Designing Surfaces with Wettability That Varies in Response to Solute Identity and Concentration

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Surfaces with solute responsive wettability can be prepared by covalent layer-by-layer assembly of PNIPAM-*c*-PNASI with 10 and 100 nm diameter aminated silica nanoparticles. These surfaces are found to exhibit reversible changes in surface wetting in response to solute anion identity and concentration, allowing surfaces to be switched from hydrophilic (advancing water contact angle 68°) to hydrophobic (advancing water contact angle 145°). The extent of the response to solute salts is found to be consistent with the Hofmeister series and with associated changes in surface roughness which result from varying degrees of polymer swelling in response to solute ion identity and concentration. The observed wettability changes on these surfaces are reversible.

"Smart" surfaces[1−3] that respond to external stimuli such as pH, temperature, or solvent are of interest in many applications. While ionizable surface grafts can be used to induce significant changes in permeability, wettability, or reactivity,[4−6] changes in surface properties solely in response to varied solutes in the same solvent or to varied concentrations of the same solute have not been reported. Here, we describe nanocomposite grafts prepared by covalent layer-by-layer assembly that exhibit striking changes in surface wetting in response to changes in solute identity or concentration that follow a Hofmeister series.

The types of changes in wettability as a function of solute ion and concentration that are seen are illustrated in Figures 1 and 2. In these figures, drops of water or salt solutions that have been allowed to stand for 3 min on the same functionalized surface have distinctly different static contact angles (Θ). As shown in Figure 1, the same surface was found to be reversibly either hydrophilic or hydrophobic depending on the identity of the solute in the water. Moreover, these solute-induced wettability changes were also found to be sensitive to the concentration of the given solute with significant differences in contact angle (Θ) for even dilute aqueous solutions of a solute such as sodium citrate (Figure 2). These visually apparent changes in wettability for the same surface are not only large, they are also reversible and reproducible. The same surface can be treated with dozens of different solute solutions but still has similar wettability on subsequent re-examination with water. While the visually different wettabilities in Figures 1 and 2 illustrate the responsiveness of these surfaces, these static water drop contact angles gradually change with time due in part to evaporation of the water drops at the surface. Thus, wettability is discussed using measurements of advancing contact angle for the various solute ions throughout the rest of this paper (see the Supporting Information).

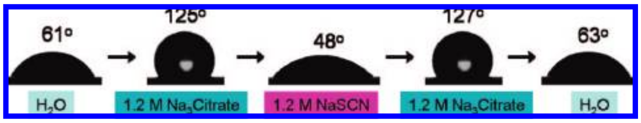

Figure 1. Contact angles for various aqueous solutions on the same surface measured after 3 min.

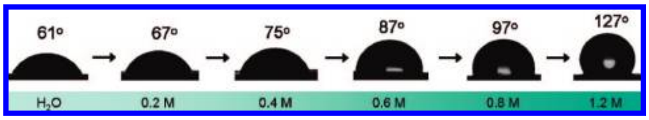

Figure 2. Contact angles for various aqueous solutions of sodium citrate on the same surface each measured after 3 min.

These varied effects are a result of solute-induced changes in hydration of a topologically complex nanocomposite surface that contains poly(*N*-isopropylacrylamide) (PNIPAM). PNIPAM is a well-known polymer whose lower critical solution temperature (LCST) and solubility varies in accord with the Hofmeister effect.[7−15] While Hofmeister effects at interfaces are known,[16−18] easily prepared surfaces with significant Hofmeister-like anion-responsive wettability have not been reported. This is surprising given the extensive number of studies of such effects and the

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(1) Kumar, A.; Srivastava, A.; Galaev, I. Y.; Mattiasson, B. *Prog, Polym. Sci.* **2007**, *32*, 1205–1237.

(2) Zhou, F.; Huck, W. T. S. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3815–3823.

