Conducting Polymers with Fibrillar Morphology Synthesized in a Biphasic Ionic Liquid/Water System

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ABSTRACT: The synthesis of poly(pyrrole), poly(terthiophene), and poly(3,4-ethylenedioxythiophene) with unusual fibrillar morphologies has been achieved by chemical polymerization in a biphasic ionic liquid/water system. Use of aqueous gold chloride as the oxidant, with the monomers dissolved in a hydrophobic ionic liquid, allows the polymerization to occur at the ionic liquid/water interface. The resultant conducting polymer fibrils are, on average, 50−100 nm wide and can be thousands of nanometers long. The polymers produced in this ionic liquid system are compared to those synthesized in a biphasic chloroform/water system.

1. Introduction

The utilization of conducting polymers now encompasses a wide range of applications,[1−3] which is fueling a continued need for materials with improved physical and chemical properties. In particular, there is an increased drive toward the fabrication of nanostructured and reduced dimensionality materials, such as thin films, nanotubes, wires, particles, etc., which can exhibit markedly different properties from those of the bulk materials.[4−6] Templating techniques,[7] such as those employing organic templates,[8] ionic surfactants,[9−11] silicates,[12] polyelectrolytes,[13] etc., are commonly employed in the synthesis of nanostructured polymers, but such techniques can have the disadvantage of having to subsequently remove the template to obtain the nanostructured polymer. Techniques that avoid the use of a template are primarily electrochemical,[14−18] utilizing nanoelectrodes, STM or AFM tips, electron beam lithography, or electrospinning, or involve the synthesis of nanocomposites containing the conducting polymer and, for example, carbon nanotubes.[7] The electrochemical synthesis of conducting polymer fractals has also been of interest for a number of years, with some success.[19−21] Here we report the use of interfacial chemical polymerization as a route to nanodimensional, fibrillar poly(terthiophene), poly(3,4-ethylenedioxythiophene) (PEDOT), and poly(pyrrole) without the aid of a template.

Interfacial polymerization is a well-established technique for the synthesis of condensation polymers, but there are few reports involving conducting polymer synthesis,[22,23] although it has attracted recent attention for the synthesis of polyaniline nanofibers.[24−26] Interfacial polymerization is traditionally performed using a volatile organic phase—chloroform, toluene, benzene, etc.—and an aqueous phase, although a recent report by Gao et al.[27] demonstrated that use of an ionic liquid/water system yields polyaniline nanoparticles rather than nanofibers. To the best of our knowledge there are no published reports of the synthesis of any other conducting polymers via interfacial polymerization using an ionic liquid.

Ionic liquids are a relatively new class of solvent, composed entirely of ions, whose advantageous physical properties can include nonflammability and negligible vapor pressure, which avoids the long-term problems of solvent evaporation from electrochemical devices.[28,29] Ionic liquids can significantly improve performance and lifetimes when used as the supporting electrolyte in conducting polymers devices,[30,31] and the potential benefits of using ionic liquids as the growth media for conducting polymers are attracting increasing interest.[32−34] Ionic liquids are ideal media for the synthesis and utilization of conducting polymers as they can exhibit excellent oxidative and reductive stability, which allows access to potentials previously prohibited by the smaller electrochemical window of molecular solvent/electrolyte systems. Further, ionic liquids have been shown to dissolve a wide range of organic and inorganic materials, which allows access to a range of monomers and chemical oxidants at significant concentrations, some of which are either insoluble in, or outside the electrochemical stability of, molecular solvents.

The ionic liquid used in this investigation was 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, which we have previously found to be an excellent choice for the electrochemical polymerization of pyrrole, EDOT, and a range of thiophene monomers.[35−37] We have also investigated the use of this ionic liquid for the one-phase chemical synthesis of a range of conducting polymers, including the synthesis of poly(thiophene) nanoparticles, and in this preliminary investigation we found that the use of gold chloride as the oxidant resulted in polymers with improved properties compared to those from the more conventional iron-based oxidants.[38] Abdou et al.[39] have shown that poly(2-hexylthiophene) containing $AuCl_4^-$ as a dopant, synthesized using $AuCl_3$ as the oxidant in either nitromethane or acetonitrile, is orders of magnitude more stable than that containing $FeCl_4^-$ and that the nature of the gold dopant depends on the solvent used. Here we have used an ionic liquid for the interfacial chemical synthesis of conducting polymers in a biphasic ionic liquid/water system, where the use of aqueous gold chloride as the oxidant, with the monomers

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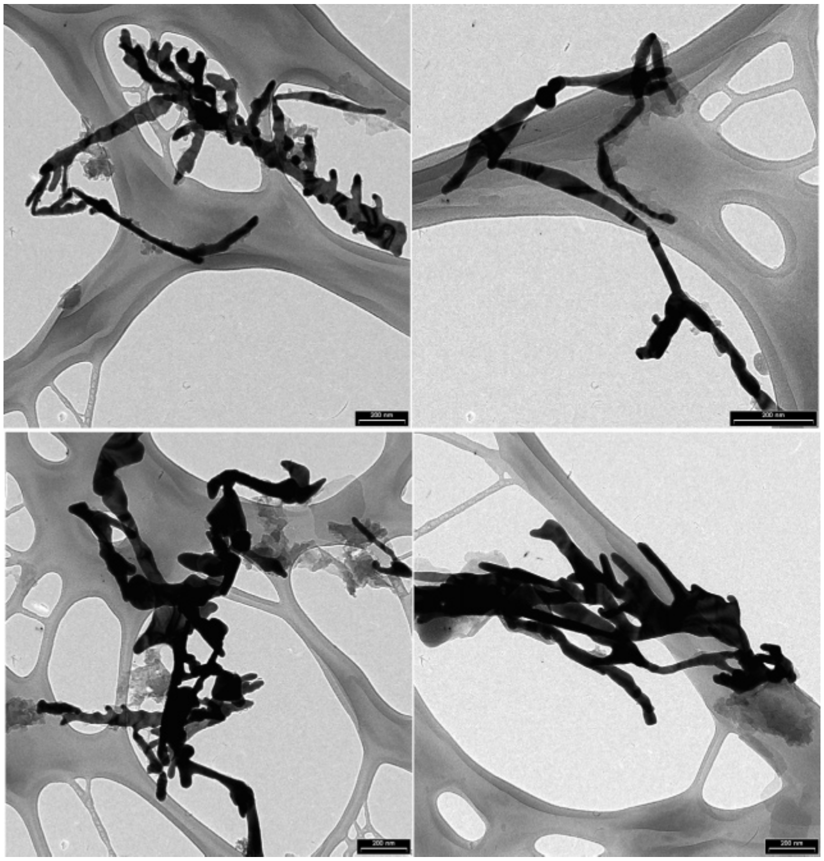

Figure 1. TEM images of the poly(terthiophene) (on lacey carbon copper grids) synthesized using gold chloride in the IL/water biphasic mixture. Scale bars are all 200 nm.

dissolved in a hydrophobic ionic liquid, allows the polymerization to occur at the ionic liquid/water interface.

