

Intermolecular Interactions between Bottlebrush Polymers Boost the Protection of Surfaces against Frictional Wear

Jimmy Faivre^{1,4}, Buddha Ratna Shrestha¹, Guojun Xie,² Mateusz Olszewski,² Vahid Adibnia¹, Florina Moldovan³, Alexandra Montembault⁴, Guillaume Sudre⁴, Thierry Delair⁴, Laurent David⁴, Krzysztof Matyjaszewski^{2*}, Xavier Banquy^{1*}

¹*Canadian Research Chair in Bioinspired Materials, Faculty of Pharmacy, Université de Montréal, Montréal, Qc, Canada*

²*Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, USA*

³*Department of Stomatology, Faculty of Dentistry, CHU Sainte Justine Research Center, Montréal QC H3T 1C5, Canada*

⁴*Université de Lyon, Université Claude Bernard Lyon 1, CNRS UMR 5223, Ingénierie des Matériaux Polymères (IMP), 15 Boulevard Latarjet, 69622 Villeurbanne Cedex, France*

Table of Contents

Experimental procedures

1. MONOBLOCK BOTTLEBRUSH POLYMER SYNTHESIS	3
2. TRIBLOCK BB POLYMER SYNTHESIS.....	5
3. DIBLOCK BB POLYMER SYNTHESIS	8

Experimental procedures

1. Monoblock bottlebrush polymer synthesis (Figure S1)

Synthesis of poly(HEMA-TMS)₄₅₉-co-PMMA₃₇₀ (A block). A dry 25 mL Schlenk flask was charged with bis(2-bromoisobutyrate) (2f-BiB, 25.8 mg, 0.0718 mmol), Cu^{II}Cl₂ (7.8 mg, 0.057 mmol), dNbpy (0.294 g, 0.718 mmol), HEMA-TMS (23.2 g, 25.0 mL, 115 mmol), MMA (11.5 g, 12.3 mL, 115 mmol) and anisole (4.1 mL). The solution was degassed by three freeze-pump-thaw cycles. During the final cycle, the flask was filled with nitrogen and Cu^ICl (28.4 mg, 0.287 mmol) was quickly added to the frozen reaction mixture. The flask was sealed, evacuated and back-filled with nitrogen five times, and then immersed in an oil bath at 70 °C. Reaction was stopped when the monomer conversion reached 25.9%. The monomers consumption was calculated by the integration of MMA and HEMA-TMS vinyl groups signal ($\text{CHH}=\text{C}-\text{CH}_3$, 6.11 ppm or 5.56 ppm) against the internal standard (anisole, *o,p*-Ar-H, 6.91 ppm). The A block was purified by three precipitations from hexane, dried under vacuum for 16 h at room temperature, and analyzed by ¹H NMR spectroscopy. The ratio of PMMA (*s*, broad, CO-O-CH₃, 3.54-3.68 ppm) to P(HEMA-TMS) (*s*, broad, O-CH₂-CH₂-O, 3.72-3.85 ppm) peaks resulted in the polymer composition, P(HEMA-TMS)₄₅₉-co-PMMA₃₇₀. Apparent molecular weights were determined using THF SEC: $M_n = 82,200$, $M_w/M_n = 1.16$.

Synthesis of polyBiBEM₄₅₉-co-PMMA₃₇₀ (A Block macroinitiator, A MI). The polymer, A **block** (0.687 g, containing 2.42 mmol of HEMA-TMS units), potassium fluoride (0.171 g, 2.90 mmol) and 2,6-di-*tert*-butylphenol (49.8 mg, 0.242 mmol) were placed in a 50 ml round bottom flask. The flask was sealed, flushed with nitrogen, and dry THF (20 mL) was added. The mixture was cooled in an ice bath to 0 °C, tetrabutylammonium fluoride solution in THF (1M, 0.02 mL, 0.02 mmol) was injected to the flask, followed by the drop-wise addition of 2-bromoisobutyryl bromide (0.36 mL, 2.9 mmol). After the addition the reaction mixture was allowed to reach room temperature and stirring was continued for 24 h. The solids were

filtered off, and the solution was precipitated into methanol:water (70:30, v/v%). The precipitate was re-dissolved in chloroform and passed through a short column filled with basic alumina. The filtrate was re-precipitated three times from chloroform into hexanes and dried under vacuum overnight at room temperature.

