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Lubrication at Physiological Pressures by Polyzwitterionic Brushes

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The very low sliding friction at natural synovial joints, which have friction coefficients of $\mu < 0.002$ at pressures up to 5 megapascals or more, has to date not been attained in any human-made joints or between model surfaces in aqueous environments. We found that surfaces in water bearing polyzwitterionic brushes that were polymerized directly from the surface can have μ values as low as 0.0004 at pressures as high as 7.5 megapascals. This extreme lubrication is attributed primarily to the strong hydration of the phosphorylcholine-like monomers that make up the robustly attached brushes, and may have relevance to a wide range of human-made aqueous lubrication situations.

The rubbing of opposing bones during the articulation of mammalian joints is mediated by layers of articular cartilage coating their surfaces that provide particularly efficient lubrication as they slide past each other (*1*, *2*). The associated very low friction at the high pressures of human joints such as hips or knees, with friction coefficients $\mu < 0.002$, has to date not been emulated in human-made systems. Model studies (*3*–*7*) between smooth sliding surfaces bearing neutral or charged polymer brushes demonstrated sliding friction coefficients as low as $\mu < 0.001$, which are values lower than with any other boundary lubricant system. As noted (*8*, *9*), in earlier studies with polymer brushes (*3*–*6*), the friction increases sharply at mean pressures $P > \sim 0.3$ MPa, which is far below the 5 MPa or more at which low friction persists in nature. In the present work, we sought to overcome the limitations of these earlier studies (*3*–*6*). We used polymer brushes, which make good boundary lubricants because they do not bridge the intersurface gap, that are strongly attached to each surface so as to resist being sheared off and that are highly hydrated so as to use the very efficient lubrication afforded by hydration sheaths that has been previously observed (*10*, *11*).

Brushes of the polymer poly[2-(methacryloyloxy)ethyl phosphorylcholine] (pMPC) were grown from the surfaces of macroinitiator-coated mica sheets that were premounted onto cylindrical lenses for surface force balance (SFB) measurements (*12*, *13*). After calibration in dry air, control measurements of the normal forces (F_n) and shear forces (F_s) between the macroinitiator-coated mica surfaces were performed (*12*, *14*) as a function of their absolute separation D and their sliding velocity v_s [$F_n(D)$ and $F_s(D, v_s)$, respectively]. Measurements were performed both in polymer-free water and after incubation in a 0.3% w/v pMPC homopolymer solution in order to compare them with the subsequent pMPC brush profiles. These controls, shown in Fig. 1, reveal the high friction associated with the macroinitiator alone (Fig. 1, B and C) before the growing of the polymer layers. They also show that the pMPC homopolymer does not adsorb onto the macroinitiator-bearing mica (Fig. 1A), which confirms that surface growth of the polymer results in true brush formation. After the polymer brushes were grown via direct polymerization from the surface, $F_n(D)$ and $F_s(D, v_s)$ profiles between the brush layers were measured in water and in aqueous $NaNO_3$ solutions up to physiological salt concentrations.

Figure 2 shows the typical F_n versus D profiles between pMPC brush–bearing mica surfaces in the standard crossed-cylinder SFB configuration in pure water and at salt concentrations of ~0.01 M and ~0.1 M $NaNO_3$ (the pMPC brush and its monomer structure are shown in Fig. 2A, inset). Some contraction of the pMPC brushes is seen in the salt solutions relative to those in the pure water. The highest normal loads F_n applied are some two or more orders of magnitude higher than those in earlier brush studies (*4*, *5*) that used the SFB. This leads to substantial flattening at the contact region, as indicated in the photo of the interference fringes (Fig. 2B and schematically in Fig. 2C), from which the contact area A between the surfaces is measured directly (the mean pressures P across the flattened contact area are given by $P = F_n/A$). Comparison with the control profiles

