<http://www.diva-portal.org>

Preprint

This is the submitted version of a paper published in *Advanced Materials Interfaces*.

Citation for the original published paper (version of record):

Pardon, G., Haraldsson, T., van der Wijngaart, W. (2016)

Simultaneous replication of hydrophilic and superhydrophobic micropatterns through area-selective monomer self-assembly.

Advanced Materials Interfaces

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:kth:diva-189595>

"This is the pre-peer reviewed version of the following article: Simultaneous replication of hydrophilic and superhydrophobic micropatterns through area-selective monomer self-assembly, which has been accepted for publication in Advanced Materials Interfaces. This article may be used for non-commercial purposes in accordance with [Wiley Terms and Conditions for Self-Archiving](#)."

DOI: 10.1002/admi.201600404

Simultaneous replication of hydrophilic and superhydrophobic micropatterns through area-selective monomer self-assembly

By Gaspard Pardon, Tommy Haraldsson, and Wouter van der Wijngaart*

[*] Dr. G. Pardon, Dr. T. Haraldsson, Prof. W. van der Wijngaart
Osquidas väg 10
10044 Stockholm (Sweden)
E-mail: tommyhar@kth.se

Keywords: surface modification; surface energy patterning; molecular self-assembly; superhydrophobicity; surface energy mimicking

Introduction

The control and permanent modification of the surface properties of polymers is a critical enabler for many applications. Here, we demonstrate a strategy, which we call surface energy mimicking, for the spontaneous replication of micropatterns of surface energies ranging from hydrophilic to superhydrophobic from a mold to several replicas.

Surface energy plays a significant role in life science applications. Hydrophobicity/-philicity notably underlies biofouling, biomolecular adhesion, and cellular growth.^[1-9] In lab-on-a-chip applications, hydrophilicity is required for self-priming of microfluidic channels and for electroosmotic flow control, whereas hydrophobicity is desirable for the creation of hydrophobic valves and passive fluidic control.^[10-21]

The most commonly used surface modification protocols are plasma treatment, chemical treatment, including grafting, and thin-film coating, all of which require elaborate back-end processes on semi-finished products.^[10,22,23] Furthermore, patterning of surface

modifications requires masking on individual devices, which entails delicate steps and cumbersome manual procedures.^[24-26] Modification on 3D-geometries, such as sidewalls or re-entrant structures, is even more problematic or may require the use of multiple materials.

In contrast, here, surface energy mimicking merges device manufacturing and surface modifications, including patterning, into a single processing step, using a single device material.

Surface energy mimicking is enabled by embedding functional mimicking monomers with specific chemical moieties in a liquid prepolymer matrix (**Figure 1**). Once the prepolymer mixture is dispensed onto a master mold, the mimicking monomers self-assemble against areas of the mold displaying a corresponding surface energy. This adaptive process is driven by surface energy minimization. During subsequent polymerization, the mimicking monomers are fixated by covalent bonds into the polymer matrix. Consequently, the surface energies and topography of the mold are simultaneously replicated in corresponding regions on the replica.

In this paper, we use an alternating thiol-ene copolymer formulation enabling surface energy mimicking to demonstrate the single-step formation of replicas containing hydrophilic, hydrophobic and superhydrophobic areas, through the simultaneous replication of surface energies (2D) and of micro-/nanostructures (2.5D). Such (super)hydrophobic/philic patterns are of general interest in many applications.^[26-36] We further demonstrate the replication of an array of hydrophilic micropatches surrounded by a hydrophobic surface, on which picoliter-droplet arrays can self-assemble. Such hydrophilic-in-hydrophobic arrays are useful for digital bioassays,

where picoliters droplets must be arrayed for digital detection of a target

bioreaction.^[16,37] Other application areas may also benefit from easily patterned surface modifications including microarrays ^[31], cell and tissue engineering ^[38,39] or block-copolymer self-assembly.^[24,40-42]

Methods and materials

Our experiments, detailed below, investigate various aspects of surface energy mimicking including the influence of the polymer composition and of the type of mold surfaces. The latter is examined using various mold materials, surface treatments and surface topography, and the former using various combinations of the polymer matrix and of the mimicking monomers. A model is derived to link and compare the contact angles of polymer replicas to those of master molds with varying surface energies, obtained by silanization. Contact angle measurements, scanning electron microscopy and bright-field and fluorescence microscopy are used to characterize the surface energy, the replication of surface topography and the self-assembly of droplet arrays, respectively.

Polymer Formulations

Several polymer formulations (PF) were investigated, using various combinations of matrix and mimicking monomers (**Table 1**). PF1 is the mimicking polymer formulation, while PF2 and 3 are used for characterization and PF4 as control.

As polymer matrix, thiol-ene monomers were used, since they form a densely cross-linked network and because they exhibit interesting features for lab-on-chip

applications, such as tunable mechanical properties, easy covalent surface bonding and surface grafting, and excellent photolithographic capabilities.^[43-47]

As functional mimicking monomers, two functional methacrylates, which can react covalently with the matrix monomers, were investigated. They were selected with a hydrophobic fluorinated moiety, and a hydrophilic hydroxylated moiety, respectively.

Preparation of Master Mold Surfaces

Several types of master mold surfaces (MMS) were tested.

MMS 1 Substrates made of various unaltered materials

Various unaltered materials, including: glass, PET, borosilicate glass, PDMS and Teflon AF, were used after thorough cleaning, immediately before use, using IPA and DI water, and drying under an N₂ gas stream. No polishing or surface treatment was performed on these substrates.

