Adaptation of a Styrene–Acrylic Acid Copolymer Surface to Water

Xiaomei Li, Simon Silge, Alexander Saal, Gunnar Kircher, Kaloian Koynov, Rüdiger Berger, and Hans-Jürgen Butt

ABSTRACT: Solid surfaces, in particular polymer surfaces, are able to adapt upon contact with a liquid. Adaptation results in an increase in contact angle hysteresis and influences the mobility of sliding drops on surfaces. To study adaptation and its kinetics, we synthesized a random copolymer composed of styrene and 11–25 mol% acrylic acid (PS/PAA). We measured the dynamic advancing $(\theta_A)$ and receding $(\theta_R)$ contact angles of water drops sliding down a tilted plate coated with this polymer. We measured $\theta_A \approx 87^\circ$ for velocities of the contact line $< 20 \mu m/s$. At higher velocities, $\theta_A$ gradually increased to $\sim 98^\circ$. This value is similar to $\theta_R$ of a pure polystyrene (PS) film, which we studied for comparison. We associate the gradual increase in $\theta_A$ to the adaptation process to water: The presence of water leads to swelling and/or an enrichment of acid groups at the water/polymer interface. By applying the latest adaptation theory (Butt et al. Langmuir 2018, 34, 11292), we estimated the time constant of this adaptation process to be $\ll 1$ s. For sliding water drops, $\theta_R$ is $\sim 10^\circ$ lower compared to the reference PS surface for all tested velocities. Thus, at the receding side of a sliding drop, the surface is already enriched by acid groups. For a water drop with a width of 5 mm, the increase in contact angle hysteresis corresponds to an increase in capillary force in the range of 45–60 $\mu N$, depending on sliding velocity.

INTRODUCTION

Many surfaces react when they are brought into contact with a liquid. Some polymer surfaces, for example, reconstruct due to a reorientation of side groups or due to selective exposure of specific segments to the liquid interface. In addition, polymers swell when liquid diffuses into the polymer. Mixed polymer brushes, or block copolymers, expose the more compatible component to the liquid interface. Adaptation of the surface typically leads to changes in surface composition upon exposure to a liquid. Consequently, adaptation contributes to contact angle hysteresis and dynamic contact angle changes. These parameters are important in the fields of printing, digital microfluidics, and fiber coatings. Despite the importance in many wetting applications, a quantitative understanding of adaptation is still in its infancy.

When adaptation is nonreversible upon exposure to air, the adaptive kinetics at the solid/liquid interface can be probed by immersing the sample in liquids for different time spans. Subsequently, the surface can be studied by X-ray photoelectron spectroscopy (XPS). However, reversible adaptation cannot be studied by XPS as it requires vacuum conditions. In addition, studying adaptation kinetics with a time scale of $< 1$ s is challenging due to the time required to immerse samples into and remove samples from the liquid. Thus, measurements located directly at, or close to, the moving three-phase contact line are beneficial.

Contact angle measurements are an elegant way of measuring adaptation kinetics. Surface adaptation leads to a change in advancing and receding contact angles, which is experimentally easily measurable. Surface adaptation kinetics have been probed by measuring time-dependent dynamic contact angles using the Wilhelmy method, or by using the infused drop method. Both methods can reveal changes in contact angles caused by surface adaptation. However, the studied adaptation processes are rather slow; they range in time from several minutes to several days. To our knowledge, no report of direct contact angle measurements exists that reveals adaptation velocities of surfaces faster than seconds.

A quantitative description of the adaptive wetting phenomena was recently outlined by Butt et al. They introduced exponentially relaxing interfacial energies and applied Young’s equation locally. The theory predicts the advancing $(\theta_A)$ and receding $(\theta_R)$ contact angles of a sliding drop on a surface exhibiting specific adaptation kinetics.
samples were heated at 150 °C for 10 min in an oven (Figure 1a). The average roughnesses of the PS/PAA surfaces were 38 ± 0.02 nm. The surface after it comes into contact with the liquid and dries was immerged in 2 wt % PS in toluene for 10 min to remove physisorbed APTES. After drying in a vacuum oven at 150 °C for 10 min between measurements. For the PS/PAA surface, we set it to 10 min as it includes a heating step at 150 °C for 10 min in an oven (Figure 1a). The average roughnesses of the PS/PAA surfaces were 38 ± 0.02 nm. The surface after it comes into contact with the liquid and dries was removed in an 8.7/1 PS/PAA surface to adjust the drop velocity. In addition, different sliding velocities of drops were accomplished by measuring the drop at different distances from the position where the drop was released. The interval between drops was 10 min for PS surfaces. PS/PAA surfaces were annealed to 150 °C for 10 min between measurements.

