Coatings

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Graft-Copolymer-Based Approach to Clear, Durable, and Anti-Smudge Polyurethane Coatings**

*Muhammad Rabnawaz and Guojun Liu**

Abstract: *Clear anti-smudge coatings with a thickness of up to tens of micrometers have been prepared through a graft-copolymer-based approach from commercial precursors. The coatings repel water, diiodomethane, hexadecane, ink, and an artificial fingerprint liquid. In addition, they can be readily applied onto different substrates using different coating methods. These coatings could find applications in protecting hand-held electronic devices from fingerprints, windows from stains, and buildings from graffiti.*

Clear coatings that are strongly repellent of both water- and oil-borne contaminants, sufficiently thick to endure wear, and readily applicable onto different substrates are highly desirable. For example, on the windows of skyscrapers, they could inhibit stain formation and reduce window cleaning costs. Alternatively, these coatings could protect buildings and statues against graffiti. However, coatings that possess all of the above-mentioned properties are currently not available. We report herein a novel and highly practical method for preparing such coatings and demonstrate their superior properties.

Currently, three types of anti-smudge coatings exist. The first type has a highly rough surface and is typically made of fluorinated nano- and/or micro-particles.[1–8] These coatings exhibit exceptional water and oil repellence and possess static contact angles that exceed 150° even for hexadecane, which has a low surface tension of $27.5\,\mathrm{mN\,m^{-1}}$ at room temperature.[9] However, this type of coating often lacks optical clarity because of light scattering by the rough architecture of the coating. Furthermore, a particulate coating made of loosely held particles normally lacks wear resistance.[10] Recent efforts to improve wear resistance have included the co-casting of a glue with fluorinated particles.[11,12] Alternatively, silica particles that are fused into a self-similar networked structure have been fluorinated for amphiphobicity.[13] This structure was able to preserve amphiphobicity after wearing because the removal of a layer on the coating surface revealed a similar structure further down into the coating.

The second type of coating consists of a monolayer of a low-surface-tension liquid polymer grafted onto a flat substrate. The contact angle of a test liquid such as water or hexadecane on such a flat coating never exceeds approximately 120°.[14–17] A test droplet still readily slips off such a coating for two reasons. First, the constant motion of molecules in a liquid coating facilitates the detachment of a test droplet. Second, being flat and physically homogeneous, the liquid coating has no “permanent” obtrusions to pin the test droplet.[14,17] Presently, such monolayer coatings are obtained by covalently grafting a liquid perfluoropolyether (PFPE) onto a flat substrate; the typically used PFPEs include poly(*n*-hexafluoropropylene oxide) ($\text{-(CF}_2\text{CF}_2\text{CF}_2\text{O)}_n\text{-}$) and poly(hexafluoroisopropylene oxide) ($\text{-(CF(CF}_3\text{)CF}_2\text{O)}_n\text{-}$ or PFPO).[18,19] However, such a monolayer disintegrates under abrasion or wear, and the anti-smudge properties of current commercial coatings on the touchscreens of smartphones or tablets disappear within weeks to months of device use.

The third type is based on polyurethane (PU) coatings, which are formed through the in situ reaction between a diol (or polyol) and a diisocyanate (or polyisocyanate) precursor. While PU has the advantages of being applied to any desired thickness and binding well to a wide range of substrates,[20] fluorinated groups[21,22] such as $\text{CF}_3\text{(CF}_2\text{)}_7$ had to be incorporated in the past to render anti-smudge properties. After incorporation, the long perfluoroalkyl groups segregated and enriched themselves on the coating surfaces because of their low surface tension. While high water and oil contact angles have been reported, perfluoroalkyl surface groups should not contract oil-based ink traces,[23] which makes these coatings ineffective in anti-graffiti applications.

