USE OF WOOD DERIVATIVES AS DOPING / DISPERSING AGENTS IN THE PREPARATION OF POLYPYRROLE AQUEOUS DISPERSIONS

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Polystyrene sulfonic acid (PSS), lignosulfonic acid (LS) sodium salts, and carboxymethylcellulose (CMC) were used as doping/dispersing agents in the chemical polymerization of polypyrrole (Ppy). Conductivity measurements performed on dry Ppy pellets showed a sharp increase in conductivity when adding the anionic polymers to the polymerization liquor. For a polyanion/pyrrole weight ratio ranging between 0.1 and 0.6, the highest conductivity was given by PpyCMC (82 S/m) and PpyPSS (80 S/m), followed by PpyLS (6 S/m). On the other hand, for a polyanion/pyrrole ratio higher than 0.6, the conductivity of PpyPSS systems sharply decreased, and for polyanion/pyrrole ratios higher than 1, the highest conductivity was given by PpyCMC (~10 S/m), followed by PpyLS (~7 S/m) and PpyPSS (~5 S/m). Zeta-potential measurements showed that the surface charge of Ppy was strongly affected by the polyanion type and amount. Cationic Ppy particles were obtained in the presence of the two polymers bearing strongly acidic moieties (PSS and LS). Anionic PpyPSS colloids were obtained at the highest PSS/Py ratio, after the degradation of the conducting properties. When using a weakly acidic dopant (CMC), PpyCMC colloids had a negative charge for all of the tested conditions.

Keywords: Carboxymethylcellulose; Lignosulfonates; Polypyrrole; Conducting polymer; Dispersion.

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INTRODUCTION

Conducting polymers are generally called synthetic metals because they have electrical, magnetic, and optical properties typical of metals and semiconductors. These characteristics arise from the conjugation of their backbone, namely, a regular succession of single and double bonds (Attias 2002). This configuration causes the formation of high-energy orbitals in which electrons are loosely bonded to their corresponding atom. Charge movement within the material can be induced by the application of an electric field. There are two energy levels, the HOMO (highest occupied molecular orbital), at lower energy, which can give up electrons, and the LUMO (lowest unoccupied molecular orbital), at higher energy, which can attract electrons. These bands are separated by an energy gap, corresponding to forbidden energy levels. The distance between the HOMO and the LUMO determines the conducting, semiconducting, or insulating character of the

material. The conduction mechanism is generated by the carrier movement (or jump) from the HOMO to the LUMO, which is easier if the HOMO-LUMO energy gap is small. Actually, most of conducting polymers display semi-conducting properties, and an oxidative doping is needed to improve the mobility of charge carriers by decreasing the HOMO to LUMO energy band gap. Some of the mostly used doping anions are: Cl^-, ClO_4^-, $Fe[CN]_6^{3-}$, NO_3^-, PF_6^-, BF_4^-. Alkylsulfonates-, alkylbenzenesulfonates-, alkylsulfate surfactants, and polystyrenesufonate are also used as dopants (Omastova et al. 2003; Lefebvre et al. 1999; Song et al. 2004). Two major properties are given by these macromolecular anions, namely, i) a reduction of the mobility of doping anions within the conducting polymers and of the ensuing degradation of electrons conduction, and ii) the stabilization of conducting polymers dispersions in water.

The doping agents are incorporated during the redox polymerisation reaction. Indeed, the dopant anion is attracted, via local resonance, to the radical formed during oxidation and acts as a counterion (Shaktawat et al. 2006). The radical-dopant combination is called a polaron, and it represents the actual charge carrier in conducting polymers. The polaron formation induces a local distortion of the chain (Attias 2002; Shaktawat et al. 2006) and the formation of energy levels within the band gap. In this way, charge carriers can move easily from the HOMO to the LUMO, promoting electrons mobility along the polymer chain (Dubois and Michel 1993).

