Self-healing behavior of a polyelectrolyte-based lubricant additive for aqueous lubrication of oxide materials

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We report on the self-healing behavior of a polyelectrolyte-based aqueous lubricant additive, poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-*g*-PEG), during aqueous lubrication of an oxide-based tribosystem. Combined pin-on-disk tribometry and fluorescence microscopy experiments have shown that stable lubricating performance was enabled by means of rapid healing of the worn tribopair surface by polymers dissolved in the adjoining bulk lubricant. This rapid 'self-healing' of PLL-*g*-PEG is attributed to electrostatic interactions between the polycationic poly(L-lysine) (PLL) backbone of the polymer and negatively charged oxide surface. In contrast, a similar healing effect was not readily achievable in the case of methoxy-poly(ethylene glycol)-trimethylsilylether (Sil-PEG), a lubricant additive that is covalently bonded to the surface prior to tribological stress.

KEY WORDS: self-healing, poly(L-lysine)-*graft*-poly(ethylene glycol), methoxy-poly(ethylene glycol)-trimethylsilylether, aqueous lubrication, fluorescence microscopy

1. Introduction

Boundary lubricants (or lubricant additives) are designed and employed to lubricate tribological contacts where asperity–asperity contact is dominant, such as under high-load and/or low-speed conditions. The mechanism of boundary lubrication is thus based upon the modification of shear strength of the tribological interface, rather than a formation of a hydrodynamic film through the entrainment of lubricants. For this reason, the continuous presence of boundary lubricants on the tribopair surface is critical in determining lubrication performance. In general, boundary-lubricating performance has been observed to improve with increasing adsorption energy [1–5]. On the other hand, if the tribostressed boundary lubricant film can heal itself following the tribostress-induced damage, it can offer an alternative efficient solution to the issue of durability under boundary lubrication.

While boundary lubricant additives are present in virtually every oil-based lubricant, the concept of adding boundary lubricants to water, in order to improve its lubrication properties, has been relatively little explored. Recently, it has been shown that a polycationic-based copolymer, poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-*g*-PEG) can be used as an effective boundary

lubricant additive for the aqueous lubrication of oxide-based tribosystems [6–8]. As schematically depicted in figure 1, this copolymer is composed of a polycationic poly(L-lysine) (PLL) backbone and non-reactive poly(ethylene glycol) (PEG) side chains. The adsorption of PLL-*g*-PEG onto oxide substrates is mainly driven by electrostatic interactions between the positively charged PLL backbone and a negatively charged oxide surface in an aqueous environment at neutral pH [6–11]. As will be detailed below in this paper, we have observed that the lubricating performance of PLL-*g*-PEG as an aqueous lubricant additive is significantly enhanced by the presence of excess copolymers in the bulk lubricant; while excess copolymers appear to cure or prevent the degradation of the lubricating performance, a monolayer of PLL-*g*-PEG on the tribopair surface in a polymer-free aqueous environment results in rapid loss of its lubricating capabilities. In this study, in parallel with several control pin-on-disk tribometry experiments, we have employed a novel fluorescence microscopy approach to determine if exchange occurs, during the tribological contact, between the PLL-*g*-PEG copolymers initially adsorbed on the tribopair surface and those dissolved in the adjoining bulk lubricant. In addition, we have also compared PLL-*g*-PEG with its analog possessing covalent-bond-based anchoring groups, methoxy-poly(ethylene glycol)-trimethylsilylether (Sil-PEG), with respect to its 'self-healing' capacity under tribological stress.

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2. Materials and methods

2.1. Polymers

The molecular structure of PLL-*g*-PEG and its conformation at the water/oxide interface are depicted in figure 1. The PLL-*g*-PEG was synthesized by the reaction of *N*-hydroxysuccinimidyl-ester-functionalized PEG (N-hydroxysuccinimidyl ester of methoxy (ethylene glycol) propionic acid, mPEG-SPA, Nektar AL, Huntsville, AL, USA) with the amino groups of PLL hydrobromide (Sigma, St. Louis, MO, USA) at a controlled stoichiometric ratio. Details on the synthesis and analytical information are available in previous publications [10,11]. The PLL-*g*-PEG employed in this work, denoted as "PLL(20)-*g*[3.4]-PEG(5)" [10,11], possesses the molecular weight of 20,000 g/mol for the PLL backbone (including HBr as a precursor), 5,000 g/mol for PEG side chains, and 3.4 for the graft ratio (lysine-mer/PEG side chains). This means that, on average, every 3.4th lysine unit carries a PEG side chain with 113 EG units. The non-functionalized lysine chains will be protonated at pH 7 and therefore responsible for binding to the surface. The polydispersities of the reagents, M_w/M_n, are 1.2 and 1.1 for the PLL backbone and the PEG side chains, respectively.

