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Fundamental Investigations of the Tribological Properties of Biological Interfaces

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14. ABSTRACT This report results from a contract tasking ETH Zurich as follows: The objective of the program was to understand the fundamental nature of structure, the influence of applied forces, and the role of solvent incorporation existing at solvated polymer-polymer under shearing conditions. This objective was to be realized through 1) the systematic elucidation of the modes of interaction between polymer surfaces, 2) the quantitative measurement of complexed solvent, and 3) the fundamental measurement of interfacial friction forces as a function of interfacial composition and structure. The experimental program was aimed at measuring interfacial forces over a range of length scales, for sets of systematically prepared and well-characterized polymer and biopolymer interfaces. The fundamental goal of the program was to predict/identify the function of aqueous-based tribological systems lubricated for military applications. The applied aim of the program was to provide design criteria and performance limitation of low-friction biological and/or bioinspired interfaces.					
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Fundamental Investigations of the Tribological Properties of Biological Interfaces

1. Introduction

This document reports the progress of a research program that began as a collaboration between the University of Houston and the Swiss Federal Institute of Technology (ETH-Zürich), originally funded by the AFOSR. The financing for the ETH part of the program has been assumed for this part of the project by EOARD. The program extended investigations of the fundamental nature of tribological interfaces found in biological systems and applied these principles to the design of future tribological systems. The work entailed molecularly specific engineering of surfaces by means of biomimetic coatings and the measurement of interfacial forces on both molecular and microscopic scales. Only work carried out at the ETH is covered in this report.

2. Objectives

The **objective** of the overall program was to understand the fundamental nature of structure, the influence of applied forces, and the role of solvent incorporation existing at solvated polymer-polymer under shearing conditions. This objective was to be realized through (i) the systematic elucidation of the modes of interaction between polymer surfaces (penetration, repulsion, compression), (ii) the quantitative measurement of complexed solvent (related to polymer swelling and conformational changes), and (iii) the fundamental measurement of interfacial frictional forces as a function of interfacial composition and structure. The experimental program was aimed at measuring interfacial forces over a range of length scales, for sets of systematically prepared and well-characterized polymer and biopolymer interfaces. The fundamental **goal** of the program was to predict/identify the function of aqueous-based tribological systems lubricated for military applications. The applied aim of the program was to provide design criteria and performance limitations of low-friction biological and/or bioinspired interfaces.

Although we had hoping to have been able to report a significant body of tribological results for hyperbranched systems, the speed of synthesis of the molecules has been slower than anticipated. There is still interest in pursuing this avenue, but it has been given lower priority until the PEG-containing hyperbranched molecules are available. Some oligoethylene glycol dendrimers have been synthesized and tested, but their lubrication performance, as anticipated, was unexceptional. On the other hand, the fact that they adsorbed to the test surfaces to form a monolayer gives us hope that the PEG versions, once synthesized, may indeed prove to be lubricious.

We have therefore focussed on dextran-based systems, since they are highly biomimetic, reasonably priced, and their temperature behavior is likely to be better than that of the previously studied PEG systems. We have been concentrating on polymers that contain a poly-lysine backbone. This allows for easier comparison with the PLL-g-PEG polymers from our previous studies. Polymers of a similar composition have also been obtained from the group of Prof. Atsushi Maruyama, Kyushu University, and this has enabled us to broaden our study of the effects of polymer architecture on both lubrication and resistance to protein adsorption.

3. Accomplishments during project

A. Synthesis of new polymers

While PAAm-g-dextran appeared at first sight to be a drop-in replacement for PLL-g-PEG, it is now suspected that subtle differences between the two backbones do indeed make a difference in tribological behavior. In particular, it was found that PLL-based polymers are not only effective on negatively charged surfaces, but also on hydrophobic surfaces such as engineering plastics. This work has recently been accepted for publication in *Lubrication Science*¹. Another advantage of combining PLL and dextran is that there are already reports of this material, used in other applications, in the literature, and we were able to obtain small (mg) quantities from Prof. Atsushi Maruyama to compare with our own material and thereby extend the scope of our study. Professor Maruyama had been using PLL-g-dextran for gene-

¹ *Poly(L-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG): A Versatile Aqueous Lubricant Additive for Tribosystems Involving Thermoplastics* Seunghwan Lee and Nicholas D. Spencer *Lubrication Science*; **2007** (in press)

therapy and drug-delivery applications, and had used a slightly different synthetic approach and starting reagents to us. The materials synthesized by us and by Prof. Maruyama are summarized in Table 1. The synthetic approach used in our lab for the polymer synthesis is similar to that used for the PAAm-based polymers, and involves the reduction of a Schiff base to the species shown in Figure 1.

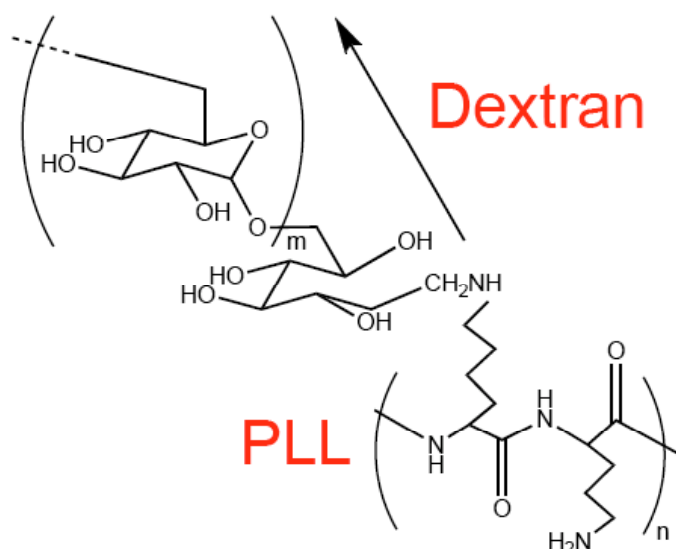


Figure 1: PLL-g-dextran

Synthesized at ETH	Synthesized at U. Kyushu
PLL(26)-g(3.4)-dex(5)	PLL(13)-g(3.9)-dex(5.9)
PLL(26)-g(3.5)-dex(5)	PLL(13)-g(7.1)-dex(5.9)
PLL(26)-g(5.3)-dex(5)	PLL(6)-g(5)-dex(5.9)
PLL(26)-g(6.6)-dex(5)	PLL(6)-g(10.2)-dex(5.9)
PLL(26)-g(7.3)-dex(5)	

Table 1. The PLL-g-dex architectures that have now been synthesized, purified and characterized by nmr and elemental analysis

B. Adsorption and protein-resistance testing of new polymers

It has been recognized in our laboratory for some time that polymer coatings that impart resistance to protein adsorption and those that provide lubricity under an aqueous environment seem to require similar architectures. With this in mind, we combined measurements of the amount of polymer attaching to a silica surface with an assay of the mass of adsorbed serum proteins. The results are shown in Figure 2:

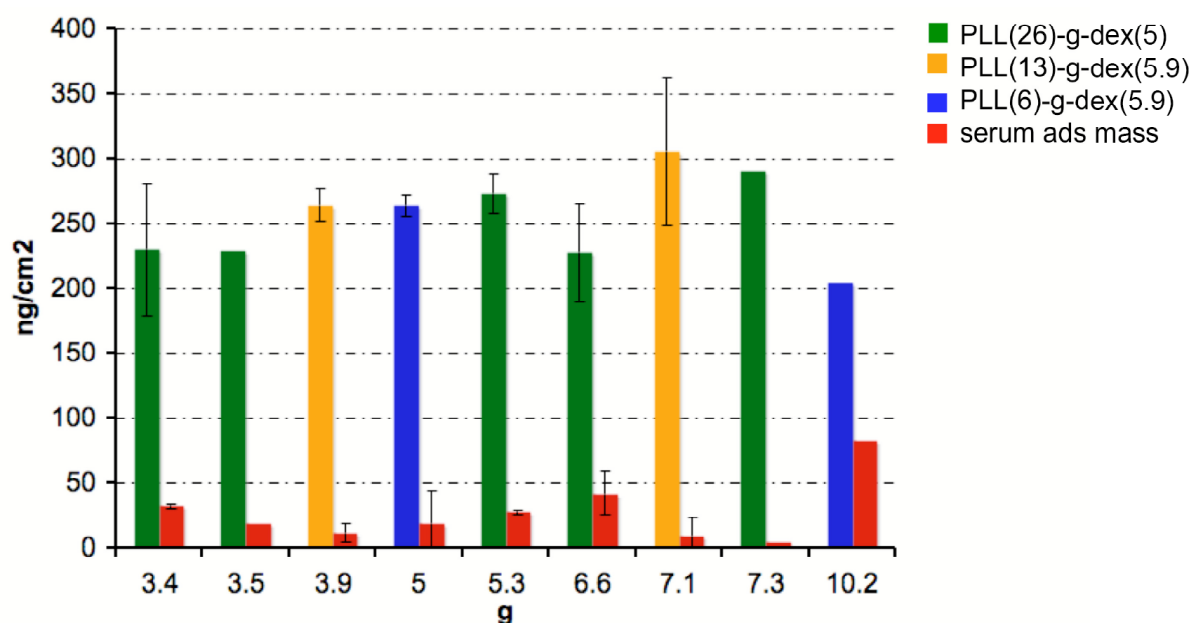


Figure 2: Optical waveguide lightmode spectroscopy (OWLS) results for the adsorption of PLL-g-dextran on silica surfaces and subsequent investigation of protein adsorption from serum. PLL(26)-based polymers were synthesized in Zurich, the others in Japan.

It can be seen that all polymers adsorb onto the silica surface, the amount corresponding to approximately monolayer coverage. Also, all were more or less protein resistant, with the exception of the grafting ratio of 10.2. This is very consistent with what we have previously observed with PLL-g-PEG. A maximum in polymer adsorption and minimum in protein adsorption seemed to occur at around a grafting ratio of 7-7.5 (a rather higher value than has been previously observed with PLL-g-PEG). No significant differences were observed between the polymers synthesized in Japan and those synthesized in our

laboratory, and the backbone and side-chain lengths did not seem to influence behavior over the range investigated.

C. Tribological testing of new polymers

Tribological testing revealed comparable behavior to that observed with PLL-g-PEG, namely an approximately 50% reduction (compared to HEPES buffer) in friction coefficient in macroscopic sliding (2N, pin-on-disk, steel ball, glass disk, Figure 3), and an order-of-magnitude reduction in friction coefficient for rolling geometry (10N, steel on glass, Figure 4). Note that dextran alone also exhibits lubricating behavior, but only at the high speeds obtainable on the mini-traction machine, indicating that the effect is rheological. Testing in an AFM (i.e. wearless sliding) between silica surfaces also revealed that the polymers display considerably better lubricating properties than buffer solution alone (Figure 5), and that the least lubricious architecture (PLL(6)-g(10.2)-dex(5.9)) is also the least effective polymer for protein adsorption resistance.

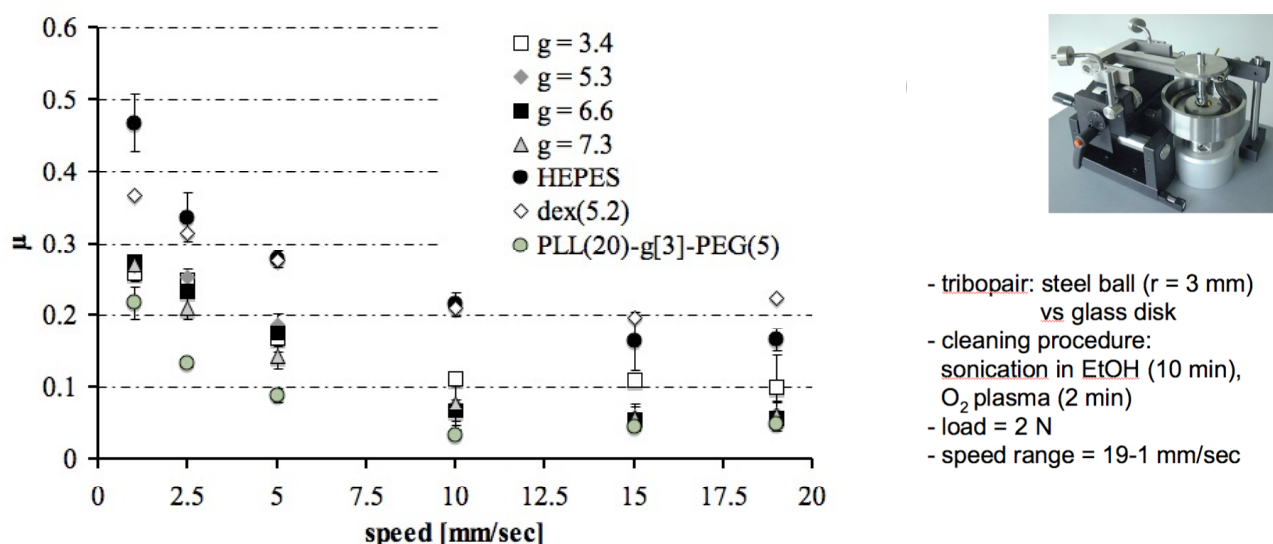


Figure 3: Pin-on-disk results for PLL-g-dex, with comparisons to dextran, HEPES, and PLL-g-PEG.

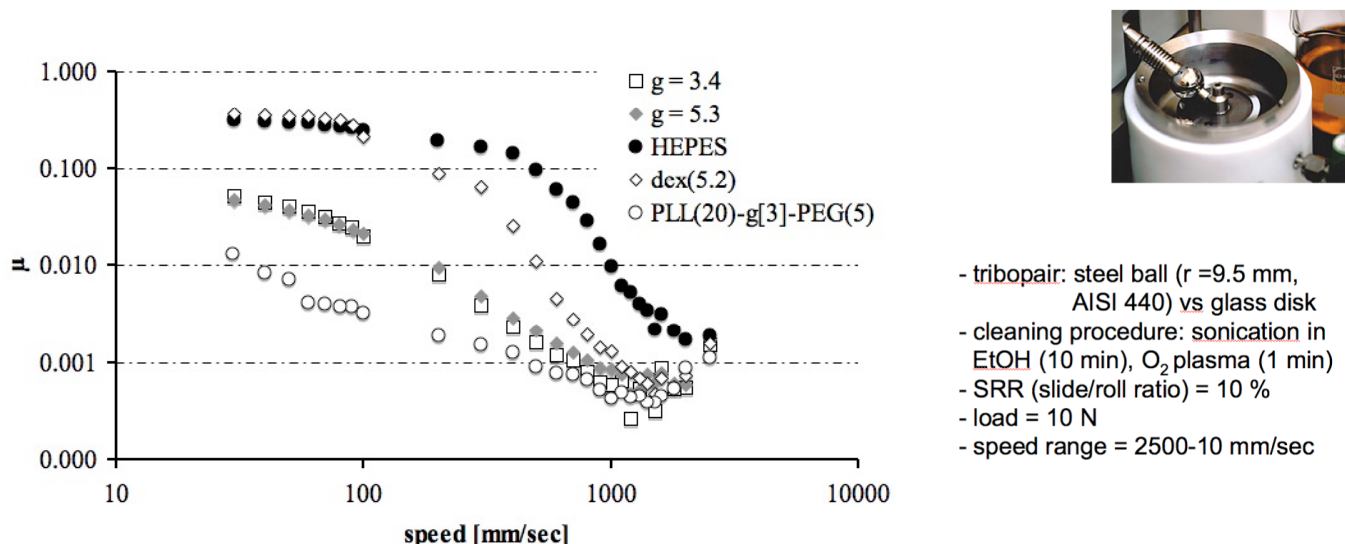


Figure 4: Rolling (MTM) results for PLL-g-dex, with comparisons to dextran, HEPES, and PLL-g-PEG.

