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Comparison of Properties and Quartz Crystal Microbalance Measurements of Poly(2-ethylaniline) in the Presence of Surfactants

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Poly(2-ethylaniline)(P2EANI) films were chemically deposited onto gold electrodes using ammonium persulfate as oxidant in the presence of the surfactants sodium dodecyl sulfate (SDS, anionic), tetradecyltrimethylammonium bromide (TTAB, cationic) and polyoxyethylene octyl phenyl ether (Triton-X 100, non-ionic). The doping and adsorption effects of surfactants onto the properties of P2EANI, were correlated with mass gain, and were determined *in situ* during polymerization of 2EANI using quartz crystal microbalance (QCM). The frequency shift of P2EANI in the presence of Triton-X 100 was very sharp and fast. TTAB exhibited the lowest frequency and mass shift among the three surfactants. P2EANIs were characterized using FTIR and UV-visible spectroscopies, TGA, conductivity measurements and SEM analysis. The latter technique showed that the polymer morphology is, as expected, affected by the incorporation of surfactants into the polymer.

Keywords: Polymers, chemical synthesis, FTIR, SEM, electrical conductivity

1 Introduction

Conducting polymers such as polyaniline (PANI), polythiophene, polypyrrole and their derivatives have been known for many years (1–5). They have many applications in battery electrodes, electrochromic devices, photoelectric cells, light-emitting diodes and biosensors (6). Polyaniline (PANI) is one of the most investigated intrinsically conducting polymers owing to its easy synthesis, environmental stability, controllable electrical conductivity, unique doping/dedoping chemistry (7); however, PANI has limited solubility. The synthesis of derivatives can, however be used to modify solubility properties of PANI (8–9). Recently, numerous works were done to improve the processibility of conducting polymers (10–12). The solubility can be improved by the synthesis of nano-to micro-scale PANI particles, which are easier to disperse in a polymer matrix, or by using an emulsifier which enhances solubility or film formation. Recently, anionic, cationic and non-ionic surfactants have been used as dopants or additives. The surfactant molecules can provide a hydrophobic micro-effect

with controlled electrochemical catalysis, effects of orientation and solubilization, and greatly improved quality of polymer films. The properties of polyaniline and polypyrrole in the presence of different surfactants were investigated by Maria et al. (13–14), and those of polythiophene by Gok (Uygun) et al. (15). These studies have shown that the surfactants have a marked effect on the polymerization conditions, kinetics, and polymer properties to an extent which depends on the type of surfactant. Therefore, the interaction between polymer and surfactant, which is still not clear, needs to be elucidated in order to develop useful materials.

The quartz crystal microbalance (QCM) has a wide range of applications in biochemistry, analytical chemistry, and other fields (16–18). The formation of polypyrrole films doped with various multiple naphthalene sulfonate anions was examined by Suematsu et al. using QCM (19). The QCM technique was used to monitor the aniline oxidation and to study PANI film formation by Ayad et al. (20). Mass changes were extracted from the shift in resonant frequency of the oscillating quartz crystal. The doping process for PANI with different strong acids and a weak acid were investigated using QCM (21). The kinetic of DBDA-doped polyaniline film formation was discussed by Zhi-hong Mo et al. (22). To date, there is no experimental work making use of the QCM technique to study the interactions of anionic, cationic and non ionic surfactants with PANI.

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In the present work, we compared the deposition rate of P2EANI in the presence of surfactants during in-situ polymerization onto the QCM electrode, and investigated the modified polymer properties using FTIR, UV-Vis, TGA, SEM and conductivity measurements.

2 Experimental

2-Ethylaniline was purified by vacuum distillation and ammonium peroxodisulfate (APS) was used as received and stored at 4°C. Sodium dodecylsulfate (SDS, anionic), tetradecyltrimethyl ammonium bromide (TTAB, cationic) and Triton-X 100 (non-ionic) (Table 1) were used as received.