In order to investigate the tribostress-induced detachment and re-adsorption, i.e. "self-healing", of PLL-*g*-PEG during the sliding contact in pin-on-disk tribometry, PLL-*g*-PEG was labeled by either of the two fluorescence markers: fluorescein 5-isothyocyanate (5-FITC) and rhodamine B isothiocyanate (RBITC) (Fluka, Deisenhofen, Switzerland). Both fluorescence markers are isothiocyanate-activated chromophores and react covalently with the PLL backbone through a thiourea linkage. The fluorescence markers were added in a ratio of roughly one chromophore per 25 lysine monomers, i.e. 3.7 per PLL-*g*-PEG on average.

For comparison, Sil-PEG possessing the identical PEG molecular weight, 5,000 g/mol, as that of PLL-*g*-PEG was purchased (Nektar, Huntsville, AL, USA) and used as received.

2.2. Preparation of substrates and polymer coating

Polymer adlayers were prepared on top of silicon oxide (SiO$_x$) substrates; thermally oxidized Si(100) wafers were used for ellipsometry (ELM) and soda-glass slides (SuperFrost, Menzel-Gläser, Braunschweig, Germany) were used for pin-on-disk tribometry. Prior to polymer coating, the substrates were first ultrasonicated in ethanol for 5 min. and blown dry with nitrogen. Then, they were cleaned in piranha solution (H$_2$SO$_4$:H$_2$O$_2 \approx 3$:1) for 10 min., rinsed with a copious amount of distilled water, and dried with nitrogen again. The substrates were then oxygen-plasma treated for 1 min. in a plasma cleaner (Harrick, Ossining, NY, USA, PDC-32) to remove contaminants and to obtain a well-defined oxide surface.
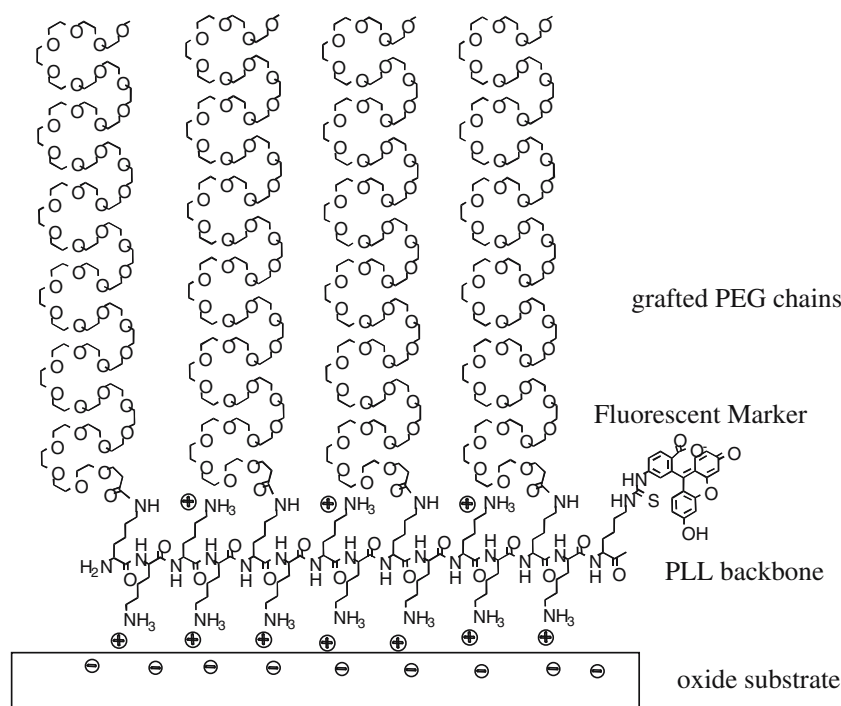

Figure 1. A schematic illustration of PLL-*g*-PEG/FITC adsorbed onto an oxide substrate surface in an aqueous environment (pH 7). Note that the ratio between the lysine monomers grafted to PEG side chains and those available for interaction with the oxide surface in this figure is 1:3 (lysine-mer/PEG side chain = 4), which is slightly different from that of the PLL-*g*-PEG employed throughout the experiments, 1:2.4 (*g* = 3.4). The FITC label is also not necessarily at the end of the PLL chain in reality.

