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Conductivity enhancement in raw polypyrrole and polypyrrole nanoparticle dispersions

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For certain commercial applications of polypyrrole (PPy), an enhancement of the electrical conductivity of the material is the key to industrial success. In this paper it will be shown that raw PPy with high conductivity (>150 S/cm) can be obtained in very good yield (>90%) by appropriate selection of both bi-functional additives and reaction conditions which increase the oxidative polymerization rate of pyrrole. The presence of new active centers for the polymerization is demonstrated by UV measurements. In addition, raw PPy synthesized according to the improved method of synthesis shows good stability of the conductivity upon aging at high temperature (150°C) in air. Finally, new PPy dispersions are reported with an average particle size of 67 nm obtained by sonochemical synthesis that can be incorporated into conventional plastic paints for direct metallization of plastics. The conductivity of the new metallization paint developed was 0.4 S/cm with a PPy content of 10 wt%. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: polypyrroles; conducting polymers; raw materials; dispersions; plastic metallization

INTRODUCTION

Intrinsically conducting polymers (ICPs) such as polypyrrole (PPy), polyaniline (PAn) or polyethylenedioxythiophene (PEDOT) are emerging electroactive materials useful for several industrial applications.[1] Among others, ICPs are employed in electronic capacitors,[2] electrochemical (bio)sensor arrays,[3] polymer light emitting displays,[4] through-hole metallization of multilayer printed circuit boards (PCBs),[5] long-term solderable lead-free tin surface finishes for PCBs,[6] transparent antistatic coatings for insulating substrates,[7] conducting fibers, textiles[8] and anticorrosion coatings.[9]

Emerging applications include electromagnetic shielding applications in electronic equipment,[10] conducting hot melt adhesives,[11] electromembranes,[12] cathode materials for lithium-ion batteries,[13] electrochromic devices,[14] organic solar cells,[15] electroactuators[16] and nanoelectronic devices.[17] For some of these applications, high electrical conductivity of the ICP is crucial. PPy is one of the ICPs that is currently being evaluated in high conductivity applications such as electromagnetic interference (EMI) shielding cans for mobile telecommunications devices[18] (PPy raw material) and for all-plastic circuits in the emerging field of organic electronics[19] (PPy dispersions).

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Chemical oxidative polymerization is a convenient technique for large scale industrial production of raw PPy.[20–25] However, this technique usually leads to materials having lower electrical conductivity (<50 S/cm) than electrochemically synthesized ICPs (>200 S/cm).[26–29] Several critical reaction parameters that affect the final conductivity of PPy have been determined such as: nature and amount of oxidant, ratio of oxidant to pyrrole, reaction medium, reaction temperature and time, and presence of organic additives.[20,30–33] In practice, iron(III) chloride is the preferred oxidant (redox potential 0.771 V) since stronger oxidants like ammonium peroxydisulfate (2.01 V) or hydrogen peroxide (1.776 V) lead to a less conducting PPy.[34] The iron(III)/pyrrole ratio is typically 2.3 since two molecules of the oxidant are required to polymerize a monomer molecule and about 0.3 iron(III) molecules per monomer are consumed in the doping (oxidation) of the polymer chains leading to the final conducting material. Water is the preferred solvent due to environmental concerns, whereas low reaction temperature increases the PPy conductivity by reducing undesired side reactions, an effect also observed by the reduction of the reaction time. Also, the presence of selected organic additives during the PPy synthesis has proved to be beneficial.[20,30–33] However, the use of such additives usually leads to a significant reduction in reaction yield, which becomes not higher than 35% and therefore limits the industrial scale-up.

PPy dispersions are usually prepared by chemical oxidative polymerization of pyrrole in water in the presence of a

polymer steric stabilizer.[35] By using different water soluble polymers during the polymerization such as poly(vinyl alcohol), poly(ethylene oxide), poly(*N*-vinylpyrrolidone), cellulose derivatives and poly(styrene sulfonate) salts, macroscopic precipitation of the ICP is prevented and submicrometer dispersed particles are obtained.[36] Reaction conditions such as temperature, oxidant, monomer concentration, etc. as well as the chemical structure, molecular weight and concentration of the polymer steric stabilizer strongly affect the size and stability of the colloidal dispersions and the conductivity of the resulting PPy film upon water removal. The presence of the insulating polymer steric stabilizer in the dried PPy film leads to lower conductivity values ($<10^{-1}$ S/cm) when compared to raw PPy. When PPy aqueous dispersions are employed as additives in water borne paints, the conductivity of the resulting coating after drying is usually very low ($<10^{-5}$ S/cm).

