Macromolecules **2005,** *38,* 3861−3866

Preferential Solvation and Its Effect on the Lubrication Properties of a Surface-Bound, Brushlike Copolymer

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Received December 9, 2004; Revised Manuscript Received February 20, 2005

ABSTRACT: We have investigated the collapse−stretching transition of a surface-bound, brushlike copolymer, poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-*g*-PEG), and the consequence of such transitions on the frictional properties of this coating. The frictional properties of the interface have been measured by colloidal-probe lateral force microscopy (LFM) in liquid environments on the nanoscale. The collapse−stretching transition has been induced through the systematic variation of the chemical composition of the binary solvent mixture comprised of an aqueous buffer solution and 2-propanol. The influence of solvent composition on the polymer conformation was monitored by comparing measurements conducted with optical waveguide lightmode spectroscopy (OWLS) and quartz crystal microbalance with dissipation monitoring (QCM-D). The combined approach employing QCM-D and OWLS has allowed the quantification of the mass of solvent molecules absorbed in the brushlike structure of PLL-*g*-PEG and has revealed a significant preferential solvation effect. This study has demonstrated preferential solvation of a surface-bound polymer and the role of such solvation in maintaining the favorable lubricating properties of a PEG brush when exposed to mixtures of good and poor solvents.

Introduction

The presence of brushlike polymers, adsorbed or end-grafted onto surfaces, is known to modify friction forces substantially.[1−10] An important parameter influencing the lubricity of brushlike polymers is the quality of the solvent with respect to the polymer brush.[2,4,5,11−13] The current study concerns the structural and frictional properties of a surface-bound, brushlike copolymer, poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-*g*-PEG), in contact with a binary mixture of solvents varying in its solvent quality with respect to PEG.

The influence of the solvent composition on the polymer conformation was investigated by combining measurements involving optical waveguide lightmode spectroscopy (OWLS) and quartz crystal microbalance with dissipation monitoring (QCM-D). Used together, these two methods enable the quantification of the mass of solvent absorbed within the structure of the brushlike copolymer. While the surface-adsorbed mass, as measured by QCM-D, includes a contribution from solvent molecules that are bound or hydrodynamically coupled to the adsorbed film,[14−16] optical techniques, such as OWLS, are sensitive only to the dry mass of a polymer adsorbed onto the surface of the waveguide.[17] As a result, a greater mass is determined using the QCM-D in liquid than that measured by optical techniques (e.g., OWLS or ellipsometry). It is therefore feasible to determine the mass of the solvent molecules per unit substrate area, defined as areal solvation, Ψ, absorbed in the structure of brushlike polymers by subtracting the “dry mass”, derived from OWLS measurements, from the “wet mass” derived from QCM-D measurements.[18−20] The areal solvation is strongly dependent on the solvent quality and has been found to be related to the tribological properties of interfaces comprised of polymer brush structures. In this study, the frictional properties were probed by colloidal-probe lateral force microscopy (LFM), which involved a silica microsphere (diameter = 5.1 μm) attached to a standard silicon nitride cantilever as one of the sliding surfaces. The influence of solvent composition was investigated for the contact of this probe with a PLL-*g*-PEG-modified, oxidized silicon wafer.

The binary solvent mixtures consisted of varying amounts of aqueous buffer solution and 2-propanol. The solvent quality of 2-propanol, with respect to the PEG brush, is clearly inferior to that of aqueous buffer solution. However, PEG is soluble in both solvents, and the two solvents are miscible in any ratio without phase separation.

Some interesting effects of conformational behavior of polymer brushes in binary[21−26] and ternary[27,28] mixtures of solvents have been reported in theoretical and, to a much less extent, in experimental studies, and these have been rationalized in terms of preferential association of one solution component with the polymer layer. The influence of a solvent mixture thus cannot be viewed simply as a combination of the effects of the different solvent components. Preferential association of a solvent component with a surface-bound, brushlike polymer has attracted some attention in the past, particularly because of its great potential for industrial applications (e.g., for filtration and separation processes).[25] However, the shear and tribological properties of surface-bound, brushlike polymers in binary solvent mixtures have, to our knowledge, not been investigated to date, and this is the subject of the present study. In engineering applications, mixtures of solvents or process-related solvent impurities are often unavoidable. Thus,

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10.1021/ma047468x CCC: $30.25

a greater understanding of preferential solvation of brushlike polymers in mixtures of solvents is of great practical importance, not only in tribology but also for many other applications and technologies where brushlike polymers are exposed to complex solvent mixtures (e.g., colloidal stabilization and destabilization, thin-film stability, or protective (antifouling) surface coatings in filtration applications).

This study clearly shows that the superior lubrication properties of surface-bound PLL-*g*-PEG in aqueous buffer solutions also prevail in the binary solvent mixtures, provided that the volume fraction of the solvent of inferior quality is maintained below a certain threshold value. Increasing the volume fraction above a critical threshold value results in both a steep decrease of the mass of solvent molecules absorbed within the polymer brush and a steep increase in the coefficient of friction.

