Diffusion of Single Polyelectrolytes on the Surface of Poly(*N*-isopropylacrylamide) Brushes

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Received May 10, 2007; Revised Manuscript Received September 25, 2007

ABSTRACT: Lateral diffusion of a single polyelectrolyte probe, poly(2-vinylpyridine) (P2VP), on the surface of thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) brushes was studied by fluorescence correlation spectroscopy. Measurements were conducted at a condition of a low pH value and a low salt concentration, under which the P2VP chain is fully charged and at its extended coil conformation. The temperature dependence of the surface diffusion coefficient (D_s) of P2VP was studied at varying PNIPAM thickness, in which D_s increased with the elevation of temperature and reached a maximum value around 32−35 °C before it dropped at further increased temperature. The experimental results indicate a linear dependence of the friction force experienced by the probe on the brush thickness. The thermovariation of D_s demonstrates the decrease of the surface friction force at temperature lower than 32−35 °C due to the decrease of the solvent viscosity and a sharp increase after the LCST transition because of the change of the PNIAPM chain rigidity.

Introduction

As an important method of surface modification, polymer brushes have been attracting considerable research interest,[1−4] as they are believed to have potential applications in lubrication, friction, micro- and nanofluidic devices, antiadsorption of biological substances, stabilization of colloidal suspensions, and so forth. It is believed that there is a close relationship between the chain structure of polymer brushes and their dynamical behavior, and it is worth exploring the physics regarding this issue.[2−4] One important topic is to understand the dynamics of the polymer chain in the brush layer and also the frictional feature of the brushes, with the presence of the solvent. There have been successful studies regarding this topic, especially by surface frictional or rheological measurements such as the surface force apparatus (SFA) and the atomic force microscope (AFM).[5−8] Particle-based microrheological measurements have also been adopted to explore the surface friction between the brush-grafted surfaces.[9] Another related method is the evanescent wave dynamical light scattering, which explores the segmental dynamics of the molecular chain consisting of the brush layer.[10−12] In terms of the measurement of friction on the polymer brush surfaces, the information obtained by most conventional research methods was based on the response of the ensemble of many molecules and polymer chains.

Biocompatible polymer brushes are believed to have their potentials in biomedical applications, such as cell culturing, drug delivery, biolubrication, substrate for biochemical reactions, and so forth. Poly(*N*-isopropylacrylamide) (PNIPAM) brush is one important kind of biocompatible brush exhibiting its thermoresponse by its phase transition of lower critical solution temperature (LCST). Considerable researches have been conducted on this material and its LCST transition.[13−17] As the surface structure of PNIPAM brushes is thermoresponsive, this effect may be utilized to control its surface friction and surface fluid flow. Also, the activities and mobilities of biomacromolecules and their responses to the temperature variation on such a polymer brush substrate are important for its future applications.

In this study, we study the surface mobility and its thermoresponse of a polyelectrolyte molecule on the PNIPAM brush surface. We explore the dynamics and surface frictional characteristics of PNIPAM brushes microscopically. Single molecule fluorescence techniques were adopted to explore the friction force experienced by single polymer electrolyte chains on this brush surface with the presence of solvent. We use fluorescence correlation spectroscopy (FCS)[18−21] to study the diffusion of single polyelectrolyte molecules, P2VP, on the surface of the PNIPAM brushes. The variation of the diffusion coefficient and the molecular friction force experienced by single P2VP chains was measured as a function of the temperature and also thickness of the brushes.

Experimental Section

The experiments were conducted in the following way in general: PNIPAM brush layers with different thickness were prepared on solid substrates, and fluorescence-labeled P2VP chains were allowed to adsorb on the surface of the brush layer. FCS experiments were conducted to study the diffusion of the single P2VP chain on PNIPAM brushes with the presence of the aqueous solution. The temperature of the system was controlled, and the variation of the surface diffusion coefficient was measured as a function of the temperature.