SRS QCM200, 5 MHz AT-cut quartz crystal device was used in conjunction with a computer program to monitor real-time formation of P2EANI films. The mass per unit area of the P2EANI film, Δm (g/cm²), grown on the crystal surface electrode, was determined from the change in its resonance frequency. The resonance frequency decreased linearly as the mass deposited on the QCM electrode increased. The relationship between the resonance frequency change Δf (Hz) and Δm is well established by Sauerbey (23) and is given in Equation 1.

$$\Delta f = -\left(2f_0^2/(\rho_0\mu_0)\right)^{1/2}\Delta m \quad (1)$$

f_0 (Hz) is the natural frequency of the quartz crystal (5 MHz), ρ_0 is the quartz density (2.649 g/cm³), and μ_0 is the shear modulus (2.947×10^{11} dyn/cm²).

Synthesis of P2EANIs in the presence of surfactants was carried out in aqueous media by *in situ* chemical polymerization. First, 0.1 M monomer + surfactant solutions were prepared in water. Mol value of each surfactant was kept constant for each solution. The QCM electrode was dipped in the glass cell which contains the monomer+surfactant solution. The chemical polymerization was started by adding APS solution in water to the monomer+surfactant solution. The APS to monomer molar ratio was kept as 1.25 for each solution. The temperature of the reaction was kept constant at 25°C. As expected, the deposition of poly(2-ethylaniline) film on the QCM electrode resulted in a decrease of resonance frequency. After polymerization, the polymer powder was filtered and purified with distilled water. As a reference material, P2EANI without surfactants was synthesized in the same conditions.

Fourier transform infrared (FTIR) spectra of P2EANIs were recorded between 400 and 4000 cm⁻¹ with a 4 cm⁻¹ resolution from KBr pellets on a Perkin-Elmer Spectrum BX FTIR system (Beaconsfield, Buckinghamshire, HP91QA, England). The electrical conductivity of P2EANIs was measured on by a standard four-probe method using PCI-DAS6014 for a current source, a voltmeter and temperature controller. Pelletized powder

samples were made for these measurements using a steel die having 13 mm diameter in a hydraulic press under a pressure of 700 MPa.

UV-Visible spectra were recorded between 270 and 900 nm using a 1 cm path length quartz cuvette and pure NMP on a Perkin-Elmer Lambda 20 spectrophotometer.

The morphology of P2EANIs samples sputter-coated with a gold layer was characterized using SEM (Philips XL-30S FEG).

Thermal stability of P2EANIs was investigated using a Perkin-Elmer model thermal parametric analyzer (Beaconsfield, Buckinghamshire, HP91QA, England) with pure nitrogen gas at a flow rate of 20 ml/min and at 20°C/min heating rate.

3 Results and Discussion

Plots of the frequency change as a function of polymerization time of P2EANI films deposited on the QCM electrodes are shown in Figures 1 and 2. Initially, P2EANI must nucleate on the electrode surface, giving rise to a slow deposition rate for P2EANI without surfactant and P2EANI/TTAB. The deposition rate of P2EANI/Triton X 100 was found to be much faster than those of other surfactants. The deposition rate typically increases and then decreases before the frequency shift attains a steady state deposition for all P2EANI/surfactants. The decrease in the deposition rate towards the end of the deposition is due to the depletion of either the oxidant or monomer or both. During the deposition step, *in situ* doping takes place due to the surfactant, and the reduction of APS. The polymerization rate of P2EANI increased in the presence of SDS and Triton X 100 surfactants whereas, it decreased in the presence of TTAB.

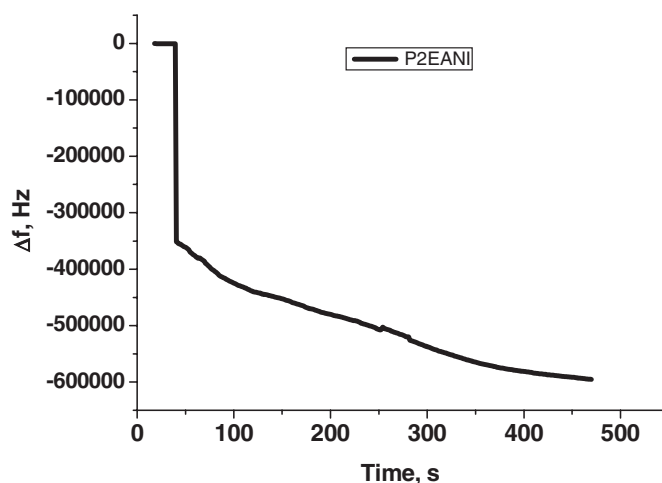


Fig. 1. Δf vs. time for P2EANI deposited in the absence of surfactants.