Materials and Methods

Poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-*g*-PEG). The synthesis of poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-*g*-PEG) molecules has been previously described.[29,30] Briefly, poly(L-lysine) hydrobromide (MW 20 kDa, Fluka, Switzerland) was dissolved at a concentration of 100 mM in a 50 mM sodium borate buffer solution, adjusted to pH 8.5, and the solution was filter-sterilized (0.22 μm pore size filter). For the grafting of PEG onto PLL, the *N*-hydroxysuccinimidyl ester of methoxy poly(ethylene glycol) propionic acid (mPEG-SPA, Nektar, Huntsville, AL) was added to PLL−HBr solution. The reaction was allowed to proceed for 6 h at room temperature, after which the reaction mixture was dialyzed (Spectra-Por, molecular weight cutoff size 6−8 kDa, Spectrum, Houston, TX) for 48 h against deionized water. The PEG graft ratio represents the number of lysine monomers per PEG chain and was determined using ^{1}H NMR. The product was freeze-dried and stored in powder form at −20 °C. The nomenclature of these polymers takes the form of PLL(x)-g[y]-PEG(z) and signifies that the graft copolymer has a PLL backbone of molecular weight x kDa, a graft ratio y (equal to the number of lysine units per PEG side chain), and PEG side chains of molecular weight z kDa. In the present study, we used PLL(20)-*g*[3.5]-PEG(5): A PLL backbone of molecular weight of 12 kDa, corresponding to 20 kDa PLL−HBr with a polydispersity of $M_w/M_n = 1.2$, was used for synthesis. The grafting ratio was $g = 3.5$, and PEG side chains were of molecular weight 5 kDa with a polydispersity of $M_w/M_n = 1.1$. The PLL-*g*-PEG was dissolved in 10 mM 4-[2-hydroxyethyl]piperazine-1-[2-ethanesulfonic acid] (HEPES) (Fluka, Switzerland) adjusted to pH 7.4 with 5.0 M NaOH, at a concentration of 0.25 mg/mL. This solution was used for all experiments.

Surface and Solvent Preparation. PLL(20)-*g*[3.5]-PEG(5) adlayers were prepared by incubating SiO_2 films (sputter-coated onto quartz crystals and optical waveguides for QCM-D and OWLS, respectively, and thermally oxidized Si(100) wafers for LFM measurements). Prior to immobilization of the polymer onto the surface, thermally oxidized Si(100) wafers were treated by the following procedure: sonicated in toluene for 2 min, sonicated in 2-propanol for 10 min, extensively rinsed with ultrapure water (18.3 MΩ) (EM Science, Gibbstown, NJ), dried in a nitrogen flow, and exposed to an oxygen plasma PDC-32G (Harrick, Scientific Corp., Ossining, NY) for 2 min. The oxidized substrates were immediately immersed in 0.25 mg/mL solutions of PLL(20)-*g*[3.5]-PEG(5) in 10 mM aqueous HEPES buffer solution for 30 min and subsequently rinsed with polymer-free aqueous HEPES buffer solution to remove free PLL-*g*-PEG from the interface. The SiO_2 sputter-coated quartz crystal sensors and optical waveguides were treated in the same manner as the Si(100) wafers. However, the plasma cleaning was reduced to 10 s in order to prevent damage to the thin SiO_2 coating through ion bombardment incurred in the oxygen plasma. For QCM-D and OWLS, the polymer was allowed to adsorb onto the substrate directly in the liquid chamber. For the binary solvent mixtures, 2-propanol (purity >99.5%, Fluka, Switzerland) was mixed in varying quantities with the aqueous HEPES buffer solution.

Optical Waveguide Lightmode Spectroscopy (OWLS). OWLS was carried out on a BIOS-I instrument (ASI AG, Zürich, Switzerland) using a Kalrez (Dupont, Wilmington, DE) flow-through cell. The waveguide chips used for OWLS measurements were purchased from MicroVacuum Ltd. (Budapest, Hungary) and consisted of a 1 mm thick glass substrate and a 200 nm thick $Si_{0.75}Ti_{0.25}O_2$ waveguide layer at the surface. A thin silicon oxide layer (ca. 12 nm) was sputter-coated on top of the waveguide layer in a Leybold dc magnetron Z600 sputtering unit. The coating conditions and the principles of OWLS investigations have been described in detail elsewhere.[17,31,32] It is important to note that the surface-adsorbed mass density determined by OWLS is regarded as a "dry mass", m_{dry}, due to the fact that solvent molecules coupled to the adsorbate do not contribute to a change in the refractive index and thus do not contribute to this measurement of adsorbate mass.

The OWLS technique is highly sensitive (detection limit ≃ 1 ng/cm^2) and allows for the direct online monitoring of macromolecular adsorption.[32] Thus, in the present study, a measurement error of less than 1% is expected.

Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D). QCM-D measurements were performed with a commercial quartz crystal microbalance with dissipation monitoring (Q-Sense, Gothenburg, Sweden).[14] The instrument was equipped with a home-built laminar flow cell with a glass window that allowed visual monitoring of the injection and exchange of the liquids in the flow cell. The sensor crystals used in the measurements were 5 MHz AT-cut crystals sputter-coated with SiO_2 (Q-Sense, Gothenburg, Sweden). All measurements were recorded at four different resonant frequencies f_0 (5, 15, 25, and 35 MHz). The QCM-D liquid chamber was temperature-stabilized to 25 ± 0.02 °C. The QCM-D response, i.e., changes in resonant frequency, f_0, and dissipation factor, D, at different overtones, is, in contrast to OWLS, sensitive to the viscoelastic properties and density of any mass coupled to the mechanical oscillation of the quartz crystal.[32] In our case, the adsorbed mass consisted of the copolymer, PLL-*g*-PEG, along with any solvent molecules coupled to the polymer. Hence, QCM-D is sensitive to the "wet mass", m_{wet}, of a polymer in contrast to the "dry mass", m_{dry}, obtained by OWLS. To determine the influence of the mixture ratio of the binary solvent mixture on the measured mass, f_0 and D of a single quartz crystal were measured in the pure solvents and in the binary HEPES/2-propanol solvent mixtures of differing relative proportions. Then, PLL-*g*-PEG was allowed to adsorb from aqueous HEPES buffer solution for 30 min, and after rinsing with polymer-free aqueous HEPES buffer solution, Δf_0 and ΔD were measured in aqueous HEPES buffer solution and in the binary solvent mixtures.

