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Thermo-Responsive Block Copolymers: Friction Control by Temperature Switch

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Abstract: **An atomic force microscope colloidal probe technique was employed to probe normal and frictional forces between silica surfaces coated with layers of diblock copolymer of the composition (N-isopropylacrylamide)$_{48}$-((3-acrylamidopropyl)trimethyl ammonium chloride)$_{20}$, abbreviated PNIPAAm$_{48}$-PN(+)$_{20}$.The architecture of these polymers allowed exploring how normal and frictional forces between polymer-coated surfaces can be tuned by temperature changes. The interaction in 0.1 mM NaCl (pH 6) solution between the PNIPAAm$_{48}$-PN(+)$_{20}$-coated surfaces at 25°C is purely repulsive. The total surface forces can be interpreted as being due to additive contributions of two components – steric and electrostatic. However, when the temperature is increased to 36°C, and subsequently to 45°C, an attractive force develops at short separations. As the temperature is increased, the PNIPAAm-water interaction becomes unfavorable and the polymer change conformation due to dehydration. Thus, at higher temperatures the surface interactions become a composition of long-range double layer repulsion and short-range attraction between the PNIPAAm blocks on the opposite surfaces. The temperature-dependent behavior of the block co-polymer also has implication on friction forces: At 25°C a frictional force that increases linearly with increasing load is observed once the surfaces are brought into close contact. At higher temperatures, as a consequence of adhesive interactions a sudden jump to higher friction forces occurs. Further, a clearly expressed hysteresis between friction forces encountered on loading and unloading is detected. Our results demonstrate that both normal and friction forces between surfaces can be controlled by temperature changes when temperature responsive polymers are employed for surface modification, and friction forces can be switched from low to high values.**

Keywords**: surface forces, friction, aqueous lubrication, AFM colloidal probe, thermo-responsive polymer, adsorption**

I INTRODUCTION

Much fundamental research related to issues of friction to date has been devoted to increase the understanding of molecular aspects of friction and to provide as good as possible lubrication to surfaces sliding past each other, that is to minimize the action of friction forces. It has been realized that friction phenomena are complex and closely related to phenomena such as adhesion, adhesion hysteresis [1] and wear. In the recent past we have made efforts to understand the relations between normal surface forces, adsorbed layer structure and frictional forces. To this end we have utilized the natural lubricant mucin and explored the effects of additives such as cationic chitosan and the anionic surfactant SDS [2]. We have also investigated bottle-brush polyelectrolytes with a variety of architectures (charge density and density of poly(ethylene oxide) side chains) [3]. Recently, we also studied the intricate friction response of organized soft matter at interfaces, employing structured polyelectrolyte-surfactant complexes [4].

The friction force, F_f, as shown in Equation 1, is related to the energy dissipation per unit time and unit area, W, as [5]:

$$F_f = \frac{WA_{eff}}{v} \quad (1)$$

where A_{eff} is the effective contact area, and v the sliding speed. Thus, any process that contributes to energy dissipation during sliding increases the friction force. For polymer-coated surfaces many such processes exist, for example i) breakage and reformation of segment-segment contacts, ii) sliding of polymer chains through the interpenetration region of the opposing polymer layers and iii) breakage and reformation of segment-surface attachment points.

Friction plays and important role in diverse systems and to achieve low friction forces is not always the ultimate goal, but rather it may be of importance to control friction forces and be able to switch them from high to low values. To achieve a tunable friction means that the surface interactions should be possible to change with a suitable external trigger such as pH, ionic strength, temperature or light exposure. In this contribution we show how this can be achieved using temperature as trigger and an electrostatically anchored layer of a temperature-responsive polymer.

II EXPERIMENTAL

A diblock copolymer, (N-isopropylacrylamide)$_{48}$-((3-acrylamidopropyl)trimethyl ammonium chloride)$_{20}$ [6], further abbreviated (PNIPAAm$_{48}$-PN(+)$_{20}$) was synthesized by utilizing atom transfer radical polymerization [7,8]. Polydispersity of the polymer is low, below 1.1, and the structure of the polymer used in the initial study is shown in Figure 1. Other compositions are available and will be explored in our further work.