MMS 2 Substrates modified using physical surface treatment

After casting, heat curing and cleaning, half of the PDMS substrates were made hydrophilic by plasma treatment. Plasma activation was performed < 5 min before use for molding or measurement, using an H₂O plasma oven (Femto 1, Diener electronic GmbH, Germany) (0.3 mbar, 40 W power, 720 cm³min⁻¹ flow, for 15 s). Each time, one substrate was used for the surface energy mimicking experiment and a second was used as control for contact angle measurement.

MMS 3 Substrates modified using chemical surface treatment

Glass substrates were made hydrophobic by silanization. After cleaning, the substrates were incubated into a silane solution (10 min at 25°C); dried using a N₂ gas stream. Reaction with the substrate was completed in an oven (120°C for

10 min). After cooling, the supernatant was washed in acetone, rinsed with IPA and dried using N₂ gas. Varying silane surface coverage was achieved using a dilution series of silane in 2-propanol, ranging from 100% w/w to 0.012% w/w, while maintaining treatment time and temperature. The contact angle as function of the silane concentration is reported in Figure S1 in Supplementary Information.

MMS 4 Substrates with micro-/nanostructured topography (2.5 D)

Substrates containing micro- and nanoscale roughness were used to investigate the simultaneous replication of surface energy and topography for generation of superhydrophobicity. Glass substrates with sandblasted areas (VWR, Sweden, part # 631-0116, Frosted end, ISO 8027/1) were used. Half of these substrates were hydrophobic silanized, as described above. Vacuum was applied prior to UV-polymerization (10 min at -0.5 bar) to remove entrapped gas bubbles.

MMS 5 Substrates with patterned surface properties (2 D)

Patterns of different surface energies were created starting from hydrophilic substrates using two approaches: 1) *MIMIC soft-lithography* ^[48,49]: Teflon AF was introduced capillarilly between a soft-bonded PDMS microstructured stamp and a glass substrate. After curing and evaporation of the solvent through the PDMS, the unprotected surface is covered by a thin layer of Teflon AF, while the areas protected by the PDMS stamp patterns remains unmodified, resulting in hydrophobic patterns corresponding to the inverse of the stamp design. 2) *Silanization lift-off*: Silicon substrates were photopatterned using a positive photoresist and thereafter silanized, as detailed above, while the photoresist protects specific surface areas. The photoresist is removed by the acetone during the washing step of the silanisation, resulting in lift-off of the silane. The

substrate only becomes silanized in areas that are not protected by the photoresist. The molecular thickness of the silanization minimally alters the surface topography and hence can more easily be applied on 3D nanostructures.

Tests for the characterization of the surface energy mimicking

The replication of 2.5D micro-/nanostructured substrates, MMS 4, and of 2D-micropatterned substrates, MMS 5, was performed using mimicking polymer formulation PF1.

Additionally, surface energy mimicking was characterized with three specific tests. Using PF1 to 4, i.e. containing none, either of, or both hydrophilic mimicking monomers, replicas were polymerized:

Test 1: onto silanized glass substrates, MMS 3, to investigate the replication of different mold surface energies obtained through silanization, and the effect of the polymer composition.

Test 2: in open-air, i.e. not in contact with any solid surface, and on untreated polished glass, to verify that surface energy mimicking is not due to material transfer.

Test 3: onto various unaltered raw materials substrates, MMS 1, as well as on plasma-modified PDMS substrates, MMS 2, to investigate the effect of the mold surface materials and of physical surface treatment, respectively. Here, the TPO-L photoinitiator was used instead and the concentration of mimicking monomers was lower, i.e. 0.5% w/w.^[37]

Manufacturing of polymer replicas

The polymer replicas were prepared by dispensing the liquid prepolymer formulation onto master mold surfaces (Figure 1), or onto a supporting substrate in the case of open-air polymerization. After photopolymerization, the replicas were carefully separated from the master mold, rinsed with IPA, dried using a N₂ gas stream, and stored in covered petri dishes until characterization.

Chemicals and Materials

Polymer matrix: Tetraallyloxyethane (TAOE) (Tokyo Chemical Industry Co., Ltd., Japan) and Pentaerythritol-tetrakis(2-mercaptoacetate) (PETMA) (Sigma-Aldrich Co., USA, mixed in 20.56% w/w and 79.34% w/w, respectively (except otherwise mentioned)).

An thiol group excess was used to enable further reactions using thiol groups after cross-linking, such as grafting or covalent bonding.[43,44] A photoinitiator, Irgacure 184 (BASF Corp. USA), was dissolved in the thiol monomer (in 0.1% w/w). In some cases (as mentioned), Lucirin TPO-L (BASF Corp., USA) was used instead (in 0.3% w/w).

Functional mimicking monomers (Sigma-Aldrich Co., USA, each mixed in 1% w/w in the polymer matrix (except otherwise mentioned)): 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,-heptadecafluorodecyl-methacrylate (FDM) (initially dissolved in 20% w/w in toluene); 2-hydroxyethyl-methacrylate (HEMA) (initially dissolved in 30% w/w in toluene (except otherwise mentioned)).

Polydimethylsiloxane (PDMS) was prepared using Sylgard® 184 (Dow Corning Europe SA, Belgium).

Other chemicals were: Teflon-AF-1601S40 (DuPont (USA)) (in 0.15% w/w in Fluorinert®-FC-40 (Sigma-Aldrich, USA)); Fluorinated silane, Dynasylan® F8263 (Evonik Industries AG (Germany)) (in various ratios in acetone); Photoresists:

Megaposit SPR-700m (Micro resist technology GmbH, Germany); and SU-8-2025

(MicroChem Corp., USA); Solvents: Isopropyl alcohol (IPA) (Sigma-Aldrich Co., USA); toluene (Merck KGaA, Germany); and acetone (Sigma-Aldrich, USA); Milli-Q water (DI water) was obtained from our cleanroom (pH was measured stable at 5.9).

