires neither sophisticated techniques nor substantial laboratory skills to perform.

## Introduction

Contact angle hysteresis complicates much of the history of wetting (liquids interacting with solid surfaces). Thomas Young<sup>1</sup> initiated modern thought on and scientific research concerning contact angle and wetting in 1804 assuming that there was no hysteresis, but rather “an appropriate angle of contact” for every liquid/solid pair. In retrospect it is apparent that Young could not have carried out many contact angle measurements and maintained his belief in this faulty assumption. Bartell,<sup>2</sup> who measured thousands of contact angles and always observed hysteresis, assumed prior to 1932 “that either an advancing or a receding angle would, within a short time, so adjust itself as to give finally a definite equilibrium angle which would be the same whether approached from the advancing or the receding angle.” Subsequently he discounted this assumption and reported, “We have since obtained good evidence that advancing angles and receding angles may each exist as definite, but different, equilibrium angles.” Wenzel<sup>3</sup> in 1936 and Cassie and Baxter<sup>4</sup> in 1944 developed theories that have been very influential on others’ perspectives of wetting. Their theories do not address hysteresis, although at least Cassie was well aware of it. A section of his 1948 *Faraday Discussion* presentation<sup>5</sup> is titled “The Problem with Receding Contact Angles.” These theories have had an arguably destructive influence<sup>6,7</sup> on wetting research and surface science education in the subsequent decades. Modern theoretical treatments of wetting describe numerous differently defined contact angles,<sup>8</sup> but not the experimentally accessible advancing and receding

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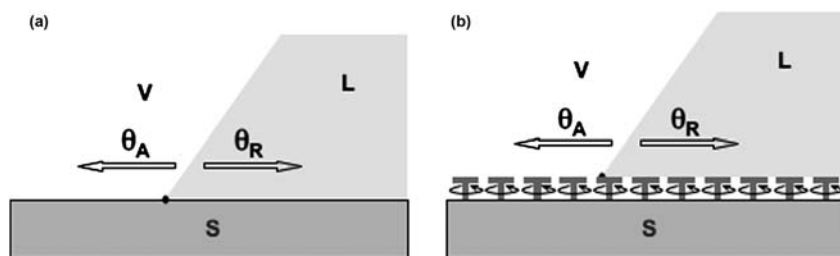
contact angles that determine hysteresis and both shear and tensile hydrophobicity. Contact angle hysteresis has been neglected, tacitly ignored and generally considered linked to defects in solid surfaces.

## Overview

We write this paper with two goals in particular: First, in preparation for a discussion on contact angle hysteresis, we present a new perspective of water drop motion on superhydrophobic surfaces. This perspective is a consolidation of views that we have presented in one 2008,<sup>9</sup> two 2006,<sup>10,11</sup> and two 1999<sup>12,13</sup> papers. This perspective could be gleaned from these manuscripts, but its formulation would be difficult. Second, we describe a simple and reproducible method (a trivial recipe) for preparing smooth surfaces with low hysteresis.

We refer to a 2006 paper<sup>10</sup> titled “*Contact Angle Hysteresis Explained*” and make only brief remarks here that summarize more detailed explanations made in the referenced paper. When a liquid drop moves on a solid surface the 3-phase contact line around the entire drop perimeter continuously redefines itself<sup>14</sup> through advancing and receding events that may be concerted, synchronous or sequential. The mechanisms of these events might be described as rolling or sliding (as extremes) and combinations/hybrids of these extremes could be operative around the contact line of a given moving drop. Some contact line sections could advance and recede back and forth between two different metastable states at greater rates, in microns per millisecond, than the macroscopic drop motion, in millimetres per second (note that the units are equivalent). Advancing and receding events are not generally the reverse of one another<sup>12</sup> and thus will almost always have different barriers. This view leads to the expectation that most surfaces should exhibit contact angle hysteresis - even if they are not dirty, rough or chemically heterogeneous. This is neither a common view nor one that a student of wetting would be taught from any textbook or almost any of the literature. Surface scientists have generally learned to view hysteresis as a “fault” that imperfect surfaces exhibit. Most have not considered that one dimensional intersections of homogeneous (at some length scale) gas, solid and liquid (3D) materials can be heterogeneous, that molecular (bond length scale) heterogeneities in solids<sup>15</sup> as well as the molecular volume and structure of liquids<sup>16</sup> can contribute to hysteresis or that contact lines do not have radial symmetry. Fig. 1a shows a cross section of a sessile drop perpendicular to the solid/liquid/vapor contact line (shown as a point). Moving the contact line to the left (advancing) will involve different barriers than moving it to the right (receding).

