Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting Information

Transparent Superhydrophobic Coatings from Amphiphilic-Fluorinated Block copolymers Synthesized by Aqueous Polymerization-Induced Self-Assembly

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I-Experimental section

I.1-Materials.

4,4-azobis(4-cyanopentanoic acid) (ACPA, >98%, Fluka), methacrylic acid (MAA, 99%, Sigma-Aldrich), 1*H*,1*H*,2*H*,2*H*-perfluorodecylacrylate (FDA, 97% Sigma-Aldrich), 1,3,5-trioxane (99%, Sigma-Aldrich), sodium hydrogencarbonate ($NaHCO_3$, 97% Sigma-Aldrich) were used as received and n-butyl acrylate (BuA, 99+%, Sigma-Aldrich) was distilled under reduced pressure to remove the stabilizer. Aerosil 200 was purchased from Keyser & Mackay and Tixosil 365 kindly provided by Solvay. The RAFT agent, 4-cyano-4-thiothiopropylsulfanyl pentanoic acid (CTPPA), was synthesized as described elsewhere.[1] Water purified with a Milli-Q reagent system (Millipore) was used in this work. All manipulations were performed by classical Schlenk techniques under argon. Single-side-polished (100) silicon wafers were purchased from ACM (France) and cut in rectangles of 2 × 2 cm^2.

I.2-Characterizations.

Prior to ^1H NMR and SEC analyses, the carboxylic acid groups of the poly(methacrylic acid) (PMAA) block were methylated by addition of trimethylsilyldiazomethane according to the reported procedure.[2]

The molar masses (M_n) and dispersities (M_w/M_n) of the polymers were determined by size exclusion chromatography (SEC) in tetrahydrofuran (THF) at 45°C at a flow rate of 1 mL/min with Viscotek 305 TDA liquid chromatograph equipped with 2 PSS SDV analytical linear M 8 mm columns protected by a PL gel 5 µm guard column and calibrated with PMMA standards.

400 MHz ^1H NMR were recorded on a Bruker AVANCE 400 MHz spectrometer.

Dynamic Light Scattering (DLS) was determined by a Delsa Nano C particle analyzer (Beckman Coulter) equipped with a laser diode source (wavelength 658 nm, power 30 mW). DLS was used to measure the hydrodynamic diameter of the triblock copolymer (PMAA-*b*-PnBuA-*b*-P(FDA-*co*-nBuA) micelles in water (diluted at 2 mg/mL). Data (treated with Delsa Nano 2.21 software) were analyzed using the CONTIN method, which is based on an inverse-

Laplace transformation of the data and gives access to a size distribution histogram for the analyzed micellar solutions. Transmission Electron Microscopy (TEM) observation was carried out on a TEM, Philips CM100. Scanning electron microscopy (SEM) analyses were performed using a 515 Philips scanning electron microscope. Transmittance spectra were taken on a U-3300 UV−Visible spectrophotometer (Hitachi). DSC measurements were acquired with a TA Instruments Q1000 DSC using standard aluminum pans, an indium standard for calibration, and nitrogen as the purge gas. T_m, ΔH_m and T_g and crystallization temperatures were determined by taking the peak values of second heating and cooling scans.

Contact angle measurements.

Water contact angle measurements were performed with an OCA-20 apparatus (Dataphysics Instruments GmbH, Germany) in the sessile drop configuration. A droplet (6 µL) of Milli-Q water was deposited onto the surface and the recorded image was analyzed by the OCA 20 software to determine the contact angle. The results are the average of 3 values measured at different locations on the surface.

Atomic force microscopy (AFM).

Surface topography and surface materials properties were characterized by atomic force microscopy (AFM). Topographic images were obtained with a Multimode microscope (Bruker) in tapping mode using PointProbes sensor (Nanosensors) with a spring constant of ~40 N m^{-1} and < 7 nm radius of curvature. AFM scratch tests were performed on a Dimension Icon (Bruker) operated in contact mode in air. Diamond coated n-type silicon AFM probes, CDT-NCLR (NanoSensors), with nominal total tip height on the order of 10-15 µm were used to test the wear resistance of the composite film. The deflection sensitivity of the cantilever was determined by measuring a force curve against a silicon substrate considered as an infinitely stiff surface; values around 70 nm.V^{-1} were obtained. The thermal tune method was use to calibrate the cantilever spring constant; values around 90 N.m^{-1} were obtained. The tip radius of curvature of the diamond-coated tips was estimated using SEM imaging (Fig. S10). Values around 175 nm were found for all the used tips.

Different regions (1 x 1 µm²) of the film surface were scanned with increasing applied normal forces (from 0.2 to 15 µN). Before and after the scratch experiments, an area of 20 × 20 µm², including all the 1 × 1 µm² scratched areas, was imaged with ScanAsyst mode using soft ScanAsyst Air probes (Bruker) and analyzed by home-made routines running to calculate the average scratch depth as a function of the applied force. Briefly, the images were flattened, and the average height of an undamaged region of the film was obtained from the distribution of pixel heights in this region; the same was done within scratched regions, leading to the average depth of the damage. The root-mean-square roughness of the film was obtained from the width of the distribution of pixel height, and averaged over three images acquired at different scan sizes (1 x 1 µm², 5 x 5 µm², 10 x 10 µm²).

