

Parallel Effects of Cations on PNIPAM Graft Wettability and PNIPAM Solubility

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ABSTRACT Stimuli-responsive surfaces grafted with thermoresponsive polymers switch from hydrophilic to hydrophobic thermally, making these surfaces attractive in applications such as in microfluidics devices, as antifouling surfaces, and in cell culture and tissue engineering. These materials exhibit changes in wettability as the polymer undergoes a phase transition above its lower critical solution temperature (LCST). Because the presence of salts affects LCSTs in accordance to the Hofmeister series, salt effects on the wettability of these thermoresponsive surfaces will dramatically impact device performance. Prior studies of such effects have focused on the influence of anions. Detailed studies of the effects of cations have not been carried out. Here, the influence of varying cation identity in a series of mono-, di-, and trivalent sulfate salts on the wettability of a stimuli-responsive grafted surface was investigated by measuring advancing water contact angle (Θ_a) changes. The cation-induced changes in Θ_a were correlated with corresponding changes in surface morphology examined by AFM. The results showed that the effects of varying cations on surface wettability are as large as the effects of varying anion identity and concentration (i.e., Θ_a changes of up to 90 degrees). Parallel studies of the effects of varying the cation identity and concentration for these same cation sulfate salts in solution show that cation variation also has a large effect on the LCST of PNIPAM, the stimuli responsive polymer component of the nanocomposite grafts that were studied. Moreover, analyses of the Θ_a and LCST data using activity showed that the Θ_a or LCST versus cation activity/concentration could be readily grouped by charge. Such differences are not seen in similar studies where anion identity, charge, and concentration are changed.

KEYWORDS: cation effects • nanocomposite graft • PNIPAM • wettability • activity • water contact angle

Stimuli-responsive or switchable surfaces that change their physical or chemical properties in response to external stimuli have recently been of considerable research interest (1–3). In particular, surfaces that can undergo reversible wettability changes under external stimuli are attractive for applications in microfluidic devices, chromatographic separations, self-cleaning and antifogging surfaces, and sensors (4). Changes of surface wetting are also be used to alter the interactions of stimuli-responsive surfaces with aqueous solutions of biomolecules and biomaterials, which are important in a variety of applications of responsive surfaces in biofouling and tissue engineering (5).

Surfaces grafted with thermoresponsive polymers, such as poly(*N*-isopropylacrylamide) (PNIPAM) and elastin-like polypeptides (ELPs) are known to reversibly switch between hydrophilic and hydrophobic states in response to temperature changes (6–10). Such thermoresponsive surfaces have been used in biomedical related applications such as in the controlled capture or release of proteins and cells (11, 12). The temperature responsiveness of surfaces in these applications derives from the fact that thermoresponsive polymers exhibit lower critical solution temperatures (LCSTs). Below the LCST, these polymers are soluble and hydrophilic with an extended coil conformation. Above the LCST, these polymers undergo a sharp phase transition to form a collapsed hydrophobic conformation (13–15). It is well-known

that the LCST of a thermoresponsive polymer changes upon the addition of salt cosolutes to an aqueous solution (16–18) and effects of salts on LCSTs follow the Hofmeister series which ranks various ions toward their ability to affect protein hydration (19, 20). Although temperature induced wettability changes of a thermoresponsive surface can be sufficient for a particular application, additional triggers such as changes in ionic strength sometimes can enhance the utility of a stimuli responsive surface. For example, ionic strength-induced hydrophilic–hydrophobic phase transitions of ELPs have been demonstrated for the reversible capture and release of an ELP fusion protein from an ELP-functionalized surface (21).

Although extensive studies have been done on the effects of salts on the LCSTs of thermoresponsive polymers in aqueous solutions, these studies have largely focused on the effects of anions. Cations are thought to play a minor role (18). However, few systematic studies have been carried out to examine the effects of salts on the wettability of thermoresponsive surfaces. Recently, we extended our studies of the effects of alkali metal anion identity and concentration on phase transitions of soluble responsive polymers to study their effects on the wettability of PNIPAM/silica nanocomposite grafts on polyethylene films (22). The so prepared $\text{PE}_{\text{oxid}}^-$ (PNIPAM/SiO₂)₆-PNIPAM nanocomposite surfaces showed roughness enhanced wetting behavior and could be reversibly switched from hydrophilic to hydrophobic by exposure to different alkali metal anion salt solutions. These studies showed that changing the anion identity and concentration of various sodium salts had a significant impact on water contact angles, an effect similar to that seen in studies of

