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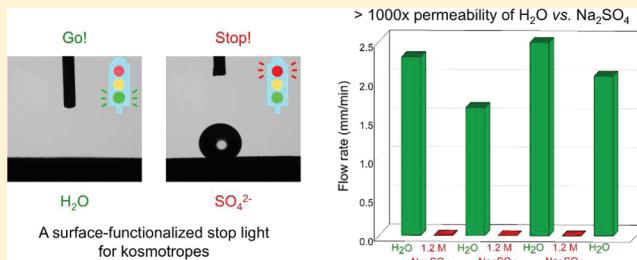
## Solute- and Temperature-Responsive “Smart” Grafts and Supported Membranes Formed by Covalent Layer-by-Layer Assembly

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### Supporting Information

**ABSTRACT:** Polymers like poly(*N*-isopropylacrylamide) (PNIPAM) exhibit lower critical solution temperature (LCST) behavior. A variety of reports have shown that brush grafts of PNIPAM on surfaces exhibit similar temperature responsiveness. We recently described an alternative synthetic approach to such surfaces that affords surfaces with similar LCST-like behavior. We also noted how such surfaces’ wettability can change in response to the identity and concentration of solutes. Here we show that this synthetic procedure can be extended to glass surfaces and to more complex surfaces present in porous glass frits. Functionalized glass surfaces exhibit solute-dependent wetting behavior analogous to that previously reported. We further show that the resulting responsive nanocomposite grafts on such frits exhibit “smart” responsive permeability with a greater than 1000-fold difference in permeability to water versus aqueous solutions of sodium sulfate. This “smart” permeability is ascribed to the solute-dependent wettability behavior of the responsive PNIPAM component of the nanocomposite graft, which is sensitive both to the identity and concentration of the solute anion and to temperature.

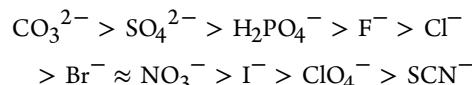


### ■ INTRODUCTION

Stimuli-responsive polymers are of broad interest in polymer science.<sup>1–3</sup> Polymers that change their shape, mechanical properties, solubility, or chemistry in response to an external stimulus such as a change in temperature, pH, solvent composition, mechanical stress, or magnetic field can be used as autonomous “smart” materials in diverse applications that include catalysis, drug delivery, surface modification, in self-repairing systems, or in the formation of responsive surfaces.<sup>4–11</sup> Poly(*N*-alkylacrylamide)s are one of the most studied types of responsive polymers with poly(*N*-isopropylacrylamide) (PNIPAM) being the most studied of a group of temperature-responsive polymers. In an aqueous solution, PNIPAM has a lower critical solution temperature (LCST) of 31–32 °C. At this temperature in water PNIPAM undergoes a phase change, reversibly precipitating above this LCST and dissolving below this LCST. This property of PNIPAM is of particular interest in many biomedical applications since the LCST is between room temperature and body temperature.<sup>12</sup> The temperature of this solubility change can be tailored by incorporating more or less hydrophilic comonomers or by adding appropriate solutes to a PNIPAM solution.

The effect of various salts on PNIPAM’s LCST reflects a particular salt’s position in the Hofmeister series. This series developed by Franz Hofmeister in 1888 was in conjunction with studies of the effect of salts on precipitation of proteins

found in egg white.<sup>13</sup> The typical order of the Hofmeister anion series is as follows:



Anions to the left of Cl<sup>-</sup> are considered kosmotropes and have a salting-out effect for proteins and PNIPAM that depends on the anion’s concentration and identity. Anions to the right of Cl<sup>-</sup> are chaotropes and have a salting-in effect for both proteins and PNIPAM.<sup>14</sup> Cations can also be salting-in or salting-out with behavior that depends on their identity and concentration.<sup>2</sup>

PNIPAM surface grafts exhibit temperature-responsive wettability that parallels the LCST behavior of PNIPAM solutions.<sup>15</sup> This effect has been used to prepare grafts on patterned flat surfaces to prepare surfaces whose wettability is alternately and reversibly superhydrophobic or superhydrophilic depending on temperature. The responsive hydration of PNIPAM grafts has also been used to modulate or control flow in certain cases. For example, Alem and co-workers were able to control the flow rate through PNIPAM brushes on a track-etched poly(ethylene terephthalate) (PET) membrane.<sup>16</sup> In this case, 80 nm pores grafted with PNIPAM were able to control the permeation rate of an electrolyte solution.<sup>16</sup> Below the LCST of PNIPAM, permeation through the membrane

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occurred though the rate was lower than that measured with an unfunctionalized membrane. At temperatures above the LCST, permeation of the electrolyte solution through the pores did not occur.<sup>16</sup>