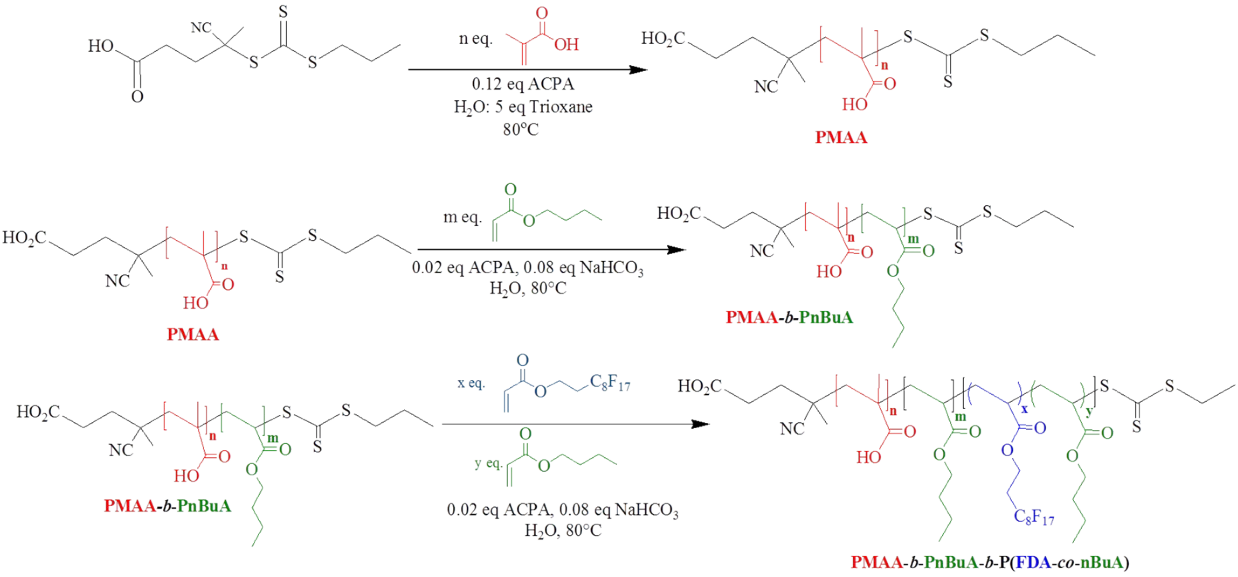
X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed on a SSX 100/206 photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized microfocused Aluminum X-ray source (1486.6 eV) operated at 20 mA and 10 kV. All binding energies are referenced to the C-(C,H) component of the C 1s peak fixed at 284.8 eV. The base pressure in the spectrometer was in the low 10^{-8} Torr range. Quantitative information was obtained from the photoemission peak areas of each element normalized according to acquisition parameters and sensitivity factors provided by the manufacturer. Peak decomposition was achieved with the Casa XPS software (CasaSoftware Ltd., UK).

Ellipsometry.

Ellipsometry measurements were performed with a spectroscopic ellipsometer Uvisel from Horiba-Jobin-Yvon at an incidence angle of ca. 70°, in a wavelength range from 400 to 850 nm. The ellipsometric data were fitted using the DeltaPsi 2 software with a three-layer model comprising silicon (bulk), native silicon oxide (1.5 nm thickness) and a single homogeneous film of adjustable thickness including the polymer layer. The refractive index of this film was modeled by a transparent Cauchy layer, and the tabulated optical constants of Si and SiO_2 were used. The measurements were carried out at least three times at different points on the sample to obtain the average thickness.

I.3- Synthesis of PMAA-*b*-PnBuA-*b*-P(FDA-*co*-nBuA)



MAA (2.06 g, 23.93 mmol, 40 eq), CTPPA (0.163 g, 0.59 mmol, 1 eq), ACPA (0.020 g, 0.07 mmol, 0.12 eq) and 1,3,5-trioxane (0.265 g, 2.95 mmol, 5 eq) were dissolved in 20 mL of deionized water under argon atmosphere (trioxane is used as an internal reference for the determination of the monomer conversion by ^{1}H NMR). After complete dissolution of reactants, the solution was purged for 30 minutes with argon and then heated at 80°C for 6 h. An aliquot was picked out of the reactor for determining the conversion (>97%) by ^{1}H NMR (using the relative integration of the protons of 1,3,5-trioxane at 5.1 ppm and the vinylic protons of MAA) and the molecular parameters of PMAA-CTPPA (M_n = 4500 g/mol and M_w/M_n = 1.17) by SEC in THF (SEC and ^{1}H NMR analyses carried out after methylation of the carboxylic acid groups). DP of PMAA block was calculated from Mn (SEC).

In the second step, nBuA (0.42 mL, 2.95 mmol, 5 eq) and 1 mL of a degassed aqueous solution of ACPA (0.003 g, 0.012 mmol, 0.02 eq) and $NaHCO_3$ (0.004 g, 0.047 mmol, 0.08 eq) was added to the reactor. After 12 hours of reaction at 80°C, an aliquot was picked out the reactor for determining the conversion (~ 98%) of nBuA, the molecular parameters of the diblock copolymer PMAA-*b*-PnBuA-CTPPA (M_n = 5100 g/mol and M_w/M_n = 1.14) by SEC in THF.

In the third step, FDA (1.68 mL, 5.31 mmol, 9 eq), nBuA (0.25 mL, 1.77 mmol, 3 eq) and 1 mL of degassed aqueous solution of ACPA (0.003 g 0.012 mmol, 0.02 eq) and $NaHCO_3$ (0.004 g, 0.047 mmol, 0.08 eq) was added to the reactor. The polymerization of the third block was carried out for 24 h at 80°C (conversion >99% as determined by ^1H NMR). During the reaction a white precipitate appears. The solution was filtrated to remove this solid (homopolymer of PFDA, m_{PFDA} = 275 mg) and the triblock copolymer in solution was analysed by SEC (M_n = 5700 g/mol and I_p = 1.14) and ^1H NMR. Before ^1H NMR and GPC analysis, the carboxylic acids groups of the final triblock copolymers and their intermediates (PMAA and PMAA-*b*-PnBuA) were methylated by addition of trimethylsilyldiazomethane according to the reported procedure elsewhere.[2] The obtained polymer was purified by precipitation in ethanol.

