Autopolymerization of Pyrrole in the Presence of a Host/Guest Calixarene

David A. Reece,[†] Jennifer M. Pringle,[‡,§] Stephen F. Ralph,[†] and Gordon G. Wallace*,[†,§]

ARC Centre for Nanostructured Electromaterials, Intelligent Polymer Research Institute, University of Wollongong, Northfields Avenue, Wollongong, NSW, Australia, 2522, School of Physics and Materials Engineering, Monash University, Clayton, Victoria, Australia, 3800

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ABSTRACT: Aqueous solutions containing pyrrole and calix-6-arenehexasulfonic acid were found to undergo polymerization in the absence of either a chemical oxidant or electrochemical oxidation. The product was an unstable colloidal suspension consisting of spherical polypyrrole particles measuring ≥500 nm in diameter. Conductivity measurements showed the material to be insulating, while cyclic voltammetry studies demonstrated that it was electroactive. Infrared spectroscopy and microanalysis confirmed that the polypyrrole produced was doped with calix-6-arenehexasulfonic acid. When the reaction was repeated using solutions containing stabilizing agents, stable colloidal dispersions were obtained. These were shown by both particle size analysis and transmission electron microscopy to contain much smaller particles than the unstabilized material, while cyclic voltammetry studies again demonstrated that the polypyrrole obtained was electroactive and sensitive to changes in the surrounding electrolyte.

Introduction

Incorporation of molecular receptors such as calixarenes into conducting polymers has attracted considerable interest in the pursuit of novel supramolecular structures. For example, the preparation of conducting polymers using pyrrole or thiophene monomers with covalently attached calixarenes has been reported,[1,2] and sulfonated calixarenes used as dopants during the electropolymerization of pyrrole.[3,4] Polypyrrole produced by the latter route was shown to trap uranyl ions, demonstrating that the molecular recognition properties of the calixarene were retained in the polymer.[4] Host−guest chemistry has also been used to facilitate the preparation of conducting polymers in aqueous solution using nonpolar monomers. For example, β-cyclodextrin has been used to render bithiophene water-soluble, and enable electropolymerization to be performed in aqueous solution.[5,6] Similarly it has also been shown that cyclodextrins can enhance the solubility of pyrrole or 3,4-ethylenedioxythiophene in water, facilitating their polymerization in this medium.[7] The products obtained by chemical oxidation of such solutions did not contain cyclodextrin, and had properties similar to that of polymers prepared using chemical oxidants and other solvents. More recently it was shown that electrode surfaces modified with cyclodextrin can be used to electrochemically produce polypyrrole consisting of nanodimensional fibers.[8]

Polypyrrole is usually obtained by oxidative polymerization of pyrrole using a chemical oxidant such as ferric chloride, or electrochemical oxidation. However, it has recently been reported that aqueous solutions containing pyrrole and strong acids undergo polymerization in the absence of a chemical oxidant or electrochemical oxidation.[9,10] In the case of solutions containing hydrochloric acid, polydisperse spheres of a nonconducting form of polypyrrole were produced.[10] When poly(vinyl alcohol) (PVA) was also present in the polymerization solution the polypyrrole produced consisted of smaller, monodisperse particles. Spectroscopic data showed that these materials consisted of polymeric chains containing pyrrole and pyrrolidine rings, as well as other units in which the pyrrole ring had undergone ring opening.

We have been recently investigating the effects of calixarene dopants on the metal ion permeability of polypyrrole membranes. During the course of our studies it was observed that solutions containing pyrrole and calix-6-arenehexasulfonic acid (C6S) contained a black precipitate after several days, in the absence of either a chemical oxidant or electrochemical oxidation. When the reaction was repeated with poly(vinyl alcohol) (PVA), poly(stryene sulfonate) (PSS), or poly(vinyl pyrrolidinone) (PVP) in the solution, stable colloidal dispersions of polypyrrole were produced. In this paper, we examine the effect of factors including solution pH and size of the calixarene on the growth and properties of unstabilized PPy/C6S colloids, and we describe the properties of stabilized colloidal materials (PPy/C6S/PVA, PPy/C6S/PSS, and PPy/C6S/PVP). These materials have been characterized by absorption spectroscopy, particle size analysis, transmission electron microscopy, and cyclic voltammetry.

Experimental Section

Reagents. Pyrrole (Merck) was distilled before use. Poly(vinyl alcohol) (PVA), poly(stryene sulfonate) (PSS) and poly(vinyl pyrrolidinone) (PVP) were obtained from Sigma. Calix-6-arenehexasulfonic acid (C6S) and calix-4-arenetetrasulfonic acid (C4S) were purchased from Acros. Indium−tin oxide (ITO) coated glass (resistance ∼ 10 Ω) was supplied by Delta

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* Corresponding author. Intelligent Polymer Research Institute, University of Wollongong. Telephone: 61 2 4221 3127. Fax:61 2 4221 3114. E-mail: gordon_wallace@uow.edu.au.

[†] Intelligent Polymer Research Institute, University of Wollongong.

[‡] Monash University.

[§] ARC Centre for Nanostructured Electromaterials, University of Wollongong.

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Technologies Ltd. All other reagents were obtained from Ajax chemicals. Solutions were prepared using deionized Milli-Q water (18 MΩ cm).