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temperature effects on the wettability of PNIPAM grafts on nanostructured surfaces. These anion effects on the wettability of PE_{oxid}-(PNIPAM/SiO₂)₆-PNIPAM nanocomposite grafts paralleled the Hofmeister-like effects of these same alkali metal anion salts on PNIPAM LCSTs, wettability changes that are larger than seen on PNIPAM grafts that do not contain silica nanoparticles (22). We have now investigated how changing cation identity, specifically changing from monovalent cations to divalent metal cations to a trivalent cation like Al(III) affects surface wettability of these nanocomposite PNIPAM-containing grafts. These wettability studies show that the effects of varying cation identity and concentration on a graft surface's wettability can be as large as the effects of anions. In addition, studies of the effects of these cation sulfate salt solutions on LCSTs show that LCST effects and surface wettability effects are comparable. Both of these studies show a correlation between cation valence and a cation's effect on LCSTs and surface wettability is seen when solution activity instead of concentration is examined. Using activities instead of concentration, the intensity of the cation effect on wettability follows the order trivalent > divalent > monovalent. Similar analyses of LCSTs show that at similar activities, trivalent and divalent aqueous solutions of metal sulfates induce more salting out than aqueous solutions of monovalent sulfates.

EXPERIMENTAL SECTION

Chemicals. Isopropylamine, 3-aminopropyltriethoxysilane, polyethylenimine (PEI, branched, $M_n = 10\,000$ Da), and the 10 nm silica nanoparticles were obtained from Aldrich and used as received. The 100 nm silica nanoparticles were obtained from Alfa Aesar. The 100 and 10 nm silica nanoparticles were aminated with 3-aminopropyltriethoxysilane following a literature procedure (23). The amine loadings of 100 and 10 nm silica nanoparticles are 0.19 and 0.74 mmol of base/g, respectively, by titrimetric analysis. The PNIPAM sample used in studies of the effects of cations on LCSTs was prepared by a conventional free radical polymerization and was fractionated by selective solvent precipitation to afford a sample with a PDI of 1.06 and a M_w value of 322 kDa (24). The PNASI and PNIPAM-*c*-PNASI used in the surface grafting were prepared according to a procedure published elsewhere (22). The PNIPAM-*c*-PNASI copolymer had a M_w value of 30 kDa and a NIPAM to NASI unit ratio of $\sim 9:1$ based on ¹H NMR analysis.

Salt Solutions. All of the inorganic salts used were ACS grade. The water used in the analyses was obtained from a Milli-Q water purification system. The solutions were prepared as necessary and had pH values between 2.1 and 7.8 depended on the identity of the cations and the concentrations of the cation sulfate salt. Buffer solutions were not used because our goal was to study the cation effect and additional electrolytes would complicate the analyses.

LCST Measurements Using an Automatic Melting Point Apparatus. A commercially available automatic melting point apparatus—OptiMelt—was used for all the LCST measurements (25). An aqueous stock solution of PNIPAM was mixed with various cation sulfate salts to prepare a solution with a desired concentration of the cation sulfate salt and a fixed PNIPAM concentration of 10 mg/mL. Then 10 μ L of the sample solution was transferred to an ordinary capillary melting point tube (Kimble 1.5–1.8 \times 90-mm) using a microsyringe. The tube was sealed before placing it into the sample holder of the melting point apparatus. The heating rate of the apparatus was set to 0.5 $^{\circ}$ C/min for all measurements. The temperatures at 50%

scattering intensity of the clouding curves were used to construct the graphs and the data used in the figures below are the average of three measurements with three separate samples.

Contact Angle Analyses. Advancing water contact angles (Θ_a) were measured on a KSV CAM 200 optical goniometer equipped with an automatic single liquid dispenser at ambient temperature. The sessile drop method was used to obtain the advancing contact angles. In a typical measurement, a 5 μ L aqueous droplet was first placed on the surface. The drop was held in place for ca. 2 min at which point the drop volume was increased by adding more of the same aqueous solution continuously until the drop volume increased to the point that the drop began to spread. The advancing contact angle was the angle recorded immediately before the contact line advanced and its value was determined using the CAM 200 software.

