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In situ chemical oxidative polymerisation for ordered conducting polythiophene nanostructures in presence of dioctyl sodium sulfosuccinate

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Polythiophenes (PTs) have been synthesized by chemical oxidative polymerization of thiophene in the presence of an anionic surfactant dioctyl sodium sulfosuccinate (AOT) using ferric chloride as an oxidant in chloroform solvent. Different monomer/surfactant ratios have been employed to study the effect of surfactant on synthesis and properties of polythiophenes. The PTs have been characterized by FT-IR spectroscopy, wide-angle powder X-ray diffraction and elemental analysis. The properties of PTs prepared using AOT surfactant have been compared with those of PT synthesized without surfactant. Four probe electrical conductivity measurements of the samples reveal that the conductivity is in the range of $(7.4–1.0)\times10^{-3}$ S cm^{-1} for AOT doped polythiophene samples. The band gap of the polymers determined from diffuse reflectance spectroscopy is in the range of 2.25–2.50 eV. Scanning electron microscopic images of the samples exhibited spherical nanoparticle morphology with size in the range of 800 ± 50 nm.

Keywords: Polymerisation, Chemical oxidative polymerisation, Polymers, Conducting polymers, Polythiophenes, Anionic surfactants

Research on conducting polymers has been extensive for the last three decades mainly due to many advantages they possess over conventional metal and inorganic based systems like flexibility, lightweight, tunable conductivity, optical properties and so on [1-9]. Conducting polymers possess electrical properties as a result of the delocalization of electrons along the polymer backbone. Some of the exclusively studied conducting polymers are polyacetylene, polythiophene, polyaniline, polyphenylene, polyphenylenevinylene and polypyrrole[4-7]. Polythiophene and its derivatives have the added advantage of good thermal and environmental stability. Polythiophenes find potential application in light-emitting diodes, polymer, electrodes, thermochromic devices, sensors, solar cells and transistors[5-9]

Polythiophene is synthesized mainly by three methods: (1) electrochemical polymerization, (2) metal-catalyzed coupling reactions, and (3) chemical oxidative polymerization[9-20]. Good quality polythiophene can be synthesized directly on the electrode by electrochemical polymerization. However, the synthetic parameters which depend on many factors such as concentration, dopants, solvents, cell geometry, and current-voltage characteristics should be optimized[5,9-11]. McCollough *et al.*[12,13] reported the synthesis of regioregular polyhexyl thiophene which has remarkable electronic and photonic properties.Yamamoto *et al*.[14] reported the polycondensation of 2, 5-dibromothiophene catalyzed by Ni(bipy)Cl_2. Similar results were also observed by Lin and Dudek[15] in their Ni, Pd, Co, and Fe catalytic system. In 1984, Yoshino *et al.*[16] found unsubstituted thiophene could be polymerized by ferric chloride in chloroform. They also explored polymerization of hexylthiophene with metal halides like Fe(III), Mo(V) and Ru(III). Direct chemical oxidative polymerization of thiophene and alkylated thiophene with ferric chloride has been reported[17-20]. *In situ* chemical oxidative polymerization is the one method for producing electrically conducting polymer backbone, since electrons removed during oxidation were replaced by charge carriers like polarons or bipolarons and the electrical charge created was neutralized by dopants[5,6].

Chemical oxidative polymerization of thiophene and its derivatives in the presence of anionic surfactant have not been studied in detail. Therefore, in the present investigation, thiophene is polymerized using ferric chloride via oxidative route in presence of AOT as a anionic surfactant. Synthetic optimization and understanding the mechanism of formation of such chemical oxidative route in presence of anionic surfactant are crucial for the polymer nanocomposite preparation and other applications. The synthesized conducting polythiophenes were characterized by FT-IR and elemental analysis. Powder X-ray diffraction of the polymer nanomaterials showed an enhancement in the solid state ordering with increase in surfactant concentration. The scanning electron microscopic studies revealed that spherical particle morphology of polythiophene. The four probe electrical conductivity measurement of the samples revealed the conductivity in the order of 10^{-3} S/cm. The band gaps of the polymer were determined by the UV-visible diffuse reflectance studies.

