

Robust Superhydrophilic Coatings by Electropolymerization of Sulfonated Pyrrole

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ABSTRACT: Superhydrophilic coatings were prepared by electropolymerization of sulfonated pyrrole from aqueous solutions. The monomer was prepared in one step from commercially available reagents. Electropolymerized polymer films exhibited significant surface roughness and porosity as evidenced by scanning electron microscopy analysis. Advancing water contact angles of the pristine coatings were as low as 12°, while receding angles were 0° for almost all samples. Soaking the films in hot water resulted in decrease in the advanced contact angles to as low as 0°. The produced coatings retained their extreme wetting characteristics even when treated in harsh environments, such as dry heat for a week. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Wettability characteristics of solid surfaces play a prominent role in applications where direct contact with water or water vapor is required. Inspired by unique wetting phenomena in nature, for example, the lotus effect,¹ much attention has been devoted to developing surfaces with extreme wettability characteristics for the design of self-cleaning surfaces.^{2–4} Most of the studies focused on the fabrication of superhydrophobic surfaces,^{5–8} while superhydrophilicity has remained relatively less explored.^{9–13} Both types of surfaces can exhibit the self-cleaning effect through either droplet flow or thin film formation, respectively. One of the major challenges associated with the preparation of superhydrophilic surfaces is to ensure that they retain their extreme wetting characteristics in harsh environments, for example, when heated or dried for prolonged periods of time, conditions that are common in some real-life applications, such as fuel cell bipolar plates.¹⁴

There has been a growing interest in recent years into wettability of conducting polymers because of potential applications in fuel cells,¹⁵ immobilization of biopolymers,¹⁶ corrosion protection,¹⁷ conductive textiles,¹⁸ and controlling the growth of living cells.¹⁹ It has been established that wettability is governed by the chemical composition and topological features of the surface of interest.^{7,20,21} As recently reemphasized by Gao and McCarthy,²² for inhomogene-

ous surfaces, the area directly under the three-phase contact line determines the water contact angle of the surface. Wettability of conducting polymers also depends heavily on the type of dopants used. For example, polypyrrole films doped with perfluorinated dopants were found to be hydrophobic, while perchlorate-doped films were hydrophilic.²³ It has also been demonstrated that changing the electrical potential across a conducting polymer controls the doping level, resulting in a reversible surface wettability. When switching between the doped (oxidized) and the dedoped (neutral) states of conducting polymers, one observes a large hysteresis ($\geq 80^\circ$) in the water contact angle, which has been used to prepare hydrophilic polypyrroles and polythiophenes.^{19,24,25}

To date, there have been many attempts at generating water-soluble polypyrroles based on self-doped polymers²⁶ bearing pendant sulfonate,²⁷ carboxylate,²⁸ and alkylammonium²⁹ polar groups. The polymerizations, however, are generally conducted in organic solvents due to poor adhesion when polymerized from aqueous solutions. A recent report provided a hydrophilic polypyrrole coating based on a two-step process using pyrrole-polyethylene oxide in water.³⁰ The two-step process still required the use of an organic solvent for the first polymerization. A hydrophilic polypyrrole derivative was recently prepared by electrochemical polymerization of *N*-butyl sulfonyl polypyrrole dimer in both acetonitrile and water.²⁹

Herein, we present a simple, economical method for the preparation of robust, superhydrophilic (advancing contact angle $< 20^\circ$) polypyrrole films exhibiting good adhesion by electrochemical deposition of an *N*-alkyl sulfonyl pyrrole from an aqueous solution. We demonstrate superior stability of the prepared coatings even when annealed at elevated temperatures under dry or aqueous conditions.

EXPERIMENTAL

Materials/Instruments

Sulfonated pyrrole **1** was synthesized according to the literature procedure.³¹ The stainless steel substrates used as working electrodes were 15 mm diameter AFM specimen discs purchased from Ted Pella (Redding, CA). The platinum wire/platinum mesh counter electrodes used were Pt gauze, 100 mesh woven from 0.0762 mm diameter wire, $50 \times 50 \text{ mm}^2$ (purchased from Alfa Aesar (Ward Hill, MA)). Current densities for polymerizations were controlled using a Princeton Applied Research (Oak Ridge, TN) Potentiostat/Galvanostat model 263A. Scanning electron microscopy was performed on a Hitachi (Schaumburg, IL) S-4000 Field Emission Scanning Electron Microscope, operated at 25 keV. Contact angle measurements were conducted on a Rame-Hart (Succasunna, NJ) model NRL A-100 Contact Angle Goniometer.