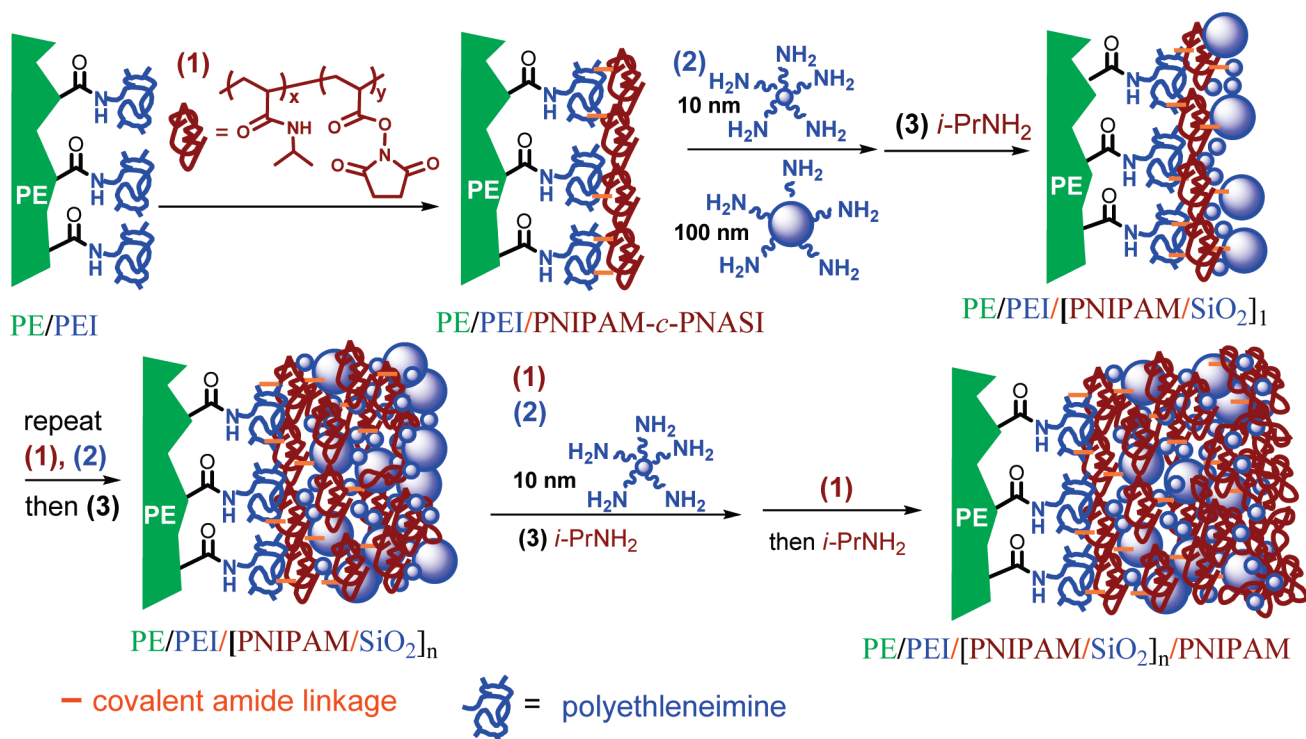
AFM Studies of the Roughness Changes. The PE_{oxid}-(PNIPAM/SiO₂)₆-PNIPAM graft surfaces were characterized by atomic force microscopy (AFM) in tapping mode using a commercial AFM (Alpha300 S, WITec, Germany). Images were collected using ultrasharp silicon AFM tips (VISTA probes, NanoScience Instruments, Phoenix, Arizona) with nominal tip radii of <10 nm, a lever resonance frequency of ~ 190 kHz and a force constant of ~ 48 N/m. The tip was modified with octadecyltrichlorosilane (OTS) prior to the measurement to minimize the adhesion between the tip and the polymer surface (22). To investigate the changes in surface morphology under varying solute concentration, the samples were scanned in the following order: ambient air, high purity water, 0.2 M ZnSO₄, 0.8 M ZnSO₄, and then again in high purity water. Between each measurement, the samples were taken out and rinsed with water, THF, and dried under a N₂ stream. For each 10 μ m \times 10 μ m topographic image, the representative surface root-mean-square (rms) roughness was determined from the average of six different randomly chosen 2.5 μ m \times 2.5 μ m regions.

Synthesis of PE_{oxid}-(PNIPAM/SiO₂)₆-PNIPAM silica nanoparticle)-PNIPAM Grafts. These grafts were prepared using oxidized high density polyethylene films primed with PEI. These PE films were subsequently modified by layer-by-layer covalent assembly with aminated silica nanoparticles and PNIPAM-*c*-PNASI copolymers following a previously reported procedure (22).

RESULTS AND DISCUSSION

We recently showed that it was possible to use covalent layer-by-layer assembly of nanoparticles (aminated SiO₂) and functional polymers to prepare surfaces that have wettability that changes dramatically from hydrophilic or hydrophobic by applying solutions of different alkali metal anion salts (22, 26). The nanocomposite graft surfaces prepared in this way exhibit multiple nanoscale roughness as determined by AFM and are analogous to thermally responsive grafts of PNIPAM and related polymers formed on nanostructured surfaces (27, 28). The assembly of these nanocomposite grafts with silica nanoparticles avoided the need for physical patterning of the underlying substrate to create a topologically complex surface. Notably, the wettability changes we observed for a PNIPAM/SiO₂ nanocomposite surface could be reversibly induced without the need for covalent modification with a hydrophobic or hydrophilic group. The polymer matrix of these grafts used PNIPAM and the grafted surfaces changed from hydrophilic to hydrophobic in a manner similar to how PNIPAM's solubility in water changed as one varied the identity and concentration of a sodium anion solute. The large anion effect on wettability seen for PNIPAM/SiO₂ nanocomposite grafts on PE films and

Scheme 1. Covalent Layer-by-Layer Self-Assembly of a PNIPAM/Silica Nanocomposite Graft on a PEI-Modified PE Film



the effects of changing the identity and concentration of the anions on LCSTs of PNIPAM prompted us to study whether varying cation identity could significantly affect surface wettability. Because surface wettability was particularly sensitive to the concentration of a solution of a kosmotropic salt like sodium sulfate, we focused our attention on various cation salts of this common anion to determine if other cation salts would be more or less effective at altering surface wettability. The results showed that changing cations can affect surface wettability in a dramatic fashion. Moreover, the analyses of the effects of various sulfate salts on wettability using activity instead of concentration provided a contrasting picture of the effect of these various metal sulfate salts.

