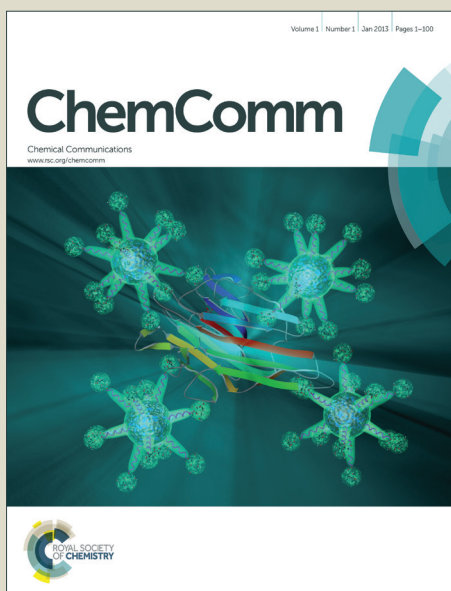


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ARTICLE TYPE

Porous polymer-based monolithic layers enabling pH triggered switch between superhydrophobic and superhydrophilic properties

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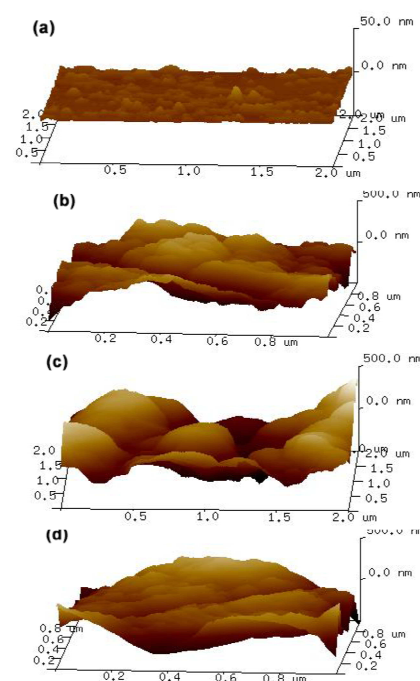
pH-Responsive surface layers consisting of porous polymer monolith containing thiol groups has been prepared via “thiol-ene” click reaction using a mixture of hydrophobic and ionizable unsaturated “ene” compounds. Proportion of these two “ene” reagents controlled wettability of the surface that varied with pH, and enabled reversible switching between superhydrophilic and superhydrophobic properties.

Introduction

Smart solid surfaces allowing reversible switching between superhydrophobicity and superhydrophilicity using an external stimulus have generated great interest in many fields including bioadhesion, water/oil separation, sensors, microfluidic devices, and drug delivery systems.¹ These so called smart surfaces are typically obtained by methods enabling control of chemical compositions and surface topography.² The external stimuli include light irradiation, temperature, pH, electric potential, and exchange of counterions.³ It has also been demonstrated that both superhydrophobicity and superhydrophilicity are enhanced by increasing surface roughness owing to the capillary effect.⁴ As a result, preparation of rough solid surfaces and control of their topology is one of the focal points driving design of smart responsive materials.

Porous polymer monoliths featuring large through pores and non-porous microglobules were introduced in the early 1990s to address the slow diffusional mass transport in stagnant mobile phase within pores of separation media in chromatographic columns.⁵ In addition to the tubular formats,⁶ the preparation of monolithic thin layers was also demonstrated.⁷ For example, monolithic thin layers with superhydrophobic surface were obtained by controlling the compositions of porogens in the polymerization mixture and functionalities of the used monomers.^{7a}

In contrast to the previously published approaches,^{3k,3p} this communication demonstrates for the first time the preparation of pH-responsive monolithic layers with tunable wettability and reversible switching between superhydrophobic and superhydrophilic properties. Another novelty is that these layers are obtained via a simple “thiol-ene” click reaction of thiol-containing monolith with the mixture of hydrophobic and polar ionizable “ene” reagents. Modulation of the proportion of “ene” compounds, 10-undecylenic acid and lauryl methacrylate, produces surface, which is superhydrophobic in acidic and superhydrophilic in basic environment. In contrast, combination



of **Figure 1** Atomic force microscopy (AFM) images of generic and functionalized poly(glycidyl methacrylate-co-ethylene dimethacrylate) monolithic layers prepared from polymerization mixtures varying in presence of porogens. (a) generic non-porous monolithic layer prepared in the absence of porogens, (b) generic porous monolithic layer prepared in the presence of cyclohexanol and 1-dodecanol as porogens, (c) porous monolithic layer functionalized via “thiol-ene” click reaction using a mixture of 75 wt% 10-undecylenic acid and 25 wt% lauryl methacrylate, (d) porous monolithic layer functionalized via “thiol-ene” click reaction with a mixture of 1 wt% [2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium betaine and 99 wt% lauryl methacrylate.

