

Bioinspired Bottle-Brush Polymer Exhibits Low Friction and Amontons-like Behavior

Xavier Banquy,^{*,1} Joanna Burdyńska,² Dong Woog Lee,³ Krzysztof Matyjaszewski,^{*,2} and Jacob Israelachvili^{*,3,4}

¹Canada Research Chair in Bio-inspired materials and Interfaces, Faculty of Pharmacy, Université de Montréal C.P. 6128, succursale Centre Ville, Montréal, QC H3C 3J7, Canada

²Department of Chemistry, Center for Macromolecular Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States

³Department of Chemical Engineering, University of California, Santa Barbara, California 93106, United States

⁴Materials Research Laboratory, University of California, Santa Barbara, California 93106, United States

S Supporting Information

ABSTRACT: We report the design of a bottle-brush polymer whose architecture closely mimics the lubricating protein lubricin. Interaction forces, assessed using a Surface Forces Apparatus (SFA), between two mica surfaces fully covered by the polymer demonstrate that the polymer adopts a loop conformation giving rise to a weak and long-range repulsive interaction force between the surfaces. Under high compression, stronger repulsive forces appear due to the strong compression of the grafted pendant chains of the polymer. When submitted to shear, the system shows extremely low frictional forces dependent on the salinity of the medium. Friction coefficients measured for this system were as low as $\sim 10^{-3}$. Interestingly, the confined lubricating fluid obeys all three Amontons' laws. We explain this peculiar observation by the strong shear thinning of the confined fluid and the osmotic repulsive forces that dominate the overall (dynamic and equilibrium) surface interactions.

This report describes the development of a multiblock polymer whose architecture was inspired from a protein known as lubricin (LUB), a major component of mammalian synovial fluids.¹ Studies have shown that LUB is a key element for providing excellent lubrication, antiadhesion, and wear protection to articular cartilage surfaces.^{2–4} These unique properties arise from the highly complex architecture of the protein, known as “bottle-brush”. As for many other mucins, lubricin can self-associate to form a highly interconnected network. It can also form dimers or multimers whose conformation on a surface can be described as a loop.^{3,5} It is this particular conformation in combination with its bottle-brush architecture that is believed to provide the excellent tribological properties to this protein.

A key requirement for a good lubricant is to reduce the friction force or friction coefficient between shearing surfaces independently over a wide range of shearing speeds, applied loads, and contact areas. Such a combination of properties is often called Amontons-like behavior and is often observed in solid contacts but rarely in lubricated ones. The lubrication effect in many systems, such as LUB³ or synthetic polymer/molecular

brushes,^{6,7} has been shown to operate independently of the contact area and/or the shearing speed, but only in a narrow range of applied loads/pressures and shear rates.

Yet, lubricating systems, such as linear polymer loops, which is also the conformation adopted by LUB, are poor lubricants, or at least not better than polymer brushes, especially under high (MPa) loads.^{8,9} The main reason for this poor behavior is the ability of polymer loops to easily bridge surfaces and to increase the adhesion between them as well as the much slower dynamics of the loop segments which tends to increase frictional dissipation under high sliding speeds.

In an effort to fill this technological gap, we designed a polymer mimic of LUB based on a triblock polymer exhibiting a central block with a bottle-brush architecture (Figure 1) and two lateral linear blocks designed to provide strong adhesion to the surfaces it adsorbs to. The arrangement of the three different blocks is expected to promote the formation of polymer loops when adsorbed on surfaces.

The ABA bottle-brush polymer^{10–12} was prepared via the combination of Atom Transfer Radical Polymerization (ATRP)^{13,14} and different postmodification techniques (Scheme S1) using the “grafting from” approach. This approach was more suitable for the present work since it allows for the preparation of a bottle-brush with a relatively long backbone ($DP \approx 800$) and controlled side chains. Since the surfaces of study are made of atomically flat mica, the adhesive (A) blocks of the polymer were composed of a positively charged amine monomer (quaternized 2-(dimethylaminoethyl) methacrylate, qDMAEMA) and a hydrophobic (methyl methacrylate, MMA) monomer. These two components strongly adsorb on negatively charged mica surfaces in aqueous solution via electrostatic and hydrophobic interactions. The bottle-brush block of the polymer was composed of a flexible MMA backbone decorated with polyzwitterionic branches of poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) (Scheme S1). The use of PMPC as side branches was motivated by the excellent biocompatibility of this polymer^{15,16} as well as recent reports showing that surface grafted brushes of PMPC exhibit extremely good lubrication

