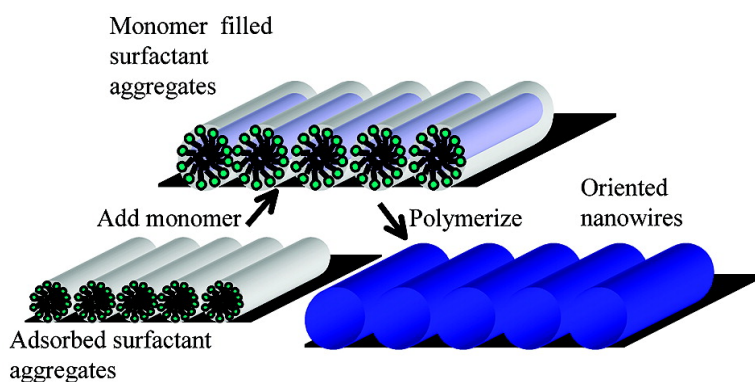Article

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Adsorbed Surfactants as Templates for the Synthesis of Morphologically Controlled Polyaniline and Polypyrrole Nanostructures on Flat Surfaces: From Spheres to Wires to Flat Films

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Abstract: Nanostructures of polyaniline (PAni) and polypyrrole (PPy) with controlled morphologies have been synthesized on atomically flat surfaces using adsorbed surfactant molecules as templates. Atomic force microscopy (AFM) has been used to investigate polymer film formation on highly oriented pyrolytic graphite (HOPG) and chemically modified HOPG. Morphological control over the resulting polymer film is possible by the addition of coadsorbing molecules, manipulation of the length of the surfactant hydrophobe, or by changing the surface chemistry of the adsorbing substrate. Phase transitions between spheres, cylinders/wires, and featureless films have been observed which exactly parallel transitions between spheres, cylinders, and flat layers in the adsorbed surfactant. Parallel arrays of PAni nanowires can be synthesized with alignment evident over large areas in a simple self-assembly technique in which fabrication and arrangement take place simultaneously. Such a technique in which one can engineer sub-100-nm-ordered nanoscale π-conjugated polymer structures of a desired shape by a simple self-assembly process presents potential as templates, sensors, and microelectronic devices.

Introduction

Surfactants are a class of molecules that form thermodynamically stable aggregates of inherently nanoscale dimensions both in solution and at interfaces. In solution, surfactant self-assembly has been investigated both theoretically and experimentally, in part because of the importance of such ordered templates in the synthesis of nanometer to micron scale structures with controlled dimensions. In 1976, Israelachvili et al. proposed the concept of the molecular packing parameter that can be used to predict the equilibrium size and shape of surfactant aggregates.[1] In this model, thermodynamic, electrostatic, and molecular packing considerations give rise to the general formula for a dimensionless parameter v_o/al_o, where v_o and l_o are the volume and length of the surfactant tail within the hydrophobic core of the aggregate and a is the effective area occupied by each surfactant headgroup at the surface of the aggregate. When the parameter lies within the ranges $0-1/3$, $1/3-1/2$, or $1/2-1$ the favored aggregate morphology in solution is spherical, cylindrical, or a flat bilayer, respectively. In addition, solution aggregate morphology can be altered by a number of external variables. The addition of electrolyte to ionic surfactant solutions reduces electrostatic repulsive forces between headgroups, whereas incorporation of *n*-alcohols causes the hydrophobic component of the aggregate to swell, and both effects cause a reduction in aggregate curvature and hence different morphologies.

Surfactants at solid−liquid interfaces have practical implications in areas such as detergency, wetting, foams, emulsions, and flotation technologies and have been the subject of two recent reviews.[2] In 1995, Manne et al. discovered via in situ atomic force microscopy (AFM) experiments that surfactants self-assemble at the solid/liquid interface into analogues of structures found in solution,[3] i.e., spheres, cylinders, and bilayers on hydrophilic surfaces and hemispheres, hemicylinders, and monolayers on hydrophobic surfaces. Phase transitions between morphologies have been observed by manipulating variables such as electrolyte concentration,[4] hydrophobe length or counterion type,[5] surface chemistry,[6] or the addition of coadsorbing molecules.[7−9] For example, adsorption of sodium dodecyl sulfate (SDS) on highly oriented pyrolytic graphite (HOPG) has been investigated by in situ AFM experiments.[10] These studies have shown that SDS self-assembles into aligned arrays of hemicylindrical aggregates that are stable over a large concentration range. This epitaxial arrangement has been attributed to an

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overlap of carbon atoms in the alkane chain of the surfactant with those of the graphite.[11] Addition of small quantities of 1-dodecanol to SDS/graphite systems induces a phase transition from hemicylinders to a planar adsorbed layer.[7] This transition is due to changes in the aggregate packing parameter described previously.

In addition to aggregation of surfactants at interfaces, aggregation of polymers at interfaces has also been extensively studied. Polymeric nanostructures, very different than those observed in bulk solution, have been observed to form on surfaces due to a combination of interfacial, intra-, and intermolecular forces.[12] Coadsorption of surfactants and polymers on surfaces has been the focus of a number of studies, although the morphology of these adsorbed structures is much less explored. In one particular case, nanoscale-aligned strands of polymer did form; these were found for ethyl(hydroxyethyl)-cellulose on the surface of graphite in the presence of surfactants.[13] However, to our knowledge, no other systems have shown such morphologies. Interactions between polymers and surfactants in the bulk have been extensively reviewed due to the relevance to many industrial applications.[14] In general, the addition of polymer to surfactant systems induces aggregation at a concentration (critical aggregation concentration, cac) well below the aggregation concentration (critical micelle concentration, cmc) for the surfactant-only system.