The changes in the resonant frequencies f_0 (15, 25, 35 MHz) were related to m_{wet} of the adsorbed layer through a Voigt-based model (software: Q-tools, version 2.0.1) where the adsorbed layer is represented by a homogeneous viscoelastic film characterized by a shear viscosity, η_{shear}, a shear modulus, E_{shear}, and a film thickness, h_{film}.[33−35] The input parameters include both the viscosity, η, and the density, ρ, of the solvent, as well as the density of the polymer film, ρ_{film}. The primary resonant frequency f_0 (5 MHz) was discarded due to its instability during data acquisition. The viscosities and densities of the solvent mixtures used in the present study were derived from a linear interpolation of the values for pure water ($\eta = 1$ mPa·s, $\rho = 0.997$ g/cm^3) and pure 2-propanol ($\eta = 2.86$ mPa·s, $\rho = 0.786$ g/cm^3).[36] However, ρ_{film} remains unknown. A fairly good approximation for ρ_{film} was derived from eq 1:

$$\rho_{\text{film}} = \frac{\Delta m_{\text{QCM-D(Sauerbrey)}} - \Delta m_{\text{OWLS}}}{\Delta m_{\text{QCM-D(Sauerbrey)}}}\rho_{\text{solvent}} + \frac{\Delta m_{\text{OWLS}}}{\Delta m_{\text{QCM-D(Sauerbrey)}}}\rho_{\text{polymer}} \quad (1)$$

where $\Delta m_{\text{QCM-D(Sauerbrey)}}$ is the mass derived from the Sauerbrey equation,[15] ρ_{polymer} is the density of PLL-*g*-PEG ($\approx$1 g/cm^3), and ρ_{solvent} denotes the density of the liquid. Finally, the adsorbed wet mass (per unit substrate area) of PLL-*g*-PEG was calculated by multiplying ρ_{film} by the film thickness h_{film} derived from the Voigt-based model.

QCM-D is highly sensitive, and the minimum detectable mass change is $\approx$1 ng/cm^2.[37]

Atomic Force Microscopy. A home-built atomic force microscope was used to probe frictional forces of the polymer-modified SiO_2 substrates under liquid environments. The microscope was equipped with a liquid cell/tip holder (Digital Instruments, Santa Barbara, CA), and controlled by SPM 1000 electronics and SPM 32 software (RHK Technology, Inc., Troy, MI). A silica microsphere (diameter = 5.1 μm), attached to an AFM cantilever (Novascan Technologies, Ames, IA), was used as the counterface to the polymer-modified SiO_2 surface. Kinetic friction data were acquired by monitoring the lateral deflection of the cantilever as a function of position across the sample surface while sliding. While the sample was rastered in a line-scan mode, the load was first increased and then decreased. During this procedure, frictional forces and normal forces were measured simultaneously at a scan speed of $\approx$1400 nm/s over a distance of 100 nm. The reported frictional data represent the average of at least six results obtained at different locations as a function of decreasing load across the surface. Valid comparisons of frictional data have been enabled through the use of the same tip/cantilever assembly throughout a set of measurements. Normal loads were limited to 30 nN in order to avoid wear of the tip and surface, which would invalidate the comparison of frictional data. AFM measurements were carried out in the sequence of pure 2-propanol, binary solutions of decreasing 2-propanol volume fraction, and pure aqueous HEPES buffer solution. The composition of the liquid environment encompassing the tip–sample interface was controlled by transferring aliquots of solution in and out of the liquid cell through the use of two 5 mL syringes.

In the reported AFM measurements, normal loads have been calibrated directly from the reported spring constant of the AFM cantilever (0.58 N/m), while the friction forces have been calibrated through an improved wedge calibration method. Briefly, the experimental force calibration was made by sliding the tip across a silicon grating surface containing two known slopes (TGG01, MikroMasch, Tallinn, Estonia) as a function of applied load. More details of this calibration method have been reported elsewhere.[38,39]

Results

PLL-*g*-PEG adsorbs readily onto SiO_2 substrates, which are negatively charged at pH 7.4, through electrostatic interaction with the positively charged PLL backbone, forcing the PEG side chains into a dense, brushlike structure.[29] The molecular structure of PLL-*g*-PEG and a schematic diagram of PLL-*g*-PEG adsorbed onto a negatively charged surface are depicted in Figures 1 and 2. From previous tribological studies, it is known that the PEG side chains of PLL-*g*-PEG are highly hydrated in aqueous solution.[40–42] In the current study, we have investigated the influence of the brush collapse transition on the frictional properties of PLL-*g*-PEG. The conformational collapse of the PEG brush was induced by varying the volume fraction of 2-propanol, Φ, in the binary solvent mixture with aqueous HEPES buffer solution. The collapse transition was monitored by determining the areal solvation, Ψ, of the surface-bound brushlike PLL-*g*-PEG structure. This was derived by comparing the results of individual QCM-D and OWLS measurements. The comparison of the two different techniques provides complementary information regarding the amount of polymer adsorbed onto the surface and the amount of solvent that is absorbed in the surface-bound PLL-*g*-PEG layer.[18–20] Thus, it is feasible to quantify the areal solvation, Ψ, of surface-bound brushlike PLL-*g*-PEG, by subtracting the dry mass, m_{dry}, obtained by OWLS, from the wet mass, m_{wet}, obtained by QCM-D.