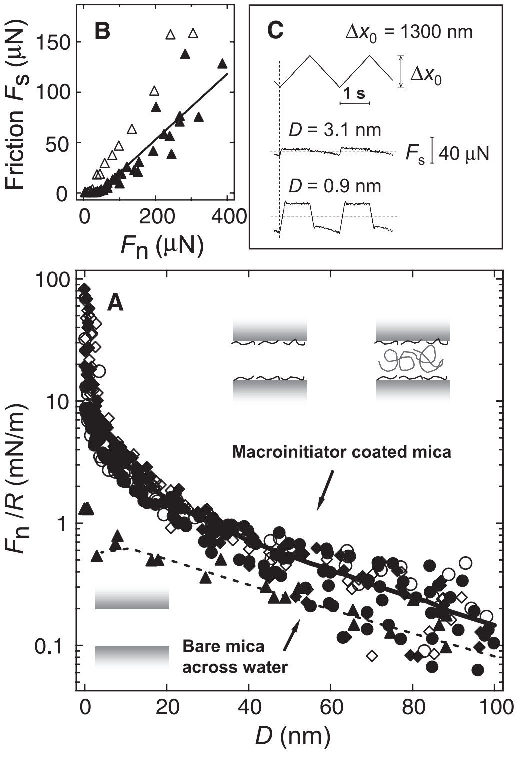

Fig. 1. Control measurements of (**A**) F_n versus D profiles and (**B** and **C**) of F_s between bare mica and between macroinitiator-coated mica surfaces across water and across a pMPC homopolymer solution. (A) Solid triangles indicate forces between bare mica in pure water on approach [normalized as $F_n(D)/R$, where $R \approx 1$ cm is the mean surface curvature radius]. The dashed line is a fit to the Derjaguin-Landau-Vervey-Overbeek theory based on a numerical solution of the nonlinear Poisson-Boltzmann equation (*32*) for a 1:1 electrolyte concentration $c = 5 \times 10^{-5}$ M, with constant surface potential $\psi_0 = -80$ mV and Hamaker constant $A = 2 \times 10^{-20}$ J. Solid and open circles indicate $F_n(D)$ profiles between macroinitiator-coated (20 min of incubation) mica in pure water on approach and separation, respectively. Solid and open diamonds indicate profiles between macroinitiator-coated mica after 13 hours of incubation in 0.3% w/v pMPC homopolymer [$M_w = 22{,}000$; $M_w/M_n = 1.3$, where M_w and M_n are, respectively, the weight and number average molecular weights] in aqueous solution on approach and separation, respectively. The solid line is a guide to the eye. The illustrations show schematically the configurations corresponding to the three control measurements; the short chains (black) represent the macroinitiator, and the longer random-coil chains represent the pMPC homopolymer in solution. (B) A summary of friction force F_s versus load, extracted from traces as in (C), between macroinitiator-coated surfaces in water (open triangles) and in 0.3% w/v MPC homopolymer solution (solid triangles); the solid line corresponds to friction coefficient $\mu = 0.33$. (C) Typical F_s versus time traces between two macroinitiator-coated mica surfaces in water at different D values in response to laterally applied motion of the top mica surface (top trace).

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from Fig. 1A in the absence of polymer brushes (the dotted and dashed curves in Fig. 2A) reveals the extension of the unperturbed brushes from the macroinitiator layer, whereas fits to the force profiles provide more detailed information on the brush characteristics (*12*, *13*). The profiles both on approach and separation of the surfaces (characteristic of brush interactions) are similar as is in particular their insensitivity to repeated shear up to the highest compressions, which shows the robustness of the layers toward resisting friction and shear-off (*15*).

Characteristic traces of F_s versus time as two pMPC brushes slide past each other under different loads or compression ratios (corresponding to different surface separations) and salt concentrations, taken directly from the SFB, are shown in Fig. 3. Traces both at low compressions (higher D values) (Fig. 3, left) and high compressions (lower D values) (Fig. 3, right) show that the shear forces remain very weak—within the noise level of the SFB—up to mean contact pressures of ~2 to 2.5 MPa and then increase measurably with the load, up to the largest loads applied. Such traces are characteristic of all pMPC brushes and salt concentrations studied; that the traces are unchanged in time indicates there is no detectable wear of the layers over the range of parameters studied. Shear force results are summarized in Fig. 4 and Table 1. These show that the friction coefficient μ (taken as the slope of the F_s versus F_n plot) is in the range of values $\mu \approx (1.5 \pm 1) \times 10^{-3}$ up to the highest mean contact pressures applied, $P \approx 7.5$ MPa (~75 atmospheres). The values of μ, though remaining very low, are seen to increase slightly within this range as the salt concentration increases. The variation of the shear or friction force with v_s is shown in Fig. 4B, revealing a weak $F_s(v_s)$ dependence over three orders of magnitude in v_s.

