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Nanoparticles preparation of pyrrole and vinyleacetaye copolymerusing various surfactants

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ABSTRACT

Poly pyrrole/poly (vinyle acetate) (Ppy/PvAc) copolymer was prepared in the aqueous /non aqueous solution by copolymerizationofPyrrole and Vinyl acetate using benzoyle peroxide and $FeCl_3$ *as an oxidant in the apesence and presence of surfactant such as hydroxy propel cellulos(commercial surfactant)and [(2,2'-1,22-diamino-8,15-dioxo-7,10,13,16-tetraazadocosane-10,13-diyl)diacetic acid](DAdAc) synthesized surfactant. In this study, the (Ppy/PvAc) copolymer was characterized by Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM). The results indicate that the intensity of peaks, morphology,particle size, andconductivity of products are dependent on the type of surfactants.*

Keywords: Nanoparticles, Surfactant, Copolymer

INTRODUCTION

Polypyrrole (Ppy), one of the most extensivelyinvestigated conducting polymers, has attracted a great deal of interest because of its good electrical conductivity, environmental stability and easysynthesis[1].Conducting polymers have attracted a great attention due to broad application areas such as energy conversion,surface coating layer, and electrochromic devices. In general, they have been synthesized by chemical orelectrochemical methods.

Poly pyrole (Ppy)is one of the most interesting conducting polymers since it is easilydeposited from aqueous and non-aqueous media, very adherent to many types ofsubstrates, and is well-conducting and stable. Electrochemical polymerization produces thinfilms with a thickness of few micrometers on an electrode surface [2], while achemical oxidation yields a fine-grained material. However,the yield and quality of theresulting polymer films are influenced by several factors, such as nature and concentrationof monomer and the counter ion, solvent, cell conditions (e.g. electrode and appliedpotential), temperature and pH [3,4].

Nanoprecipitation is also called solvent displacement method. It involves the precipitation of a preformed polymer from an organic solution and the diffusion of the organic solvent in the aqueous medium in the presence or absence of a surfactant[5-8].

Polymer deposition on the interface between the water and the organic solvent, caused by fast diffusion of the solvent, leads to the instantaneous formation of a colloidal suspension[9]. To facilitate the formation of colloidal polymer particles during the first step of the procedure, phase separation is performed with a totally miscible solvent that is also a non solvent of the polymer[10].

All surfactants have both hydrophilic and lipophilic properties and are characterized by their hydrophilic–lipophilic balance (HLB) values. HLB system is the relationship (or balance) betweenthe hydrophilic portions of the nonionic surfactant to the lipophilic portion. HLB values of thestabilizing agents affect the qualities of nanoparticles. A stabilizing agent with high HLB can causedestabilization of the double structure while a stabilizing agent with low HLB may lead to instability between globules [11].

Emulsion polymerization is one of the fastest methodsfor nanoparticle preparation and is readily scalable [12]. Themethod is classified into two categories, based on the use ofan organic or aqueous continuous phase.

Adsorptionof the surfactant on the Ppy particles is primarily due to the hydrophobiccomponent of the surfactants, probably via a hydrogen bonding mechanism withthepyrrole N-H group [13].The type of surfactant is known to influence the rate of polymer formation, particlesize, size distribution, morphology, and homogeneity [14-16]. The interaction between surfactant and polymeror copolymer affects the electrical conductivity and morphology of resultantproducts [17].

In this study, Polypyrrole/Poly(vinyl acetate) copolymer was prepared in the aqueous/non-aqueous solution by copolymerization of Pyrrole and (vinyl acetate) using benzoyle peroxide and $FeCl_3$ as an oxidant in thepresence of various surfactants.

MATERIALS AND METHODS

The Materials used in this work were vinyl acetate (d=0.93g/ml)and benzoyle peroxide frome (Merk), hydroxy propyl cellulose,pyrrol (d=0.97g/ml),ferric chloride frome (Aldrech), (2,2'-1,22-diamino-8,15-dioxo-7,10,13,16-tetraazadocosane-10,13-diyl)diacetic acid (DAdAc) [18]. Distilled water. Pyrrole was purify by simple distilation.