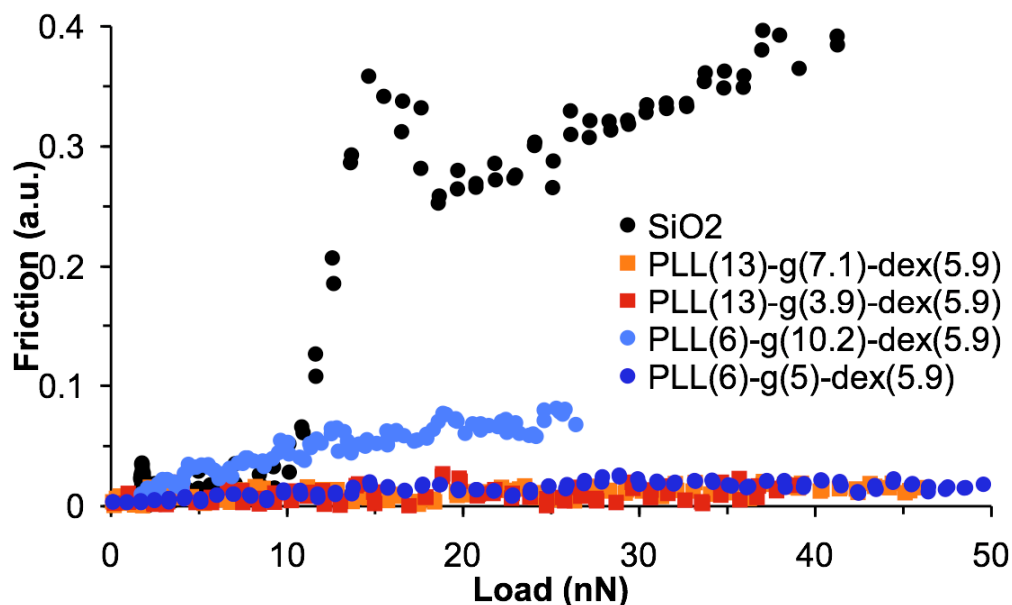


Figure 5: AFM friction results for PLL-g-dex adsorbed on silica surfaces, tested with a silicon nitride tip, in a HEPES buffer environment.

4. Conclusions

Comb-like graft-copolymers with dextran side chains (PLL-g-dex) have been developed and investigated as biomimetic lubricant additives in an aqueous environment. The synthesized copolymers have been shown to adsorb spontaneously onto metal oxide surfaces, similarly to PLL-g-PEG, and to behave as boundary lubricants, both in the pure sliding and in mixed sliding/rolling contact regimes.

Compared to PLL-g-PEG, the PLL-g-dex polymers employed in this work showed marginally inferior lubricating performance, especially in the boundary lubrication regime. This is mainly attributed to the significant difference in the fully extended chain lengths of dextran(5.2) and PEG(5), since the structures of the chains are completely different (rings vs. single strands). In fact the fully extended chain length of dex(5.2) is estimated to be roughly half of that of PEG(5), which is likely to impact on the performance of the lubricating films. This leaves the possibility that the lubricating properties of PLL-g-dex could be further improved by employing longer dextran chains. This is currently under investigation.

Dextran has higher solubility at higher temperatures than PEG, as well as being very inexpensive, and therefore may be more relevant for applications. Furthermore, the undesirable oxidation of PEG to peroxides in air is not a problem with sugar chains. The macrotribological work on dextrans is now completed and has been prepared as a manuscript for *Tribology Letters*. A manuscript on the nanotribological work is now in preparation.

The PI and his team have been invited to prepare a “Perspectives” article for *Science* on the general area of water-based lubrication. Clearly our AFOSR/EOARD-supported research in this field has led to our being honored in this way, and for this we are most grateful.

4. Inventions

I certify that there were no subject inventions to declare as defined in FAR 52.227-12, during the performance of this contract.

5. Declaration

The Contractor, Nicholas D. Spencer, hereby declares that, to the best of his knowledge and belief, the technical data delivered herewith under Contract No. FA8655-05-1-3042 is complete, accurate, and complies with all requirements of the contract.

November 27th, 2007

Nicholas D. Spencer

Relevant Publications Published, Submitted, or Prepared During the Funded Period

Surface-grafted Sugar Chains as Aqueous Lubricant Additives: Synthesis and Macrotribological Tests of Poly(L-lysine)-graft-Dextran (PLL-g-dex) Copolymers

Chiara Perrino, Seunghwan Lee and Nicholas D. Spencer
Tribology Letters; **2007** (Manuscript attached, to be submitted)

Poly(L-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG): A Versatile Aqueous Lubricant Additive for Tribosystems Involving Thermoplastics

Seunghwan Lee and Nicholas D. Spencer
Lubrication Science; **2007** (in press)

Nanotribology of surface-grafted PEG layers in an aqueous environment

Tanja Drobek and Nicholas D. Spencer
Langmuir; **2007** (in press)

Macroscopic Tribological Testing of Alkanethiol Self-Assembly Monolayers (SAMs): Pin-on-Disk Tribometry with Elastomeric Sliding Contacts

Seunghwan Lee, Raphael Heeb, Nagaiyanallur V. Venkataraman, and Nicholas D. Spencer
Tribology Letters; **2007** 28(3) 229

Achieving Ultralow Friction by Aqueous, Brush-Assisted Lubrication

Seunghwan Lee and Nicholas D. Spencer
Ch. 21 in “*Superlubricity*”, Ed. Ali Erdemir and Jean-Michel Martin
Elsevier **2007**

Self-Healing Behavior of A Polyelectrolyte-Based Lubricant Additive for Aqueous Lubrication of Oxide Materials

Seunghwan Lee, Markus Müller, Raphael Heeb, Stefan Zürcher, Samuele Tosatti, Michael Heinrich, Fabian Amstad, Sebastian Pechmann, and Nicholas D. Spencer
Tribology Letters; **2006** 24(3), pp217-223

Aqueous Lubrication of Polymers: Influence of Surface Modification

S. Lee, N.D. Spencer
Tribology International; **2005**; 38, pp 922-930

Lubrication properties of a brush-like copolymer as a function of the amount of solvent absorbed within the brush

M. Müller, X. Yan, S. Lee, S. Perry, and N.D. Spencer
Macromolecules; **2005**; 38(13), pp 5706-5713.

Compressing PEG brushes

T. Drobek, M. Heuberger, and N.D. Spencer
Macromolecules; **2005**; 38(12) pp 5254-5259

(submitted to *Tribology Letters*)

**Surface-grafted Sugar Chains as Aqueous Lubricant Additives: Synthesis and
Macrotribological Tests of
Poly(L-lysine)-*graft*-Dextran (PLL-g-dex) Copolymers**

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Abstract: Comb-like graft copolymers with carbohydrate side chains have been developed as aqueous lubricant additives for oxide-based tribosystems, in an attempt to mimic biological lubrication systems, whose surfaces are known to be covered with sugar-rich layers. Following previous studies of the graft copolymer, poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-g-PEG), which showed both excellent lubricating¹⁻⁴ and antifouling properties,⁵⁻¹⁰ a similar approach has been chosen to graft dextran¹¹ chains onto the same backbone, thus generating PLL-g-dex. PLL-g-dex copolymers were found to adsorb readily from aqueous solution onto negatively charged oxide surfaces. Tribological characterization at the macroscopic scale, either under pure sliding conditions or a mixed sliding/rolling contact regime, showed that PLL-g-dex is very effective for the lubrication of oxide-based tribosystems. In comparison with a PLL-g-PEG possessing similar architectural features in terms of molecular weight, the lubricating capabilities of PLL-g-dex were observed to be only marginally inferior to those of PLL-g-PEG.