Substrate materials were: Glass substrates: microscopy slides and borosilicate microscope cover slips glass (VWR, Sweden); Polyethylene terephthalate (PET) films (AGFA, Belgium); PDMS substrates were prepared in-house within an hour before the experiments (in 10:1 weight ratio) and cured against polished glass; Teflon substrates were prepared on polished glass by spin-coating Teflon AF (1200 rpm for 60 s, followed by 10 min at 110° annealing), measured 8 nm thick by ellipsometry.

Other materials were: Flexible photomasks (Micro Lithography Services Ltd, UK); Rhodamine B-marked and carboxylate-modified melamine resin microparticles (Sigma-Aldrich, USA).

Polymerization was performed using a collimated (3° half-angle) near-UV short-arc mercury lamp (12 mW cm⁻²) (OAI, Milpitas, USA). Exposure dose was 100s of mJ cm⁻² and varied to match the photoinitiator concentration and polymer formulation.

Contact angle measurements were performed using a Theta-lite optical tensiometer (Biolin AB, Sweden), using 3 µL Milli-Q water droplets. At least five droplets per sample were measured and averaged. Each measurement is an average of ten images taken every 0.1 sec, 8 sec after droplet deposition, for proper stabilization and to avoid evaporation. Contact angles were measured on each master mold < 10 min before use for molding and on the polymer replicas < 30 min after separation from the mold and IPA rinse.

Modeling

In the case of Test 1, i.e. using MMS 3, made of silanized polished glass, the surface energy mimicking can be modeled. For both the master molds and the polymer replicas, the surface energy results from heterogeneous surface constituents, i.e. constituents i = glass and silanes for the mold, and constituents j = matrix, hydrophilic and hydrophobic mimicking monomers for the replicas, which can be assumed to form surface domains in the micro-/nanometer range. The energy of the heterogeneous surface can be estimated as the surface area weighted-average of the surface energy of each constituents, using the Cassie equation:[50-52]

$$\theta_{\text{replica_Cassie}} = h(\theta_{\text{master}},) = \arccos\left(\sum_i \sum_j f_i(\theta_{\text{master}}) \cdot g_{i,j} \cdot \cos(\theta_j)\right) \quad (1)$$

or, in the case of nanoscale domains, using a modified version of the latter proposed by

Israelachvili *et al.*:[53]

$$\theta_{\text{replica_Israelachvili}} = \arccos\left(\left(\sum_i \sum_j f_i(\theta_{\text{master}}) \cdot g_{i,j} \cdot (1 - \cos(\theta_j))^2\right)^{1/2} - 1\right) \quad (2)$$

(The model derivation is detailed in Supplementary information)

Furthermore, the surface fraction of the different constituents in the polymer replica can be assumed to result from an adsorption process. At first approximation, this can be

described by an adsorption isotherm of the type: $g_{i,j} = \frac{c_{s,i,j}}{c_{s,0}} = \frac{K_{i,j}c_{b,j}}{1 + \sum_j K_{i,j}c_{b,j}}$ (4), where $c_{s,0}$

is the surface concentration of adsorption sites, and $K_{i,j}$ the adsorption equilibrium constant of constituent j on surface i . Equation (4) enables comparing the $K_{i,j}$ obtained from measurements using PF1 with those obtained using PF2 and 3.

Results

Replication of 2.5D micro-/nanostructures of different surface energies

Figure 2 a shows the replication of micro-/nanostructures of different surface energies, (MMS 4). The glass master mold contains four regions, i.e. the combinations of: polished or micro-/nanostructured geometry; and hydrophobic or hydrophilic surface energy. SEM images show close-ups of hydrophobic areas on the polymer replica (Figure 2 b). The replicated surface of the polished region is very smooth, while that of the micro-/nanostructured region demonstrates fine replication of the mold 2.5D structures. In both regions, nanometer sized dots are visible at increased image contrast, indicating some material heterogeneity.

Contact angle measurements on each of the four replicated regions are indicated in Figure 2 a. Interestingly, the replicated surface corresponding to the structured hydrophobic mold region displays superhydrophobicity, with a contact angle of up to 165° (Figure 2 c). This demonstrates that surface energy mimicking enables generating hydrophilic, hydrophobic and superhydrophobic areas on a single replica in a single molding step.

Replication of 2D micropatterns of different surface energies

Figure 2 d shows the replication of an array of hydrophilic micropatches surrounded by a hydrophobic surface area (MMS 5). After replication, an array of nano-/femtoliter droplets can be self-assembled on the replica surface. A self-assembled droplets array, with $200\ \mu\text{m}$ patch diameter and $500\ \mu\text{m}$ pitch is shown in Figure 2 e. Fluorescent images show microparticles deposited on the rim of hydrophilic patches of $250\ \mu\text{m}$ and $50\ \mu\text{m}$ diameter, due to coffee stain effect during evaporation of the self-assembled droplets (Figure 2 f). The deposited microparticles indicate the excellent replication of the circular patch pattern, with a very sharp and regular contour. The images shown

were obtained from the fifth replica produced using the same master mold and do not reveal any pattern degradation. These results demonstrate that surface energy mimicking accurately replicates 2D micropatterns in a single step.