Some of the most widely diffused intrinsic conducting polymers (ICP), namely PEDOT and polypyrrole (Ppy), are currently obtained via electrochemical or chemical polymerization (Toshima and Hara 1995). Polymers synthesized by electrochemistry are characterized by high purity, i.e. absence of residual chlorides and iron cations, and appear to be ideal candidates for sensor, electronic, and opto-electronic applications (Stenger-Smith 1998). Nevertheless, the use of this technique is restrained to the preparation of smooth polymer films, and conventional redox polymerization remains the major method to obtain ICP's aqueous dispersions for the formulation of conducting printing inks. In this context, anionic polyelectrolytes / surfactants added in the polymerization liquor have the double role of doping and dispersing agents, boosting conductivity and modifying the morphology of polymer particles (Omastova et al. 2003; Lefebvre et al. 1999). Until now, some modified cellulose and lignin derivatives have been used for the electrochemical synthesis (Mahmud et al. 2005; Otero and Vazquez 1995; Otero et al. 1998) of Ppy, but only little interest has been shown to their use in chemical synthesis (Mandal and Mandal 1995; Underhill-Shanks and Viswanathan 1996; Welch and Viswanathan 1996), and their role as doping/dispersing agents remains rather unexplored.

In this study, the doping/dispersing action of polystyrene sulfonic acid sodium salt was compared to that of carboxymethylcellulose and lignosulfonic acid sodium salt in order to evaluate their potential use in the formulation of conducting polymer dispersions.

EXPERIMENTAL

Chemical polymerization of pyrrole was run at a fixed concentration of oxidant and monomer in the presence of a strong excess of Fe^{3+} to ensure the complete

polymerization of pyrrole ($Fe^{3+}/Py = 4$). In order to avoid the contact between highly concentrated reagents, ferric chloride (Aldrich, 99%), pyrrole (Aldrich, 98%), and the dopant (Fig. 1), namely carboxymethylcellulose (CMC), lignosulfonates (LS), or polystyrene sulfonic acid sodium salt (PSS), were separately dissolved in 100 mL deionized water at 5×10^{-2} mol/L, 1.25×10^{-2} mol/L, and 0.3-2 g/L, respectively. All polyanions used as dopants were purchased from Aldrich (analytical grade). The dopant solution was slowly poured into the $FeCl_3$ solution under vigorous stirring in order to prevent the precipitation of polyanion-iron complexes and to obtain a cloudy suspension. The monomer solution was then added, and a 24 h polymerization was run at room temperature under gentle stirring. Ppy suspensions were dialyzed during 24 h (20 kDalton membrane) in order to remove residual HCl and iron compounds. Particle size distribution (Malvern, Mastersizer 2000) and ζ-potential (Malvern, Nanosizer nanoZS) of Ppy particles were measured after adjusting the ionic strength with KCl (5×10^{-2} mol/L) and 5 min sonication (Branson sonifier 250, output 40%). The dispersion stability was evaluated by visual analysis of the suspension after 24 h at rest. Aqueous dispersions were dried in a vacuum oven (0.2 bar, 40°C) to prevent polymer oxidation, and 10 mm diameter x 0.9 mm thickness pellets were obtained by pressing 0.95 g of Ppy powders at 1 GPa. The surface resistance of Ppy pellets was measured using the four points-point-probe technique (Jandel, Universal Probe) with an electrode load of 600 N. Sheet resistance data were used to calculate the corresponding conductivity, $C = 1/(R\ e)$, where R is the surface resistance and e is the sample thickness.

The electric charge carried by polyanions was evaluated by polyelectrolyte titration (Pelton et al. 2007) of PSS, CMC, and LS solutions in deionized water, using polyethyleneimine (Aldrich, 0.9 meq/g) and a streaming current detector (BTG Mütek, PCD03). Weak acids, namely R-COOH, borne on tested polyelectrolytes were dosed by conductimetric titration of polyelectrolyte solutions acidified with HCl at pH 2 and using NaOH as titrant (Katz et al. 1984).
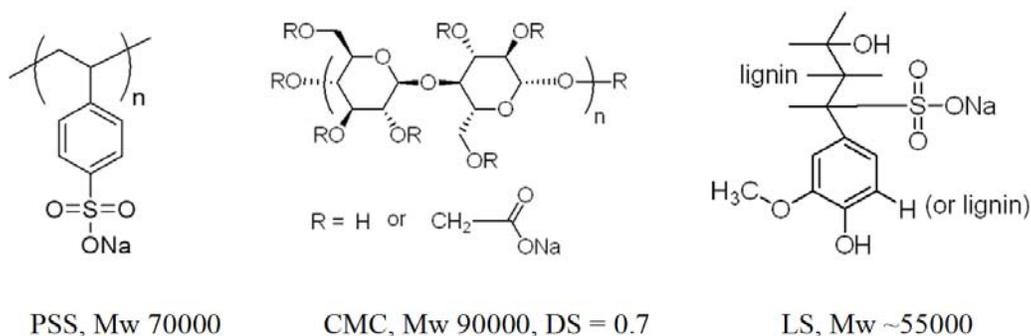