PFPE has also been incorporated into PU by replacing a part of a hydrogenated oligomeric diol with a PFPE diol.[24,25] As the oligomeric diol chains can be long, such a coating may not be highly crosslinked. Thus, undesirable surface reconstruction that involves the upward migration by hydrogenated components during coating contact with liquids could occur.[24,25] We have also incorporated a PFPE diol into PU. Our own experiment, which involved three protocols and recipes, showed that the resultant PU coatings were always cloudy (Figures S19–S21, Supporting Information). In addition, two of the three coatings had poor anti-writing (anti-graffiti) properties. The coating opacity must be a result of the high incompatibility between the fluorinated and hydrogenated components, which eventually caused the non-uniform distribution of the different components within a PU coating.

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[*] Dr. M. Rabnawaz, Prof. G. Liu
Department of Chemistry, Queen’s University
90 Bader Lane, Kingston, Ontario, K7L 3N6 (Canada)
E-mail: gliu@chem.queensu.ca

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We resolved the surface reconstruction issue by using oligomeric polyols that contained not two, but up to tens of hydroxy groups per oligomeric chain to increase the degree of crosslinking of our fluorinated PU. Further, we used a monohydroxy PFPE to replace a PFPE diol in our PU formulations. Compared with PFPE diol chains, which were tied into a PU matrix by two ends, a grafted monohydroxy PFPE should possess higher mobility and more readily escape and concentrate on the coating surface (Structure 5, Figure 1 A). In addition, our PU matrix contained interspersed PFPE nanodomains. The removal of the surface layers by wear exposed the embedded fluorinated domains, which replenished the new surface with fresh PFPE chains (Structure 6, Figure 1 A). Thus, the surface PFPE layer of our coatings was self-replenishing or regenerating.[26–28]

We prepared PU infused with PFPE nanodomains using a graft-copolymer-based approach. In this method, a polyol that bore only one or two fluorinated side chains, but many hydroxy groups per polyol chain (Structures 1, 2, and 3 in Figure 1 A) was used. We imagined that these polyols would self-assemble, in a hydrogenated solvent that selectively solubilized the polyol backbone, into micelles with the fluorinated side chains as the core and the backbone as the corona (Structure 4, Figure 1 A).[29] These micelles were then mixed with the hydrogenated polyol precursor and a diisocyanate, and their subsequent reactions produced a PU. Our premise was that the corona-crosslinked fluorinated polyol micelles would be evenly distributed inside the cured PU bulk, because the coronal chains of the micelles were structurally identical to their polyol precursor and the two should mix well. We further speculated that the cured PU films would be optically clear if the sizes of the final embedded PFPE domains were considerably smaller than the wavelength of visible light.