In this paper the synthesis of raw PPy of high conductivity in a good yield (>90%) will be described. The appropriate selection of bifunctional additives (selected to have both polar substituents as ligands for iron(III) and heterocyclic nature to mimic the pyrrole chemical structure) together with the reaction conditions increase the reaction rate (high molar ratio of iron(III) to pyrrole) leading to raw PPy which retains good conductivity after aging at high temperature (150°C). Furthermore, it will be shown that using sonochemical techniques during the oxidative polymerization of pyrrole leads to new PPy dispersions with average particle size below 100 nm, that can be incorporated into conventional paints for direct metallization of plastics.

EXPERIMENTAL

All chemical compounds employed in this work were purchased from Aldrich Co. with at least 98% purity and used without further purification.

In a typical synthesis of raw PPy, a solution was prepared by mixing at room temperature *N*-(2-hydroxyethyl)-2-pyrrolidinone (HEP, 12.5 ml, 110 mmol) and water (37.5 ml) in a 250 ml flask. To this solution, iron(III) chloride (47.3 g, 175 mmol) was slowly added and after 30 min of stirring, the solution was cooled to −5°C. Pyrrole (1.2 ml, 17.3 mmol) was poured then in a single portion under vigorous stirring. After a reaction time of 30 min, the resulting black PPy precipitate was filtered, repeatedly washed with methanol and finally dried under dynamic vacuum to constant weight. Characterization of the raw PPy samples and the reaction medium was performed as described previously.[20]

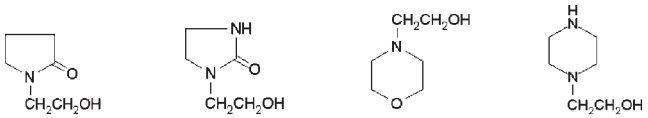
PPy aqueous dispersions were prepared by using an Ultrasonic Processor (model UP 400 S from Dr Hielscher, GmbH) during the synthesis. As an example, pyrrole (2 ml, 28.8 mmol) and 3.5 g of poly(styrene sulfonate, sodium salt) were dissolved in 100 ml of distilled water. To this mixture, an equimolar amount of ammonium peroxydisulfate (6.58 g, 28.8 mmol) dissolved in 50 ml of water was added dropwise over a period of 4 min. After 1 hr of reaction a black PPy aqueous dispersion was obtained. Dispersion particle sizes were measured using a Beckman Coulter N5 Submicron Particle Size Analyzer.

The PPy dispersion was mixed with commercial grade polyurethane paint (ABS-1K from Desmopur) and deposited by dip coating onto ABS specimens of different roughness. Drying of the coated ABS specimens was performed in an oven under dynamic vacuum at room temperature. The PPy content in the metallization paint was typically 10 wt%. Copper was electrodeposited onto the coated ABS specimens in an industrial plating bath following conventional procedures.

RESULTS AND DISCUSSION

Conductivity enhancement in raw polypyrrole

For the chemical oxidative polymerization of pyrrole in water with iron(III) chloride as oxidant, improvements in reaction yield could be expected if a better solvent for the monomer is used, since pyrrole has a limited solubility in water (7.5%). However, such a solvent should also have a certain, but limited, solvation power towards iron(III). It is well known that no PPy is formed in strong donor solvents such as dimethylsulfoxide (DMSO) or pyridine.[33] Following this line of reasoning, several *N*-hydroxyethyl heterocylic compounds have been selected as co-solvents for chemical oxidative polymerization of pyrrole in water:



1

These compounds incorporate: (1) a polar hydroxyethyl substituent able to act as a ligand for iron(III) ions, and (2) an N-containing heterocyclic structure for improved affinity towards pyrrole. Additionally, rapid and uniform consumption of the pyrrole monomer could be a complementary way to improve the electrical conductivity of the resulting material. In this sense, the probability of instantaneous oxidation of most pyrrole molecules to the starting radical cation species should increase by using a high iron(III)/pyrrole ratio. Enhancement of the polymerization rate is also expected under such conditions.

Figure 1 shows the evolution of the conductivity and the reaction yield of raw PPy synthesized in binary mixtures of water and HEP as a function of composition. Interestingly, a synergic effect is found in both conductivity and yield by using binary mixtures of water and HEP and an iron(III)/pyrrole molar ratio of 10:1. It is worth noting that the maximum conductivity at 152 ± 7 S/cm is found with a HEP/iron(III) molar ratio of 0.63:1, with a simultaneous very good yield (94%). Higher or lower HEP/iron(III) molar ratios lead to raw PPy of lower conductivity. Moreover, chemical oxidative polymerization of pyrrole in pure HEP was unsuccessful.