Synthesis of poly[(BiBEM₄₀₀-g-MPC₄₁)-stat-MMA₄₀₀] (Monoblock BB polymer). A dry 5 mL Schlenk flask was charged with polymer **A MI** (10.2 mg, 2.8 μ mol of BiBEM), 2-methacryloyloxyethyl phosphorylcholine (2.5 g, 8.5 mmol), 2,2'-bipyridyl (15.0 mg, 0.0960 μ mol), Cu^{II}Cl₂ (as a stock solution, 0.76 mg, 0.056 mmol), acetonitrile (3.0 mL) and methanol (7.0 mL). The solution was degassed by three freeze-pump-thaw cycles. After the final cycle Cu^ICl (4.2 mg, 0.042 μ mol) was added followed by thawing reaction mixture under nitrogen atmosphere, and the flask was immersed in an oil bath thermostated at 50 °C. The reaction was stopped by exposing the solution to air when the monomer conversion reached 13.8%, achieving the monoblock BB polymer. The brush was purified by dialysis against MeOH for 48 h using tubes with a pore size molar mass cut off 10,000 kDa. The Monomer conversion was calculated by ¹H NMR analysis, resulting in the average degree of polymerization of the side chains, DP~41.

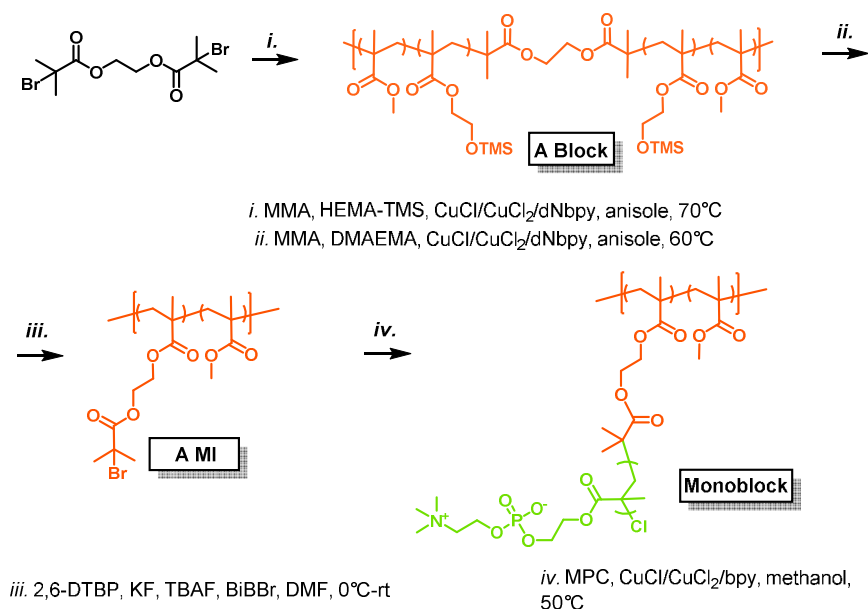


Figure S1. Synthesis of the monoblock BB polymer

2. Triblock BB polymer synthesis (Figure S2)

Synthesis of poly[(DMAEMA₉₈-stat-MMA₆₅)-*b*-(HEMA-TMS₄₅₉-stat-MMA₃₇₀)-*b*-(DMAEMA₉₈-stat-MMA₆₅)] (BAB). A dry 10 mL Schlenk flask was charged with **the previous A block** (1.02 g, 0.0081 mmol), Cu^{II}Cl₂ (as a stock solution, 0.54 mg, 4.0 μmol), dNbpy (0.0330 g, 0.0808 mmol), DMAEMA (2.03 g, 2.17 mL, 12.9 mmol), MMA (1.29 g, 1.38 mL, 12.9 mmol) and anisole (3.6 mL). The solution was degassed by three freeze-pump-thaw cycles. During the final cycle, the flask was filled with nitrogen and Cu^ICl (0.0034 g, 0.035 mmol) was quickly added to the frozen reaction mixture. The flask was sealed, evacuated and back-filled with nitrogen five times, and then immersed in an oil bath at 60 °C. Reaction was stopped via exposure to air when the monomer conversion reached 15.3%. The product was precipitated from hexanes (twice) and water, re-dissolved in chloroform and passed through neutral alumina. The solvent was removed and the purified product was dried overnight under vacuum at room temperature. The ¹H NMR spectra of a pure **BAB** was used to evaluate its final composition, giving poly[(DMAEMA₉₈-stat-MMA₆₅)-*b*-(HEMA-TMS₄₅₉-

stat-MMA₃₇₀)-*b*-(DMAEMA₉₈-*stat*-MMA₆₅)] (**BAB**). The structure of the polymer was determined from the ratio of selected polymer signals: PMMA (*s*, broad, CO-O-CH₃, 3.54-3.68 ppm), P(HEMA-TMS) (*s*, broad, O-CH₂-CH₂-O, 3.72-3.85 ppm) and PDMAEMA (*m*, CH₂-NMe₂, 2.55-2.65 ppm). Apparent molecular weights were obtained using THF SEC: $M_n = 110,000$, $M_w/M_n = 1.33$.