We recently described strategies for synthesis of grafts using covalent layer-by-layer assembly procedures.<sup>17</sup> These studies included synthesis of grafts that contained silica nanoparticles within a responsive PNIPAM matrix on polyethylene films that exhibited responsive wettability.<sup>15</sup> We showed that the surface wettability depended both on the concentration of salts in aqueous solutions and on the specific types of cations and anions.<sup>15,18</sup>

The discussion below shows that similar nanocomposite PNIPAM/silica grafts can be prepared via this covalent layer-by-layer assembly process on both flat and topologically complex glass surfaces. Such grafts also have temperature and solute responsive properties. Most notably, when these PNIPAM/silica grafts were prepared on porous glass frits, the modified frits had solute dependent and temperature responsive permeability with passive permeability differences as large as 1000-fold seen when using solutions of water, a kosmotropic salt, or a chaotropic salt.

## ■ EXPERIMENTAL SECTION

**Materials.** Polyethylenimine (PEI, branched,  $M_w = 25\,000$ ), isopropylamine, and *sec*-butylamine were purchased from Sigma-Aldrich and used as received. 3-Aminopropyltriethoxysilane was obtained from Alfa Aesar and used as received. *N*-Isopropylacrylamide was purchased from Sigma-Aldrich and TCI Japan and recrystallized from 9:1 hexanes/benzene. Microscope glass slides obtained from VWR and medium porosity (pore size 10–20  $\mu\text{m}$ ) glass frits purchased from ACE Glass (ACE #5848-33) were used for surface functionalization. Both 10 and 100 nm silica ( $\text{SiO}_2$ ) nanoparticles were obtained from Sigma-Aldrich and Fiber Optic Center Inc., respectively. Poly(*N*-acryloxysuccinimide) (PNASI), poly(*N*-isopropylacrylamide)-*c*-poly(*N*-acryloxysuccinimide) (PNIPAM-*c*-PNASI), and poly(*N,N*-diethylacrylamide)-*c*-poly(*N*-acryloxysuccinimide) (PDEAM-*c*-PNASI) used for surface grafting were prepared from *N*-acryloxysuccinimide, *N*-isopropylacrylamide, and *N,N*-diethylacrylamide using reported procedures.<sup>15</sup> <sup>1</sup>H NMR analysis showed that the ratios of *N*-alkylacrylamide to NASI groups in copolymers PNIPAM-*c*-PNASI and PDEAM-*c*-PNASI were 9:1 and 6:1, respectively. Amination according to a literature procedure<sup>19</sup> afforded aminated 10 and 100 nm  $\text{SiO}_2$  nanoparticles whose  $-\text{NH}_2$  loading by titrimetric analysis was 0.59–1.87 (different batches) and 0.24 mmol of  $-\text{NH}_2$  groups/g of  $\text{SiO}_2$ , respectively. A Barnstead Nanopure Diamond water purification system was used to obtain high-purity water with low conductivity (18.2 M $\Omega$ ·cm).

**Functionalization of Glass Slides by Covalent Layer-by-Layer Assembly.** The procedure for functionalizing glass slides was modified from the surface grafting procedure for polyethylene films.<sup>15</sup> Briefly, the slides were placed in a Teflon holder and thoroughly cleaned. Following amination of the surface by 3-aminopropyltriethoxysilane, the slides were primed by two cycles of treatment with solutions of PNASI, PEI, and a primary amine (isopropyl- or *sec*-butylamine) in *N,N*-dimethylformamide (DMF). The layer-by-layer assembly was achieved by five cycles of reaction using successively an electrophilic copolymer of a polyacrylamide and PNASI, a suspension of both 100 and 10 nm aminated  $\text{SiO}_2$  nanoparticles, and a primary amine (isopropyl- or *sec*-butylamine) in DMF. Finally, the slides were treated with DMF solutions or suspensions of the electrophilic copolymer, 10 nm  $\text{SiO}_2$  nanoparticles, the primary amine (isopropyl- or *sec*-butylamine), the electrophilic copolymer, and the primary amine (isopropyl- or *sec*-butylamine). Slides with these poly(*N*-alkylacrylamide)/silica nanocomposite grafts were then washed extensively with high-purity water, followed by methanol or tetrahydrofuran and dried with nitrogen.

**Synthesis of Responsive Glass Frits by Covalent Layer-by-Layer Assembly.** The method for functionalizing porous glass frits was modified from the surface grafting procedure established for glass slides, as described above. PNIPAM-*c*-PNASI and isopropylamine were used as the electrophilic copolymer and the primary amine, respectively. Upon completion of the grafting process, the frit was washed extensively with high-purity water, followed by methanol and dried with nitrogen.

**Contact Angle Measurements.** Advancing contact angles ( $\Theta_a$ ) were measured using a KSV CAM 200 optical goniometer at ambient temperature, using the CAM 200 software. Aqueous  $\text{Na}_2\text{SO}_4$  or water was dispensed with an automatic syringe.