For solutions of $FeCl_3 \cdot 6H_2O$ in water in high concentration ([iron(III)] = 4.23 M), three main iron(III) complexes have been determined by X-ray diffraction studies in solution:[37] *trans*-$Fe(H_2O)_4Cl_2^+$ with [*trans*-$Fe(H_2O)_4Cl_2^+$]/[total iron(III)] = 0.33, $Fe(H_2O)_3Cl_3$ with [$Fe(H_2O)_3Cl_3$]/[total iron(III)] = 0.34,

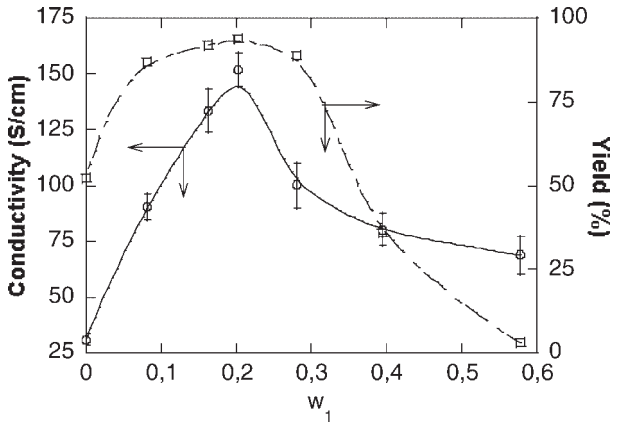


Figure 1. Electrical conductivity (○) and reaction yield (□) of raw PPy chemically synthesized in binary mixtures of water and HEP as a function of the HEP weight fraction in the mixture (w_1).

and $FeCl_4^-$ with $[FeCl_4^-]/[\text{iron(III)}] = 0.33$. Replacement of a water molecule in the above octahedral *trans*-$Fe(H_2O)_4Cl_2^+$ and $Fe(H_2O)_3Cl_3$ complexes by a molecule of HEP could lead to new active species and account for the optimum [HEP]/[iron(III)] ratio experimentally found.

Evidence of the formation of new active centers is provided by UV spectroscopy as illustrated in Fig. 2. In the presence of such new species, the use of high iron(III)/pyrrole molar ratios and, hence, enhanced reaction rates without loss of conductivity in the resulting PPy is allowed. When *N*-(2-hydroxyethyl)-2-imidazolidinone (HEI), *N*-(2-hydroxyethyl)morpholine (HEM) and *N*-(2-hydroxyethyl)piperazine (HEPI) are used as co-solvents instead of HEP at a molar ratio of 0.63:1 with respect to iron(III), PPy conductivity values of 133, 78 and 0.02 S/cm, were found with reaction yields of 93, 99 and 58%, respectively.

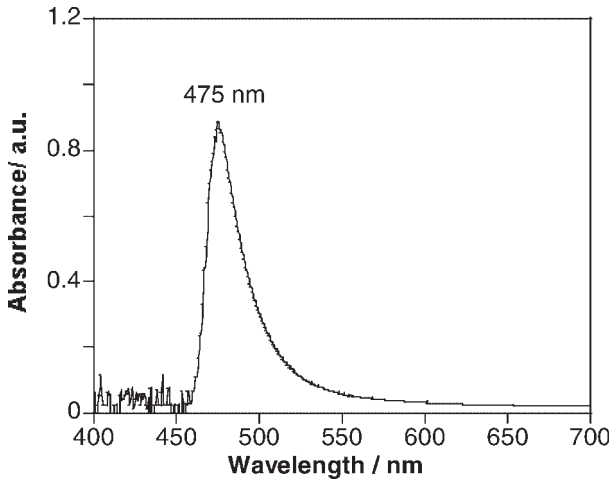


Figure 2. UV absorption spectrum of the HEP/iron(III) chloride/water solution containing 110 mmol of HEP after subtraction of the UV absorption spectrum of the reference iron(III) chloride/water solution. The new band centred at 475 nm is attributed to the formation of charge-transfer complexes between HEP as electron donor and iron(III) as electron acceptor.