Preparation of PPy/C6S Colloids by Autopolymerization. Solutions containing 0.2 M pyrrole and 1.7 mM C6S (pH ~ 2) produced a black precipitate (PPy/C6S) over a number of days. Stabilized PPy/C6S/PVA colloids were produced using solutions containing 0.3% (w/v) PVA, PSS or PVP in addition to the above reagents. Particle size analysis and transmission electron microscopy (TEM) was performed on products obtained from solutions containing 0.2 M pyrrole, 1.7 mM C6S and, in some instances, 0.3%(w/v) PVA, PSS, or PVP that had been allowed to undergo autopolymerization for 2 weeks. In the case of TEM studies, the resulting solutions were diluted and allowed to evaporate on a copper grid prior to analysis. Cyclic voltammetry studies were performed using solutions that had been prepared in an identical manner to those used for particle size analysis and then dialyzed against distilled water.

Preparation of PPy/C6S Membranes by Electrochemical Oxidation. Films of PPy/C6S were grown from solutions containing 0.2 M pyrrole and 1.7 mM C6S. A two-electrode electrochemical cell consisting of a reticulated vitreous carbon (RVC) auxiliary electrode and stainless steel plate (surface area ~ 9 cm^2) working electrode was used. Polymerization was performed by applying a constant current density of 2 mA cm^{-2} for 1 h. After synthesis the PPy/C6S membrane was peeled from the stainless steel plate, washed with water and then dried in air.

Instrumentation. UV–visible absorption spectra were obtained using a Shimadzu UV-1601 spectrophotometer and 1 cm path length cuvettes. Infrared spectra of samples prepared as pressed KBr pellets were measured between 4000 and 400 cm^{-1} on a Bomem MB-100 Fourier Transform infrared spectrophotometer. Cyclic voltammetry studies were conducted using a three-electrode electrochemical cell consisting of a platinum working electrode, Ag/AgCl reference electrode, and platinum mesh auxiliary electrode. Particle size analysis was performed using a MALVERN zetasizer. TEM studies were conducted by staff of the School of Chemistry, University of New South Wales, using a HITACHI H-7000 transmission electron microscope. Solid state ^{13}C NMR spectra were obtained using a Bruker AM-300 MHz NMR spectrometer operating at 75.48 MHz, located in the School of Physics and Materials Engineering, at Monash University. All NMR measurements were performed with magic angle spinning (mas) and cross-polarization on crushed samples mixed with calcined MgO, at a spin rate of 5K. Cross-polarization times of between 500 and 2000 μs, and a delay time of 3 s were used in all spectra, which were obtained using a line-broadening factor of 50 Hz. All ^{13}C spectra were referenced to the resonance from the methylene carbon in glycine. Electrical conductivity measurements were performed using the four point probe method. Elemental analyses were performed by staff of The Microanalysis Unit at The Australian National University.

Results and Discussion

Preparation and Characterization of Unstabilized PPy/C6S Colloids. When aqueous solutions containing 0.2 M pyrrole and 0.01 M *p*-toluenesulfonic acid (pTSA) were allowed to stand for 1 week, the UV–visible spectra of the resulting solution contained no absorption bands attributable to polypyrrole. In contrast, aqueous solutions containing 0.2 M pyrrole and 1.7 mM C6S, which contain the same effective concentration of sulfonic acid groups as solutions containing 0.01 M pTSA, slowly produced a black solid. Figure 1 shows the changes in the visible absorption spectrum of such a solution over a 2-week period. After 2 weeks the spectrum contained a broad, weakly absorbing band centered around 1000 nm, and a second absorption band at approximately 450 nm, that is actually two overlapping bands. The intensity of these absorption bands was still increasing after 2 weeks, suggesting that a reaction was still occurring. The above spectral features are similar to, but not identical with, those seen in spectra of highly doped polypyrrole. The latter typically exhibit two bands assigned to electronic transitions associated with bipolaron energy levels, at around 475 and 1240 nm, as well as a $\pi-\pi^*$ transition at shorter wavelengths.[11,12] Of the two bipolaron bands, the one at longer wavelengths is much broader and often the more intense. Figure 1 contains a broad absorption band centered around 1000 nm that is consistent with assignment to a bipolaron band. Although the intensity of this band is not as great as typically seen, this may be a result of the polymer not being fully doped, and is consistent with its low conductivity (see below). Another difference between Figure 1 and the spectrum of a typical polypyrrole is the absence of a distinct band assignable to a $\pi-\pi^*$ transition in the spectrum of the former. This may be due to the polymer having a low level of conjugation, consistent with its low conductivity, and consequent shift in the position of this absorption band to below 300 nm. The final absorption bands in Figure 1, centered around 450 nm, are also assigned to electronic transitions associated with the presence of polarons and/or bipolarons in the material.

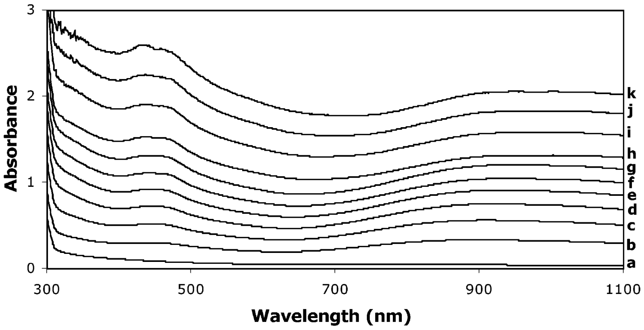

Figure 1. Absorption spectra of an aqueous solution containing 0.2 M pyrrole and 1.7 mM C6S obtained at different times after preparation: a, 0 days; b, 1 day; c, 2 days; d, 3 days; e, 4 days; f, 5 days; g, 6 days; h, 8 days; i, 10 days; j, 12 days; k, 14 days.