Nanocomposite grafts were prepared on oxidized PE films following the procedure we reported earlier. This procedure shown in Scheme 1 afforded PNIPAM/SiO₂ nanocomposite grafts on oxidized polyethylene films. The product surfaces had an rms roughness of 224 ± 17 nm (air). As in our original work, the substrate oxidized PE film was first “primed” by reaction with the polyvalent nucleophile polyethyleneimine (PEI) to facilitate the initial grafting steps. This afforded us a surface with multiple primary and secondary amine groups that could in turn react with the active esters of the copolymer PNIPAM-*c*-PNASI ($M_n = 30\,000$ Da). A portion of the electrophilic NASI groups in this copolymer reacted with the surface-bound amines to form amides. However, although this copolymer PNIPAM-*c*-PNASI presumably covalently bonded to multiple surface sites, surface constraints preclude complete consumption of the NASI groups and the remaining unreacted NASI groups were thus available after this initial step for reaction with other nucleo-

philic species in a subsequent step. Our procedures used amine-functionalized 10 and 100 nm diameter silica nanoparticles as polyvalent amine nucleophiles in this second step. This second treatment then reformed an amine-rich nucleophilic surface. Any unreacted reactive NASI esters were then capped with isopropylamine at the following step. Subsequent reactions using PNIPAM-*c*-PNASI, aminated silica nanoparticles, and isopropylamine continued the covalent layer-by-layer assembly process. After 6 stages of this PNIPAM-*c*-PNASI/10 and 100 nm aminated silica nanoparticles/*i*-PrNH₂ treatment, the covalently assembled layer-by-layer nanocomposite graft was capped with PNIPAM-*c*-PNASI followed by reaction with excess *i*-PrNH₂ to ensure the outmost layer of the surface was covered with PNIPAM.

Studies of the effects of aqueous solutions of trivalent, divalent, and monovalent cations on wettability of PNIPAM/silica nanocomposite grafts on PE film were then carried out. In these studies, we opted to investigate cation salts of a common anion. These studies are more complicated in some ways than studies that use simpler sodium salts because the divalent and trivalent metal cations have relatively more complex and concentration-dependent structures in aqueous solution (29, 30). For example, the identity of the metal cationic species in aqueous solutions in the 0.1–1.0 M regime is complicated with a trivalent salt like Al₂(SO₄)₃. Although Al³⁺ species like Al(H₂O)₆³⁺ can be present, changes in pH or the presence of additives can lead to formation of a variety of other species (31, 32). The situation with divalent metal salts is somewhat less complex but these species too are present in many forms. Hexahydrates of cations as well as other more complex cations can all be present (33). Moreover, depending on the cation and

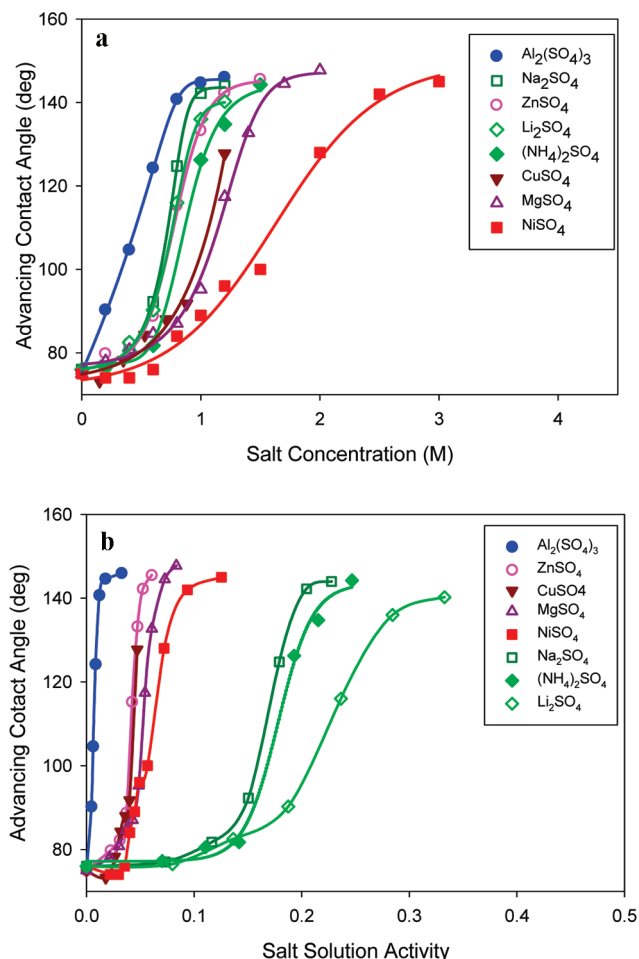


FIGURE 1. Cation effects on wettability of PNIPAM grafted nano-composite surface. (a) The advancing contact angles of various cation sulfate salts versus salt concentration. (b) The advancing contact angles of various cation sulfate salts versus salt solution activity.