Scaning electron microscope (SEM)modelKYKY-EM3200. A magnatic mixer model VELP scientifica, fourier transform infra red(FTIR) spectrometer model THERMO-NICOLET IR 100,Thermogravimatricanalysis:TGA Q 50 (U.S.A) A four-point probe method was used to measure the volume resistivity of conducting polymer films.

Synthetic methods, analytical and spectral data

Chemistry

Copolymerization of PPy/PvAc

The reaction was carried out in aqueous/non-aqueous media at room temperature for 5 hours. In a typical experiment3ml of vinyle acetate monomer was added to stirred aqueous/ nonaqeous solution 100ml (water /toluene ,75/25%v/v) containing 2g of benzoilperoxide,5.4gof $Fecl_{3,}$ 0.2g one of the surfactants. after afew minutes,1ml pyrrol was added to stirred solution. After 5 hours, the polymer was filtered, and washed several time with deionized water, andthen dried at room temperature.

Table1.FTIR of poly pyrrole and copolymers

Type of band	Ppy cm^{-1}	Withoutsurfactant cm^{-1}	hydroxy propyl cellulose cm^{-1}	(DAdAc) cm^{-1}
Pyrrole unit	1550	1542.28	1552.24	1542.09
(C-N) stretching vibration	1306	1302	1298.93	1292.54
(C-H) in plan deformation	1190	1183.96	1177.59	1174.54
(N-H) in plan deformation	1037	1043.97	1048.19	1037.22
(C-H)outofplane deformation.	901	919.55	929.43	905.45
New peak of Ppy/PvAcparticles	-------	1699.58	1690.94	1697.63

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 the4000-400 cm^{-1}region for poly pyrolle and various copolymers are shown in Figs(1,2,3,4) as can be seen. The FTIR spectrum changes when the copolymer is formed by copolymerization. New peaks which are due to pyrrole /vinyl acetate uniteappear in the new copolymers as can be seen in the Table (1) the presence of the characteristic bands of these bring strong evidence for the effective in corporation of vinyl acetate into the conjugated pyrrole polymer.