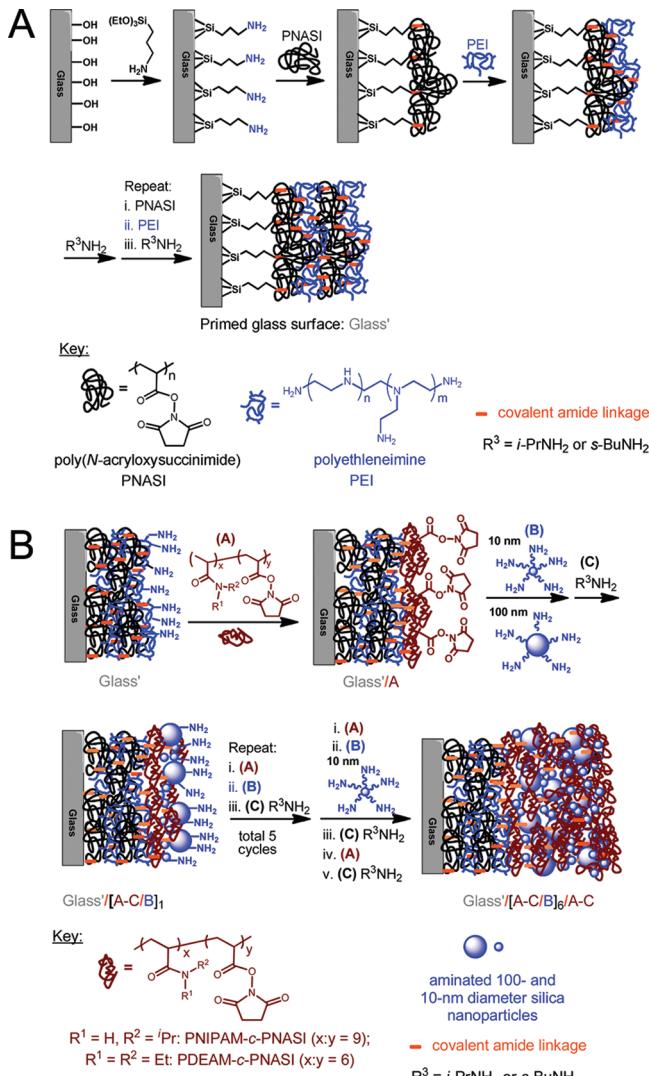
**Measuring the Frit Flow Rates for Water or Salt Solutions.** A functionalized frit was inserted into a chromatography column to tubing adapter (ACE #5838-91), which was secured to a 15 mm i.d. column (ACE #7644-15). Approximately 4 cm column height (~7 mL) of water followed by 2 cm column height of methanol (~3.5 mL) was allowed to passively flow through the frit. After nitrogen was flushed through the frit for 3 h, 5 cm column height (~9 mL) of various salt solutions at the desired concentration was added to the column, and the volume change was studied until 1 cm (~1.7 mL) of the solution volume had passed through the frit. If the volume change was less than this after 12 h, the study was stopped. The remaining salt solution was discarded, and the frit assembly was rinsed with ~50 mL of high-purity  $\text{H}_2\text{O}$  four times before filling the column to 8 cm above the frit top with water. After 3 cm (~5 mL) of water had flowed through the frit the water level was 5 cm above the top of the frit, and the flow rate for water was measured over the next 1 cm. The remaining water was removed, and 2 cm (~3.5 mL) of methanol was allowed to flow through the frit before it was dried for 3 h with nitrogen. The process was then repeated starting with a fresh salt solution with the same concentration and salt (repeatability studies) or with a different salt solution containing a different concentration or a different salt. For temperature effects on flow rate, measurements were performed in an 8 °C cold room and at room temperature.

**Measuring the Effects of  $\text{Na}_2\text{SO}_4$  Concentration on Frit Permeability.** Frits were placed in the glass column to tubing adapters and cleaned by submerging in cold water, which was stirred with an overhead stirrer at ~8 °C for 3 h. After attachment to a glass column, ~18 mL of methanol was passed through the frit before it was dried by flushing nitrogen through the column and frit for 4 h. The column above the dry frit was then filled to a 5 cm height (~9 mL) with  $\text{Na}_2\text{SO}_4$  solution and the flow rate measured in the manner described above. In between measurements, the frits were cleaned using the procedure described consisting of soaking in cold water, washing with methanol and flushing with nitrogen. The passive permeability of frits to  $\text{Na}_2\text{SO}_4$  at concentrations of 1.2 to 0 M was measured using progressively lower salt concentrations. These  $\text{Na}_2\text{SO}_4$  flow rate measurements were repeated in decreasing salt concentrations to determine a standard deviation for these flow rates.