Fig. 1. The anionic polyelectrolytes used in this study as Ppy dopants/dispersing agents.

RESULTS AND DISCUSSION

Figure 2 shows that the surface charge of Ppy particles was strongly affected by both the dopant concentration and by the acidic moiety. In the absence of polymeric dopants, the low doping density of Cl^- ions, i.e. ~0.25-0.3 per pyrrole unit (Kang et al. 1991), and Cl^- anions release (Stéphan et al. 1995; Zhang and Bai 2003) are expected to

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contribute to the generation of positive surface charges and therefore of the positive ζ-potential measured for PpyCl particles. The addition of sulfonates induced an increase in ζ-potential, which was followed by a progressive decrease and, for PSS, the reversal of the surface charge. Since polyanions incorporation in Ppy is irreversible (Stéphan et al. 1995), the increase of ζ-potential cannot be attributed to the release of anions. The observed trend was interpreted as reflecting iron complexation with sulfonate anions and the ensuing increase of iron inclusion in Ppy particles (Arribas and Rueda 1996). When increasing PSS concentration, the charge balance between $R\text{-}SO_3^-$ and Fe^{n+} ions turns in favour of sulfonate anions, and the net charge of PSS/iron complexes and Ppy particles sharply decreases until charge reversal. The total charge density of CMC and PSS (Table 1) was similar, i.e. 3.6 and 3.8 meq/g; however, the surface charge of PpyCMC particles was significantly different from that of PpyPSS.
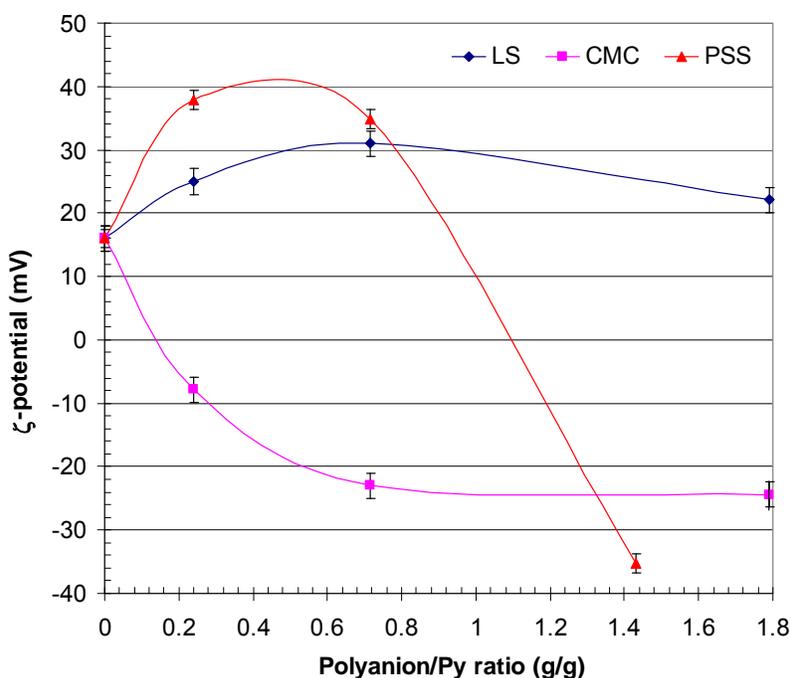

Fig. 2. ζ-potential of Ppy aqueous dispersions plotted as a function of the polyanion/monomer ratio. Full lines were added to guide the eye.