2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl) ammonium betaine and lauryl methacrylate provides surfaces exhibiting superhydrophobicity in basic and superhydrophilicity in acidic media.

The initial generic monolithic polymer layer was prepared using *in-situ* photopolymerization of a mixture comprising glycidyl methacrylate (GMA), ethylene dimethacrylate (EDMA), and 2,2-dimethoxy-2-phenylacetophenone as an initiator. Due to the absence of porogens, we obtained polymer film with a smooth

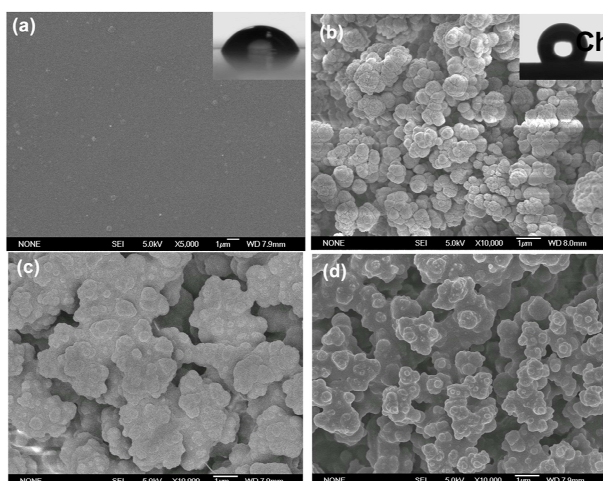


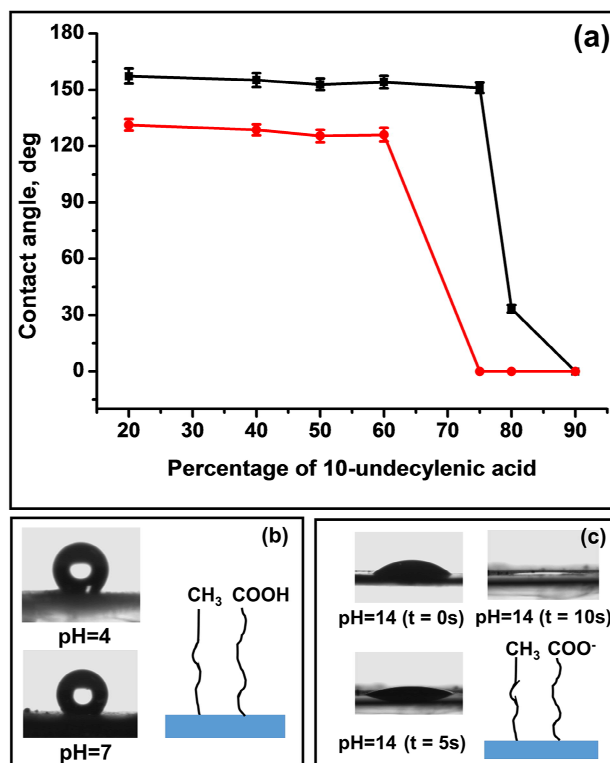
Figure 2 Scanning electron micrographs (SEM) of generic and clicked poly(glycidyl methacrylate-co-ethylene dimethacrylate) monolithic layers prepared from polymerization mixtures varying in presence of porogens. (a) Generic non-porous monolithic layer prepared in the absence of porogens, (b) generic porous monolithic layer prepared in the presence of cyclohexanol and 1-dodecanol as porogens, (c) porous monolithic layer functionalized via “thiol-ene” click reaction using a mixture of 75 wt% 10-undecylenic acid and 25 wt% lauryl methacrylate, (d) porous monolithic layer functionalized via “thiol-ene” click reaction with a mixture of 1 wt% [2-(methacryloyloxy)ethyl]-dimethyl-(3-sulfopropyl) ammonium betaine and 99 wt% lauryl methacrylate.

surface and a roughness parameter R_a of about 1.6 nm as measured using atomic force microscopy (AFM) (Figure 1a). The water contact angle (WCA) on this surface is only 67° . In order to obtain potentially superhydrophobic materials, the chemistry of this material must be accompanied with surface roughness.^{4b} The roughness of our layer was achieved by preparing porous poly(GMA-co-EDMA) thin layers from the above polymerization mixtures to which we added cyclohexanol and 1-dodecanol as porogens. The surface morphology and roughness of porous monolithic thin layer were observed using SEM and AFM. The surface shown in Figure 2a is smooth and typical of non-porous monolithic substrates. In contrast, Figure 2b presents SEM image of a monolithic polymer layer featuring structured morphology formed from clusters of non-porous microglobules with large through pores between them. The AFM image shown in Figure 1b confirms roughness of the surface with a parameter R_a significantly enhanced to 82.7 nm. This surface roughness, as produced by introduction of porosity in the layer alone, leads to an increase in WCA to 121° .