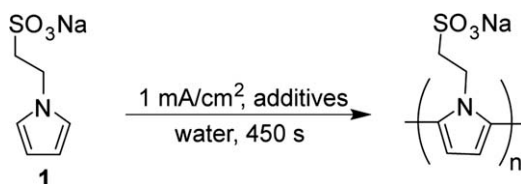
Polymerization Conditions

Electropolymerizations were carried out in a typical one cell setup, using a stainless steel working electrode with a platinum wire/platinum mesh counter electrode, and an Ag/AgCl (sat) reference electrode.

RESULTS AND DISCUSSION

Sulfonated pyrrole **1** was synthesized in one step from commercially available reagents by a modified Paal-Knorr method.³¹ Thus, a reaction between 2,5-dimethoxytetrahydrofuran and taurine provided pure **1** after recrystallization in high yields ($>80\%$). The reaction proceeds under mild conditions and is readily amenable to scale up.

Monomer **1** was then electrochemically polymerized under a constant current density of 1 mA/cm^2 for 450 s, using a variety of supporting electrolytes (Scheme 1). The use of sodium sulfate or sodium perchlorate in the presence of oxalic acid resulted in the formation of a black polymer film. The use of sodium phosphate as a supporting electrolyte in the absence of oxalic acid was also successful. It has been shown that acidic solutions favor polymerization of pyrrole,^{32,33} which may provide an explanation for the necessity for a protic acid source in the successful entries. On the other hand, polymerization did not proceed in the presence of sodium chloride.



Scheme 1. Synthesis of Sulfonated Polypyrrole.

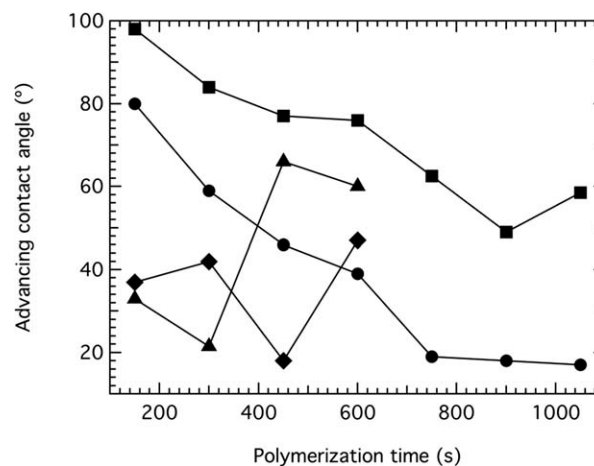


Figure 1. Evolution of water contact angles of the electrodeposited polymer films with polymerization time at different current densities (squares: 0.1 mA/cm^2 , circles: 0.5 mA/cm^2 , diamonds: 1 mA/cm^2 , triangles: 2 mA/cm^2).

We have conducted electropolymerizations for various times and at different current densities to evaluate how these parameters affect the water contact angle of the prepared films. For these studies, polymerizations were carried out at an acid concentration of 0.04 M , a monomer concentration of 0.1 M , and a sodium sulfate concentration of 1.0 M . Figure 1 shows advancing contact angles for coatings electrodeposited at different current densities for different periods of time. Clearly, hydrophilic coatings are produced faster at higher current densities. We attribute the initial decrease in contact angle due to coverage of steel surface by the newly formed polypyrrole film. In all cases, the contact angle decreases with polymerization time until a certain point, when the behavior drastically reverses and the contact angle goes up or remains steady. For example, this transition occurs at 900 s for the sample polymerized at 0.1 mA/cm^2 and at 450 s for the sample deposited at 1 mA/cm^2 . These results are consistent with polymer degradation at higher conversions, and the degradation starting sooner when higher current densities are used.^{33,34} For all current densities, except the lowest one of 0.1 mA/cm^2 , we were able to produce superhydrophilic coatings with advancing contact angles below 20° . The most consistent results were obtained using the current density of 0.5 mA/cm^2 . In all cases, the receding contact angle was 0° . The static water droplets were unstable and quickly spread on the surface within seconds for all samples (Figure 2), with the exception of those that were prepared at 0.1 mA/cm^2 under 300 s. Such a large hysteresis between the advancing and receding contact angles can be attributed to surface roughness and porosity.^{9,20,35}

The morphology of the electrodeposited films was inspected by scanning electron microscopy. The characterized surfaces exhibited micron-scale roughness and contained clearly distinguishable pores (Figure 3). Such a morphology is consistent with typical results obtained for electropolymerization of pyrrole and is a major factor contributing to the large hysteresis in water contact angles and to the observed extreme wetting behavior for the prepared coatings.