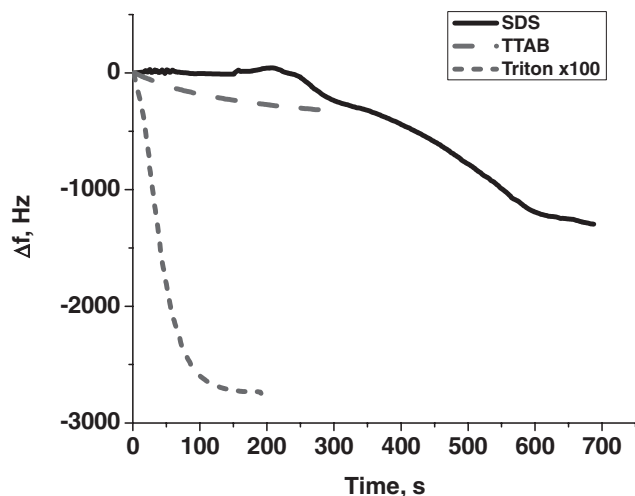


Fig. 2. Δf vs. time for P2EANI deposited in the presence of surfactants.

The frequency shifts calculated at the end of polymerization are 550, 2730, 1295 and 325 Hz for P2EANI without surfactant and with Triton X 100, SDS and TTAB surfactants, respectively, with the latter having the lowest frequency shift, presumably due to the weak interaction between TTAB surfactant and P2EANI polymer. However, the polymerization rate is lower than that of P2EANI without surfactant, which indicates that TTAB has also an effect on the polymerization. The non-ionic surfactant is less sensitive to pH than ionic ones and thus, its ability to stabilize the P2EANI should be better. Therefore, the fastest polymerization was observed in the presence of Triton X 100. The frequency shift of P2EANI/Triton X 100 is higher than that of PANI polymerized in 0.1 M H_2SO_4 (20). P2EANI/SDS has the lowest deposition rate and the polymerization reaction time is longer than those of others. The anionic SDS hydrophilic region neutralizes the P2EANI positive charge leading to an association between the hydrophobic region and the polymer chain.

Figures 3 and 4 show the plots of Δm vs. time for P2EANI films obtained in the same experimental conditions for the three surfactants. It can be seen that Δm increases with increasing polymerization time and reaches a maximum value after approximately 150, 100, 175 and 600 seconds for P2EANI (without surfactant), P2EANI/Triton X 100, P2EANI/TTAB and P2EANI/SDS, respectively. The highest mass increase is obtained for the non-ionic surfactant during the shortest polymerization time.

Figure 5 shows the FTIR spectra of P2EANI with and without surfactants. All spectra have the major characteristic vibrational bands of P2EANI at 3445–3448, 1593–1622, 1486–1505, 1206–1225 cm^{-1} (24). The peaks at 3445–3448 cm^{-1} are due to N-H vibration and deformation. The ring stretching of N=Q=N (Q denoted quinone ring) and N-B-N (B denoted benzene ring) forms appear at 1593–1622 and 1486–1505 cm^{-1} respectively. The C-N stretching

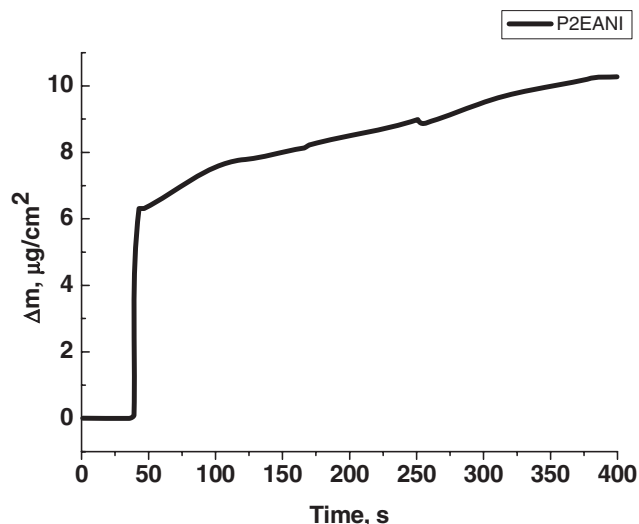


Fig. 3. Δm vs. time for P2EANI deposited in the absence of surfactants.