(3) Luzinov, I.; Minko, S.; Tsukruk, V. V. *Soft Matter* **2008**, *4*, 714–725.

(4) Peez, R. F.; Dermody, D. L.; Franchina, J. G.; Jones, S. J.; Bruening, M. L.; Bergbreiter, D. E.; Cooks, R. M. *Langmuir* **1998**, *14*, 4232–4237. Zhao, M.; Liu, Y.; Crooks, R. M.; Bergbreiter, D. E. *J. Am. Chem. Soc.* **1999**, *121*, 923–930.

(5) Wang, S.; Liu, H.; Liu, D.; Ma, X.; Fang, X.; Jiang, L. *Angew. Chem., Int. Ed.* **2007**, *46*, 3915–3917.

(6) Connal, L. A.; Li, Q.; Quinn, J. F.; Tjipto, E.; Caruso, F.; Qiao, G. G. *Macromolecules* **2008**, *41*, 2620–2626.

(7) Fu, Q.; Rao, G. V. R.; Basame, S. B.; Keller, D. J.; Artyushkova, K.; Fulghum, J. E.; Lopez, G. P. *J. Am. Chem. Soc.* **2004**, *126*, 8904–8905.

(8) Sun, T.; Wang, G.; Feng, L.; Liu, B.; Ma, Y.; Jiang, L.; Zhu, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 357–360.

(9) Jonas, A. M.; Glinel, K.; Oren, R.; Nysten, B.; Huck, W. T. S. *Macromolecules* **2007**, *40*, 4403–4405.

(10) Ivanov, A. E.; Ekeroth, J.; Nilsson, L.; Mattiasson, B.; Bergenstahl, B.; Galaev, I. Y. *J. Colloid Interface Sci.* **2006**, *296*, 538–544.

(11) Yuan, W.; Jiang, G.; Wang, J.; Wang, G.; Song, Y.; Jiang, L. *Macromolecules* **2006**, *39*, 13001303.

(12) He, Q.; Küller, A.; Grunze, M.; Li, J. *Langmuir* **2007**, *23*, 3981–3987.

(13) Song, W.; Xia, F.; Bai, Y.; Liu, F.; Sun, T.; Jiang, L. *Langmuir* **2007**, *23*, 327–331.

(14) Yusa, S.; Fukuda, K.; Yamamoto, T.; Iwasaki, Y.; Watanabe, A.; Akiyoshi, K.; Morishima, Y. *Langmuir* **2007**, *23*, 12842–12848.

(15) Kurkuri, M. D.; Nussio, M. R.; Deslandes, A.; Voelcker, N. H. *Langmuir* **2008**, *24*, 4238–4244.

(16) Boström, M.; Williams, D. R. M.; Ninham, B. W. *Langmuir* **2002**, *18*, 8609–8615.

(17) Chen, X.; Yang, T.; Kataoka, S.; Cremer, P. S. *J. Am. Chem. Soc.* **2007**, *129*, 12272–12279.

(18) Ishida, N.; Biggs, S. *Macromolecules* **2007**, *40*, 9045–9052.

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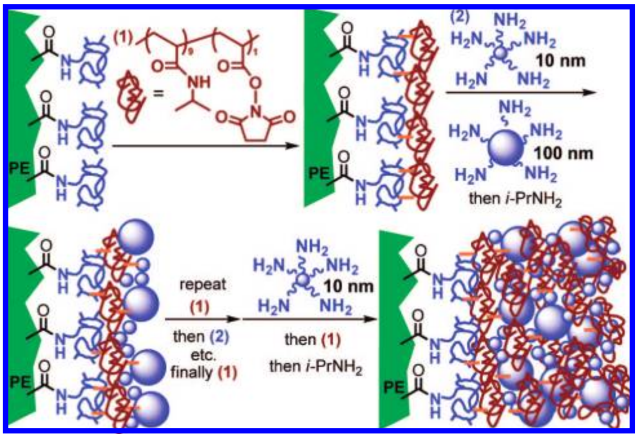
Scheme 1. Covalent Layer-by-Layer Self-Assembly of a PNIPAM-*c*-PNASI/Aminated Silica Nanoparticle/PNIPAM Graft on a PEI Modified PE Film (the Final Structure Is Not Drawn to Scale)



sharp and visually obvious phase transitions seen for many polymers in salt solutions.[1,19−21]