Characterization of the surface energy mimicking

Test 1: Replication of silanized glass substrates

The contact angles of the replicas versus those of the master mold, for Test 1 and PF1, show that hydrophilic molds generate hydrophilic replicas, and hydrophobic molds generate hydrophobic replicas (**Figure 3 a**). The slope, $d\theta_{\text{replica}}/d\theta_{\text{master}}$, plotted in the right inset, shows a good correlation between the surface energies, with a value > 0.6 in the range 55 to 110° of contact angle on the master mold. The left inset shows the calculated surface fraction of silane, f_{silane} , versus θ_{master} . Equations (1) and (2) were fitted to the measurements using a non-linear least-square regression, (blue lines). The $R^2 = 0.9274$ and 0.9375 show a good fit for both models. **Table 2** summarizes the fitting parameters $g_{i,j}$, as well as the corresponding $K_{i,j}$ and the $g_{i,j}$ parameters, back calculated using equation (3) and the model fitting parameter on measurements for FP2 and FP3. The model computed with the calculated $g_{i,j}$ is plotted with light-grey line.

Figure 3 b shows a comparison of contact angles for PF1 with those for PF2, 3 and 4. To the contrary of the mimicking formulation PF1, containing both functional mimicking monomers, the surface energy of the pure polymer matrix PF4 does not vary significantly for different mold surface energies. For PF2, only containing hydrophilic mimicking monomers, the replica surface only becomes more hydrophilic than PF4; while for PF3, only containing hydrophobic mimicking monomers, the opposite is true.

This demonstrates that surface energy mimicking originates from surface self-assembly of the functional mimicking monomers.

Test 2: Polymerization in open air

To verify that replication of the mold surface energy is not due to transfer of silane monomers from the master to the replica, measurements were also performed on replica polymerized in open air, i.e. not in contact with any surface. Air is equivalent to a low surface energy substrate and is expected to produce similar results to hydrophobic molds. In Figure 3 c, the results from replication in open air are compared with those from replication on bare glass and on fully silanized glass. As indicated with *I*, the open-air results for PF1 and 3 are similar to those obtained on hydrophobic substrates, i.e.

$\theta_{\text{replica,open-air}} \approx \theta_{\text{replica,silanized glass}}$; while the open-air results for PF2 and 4 stay similar to those obtained on hydrophilic substrates, i.e. $\theta_{\text{replica,open-air}} \approx \theta_{\text{replica,glass}}$.

This demonstrates that the surface energy mimicking is not due to material transfer from the master to the replica.

Furthermore, as indicated with *II*, the open-air results for PF2 are similar to those on the hydrophobic substrate, $\theta_{\text{replica,open-air}} \approx \theta_{\text{replica,silanized glass}}$, confirming that the hydrophilic moieties are repelled from hydrophobic interfaces.

Test 3: Replica of the surface energy of various materials

In Figure 3 d, the contact angles of the polymer replicas versus those of the master mold for Test 3 and formulations PF1 to 4 show that surface energy mimicking also works on various unaltered materials. Surface energy mimicking is also shown sensitive to

physical modification of the surface energy of master surfaces, such as for plasma-treated PDMS.

Because of the homogeneous mold materials in Test 3, equation (1) or (2) are not applicable and a linear regression was fitted instead. The slope value of 0.42 for PF1 is slightly lower than that observed with the fitted models in Figure 3 a. This may result from measurement errors or from nanoscale roughness on the mold material surfaces, as suggested by the non-zero slope for the pure matrix PF4 (Figure 3 d), or of the replica surface, as suggested by the SEM images (Figure 2 b).

Discussion

Beyond the functional demonstration of superhydrophobicity generation and of surface energy micropattern replication, our investigation provides interesting insight into the mechanisms underlying surface energy mimicking. The good match between model and experiments (Figure 3 a and b) supports the hypothesis that surface energy mimicking results from area-selective self-assembly of functional mimicking monomers. The model parameters indicate that, in the hydrophobic case, the polymer replica surface is mostly composed of hydrophobic mimicking monomers, while, in the hydrophilic case, the replica surface is mostly composed of a mix of the polymer matrix and of hydrophilic mimicking monomers. Deviation from the model at higher contact angles may result from nanoscale roughness, as visible in Figure 2 b. The latter may result from clustering of hydrophobic mimicking monomers. Curing conditions may also explain the variation in surface energy of the pure thiol-ene matrix PF4 formulation.^[54]

As surface energy mimicking originates spontaneously from within the polymer, replication of surface energy patterns on 3D topography, such as sidewalls or reentrants structures, can be expected. Furthermore, as it originates from molecular self-assembly, replication of nanoscale surface energy patterns may be possible. The manufacturing of the mold and the separation of the replica from the mold may ultimately limit the applicability of surface energy mimicking.

One critical aspect for industrial application of surface energy mimicking may result from the maximum number of molding cycles for a single mold before extensive cleaning or regeneration is needed. In this respect, the results of Figure 2 were tested for at least five replication cycles. The contact angle for six superhydrophobic replicas obtained from a single mold is stable within the measurement error (Figure 2 c). The self-assembly of droplet arrays was verified on the fifth replica from the same mold, and no feature degradation was observed (Figure 2 f), despite the molecular thickness of the surface modification of the silanized mold. The latter observation was further verified after > 6 months of storage in ambient condition in closed transparent petri dishes.

The model reveals two strategies for further improving surface energy mimicking: the surface energy of the mimicking monomers moiety should cover the largest possible range, i.e. $\theta_{hpl} \ll$ and $\theta_{hpb} \gg$; and the surface-specific interaction of the mimicking monomers should be minimized for surfaces with a corresponding surface energy and maximized otherwise, i.e. $K_{silane,hpl}$ and $K_{glass,hpb} \ll$ and $K_{glass,hpl}$ and $K_{silane,hpb} \gg$. In this respect, functional monomers, such as polyhedral silsesquioxanes,^[55-57] or long polyethylene glycol (PEG) monomers, may help further improving the results, notably for replication of hydrophilicity.