## ■ RESULTS AND DISCUSSION

The procedure we used previously to prepare covalent layer-by-layer nanocomposite grafts on functionalized polyethylene films was extended to glass slides and followed the general scheme shown in Scheme 1. In this scheme, the glass surface was first functionalized with amines using aminopropyltriethoxysilane. Two cycles of treatments of this surface alternately with PNASI ( $M_w = 380\text{ kDa}$ ) and then with commercially available PEI ( $M_w = 25\text{ kDa}$ ) followed by quenching of any unreacted active ester groups of PNASI with a primary amine primed this glass surface with sufficient reactive amines for further layer-by-layer covalent grafting. This grafting used alternately a polyvalent electrophile (poly(*N*-isopropylacrylamide)-*c*-poly(*N*-acryloxysuccinimide) or poly(*N,N*-diethylacrylamide)-*c*-poly(*N*-acryloxysuccinimide)) followed by reaction with a mixture of polyvalent aminated silica nanoparticles (a mixture of 10 and 100 nm diameter particles was used). Unreacted esters were

**Scheme 1. (A) Synthesis of Functional Responsive Nanocomposite Grafts on Glass Slides and Frits;<sup>a</sup> (B) Following Priming of the Surface, Layer-by-Layer Assembly of the Copolymer and Aminated Silica Nanoparticles Is Carried out To Form a Responsive Surface with a Topologically Complex Structure<sup>b</sup>**



<sup>a</sup>A priming step is first completed with the deposition and formation of covalent amide linkages within the PNASI and PEI layers. <sup>b</sup>Note the final structure is not drawn to scale.

then quenched with a primary amine. A primary amine was used in this last step because experiments showed secondary amines like diethylamine react much slower with the active ester of the PNASI.

The syntheses of nanocomposite grafts on glass slides involved six cycles of a polyvalent electrophile/polyvalent nucleophilic nanoparticle treatment analogous to the procedures we used earlier to prepare functional, responsive nanocomposite grafts on polyethylene.<sup>15</sup> As in our prior work, these six cycles were followed by a series of capping steps that concluded with a final reaction using only the polymeric electrophile and the primary amine to form a surface with a polyacrylamide interface. The incorporation of nanoparticles had previously been shown to generate surfaces with nanoscopic roughness, yielding a topologically complex surface that when combined with the PNIPAM-*c*-PNASI copolymer results in a responsive surface.<sup>15,18</sup> The number of cycles used for the LbL deposition was determined based on the stability of the responsive nature of the film. Following six layers, no notable change was observed in the resulting surface contact angle for water, or a 1.2 M  $\text{Na}_2\text{SO}_4$  solution, as described in our earlier work.<sup>15</sup> While these findings were for assembly on polyethylene surfaces, the same result was observed for assembly on Si wafers or on the glass slides used here (see Supporting Information).

We first showed that these surfaces had very similar solute responsive wettability like earlier nanocomposite grafts on polyethylene that we have prepared using aminated silica particles and a PNIPAM matrix.<sup>15</sup> The results (Table 1, entry 2) showed that glass surfaces prepared using poly(*N*-isopropylacrylamide)-*c*-poly(*N*-acryloxysuccinimide), aminated nanoparticles, and isopropylamine as the primary amine had a  $\Theta_a$  of  $74^\circ$  using water as a test fluid and a  $\Theta_a$  of  $>170^\circ$  using 1.2 M  $\text{Na}_2\text{SO}_4$ . These values are very comparable to values for similar grafts on polyethylene (Table 1, entry 1).<sup>15</sup>

Next we probed the effect of using other respsonsively soluble acrylamide copolymers instead of poly(*N*-isopropylacrylamide) copolymer and of using *sec*-butylamine in place of isopropylamine as a quenching agent for unreacted NASI ester groups. The results of these experiments are shown in entries 3, 4, and 5 in Table 1. All the polyacrylamide/silica nanocomposite surfaces prepared had differential wettability to water and 1.2 M  $\text{Na}_2\text{SO}_4$ . However, while poly(*N,N*-diethylacrylamide) has an LCST in solution like poly(*N*-isopropylacrylamide), nanocomposite grafts with a poly(*N,N*-diethylacrylamide) matrix were significantly less effective than those containing a poly(*N*-isopropylacrylamide) matrix in forming a solute responsive surface. While the largest effects in Table 1 reflect the