Experimental

Thiophene, dioctyl sodium sulfosuccinate (AOT), ferric chloride and ammonium persulfate were purchased from Sigma Aldrich. Solvents like chloroform, deionised water and acetone were purchased from Merck.

FT-IR spectra of the samples were recorded on a Shimadzu FT-IR spectrometer with KBr pellets in the range of 4000–400 cm^{-1}. The elemental analysis (CHNS) of the samples was recorded by Elementar Vario EL III. Powder X-ray diffraction of the samples was recorded using Anton Paar, TTK 450 diffractometer with the 2θ values ranging from 3°- 80°. For scanning electron microscopy, polymer samples were subjected to a thin gold coating and images were recorded on JOEL model JSM - 6390LV instrument. Thermogravimetric analysis (TGA) of the samples was carried out on a Perkin Elmer, Diamond TG/DTA instrument at heating rate of 10 °C per min. Conductivity was measured using Kiethley 6221 DC and AC current source and 2191A nanovoltmeter. The resistance of the samples was measured at five different positions. Diffuse reflectance spectra of the samples were recorded on a Varian, Cary 5000 UV-visible spectrometer using an external DRA 2500.

For the synthesis of PT-0, the monomer:surfactant ratio for PT-0 was kept as 1:0. Thiophene (1 mL, 12.5 mmol) was added to 20 mL chloroform and sonicated for 5 min. Ferric chloride (15.0 mmol, 2.43 g) was dispersed in 10 mL chloroform was added dropwise to the monomer solution. It was sonicated for 15 min and then stirred using a magnetic stirrer for 3 h at 30 °C. The resultant polymer was filtered and washed using water and then with acetone. The polymer was dried in vacuum oven at 60 °C. Yield = 62%. FT-IR (KBr, cm^{-1}) 1614, 1325, 1196, 1104, 1021, 784, 686; Elemental comp. : Calc. wt%: C = 44.97, S= 26.71, H= 2.89.

For the synthesis of PT-25, the monomer:surfactant ratio for PT-25 was kept as 1:1/25. AOT (22 mg, 0.50 mmol) was dissolved in 20 mL chloroform and to this solution was added thiopene (1 mL, 12.5 mmol). The above solution was sonicated for 5 min. Ferric chloride (15 mmol, 2.43 g) dispersed in 10 mL chloroform was added dropwise to the monomer solution, sonicated for 15 min and stirred using a magnetic stirrer for 3 h at 30 °C. The resultant polymer was filtered and washed first with water and then with acetone. The polymer was dried in vacuum oven at 60 °C. Yield = 62%. FT-IR (KBr, cm^{-1}) 1650, 1521, 1315, 1207, 1114, 1026, 778, 691; Elemental comp. : Calc. wt% : C=53.73,S= 31.21, H=3.74

Similar synthesis was carried out for PT-50, PT-75 and PT-100 by changing monomer surfactant ratio to 1:1/50, 1:1/75 and 1:1/100 repectively (see Supplementary data).

Results and discussion

Polythiophenes (PTs) were synthesized via the chemical oxidative polymerization route using ferric chloride as the oxidizing agent in chloroform. In the present investigation, polymerizations were carried out both in the presence and in the absence of the anionic surfactant, dioctyl sodium sulfosuccinate (Fig. 1). AOT is an anionic surfactant which has a double tail and a polar head and forms micelles in both aqueous and non-polar solvents[21,22]. Monomer/surfactant ratio was varied to study the role of anionic surfactant on solid state ordering and morphology of the nanomaterial. We have carried out the polymerization in hexane (non-polar) and aqueous (polar) medium using anhydrous ferric chloride and ammonium persulfate. No polymer formation was observed with ammonium persulfate as oxidizing agent both in aqueous and organic phase in the present conditions. Ferric chloride polymerizes thiophene in chloroform and hexane; however polymerization was effective only in chloroform. Formation of polythiophene by ferric chloride as oxidizing agent has been reported similarly in literature without surfactant or with surfactant other than AOT[16-20].