The engineering of other surface properties than the lone hydrophobicity/philicity, such as specific biointeractions, is also possible by using mimicking monomers with different or multifunctional moieties. Furthermore, while in this paper a thiol-ene polymer system was used, other thermoset polymers, such as (meth)acrylates, epoxies, etc., could also be considered.

Through our results, surface energy mimicking demonstrates promising features for applications requiring patterned surface modifications, with or without micro-/nanostructures. In microarray technology for example, the results of Figure 2 may be directly applicable to improve spot uniformity and read-out sensitivity.^[25,58]

Generally, surface energy mimicking bears similarities with other technologies, such as surface grafting of polymer brushes, molecular imprinting, block-copolymer self-assembly, or self-assembly of Langmuir-Blodgett films and surfactants, all relying on specific energetic interactions at a material or phase interface. Hence, surface energy mimicking complements and may be inspiring for other application areas.

Conclusion

We demonstrated a strategy, surface energy mimicking, enabling merging device manufacturing and surface energy patterning in a single step. Through the simultaneous replication of 2.5D micro-/nanostructures and of surface energy micropatterns, polymer replicas displaying surface energies ranging from hydrophilic to superhydrophobic were obtained. Surface energy mimicking was shown to originate from a spontaneous and adaptive surface arrangement of mimicking monomers as a function of their environment, which is similar to many natural processes. It may hence open new

possibilities for novel biomimetic or biocompatible materials, through the engineering of more elaborate surface properties.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] D. M. Yebra, S. Kiil, K. Dam-Johansen, *Progress in Organic Coatings* **2004**, 50, 75.
- [2] R. F. Brady Jr., *Progress in Organic Coatings* **1999**, 35, 31.
- [3] C. M. Magin, S. P. Cooper, A. B. Brennan, *Materials Today* **2010**, 13, 36.
- [4] S. Krishnan, N. Wang, C. K. Ober, J. A. Finlay, M. E. Callow, J. A. Callow, A. Hexemer, K. E. Sohn, E. J. Kramer, D. A. Fischer, *Biomacromolecules* **2006**, 7, 1449.
- [5] D. L. Schmidt, R. F. Brady, K. Lam, D. C. Schmidt, M. K. Chaudhury, *Langmuir* **2004**, 20, 2830.
- [6] M. Salta, J. A. Wharton, P. Stoodley, S. P. Dennington, L. R. Goodes, S. Werwinski, U. Mart, R. J. K. Wood, K. R. Stokes, *Philos Trans A Math Phys Eng Sci* **2010**, 368, 4729.
- [7] J. L. Dalsin, P. B. Messersmith, *Materials Today* **2005**, 8, 38.
- [8] A. R. Statz, R. J. Meagher, A. E. Barron, P. B. Messersmith, *Journal of the American Chemical Society* **2005**, 127, 7972.
- [9] M. L. Carman, T. G. Estes, A. W. Feinberg, J. F. Schumacher, W. Wilkerson, L. H. Wilson, M. E. Callow, J. A. Callow, Brennan, AB, *Biofouling* **2006**, 22, 11.
- [10] H. H. Becker, C. C. Gärtner, *Analytical and bioanalytical chemistry* **2007**, 390, 89.
- [11] S. A. Soper, A. C. Henry, B. Vaidya, M. Galloway, M. Wabuye, R. L. McCarley, *Analytica Chimica Acta* **2002**, 470, 87.
- [12] L. E. Locascio, A. C. Henry, T. J. Johnson, D. Ross, in *Lab-on-a-Chip* (Eds.: R.E. Oosterbroek, A. van der Berg), Elsevier, **2003**, pp. 65–82.

- [13] D. D. Belder, M. M. Ludwig, *Electrophoresis* **2003**, 24, 3595.
- [14] Yun Wang, Bikas Vaidya, Hannah D Farquar, Wieslaw Stryjewski, Robert P Hammer, A. Robin L McCarley, S. A. Soper, Y.-W. C. and, F. Barany, *Anal. Chem* **2003**, 75, 1130.
- [15] G. A. Diaz-Quijada, R. Peytavi, A. Nantel, E. Roy, M. G. Bergeron, M. M. Dumoulin, T. Veres, *Lab Chip* **2007**, 7, 856.
- [16] D. Witters, K. Knez, F. Ceyssens, R. Puers, J. Lammertyn, *Lab Chip* **2013**, 13, 2047.
- [17] D. M. Dankbar, G. Gauglitz, *Analytical and bioanalytical chemistry* **2006**, 386, 1967.
- [18] H. Bi, S. Meng, Y. Li, K. Guo, Y. Chen, J. Kong, P. Yang, W. Zhong, B. Liu, *Lab Chip* **2006**, 6, 769.
- [19] R. Safavieh, D. Juncker, *Lab Chip* **2013**, 13, 4180.
- [20] H. Andersson, W. van der Wijngaart, P. Griss, N. Sandström, G. Stemme, *Sensor Actuat B-Chem* **2001**, 75, 136.
- [21] H. Andersson, W. van der Wijngaart, G. Stemme, *Electrophoresis* **2001**, 249.
- [22] P. Mansky, Y. Liu, E. Huang, T. P. Russell, C. Hawker, *Science* **1997**, 275, 1458.
- [23] A. Rastogi, M. Y. Paik, M. Tanaka, C. K. Ober, *Acs Nano* **2010**, 4, 771.
- [24] S. Tawfick, M. De Volder, D. Copic, S. J. Park, C. R. Oliver, E. S. Polsen, M. J. Roberts, A. J. Hart, *Adv. Mater. Weinheim* **2012**, 24, 1628.
- [25] J. M. Moran-Mirabal, C. P. Tan, R. N. Orth, E. O. Williams, H. G. Craighead, D. M. Lin, *Anal. Chem* **2007**, 79, 1109.
- [26] S. P. R. Kobaku, A. K. Kota, D. H. Lee, J. M. Mabry, A. Tuteja, *Angewandte Chemie International Edition* **2012**, 51, 10109.
- [27] J. S. Li, E. Ueda, A. Nallapaneni, L. X. Li, P. A. Levkin, *Langmuir* **2012**, 28, 8286.
- [28] Y. Han, P. Levkin, I. Abarientos, H. Liu, F. Svec, J. M. J. Fréchet, *Anal. Chem* **2010**, 82, 2520.