Friction and normal force measurements were performed in a fused silica liquid cell using an atomic force microscope Nanoscope Multimode III Pico Force (Veeco Instruments Inc.). Tipples rectangular cantilevers (CSC12, MicroMasch, Madrid, Spain) with the approximate dimensions of 150 µm in length and 35 µm in width, and normal spring constants in the range of 0.6 – 1.2 N/m were used. The exact values of the

spring constants (normal, k_N and torsional, k_ϕ) were determined by the method based on thermal noise with hydrodynamic damping [9, 10] using the AFM tune IT v 2.5 software (Force IT, Sweden). The thermal frequency spectra of the cantilevers were measured at room temperature without any particles attached. The lateral photodetector sensitivity, δ (V/rad), was calibrated using the method of tilting the AFM head as suggested by Pettersson *et al.* [11]. Silica particles with diameter of approximately 7 µm were attached, with the aid of an Ependorf Micromanipulator 5171 and a Nikon Optiphot 100S reflection microscope, to the end of the cantilever by using a small amount of high-temperature melting epoxy glue (Shell Epikote 1009) [12, 13].

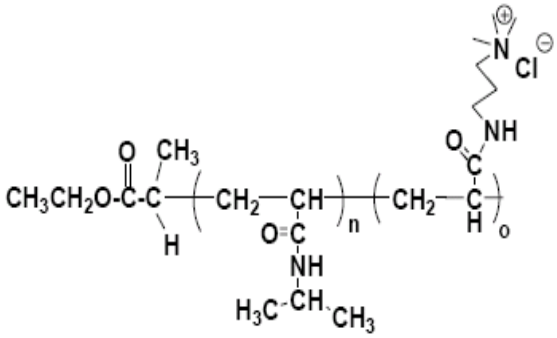

Fig. 1. Chemical structure of (N-isopropylacrylamide)$_{48}$-((3-acrylamidopropyl)trimethyl ammonium chloride)$_{20}$.

III RESULTS AND DISCUSSION

The block copolymer PNIPAAm$_{48}$-PN(+)$_{20}$ adsorbs to silica surfaces at low ionic strength and pH 6 to an amount of 0.6 mg/m^2, as determined by reflectometry. Once adsorbed the polymer does not desorb from the surface to any measurable degree. This, together with the fact that the solvent quality of water for the PNIPAAm block decreases with temperature were utilized for studying the influence of temperature on normal and frictional forces between silica surfaces coated with PNIPAAm$_{48}$-PN(+)$_{20}$. Any change in the forces acting between the surfaces is thus primarily due to changes in segment-segment interactions (and possibly segment-surface interactions).

The normal forces measured between two silica surfaces coated with PNIPAAm$_{48}$-PN(+)$_{20}$ at 25°C are illustrated in Figure 2.

The long-range repulsion between the surfaces decays exponentially with surface separation, and the decay-length is in agreement with that of the expected double-layer force. The large magnitude of he surface potential, 68 mV, demonstrates that adsorption of the polymer significantly overcompensates the surface charge of the silica surface. This is different compared to what usually is found for linear highly charged homopolyelectrolytes [14] where adsorption proceeds to close to charge neutrality. The significant overcharging in the present case is suggested to be a consequence of a non-electrostatic affinity between PNIPAAm and silica. At close separation a steric repulsion between the polymer chains become noticeable and at no attractive force is observed at any surface separation. Further, there is no, or only a very small, hysteresis between the forces measured on approach and on separation.

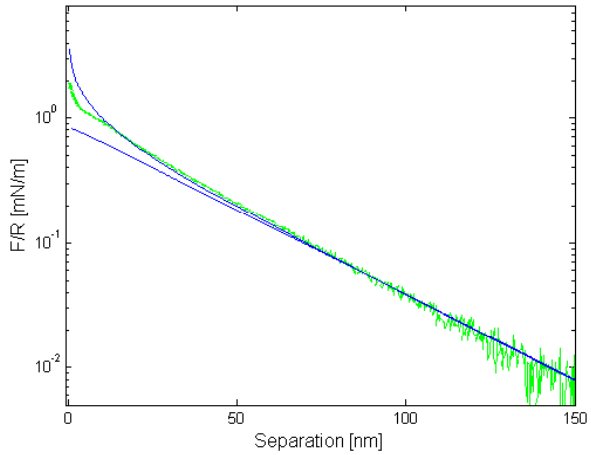

Fig. 2. The force normalized by radius as a function of separation from hard wall contact. The forces were measured between two silica surfaces precoated with a layer of PNIPAAm$_{48}$-PN(+)$_{20}$ across a 0.1 mM NaCl solution at 25°C. The upper and lower lines are calculated double-layer forces using constant surface charge and constant surface potential boundary conditions, respectively. In the calculations the Debye-length is given by the ionic strength of the solution and the surface potential was found to be 68 mV.

