

Supporting information for

**Stable Superhydrophobic Porous Coatings from Hybrid
ABC Triblock Copolymers and their Anti-Corrosive
Performance**

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1. Synthesis and Characterization of polymers

Synthesis of PDMS-PS diblock copolymer. The diblock copolymer was synthesized by atom transfer radical polymerization (ATRP). The functional PDMS-Br macroinitiator was prepared from monocarbinol-terminated poly(dimethylsiloxanes) by using BiBB and TEA (ratio 1:10:10) in anhydrous DCM with a final polymer concentration of 15 wt% in solution. The TEA/PDMS solution was cooled using a water/ice bath under nitrogen circumstance for 15 min, followed by dropwise addition of BiBB. This reaction solution was stirred at 23 °C for 24 h. Subsequently, the polymer solution was filtered to remove precipitates, and then washed with a saturated NaHCO₃ solution and deionized water, respectively. The solvent was removed by a rotary evaporator and the polymer was further washed with methanol to yield a colorless clear liquid. The PDMS-Br macroinitiator (0.38 g), PMDETA ligand (20 µL, 0.08 mmol) were firstly added to a 50 mL Schlenk tube. After three vacuum-nitrogen purging cycles, the monomer (styrene) (3 mL, 26 mmol) and toluene (1 mL) were added under nitrogen flow. The solution was further bubbled with nitrogen for 20 min, and then CuBr powder (12 mg, 0.08 mmol) was added quickly under nitrogen flow. Subsequently, the Schlenk tube was placed in an oil bath (100 ± 0.1 °C) and stirred (600 rpm) for 6 h. The reaction was quenched by cooling and exposing to air, followed by diluting with THF. The copper catalyst was removed by passing through a neutral alumina column. Finally, the polymer solution was precipitated in cold methanol, the resultant white solid was dried under vacuum at 45 °C for 24 h.

Synthesis of PDMS-PS-PiBuPOSSMA triblock copolymer. The chain extension with iBuPOSSMA monomer was also achieved by ATRP. Typically, the PDMS-PS-Br

macroinitiator (0.5 g), PMDETA ligand (6 μ L, 0.03 mmol) and iBuPOSSMA (1.24 g, 1.5 mmol) were firstly added to a 50 mL Schlenk tube. After three vacuum-nitrogen purging cycles, toluene (2.5 mL) was added and further bubbled with nitrogen for 20 min, and then CuBr powder (5 mg, 0.03 mmol) was added quickly under nitrogen flow. The Schlenk tube was placed in an oil bath (45 ± 0.1 °C) and stirred (600 rpm) for 24 h. The polymer was recovered by using the method described above.