The ability of surfactants to self-assemble into organized templates in the bulk offers potential to fabricate materials that retain this molecular imprint. Examples of these materials include latexes and mesoporous inorganic materials with controlled pore size, i.e., the extremely important commercial structures known as MCM catalysts.[15] Because this current work focuses on π-conjugated polymer nanowires, this paragraph briefly reviews other methods to produce nanowires in bulk. Mesoporous inorganic materials with controlled pore sizes have been used to synthesize π-conjugated polymer nanowires within the confined reaction channels afforded by the pores.[16] Ordered π-conjugated polymer/silica nanocomposites have been prepared by using polymerizable surfactants, monomer, and tetraethyl ortho-silicate so that the ordering of the silica and polymer occurs simultaneously.[17] Surfactants have also been used to produce 1-D nanostructures of electrically conducting polymers in the presence of inorganic acids[18] and also in a reverse

microemulsion technique.[19] In addition to this, nonionic surfactants have been shown to act as templates for individual poly-(3,4-ethyldioxythiophene) (PEDOT) chains producing films with individual PEDOT chains having a high level of orientation.[20] Amphiphilic molecules have been used directly by Wan et al. to synthesize PAni and PPy micro/nanotubules or fibrils in the bulk. In this technique, β-naphthalene sulfonic acid (β-NSA) is used as a "surfactant-like" molecule which simultaneously controls the cylindrical structure and acts as a dopant to the polymer product.[21] Other amphiphilic organic acids have been used as dopants to form nanoscale tubes or fibers of conducting polymers.[22] In a different technique, the self-organization of preformed polymers in conjunction with amphiphilic molecules has been used to fabricate ordered materials.[23] Nanoscale cylinders with repeat distances of 3.5 nm have been created in the bulk due to hydrogen bonding between PAni chains and camphorsulfonic acid (CSA) and 4-hexylresorcinol (Hres) appendage molecules.[24]

As well as synthesizing π-conjugated polymeric nanostructures in bulk solution, the ability to engineer ordered thin films of conducting polymers on flat surfaces is attractive in the fabrication of macromolecular electronic devices for applications such as electrooptics, microelectronics, and photonics.[25] Thin films of PPy have been successfully rendered on surfaces by a technique termed admicellar polymerization (AP). AP can be visualized as the surface analogue to emulsion polymerization as adsorbed bilayered surfactant aggregates are used as templates to form thin polymer films on various surfaces. Thin polymer films of PPy have been successfully fabricated on surfaces such as alumina,[26−28] mica,[28,29] and HOPG[29] using AP, although no attempts have been made to control the morphology of the resulting polymer film. For many applications, spatial control of the deposition on the surface is desired. Typical routes to pattern surfaces with π-conjugated polymers include laser writing,[30] surface-templated deposition,[31] screen printing,[32] photolithography,[33] and e-beam writing.[34] Limitations to these techniques include resolution and possible damage of the polymer.

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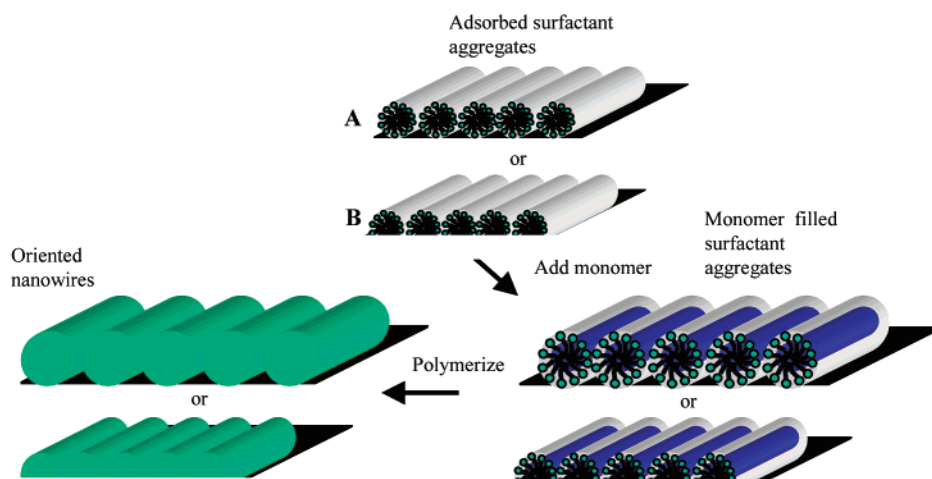(32) Garnier, F.; Hadjlaoui, R.; Yasser, A. Scivastava, P. *Science* **1994**, *265*, 1684.

Figure 1. Illustration of the process to fabricate morphologically controlled nanostructures of electrically conducting polymers on surfaces using surfactant templates. This particular schematic represents the proposed schematic of wire formation on (A) chemically treated HOPG and (B) HOPG.

