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Feature Article

Polyzwitterionic brushes: Extreme lubrication by design

Meng Chen^{a,*}, Wuge H. Briscoe^{a,1}, Steven P. Armes^b, Hagai Cohen^c, Jacob Klein^{a,c,*}^a Department of Chemistry, University of Oxford, Oxford OX1 3QZ, UK^b Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK^c Weizmann Institute of Science, Rehovot 76100, Israel

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ABSTRACT

Polymers offer the advantage that they may independently combine desirable supramolecular structure with useful local monomeric properties to yield optimal performance of different tasks. Here we utilise the remarkable lubricating properties both of dense polymer brushes, and of hydration sheaths about charges via the emerging paradigm of hydration lubrication, to design a grafted-from polyzwitterionic brush system, where each of the monomers has a structure similar to the highly-hydrated phosphorylcholine headgroups of phosphatidylcholine lipids. Such polyzwitterions are grown from a macroinitiator coating the substrate (mica) surface using atom transfer radical polymerisation (ATRP) of 2-(methacryloyloxy)ethyl phosphorylcholine (MPC) to form exceptionally robust poly(MPC) brushes. We have characterized these brush layers via X-ray reflectometry, X-ray photoelectron spectroscopy, surface forces measurements and atomic force microscopy. Such brushes, designed to optimise their lubrication properties, are indeed found to provide state of the art boundary lubrication, achieving friction coefficients as low as 0.0004 at pressures up to 75 atmospheres over a wide range of sliding velocities. Such low friction is comparable with that of articular cartilage in healthy mammalian joints, which represents nature's benchmark for boundary lubrication in living organisms, and suggests that hydration lubrication plays a major role in reducing friction in biological systems.

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1. Introduction

Polymers offer the advantage that they may independently combine desirable supramolecular structure with useful local monomeric properties to yield optimal performance of different tasks. Polymer brushes are a particular example of such supramolecular assemblies, which have become a widely-used means for modifying surface properties. Such brushes are an assembly of non-adsorbing polymer chains end-grafted to surfaces at a sufficiently

high grafting density in a good solvent. They have attracted considerable attention since the discovery of their exceptional performance, in contrast with adsorbed polymers, in colloidal stabilization [1,2] due to strong osmotic repulsion between opposed brushes combined with the absence of bridging. Subsequent work led to the concept that such nanometer-scale brushes can act as an efficient lubricant in friction and wear processes, especially at the pressures and aqueous environment typical of frictional processes in biological systems, such as sliding of one tissue over another, which is common in articular cartilage of mammalian joints and cornea tissue. Lubrication and wear properties of some model systems for polymer brushes [3–7] have been studied using the surface force balance (SFB) technique, as it is believed that understandings of underlying friction mechanisms achieved in this way can be largely applied to real biological situations.

* Corresponding authors. Present address: Procter and Gamble Technology (Beijing) Co. Ltd., 35 Yu An Road, Tianzhu Konggang Development Zone B, Beijing 101312, PR China (Meng Chen).

E-mail addresses: mengeva@gmail.com (M. Chen), jacob.klein@weizmann.ac.il (J. Klein).

¹ Present address: School of Chemistry, University of Bristol, Bristol BS8 1TS, UK.

To construct such a model polymer brush system, both 'grafting to' and 'grafting from' approaches have been employed. 'Grafting to' involves tethering of preformed, non-adsorbing, end-functionalised polymer chains onto surfaces by one end, which can be divided into two groups – physical and chemical grafting, depending on the nature of the interaction between their end-groups and substrates. Physical grafting (or physigrafting) refers to chain anchoring via hydrophobic attraction [8], dipole–dipole interaction [9], charge–charge interaction [5], or using diblock copolymers in a selective solvent [9,10]. Chemical grafting concerns the formation of chemical bonds between functionalised chain ends and reactive groups attached to surfaces, for example, via photochemical reaction [11]. The mechanism for irreversible deposition of polymer chains via silane chemistry [12,13] or thiol–gold interaction [14] is unclear and regarded as between physical and chemical grafting. Typical examples are summarised in Fig. 1.