2. Experimental Section

2.1. Materials and Synthesis. The ionic liquid used was 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, prepared according to the literature procedure,[40] dried (water typically <40 ppm by Karl Fisher), and degassed before use. The gold(III) chloride oxidant (Sigma) was used without further purification.

Gold chloride in Milli-Q water (1 mL, 0.05 M for the terthiophene reactions, 0.1 M for pyrrole and EDOT) was carefully added to the monomer in ionic liquid (1 mL, 0.05 M for terthiophene, which required gentle heating to achieve dissolution in the ionic liquid at this concentration, 0.1 M for pyrrole and EDOT), resulting in an immediate darkening of the ionic liquid in contact with the water layer. Care was taken to minimize any mixing of the two solutions during addition, and upon standing the solutions became progressively darker and polymer could be seen to form at the ionic liquid/water interface. The pyrrole reaction appeared to result in synthesis of the polymer at the interface and in the water layer, whereas the PEDOT synthesis resulted in polymer formation at the interface and darkening of the ionic liquid layer, with little decoloration of the water layer. The poly(terthiophene) formed a “film” at the solution interface, and the water layer remained colorless.

The same experimental conditions were used for synthesis in the biphasic chloroform/water systems and in the systems composed of two immiscible ionic liquids. In the latter system, a phosphonium ionic liquid, tri(hexyl)tetradecylphosphonium bis(trifluoromethanesulfonyl)amide (Cytec), was used as the upper layer, with the 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide as the lower layer. These reactions were performed with the monomer in the top layer and the oxidant in the bottom layer, which appeared to be preferable to the opposite arrangement, probably as a result of the different solubilities of the reagents in the different ionic liquids. The reactions in the one-phase systems were performed using 0.1 M $AuCl_3$ in 1 mL of water, with pyrrole in water (0.1 M, 1 mL) and EDOT in acetonitrile (0.1 M, 1 mL).

The reactions were performed in small (50 × 12 mm) sample vials—the effect of using a wider vessel, thus creating a larger interfacial area, is under investigation. The reaction solution was left to stand for 24 h, and then the polymer was isolated and washed by repeated additions of ethanol, in which the ionic liquid is soluble, and decantation of the supernatant liquid after the polymer had settled. The use of a centrifuge to separate the polymers was avoided in order to minimize polymer aggregation, which would be detrimental to the studies of the polymer morphology by TEM analysis. The polymers were retained as a solution in ethanol for the TEM, CV, and UV−vis spectroscopic analysis. The dry yields of the polymers were over 80%, calculated using the XPS analysis data to determine the quantity of each dopant present, with the exception of poly(terthiophene) from the chloroform/water system, which was below 50%.

2.2. Instrumentation. The cyclic voltammograms were recorded by casting films from ethanol/chloroform onto a glassy carbon working electrode (0.07 cm^2) and cycling in 0.1 M tetrabutylammonium perchlorate/acetonitrile at 100 mV/s, starting at 0 V and scanning to positive potentials first, using a Pt counter electrode and a Ag/Ag^+ (0.1 M tetrabutylammonium perchlorate/acetonitrile) reference electrode, unless stated otherwise. The magnitude of the current recorded depends on the quantity of the polymer solvent-cast onto the working electrode. The UV−vis spectra of the polymers, dispersed in ethanol, were recorded using a Shimadzu UV-1601 UV−vis spectrophotometer. The transmission electron microscopy (TEM) was performed with the samples supported on lacey Formvar/carbon 300 mesh Cu grids (ProSciTech), using a Philips CM200 HRTEM at 75 eV, with the exception of those in Figure 7, which were collected using a JEOL 100S at 80 keV. X-ray photoelectron spectroscopy (XPS) was performed using an Axis Ultra spectrometer (Kratos Analytical, UK), equipped with a

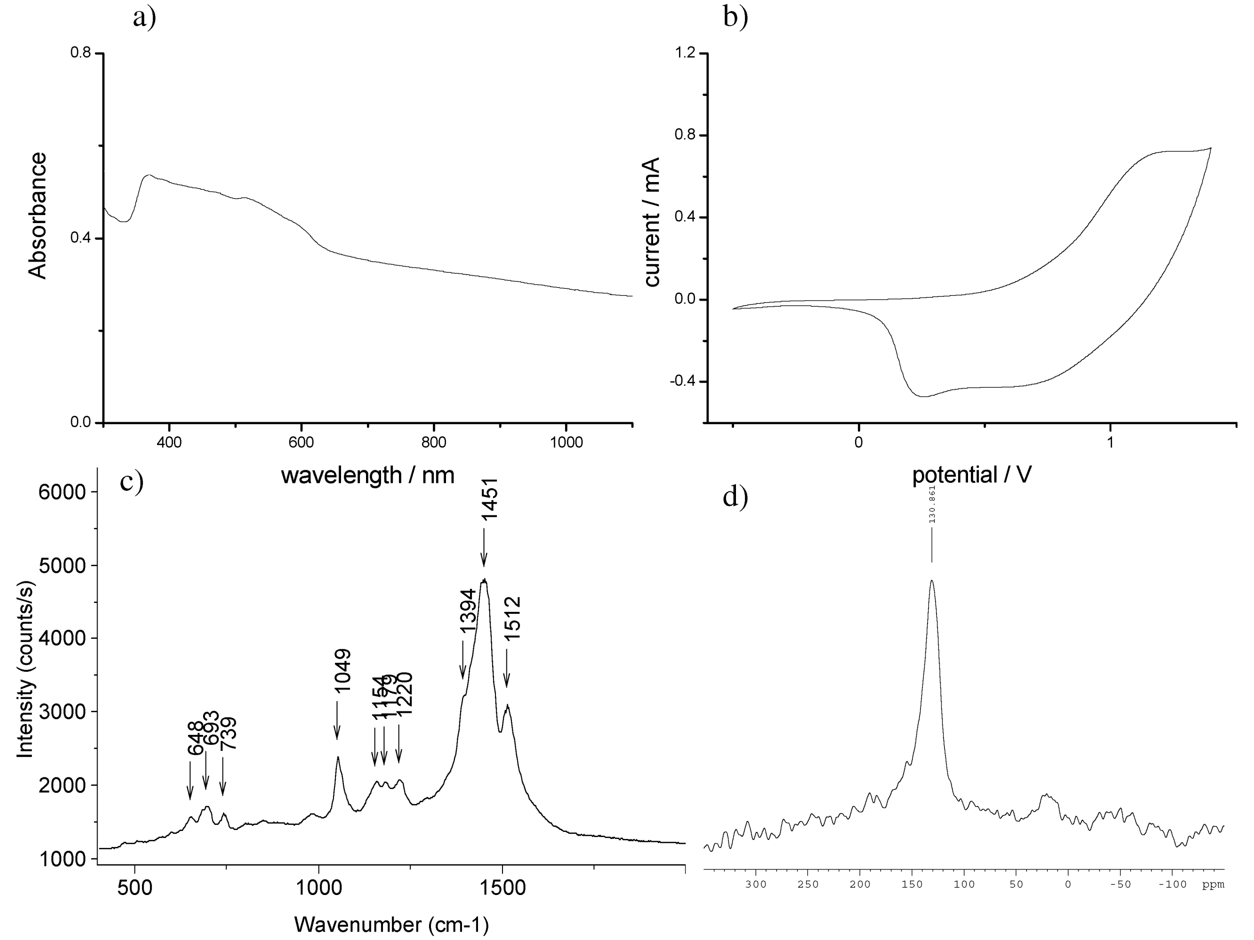

Figure 2. (a) UV−vis spectrum, (b) cyclic voltammogram, (c) Raman spectrum, and (d) ^{13}C CP-MAS solid-state NMR spectra of the poly(terthiophene) fibrils formed using the biphasic ionic liquid/water system.