PNIPAM brushes were prepared on silicon wafers and fused silica slides by surface-initiated atom transfer radical polymerization (ATRP).[22−23] The substrates, silicon wafers of ⟨111⟩ orientation and fused silica, were carefully cleaned, and the reagents were purified before use. To prepare PNIPAM brushes, the initiators were immobilized on the substrates' surfaces by the self-assembled monolayer technique. After being treated successively in ozone, piranha solution and a mixed solution of ammonia, hydrogen peroxide, and water, the clean and hydroxyl group-rich substrates were used to prepare self-assembled monolayer in toluene solution of 3-aminopropyltrimethoxysilane (APTMS), following the published protocol.[24] The initiators were then tagged onto the substrate

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10.1021/ma0710535 CCC: $37.00
Published on Web 11/29/2007

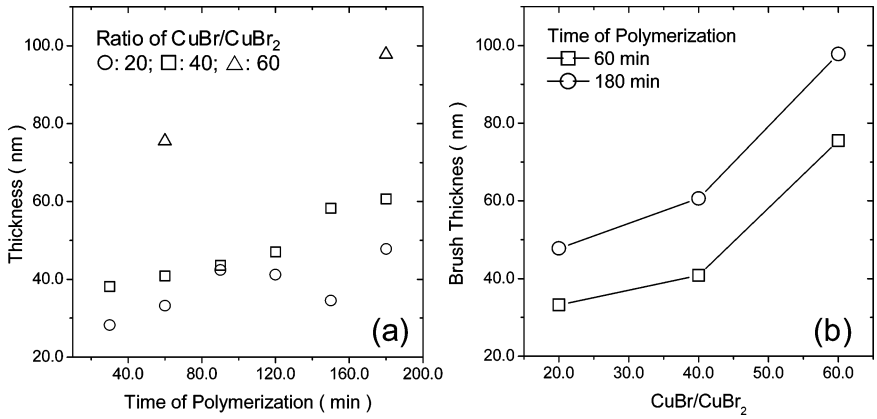

Figure 1. Thickness of PNIPAM brushes as a function of the time of polymerization and reaction condition. (a) Brush thickness as a function of polymerization time under the concentration of ratio between CuBr and $CuBr_2$: 20:1 (○), 40:1 (□), and 60:1 (△). (b) Brush thickness as a function of ratio of $CuBr/CuBr_2$ for two different times of polymerization: 60 and 180 min.

by reacting with 2-bromoisobutyl bromide (2-BiB). Afterward, the polymerization was conducted in the polymerization solution. A detailed description of the polymerization process can be found in the Supporting Information I.

The thickness of the brushes was controlled by tuning the time of polymerization and also the ratio of activator/deactivator in the reaction solution. The characterization of brush thickness was conducted by an atomic force microscope (AFM) (Nanoscope III, Digital Instrument) and an ellipsometer (SOPRA), and the measurements were conducted on the films at their "dry" state, i.e., when the solvent was not present. AFM characterization on the brush layer in water was conducted by measuring the height difference of a scratch created in the film. For a 90.0 nm thick "dry" brush layer, the thickness in water was 135.0 nm, showing the brush layer was about 1.5 times swelled. Later in this paper, the thickness of the brush layer was indicated by their "dry" thickness.

The probe molecule is poly(2-vinylpyridine) (M_n = 109 800 g mol^{-1}, M_w/M_n = 1.03), purchased from Polymer Source (Quebec, Canada). The P2VP chain was terminated with an amino group, through which a bright and stable fluorescence dye molecule, Alexa 488 (Invitrogen Corp.), was chemically attached. The samples were purified by both size exclusion chromatographic column and dialysis.[25]

The probe molecule was allowed to adsorb to the surface of PNIPAM brushes from its aqueous solution at the pH of 2.0. At this pH value, the P2VP molecule is fully charged and the chain is taking an extended coil conformation.[25] In the experiment, a fluid cell was fabricated with the silica substrate grafted with PNIPAM brushes. The cell was first filled with the blank HCl solution at pH of 2.0 and then rinsed with fluorescent-labeled P2VP solution at a concentration of 1.0×10^{-9} M. The pH value of the solution was controlled by adjusting the concentration of HCl, and no buffer solution was used here to keep a very low ionic strength. Usually, 15−30 min was allowed to let P2VP chains adsorb onto the surface of PNIPAM brush layer. Afterward, the cell was rinsed copiously with the blank solution of pH 2.0 to remove any residual P2VP molecules in the solution. After all of these processes, we waited 1−2 h in order to allow the sample to equilibrate. The temperature of the sample was controlled by a hot-and-cold stage (HCS60, INSTEC).