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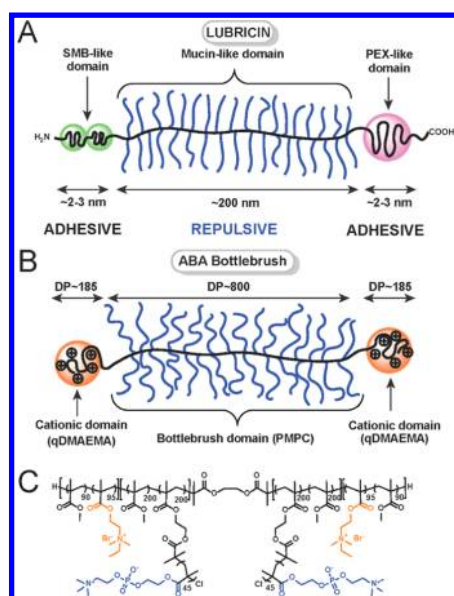


Figure 1. Schematic representations of the protein LUB found in mammalian synovial fluids (A) and the bottle-brush polymer mimicking LUB (B–C).

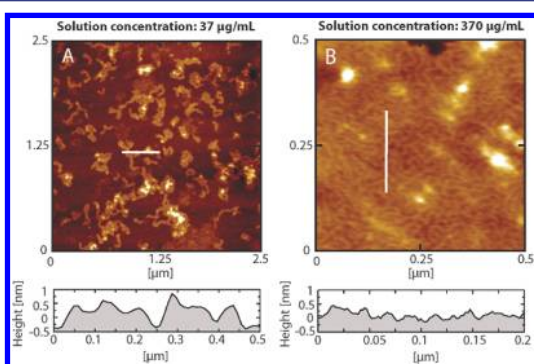


Figure 2. Atomic force microscopy imaging in air of the polymer chains adsorbed on a freshly cleaved mica surface from a solution at (A) 37 $\mu\text{g/mL}$ and (B) 370 $\mu\text{g/mL}$.

under physiological pressure (between 2 and 7.5 MPa).^{6,16} When adsorbed on a mica surface from a diluted solution (see Figure 2A), individual polymer chains can be resolved by atomic force microscopy (AFM). Figure 2A and B show a significant difference in organization of the polymer chains when adsorbed from solutions at 37 and 370 $\mu\text{g/mL}$ (Figure 2A and B, respectively). At 37 $\mu\text{g/mL}$, isolated chains are rarely observed. Most of the chains tend to form small aggregates of two to five molecules. At 370 $\mu\text{g/mL}$, the surface is almost fully covered by a monolayer of polymer chains (see also Figures S2 and S3). In the monolayer, the polymer chains tend to maximize possible contacts with their neighboring molecules by adopting an extended conformation.

Figure 3 shows the interaction forces, reported as F_{\perp}/R , F_{\perp} being the normal interaction force and R the surface curvature, between mica surfaces immersed in a solution of polymer at 370 $\mu\text{g/mL}$ in phosphate buffer saline (PBS) or pure water were measured at 25 °C using the SFA. In both media, the interaction forces present a strong dependence on the approach speed, v_{\perp} . Long range interaction forces, starting from 60 nm in PBS and 100 nm in pure water, were systematically detected at $v_{\perp} = 4 \text{ nm/s}$. The final polymer film thickness, measured at the highest

compression force (pressure 1.5 MPa), was found to be independent of v_{\perp} and equal to $\sim 5 \text{ nm}$.