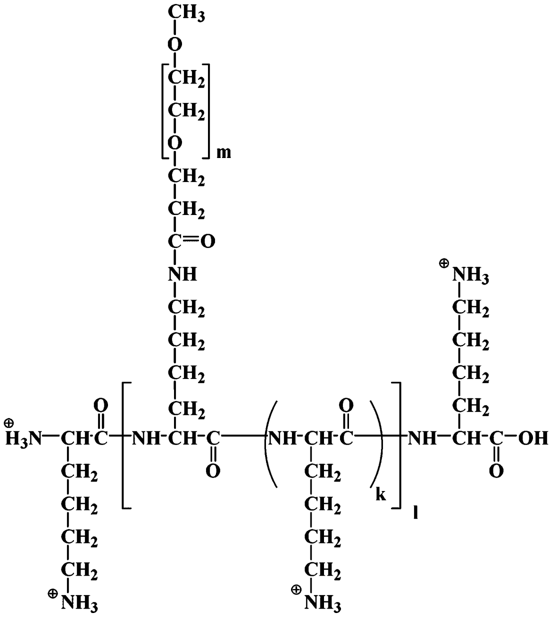

Figure 1. Structure of PLL-*g*-PEG.

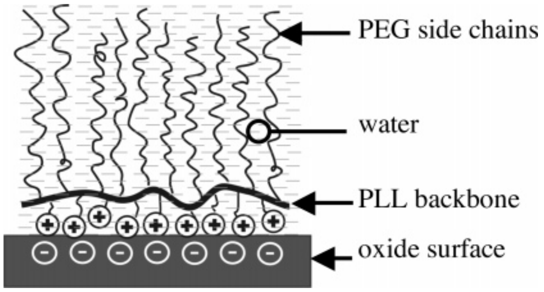

Figure 2. Schematic diagram of PLL-*g*-PEG adsorption onto a negatively charged oxide surface in aqueous solution.

Both QCM-D and OWLS revealed a rapid adsorption of PLL-*g*-PEG in aqueous HEPES buffer solution onto the SiO_2 substrates. Approximately 95% of the total adsorbed mass was reached within the first 5 min of exposure to the polymer-containing solution. For the purposes of standardization, the adsorption process was regarded to be complete 30 min after injection of PLL-*g*-PEG. Following rinsing with polymer-free aqueous HEPES buffer solutions, no apparent polymer desorption could be observed. The wet and the dry mass of a PLL(20)-g[3.5]-PEG(5) adlayer, adsorbed from aqueous HEPES buffer solution onto a SiO_2 substrate, are m_{wet} = 1240.6 ng/cm^2 and m_{dry} = 197.8 ng/cm^2, respectively, resulting in Ψ = 1042.8 ng/cm^2. In other words, the ratio of the mass of buffer solution to the mass of polymer in the adlayer is $\approx$6.3, indicating that a significant amount of aqueous buffer solution has been absorbed within the structure of the surface-bound PEG brush.

Figure 3 shows the change in the areal solvation, Ψ, as a function of the volume fraction of 2-propanol, Φ,

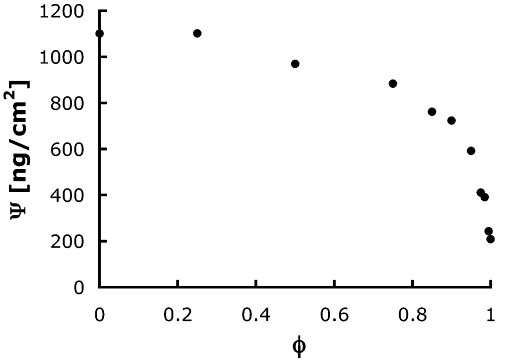

Figure 3. Areal solvation, Ψ, of surface-bound PLL-*g*-PEG as a function of the composition of the binary solvent mixture, Φ (Φ = 1, pure 2-propanol; Φ = 0, pure aqueous HEPES buffer solution).

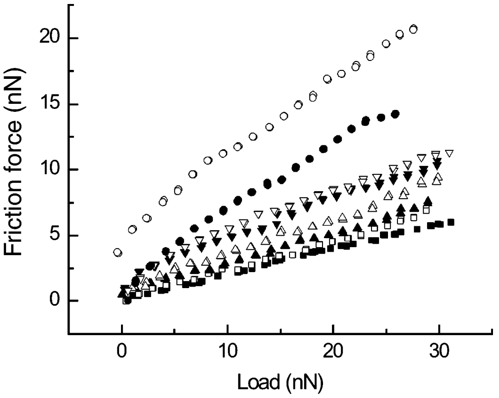

Figure 4. Friction force measured as a function of decreasing load for different compositions of the binary solvent mixture: ■, Φ = 0; □, Φ = 0.25; ▲, Φ = 0.5; △, Φ = 0.75; ▼, Φ = 0.85; ▽, Φ = 0.9; ●, Φ = 0.95; ○, Φ = 1. Friction was measured between a bare silica sphere (5.1 μm diameter) and a PLL-*g*-PEG-modified oxidized silicon wafer.

