Thickness-Dependent Properties of Polyzwitterionic Brushes

Nan Cheng, Andrew A. Brown, Omar Azzaroni, and Wilhelm T. S. Huck*

Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

ABSTRACT: This paper describes detailed studies on the controlled synthesis of poly[2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)ammonium hydroxide (polyMEDSAH) from initiator-modified gold surfaces and the properties of these brushes as a function of grafting density and thickness. Improved control over polymerization was achieved by preforming the catalytically active complex to ensure that the monomers did not coordinate to the catalyst. We observed an intriguing transition thickness (h_{crit}) in which the polyMEDSAH brushes switched from hydrophilic to hydrophobic due to the strong inter- and intrachain associations. We studied this transition as a function of the rate of polymerization and grafting density and found that both factors strongly influence the value of h_{crit}. Faster grown polyMEDSAH brushes have higher h_{crit} values, and brushes grown from higher grafting density have higher h_{crit} value. These observations suggest that the h_{crit} is governed by the density of the brushes, the polymer chain length, and the degree of alignment. Furthermore, the inter- or intrachain associations can be reversed by increasing the temperature, leading to a hydrophobic to hydrophilic switch, where the magnitude of the switching is governed by the grafting density.

1. Introduction

There have been significant theoretical and experimental efforts to study the equilibrium thickness of both weak and strong polyelectrolyte brushes in water and their responsive properties upon changes in pH or addition of salts.[1–6] However, both theoretical and experimental studies have focused almost exclusively on polyelectrolytes that contain either positive or negative charges and where the stretching of the chains is due to repulsive interactions between charged monomers. A different and completely new situation arises in polyelectrolyte brushes that also contain *attractive* noncovalent interactions. In a recent publication,[7] we demonstrated the growth of up to 100 nm thick films of zwitterionic poly[2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)ammonium hydroxide (polyMEDSAH) polymers using atom transfer radical polymerization (ATRP). These are sulfobetaine polymer brushes bearing an anionic sulfonate (SO_3^-) and a cationic quaternary ammonium (QA^+) group on each monomer unit.

Polyzwitterions are isoelectric at neutral pH, with typical dipole moments in the 20–30 D range.[8,9] The salt-free solution properties of polyzwitterions are dominated by attractive electrostatic interactions between the monomeric units, generally rendering them insoluble. This behavior is strongly dependent on temperature and molecular weight, which strongly influence the inter- and intrachain ion-pairing interactions.[10–13] For certain polyzwitterionic hydrogels this reversible self-association manifests itself experimentally as an upper critical solubility temperature (UCST);[12] i.e., only at sufficiently high temperatures are the dipolar, electrostatic, interactions broken, yielding isolated polymer chains that are completely solvated.[14–16] Polyzwitterionic polymers exhibit excellent hemo- and biocompatibility.[17–22] Like other biocompatible surfaces, such as poly(ethylene glycol),[23] biocompatibility is attributed to hydration of the zwitterionic surface to form a dynamic boundary layer.[24] The modification of surfaces with zwitterionic structures is therefore of general interest in the area of biomaterials science, and there are numerous literature examples on the use of self-assembled monolayers and polymeric coatings containing zwitterionic groups.[22,25,26] We,[7] and others,[27,28] have recently shown the formation and protein-resistant properties of zwitterionic polymer brushes. However, thus far, the synthesis of these brushes has been rather difficult to control, with the polymerization terminating after the formation of around 100 nm thick brushes and significant amounts of solution polymerization occurring.

Here we present the formation of up to 600 nm thick brushes of polyMEDSAH and demonstrate how control over the polymerization rate as well as grafting density gives an insight into the unusual properties of these brushes, which show a sudden and significant change in wettability at a relatively precise thickness and grafting density.

2. Experimental Section

Materials. MEDSAH (97%), copper(I) chloride (99.995+%) (CuCl), copper(II) chloride (99.995+%) (CuCl$_2$), and 2,2′-dipyridyl (99+%) (bipy) were purchased from Aldrich and used as received. CuCl was stored under vacuum until needed. Analytical Reagent grade methanol (99.99%) was purchased from Fisher Scientific and used as received. Deionized water with a resistance of 18.2 MΩ·cm was obtained form a Millipore Simplicity 185 system.