band of amine appears around 1200 cm^{-1} (8). The FTIR spectrum of P2EANI-TTAB exhibits additional bands at 2919 (sharp), 2850, 3016 (weak), 966 and 720 cm^{-1} due to the presence of TTAB in the polymer structure. The presence of non-ionic Triton X-100 surfactant decreased the intensities of 3446 and 2900 cm^{-1} bands in the spectrum of P2EANI, however, a new band appears at 1103 cm^{-1} . Additionally, the spectrum of P2EANI-SDS exhibits bands at 3225, 990 and 910 cm^{-1} (sharp) due to SDS (5). Moreover, the wavenumbers of the benzenoid and quinoid bands of P2EANI have shifted to different values due to the interaction between the surfactant and P2EANI. Therefore, the FTIR results, just as in the case of the QCM results, have confirmed the different effects of surfactants on the materials properties.

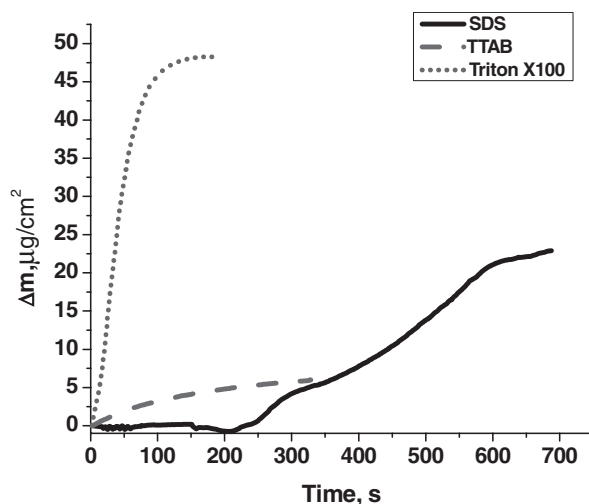


Fig. 4. Δm vs. time for P2EANI deposited in the presence of surfactants.