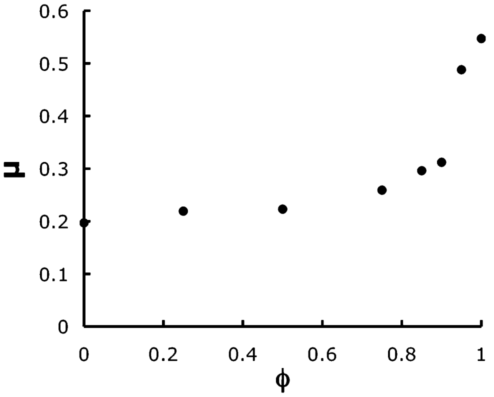

Figure 5. Coefficients of friction, μ, vs the chemical composition of the binary solvent mixture, Φ (Φ = 1, pure 2-propanol; Φ = 0, pure aqueous HEPES buffer solution). Coefficients of friction were derived from a linear regression of the friction−load plots shown in Figure 4.

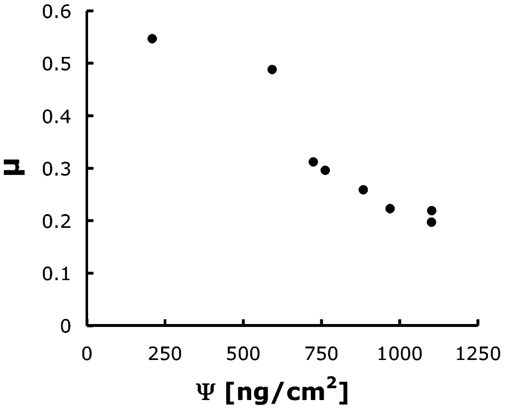

Figure 6. Coefficient of friction, μ, vs areal solvation*,* Ψ.

in the binary solvent mixture (Φ = 1, pure 2-propanol; Φ = 0, pure aqueous HEPES buffer solution). It is noted that PLL-*g*-PEG was allowed to adsorb only from pure aqueous HEPES buffer solution. Subsequent variation of Φ in the range of 0 to ≈0.85 caused a uniform, slow decrease in the mass of solvent molecules found within the brushlike PEG structure from Ψ = 1101.3 ng/cm^2 to Ψ = 761.8 ng/cm^2. However, in the narrow range of $0.85 < \Phi < 1$, Ψ drops dramatically and reaches a value of Ψ = 208.7 ng/cm^2 for pure 2-propanol. The highly solvated and extended PEG brush thus collapses to a poorly solvated, random coillike conformation within a very narrow range of 15% of the solvent mixture ratio. Figure 4 displays friction−load plots measured by colloidal-probe LFM in different solution mixtures between a bare silica sphere and a PLL-*g*-PEG-modified, oxidized silicon wafer. No velocity dependence was detected over the range accessible to our AFM (maximum speed ≈ 2 μm/s). The relationship between the friction force and the load, depicted in Figure 4, is approximately linear above 10 nN, while adhesion is negligible compared to the magnitude of frictional forces measured, suggesting that the data may be fitted using Amonton's law. The resulting coefficients of friction, μ, determined by linear regression, are shown in Figure 5 as a function of Ψ. A variation of $0 < \Phi < 0.85$ results in a slow increase of the coefficient of friction from μ = 0.20 to μ = 0.30. Similarly, the coefficient of friction increases sharply when the 2-propanol fraction exceeds Φ ≈ 0.85 and reaches a value of μ = 0.55 in pure 2-propanol. A plot of μ vs Ψ, as depicted in Figure 6, demonstrates a strong correlation between the mass of solvent molecules absorbed within the brushlike structure of PLL-*g*-PEG and the film's lubricity. The coefficient of friction is observed to decrease uniformly with increasing number of solvent molecules within the polymer−brush structure.

To eliminate the possibility of a systematic change in solvation and friction with time, several measurements were repeated in a random order. The results were in excellent agreement with the previous measurements and did not show any dependence on the sequence of solvent exchange. Thus, the solvent exchange within the PEG brush appears to be fully reversible.

Discussion

We have investigated the structural and the frictional properties of the brushlike copolymer PLL(20)-*g*[3.5]-PEG(5) in binary mixtures of an aqueous HEPES buffer solution and 2-propanol. An aqueous HEPES buffer solution is regarded as a good solvent whereas 2-propanol is clearly inferior in quality with respect to PEG structures.

By applying the combined experimental approach of OWLS and QCM-D, it was feasible to quantify the areal solvation, Ψ, of the surface-bound brushlike copolymer PLL-*g*-PEG. As shown in Figure 3, the PEG brush was found to change from a highly solvated to a poorly solvated state in an abrupt and nonuniform way within a very narrow range of solvent conditions involving high 2-propanol concentrations ($0.85 < \Phi < 1$). The change in friction forces exhibited a similar trend; the coefficient of friction, μ, sharply increases when the volume fraction of 2-propanol exceeds $\Phi \approx 0.85$, whereas μ is only moderately influenced in the range of $\Phi < 0.85$. The roughly linear relationship between μ and Ψ, as revealed in Figure 6, is indicative of a strong correlation between the friction properties of PLL-*g*-PEG and the mass of solvent absorbed within the polymer brush.