The ζ-potential of Ppy/CMC particles was negative for the lowest CMC concentration, and it progressively became more negative until a plateau value of -25 mV. This difference was ascribed to the different ionization of sulfonic and carboxylic acids. At the polymerization pH (1.8-2), carboxylic moieties ($R\text{-}COOH$, $pK_a = 5$) are protonated, and iron/CMC complexation occurs via the C-O group in the carboxylate anion (Hosny 1997). Sulfonate moieties ($Ar\text{-}SO_3H$, $pK = -6.5$) are in the anionic form and can form complexes with iron ions by electrostatic interaction. During the dialysis of Ppy dispersions the pH increased from 2 to 5.5-6.5, and the generation of a negative charge on PpyCMC particles was correlated to the deprotonation of R-COOH moieties.

Table 1. Anionic Charge (tot.) and Carboxylate Anions (R-COO⁻) Density of Tested Polyanions as Obtained by Polyelectrolyte and Conductimetric Titration, respectively. (Theoretical charge (th.) was calculated using polymer formula given in Fig. 1.)

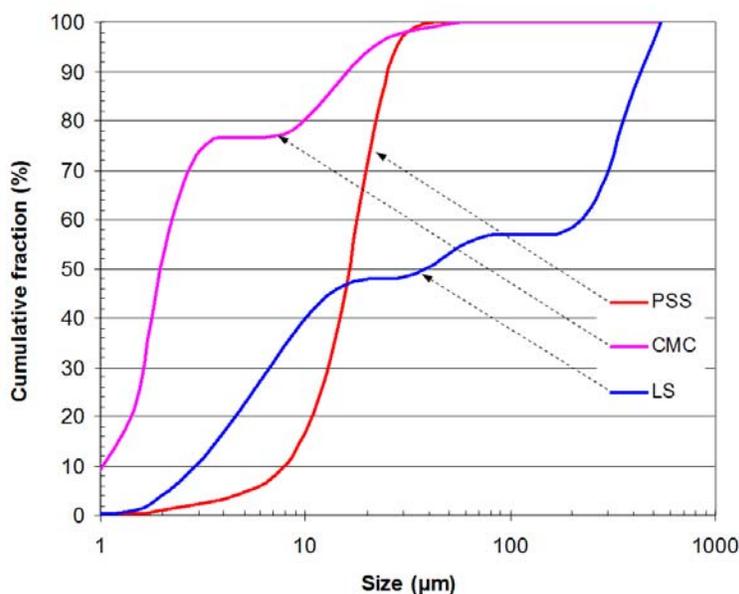| $PSS_{tot.}$ (meq/g)	PSS_{COO^-} (meq/g)	$PSS_{th.}$ (meq/g)	$CMC_{tot.}$ (meq/g)	CMC_{COO^-} (meq/g)	$CMC_{th.}$ (meq/g)	$LS_{tot.}$ (meq/g)	LS_{COO^-} (meq/g)
3.8	~0.05	4.8	3.6	2.4	2.4	1.4	0.5

Fig. 3. Comparison of cumulative particle size distributions obtained with a constant polyanion/Py ratio of 0.7.

Despite the presence of a maximum in ζ-potential, charge neutralization and inversion was not observed for PpyLS. Polyelectrolyte and conductimetric titration of LS, Table 1, show that the anionic charge density of LS was 2.5 times lower than that of PSS and CMC, and it was mainly due to sulfonate and a small amount of carboxylate moieties. The low charge density of LS was not sufficient to ensure a charge inversion within the range of tested LS concentrations. Moreover, deprotonation of carboxylic moieties in LS did not affect Ppy particle charge when compared to CMC (R-COO⁻ concentration in LS is 5 times lower than in CMC).