I.4- Preparation of FBC coating

The as-prepared FBC micellar solution (20 wt%) was spin-coated (700 rpm for 30 seconds and 1200 rpm for 60 seconds) onto microscope glass substrates (cleaned by washing with isopropanol, water and acetone) and dried at room temperature. To obtain hydrophobic coating, the coated glass substrates were heated at different temperatures (between 100°C and 200°C) for 2h in order to found the optimal (and minimal) temperature that was required for the migration of the fluorinated block at the surface. Water contact angle was then measured on the different coated glasses (Table S1). The optimal temperature was found to be 150°C for the block copolymer and was therefore selected for our study.

Table S1: water contact angles measured for the coatings obtained for the different annealing temperatures

Temperature of annealing	Water contact angle
100°C	100 – 102°
120°C	110 - 115°
150°C	124 - 127°
170°C	122 – 126°
200°C	112 – 115°

I.5- Preparation of FBC-Silica coating (62 wt%FBC, 30 wt% Aerosil 200, 8 wt% Tixosil 365)

10 g of the original FBC micellar solution (20 wt%) was diluted to 15 wt% by adding deionized water. Aerosil 200 (0.97 g) and Tixosil 365 (0.26 g) silica particles were added to this solution, and the mixture was ultrasonicated for 30 min with an ultrasonic probe Omni Sonic Ruptor 400 working at 400 W and 20 kHz. The FBC/silica mixture dispersed in water was spin-coated onto microscope glass slide. Finally, the coated glass substrate was dried at room temperature and then heated in an oven at 160°C for 12 hours under ambient atmosphere.

It is important to note here that the presence of silica particles decreases the polymer chains mobilities. Therefore, it was necessary to increase both the annealing temperature and time to 160°C and 12 hours (compared to the coating without silica), respectively, to efficiently promote the migration of fluorinated block to the surface. Furthermore, the film thickness of the coating with silica (~ 500 nm) was higher than the coating without silica (< 200 nm), which also justifies why a higher annealing temperature and time are required for this migration.

II-Supporting Figures

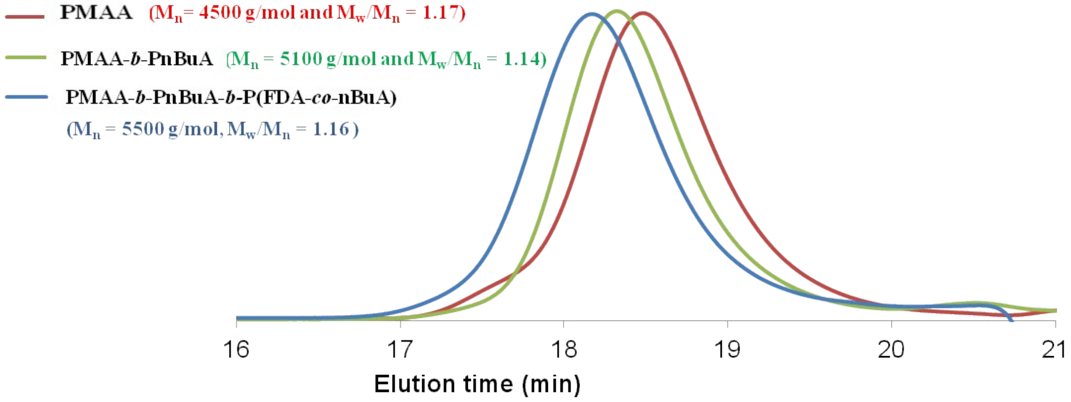


Fig. S1 SEC chromatograms of PMAA, PMAA-*b*-PnBuA and PMAA-*b*-PnBuA-*b*-P(FDA-*co*-FDA) after methylation of the carboxylic acid groups of PMAA.

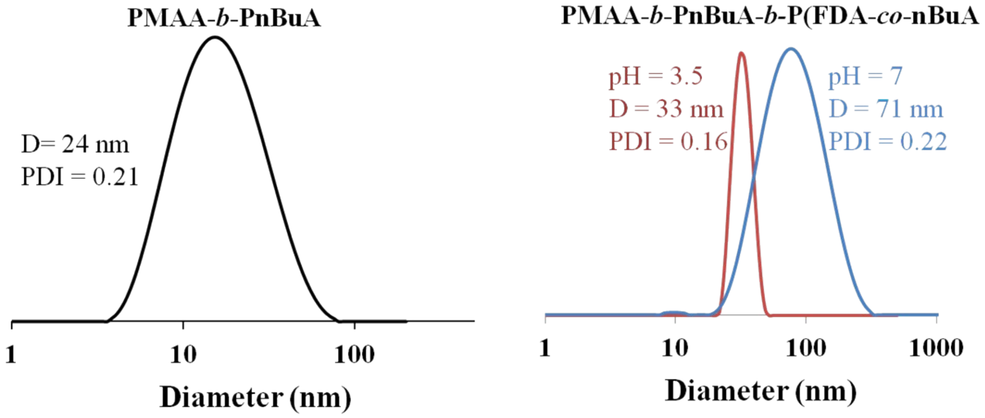


Fig. S2 DLS analyses of PMAA-*b*-PnBuA and PMAA-*b*-PnBuA-*b*-P(FDA-*co*-nBuA) (5 wt%, pH = 3.5 and 7).

The DLS measurement was performed at pH = 3.5 (that corresponds to the pH of the as-prepared micellar solution). At this pH the PMAA shell of the micelles is protonated. Therefore, this shell is not in an extended conformation although the micelles are highly stable. Under these conditions, the measured diameter by DLS is thus very close to the diameter of dried micelles (measured par TEM). When the pH of the solution is increased to 7 by the addition of KOH, the measured diameter by DLS increased to about 70 nm. This increase of the diameter of the micelles is due to the solvation of the deprotonated PMAA shell.