Interestingly, the interaction forces measured upon compression of the surfaces at the highest confinement speed ($v_{\perp} = 4 \text{ nm/s}$) exhibited quasi-periodic instabilities (see insert in Figure 3 A and B) on the first approach. These instabilities correspond to transient accelerations of the surfaces (jumps in) over separation distances ΔD of 3–5 nm due to the squeezing out of 1 to 2 molecular layers of polymer chains. Such instabilities systematically disappeared during the separation of the surfaces as well as in subsequent approaches performed immediately after separation of the polymer film. Such phenomena are remarkably similar to previously reported experiments on molecular fluids such as linear alkanes¹⁷ where the confinement speed was also found to affect the number of molecular layers trapped between the surfaces as well as their fluidity. Independently of the confinement speed, the measured interaction forces were found to be repulsive and reversible although a small hysteresis was systematically found during the first approach–separation cycle in PBS.

The force curves shown in Figure 3B and D were measured at a confinement speed of $v_{\perp} = 0.2 \text{ nm/s}$, which corresponds to quasi-equilibrium conditions. The forces present a long-range exponential interaction component with a decay length of $\sim 2 \text{ nm}$ in PBS and 9 nm in pure water. If the long-range component of the interaction was of electrostatic origin, the decay length should be the Debye length, λ_D , which in the present case was estimated to be $< 1 \text{ nm}$ in PBS and 60 nm in pure water (taking into account the electrostatic charges and counterions coming from the polymer free in solution¹⁸). The difference between the calculated Debye length, λ_D , and the measured decay length in PBS and pure water are sufficiently large to confirm that the long-range repulsive forces are not electrostatic but of steric origin.

Given the architecture of the polymer and its expected loop conformation on the surfaces, we used an effective brush interaction model to describe the long-range component of the interaction forces.¹⁹ In this model, the polymer loop is assumed to be equivalent to two diblock polymers of half the bottle-brush domain molecular weight. The short-range interaction forces were assumed to be dominated by the direct interaction between the bottle-brush domains and were modeled by a brush–brush interaction model. The general expression of the model is²⁰

$$\frac{F_{\perp}(D)}{R} = 2\pi W = 2\pi(W_{\text{LR}} + W_{\text{SR}}) \quad (1)$$

where W is the interaction energy between flat surfaces and LR and SR stand for Long Range and Short Range, respectively. The expression of the LR and SR components can be written as^{21,22}

$$W_i = p_0 L_i \left[\frac{1}{u} + u^2 - \frac{u^5}{5} - \frac{9}{5} \right] \quad (2)$$

where p_0 is the intrinsic scale for the pressure and L is the unperturbed brush height, $u = D/2L$ and $i = \text{LR or SR}$.

Figure 3B and D show the agreement between the proposed model and the experimental data. The fitted values of L_{SR} (Table S1) are independent of the media (pure water or PBS) which suggests that the conformation of the PMPC brushes is insensitive to the salt concentration. This observation is consistent with recent reports showing that the conformation of PMPC grafted brushes or PMPC chains free in solution are almost insensitive to salt concentration.^{6,23} The value of the unperturbed length of the brush L_{SR} was found to be 6.5 nm