Keywords: poly(L-lysine)-*graft*-dextran (PLL-g-dex), biomimetic lubrication, surface modification, carbohydrates

1. Introduction

Water-based lubricants possess distinctive advantages (environmental compatibility, biocompatibility, availability, cost effectiveness), and could represent a viable alternative to oil-based lubricants in certain applications. Their environmental compatibility makes them suitable for a number of industrial applications, such as food processing or textile and pharmaceutical manufacturing, where the use of oil-based lubricants can be problematic due to contamination issues.^{12, 13} In the biomedical field, aqueous lubrication is particularly important, since water is virtually the only acceptable base lubricant. Any attempts to improve lubrication properties in biomedical applications (such as lubricious coatings for catheters) should therefore take both water compatibility and biocompatibility into account.¹⁴

Poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-g-PEG), a graft copolymer consisting of a polycationic PLL backbone and PEG side chains, has proven to be highly effective at both preventing non-specific adsorption of proteins onto and lubricating oxide surfaces in an aqueous environment.^{1-3, 6-9, 15} PLL-g-PEG has been shown to adsorb spontaneously from aqueous solutions onto negatively charged surfaces via electrostatic interactions; the positive charges present on the protonated primary amine groups of the PLL backbone in neutral aqueous environment lead to its rapid immobilization onto negatively charged surfaces. PEG side chains, which are radially distributed along the backbone in bulk solution in order to minimize steric repulsion, stretch out into the solution once the copolymers have adsorbed on the surface, forming a polymer brush, providing the inter-PEG spacing is sufficiently close. PEG, however, has some disadvantages, such as lower solubility with increasing temperature and oxidation to peroxides in air,^{16, 17} which could limit the usage of PLL-g-PEG in certain applications. An alternative approach is to mimic

biological membrane surfaces, which are typically covered with carbohydrate-rich layers. *In vivo* cellular interactions can be strongly influenced by pendant oligosaccharides chains—principle components of the highly hydrated *glycocalyx*, which surrounds certain kinds of cell, and is known to prevent undesirable, non-specific adsorption of proteins.¹⁸⁻²² Carbohydrates are also known to play an important role in natural lubrication mechanisms, which often involve a brush-like structure of sugar chains, anchored to a protein backbone. Proteoglycans, for instance, have been suggested to play a role in natural joint lubrication,^{23, 24} and mucins, large glycoproteins that make up the mucosal hydrogel coating covering epithelial cell surfaces, act as protective and lubricious layers.^{5, 25-27}

Based on this natural model, sugar-based copolymers have been developed for use as aqueous lubricant additives. In the present work, encouraged by the successful lubricating performance of PLL-g-PEG in previous studies,¹⁻³ we have chosen to maintain the comb-like graft polymer structure, selecting the same PLL backbone, and replacing the PEG side chains with dextran chains. Dextran is a natural and neutral polysaccharide consisting of an $\alpha(1\rightarrow6)$ -linked glucan with side chains attached to the 3-positions of the backbone glucose units (Figure 1). Our choice of dextran for the carbohydrate chains was motivated by several factors. Firstly, there are already reports on the synthesis and applications for drug/gene delivery of poly(L-lysine)-g-dextran (PLL-g-dex) in the literature.²⁸⁻³⁴ Secondly, since the dextran is neutral, it does not present problems due to electrostatic interactions when grafted onto a polycationic backbone (PLL). Finally, previous studies have shown the effectiveness of dextran coatings at preventing non-specific protein adsorption,^{19-22, 35-41, 18, 42} this being a property that often seems to be closely associated with good aqueous lubricating properties.

We have focussed on the characterization of adsorption and aqueous lubricating properties of PLL-*g*-dex copolymers on oxide surfaces under standard, macroscopic tribological conditions at ambient temperatures, including sliding and mixed sliding/rolling contacts. We compare these properties with those of PLL-*g*-PEG copolymers.

2. Materials and Methods

2.1 Poly(L-lysine)-graft-dextran (PLL-*g*-dex)

Poly(L-lysine)-*graft*-dextran (PLL-*g*-dex) copolymers were synthesized by a reductive amination reaction of PLL HBr (15-30 kDa, polydispersity 1.1, Sigma-Aldrich, Switzerland) with dextran (dextran T5, 5 kDa, polydispersity 1.8, Pharmacosmos A/S, Denmark). Borate buffer (0.1 M, pH 8.5) was used as solvent for the reaction. The reaction proceeded in two steps: first, the formation of a Schiff base between the terminal dextran aldehyde group and primary amine groups of PLL, and second, the reduction of the unstable Schiff base to secondary amines. PLL was dissolved in borate buffer solution at 40 °C, and dextran was subsequently added to the solution, and the mixture was incubated with stirring overnight for the formation of the Schiff base. Sodium cyanoborohydride (NaBH₃CN, Fluka Chemika, Switzerland) was then added to the mixture (10x molar excess to dextran was used) and it was kept under stirring for two more days. The resulting copolymers were isolated by ultracentrifugation (Vivaspin 15R centrifugation tubes, 30000 MWCO, Sartorius AG, Switzerland) to remove the unreacted starting materials. Varying the ratio of Lys/dex ratio allowed us to control the degree of grafting of dextran chains onto PLL backbone (see below for the definition of the grafting ratio, *g*). PLL-*g*-dex molecules were characterized by ¹H-NMR spectroscopy and elemental analysis (EA).

^1H -NMR spectra of the copolymers in D_2O were recorded on a Bruker spectrometer (300 MHz) and both NMR spectra and elemental analysis data were used to determine the grafting ratio.

The notation PLL(x)-g[y]-dex(z) for the copolymers was used to represent the molar mass of PLL in kDa (x) (including the counterions, Br $^-$, as precursor), the molar mass of dextran in kDa (z), and the grafting ratio (y) (defined as y = the number of lysine monomers/dextran side chain). While it is possible, in principle, to control all three structural parameters, we have varied only the grafting ratio, y , whereas the molecular weights of PLL and dex were kept constant at 26.3 kDa and 5.2 kDa, respectively, in this work. For comparison purposes, PLL(20)-g[3.0]-PEG(5), a copolymer with the PEG(5) side chains (molecular weight, 5 kDa) onto PLL(20) backbone at the grafting ratio of $g = 3.0$, has also been employed.

2.2 Optical Waveguide Lightmode Spectroscopy (OWLS)

Optical waveguide lightmode spectroscopy (OWLS) was employed to characterize the adsorption properties of the polymers. Experiments were performed using an OWLS 110 instrument (Microvacuum, Budapest, Ungary).

OWLS is an optical biosensing technique for the *in situ* label-free analysis of adsorption processes. Briefly, linearly polarized light (He-Ne laser) is coupled with a diffraction grating into a planar waveguide, provided that the in-coupling condition is fulfilled. The light is guided by total internal reflection to the ends of the waveguide layer, where it is detected by a photodiode detector. The adsorbed mass is calculated from the change in the refractive index in the vicinity of the waveguide surface upon adsorption of molecules.⁴³⁻⁴⁵ A refractive index increment (dn/dc) value of 0.139 was used to calculate the mass of polymer adsorbed.

Prior to the experiments, optical waveguides chips (standard: $\text{Si}_{0.75}\text{Ti}_{0.25}\text{O}_2$ on glass, $1.2 \times 0.8 \text{ cm}^2$, Microvacuum, Budapest, Hungary) were ultrasonicated in 0.1 M HCl for 10 min, rinsed with Millipore water, ultrasonicated in 2-propanol for 10 min, rinsed again with Millipore water, and then dried under a dry nitrogen stream. The substrates were subsequently cleaned by UV/ozone cleaner (Boeckel industries Inc., model 135500) for 30 min.

The cleaned waveguides were assembled into the OWLS flow cell and equilibrated by exposing to HEPES buffer solution (10 mM 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (Sigma, St. Louis, MO, USA), adjusted to pH 7.4 with 6.0 M NaOH solution) overnight in order to obtain a stable baseline. The waveguides were then exposed to a polymer solution (0.25 mg/ml in HEPES buffer) for at least 30 min, resulting in the formation of a polymer adlayer, and rinsed three times with buffer solution for another 30 min.

2.3 Pin-on-disk tribometry

A pin-on-disk tribometer (CSM Instruments, Switzerland) was employed to investigate the lubricating properties of the polymer solutions under pure sliding conditions.