Surface modification of the cleaned substrates with polymers was carried out either *ex situ* (pre-coating) or *in situ*. The pre-coating was achieved by incubating the substrates in the polymer solutions; in PLL-*g*-PEG solution (0.25 mg/ml in HEPES aqueous buffer (10 mM, 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (Sigma) for 30 min. or in Sil-PEG solution (1 mg/ml in toluene or 1 mg/ml in distilled water with 0.05% (v/v) of hydrochloric acid (36–38%) [12]) overnight, respectively. The modified substrates were then rinsed with the respective solvent to remove the unbound or loosely bound polymers. This approach was employed for all of the ELM measurements and some of the pin-on-disk tribometry measurements. For some control pin-on-disk tribometry measurements, *in situ* polymer coating was carried out either by employing polymer solutions as lubricants or injecting the polymer solution into the pin-on-disk tribometer cup during the measurements (see figure 3 for the schematic of the pin-on-disk tribometer).

2.3. Ellipsometry

A Variable Angle Spectroscopic Ellipsometer of the type M200-F (J.A. Woollam Co. Inc., Lincoln, USA) with a spectral range from 245 to 995 nm was used to determine the thickness of the adsorbed polymer layers. Measurements were performed in ambient at three different angles (65, 70, and 75° with respect to the surface normal). For each polymer adlayer, i.e. Sil-PEG (from toluene), Sil-PEG (from acidic aqueous solution), and PLL-*g*-PEG (from aqueous HEPES buffer), five samples were prepared to obtain statistical data. The measurements were fitted with multilayer models using WVASE32 analysis software. The analysis of optical constants was based on a bulk silicon/ SiO_x layer, fitted in accordance with the Jellison model. After adsorption of the molecules, the adlayer thickness was determined using a Cauchy model ($A = 1.45$, $B = 0.01$, $C = 0$).

2.4. Pin-on-disk tribometry

Tribological measurements were performed by means of pin-on-disk tribometry (CSEM, Neuchâtel, Switzerland) [6, 7]. In this setup, a fixed, spherical steel pin (6 mm in diameter, DIN 5401-20, G100, Hydrel AG, Romanshorn, Switzerland) was loaded against a flat glass disk by placing dead weights on top of the pin holder. The sliding speed was controlled with a motor underneath the disk. Friction signals were recorded as a function of the number of revolutions over a fixed sliding track with a Macintosh Power PC using Labview 5.0 (National instruments, Austin, TX, USA). All the measurements were performed in aqueous solution, employing a load and sliding speed of 2 N and 5 mm/s, respectively. The temperature was ca. 20°C. The mean

Hertzian contact pressure for this pair is estimated to be 0.51 GPa under the experimental conditions used in this work. The surface roughness of the steel pin and disk were 10 and 2 nm, respectively.

Generally, the revolution of a pin against a disk was allowed to proceed for up to 50 cycles. For measurements involving fluorescence-labeled PLL-*g*-PEG and subsequent fluorescence microscopy, however, the number of revolutions was carefully controlled over the four adjacent tracks on a single disk.

The steel pins were cleaned by consecutive sonication in toluene for 5 min., in ethanol for 10 min., and distilled water for 5 min. Then, they were oxygen-plasma cleaned for 2 min.

2.5. Fluorescence microscopy

Fluorescence microscopy (Zeiss Axiovert 135 TV, Carl Zeiss, Jena, Germany, equipped with a CCD camera (ORCA-ER, Hamamatsu, Japan)) was employed to visualize the exchange between the pre-adsorbed PLL-*g*-PEG polymers and those dissolved in the adjoining solution during pin-on-disk tribometry measurements. As described above, the PLL-*g*-PEG copolymers from the same batch were marked either by fluorescein isothyocyanate (FITC) or by RBITC. The FITC absorbs light at 490 and 494 nm, and re-emits light at 520 and 525 nm (green). These wavelengths were filtered out with the Zeiss Filter-set No. 10. RBITC absorbs light at 555 nm and emits at 576 nm (red). These wavelengths were filtered out with the Zeiss Filter-set No. 15. In pin-on-disk tribometry, the tribopair was pre-coated with PLL-*g*-PEG labeled with a different chromophore FITC than the excess PLL-*g*-PEG dissolved in the solution RBITC. By changing the wavelength of excitation in the fluorescence microscopy, it was possible to distinguish the two differently labeled polymers and, therefore, verify the exchange between the two in the course of the sliding contacts. The intensity of each fluorescence signal was quantified by means of a brightness profile measured with ImageJ 1.33U (National Institute of Health, Washington, DC, USA) from bitmap files exported from AxioVision 4.2 (Carl Zeiss Vision GmbH).