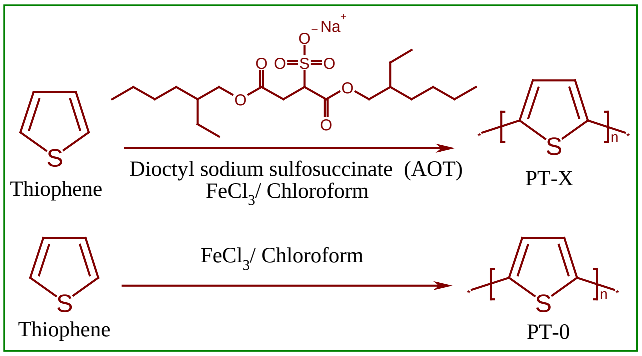

Fig. 1 – Synthesis of polythiophene using ferric chloride as oxidizing agent with and without anionic surfactant AOT.

Table 1 – Experimental conditions, yield of the product and conductivity of the polythiophene samples

Sample	Thiophene (moles)	AOT (moles)	Thiophene/AOT (Mole ratio)	Elemental sulfur (%)	Yield (g)	Conductivity (S/cm)
PT-0	0.0125	0.00000	1:0	26.71	0.6220	4.7×10^{-5}
PT-25	0.0125	0.00050	1:1/25	31.21	0.6240	7.39×10^{-3}
PT-50	0.0125	0.00024	1:1/50	31.72	0.6101	2.93×10^{-3}
PT-75	0.0125	0.00016	1:1/75	32.23	0.5173	1.93×10^{-3}
PT-100	0.0125	0.00012	1:1/100	32.51	0.3822	1.00×10^{-3}

In a typical synthesis of PT-25 (monomer: surfactant ratio [1:1/25]), thiophene was added to AOT dissolved chloroform solution by sonication. Sonication of the monomer-surfactant mixture provides stabilization of monomer-surfactant complex in solution, which acts as a soft template for polymer formation. To the monomer-surfactant mixture, ferric chloride dispersed in chloroform was added drop wise to the monomer solution. The chemical oxidative polymerization of thiophene initiated by sonication during the first 15 min and then magnetically stirred for remaining 3 h (Supplementary data, Fig. S1). The resultant brown colored polymer was filtered and washed with water to remove water soluble ions and then with acetone to remove oligomeric species. The polymer was dried in vacuum oven at 60 °C. The number of moles of the AOT used for PT-25 synthesis was lower than about 1/25 moles of the monomer. The monomer-oxidant ratio was kept as 1:2. Similarly, the synthesis of PT-50, PT-75, PT-100 were carried out by varying the thiophene: AOT mole ratio as 1:1/50, 1:1/75 and 1:1/100 respectively (see Table 1). Synthesis of polythiophene without the addition of AOT was denoted as PT-0.

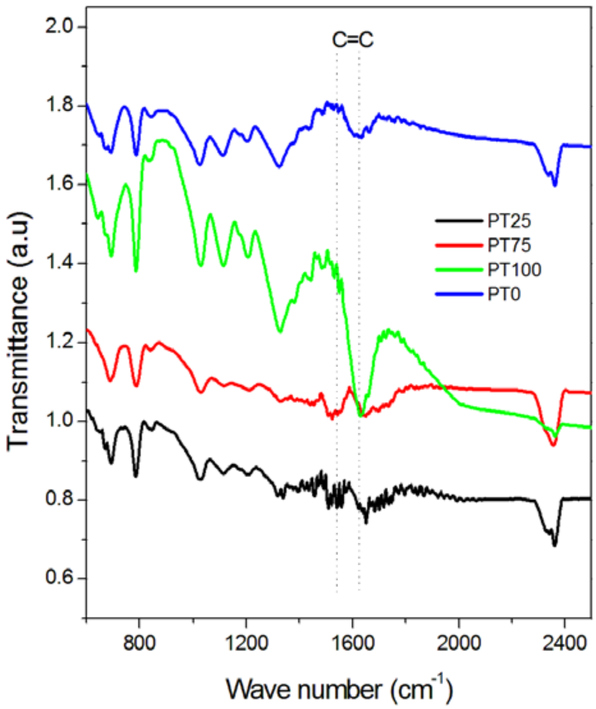

Fig. 2 – FT-IR spectra of PT-0, PT-25, PT-75 and PT-100.

