

## Arrangement of Monomer Injection in the Characteristics of Copolymer

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**Abstract:** Polypyrrole/Poly(vinyl acetate) (PPy/PVAc) copolymer was prepared by the copolymerization of vinyl acetate and pyrrole using  $\text{FeCl}_3$  and benzoylperoxide as an oxidant in the presence of various surfactants such as sodium dodecylbenzenesulfonate and poly(ethylene glycol) in the aqueous/non-aqueous media. The PPy/PVAc copolymer was characterized in terms of conductivity, morphology, chemical structure, particle size and yield. The results indicate that the morphology, particle size, yield and electrical conductivity of the products are dependent on the type of surfactant and the arrangement of monomer injection. The chemical structure of obtained product was determined by FTIR spectroscopy. By comparison FTIR spectra between pure PPy and PPy/ PVAc copolymer, the PPy/ PVAc copolymer had additional bands. All these bands indicate the formation of copolymer.

**Keywords:** Copolymer, surfactant, monomer injection, morphology, conductivity, structure

### 1 Introduction

During the last decade there has been widespread interest in conducting polymers both for academic purposes and for potential applications. Conductive electroactive polymers such as polypyrrole (PPy) possess some unique chemical and electrochemical properties. The insolubility in common solvents and infusibility of conducting polymers, in general, make them poorly processable either by solution technique or by melt processing methods (Yin et al., 1988; Machado et al., 1988). Improvement properties of these materials can be achieved either by forming copolymers, or composites and blends with commercially available polymers or inorganic materials which offer better mechanical and optical properties, stability

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and processability (Eisazadeh, 2007; Ghorbani and Eisazadeh, 2008; Paoli et al., 1984; Lindsey et al., 1984; Bhat et al., 2001; Cassagnol et al., 1999)

Chemical grafting (copolymers) of aniline onto the backbone of the polymeric surfactant is a novel way to obtain colloidal forms of this conducting polymer (Armes et al., 1990; Aldissi and Armes, 1991). The chemical grafting technique offers the advantage, compared to physical adsorption, in the case of polypyrrole, of forming more stable materials in which desorption of the stabilizers does not take place.

Suspension polymerization of aniline in the presence of dodecylbenzenesulfonic acid (DBSA) with styrene-butadiene-styrene (SBS) and without SBS was carried out and results indicate that DBSA acts simultaneously as a surfactant (emulsifier) and as a dopant (Xei et al., 1998; Osterholm et al., 1994). Also surfactant affect on the morphology (degree of crystalline order and orientation) (Osterholm et al., 1994).

Polypyrrole is a conjugated polymer with alternating single and double bonds. The conductivity of PPy originates from the  $\pi$  electrons delocalized over the conjugated system and from the doping ions. These ions are interstitially positioned between the polymer chains and may considerably increase the conduction of the polymer.

PPy is attractive as an electrically conducting polymer because of its selective ease of synthesis. Bulk quantities of PPy can be obtained as fine powders using the oxidative polymerization of the monomer by selected transition metal ions in water or various other solvents (Machida et al., 1989; Armes, 1987; Rapi et al., 1988). Adsorption of the surfactant on the PPy particles is primarily due to the hydrophobic component of the surfactants, probably via a hydrogen bonding mechanism with the pyrrole N-H group (Armes et al., 1990).

The type of surfactant is known to influence the rate of polymer formation, particle size, size distribution, morphology, and homogeneity (Aldissi, 1993; Eisazadeh, 1994, 1995; Dipankar et al., 2001). The interaction between surfactant and polymer or copolymer affects the electrical conductivity and morphology of resultant products (Ruckenstein and Yuan, 1998; Goh et al., 1996).

The size and type of the dopant (anion) affect the morphology, size and electrical conductivity of resulting polymers (Hayashi et al., 1987; Tang et al., 2003). The polarity of the counterion plays an important role in the conductivity as well as in the chemical properties. Conductivity increased when small counterions were used (Myers, 1986).

From the beginning, interest in conducting polymers has its origins in the possible commercial applications of these materials. The commercial applications are based on the promise of a novel combination of light weight, processability and electrical conductivity.

A wide range of possible applications have been proposed for conducting polymers such as rechargeable batteries (Scrosati, 1998) conductive paint (Eisazadeh et al., 1993), heavy metals separation (Eisazadeh, 2007, 2008), optical devices (Falcao et al., 2002) membrane (Misoska et al., 2001), sensors and biosensors (Guernion et al., 2002, Yamato et al., 1997), electromagnetic interference (EMI) shielding (Dhawan et al., 2002), antistatic coating (Ohtani et al., 1993), and biomedical applications (Benabderrahmane et al., 2005), etc.