Sample Preparation. Gold substrate coated with ω-mercaptoundecyl bromoisobutyrate to form a thiol initiator monolayer was prepared as described previously for surface-initiated ATRP.[3] The polymerization solutions were prepared as follows: MEDSAH (25 g, 89 mmol) was degassed and left under nitrogen. CuCl (0.18 g, 1.8 mmol), CuCl$_2$ (48 mg, 0.36 mmol), and 2,2′-dipyridyl (0.70 g, 4.5 mmol) (bipy) were degassed and left under nitrogen. A mixture of methanol (40 cm^3) and water (10 cm^3) was freeze–pump–thaw degassd at least four times. The monomer was then dissolved in degassed solvent (45 cm^3), and the copper/ligand mixture was dissolved in degassed solvent (5 cm^3). After 10 min the catalyst mixture was added to the monomer solution and mixed thoroughly at room temperature. Initiator-coated samples (~1 cm^2) were sealed in reaction vessels, degassed, and left at room temperature under nitrogen. The polymerization solution was then injected into each reaction vessel, adding enough solution to submerge each sample completely. After various polymerization times the samples were removed, washed with warm Milli-Q water (65 °C), and dried under a stream of nitrogen. Polymerizations with different monomer-to-copper ratios and different grafting density[7] (adopted the system previously published by our group) were carried out to study the kinetics and conformation effects on the properties of this polyelectrolyte zwitterionic brushes.

* To whom correspondence should be addressed: Tel (+44)1223-334-370; Fax (+44)1223-334-866; e-mail wtsh2@cam.ac.uk.
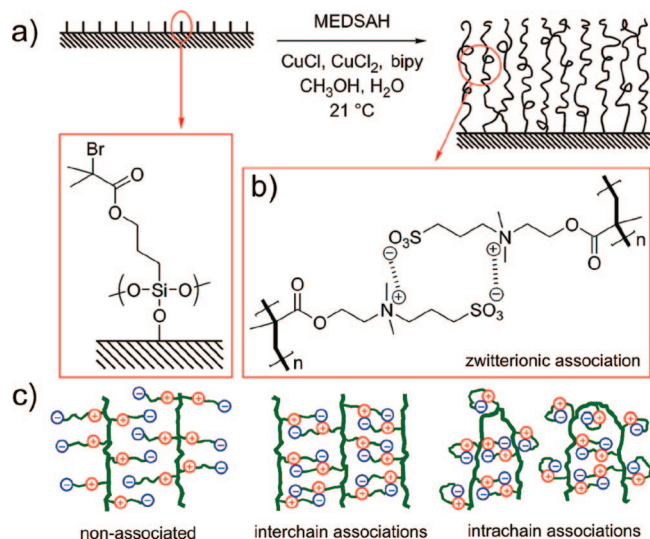
Figure 1. (a) Synthesis of poly[2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)ammonium hydroxide (polyMEDSAH) brushes using surface-initiated atom transfer radical polymerization (ATRP). (b) Ion-pairing interactions between zwitterionic monomers. (c) Different conformational states of polymers in brushes ranging from fully hydrated, nonassociated chains to collapsed chains with interchain and intrachain associations.

Table 1. Relative Concentrations of Catalyst, Deactivator, Monomer ([2-(Methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)ammonium Hydroxide, MEDSAH), and Ligand (2,2′-Dipyridyl, bipy) Used for Polymer Brush Growth from Initiator-Modified Gold Substrates[a]