Contact Angle Measurement Using the Tilted-Plate Setup. A 33 ± 1 μL water drop was pipetted onto the tilted surface using a syringe pump (KD Scientific, Legato 100 Syringe Pump). The tilt angles of the surface were varied from 33° to 70° for an 8.7/1 PS/PAA surface to adjust the drop velocity. In addition, different sliding velocities of drops were accomplished by measuring the drop at different distances from the position where the drop was released. The interval between drops was 10 min for PS surfaces. PS/PAA surfaces were annealed to 150 °C for 10 min between measurements.

To check if the interval between drops was long enough to dry the surface, a series of 40 drops with a volume of 33 ± 1 μL was pipetted onto the 67 nm 8.7/1 PS/PAA surface and the PS surface using the syringe pump. We set the interval between individual drops to 1 min for PS surfaces. For the PS/PAA surface, we set it to 10 min as it includes a heating step at 150 °C. The inclination angle was kept constant: α = 30° for the PS/PAA surface, and α = 16° for the PS surface. The distance between the pipet and the camera’s field of view ranges from 3 to 6 cm. To prevent the results being affected by surface inhomogeneity, the contact angle was always measured at the same spot on the samples.

Confocal Laser Scanning Microscopy Measurement. Confocal laser scanning microscopy (CLSM) experiments were performed on a commercial confocal microscope, LSM 510 (Carl Zeiss, Jena, Germany) equipped with a C-Apochromat 40/1.2 W water-immersion objective. For excitation, the 488 nm line of an argon laser fiber-coupled to the microscope was used. Emitted fluorescence light was collected with the same objective and then passed through a photomultiplier detector. A stainless-steel chamber Attoliner (Thermo Fisher Scientific) holding the 25 mm round coverslip was used as a sample cell. A glass coverslip functionalized with pHrodo dye and covered (or not) with a polymer film was mounted in the sample holder, and a droplet of buffer solution with pH = 9.0 (ROT1 Calipure) was added. For CLSM experiments, the functionalized glass surface was positioned in the middle of the confocal volume (in a vertical direction), and horizontal scans of different regions of the droplet contact line were acquired.

RESULTS AND DISCUSSION

As an adaptive surface, a random PS/PAA copolymer surface was prepared on Si wafers by spin-coating. Subsequently, we annealed the samples at 150 °C for 10 min in an oven (Figure 1a). The average roughnesses of the films were 0.2 ± 0.02 nm on a 500 × 500 nm² scale (Figure S1). The thicknesses of the films were 38 ± 1 and 67 ± 1 nm, respectively, as measured by a profilometer (KLA-Tencor Stylus-Profiler model P7). By annealing, we expected the hydrophobic styrene side groups to
enrich at the surface to lower the surface energy. When the PS/PAA films were exposed to water, they were able to change their wetting properties by swelling and by reorientation of the polymer chain segments at the surface.

We synthesized PS/PAA surfaces with three different styrene/acrylic acid molar ratios: 8.7/1, 4.2/1, and 2.9/1 (details are in the Methods section). The ratios were revealed by NMR (Figure S2). The glass transition temperature $T_g$ of all three PS/PAA copolymers was measured to be between 100 and 130 °C (Figure S3).

When measuring the contact angles of films by the traditional sessile drop method, the advancing contact angle of PS and all PS/PAA copolymers were in the range from 5° to 98°. However, the receding contact angle decreased by 21° when increasing the acrylic acid content from 8.7/1 to 2.9/1 (Table 1). Compared to pure PS, the receding angle for 2.9/1

(PS/PAA) even decreased by 25°. Accordingly, the contact angle hysteresis varies between 27° and 50°. In this contact angle measurement, the advancing side of the drop always wets a dry surface. In contrast, when measuring the receding contact angles, the surface stayed in contact with water for seconds. Thus, the response of the receding contact angle may indicate the adaptation of the surface, and phenol rings remain on the surface compared to 95° ± 10/0.