The diffusion of fluorescent-labeled P2VP was measured by the FCS technique.[18−21,25] The experimental setup is based on an inverted microscope (Olympus IX-71) equipped with an oil-immersion objective lens (Plan Apochromat 60×, numerical aperture = 1.4). The excitation light source is the 488 nm output of an argon laser (Melles Griot), and the fluorescence excitation and collection were conducted at the confocal detection geometry. The background noise was greatly suppressed by a combination of optical filters and a dichroic mirror (Chroma Tech), and the fluorescence was detected separately by two single photon counting modules (Hamamatsu, Japan). The fluorescence photon count signal was coupled into a multichannel FCS data acquisition board, and the data analysis was conducted by its software (ISS). The dimension of the excitation spot at the room temperature (∼20 °C) was calibrated as ∼260 nm in the lateral direction and ∼2 μm in the vertical direction by measuring the diffusion of standard samples with known diffusion coefficients (D), such as Rhodamine 6G and fluorescein. The determination of the excitation spot at varying temperature was conducted (detailed description later in the text).

To measure the surface diffusion of the P2VP chain on PNIPAM brushes, the focus of the microscope was adjusted to the surface, judging by the criterion that the fluorescence photon counting signal reached its maximum value, demonstrating adsorption of P2VP on PNIPAM brushes and guaranteeing that the focal point of the objective lens was at the surface of the brush layer. The FCS measurement was conducted for every sample at different temperatures. Usually, for each temperature, more than 15 measurements were conducted at different locations across the sample's surface. When changing the temperature, the sample was kept for more than 1 h in order to let the sample equilibrate before the measurements at this temperature were made.

Results and Discussion

Characterization of the PNIPAM Brushes. The thickness of PNIPAM brush layer was controlled by adjusting the reaction condition and the time of polymerization. Figure 1 shows the PNIPAM brush layer as a function of the time of polymerization and under different concentration ratio of the activator/deactivator, CuBr and $CuBr_2$. Apparently, the kinetics of the polymerization was vastly adjusted by the ratio of CuBr and $CuBr_2$. For a certain time of polymerization, a thicker brush layer was generated with a higher ratio of $CuBr/CuBr_2$. Also, the layer thickness increased with the time of polymerization. It was with the combination of these methods that the brush thickness was controlled effectively. The grafting density of the brushes was characterized by the method of "sacrificial initiator", and the results showed an average value of 0.4 chain/nm^2. (Please refer to the Supporting Information I for details on grafting density characterization.)

The fabricated PNIPAM brush layers exhibited their thermoresponse and this was demonstrated by the measurements of the water contact angle and film thickness in water at different temperatures. The results for PNIPAM brushes of two thicknesses are displayed in Figure 5. (For the sake of the length of the paper, water contact angle data are not displayed separately and are put together with the surface friction data for comparisons.) The value of water contact angle was found to be about 60° at room temperature, and it started to increase around 30 °C until it reached a stable value around 80° at 40 °C.

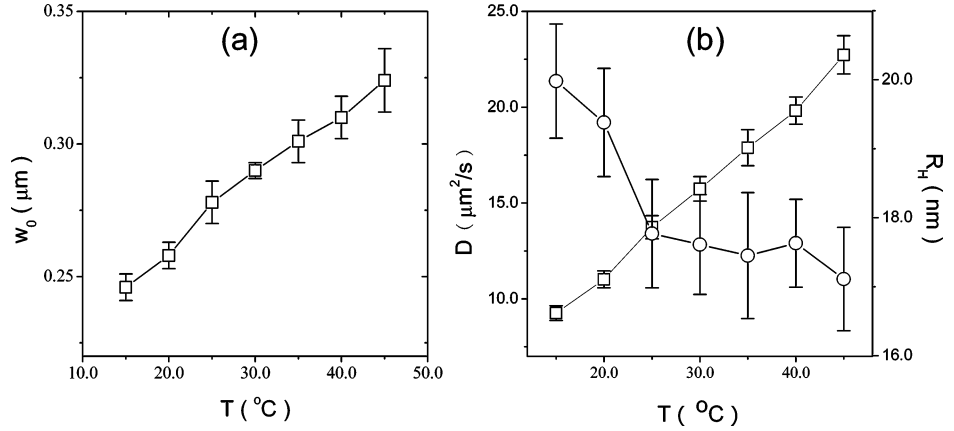

Figure 2. (a) Diameter of the excitation volume (w_0) in aqueous solutions as a function of the temperature. (b) Diffusion coefficient, D (□), and hydrodynamic radius, R_H (○), of P2VP in its aqueous solution as a function of the temperature.