Table 1. Microanalytical Data for PPy/C6S Grown Electrochemically and by Autopolymerization[a]

element	electrochemically prepared PPy/C6S	PPy/C6S grown by autopolymerization
carbon	52.1%	37.5%
hydrogen	3.6%	3.7%
nitrogen	10.4%	6.6%
sulfur	4.6%	2.9%

[a] The difference between the above percentages and 100% is accounted for by the presence of oxygen.

The above results suggest that pyrrole had undergone polymerization in the absence of a either a chemical oxidant (other than oxygen) or electrochemical oxidation. Evidence in support of the formation of polypyrrole doped with C6S was provided by elemental analysis of the black solid obtained after the reaction had been allowed to proceed for 1 week. Table 1 compares microanalytical data obtained for unstabilized colloidal PPy/C6S prepared by autopolymerization, with that for a PPy/C6S membrane grown using electrochemical oxidation. The ratio of nitrogen to sulfur in the two materials was very similar. In the case of electrochemi-

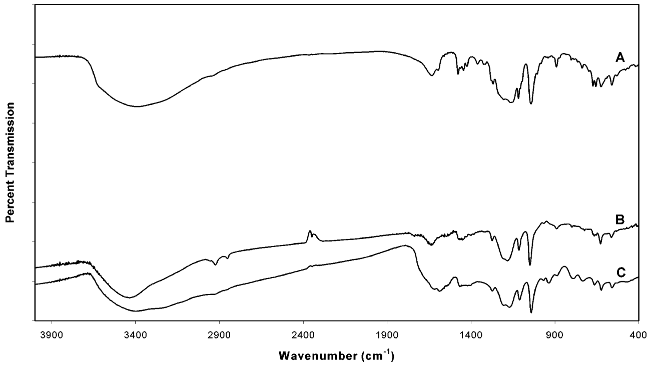

Figure 2. Infrared absorption spectra: (a) C6S; (b) PPy/C6S grown by electropolymerization; (c) PPy/C6S grown by autopolymerization.

cally prepared PPy/C6S the N:S ratio was 5.2:1, while for autopolymerized PPy/C6S it was 5.3:1. Both values are higher than typical pyrrole:dopant ratios for polypyrrole,[13,14] and they suggest that there is one fully deprotonated calixarene dopant (containing six sulfonate groups) for approximately every 30 pyrrole units in the conducting polymer. The ratios of carbon to nitrogen for electropolymerized and autopolymerized PPy/C6S were found to be 5.9:1 and 6.6:1, respectively. The slightly higher value for the autopolymerized material may indicate that ring opening reactions, and accompanying side reactions leading to loss of pyrrole nitrogen atoms and formation of carbonyl functional groups, may have occurred to a significantly greater extent for this material. Such reactions were proposed to account for the lower than expected C:N ratios found for polypyrroles prepared by autopolymerization in hydrochloric acid solution.[10]

Further evidence that the sulfonated calixarene was present in the product obtained by autopolymerization, was provided by comparison of its infrared spectrum to that of both a PPy/C6S membrane grown electrochemically, and C6S itself (Figure 2). For C6S the infrared absorption bands associated with the sulfonic acid group (asymmetric and symmetric ν_{SO3}) were reported at 1160 and 1040 cm^{-1}, respectively.[15] Infrared bands are clearly evident at these wavelengths in all three spectra shown in Figure 2. In addition all three spectra have a number of other infrared bands in common, including those at ~1475–1480, 1275–1280, 1115–1120, 895–900, 625–630, and 565–570 cm^{-1}. The only significant difference between the infrared spectra of PPy/C6S grown electrochemcially and by autopolymerization is that there was much stronger absorption in the region between 1525 and 1775 cm^{-1} in the spectrum of the autopolymerized material. This may reflect that the latter product contains pyrrolidine units and functional groups (e.g., carbonyl groups) produced by ring-opening reactions. These were reported to be present in the structure of the product formed by autopolymerization of pyrrole in the presence of hydrochloric acid.[10] Overall, the spectra of both PPy/C6S samples are very similar to each other and that of free C6S. This indicates that there is little interaction between the calixarene dopant and polypyrrole backbone in the different conducting polymer samples.

Solid state ^{13}C NMR spectroscopy was also used to compare the structures of PPy/C6S prepared electrochemically and by autopolymerization. Figure 3 illustrates the spectra of both polymer samples and free C6S. For the latter compound the ^{13}C NMR spectrum (Figure 3a) showed a single resonance assigned to the methylene carbons at 25.5 ppm, and additional resonances owing to aromatic carbons at 120.3, 128.4, 146.2, and 150.2 ppm. The asymmetric shape of the intense resonance at 120.3 ppm indicates that it consists of at least two overlapping resonances. Both PPy/C6S samples gave ^{13}C NMR spectra (Figure 3b,c) that are qualitatively very similar to that of free C6S. Each spectrum contains a single resonance between 26 and 28 ppm that can be assigned primarily to the methylene carbons of the dopant. In addition the spectra contain an intense, asymmetric resonance between 124 and 125 ppm, that is assigned to the aromatic carbons of C6S. One significant difference between the spectra of the two polymer samples and that of free C6S is that the former displays only a single aromatic resonance between 150 and 152 ppm. In contrast the spectrum of free C6S contained resonances at both 146.2 and 150.2 ppm. Despite this difference, the spectra of both samples clearly provide additional strong evidence for incorporation of the calixarene in to the polymers as a dopant.