monochromatized X-ray source (Al Kα, $h\nu = 1486.6$ eV) operating at 150 W. The spectrometer energy scale was calibrated using the Au 4f$_{7/2}$ photoelectron peak at binding energy ($E_B = 83.98$ eV). Survey scan spectra were acquired from 0 to 1200 eV binding energy at a pass energy of 160 eV. Region spectra were scanned at a pass energy of 20 eV to obtain higher resolution spectra. The analysis area was 700 μm × 300 μm. The peaks were fitted with synthetic Gaussian−Lorentzian components and quantified using the sensitivity factors for the Kratos instrument. The doping level of the polymer was calculated from the XPS data using the relative intensities of the relevant carbon peaks in comparison to those from the TFSA and Cl$^-$ anions. This calculation requires the assumption that no cations from the ionic liquid are incorporated into the polymer as these cannot be clearly distinguished from the polymer backbone; negligible cation incorporation into the polymers was detected by solid-state NMR. For solid-state NMR analysis, the polymers were crushed and ground up under N_2 with calcined MgO, to avoid problems of arcing in the magnetic field, and packed into a 4 mm zirconium oxide rotor with Kel-F end caps. Magic angle spinning was used with a spinning speed of 8 kHz. Analysis was performed using a Bruker AM300 instrument equipped with a Bruker 4 mm solid-state probe operating at 75.5 MHz for ^{13}C, with chemical shifts referenced to external samples of glycine. The ^{13}C NMR signal was enhanced using cross-polarization techniques, where the ^{1}H polarization is transferred to the ^{13}C nuclei. A contact time of 800 μs was used, with a 3.75 μs pulse, a recycle delay of 2 s, and line broadening of 300 Hz, collected over at least 24 h. The conductivity of the polymers was measured by pressing the dried polymer into pellets and using a Jandel square array four-point probe head and RM2 test unit.

3. Results and Discussion

3.1. Synthesis of Poly(terthiophene). The synthesis of poly(terthiophene) is of significant interest as it has been shown to exhibit excellent performance in photovoltaic devices.[41] The high oxidation potential of thiophene can be problematic, for both chemical and electrochemical polymerization, commonly resulting in the overoxidation of the resultant polymer.[42] However, the oxidation potential of terthiophene is considerably lower than thiophene and may increase the stereoregularity of the polymer by reducing the number of β,β or α,β mislinkages, although it has also been reported that poly(terthiophene) can display a detrimental reduction in polymer chain length compared to poly(thiophene).[43] Synthesis of poly(terthiophene) is often hampered by the poor solubility of the monomer, but terthiophene can easily be dissolved in this ionic liquid at concentrations up to 0.05 M with gentle heating. As terthiophene is of only very low solubility in water there will be only minimal diffusion of the monomer from the ionic liquid into the water layer during the reaction. Transmission electron microscopy (TEM) analysis of the poly(terthiophene) synthesized in the biphasic ionic liquid/water system, formed as a film at the liquid−liquid interface and after isolation, revealed a polymer with an almost entirely fibrillar morphology (Figure 1), forming structures ∼50 nm wide and hundreds of nanometers long.

This reaction was also repeated in the presence of a second salt, 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$), in the ionic liquid, to explore the effect of further ionic components.[44] More rapid coloration of the reaction media

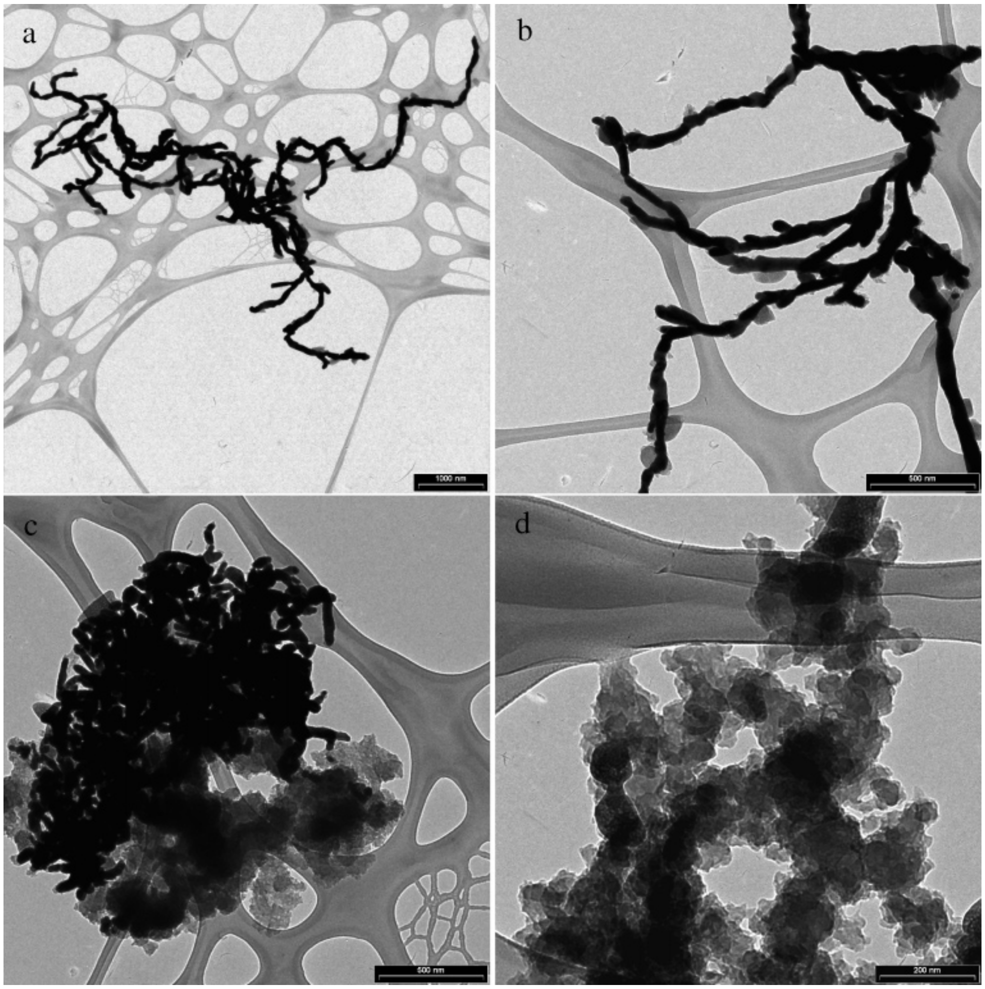

Figure 3. TEMs of PEDOT (on lacey carbon copper grids) synthesized using an ionic liquid/water biphasic mixture. Scale bars are (a) 1000, (b) 500, (c) 500, and (d) 200 nm.

indicated a faster polymerization reaction had occurred, and TEM analysis again showed that the resultant polymer was almost entirely fibrillar in structure (not shown). Some of the polymer fibrils produced are of considerable length—thousands of nanometers—suggesting a kinetic influence on the length of the fibrils produced. However, analysis of the resultant polymer by cyclic voltammetry, UV−vis, and Raman spectroscopy indicated no significant difference in properties between the polymers synthesized with or without $TBAPF_6$ in the ionic liquid.