Synthesis of poly[(qDMAEMA₉₈-*stat*-MMA₆₅)-*b*-(HEMA-TMS₄₅₉-*stat*-MMA₃₇₀)-*b*-(qDMAEMA₉₈-*stat*-MMA₆₅)] (quaternized BAB, qBAB). BAB (0.8962 g, containing 1.16 mmol DMAEMA units) was placed in 50 mL flask and dissolved in acetone (25 mL). The solution was cooled in an ice bath to 0 °C, followed by a slow addition of bromoethane (0.48 g, 0.33mL, 4.4 mmol). The reaction was stirred at room temperature for the next 48 h. The solvent was removed and the product was dried under vacuum at room temperature. ¹H NMR spectra of the product, **qBAB**, showed the quantitative quaternization of -NMe₂ groups, as confirmed by the disappearance of signals corresponding to methylene (CH₂-NMe₂, 2.55-2.65 ppm) and methyl groups (*m*, CH₂-N(CH₃)₂, 2.27-2.35) of PDMAEMA.

Synthesis of poly[(qDMAEMA₉₅-*stat*-MMA₉₀)-*b*-(BiBEM₄₀₀-*stat*-MMA₄₀₀)-*b*-(DMAEMA₉₅-*stat*-MMA₉₀)] (qBAB macroinitiator, qBAB MI). The polymer, **qBAB** (2.38 g, containing 1.96 mmol of HEMA-TMS units), potassium fluoride (0.139 g, 2.35 mmol) and 2,6-di-*tert*-butylphenol (40.4 mg, 0.196 mmol) were placed in a 100 ml round bottom flask. The flask was sealed, flushed with nitrogen, and dry DMF (30 mL) was added. The mixture was cooled in an ice bath to 0 °C, tetrabutylammonium fluoride solution in THF (1M, 0.02 mL, 0.02 mmol) was injected to the flask, followed by the drop-wise addition of 2-bromoisobutryl bromide (0.29 mL, 2.35 mmol). After the addition the reaction mixture was

allowed to reach room temperature and stirring was continued for 24 h. The product was purified by dialysis against DMF using dialysis tubes with a pore size molar mass cut off 10 kDa..

Synthesis of poly[(qDMAEMA₉₈-stat-MMA₆₅)-b-((BiBEM-g-poly(MPC)₃₅)₄₅₉-stat-MMA₃₇₀)-b-(qDMAEMA₉₈-stat-MMA₆₅)] (triblock BB polymer). A dry 50 mL Schlenk flask was charged with polymer **qBAB MI** (32.6 mg in 3 wt% DMF stock solution, containing 0.056 μ mol of BiBEM), 2-methacryloyloxyethyl phosphorylcholine (5.00 g, 17.0 mmol), 2,2'-bipyridyl (30.0 mg, 0.192 mmol), Cu^{II}Cl₂ (1.5 mg, 0.011 mmol), and methanol (22.0 mL). The solution was degassed by three freeze-pump-thaw cycles. After the final cycle, Cu^ICl (8.4 mg, 0.085 mmol) was added followed by thawing reaction mixture under nitrogen atmosphere, and the flask was immersed in an oil bath thermostated at 45 °C. The reaction was stopped when monomer conversion reached 11.8%. The resulting brush was purified by dialysis against MeOH for 48 h using dialysis tubes with a pore size molar mass cut off 10 kDa. The Monomer conversion was calculated by ¹H NMR analysis, resulting in the average degree of polymerization of the side chains, DP~35.