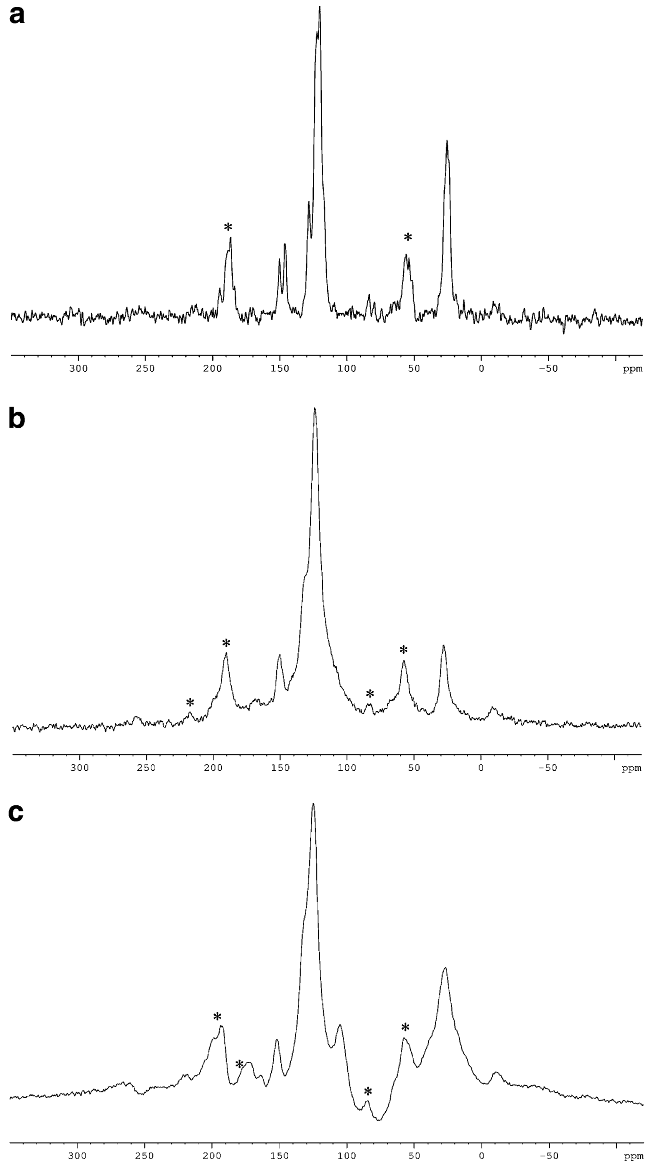

Figure 3. Solid-state magic angle spinning ^{13}C NMR spectra: (a) C6S; (b) PPy/C6S grown by electropolymerization; (c) PPy/C6S grown by autopolymerization. $*$ = spinning sideband.

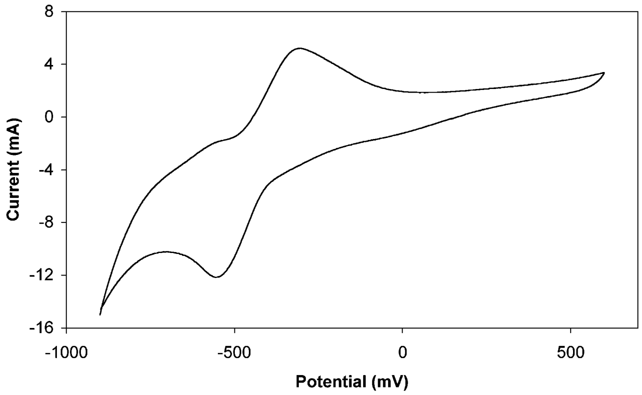

Figure 4. Cyclic voltammogram of a solution containing 0.2 M pyrrole, 1.7 mM C6S after 2 weeks. Scan rate = 100 mV s^{-1}.

No additional, distinct resonances that could be assigned to polypyrrole are present in the spectrum of PPy/C6S prepared electrochemically (Figure 3b). This indicates that the resonances assignable to PPy must overlap to a large extent with the aromatic resonances owing to the calixarene. However, the spectrum of PPy/C6S prepared by autopolymerization (Figure 3c) contains resonances at 104.8 and 173.6 ppm that are not present in the spectrum of free C6S. These are assigned to methylene carbon atoms present in the polypyrrole backbone, and carbonyl carbon atoms, on the basis of a comparison with solid state ^{13}C NMR data reported for PPy/Cl prepared by autopolymerization.[10] The presence of resonances owing to carbonyl functional groups only in the spectrum of PPy/C6S prepared by autopolymerization indicates that this material has undergone ring-opening to a much greater extent than PPy/C6S prepared electrochemically. Such reactions would also produce other unique environments for the carbon atoms present in the conducting polymer, and may therefore explain the greater broadness of the resonance at 26.8 ppm in Figure 3c, compared to analogous resonances in the other two spectra.