The UV−vis spectra of the poly(terthiophene) (Figure 2a) show significant absorption over the range 365−600 nm, but only a weak bipolaron band at 400−600 nm. The terthiophene monomer has an absorption maximum at 355 nm,[45] and absorption above this wavelength can be assigned to longer chained oligomers; this spectrum indicates the presence of predominantly short-chained or undoped polymer, which is consistent with the suggested difficulties in forming long-chain poly(terthiophene).[43] It may also suggest that here the polymer is in its reduced form, possibly as a result of using ethanol as the solvent. This spectrum is very similar to that which we have previously observed for poly(terthiophene) chemically synthesized using gold chloride in a one-phase ionic liquid system,[46] which displayed advantageous features compared to those obtained using iron-based oxidants, indicating that these advantages are retained when an aqueous gold chloride system is used. The electrochemical activity of the fibrillar poly(terthiophene) was analyzed by cyclic voltammetry (Figure 2b) and shows well-clarified oxidation reduction responses, which we also observed for poly(terthiophene) synthesized chemically and electrochemically in this ionic liquid, at similar potentials.[36,37] Raman analysis of the poly(terthiophene) (Figure 2c) is consistent with the formation of the polymer, with bands assigned to the C═C antisymmetric stretching vibration (1512 cm^{-1}), C═C symmetric stretching (1451 cm^{-1}), inter-ring C−C stretch (1220 cm^{-1}), C−H in-plane bending (1049 cm^{-1}), and inter-ring C−C stretching (1179 and 1154 cm^{-1}).[47] Solid-state ^{13}C CP-MAS NMR analysis of the polymer (Figure 2d) is consistent with the formation of poly(terthiophene),[48] with only a small intensity in the region of 0−50 ppm indicative of the incorporation of the ionic liquid cation into the polymer. The sharpness of the polymer peak is indicative of a low polydispersity, again consistent with the formation of predominantly short-chained polymer. XPS analysis of poly(terthiophene) samples synthesized in this way indicated an average doping level of ∼0.27 charges per terthiophene unit, with the majority (ca. 75%) of the dopant anions being TFSA anions from the ionic liquid rather than Cl^- from the oxidant. The gold was incorporated into the polymer at an average concentration of ca. 0.5 atom % Au^+ and 0.14 atom % Au^{3+}. The conductivity of the polymers, pressed into a pellet and measured using a four-probe method, was 6.5 ± 0.16 S cm^{-1}.

3.2. Synthesis of Poly(3,4-ethylenedioxythiophene). 3,4-Ethylenedioxythiophene (EDOT) is a popular choice of substituted monomer as it forms a low-band-gap polymer with high

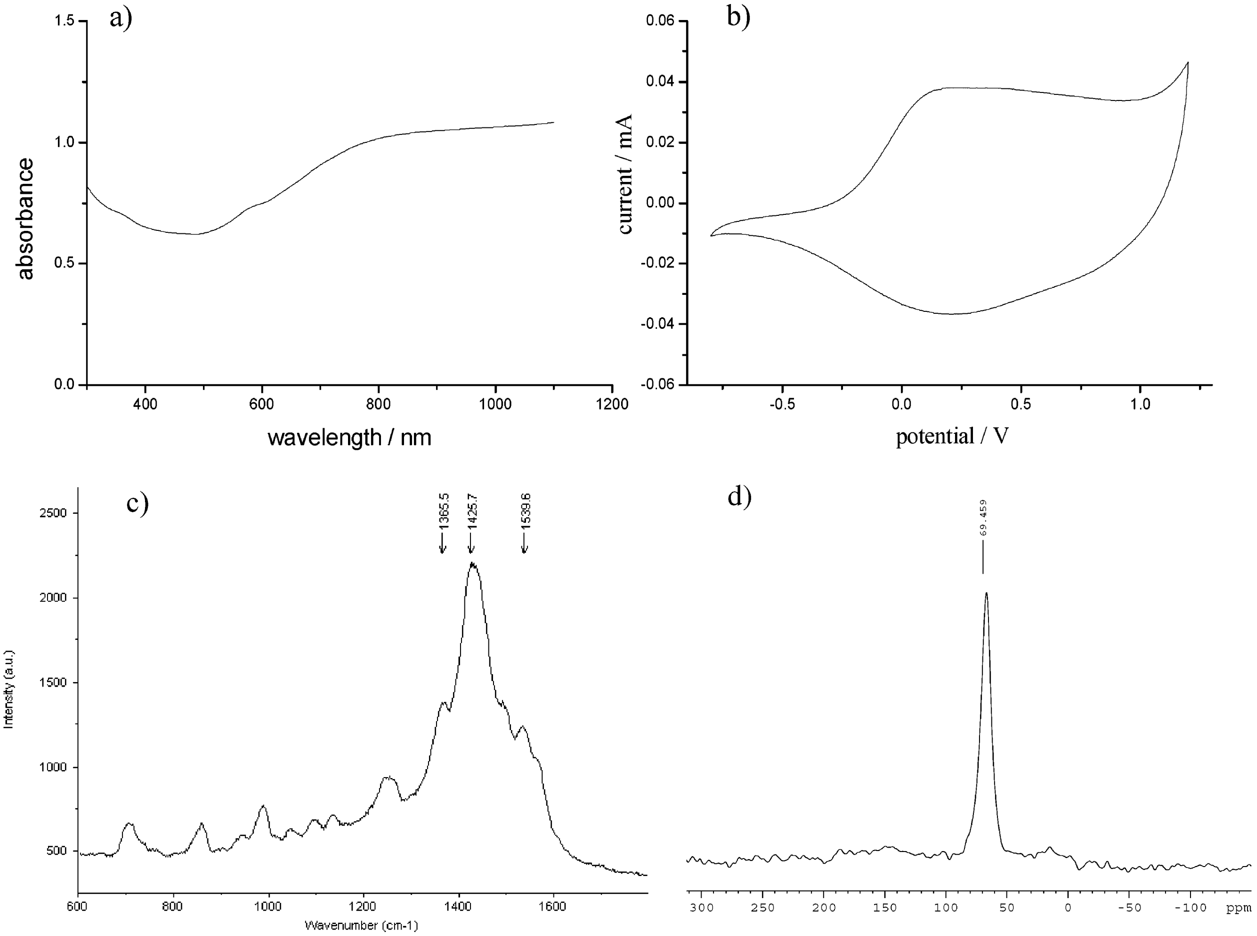

Figure 4. (a) UV−vis spectrum, (b) cyclic voltammogram, (c) Raman spectrum, and (d) ^{13}C CP-MAS solid-state NMR spectrum of the PEDOT synthesized using the biphasic ionic liquid/water system.