An increase in temperature to 36°C worsens the solvent quality of water for PNIPAAm, and under these conditions the segments attract each other. This is reflected in the forces between the adsorbed layers as illustrated in Figure 3. At large separations a repulsive double-layer force still dominates the interaction. However, at a surface separation of about 10 nm an attractive force component, identified as being due to segment-segment attraction is noticeable and this force contribution results in an inward jump (shown as a straight line in the force curve depicted in Figure 3).

On separation a relatively strong adhesion force (≈ 1 mN/m) is measured. Once this adhesion force is overcome the surfaces jump apart. A further increase in temperature results in a further increase in the magnitude of the adhesion force (data not shown).

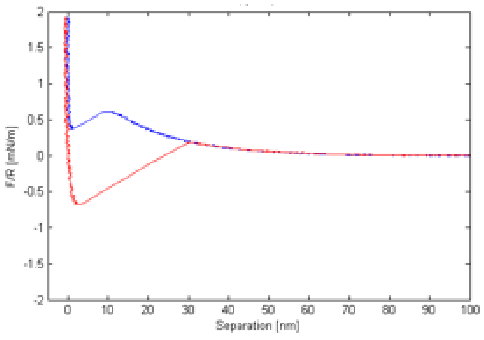

Fig. 3. The force normalized by radius as a function of separation from hard wall contact. The forces were measured between two silica surfaces precoated with a layer of PNIPAAm$_{48}$-PN(+)$_{20}$ across a 0.1 mM NaCl solution at 36°C. The upper curve is measured on approach and the lower curve on separation.

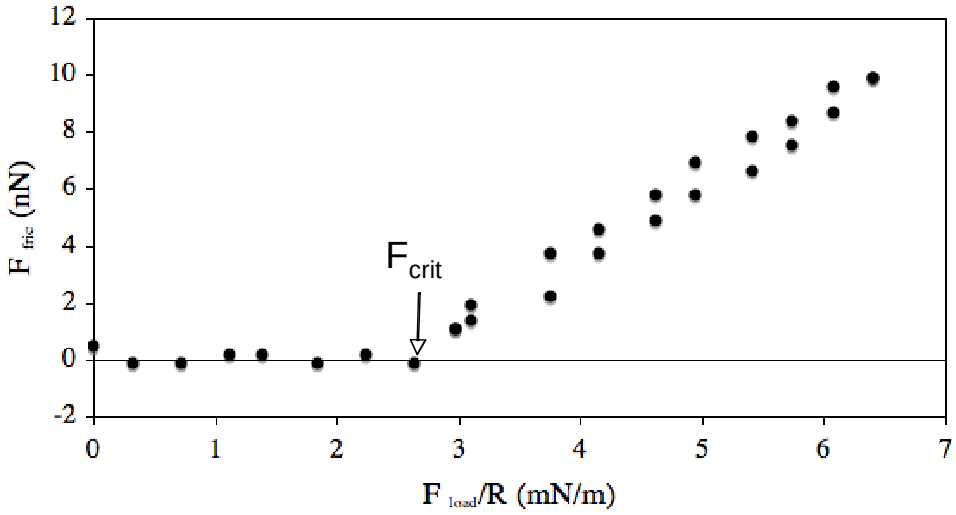

Fig. 4. The friction force as a function of load for two silica surfaces coated with PNIPAAm$_{48}$-PN(+)$_{20}$ at 25°C

Thus, it is clear that by increasing the temperature and making water a less good solvent for PNIPAAm changes the short-range interaction from repulsive to attractive. We conclude that colloidal particles coated with PNIPAAm$_{48}$-PN(+)$_{20}$ would form a stable dispersion at low temperatures but flocculate at higher temperatures where the segment-segment interaction becomes attractive. We will now turn our attention to how the change in short-range interaction influences the friction force.

The friction force observed between two silica surfaces precoated with PNIPAAm$_{48}$-PN(+)$_{20}$ is illustrated in Figure 4.

At low loads the surfaces are kept apart by the repulsive double-layer force. As long as this is the case, the interface remains fluid and the friction force is below the detection limit of our AFM instrument. However, when the polymer layers are pressed more firmly together the friction force begins to increase linearly with the applied load. We suggest that interpenetration of the two polymer layers occurs and that the main energy dissipative mechanism arises from polymer chains being dragged through the interpenetration region. For the PNIPAAm$_{48}$-PN(+)$_{20}$ coated surface at 25°C the following friction force law describes the data well (Equation 2).

$$F_f = (F_n - F_{crit})\mu \quad \text{valid for } F_n > F_{crit} \qquad (2)$$

where F_n is the normal load, F_{crit} is the critical load defined in Figure 4, and μ is the friction coefficient. The friction force was found to be slightly larger on decompression than on compression, but the difference was small.