Table 1. Dynamic Contact Angles of Copolymer Surfaces with Different PS-to-PAA Ratios

| polymer (PS/PAA) | $\theta_a$ (deg) | $\theta_r$ (deg) | $\Delta \theta$ (deg) |
|------------------|------------------|------------------|---------------------|
| 10/0             | 97 ± 1           | 70 ± 1           | 27 ± 2              |
| 8.7/1            | 98 ± 1           | 66 ± 1           | 32 ± 2              |
| 4.2/1            | 96 ± 1           | 50 ± 1           | 46 ± 2              |
| 2.9/1            | 95 ± 1           | 45 ± 1           | 50 ± 2              |

The advancing and receding angles were measured using the sessile drop method.

To estimate the order of the relaxation time $\tau_{SL}$ for this process, we fitted eq 1 to the measured advancing angles of the PS/PAA surface. For the fit, we used $\theta_a^0 = 87^\circ$, $\Delta \gamma_{SL} = 0.013$ N/m, and $r_{SL} = 0.072$ N/m in the velocity range of $5 \times 10^{-6}$ to 0.1 m/s (red continuous line in Figure 2b). The fit revealed a ratio of $\frac{\tau_{SL}}{\tau_{in}} = (5 \pm 2) \times 10^{-5}$ m/s. Assuming a peripheral thickness on the order of $l_{per} = 10$ nm results in a relaxation time $\tau_{SL}$ of ~0.2 ms. With $l_{per} = 100$ nm, one would estimate $\tau_{SL} = 2$ ms.
The presence of acid groups at the surface may be correlated with a diffusion of water into the polymer film. Assuming a diffusion constant $D$ for the PS/PAA film on the order of $10^{-13}$ m$^2$/s, we obtained a diffusion depth of $4-40$ nm ($D = h^2/2D$). Thus, a likely scenario is that water diffuses into the copolymer, swelling occurs, and the topmost side groups of the copolymer reorient.

Our next step was to demonstrate that the adaptation of the surface to water was also visible at the receding side of the drop. We used a 33 $\pm$ 1 $\mu$L drop volume in the tilted-plane experiment. This volume resulted in a drop length of $8.1$ mm, when the drops slid at a maximum velocity of $0.35$ m/s in our setup. Thus, the drop stayed in contact with the surface for $23$ ms. This contact time is $10-100$ times the relaxation time for the PS/PAA surface. Thus, the surface was able to adapt during all the different velocities applied in our measurement setup. The adaptation was reflected in the lower receding contact angles of the PS/PAA surface compared to the reference PS surface for all velocities measured (Figure 2b). Thus, contact angle hysteresis was larger for the PS/PAA surface compared to the pure PS surface. Despite the offset in the receding contact angle, the characteristics of velocity-dependent receding contact angles of PS surface and 8.7/1 PS/PAA surface were quite similar (Figure 2b). This indicates that the reverse adaptation time at the receding side of the drop, $\tau_r$, was much larger compared to $\tau_{sl}$. Thus, the topmost side groups of the copolymer did not return to their original positions before contact with water, and it is possible that water stayed partially in the films. We attribute the slight decrease of the receding angles of the PS/PAA copolymer at a velocity of $\leq 1 \times 10^{-4}$ m/s to the prolonged time that the surface was in contact with water ($\sim 80$ s). For such contact times, the surface became more and more hydrophilic, as we will report later. The increase in advancing angles and decrease in receding angles observed for PS and PS/PSA surfaces at a velocity of $\geq 0.1$ m/s were both caused by viscous dissipation and the Marangoni effect.

When surfaces adapt to a liquid, the contact angle hysteresis and dynamic contact angles change. Accordingly, the mobility of the drop is affected due to changes in the capillary force,

$$F_{\text{capillary}} = kw \frac{\gamma}{\cos \theta_R - \cos \theta_A}$$

Exemplarily, we calculate the capillary force for a drop volume of 33 $\mu$L, corresponding to a drop width of 5 mm. In comparison to a pure PS surface, the decrease in receding angle on PS/PAA surfaces leads to an increase in capillary force from $\sim 87$ to $148$ $\mu$N at $0.2$ mm/s $\leq v \leq 20$ mm/s. At lower velocity, $\leq 20$ $\mu$m/s, where the advancing and receding contact angles adapt, the capillary force increases from $\sim 87$ to $\sim 132$ $\mu$N. That is, the adaptation of the PS/PAA copolymer surface with a water drop leads to the increase in contact angle hysteresis of $22^\circ-25^\circ$, corresponding to an increase in capillary force in the range of 45-60 $\mu$N, depending on the sliding velocity.