However, both physical and chemical grafting methods suffer from kinetic limitations, and it is difficult to obtain dense brushes as it takes a long time for free chains to diffuse to the substrate through the potential barrier presented by the existing end-tethered chains [15]. Physigrafting results in weak chain anchoring, which has caused a general problem in previous surface force measurements between polymer brushes prepared in this way. Simply stated, this is that at the highest compressions and therefore highest frictional forces between the surfaces, the surface-attached brushes can slide across or entirely detach from the surfaces, because the adhesive interactions at the end of each chain are insufficient to anchor it firmly enough to the surface. Thus, Klein et al. [4] observed an erratic stick–slip shear behavior at the highest compressions, which suggests a shift of slip-plane from the mid-plane to the polymer–substrate interface arising from sufficiently high viscous dissipation in heavily entangled polymer layers and weak attachment of zwitterionic end-groups onto mica. Raviv et al. [6] reported that brushes of charged polymers attached to surfaces rubbing across an aqueous medium can deliver superior lubrication compared to other polymeric surfactants. Effective friction coefficients with this polyelectrolyte brush in water are lower than about 0.0006–0.001 up to loads corresponding to a mean pressure of a few atmospheres ($P \sim 0.3$ MPa). This is indeed comparable with the friction between articular cartilage surfaces in human synovial joints, for which

$\mu < 0.002$, but the maximum pressure is far below the physiological pressures (up to 5 MPa or more) at natural synovial joints. The sharp increase in friction above the maximum pressure is due to the shearing away from the intersurface gap of most confined chains that are only weakly end-attached to the surface. These studies show insufficiently strong anchoring of physigrafted brushes, which limits their lubricating performance and also limits our exploration of friction mechanisms of polymer brushes in the high pressure regime. Therefore, the 'grafting to' approach cannot provide dense, strongly anchored polymer brushes, and 'grafting from' should be used for the purpose of designing a robust brush that can effectively provide good lubrication and wear properties to the surface even at high loads.

'Grafting from' consists of two steps, attachment of initiators onto surfaces and subsequently, polymer growth from initiator sites monomer by monomer via covalent bonding. This can lead to much stronger anchoring and give another advantage that the polymer conformation can be easily tuned via varying the initiator surface density and the polymerisation time. In this study, zwitterionic polymer brushes, poly(2-(methacryloyloxy)ethyl phosphorylcholine) (pMPC), have been directly grown from planar mica pre-coated with macroinitiator using atom transfer radical polymerisation (ATRP). ATRP was first discovered by Matyjaszewski [16] and Sawamoto [17] in 1995, which reversibly generates free radicals via catalysis by transition-metal complex to continuously promote monomer addition. A surface-initiated ATRP system [18–21] in the absence of free initiator is typically composed of monomer, surface-bound initiator, activator/deactivator formed by transition-metal salts complexed with ligand, solvent and reaction conditions (e.g., temperature and inert atmosphere) as well as some additives if necessary. The synthesis is implemented in two processes that are initiator immobilisation and polymer growth by ATRP from initiating sites.

Polyzwitterionic brushes are usually hydrated due to the charged segments, similar to polyelectrolyte brushes, and pMPC is especially hydrated due to its phosphorylcholine (PC) headgroups with water molecules tightly bound to its phosphate group in the primary hydration shell [22]. The combination of 'grafting from' strategy and highly hydrated pMPC polyzwitterionic brushes can allow the idea of hydration as the lubrication mechanism to be well tested using the SFB. Classical lubrication mechanisms for

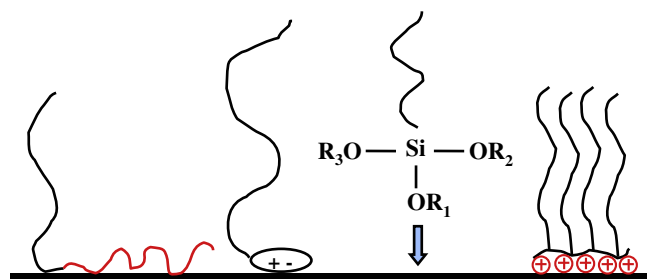


Fig. 1. Examples of polymer chains grafted to surfaces to form brushes via (from left to right) hydrophobic attraction, dipole–dipole interaction, silane chemistry and multi-point electrostatic interaction.

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