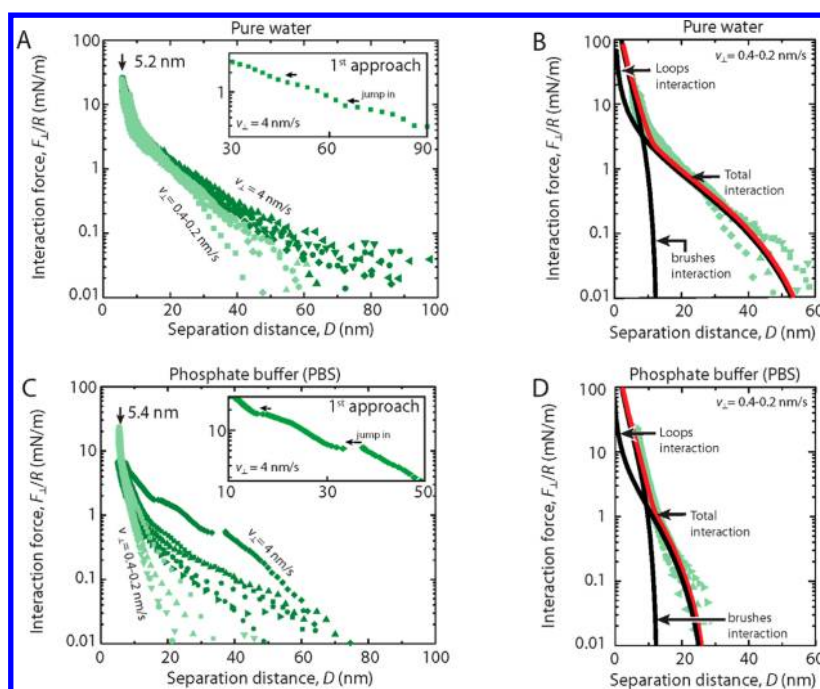


Figure 3. Normal interaction forces between two mica surfaces immersed in a polymer solution in pure water (A, B) and in PBS (C, D). A and C show the effect of the confinement speed on the range of the interaction forces and the structuring of the polymer solution at the interfaces. High confinement speed generates longer range repulsive interaction forces mostly due to the extra contribution of the viscous forces (compared to low approach speed). B and D show the good agreement between the loop and brush models (eqs 1 and 2) and the experimental data obtained at low v_{\perp} .

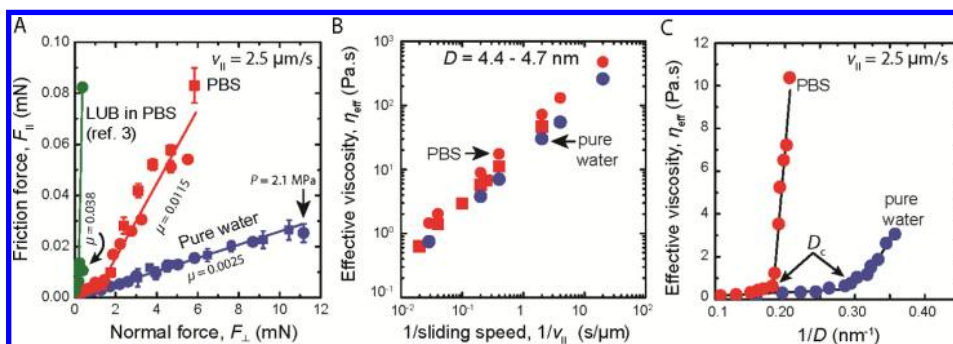


Figure 4. Experimental observation of Amontons-like behavior of the molecular brushes thin film in pure water and PBS. (A) Experimental data showing that the friction coefficient μ is independent of the applied load. (B) Results showing that the viscosity of the confined film is inversely proportional to sliding speed at constant separation distance. (C) Results showing that the viscosity is inversely proportional to the separation distance above and below a critical separation distance D_c .

(Table S1) which is close to the expected theoretical value of 6 nm (see Supporting Information) and about one-third of the contour length $L_c = 2nl = 18$ nm, n being the number of monomer units in one side chain ($n = 45$) and l the characteristic segment length (estimated to be ~ 0.2 nm).^{23,24} The unperturbed height of the loops, L_{LR} , obtained from the long-range component of the interaction forces was found to be 15 nm in PBS and 33 nm in pure water which correspond respectively to approximately 30% and 65% of the fully extended loop height (based on a contour length of 200 nm estimated by AFM imaging).

The conformational change in the distal part of the adsorbed polymer from the increase in salt concentration can be ascribed to two main factors, namely, the increased affinity of the bottle-brush domain to the surface and the screening of the electrostatic interaction between the lateral blocks of the polymer and the surface. From these observations we expect the conformation of a polymer chain at the surface in pure water to be a single loop

while in PBS it is expected to adopt multiple loops and train conformations.

The lubrication properties of the polymer were also found to be sensitive to the surrounding media (see Figure 4A). When the surfaces were sheared in pure water, the measured friction force, F_{\parallel} , was found to depend linearly on the applied normal load, F_{\perp} , and to vanish at $F_{\perp} = 0$, which is consistent with the previous observation that no adhesion forces were measured in this system.