The receding contact angles decreased with decreasing PS-to-PAA ratio (Table 1). We measured the velocity-dependent dynamic contact angles on a PS/PAA surface made by a copolymer with a ratio of 4.2/1 (Figure S6). Then we also fitted eq 1 to the measured advancing angles, leading to $l_{sl}/\lambda_{sl} = 0.04$ m/s. Again, assuming $l_{sl} \approx 10-100$ nm, we obtained a relaxation time of $\tau_{sl} \approx 0.25-2.5$ $\mu$s. Thus, in comparison to the 8.7/1 PS/PAA the 4.2/1 PS/PAA copolymer surfaces, it required less time to adapt to water. For the sliding drop, the magnitude of the advancing contact angle change is similar for
the surfaces made from 8.7/1 and 4.2/1 PS/PAA copolymers. Thus, we conclude that water diffuses faster into the copolymer that has more acrylic acid content. For the receding side, the 4.2/1 PS/PAA surface has also already completely adapted to the water. We measured a receding angle of 55° ± 2°, which is almost 15° lower than that of the 8.7/1 PS/PAA surface (Figure S6).

To study the adaptation upon contact with water over a longer time scale, we measured the advancing and receding contact angles of PS/PAA films by repeatedly inflating and deflating a water drop. The flow rate used during the measurement was 0.5 μL/s (this is the lowest flow rate that our instrument could achieve), corresponding to a contact line velocity of (8 ± 1) × 10⁻⁵ m/s (beginning with small drop volumes) to (6 ± 1) × 10⁻⁵ m/s (ending with the maximum inflated drop volume). The first contact angle measurement was performed on a pristine PS/PAA surface, as used in the sliding drop experiments (blue data points in Figure 3a). In the first cycle of the contact angle measurement during inflation, the advancing angle was 95° ± 1°. The receding contact angle measured during deflation was 66° ± 1°. This contact angle slightly decreased during deflation of the drop. We inflated the

Figure 3. (a) Contact angle vs contact base diameter on the 67 nm PS/PAA (8.7/1) surface. The cycle’s orders of repeated inflating and deflating processes are represented by 1st–5th. The 5 repeated tests required 4 ± 0.5 min, corresponding to 50 ± 1 s for each cycle. (b) Possible arrangement of the PS/PAA copolymer at the interface corresponding to positions 2 and 3 in (a). In particular, state 1 in air is the original state of the copolymer before a drop was deposited on the surface.

Figure 4. Schematic drawing of water penetration into the copolymer film using confocal microscopy. The images show fluorescence intensity maps (a) before a drop (pH = 9) was deposited on a glass surface grafted with a pH-sensitive dye, (b) after a drop (pH = 9) was deposited on the dye-grafted glass surface, (c) after a drop (pH = 9) was deposited on a 8.7/1 PS/PAA film spin-coated above the dye-grafted glass surface, and (d) after a drop (pH = 9) was deposited on a PS film spin-coated above the dye-grafted glass surface. The detected area for (b), (c), and (d) was a three-phase area.
drop again (red, round symbols in Figure 3a). In the second cycle, the advancing contact angle decreased to 92° ± 1°. The corresponding receding contact angle decreased to 64° ± 1°. Subsequently, the drop was inflated again three more times. In the 3rd–5th cycles, the advancing contact angle only slightly decreased to 90° ± 1°. The corresponding receding contact angles kept decreasing continuously for each cycle by ~1°. At the fifth cycle, a receding contact angle of 62° ± 1° was measured (Figure 3a).

We attributed the decrease in advancing and receding contact angles to water penetrating into the PS/PAA film and staying in the film for the subsequent cycles. Thus, in the 2nd–5th cycles, the surface appears more hydrophilic. In addition, the presence of water in the film allows the hydrophilic PAA segment to move to the interface (Figure 3b, states 2 and 3). Therefore, the advancing angles and receding angles gradually decreased after every cycle.

It is worth mentioning that during successive inflations of the drop the advancing contact angle never reached the value of the pristine sample. Thus, τ is longer than the time for one measurement cycle, which is 50 ± 5 s. For comparison, we used pure PS surfaces as a reference. Both the advancing and receding angles on the PS surfaces remained almost constant \( \theta_A = 97°, \theta_R = 73° \) even after five inflation/deflation cycles (Figure S7). The small differences in the contact angles measured by sliding drop and sessile drop for the same samples at their original state and final state can be caused by the different measuring methods and fitting models. We used a polynomial model for sliding drop and an elliptical model for sessile drop experiments.