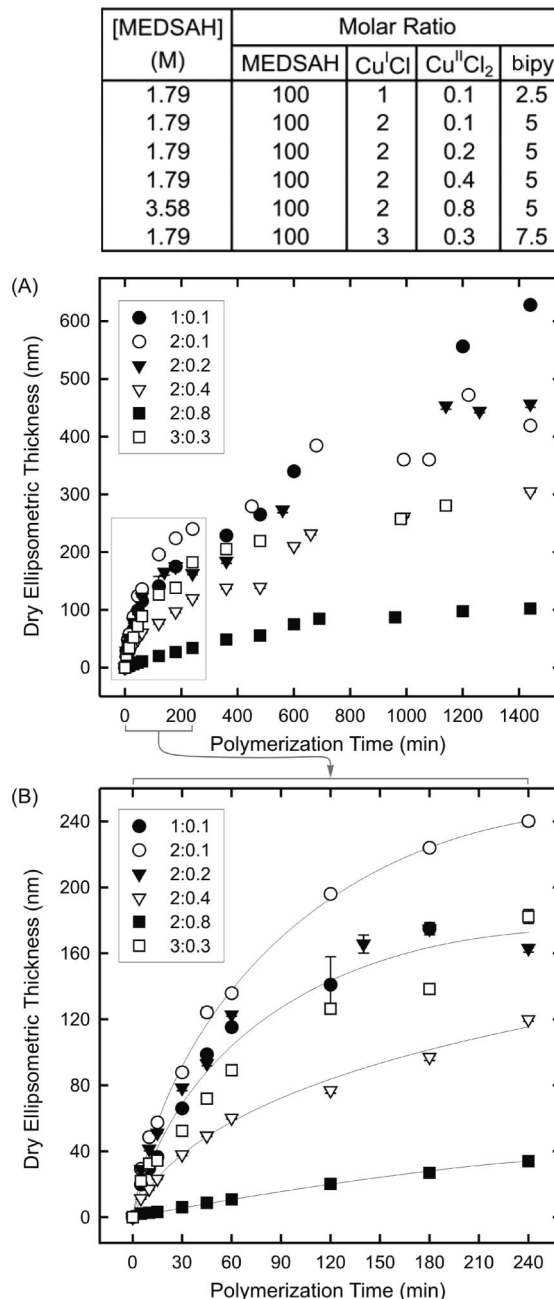| MEDSAH (M)	molar ratio			
	MEDSAH	Cu^ICl	$Cu^{II}Cl_2$	bipy
1.79	100	1	0.1	2.5
1.79	100	2	0.1	5
1.79	100	2	0.2	5
1.79	100	2	0.4	5
3.58	100	2	0.8	5
1.79	100	3	0.3	7.5

[a] All polymerizations were performed at room temperature using water/methanol (20% v/v) as solvent.

Ellipsometry. Ellipsometric measurements were carried out with a spectroscopic ellipsometer (α-SE from J.A. Woollam Co, Inc.). The data were fit using a Cauchy model for the index of refraction of the organic layer and tabulated values for the index of refraction of gold substrate. At least three measurements across each sample were taken.

Contact Angle Measurements. Contact angle goniometry was performed using a homemade stage with a computer-controlled microsyringe and digital camera. Infusion and withdrawal rates of $2 \mu L min^{-1}$ were used. Advancing water contact angles (θ_{AW}) were recorded.

3. Results and Discussion

We previously outlined a synthetic route to polyMEDSAH brushes up to 100 nm thick with potentially interesting surface properties in the form of an UCST transition for brushes over 90 nm thick.[3] The general synthetic route is shown in Figure 1. In our first series of detailed experiments into the growth of these brushes, we used a polymerization solution containing MEDSAH, CuCl, CuCl₂, and 2,2′-bipyridine at molar ratios ranging from 100:1:0.1:2.5 to 100:3:0.3:7.5, respectively (as shown in Table 1), with a monomer concentration of 1.79 M, with water in methanol (20% v/v) as solvent. The solution was rigorously degassed using four freeze−thaw cycles to minimize uncontrolled polymerization in solution. The different ratios of

[MEDSAH]	Molar Ratio			
(M)	MEDSAH	Cu^ICl	$Cu^{II}Cl_2$	bipy
1.79	100	1	0.1	2.5
1.79	100	2	0.1	5
1.79	100	2	0.2	5
1.79	100	2	0.4	5
3.58	100	2	0.8	5
1.79	100	3	0.3	7.5

Figure 2. Time-resolved growth of poly[2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)ammonium hydroxide (polyMEDSAH) brushes on gold: (A) 0−24 h polymerization time; (B) 0−240 min polymerization time. All polymerizations used a monomer concentration of 1.79 M in water/methanol (20% v/v) at room temperature. Legend values refer to the molar ratio of $[Cu^+]/[Cu^{2+}]$ molar ratios used, as outlined in Table 1. Lines are added to guide the eye.

Cu^+ to Cu^{2+} provide a synthetic tool to improve the "living" character of the brush growth.[29,30] The ellipsometric data for the thickness of the polymer brushes formed under different conditions is shown in Figure 2. Some general trends can be observed during the first 200 min of the polymerization (which are partly lost during later stages of the reaction):