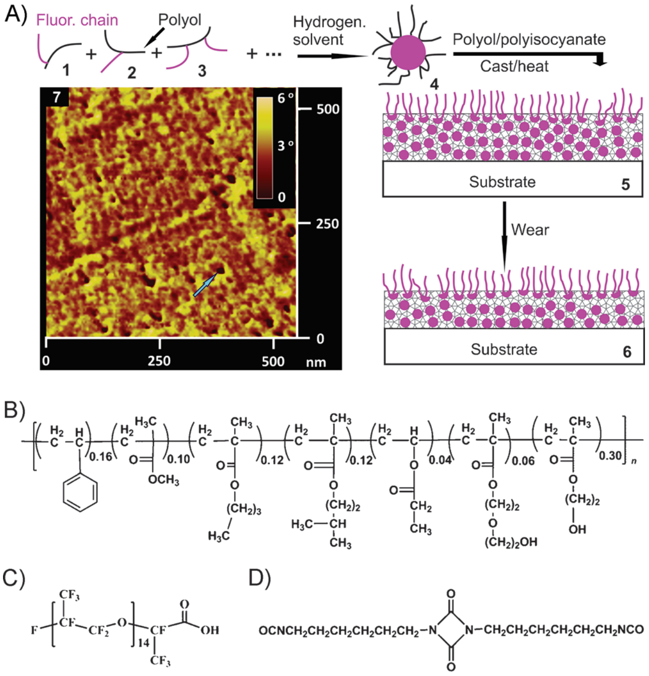

Figure 1. A) Schematic diagram of the coating process ((1–3)→4→5), the coating structure (5), and the structure of a partially worn coating (6). Also shown is an atomic force microscopic phase image (7) of a cross section generated from microtoming a PU coating containing 25 wt% of fluorine. In a hydrogenated solvent, the fluorinated side chains of a modified polyol do not dissolve but form the cores of micelles that are dispersed by the polyol backbone, which forms the micellar corona chains (Structure 4, cross-sectional view of a micelle). Upon the addition of the normal polyol and a polyisocyanate, the mixture can be partially reacted and then cast onto a substrate. Solvent evaporation and heating gives a cured coating (Structure 5). Partial wearing of the coating exposes fluorinated domains within the coating matrix (Structure 6). B–D) Chemical structures of P1 (B), PFPO-COOH (C), and the hexamethylene diisocyanate dimer (HDID, D) used in this study.

We note that there have been several publications on graft copolymers bearing PFPE side chains.[30–33] However, the reported graft copolymers were not incorporated into PU formulations. In our proof-of-concept experiments, we synthesized our fluorinated graft copolymer by modifying a commercial polyol with PFPE. The polyol that we used was polymer 1, denoted as P1, which we obtained as a solid by precipitating a commercial polyol P1-0, which we obtained as a solution in a solvent mixture including acetone from a proprietary source, in poor solvents. While the specific composition of P1 is shown in Figure 1 B, structural information regarding P1-0 is provided in the Supporting Information. The polymers were unduly complex because different monomers were incorporated by the manufacturer to improve various properties of the coating solution and the final coating. However, the key monomers were 2-hydroxyethyl methacrylate and 2-(2′-hydroxyethoxy)ethyl methacrylate, which provided the desired hydroxy groups for the reaction with isocyanate moieties. From size-exclusion chromatography analysis based on narrowly dispersed polystyrene standards, the approximate total repeat unit number *n* was 20 for P1.

The fluorinated oil that we used was PFPO-COOH, which was purchased from DuPont. This polymer had a molar mass of 2.5×10^{3} g mol^{-1} and its structure is shown in Figure 1 C. To graft it to P1, the terminal carboxy group of PFPO-COOH was first reacted with oxalyl chloride to convert it into an acid chloride. The subsequent reaction between the acid chloride and some hydroxy groups of P1 gave a graft copolymer P3. Our NMR analysis indicated that P3 contained 6.2 mol% PFPO-bearing units, which corresponded to 1.3 PFPO units per P3 backbone chain or a PFPO weight fraction of 54% in P3 (Supporting Information).

To prepare a coating, P3 was first dispersed into THF. Our DLS analysis of a dilute version of this solution gave an average hydrodynamic diameter of 36 nm for P3. Thus, this polymer formed micelles in THF following our design. Subsequently, P1-0 and a hexamethylene diisocyanate dimer (HDID, Structure D, Figure 1) were added. We adjusted the fluorine content in the final mixture by changing the mass ratio between P1-0 and P3 and maintained a molar ratio of approximately 1.23:1 between the isocyanate and hydroxy groups. Excess HDID was used to account for its possible reaction with atmospheric moisture. To form a film on a glass plate, the mixture obtained after partial reaction was cast onto the plate and leveled with a surgical blade. The solvent was then evaporated in a desiccator under gentle N_2 flow. The dried film was finally cured at 120 °C for 12 h. The complete consumption of the isocyanate groups under these conditions was confirmed by attenuated total reflectance infrared analyses (ATR-IR) of the curing films (Supporting Information).