anion, various amounts and types of ion pairs are present. The complexity of such solutions over the concentration range of 0.05–1.0 M is seen in prior studies of divalent sulfates where both contact and solvent separated ion pairs are present (34–36). Similar complexity is seen in NMR studies where metal cationic species form various types of contact and solvent separated ion pairs with anions that range from halides to sulfates (37–39). The solvated cationic species that are likely present at a solid/solution interface are certainly no less complex (40). Such complications affect studies of the effect of an aqueous solution of any trivalent and divalent metal salt (41). We opted to focus on a common anion that has a large effect on wettability. Because the kosmotropic sulfate anion was found to have a large effect on surface wettability in our prior studies of sodium salts, we examined the effect of varying the identity and concentration of the cation in sulfate salts on wettability.

Our studies measured advancing water contact angles as a function of the concentration of the various sulfate salt solutions. The results shown in Figure 1a show that changing the identity of the cation in aqueous solutions of sulfate salts does indeed have a large effect on surface wettability. The effects were seen in comparing tri-, di-, and monovalent as well as in comparing monovalent sulfate salts alone. These

effects were also reversible. For example, a $\text{PE}_{\text{oxid}}(\text{PNIPAM}/\text{SiO}_2)_6$ -PNIPAM surface analyzed with a 1.0 M $\text{Al}_2(\text{SO}_4)_3$ solution had a Θ_a of 145° . Washing this surface first with water and then with THF yielded a film was then dried and reanalyzed with water. That analysis showed that the film had a Θ_a of 76° , a value that was identical to that of the Θ_a for water on the film before the original analysis with $\text{Al}_2(\text{SO}_4)_3$. Similar reversible wettability was seen in reanalysis with all of the other cation salts. This sort of reversible behavior was also seen in our earlier studies of the effects of anions on surface wettability.

Although the effect of changing cation identity in Figure 1a was significant, the results in Figure 1a suggested that the changes in wettability were not correlated with the cation valence. Specifically Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and Li_2SO_4 had a greater effect on surface wettability than MgSO_4 , CuSO_4 or NiSO_4 . ZnSO_4 was however very much like the monovalent sulfate salts in its effect on wettability. The wettability of these grafts was most sensitive to cation sulfate salt concentration in $\text{Al}_2(\text{SO}_4)_3$ solutions. Plots of advancing water contact angle (Θ_a) versus SO_4^{2-} concentration (see the Supporting Information) also showed that the effects of divalent salts and monovalent salts on surface wettability are intermingled. We also plotted advancing water contact angle versus ionic strength (see the Supporting Information). These plots showed that mono-, di-, trivalent cations' effects on wettability decrease with ionic strength though Zn^{2+} is nearly indistinguishable from NH_4^+ . Given the complexity of cation species in these solutions, we thus looked at the variation in Θ_a for various cation sulfates versus salt solution activity. The activity coefficients for the various sulfate salts were obtained either directly from the literature (42–44) or were calculated by using Pitzer's method (which was used mainly for salt concentrations lower than 0.1 M for which the activity coefficients were not listed) (45, 46). The resulting plot of Θ_a versus activity shown in Figure 1b differed from the analogous plot of Θ_a versus concentration in that the divalent cations and monovalent cations were both slightly distinguishable from one another but also were present in distinct groupings. The single trivalent cation examined exhibited similarly distinct behavior. The differences seen for plots using concentration (Figure 1a) or activity Figure 1b were not observed in studies of the effects of sodium salts of anions on wettability. Plots of Θ_a versus concentration and Θ_a vs activity in panels a and b in Figure 2 show only modest differences. In these cases, the activity coefficients of the various sodium salts did not change appreciably as the concentration of the anion changes from 0.1 to 1.0 M. Because the changes in activity over this concentration range paralleled the changes in anion concentration, the shape and sequential order of the curves in the activity plot are generally similar to what is seen in plots of Θ_a versus concentration.