Our findings show that brushes of pMPC, a polyzwitterion whose monomers carry the phosphorylcholine (PC) group (as occurs in naturally occurring phospholipid headgroups), can reduce friction to levels previously seen only in natural joints (μ on the order of 0.001 at pressures of 5 MPa or more). Earlier studies (*4*, *5*) between polymer brush–coated surfaces showed similarly low friction coefficients but only at very much lower pressures. At higher pressures, the coefficient of friction became large, either because of entanglement or vitrification of the brushes (*4*) or as a result of the increasing frictional shear at these pressures removing from the surface the relatively weakly attached charged brushes (*5*). What is the

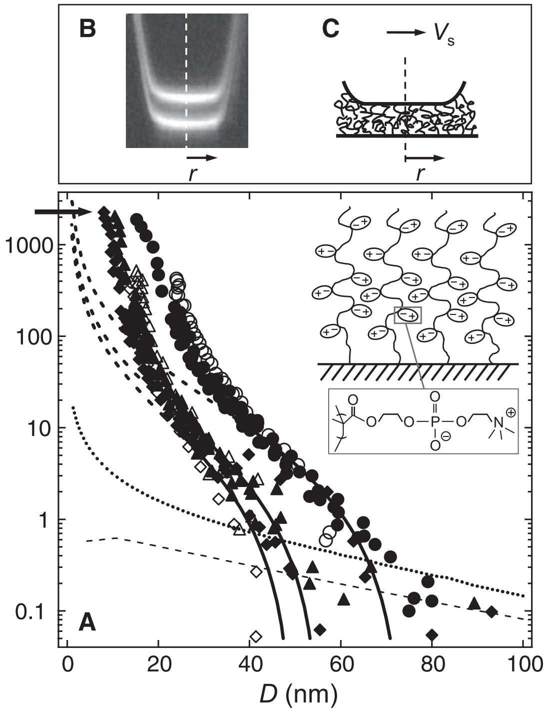

Fig. 2. Normal interactions between pMPC brush–coated mica surfaces across water and across aqueous salt solutions (normalized as above). (**A**) Normal force profiles: circles, water (no added salt); triangles, 8.7 mM $NaNO_3$; diamonds, 88.6 mM $NaNO_3$. Solid and open symbols indicate compression and decompression, respectively. Different incubation times in the macroinitiator solution (20 min and 2 hours) were used, with a polymerization time of 1.5 hours in each case (the layers are designated as 20-1.5 and 2-1.5, respectively). The pMPC layers are 2-1.5 brushes (*12*). Before solvation, the brushes were characterized (*12*, *13*) with x-ray photoelectron spectroscopy, multiple-beam interference, x-ray reflectometry, and atomic force micoscopy, which revealed a uniform smooth layer (root mean square roughness, 0.4 nm), whereas from a fit to the data (solid curves) (*12*) we estimate mean interanchor spacings $s = 3.5 \pm 1$ nm and unperturbed brush-heights $L = 37 \pm 5$, 28 ± 5, and 25 ± 5 nm for the solvated brushes at respective increasing salt concentrations. The brush-chain polydispersity is estimated at ~1.2 (*12*, *13*). The pMPC brush-like configuration and its monomer structure are also shown. The dashed and dotted lines summarize the brush-free controls between bare and between macroinitiator-coated mica, respectively, from Fig. 1A. (**B**) Equal chromatic order interference fringes revealing the flattening of the mica surfaces at a high load, indicated by the arrow in (A). (**C**) The schematic configuration corresponding to (B) (with contact area $A \cong \pi r^2$).

