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Effect of solvent quality and chain density on normal and frictional forces between electrostatically anchored thermoresponsive diblock copolymer layers

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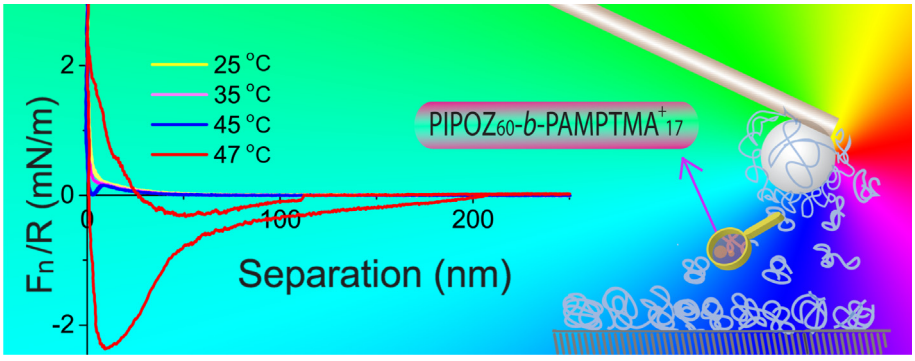
GRAPHICAL ABSTRACT



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ABSTRACT

Equilibration in adsorbing polymer systems can be very slow, leading to different physical properties at a given condition depending on the pathway that was used to reach this state. Here we explore this phenomenon using a diblock copolymer consisting of a cationic anchor block and a thermoresponsive block of poly(2-isopropyl-2-oxazoline), PIPOZ. We find that at a given temperature different polymer chain densities at the silica surface are achieved depending on the previous temperature history. We explore how this affects surface and friction forces between such layers using the atomic force microscope colloidal probe technique. The surface forces are purely repulsive at temperatures <40 °C. A local force minimum at short separation develops at 40 °C and a strong attraction due to capillary condensation of a polymer-rich phase is observed close to the bulk phase separation temperature. The friction forces decrease in the cooling stage due to rehydration of the PIPOZ chain. A consequence of the adsorption

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Poly(2-isopropyl-2-oxazoline)
Thermoresponsive polymer
Adsorption hysteresis

hysteresis is that the friction forces measured at 25 °C are significantly lower after exposure to a temperature of 40 °C than prior to heating, which is due to higher polymer chain density on the surface after heating.

1. Introduction

Many applications of temperature-responsive polymers utilize their temperature-induced conformational transition when tethered onto a solid substrate. For instance, the conformational transition can lead to changes in wetting [1], adhesion [2] and lubrication [3]. Temperature-responsive polymers that have been explored and applied to build temperature-responsive surfaces include, poly(*N*-isopropylacrylamide) (PNIPAAM) [4,5], poly(ethylene oxide) (PEO) [6] also known as poly(ethylene glycol) (PEG), poly(propylene oxide) (PPO) [7,8], methylcellulose (MC) [9] and poly(2-alkyl-2-oxazoline) [10,11]. Among these, surfaces bearing PNIPAAM chains have been widely investigated in many potential applications, like protein resistance surfaces [12], cell adhesion and detachment in cell sheet engineering [13,14] and dynamic control of gliding microtubule mobility [15]. Poly(2-oxazoline)s, discovered in 1966 [16,17], have been studied in great detail since then. In 2012, Macromolecular Rapid Communications devoted a special issue on poly(2-oxazoline)s and related pseudo-polypeptides [18]. However, these studies mainly focused on polymerization methods [19] and on the properties of poly(2-oxazolines) in bulk solution [10,11,20–24]. In recent years poly(2-oxazoline)s and derivatives have attracted increasing attention because of their promising properties in biomedical applications [25–28] and as antifouling materials [29–31].