As was true for our earlier studies where anion identity and concentration were varied, the change of Θ_a with salt activity or concentration produced a curve similar to a titration curve with an inflection point that was significantly different with different salts. Plots of Θ_a for different cations on the wettability

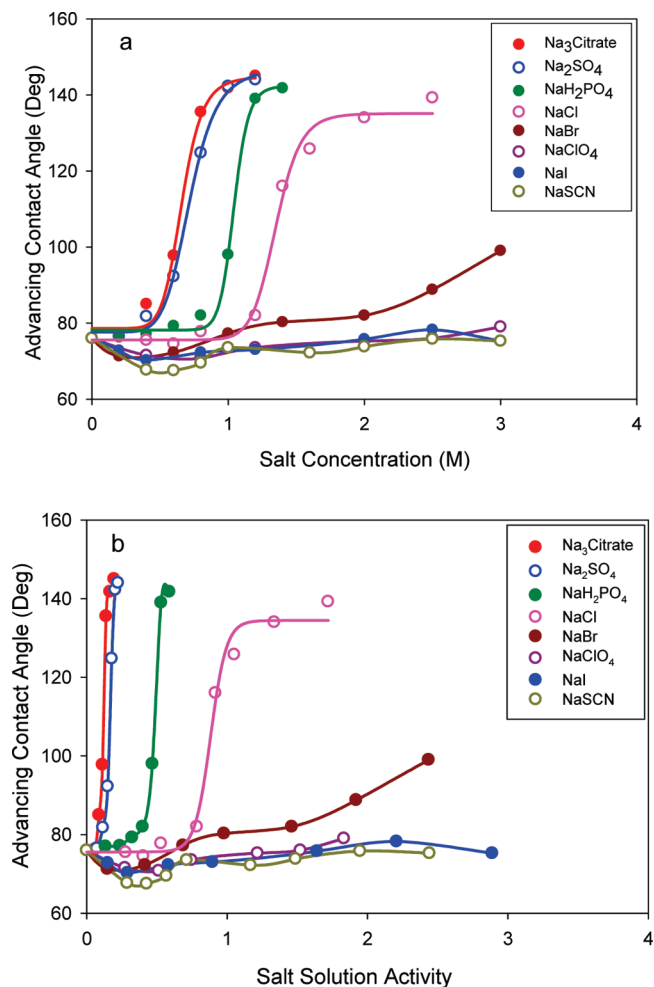


FIGURE 2. Anion effects on wettability of PNIPAM grafted nanocomposite surface. (a) The advancing contact angles of various sodium salts versus salt concentration. (b) The advancing contact angles of various sodium salts versus salt solution activity.

of these PNIPAM nanocomposite grafts differed most for cations of different valence. In Figure 1b, the inflection point for the wettability changes induced by the trivalent Al(III) sulfate solution was about 0.01, whereas the average inflection points for the wettability changes induced by di- and monovalent sulfate salts were 0.05 and 0.19, respectively. Lesser but measurable differences were observed among cations that have the same valence. For example, the wettability curves in Figure 1b for Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and Li_2SO_4 had inflection points at solution activities of 0.17, 0.18, and 0.23 respectively.

Our prior studies of the effect of varying anion identity and concentration in reversibly changing wettability of PNIPAM/ SiO_2 nanocomposite grafts showed that the wettability changes were correlated with changes in surface roughness presumably due to solvation/desolvation of the PNIPAM matrix. A similar correlation between surface roughness and surface wettability with different cation sulfate solutions was also found by AFM on the $\text{PE}_{\text{oxid}}(\text{PNIPAM}/\text{SiO}_2)_6\text{-PNIPAM}$ surfaces (Figure 3). The $10 \times 10 \mu\text{m}^2$ AFM images were acquired multiple times under each condition. Similar morphology and roughness were observed between each measurement under the same conditions. Figure 3 shows typical topographic images and the average surface roughness of $\text{PE}_{\text{oxid}}(\text{PNIPAM}/\text{SiO}_2)_6\text{-PNIPAM}$ surfaces in air, water, 0.8 M ZnSO_4 , and 1.2 M ZnSO_4 . The PNIPAM/ SiO_2 nanocomposite surface had both macro- and nanoscale roughness like the samples we prepared previously in air. This 224 nm rms roughness changed when the surface was exposed to water, dropping to a value of ~ 157 nm rms. This 157 nm rms roughness did not change significantly in the presence of 0.2 M aqueous ZnSO_4 (134 nm rms). However, treatment with a 0.8 M ZnSO_4 solution increased rms roughness to ~ 257 nm rms, which further increases to ~ 307 nm in the presence of 1.2 M