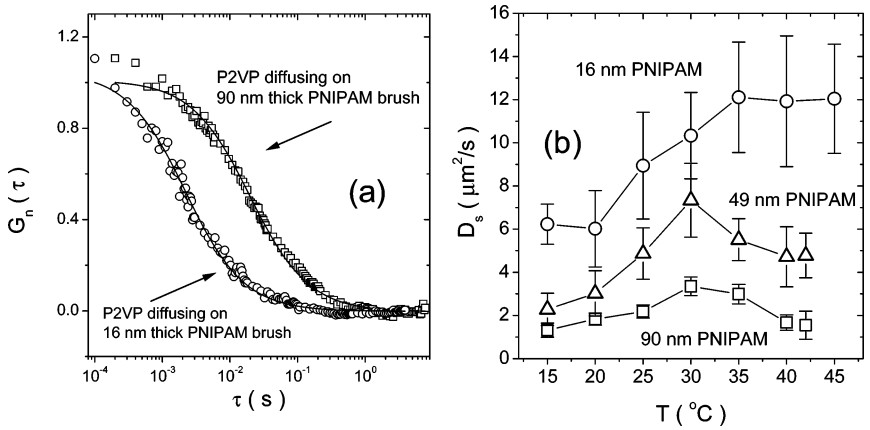

Figure 3. (a) Normalized autocorrelation functions of P2VP diffusing on PNIPAM brushes at the temperature of 25 °C. (b) Surface diffusion coefficient of P2VP as a function of temperature on PNIPAM brushes with three thicknesses: 16.0 (○), 49 (△), and 90.0 nm (□).

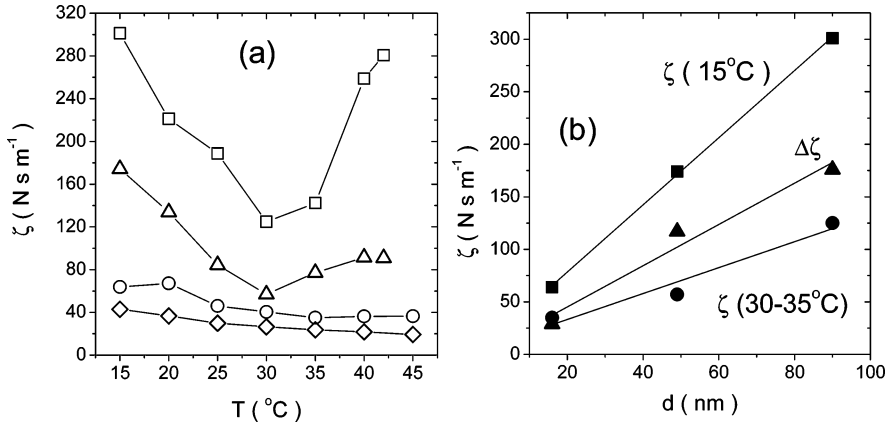

Figure 4. (a) Surface friction (ζ) experienced by single P2VP chain as a function of temperature on PNIPAM brushes of three thicknesses: 16.0 (○), 49.0 (△), and 90.0 nm (□). Friction force in solution is also displayed (◇). (b) Dependence of friction force on the brush thickness, in which ζ(15 °C) is for friction at 15 °C, ζ(30−35 °C) for the minimum friction around the transition point, and Δζ for the difference of these two values.

An in-situ observation of the brush thickness by AFM showed that the brushes with 135 nm "wet" thickness shrank to 110 nm upon LCST transition. (Please refer to the Supporting Information II for details).