For all tested polyanions, the increase in their concentration in the polymerization liquor gave a corresponding decrease in the average size of Ppy particles. Cumulative particle size distribution shown in Fig. 3 shows that, at a fixed polyelectrolyte concentration, the best dispersing action was given by CMC, followed by PSS and LS, respectively. The effect of polyanions on particle size was directly correlated with the stability of Ppy suspensions. For all tested conditions, an increase in the amount of polyanions gave a decrease in the sedimentation rate. Nevertheless, as shown in Fig. 4, only PpyCMC dispersions obtained with CMC/Py ratio of 0.7 and 1.8 did not sediment appreciably during 24 h at rest.
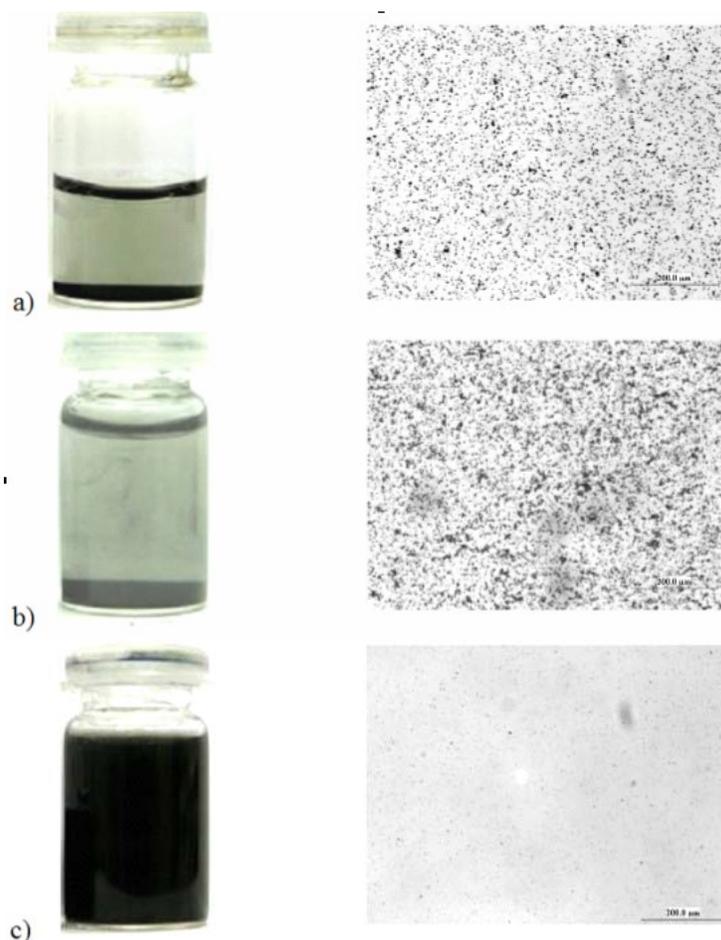
Fig. 4. Evaluation of Ppy dispersions stability after 24 h at rest and corresponding optical microscopy micrographs taken after sonication (magnification x120). a) PpyPSS with polyanion/Py ratio 1.4, b) PpyLS with polyanion/Py ratio 1.8, c) PpyCMC with polyanion/Py ratio 1.8.

Ppy conductivity sharply increased by four orders of magnitude when adding polyanions in the polymerization liquor, i.e. from 2×10^{-3} for PpyCl to ~20 S/m (Fig. 5). The shape of conductivity curves shown in Fig. 5 was attributed to different charge densities of PSS and LS. The doping action of PSS took place in a narrow range of PSS/Py ratios, i.e. conductivity increased for $0 < PSS/Py < 0.2$ and decreased for $0.2 < PSS/Py$. With LS this trend was less pronounced, and after an increase for $0 < LS/Py < 0.4$, PpyLS conductivity reached a nearly stable value. CMC had a doping action similar to that obtained with PSS. However, conductivity slightly decreased for CMC/Py ratios above 0.4. Since the tested polyanions did not display any intrinsic conducting property, the degradation of Ppy conductivity obtained when increasing the polyanion/Py ratio was associated with the increase of the non-conducting phase in Ppy-polyanion composites.