In order to make this porous layer ready for the targeted thiol-ene click reaction, the generic porous poly(GMA-co-EDMA) layer was reacted with cystamine followed by cleaving the disulfide bond using tris(2-carboxylethyl)phosphine to liberate the desired thiol groups.^{6a,c} Energy-dispersive X-ray spectroscopy revealed 1.2 at% of S in the resulting monolithic layer. We selected a mixture of unsaturated ionizable and hydrophobic compounds, 10-undecylenic acid and lauryl methacrylate, to functionalize the thiol-containing layer using photoinitiated “thiol-ene” click reaction. In this binary mixture, the unsaturated acid is the pH-sensitive component while the methacrylate provides the hydrophobicity. It is worth noting that functionalization of the porous monolithic layer via photoinitiated “thiol-ene” click chemistry covers all the pores with the grafted layer. As a result the tiny morphological features observed on SEM image of the generic monolith in Figure 2b are less pronounced in images of both functionalized layers (Figures 2c and 2d). The surface of globular clusters is smoother but the

size of the clusters increased. This fact is confirmed by the AFM images presented in Figure 1. For example, the monolithic layer functionalized with a 75:25 wt% mixture of 10-undecylenic acid and lauryl methacrylate exhibits an increased surface roughness characterized with a roughness parameter R_a of 130 nm. Layer modified with the 1:99 wt% mixture of [2-(methacryloyloxy)ethyl]-dimethyl-(3-sulfopropyl) ammonium betaine and lauryl methacrylate also features an enhanced R_a value of 82.3 nm.

We then investigated the effect of chemical compositions on the wetting property of the layers, which were characterized using water contact angle (WCA). As shown in Figure 3a, a superhydrophobicity with a WCA of more than 150° was observed after placing acidic water droplet (pH=4, adjusted by acetic acid) at surfaces functionalized with “ene” mixtures containing less than 60% of the unsaturated acid. A basic aqueous droplet (pH=14, 1 mol/L NaOH) exhibits a WCA of 130° at the same surface. In contrast, superhydrophilicity with a WCA of less than 5° for both Figure 3 Effect of composition of the mixture used for click reaction and pH-responsive wettability of a monolithic layer formed by porous polymer functionalized with a 75:25 w/w mixture of 10-undecylenic acid and lauryl methacrylate. (a) Water contact angle as a function of percentage of 10-undecylenic acid in mixture with lauryl



methacrylate for acidic (pH=4, squares) and basic (pH=14, circles) droplets placed on surface of the porous polymer monolith. (b,c) Images of shape of acidic, neutral, and basic droplets on modified monolithic surfaces and schematic illustration of the pH-responsive wettability. The WCA for acidic and neutral droplets was 152° and 141° , respectively, for basic droplet was less than 90° in 0.5 s, 24° in 5 s, and finally 0° after 10 s.

acidic and basic droplets is detected at surfaces functionalized with mixtures containing more than 90% of the unsaturated acid. The repeatable reversibility of switching between superhydrophilic and superhydrophobic surface properties was

obtained with the thiol-containing monolithic layer functionalized using a 75:25 mixture of 10-undecylenic acid and lauryl methacrylate. The surface exhibited a WCA of 152° for aqueous droplet with pH 4, while a basic droplet with pH 14 reached a WCA of less than 90° , and then within 10 s dispersed on the surface to decrease to 0° (Figure 3b,c). This effect resulted from protonation at low pH that forms relatively hydrophobic carboxylic acid groups. In contrast, carboxylic acid groups are ionized at high pH and the carboxylate anions are hydrophilic.^{4b, 8}

The amount of the attached undecylenic acid is just sufficient to totally reverse the surface polarity. The previous example demonstrated superhydrophobicity for acidic solution. We have also found that 1:99 wt% mixture of zwitterionic [2-(methacryloyloxy)ethyl]-dimethyl-(3-sulfopropyl) ammonium betaine and lauryl methacrylate clicked at the monolith produced a system that operates the opposite way, i.e. the surface is superhydrophobic under basic conditions. As illustrated in Figure 4, the surface is superhydrophobic at pH 14 with a WCA of 157° . Decreasing the pH value to 7 led to a slight decrease in WCA to 139° . However, applying an acidic droplet with pH 4, the liquid penetrated immediately into the polymer layer confirming the superhydrophilicity with a WCA of 0° .