- [29] D. Zahner, J. Abagat, F. Svec, J. M. J. Fréchet, P. A. Levkin, *Adv. Mater* **2011**, 23, 3030.
- [30] J. Zimmermann, M. Rabe, G. R. J. Artus, S. Seeger, *Soft Matter* **2008**, 4, 450.
- [31] A. Ressine, G. Marko-Varga, T. Laurell, *Biotechnol Annu Rev* **2007**, 13, 149.
- [32] M. Nosonovsky, B. Bhushan, *Advanced Functional Materials* **2008**, 18, 843.
- [33] M. Nosonovsky, B. Bhushan, *Langmuir* **2008**, 24, 1525.
- [34] M. Nosonovsky, B. Bhushan, *Nano Lett* **2007**, 7, 2633.
- [35] B. Bhushan, Y. C. Jung, *Progress in Materials Science* **2011**, 56, 1.
- [36] B. BHUSHAN, J. N. ISRAELACHVILI, U. Landman, *Nature* **1995**, 374, 607.
- [37] G. Pardon, T. Haraldsson, W. van der Wijngaart, in *2014 IEEE 27th International Conference on Micro Electro Mechanical Systems (MEMS)*, Ieee, **2014**, pp. 96–99.
- [38] T. Ishizaki, N. Saito, O. Takai, *Langmuir* **2010**, 26, 8147.
- [39] S. Lindstrom, H. Andersson-Svahn, *Lab Chip* **2010**, 10, 3363.
- [40] J. Y. Cheng, C. A. Ross, H. I. Smith, E. L. Thomas, *Adv. Mater* **2006**, 18, 2505.
- [41] Xiao M Yang, A. Richard D Peters, P. F. Nealey, H. H. S. and, F. Cerrina, *Macromolecules* **2000**, 33, 9575.
- [42] E. Han, M. Kim, P. Gopalan, *Acs Nano* **2012**, 6, 1823.
- [43] C. F. Carlborg, T. Haraldsson, K. Öberg, M. Malkoch, W. van der Wijngaart, *Lab Chip* **2011**, 11, 3136.
- [44] G. Pardon, F. Saharil, J. M. Karlsson, O. Supekar, C. F. Carlborg, W. van der Wijngaart, T. Haraldsson, *Microfluidics and Nanofluidics* **2014**, 17, 773.
- [45] M. Hillmering, G. Pardon, A. Vastesson, O. Supekar, C. F. Carlborg, B. D. Brandner, W. van der Wijngaart, T. Haraldsson, *Microsyst. Nanoeng. (Nature Publ. Group)* **2016**, 2, 15043.

- [46] J. Hansson, H. Yasuga, T. Haraldsson, W. van der Wijngaart, *Lab Chip* **2016**, 16, 298.
- [47] D. Sticker, M. Rothbauer, S. Lechner, M.-T. Hehenberger, P. Ertl, *Lab Chip* **2015**, 15, 4542.
- [48] Y. Xia, E. Kim, G. M. Whitesides, *Chem. Mater* **1996**, 8, 1558.
- [49] E. Kim, Y. Xia, G. M. Whitesides, *Nature* **1995**, 581.
- [50] D. K. Owens, R. C. Wendt, *Journal of Applied Polymer Science* **1969**, 13, 1741.
- [51] A. B. D. Cassie, *Discuss. Faraday Soc.* **1948**, 3, 11.
- [52] J. N. Israelachvili, *Intermolecular and Surface Forces: Revised Third Edition*, Academic Press, London, New York, **2011**.
- [53] J. N. Israelachvili, M. L. Gee, *Langmuir* **1989**, 5, 288.
- [54] S. M. Tähkä, A. Bonabi, M.-E. Nordberg, M. Kanerva, V. P. Jokinen, T. M. Sikanen, *J Chromatogr* **2015**, 1426, 233.
- [55] J. M. Mabry, A. Vij, S. T. Iacono, B. D. Viers, *Angew. Chem. Int. Ed. Engl.* **2008**, 47, 4137.
- [56] A. Tuteja, W. Choi, M. Ma, J. M. Mabry, S. A. Mazzella, G. C. Rutledge, G. H. McKinley, R. E. Cohen, *Science* **2007**, 318, 1618.
- [57] G. Li, L. Wang, H. Ni, C. U. Pittman Jr, *Journal of Inorganic and Organometallic Polymers* **2001**, 11, 123.
- [58] L. H. Mujawar, W. Norde, A. van Amerongen, *Analyst* **2013**, 138, 518.

Figure 1 Illustration of the surface energy mimicking principle. **a)** The prepolymer formulation is dispensed onto a master mold surface with varying surface energies. **b)** The functional mimicking monomer molecules diffuse in the prepolymer matrix and self-assemble against the surface areas on the master mold displaying a corresponding surface energy corresponding to the mimicking monomer respective moiety. The prepolymer is subsequently cross-linked using light or heat. **c)** After demolding, the polymer replica exhibits at its surface a replica of the surface energies of the master mold, as the specific chemical moieties of the embedded mimicking monomers are displayed in the corresponding areas. The mold can be reused for the manufacturing of several replicas.