As a tribopair, we chose steel balls (6 mm in diameter, DIN 5401-20 G20, Hydrel AG, Romanshorn, Switzerland) against flat glass squares ($2.5 \times 2.5 \text{ cm}^2$, 1 mm thick), cut from microscopes slides (Medite Medizintechnik AG, Switzerland, approximate chemical composition according to the manufacturer: 72.2 % SiO_2 , 14.3 % Na_2O , traces of K_2O , CaO , MgO , Al_2O_3 , Fe_2O_3 , SO_3). The lubricating properties of the polymers were evaluated by acquiring the coefficient of friction, μ (= friction

force/load), as a function of speed under a fixed load (2 N, dead weights) at room temperature. The maximum Hertzian contact pressure in this configuration is estimated to be 0.34 GPa. The sliding speed was controlled to vary from 1 to 19 mm/s using the instrument's software (InstrumX version 2.5A, CSM Instruments, Switzerland). The concentration of the polymer solutions was 0.25 mg/ml, as with the OWLS experiments. The number of rotations was fixed at 200. For each measurement with a given copolymer, the same pair of pin and disk was used. However, the position of the ball and the radius of the track on the disk was changed for each speed, to provide fresh tribocontact points. Balls and disks were cleaned right before each measurement as follows; they were ultrasonicated in ethanol for 10 min, dried under a nitrogen stream and then oxygen-plasma cleaned for 2 min. All instrumental parts expected to be in contact with the polymer solution were cleaned by rinsing with ethanol and water.

2.4 Mini-traction Machine

A mini-traction machine (MTM, PCS Instruments, London, UK) was employed to characterize the lubricating behavior of the copolymer solutions in a mixed sliding/rolling contact regime over a speed range of 0-2500 mm/s. AISI 440 steel balls (9.5 mm in radius, PCS instruments, London, UK) and flat silicate glass disks (46 mm in diameter, PCS Instruments, London, UK) were used as tribopairs. The ball is loaded against the disk and ball and disk driven independently to create a mixed sliding/rolling contact. The slide/roll ratio (SRR) is defined as the percentage ratio of the difference to the mean of the ball speed (u_{ball}) and disk speed (u_{disk}); i.e., $\text{SRR} = [(u_{\text{ball}} - u_{\text{disc}})/(u_{\text{ball}} + u_{\text{disc}})/2] \times 100\%$. Thus, $\text{SRR} = 0\%$ (i.e. $u_{\text{ball}} = u_{\text{disk}}$) represents a pure rolling contact and higher SRR values represent a higher portion of

the sliding character. With the software provided by the manufacturer (PCS Instruments, MTM version 1.0, London, UK), values in the range SRR 1 to 200% are accessible. For the present work, an SRR value of 10% was chosen, which enables friction measurements in conditions close to pure rolling. Speed-dependence tests on polymer solutions (0.25 mg/ml) were carried out at a constant load of 10 N (Hertzian contact pressure, 0.42 GPa) and at a controlled temperature (25 °C). The disk track radius was fixed at 21 mm and for each measurement a new ball and a new disk were used. Balls and disks were cleaned according to the same procedure used for pin-on-disk tribometry experiments, except that air-plasma was used instead of oxygen-plasma. The instrumental parts expected to be in contact with the polymer solution were cleaned with a commercial cleaner (Hydrochloric acid 300 mmol/L and detergent 1 %, Roche Diagnostics GmbH, Mannheim, Germany).

3. Results and Discussion

3.1 Synthesis and structural features of PLL-g-dex copolymers

PLL-g-dextran copolymers with different grafting ratios were successfully synthesized and characterized by ^1H -NMR. The grafting ratio was varied between roughly 3 and 7 and evaluated by means of NMR and EA. In Table 1, the structural features of the synthesized copolymers and the yield of the synthesis are presented in detail.

It should be noted that the selection of the molecular weight of dextran chains in this work (5.2 kDa) was mainly motivated to keep it comparable with that of PEG (5 kDa) in PLL(20)-g[3.0]-PEG(5). For this reason, however, the number of monomer

units of the dex(5.2) chain, 32 sugar rings, is significantly less than that of corresponding EG units of PEG(5), 113.6. In turn, the fully extended chain length of dextran (5.2), 22.4 nm, is also expected to be shorter than that of PEG(5), 40.5 nm (based on the molecular length of monomers: 0.7 nm for dextran ⁴⁶ and 0.358 nm for ethylene glycol (EG) ⁴⁷). For this reason, the adsorption behavior of the two types of copolymers, PLL-g-dex and PLL-g-PEG, can be fairly assessed by comparison of adsorbed mass data from OWLS experiments, but a potential influence of the difference in the extended chain lengths on the lubricating properties should be borne in mind when interpreting the tribological results, as will be addressed below.

3.2 Adsorption behavior of PLL-g-dex: OWLS

A representative adsorption profile for PLL-g-dex copolymer onto the oxide surface as characterized by OWLS is presented in Figure 2 (shown in Figure 2 is the case for the PLL(26.3)-g[3.4]-dex(5.2)). Upon exposure of a waveguide surface to the polymer solution (at $t \approx$ ca. 60 min), the adsorption of PLL-g-dex proceeded very rapidly so that more than the 90% of the final mass of adsorbed polymer was reached within the first 5 min. Since the raw data signals (change in the refractive index) at this stage reflect the contributions from both the surface-bound polymers and the bulk polymer solution, the final adsorbed mass was determined after the flow cell was rinsed with buffer solution (at $t \approx$ ca. 110 min) to exclude the contribution from the bulk solution and loosely bound polymers. The negligible reduction in the adsorbed mass after the rinse indicates that no noticeable polymer desorption occurred during rinsing and assures the formation of a stable polymer adlayer. The same procedure was repeated for all the PLL-g-dex copolymers, as well as dex(5.2), and the results are presented in Figure 3. From the adsorbed mass and the compositional features of

the copolymers, it is possible to calculate the surface concentration of dextran chains, n_{dex} and PLL backbone chains, n_{Lys} , and the spacing between the dextran chains, s , and finally to estimate the conformation of the surface-grafted dextran chains by comparing the spacing and the radius of gyration of dextran chains, $s/2R_g$.⁷ The results of these calculations are summarized in Table 2.

All the PLL-g-dex copolymers employed in this study showed a significant amount of adsorption onto the OWLS waveguide surfaces, ranging from ca. 230 to 290 ng/cm² on average, whereas dextran alone revealed negligible adsorption onto the surfaces (5.3 ± 3.5 ng/cm²). This observation supports the hypothesis that the adsorption mechanism and the conformation of PLL-g-dex copolymer on negatively charged surfaces are very similar those of PLL-g-PEG copolymer,^{1, 6, 7}; the adsorption of the copolymer proceeds through the electrostatic interaction between PLL backbone and the surface in aqueous environment, and thus the PLL backbone lies generally flat on the substrate surface, whereas the dextran side chains stretch into bulk aqueous solution due to their hydrophilic characteristics, forming comb-like brush layers.

Compared to PLL(20)-g[3]-PEG(5), all the PLL-g-dex copolymers examined showed higher adsorbed masses (230 to 290 ng/cm² vs 161 ± 1 ng/cm²). This is thought to be closely associated with the smaller radius of gyration, R_g , of dextran(5.2), 2.35 nm,¹¹ than PEG(5), 2.82 nm.⁴⁸ Assuming that the other structural parameters are identical, a smaller R_g of the side chains of the graft copolymers is expected to enhance the surface adsorption due to weaker shielding of the anchoring groups (charged backbone) by the side chains as well as the weaker steric interactions between neighboring side chains. Furthermore, the hindrance of the side chains for the surface adsorption is exacerbated for the PLL-g-PEG employed in this work due

to the higher number of grafted side chains, $g = 3.0$, than those of the examined PLL-g-dex copolymers, $g = 3.4$ to 7.3 . A more detailed explanation of the factors affecting the adsorption behavior is given below.