From a practical (experimental) perspective, the task of preparing surfaces that exhibit negligible or low hysteresis is not a small one. There is ample literature to refer to, but filtering reproducible methods and legitimate contact angle data from the mass of information is nearly impossible. The recent attention to “superhydrophobicity” has complicated this task.<sup>17</sup> Some rough surfaces exhibit little or no

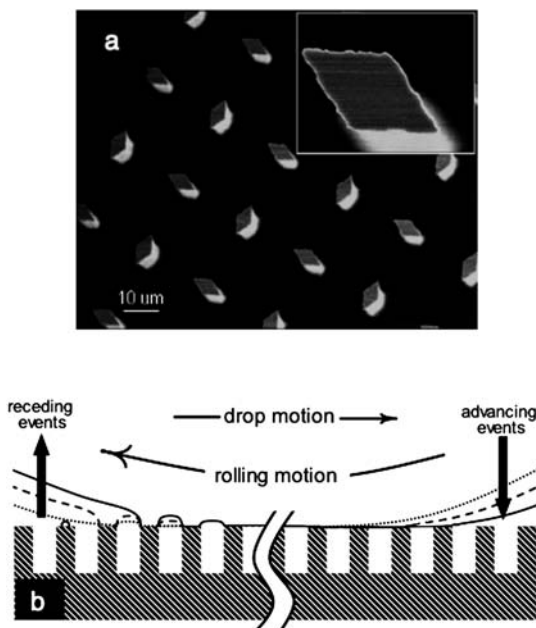


**Fig. 1** Cross sectional views of contact lines at solid/liquid/vapor interfaces on rigid (a) and liquid-like (b) surfaces.

hysteresis while others exhibit extremely high hysteresis. These surfaces have been described as “slippy superhydrophobic” and “sticky superhydrophobic” as well as other adjectives.<sup>9</sup> This terminology has been criticized<sup>9</sup> and we discuss these issues below. Our group has reported preparations of smooth surfaces that exhibit negligible hysteresis,<sup>13,18,19</sup> but these involve techniques of air-sensitive organic synthesis and silane monolayer preparative chemistry. These methods are inherently irreproducible due to “holes,” that are reagent size but larger than the probe fluid, which occur as the result of random covalent attachment. Defects and heterogeneities (even at molecular length scales, for example an ethyl group rather than a methyl group<sup>15</sup>) contribute to hysteresis and the contact line will locate and focus on these defects during advancing and receding contact angle measurements. Our strategy for minimizing hysteresis has been to prepare randomly covalently attached monolayers that are not “close packed,” but in which the attached molecules are free to rotate (exhibiting liquid-like or disordered plastic crystalline behavior - Fig. 1b), heal defects in the surface, and lower activation barriers to the level that the contact line is dynamic at room temperature.

### Contact angle hysteresis on superhydrophobic surfaces

Droplets roll on superhydrophobic surfaces containing topographical features that minimize contact between liquid and solid. This rolling motion and the ability of rolling droplets of water to pick up debris from the solid surface is termed the “lotus effect.” Surfaces containing “posts” have been used to model this effect and we have reported<sup>20</sup> water contact angle data for surfaces containing posts of different size, shape, spacing and surface chemistry (covalently attached alkyl, perfluoroalkyl and silicone groups). A scanning electron micrograph of one of these surfaces is shown in Fig. 2a. This surface was prepared<sup>20</sup> using standard photolithography techniques and contains staggered rhombus-shaped posts that are smooth on their tops