stability and good conductivity. The use of ionic liquids for the chemical synthesis of poly(3,4-ethylenedioxythiophene) has been investigated by ourselves[36] and others,[49−52] but to the best of our knowledge the chemical synthesis of PEDOT in ionic liquids has not been previously explored. Unlike terthiophene, EDOT is partially soluble in water (2.1 g/L), and thus some degree of diffusion of the monomer into the water layer during the reaction is predicted. However, during the interfacial polymerization the polymer was observed to form at the interface, with decolorization only of the ionic liquid layer, and the polymer produced fell to the bottom of the reaction vessel. TEM analysis of the polymer (Figure 3) shows the formation of fibrillar structures similar to those of poly(terthiophene), although the proportion is lower, with the synthesis also producing some round polymers nanoparticles (Figure 3d). The parameters that determine this distribution of polymer morphologies is the focus of our future work in this area. As for poly(terthiophene), the synthesis was also performed in the presence of TBAPF$_6$ in the ionic liquid layer, which yielded some similar fibrillar polymer structures (not shown) that again displayed similar material properties (CV, UV−vis, Raman) to the polymer synthesized in the absence of TBAPF$_6$.

The UV−vis spectrum of the PEDOT (Figure 4a) displays a small peak at 600 nm, which corresponds to the $\pi-\pi$ * transition,[53] plus a strong, broad absorption over higher wavelengths (the free carrier tail), indicating the presence of delocalized charges on the polymer chains. It is known that during the doping of PEDOT the peak near 600 nm decreases, and the doped polymer absorbs in the infrared range, near 1200 nm,[54] as suggested here. This spectrum is also similar to that observed for PEDOT chemically synthesized in alcohol solvents.[55] The intensity at low wavelengths may be due to the presence of some ionic liquid, either incorporated into or coating the polymer, which absorbs at wavelengths below 400 nm. The electrochemical activity of the PEDOT was analyzed by cycling in 0.1 M tetrabutylammonium perchlorate/acetonitrile (Figure 4b). The polymer shows well-defined oxidation and reduction peaks, at potentials similar to those observed for PEDOT electrochemically synthesized in this ionic liquid.[36] The Raman spectrum (Figure 4c) is typical of PEDOT, dominated by the strong C═C symmetric stretching vibration at 1426 cm^{-1}, whose position indicates significant doping, and a weaker $C_\beta-C_\beta$ stretching band at 1364 cm^{-1}.[53] The ^{13}C solid-state NMR of the polymer (Figure 4d) shows a strong signal due to the ether carbons at 69 ppm[56] and also indicates little incorporation of the ionic liquid cation. There is negligible intensity for the aromatic carbons (128 and 140 ppm), possibly because the radical character of the polarons in the doped polymer result in significant paramagnetic broadening,[56,57] which is severe for the aromatic carbons but much less so for the more remote oxyethylene bridge and/or is a result of the absence of any coordinated protons that are key to this cross-polarization NMR technique. The conductivity of the polymer, pressed into a pellet and measured using a four-probe method, was 1.5 ± 0.08 S cm^{-1}.

3.3. Synthesis of Poly(pyrrole). We have also investigated the synthesis of poly(pyrrole) in this biphasic ionic liquid/water system using gold chloride and have observed the formation of

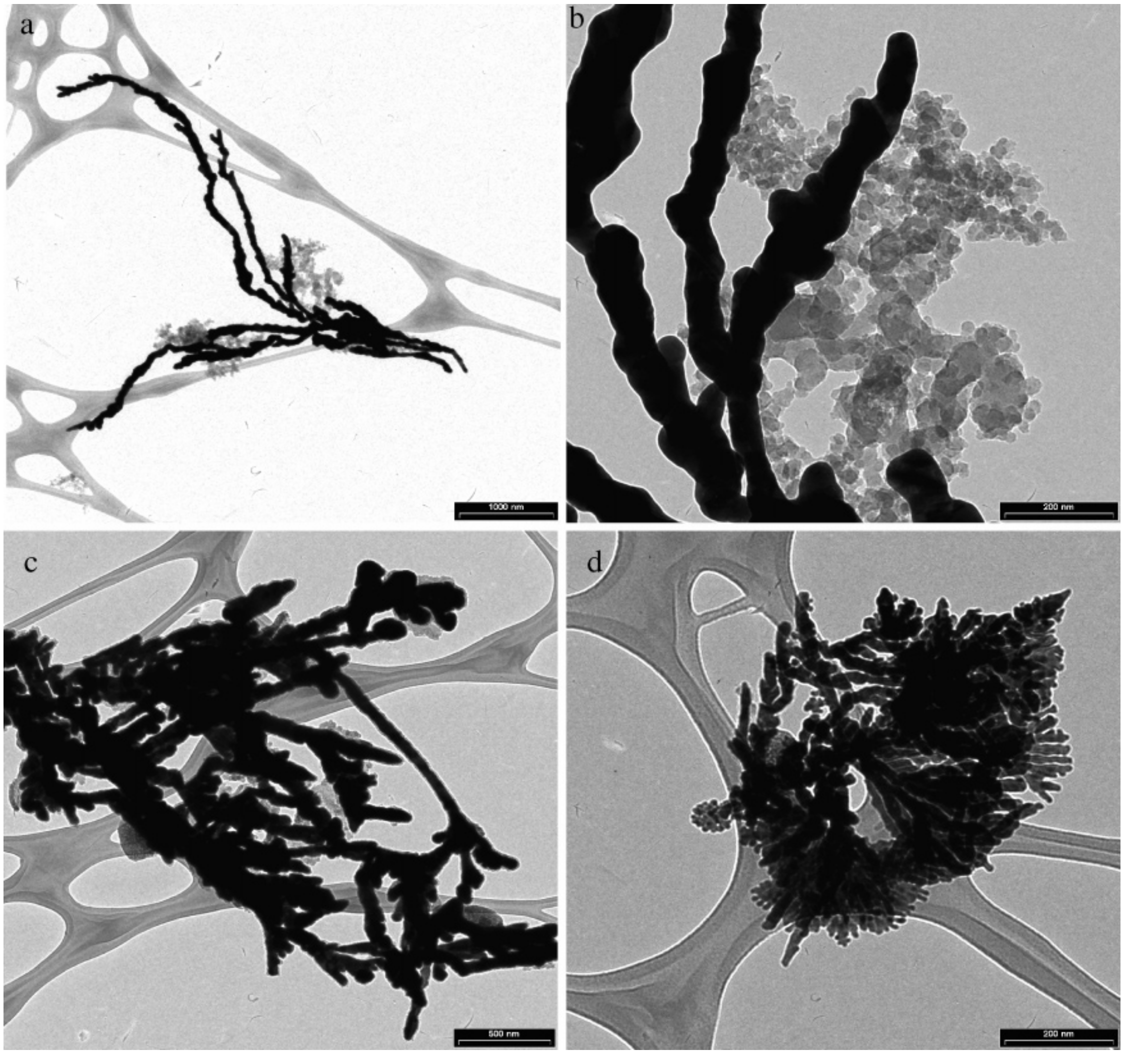

Figure 5. TEMs of the poly(pyrrole) (on lacey carbon copper grids) synthesized in the biphasic ionic liquid/water system. Scale bars are (a) 1000, (b) 200, (c) 500, and (d) 200 nm.

similar fibrillar structures (Figure 5). However, the proportion of the resultant polymer that displays this morphology is lower than in the poly(terthiophene) or PEDOT cases. As separation of the fibrillar polymer from the round species is not at this stage possible, analysis of the polymer was performed on the bulk material, and thus the results are not specific to the fibrillar polymer.

