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Tunable friction by employment of co-non-solvency of PNIPAM brushes

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ABSTRACT

We present a simple method to control the tribological properties of contacts between polymer brushes and a solid counter surface. We show, using atomic force microscopy (AFM) experiments, that the friction force, upon relative sliding of a poly(*N*-isopropyl acrylamide) (PNIPAM) brush and a gold colloid on an AFM cantilever, varies over two orders of magnitude when changing the composition of an ethanol-water mixture that solvates the brush. We achieve this large variation in friction via a co-non-solvency effect: In pure water or ethanol, the PNIPAM brush is swollen and the friction is low, while in a 10–90 vol % ethanol-water mixture, the brush is partly collapsed and polymer-stretching causes the friction to be high.

1. Introduction

Friction between surfaces in relative motion is generally required to be either high or low: When walking, braking or picking up material, sufficiently high friction is of critical importance, while smooth sliding is preferred in systems where friction results in major costs due to energy-loss. However, for some advanced applications, it is necessary to be able to switch between high and low friction. Examples include robots that can walk on walls [1] and smart tweezers [2]. Polymer brushes provide a versatile platform for controlling surface properties [3–6] including tribo-mechanical properties [4,7–9] and, therefore, hold great potential for applications as surfaces with variable (switchable) friction [10,11].

Polymer brushes can be created by end-anchoring polymers to a surface or interface at an adequately high density [12]. When brushes are dry or kept in a poor solvent in their collapsed state, the polymers form a dense layer on the surface. The adhesion and friction between these dense polymer films and a solid counter-surface are generally high [13]. When a polymer brush is kept in a good solvent, the polymers stretch out and absorb the solvent into brush. Under these conditions, the friction and adhesion are typically low [14]. By employing polymers that respond to an applied external stimulus (e.g. by changes in temperature [15], solvents [16], pH [17], electric [18] and magnetic field [19] *etc.*), the effective solvent-quality can be readily changed such that friction and adhesion can be controlled [7,14,20–22]. A particularly easy method to change the solvent quality is the employment of the so-called co-non-solvency of the polymers [23–27] where a coil-to-globule transition of polymers can be triggered by simply adding a relatively small amount of co-solvent to the solvent.

When polymers are in a swollen, coiled state in pure solvent or co-solvent, but form a collapsed globule in a mixture of the two solvents, it is called a co-non-solvency effect. A well-studied example is poly(*N*-isopropyl acrylamide) (PNIPAM) in a mixture of water and alcohols such as methanol, ethanol or isopropanol [28,29]. At room temperature, PNIPAM polymers are found to be swollen in water or one of these alcohols, while the polymers are collapsed e.g. for 10–20 vol% methanol in a methanol-water mixture for polymers free in solution [16] (at 30 vol % for gels

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and brushes [24,30]). The origin of co-non-solvency is still under debate [25,31,32]. Koga et al. [25] proposed that co-non-solvency is a result of competitive hydrogen bonding where bonds between water and alcohol-molecules can be favored over hydrogen bonds between PNIPAM and the solvent-molecules. In a different study, Sheng et al. [31] conclude from their Fourier transform infrared spectroscopy experiments that the formation of "water-methanol clusters" $(H_2O)_n(MeOH)_m$ of concentration-dependent size ($n = 1, 2, 3, 4, 5$; $m = 1$) induces a coil-globule-coil transition. Depending on their size, these clusters create either good or poor solvent conditions for PNIPAM. Recently, Mukherji et al. [33] reported that the Flory-Huggins theory cannot explain the co-non-solvency mechanism. They show using coarse-grained molecular dynamics simulations [32] that a possible explanation for the phenomenon might be that, at low concentration of the better solvent, bridges are formed between parts of the PNIPAM polymer by the better solvent, which induces a collapse. Nevertheless, irrespective of the exact explanation for the origin, the manifestation of the phenomenon of co-non-solvency is well established and has been widely observed for different combinations of polymers, solvents and co-solvents [24,26,27,34,35]. Moreover, it has been employed in the development of applications such as gating [36] and in alcohol sensing [37]. However, for tuning friction, it has been relatively unexplored.

In this article we show using friction force atomic force microscopy (AFM) experiments, that co-non-solvency of PNIPAM in ethanol-water mixtures can be used to tune friction over two orders of magnitude. In a recent publication Chen et al. [14] reported on obtaining variable friction between PNIPAM and a silicon colloid using co-non-solvency. They observe that, in a 50-50 vol % mixture of methanol and water, the friction coefficient is approximately 4 times higher than in pure water. We built on these results and study the frictional response upon sliding a gold colloid over a PNIPAM brush at room temperature, while we systematically vary the relative amount of ethanol in ethanol-water mixtures. We find that for 10% of ethanol, the friction is the highest. At this concentration the friction is 120 ± 10 times higher than in pure ethanol. Surprisingly, we find that the concentration for the highest friction force does not coincide with the concentration of minimal brush swelling at 30% of ethanol. Thus, the observed frictional response cannot be explained by brush-swelling alone. Instead, we show, using AFM measurements in which the colloid probe is approached towards and retracted from the surface, that the partly collapsed polymers in 10% ethanol have become strongly stretched when the colloid is moved away from its initial contact with the brush. This can explain the enhanced frictional response found at 10 vol % of ethanol in the mixture. Because our results show that the friction can be varied over two orders of magnitude, we propose that PNIPAM in these solvent-co-solvent mixtures holds great potential for application in e.g. robots that can walk on walls or smart tweezers.