FT-IR spectra of the polymer samples were recorded to confirm the formation of the polythiophene using KBr pellet method (Fig. 2). The FT-IR spectrum of PT-25 show peaks at 1628 cm^{-1}, 1526 cm^{-1}, 1325 cm^{-1}, 1211 cm^{-1}, 1025 cm^{-1}, 841 cm^{-1}, 787 cm^{-1} and 688 cm^{-1}. The strong peaks at 1628 and 1526 cm^{-1} represent asymmetric and symmetric ring stretching contribution from –C=C- and –C-C– of the thiophene rings in polythiophene. The peak at 1326 cm^{-1} is due to ring breathing. The peaks present at 1199 (w), 1112 (m) and 1025 (m) cm^{-1} are due to the C-H in plane deformations. The peaks present at 787 (m) and 688 (m) are due to C-S stretching mode and C-H out of plane deformation, respectively[17-19]. FT-IR peaks are in accordance with characteristic peaks of polythiophene. Interestingly, the carbonyl C=O and S=O peaks of AOT were missing in all the PT samples (PT-25, PT-50, PT-75 and PT-100) and their peaks observed matched with that of PT-0. The very low concentration of AOT surfactant used in PT-25, PT-75 and PT-100 may be the reason for absence of the surfactant peak. The elemental analysis of the PTs (PT-25 to PT-100) in comparison with PT-0 reveals only 5% increase in the sulfur content in these doped samples, which comes from the surfactant (see Table 1). Therefore, it is very difficult to quantify the amount of AOT present in the doped samples from the spectroscopic techniques.

The solid state ordering of the samples was analyzed by powder X-ray diffraction analysis (Fig. 3a). Polythiophene samples synthesized using AOT (PT-25, PT-50, PT-75 and PT-100) show a characteristic broad peak between 2θ values 15° and 23° and the maximum centered at 18°. This peak usually arises due to the polymer chain arrangement from amorphous domain. Interestingly, with increase in surfactant concentration (from PT-100 to PT-25) the amorphous chains become ordered, as is evident from