Interestingly, the PU coatings thus prepared were transparent in the visible region possessing more than 90% transmittance at thicknesses of up to 20 μm. Figure 2a shows a smartphone with one half of its touchscreen coated by a P3-modified PU. At a thickness of 15 μm and a fluorine mass fraction of 7.2 wt%, the screen remained clear. Furthermore, one could input letters such as i, p, o, u, y on the coated side of the touchscreen's "virtual" keyboard. Therefore, this PU coating did not harm the display quality or affect the electronic response of the touchscreen, and this formulation has potential for the coatings of hand-held electronic devices. Figure 2b shows transmittance variations of P3-modified coatings as a function of film thickness at a fixed fluorine content of 6.6 wt% and also as a function of the fluorine content at a fixed thickness of (15 ± 2) μm. The optical transmittance improved as the fluorine content or film thickness decreased.

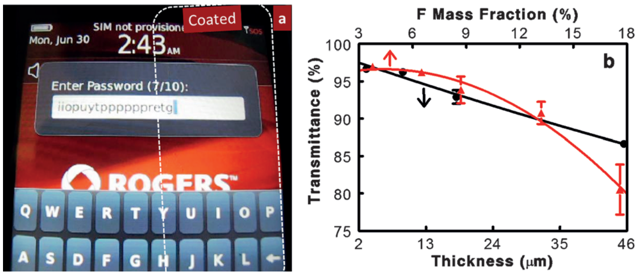

Figure 2. a) Photograph of a smartphone that was coated in the region enclosed by the dashed box. The P3-modified coating was 15 μm thick and had a fluorine content of 7.2 wt%. b) Transmittance variation at 500 nm for P3-modified coatings as a function of film thickness at 6.6 wt% fluorine (black curve) and as a function of the fluorine mass fraction at a fixed thickness of (15 ± 2) μm (red curve).

The films were clear because the incorporated PFPO did not undergo macrophase separation from the hydrogenated components. This conclusion was supported by our atomic force microscopic analysis of cross sections of P3-modified PU at different fluorine contents. Shown in Figure 1A (Structure 7) is a phase image of a cross section generated from microtoming a sample that contained 25 wt% of fluorine. We note the existence of several dark circles (one marked with an arrow), which could be cavities that were generated as a result of matrix shrinkage during coating formation and curing (crosslinking). More importantly, phase contrast was seen throughout the remaining regions of the image and the yellow and brown domains, which probably corresponded to the hard (polyol backbone) and the soft (PFPO and HDID) domains,[34] both had sizes smaller than tens of nanometers. The presence of only nanodomains agreed with Structure 6 (Figure 1A), which we proposed for the coating matrix.

The wetting properties of P3-modified coatings were evaluated by determining on them the static, advancing, and receding contact angles and the sliding angles of water, diiodomethane, and hexadecane droplets. Between the fluorine contents of 3.7 and 17.6 wt%, all test liquids slid down the coatings and the dewetting properties improved as the fluorine content increased. While the detailed results are presented and discussed in the Supporting Information, qualitative behaviors of 20 μL water and hexadecane droplets on P3-modified PU coatings containing 6.6 wt% fluorine are compared in Figure 3a and 3b. These coated glass plates were initially kept level and the liquid droplets sat at their dispensing sites for 2 h. After the plates were tilted above certain angles, the droplets readily glided down the plates. Strikingly, these droplets left no noticeable traces along their paths or on their original sites. The fact that film swelling was not noticed beneath the original spots of the test droplets suggests that the films were not permeated by the liquids, most likely because of the high crosslinking degree of the PU matrix. As designed, this heavy crosslinking eliminated surface reconstruction because all of the test liquid droplets readily glided down the coating, even after 2 h of a droplet resting on it.