A simple technique to pattern π-conjugated polymers with nanoscale dimensions is in great demand. Although chemical vapor deposition has proven effective in rendering ordered nanostructures on surfaces,[35] this technique is not suitable for orienting polymeric materials. Ordered rodlike structures of polymerizable surfactants have been observed by AFM at the mica/water interface,[36] and polyelectrolyte ribbonlike structures have been observed at the graphite/water interface.[37] With respect to oriented conducting polymers on surfaces, there have been few reports in the literature. Sub-100-nm lines of conducting polymer have been "drawn" on surfaces using the tip of a scanning tunneling microscope[38] and with the tip of an atomic force microscope in a direct-writing technique.[39] Oriented arrays of PAni nanowires have been grown normal to surfaces by an electrochemical method in which no template is used.[40]

In this article, a new way to pattern π-conjugated polymers with nanoscale dimensions on a solid surface is described, with some advantages over other processes. We show that by means of a three-step process, equilibrium adsorbed surfactant aggregates can be used as templates to synthesize organized polymer films on flat surfaces in which one has morphological control over the resulting polymer film. In the first stage, the monomer and surfactant are allowed to aggregate on the surface of the substrate, in the second stage an oxidizing agent is added to begin the polymerization reaction, and in the third stage the substrate is rinsed to remove excess ingredients. Figure 1 indicates a schematic representation of the process. Unique to our work is the fact that, in the case of the polymer nanowires,

we can fabricate aligned arrays over large areas quickly in which orientation is dictated by the surface and alignment is parallel to the surface. The polymer structures have sub-100-nm features, are highly aligned, and are not trapped within a solid support.

Results and Discussion

Polyaniline. In Figure 2A we show ordered arrays of PAni nanowires on HOPG using adsorbed SDS aggregates as a template. Orientation of the wires is maintained over large distances, with directional changes seen at grain boundaries or steps inherent in the graphite surface. Such abrupt changes in orientation of SDS hemicylinders on HOPG have been observed previously.[7,10] Separations, or cracks in the film, are observed along the long axis of the wires. These cracks are believed to form during drying, and no attempts were made to try to stabilize these films during drying. A cross-sectional view of the film (Figure 2A) identifies a distinct periodicity with a repeat distance of 16.7 ± 1.2 nm. Hemicylinder SDS aggregates adsorbed on HOPG have been shown to have diameters of approximately 6 nm, although addition of 1-dodecanol causes the aggregates to swell to around 12 nm.[7] It is therefore likely that incorporation of aniline and aniline−HCl into adsorbed SDS aggregates causes a swollen aggregate to form. A recent study concerning the solubilization locus of aniline−HCl in SDS micelles showed that the phenyl moiety resides within the hydrophobic region and the positively charged polar group between negatively charged SDS headgroups at the surface of the micelle.[41] The incorporation of bulky phenyl groups within the hydrophobic core of the aggregate coupled with charge stabilization at the surface of the aggregate could lead to an enlarged incipient structure. Height measurements have not been included due to geometric limitations of the tip and the fact that naked HOPG may not be exposed between the wires. PAni nanowires can be transitioned into a featureless PAni film by the addition of 1-dodecanol (Figure 2B). Cross-sectional analysis shows that the periodicity is lost and the roughness of the film is reduced, although the roughness is slightly larger (rms = 0.12 nm) than the roughness of the underlying graphite (rms = 0.07 nm). Additionally, no cracks are present in the film indicative of surface homogeneity. Addition of 1-dodecanol causes a change

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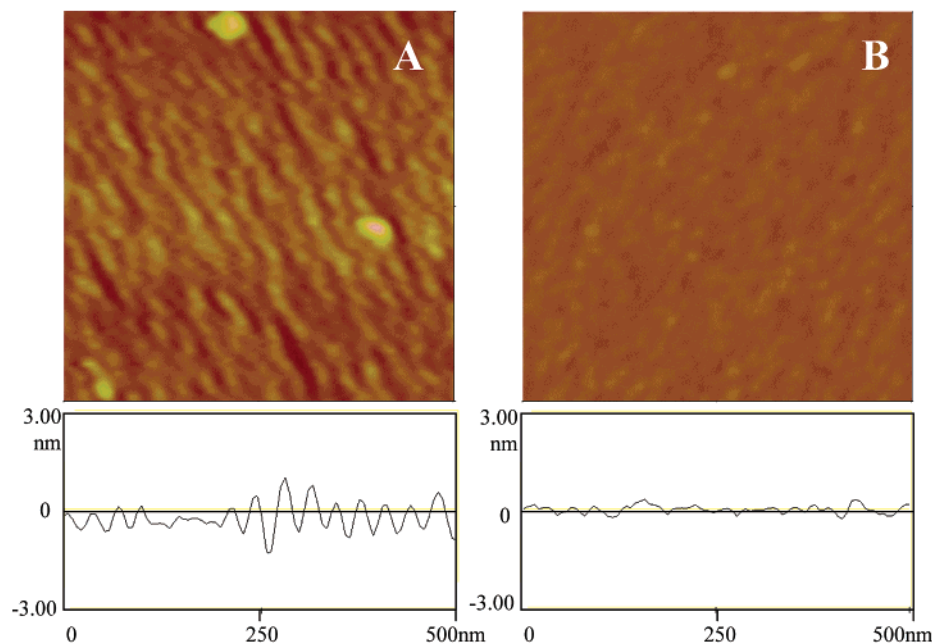
Figure 2. 500×500 nm^2 AFM images of PAni films on HOPG with 0 mM 1-dodecanol (A) and 0.5 mM 1-dodecanol (B). Both images shown at a height scale of 12 nm.

in aggregate packing parameter due to its smaller headgroup yet same-length hydrophobe.