First, in agreement with the general rate equation for ATRP reactions,[31,32] increasing the concentration of deactivating CuCl₂ slowed down the kinetics of polymerization, as can be seen for the series 2: 0.1; 2: 0.2; 2: 0.4; 2: 0.8. Second, changing the ratio of total catalyst to monomer, while keeping the $[Cu^+]$/$[Cu^{2+}]$ molar ratios constant had little influence on the rate of polymerization, as can be seen for the series 1: 0.1; 2: 0.2; 3: 0.3.
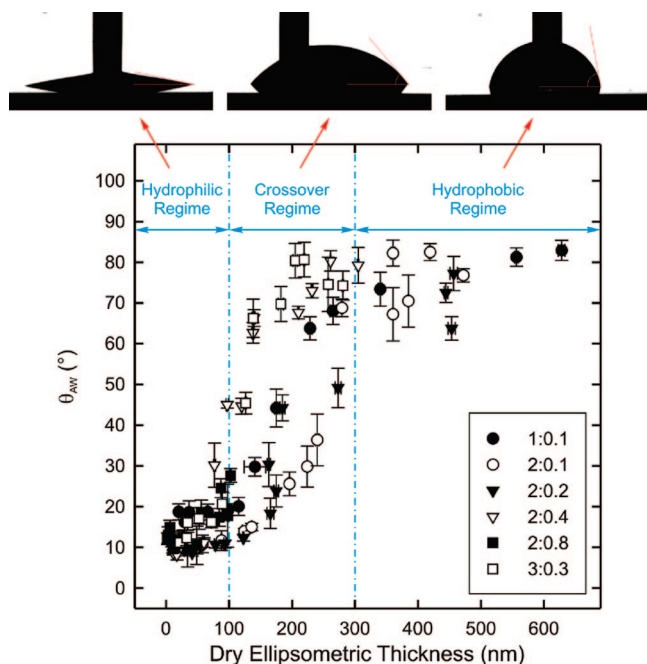
Figure 3. Plot of advancing water contact angle (θ_{AW}) as a function of the thickness of poly[2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)ammonium hydroxide (polyMEDSAH) brushes on gold. Same polymerization conditions as listed in Table 1. The legend labels refer to the corresponding [Cu$^+$]/[Cu^{2+}] molar ratios for that experiment.

The samples were further analyzed by contact angle goniometry, the results of which are depicted in Figure 3. We intuitively expect the results to be independent of film thickness since the material of the film is uniform throughout, but we previously[7] observed that thick (>90 nm) polyMEDSAH brushes were markedly more hydrophobic than thin brushes. Looking at our contact angle data, it becomes quite obvious that the thickness-dependent properties of polyMEDSAH brushes are quite complicated.

In general, films below a thickness of ~90 nm are hydrophilic with θ_{AW} between 10° and 20°. Above a film thickness of ~300 nm the films are hydrophobic with θ_{AW} up to ~80°. Between these thicknesses a broad crossover regime is observed. Looking closely at Figure 3, the critical switching thickness (h_{crit}) for the series 2: 0.4 occurs close to the lower boundary of 100 nm. Conversely, h_{crit} for the series 2: 0.1 occurs near the upper limit of 300 nm.

Figure 3 also indicates that increasing the CuCl$_2$ concentration reduces the critical thickness at which a change in wettability occurs. By combining these observations for the kinetics and wetting, the beginnings of a theory can be proposed. Increasing the polymerization rate and/or losing control over the polymerization will result in an extended hydrophilic regime, switching to a hydrophobic regime at a higher h_{crit}. Slow growing, well-controlled brushes will exhibit narrow molecular weight distributions and similar polymer chain densities throughout their profile. Conversely, rapid polymer brush growth would be expected to yield films with broader molecular weight distributions, and therefore a reduced polymer chain density, due to the burial of active end groups by surrounding chains and an increased probability of termination. These differences in brush morphology may explain the spread of data for the wetting characteristics shown in Figure 3.

These initial experiments prompted us to further improve the control over the polymerization reaction. The key to further control was found in changing the procedure for mixing the brush growth solution. We noticed that no polymers formed in solution before the addition of copper catalyst and that more

solution polymer formed with larger amounts of catalyst added. A possible explanation for this is the formation of sulfobetaine copper complexes which may lead to unwanted side reactions.[33] In order to overcome this problem, the copper catalyst was precoordinated and degassed separately from the MEDSAH monomer. In a typical experiment, water in methanol (20% v/v) was freeze−pump−thaw degassed at least four times. The monomer MEDSAH was degassed and left under nitrogen in a separate flask. The CuCl, CuCl$_2$, and bipy were degassed and left under nitrogen in a third flask. Once the solvent was degassed, 10% of the total solvent volume required was added to the catalyst flask; the solution was stirred for at least 10 min to precoordinate the copper, forming the copper−(bipy)$_2$ complexes. The remaining 90% of the total solvent needed was added to the monomer. Once the monomer had dissolved, the precoordinated catalyst was added to the monomer solution. After thorough mixing, the polymerization solution was injected over initiator-coated wafer samples held under nitrogen and left to polymerize for various times. After polymerization the samples were washed with warm Milli-Q water at 65 °C and dried under a stream of nitrogen before analysis. Masses and volumes of the starting materials were chosen such that in the final polymerization solution the monomer concentration was 1.79 M, and the ratio of monomer to catalyst followed a selection of those given in Table 1. The polymerization was now much more reproducible (although slower), and no solution polymerization was observed for the first 20 h of the reaction. The reaction follows a similar trend as observed for the conditions described above, with more Cu^{2+} leading to slower brush growth.