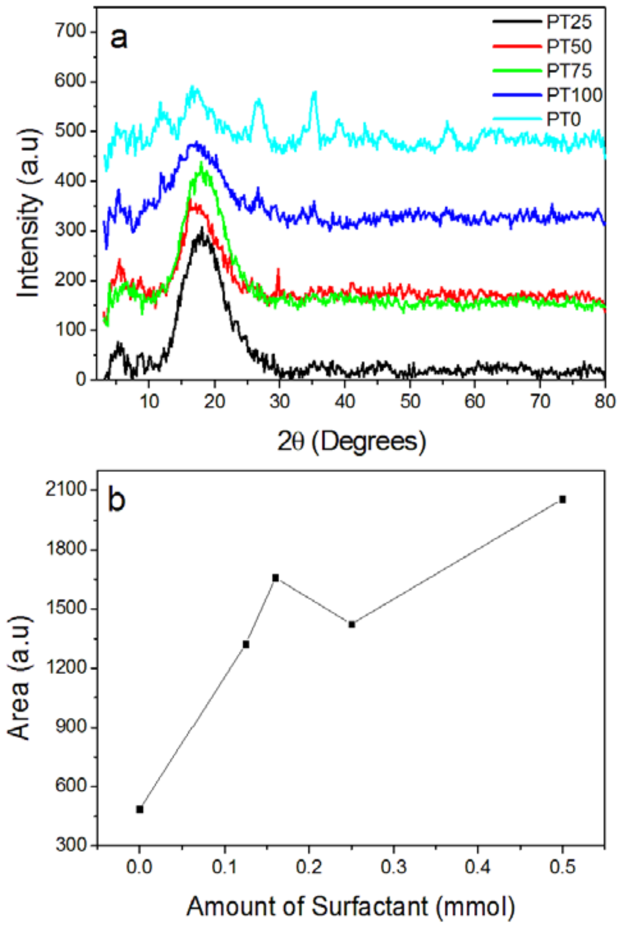

Fig. 3 – (a) Powder WXRD studies of PT-25, PT-50, PT-75, PT-100 and PT-0. (b) Plot showing peak area versus surfactant concentration.

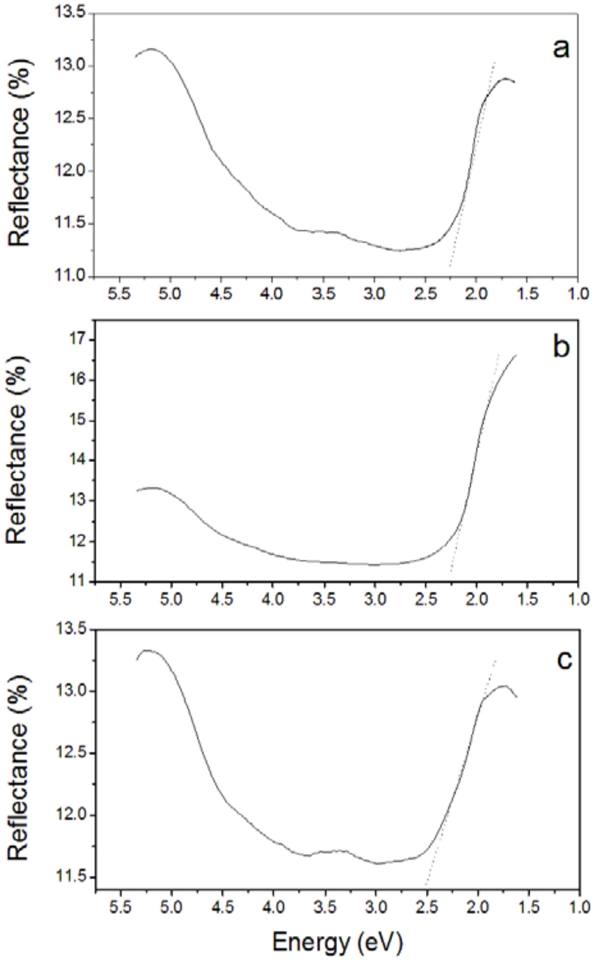

Fig. 4 – Diffuse reflectance spectra of the (a) PT-25, (b) PT-50 and (c) PT-0.

increase in sharpness and intensity of the peaks[23, 24]. Solid state ordering of the PT-0 was least intense among all the samples. X-ray diffraction studies indicate that the surfactant plays a crucial role in the ordering of the polythiophene materials. To support the above observation, peak area was calculated by Gaussian method and plotted against surfactant concentration (Fig. 3b and Supplementary data, Fig. S2). On increase in surfactant concentration from PT-100 to PT-25, peak area of the samples increased from 500 a.u to 2100 a.u. Lower angle peaks (below 10θ values) were not prominently present in the PT samples, indicating that lamellar kind of surfactant arrangement was absent. This could be due to poor doping of the AOT and low concentration used in the present conditions, which is in accordance with our previous observations of FT-IR spectra and CHNS analysis.