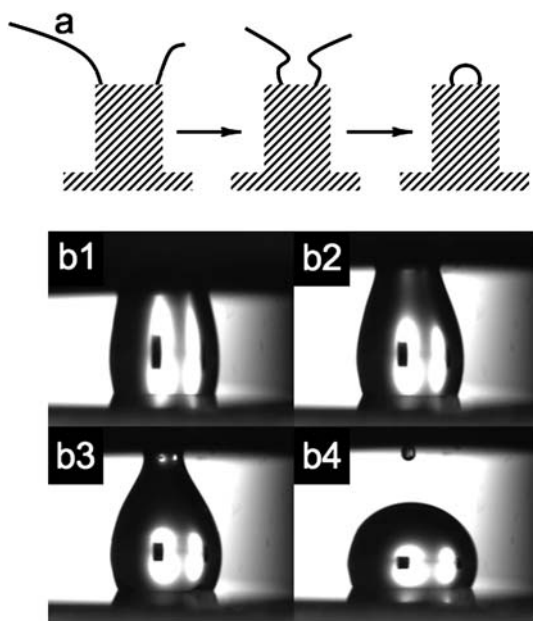


**Fig. 2** (a) SEM of a superhydrophobic modified silicon surface containing staggered rhombus posts ( $8 \times 4 \times 40 \mu\text{m}$ ). (b) Advancing and receding events that occur at the contact lines of a rolling water drop on a surface such as the one shown in (a).

and are all the same height. This surface, when modified with dimethyldichlorosilane,<sup>11</sup> exhibits water contact angles of  $\theta_A/\theta_R = 176^\circ/156^\circ$ . The smooth surfaces of the post tops exhibit contact angles of  $\theta_A/\theta_R = 104^\circ/103^\circ$ .

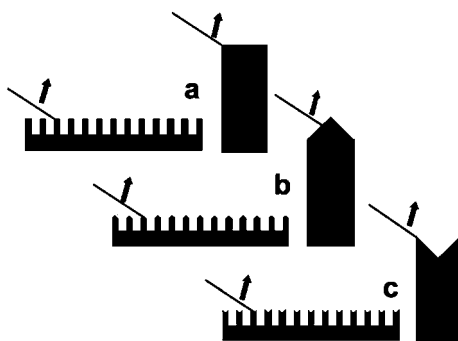
Drops of water roll easily on this surface when it is tilted a few degrees from the horizontal (the minimum tilt angle depends on the drop volume), but are pinned when the surface is horizontal. The  $20^\circ$  hysteresis requires the rolling drop on a tilted surface to distort from a section of a sphere to a shape that exhibits a  $176^\circ$  contact angle (advancing) at the downhill edge and a  $156^\circ$  contact angle (receding) at the uphill-most section of the contact line. Fig. 2b describes the advancing and receding events that must occur at the contact lines. The advancing contact line does not move, but a new one forms as the liquid–vapor surface descends onto the next posts to be wet. The advancing contact angle of the post tops is  $104^\circ$  and the macroscopic drop contact angle is  $176^\circ$  so the drop spontaneously wets the post tops (no activation barrier). The receding events at the rolling drop contact line involve tensile hydrophobicity.<sup>9</sup> The rolling drop with the macroscopic receding contact angle,  $\theta_R = 156^\circ$ , cannot recede across the post tops ( $\theta_R = 103^\circ$ ) and must disjoin from the posts being dewet in a near vertical (tensile) manner. This must involve the cohesive failure of a capillary bridge (Fig. 3a) and the formation of small sessile droplets on the recently dewet post tops. We have not observed these small droplets, but have not yet looked for them. We have studied capillary bridge rupture between smooth hydrophobic surfaces and small droplets are retained by the dewet surfaces. Fig. 3b shows frames from a movie of a capillary bridge rupturing as two smooth hydrophobic surfaces are separated. A small droplet of water is apparent on the upper surface.