However, Figure 4 shows that in all cases there is now a dramatic and sudden change of the contact angles from hydrophilic to hydrophobic when the thickness of the brushes reaches a critical thickness (h_{crit}). The transition is clearly strongly correlated to the Cu$^+$/Cu^{2+} ratio and can be tuned to occur anywhere between 50 and 250 nm brush thickness. Slower growing brushes show lower h_{crit}, which suggests that it is not the length of the chains (i.e., the molecular weight of the brushes) that is the key parameter that determines the value of h_{crit}. Instead, slower growing brushes are more dense,[30] and it is the grafting density of the polymer brushes that apparently controls the collapse transition of the brushes.

In order to study the influence of grafting density in a more controlled way, a set of experiments using different initiator densities but the same polymerization condition ([Cu$^+$]/[Cu^{2+}] = 2:0.8) was carried out. The exact grafting density is difficult to determine as not all initiator molecules in the self-assembled monolayers will carry a polymer chain.[34] We varied the grafting density from 10% to 100% by mixing the thiol initiator with different amounts of undecanethiol, and the kinetic plots are shown in Figure 5. All polymerizations used a monomer concentration of 1.79 M in water/methanol (20% v/v) at room temperature. The legend labels refer to the corresponding initiator concentration for the experiment.

When decreasing the initiator concentration, i.e., decreasing the initial grafting density on the polyzwitterionic brushes, the polymerization reactions are not so well controlled as the 100% initiators ones. However, with lower initiator concentration, the thickness increased slower and terminated at a lower brushes thickness, which agrees with the rate equation, as the rate of polymerization is proportional to the initiator concentration while the rest of the parameters are the same. When decreasing the initial grafting density, the polymer brushes conformation changes from the so-called "brushes regime" to the so-called "mushroom regime".[35−37] If we look at the thickness vs advancing contact angle plots (Figure 5b), there is a transition point of thickness for all cases. However, the transition thickness
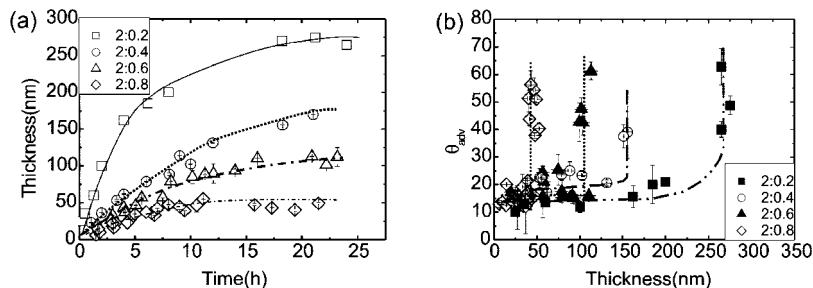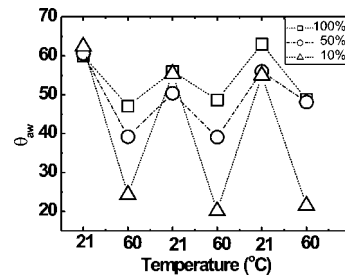
Figure 4. (a) Time-resolved growth of poly[2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)ammonium hydroxide (polyMEDSAH) brushes on gold with different $[Cu^+]/[Cu^{2+}]$ ratios. (b) Advancing water contact angles (θ_{AW}) as a function of brush thickness. All polymerizations used a monomer concentration of 1.79 M in water/methanol (20% v/v) at room temperature. The legend labels refer to the corresponding $[Cu^+]/[Cu^{2+}]$ molar ratios.
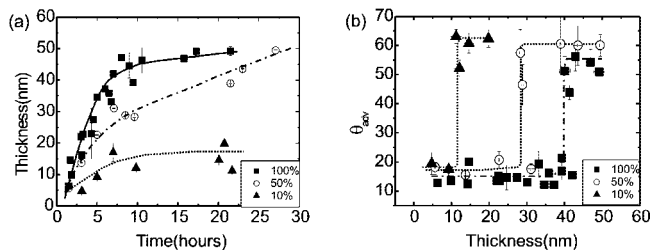
Figure 5. (a) Plots of dry poly[2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)ammonium hydroxide (polyMEDSAH) brushes thickness as a function of polymerization time with different initiator concentrations. (b) Plot of advancing water contact angle (θ_{AW}) as a function of the brush thickness with respect to different initiator concentration. All polymerizations used a monomer concentration of 1.79 M in water/methanol (20% v/v) at room temperature.