Calibration of FCS at Varying Temperatures. FCS measurement is highly dependent on the confocal excitation profile in the sample, which is closely related to the refractive index of the media.[26−29] An accurate calibration of the excitation volume is necessary in order to guarantee measurement precision, and this is realized by measuring the autocorrelation function of standard samples. Fluorescent silica particles were adopted as the standard sample. The particles were monodispersed fluorescent silica particles without surface functionalization and 62.0 nm in diameter (Corpuscular Inc.). Dynamic light scattering measurements proved that there was no observable change of the hydrodynamic radius of the particle at varying temperatures (15−50 °C). Taking the known viscosity of water at different temperature, the diffusion coefficient of the particle is calculated as the reference value. By numerical fitting the autocorrelation function of the diffusing particles, the dimension of the excitation volume was determined. Figure 2a shows the measured lateral diameter of the excitation spot in aqueous medium as a function of temperature. Apparently, there is an expansion of the excitation volume with the elevation of

temperature due to the decrease of refractive index of water at higher temperatures. It has been known that the mismatch of refractive index of the sample medium and the immersion fluid of the objective lens will cause an aberration of the confocal detection volume, and the current results clearly demonstrates that this effect is even more enlarged by further index mismatching.[26−29]

After the calibration of the excitation volume, the diffusion coefficient of the probing molecule, fluorescence-labeled P2VP, in its aqueous solution at pH of 2.0 was measured at different temperatures. Figure 2b shows the diffusion coefficient and hydrodynamic radius of the probing P2VP molecule in aqueous solution at pH of 2.0 as a function of the temperature. The hydrodynamic radius (R_H) of the P2VP in solution was calculated from the diffusion coefficient by the application of the Stokes−Einstein equation, $D = kT/6\pi\eta R_H$, where the viscosity of water (η) is taken as a function of the temperature. The hydrodynamic radius of single P2VP chains decreased upon the increase of the temperature. This is a reasonable result because the hydration of the charged pyridine group is believed to decrease at the elevated temperature as the thermal excitation weakens the interaction between the water molecules and the charged pyridine groups. This calibration and correction have been proved to be essential for FCS measurement under varying temperatures. (A detailed description of this issue will be published elsewhere.) Without such a careful calibration and correction, the diffusion of P2VP in solution appeared to slow down with the elevated temperatures (data not shown for clarity), meaning a more swollen conformation of P2VP in its aqueous solution at higher temperature, which apparently deviated from the real situation.

FCS Measurement of P2VP Diffusing at PNIPAM Brushes at Varying Temperatures. Figure 3a shows the typical normalized FCS autocorrelation functions of P2VP probe diffusing on the surface of PNIPAM brush layers with two different thicknesses at the temperature of 25 °C, and Figure 3b demonstrates the surface diffusion coefficient of P2VP as a function of the temperature on the surface of PNIPAM brush layer of three different thicknesses: 16.0, 49.0, and 90.0 nm. Two features were obviously observed: (1) the surface diffusion coefficient (D_s) of probe P2VP chain decreases as the PNIPAM brushes get thicker; (2) D_s on PNIPAM brush layers experienced a variation vs temperature. There was an increase of D_s when the temperature increased from 15 to 32−35 °C, and afterward, the D_s value of the probe was almost constant on the 16 nm thick PNIPAM brush layer while that on 49 and 90 nm thick brushes experienced a drop. Compared with the temperature dependence of the diffusion coefficient of P2VP in bulk solution, which increased monotonously with the temperature, this behavior of the surface diffusion coefficient originates from the effect of the PNIPAM brush layers.

Experimentally, it is hard to distinguish experimentally whether the prove P2VP chain is on the surface or inside the PNIPAM brushes due to the limitation of the spatial resolution of the optical microscope in the direction of the optical axis (1−2 μm). We believe that the location of the adsorbed P2VP chain was at the surface of the brushes because the penetration of the probe chain into the inner brush layer should be hindered by the high osmotic pressure inside the PINIPAM brushes. On the basis of the grafting density data, the probe polymer chain inside such a dense brush layer should have had a much lower diffusion coefficient than what was measured.

It is interesting to discuss the interaction between the P2VP probe and the PNIPAM brushes. Considering the chemical structure of the chains, the possible interaction between the P2VP probe and PNIPAM brushes is hydrophobic interaction, van der Waals interaction, and the interaction between the polar groups of the two chains. The possible effect of electrostatic attraction between the positive-charged P2VP chain and the residual silanol groups at the substrate's surface can be excluded for the following reasons: (1) The silanol groups have a less chance to be dissociated under pH 2.0, as its isoelectric point is above pH of 2.0.[30] Therefore, at the low pH value in this study, the possible residual silanol groups are mostly neutral. (2) The adsorption is dependent on the thickness of the brushes, as it was verified in the experiments: it took much longer time for the thinner brush surface to reach a comparable adsorbed amount than the thicker brushes (measured by the fluorescence intensity at the surface.) Provided the adsorption was by the interaction with the silanol groups, it should have had an inversed dependence on brush thickness due to the weakened interaction by the brush in between.