We have shown<sup>11</sup> that introducing a second level, submicron topography to the post tops relieves the receding contact line pinning and eliminates hysteresis. We expect, however, that this pinning could also be eliminated by introducing positive curvature to the post tops. Surfaces with posts containing pyramidal, conical or

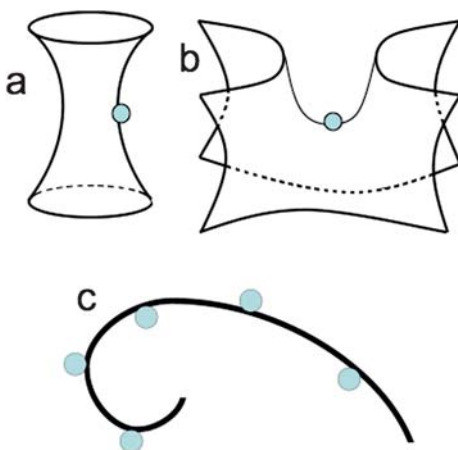


**Fig. 3** (a) Depiction of a capillary bridge rupturing during a receding event at the contact line. (b) Selected frames from a movie of a capillary bridge rupturing as two smooth hydrophobic surfaces are separated.

spherical caps should exhibit higher receding contact angles. Surfaces with pyramidal, conical or spherical depressions should exhibit lower receding angles and greater pinning (Fig. 4). This intuitively obvious prediction is based essentially only on the simple contact line arguments<sup>21</sup> made by Bartell in 1953 to explain differences in hysteresis on surfaces containing pyramid-shaped asperities. We have not prepared surfaces with the constructs shown in Fig. 4, but include these to stimulate discussion at the meeting. We note that pairs of surfaces with positive and negative curvature post caps would exhibit an identical liquid–solid contact area (have the same Cassie & Baxter  $f_1$  and  $f_2$  values), but very different receding contact angles. In Fig. 5 we show two surfaces with constant mean curvature that should exhibit direction-dependent receding contact angle pinning and a surface with a constantly changing curvature (French curve) that should exhibit and could test curvature-dependent tensile hydrophobicity.



**Fig. 4** Compared with flat post tops (a), surfaces with posts containing pyramidal, conical or spherical caps (b) should exhibit higher receding contact angles and reduced receding contact line pinning. Surfaces with pyramidal, conical or spherical depressions (c) should exhibit lower receding angles and greater pinning.



**Fig. 5** Two surfaces (a and b) with constant mean curvature, that should exhibit direction-dependent receding contact angle pinning, and a surface (c) with constantly changing curvature (French curve) that should exhibit curvature-dependent tensile hydrophobicity and direction-dependent shear hydrophobicity.



## Smooth surfaces without contact angle hysteresis

As mentioned above, preparing non-hysteretic surfaces is a synthetic challenge that the literature does not readily aid. Two publications that stand out as having the potential to impede the task of preparing smooth low hysteresis surfaces are (1) a 1994 *Langmuir* paper,<sup>22</sup> entitled “*Silanization of Solid Substrates: A Step toward Reproducibility*,” that claims to prepare surfaces with “less than 1°” hysteresis and (2) a 2005 *J. Am. Chem. Soc.* paper,<sup>23</sup> entitled “*Mixed Self-Assembled Monolayers of Alkanethiolates on Ultrasoother Gold Do Not Exhibit Contact-Angle Hysteresis*.” Another paper<sup>24</sup> that demonstrates the authors’ significant insight into wetting, reports hysteresis values of 1–2° using hexadecane as a probe fluid and that hysteresis using water “is larger.” In a subsequent paper<sup>25</sup> by the same authors, the water contact angle data were reported and hysteresis was indeed higher than 1–2°: reported values ranged from 23° to 61°.

We report here a procedure to prepare low hysteresis hydrophobic solid surfaces that uses a similar strategy (monolayer flexibility) as the one described above, but is improved over previous ones. This method neither produces surfaces that have lower hysteresis nor is it more reproducible in skilled hands than those we reported in the past,<sup>13,18,19</sup> however it does not involve air-sensitive reactive silanes, requires no cleaning of glassware, is not dependent on air humidity or the water content of solvents and does not require the skills of an experienced chemist. The procedure is simple: A silicon wafer sample<sup>26</sup> is cleaned in a commercial plasma cleaner,<sup>27</sup> placed in a just-opened commercial screw cap vial,<sup>28</sup> and wet with as-received trimethylsilyl-terminated linear poly(dimethylsiloxane) (PDMS).<sup>29</sup> The cap is replaced and the vial is placed in an oven at 100 °C for 24 h. After the vial cools to room temperature, the sample is rinsed with copious solvent<sup>30</sup> and allowed to dry.