Figure 6. Changes of the wetting characteristics of hydrophobic poly[2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)ammonium hydroxide (polyMEDSAH) brushes after raising the temperature from 20 to 60 °C. All polymerizations used a monomer concentration of 1.79 M in water/methanol (20% v/v) at room temperature with varied initiator concentrations. The legend refers to the fraction of initiator molecules on the substrate.

appears at lower thickness in case of lower initial grafting density.

To rule out differences in surface morphology for the different grafting densities, we characterized these samples using AFM. For the dense brushes (100% initiator), the roughness (rms, as determined by AFM software) of the brushes changed from 0.5 to 1.2 nm^2 when the thickness increased from 27 to 40 nm and the contact angle changed from about 15° to 51°. However, for the 50% initiator brushes the rms roughness remained more or less constant (0.8 nm^2) when the thickness changed from 28 to 39 nm. These differences are quite minimal and are not expected to make a significant contribution to the contact angles. However, Figure 5b shows different h_{crit} values for different grafting densities; the brushes were grown for approximately similar amounts of time (polymerization for 7−8 h resulted in ~40−45 nm thick brushes on 100% initiator density SAMs and 10−15 nm thick brushes on 10% initiator SAMs) when the polymer brushes hit the h_{crit} and changed from hydrophilic to hydrophobic. Under the conditions used, brush growth was controlled, and therefore the molecular weights of these brushes should all be quite similar. This result strongly indicated that a critical molecular weight (or length) of the polymer brushes is a determining factor for the collapse transition. Combining these data with the results on less controlled polymerizations, we believe that it is molecular weight that determines the value for h_{crit}. However, if the length of the polymer chains would be the only deciding factor, then the very thick (≫100 nm) brushes reported previously should all be hydrophobic, as we observe hydrophobic transitions at around 40 nm here. Therefore, we believe that the transition must also be associated with the specific *intrachain* and *interchain* interactions between *neighboring* chains (Figure 1). This strongly indicates that alignment of the chains, which is a unique property of polymer brushes, and thereby an increased organization of the interacting dipole−dipole associations, the trigger that provides hydrophobic collapse, provided that the chains are of sufficient molecular

weights. However, we cannot measure the absolute grafting density of these brushes as we cannot measure the molecular weights of the chains. (The polymers would be very insoluble in water, and we can only obtain minute amounts of polymer after dissolving the Au substrates.) The alignment in the brushes will occur in dense brushes as well as in dilute brushes (dilute due to more rapid growth or grown from 10% initiator SAMs) once the size of the chains is larger than the distance between grafting points. However, the brushes grown at different speeds will also show differences in polydispersity.[30] We believe that the increased polydispersity of the rapidly and uncontrolled growing chains will broaden the wetting transition and obscure the influence of molecular weight and alignment of the chains.

In our previous work on polyMEDSAH brushes,[7] we reported that these brushes show a reversible wetting transition at around 52 °C, which we attributed to the UCST of the polyzwitterionic polymers. This UCST is normally strongly influenced by the molecular weight and concentration of the polymers and the nature and concentration of added salts.[12,38] Here, we show a marked influence of the grafting density on the wetting transition. Figure 6 shows the reversible transition between hydrated (hydrophilic) brushes at temperatures above the UCST (60 °C) and the more hydrophobic, dehydrated brushes at room temperature. All brushes became more hydrophilic at high temperatures, but the magnitude of contact angle change ranged from 10−15° for the 100% brushes to 30−35° for the 10% initiator brushes, showing a strong dependency on the grafting density. The more dilute brushes showed much lower contact angles when hydrated (and slightly lower contact angles at room temperature). This effect can be explained by considering that hydrated brushes of lower grafting densities will contain a significantly larger fraction of water and therefore will show lower contact angles. Probing the UCST transition using contact angles should more appropriately be measured using "captive bubble" contact angles of air in water.[39] In this study, we only

probed a number of both hydrophilic and hydrophobic brushes using this method and found no qualitative differences.