It has previously been shown that films composed of PPy/C6S are electroactive and can electrochemically detect the binding of both the uranyl ion and trimethyl(ferrocenylmethyl)ammonim ion.[3,4] Figure 4 shows the cyclic voltammogram obtained by immersing a platinum working electrode, Ag/AgCl reference electrode, and platinum mesh auxiliary electrode, in a sample of autopolymerized PPy/C6S prepared by allowing a solution containing 0.2 M pyrrole and 1.7 mM C6S to react for 2 weeks. Distinct features attributable to oxidation and reduction of PPy/C6S are evident, confirming that it is electroactive. Since solutions containing C6S alone are not electroactive, and do not yield an electroactive material on standing, this indicates that the electroactivity of PPy/C6S is due to the polypyrrole component. However, because PPy/C6S was not stable for extended periods, it was decided to use stabilized PPy/C6S colloids to investigate the effect of changes in supporting electrolyte on electroactivity (see below). Measurement of the electrical conductivity of a solid pellet prepared from autopolymerized PPy/C6S showed that it was insulating. This is consistent with the lack of electrical conductivity displayed by polypyrroles prepared by reacting pyrrole with 6 M solutions of hydrochloric, hydrobromic, hydrofluoric, orthophosphoric, or nitric acid[9] and indicates that there is a low level of conjugation along the polymer backbone in autopolymerized PPy/C6S. In addition, the sharp peaks observed in solid state ^{13}C NMR spectra of PPy/C6S prepared either electrochemically or by autopolymerization is consistent with both materials having very low electrical conductivities.

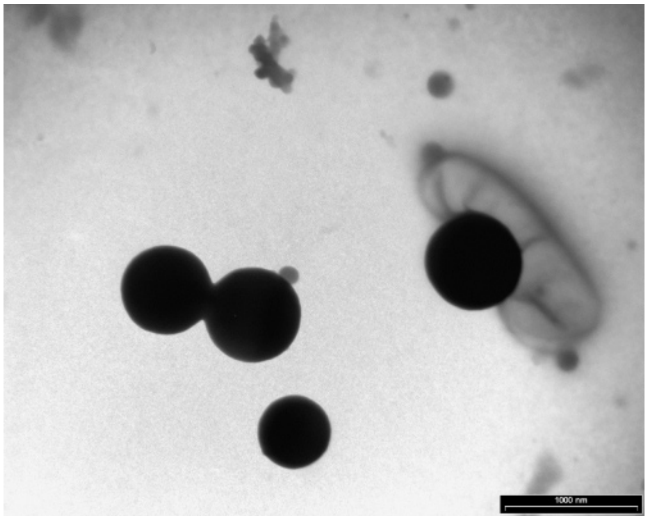

Figure 5. Transmission electron micrograph of PPy/C6S particles prepared by allowing a solution containing 0.2 M pyrrole and 1.7 mM C6S to undergo autopolymerization for 2 weeks. Magnification = 20000.

Attempts to perform particle size measurements using the zetasizer on a solution that initially contained 0.2 M pyrrole and 1.7 mM C6S, and had been allowed to undergo autopolymerization for 2 weeks met with limited success. This was attributed to the solution containing PPy/C6S particles that were too large for measurement by this technique, which cannot generally be used for analysis of particles greater than 1 μm in diameter. Figure 5 shows a transmission electron micrograph of the same solution, which provides evidence in support of the above hypothesis. The micrograph shows round PPy/C6S particles $\geq$approximately 500 nm in diameter, and particle aggregates that are even larger. Figure 5 also shows an individual PPy/C6S particle bonded to what is presumably a thin membrane of polymer.

Factors Promoting Autopolymerization. Several different mechanisms have been proposed for the polymerization of pyrrole, which is known to be influenced by a variety of factors including solvent, temperature, electrochemical method, and electrolyte.[16] Variations in solution pH have also been shown by several workers to have a significant effect on the properties of polypyrrole.[16−20] For example, Zhou and Heinze showed that different forms of polypyrrole were produced by electropolymerization in acetonitrile, depending on whether small quantities of water or hydrochloric acid were also present in the solvent.[20] One of the most important properties of polypyrrole that has been shown to be affected by the presence of acid in the polymerization solution is conductivity. At very low pH the conductivity of electrochemically prepared polypyrrole decreases. This has been reported to be a result of the acid catalyzed formation of nonconjugated pyrrole trimers in the early stages of the reaction mechanism, and subsequent incorporation of trimers into polypyrrole molecules.[16]

Autopolymerization did not occur when aqueous solutions containing pyrrole, and C6S, both of which had