The PLL-g-dex copolymers employed in this work are designed such that the structural features of PLL backbone and the dextran side chains are virtually identical, whereas the density of the grafted dextran side chains along the PLL backbone is systematically varied, $g =$ from 3.4 to 7.3 . Nevertheless, the adsorbed masses obtained from the series of PLL(26.3)-g-dex(5.2) copolymers employed in this work showed no clear and consistent trend with the change of grafting ratio, and are nearly constant within the standard deviations (Figure 3). This can be ascribed mainly to the opposing effects of the molecular weight of a single PLL-g-dex copolymer and the probability of adsorption onto surfaces as a function of grafting ratio. As is summarized in Table 1, the variation of grafting ratio, g , from 3.4 to 7.3 , for PLL(26)-g-dex(5.2) can also be viewed as the total number of the grafted dextran chains on a single copolymer molecule ranging from 37.0 ($g = 3.4$) to 17.2 ($g = 7.3$), and, in turn, the molecular weight of the PLL-g-dex copolymers ranging from 207.0 kDa ($g = 3.4$) to 105.1 kDa, on average. In terms of molecular weight, the copolymers with lower g values, such as PLL(26.3)-g[3.4]-dex(5.2), are more likely to be associated with a higher mass of surface adsorption due to the higher number of dextran chains per single copolymer. On the other hand, in terms of adsorption probability and/or stability, the copolymers with higher g values, such as PLL(26.3)-g[7.3]-dex(5.2), are more advantageous, due to the higher number of anchoring groups (un-grafted free lysine units, see Table 1) per single copolymer molecule. Furthermore, the copolymers with higher g values can more readily pack onto the surface with a higher surface density, as a result of the smaller steric hindrance between neighboring dextran side chains. This trend is

clearly manifested in the plot of the PLL backbone chain density, n_{Lys} , and the dextran chain density of PLL(26.3)-g-dex(5.2) series on surface, n_{dex} , as a function of grafting ratio, g , as shown in Figure 4. While the n_{Lys} , which represents the density of the copolymer itself as well, is gradually increasing with increasing grafting ratio, g , the surface density of dextran chains, n_{dex} , which represents the ultimate efficacy of each copolymer to graft dextran chains onto surfaces, is nearly constant due to compensation by the opposing effect of the number of dextrans per copolymer chain.

It should be noted though that the trend described above is specific to the comb-like copolymers with high-molecular-weight side chains. A previous adsorption study of PLL(20)-g-PEG⁷ onto oxide surfaces employing a broad range of grafting ratio (g = from ca. 2 to 20) and the molecular weight of PEG (1, 2, and 5 kDa) has shown that the surface density of PEG chains, n_{PEG} , is monotonically proportional to the inverse of the grafting ratio, i.e. $1/g$, for the case of PLL(20)-g-PEG(1), whereas a ‘leveling-off’ in adsorbed mass from a threshold of grafting ratio becomes gradually more significant with increasing molecular weight of PEG side chains (the threshold being $1/g \approx 0.3$ for PLL(20)-g-PEG(2) series and $1/g \approx 0.2$ for PLL(20)-g-PEG(5) series). This, in turn, suggests that the nearly constant adsorption mass of PLL(26.3)-g-dex(5.2) as well as PLL(20)-g-PEG(5) over a range of g = roughly 3 - 7 is mainly due to the steric hindrance between grafted side chains, rather than the availability of the anchoring groups.⁷

3.3 Lubrication properties of PLL-g-dex

In order to evaluate the lubricating properties of PLL-g-dex copolymer solutions and compare them with other standard aqueous solutions, including HEPES buffer solution, dextran solutions (dex(5.2)), as well as PLL(20)-g[3.0]-PEG(5)

solutions, μ vs. speed plots were acquired under both sliding and mixed sliding/rolling conditions using a pin-on-disk tribometer and MTM, respectively.

3.3.1. Lubrication at sliding contacts: pin-on-disk tribometry

Sliding-contact experiments, carried out by pin-on-disk tribometry, were intended to assess the lubricating capabilities of the polymer solution in the boundary-lubrication regime. As shown in Figure 5, μ values obtained in all cases (load = 2 N) revealed an initial reduction with increasing speed, but they started to level off from roughly 10 mm/s to the highest speed investigated. With respect to the HEPES buffer solution, for which the μ values are roughly 0.2 above 10 mm/s and as high as 0.47 ± 0.04 at the lowest speed (1 mm/s), the dextran solution revealed nearly no improvement in the lubricating properties. This behavior is consistent with the negligible adsorption of dex(5.2) onto the oxide surfaces, as determined by OWLS measurements (Figure 3). However, all PLL-g-dex solutions showed an approximately 50% reduction in μ values compared to those of HEPES solution over the entire speed range investigated; the μ values were generally lower than 0.1 for all polymers tested at speeds above 10 mm/s, although they increased to values between 0.2 and 0.3 at lower speeds (below 2.5 mm/s). As in the case of PLL-g-PEG copolymers^{1, 3}, surface-grafted dextran chains that are stretched out towards the bulk aqueous solution are thought to function as a boundary lubricant.

Although the μ values of all PLL-g-dex solutions were observed to be generally very similar, consistent with their adsorption behavior (Figure 3), those of PLL(26.3)-g-[3.4]-dex(5.2) are slightly, yet noticeably, higher than the others, especially at high-speed regime (≥ 10 mm/s). As was discussed in the section 3.1, the efficacy of all the PLL-g-dex copolymers employed in this work to surface-graft

dextran chains are comparable, as expressed by the n_{dex} values in OWLS experiments (see the Table 2). However, unlike OWLS experiments, which characterize the adsorption behavior of polymers under *static* conditions, the tribological properties are sensitive to the adsorption of the lubricant additives *under tribological stress*. As was addressed in a previous study employing fluorescently labeled PLL-g-PEG copolymers,⁴⁹ the electrostatically adsorbed polymer layers are easily scraped away from the surface during sliding contact in pin-on-disk tribometry, and yet the excess polymers in bulk solution re-adsorb, i.e. ‘self-heal’ the tribostressed area. Thus, the capabilities of the copolymers to quickly re-adsorb onto the surfaces following tribostress-induced desorption becomes of critical importance to maintain effective lubricating performance under cyclic tribological contact. Among the PLL-g-dex copolymers employed in this work, PLL(26.3)-g[3.4]-dex(5.2) is expected to be least effective in ‘self-healing’ capabilities due to the steric hindrance between dextran side chains and the smaller number of anchoring groups, as discussed in the previous section.

Despite the effective lubricating behavior of PLL-g-dex copolymers under sliding-contact conditions, their performance was observed to be slightly inferior to that of PLL(20)-g[3.0]-PEG(5), especially at speeds below 10 mm/s. Since the estimated conformation of PEG and dextran chains, as described by $s/2R_g$, are comparable for the two types of copolymers (see the Table 2), it is unlikely that differences in the conformation of the polymer chains on the surface are the principal cause of this difference. We propose two alternative possibilities. While the surface density of PEG chains, n_{PEG} was lower than that of dextran chains, n_{dex} (see Table 2), dextran and PEG chains may also possess different innate water-based lubricating capabilities, arising from different degrees and mechanisms of hydration and/or

differences in the stiffness of the chains. Secondly, as has already been mentioned in section 3.1, although the molecular weights of the two hydrophilic chains were chosen to be nearly identical in this work, the fully extended dextran chain is significantly shorter than that of the PEG, simply as a consequence of the different chain structures. In addition, unlike the PEG chains, the dextran chains have a small degree of branching,⁵⁰ which will further reduce the extended chain length. Since the fully extended chains length of the dex (5.2) is roughly a half of that of PEG(5), the film thickness of the lubricant layer is expected to be lower for PLL-g-dex than PLL-g-PEG. Further studies to elucidate both factors in detail are currently under way.

3.3.2. Lubrication at mixed sliding/rolling contacts: MTM

The lubricating properties of the PLL-g-dex copolymer solutions under mixed sliding/rolling contact conditions have been characterized by means of MTM. The MTM experiments serve primarily to assess the lubricating properties of the copolymers under milder contact conditions than the pure sliding contacts characteristic of pin-on-disk tribometry. Additionally, due to the much higher speed range available from MTM (up to 2500 mm/s), the formation of a full fluid-film lubricant layer by the polymer solutions can be investigated. Based on the pin-on-disk tribometry results above, two PLL-g-dex copolymers, PLL(26.3)-g[3.4]-PEG(5.2) and PLL(26.3)-g[5.3]-PEG(5.2), which showed slightly different lubricating behavior in sliding contact, have been employed, together with other lubricant solutions. The results are shown in Figure 6.

