



Morphological and electrical conductivity properties of unsubstituted polythiophene nanostructures prepared by surfactant-assisted chemical polymerization method

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Abstract: Unsubstituted polythiophene (UPT) nanostructures were successfully prepared via soft template oxidative polymerization method using SDS, TTAB and Triton X-100 as anionic, cationic and nonionic surfactants respectively. During the polymerization, unsubstituted thiophene monomer was polymerized into unsubstituted polythiophene at the presence of surfactants and which confined the polymerization of thiophenes into low dimensional nanostructures. The synthesized UPT samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Field emission scanning electron microscopy (FE-SEM) and High resolution-transmission electron microscopy (HRTEM). Also electrical conductivity of the UPT samples checked by standard four-point probe method. The effects of different surfactants on the morphology and electrical conductivity of UPT were studied and compared. FTIR spectroscopy confirmed the incorporation of surfactants into UPT. FESEM and HR-TEM studies proved that the surfactants affected the morphology of final products. Additionally, SDS was found capable of increasing the electrical conductivity of UPT.

Keywords: Unsubstituted polythiophene, Surfactants, Morphology, Electrical conductivity.

1. Introduction

The great work to get metallic levels of conductivity in doped polyacetylene films was published by Shirakawa et al (1977) sparked the interest in conducting polymers [1]. Synthesis and characterization of conducting polymers rapidly expanded in the mid-1980s [2-7]. At this time researchers achieved metallic range of conductivity in many conjugated polymers by doping. Optical non linearly were also thoroughly analyzed to use conjugated polymers in modulators and optical switches. The conjugated polymers were well examined for the application in organic field-effect transistors [8-9]. In organic field effect transistor, polythiophenes can be used as a channel between the two electrodes. Unsubstituted and substituted polythiophene both have been widely studied due to their potential application in organic electronics field [10-11]. High conductivity is achieved in polythiophene by $\alpha - \alpha$ linkages. The first chemical synthesis of polythiophenes was published in 1980 using dibromo thiophene as a monomer [12]. A wide range of alky and alkoxy-substituted polythiophenes with high solubility were prepared using the various synthetic approaches. Water-soluble polythiophenes with propionic acid group was reported by McCullough et al [13-14]. However, the synthetic procedures of substituted polythiophenes are quite complex owing to the intolerance of the functional group of monomer to the synthetic conduction. One of the alternative way for enhancing physical and chemical properties of UPT is to synthesis UPT in the presence of suitable surfactants. Recently some researchers reported the effect of various surfactants on the electrical properties of conjugated polymers [15-16]. Colloidal solubility and processibility also improved for the conjugated polymers by adding required surfactants during polymerization

[17]. Jaroslov stejskal et al indicated that locus and the course of polymerization can be altered by the presence of surfactant micelles, and the incorporation of surfactants has greater effect on the structure and conductivity of the conducting polymers [18]. By using this soft template synthesis or self assembly method, surfactant micelles were employed to confine the polymerization to produce various nano structures of conducting polymers [19]

We present here a soft template chemical oxidative synthesis of Unsubstituted polythiophene (UPT) nanostructures with various morphology using SDS, TTAB, and Triton X-100 as anionic, cationic and non-ionic surfactants respectively. To compare the properties, UPT nanomaterial prepared without surfactants also. The structure, morphology and electrical conductivity of the UPT samples were thoroughly investigated using XRD, FT-IR, FE-SEM, HR-TEM and four probe conductivity methods.

2. Materials and Methods

2.1. Materials

Thiophene monomer (Sigma – Aldrich) was purified by distillation at reduced pressure and stored in the refrigerator before use. Chloroform (Merk), the oxidant ferric chloride (FeCl_3 , Merk), and all the surfactants: Sodium dodecyl sulfonate (SDS, Fluka), Tetra decyltrimethyl ammonium bromide (TTAB, Fluka), Poly (ethylene oxide) (10) iso – octylphenyl ether (Triton X-100, Fluka) were used as received without further purification.

2.2. Characterizations

Rigaku X – ray diffractometer (XRD) was used to analyze the crystalline nature of UPT samples. Using JASCO 460 plus FTIR spectrometer, the functional groups of UPT samples were confirmed by recording Fourier transform infrared (FTIR) spectrum in the range of $4000 - 400\text{cm}^{-1}$. Morphologies of the synthesized samples were observed by field – emission scanning electron microscope (FE-SEM, SUPRA55) and high resolution transmission electron microscope (HRTEM, JEOL 3010). Standard four- point probe method (RT-70, Jandel) was used to determine the electrical conductivity of pelletized nano scale UPT samples at room temperature.