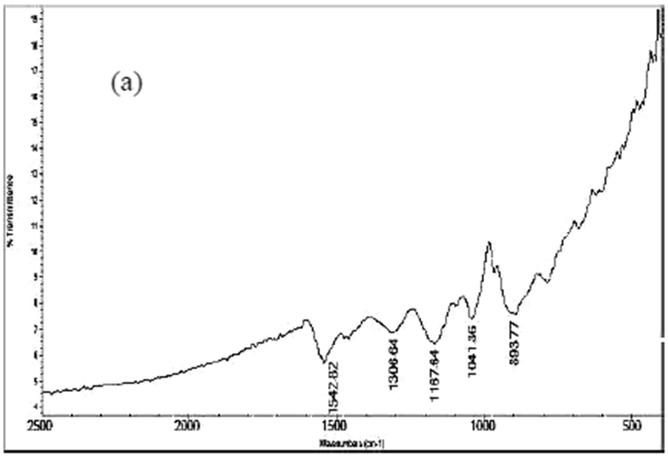

Fig. 1. FTIR spectrum of pure poly pyrrole

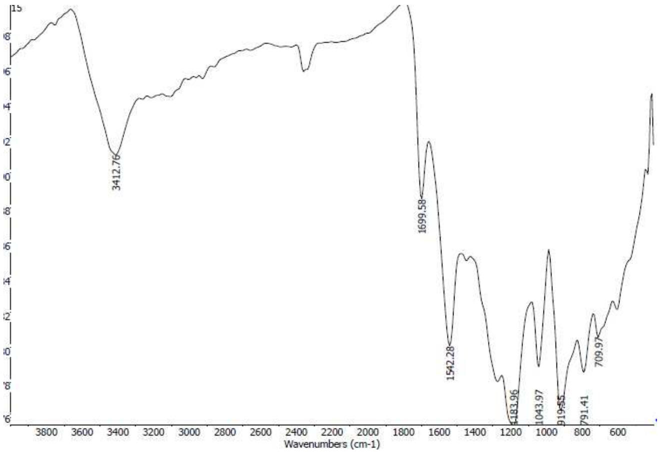

Fig. 2. FTIR spectrum of Ppy/pvAc without surfactant

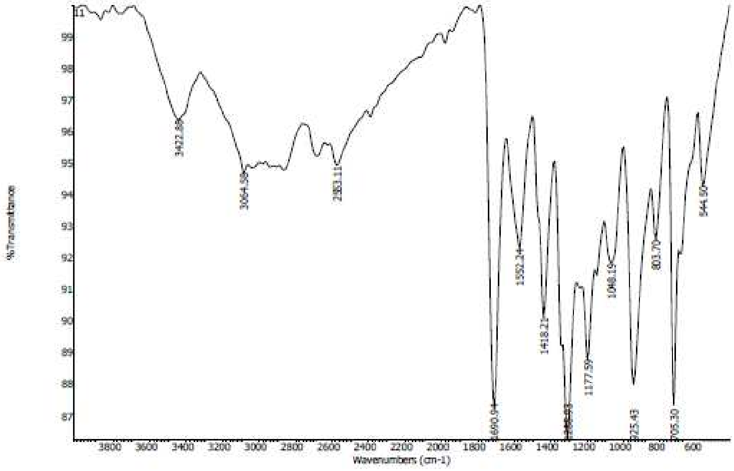

Fig. 3. FTIR spectrum of copolymer using hydroxy propyl cellulose

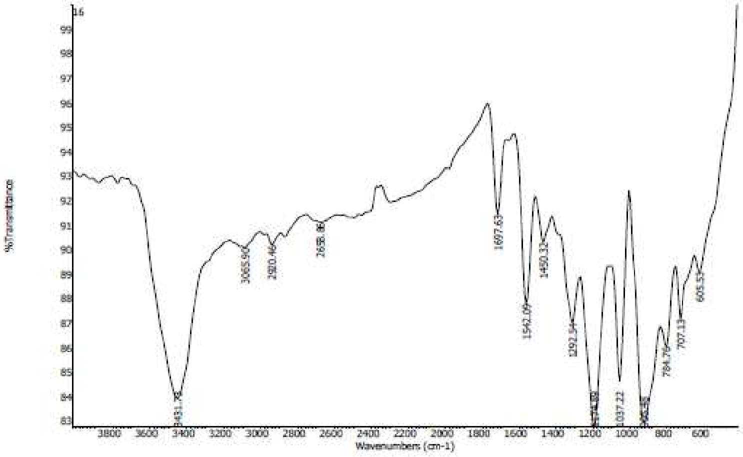

Fig.4. FTIR spectrum of copolymer using(DAdAc)

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 compressed pellets was measured using four point probe method. The particle size and electrical conductivity of copolymers using various surfactants are listed in Table 2 an the Figures (5,6,7). As can be seen the particle size and electrical conductivity are dependent on the type of surfactant, because the surfactant, influence the rate of polymerization and also surfactants are adsorbed physically or chemically (graft copolymer) by the growing polymer [19]. The particles size and electrical conductivity are listed in Table (2). As can be seen, the particle size of the copolymer without surfactant in rang (133.1-355.6nm), the particle size of the copolymer using surfactant in range (147.5-253,2nm), (100-197.4nm) to hydroxyl propyl cellulos, and (DAdAc) respectivity. The electrical conductivities were measured on pressed pellets of the copolymer powders.

Table 2.The conductivity and particles size of the copolymer

Type of copolymer	Type of surfactant	Particles size(nm)	Electrical conductivity (Scm^{-1})
Ppy/ PvAc	Without surfactant	206.6-274.4	$6.3*10^{-5}$
Ppy/ PvAc	Hydroxy propyl cellulose	162.8-209.0	$7.4*10^{-6}$
Ppy/ PvAc	(DAdAc)	102.9-135.3	$5.3*10^{-6}$