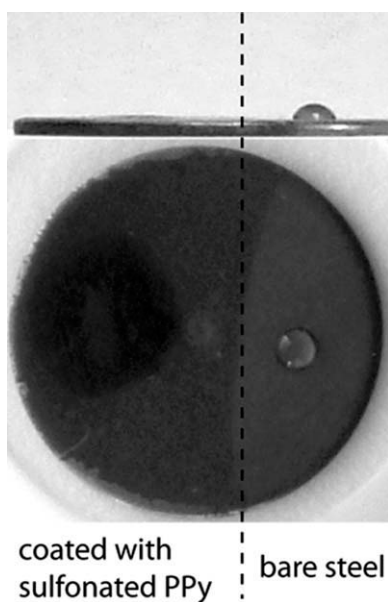


Figure 2. Water droplets on a steel substrate before and after coating with a sulfonated polypyrrole film.

Thermal stability of the polymer films and their wettability properties were studied in a heated dry environment as well as a heated aqueous environment. The samples were placed in a water filled vial in an oven at 80°C for 1 week, and the water was exchanged daily. The contact angles were obtained after samples were dried in vacuum. The same samples were then placed in a dry vial in the oven for 1 week at 80°C and contact angles were measured again (Table I). Superhydrophilic polypyrrole surfaces retained their low advancing contact angles after heating in aqueous solution and only slightly increased after dry heating (Table I, Entry 1). We attribute this remarkable stability of the wettability characteristics to the highly crosslinked nature of the electrodeposited polymer films. In the cases where the original surface was mildly hydrophilic (Table I, Entries 2 and 3), an 80°C soak for a week drastically lowered the contact

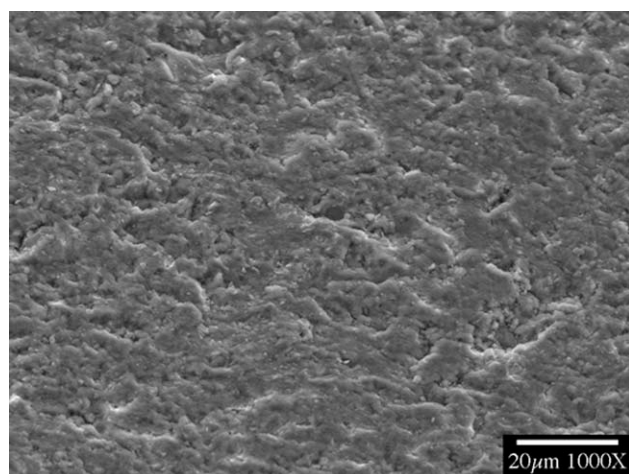


Figure 3. Scanning electron micrograph of an electrodeposited sulfonated polypyrrole film.

Table I. Thermal Stability of Electrodeposited Polymer Films^a

Entry	Polymerization conditions	CA	CA after 80°C 1 week (H ₂ O)	CA after 80°C 1 week (air)
1	1 mA cm ⁻² /450 s	13	13	17
2	1 mA cm ⁻² /300 s	34	12	17
3	1 mA cm ⁻² /600 s	41	0	9

^aOnly advancing contact angles are reported. Receding contact angles are all 0°, and all static contact angles quickly obtain a value of 0°.

angle to obtain a superhydrophilic surface, in essence an “aqueous annealing.” This could be explained by reorientation of polar groups near the polymer/water interface, placing the more polar sulfonate groups at the interface. Low contact angle surfaces obtained by this method were stable to prolonged heating, as it only slightly raised the contact angle. Thus, stable superhydrophilic surfaces were obtained either by direct electrodeposition of polymer films, or by aqueous annealing of mildly hydrophilic polymer films at elevated temperatures. The samples made at high current densities (>2 mA cm⁻²) did not exhibit good adhesion, and the integrity of the films lasted only a few days at elevated temperatures, leading to desorption of the polymer film.

CONCLUSIONS

Stable, superhydrophilic sulfonated polypyrrole films were prepared by electrodeposition from aqueous solutions. Scanning electron microscopy images of the polymer deposits revealed surfaces with significant roughness and porosity. An electrolyte screening revealed the necessity for a proton source in the polymerization medium, and advancing water contact angles ranged from 112° down to 12°. In the vast majority of cases, the receding water contact angles were 0°. Thermal studies revealed that most substrates exhibited good adhesion, and film integrity was maintained when exposed to 80°C for extended periods of time. An “aqueous annealing” process was discovered, where the contact angle of the polymer deposits drastically decreased on exposure to 80°C water for 1 week. The obtained coatings retained their superhydrophilic characteristics after prolonged heating in air (1 week). The developed coatings are of direct importance to applications requiring self-cleaning surfaces and interfaces.

The described method provides a convenient and scalable approach to superhydrophilic coatings on metal surfaces. One of the unique features of such coatings is their remarkable performance under harsh environmental conditions where they retain their wettability characteristics even after prolonged heating and drying. Such remarkable stability will facilitate the utilization of these materials in real-life applications.

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