Conductivities of some Ppy-wood derivative composites listed in Table 2 show that electric properties obtained in this study (Fig. 5) were in line with data published for similar systems. Indeed, the conductivity of chemically synthesised PpyCMC and PpyLS

composites ranges between 1 and 110 S/m (Yin et al. 2001) and 3 and 8 S/m (Underhill-Shanks and Viswanathan 1996), respectively. Higher conductivities, i.e. 1200-3800 S/m, can be obtained by electrochemical polymerization of PpyCMC films on indium thin oxide (ITO) substrates the presence of a co-dopant (Mahmud et al. 2005).
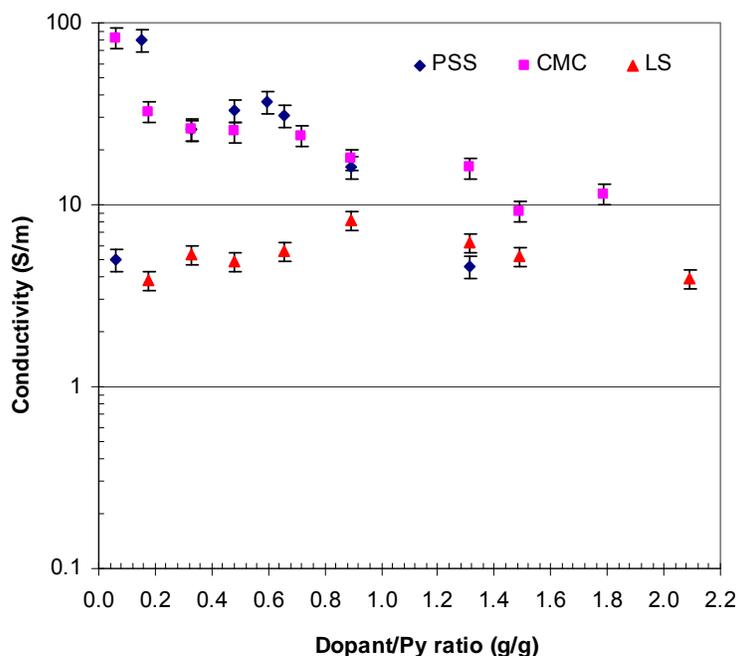
Fig. 5. Conductivity of doped Ppy pellets plotted as a function of polyanion type and polyanion to monomer ratio.

Table 2. Conductivity and Polymerization Conditions of some Ppy-wood Derivative Composites

Wood derivative	Polymerization	T (°C)	Conductivity (S/m)	Author
Cross linked CMC films	$FeCl_3$, Py condensation from vapour	-8	0.04-110	Yin et al. 2001
CMC (with p-toluene sulfonate dopant)	Electrochemical	Room	1240-3850	Mahmud et al. 2005
Ethylhydroxyethyl cellulose	$FeCl_3$, water/ethanol (50/50)	2	161-734	Mandal and Mandal 1995
Hydroxypropyl cellulose	$FeCl_3$, in water	0	10	Amaike and Yamamoto 2006
Methylcellulose	$FeCl_3$, in water	Room	≤ 20	Bjorklund and Liedberg 1986
Lignosulfonic acid sodium salt	$(NH_4)_2S_2O_8$, in water	0	1-5	Underhill-Shanks and Viswanathan 1996

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All tested polyanions had the double role of dopants and dispersing agents. The best compromise between Ppy particle size, conductivity, and dispersion stability was with CMC, followed by PSS and LS, respectively. The results show that wood derivatives represent a potential alternative to PSS in the chemical synthesis of Ppy dispersions.

CONCLUSIONS

1. This study showed that water-soluble wood derivatives can be used in the chemical polymerization of polypyrrole (Ppy) and, as polystyrene sulfonic acid (PSS), they have the double role of dopants and dispersing agents.
2. Lignosulfonic acid (LS) displayed a doping-dispersing action lower than that obtained with PSS. This behaviour was associated to the low density of charged sites ($R\text{-}SO_3^-$, $R\text{-}COO^-$) borne on tested LS. Furthermore, cationic Ppy particles were obtained when using LS.
3. The doping action of carboxymethylcellulose CMC was similar to that obtained with PSS. PpyCMC dispersions were more stable than those obtained with PSS and LS and suspended particles were negatively charged.
4. After a first increase in conductivity, excessive polyanion dosage induced a drop in conductivity with PSS and a less pronounced decrease with CMC. This conductivity drop was not observed in the presence of LS. The conductivity of PpyLS pellets levelled off to ~5 S/m whatever the LS/Py ratio.
5. CMC gave the best compromise between Ppy dispersion and conductivity.

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