Analysis of the chemical form of PAni can be ascertained by X-ray photoelectron spectroscopy (XPS), sometimes called electron spectroscopy for chemical analysis (ESCA). PAni can be present in one of three oxidation states: leucoemeradine, emeraldine, and pernigraniline referring to reduced, reduced/oxidized, and oxidized states, respectively. The particular form of PAni can be characterized by XPS by way of three different nitrogen environments with specific N$_{1s}$ binding energies: <399, 399−400, and >400 eV representing −N=, −NH−, and −N$^{\bullet+}$−, respectively.[42] Evaluation of the N$_{1s}$ peak from XPS indicates that in both cases the polymer is in the emeraldine salt (conductive) form. Figure 3 represents spectra for the film shown in Figure 2A. Analysis of the area corresponding to positively charged nitrogen (>400 eV) suggests that two different species exist. These two different environments can be interpreted, in order of increasing binding energy, as polaron and bipolaron states, respectively.[43] Evaluation of the relative area of the two peaks >400 eV with respect to total nitrogen (N$^+$/N) shows a doping degree of 0.45.[44] Ordered films of PAni should provide improved electrical properties, and therefore, evaluation of the conductivity of these films is currently under investigation.

To study PAni film formation on a less hydrophobic surface, chemical treatment of freshly cleaved HOPG was carried out by exposure to ammonium persulfate under acidic conditions prior to the addition of monomer and surfactant. Contact angle measurements show that the contact angle of the HOPG block with water changes from 90° to around 75° after surface treatment. XPS analysis of treated HOPG indicates peaks corresponding to specific binding energies associated with
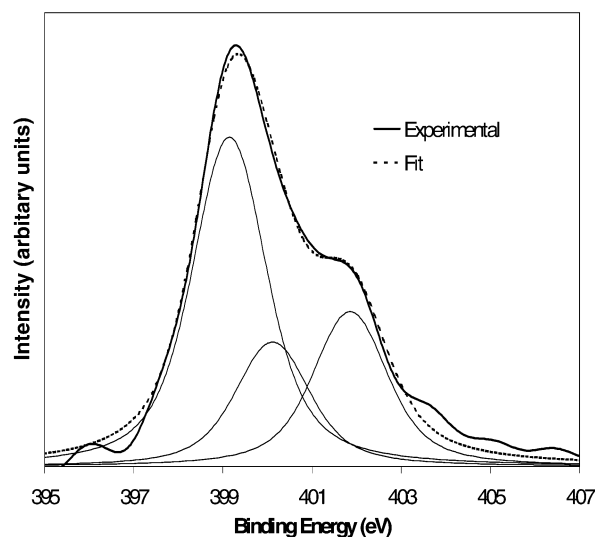
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(44) We cannot rule out that some contribution to positively charged nitrogen may come from intercalated ammonium ions beneath the polymer film.

Figure 3. X-ray photoelectron spectroscopy of PAni wires on freshly cleaved HOPG. Three nitrogen environments can be observed by curve fitting.

carbon, nitrogen, oxygen, and sulfur (Figure 4). A slight amount of oxygen is present in freshly cleaved HOPG (Figure 4C), possibly due to the sample being cleaved 3 days prior to analysis (the treated sample was treated and then also stored for 3 days before analysis). Since the binding energies for nitrogen, oxygen, and sulfur are 402.2, 532.5, and 168.7 eV, respectively, we believe that the mode of surface modification is intercalation of ammonium persulfate ions into the graphene lattice. STM studies of the intercalation of various ions into HOPG have shown the existence of large periodic superstructures.[45]

Following surface treatment of HOPG with ammonium persulfate, PAni synthesis was then carried out in an identical fashion as described previously. The resulting polymer films