The friction forces determined at 36°C, when the segment-segment interaction is attractive, are illustrated in Figure 5.

As the surfaces are pushed together under a very low load (<0.7 mN/m) the repulsive double layer force separates the surfaces and the friction force is very low. However, as soon as the polymer layer come in direct contact a large friction is observed, which increases substantially with increasing load. As the load is released, we notice a significant hysteresis in the friction force, which for a given load is higher on unloading than on loading. This is related to the hysteresis observed in the normal force measurements, Figure 3, and indicates that the adsorbed layer at any given load contains less water on unloading than on loading. This decreases the fluidity of the interface and increases the friction force. We also note that the surfaces are held together also under low negative loads as a direct consequence of the adhesion, and on unloading a significant friction force is observed also at zero loads.

After compression the friction force can be described as being adhesion controlled, i.e. it is the intermolecular attraction between the surfaces rather than the applied load that dictates the friction behavior (at the sufficiently low loads of this investigation where the highest force applied corresponds to a pressure of about 15 MPa). In this situation the friction force law can be described as shown in Equation 3:

$$F_f = S_c A + \mu F_n \qquad (3)$$

where S_c is the critical shear stress and A is the effective contact area, which can be calculated from contact mechanics theories [15].

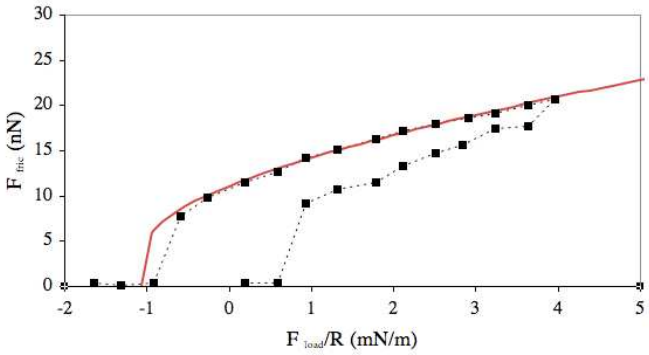

Fig. 5. The friction force as a function of load for two silica surfaces coated with PNIPAAm$_{48}$-PN(+)$_{20}$ at 36°C.

The fit to the data shown in Figure 5 was calculated with the equation given above, and a zero value for the friction coefficient. The very good agreement between theory and

experiments demonstrate that the major cause for the increase in friction force with the applied load in the present case is due to the increase in the contact area with load, which increases the intermolecular attraction forces.

IV CONCLUSIONS

The block copolymer $PNIPAAm_{48}$-$PN(+)_{20}$ adsorbs irreversibly with respect to dilution on silica surfaces at pH 6. The forces acting between such layers are at large distances dominated by a repulsive double-layer force and at shorter separations by interactions between the PNIPAAm segments. At low temperature (25°C) the segment-segment interaction is repulsive and consequently the forces acting between $PNIPAAm_{48}$-$PN(+)_{20}$ coated silica surfaces are repulsive at all separations. The friction force between these layers is exceedingly low at low loads when the surfaces are separated by the repulsive double-layer force. However, as the polymer layers start interpenetrating a significant friction force that increases linearly with the applied load is observed.

An increase in temperature to 36°C makes water a poor solvent for PNIPAAm, and consequently the segment-segment interaction becomes attractive. This changes the surface forces acting between $PNIPAAm_{48}$-$PN(+)_{20}$ coated silica surfaces, and an attractive force is now noticed at short distances (< 10 nm), and on separation the surfaces adhere to each other. The change in segment-segment interaction from repulsive to attractive has also dramatic effects on the friction forces. Under conditions of segment-segment attraction, the friction force is controlled by the attractive intermolecular interactions rather than by the applied load. The friction as a function of load curve can now be rationalized in terms of a critical shear stress and an increase in the effective contact area due to an increasing applied load.