2.3. Synthesis

The UPT nano scale samples were prepared via in situ chemical oxidative polymerization using thiophene as a monomer. Anhydrous FeCl_3 was used as the oxidant. SDS, TTAB and Triton X-100 were chosen as anionic, cationic and non-conic surfactants respectively. The reaction was carried out in a 500 ml round-bottomed flask equipped with magnetic stirring bar. In a typical polymerization, 0.01mol of thiophene and 0.001mol of surfactant was dissolved in 100ml of chloroform in the round-boltomed flask and stirred for 20 min. Subsequently, 0.05mol of anhydrous FeCl_3 dissolved in 150ml of chloroform was added drop wise into the above solution under stirring. The reaction mixture was stirred for 24 h at room temperature. The brown UPT precipitate was filtered and washed thoroughly with methanol and double distilled water and then dried at 60°C for 24h in a vacuum oven. The UPT smaple without surfactant was synthesized by a similar procedure in the absence of surfactant.

3. Results and Discussions

3.1. XRD

The crystalline orientation and the degree of crystallinity can be determined with the help of XRD. In general, nano scale in the thickness direction was reported as a crystallite size of conducting polymers. The molecular order and crystallinity of the conducting polymers are chiefly characterized by diffraction of X-rays where scattering angle of incident X-rays highly related with spacing between molecular layers. The power XRD spectra of UPT and surfactants incorporated UPT are shown in Fig. 1(a-d). In the XRD spectrum of pure UPT, It is observed that a broad pack reflection at 21.5° . This peak broadening shows that polythiophene crystallites are very small with a large surface to volume ratio. After incorporating with surfactants (SDS, TTAB, Triton X-100), this peak was found to have shifted. UPT-SDS was shifted to 23.5° . UPT-TTAB was shifted to 23° and

UPT-Triton X -100 was shifted 21.3° . These shiftings show the modification of crystalline structure after doping. Already such kinds of shiftings have been reported in the literature [20]. The combination of chain to chain stacking structure and amorphous nature was revealed by XRD for UPT and surfactants incorporated UPT.