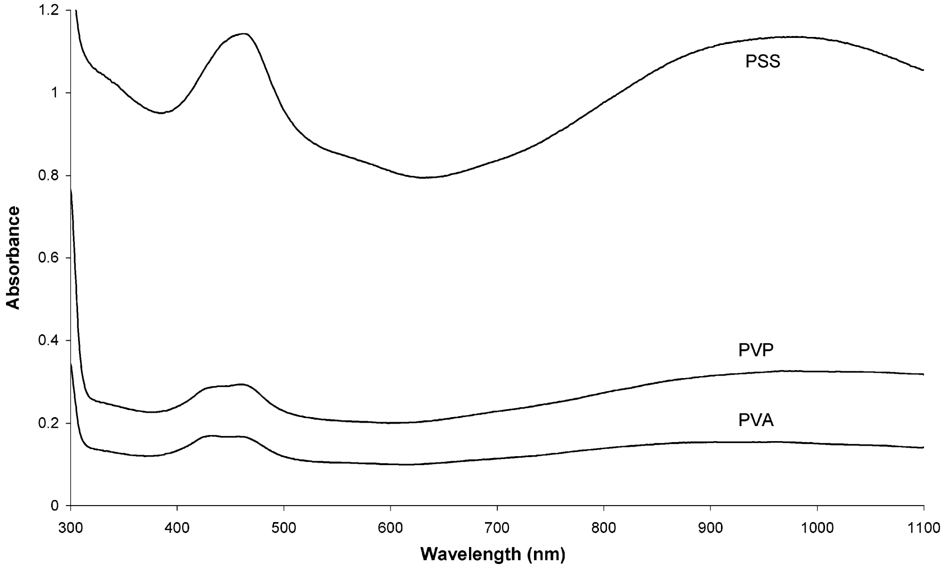

Figure 6. Absorption spectra of stabilized PPy/C6S colloids prepared by allowing aqueous solutions containing 0.2 M pyrrole, 1.7 mM C6S, and either 0.3% PVA, 0.3% PSS, or 0.3% PVP to react for 1 week.

previously been neutralized with ammonia, were combined. This confirms that the reaction medium must be acidic for pyrrole to undergo polymerization in the absence of chemical or electrochemical oxidation. However, as noted previously, solutions containing 0.2 M pyrrole and 0.01 M pTSA do not undergo autopolymerization. This result suggests that the identity of the acid is also crucial to the autopolymerization process. When aqueous solutions containing pyrrole (0.2 M) and the smaller calix-4-arenetetrasulfonic acid (2.5 mM) were allowed to stand for 1 week, a gray colloidal dispersion developed. However, the absorption spectrum of the resulting solution did not show any bands attributable to polypyrrole. This reinforces the conclusion that the identity of the dopant/acid is critical to the autopolymerization reaction, and suggests that specific interactions involving pyrrole and the calixarene may play an important role in the reaction. Favorable host−guest interactions have previously been used to explain why bithiophene can be electrochemically polymerized in aqueous solution in the presence of hydroxypropyl-β-cyclodextrin.[5,6] Further evidence illustrating the importance of host−guest interactions for autopolymerization of pyrrole was provided by the lack of reaction observed when pyrrole was replaced by either 3-methylpyrrole-4-carboxylic acid or aniline in polymerization reaction mixtures.

Pyrrole has previously been reported to undergo polymerization in acidic solutions in the absence of a chemical oxidant or electrochemical oxidation,[9,10] however this reaction has attracted little attention. On the basis of microanalytical and spectroscopic data, Hawkins and Ratcliffe proposed a mechanism for polymerization of pyrrole in which the first step is protonation of pyrrole at the beta carbon position.[10] The resulting protonated pyrrole then reacts with unprotonated monomer to give a dimer, which after a series of further steps produces a polymeric molecule consisting of an alternating sequence of pyrrole and pyrrolidine units. Evidence in support of this mechanism was provided by microanalytical and spectroscopic data, and by the isolation of significant quantities of a trimeric molecule contining two pyrrole molecules bound to pyrrolidine soon after addition of pyrrole to 6 M HCl. Recently it was also shown that aniline will spontaneously deposit onto the surface of either platinum or palladium foil from aqueous solutions containing H_2SO_4 or $HClO_4$.[21] The polyaniline produced was 75% oxidized and underwent protonation/deprotonation equilibria. When HCl was used as the acid or oxygen excluded from the reaction medium polymerization did not occur as readily.

The first step in the autopolymerization of pyrrole in the presence of C6S probably also involves protonation at the beta carbon. However, the fate of the protonated pyrrole formed and the role of the calixarene in the polymerization process is unclear. One possible role for the calixarene is to reduce the oxidation potential required for polymerization, owing to encapsulation of pyrrole within the cavity of the ligand. However, using cyclic voltammetry measurement of the redox potentials for solutions containing 0.001 M pyrrole and either 1.7 mM C6S or 0.01 M pTSA gave values of 0.43 and 0.22 V, respectively vs Ag/AgCl. These results therefore do not support the hypothesis that inclusion of pyrrole within the calixarene results in the monomer being more readily oxidized. Despite this it is clear that the appropriate calixarene must be present for autopolymerization to occur.

Preparation and Characterization of Stabilized PPy/C6S/PVA, PPy/C6S/PVP and PPy/C6S/PSS Colloids. Solutions containing pyrrole and C6S darkened as autopolymerization occurred and then deposited a black solid after 1−2 days. When the reaction was repeated with either poly(vinyl alcohol) (PVA), polystyrene sulfonate (PSS), or poly(vinyl pyrrolidinone) (PVP) also in the reaction mixture the solution again darkened, but there was no deposition of a black solid even after 1 month. These observations are consistent with PVA, PVP, and PSS coating the colloidal PPy/C6S particles as they are formed and preventing them from forming larger, insoluble aggregates. Figure 6 shows UV−visible spectra of reaction mixtures initially containing 0.2 M pyrrole, 1.7 mM C6S, and either 0.3% PVA, 0.3% PSS, or 0.3% PVP, after 1 week. Qualitatively each spectrum is very similar in appearance to each other and to that of unstabilized PPy/C6S colloids shown in Figure 1, indicating that the materials being measured all contain the same chromophore. All spectra contained bands assigned to polaron charge transfer transitions between 400 and 500 nm, as well as a broad