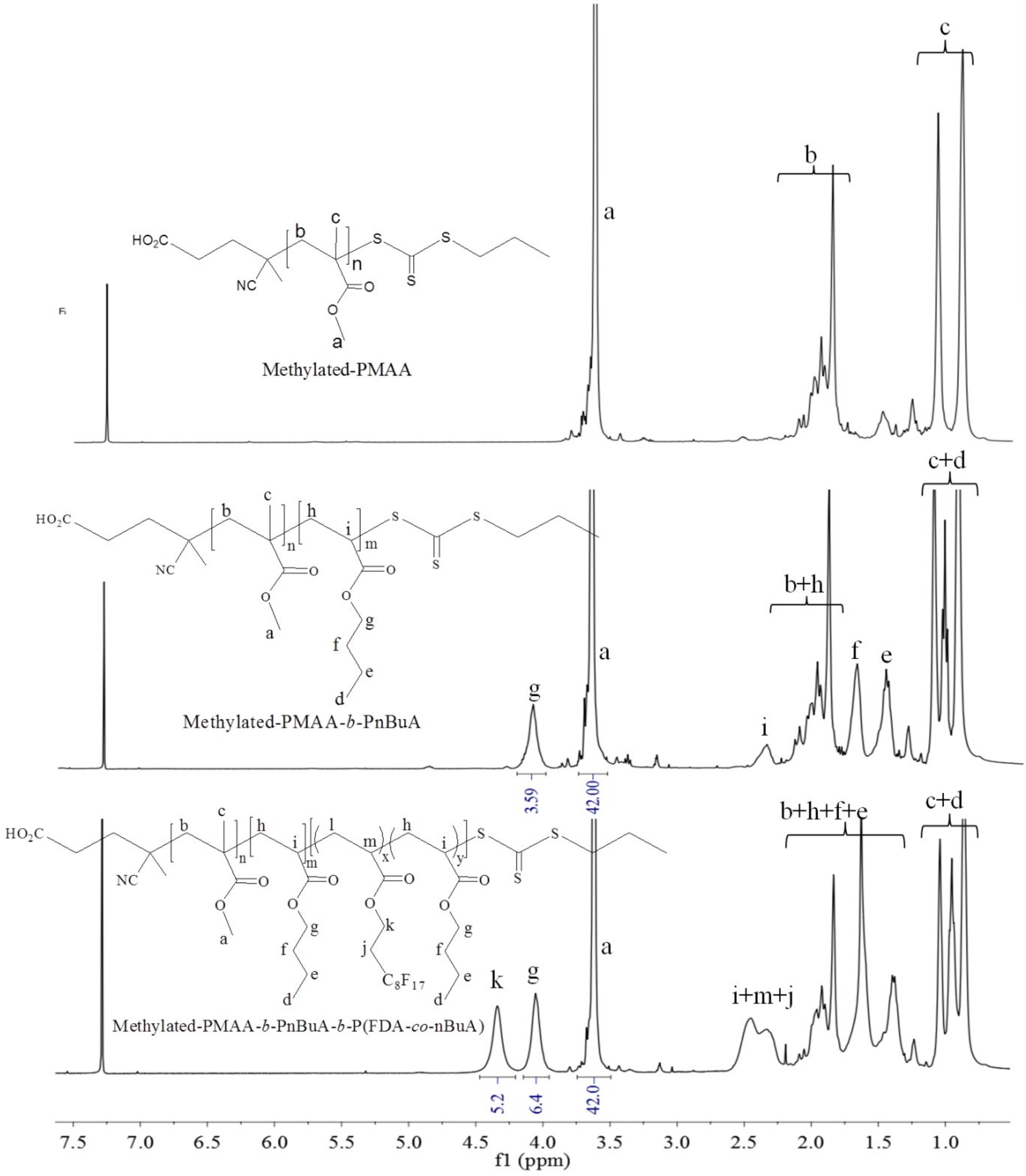


Fig. S3 ^{1}H NMR spectra in $CDCl_3$ of methylated PMAA, PMAA-*b*-PnBuA and PMAA-*b*-PnBuA-*b*-P(FDA-*co*-FDA).

The degree of polymerization (DP) of the second block (PnBuA) was determined on the basis of resonances characteristic of the repeating unit of methylated PMAA (protons **a**, CH_3-O-, 3.6ppm) and of the repeating unit of PnBuA (protons g, -CH_2-O-, 4.05ppm), and taking into account that DP of PMAA first block is 42 as determined by SEC (PMMA calibration) after methylation of carboxylic acid groups of PMAA. DP of the third block was determined by comparing the integrals of protons **a** of methylated PMAA first block with protons **k** (-O-CH_2-, 4.3 ppm) of the repeating unit of PFDA.

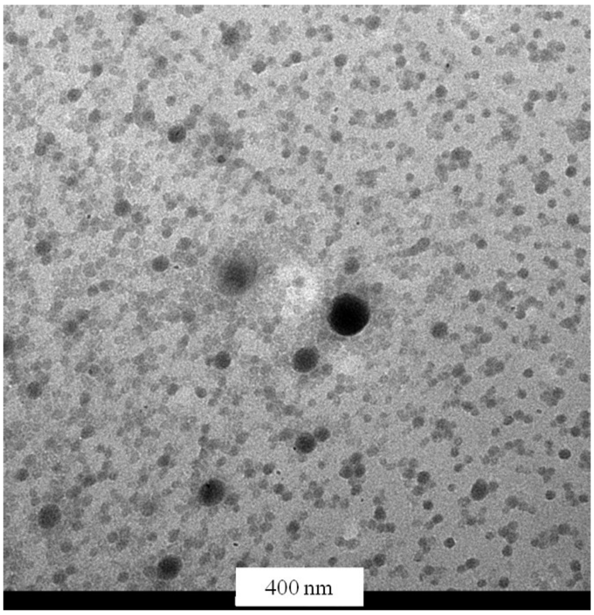


Fig. S4 TEM image of PMAA-*b*-PnBuA-*b*-P(FDA-*co*-nBuA) micelles.