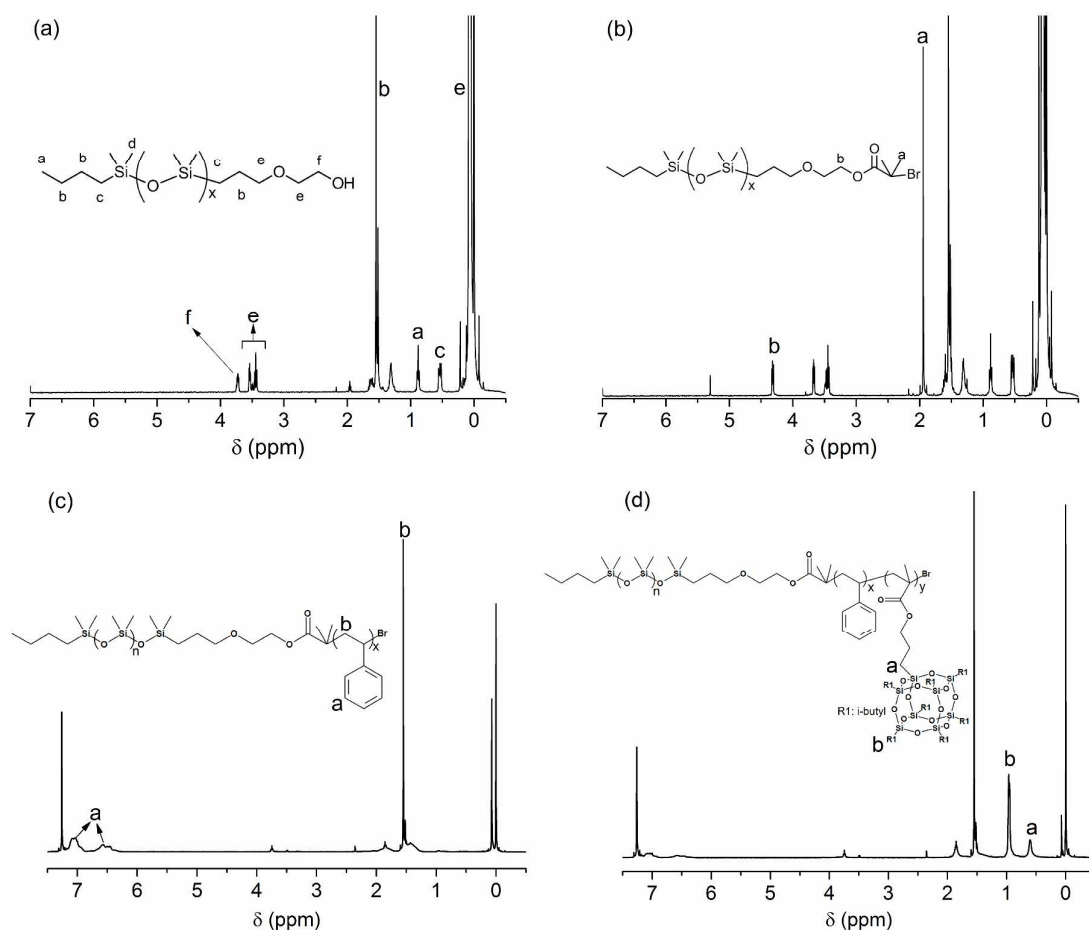


Figure S1. ^1H NMR (400 MHz) spectra of polymers in CDCl_3 . (a) PDMS-OH, (b) PDMS-Br, (c) PDMS-PS, (d) PDMS-PS-PiBuPOSSMA.

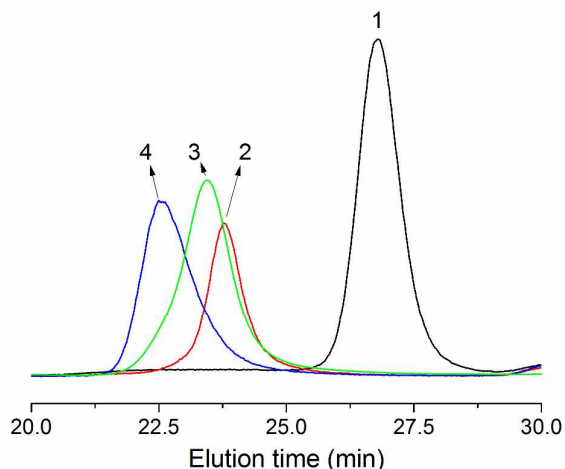


Figure S2. The GPC traces of polymers: (1) PDMS₅₈-Br, (2) PDMS₅₈-PS₂₁₄, (3) PDMS₅₈-PS₂₁₄-PiBuPOSSMA₃₅, (4) PDMS₅₈-PS₂₁₄-PiBuPOSSMA₇₀.

The structure of the polymer was verified by ^1H NMR spectroscopy (Figure S1). In the ^1H NMR spectra of all polymers, the signals of the protons of methyl groups on PDMS backbone are present at 0.07 ppm. The presence of methyl group next to the bromide ($\delta = 1.9$ ppm) confirms the successful reaction between PDMS-OH and 2-bromoisobutyryl bromide (Figure S1b). In the case of PDMS-PS, broad peaks at 1.2-2.0 ppm (aliphatic backbone) and 6.3-7.3 ppm (aromatic side chain) represent the PS block. Comparing the ^1H NMR spectrum of PDMS-PS, additional peak ($\delta = 0.96$) due to the isobutyl on pendant POSS clearly indicates the chain extension (Figure S1d). All GPC traces (Figure S2) of the polymers are unimodal and display a clear shift toward higher molar mass when compared with the PDMS macroinitiator. The ^1H NMR and GPC provide a complementary evidence of the successful synthesis of the hybrid triblock copolymers in this study.