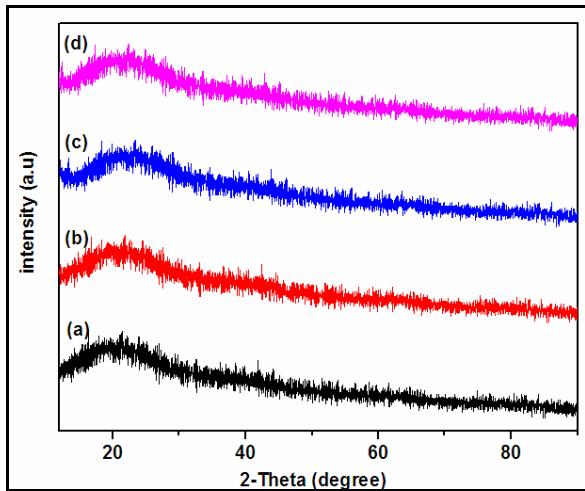


Fig. 1. XRD pattern of (a) UPT, (b) UPT-Triton X-100, (c) UPT-SDS, (d) UPT-TTAB

3.2. FTIR

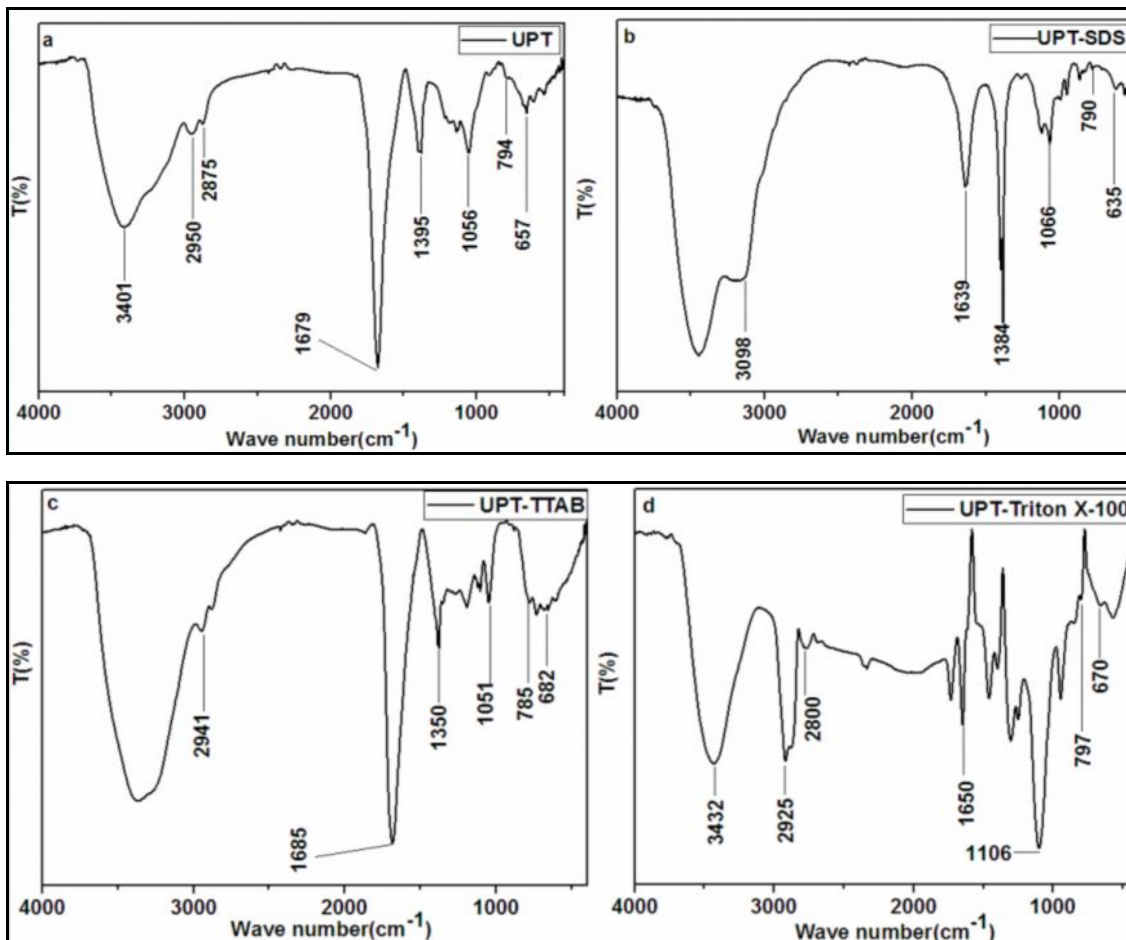


Fig. 2. FTIR spectra of (a) UPT, (b) UPT-SDS, (c) UPT-TTAB, (d) UPT-Triton X-100

The vibronic techniques are generally used to investigate the structure of polythiophene and its derivatives. FTIR is more useful tool for the characterization of vibrational structure of conducting polymers.

Information and identification of functional groups can be known from FTIR spectra. FTIR spectra of UPT and UPT prepared in the presence surfactants were taken from the pellets which were made from powdered UPT samples in KBr. The infrared spectra of UPT and surfactant incorporated UPT samples in the region from 4000 to 400 cm^{-1} are shown in Fig. 2(a-d). The FTIR spectra of UPT exhibited all the characteristic peaks. In Fig. 2a, the peaks in between 3100 cm^{-1} and 2800 cm^{-1} indicate C-H stretching mode vibrations. The peak at 1395 cm^{-1} belongs to C=C characteristic vibration of UPT. The peak around 1056 cm^{-1} was attributed to the C-H in plane deformation. Whereas the peaks at 794 cm^{-1} and 657 cm^{-1} were attributed to C-H out of plane deformation and C-S stretching vibrations respectively. UPT samples prepared in the presence of surfactants (SDS, TTAB, Triton X-100) also display the characteristic bands of polythiophene with shifting. The doping process of surfactants leads to dramatic changes in the vibrational structure of UPT.

3.3. FE-SEM

The morphology of various UPT samples prepared by soft template method was probed using Field Emission Scanning Electron Microscope (FE-SEM). Comparison of the various morphologies based on three different surfactants has shown that the type of surfactant is a key factor for controlling the morphology of UPT. In the FE-SEM, a high energy electron beam is inelastically scattered when it strikes the surface of a solid sample. Now the signals from the sample are collected and amplified to form an image. FE-SEM micrographs of various UPT samples prepared in the presence and absence of surfactants are shown in Fig. 3(a-d). The morphology of UPT varied much with different surfactants. The FESEM study of UPT without any surfactants reveals the presence of globular particles (Fig.3a) with a particle size range of 150-200 nm. UPT nanostructures with regular nanofiber morphology were prepared using SDS as surfactant, whose thickness falls in the range of 50-80 nm (Fig.3b). But, the UPT sample with highly irregular bulk nano fibrillar morphology was obtained using TTAB as surfactant (Fig. 3c). Using Triton X-100 as surfactant leads to the formation of somewhat spherical UPT nanoparticles with the diameter of 100-150 nm.