The UV−vis spectrum of the poly(pyrrole) (Figure 6a) exhibits the typical poly(pyrrole) $\pi-\pi^*$ transition at 440 nm and a strong bipolaron absorption at higher wavelengths. The cyclic voltammogram (Figure 6b) shows well-defined oxidation and reduction peaks, at ca. 0.8 and −0.25 V, respectively. The Raman spectrum (Figure 6c) is characteristic of poly(pyrrole), with a strong C═C stretching at 1596 cm^{-1}, consistent with the presence of polarons, but little intensity at higher wavenumbers (i.e., 1613 cm^{-1}) due to the presence of bipolaron/quinoidal structures.[58] The spectrum also shows the skeletal band at 1497 cm^{-1}, an antisymmetrical C−N stretching at 1411 cm^{-1}, the double peaks from the symmetrical C−H in-plane bending (1047 cm^{-1}), and the ring deformation (939 cm^{-1}), although the expected antisymmetric C−H in-plane bending is very weak (expected in the range 1000−1150 cm^{-1}). The solid-state ^{13}C CP-MAS NMR spectrum shows a broader polymer peak that was observed for the poly(terthiophene) or PEDOT, possibly due to a wider range of conjugation lengths and the presence of the different polymer morphologies within the sample. The spectrum shows the expected polymer peak (130 ppm) in addition to some higher frequency resonances (143 ppm) which suggest the presence of quinoidal structures that are indicative of an oxidized polymer.[59] There is also significant intensity between 0 and 50 ppm due to the incorporation of the ionic liquid cation into the polymer. XPS analysis of poly(pyrrole) samples synthesized using this technique indicated an average doping level of ca. 0.2 anions per pyrrole unit, with more Cl^- than TFSA dopant. Gold was only incorporated into the polymer as Au^+, at an average concentration of ca. 1 atom %.

The lower proportion of fibrillar structures in the poly(pyrrole) compared to the poly(terthiophene) or PEDOT suggests that the sulfonated polymers have a higher propensity for forming such fibrils than the nitrogen-containing analogues. This may be related to the stronger interaction that exists between gold and sulfur atoms compared to gold−nitrogen, suggesting an interaction between the gold and the monomer during polymerization.

The kinetics of the polymerization reactions are also expected to play a significant role in determining the polymer morphology. However, the polymerization of pyrrole, which has a lower oxidation potential and appears to proceed faster than the terthiophene polymerization, would thus have been expected to yield the most fibrillar structures, actually forms a relatively smaller amount, suggesting that kinetics may not be the dominant factor.

Possibly most significantly, the miscibility of the monomer in the water layer may influence the polymer morphology;

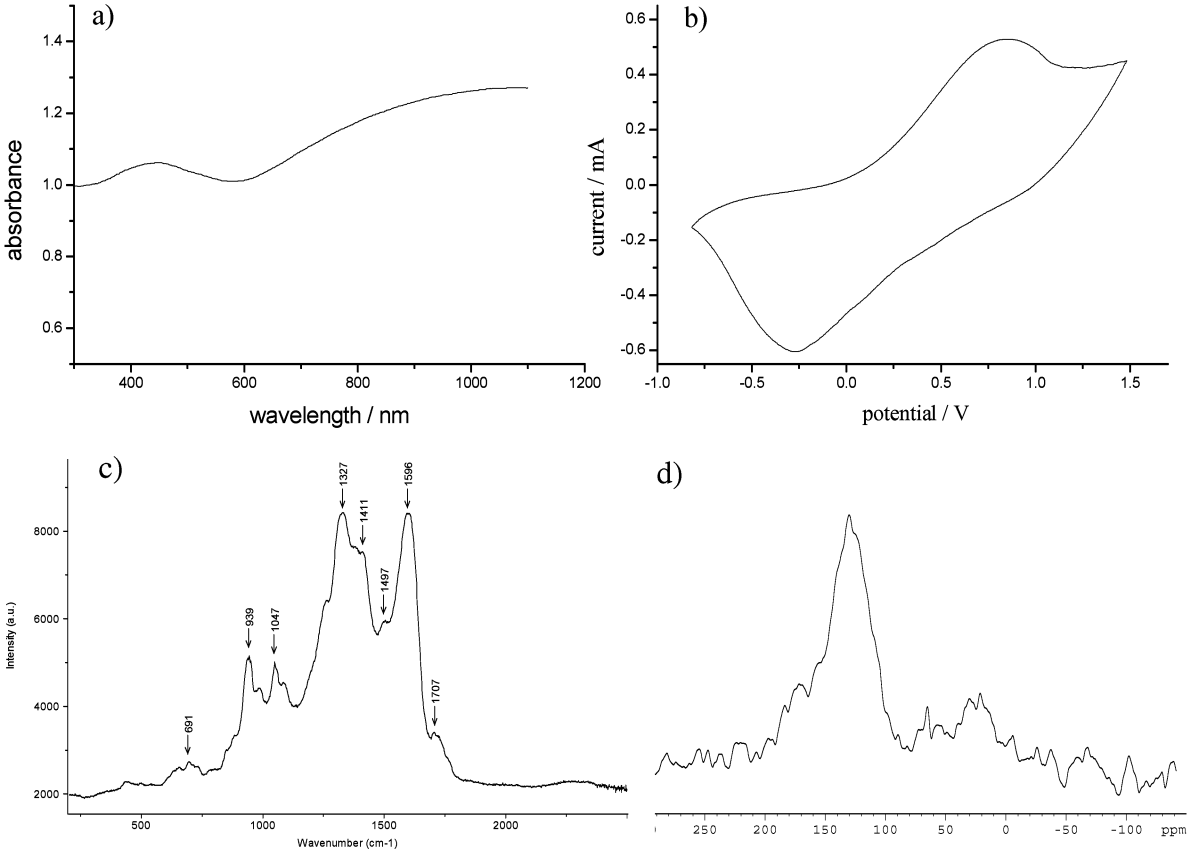

Figure 6. (a) UV−vis spectrum, (b) cyclic voltammogram, (c) Raman spectrum, and (d) ^{13}C solid-state CP-MAS NMR spectrum of the poly(pyrrole) formed by chemical polymerization in an ionic liquid/water system.