Table S1. Molecular Parameters of Polymers

sample ^a	M _w (Da) ^b	M _n (Da) ^b	PDI ^b
PDMS ₅₈ -Br	8543	8040	1.06
PDMS ₅₈ -PS ₂₁₄	47213	40600	1.16
PDMS ₅₈ -PS ₂₁₄ -PiBuPOSSMA ₃₅	70781	60840	1.16
PDMS ₅₈ -PS ₂₁₄ -PiBuPOSSMA ₇₀	85924	72414	1.18

^a Subscripts correspond to the number-average degrees of polymerization of corresponding block as determined by ¹H NMR. ^b Measured by GPC analysis.

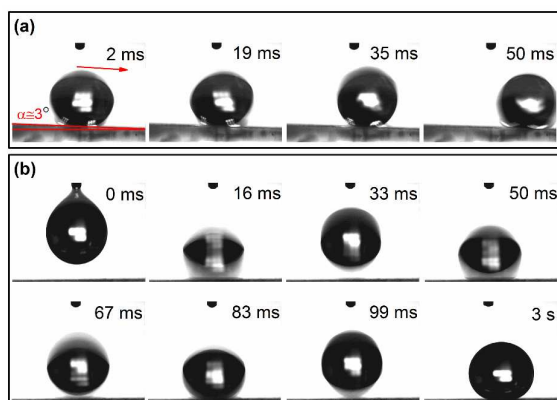


Figure S3. The time-lapse frames of (a) water droplets (7 μL) rolling off on an inclined surface and (b) water-droplet-bouncing phenomena on a coating surface (7 μL) for PDMS₅₈-PS₂₁₄-PiBuPOSSMA₇₀ SH surface.

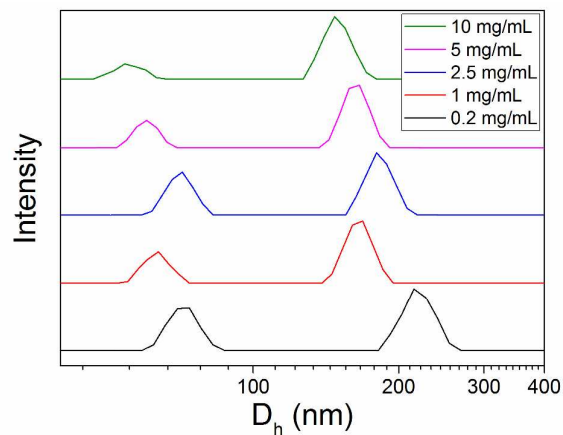


Figure S4. Concentration dependence of particle size distributions of PDMS-b-PS-b-PiBuPOSSMA self-assemblies in 1:1 (v/v) DCM/DMF.

Table S2. Electrochemical parameters obtained from polarization curves by the Tafel extrapolation method.

Samples	E _{corr} (mV)		J (nA/cm ²)		Corrosion rate (mm/year)		Polarization resistance (kΩ)	
	Day 1	Day 7	Day 1	Day 7	Day 1	Day 7	Day 1	Day 7
Bare SS	-234.8	-207.5	152.5	279.6	1.8×10 ⁻³	3.2×10 ⁻³	50.7	43.3
Dense coating	-188.4	-154.3	0.94	3.98	1.4×10 ⁻⁵	4.6×10 ⁻⁵	3.0×10 ⁴	3.5×10 ³
C10 coating	-173.8	-101.1	0.3	2.5	3.5×10 ⁻⁶	2.9×10 ⁻⁵	7.6×10 ⁴	3.6×10 ³
C5 coating	-158.2	-155.3	0.067	0.133	7.8×10 ⁻⁷	6.8×10 ⁻⁷	5.7×10 ⁵	2.8×10 ⁵

Reference

1. Raus, V.; Cadova, E.; Starovoytova, L.; Janata, M., ATRP of POSS Monomers Revisited: Toward High-Molecular Weight Methacrylate-POSS (Co)Polymers. *Macromolecules* **2014**, *47*, 7311-7320.