In this study, polypyrrole/poly(vinyl acetate) copolymer was prepared in aqueous/non-aqueous solution by the copolymerization of vinyl acetate and pyrrole using  $\text{FeCl}_3$  and benzoylperoxide as an oxidant in the presence of various surfactants.

## **2 Experimental**

### **2.1 Instrumentation**

A magnetic mixer model MK20, digital scale model FR200, scanning electron microscope (SEM) model XL30 and fourier transform infrared (FTIR) spectrometer model shimadzu 4100 were employed. A four-point probe method was used to measure the volume resistivity of conducting polymer films.

### **2.2 Reagents and standard solutions**

Materials used in this work were pyrrole ( $d = 0.97 \text{ g/mL}$ ), poly(ethylene glycol) (PEG,  $M_w = 35000$ ) from Aldrich, sodium dodecylbenzenesulfonate (DBSNa) from Loba chemie, vinyl acetate ( $d = 0.93 \text{ g/mL}$ ), ferric chloride and benzoylperoxide from Merck. All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Pyrrole was purified by simple distillation.

### **2.3 Copolymerization of PPy/PVAc (pyrrole monomer was injected first)**

The reaction was carried out in aqueous/non-aqueous media at room temperature for 5 hours. The conditions for copolymer formation are summarized in Table 1.

In a typical experiment 1 mL pyrrole monomer was added to a stirred aqueous/non-aqueous solution 100 mL (water/toluene, 75/25 % v/v) containing 5.4 g of  $\text{FeCl}_3$ , 2 g of benzoylperoxide and 0.2 g one of the surfactants. After few minutes, 3 mL vinyl acetate monomer was added to the stirred solution. After 5 hours, the polymer was filtered, and in order to separate the oligomers and impurities, the product was washed several times with deionized water, and then dried at room temperature.

## 2.4 Copolymerization of PPy/PVAc (vinyl acetate monomer was injected first)

The reaction was carried out in aqueous/non-aqueous media at room temperature for 5 hours. The conditions for copolymer formation are summarized in Table 2.

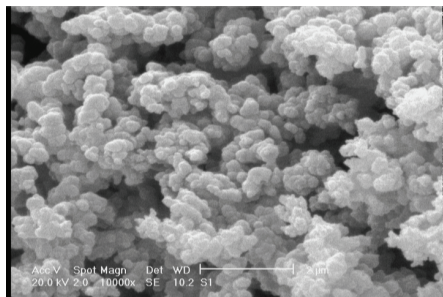


Figure 1: Scanning electron micrograph of PPy in aqueous/non-aqueous media. Reaction conditions: ( $\text{FeCl}_3 = 54 \text{ g/L}$ , pyrrole monomer  $14.45 \times 10^{-2} \text{ mol/L}$ , volume of solution 100 mL (water/toluene, 75/25 % v/v), reaction time 5 hours at room temperature.

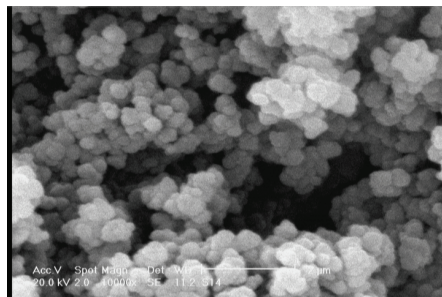


Figure 2: Scanning electron micrograph of PPy/PVAc in aqueous/non-aqueous media. Reaction conditions: ( $\text{FeCl}_3 = 54 \text{ g/L}$ , benzoylperoxide = 20 g/L, poly(ethylene glycol) = 20 g/L, pyrrole monomer  $14.45 \times 10^{-2} \text{ mol/L}$ , vinyl acetate monomer  $32.44 \times 10^{-2} \text{ mol/L}$ , volume of solution 100 mL (water/toluene, 75/25 % v/v), reaction time 5 hours at room temperature, when pyrrole monomer was injected first).

In a typical experiment 3 mL vinyl acetate monomer was added to a stirred aqueous/non aqueous solution 100 mL (water/toluene, 75/25 % v/v) containing 5.4 g of  $\text{FeCl}_3$ , 2 g of benzoyl peroxide and 0.2 g one of the surfactants. After few minutes, 1 mL pyrrole monomer was added to the stirred solution. After 5 hours, the polymer was filtered, and in order to separate the oligomers and impurities, the product was washed several times with deionized water, and then dried at room temperature.

## 3 Results and Discussion

The electrical conductivities of various copolymers produced under different reaction conditions were measured on pressed pellets of the copolymer powders. The electrical conductivity of the compressed pellets was measured using four point probe method and the particle size was measured using measurement software.