We prepared these responsive surfaces by covalent layer-by-layer grafting chemistry.[4,22] These syntheses drew inspiration from our prior work on the assembly of superhydrophobic surfaces. In that work, we had shown first that condensation of an electrophilic anhydride-containing polymer with polyvalent nucleophilic polymers or aminated MWNTs (multiwall nanotubes) led to covalent grafts that exhibited significant pH-responsive wettability. We had also shown that nanocomposite grafts formed with polydisperse MWNTs were topologically complex and that these grafts when chemically modified could be either superhydrophobic or superhydrophilic depending on whether the grafts were modified with hydrophobic or hydrophilic reagents. We reasoned that similar nanocomposite grafts whose hydrophobic or hydrophilic character changes in response to solute concentration could also be prepared without chemical derivatization if they were prepared with a responsive polymer. This proved to be the case, and we see responsive solute dependent wettability for grafts formed by covalent layer-by-layer assembly of a copolymer of NIPAM and *N*-acryloxysuccinimide (NASI) (PNIPAM-*c*-PNASI) with an aminated silica nanoparticle mixture (Scheme 1).

Our synthesis of these responsive nanocomposite grafts involved assembling a covalent graft using the copolymer **1**, PNIPAM-*c*-PNASI (M_n = 30 000 Da), and an admixture of aminated 10 and 100 nm fused silica particles as polyvalent electrophilic and nucleophilic reagents, respectively. In the first step of this process, the NASI groups in the copolymer **1** are allowed to react with the amine groups of an aminated surface derived from the reaction of an activated, oxidized polyethylene with polyethyleneimine (PEI).[23] This leads to covalent binding of **1** to this surface via amide bonds. However, spatial constraints preclude complete consumption of all of the NASI groups of **1**. This results in a surface having unreacted electrophilic NASI groups that can react with amine groups of amine-functionalized 10 and 100 nm diameter silica nanoparticles in a second step. As shown in Scheme 1, this second step produces a nucleophilic amine-rich surface. While this surface could be used as is for further grafting, we treated this surface with excess *i*-PrNH$_2$. This quantitatively converts any unreacted NASI groups into NIPAM groups.[24,25] The covalent layer-by-layer assembly then continues with further stages of PNIPAM-*c*-PNASI/10 and 100 nm aminated silica nanoparticle/*i*-PrNH$_2$ treatment. After six such stages, the surface was capped with PNIPAM-*c*-PNASI and treated with excess *i*-PrNH$_2$ to form the PNIPAM-*c*-PNASI/aminated silica nanoparticle/PNIPAM graft on a PEI modified PE film. These grafts contain carboxamides based on peaks at 1670 and 1640 cm^{-1} in the attenuated total reflection infrared (ATR-IR) spectrum (see the Supporting Information). This surface was further characterized by atomic force microscopy (AFM) (Figure 3) and in air had an average surface roughness of ∼287 nm based on analysis of a random series of 2.5 μm × 2.5 μm regions.