The low conductivity value and reaction yield obtained using HEPI demonstrates a negative effect of the –NH– group of the heterocycle (by comparison with HEM containing an –O– group at the same position). This effect is not present, to a significant extent, for HEI with a –NHCO– group in the structure. Elemental analysis data reveals that incorporation of the *N*-hydroxyethyl heterocyclic compounds into the PPy chains has not taken place.

Concerning the evolution of the conductivity upon aging, raw PPy synthesized in water at a molar ratio of 0.63:1 with respect to iron(III) without *N*-hydroxyethyl heterocyclic compounds and aged for 5 hr at 150°C in air showed a conductivity value of 0.2 S/cm, whereas raw PPy synthesized in binary mixtures of water and HEP, HEI and HEM showed conductivity values of 138, 82 and 2 S/cm after aging, respectively.

Conductivity enhancement in polypyrrole dispersions

Aqueous PPy dispersions synthesized with mechanical stirring led to a broad distribution of particle sizes from tens of nanometers to several microns with a typical average size of 368 nm. When such PPy dispersions were incorporated into conventional water borne paints for plastics, the conductivity of the resulting coating after drying was very low ($<10^{-5}$ S/cm), as expected. In addition, the surface roughness of the coatings was significantly enhanced as a consequence of the presence of large PPy particle sizes.

Sonochemical techniques such as ultrasound irradiation, were first employed to reduce the particle size in PAn dispersions to 10–60 nm.[38,39] Recently, colloidal dispersions of hybrid nanocomposite composed of gold nanoparticles and PPy (core-shell, 8 nm in size) have been prepared by a sonochemical method, in which gold ion and pyrrole monomer in an aqueous solution were reduced and oxidized, respectively, by ultrasonic irradiation in the presence of poly(*N*-vinyl-2-pyrrolidone).[40]

In this work, ultrasound irradiation has been employed during the synthesis of the PPy dispersions in the presence of ammonium peroxydisulfate, as oxidant, and poly(styrene sulfonate) as steric stabilizer and dopant. Figure 3 illustrates

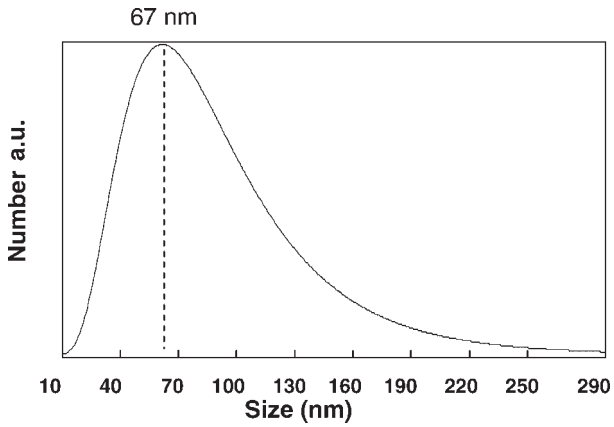


Figure 3. Distribution of particle sizes in PPy dispersions prepared with ultrasonic irradiation. The PPy average particle size reduces from 368 to 67 nm with the aid of sonochemical techniques.

Figure 4. Direct metallization of plastics with PPy paints. From left to right: (a) raw ABS specimen, (b) PPy painted ABS specimen, (c) Cu-metallized PPy painted ABS specimen with rough surface and (d) Cu-metallized PPy painted ABS specimen with smooth surface.

the distribution of particle sizes obtained using the sonochemical technique. In this case, the average size of the particles in the ultrasonic irradiated PPy dispersion was 67 nm.

When such dispersions were incorporated into the aforementioned conventional water borne paint for plastics, the conductivity of the coating formed upon water removal was 0.4 S/cm with PPy contents of 10 wt%, with no increase in surface roughness. The increase in conductivity without loss in surface roughness is optimal for certain applications such as the direct metallization of plastics. As an example, Fig. 4 shows ABS sheets of different roughness metallized with the new conducting formulation developed in this work.

CONCLUSIONS

In summary, two different strategies have been followed to enhance the conductivity of PPy for their use in industrial applications. For raw PPy, an efficient chemical synthesis method for obtaining highly conducting PPy has been reported that relies on: (1) the use of bi-functional additives that both mimic monomer structure and interact with the oxidant during polymerization, and (2) the use of a high iron(III)/pyrrole molar ratio to enhance the polymerization rate. For PPy dispersions, sonochemical techniques have been employed during the synthesis in order to reduce the average PPy particle size and increase the conductivity of the corresponding PPy based coatings. Further studies are in progress to confirm the validity of these strategies for other conducting polymers.

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