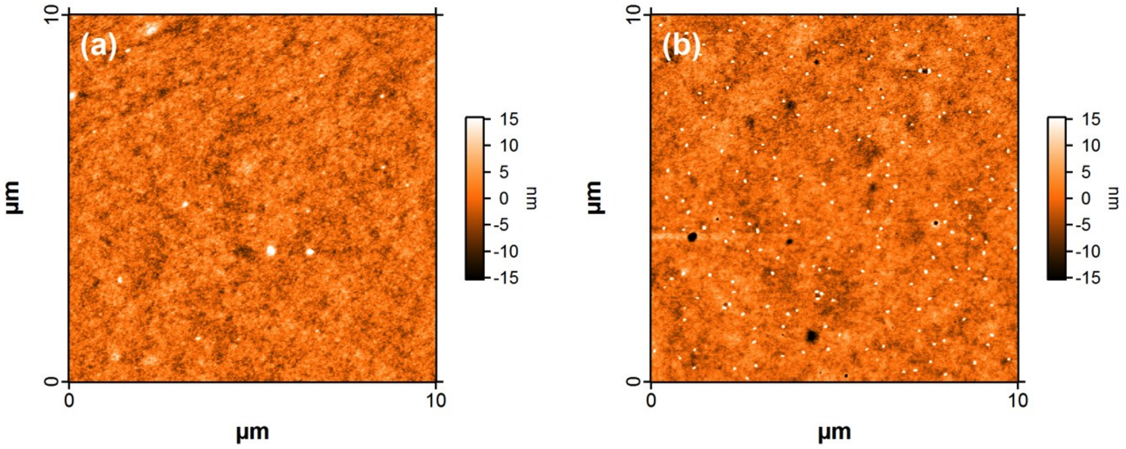


Fig. S5 AFM topographic images of FBC micelles deposited on silicon (a) before and (b) after thermal annealing.

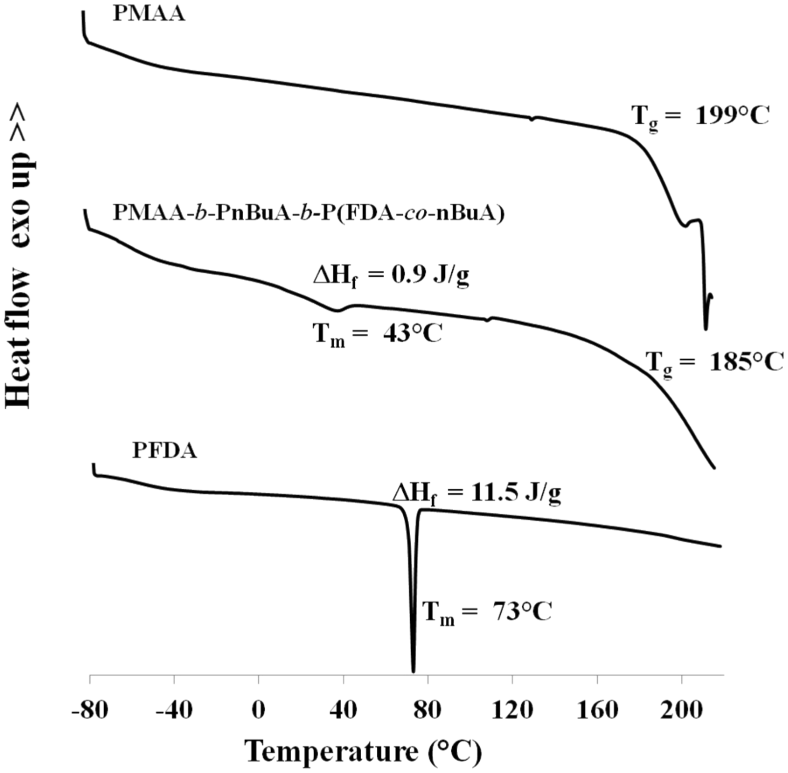
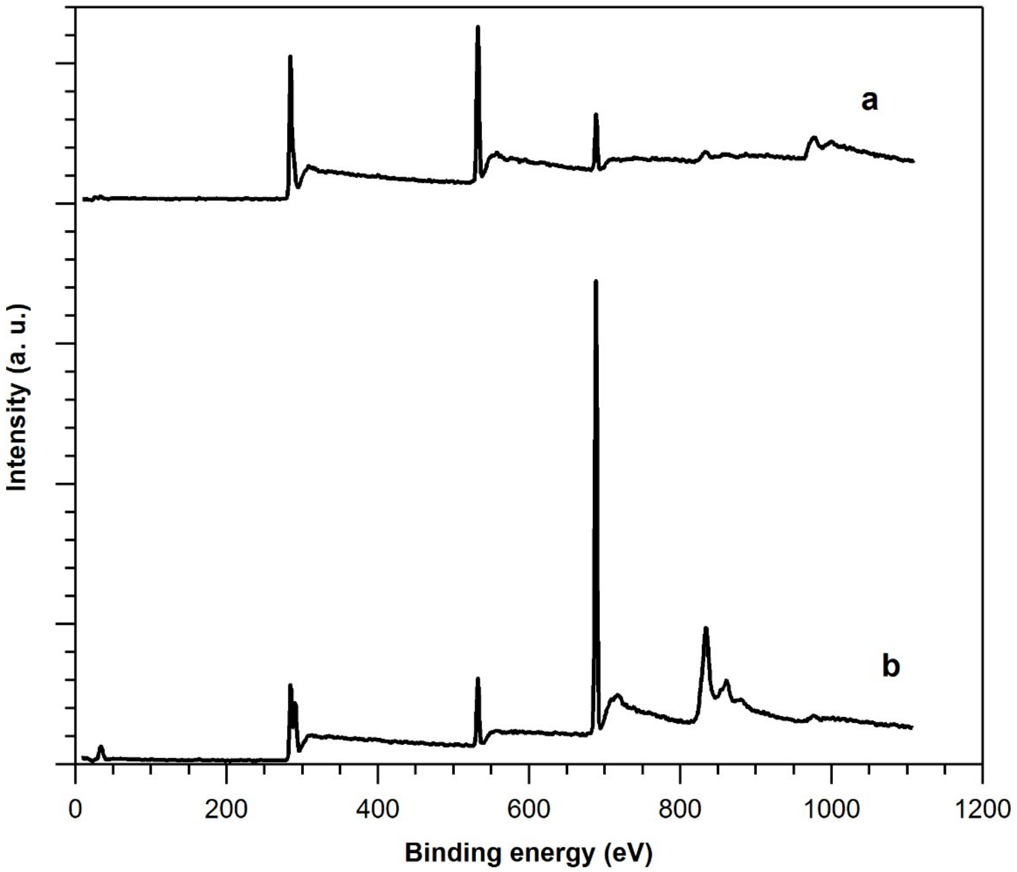