It is important to note that areal solvation was measured in the unperturbed brushlike structure of the PEG chains. The coefficient of friction, however, was measured in the tribocontact of a colloidal probe and a flat substrate surface, where the brushlike structure of the PEG chains is compressed as a function of the applied load. Solvent molecules will be released from the compressed polymer interface, causing a reduction in the areal solvation. The release of solvent molecules depends on the polymer/solvent interaction strength. Thus, under compression, the binary solvent composition may deviate from that measured in the ideal case of zero compression. Nonetheless, the reports presented here clearly portray a systematic trend in the correlation between interfacial friction and areal solvation, suggesting that the effect of solvent release due to compression under these light loads is not dominant. Under alternative geometries and higher loads such effects may well play a more significant role.

PEG solubility in an aqueous environment has been widely investigated as it is thought to be directly related to its unique capacity for protein resistance, which has led to PEG occupying a key role in biomedical and biotechnical applications. At room temperature, PEG displays a distinctive solubility behavior in water, as it is fully miscible at all concentrations and is known to form extended brushlike structures when grafted to flat surfaces.[29,43] This characteristic stands in sharp contrast to the water solubility of other polyethers, such as poly(oxypropylene) $-[CH_2CH(CH_3)O]_n$ and poly(oxytrimethylene) $-[CH_2CH_2CH_2O]_n$, which slightly differ in the number of methylene groups within one monomer unit and are completely insoluble in water.[44] Despite intensive theoretical and experimental studies on the solubility of PEG and related polyethers, it is still not clear to what extent different characteristics of the polymers contribute to their solubilities.[45−48] However, it is generally accepted that PEG has a strong tendency to form hydrogen-bonded water complexes, on average comprising three water molecules per EG repeat unit. The opportunity for hydrogen bonding and the presence of such complexes in a polar medium favor a trans−trans−gauche (*ttg*) conformation of the majority of EG chain segments.[49] In 2-propanol, however, the formation of stabilized solvent structures associated with repeating EG units is absent because the ability of 2-propanol to form hydrogen bonds is significantly weaker than that of water. Thus, in 2-propanol, PEG adopts a more random-coil-like conformation, which is entropically favored.[49] In addition, because of the poorer solvent quality, the EG−EG interactions become relatively more attractive in 2-propanol, further hindering the formation of the extended brushlike structure of the PEG chains in aqueous solutions.

The nonlinear change of both Ψ and μ upon increasing the volume fraction of 2-propanol is ascribed to partial solvent demixing. As a result, the relative proportions of aqueous HEPES buffer solution and 2-propanol are different inside and outside the PEG brush. Partial solvent demixing of separate polymer coils in solvent mixtures was first studied in the late 1960s by Dondos and co-workers.[50−53] Some 20 years later, partial solvent demixing was theoretically and experimentally investigated for surface-bound brushlike polymers.[21−28] Auroy et al.[25] were the first to experimentally verify the effect of preferential solvation for surface-grafted, brushlike polymers. By means of small-angle neutron scattering (SANS) experiments, they found that the collapse−stretching transition of surface-grafted poly(dimethylsiloxane) chains in the binary solvent mixture of methanol−dichloromethane is associated with the preferential solvation of brush structure by the good solvent component.

When PEG is exposed to a binary mixture of water and an organic solvent, we postulate that the strong affinity between water and the EG monomers creates enthalpic penalties for the disruption of the EG−water bonds. This is the reason for the exclusion of the organic solvent molecules from the PEG brush, which remains highly hydrated up to high volume fractions of 2-propanol. However, above a critical volume fraction of $\Phi \approx 0.85$, the discrepancy in entropy between the solvent composition inside and outside the brush can no longer be maintained, and any further increase in 2-propanol fraction results in a sudden collapse of the brushlike polymer structure to a more random-coil-like polymer conformation. As shown in the present study by means of LFM, the collapse transition of the PEG brush is accompanied by a significant increase in friction between the bare colloidal LFM tip and the PLL-*g*-PEG-modified SiO_2 substrate. The importance of the solvency state of a brushlike copolymer with respect to its lubrication properties is clearly seen in the roughly linear relationship between Ψ and μ shown in Figure 6. We propose that this relationship is related to the location and nature of interfacial shear. In the presence of highly solvated structures shear is likely to occur in the region of liquidlike structures. Thus, under good solvent condition the resulting friction is relatively low ($\mu \approx 0.2$) while friction increases under poor solvent conditions up to a value of $\mu \approx 0.6$. Raviv et al.[54] have reported on the properties and interactions of physigrafted, end-functionalized PEG layers measured by means of SFA. For the symmetrically PEG-grafted ($M_w = 3400$ Da) tribointerface, Raviv et al.[54] reported a coefficient of friction measured from the onset of detectable shear forces of $\mu = 0.03$ that sharply increased at higher compression ratios by an order of magnitude. In contrast to Raviv et al.'s data, the friction measurements in this work were performed in the asymmetric configuration, where only the flat substrate surface was coated by the polymer and the colloidal probe remained bare. Thus, no superior lubrication properties, as reported by Raviv et al.[54] for the ideal triboconditions, are expected in the present study. However at higher contact pressure, the coefficients of friction obtained in the present study under good solvent conditions are similar to those obtained by Raviv et al.[54]

Conclusions

We have investigated the behavior of the brushlike copolymer PLL-*g*-PEG, exposed to binary mixtures of an aqueous HEPES buffer solution and 2-propanol. The frictional properties of a PLL-*g*-PEG modified silica wafer were probed by colloidal-probe LFM and entailed the contact of a bare silica microsphere (diameter = 5.1 μm) with the polymer-modified silica substrate.