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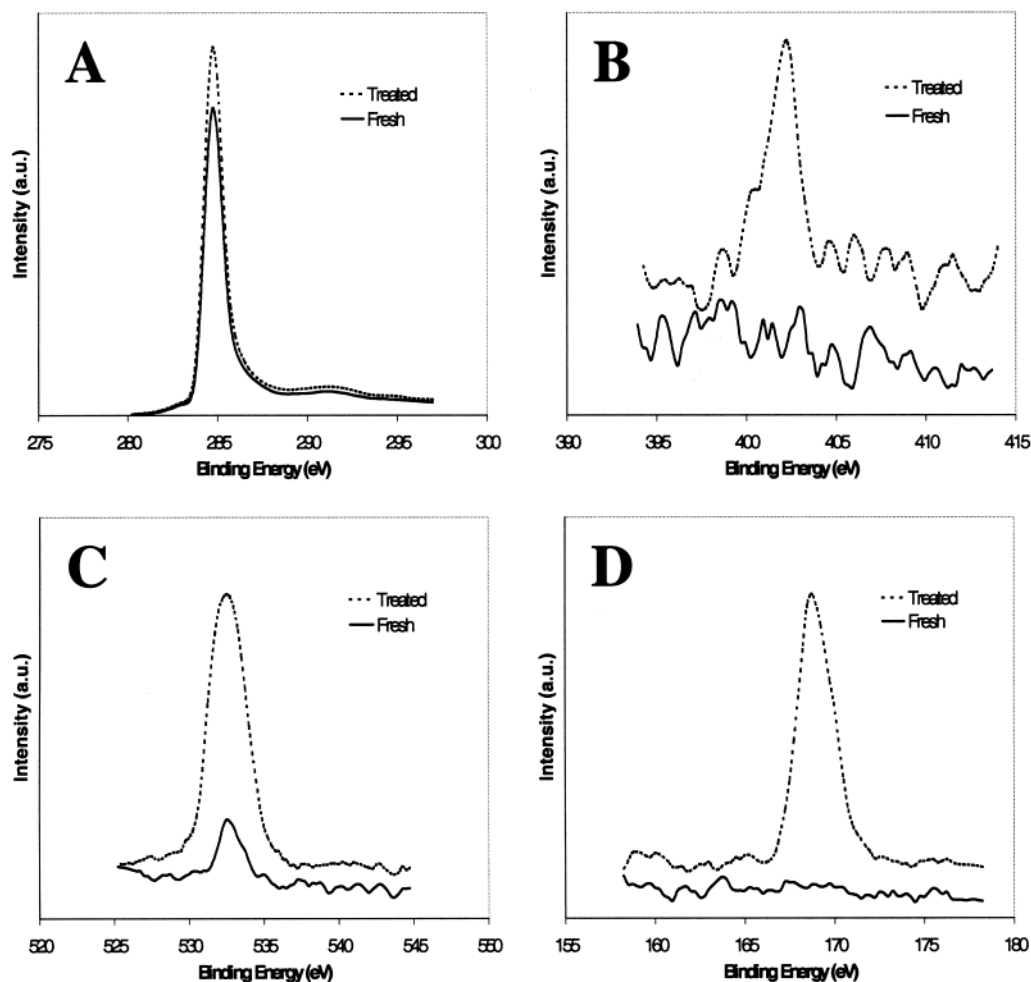
Figure 4. X-ray photoelectron spectroscopy of HOPG before and after chemical treatment. (A) Carbon, (B) nitrogen, (C) oxygen, and (D) sulfur.

are shown in Figure 5A; compare these films with those synthesized on freshly cleaved HOPG (Figure 2A). Spherical PAni structures are fabricated with a diameter of 44.9 ± 2.6 nm covering the entire surface of the substrate. Many cracks are apparent in the film and appear to follow steps in the underlying graphite. Using the cracks as a reference point for the location of the underlying graphite, we can measure a typical height of the film to be approximately 40 nm which corresponds well to the measured diameter indicating that the film morphology is indeed spherical. Addition of small quantities of 1-dodecanol causes the spheres to align into what looks like wires composed of connected spheres in a "pearl necklace-like" conformation (Figure 5B). Interestingly, increasing the reaction time from 1 to 3 h at the same 1-dodecanol concentration causes the globular texture of the wires to diminish, rendering well-formed PAni nanowires with a similar diameter of 44.5 ± 1.8 nm (Figure 5C). Analysis by XPS indicates that PAni is in the conductive emeraldine salt form with a typical doping degree of 0.46 (Figure 6).[44] Featureless PAni films were not observed for this system at the highest 1-dodecanol concentrations investigated.

Differences in film morphology with respect to surface treatment can be explained by a change in interaction between the surfactant and surface. For freshly cleaved HOPG, the interaction between the surfactant and surface is primarily due to interactions between the tail group and surface, consistent with monolayer coverage. In the case of a less hydrophobic substrate, i.e., graphite chemically treated with ammonium persulfate, interactions between the headgroup and surface predominate leading to bilayer coverage, which in turn leads to features with larger dimensions (see proposed mechanism in Figure 1). Measurements of the height differences are consistent with this explanation; the height of the film shown in Figure 2A (periodicity of 16.7 nm) has been measured as 1.5 ± 0.4 nm, while Figure 5C (periodicity of 44.5 nm) has a height of 4.7 ± 1.9 nm. As mentioned previously, the tip is likely not contacting the surface of the graphite, and almost certainly these height values are not quantitatively correct although this difference certainly represents a difference in polymer morphology.

If APS-treated graphite is soaked in water for a few hours prior to reaction, the results are the same as using freshly cleaved HOPG, indicating that intercalated ions diffuse back out of the graphene lattice. Conversely, even though APS is present in reactions with freshly cleaved HOPG, we believe that adsorption of surfactant occurs before addition of APS and therefore retards (or at least slows down the kinetics of) APS intercalation, and hence, the surface is hydrophobic with respect to surfactant adsorption and subsequent polymerization.