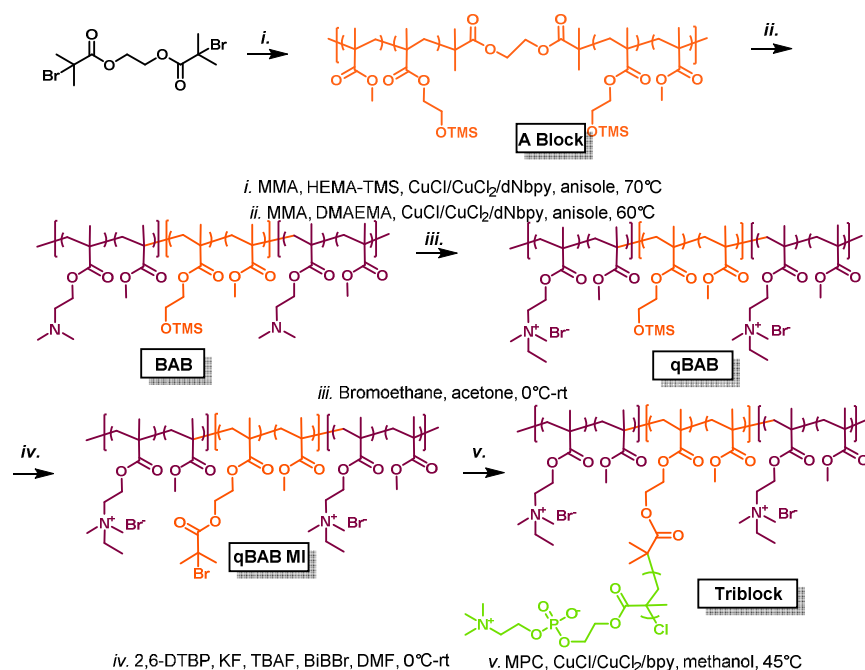


Figure S2. Synthesis of the triblock BB polymer

3. Diblock BB polymer synthesis (Figure S3)

Synthesis of poly(HEMA-TMS)₅₅₁-co-PMMA₃₃₈ (A block): A dried round bottom flask was charged with BBiB (3.4 μ L, 0.023 mmol), dNbpy (112.8 mg, 0.276 mmol), HEMA-TMS (10.0 mL, 45.9 mmol), MMA (4.9 mL, 45.9 mmol) and anisole (3.0 mL). The solution was bubbled with argon for 30'. Cu^IBr (0.0158 g, 0.110 mmol), and Cu^{II}Br₂ (0.0061 g, 0.028 mmol) were charged in a dried 50 mL round bottom flask and 3 argon-vacuum cycles were performed to remove oxygen. The flask was sealed, and then immersed in an oil bath at 40 °C. After bubbling, the monomer solution was injected into the catalyst solution. Reaction was stopped after 14 h via exposure to air, reaching the degree of polymerization of the product 500. The monomers consumption was calculated by the integration of MMA and HEMA-TMS vinyl groups signal (CHH=C-CH₃, 6.11 ppm or 5.56 ppm) against the internal standard (anisole, *o,p*-Ar-H, 6.91 ppm). The product A was purified by three precipitations from methanol, dried under vacuum overnight at room temperature, and analyzed by GPC and ¹H NMR spectroscopy. The ratio of PMMA (*s*, broad, CO-O-CH₃, 3.54-3.68 ppm) to P(HEMA-TMS) (*s*, broad, OCO-CH₂, 3.90-4.17 ppm) signals gave the polymer composition.

Synthesis of (PDMAEMA₉₄-*stat*-PMMA₁₅₃)-*b*-[P(HEMA-TMS₅₅₁-*stat*-PMMA₃₃₈] (BA): A dried round bottom flask was charged with **A block** (1.0 g, 0.0094 mmol), dNbpy (70 mg, 0.17 mmol), DMAEMA (1.2 mL, 7.0 mmol), MMA (0.75 mL, 7.0 mmol) and anisole (4.0 mL). The solution was bubbled with argon for 30'. Cu^ICl (0.0074 g, 0.0752 mmol), and Cu^{II}Cl₂ (0.0010 g, 7.46 μmol) were charged in a dried 25 mL round bottom flask and 3 argon-vacuum cycles were performed to remove oxygen. The flask was sealed, and then immersed in an oil bath at 60 °C. After bubbling, the monomer solution was injected into the catalyst solution. Reaction was stopped after 48 h via exposure to air. The product was diluted in dichloromethane, passed through a neutral alumina column, concentrated under vacuum and precipitated twice from hexanes and water. The solvent was removed under vacuum and the product was dried overnight under vacuum at room temperature. The structure of the polymer was determined from the ratio of selected polymer signals: PMMA (*s*, broad, CO-O-CH₃, 3.54-3.68 ppm), P(HEMA-TMS) (*s*, broad, O-Si(CH₃)₃, 0.11-0.21 ppm) and PDMAEMA (*m*, CH₂-NMe₂, 2.55-2.65 ppm).