Four probe electrical conductivity of samples were measured by four probe conductivity meter setup using Kiethlys current source and nanovoltmeter. Polythiophene samples, P-25, P-50, P-75 and PT-100, show a semiconducting behavior with conductivities of 7.39×10^{-3}, 2.93×10^{-3}, 1.93×10^{-3} and 1.00×10^{-3} S/cm respectively (Table 1 and Supplementary data). The observed conductivity of the polythiophene samples decreases with decrease in surfactant concentration, which was similar to one that reported in literature[25]. The conductivity studies reveal that synthesized polythiophene samples exhibit conductivity within the range reported for polythiophene[17-19]. The conductivity of the polythiophene samples was due to the movement of charge carriers like polarons and bipolarons. Poor doping prevents higher conductivity and generation of high band gap in the polymers. The band gap of the polythiophene synthesized was determined from the UV-visible diffuse reflectance spectra (Fig. 4). The band gap of the polymer PT-0 was found to be 2.50 eV, while PT-25 and PT-50 had the values of

2.25 eV. The semiconducting nature of the materials can be attributed to this band gap values. Polythiophene derivatives like poly(3-hexylthiophene) and poly(3,4-ethyledioxythiophene) show a higher conductivity than this due to good doping conditions and special methods used to inject charge carriers[25-30]. The AOT is an efficient micellar structure directing molecule in water and non-aqueous medium. Therefore, it would be interesting to understand the morphology features of the polymer materials. Polythiophene samples were subjected to scanning electron microscopic studies (SEM) to understand the morphology. SEM images of PT-25, PT-75 and PT-0 are shown in Fig. 5. PT-25 and PT-75 has spherical with size in the range of 800 ± 50 nm. On the other hand, PT-0 shows an irregular shape throughout the sample. The spherical shape of the polymer nanomaterial may be attributed to the formation of spherically shaped monomer-surfactant complex that may act as a template for the polythiophene nanospheres[31-36].

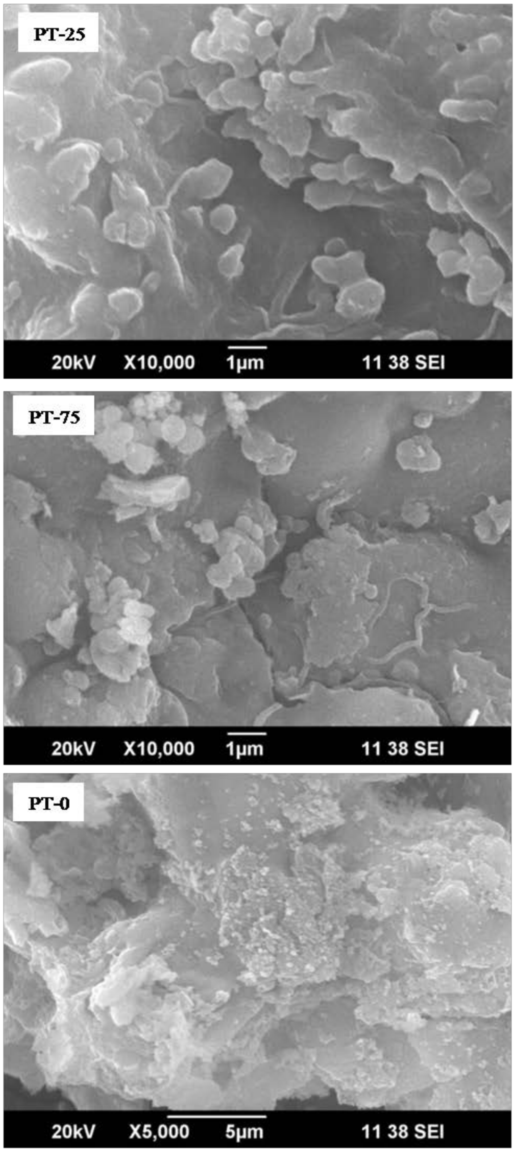

Fig. 5 – SEM images of PT-25, PT-75 and PT-0.

Thermal stability of the polymer samples were studied by thermogravimetric analysis at a heating rate 10 °C per minute under nitrogen atmosphere (Fig. 6). All the samples (PT-25, PT-50, PT-75, PT-100) show only 10% weight loss around 260 °C indicating the thermal stability of the polymer. However, the mass loss increases to 50-60% on raising the temperature 500 °C due to the decomposition of carbon from polymer chain[16].