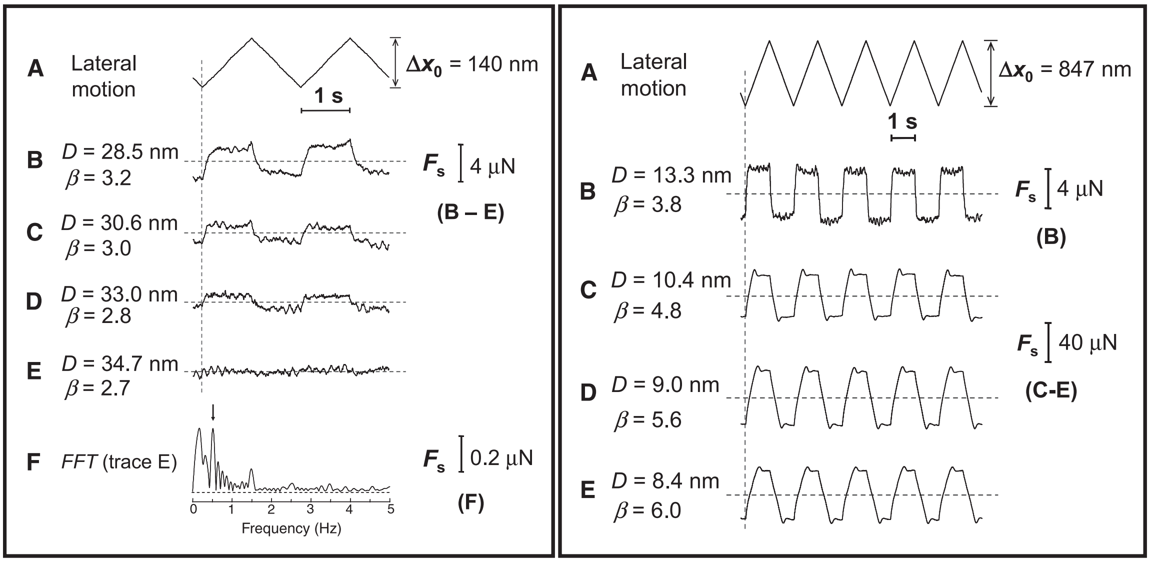

Fig. 3. Typical F_s versus time traces between pMPC-coated mica surfaces taken directly from the SFB. (**Left**) 20-1.5 brushes in pure water. (**Right**) 2-1.5 brushes in ~0.1 M salt solution (*12*). The top trace A in each column is the lateral motion applied to the top surface, whereas traces B to E are the corresponding shear forces transmitted between the surfaces at the compression ratios β (2*L*/*D*) shown. Trace F is a frequency (ω) analysis of trace E, where the magnitude of F_s (ω) at the drive frequency (arrow) is used to reveal the onset of frictional force above any systematic signal (*5*, *10*) at large *D* values.

mechanism underlying the very low friction in the present study?

Earlier studies with charged brushes attributed comparably low friction coefficients (at much lower pressures) to a combination of factors. At low to moderate pressures, interpenetration (and therefore entanglement) of the opposing brushes was suppressed by configurational entropy effects (*4*, *6*, *16*). At the higher compressions of the present study, such interpenetration during the sliding is attributed instead to a self-regulation mechanism within the interfacial region (*6*, *17*). According to this, the mutual interpenetration zone of the sliding brushes, where the viscous dissipation leading to frictional drag occurs, has a thickness δ. This thickness varies so that the relaxation rate of the polymer moieties within it equals the shear rate within the zone; that is, $[1/\tau(\delta)] \approx (v_s/\delta)$, where τ is the relaxation time of the polymer moieties. Such self-regulation can readily be seen to lead to a weak dependence of friction on v_s, which is in line with the observed data at high loads (Fig. 4B), and a similar variation has been seen earlier for friction between sliding highly compressed brushes (*17*). Qualitatively, this occurs because at higher sliding velocities the extent of brush interpenetration decreases so that the overall frictional drag varies more weakly with increasing v_s than if the interpenetration zone remained at a constant thickness (*6*, *17*). At elevated pressures, lubrication by charged brushes was previously attributed to counterion osmotic pressure (*5*), together with the lubricating action of hydration layers surrounding the charged monomers. In the present study, the overall-neutral zwitterionic chains have no counterions associated with them so that osmotic pressure due to trapped counterions cannot be playing a role. The effect of any counterions associated with the residual charge of the underlying macroinitiator-coated mica is negligible. The primary mechanism underlying the low friction observed must therefore be attributed almost exclusively to the high level of hydration of the zwitterionic PC groups on the monomers. These are known to bind around 15 to 25 or more water molecules per monomer [depending on the method of measurement (*18*–*23*)]. Similar strongly bound hydration layers about such phosphorylcholine-coated biomaterials are also responsible for repelling proteins from their surfaces (*22*, *24*).