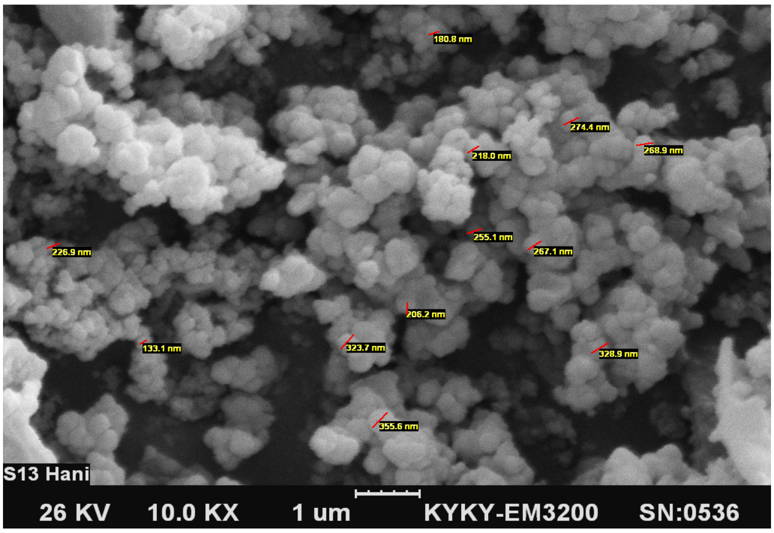

Fig. 5.Scanning electron micrograph of PPy/PvAc in aqueous/non-aqueous media without surfactant

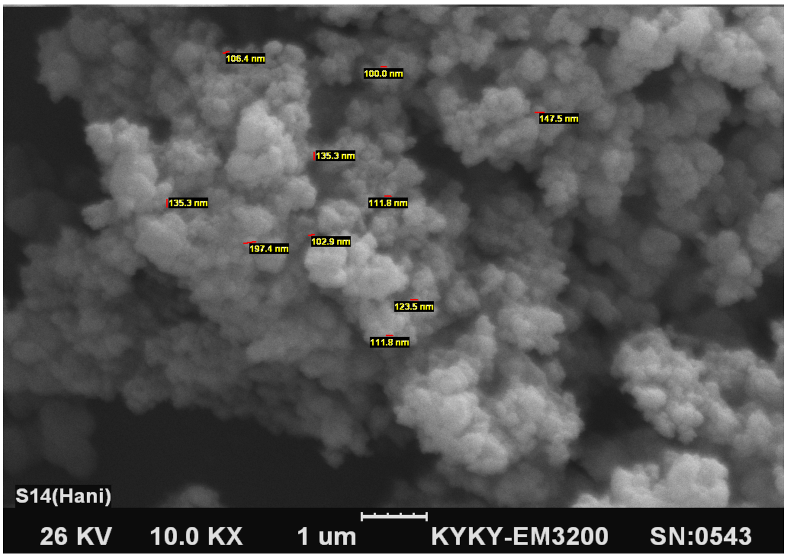

Fig. 6. Scanning electron micrograph of PPy/PvAc in aqueous/non-aqueous media with hydroxyl propyl cellulose surfactant

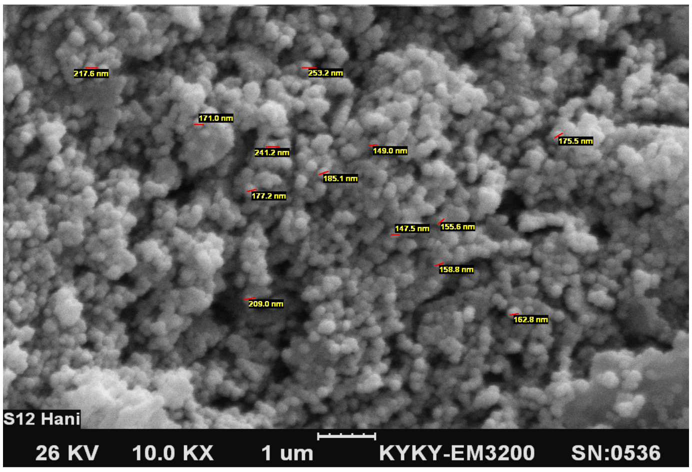

Fig. 7.Scanning electron micrograph of PPy/PvAc in aqueous/non-aqueous mediawith(DAdAc)surfactant

CONCLUSION

In this work the characteristics of PPy/PVAc copolymers, such as conductivity, morphology and particle size, were investigated in aqueous/non-aqueousmedia. The SEM micrographsshow that the type of surfactant play a major role on the surface morphology and homogeneity of particles. The structure of productswas determined by FTIR spectrum. By comparison FTIR spectra between pure PPyand copolymers, the copolymers have additional bands. All these bands indicate the formation of copolymers.

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