terthiophene is insoluble in water, and thus no phase transfer of the monomer will occur during the reaction time (24 h), whereas pyrrole is significantly soluble in water and, thus, some diffusion of the monomer between the ionic liquid and water may occur. Further, once the polymerization of pyrrole has been initiated, some oligomeric poly(pyrrole) may be expected to diffuse into the water layer and undergo secondary oxidation processes. Similarly, gold chloride is sparingly soluble in the ionic liquid, and thus some transfer of oxidant from the water to the ionic liquid may occur during the reaction, resulting in polymerization in the ionic liquid itself rather than at the ionic liquid/water interface. However, during the polymerization of the terthiophene the formation of the hydrophobic poly(terthiophene) effectively blocks the interface (similar to the effect observed during the interfacial chemical synthesis of Nylon in an organic solvent/water). Thus, the polymerization of terthiophene may be considered to be a more exclusively interfacial polymerization than that of the pyrrole. Once polymerization of the terthiophene is initiated at the interface, negligible mixing occurs, and the polymer is not exposed to further monomer and/or oxidant. Hence, no secondary growth can occur, and thus the product may be considered to be the result of only primary growth. The polymer grows only at the interface and in a fibrillar fashion. This appears to be consistent with the studies by Huang and Kaner,[26] who have shown that during the chemical polymerization of aniline in water nanofibers are the initial product formed, and it is only the secondary growth processes that result in the formation of particles. Thus, the key to achieving a polymer product with entirely fibrillar morphology may simply lie in the choice of an appropriate oxidant and/or biphasic solvent system in which the oxidant and the monomer are completely insoluble in the opposing phase.

In order to investigate the role of the water, the interface, and the ionic liquid on the production of polymer fibrils, we have also performed the polymerizations in a one-phase system (in water for pyrrole and in acetonitrile/water for EDOT, not possible for terthiophene due to monomer insolubility), in a two-phase ionic liquid system composed of two immiscible ionic liquids,[60] and in a two-phase system composed of chloroform/water. TEM analysis of the poly(pyrrole) and PEDOT synthesized in the one-phase systems, neither of which could be as well dispersed in ethanol as the products from the ionic liquid/water reactions, showed only round polymer particles (not shown). The synthesis of poly(terthiophene) in the two-phase ionic liquid system (with the monomer in the bottom layer, in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide) proceeded very slowly, without the immediate color change evident when aqueous gold chloride is used. TEM analysis indicated the presence of some fibrillar polymer structures, but they appeared to only constitute a small percentage of the sample. We have tentatively concluded that this is due to the reduced kinetics in this more viscous, less conductive medium. However, when a biphasic chloroform/water system was used (with the monomer in the chloroform layer), a significant percentage of the poly(terthiophene) and PEDOT synthesized had a fibrillar morphology (Figure 7). Very few fibrils were observed for poly(pyrrole) synthesized in this system, which is consistent with the observations made for the ionic liquid/water system. It is interesting to note that the poly(terthiophene) fibrils appear to be longer and thinner than those of the PEDOT, which also appear to be much shorter and wider

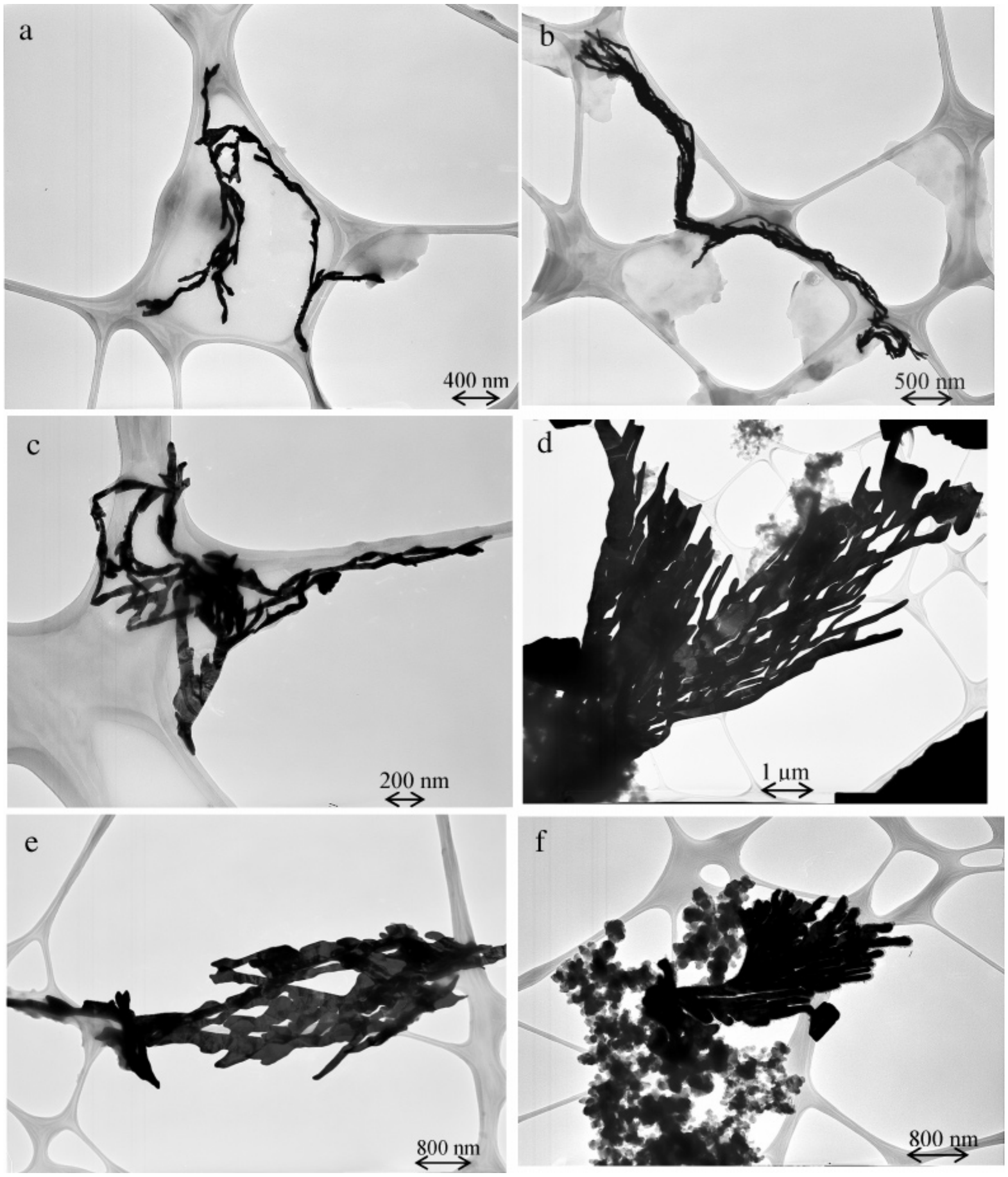

Figure 7. Poly(terthiophene) (a−c) and PEDOT (d−f) (on lacey Formvar/carbon mesh) synthesized using gold chloride in a biphasic chloroform/water system. Scale bars are (a) 400 nm, (b) 500 nm, (c) 200 nm, (d) 1 μm, (e) 800 nm, and (f) 800 nm.

than those made in the ionic liquid/water system (Figure 3). The direction of polymer growth is clearly evident in some of these PEDOT structures, more reminiscent of the evolution of fractal polymer structures[21] than the reports of, for example, poly(aniline) nanofibers produced by interfacial chemical polymerization.[26] The polymerization reactions performed in the chloroform/water appeared to be predominantly interfacial, with less color change of the lower layer observed in this system than for the same reactions in the ionic liquid/water reaction, which may explain the considerable proportion of fibrillar polymer formed.