4. Conclusions

We have described a detailed investigation into the controlled synthesis of PMEDSAH brushes by ATRP. The impetus for this work was provided by our observation that uncontrolled polymerization yielded very thick brushes (>500 nm), but the brush growth was accompanied by polymer formation in solution. Furthermore, these brushes showed fairly unusual surface wettability characteristics as a function of the thickness. However, the transition from hydrophilic to hydrophobic brushes took place in a very wide (200 nm) thickness window which made it impossible to draw any conclusions about the underlying mechanism. Significantly better control over the polymerization was achieved by performing the Cu−bipy complex to ensure that the monomers did not coordinate to the catalysts. Furthermore, we explored a wide range of different $[Cu^+]/[Cu^{2+}]$ molar ratios to maximize reproducibility in the brush growth. To corroborate faster brush growth with our assumption that such brushes would be have a lower grafting density, we also initiated polymer brushes from monolayers with different initiator densities. As a result of the improved synthetic procedure, the wettability transition now occurred at precise thicknesses (h_{crit}), below which all brushes showed the same hydrophilic character and above which the brushes were more or less equally hydrophobic. We studied the transition as a function of rate of polymerization and grafting density and found that both factors strongly influence the value of h_{crit}. Overall, our experiments strongly point in the direction of an interplay between intrachain associations between zwitterionic groups on monomers on the same chains and interchain associations between neighboring polymer chains. This interplay is governed by the density of the brushes, the polymer chain length, and the degree of alignment. Clearly, low molecular weight and dilute brushes will always be hydrophilic, higher molecular weight, but dilute (and/or polydisperse) brushes will also be hydrophilic, until the chains stretch away from the surface, have a sufficient molecular weight, and are sufficiently dense and monodisperse to form interchain associations. We have previously suggested that some form of supercollapsed state[40] could be responsible for the rapid transition: once these associations form, the polymers rapidly "zip" together, as the dipole−dipole pairing leads to an avalanche of further associations in the locally less polar environment. Such a supercollapse transition would explain the "sudden" collapse of the brushes at a particular thickness, rather than a slow increase in the contact angles with increasing thickness or grafting density. Finally, the self-associated state can be reversed by increasing the temperature, leading to a hydrophobic-to-hydrophilic switch, and we show that the magnitude of the switching is governed by the grafting density. The increased control over the brush growth and the reversible switching in wettability, in combination with the reported biocompatibility and protein-resistance properties of polyzwitterionic polymers, make these brushes interesting candidates for new types of adaptive surfaces with applications in microfluidics, sensors, and protein diagnostics.