Tables 1 and 2 show water contact angle<sup>31</sup> data for silicon wafer surfaces prepared using two different commercial PDMS samples with reported molecular weights of 2,000 and 9,400 g mol<sup>-1</sup>. 12 individual reactions were carried out with PDMS<sup>2 K</sup> and 10 with PDMS<sup>9 K</sup>. Each of the reported  $\theta_A$  and  $\theta_R$  values are the averages of 18 measurements made at 3 locations on each sample. Individual measurements were recorded to the nearest degree and the values to one decimal place reported in the tables are averages of the 18 measured values. The averages and standard deviation values of 216 measurements for surfaces prepared with PDMS<sup>2 K</sup> are  $\theta_A/\theta_R = 104.0^\circ \pm 0.8^\circ/102.4^\circ \pm 1.4^\circ$ . The 180 measurements on PDMS<sup>9 K</sup>-derived surfaces averaged  $\theta_A/\theta_R = 105.6^\circ \pm 0.7^\circ/104.8^\circ \pm 0.9^\circ$ .

These easily prepared surface-modified silicon wafers exhibit water contact angle behavior that is indistinguishable from numerous other surfaces that we have

**Table 1** Water contact angles of PDMS<sup>2 K</sup>-derived silicon wafers

Sample	$\theta_A$ (°)	$\theta_R$ (°)
PDMS <sup>2 K</sup> -A	104.7	102.3
PDMS <sup>2 K</sup> -B	105.8	105.0
PDMS <sup>2 K</sup> -C	104.2	103.2
PDMS <sup>2 K</sup> -D	104.3	103.7
PDMS <sup>2 K</sup> -E	103.7	103.2
PDMS <sup>2 K</sup> -F	104.2	100.2
PDMS <sup>2 K</sup> -G	104.0	102.2
PDMS <sup>2 K</sup> -H	104.2	102.7
PDMS <sup>2 K</sup> -I	103.3	99.8
PDMS <sup>2 K</sup> -J	103.7	102.0
PDMS <sup>2 K</sup> -K	103.3	101.7
PDMS <sup>2 K</sup> -L	103.2	102.7

**Table 2** Water contact angles of PDMS<sup>9 K</sup>-derived silicon wafers

Sample	$\theta_A$ (°)	$\theta_R$ (°)
PDMS <sup>9 K</sup> -A	105.0	105.0
PDMS <sup>9 K</sup> -B	106.0	105.7
PDMS <sup>9 K</sup> -C	106.0	104.0
PDMS <sup>9 K</sup> -D	106.0	106.0
PDMS <sup>9 K</sup> -E	106.5	106.3
PDMS <sup>9 K</sup> -F	104.3	103.7
PDMS <sup>9 K</sup> -G	105.7	104.2
PDMS <sup>9 K</sup> -H	105.0	104.3
PDMS <sup>9 K</sup> -I	105.5	103.8
PDMS <sup>9 K</sup> -J	105.8	104.5

prepared in our laboratory using discrete sterically hindered monochlorosilane compounds, chloro-terminated (difunctional) silicone oligomers and certain mixtures of methylchlorosilanes. We have reported values of  $\theta_A/\theta_R = 105^\circ/104^\circ$ ,  $106^\circ/104^\circ$  and  $104^\circ/103^\circ$  for some of these surfaces<sup>11,13,19</sup> and some of these data have been reproduced many times by multiple researchers including both authors of this paper. We have also reported<sup>18,20,32</sup> values of  $\theta_A/\theta_R = 101^\circ/99^\circ$ ,  $104\text{--}105^\circ/101\text{--}103^\circ$  and  $107^\circ/102^\circ$  for one of these surfaces (prepared by vapor phase reaction with dimethyldichlorosilane) because these were the data obtained during a particular study by a particular researcher. In all of these studies, a fraction of surfaces prepared with reactive silanes were discarded because of low receding contact angles caused by defects or contaminants. We report the multiple experiments and redundant data in Tables 1 and 2 to emphasize the reproducibility and ease of this modification method.