Table 1. Friction coefficients between pMPC brush–coated mica surfaces sliding past each other at mean pressures *P* (in the range of 2 to 7.5 MPa) at different salt concentrations. Details about the water purification can be found in (*12*).

Aqueous solution	Friction coefficient
Pure water	0.00043 ± 0.0001
0.01 M $NaNO_3$	0.001 ± 0.0004
0.1 M $NaNO_3$	$0.0026^{+0.0005}_{-0.001}$

Water molecules in hydration layers have been shown to act as very efficient lubricants in the case of hydrated ions trapped between charged surfaces (*10*). This results from the water molecules being tenaciously attached, on an average over time, to the enclosed ionic charges so that the resistance to dehydration leads to their ability to support a large pressure. At the same time, the hydration water molecules are able to rapidly exchange with other hydration or free water molecules (*10*, *25*) and so are able to behave fluidly when sheared at rates lower than these exchange (relaxation) rates. This, we believe, is also the origin of the low friction in the present system and, together with the stronger attachment of the chains grown directly from the surface, ensures the robust nature of the brushes when compared with the polyelectrolyte chains that were sheared off (*15*). We attribute the ability of the hydration shells about the (methacryloyloxy)ethyl phosphorylcholine (MPC) monomers to lubricate at much higher mean pressures (relative to those at which previously studied polyelectrolyte brushes were removed by friction) to the higher and more tenacious hydration (*18*–*21*, *23*) of their PC groups. The slight increase in the friction coefficient with increasing salt concentration (Table 1) may be attributed to some salting-out of the pMPC monomers at the higher salt concentration [as has been observed in other PC systems (*26*)], leading to reduced hydration of the monomers and thus to less efficient lubrication. Such an effect would also explain the small contraction of the brush height at the higher salt concentrations (Fig. 2).

A large reduction in wear of polymer/metal hip implants has recently been achieved (*27*) by growing a pMPC layer from a polyethylene acetabular surface. The corresponding μ ~ 0.1 was not especially low. It is likely that this value of μ is dominated by a small number of high-friction asperity contacts between the sliding surfaces, which are far rougher than the mica substrate in our experiments, or by the bridging of the pMPC chains between the acetabular surface and the metal countersurface to which they may adsorb. This would result in higher friction relative to the values we measured between two pMPC brushes. A comparably high friction coefficient, ~0.1, was also measured (*28*) in a recent pin-on-disk tribological study between pMPC-coated surfaces under water.

Finally, in view of their similarly low friction at comparably high pressures, it is of interest to consider the relevance of our study to mechanisms of