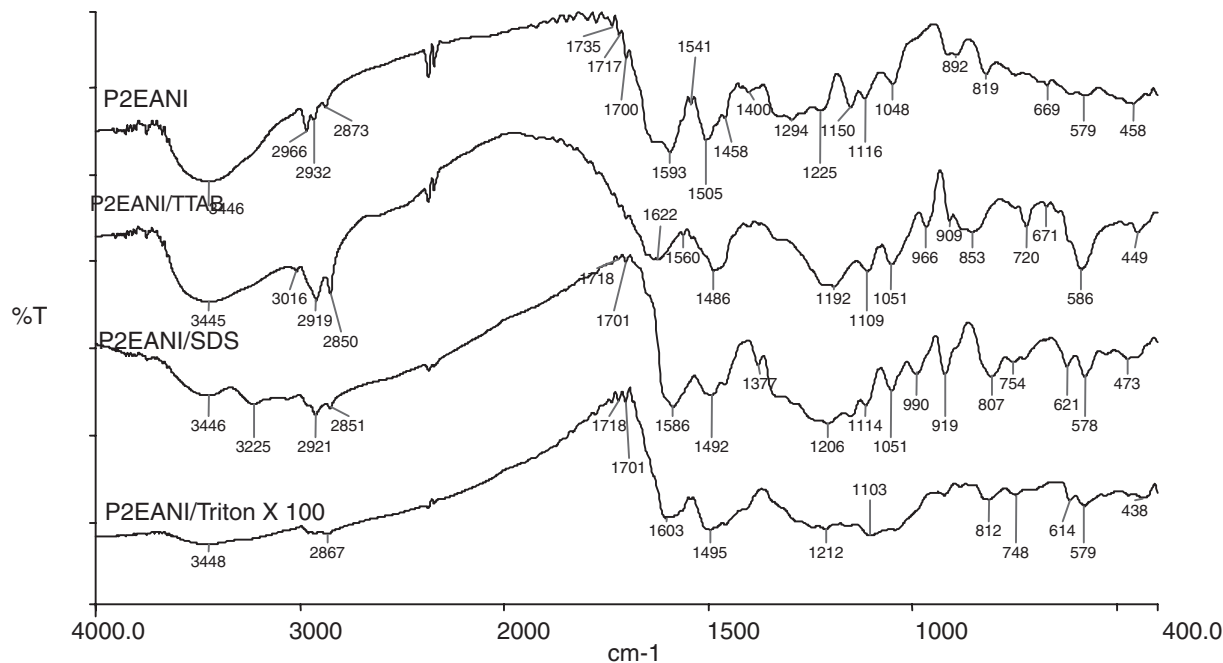


Fig. 5. FTIR spectra of P2EANI samples.

UV-visible spectra of P2EANIs in NMP exhibit two characteristic absorption bands at 305–325 and 555–620 nm (Fig. 6). The first absorption is due to the excitation of the nitrogen in the benzenoid segments ($\pi-\pi^*$ transition) while the second ($\rightarrow \pi^*$) is ascribed to the polaron/bipolaron transition (8, 1) that occurs in doped P2EANI. The characteristic bands have the highest maximum absorbance and wavelength values for P2EANI and P2EANI/TTAB, indicating more conjugated structures

than those of P2EANI-SDS and P2EANI-Triton X-100. Moreover, these results have been confirmed by the conductivity values. P2EANI and P2EANI-TTAB have higher conductivity values (6.3×10^{-4} and 1.3×10^{-4} S/cm) than those of P2EANI-SDS and P2EANI-Triton X-100 (3.6×10^{-5} and 6.9×10^{-5} S/cm).

TGA curves of P2EANIs are given in Figure 7. P2EANIs have different thermal properties due to the presence of surfactant materials. P2EANI and P2EANI-Triton X-100

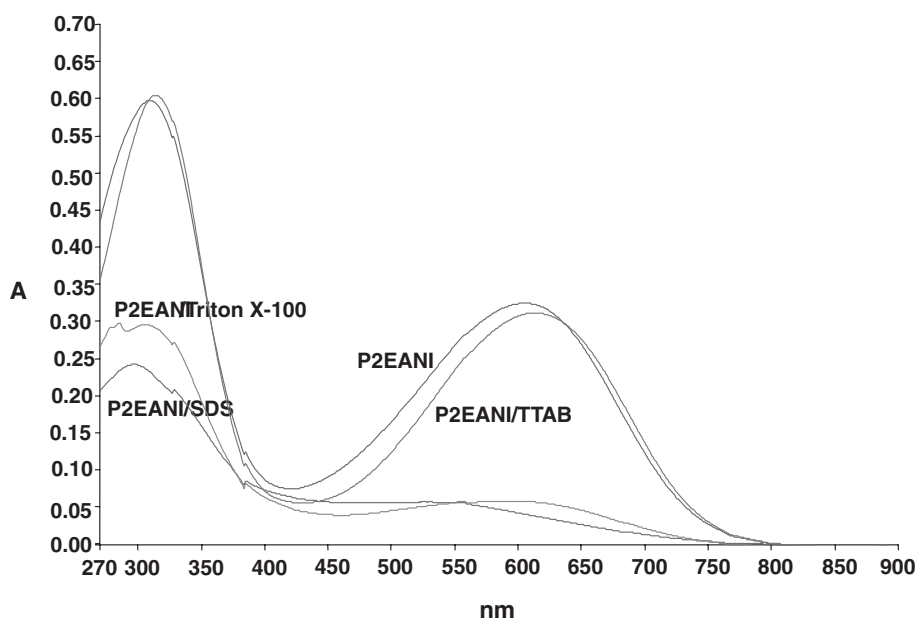


Fig. 6. UV-visible spectra of P2EANI samples.