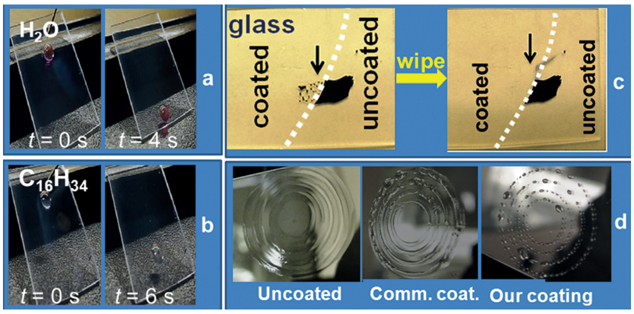

Figure 3. Anti-smudge properties of P3-modified PU films containing 6.6 wt% fluorine. Snapshots of a) sliding water droplets and b) hexadecane droplets on coated glass plates. c) Ink traces left behind by a permanent ink marker on uncoated and fluorinated PU-coated regions of a glass plate (left) before and (right) after the surface was wiped with a tissue. d) Photographs of traces impressed by a stamp freshly wetted by an artificial fingerprint liquid (left) on an uncoated glass plate, (middle) on a glass plate treated by a commercial anti-fingerprint coating, and (right) on a glass plate coated by a P3-modified PU film.

The anti-smudge properties of our designer coatings were further demonstrated in Figure 3c. While a permanent marker readily wrote and left a uniformly dark trace on the uncoated portion of a glass plate, the ink contracted on the region coated by the P3-modified PU film containing 6.6 wt% fluorine and left behind an uneven trace. After the ink had been dried, the faint trace on the coated side was readily removed by gentle wiping with a tissue. However, the trace on the uncoated side was "permanent" and could not be removed. Additional control experiments demonstrated that glass plates coated by a normal PU film prepared from P1-0 and HDID alone behaved similarly as the uncoated glass plate. Thus, the incorporated PFPO endowed the ink-repellant properties. That fluorinated PU not only inhibited ink deposition, but also facilitated ink removal suggests that it has tremendous potential in anti-graffiti applications.

In a third test, a rubber stamp bearing protruded concentric rings was wetted with an artificial fingerprint liquid (consisting of lactic acid, acetic acid, sodium chloride, sodium hydrogen phosphate, 1-methoxy-2-propanol, hydroxy-group-terminated polydimethylsiloxane, and deionized water)[35] before it was pressed onto a test substrate. Figure 3 d compares the impressions left behind by the stamp on an uncoated glass plate, a plate bearing a commercial anti-fingerprint coating for smartphones and tablets, and a plate coated by the P3-modified PU film containing 6.6 wt % fluorine. The "fingerprint" liquid readily wetted the uncoated plate, and the concentric ring patterns of the stamp were reproduced by the liquid. On the commercial monolayer-based type 2 coating, undulations or beaded sections were seen in the stamped rings, suggesting that this coating exhibited repellency against the "fingerprint" liquid. On our coating, the test liquid dewetted completely into distinct droplets, and no concentric rings were formed. Thus, our coating rejected the "fingerprint" liquid better than a product currently on the market.

Our coatings are also wear resistant. After a P3-modified PU coating containing 6.6 wt % fluorine was rubbed with a cotton-wrapped probe at a pressure of 7.7×10^3 Pa for 3600 cycles using a home-built apparatus (Supporting Information), the hexadecane static contact angle and sliding angle were $(58\pm1)^\circ$ and $(46\pm1)^\circ$. These values were essentially unchanged from $(60\pm1)^\circ$ and $(45\pm1)^\circ$ that were observed before the rubbing test. This wear resistance was much better than that of a particulate coating, made of fluorinated silica embedded in an epoxy glue, which we have tested before.[11]

In a second test, another coating containing 6.6 wt % fluorine was rubbed with the probe covered by sandpaper at an average pressure of 5.0×10^3 Pa for eight cycles. The protruded particles made circular scratches in certain regions of the coating (Figure 4 a). We then measured the static contact angles and sliding angles of water in the highly scratched region around the droplet shown in the first frame of Figure 4 a. These angles were $(109\pm3)^\circ$ and $(60\pm8)^\circ$, respectively, and differed from $(113\pm1)^\circ$ and $(47\pm2)^\circ$ measured on the original unscratched coating. Thus, the spreads in the measured contact and sliding angles increased, the average static contact angle decreased, and the average sliding angle increased after coating scratching. However, these changes could all be reasonably explained by Wenzel's theory[36] because of a roughness increase, and might have nothing to do with a decrease in the intrinsic repellency of the coating. The latter point was supported by the fact that both water and hexadecane droplets still slid down the scratched coating, leaving no visible trace behind (Figure 4 a).