To determine whether water molecules are able to diffuse in the PS/PAA film and if they can reach the SiO\(_2\) substrate interface, we grafted a pH-sensitive fluorophore (pHrodo iFL STP eater, ThermoFisher) to the surface of a glass coverslip. This fluorophore emits green light with an emission maximum at a wavelength of 525 nm after excitation by a 488 nm laser. Fluorescence decreases when it comes into contact with basic water \((\text{pH} = 9)\). To confirm the activity of the pH-sensitive dye, we deposited a drop with \(\text{pH} = 9\) on the surface of a dye-grafted glass surface and recorded the fluorescence intensity using a confocal microscope. The fluorescence intensity of the dry area is higher than that in the wet area (Figure 4a and b). We used this fluorophore to verify the presence of water at the PS/PAA/substrate interface. We spin-coated the PS/PAA polymer film (thickness = 45 nm) on a dye-grafted glass surface and added a drop \((\text{pH} = 9)\) onto the polymer surface. The fluorescence image recorded ~1 min after adding the drop showed a slight decrease in fluorescence (Figure 4c). Thus, we concluded that water had penetrated through the polymer film and reached the dye layer grafted on the glass surface. In comparison, the pure PS film showed no decrease in fluorescence (Figure 4d). The latter rules out optical artifacts due to the presence of a water drop on top of the surface, which could also lead to changes in the intensity of the backscattered light.

**CONCLUSION**

The surface of a PS/PAA copolymer film adapts upon contact with water. Most likely, water penetrates in the uppermost layer and acrylic acid groups become exposed to the water interface. On the basis of a recently proposed theory, we estimated the time scale of the swelling and reorganization process to be \(\ll 1\) s. For a 8.7/1 PS/PAA surface and for sliding velocities of drops \(\geq 7 \times 10^{-4} \text{m/s}\), the advancing contact line “sees” a styrene-dominated surface. For a sliding velocity \(\leq 7 \times 10^{-4} \text{m/s}\), the acrylic acid groups have sufficient time to get exposed so that the advancing contact line of the drop can be influenced by the acrylic acid groups. This adaptation gradually leads to the decrease of advancing angle. In the case of a 4.2/1 PS/PAA surface, the critical sliding velocity increases to \(3 \times 10^{-2} \text{m/s}\). In both cases, at the receding contact line, the surface has adapted and more acid groups are exposed. In particular, the adaptation time scale could depend on phase separation of PAA and PS moieties. The latter would be even more pronounced for block copolymer morphologies. The adaptation processes of the surface influence the mobility of drops by increasing the capillary force in the range of 45–60 \(\mu\text{N}\) in comparison to a pure PS reference surface.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c03226.

Surface morphology characterization by scanning force microscopy; copolymer composition characterization by NMR; \(T_g\) of PS, PAA, and PS/PAA copolymers; data processing of sliding drops; evidence of drying “wet” surfaces by annealing; adaptation on 4.2/1 PS/PAA surface by sliding drops; and dynamic contact angles of PS surface measured by sessile drop (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Rüdiger Berger – Max Planck Institute for Polymer Research, SS128 Mainz, Germany; orcid.org/0000-0002-4084-0675; Email: berger@mpip-mainz.mpg.de

**Authors**

Xiaomei Li – Max Planck Institute for Polymer Research, SS128 Mainz, Germany
Simon Silge – Max Planck Institute for Polymer Research, SS128 Mainz, Germany
Alexander Saal – Max Planck Institute for Polymer Research, SS128 Mainz, Germany
Gunnar Kircher – Max Planck Institute for Polymer Research, SS128 Mainz, Germany
Kaloian Koynov – Max Planck Institute for Polymer Research, SS128 Mainz, Germany; orcid.org/0000-0002-4062-8834
Hans-Jürgen Butt – Max Planck Institute for Polymer Research, SS128 Mainz, Germany; Email: butt@mpip-mainz.mpg.de

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.langmuir.0c03226

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Our thanks go to Jürgen Thiel for synthesizing the PS polymer and to Uwe Rietzler and Helma Burg for their technical support. We acknowledge partial funding by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), Project-ID 265191195-SFB 1194, and within the German Priority Program 2171.
REFERENCES