We were initially surprised by the results that we report here, but in retrospect should not have been. We had ignorantly regarded linear unfunctionalized methylsilicones as unreactive polymers and did not expect that they would react with silica surface silanols. Silicones, however, have long been known to equilibrate<sup>33–36</sup> to most probable molecular weight distributions and equilibrium cyclic oligomer concentrations by both acid and base catalysis. It is reasonable and expected that surface silanols participate in these equilibrations at 100 °C. We have not carried out experiments to distinguish whether the mechanism involves silanols protonating silicone oxygen atoms or silanols reacting as nucleophiles with silicone chains. Both protonated silicones and silanols may be involved. Silica has been reported to be acidic<sup>37,38</sup> with an isoelectric point of  $\sim 3$ , but whether this is meaningful at PDMS interfaces at 100 °C is questionable. The hydrolytic cleavage and equilibration of silicones is reported to be Lewis acid-catalyzed by inorganic solids.<sup>39,40</sup>

We plan to report data based on work currently in progress, but make 7 additional observations that are currently only qualitative, involving control experiments that substantiate the results reported here: (1) Ellipsometry and XPS data indicate that PDMS<sup>9 K</sup>-derived grafted layers are about twice as thick as those prepared with PDMS<sup>2 K</sup>. (2) Initial AFM studies suggest that the PDMS<sup>2 K</sup>-derived surfaces are about as smooth as the initial silicon wafer. (3) These surfaces show low contact angle hysteresis with hexadecane and diiodomethane probe fluids, thus are “shear lyophobic.” (4) Other linear dimethylsilicones of both higher and lower molecular weight react to hydrophobize silicon wafers. (5) Silicon wafers cleaned using chromic acid<sup>19</sup> react with PDMS<sup>2 K</sup> to form surfaces that exhibit contact angles indistinguishable from those cleaned with oxygen plasma. (6) As-received silicon wafers (not cleaned) react with PDMS<sup>2 K</sup>, but receding contact angles reveal that many defects are present in the resulting surfaces. (7) The reaction occurs in vessels other than the disposable vials<sup>28</sup> including Teflon bottles, however the cleanliness of the vessel is important and the disposable vials that are purchased with caps attached are cleaner

than vessels that have been exposed to our laboratory and we expect cleaner also than vessels cleaned and dried in any preparative chemistry lab.

## Summary

Contact angle hysteresis on superhydrophobic surfaces, modeled by surfaces containing posts, is due to receding contact line pinning. This pinning is based on the force required for cohesive failure of capillary bridges, thus a tensile analysis is appropriate. The sign of the curvature of the tops of posts is critical to whether hysteresis will be negligible or significant. Low hysteresis smooth surfaces can be conveniently prepared using disposable vials, commercial silicone oil and plasma-cleaned silicon wafers.

## Acknowledgements

We thank Shocking Technologies and the Centers for Materials Research Science and Engineering (DMR-0213695) and Hierarchical Manufacturing (CMMI-0531171) at the University of Massachusetts for support.

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- 27 Samples were exposed to oxygen plasma in a Harrick Expanded Plasma Cleaner at 18 W and 300 mTorr (flowing oxygen) for 30 min.
- 28 20 mL borosilicate glass scintillation vials capped with pulp-backed metal liners were purchased from Fisher and supplied in boxes of polyethylene film - wrapped trays containing 100 closed vials. These vials are apparently closed in a much cleaner and much more dust-free environment than our laboratories. We regard them as "a clean room in a bottle".
- 29 PDMS<sup>2 K</sup> and PDMS<sup>9 K</sup> were purchased from Gelest. Product codes are DMS-T12 and DMS-T22.
- 30 The data reported here were obtained using samples that were rinsed sequentially with copious toluene, acetone and house-purified water from polyethylene squirt bottles. Samples rinsed with only heptane exhibited contact angle values that are indistinguishable from data obtained with toluene/acetone/water rinsing.
- 31 Contact angle measurements were made with a Rame-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Dynamic advancing ( $\theta_A$ ) and receding angles ( $\theta_R$ ) were recorded while the probe fluid was added to and withdrawn from the drop, respectively.
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