In a third test, a 22 μm-thick P3-modified coating was cut with a surgical blade to create a 0.4 mm-wide trough. As shown in Figure 4 b, this trough did not stop a hexadecane droplet from sliding down the surface either, although this feature, as the scratches in Figure 4 a, did pin or drag the tail end of the sliding drop.

The damaged regions shown in Figure 4 a and b were still able to repel hexadecane and other liquids because the PFPO chains were interspersed throughout the PU matrix and the removal of the surface layer from a coating would expose the PFPO chains underneath, as depicted in Structure 6 of Figure 1 A. Therefore, our PU coatings not only had an improved wear resistance, but also were wear-tolerant because of their thickness. The thick coatings retained their anti-smudge properties as long as there was still some coating materials left to release PFPO chains.

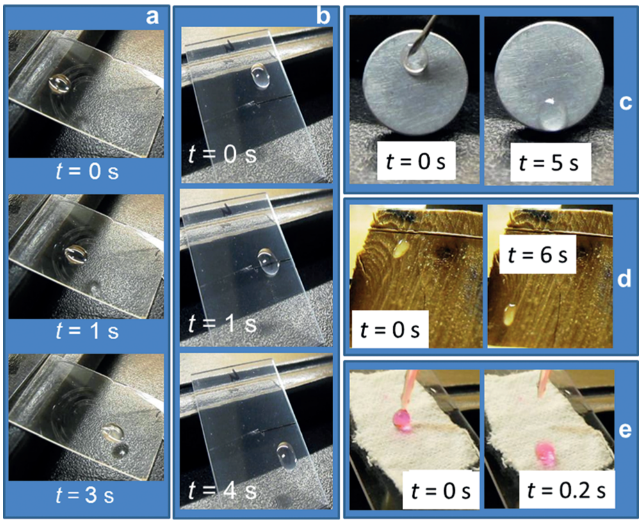

Figure 4. Snapshots showing the movement of hexadecane (a–d) and water (e) droplets on coatings that were damaged or were applied onto different substrates: a) on a coating that has been rubbed for eight cycles by a sandpaper-covered probe, b) on a coating that was 22 μm thick and was impaired by excavating a 0.4 mm-wide trough using a surgical blade, c) on a coated stainless-steel disk, d) on a coated wooden plate, and on a coated cotton fabric. All coatings were P3-modified PU containing 6.6 wt % fluorine.

While the reported anti-smudge and self-regenerating properties are readily justified by the structural model we provided in Figure 1 A for our coatings, further support for this model was gleaned from an X-ray photoelectron spectroscopic (XPS) study (Supporting Information). Using an electron take-off angle of 45° and an XPS sampling depth of around 6.6 nm,[37] we obtained a surface fluorine atomic composition of 46 % for a coating that had a bulk fluorine atomic fraction of 5.3 % (6.6 wt %). The former was much larger than the latter, suggesting PFPO enrichment on the surface. The value of 46 % was still substantially less than 60 % expected for neat PFPO, because the PFPO chains were short compared to the sampling depth of 6.6 nm. The more interesting result was that the fluorine content barely changed and was 45 % after a sample had been subjected to 3600 rubbing cycles. This result suggested that either the coating was very wear resistant, or the PFPO chains were self-regenerating on the worn coating surface.