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Asta Dedinaite, Esbens Thormans, Džeofrijs Olanya, Pers M. Claesson, Bo Nīstrēms, Kaizhengs Zū. Termojutīgi blokkopolimēri: berzes kontrole ar termopērslēgšanos.
Atomspēku mikroskopa koloidālā parauga metodi izmantoja, lai pārbaudītu normālos un berzes spēkus starp silīcija dioksīda virsmām, kuras bija pārklātas ar diblokkopolimēra – $(N\text{-izopropilakrilamīds})_{48}$-$((3\text{-akrilamidopropil})\text{trimetil amonija hlorīds})_{20}$, $PNIPAAm_{48}$-$PN(+)_{20}$, – slāniem. Šo polimēru uzbūve ļāva spriest par to kā normālie un berzes spriegumi starp ar polimēru pārklātām virsmām var tikt saskaņoti ar temperatūras izmaiņām. Mijiedarbība 0.1 mM NaCl (pH 6) šķīdumā starp $PNIPAAm_{48}$-$PN(+)_{20}$ pārklātām virsmām 25°C temperatūrā ir tīri atgrūdoša. Kopējos virsmas spēkus var interpretēt kā additīvus starp divām komponentēm – sterisko un elektrostatisko. Tomēr, kad temperatūra tiek paaugstināta līdz 36°C un vēlāk līdz 45°C, attīstās arī pievilkšanās spēki. Temperatūrai pieaugot, PNIPAA-m-ūdens mijiedarbe kļūst nelabvēlīga un polimērs maina konfigurāciju pateicoties dehidratācijai. Tādējādi pie augstākām temperatūrām virsmas mijiedarbes veido kombinācija no tālās darbības dubultslāņa atgrūšanās un tuvās darbības pievilkšanās starp PNIPAAm blokiem uz kontaktējošajām virsmām. Blokkopolimēru no temperatūras atkarīgajai uzvedībai ir arī ietekme uz berzes spēkiem: 25°C temperatūrā, tikko kā virsmas nonāk savstarpējā kontaktā, līdz ar slodzes palielināšanos, novērots lineārs berzes spēka pieaugums. Pie augstākām temperatūrām, pateicoties adhezīvajai mijiedarbei, notiek lēcienveidīgs bīdes spriegumu pieaugums. Bez tam, vērojama skaidri izteikta histerēze starp slogošanas un atslogošanas procesu berzes spriegumiem. Mūsu rezultāti parāda, ka gan normālos, gan berzes spēkus starp kontaktējošām virsmām var kontrolēt ar temperatūras izmaiņām, ja to virsmas modificēšanai tiek izmantoti termojutīgi polimēri, kas sekojoši ļauj pārslēgties no zemām berzes spriegumu vērtībām uz augstām.

Аста Дединайте, Есбен Тхорманн, Геофрий Оланиа, Пер М. Клаессон, Бо Нистром, Кайзхенг Зху. Термочуствительные блок-полимеры: Контроль трения переключением температур.

Метод коллоидальной пробы атомно-силовой микроскопии был использован для исследования нормальных сил и сил трения между поверхностями кремния, покрытыми слоями сополимера N-изопропилакриламида и **(**3-акриламидопропил)триметиламмония хлорида ($PNIPAAm_{48}$-$PN(+)_{20}$). При взаимодействии $PNIPAAm_{48}$-$PN(+)_{20}$ покрытых поверхностей в 0.1 mM растворе NaCl (pH 6) при температуре 25^{o}C было обнаружено чисто отталкивающее поведение. Поверхностные силы могут быть интерпретированы, как состоящие из двух аддитивно взаимодействующих силовых компонентов - стерического и электростатического. При повышении температуры до 36^{o}C, а затем до 45^{o}C, на близких расстояниях развиваются силы притяжения. В связи с дегидратацией при повышении температуры взаимодействие между PNIPAAm и водой становится неблагоприятным, и полимер изменяет свою конформацию. Таким образом, при более высоких температурах поверхностные взаимодействия объединяют отталкивание двойного слоя дальнего порядка и притяжение близкого порядка между блоками PNIPAAm на противоположных поверхностях. Температурная зависимость поведения блок-сополимера так же влияет на силы трения: при возникновении контакта между поверхностями при 25^{o}C наблюдается увеличение силы трения линейно увеличению нагрузки. При более высоких температурах в связи с адгезионным взаимодействием наблюдается резкий скачок сил трения. Кроме того, обнаружен явный гистерезис сил трения между процессами нагрузки и разгрузки. Полученные результаты показали, что нормальные силы и силы трения между поверхностями можно контролировать изменением температуры, если для модификации поверхности использовались термочувствительные полимеры.