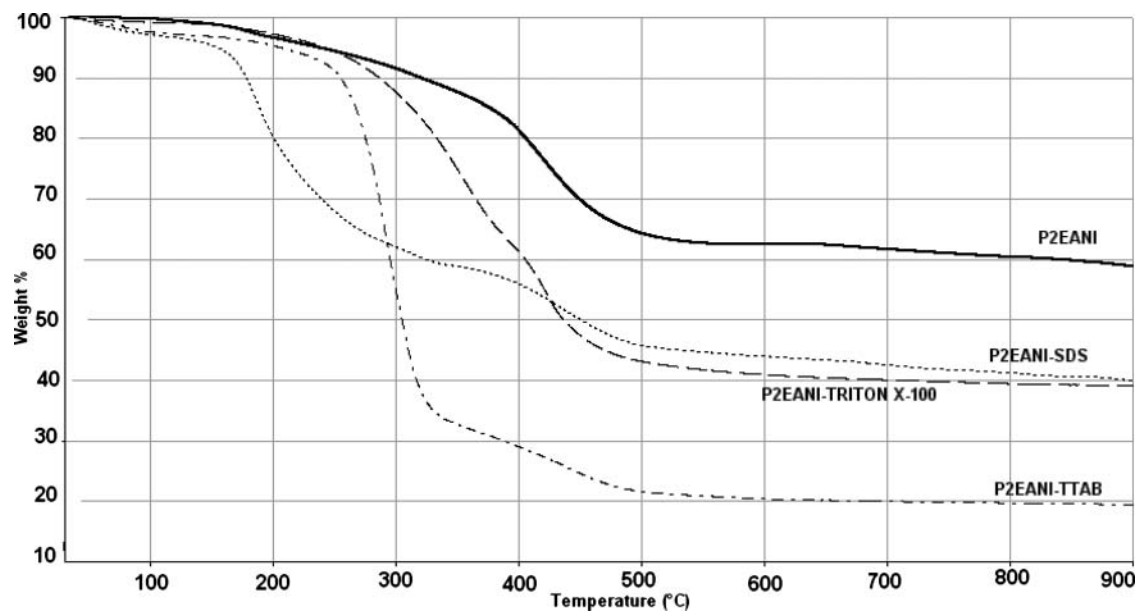
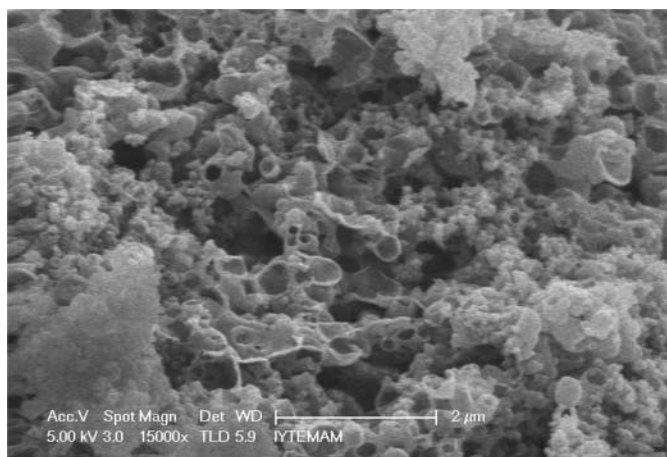
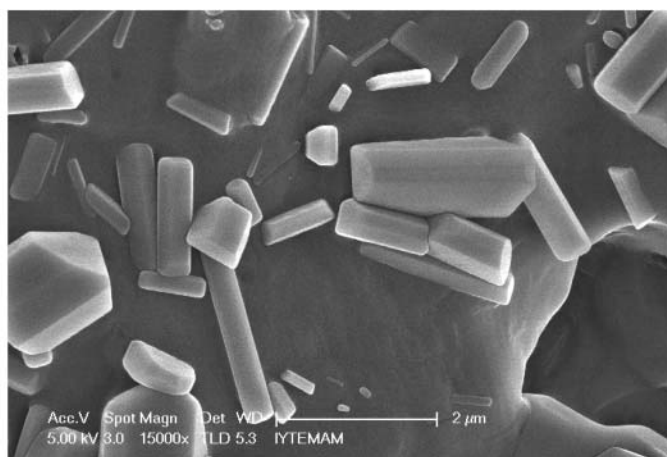