Polypyrrole. In the studies of PAni described above, the morphology of the synthesized polymer was controlled by varying the template morphology using either the surfactant
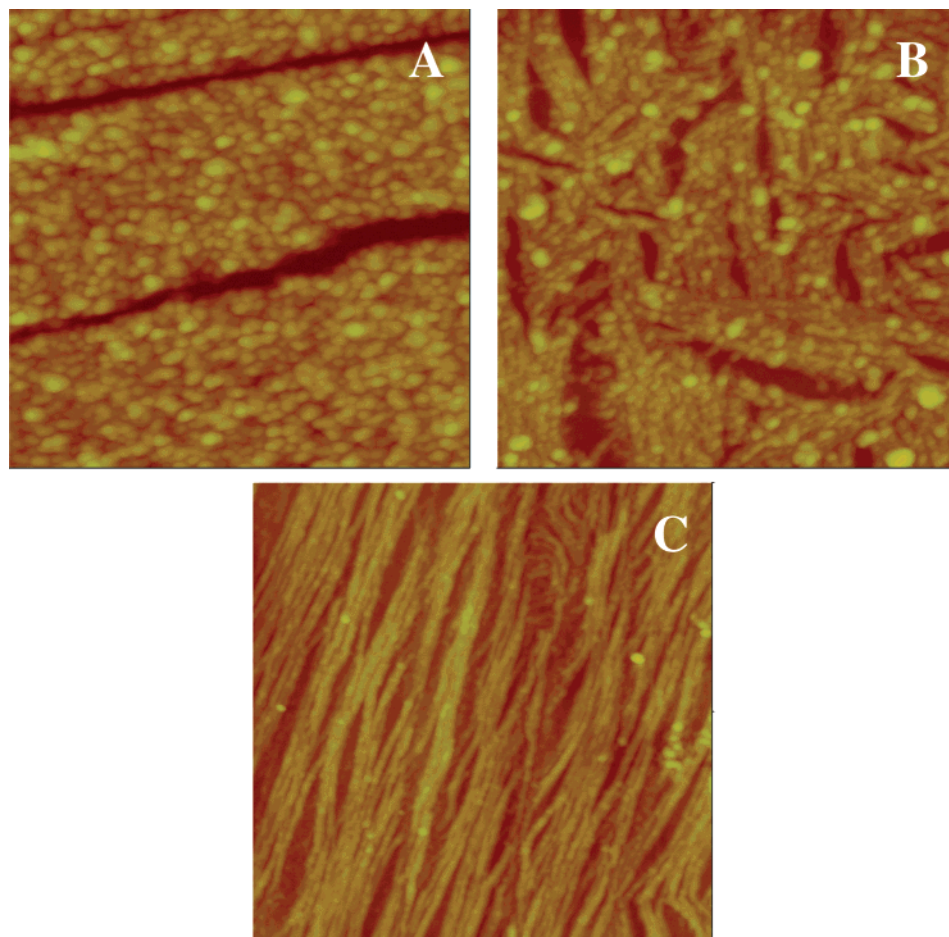
Figure 5. $2 \times 2 \ \mu m^2$ AFM images of PAni films on oxidized HOPG with 0 mM 1-dodecanol (A), 0.1 mM 1-dodecanol (B), and 0.1 mM of 1-dodecanol and 3 h of polymerization (C).
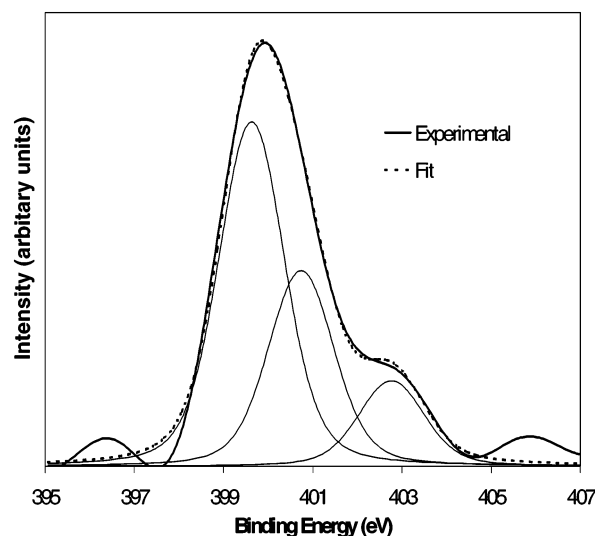

Figure 6. X-ray photoelectron spectroscopy of PAni wires on chemically treated HOPG, indicating curve fitting and the different nitrogen environments.

surface energetic interaction or the addition of a coadsorbing molecule. Another parameter we wished to examine was hydrophobe length, and further, we wished to determine whether the templating effect could be induced with a monomer other than aniline. Hence, three sodium sulfonate surfactants were used: 1-octanesulfonate, 1-decanesulfonate, and 1-dodecane-

sulfonate. Sulfonate surfactants were used because the adsolubilization of pyrrole is somewhat limited in sulfate aggregates without the addition of electrolyte.[46] The disadvantage of this choice is that the adsorption of sodium sulfonate surfactants on atomically smooth surfaces has not been studied by AFM to our knowledge; therefore, the initial morphology of the surfactant aggregates in the absence of pyrrole is unknown.

In Figure 7, one can see the effect of varying the length of the hydrophobic moiety in the surfactant on PPy film formation. In Figure 7A, PPy spheres are observed for C_8 with a diameter of approximately 25.6 ± 2.8 nm. Increasing the length of the hydrophobe by two methylene groups to C_{10} creates a smaller spherical morphology (18.2 ± 1.9 nm) and a reduced film roughness indicated by the AFM cross section analysis (Figure 7B). A smaller spherical diameter in the case of C_{10} is somewhat counterintuitive, although it can be explained in terms of the cmc. As the same concentration of surfactant is used in all cases, experimental conditions for C_{10} are closer to the cmc than for C_8, and hence, the number density of spheres adsorbed on the surface is expected to be greater for the C_{10} surfactant, which in turn limits the size of polymer spheres. In contrast to spherical structures observed for C_8 and C_{10} hydrophobes, a featureless film is found in the case of C_{12} (Figure 7C). The transition from spherical to flat morphologies is predicted by the packing parameter of solution aggregates for an increase in length of