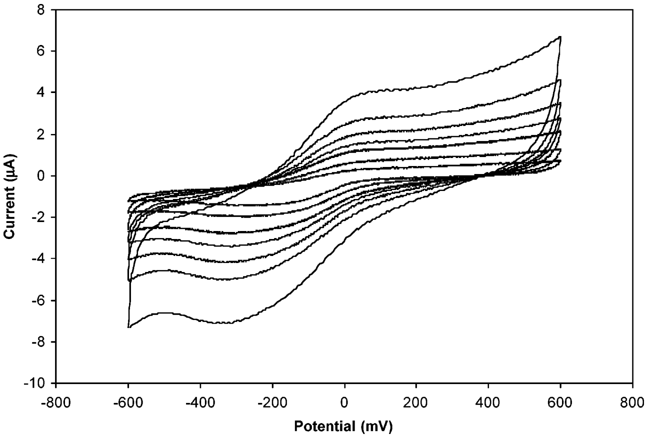

Figure 7. Effect of variations in scan rate on the cyclic voltammogram of PPy/C6S/PVP dispersed in 0.1 M $NaNO_3$, obtained using a platinum working electrode, Ag/AgCl reference electrode and platinium mesh auxiliary electrode. Scan rates used = 10, 25, 50, 75, 100, 150, 250 mV s^{-1}.

bipolaron charge transfer band at higher wavelengths. Despite these similarities, it is also apparent that the intensities of the absorption bands present in the spectrum of the reaction mixture containing PSS are significantly greater than that of the corresponding bands in spectra of reaction mixtures containing the other stabilizing agents. This strongly suggests that autopolymerization occurred to a much greater extent in the presence of this stabilizing agent. Determination of the yields of polypyrrole formed after 2 weeks supports this conclusion. When the stabilizing agent used was PSS the yield was 16%, identical to that obtained in the absence of stabilizing agent, and greater than the values obtained for PPy/C6S/PVA and PPy/C6S/PVP which were 13% and 11%, respectively. The differences in absorption spectra and product yields may both be attributed to a faster rate of autopolymerization when PSS was used as the stabilizer.

Each of the stabilized colloids was shown by cyclic voltammetry to be electroactive. For example, Figure 7 illustrates the effect of varying the scan rate from 10 to 250 mV s^{-1} on the cyclic voltammogram of PPy/C6S/PVP dispersed in 0.1 M $NaNO_3$. A single anodic and cathodic process is evident at each scan rate, consistent with the presence of electroactive polypyrrole. Plots of peak anodic or peak cathodic current against the square root of the scan rate were linear (correlation coefficient > 0.98), indicating the electrochemical processes are diffusion-controlled. The separation between the peak anodic and cathodic potentials, ΔE, decreased from 280 mV at 250 mV s^{-1}, to 196 mV at 50 mV s^{-1}. However, on further decreasing the scan rate to 10 mV s^{-1} ΔE increased to 263 mV. In addition the ratio peak anodic current:peak cathodic current (i_{pa}:i_{pc}) decreased dramatically from 0.94 at 250 mV s^{-1} to 0.46 at 10 mV s^{-1}. This may be attributed to the more efficient electrochemical reduction of the conducting polymer colloids at the very slow scan rates rendering them less conductive and more difficult to oxidize. Alternately, the reduced polymer colloid forms aggregates that are significantly more difficult to reoxidize. Coagulation and indeed deposition of conducting polymer colloids at negative potentials have been described previously and would be expected to be more important at lower scan rates.

Table 2. Particle Size Analysis for Stabilized and Unstabilized PPy/C6S Colloids

type of colloid	particle size distribution (nm)
PPy/C6S	$>500^a$
PPy/C6S/PVP	270 ± 120^b
PPy/C6S/PSS	120 ± 250^b
PPy/C6S/PVA	50 ± 60^b

[a] Estimated by transmission electron microscopy [b] Determined using a Malvern zetasizer. The first value gives the most abundant particle size, while the second value is determined by the size of the largest particle present in the sample.

Similar electrochemical behavior was observed with both PPy/C6S/PVA and PPy/C6S/PSS. For each system, a single anodic and cathodic feature was present in the cyclic voltammogram, and the separation between peak anodic and cathodic potentials initially decreased as the scan rate was lowered. However, at relatively low scan rates (below 25 or 50 mV s^{-1}) ΔE increased, while the ratio i_{pa}:i_{pc} decreased in a regular fashion as the scan rate was lowered for both systems. Changing the identity of the stabilizer therefore had little effect on polymer electrochemistry. In comparison, a PPy/C6S coated platinum electrode immersed in aqueous 0.1 M $NaNO_3$ showed behavior typical of a conducting polymer when the scan rate was varied.