3. Results and discussion

3.1. Characterization of polymer film thickness

Table 1 shows the results of thickness measurements of the three polymer adlayers by ELM: Sil-PEG from toluene, Sil-PEG from acidic aqueous solution, and PLL-*g*-PEG from HEPES buffer. The highest adlayer thickness was obtained from Sil-PEG adsorbed from toluene (2.21 ± 0.25 nm), followed by PLL-*g*-PEG (1.41 ± 0.05 nm) adsorbed from aqueous HEPES buffer

Sil-PEG (adsorbed from toluene)	Sil-PEG (adsorbed from acidic aqueous solution)	PLL-g-PEG (adsorbed from HEPES buffer solution)
2.21 ± 0.25 nm	0.49 ± 0.06 nm	1.41 ± 0.05 nm

solution, and finally Sil-PEG adsorbed from aqueous buffer solution (0.49 ± 0.06 nm).

Previous studies have shown that the film thickness of PLL-*g*-PEG adlayer is strongly influenced by its architectural features [10, 11], including grafting ratio, (number of lysine units per PEG chain), which simultaneously determines the spacing of PEG chains along the PLL backbone and the number of free protonated amine groups that can serve as surface-anchoring units. Generally, a higher film thickness is expected for smaller grafting ratios, unless the number of free amino groups is too small (e.g. *grafting ratio* ≤ 2.0) [11]. The higher film thickness obtained from Sil-PEG (from toluene) than PLL-*g*-PEG suggests that the lateral spacing between PEG chains of Sil-PEG on the substrate surface is probably closer than that of the PLL-*g*-PEG employed in the present work. Considering that most organic solvents, including toluene, are not 'good' solvents for PEG [9], the collapsed PEG structure of Sil-PEG in toluene can be advantageous for compact adsorption onto substrate surfaces. Although densely packed PEG films can be readily achieved on SiO_x surfaces by adsorption of Sil-PEG from organic solvents, as shown in this work, its usage as an aqueous lubricant additive can be rather inconvenient since the film preparation must always be carried out outside the tribosystem. For this reason, the adsorption of Sil-PEG from aqueous solution, following the method suggested by Papra *et al.* [12], has been employed as an alternative in this work. However, the film thickness of Sil-PEG generated from this approach is clearly smaller than for the other two protocols and molecules considered, while still being readily detectable. This is attributed to uncontrolled polymerization of siloxanes in the presence of water [13–15].

3.2. Pin-on-disk tribometry: poly(L-lysine)-graft-poly (ethylene glycol)

In figure 2(a), the pin-on-disk tribometry measurements for steel/glass tribopairs employing PLL-*g*-PEG as the aqueous lubricant additive are presented. Three sets of experiments with varying surface modification of the tribopair and composition of lubricant are included: (i) an unmodified steel/glass pair in HEPES (○); (ii) a steel/glass pair in PLL-*g*-PEG solution (0.25 mg/ml in HEPES); (□) (iii) a steel/glass pair pre-coated with

PLL-*g*-PEG, then transferred into HEPES (●). For the case of the steel/glass pair in PLL-*g*-PEG solution, i.e. case (ii), the measurement was started 30 min. after immersion of the tribopair into the lubricant (PLL-*g*-PEG solution), to provide sufficient time for the adsorption of polymers onto the tribopair surface. Thus, the difference between the cases (ii) and (iii) is only the presence of the solution-phase PLL-*g*-PEG in the case of (ii).