**Table 1. Differential Wettability of Solute Responsive Surfaces toward Water or 1.2 M  $\text{Na}_2\text{SO}_4$  at Room Temperature as a Function of the Nature of the *N*-Alkyl Groups in the Polymer Matrix and as a Function of the Identity of the Primary Amine Used To Quench Unreacted Active Esters in the Covalent Layer-by-Layer Assembly Process**

substrate and polymer matrix	R <sup>1</sup> , R <sup>2</sup>	primary amine	$\Theta_a$ (H <sub>2</sub> O) (deg)	$\Theta_a$ (1.2 M $\text{Na}_2\text{SO}_4$ ) (deg)	$\Delta\Theta_a$ (deg)
polyethylene <sup>15</sup>	H, $-\text{CH}(\text{CH}_3)_2$	$\text{H}_2\text{NCH}(\text{CH}_3)_2$	76	144	polyethylene <sup>15</sup>
glass	H, $-\text{CH}(\text{CH}_3)_2$	$\text{H}_2\text{NCH}(\text{CH}_3)_2$	74	>170	glass
glass	H, $-\text{CH}(\text{CH}_3)_2$	$\text{H}_2\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	69	146	glass
glass	$-\text{CH}_2\text{CH}_3$ ,	$\text{H}_2\text{NCH}(\text{CH}_3)_2$	33	72	glass
glass	$-\text{CH}_2\text{CH}_3$ ,	$\text{H}_2\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	44	82	glass
	$-\text{CH}_2\text{CH}_3$				

polyacrylamide matrix, the choice of primary amine for quenching unreacted ester groups affected both  $\Theta_a$  and  $\Delta\Theta_a$  in wettability by solutions of water and 1.2 M Na<sub>2</sub>SO<sub>4</sub>. Subtle changes in the identity of an N-alkyl substituent are known to lead to changes in a responsive polymer's LCST or in a polymer's solubility in polar vs nonpolar solvents.<sup>20,21</sup> These results suggest that a graft's solute responsive wettability is similarly sensitive to such structural changes and that the responsive character of these surfaces could be even higher with other polymer matrices.

This covalent layer-by-layer assembly process is a conformal synthetic process and was therefore extended to functionalize porous glass frits to form a responsive supported membrane. The surface-grating procedure followed the procedure used for glass slides above (Scheme 1A,B) but only used the PNIPAM-*c*-PNASI copolymer polyelectrophile, 10 and 100 nm aminated SiO<sub>2</sub> nanoparticles, and isopropylamine in the covalent assembly process since this combination of reagents afforded the most differentially responsive solute sensitive wettability in experiments with glass slides. Since nanocomposite grafts on glass slides exhibited solute-responsive wettability, depending on solute identity and concentrations of anions and cations according to the Hofmeister series,<sup>15,18</sup> we anticipated that a similar responsive behavior would be seen with these functionalized glass frits and that this responsive behavior would lead to solute-responsive permeability in a porous frit.

To test the successful functionalization of a frit, a drop of water or 1.2 M Na<sub>2</sub>SO<sub>4</sub> was placed on the surface of either a functionalized or unfunctionalized frit. In the case of the unfunctionalized frit, the drop rapidly (<10 s) was absorbed into the frit for both the water and the salt solution. However, in the case of the functionalized frit, very different behavior was observed (Figure 1). In this case, the droplet of pure water was rapidly absorbed into the frit, but the 1.2 M Na<sub>2</sub>SO<sub>4</sub> solution hardly wet the frit. Qualitative experiments carried out with aqueous solutions containing lower concentrations of Na<sub>2</sub>SO<sub>4</sub> further showed that the drop behavior depended on the concentration of Na<sub>2</sub>SO<sub>4</sub>. These experiments indicated that

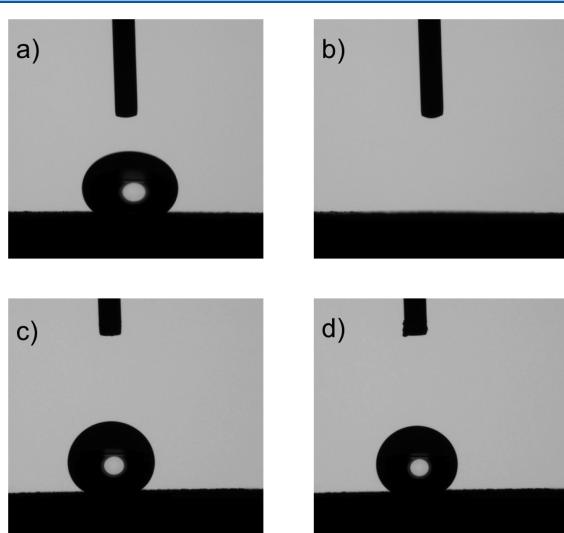
drops with Na<sub>2</sub>SO<sub>4</sub> concentrations >0.6 M did not readily absorb into functionalized frits.

Given the results of these preliminary studies of droplet behavior, we began a study of the solute responsive permeability of frits modified with nanocomposite grafts. These studies tested the passive permeability of functionalized frits as a function of salt identity, salt concentration, and temperature as well as tested the reversibility of the permeability response. These tests involved measuring flow rates for frits, which were placed in a Teflon adapter that were in turn attached to a glass column. In the experiments, the column was filled with water or salt solutions, and the time required for 1.7 mL of solution to flow through the frit was measured by measuring the time required for the solution height above the frit to decrease by ca. 1 cm. The solutions were all initially 4.5 ± 0.5 cm above the frit to minimize variations in flow rates caused by hydrostatic pressure. The flow rate measurements for salt solutions included the response time before percolation through the frit, if it occurred.