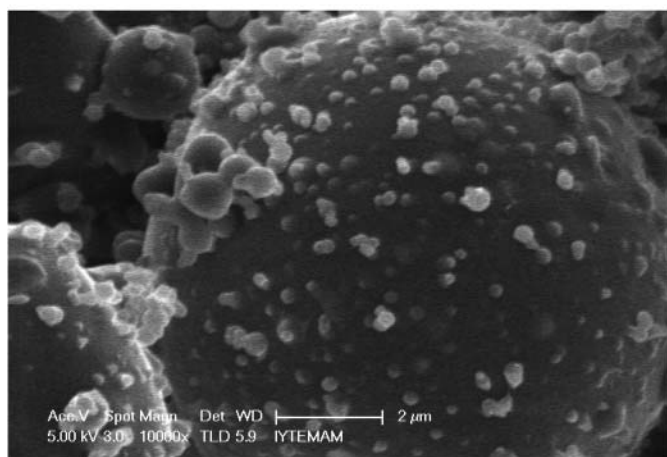
Fig. 7. TGA curves of P2EANI samples.



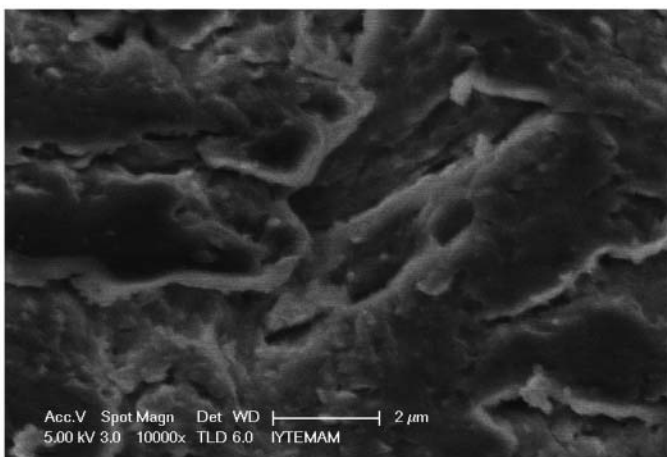
(a)



(b)



(c)



(d)

Fig. 8. SEM micrograph of P2EANI (a), P2EANI/TTAB (b), P2EANI/SDS (c), P2EANI/Triton X-100 (d).

are quite stable until 150°C whereas, P2EANI-SDS and P2EANI-TTAB suffer a low weight loss (5%) towards 150°C. All samples follow a one-step decomposition profile due to degradation of the polymer backbone (6). Based on our data, the thermal stability (T_i : initial degradation temperature) is in the following order:

$$T_i(\text{P2EANI}) > T_i(\text{P2EANI} - \text{TritonX} - 100) > T_i(\text{P2EANI} - \text{TTAB}) > T_i(\text{P2EANI} - \text{SDS}).$$

P2EANI-SDS has the lowest initial decomposition value with 180°C whereas P2EANI-TTAB has the lowest residue amount (20%).

Figure 8(a-d) shows SEM images of P2EANI samples where each surfactant yields a different morphology: shell-like structure (P2EANI), spherical structure (P2EANI-SDS), a mix of seemingly crystalline parts onto platelets (P2EANI-TTAB) and broken disordered layers (P2EANI-Triton X-100).

4 Conclusions

Our results indicate that the polymerization of poly(2-ethylaniline) in the presence of different bulky surfactants, such as SDS, TTAB and Triton X-100, leads to deposition of P2EANIs having specific properties that are surfactant dependent. Moreover, the polymerization was shown to proceed without addition of an acid, and at low temperatures. QCM results have shown that each surfactant results in different kinetics with P2EANI and P2EANI-TTAB having different polymerization times, Δf and Δm changes in the QCM results. Thus, their electrical and optical absorption characteristics are very close to each other but different from those of P2EANI-SDS and P2EANI-Triton X-100. The highest and lowest polymerization rates were found in the presence of Triton X-100 and SDS surfactants respectively due in part to their effect on the polymerization induction period.

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