For the bare steel/glass pair in HEPES, (i), the friction coefficient μ (= friction/load) increased erratically during the initial few revolutions ("running-in" process) and then settled down to a constant value of $\mu \approx 0.5$. On the other hand, the steel/glass pair in PLL-*g*-PEG solution, (ii), showed $\mu \approx 0.1$ from the initial contact, and this value persisted to the end of the measurement without significant variation. Finally, the tribopair pre-coated with PLL-*g*-PEG but tested in polymer-free HEPES aqueous buffer, (iii), exhibited a significant change of μ over the initial ca. five revolutions, then
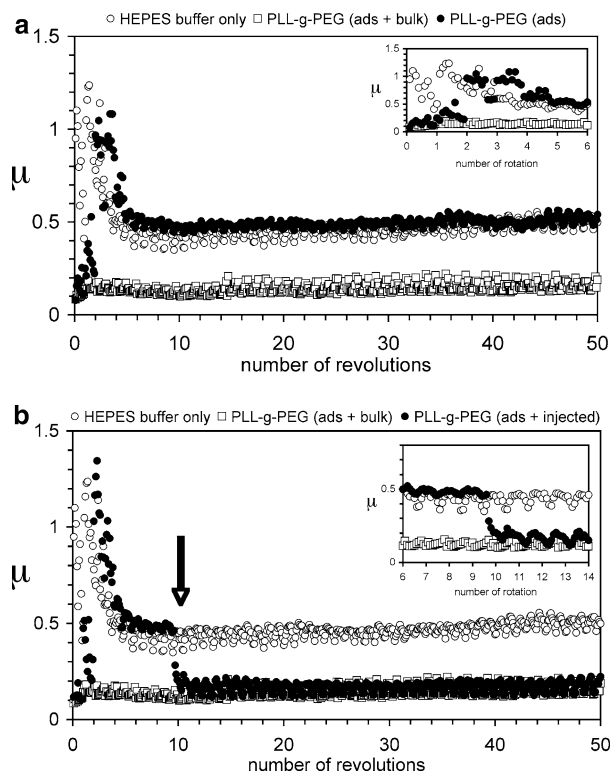

Figure 2. μ versus number of revolutions for sliding contact of a steel/glass (pin/disk) tribopair, by means of pin-on-disk tribometry: (a) in HEPES buffer solution (○); in PLL-*g*-PEG solution (0.25 mg/ml in HEPES buffer solution) (□); and in HEPES buffer solution with PLL-*g*-PEG coating at surfaces (●); (load: 2 N, sliding speed: 5 mm/s, radius of pin: 3 mm). Inset: expanded display of the data for the initial six revolutions, (b) in HEPES buffer solution (○); in PLL-*g*-PEG solution (0.25 mg/ml in HEPES buffer solution) (□); and in HEPES buffer solution with PLL-*g*-PEG coating at surfaces, followed by the injection of concentrated PLL-*g*-PEG solution (●); (final concentration: 0.25 mg/ml) at ∼10th rotation, as indicated by the arrow (load: 2 N, sliding speed: 5 mm/s, radius of pin: 3 mm). Inset: expanded display of the data for the sixth–14th revolutions.

displaying a constant value, similar to that observed for the bare tribopair in HEPES, (i), until the end of the measurement. The detailed variation of μ in the initial testing period is displayed in the inset of figure 2(a); while the μ values for the first one or two revolutions are as low as with those for the steel/glass in PLL-*g*-PEG solution, (ii), those during the third to the fifth revolutions are much higher, and are similar to those of the bare steel/glass pair in HEPES, (i). This observation suggests that some apparently irreversible change in the pre-coated PLL-*g*-PEG film, such as removal or permanent disruption of the film structure, appears to have occurred during the initial sliding period for case (ii). Meanwhile, the consistently low μ values observed in case (iii) imply that such effects can be either prevented or instantaneously repaired by the presence of PLL-*g*-PEG polymers in the bulk lubricant.

To investigate this behavior in more detail, another pin-on-disk tribometry measurement involving a steel/glass tribopair pre-coated with PLL-*g*-PEG, i.e. case (iii), was carried out; for this run, however, an aliquot (5 ml) of concentrated PLL-*g*-PEG solution (1 mg/ml) was injected into the tribometer cup in which a pin-on-disk test was in progress under HEPES (15 ml). Thus, the final concentration was 0.25 mg/ml. The results are shown in figure 2(b). In this plot, the data obtained from two other tribopairs in figure 2(a), (i) and (ii), are also presented for comparison. The initial 10 revolutions are basically a reproduction of the data shown in figure 2(a). However, upon injection of the PLL-*g*-PEG solution at ~10th revolution (as indicated by the arrow), the μ values immediately decreased to the level of the steel/glass pair in PLL-*g*-PEG solution, the case (ii). As shown in the inset of figure 2(b), where the data for the sixth–14th revolutions are magnified, the reduction of μ upon injection of the PLL-*g*-PEG solution is completed even before a single revolution has elapsed. Another injection measurement was carried out, starting with a bare steel/glass tribopair; as in figure 2(b), upon injection of the polymer solution, a rapid reduction of μ was again observed to the level of the tribopair in PLL-*g*-PEG solution (data not shown).