The UV−vis spectrum (Figure 8a) of the poly(terthiophene) from the chloroform/water system shows a broad absorption over ca. 250−500 nm, but only a weak free carrier tail, similar to the poly(terthiophene) synthesized in the ionic liquid system and consistent with the formation of predominantly short-chained or undoped polymer,[43] whereas the PEDOT again shows strong absorption over higher wavelengths. The cyclic voltammograms of the two polymers (Figure 8b) indicate good electrochemical activity. The poly(terthiophene) again displays two reduction peaks, but these occur at relatively high potentials compared to that of the polymer made in the ionic liquid/water system (Figure 2), which again suggests a shorter conjugation length. The PEDOT displays very broad oxidation and reduction processes, which is typical of this polymer and suggests a high charge capacity. The Raman spectra of the PEDOT (Figure 8c) and poly(terthiophene) (Figure 8d) from the chloroform/water system are quite similar to those from the ionic liquid/water systems, although the PEDOT spectrum is less well-defined and there are some slight differences in the higher-wavelength region of the poly(terthiophene) spectrum, which exhibits a weaker C═C antisymmetric stretching vibration (1501 cm^{-1}) and a shaper C═C symmetric stretching (1450 cm^{-1}) than the polymer from the ionic liquid.

The yields of poly(pyrrole) and PEDOT (dry weight) obtained from the chloroform/water reactions were comparable to that from the ionic liquid/water system, allowing for uncertainties in dopant level, the nature of the dopant anions, and the quantity of gold incorporated into the polymer, but the yield of poly(terthiophene) was considerably lower using the chloroform/

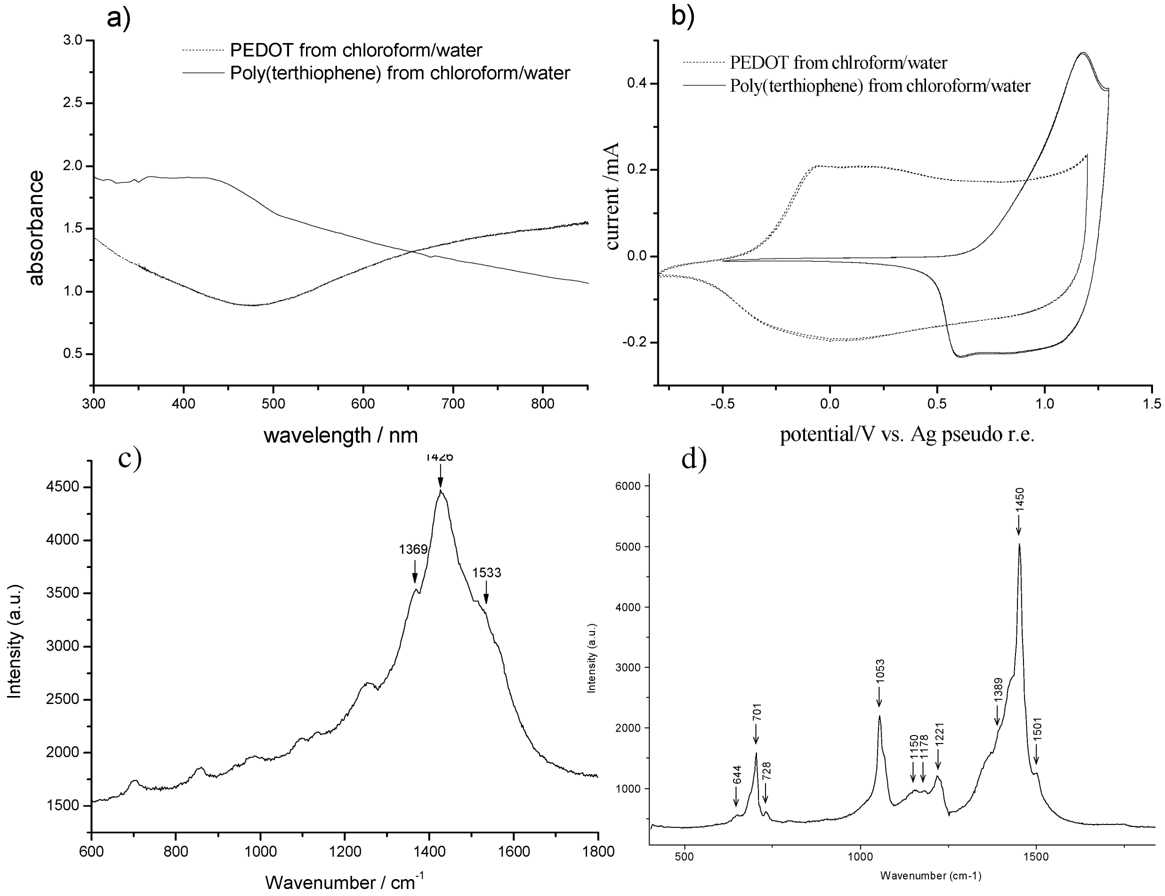

Figure 8. (a) UV−vis spectra, (b) cyclic voltammograms, (c) Raman spectrum of PEDOT, and (d) Raman spectrum of poly(terthiophene), synthesized in a chloroform/water biphasic system.

water system. The conductivities of the polymers from chloroform/water were 0.9 ± 0.1 S cm^{-1} for poly(terthiophene) and 28 ± 5 S cm^{-1} for PEDOT.

4. Conclusions

The chemical polymerization of pyrrole, EDOT, and terthiophene using a biphasic ionic liquid/water system results in the formation of conducting polymers fibrils. Our preliminary investigation into this phenomenon suggests that the sulfonated polymers have a higher propensity for fibril formation in this system, which may reflect the lower solubility of these monomers in water, minimizing interphase transfer of the monomer/oligomers during the polymerization process, hence discouraging secondary growth. We have performed analogous experiments in a one-phase water system and also a biphasic system composed of two immiscible ionic liquids in an attempt to elucidate the factors that predominantly influence the polymer morphology and result in these unusual fibrillar structures. The use of a biphasic chloroform/water system was also found to result in the formation of poly(terthiophene) and PEDOT fibrillar structures, but with a lower poly(terthiophene) yield than from the ionic liquid/water system.

The formation of the polymers was confirmed by UV−vis, cyclic voltammetry, and Raman analysis, which suggested that the physical properties of these materials were similar to those of the bulk polymer material. However, these nanodimensional polymer fibrils will possess a significantly larger surface area and, thus, charge accessibility, than any of the larger polymer particles prepared by conventional chemical polymerization, which may be key to improving the device performance of these conducting polymers.

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