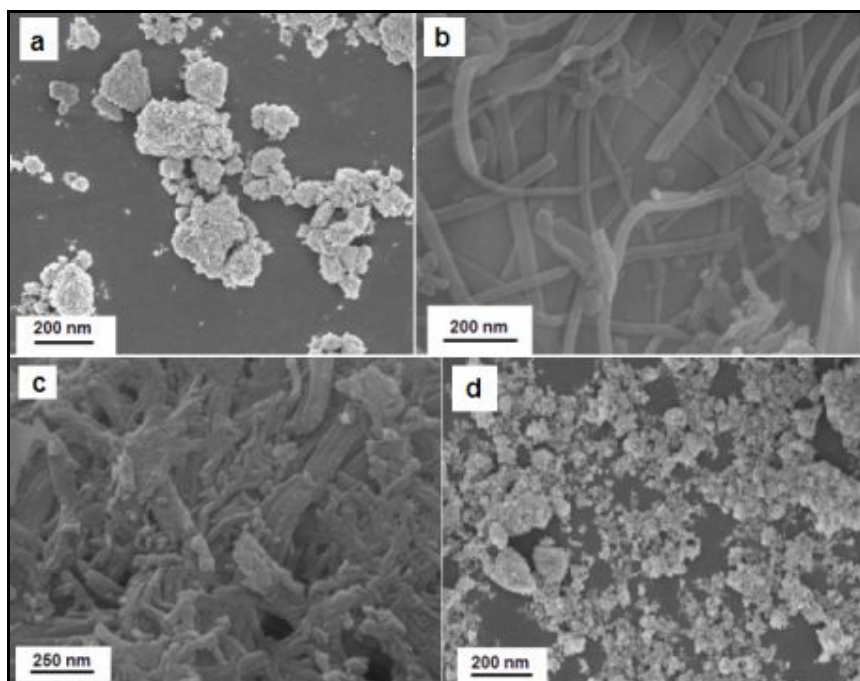


Fig. 3. FE-SEM images of (a) UPT, (b) UPT-SDS, (c) UPT-TTAB, (d) UPT-Triton X-100

3.4. HR-TEM

One of the importances of soft template synthesis method is their efficiency to create extremely small size conducting polymer nanostructures with various morphologies. Direct imaging of individual nanostructures can be achieved only by using TEM. It can provide a real space image of nanoscale conducting polymers. High resolution transmission electron microscopy (HR-TEM) images of UPT samples are shown in Fig. 4(a-d). The combination of nano fibrillar and globules structures were synthesized by the chemical oxidative polymerization method without using any surfactants (Fig. 4a). UPT nanofibers and nano fiber networks have

also been obtained by the presence of SDS and TTAB respectively (Fig.4b and c). The approximate thickness of PT-SDS nanofiber is around 29nm. The aggregated spherical UPT nanostructures with diameter of around 30nm were also prepared in the presence of Triton X-100 (Fig.4d). HR-TEM studies clearly showed that UPT nano fibers are naturally formed during the polymerization of thiophene. The morphological results from FE-SEM and HR-TEM show that the type of surfactant strongly affects the final morphology of UPT.

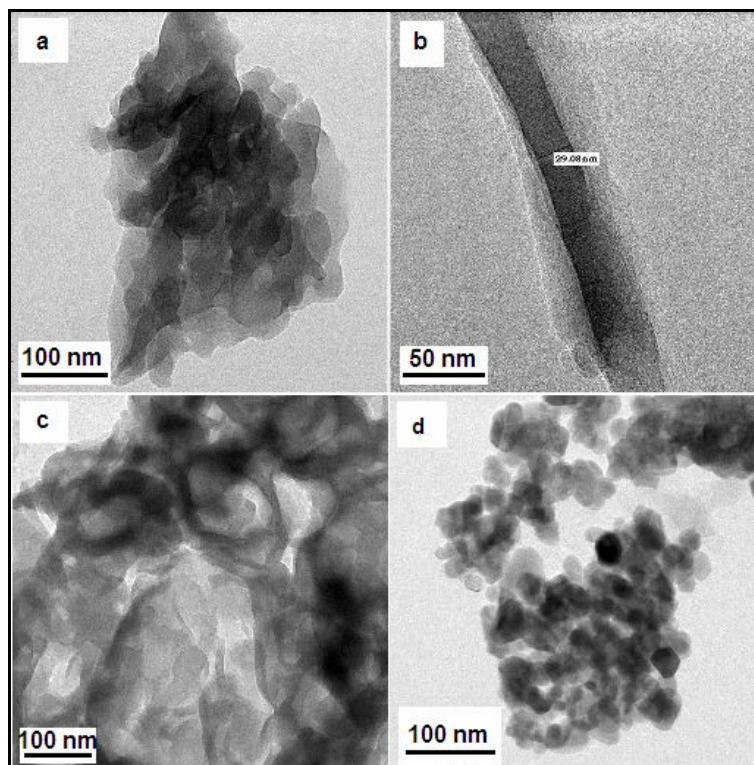


Fig. 4. HR-TEM images of (a) UPT, (b) UPT-SDS, (c) UPT-TTAB, (d) UPT-Triton X-100