Just as traditional PU formulations, our fluorinated PU formulations in THF can be applied onto various substrates using different coating methods. For example, we coated a stainless-steel disk by solution casting and a wooden substrate by aero-spraying (spraying an atomized coating mixture as a mist, as described in the Supporting Information). To coat a cotton fabric swatch, dip-coating was used. This process involved immersing the fabric into a coating solution, subsequently removing the swatches from the solution and evaporating the solvent in air, and lastly annealing the deposited coating at 120 °C in an oven. Both the coated metal disk and the wooden plate repelled water and hexadecane, and droplets of these liquids readily glided down the surface. However, the hexadecane droplet shown in Figure 3c on the wood appeared elongated because the substrate was not flat and presented solid protrusions that pinned the liquid. Meanwhile, the droplets behaved differently on the coated fabric because this substrate was very rough and a different wetting regime was experienced by this system.[1,2] The static contact angles of diiodomethane and water on this coated substrate were both high at (135 ± 2)° and (146 ± 2)°, respectively. Moreover, these droplets rolled rather than slid off the coatings at the rolling angles of 45° and 18°, respectively, for these two liquids.

In summary, by grafting a monofunctional PFPE to a polyol, we have produced a fluorinated polyol from these commercial reagents. Using this graft copolymer without a fluorinated solvent, clear fluorinated PU coatings at thicknesses of up to tens of micrometers were prepared. The coatings could be applied to a wide range of substrates using a variety of methods. The coatings on flat substrates repelled water, diiodomethane, hexadecane, ink, and an artificial fingerprint liquid. Moreover, they did not undergo noticeable surface reconstruction during contact with testing liquids and retained their anti-smudge properties after extensive wear. Furthermore, they did not interfere with the functions of the touchscreen of a smartphone. Thus, such coatings may find many applications, for example in the protection of hand-held electronic devices from fingerprint/smudge deposition and the protection of historical buildings from graffiti.