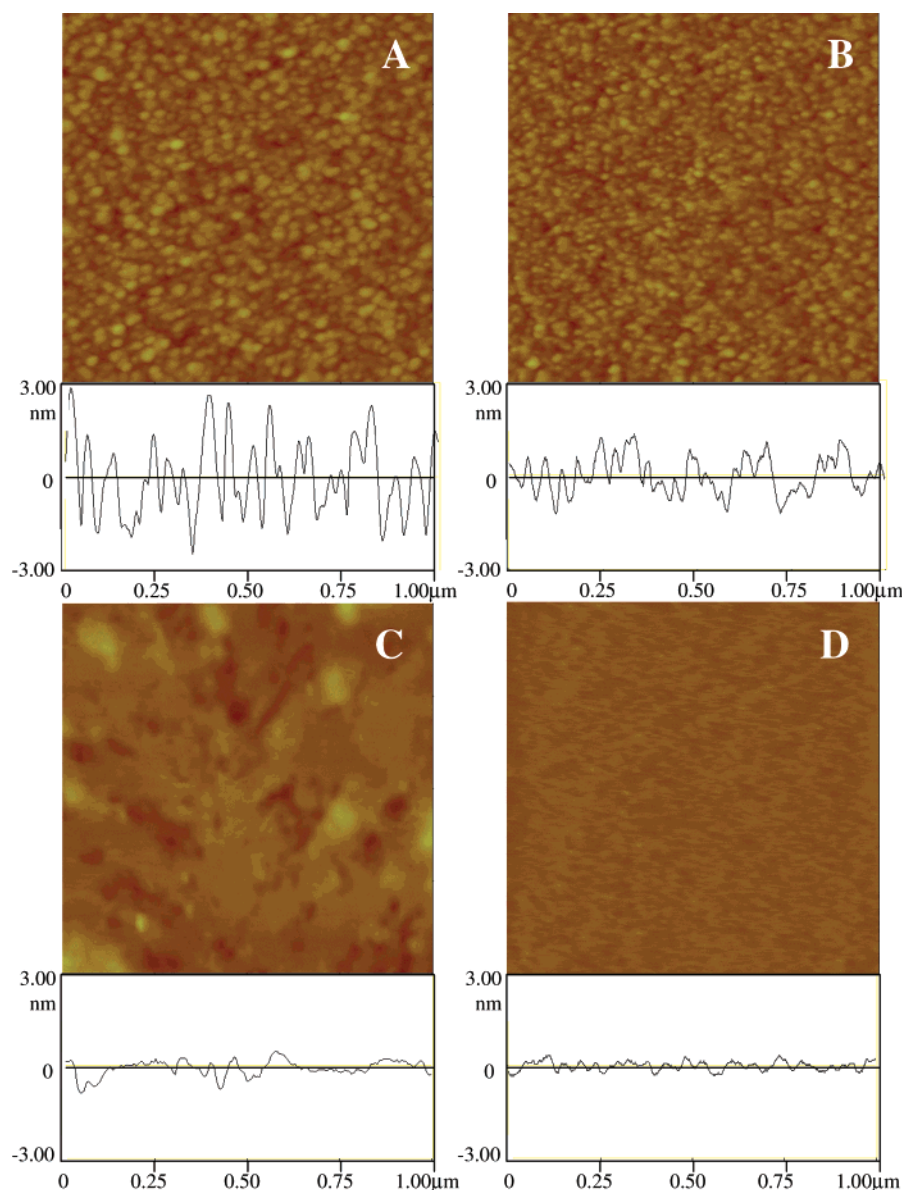(46) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; Wiley-Interscience: New York, 1989.

Figure 7. 1×1 μm^2 AFM images of PPy films on HOPG 1-sodiumoctanesulfonate (A), 1-sodiumdecanesulfonate (B), 1-sodiumdodecanesulfonate (C), 1-sodiumdecanesulfonate with 0.8 mM decanol (D).

the hydrophobe. Addition of 1-octanol to the C$_8$ system did not appear to affect the size or curvature of the PPy spheres as spheres with an average diameter of 27.5 ± 3.2 nm were observed at the highest concentration of 1-octanol investigated. However, 1-decanol did induce a phase transition to reduced curvature PPy films in the C$_{10}$ system and subsequently to a featureless layer as evidenced by the cross section (Figure 7D). Addition of 1-dodecanol to the C$_{12}$ system was not investigated as a featureless layer was already present. Rodlike morphologies do not appear to be favorable for sodium sulfonate surfactants and pyrrole under these particular reaction conditions.

Although films of PPy on HOPG appear to be spherical, one would expect that the films are hemispherical by considering the hydrophobicity of HOPG. The film thickness was measured by masking a portion of the HOPG from reaction. Surface masking was accomplished by trapping a bubble against the side of the vial and over a section of HOPG so that an edge was created across which one could measure the film thickness. Figure 8A represents the edge of the PPy film for the case of

C$_8$. There is a slight disruption in film thickness at the edge of the bubble, although the height can be estimated by placing cursors at selected points as shown in Figure 8B. Multiple measurements indicate that the film thickness is very close to the measured diameter of the spheres (28 nm), indicating that indeed the film is composed of PPy nanospheres, not hemispheres. The same experiment was carried out for PPy films on HOPG in the case of C$_{10}$ (Figure 8C). Once again the film thickness is found to correlate well with the measured diameter of the PPy structures at 16 nm. Therefore, PPy nanospheres are also synthesized on HOPG in the C$_{10}$ system.