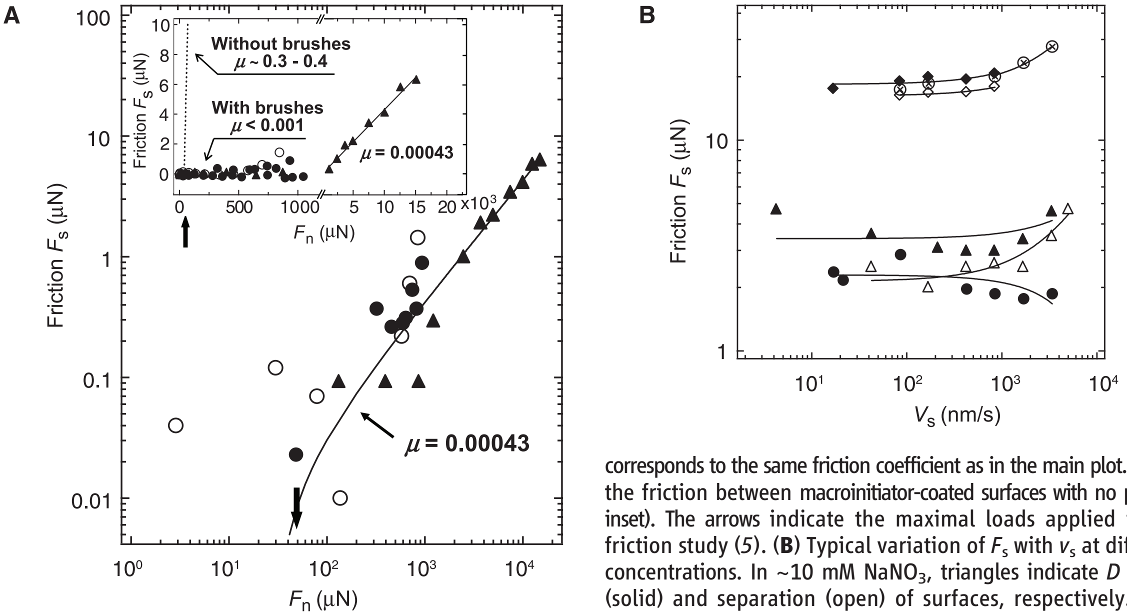

Fig. 4. Variation of friction F_s with load F_n and with sliding velocity v_s between pMPC brush–coated surfaces. (**A**) Variation of F_s with F_n for both 20-1.5 (circles) and 2-1.5 (triangles) brushes across water; within the scatter there is little systematic difference between these two brushes. Solid circles, approach; open circles, separation. There is a double logarithmic scale; the solid curve corresponds to μ = 0.00043. (Inset) The same data on a linear scale; the solid line for F_n > 1.5 mN corresponds to the same friction coefficient as in the main plot. The sharply rising dotted line is the friction between macroinitiator-coated surfaces with no pMPC brushes (based on Fig. 1, inset). The arrows indicate the maximal loads applied in the polyelectrolyte brush friction study (*5*). (**B**) Typical variation of F_s with v_s at different compressions and salt concentrations. In ~10 mM $NaNO_3$, triangles indicate *D* = 13 ± 0.3 nm on approach (solid) and separation (open) of surfaces, respectively. In ~100 mM $NaNO_3$, solid circles indicate *D* = 13.3 ± 0.3 nm in approach run; diamonds indicate *D* = 10.2 ± 0.3 nm, on approach (solid) and separation (open) of surfaces, respectively; and crossed circles indicate *D* = 8.5 ± 0.3 nm, in separation run. There is little variation between data sets whether on approach or separation of surfaces and whether in ~10 mM or 100 mM salt.

lubrication between articular cartilage surfaces. Biological lubrication at such synovial joints, despite many decades of study, is not yet well understood at the molecular level (*29–31*). Recent models have focused on the role of pressurized interstitial water (*31*) and of macromolecules at the outer cartilage surface (*30*). Our system of synthetic polyzwitterionic brushes polymerized from molecularly smooth mica surfaces does not have a clear analog at the cartilage surface, at which macromolecular components of the cartilage and the synovial fluid surrounding it are likely to be present [including proteins, hyaluronic acid, proteoglycans, glycoproteins, and lipidic molecules (*30*)]. The detailed role of these in the lubrication process, as well as of the cartilage substrate itself, has yet to be clarified. Moreover, cartilage is softer and much rougher than mica, though at these high pressures it may deform affinely (*30*); experiments on similarly soft and roughened brush-coated surfaces could potentially provide insight into the mechanisms that are operative in cartilage-cartilage friction. The highly hydrated PC-like monomers on our pMPC chains provide very efficient lubrication. The structure of these is similar to that of lipid headgroups, which provides some context for the recent controversial suggestion that lipid multilayers may have a role in mediating synovial lubrication (*29*), particularly in view of recent findings on the mechanism of boundary lubrication under water (*11*). Finally, although our polyzwitterionic brushes have no direct analog at cartilage surfaces, our results underline the possible importance at such surfaces of highly hydrated macromolecules in both chondroprotective and lubrication roles.