Keywords: coatings · graft copolymers · polyols · polyurethane · self-assembly

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[1] A. Tuteja, W. Choi, M. L. Ma, J. M. Mabry, S. A. Mazzella, G. C. Rutledge, G. H. McKinley, R. E. Cohen, *Science* **2007**, *318*, 1618–1622.
[2] A. Tuteja, W. J. Choi, G. H. McKinley, R. E. Cohen, M. F. Rubner, *MRS Bull.* **2008**, *33*, 752–758.
[3] X. Deng, L. Mammen, H. J. Butt, D. Vollmer, *Science* **2012**, *335*, 67–70.
[4] Z. Xue, M. Liu, J. Lei, *J. Polym. Sci. Part B* **2012**, *50*, 1209–1224.
[5] D. A. Xiong, G. J. Liu, J. G. Zhang, S. Duncan, *Chem. Mater.* **2011**, *23*, 2810–2820.
[6] D. Xiong, G. J. Liu, L. Z. Hong, E. J. S. Duncan, *Chem. Mater.* **2011**, *23*, 4357–4366.
[7] W. J. Jiang, C. M. Grozea, Z. Q. Shi, G. J. Liu, *ACS Appl. Mater. Interfaces* **2013**, *6*, 2628–2637.
[8] J. P. Zhang, S. Seeger, *Angew. Chem. Int. Ed.* **2011**, *50*, 6652–6656; *Angew. Chem.* **2011**, *123*, 6782–6786.
[9] R. C. Weast, D. R. Lide, M. J. Astle, W. H. Beyer, *CRC Handbook of Chemistry and Physics*, 70 ed., CRC Press, Boca Raton, **1990**.
[10] T. Verho, C. Bower, P. Andrew, S. Franssila, O. Ikkala, R. H. A. Ras, *Adv. Mater.* **2011**, *23*, 673–678.
[11] D. A. Xiong, G. J. Liu, E. J. S. Duncan, *Polymer* **2013**, *54*, 3008–3016.
[12] R. Campos, A. J. Guenthner, A. J. Meuler, A. Tuteja, R. E. Cohen, G. H. McKinley, T. S. Haddad, J. M. Mabry, *Langmuir* **2012**, *28*, 9834–9841.
[13] H. Jin, X. L. Tian, O. Ikkala, R. H. A. Ras, *ACS Appl. Mater. Interfaces* **2013**, *5*, 485–488.
[14] D. F. Cheng, C. Urata, M. Yagihashi, A. Hozumi, *Angew. Chem. Int. Ed.* **2012**, *51*, 2956–2959; *Angew. Chem.* **2012**, *124*, 3010–3013.
[15] D. F. Cheng, C. Urata, B. Masheder, A. Hozumi, *J. Am. Chem. Soc.* **2012**, *134*, 10191–10199.
[16] T. S. Wong, S. H. Kang, S. K. Y. Tang, E. J. Smythe, B. D. Hatton, A. Grinthal, J. Aizenberg, *Nature* **2011**, *477*, 443–447.
[17] A. Y. Fadeev, T. J. McCarthy, *Langmuir* **1999**, *15*, 3759–3766.
[18] D. F. Cheng, B. Masheder, C. Urata, A. Hozumi, *Langmuir* **2013**, *29*, 11322–11329.
[19] S. Block, D. Kleyer, P. Hupfield, E. Kitaura, Y. Itami, T. Masutani, Y. Nakai in *11th Annual Coatings for Plastics Symposium*, Paint & Coating Industry, Chicago, **2008**, pp. 88–92.
[20] D. K. Chattopadhyay, K. Raju, *Prog. Polym. Sci.* **2007**, *32*, 352–418.
[21] W. Ming, M. Tian, R. D. van de Grampel, F. Melis, X. Jia, J. Loos, R. van der Linde, *Macromolecules* **2002**, *35*, 6920–6929.
[22] W. H. Ming, J. Laven, R. van der Linde, *Macromolecules* **2000**, *33*, 6886–6891.
[23] D. Macoretta, M. Rabnawaz, C. M. Grozea, G. J. Liu, Y. Wang, A. Crumblehulme, M. Wyer, *ACS Appl. Mater. Interfaces* **2014**, *6*, 21435–21445.
[24] T. Trombetta, P. Iengo, S. Turri, *J. Appl. Polym. Sci.* **2005**, *98*, 1364–1372.
[25] A. Vaidya, M. K. Chaudhury, *J. Colloid Interface Sci.* **2002**, *249*, 235–245.
[26] Y. Li, L. Li, J. Q. Sun, *Angew. Chem. Int. Ed.* **2010**, *49*, 6129–6133; *Angew. Chem.* **2010**, *122*, 6265–6269.
[27] H. Zhou, H. X. Wang, H. T. Niu, A. Gestos, X. G. Wang, T. Lin, *Adv. Mater.* **2012**, *24*, 2409–2412.
[28] X. L. Wang, X. J. Liu, F. Zhou, W. M. Liu, *Chem. Commun.* **2011**, *47*, 2324–2326.
[29] F. He, T. Gadt, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **2011**, *133*, 9095–9103.
[30] J. C. Yarbrough, J. P. Rolland, J. M. DeSimone, M. E. Callow, J. A. Finlay, J. A. Callow, *Macromolecules* **2006**, *39*, 2521–2528.
[31] M. Krupers, P. J. Slangen, M. Moller, *Macromolecules* **1998**, *31*, 2552–2558.
[32] R. Bongiovanni, G. Malucelli, V. Lombardi, A. Priola, V. Siracusa, C. Tonelli, A. Di Meo, *Polymer* **2001**, *42*, 2299–2305.
[33] E. Casazza, A. Mariani, L. Ricco, S. Russo, *Polymer* **2002**, *43*, 1207–1214.
[34] S. N. Magonov, V. Elings, M. H. Whangbo, *Surf. Sci.* **1997**, *375*, L385–L391.
[35] L. Y. L. Wu, S. K. Ngian, Z. Chen, D. T. T. Xuan, *Appl. Surf. Sci.* **2011**, *257*, 2965–2969.
[36] R. N. Wenzel, *Ind. Eng. Chem.* **1936**, *28*, 988–994.
[37] C. Ton-That, A. G. Shard, R. H. Bradley, *Langmuir* **2000**, *16*, 2281–2284.

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