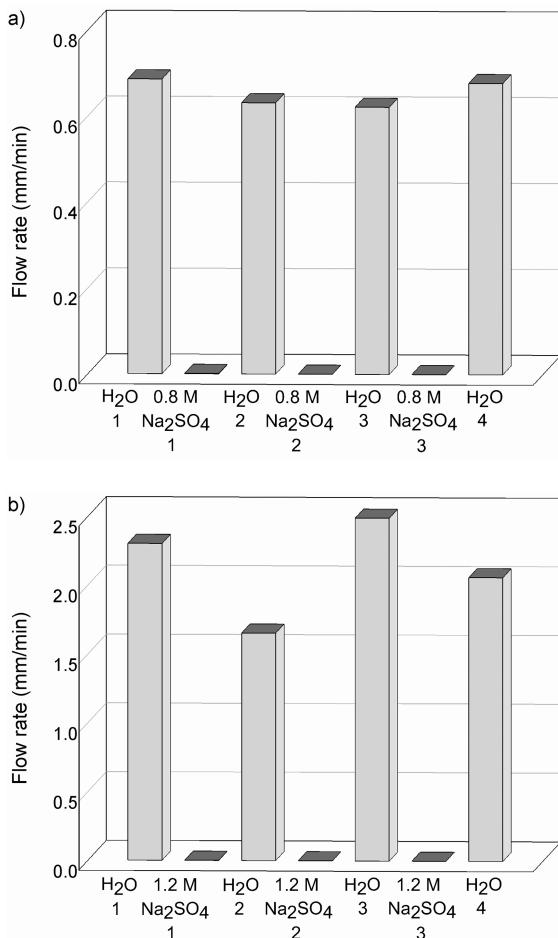
Our initial experiments confirmed the impermeability of these frits to 1.2 M Na<sub>2</sub>SO<sub>4</sub> and the permeability of the frits to water. However, initial attempts to reproduce flow rates for a single frit led to poor reproducibility of flow rates after washing and drying the frit, with flow rates sometimes varying by up to 40% from experiment to experiment. This irreproducibility in flow rates for a given frit in response to water and Na<sub>2</sub>SO<sub>4</sub> solutions was found to be due to a lack of consistency in the washing and drying processes. When experimental procedures were carefully modified to standardize the water wash, flow rate measurement, methanol rinse, and nitrogen drying time, such that a frit was exposed to the same conditions each time after a set of flow rate studies, flow rate measurements with a second set of a salt solution and water yielded more consistent results. In these experiments the standard deviation for successive measurements for flow rates for one frit with a Na<sub>2</sub>SO<sub>4</sub> solution and a water solution showed little variation (standard deviation of these measurements was less than 25%). We believe these effects arise from the fact that the extent to which the nanocomposite grafts rehydrate depends on the extent to which the graft was dried. Similar effects are known for dissolution/precipitation of linear PNIPAM in that fully dehydrated PNIPAM can require hours to dissolve while PNIPAM containing significant amounts of water can redissolve in less than a minute after an LCST event.<sup>22,23</sup>

When flow rate studies were more carefully controlled, the frits with a PNIPAM/silica nanocomposite graft exhibited reversible solvent dependent permeability for solutions of Na<sub>2</sub>SO<sub>4</sub> and water. This is illustrated by the data in Figure 1 for both a 0.8 and a 1.2 M Na<sub>2</sub>SO<sub>4</sub> solution and water. In these experiments, the flow rate of the Na<sub>2</sub>SO<sub>4</sub> was >1000 times lower than that of water for either the 0.8 or 1.2 M Na<sub>2</sub>SO<sub>4</sub> over a 12 h period at room temperature.

While Figure 2 demonstrates solute-dependent passive permeability for these functionalized frits, it also illustrates that deviation of water flow rates through a frit varied from frit to frit. The ca. 3-fold difference in water flow rate for the separately functionalized frits in Figure 2 was not unusual and was attributed to the significant deviations between the frits' range of porosity (10–20 μm). This range of porosities led to differences in the extent of functionalization from frit to frit. However, while flow rates for water at room temperature for separately functionalized frits varied, flow rates for Na<sub>2</sub>SO<sub>4</sub>



**Figure 1.** Images of 10 μL droplets on PNIPAM-*c*-PNASI copolymer/silica nanocomposite functionalized frits captured using an optical goniometer: (a) initial water drop; (b) water drop after 12 s; (c) drop of 1.2 M Na<sub>2</sub>SO<sub>4</sub> after 2 min; and (d) drop of 1.2 M Na<sub>2</sub>SO<sub>4</sub> after 12 min.