We have shown that brushes of a biocompatible polyzwitterion, pMPC, are capable of providing extremely efficient lubrication in aqueous media with coefficients of friction $\mu \approx 0.001$ at mean pressures up to 7.5 MPa, which are comparable to values in human synovial joints. We attribute the low friction at the high pressure primarily to the lubricating action of tenaciously attached but labile water molecules about the strongly hydrated MPC monomers. Our results may have relevance for boundary lubrication in human-made systems in aqueous or physiological media, as in biomedical devices, in which friction and wear are often an issue.

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15. This robustness is consistent with the nature of the pMPC brushes' attachment to the mica and the shear forces applied. For an area per macroinitiator $A_m \approx 16$ nm^2 (*13*) and a mean pressure P, the shear force acting on a single macroinitiator molecule [$F_{s(m)}$] through the chains growing from it is given by $F_{s(m)} = \mu P A_m$. Because the chains are attached covalently to the initiation sites, any detachment due to shear is expected to commence at the weaker bonds attaching the macroinitiator to the mica. These bonds (on average ~18 such bonds per macroinitiator) each have a net adhesion energy $\varepsilon_1 \approx k_B T$ (k_B is the Boltzmann constant and T is the temperature) arising from replacement of counterions at the negatively charged mica surface by the positively charged quaternary $-N^+(CH_3)_3$ groups on the macroinitiator. In the worst-case scenario, all the $F_{s(m)}$ during sliding will act on one of the quaternary groups at the surface, and this may initiate the "unzipping" of the macroinitiator from the mica. Putting $\mu = 0.001$ and $P = 7.5$ MPa gives $F_{s(m)} = 1.2 \times 10^{-13}$ N. This is smaller than the force $f_1 \approx \varepsilon_1/\delta$ that is needed to detach a single $-N^+(CH_3)_3$ group from the mica, where δ is on the order of 1 Å or less. Putting $\delta = 1$ Å gives $f_1 \approx 4 \times 10^{-11}$ N. Thus, the friction force on a macroinitiator at the highest pressures we apply is too weak (by a factor of 100 or more) to detach even a single bond anchoring the macroinitiator to the mica surface, which is consistent with our observations of the robustness of the pMPC layer toward resisting shear under all conditions in our study.
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Controlled Formation of Sharp Zigzag and Armchair Edges in Graphitic Nanoribbons

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Graphene nanoribbons can exhibit either quasi-metallic or semiconducting behavior, depending on the atomic structure of their edges. Thus, it is important to control the morphology and crystallinity of these edges for practical purposes. We demonstrated an efficient edge-reconstruction process, at the atomic scale, for graphitic nanoribbons by Joule heating. During Joule heating and electron beam irradiation, carbon atoms are vaporized, and subsequently sharp edges and step-edge arrays are stabilized, mostly with either zigzag- or armchair-edge configurations. Model calculations show that the dominant annealing mechanisms involve point defect annealing and edge reconstruction.

Graphene, a single sheet of graphite, has attracted a lot of research interest since it first became experimentally accessible in 2004 (*1–5*). Its two-dimensional (2D) structure and the near massless behavior of its charge carriers provide unique transport properties. Graphene nanoribbons, which are quasi-1D graphene nanostructures, exhibit a bandgap between the valence and conduction band states. The bandgap depends on both the edge type and ribbon width (*6*), which is typically a few nanometers, making graphene nanoribbons a very interesting material for potential electronics applications (*7*). Theoretical and experimental studies show that the edges of graphene nanoribbons strongly influence their electronic and magnetic properties (*8*, *9*). Therefore, much effort has been devoted to studying the edges in graphitic nanomaterials (*10–18*). Although atomically smooth edges are essential for many applications, it is difficult to produce such edges by conventional physico-chemical methods. For example, lithographic etching and