The diffusion rate of the probe molecule is closely related to the friction force experienced by it. Here, the major friction force originates from the interaction between the probe molecule and the surface. In order to estimate this surface friction force on P2VP molecules, we adopt the Einstein equation, $D = kT/\zeta$, where D and ζ are the diffusion coefficient and friction force, respectively. The Einstein equation is applicable to diffusion problems of different dimensions, and it is valid for the current case of the semi-two-dimensional diffusion. The polymer brush surface is a "soft" surface with numerous PNIPAM segments fluctuating at the interface between the brushes and solvent, and it is reasonable to treat the diffusion of the P2VP chain on such a surface as the stochastic process, i.e., the Brownian motion, which is best expressed mathematically by Langevin equation and Einstein equation.[31] On the basis of these two reasons, the Einstein equation was adopted here to estimate the friction force.

The results of the friction force experienced by P2VP on PNIPAM brushes as a function of the temperature are displayed in Figure 4a, in which the friction force experienced by P2VP in solution is also displayed (data calculated from the diffusion coefficient of P2VP in solution, Figure 2b). In general, the friction force experienced by P2VP is roughly proportional to the brush thickness. The change of surface friction with the increase of the temperature experienced a decrease before the temperature reached about 32−35 °C, and when the temperature increased further beyond, the friction force increased again for thicker brushes (49 and 90 nm thick) while it stayed at a constant level for the 16 nm thick brushes.

The data for such a comparison are shown in Figure 4b, in which a few features are revealed: (1) the level of friction force on the brush layer is roughly proportional to the thickness of the brush layers (for low and high temperatute, 15 and 32−35 °C); (2) the amount of the friction force decrease with the temperature change before 32−35 °C is also proportional to the layer thickness. These features lead us to the conclusion that the friction force by PNIAPM brushes is related to the length of the PNIPAM chain, i.e., the molecular weight, and each segment contributes to the overall friction force exerting on the P2VP probe.

The friction force experienced by the probe comes from two origins: the viscous drag force from the bulk solvent and the surface friction from the PNIPAM chain. From Figure 4a, it is clear that the surface friction is higher than the viscous force from the solution, and this is true especially for the thicker brush layer. This indicates that the surface friction force comes largely

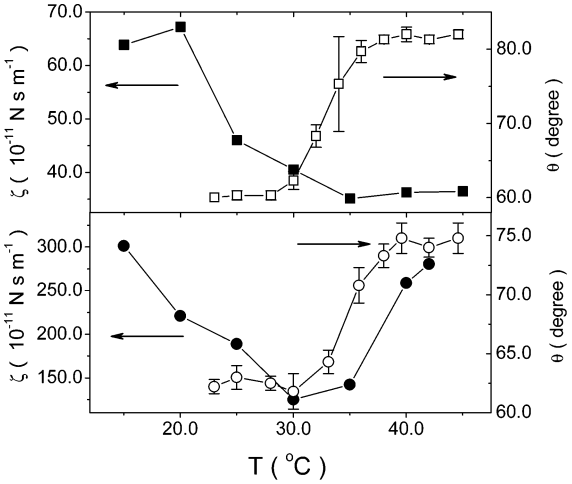

Figure 5. Surface friction (ζ) experienced by single P2VP chain and water contact angle (θ) as a function of the temperature on PNIPAM brushes of 16 nm (top panel) and 90 nm thickness (bottom panel).

from the hydrodynamic force from the PNIPAM chain. We attribute this to the coupling of the motion of P2VP probe and the PNIPAM chains. One possible picture can be that the PNIPAM chains wag in the solvent as the P2VP probe chain moves laterally. This coupling makes the probe chain experience the hydrodynamic force exerted on PNIPAM chains, which should have a linear dependence on the chain dimension or the thickness of the brushes. The hydrodynamic drag force from the brush chain is also dependent on the viscosity of the solvent. An increase of the temperature decreases the viscosity of solvent inside the brushes (water), and therefore a lower hydrodynamic force is experienced by the wagging PNIPAM chain, resulting in the decrease in the friction force on the probe P2VP chain with the increase of the temperature below 32−35 °C.