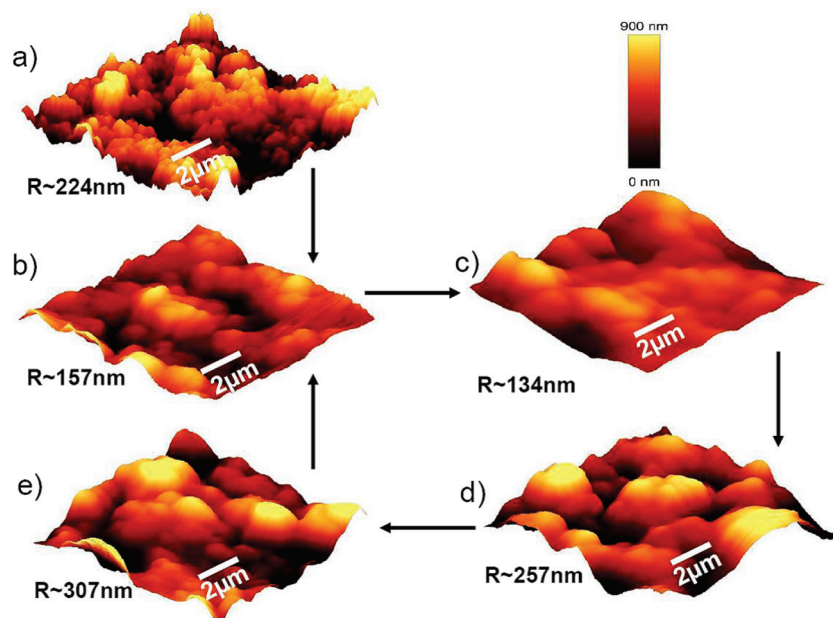


FIGURE 3. Tapping mode AFM images of a $\text{PE}_{\text{oxid}}(\text{PNIPAM}/\text{SiO}_2)_6\text{-PNIPAM}$ nanocomposite surface obtained in (a) air, (b) water, (c) 0.2 M ZnSO_4 , (d) 0.8 M ZnSO_4 , and (e) 1.2 M ZnSO_4 . The average rms roughness of the surface in each environment was taken from six random $2.5 \mu\text{m} \times 2.5 \mu\text{m}$ regions and the data were listed below each image (scale bar: $2 \mu\text{m}$).

ZnSO₄. As suggested above, these changes in roughness likely are due to changes in solvation of the nanocomposite graft. These changes in surface morphology are akin to those we observed in our earlier work. These changes observed by AFM correlate with the changes in wettability and are consistent with the notion that these cation sulfate salt solutes produce solute responsive swelling or chain collapse that altered the hydrophobicity of the PNIPAM component of the nanocomposite graft (47–49).

Since our earlier studies of the effects of changing the identity and concentration of anions on wettability of responsive grafts were based on prior studies of LCSTs of PNIPAM in sodium salt solutions, we chose to also study the effects of varying the identity and concentration of these sulfate salts on PNIPAM LCSTs to see if these solution studies of cation effects on LCSTs could be predictive of stimuli responsive surface wettability changes. These studies employed the same automated melting point apparatus and procedures we used previously to study clouding curves for solutions of PNIPAM and other thermoresponsive polymers (25). We used a fractionated sample of atactic PNIPAM with a M_n of 322 kDa (PDI = 1.06) as the polymer substrate. This PNIPAM was made from conventional radical polymerization and was purified by solvent precipitation (25). The sample solutions were prepared as described in the experimental section and each sample had a constant PNIPAM concentration of 10 mg/mL. Plots of the LCST versus sulfate salt concentration and activity are shown in panels a and b in Figure 4, respectively. The LCSTs in these curves were based on the temperature at which 50% clouding was observed. Plots of the LCST versus cation sulfate salt concentration or activity based on the 10% value for clouding were roughly similar (see the Supporting Information). In either case, distinguishable cation sulfate salt effects were also seen for the phase transition temperature of PNIPAM solutions when we plotted the LCSTs versus cation sulfate salt concentrations (Figure 4a). Just as was true in studies of surface wettability, plots of the LCST versus cation sulfate salt concentration did not distinguish between divalent and monovalent sulfates, e.g., Na₂SO₄ and ZnSO₄ are quite similar. NiSO₄, MgSO₄, and CuSO₄, in contrast, behaved like “salting in” cations in accord with conventional Hofmeister effects (20). Plots of salt concentration versus LCST with Al₂(SO₄)₃ showed this salt is the most kosmotropic. However, just as seen earlier for the cation sulfate effect on advancing contact angle, a plot of LCST versus cation sulfate salt solution activity showed distinctly different behavior for monovalent, divalent and trivalent sulfate salts. Because the activity coefficient of the tri- and divalent cations was less than that of the monovalent cations, the salting-out effects of different cations followed a different order with trivalent salts being the more salting out than divalent sulfate salts, which were in turn more salting out than monovalent sulfate salt solutions. These activity plots also were curved while more linear plots though were obtained when sulfate solution concentrations were plotted versus LCSTs.