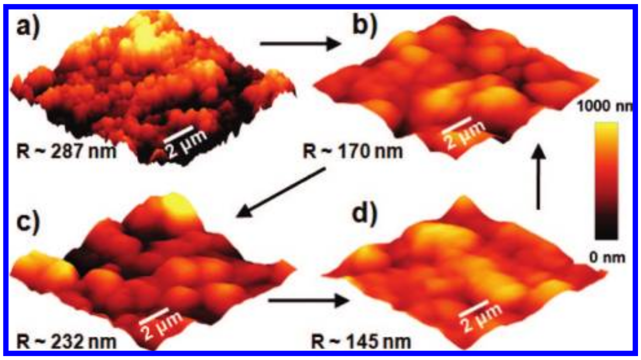


Figure 3. Tapping mode AFM images of PE$_{oxid}$-(PNIPAM-*c*-PNASI/aminated silica nanoparticles)$_6$-PNIPAM obtained in (a) air, (b) water, (c) 1.4 M Na$_2$SO$_4$, and (d) 1.2 M NaSCN. Returning the sample to water yields an surface similar to (b). The average rms roughness of the surface in each environment taken from a random series of 2.5 μm × 2.5 μm regions is listed below each figure.

Most interestingly, this surface exhibited solute dependent wettability. To avoid any time dependent changes in contact angle, here we report the differences in advancing water contact angles for various solutes. With pure water, the advancing contact angle (Θ_a) was 76°, while with 1.4 M Na$_2$SO$_4$ (a Hofmeister kosmotrope) the Θ_a was 144°. This 68° difference in Θ_a between water versus 1.4 M Na$_2$SO$_4$ ($\Delta\Theta_a$) was much larger than the $\Delta\Theta_a$ seen using these same solutions on glass, unfunctionalized PE, oxidized PE, or a PEI/Gantrez graft on PE that was grafted with PNIPAM.[8] Those surfaces had smaller $\Delta\Theta_a$ values of 14°, 0°, 8°, and 25°, respectively.

The AFM measurements of the PE$_{oxid}$-(PNIPAM-*c*-PNASI/aminated silica nanoparticle)$_6$-PNIPAM surfaces show visible changes in surface texture when changing from one solute to the next (Figure 3). In air, the surfaces are rough and the larger silica particles (ca. 100 nm) dominate the surface morphology. Upon immersion in water, the film swells and the surface roughness decreases from ∼287 nm rms to ∼170 nm rms. Replacement of water by 1.4 M Na$_2$SO$_4$ results in an increase in roughness (ca. 232 nm rms) along with the $\Delta\Theta_a$ of 68°. In 1.2 M NaSCN, the surface roughness decreased to ∼145 nm rms and the Θ_a changed to 72° ($\Delta\Theta_a$ of −4°). These changes show that these surfaces reconstruct in response to different solutes and suggest that the changes in water contact angle are likely due to a combination

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(19) Zhang, Y.; Furyk, S.; Bergbreiter, D. E.; Cremer, P. S. *J. Am. Chem. Soc.* **2005**, *127*, 14505–14510.

(20) Bergbreiter, D. E.; Fu, H. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 186–193.

(21) Zhang, Y.; Cremer, P. S. *Curr. Opin. Chem. Biol.* **2006**, *10*, 658–663.

(22) Liao, K.-S.; Wan, A.; Batteas, J. D.; Bergbreiter, D. E. *Langmuir* **2008**, *24*, 4245–4253.

(23) Kim, Y.-S.; Liao, K.-S.; Jan, C. J.; Bergbreiter, D. E.; Grunlan, J. C. *Chem. Mater.* **2006**, *18*, 2997–3004.

(24) Batz, H. G.; Franzmann, G.; Ringsdorf, H. *Angew. Chem., Int. Ed.* **1972**, *11*, 1103–1104.

(25) Bergbreiter, D. E.; Aviles-Ramos, N. A.; Ortiz-Acosta, D. *J. Comb. Chem.* **2007**, *9*, 609–617.