The experimental results of this study show that the adsorbed polymer changes from an expanded brushlike structure to a more random-coil-like polymer conformation within a very narrow (15%) range of binary solvent composition, $0.85 < \Phi < 1$. The collapse transition is accompanied by a dramatic increase in the friction coefficient. For values of $\Phi < 0.85$, both solvation and the coefficient of friction were only moderately affected by the solvent-mixture composition. These effects were related to a preferential solvation of the PEG brush by the good solvent component, driven by the strong affinity existing between water molecules and the EG monomers. Enthalpic barriers prevent the disruption of favorable EG−water interactions, thus excluding the 2-propanol solvent molecules from the PEG brush at mixing ratios of $\Phi < 0.85$. However, the discrepancy between the solvent mixing ratio inside and outside the brush, caused by the partial demixing, cannot be maintained above a critical mixing ratio, $\Phi \approx 0.85$, and the PEG brush rapidly collapses to a dense layer accompanied by a considerable increase in the measured friction forces.

In summary, these results demonstrate that preferential solvation effectively extends the favorable tribological properties of PLL-*g*-PEG found in aqueous solutions into the regime of solvent mixtures, including those containing components characterized as poor solvents. Preferential solvation is seen to facilitate the use of brushlike polymers as effective boundary lubricants in nonideal environmental conditions where the polymer is exposed to mixtures of good and bad solvents. This is particularly interesting for potential industrial applications of brushlike polymers as lubricant additives, where solvent mixtures are more often the rule than the exception (e.g., contamination or process-related solvent impurities). The extent of this effect, however, will vary considerably for different solvent mixtures, depending heavily on the energetics of solvent/solvent and solvent/PEG interactions.

Acknowledgment. This work was financially supported by the Council of the Swiss Federal Institutes of Technology (ETH-Rat TopNano 21) and the US Air Force Office of Scientific Research (Contract F49620-02-1-0346). We are also grateful to Dr. Janos Vörös of the Laboratory of Surface Science and Technology (LSST), ETH Zürich, Switzerland, for his valuable advice and assistance in the QCM-D and OWLS experiments.