(1) Lavielle, L.; Schultz, J. Surface properties of graft polyethylene in contact with water: I. Orientation phenomena. J. Colloid Interface Sci. 1985, 106 (2), 438–445.
(2) de Crevoisier, G.; Fabre, P.; Corpard, J.-M.; Leibler, L. Switchable tackiness and wettability of a liquid crystalline polymer. Science 1999, 285 (5431), 1246–1249.
(3) Grundke, K.; Pößchl, K.; Syntyska, A.; Frenzel, R.; Drechsler, A.; Nitschke, M.; Cordeiro, A. L.; Uhlmann, P.; Welzel, P. B. Experimental studies of contact angle hysteresis phenomena on polymer surfaces—toward the understanding and control of wettability for different applications. Adv. Colloid Interface Sci. 2015, 222, 350–376.
(4) Sui, X.; Zapotoczny, S.; Benetti, E. M.; Memesa, M.; Hempenius, A. M.; Vancso, G. J. Grafting mixed responsive brushes of poly(N-isopropylacrylamide) and poly(methacrylic acid) from gold by selective initiation. Polym. Chem. 2011, 2, 879–884.
(5) Liu, C.; Lopes, M. C.; Pihan, S. A.; Fell, D.; Sokuler, M.; Butt, H.-J.; Auernhammer, G. K.; Bonaccorso, E. Water diffusion in polymer nano-films measured with microcantilevers. Sens. Actuators, B 2011, 160 (1), 32–38.
(6) Yoon, J.; Cai, S.; Soo, Z.; Hayward, R. C. Polerostatic swelling kinetics of thin hydrogel layers: comparison of theory and experiment. Soft Matter 2010, 6 (23), 6004–6012.
(7) Zhang, H.; Gao, X.; Chen, K.; Li, H.; Peng, L. Thermo-sensitive and swelling properties of cellouronic acid sodium/poly(acrylamide-co-diallyldimethylammonium chloride) semi-IPN. Carbohydr. Polym. 2018, 181, 450–459.
(8) Ionov, L.; Minko, S. Mixed polymer brushes with locking switching. ACS Appl. Mater. Interfaces 2012, 4 (1), 483–489.
(9) Ochsman, J. W.; Lena, S.; Lellig, P.; Emmerling, S. G. J.; Golzir, A. A.; Reichert, P.; You, J.; Perlisch, J.; Roth, S. V.; Berger, R.; Gutmann, J. S. Stress-Structure Correlation in PS-PMMA Mixed Polymer Brushes. Macromolecules 2012, 45 (7), 3129–3136.
(10) Lee, S.; Flores, S. M.; Berger, R.; Gutmann, J. S.; Brehmer, M.; Conrad, L.; Funk, L.; Theato, P.; Yoon, D. Y. Sheeting, Temperature dependence of surface reorganization characteristics of amphiphilic block copolymer in air and in water studied by scanning force microscopy. J. Plast. Film Sheeting 2015, 31 (4), 434–448.
(11) Butt, H. J.; Berger, R.; Steffen, W.; Vollmer, D.; Weber, S. A. L. Adaptive Wetting-Adaptation in Wetting. Langmuir 2018, 34 (38), 11292–11304.
(12) Dupont-Gillain, C. C.; Adriaensen, Y.; Derclaye, S.; Rouxhet, P. G. Plasma-oxidized polystyrene: wetting properties and surface reconstruction. Langmuir 2000, 16 (21), 8194–8200.
(13) Vaidya, A.; Chaudhury, M. K. Synthesis and surface properties of environmentally responsive segmented polyurethanes. J. Colloid Interface Sci. 2002, 249 (1), 235–45.
(14) Honda, K.; Morita, M.; Sakata, O.; Sasaki, S.; Takahara, A. Effect of Surface Molecular Aggregation State and Surface Molecular Motion on Wetting Behavior of Water on Poly(fluoroalkyl methacrylate) Thin Films. Macromolecules 2010, 43 (1), 454–460.
(15) Honda, K.; Yamamoto, I.; Morita, M.; Yamaguchi, H.; Arita, H.; Ishige, R.; Higaki, Y.; Takahara, A. Effect of α-substituents on molecular motion and wetting behaviors of poly(fluoroalkyl acrylate) thin films with short fluoroalkyl side chains. Polymer 2014, 55 (24), 6303–6308.
(16) Zhao, J.; Wang, M.; Gleason, K. K. Stabilizing the Wettability of Initiated Chemical Vapor Deposited (iCVD) Polydivinylbenzene Thin Films by Thermal Annealing. Adv. Mater. Interfaces 2017, 4 (18), 1700270.