Poor solubility of the polythiophene nanomaterials in organic and aqueous media prevents the practical applications of the material in solution. However, the *in situ* chemical oxidative synthesis of polythiophene in presence of a soft micellar template like AOT could be further extended as an attractive approach for polythiophene-carbon nanocomposite preparation[37,38]. Both polythiophene and multiwalled carbon nanotubes (MWCNT) have poor dispersibility in common solvents. The huge aspect ratio and the non covalent forces present in carbon nanotubes enable them to aggregate in bundle. The aggregation of MWCNT can be rectified by composite preparation via *in situ* polymerization of thiophene in presence of MWCNT[39,40].

In the present study, polythiophenes were prepared by chemical oxidative polymerization of thiophene using an anionic surfactant, AOT, in chloroform, and characterized by FT-IR, elemental analysis and WXRD. FT-IR spectra of samples confirm the

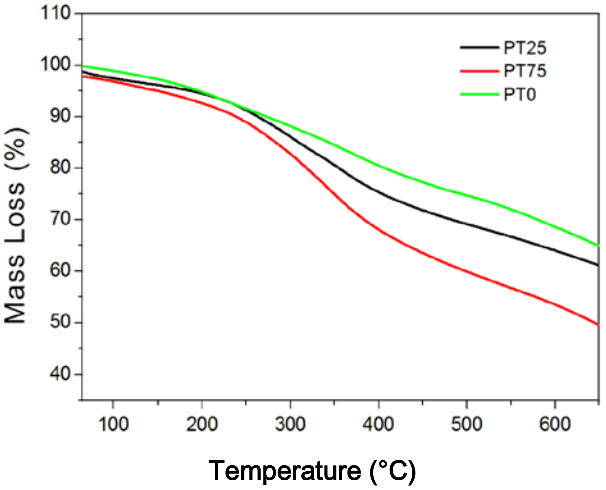

Fig. 6 – TGA analysis of the PT-25, PT-75 and PT-0.

formation of the polythiophenes and the peaks obtained were in accordance with those reported for polythiophene in literature. The C=O and S=O peaks of the dopant were not observed in FT-IR spectra, probably due to lower dopant concentration. CHNS analysis indicates that there was only 5% difference in the sulfur content between PT-0 and other samples (PT-25, PT-50, PT-75 and PT-100). Poor doping of anionic surfactant could be attributed to low amount of dopant taken in the present study or weak electrostatic interaction between polymer and dopant. Powder x-ray diffraction studies indicate the increase in solid state ordering with increase in amount of surfactant. The four probe solid state conductivity of the polythiophene samples was in the range of $(7–1)\times10^{-3}$ S cm^{-1}. The SEM images indicate that of most of polythiophene samples are of spherical nature with size of in the range 800 ± 50 nm. The polymer samples showed a 10% weight loss around 200 °C. The study shows that the presence of an anionic surfactant controlled the solid state ordering and morphology of the polythiophene nanomaterials. *In situ* chemical polymerization used in the present study, can an easy applied for producing PT-CNT nanocomposite for producing good dispersion in chloroform.

Supplementary data

Supplementary data associated with this article, i.e., details of syntheses of PT-50, PT-75 and PT-100, and, Figs S1 and S2, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(03)292-297_SupplData.pdf.