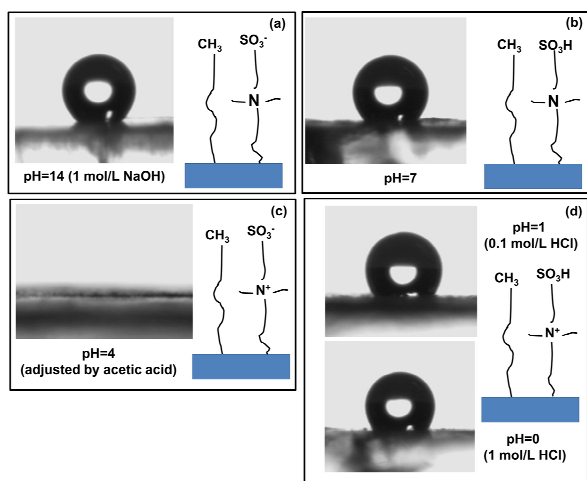


Figure 4 Images of basic (a), neutral (b), and acidic (c,d) droplets on surface of a porous polymer monolithic layer functionalized with a mixture containing 1 wt% [2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl) ammonium betaine and 99 wt% lauryl methacrylate and schematic illustration of the pH-responsive wettability. WCA droplets at pH 14, 7, 4, 1, and 0 were 157° , 139° , 0° , 135° , and 132° , respectively.

Once again, Figure 4 shows that the quaternary amine group was no longer ionized at pH 14, turning the surface in superhydrophobic. The lack of the amine ionization was sufficient to offset the hydrophilic nature of the ionized sulfonic acid groups. However, the situation changed at a pH value of 4. The amine groups were mostly ionized and at the same time, the sulfonic acid functionalities were not protonated to a significant extent due to their strong acidity. The hydrated surface then exhibited superhydrophilicity. However, applying a droplet with pH 1 and 0 adjusted by hydrochloric acid, the protonation of the sulfonic groups occurred and the surface was converted to hydrophobic again with a WCA of 130° . It is worth noting that

the properties of the switchable monolithic polymer layers remain reversible and stable even after more than 20 cycles.

In conclusion, we demonstrated the preparation of pH-responsive monolithic layers using photo-initiated “thiol-ene” click reaction. The smart surface enabled reversible switching between superhydrophobicity and superhydrophilicity affected by external pH. For the monoliths grafted with unsaturated carboxylic acid/alkylene system, water droplet with acidic pH 4 had a WCA of 152° , while the same layer was superhydrophilic after placing a droplet with basic pH on the layer. Thiol-ene grafting of a mixture of zwitterionic monomer and alkylene produced a layer which surface exhibited WCA of 157° , 0° , and 135° at pH 14, 4, and 1, respectively. In continuation of this research, we plan to prepare dual- and multi-responsive layers for applications in separation devices, microfluidic chips, and for biological detection.

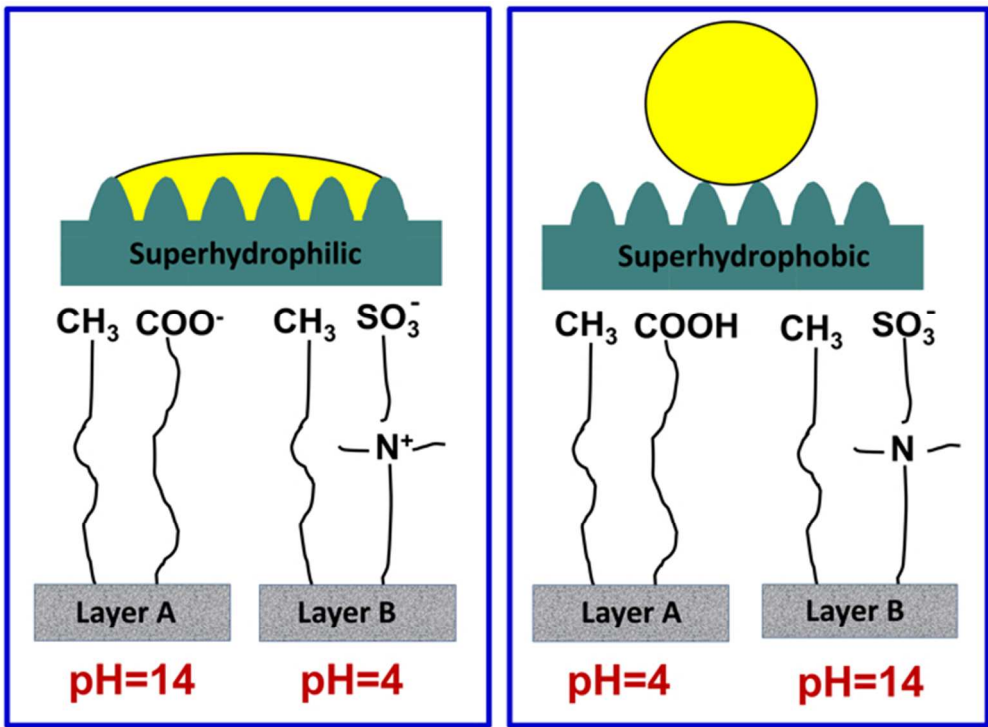
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