Cyclic voltammograms obtained using PPy/C6S/PVP and 0.1 M solutions of $NaNO_3$, KNO_3, $Mg(NO_3)_2$ and $Ca(NO_3)_2$ and a scan rate of 100 mV s^{-1} all showed cathodic processes attributable to polymer reduction. However, only the cyclic voltammogram obtained using $NaNO_3$ as the supporting electrolyte displayed a prominent feature attributable to an anodic process. This shows that changing the supporting electrolyte that the colloid was dispersed in has a significant effect on its electrochemical behavior. This is further supported by the observation that the cathodic peak potentials varied by several hundred millivolts when the supporting electrolyte was changed. The fact that peaks attributable to polymer oxidation were only seen when the supporting electrolyte was $NaNO_3$ may indicate that in most supporting electrolytes the reduced polymer is undergoing aggregation, particularly at slow scan rates. Aggregation would be expected to be affected by changes to the supporting electrolyte, as observed.

The results of particle size measurements are shown in Table 2. Particle size measurements revealed that each of the three types of stabilized colloids were present in a monomodal distribution, and contained particles that were significantly smaller than those found in unstabilized PPy/C6S. Furthermore, there were significant variations in the size of particles present in each of the three stabilized colloids. For PPy/C6S/PVA the particle size distribution was centered at 50 nm, while for PPy/C6S/PSS and PPy/C6S/PVP this value was 120 and 270 nm, respectively. These results are consistent with previous studies that showed the particle size of polypyrrole colloids is highly dependent on the reaction conditions, including the molecular weight and nature of the stabilizer,[22,23] and is supported by results obtained using transmission electron microscopy (TEM). For example, Figure 8 illustrates the TEM image of PPy/C6S/PVA, and shows all particles to be roughly spherical in shape, and less than 100 nm in diameter. The smaller size of PPy/C6S/PVA colloids, relative to the two other types of stabilized colloids, may be due to the fact that it was the only steric stabilizer used, combined with its relatively low molecular weight (70000 Da). In contrast

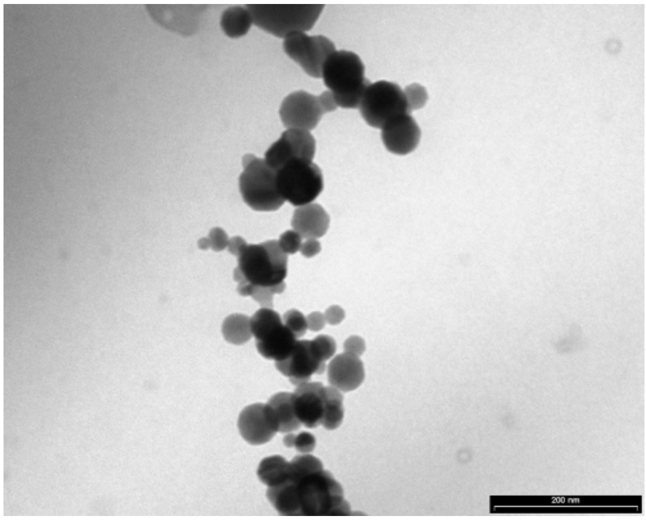

Figure 8. Transmission electron micrograph of PPy/C6S/PVA particles prepared by allowing a solution containing 0.2 M pyrrole, 1.7 mM C6S, and 0.3% (w/v) PVA to undergo autopolymerization for 2 weeks.

PPy/C6S/PVP colloids were on average the largest prepared, which may be largely a consequence of the much larger size of PVP (mol wt 630000 Da) compared to either PVA or PSS (mol wt 70000).

Conclusion

Aqueous solutions containing pyrrole and calix-6-arenehexasulfonic acid undergo autopolymerization to give an insulating, electroactive form of polypyrrole that is doped with the calixarene. Owing to the large size of polymer particles produced by this method, the solution is unstable and deposits a powder over a period of 1−2 days. Addition of stabilizers to the polymerization solution results in the formation of colloidal dispersions that are considerably more stable. This is a consequence of the presence of conducting polymer particles in solution that are up to 10 times smaller than those formed in solutions that contain no stabilizer. The resulting colloidal dispersions are stable for extended periods, electroactive, and responsive to changes in the surrounding electrolyte. When the calixarene and pH were varied the products obtained were different, clearly indicating that both acid and a specific guest molecule must be present for the reaction to proceed.

While the ability of strong acids to induce polymerization of pyrrole has been reported previously,[9,10] we believe this is the first instance where both acid and specific host/guest interactions have been demonstrated to be essential to the reaction mechanism. There have previously been only a relatively small number of studies describing the polymeric products obtained upon treating heterocycles with acid. One of the earliest of these was an investigation into the polymerization of isothianaphthalene.[24] Anodic polymerization of this monomer yielded a white nonconducting polymeric product. In contrast, treatment of isothianaphthalene with sulfuric acid in dichloromethane produced conducting, doped poly(isothianaphthalene). The later compound could also be obtained by dehydrogenating the white polymer produced by anodic polymerization.[24,25] This provided evidence that the white polymer was a polyhydrogenated form of poly(isothianaphthalene).

Both thiophene and pyrrole have been reported to undergo polymerization in the presence of acid to form polymers containing both saturated and unsaturated heterocyclic ring systems.[10,26] In the case of pyrrole, the mechanism of polymerization was proposed to involve initially protonation of pyrrole at the C-3 position.[10] This results in a protonated pyrrole molecule, which then reacts with unprotonated pyrrole to form a dimer, that subsequently undergoes further reaction with either protonated or unprotonated pyrrole. A similar mechanism may account for the formation of PPy/C6S. If this is indeed the case then it may be possible to treat PPy/C6S with oxidizing agents to yield a more highly conducting and highly doped polymer. Future experiments are planned which will examine this possibility.

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