The instantaneous reduction of μ upon injection of PLL-*g*-PEG solution into the tribometer is ascribed to the fast adsorption kinetics of PLL-*g*-PEG onto oxide surfaces at neutral pH. Previous optical waveguide lightmode spectroscopy (OWLS) studies have already revealed that the adsorption of PLL-*g*-PEG onto oxide surfaces, including SiO_x [6, 10] and iron oxide [6], which comprise the tribopair of this work, starts to occur within seconds, upon exposure of an oxide substrate to the polymer solution, and is virtually completed within a few minutes. However, fast adsorption of PLL-*g*-PEG is feasible only when the concentration of the polymer solution is sufficiently high, e.g. > 0.1 mg/ml. In fact, in the low-concentration regime, the lubricating capabilities

of PLL-*g*-PEG solution are clearly inferior, even if excess polymers are present in the bulk solution. Thus, the 'irreversible' change of μ in the initial few revolutions for the tribopair with the pre-coated PLL-*g*-PEG alone (the case (iii) in figure 2(a)) can be understood in terms of the concentration of the PLL-*g*-PEG in bulk solution, which may come from the tribostressed detachment from the tribopair surface, being too low. In other words, at such low concentrations, the tribostress-induced desorption of PLL-*g*-PEG polymers is always faster than their re-adsorption onto the substrate under the experimental condition employed. In the same context, the stable lubricating performance of the PLL-*g*-PEG solution from the initial tribological contact (case (ii) in figure 2(a)) can be attributed to the solution concentration of PLL-*g*-PEG being sufficiently high to replenish, or repair, the worn area instantaneously. Based upon the results in figure 2(a) and (b), it can be inferred that the 'irreversible' change observed for the tribopair only possessing the surface PLL-*g*-PEG film (case (iii) in figure 2(a)) in the initial contact stage is, in fact, simple removal as entire molecules, rather than irreversible disruption of the film structure. Since PLL-*g*-PEG is mainly adsorbed onto SiO_x surfaces through electrostatic attraction in a neutral aqueous environment, adsorption is rapid when bare oxide surfaces are exposed.

3.3. Fluorescence microscopy: poly(L-lysine)-graft-poly (ethylene glycol)

The tribostress-induced desorption of PLL-*g*-PEG and exchange with excess polymers dissolved in the bulk solution has been manifested in a more striking manner by means of fluorescence microscopy. As schematically shown in figure 3, a steel/glass tribopair was pre-coated with PLL-*g*-PEG labeled with FITC (green), and was then transferred into the tribometer cup containing a solution of PLL-*g*-PEG labeled with RBITC (red). On the same disk, four adjacent tribostressed tracks with
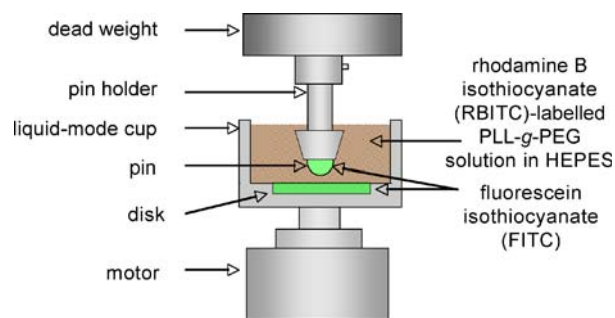

Figure 3. A schematic illustration of the pin-on-disk tribometer and the location of the two different fluorescently labeled PLL-*g*-PEG copolymers (fluorescein isothiocyanate (FITC-PLL-*g*-PEG), pre-coated onto both pin and disk, RBITC-PLL-*g*-PEG, in the lubricant solution, dissolved in HEPES buffer).
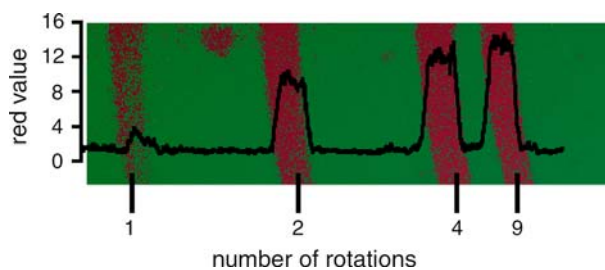
Figure 4. Fluorescence microscopy image of the disk following pin-on-disk tribometry experiment. The number of revolutions was 9, 4, 2, and 1 (in the order of the experiment) in the tracks of radius 1.6, 2.0, 2.4, and 2.8 mm. The load and sliding speed were fixed at 2 N and 5 mm/s, respectively.

varying numbers of revolutions, 1, 2, 4, 9, were generated. Because of their low concentration and small size, the chromophores were assumed to have negligible influence on the tribological properties. Fluorescence microscopy was performed *ex situ* after a drying stage in ambient following pin-on-disk tribometry. The results are shown in figure 4.