2. Materials and methods

2.1. Materials

N-Isopropylacrylamide (NIPAM, Aldrich, 97%) was dissolved in toluene/hexane solution (50% v/v), and recrystallized twice in the refrigerator, then dried under vacuum for 48 h at room temperature. Copper (I) bromide (CuBr, Aldrich, 98%) was purified by stirring in excessive acetic acid and filtered until the suspension solution is light gray, and dried under approximate vacuum conditions at room temperature overnight. *N,N,N′,N′,N′*-pentamethyldiethylenetriamine (PMDETA) (98%), (3-aminopropyl) triethoxysilane, 2-bromo-2-methylpropionyl bromide (98%), triethylamine (TEA, ≥99%), copper (II) bromide (≥99%), ethylenediaminetetraacetic acid tetrasodium salt di-hydrate (EDTA, 99–102%) were purchased from Sigma-Aldrich, and used as received without purification. Methanol (absolute), sulfuric acid (95–97%), tetrahydrofuran (THF), hexane and toluene (AR) were purchased from Biosolve, and hydrogen peroxide H_2O_2 and ethanol were purchased from Merck and used as received. MilliQ water was obtained from a MilliQ Advantage A 10 purification system (Millipore, Billerica, Ma, USA).

2.2. Brush preparation and characterization

The PNIPAM brushes were grafted from pieces of a silicon wafer (1×1 cm^2) via surface-initiated ATRP [7]. First, the silicon wafer was cleaned by Piranha solution (H_2SO_4:H_2O_2 = 3:1, v/v). (Caution: Piranha is very dangerous, extreme caution should be taken when handling it.) Next, a monolayer with an amine group ((3-aminopropyl)triethoxysilane) was attached through vapor deposition. Then, the initiator was attached to the surface using 2-bromo-2-methylpropionyl bromide by a one-step replacement reaction. The NIPAM solution mixed with PMDETA, CuBr and $CuBr_2$ was degassed and injected into a vial containing pieces of Si wafer substrates to conduct the ATRP polymerization at room temperature. Finally, specimens featuring the polymer brush were soaked in EDTA solution overnight to remove the copper, and dried with nitrogen. More details on the sample preparation can be found in Ref. [38]. For a movie showing the sample preparation procedure see Ref. [39]. The grafting density and molar mass of the PNIPAM brush were estimated by the swelling ratio [4] For the specimens used the values of 0.45 ± 0.2 chains/nm^2 and $2.5 \pm 1.0 \times 10^5$ g/mol were obtained, respectively. The absolute molar mass of PNIPAM brush-polymers from reference samples with a dry height of 120 nm was determined to be $M_n = 1 \times 10^5$ g/mol (typical PDI = 4 for the detached chains) [40] by gel permeation chromatography in THF after detachment from the silicon substrate using *p*-toluene sulfonic acid [41].

Static contact angle measurements were carried out on an optical contact angle device equipped with an electronic syringe unit (OCA15, Dataphysics, Germany). Contact angle values of the modified substrates at each reaction step were measured, and at least three samples were assessed for each step. Typical results can be found in the supporting information Fig. S1.

Fourier transform infrared spectroscopy (FTIR) was employed to characterize the chemical composition of the polymer brush tethered on the silicon substrates. A Bruker Vertex 70v spectrometer was used to obtain the FTIR spectra with a spectral resolution of 4 cm^{-1}. Background data was obtained by scanning a clean silicon wafer before sample measurement. A typical absorbance spectrum of a polymer brush is shown in Fig. S2.

Swelling and co-nonsolvency properties were investigated by measuring brush thickness using a Variable Angle Spectroscopic Ellipsometer (VASE, J. A. Woollam). Measurements were performed as a function of photon energy (in ambient: 0.8–4.0 eV, corresponding to a wavelength range of 276–1550 nm; in ethanol-water mixture: 1.1–4 eV, i.e. 276–1127 nm) with a step size of 0.1 eV. In liquid, the accessible range is limited due to absorption of infrared light. The experiments were performed at room temperature (25 °C) in air and in different compositions of ethanol/water mixtures, as outlined in the supporting information. A dedicated custom-built liquid cell was used, which enables optical access at a fixed angle of incidence of 63°. Spectra on dry samples were performed at three different angles of incidence (65, 70 and 75°). The detailed analysis of the spectra is shown in supporting information.

AFM force measurements were conducted on a Multimode 8 AFM with a NanoScope V controller, a JV vertical engage scanner