Synthesis of [PBiBEM-*stat*-PMMA]-*b*-(PDMAEMA-*stat*-PMMA) (BA macroinitiator, BA MI): BA (0.1840 g), potassium fluoride (0.030 g, 0.52 mmol) and 2,6-di-*tert*-butylphenol (0.0090 g, 0.0439 mmol) were placed in a 20 ml round bottom flask. The flask was sealed, flushed with argon, and finally anhydrous THF (7 mL) was added. The mixture was cooled in an ice bath to 0 °C, tetrabutylammonium fluoride solution in THF (1M, 0.44 mL, 0.44 mmol) was injected to the flask, followed by a drop-wise addition of 2-bromoisobutyryl bromide (0.121 g, 65 μL, 0.526 mmol). After the addition the reaction mixture was allowed to reach room temperature and stirring was continued for 24 h. The solution was passed through a short column filled with basic alumina, precipitated into hexanes and then methanol:water (70:30, v/v%) three times. The filtrate was dried under vacuum overnight at room temperature.

Synthesis of [(PBiBEM-*g*-PMPC)-*stat*-MMA]-*b*-(PDMAEMA-*stat*-PMMA) (BAC): A dry 10 mL round bottom flask was charged with polymer **BA MI** (2mg), 2-methacryloyloxyethyl phosphorylcholine (MPC) (0.2540 g, 0.860 mmol), 2,2'-bipyridyl (bpy) (22 mg, 14.23 μmol), Cu^ICl (6 mg, 60 μmol), and copper (II) chloride (Cu^{II}Cl₂) (1 mg, 7.40 μmol). A dry 10 mL round bottom flask

was charged with methanol (3.0 mL) and anisole (500 μ L). The solution was bubbled with argon for 15'. The flask was sealed, and then immersed in an oil bath at 50 $^{\circ}$ C. After bubbling, the solvent solution was injected into the catalyst/monomer solution. Time of reaction was determined thanks to MPC conversion measurement by 1 H NMR to reach a DP of 35. Reaction was then stopped via exposure to air achieving PMPC diblock brush. The resulting brush was purified by ultrafiltration against MeOH under pressure using regenerated cellulose membrane (Milli Pore) with a pore size molar mass cut off 30,000 Da.

Synthesis of [(PBiBEM-*g*-PMPC)-*stat*-MMA]-*b*-(PqDMAEMA-*stat*-PMMA) (diblock BB polymer) was placed in 20 mL vial and dissolved in Methanol (10 mL). The solution was cooled in an ice bath to 0 $^{\circ}$ C, followed by a slow addition of bromoethane (0.5mL, 6.7 mmol). The reaction was stirred at room temperature for the next 48 h. The solvent and the unreacted reagent were evaporated under gentle pressure and solvent was exchanged for water by ultrafiltration. The polymer was freeze-dried and stored at -20 $^{\circ}$ C in a dark container. The quantitative quaternization of -NMe₂ groups of **diblock BB polymer** was determined by 1 H NMR.

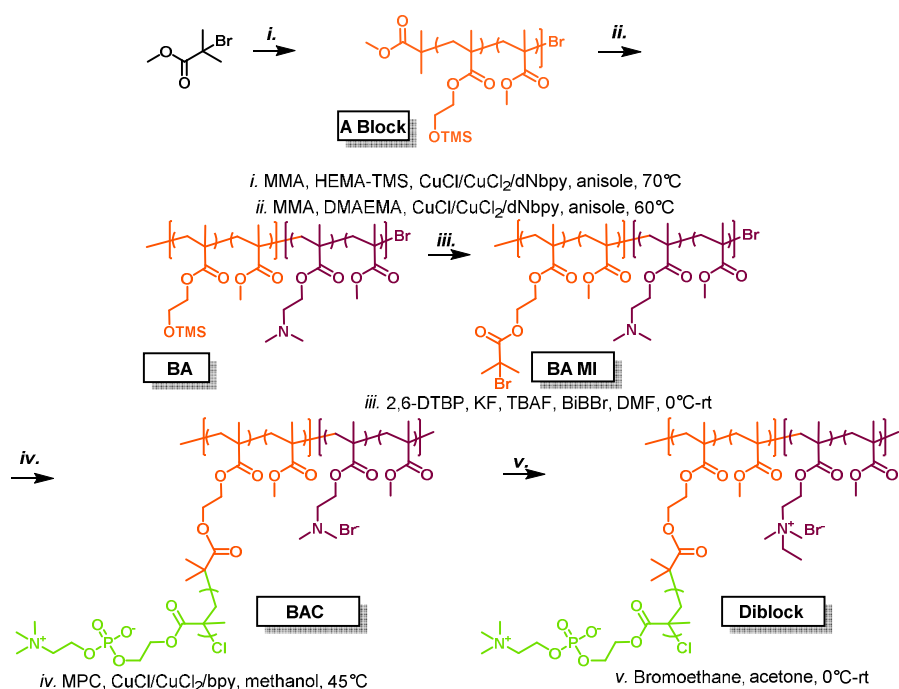


Figure S3. Synthesis of the diblock BB polymer