(17) Neto, C.; James, M.; Telford, A. M. On the Composition of the top layer of microphase separated thin PS-PEO films. Macromolecules 2009, 42, 4801–4808.
(18) Inutsuka, M.; Tanoue, H.; Yamada, N. L.; Ito, K.; Yokoyama, H. Dynamic contact angle on a reconstructive polymer surface by segregation. RSC Adv. 2017, 7, 17202.
(19) Crowe, J. A.; Genzer, J. Creating responsive surfaces with tailored wettability switching kinetics and reconstruction reversibility. J. Am. Chem. Soc. 2005, 127 (50), 17610–17611.
(20) Farris, S.; Intorozzi, L.; Biagioli, P.; Holz, T.; Schiraldi, A.; Piergiovanni, L. Wetting of biopolymer coatings: contact angle kinetics and image analysis investigation. Langmuir 2011, 27 (12), 7563–7569.
(21) Holly, F. J.; Refojo, M. F. Wettability of hydrogels I. Poly(2-hydroxyethyl methacrylate). J. Biomed. Mater. Res. 1975, 9 (3), 315–326.
(22) Yasuda, H.; Sharma, A. K.; Yasuda, T. Effect of orientation and mobility of polymer molecules at surfaces on contact angle and its hysteresis. J. Polym. Sci., Polym. Phys. Ed. 1981, 19 (9), 1285–1291.
(23) Lee, S. H.; Ruckenstein, E. Surface restructuring of polymers. J. Colloid Interface Sci. 1987, 120 (2), 529–536.
(24) Wong, W. S. Y.; Hauer, L.; Naga, A.; Kaltbeitzel, A.; Baumli, P.; Berger, R.; D’Aruncu, M.; Vollmer, D.; Butt, H. J. Langmuir 2020, 36 (26), 7236–7245.
(25) Bartell, F. E.; Bjorklund, C. W. Hysteresis of contact angles. J. Phys. Chem. 1952, 56 (4), 453–457.
(26) Ruckenstein, E.; Gourisankar, S. V. Surface restructuring of polymeric solids and its effect on the stability of the polymer—water interface. J. Colloid Interface Sci. 1986, 109 (2), 557–566.
(27) Sedev, R. V.; Budziak, C. J.; Petrov, J. G.; Neumann, A. W. Dynamic contact angles at low velocities. J. Colloid Interface Sci. 1993, 159 (2), 392–399.
(28) Furmidge, C. G. L. Studies at phase interfaces. I. The sliding of liquid drops on solid surfaces and a theory for spray retention. J. Colloid Interface Sci. 1962, 17 (4), 309–324.
(29) Olsen, D. A.; Joynor, P. A.; Olson, M. D. The sliding of liquid drops on solid surfaces. J. Phys. Chem. 1962, 66 (5), 883–886.
(30) Wolfram, E. Liquid drops on a tilted plate, contact angle hysteresis and the Young contact angle. Wetting, Spreading Adhes. 1978, 213–222.
(31) Dussan, V. E. On the ability of drops or bubbles to stick to non-horizontal surfaces of solids. Part 2. Small drops or bubbles having contact angles of arbitrary size. J. Fluid Mech. 1985, 151, 1–20.
(32) Estrand, C. W.; Gent, A. N. Retention of liquid drops by solid surfaces. J. Colloid Interface Sci. 1990, 138 (2), 431–442.
(33) ElSherbini, A. I.; Jacob, A. M. Retention forces and contact angles for critical liquid drops on non-horizontal surfaces. J. Colloid Interface Sci. 2006, 299 (2), 841–849.
(34) Antonini, C.; Carmona, F. J.; Pierce, E.; Marenco, M.; Amirfazli, A. General methodology for evaluating the adhesion force of drops and bubbles on solid surfaces. Langmuir 2009, 25 (11), 6143–6154.
(35) Fike, L. R. Transport properties of polystyrene above and below the glass transition temperature; Texas Tech University: 1983.
(36) Heinrich, F.; Fell, D.; Truszkowska, D.; Weirich, M.; Anyfantakis, M.; Nguyen, T.-H.; Wagner, M.; Auernhammer, G. K.; Butt, H.-J. Influence of surfactants in forced dynamic dewetting. Soft Matter 2016, 12 (37), 7782–7791.