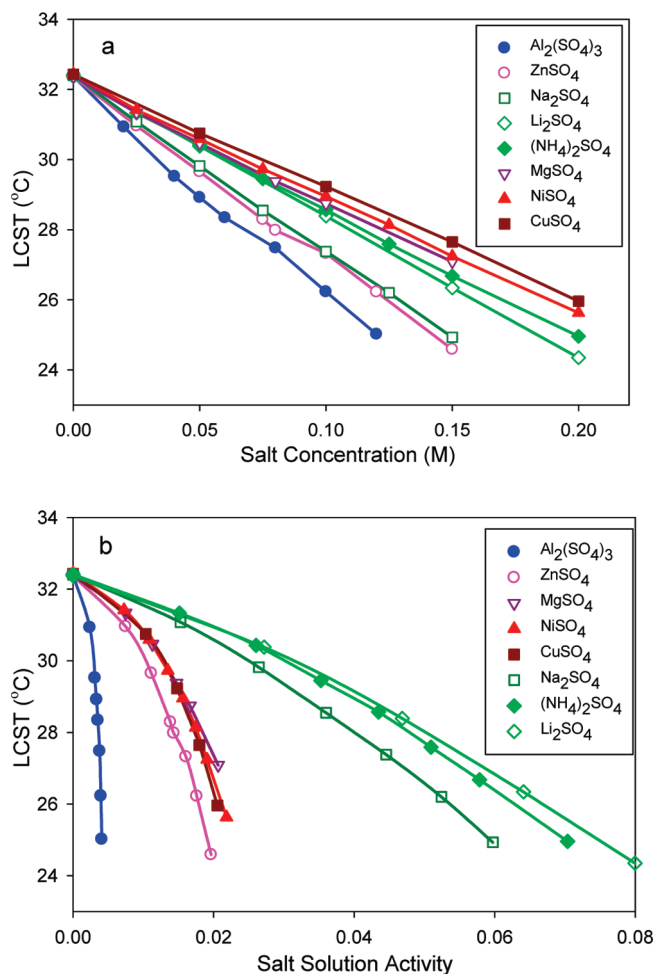


FIGURE 4. Cation effects on the LCST of PNIPAM in aqueous solution. (a) The LCSTs of PNIPAM in various cation sulfate salt solutions versus salt concentration (M). (b) The LCSTs of PNIPAM in various cation sulfate salt solutions versus salt activity. The concentration of PNIPAM was fixed to 10 mg/mL for all samples.

Although it is possible to speculate about the origin of these differences (e.g., Al³⁺ bears the most positive charge, Al₂(SO₄)₃ has the highest ionic strength (50), and Al₂(SO₄)₃ produces the most ions when it dissociates), speculation on the specific interactions of cations with a polymer are likely to be oversimplified given the complexity and number of species present in aqueous solutions of aqueous solutions that contain tri-, di-, and monovalent sulfate salts. Given this complexity, a simplified picture where cation hydrates of whatever structure affect the ability of water to hydrate the macromolecules is perhaps the best way to try to understand the different effects seen here. A similar interpretation of cation effects was advanced by Guo and Friedman in a recent report. From their Gadolinium (Gd³⁺) vibronic sideband luminescence spectroscopy (GVSBL) experiments, they concluded that the effect of a cation on a macromolecule hydration was charge density-dependent and that high charge density cations change water configuration which in turn weakens its hydrogen bonds to neighboring waters (40, 51). However, the specific interactions will obviously vary depending on the relative concentrations of the various species present in these complex solutions. Moreover, these solutions' components' relative concentrations vary in a

concentration-dependent manner. Thus, the effects are not likely to be linear with concentration. Interestingly, plots that compare wettability or LCSTs versus wettability are nonlinear, as might be expected for solutions where the components' relative abundance changes with concentration.

CONCLUSION

These studies show that cations have large effects on phase separation of PNIPAM solutions and surface wettability of PNIPAM nanocomposite grafts. These effects on surface wettability are correlated with changing solvation/swelling and changing surface roughness of these nanocomposite grafts. Overall, the effects of varying the identity and concentration of cations on surface wettability are as marked as those seen with anions. This suggests that the design of solute responsive interfaces will need to consider cation identity and concentration in addition to anion identity and concentration. As was true in the case of our studies of wettability effects of solute anions, the effect of varying cation identity and concentration seen in wettability are paralleled in studies of changes in LCST for PNIPAM solutions. However, plots of the physical changes of either the wettability or the LCST of these responsive polymer systems with varying cation concentration and identity vary significantly from plots where activity is used in place of concentration. Such marked differences are not seen for plots of wettability or LCST for less complex solutions where the identity of an anion is varied with a constant cation (Na^+). Generally speaking, the activity coefficients take into account both the dissociation of the electrolytes and the electrostatic forces between the dissociated ions. Thus, it might be more appropriate to use activity rather than concentration to analyze data especially when complicated electrolytes are under consideration or to at least consider activity as an alternative to concentration in analyses.

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Supporting Information Available: The plots of advancing contact angle vs $[\text{SO}_4^{2-}]$, advancing contact angle vs solution ionic strength, and PNIPAM LCST vs salt concentration based on 10% clouding temperature (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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