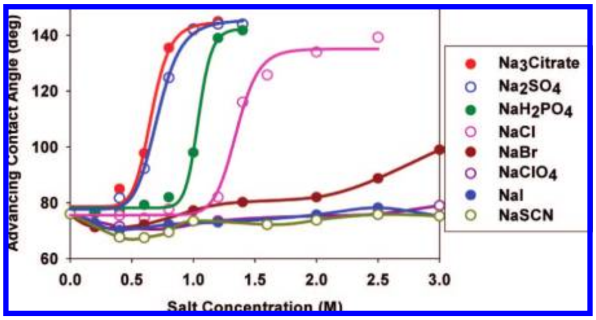

Figure 4. Changes in advancing contact angle (Θ_a) of a PE$_{oxid}$-(PNIPAM-*c*-PNASI/aminated silica nanoparticle)$_6$/PNIPAM surface measured with solutions of various salts as a function of salt concentration. Each data point is the average of three individual measurements and has an error of ±2°.

of changes in surface roughness induced by solute dependent swelling or chain collapse that alters the hydrophobicity of the PNIPAM. Hence, the swelling of the polymer on the textured surface follows the expected Hofmeister series which predictably alters the surface roughness and the associated wetting and dewetting of the surface.

The large solute responsive wettability of these PE$_{oxid}$-(PNIPAM-*c*-PNASI/aminated silica nanoparticle)$_6$-PNIPAM surfaces allowed us to examine the concentration dependence of wettability changes with solute anions. These studies used advancing water contact angle measurements, and results are shown in Figure 4. For the kosmotropic anions, the results generally show a gradual increase in Θ_a values with increased salt concentration until a certain critical concentration of salt is reached. This is illustrated by the results for sodium citrate, Na_2SO_4, NaH_2PO_4, and NaCl, where the increase in Θ_a with increased salt concentration exhibited sigmoidal behavior with inflection points that varied from around 0.6 M (sodium citrate) to 1.2 M (NaCl). In the case of chaotropic anions such as thiocyanate, salting-in behavior similar to that seen in the LCST behavior of PNIPAM,[19] hydroxymethylcellulose,[26] and other macromolecules[27] occurred. Salt-enhanced wetting is also seen for NaI, though the changes in Θ_a in this case are close to the error in contact angle measurements. All these surfaces had Θ_r values of $<10°$.

The wettability changes and hydration changes seen in AFM are reversible. When a film prepared as shown in Scheme 1 had its Θ_a analyzed using 1.4 M Na_2SO_4, the Θ_a value was 144°. Washing this film with distilled water and tetrahydrofuran (THF), drying, and reanalysis showed it had a Θ_a of 76° with water, the same Θ_a as it had before it was ever exposed to Na_2SO_4. After a month of treatment with various salt solutions, surfaces did exhibit minor changes. After ~100 cycles using various salt solutions, THF, and water, the $\Delta\Theta_a$ values (1.4 M Na_2SO_4 versus H_2O) gradually decreased from 68° to ~50° though the trends of Figure 4 were still seen.

As noted above, changes in Θ_a values with salts are modest with other surfaces. This may explain why studies of the effect of solute concentration or solute identity on surface wettability are not known, as the errors inherent in studying water contact angles and these modest changes seen in Θ_a values for other surfaces with changes in solute preclude definitive studies of wettability changes. Further improvement in our synthetic procedures to form surfaces with even larger solute responsive $\Delta\Theta_a$ values and further work to study other solutes and to characterize other possible consequences of the solute responsive morphological changes in these smart surfaces such as modulation of adhesion or changes in surface mechanical properties are continuing. This facile approach to surface modification allows such films to be prepared on virtually any surface and should be a general route to materials with solute responsive wettability.

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Supporting Information Available: Synthesis and characterization of polymers and aminated silica nanoparticles; procedures for covalent layer-by-layer self-assembly; and ATR-IR spectra of the assembled film. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Nishio, Y.; Chiba, R.; Miyashita, Y.; Oshima, K.; Miyajima, T.; Kimura, N.; Suzuki, H. *Polym. J.* **2002**, *34*, 149–157.

(27) Bauduin, P.; Wattebled, L.; Touraud, D.; Kunz, W. *Z. Phys. Chem.* **2004**, *218*, 631–641.