Figure 2 a) Schematics showing the replication of 2.5D micro-/nanostructures of different surface energies using surface energy mimicking. The master mold (MMS 4) consists of a glass substrate with one half being nanostructured and the other polished. Half of each area was made hydrophilic by silanization. The contact angle of water on each four replicated areas are indicated. The area replicating the silanized nanostructures exhibits superhydrophobicity. **b)** SEM images of the replica surface areas corresponding to the silanized polished and silanized nanostructured areas on the master mold. **c)** Image and measurements of the superhydrophobic contact angle of water on several replicas from a same mold, on area corresponding to the silanized 2.5D structured area on the master mold. **d)** Schematics showing the replication of 2D micropatterns of different surface energy using surface energy mimicking. Using a pattern consisting of an array of hydrophilic patches, an array of picoliter droplets can be formed by self-assembly. The master molds (MMS 5) consist of a hydrophilic silica

substrates, on which a hydrophobic pattern was created by hydrophobic silanization. **e)**

Micrographs of a nanoliters droplets array (blue dye solution) formed by self-assembly

on hydrophilic patches of 200 μm diameter on a polymer replica, demonstrating

successful replication of the 2D-micropatterns. **f)** Fluorescent images showing

hydrophilic, Rhodamine B-labeled microparticles seeded on the hydrophilic patches

after evaporation of the self-assembled droplets. The droplet volume can be estimated to

tens of picoliters on the 50 μm patches and a few nanoliters on the 250 μm patches.

Table 1 Summary of the polymer formulations studied

Polymer formulations	Matrix	Hydrophilic mimicking monomers	Hydrophobic mimicking monomers
	Thiol-ene	HEMA	FDMA
PF1	X	X	X
PF2	X	X	-
PF3	X	-	X
PF4	X	-	-

Figure 3 a) Test 1: Measurements of the contact angle of polymer replicas versus that of the silanized glass master molds (MMS 3) used for replication, using polymer formulation PF1, containing the matrix monomers and both hydrophilic HEMA and hydrophobic FDMA mimicking monomers. The blue lines show the models for the Cassie and Israelachvili (dashed lines) equations, fitted using a non-linear least-square method, and the light-grey lines show the models with fixed calculated K_{ij} parameters. **b)** Comparison of the contact angles for the polymer formulations PF1 to PF4, containing the matrix monomers with both (PF1 – grey line –), either of (PF2 – orange line – and PF3 – brown line –), or none (PF4 – blue line –) of the hydrophilic HEMA and hydrophobic FDMA mimicking monomers, using MMS 3. The full and dashed lines show the models using Cassie or Israelachvili equations, respectively, fitted using the least-

square method. **c)** Test 2: Comparison of the contact angles after replication on, respectively, a glass surface, $\theta_{glass} = 8.02^\circ \pm 0.65$, , and hydrophobic silanized glass surface, $\theta_{silane} = 108.32^\circ \pm 0.43$, and when polymerized in open air, i.e. not in contact with any solid surface, for the four different polymer formulations. **d)** Test 3: Contact angle of polymer replica versus contact angle of various raw materials and of plasma-treated PDMS (MMS 1 and MMS 2). A linear regression was fitted using the least-square method to the data for FP1 and FP4 and the corresponding equations and R^2 are displayed.

Table 2 Model parameters and resulting surface fractions in % after fitting on the measurements and as calculated with equation (3).

	f_{glass}				f_{silane}			
	Fitted		Calculated		Fitted		Calculated	
	$g_{glass,j}$	$K_{glass,j}$	$g_{glass,j}$	$K_{glass,j}$	$g_{silane,j}$	$K_{silane,j}$	$g_{silane,j}$	$K_{silane,j}$
Polymer matrix	0.48	-	0.38	-	$10^{-9} *$	-	$10^{-9} *$	-
Hydrophilic mimicking monomers	0.47	2.59	0.62	1.54	$10^{-9} *$	0.12	$10^{-9} *$	15.65
Hydrophobic mimicking monomers	0.054	6.4×10^{-9}	$10^{-9} *$	0.73	$0.99 *$	5.82×10^9	$0.99 *$	6.40×10^{10}

* Fixed at bound

Remark: $g_{i,j} \in [0,1]$ and the fit starting values were: $g_{glass,j} = [1 \ 0]$ and $g_{silane,j} = [0 \ 1]$

We introduce surface energy mimicking, enabling spontaneous replication of micropatterns (2D and 2.5D) of different surface energies, and enabled by self-assembly of functional mimicking monomers within a polymer matrix. We demonstrate replication of surface energies ranging from hydrophilic to superhydrophobic, and self-assembly of picoliter-droplet arrays on replicated micropatterned arrays containing hydrophilic patches in a hydrophobic surface.

Keyword (see list)

T. Haraldsson, W. van der Wijngaart, G. Pardon*

Title ((no stars))

ToC figure

Supplementary information

Modeling

In the case of master mold of MMS 3, i.e. made of flat unstructured silanized glass, the surface energy mimicking can be modeled. For both the master molds and the polymer replicas, the surface energy is provided by a combination of heterogeneous constituents at the surface, i.e. glass and silanes for the molds, and matrix and mimicking monomers for the replicas. These constituents can be assumed to form surface domains in the micro-/nanometer size range. Based on this assumption, the surface energy of the heterogeneous surface can be estimated as the surface area weighted-average of the surface energy of each domain constituents, i =glass or silane.^[50]

For the silanized glass surface, the surface contact angle can thus be expressed using the Cassie equation,^[51,52] as:

$$\cos(\theta_{master}) = \sum_i f_i \cdot \cos(\theta_i) = f_{glass} \cdot \cos(\theta_{glass}) + f_{silane} \cdot \cos(\theta_{silane}) \quad (S1)$$

with the condition $f_{glass} + f_{silane} = 1$, and where f_i are the surface fractions for each constituents and θ_i are the contact angle of a surface entirely made of constituent i .