The question now arises as to why the PPy films are spherical and not hemispherical in nature. To answer this, fresh HOPG was chemically modified with APS as previously described to form a more hydrophilic surface, and the synthesis of PPy was carried out in an identical fashion as before. Resulting PPy films were identical in morphology and thickness to those obtained with freshly cleaved HOPG. From this result we believe that the surface of the freshly cleaved HOPG is chemically altered
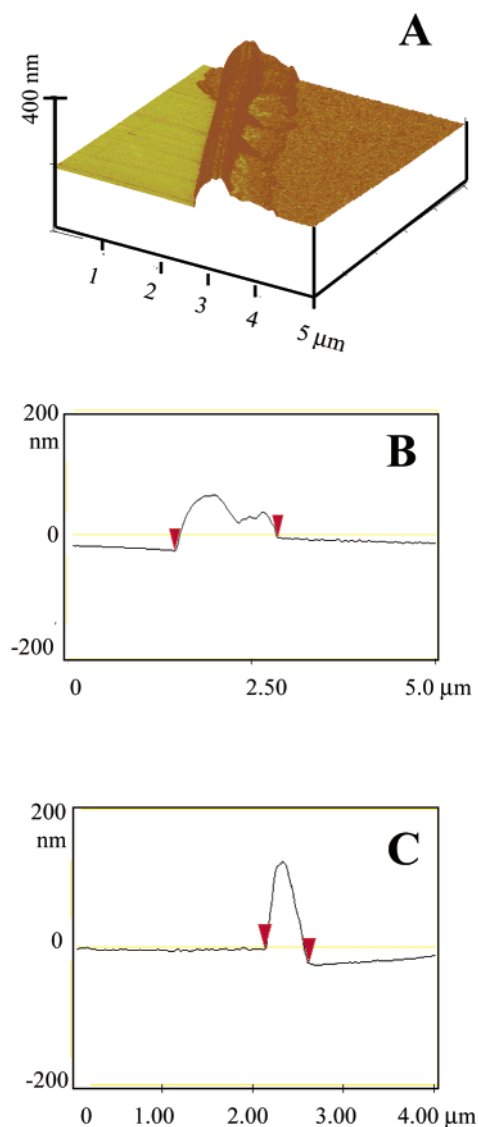
Figure 8. Cross-sectional analysis of PPy films for C_8 system indicating polymer film on the right side of the image and bare HOPG on the left side of the film edge (A). Height of the film measured between the markers for C_8 (B) and C_{10} (C) with heights of 26 and 16 nm, respectively.

0.03*cmc, 0.13*cmc, and 0.45*cmc for C_8, C_{10}, and C_{12}, respectively,[46] where the cmc's correspond to those measured without monomer. In a different set of experiments, surfactant concentrations were fixed at 0.67*cmc and the monomer concentration fixed at 2.7 mM. For C_8 and C_{10} systems, which had much higher surfactant concentrations than 5.4 mM, there was no noticeable coverage of polymer on the substrate, indicating not enough monomer was localized at the surface. Increasing the monomer concentration so that the surfactant to monomer concentration was kept at a 2:1 ratio, as used for the other experiments, leads to large amounts of solution polymerization which in turn deposits on the graphite and obscures the surface.

Conclusion

Adsorbed surfactant aggregates function as templates for the formation of morphologically controlled polymer films of π-conjugated polymers with sub-100-nm features. The capability to synthesize and arrange the polymer in one step to retain the properties of the material by eliminating subsequent treatment or processing is key to producing organic electronic devices. The structure of the polymer film can be controlled by the addition of coadsorbing molecules which induce phase transitions in the order of spherical $\rightarrow$ cylindrical $\rightarrow$ planar. Additionally, film morphologies are shown to be sensitive to the length of the surfactant hydrophobe, with the same sort of phase transitions occurring with changes in hydrophobe length, i.e., spherical $\rightarrow$ cylindrical $\rightarrow$ planar with increasing hydrophobe length. Unique to surface aggregation, a third variable, the interaction between the surface and the surfactant, can be used to alter the morphology in a manner which agrees qualitatively with expectations. Other variables are also probably available to elicit structural control, including electrolyte concentration, temperature, pH, or possibly monomer type and concentration. Thorough experimentation and theoretical modeling will yield a better understanding of this phenomenon and should lead to a technique that can be tailored to many polymers and surfaces in which one can not only synthesize, but also pattern at nanoscale dimensions.

Supporting Information Available: Experimental details and procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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upon addition of APS even after the adsorption of surfactant and monomer. With SDS, the surface maintained its hydrophobicity in the presence of APS if surfactant and monomer were already adsorbed. This difference is probably due to low surface coverage of the sulfonate surfactants; the concentration used was far below the cmc for the C_8 and C_{10} systems (0.03*cmc and 0.13*cmc, respectively), while for SDS the concentrations used were roughly 0.7*cmc.

In this study, we chose to keep the surfactant and monomer concentrations the same for all three surfactants (5.4 and 2.7 mM, respectively), irrespective of the surfactant's cmc. Surfactant concentrations of 5.4 mM correspond to approximately