Fig. S6 Heating DSC thermograms (10°C/min) of $PMAA_{42}$, $PFDA_{10}$, $PMAA_{42}$-*b*-$PnBuA_5$ and $PMAA_{42}$-*b*-$PnBuA_5$-*b*-P(FDA_7-*co*-$nBuA_4$).



Sample	C (%)	O (%)	F (%)
Before annealing (a)	66	26	6
After annealing (b)	45	9	45
Theoretical data for homopolymer of FDA	33	5	43

Fig. S7 XPS spectra of FBC micelles a) before and b) after thermal annealing; the table summarized the chemical composition of the sample surface computed from XPS spectra, and the theoretical compositions of homopolymer of FDA.

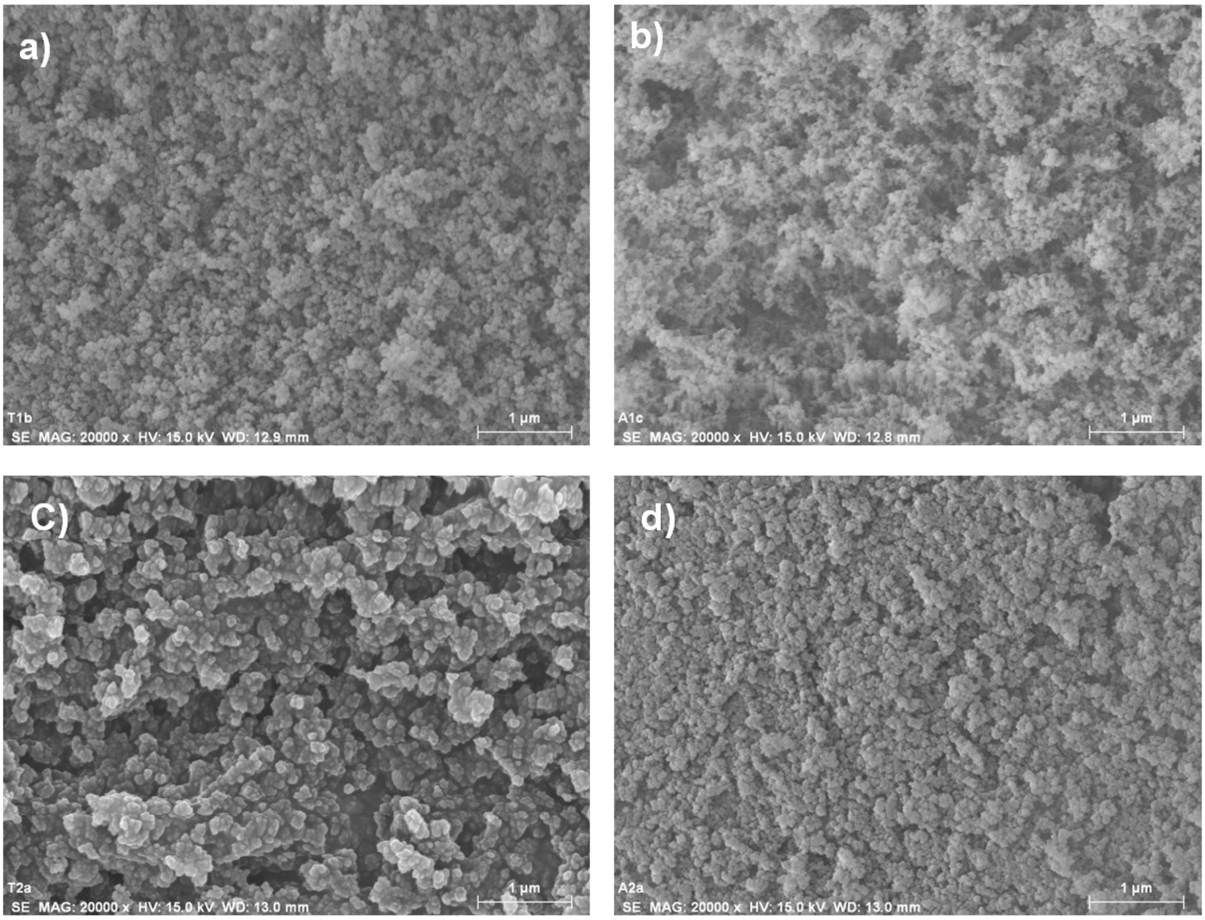


Fig. S8 SEM images of Aerosil 200 (a) without (b) after 30 min of ultrasonication and Tixosil 365 (c) without (d) after 30 min of ultrasonication