However, Israelachvili *et al.* suggested that this model may not be adequate when surface domains are of atomic or molecular scale, in which case the polarizability, the dipole moments and the surface charge of the surface should be considered, rather than simply the Van der Waals and electrostatic forces as in equation (1).^[53] They suggested a modified model to cover this case, which we also examine in this manuscript along with the model of equation (1):

$$(1 + \cos(\theta_{master}))^2 = \sum_i f_i \cdot (1 + \cos(\theta_i))^2 \quad (S2)$$

With either model, the surface fraction f_{silane} can be determined by measuring the material contact angles.

For the polymer replica, the surface will be composed of two or more constituents, depending on the formulation, and the models of equation (1) and (2) can be used as well. For the sake of conciseness, the following development will only be written for equation (1), but is similar for equation (2).

As a first approximation, we assume the surface consisting of three main constituents, i.e. the polymer matrix material, hydrophilic mimicking monomers and hydrophobic mimicking monomers, with respective contact angle θ_j , where $j = \text{matrix, hpb or hpl}$, and surface fraction $g_j = \frac{c_{s,j}}{\sum_j c_{s,j}}$ where $c_{s,j}$ is the surface concentration. The Cassie equation for the replica contact angle is then:

$$\cos(\theta_{replica}) = \sum_j g_j \cdot \cos(\theta_j) = g_{matrix} \cdot \cos(\theta_{matrix}) + g_{hpl} \cdot \cos(\theta_{hpl}) + g_{hpb} \cdot \cos(\theta_{hpb}) \quad (S3)$$

Furthermore, since we are interested in the surface energy mimicking, it is of interest to divide the surface fractions in the polymer replica, g_j , in two separate contributions $g_{glass,j}$ and $g_{silane,j}$ representing, respectively, the fraction adsorbed on the glass domains or on the silane domains of the master mold, as:

$$g_j = \sum_i f_i \cdot g_{i,j} = f_{glass} \cdot g_{glass,j} + f_{silane} \cdot g_{silane,j} \quad (S4)$$

with the condition $\sum_j g_{ij} = g_{i,matrix} + g_{i,hpl} + g_{i,hpb} = 1$.

Using this expression, the contact angle of the polymer replica can be expressed as a function, $h(\theta_{master})$, of the contact angle of the master mold with up to five problem (experimentally accessible) parameters, i.e. the contact angle of the pure substances θ_j or θ_i , and of up to four independent (fitting) parameters, i.e. $g_{hpl,j}$ and $g_{hpb,j}$, as:

$$\theta_{replica_Cassie} = h(\theta_{master}) = \arccos\left(\sum_i \sum_j f_i(\theta_{master}) \cdot g_{i,j} \cdot \cos(\theta_j)\right) \quad (S5)$$

$$\theta_{replica_Israelachvili} = \arccos\left(\left(\sum_i \sum_j f_i(\theta_{master}) \cdot g_{i,j} \cdot (1 - \cos(\theta_j))\right)^{1/2} - 1\right) \quad (S6)$$

The contact angles for each of the surface domains materials were measured separately and used in the models: $\theta_{glass} = 8.02^\circ \pm 0.65$, $\theta_{silane} = 108.32^\circ \pm 0.43$, $\theta_{matrix} = 71.82^\circ \pm 0.41$, $\theta_{hpl} = 110.59^\circ \pm 3.38$ and $\theta_{hpb} = 27.5^\circ \pm 5.2$.

In the case of a perfect match between the mimicking monomers moiety surface energy, i.e. $\theta_{hpl} = \theta_{glass}$ and $\theta_{hpb} = \theta_{silane}$, and of a one-to-one adsorption onto the corresponding surface energy fraction, i.e. $g_{glass,hpl}$ and $g_{silane,hpb} = 1$, and $g_{silane,hpl}$ and $g_{glass,hpb} = 0$, the model would reduce to a direct linear relation:

$$\theta_{replica} = \theta_{master}$$

Furthermore, the surface fraction of the different constituents in the polymer replica can be assumed to result from an adsorption process occurring before solidification of the matrix. This can be described, at first approximation, by an adsorption isotherm of the type:

$$g_{i,j} = \frac{c_{s,i,j}}{c_{s,0}} = \frac{K_{i,j}c_{b,j}}{1 + \sum_j K_{i,j}c_{b,j}} \quad (S7)$$

where $c_{s,i,j}$ is the surface concentration of the adsorbed species, $c_{s,0}$ is the surface concentration of available adsorption sites, and $K_{i,j}$ is the equilibrium constant for species $j = \text{matrix, hpb or hpl}$, on the surface domain $i = \text{glass or silane}$.

Equation 7 allows comparing the $K_{i,j}$ obtained of the measurements using PF1 with those made using PF2 and 3, as reported in **Table 2**. The model results using the calculated $K_{i,j}$ are shown with light-grey lines in **Figure 3 a)**, and are in reasonable agreement with the data and with the otherwise fitted model (blue lines).

Silanization of glass slide

Figure S 1 Contact angle of glass slides after hydrophobic silanization as a function of the silane concentration in the solution.