It can be clearly seen that, as a function of the number of rotations, part of the FITC-labeled (green) PLL-*g*-PEG, initially adsorbed on the glass disk, has been exchanged by the RBITC-labeled (red) PLL-*g*-PEG during the course of the pin-on-disk tribometry experiment. Since the choromophores are located exclusively on the PLL backbone, this exchange supports the idea that the tribostress applied to the sliding track mainly induces simple, molecular desorption of the entire PLL-*g*-PEG rather than disruption of the film structure or partial removal of the polymer involving the breaking of covalent bonds. It is also noted that the intensity of the red color in the sliding tracks increases upon increasing the number of revolutions. The fluorescence image shown in figure 4 confirms that the exchange of the pre-adsorbed polymer with polymer molecules dissolved in the bulk volume does occur, and that it accounts for the stable lubricating performance of aqueous PLL-*g*-PEG solution, as shown in figure 2(a) and (b). From the absence of color change in the regions between the test tracks, it can readily be observed that exchange of PLL-*g*-PEG between surface and solution does not occur to a detectable extent in the absence of tribological stress.

3.4. Pin-on-disk tribometry: methoxy-poly(ethylene glycol)-trimethylsilylether

In figure 5(a), the pin-on-disk tribometry measurements employing a steel pin and a glass disk pre-coated with Sil-PEG are presented. The data for the unmodified steel/disk in HEPES are also plotted as a reference in this figure. In a similar way to the steel/glass tribopair pre-coated with PLL-*g*-PEG ((iii) in figure 2(a)), the steel/glass tribopair involving the Sil-PEG adlayer on the disk
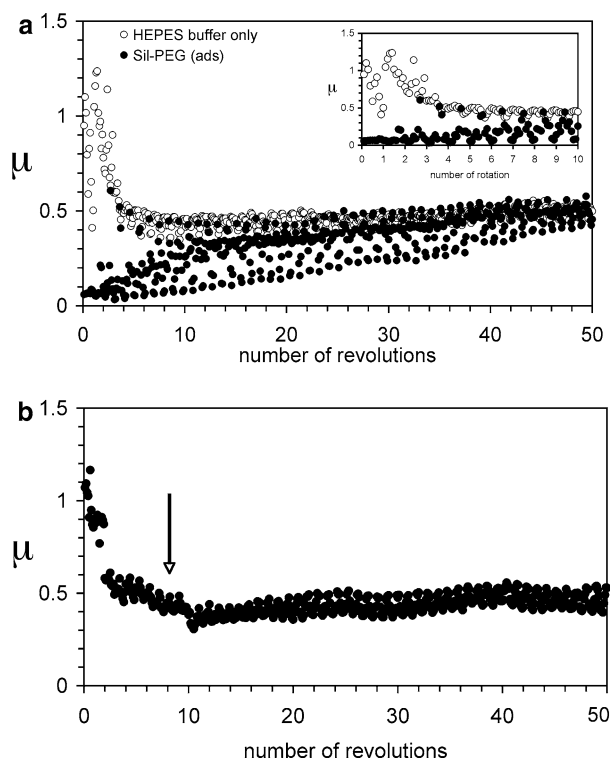

Figure 5. μ versus number of revolutions plots for sliding contact of a steel/glass (pin/disk) tribopair by means of pin-on-disk tribometry: (a) in HEPES buffer solution ($\bigcirc$); and in HEPES buffer solution with Sil-PEG coating at surfaces ($\bullet$); (load: 2 N, sliding speed: 5 mm/s, radius of pin: 3 mm). Inset: enlarged display of the data for the initial 10 revolutions, (b) an aliquot (5 ml) of concentrated PLL-*g*-PEG solution was injected (final concentration, 1.0 mg/ml) at the ~10th rotation, as indicated by the arrow (load: 2N, sliding speed: 5 mm/s, radius of pin: 3 mm).

also exhibited much lower μ values (≈ 0.08) than the *bare* steel/glass tribopair in HEPES, yet only in the initial revolutions. With increasing number of revolutions, the μ values gradually increased, reaching the level of the bare steel/glass tribopair by the end of the measurement. In this plot, 10 data points correspond to one revolution of the sliding contact. Thus, the scatter in friction signals within a single cycle in the majority of the data, ca. fifth–45th revolutions, suggests that the damage to the Sil-PEG coating may be initially occurring due to local asperities, eventually spreading over the entire track.