When the temperature increased further above the range of 32−35 °C, the surface friction force started to increase, and this is related to the LCST transition of the PNIPAM chain. It is well-known that the LCST transition of PNIPAM occurs at the temperature of 32 °C in bulk solution.[13,14] This process involves the breaking of the hydrogen bonding formerly established between the solvent water molecules and the amide groups on the PNIPAM chain and, at the same time, the formation of the intramolecular hydrogen bonding between the amide groups along the PNIPAM chain. Meanwhile, the PNIPAM chains become dehydrated, and water is excluded from the brush layer. Furthermore, there is a strong aggregation between the PNIPAM chains together with the dehydration. This results in the change of the layer structure from a hairy and fluffy layer to a shrunk and closely packed layer, i.e., the surface changes from a "soft" surface to a "hard" one. Also, there is an increase of the chain rigidity of PNIPAM; i.e., they change from flexible to stiffer chains. The recovery of the friction force after 32−35 °C means the "hardened" surface, and the stiffening of the brush chain render a much higher friction force on the probes.

The LCST transition of the PNIPAM brushes has been found to be broader than that in the bulk solution.[2,32−34] In the present case, both water contact angle and friction force exhibit this broad transition (Figure 5). For water contact angle, its changes on 16 and 90 nm thick PNIPAM brushes occurred at 30−40 °C. For the friction force, its change by LCST transition is even broader. This is clearly evidenced by the fact that, for the 90 nm thick brushes, the increase of the friction force continues even after the contact angle value has stabilized when the temperature went beyond 40 °C. This demonstrates a vast difference in the characterization of the LCST process by contact angle and friction force: the contact angle characterizes the surface property of the brush layer while the friction force reflects the property of the whole grafted chain. The results indicate that the LCST process of the PNIPAM chain inside the brush continues when the change of the surface properties finishes. This is believed to be the confinement effect to the PNIPAM chain inside the brushes, and the portion of the chain near the brush surface has a higher mobility than that near the substrate surface. This result is consistent with the multistep LCST process of PNIPAM brush, as demonstrated by surface force apparatus (SFA) and neutron reflectivity measurements.[7,34]

For the thin brush layer (16 nm), the change of friction force is delayed; i.e., it occurs at a higher temperature (35 °C) in comparison with the change of contact angle, showing that the change of friction force is less sensitive than that of contact angle. The contact angle tells the change of the interaction between the water molecules and the PNIPAM chain, but the interaction between the P2VP chain and the brushes does not necessarily change. The molecular interaction between the P2VP and PNIPAM is considered to be hydrophobic interaction, van der Waals interaction, and the interaction between the polar groups of the two chains, none of which experiences a sudden change around 32 °C. It is only when the LCST transition occurs to a considerable portion of the PNIPAM chain that friction force will start to change. We believe that this effect is also dependent on the length of the grafted chain, and a detailed investigation on the brush thickness is underway.

Conclusion

With the sensitivity at single molecular level and the suitable time window of detection, fluorescence correlation spectroscopy (FCS) has been used to study the diffusion of single fluorescence-labeled polyelectrolyte probe, poly(2-vinylpyridine), on the surface of PNIPAM brushes. The observed temperature dependence of diffusion coefficient provides rich information on the friction force generated by the thermoresponsive brushes at its different states. When the temperature is below the LCST transition point, the decrease of viscosity of the solvent water brought about the decrease of the friction force because of the coupling of the lateral diffusion of the probe and the motion of the brush chain. The LCST transition induced stiffening of the PNIPAM chain and the hardening of the PNIPAM brushes above 32−35 °C resulted in a large increase of the friction force.

Acknowledgment. The authors thank Charles C. Han for providing dynamical light scattering (DSL) facilities and Pengxiang Jia for his experimental DLS measurements of the particles for FCS calibration. Experimental help from Hongwei Ma of Peking University is also acknowledged. The current study is under the Project 20474071 and 50730007 supported by National Natural Science Foundation of China.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0710535