The μ vs. speed plots shown in Figure 6 revealed significant reduction of μ values in the high-speed regime (starting from ca. 200 mm/s) for all aqueous lubricants employed, including polymer solutions and polymer-free HEPES buffer

solution. The lowest μ value for HEPES buffer solution, 1.9×10^{-3} , which was achieved at the highest speed (2500 mm/s), for instance, represents roughly two orders of magnitude reduction compared with the highest μ value, 0.3, observed from the lowest speed (10 mm/s). This observation suggests that the entrainment of base lubricant, water, is starting to contribute to the lubrication of this mixed sliding/rolling contacts (SRR = 10%) in the high-speed regime. Nevertheless, all the polymer solutions investigated have been observed to further improve the lubricating properties, either in high-speed regime alone or both in low- and high-speed regimes, depending on the type of polymers. For instance, the dextran solution revealed virtually identical μ vs. speed behavior to that of HEPES buffer in the low-speed regime (≤ 100 mm/s), whereas a significant reduction in μ was observed in high-speed regime, as mentioned above. Although dex(5.2) chains do not display noticeable surface-adsorption properties (Figure 3(a)), and thus are poor boundary-lubricant additive, they appear to facilitate the entrainment of aqueous lubricant due to their hydrophilic characteristics.

Meanwhile, the two PLL-g-dex copolymer solutions showed a distinctive reduction in μ values both in low- and high-speed regimes, reflecting their adsorption onto the tribopair surfaces; compared to the dextran solution, the μ values are observed to be consistently lower over nearly the entire speed range investigated. This observation implies that the reduction in μ values in the high-speed regime is not entirely due to the formation of fluid-film, but also due to the improvement in the boundary lubrication properties to a certain extent. In fact, previous combined studies of the film thickness and frictional properties by means of ultra-thin film interferometry and MTM, respectively, have shown that the mixed lubrication mechanism is dominant for the tribological contacts lubricated by PLL-g-PEG

aqueous solutions.³ In contrast to the results for sliding contacts, however, the two PLL-g-dex copolymers showed no noticeable difference in their lubricating properties, presumably because of the characteristics of the tribological contacts provided by MTM; firstly, the contact is much milder due to the dominance of rolling contact (SRR = 10%) under these conditions, and thus the readsoption properties of the molecules are less critical, and secondly the entrainment of the base lubricant, water, becomes more likely, even in the absence of additives with increasing speed.

Lastly, similarly to the case of sliding contacts, the lubricating performance of the PLL-g-dex copolymers under mixed sliding/rolling contact conditions was observed to be inferior to that of PLL(20)-g[3.0]-PEG(5). This difference is more noticeable under low-speed conditions, and starts to diminish with increasing speed, which again suggests that the PLL-g-dex copolymers employed in this study do not perform as effectively as boundary lubricant additives as does PLL(20)-g[3.0]-PEG(5).

4. Conclusions

Comb-like graft-copolymers with dextran side chains (PLL-g-dex) were developed and investigated as biomimetic lubricant additives in an aqueous environment. The synthesized copolymers have been shown to adsorb spontaneously onto metal oxide surfaces, similarly to PLL-g-PEG, and to behave as boundary lubricants, both in the pure sliding and in mixed sliding/rolling contact regimes. The variation of the grafting ratio of the dextran side chains on the PLL backbone revealed no significant influence on either the adsorption or the tribological properties within the range selected in this work: $g = 3.4$ to 7.3 , corresponding to 29.4 to 13.7 % of the available lysine units along the PLL backbone being grafted with dextran chains.

Compared to PLL-g-PEG, the PLL-g-dex polymers employed in this work showed slightly inferior lubricating performance, especially in the boundary lubrication regime. This is mainly attributed to the significant difference in the fully extended chain lengths of dextran(5.2) and PEG(5), since the structures of the chains are completely different (rings vs. single strands). In fact the fully extended chain length of dex(5.2) is estimated to be roughly half of that of PEG(5), which is likely to impact on the performance of the lubricating films. This leaves the possibility that the lubricating properties of PLL-g-dex could be further improved by employing longer dextran chains. This is currently under investigation.

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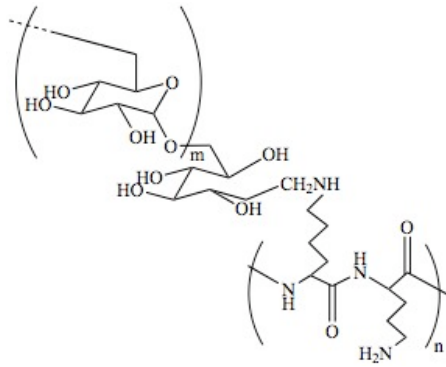


Fig. 1 A schematic illustration of the chemical structure of PLL-g-dextran

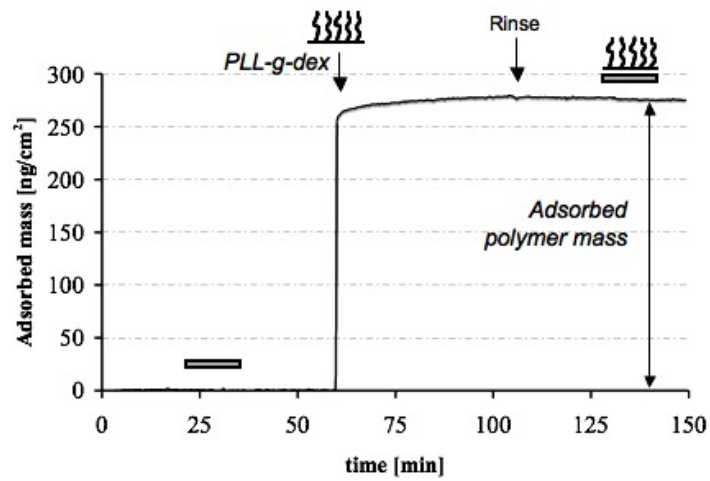


Fig. 2 In situ OWLS measurement of the polymer adsorption from solution onto uncoated waveguide chips

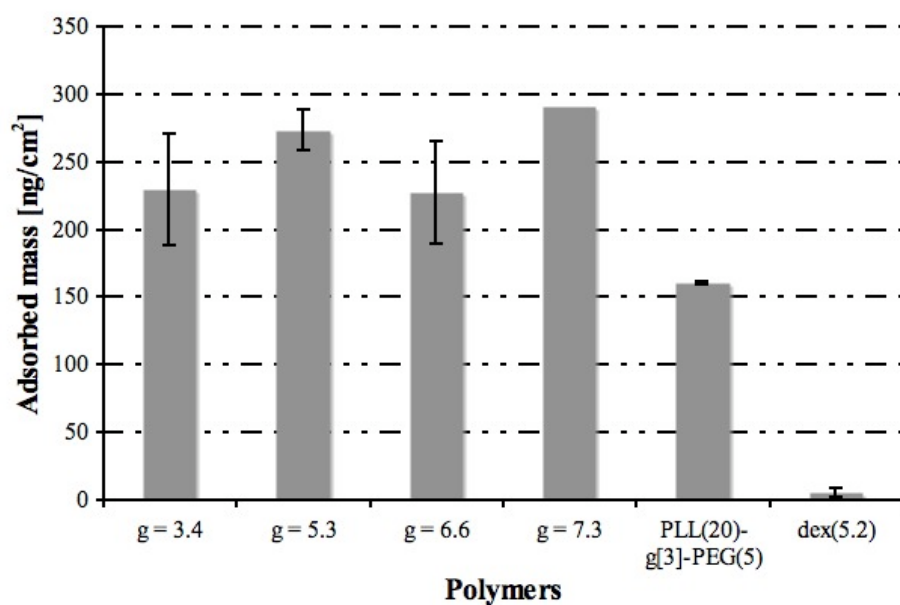


Fig. 3 OWLS results for the adsorption of several PLL-g-dex copolymers (indicated by their grafting ratio, g), PLL-g-PEG and dextran (5.2 kDa) onto bare silica waveguides