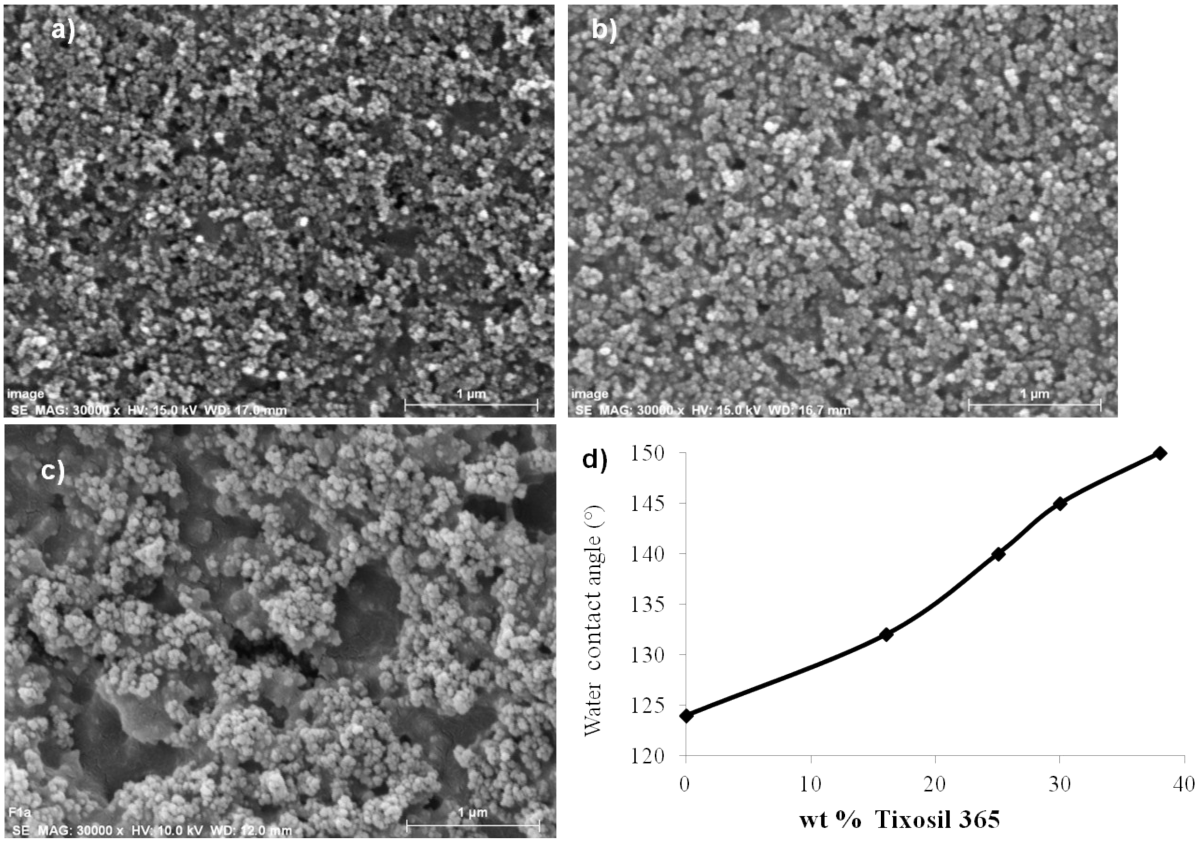


Fig. S9 SEM images of coatings based on (a) 60 wt% of FBC+ 40 wt% of Aerosil 200 (b) 62 wt% of FBC+ 30 wt% of Aerosil 200 + 8 wt% of Tixosil 365 (c) 62 wt% of FBC+ 38 wt% of Tixosil 365 and (d) Evolution of water contact angle of (FBC + Tixosil 365) coatings with different Tixosil 365 contents.

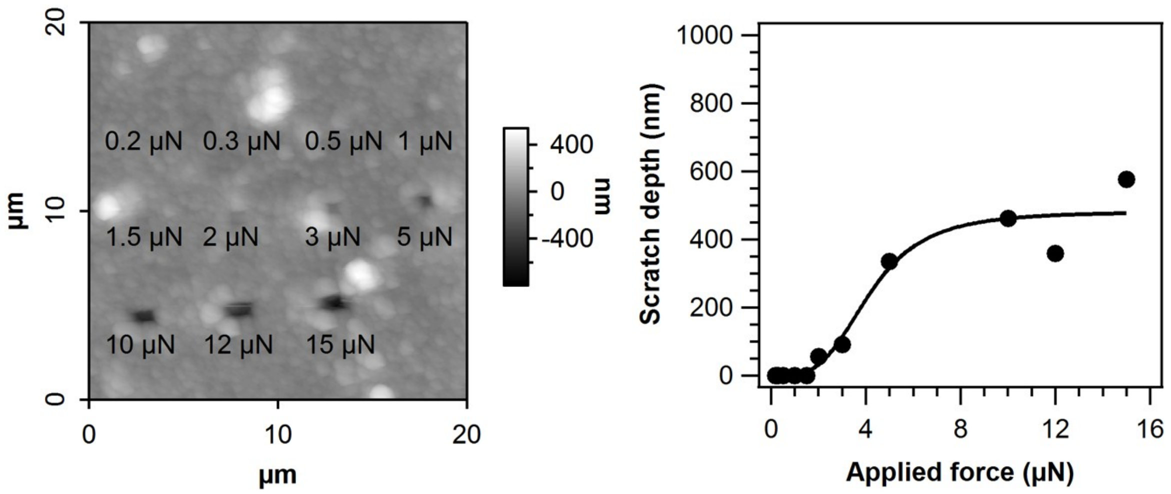


Fig. S10 AFM scratch tests on 62 wt% of FBC+ 30 wt% of Aerosil 200 + 8 wt% of Tixosil 365 coating obtained after annealing. (Left) AFM topography image recorded after scratching with different applied normal forces; (right) Average scratch depth as a function of the applied force. The line is drawn as guide for eye.