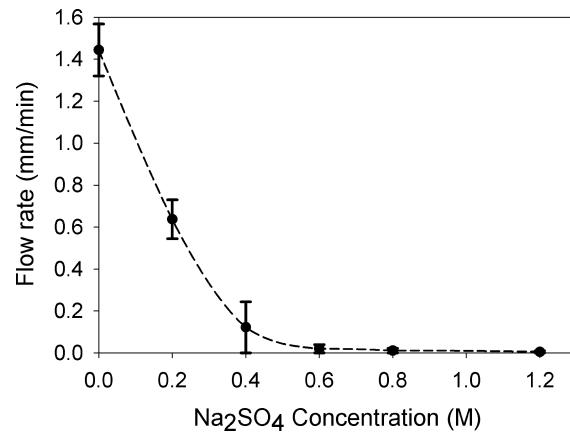
**Figure 2.** Variation of flow rates for aqueous  $\text{Na}_2\text{SO}_4$  and high-purity water measured for two separate frits at room temperature: (a) 0.8 M  $\text{Na}_2\text{SO}_4$  and water; (b) 1.2 M  $\text{Na}_2\text{SO}_4$  and water.

solutions were always consistently several orders of magnitude slower.

The premise that the difference in flow rates of 1.2 M  $\text{Na}_2\text{SO}_4$  solutions and water was due to the presence of a kosmotropic salt was tested by examining two other salt solutions. Sodium citrate, another kosmotropic salt whose solutions do not wet PNIPAM/silica nanocomposite grafts on polyethylene or glass, was also found to have a 1000-fold lower flow rate than water. On the other hand, sodium thiocyanate ( $\text{NaSCN}$ ), a chaotropic salt, did not affect the flow rate in the same manner as  $\text{Na}_2\text{SO}_4$  or sodium citrate and a 1.2 M  $\text{NaSCN}$  solution flowed through a frit with a flow rate that was ca. 70% of the flow rate of water. The similarity in flow rates of water and  $\text{NaSCN}$  solution, in contrast with the lack of flow for 0.8 M  $\text{Na}_2\text{SO}_4$  and 0.8 M sodium citrate, both indicate the solute responsiveness of these PNIPAM-grafted frits' permeability and the correlation of these permeability changes to the Hofmeister effect.

Our preliminary experiments of the rate of absorption of droplets into frits suggested that varying concentrations of  $\text{Na}_2\text{SO}_4$  could also affect flow rates and experiments showed that solutions of  $\text{Na}_2\text{SO}_4$  with concentrations of 0.4–0.6 M  $\text{Na}_2\text{SO}_4$  would penetrate through a PNIPAM/silica grafted frit during the 12 h experiments. To examine the effect of varying  $\text{Na}_2\text{SO}_4$  concentrations on flow rates and to ensure that residual  $\text{Na}_2\text{SO}_4$  from one experiment did not compromise

results for a succeeding experiment, the frit washing process was changed. In this case, a frit used in one flow rate experiment was soaked for 3 h in a beaker of cold water (8 °C) which was stirred with an overhead stirrer. This ensured that the PNIPAM matrix was fully rehydrated and that any residual  $\text{Na}_2\text{SO}_4$  was removed before the next flow rate measurement. Using this protocol, we observed a smooth change in flow rates for varied concentrations of  $\text{Na}_2\text{SO}_4$  (Figure 3), consistent with



**Figure 3.** Flow rates of  $\text{Na}_2\text{SO}_4$  solutions of varying concentrations measured on the same frit. Error bars not shown are smaller than the marker.

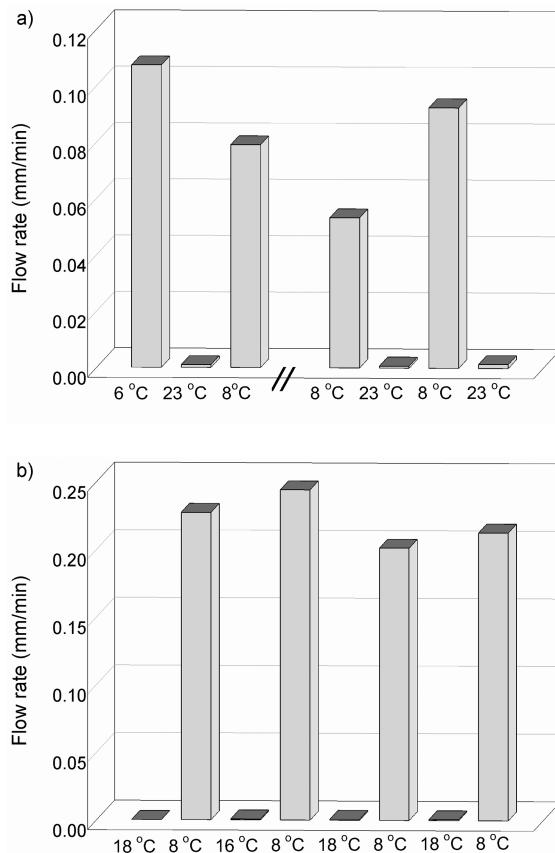
the Hofmeister effect where solubility of linear PNIPAM or wettability of a PNIPAM/silica nanocomposite graft vary with the concentration of salt.