3.5. Electrical Conductivity

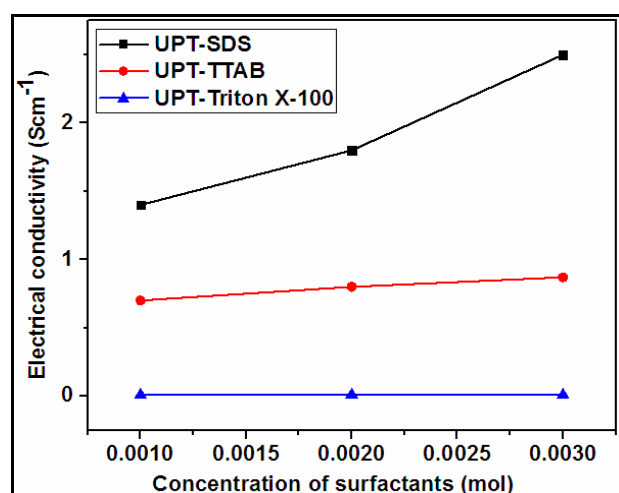
Electrical conductivity of the UPT nano scale samples in pellet form was measured by four probe method. These measurements showed that electrical conductivity of the UPT samples are influenced by the concentration and types of surfactants used during polymerization. Fig.5 shows the effect of concentration of the surfactants on the electrical conductivity of UPT samples at room temperature. There is a significant effect of the presence of SDS on the electrical conductivity of UPT. On the contrary, there is no positive effect of TTAB and Triton X-100 on the conductivity of UPT (Table. 1 and 2). By increasing the concentration of SDS from 0.001 to 0.003 mol, the conductivity increases up to 2.5 from 1.4 Scm^{-1} . The electrical conductivity reached a maximum of 0.87 Scm^{-1} only for the UPT sample prepared at the presence of 0.003mol TTAB. However, electrical conductivity slightly decreased for the sample UPT-Triton X-100 at all the concentrations (0.001 to 0.003mol) of Triton X-100 (Table 2). In Fig. 5, concentration of surfactant is found as a critical factor affecting electrical conductivity of UPT. From the above measurements, it can be noted that optimal doping of SDS would be the best way for preparing UPT with high conductivity. Such kinds of variations in conductivity of UPT samples are the reflection of change in morphology produced by the presence of different types of surfactants.

Table 1: Effect of surfactants (at 0.001 mol) on electrical conductivity of UPT

Samples	Electrical conductivity (Scm^{-1})
UPT	0.5
UPT-SDS	1.5
UPT-TTAB	0.7
UPT-Triton X-100	0.00875

Table 2: Electrical conductivity of UPT samples at different concentration of surfactants

Samples	Concentration of surfactants	Electrical conductivity (Scm^{-1})
UPT-SDS	0.001 mol	1.4
UPT-SDS	0.002 mol	1.8
UPT-SDS	0.003 mol	2.5
UPT-TTAB	0.001 mol	0.7
UPT-TTAB	0.002 mol	0.8
UPT-TTAB	0.003 mol	0.87
UPT-Triton X-100	0.001 mol	0.00875
UPT-Triton X-100	0.002 mol	0.00865
UPT-Triton X-100	0.003 mol	0.00825

**Fig. 5. Comparison of electrical conductivity of surfactant incorporated UPT samples**

4. Conclusions

In summary, UPT and various types of surfactants incorporated UPT nanoscale samples were successfully synthesized by oxidative polymerization method. XRD study confirmed $\pi - \pi$ stacking structure of UPT. FTIR analyses suggest the interaction between surfactants and UPT. Characteristic functional groups of UPT were also confirmed by FTIR spectroscopy. FE-SEM and HR-TEM results indicated that type of surfactants played a significant role in control over the morphology of UPT. The morphology of UPT could be controlled as globular, fibers, and spherical particles by changing the type of surfactants. We have demonstrated that the modification in structure brought on by the incorporation of different types of surfactants can have a profound effect on the electrical conductivity of the resultant UPT sample. It was also found that the UPT nano scale sample prepared with SDS exhibited fibril like structure, resulting in higher electrical conductivity than other samples.

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