Table 1: Conditions for copolymer formation (pyrrole monomer was injected first)

Type of solution	Type of surfactant	Type and concentration of oxidant (g/L)	Concentration of surfactant (g/L)	Yield of 3.76 gram monomers (pyrrole + vinyl acetate) to copolymer (g)	Monomers to copolymer (% w/w)	Particle size (nm)	Electrical conductivity (S/cm)
water+toluene (75/25 % v/v)	PEG	FeCl <sub>3</sub> = 54 + Benzoyl peroxide = 20	2	1.45	39	315	$4.3 \times 10^{-4}$
water+toluene (75/25 % v/v)	DBSNa	FeCl <sub>3</sub> = 54 + Benzoyl peroxide = 20	2	1.5	40	180	$4.4 \times 10^{-4}$

Table 2: Conditions for copolymer formation (vinyl acetate monomer was injected first)

Type of solution	Type of surfactant	Type and concentration of oxidant (g/L)	Concentration of surfactant (g/L)	Yield of 3.76 gram monomers (pyrrole + vinyl acetate) to copolymer (g)	Monomer to copolymer (% w/w)	Particle size (nm)	Electrical conductivity (S/cm)
water+toluene (75/25 % v/v)	PEG	FeCl <sub>3</sub> =54 + Benzoyl peroxide=20	2	1.1	29	158	7.1×10 <sup>-6</sup>
water+toluene (75/25 % v/v)	DBSNa	FeCl <sub>3</sub> =54 + Benzoyl peroxide=20	2	1.1	29	127	1.2×10 <sup>-5</sup>

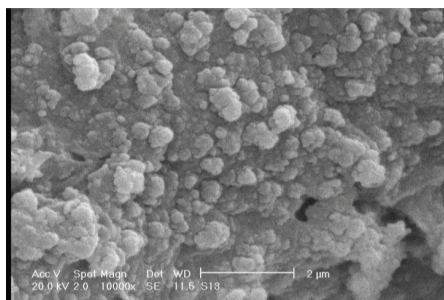


Figure 3: Scanning electron micrograph of PPy/PVAc in aqueous/non-aqueous media. Reaction conditions: ( $\text{FeCl}_3 = 54 \text{ g/L}$ , benzoylperoxide =  $20 \text{ g/L}$ , sodium dodecylbenzenesulfonate =  $20 \text{ g/L}$ , pyrrole monomer  $14.45 \times 10^{-2} \text{ mol/L}$ , vinyl acetate monomer  $32.44 \times 10^{-2} \text{ mol/L}$ , volume of solution  $100 \text{ mL}$  (water/toluene,  $75/25 \%$  v/v), reaction time 5 hours at room temperature, when pyrrole monomer was injected first)

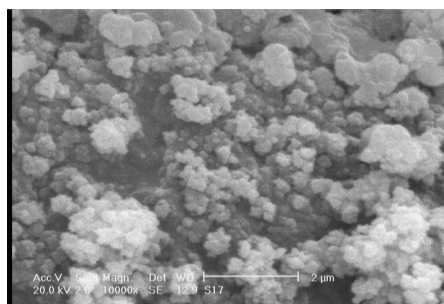


Figure 4: Scanning electron micrograph of PPy/PVAc in aqueous/non-aqueous media. Reaction conditions: ( $\text{FeCl}_3 = 54 \text{ g/L}$ , benzoylperoxide =  $20 \text{ g/L}$ , poly(ethylene glycol) =  $20 \text{ g/L}$ , pyrrole monomer  $14.45 \times 10^{-2} \text{ mol/L}$ , vinyl acetate monomer  $32.44 \times 10^{-2} \text{ mol/L}$ , volume of solution  $100 \text{ mL}$  (water/toluene,  $75/25 \%$  v/v), reaction time 5 hours at room temperature, when vinyl acetate monomer was injected first)

The yield, particle size and electrical conductivity of copolymers are listed in Tables 1, 2. As can be seen, the yield, particle size and the electrical conductivity are dependent on the arrangement of monomer injection.

As shown in tables, the yield and particle size are dependent on the type of surfactant, because surfactant influences the chemical and physical properties of solution and rate of polymerization. Also DBSNa is a molecular and anionic surfactant, but PEG is a polymeric surfactant.

As can be seen in table 1, 2, by comparison between copolymer obtained using DBSNa and PEG as surfactant respectively, particle size decreased and electrical conductivity increased using DBSNa as surfactant, because probably DBSNa simultaneously acts as emulsifier and dopant [12, 13]. Electrical conductivity, particle size and yield of monomers to polymer, decreased when vinyl acetate monomer was injected first.