References and Notes

(1) Klein, J.; Kumacheva, E.; Mahalu, D.; Perahia, D.; Fetters, L. J. *Nature (London)* **1994**, *370*, 634−636.
(2) Klein, J.; Kumacheva, E.; Perahia, D.; Mahalu, D.; Warburg, S. *Faraday Discuss.* **1994**, *98*, 173−188.
(3) Tadmor, R.; Janik, J.; Klein, J.; Fetters, L. J. *Phys. Rev. Lett.* **2003**, *91*, art. no. 115503.
(4) Grest, G. S. *Adv. Polym. Sci.* **1999**, *138*, 149−183.
(5) Schorr, P. A.; Kwan, T. C. B.; Kilbey, S. M.; Shaqfeh, E. S. G.; Tirrell, M. *Macromolecules* **2003**, *36*, 389−398.
(6) Joanny, J. F. *Langmuir* **1992**, *8*, 989−995.
(7) Klein, J.; Kumacheva, E.; Perahia, D.; Fetters, L. J. *Acta Polym.* **1998**, *49*, 617−525.
(8) Klein, J. *J. Annu. Rev. Mater. Sci.* **1996**, *26*, 581−612.
(9) Grest, G. S. *Phys. Rev. Lett.* **1996**, *76*, 4979−4982.
(10) Granick, S.; Kumar, S. K.; Amis, E. J.; Antonietti, M.; Balazs, A. C.; Chakraborty, A. K.; Grest, G. S.; Hawker, C.; Janmey, P.; Kramer, E. J.; Nuzzo, R.; Russell, T. P.; Safinya, C. R. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 2755−2793.
(11) Granick, S.; Demirel, A. L.; Cai, L. L.; Peanasky, J. *Isr. J. Chem.* **1995**, *35*, 75−84.
(12) Cai, L. L.; Peanasky, J.; Granick, S. *Trends Polym. Sci.* **1996**, *4*, 47−51.
(13) Dhinojwala, A.; Cai, L.; Granick, S. *Langmuir* **1996**, *12*, 4537−4542.
(14) Rodahl, M.; Höök, F.; Krozer, A.; Brzezinski, P.; Kasemo, B. *Rev. Sci. Instrum.* **1995**, *66*, 3924−3927.
(15) Rodahl, M.; Kasemo, B. *Sens. Actuators, A* **1996**, *54*, 448−456.
(16) Marx, K. A. *Biomacromolecules* **2003**, *4*, 1099−1120.
(17) Vörös, J.; Ramsden, J. J.; Csucs, G.; Szendro, I.; De Paul, S. M.; Textor, M.; Spencer, N. D. *Biomaterials* **2002**, *23*,3699−3710.
(18) Craig, V. S. J.; Plunkett, M. *J. Colloid Interface Sci.* **2003**, *262*, 126−129.
(19) Stalgren, J. J. R.; Eriksson, J.; Boschkova, K. *J. Colloid Interface Sci.* **2002**, *253*, 190−195.
(20) Boschkova, K.; Feiler, A.; Kronberg, B.; Stalgren, J. J. R. *Langmuir* **2002**, *18*, 7930−7935.
(21) Lai, P. Y.; Halperin, A. *Macromolecules* **1992**, *25*, 6693−6695.
(22) Lyatskaya, Y.; Balazs, A. C. *Macromolecules* **1997**, *30*, 7588−7595.
(23) Magda, J. J.; Fredrickson, G. H.; Larson, R. G.; Helfand, E. *Macromolecules* **1988**, *21*, 726−732.
(24) Marko, J. F. *Macromolecules* **1993**, *26*, 313−319.
(25) Auroy, P.; Auvray, L. *Macromolecules* **1992**, *25*, 4134−4141.
(26) Birshtein, T. M.; Mercurieva, A. A.; Zhulina, E. B. *Macromol. Theory Simul.* **2001**, *10*, 719−728.
(27) Birshtein, T. M.; Lyatskaya, Y. *Colloids Surf. A* **1994**, *86*, 77−83.
(28) Birshtein, T. M.; Lyatskaya, Y. V. *Macromolecules* **1994**, *27*, 1256−1266.
(29) Kenausis, G. L.; Vörös, J.; Elbert, D. L.; Huang, N. P.; Hofer, R.; Ruiz-Taylor, L.; Textor, M.; Hubbell, J. A.; Spencer, N. D. *J. Phys. Chem. B* **2000**, *104*, 3298−3309.
(30) Huang, N. P.; Michel, R.; Vörös, J.; Textor, M.; Hofer, R.; Rossi, A.; Elbert, D. L.; Hubbell, J. A.; Spencer, N. D. *Langmuir* **2001**, *17*, 489−498.
(31) Kurrat, R.; Textor, M.; Ramsden, J. J.; Böni, P.; Spencer, N. D. *Rev. Sci. Instrum.* **1997**, *68*, 2172−2176.
(32) Vörös, J. *Biophys. J.* **2004**, *87*, 553−561.
(33) Bandey, H. L.; Hillman, A. R.; Brown, M. J.; Martin, S. J. *Faraday Discuss.* **1997**, *107,* 105−121.
(34) Voinova, M. V.; Rodahl, M.; Jonson, M.; Kasemo, B. *Phys. Scr.* **1999**, *59*, 391−396.
(35) Larsson, C.; Rodahl, M.; Höök, F. *Anal. Chem.* **2003**, *75*, 5080−5087.
(36) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 72nd ed.; CRC Press: London, 1992.
(37) Rickert, J.; Brecht, A.; Göpel, W. *Biosens. Bioelectron.* **1997**, *12*, 567−575.
(38) Ogletree, D. F.; Carpick, R. W.; Salmeron, M. *Rev. Sci. Instrum.* **1996**, *67*, 3298−3306.
(39) Varenberg, M.; Etsion, I.; Halperin, G. *Rev. Sci. Instrum.* **2003**, *74*, 3362−3367.
(40) Lee, S.; Müller, M.; Ratoi-Salagean, M.; Vörös, J.; Pasche, S.; De Paul, S. M.; Spikes, H. A.; Textor, M.; Spencer, N. D. *Tribol. Lett.* **2003**, *15*, 231−239.
(41) Müller, M.; Lee, S.; Spikes, H. A.; Spencer, N. D. *Tribol. Lett.* **2003**, *15*, 395−405.
(42) Yan, X. P.; Perry, S. S.; Spencer, N. D.; Pasche, S.; De Paul, S. M.; Textor, M.; Lim, M. S. *Langmuir* **2004**, *20*, 423−428.
(43) Lin, Y. S.; Hlady, V.; Golander, C.-G. *Colloids Surf. B* **1994**, *3*, 49−62.
(44) Tasaki, K.; Abe, A. *Polym. J.* **1985**, *17*, 641−655.
(45) Bailey, F. E.; Koleske, J. V. *Poly(ethylene oxide)*; Academic Press: New York, 1976.
(46) Karlstrom, G.; Engkvist, O. 213th National Meeting of the American Chemical Society, 1997, pp 16−29.
(47) Tasaki, K. *J. Am. Chem. Soc.* **1996**, *118*, 8459−8469.
(48) Liu, K.-J.; Parsons, J. L. *Macromolecules* **1969**, *2*, 529−533.
(49) Rixman, M. A.; Dean, D.; Ortiz, C. *Langmuir* **2003**, *19*, 9357−9372.
(50) Dondos, A.; Benoit, H. *Makromol. Chem.* **1970**, *133*, 119.
(51) Dondos, A.; Benoit, H. *J. Polym. Sci., Part B: Polym. Lett.* **1969**, *7*, 335.
(52) Dondos, A.; Patterso. D. *J. Polym. Sci., Part A2: Polym. Phys.* **1969**, *7*, 209.
(53) Dondos, A.; Benoit, H. *Eur. Polym. J.* **1968**, *4*, 561.
(54) Raviv, U.; Frey, J.; Sak, R.; Laurat, P.; Tadmor, R.; Klein, J. *Langmuir* **2002**, *18*, 7482−7495.

MA047468X