References and Notes

(1) Konradi, R.; Ruhe, J. *Macromolecules* **2004**, *37*, 6954–6961.
(2) Tran, Y.; Auroy, P.; Lee, L. T.; Stamm, M. *Phys. Rev. E* **1999**, *60*, 6984–6990.
(3) Zhou, F.; Huck, W. T. S. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3815–3823.
(4) Wu, T.; Gong, P.; Szleifer, I.; Vlcek, P.; Subr, V.; Genzer, J. *Macromolecules* **2007**, *40*, 8756–8764.
(5) Israels, R.; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B. *Macromolecules* **1994**, *27*, 3249–3261.
(6) Zhulina, E. B.; Birshtein, T. M.; Borisov, O. V. *Macromolecules* **1995**, *28*, 1491–1499.
(7) Azzaroni, O.; Brown, A. A.; Huck, W. T. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 1770–1774.
(8) Bredas, J. L.; Chance, R. R.; Silbey, R. *Macromolecules* **1988**, *21*, 1633–1639.
(9) Galin, M.; Chapoton, A.; Galin, J. C. *J. Chem. Soc., Perkin Trans. 2* **1993**, 545–553.
(10) Georgiev, G.; Tzoneva, A.; Lyutov, L.; Iliev, S.; Kamenova, I.; Georgieva, V.; Kamenska, E.; Bund, A. *Macromol. Symp.* **2004**, *210*, 393–401.
(11) Rubinstein, M.; Dobrynin, A. V. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 83–87.
(12) Schulz, D. N.; Peiffer, D. G.; Agarwal, P. K.; Larabee, J.; Kaladas, J. J.; Soni, L.; Handwerker, B.; Garner, R. T. *Polymer* **1986**, *27*, 1734–1742.
(13) Soto, V. M. M.; Galin, J. C. *Polymer* **1984**, *25*, 254–262.
(14) Moelbert, S.; De los Rios, P. *Macromolecules* **2003**, *36*, 5845–5853.
(15) Lee, W. F.; Chen, C. F. *J. Appl. Polym. Sci.* **1998**, *69*, 2021–2034.
(16) Chen, L.; Honma, Y.; Mizutani, T.; Liaw, D. J.; Gong, J. P.; Osada, Y. *Polymer* **2000**, *41*, 141–147.
(17) West, S. L.; Salvage, J. P.; Lobb, E. J.; Armes, S. P.; Billingham, N. C.; Lewis, A. L.; Hanlon, G. W.; Lloyd, A. W. *Biomaterials* **2004**, *25*, 1195–1204.
(18) Yuan, Y. L.; Zang, X. P.; Ai, F.; Zhou, J.; Shen, J.; Lin, S. C. *Polym. Int.* **2004**, *53*, 121–126.
(19) Moro, T.; Takatori, Y.; Ishihara, Y.; Konno, T.; Takigawa, Y.; Matsushita, T.; Chung, U. I.; Nakamura, K.; Kawaguchi, H. *Nat. Mater.* **2004**, *3*, 829–836.
(20) Yuan, J. A.; Bian, R. B.; Ling, T.; Jian, S.; Lin, S. C. *Colloids Surf., B* **2004**, *36*, 27–33.
(21) Lowe, A. B.; Vamvakaki, M.; Wassall, M. A.; Wong, L.; Billingham, N. C.; Armes, S. P.; Lloyd, A. W. *J. Biomed. Mater. Res.* **2000**, *52*, 88–94.
(22) Chang, Y.; Chen, S. F.; Zhang, Z.; Jiang, S. Y. *Langmuir* **2006**, *22*, 2222–2226.
(23) Pertsin, A. J.; Grunze, M. *Langmuir* **2000**, *16*, 8829–8841.
(24) Ostuni, E.; Chapman, R. G.; Holmlin, R. E.; Takayama, S.; Whitesides, G. M. *Langmuir* **2001**, *17*, 5605–5620.
(25) Holmlin, R. E.; Chen, X. X.; Chapman, R. G.; Takayama, S.; Whitesides, G. M. *Langmuir* **2001**, *17*, 2841–2850.
(26) Chen, S. F.; Zheng, J.; Li, L. Y.; Jiang, S. Y. *J. Am. Chem. Soc.* **2005**, *127*, 14473–14478.
(27) Feng, W.; Brash, J. L.; Zhu, S. P. *Biomaterials* **2006**, *27*, 847–855.
(28) Cho, W. K.; Kong, B. Y.; Choi, I. S. *Langmuir* **2007**, *23*, 5678–5682.
(29) Pyun, J.; Kowalewski, T.; Matyjaszewski, K. *Macromol. Rapid Commun.* **2003**, *24*, 1043–1059.
(30) Cheng, N.; Azzaroni, O.; Moya, S.; Huck, W. T. S. *Macromol. Rapid Commun.* **2006**, *27*, 1632–1636.
(31) Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* **2001**, *101*, 2921–2990.
(32) Matyjaszewski, K.; Gaynor, S. G.; Muller, A. H. E. *Macromolecules* **1997**, *30*, 7034–7041.
(33) Song, Y. J.; Doomes, E. E.; Prindle, J.; Tittsworth, R.; Hormes, J.; Kumar, C. *J. Phys. Chem. B* **2005**, *109*, 9330–9338.
(34) Jones, D. M.; Brown, A. A.; Huck, W. T. S. *Langmuir* **2002**, *18*, 1265–1269.
(35) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 983–987.
(36) Liu, G. M.; Yan, L. F.; Chen, X.; Zhang, G. Z. *Polymer* **2006**, *47*, 3157–3163.
(37) Milner, S. T. *Science* **1991**, *251*, 905–914.
(38) Koberle, P.; Laschewsky, A.; Tsukruk, V. *Makromol. Chem.* **1992**, *193*, 1815–1827.
(39) Jonas, A. M.; Glinel, K.; Oren, R.; Nysten, B.; Huck, W. T. S. *Macromolecules* **2007**, *40*, 4403–4405.
(40) Khokhlov, A. R.; Kramarenko, E. Y. *Macromol. Theory Simul.* **1994**, *3*, 45–59.

MA800625Y