The morphology of the copolymer was studied by using scanning electron microscope. As shown in Figs. 2-5, the size and homogeneity of the particles are dependent on the type of surfactant and arrangement of monomer injection. By com-

parison between Figs 2, 4 (copolymer obtained using PEG as surfactant) and Figs 3, 5 (copolymer obtained using HPC as surfactant) the arrangement of monomer injection influence the electrical conductivity and particle size of resulting product. The electrical conductivity and particle size decreased when vinyl acetate monomer was injected first. This is probably due to the resulting poly(vinyl acetate) acts as steric stabilizer.

The chemical structure of obtained product was determined by FTIR spectrum. FTIR analysis has been done to identify the characteristic peaks of product.

The FTIR spectra in the 2500-400  $\text{cm}^{-1}$  region for various polymers are shown in Fig. 6. As can be seen, the FTIR spectrum changes when the copolymer is formed by copolymerization. For instance, the one characteristic of the pyrrole unit at 1542.82  $\text{cm}^{-1}$ . The peaks are at 1306.64  $\text{cm}^{-1}$  (C-N stretching vibration), 1167.64  $\text{cm}^{-1}$  (C-H in-plane deformation), 1041.86  $\text{cm}^{-1}$  (N-H in-plane deformation) and 893.77  $\text{cm}^{-1}$  (C-H out-of-plane deformation).

New peaks which are due to pyrrole/vinyl acetate unites appear at 1700.62  $\text{cm}^{-1}$  in the spectra of PPy/PVAc particles. The presence of the characteristic bands of these brings strong supporting evidence for the effective incorporation of vinyl acetate into the conjugated pyrrole polymer.

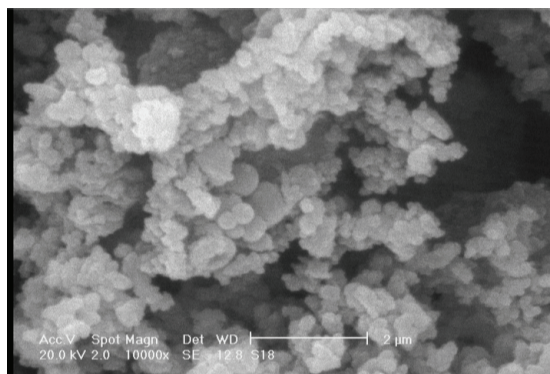


Figure 5: Scanning electron micrograph of PPy/PVAc in aqueous/non-aqueous media. Reaction conditions: ( $\text{FeCl}_3 = 54 \text{ g/L}$ , benzoylperoxide = 20 g/L, sodium dodecylbenzenesulfonate = 20 g/L, pyrrole monomer  $14.45 \times 10^{-2} \text{ mol/L}$ , vinyl acetate monomer  $32.44 \times 10^{-2} \text{ mol/L}$ , volume of solution 100 mL (water/toluene, 75/25 % v/v), reaction time 5 hours at room temperature, when vinyl acetate monomer was injected first)



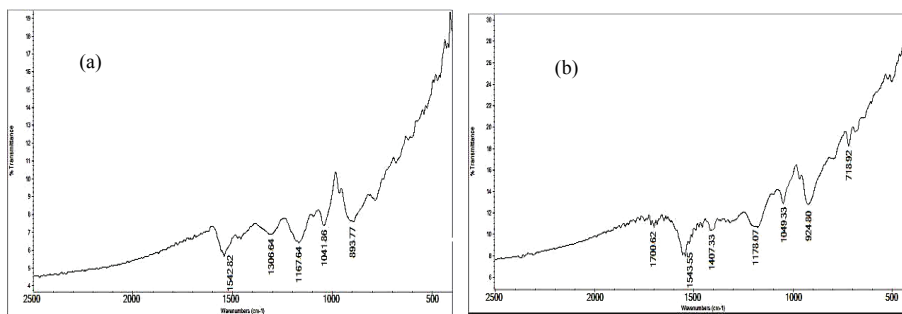


Figure 6: FTIR spectra of (a) pure polypyrrole, (b) PPY/PVAc copolymer with DBSNa as surfactant in aqueous /non-aqueous media (water/toluene,75/25 % v/v)

#### 4 Conclusion

In this work the characteristics of PPY/PVAc copolymers, such as conductivity, yield, morphology and particle size, were investigated in aqueous/non-aqueous media. The arrangement of monomer injection has a considerable effect on the conductivity particle size and morphology of the resulting product. The SEM micrographs show that the arrangement of monomer injection plays a major role on the surface morphology and homogeneity of particles. In the case of injection of vinyl acetate monomer before pyrrole monomer, particle size, electrical conductivity and yield of monomers to polymer were decreased. The structure of products was determined by FTIR spectrum. By comparison FTIR spectra between pure PPY and copolymers, the copolymers have additional bands. All these bands indicate the formation of copolymers.

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