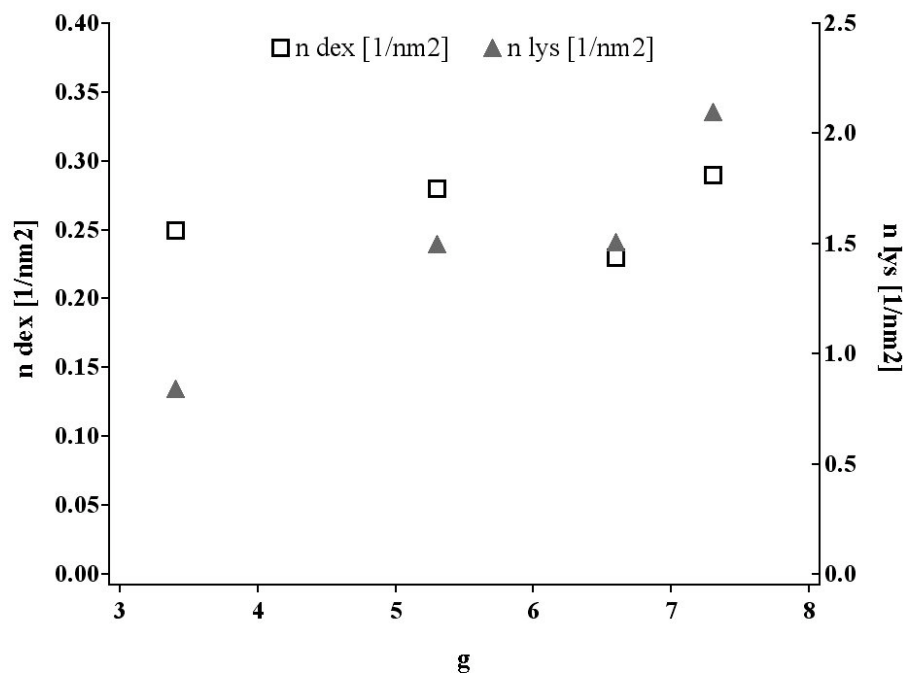


Fig. 4 PLL backbone chain density and dextran chain density of PLL(26.3)-g-dex(5.2) on the silica surface

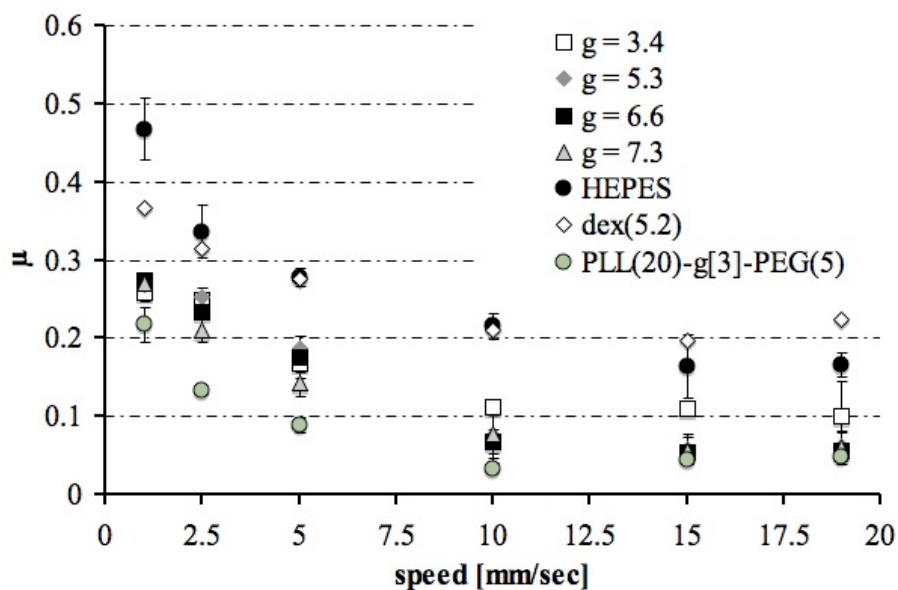


Fig. 5 Sliding pin-on-disc results: coefficients of friction (μ) as a function of the sliding speed. PLL(26.3)-g-dex(5.2) copolymers are indicated by their grafting ratio, g .

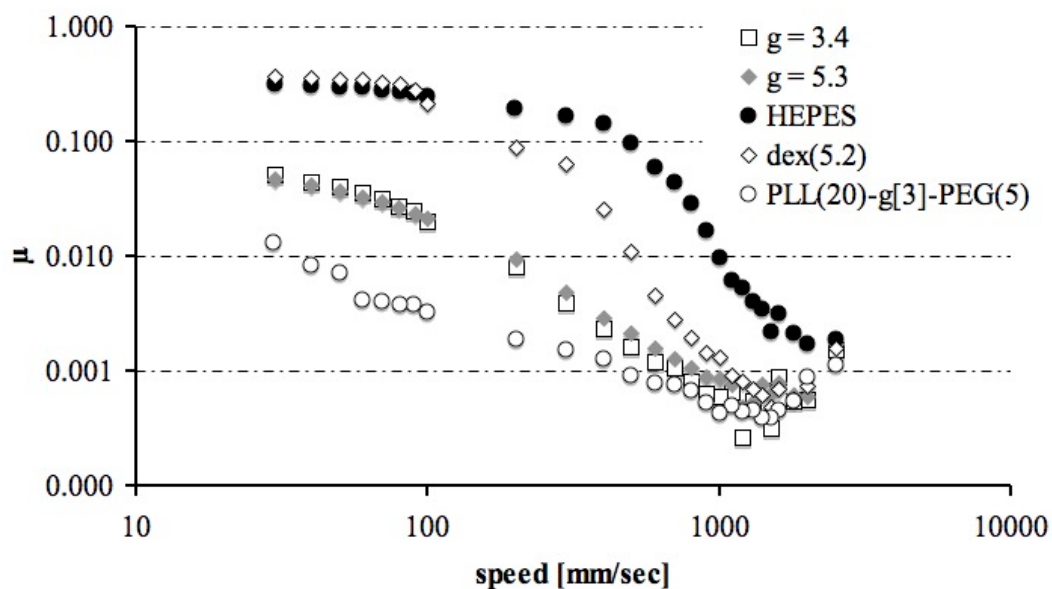


Fig. 6 Mixed sliding/rolling MTM results: coefficients of friction as a function of the sliding speed. PLL(26.3)-g-dex(5.2) copolymers are indicated by the grafting ratio.

Table 1. Synthesized PLL-g-dex copolymers

Polymer	Synthesis yield [%]	No. of grafted side chains per PLL	No. of free lysines per PLL	Percentage of side-chain grafting (%)	M.W. of copolymer (kDa)
<i>PLL(26.3)-g[3.4]-dex(5.2)</i>	30	37.0	88.8	29.4	207.0
<i>PLL(26.3)-g[5.3]-dex(5.2)</i>	60	23.7	102.1	18.9	138.6
<i>PLL(26.3)-g[6.6]-dex(5.2)</i>	56	19.1	106.8	15.2	114.5
<i>PLL(26.3)-g[7.3]-dex(5.2)</i>	27	17.2	108.6	13.7	105.1
<i>PLL(20)-g[2.9]-PEG(5)</i>	-	37.9	75.7	33.4	203.9

(The number of lysine units for the PLL-HBr (26.3 kDa) and PLL-HBr (20 kDa), before grafting with dextran or PEG, is 125.8 and 95.7, respectively. The number of monomer units for the PEG (5 kDa) and dex (5.2 kDa) is 113.6 and 31.8, respectively)

Table 2. Summary of the adsorption data determined by OWLS for the synthesized PLL-g-dex polymers

Surface	m_{pol} [ng/cm ²]	n_{Lys} [1/nm ²]	$n_{dex/EG}$ [1/nm ²]	s [nm]	$s/2Rg$
<i>PLL(26.3)-g[3.4]-dex(5.2)</i>	230 ± 41	0.84	0.25	2.16	0.46
<i>PLL(26.3)-g[5.3]-dex(5.2)</i>	274 ± 15	1.5	0.28	2.02	0.43
<i>PLL(26.3)-g[6.6]-dex(5.2)</i>	228 ± 38	1.51	0.23	2.25	0.48
<i>PLL(26.3)-g[7.3]-dex(5.2)</i>	291	2.1	0.29	2.00	0.43
<i>PLL(26)-g(3)-PEG(5)</i>	161 ± 1	0.54	0.18	2.53	0.45