Although both of the pre-coated polymer films had completely lost their lubricating properties by the 50th rotation, the rate of increase in μ is much slower for the case of Sil-PEG. This difference is clearly demonstrated in the enlarged display of the initial 10 revolutions for the Sil-PEG coating, as shown in the inset of figure 5(a). While the removal of the PLL-*g*-PEG film appears to be virtually completed within the first five revolutions (see the inset of figure 2(a)), it took almost the entire 50 revolutions for the μ of Sil-PEG to reach the same level; the average μ values for the five revolutions are 0.58 ± 0.31 and 0.13 ± 0.13 for the PLL-*g*-PEG and Sil-PEG coatings, respectively. This difference implies that

Sil-PEG adlayer may be more durable than the PLL-*g*-PEG adlayer upon encountering the tribostress applied in this study, at least for the initial revolutions. This is presumably due to the stronger, covalent bonds that join the Sil-PEG coating to the surface as well as the higher initial thickness, leading to a better shielding of small asperities [16].

Previous studies on alkylsilane or alkanethiol self-assembled monolayers (SAMs) have shown that the chemical and structural properties of covalently bound films that have undergone tribostress in macroscopic contacts are diverse, and depend on the detailed experimental conditions, such as load, sliding speed, accumulated number of tribological interactions, and the details of film preparation, as well as bonding characteristics, etc. [17–20]. In the present work, the nature of the damage that occurred to the Sil-PEG films has not been investigated in detail. We were particularly interested in whether the 'self-healing' process, which was observed for PLL-*g*-PEG, could also occur for a covalently bound lubricant additive, such as Sil-PEG. In this sense, even though the film thickness of Sil-PEG adsorbed from acidic aqueous solution was smaller than that adsorbed from toluene (see table 1), an aqueous Sil-PEG solution has the potential to 'heal' the worn surface *in situ* since the liquid phases for both the film preparation and operation are aqueous. However, as shown in figure 5(b), when an aliquot (5 ml) of concentrated acidic aqueous Sil-PEG solution (4 mg/ml) was added into the tribometer cup during a steel/glass tribological test (at $\sim$10th revolution, the final concentration being 1 mg/ml), no noticeable reduction of μ occurred, except for a very transient and minor change at the moment of polymer solution injection. This can be attributed to slower adsorption kinetics of Sil-PEG, as well as a lower adsorption amount from aqueous solution, or a combination of both effects.

4. Summary

We have shown that a polyelectrolyte-based copolymer, PLL-*g*-PEG, displays the unique feature of forming a self-healing lubricating layer for oxide tribosystems in an aqueous environment. When a steel/pin tribopair, pre-coated with a PLL-*g*-PEG adlayer, was subjected to tribological contact by means of pin-on-disk tribometry in polymer-free aqueous buffer solution, the μ values quickly increased to the level of the unmodified tribopair ($\approx$0.5) within only a few revolutions. Meanwhile, the same measurement repeated in PLL-*g*-PEG solution revealed consistently low μ values ($\approx$0.1) from the very initial contact to the end of measurement (50 revolutions). This was attributed to the tribostress-desorbed PLL-*g*-PEG polymers being quickly replaced by the polymers from the bulk lubricant. The exchange between the initially adsorbed PLL-*g*-PEG and that dissolved in the bulk lubricant was most directly manifested by functionalizing the adsorbed and solution-phase polymers with different fluorescing moeities. This behavior is chiefly ascribed to the unique adsorption kinetics of the PLL-*g*-PEG; the polycationic PLL backbone is rapidly attracted to negatively charged SiO_x surface in aqueous solution at neutral pH, due to electrostatic interactions. Although a covalently bonded analogue of PLL-*g*-PEG, Sil-PEG, showed higher durability in the initial stages of sliding, if the film was prepared from toluene, a complete loss of lubricating ability was observed by the end of the measurement. Moreover, *in situ* healing of the worn tribopair did not appear to be feasible when Sil-PEG was used as an aqueous lubricant.

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