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References

1 Roncali J, *Chem Rev,* 92 (1992) 711.
2 Roncali J, *Chem Rev,* 97 (1997) 173.
3 McCullough R D, *Adv Mater,* 10 (1998) 93.
4 Reddinger J L & Reynolds J R, *Adv Polym Sci,* 145 (1999) 57.
5 Nalwa H, *Handbook of Conductive Molecules and Polymers,* Vol. 2, (Wiley, New York) 1997.
6 Skotheim T A, *Handbook of Conducting Polymer,* 2nd Edn (CRC Press, New York) 1997.
7 Chandrashekar P, *Conducting Polymers, Fundamentals and Applications: A Practical Approach,* (Kluwer, USA) 1999.
8 McQuade D T, Pullen A E & Swager T M, *Chem Rev,* 100 (2000) 2537.
9 Rudge A, Raistrick I, Gottesfeld S & Ferraris J P, *Electrochim Acta,* 39 (1994) 273.
10 Zotti G & Schiavon G J, *Electroanal Chem,* 163 (1984) 385.
11 Mastragostino M & Soddu L, *Electrochim Acta,* 35 (1990) 463.
12 McCullough R D & Williams S P, *J Am Chem Soc,* 115 (1993) 11608.
13 McCullough R D, Tristram-Nagle S, Williams S P, Lowe R D L & Jayaraman M, *J Am Chem Soc,* 115 (1993) 4910.
14 Yamamoto T, Sanechika K & Yamamoto A, *J Polym Sci Polym Lett Ed,* 18 (1980) 9.
15 Lin J W P & Dudek L P, *J Polym Sci Polym Chem Ed,* 18 (1980) 2869.
16 Yoshino K, Hayashi S & Sugimoto R, *Japan J Appl Phys,* 23 (1984) 899.
17 Gok A, Omastova M & Yavuz A G, *Synth Met,* 157 (2007) 23.
18 Ruochen L & Zheng Ping L, *Chinese Sci Bull,* 54 (2009) 2028.
19 Qiao X, Wang X & Mo Z, *Synth Met* 122, (2001) 449.
20 Loponen M, Taka T, Laakso J, Vakiparta K, Suuronen K, Valkeinen P & Osterholm J, *Synth Met,* 41 (1991) 479.
21 Jang J & Yoon H, *Langmuir,* 21 (2005) 11484.
22 Mitsionis A I & Vaimakis T C, *Chem Phys Lett,* 547 (2012) 110.
23 Gnanakan S R P, Rajasekhar M & Subramania A, *Int J Electrochem Sci,* 4 (2009) 1289.
24 Lee S J, Lee J M, Cheong I W, Lee H & Kim J H, *J Polym Sci Part A: Polym Chem,* 46 (2008) 2097.
25 Alveroglu E, *J Mol Struct,* 1086 (2015) 86.
26 Gao J, Stein B W, Thomas A K, Garciia J A, Yang J, Kirk M L & Grey J K, *J Phys Chem C,* 119 (2015) 16396.
27 Karim M R, *J Nanomater,* 2012 (2012) 1.
28 Hsiao Y-S, Wang W-T, Chen C-P & Chen Y-C, *J Mater Chem,* 18 (2008) 5948.
29 Obrzut J & Page K A, *Phys Rev B,* 80 (2009) 195211.
30 Singh R K, Kumar J, Singh R, Kant R, Rastogi R C, Chand C & Kumar V, *New J Phys,* 8 (2008) 112.
31 Antony M J & Jayakannan M, *J Phys Chem B,* 115 (2011) 6427.
32 Antony M J & Jayakannan M, *J Phys Chem B,* 114 (2010) 1314.
33 Antony M J & Jayakannan, M, *J Polym Sci Polym Phys,* 47 (2009) 830.
34 Antony M J & Jayakannan M, *J Phys Chem B,* 111 (2007) 12772.
35 Antony M J & Jayakannan M, *Langmuir* 27 (2011) 6268.
36 Das K R & Antony M J, *Polymer,* 87 (2016) 215.
37 Saini V, Li Z, Bourdo S, Dervishi E, Xu Y, Ma X, Kunets V P, Salamo G J, Viswanathan T, Biris A R, Saini D & Biris A S, *J Phys Chem C,* 113 (2009) 8023.
38 Kuila B K, Malik S, Batabyal S K & Nandi A K, *Macromolecules,* 40 (2007) 278.
39 Gangopadhyay R & De A, *Chem Mater,* 12 (2000) 608.
40 Rajesh A T & Kumar D, *Sensors Actuators B-Chem,* 136 (2009) 275.