The effect of temperature on flow rate control for glass frits with PNIPAM/silica nanocomposite grafts due to the presence of kosmotropic salts was also briefly examined. In these cases, the low-temperature flow rates were measured by first equilibrating all solutions and the apparatus in a cold room overnight. Since the maximum solubility of  $\text{Na}_2\text{SO}_4$  is 0.48 M at 5 °C,<sup>24</sup> 0.5 M  $\text{Na}_2\text{SO}_4$  was used to measure flow rates at 8 and 23 °C. These temperatures were chosen so as to be below and above the LCST of PNIPAM in 0.5 M  $\text{Na}_2\text{SO}_4$ . The reported LCST of PNIPAM in 0.33 M  $\text{Na}_2\text{SO}_4$  is ~23 °C,<sup>14</sup> and the LCST of PNIPAM at higher concentrations of  $\text{Na}_2\text{SO}_4$  (i.e., in 0.5 M  $\text{Na}_2\text{SO}_4$ ) should be lower than 23 °C.

The flow rates obtained for a 0.5 M  $\text{Na}_2\text{SO}_4$  solution through a PNIPAM/silica nanocomposite-functionalized glass frit at 8 and 23 °C are shown in Figure 4. Inside a cold room at 8 °C the 0.5 M  $\text{Na}_2\text{SO}_4$  solution flowed 100 times faster compared to the same experiment conducted at room temperature within the time frame of the experiment (12 h). In addition, the flow rate changes due to temperature were fully reversible for eight cycles. Similar temperature effects were also observed for 0.8 M sodium citrate solutions. Again, a 0.8 M sodium citrate solution flowed through a functionalized frit 2 orders of magnitude faster at 8 °C than at 18 °C. These temperature-dependent flow rates were also reversible with cooling and warming to room temperature. Thus, these PNIPAM-grafted frits responded to temperature in the presence of these kosmotropic salts by allowing flow when the temperature is below its LCST.

## CONCLUSIONS

Responsive nanocomposite grafts were successfully synthesized by a covalent layer-by-layer approach, using a surface grafting procedure recently developed by our group on both glass slides



**Figure 4.** Reversible flow rates of a PEI/[PNIPAM/SiO<sub>2</sub>]<sub>n</sub>/PNIPAM-functionalized frit at room temperature and in a cold room in the presence of (a) 0.5 M Na<sub>2</sub>SO<sub>4</sub> and (b) 0.8 M sodium citrate.

and macroporous glass frits. Grafts prepared with poly(*N,N*-diethylacrylamide) in place of poly(*N*-isopropylacrylamide) as a matrix had a significantly differential wetting response to solutions of a kosmotropic salt like 1.2 M Na<sub>2</sub>SO<sub>4</sub> even though poly(*N,N*-diethylacrylamide) solutions have an LCST similar to that of poly(*N*-isopropylacrylamide). The differential wetting response of these grafts on planar surfaces could also be affected by the primary amine component of the grafting chemistry. Macroporous glass frits could be similarly functionalized to form a supported membrane that exhibited similar differential wetting in response to solutions of kosmotropic salts, chaotropic salts, and water, resulting in dramatic changes in passive permeability of these frits as measured by the flow rates of water as compared to aqueous solutions of various salts. At room temperature, high concentrations of kosmotropic salt solutions were not capable of permeating the hydrophobic pores, and no permeation occurred. In contrast, water and aqueous solutions of chaotropic salts wet these frits and flowed through these frits ~1000 times faster. This phenomenon was readily correlated to the LCST of behavior of PNIPAM in the presence of kosmotropic or chaotropic salt solutions and water, respectively. By measuring flow rates from 1.2 to 0.0 M of Na<sub>2</sub>SO<sub>4</sub>, it was determined that the permeability of these frits to solutions of kosmotropic salts was concentration dependent. Permeation and flow began through PEI/[PNIPAM/SiO<sub>2</sub>]<sub>n</sub>/PNIPAM-grafted frits at concentrations between 0.6 and 0.4 M. Additionally, the permeability of these nanocomposite PEI/[PNIPAM/SiO<sub>2</sub>]<sub>n</sub>/PNIPAM-grafted frits was demonstrated as 0.5 M Na<sub>2</sub>SO<sub>4</sub> and 0.8 M sodium citrate solutions flowed 2

orders of magnitude faster at subambient temperature at room temperature.

## ASSOCIATED CONTENT

### S Supporting Information

Synthetic procedures for polymeric precursors, aminated silica nanoparticles, and details for layer-by-layer grafting onto glass slides and frits. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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