Surfaces bearing poly(2-alkyl-2-oxazoline) chains, where the alkyl group is methyl, ethyl, or isopropyl, have been prepared by different methods, including grafting to [32,33], grafting from [31,34,35] and physisorption [29,30]. For example, the grafting to method was used by Yan et al. to covalently immobilize poly(2-ethyl-2-oxazoline) on silicon wafers and gold slides in order to form protein-resistant surfaces [31]. These films were employed in fabrication of carbohydrate microarrays and shown to reduce non-specific adsorption of lectins and, consequently, to lower the background noise [31]. Konradi et al. studied the protein-repellent properties of a poly(2-methyl-2-oxazoline) (PMOXA) based coating [30]. The polymer was electrostatically anchored to a negatively charged Nb_2O_5-coated silicon wafer via a positively charged block of poly(L-lysine). They found that the PMOXA-based coating with an optimal side-chain grafting density, approximately 10–12 monomer units per nm^2, eliminates protein adsorption as effectively as the best PEG-based coatings [30]. Our group has studied the interfacial properties of electrostatically anchored poly(2-isopropyl-2-oxazoline) (PIPOZ) layers on silica substrates, focusing particularly on the changes of the film thickness and water content within the temperature range from 25 °C to 45 °C. We observed a significant adsorption hysteresis during a heating-cooling cycle [36]. Furthermore, the interactions between such preadsorbed layers across polymer-free aqueous solutions, i.e. under conditions of temperature-independent adsorbed amount, were found to change from purely repulsive at low temperature to partly attractive at higher temperatures due to worsening of the solvent condition. The observed temperature-dependence was reproduced by mean-field modeling, which also demonstrated that the segment density profile and the degree of chain interpenetration under a given load change significantly with increasing temperature [37].

In this work, we explore how the slow equilibration affects surface and friction forces under a given condition. To this end we affect the adsorbed polymer chain density by the temperature history and utilize the atomic force microscopy (AFM) colloidal probe technique to determine surface and friction forces between $PIPOZ_{60}$-*b*-$PAMPTMA_{17}$ layers across a solution containing this polymer, covering the temperature range from 25 °C to 47 °C. Thus, unlike the previous work with pre-adsorbed layers [37], the polymer surface excess will change with temperature providing insight on how the physical properties are affected by the temperature history. Only a few reports can be found that discuss surface forces and/or friction forces between temperature-responsive surfaces under conditions that allow the surface excess to vary with temperature. These include studies of surface forces between ethyl (hydroxyethyl)cellulose (EHEC) coated hydrophilic [38] and hydrophobic surfaces [39], and electrostatically tethered PEO layers on mica surfaces [40], as well as investigations of surface and friction forces between methylcellulose (MC) coated hydrophobic surfaces [9]. Studies of this type are not only of fundamental interest, but also of high relevance for applications where products containing thermoresponsive components are exposed to varying temperatures during their storage or in processes there they are used.

2. Materials and methods

2.1. Materials

$PIPOZ_{60}$-*b*-$PAMPTMA_{17}$, see Fig. 1, with a number average molecular weight (M_n) of 10.3 kDa, was prepared as described previously [10]. The cationic PAMPTMA block, containing one charge per repeat unit, promotes the adsorption onto negatively charged silica [36]. The number of charged units per copolymer was determined to be ~17 by 1H NMR spectroscopy [10]. The non-ionic PIPOZ block (M_n = 7.0 KDa) is thermoresponsive. The phase transition temperature (cloud point) of this diblock copolymer in 0.1 mM NaCl at pH 9 with a concentration of 0.1 g/L (100 ppm) is around 49 °C (see Fig. S1). The cloud point was determined by turbidimetry measurement as described in the Supporting information. Sodium chloride (NaCl, BioXtra, ⩾99.5%) was purchased from Sigma-Aldrich and used as received. All water used was purified to a resistivity of 18.2 MΩ cm by employing a Milli-Q Purification System (Millipore, Malsheim, France) and the total organic carbon content of the water did not exceed 2 ppb.

Aqueous 0.1 mM NaCl solutions of $PIPOZ_{60}$-*b*-$PAMPTMA_{17}$ with a weight concentration of 500 ppm were prepared, and they were diluted with 0.1 mM NaCl to reach the intended concentration, 100 ppm, before use. The pH of the solutions was monitored using a pH meter (PHM 210, Meterlab) and adjusted to pH 9 by adding small amounts of HCl (0.6 M) or NaOH (1 M).

Silicon wafers (Wafer net, Germany) with a 33 nm silica layer were used as substrates and they were cut into proper size, squares with 12–14 mm sides, for the AFM experiments. The silicon wafers were cleaned by immersion in a 2% Hellmanex (Hellma GmbH) solution for 30 min, followed by rinsing with Milli-Q water excessively. They were then left in Milli-Q water overnight until