The measured friction coefficient, μ , defined as $dF_{\parallel}/dF_{\perp}$, was equal to 0.0025 ± 0.0001 in pure water solution and 0.0115 ± 0.0003 in PBS solution at a normal pressure of 2.1 MPa, well into the physiological range. These values are well below the friction coefficient of 0.038 reported for lubricin under similar conditions of sliding speed and concentration (Figure 4A).³ Interestingly, above a normal force of 0.4 mN ($P = 0.4$ MPa), the friction coefficient of lubricin was reported to increase sharply which was also accompanied by the triggering of surface wear. Such drastic

changes in lubrication properties were similarly observed in the present system in PBS only for $F_{\perp} > 1.5$ mN (or $D < 5$ nm). Below this value, the friction coefficients of the mimetic polymer measured in PBS and pure water were found to be nearly identical.

The separation distance D at which the sudden increase in friction force occurs in PBS corresponds to the transition from a two-layer film to a single monolayer film. The increase in friction force in the monolayer film is first due to the increase of the attractive interaction between the bottle-brush domains and the mica surfaces which, as mentioned earlier, causes a partial collapse of the loop conformation, and second to the partial screening of the attractive electrostatic interaction between the lateral blocks of the polymer chains and the surface. The screening of the electrostatic attraction enhances the mobility of the lateral blocks allowing transient (weak) adhesive bridges to form during shear via the still remaining hydrophobic forces.

The observed linear relationship between F_{\parallel} and F_{\perp} already suggests that the system exhibits Amontons-like behavior.

Such behavior, most commonly observed for non lubricated “solid” contacts, is essentially due to the peculiar rheological properties of the confined fluid. Thus, Figure 4B and C show that the effective viscosity of the confined thin film, η_{eff} is inversely proportional to the sliding speed and to the separation distance and can therefore be written as $\eta_{\text{eff}} = B/v_{\parallel}D$, where B is a constant. In addition, in the purely osmotic compression regime (very small D), the normal pressure between the surfaces can be written as $P_{\perp} = -\partial W_{\text{SR}}/\partial D = +C/D^2$. Thus, assuming Couette flow between the surfaces, the expression of the friction coefficient, μ , becomes

$$\mu = \frac{F_{\parallel}}{F_{\perp}} = \left(\frac{\eta_{\text{eff}} A v_{\parallel}}{D} \right) / F_{\perp} \quad (3)$$

where A is the contact area. Substituting for the expressions for η_{eff} and $P_{\perp} = F_{\perp}/A$, the friction coefficient can be written as

$$\mu = \frac{B}{C} \quad (4)$$

which is independent of A , v_{\parallel} , and F_{\perp} and therefore follows all three Amontons’ laws.

Amontons-like behavior has been reported for single component fluids such as linear alkanes or polymer melts. Our results suggest that such behavior can be obtained, or even designed, in polymer solutions as well. Key properties leading to such behavior are the shear thinning of the confined fluid, the increase of η_{eff} with confinement, and a repulsive, roughly $1/D^n$, force–distance or pressure–distance dependence.

Our results show that excellent lubricating properties and Amontons-like behavior can be obtained simultaneously for the first time from adsorbed polymer brushes, which expands drastically the arsenal of strategies for the development of efficient artificial synovial fluids.

In this study we show that molecular brushes having a triblock architecture can form polymer loops when strongly adsorbed on a surface. The excellent lubricating properties of these polymers even when confined to a monolayer arise from the strong osmotic repulsion between the side chains of the molecular brushes and the surfaces which favors the flow of water molecules during shear and thereby improves lubrication. The results show that the excellent lubricating properties of the polymer are maintained independently of the shearing speed or applied load even under molecular confinement. Our approach suggests new

ways to design polymeric lubricants custom designed to work on specific surfaces or solvent conditions.

■ ASSOCIATED CONTENT

■ Supporting Information

Synthesis of the polymer and SFA as well as AFM characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

xavier.banquy@umontreal.ca

km3b@andrew.cmu.edu

jacob@engr.ucsb.edu

Notes

The authors declare no competing financial interest.

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