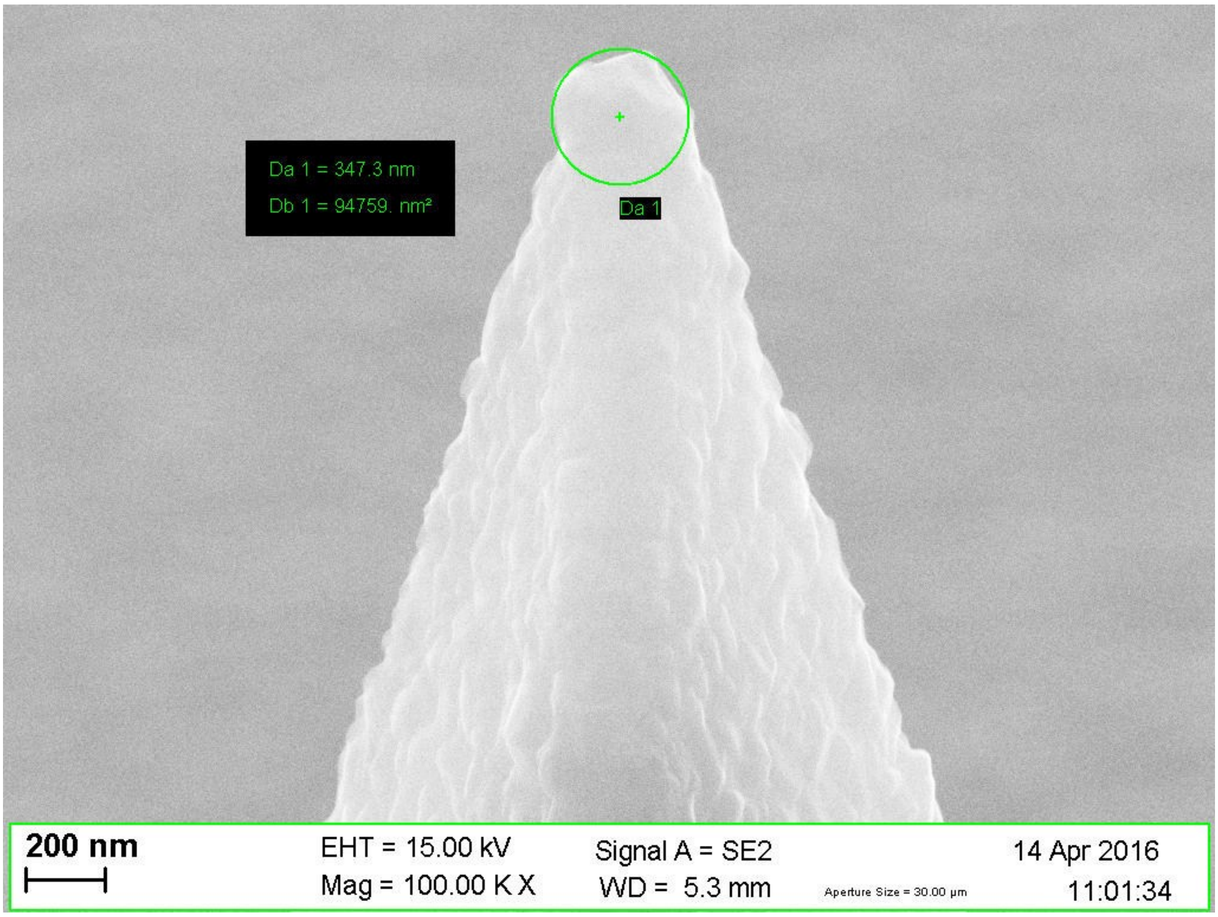


Fig. S11 SEM image of the diamond-coated AFM tip used for the scratch tests. The radius of curvature of the apex is estimated to be around 175 nm.

Table S2: Macromolecular characteristics of PMAA, PMAA-*b*-PnBuA and PMAA-*b*-PnBuA-*b*-P(FDA-*co*-FDA).

PMAA				**PMAA-*b*-PnBuA**			**PMAA-*b*-PnBuA-*b*-P(FDA-*co*-nBuA)**		
$[MAA]_0$/ [CTPPA]°	M_n (g/mol)^a	M_w/M_n ^{a}	DP_n^{a}	M_n (g/mol)^a	M_w/M_n ^{a}	DP_n^{b} (nBuA)	M_n (g/mol)^a	M_w/M_n ^{a}	DP_n^{b} (FDA+nBuA)
40	4500	1.17	42	5100	1.14	6	5700	1.14	7+4

$^{a)}$Estimated from SEC analysis (*vs* PMMA standards) in THF $^{b)}$ Estimated from ^{1}H NMR spectroscopy

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[1] Boursier, T.; Chaduc, I.; Rieger, J.; D'Agosto, F.; Lansalot, M.; Charleux, B. *Polym. Chem*. 2011, **2**, 355−362.

[2] Couvreur, L.; Lefay, C.; Belleney, J.; Charleux, B.; Guerret, O.; Magnet, S. *Macromolecules*. 2003, **36**, 8260−8267.