Pattern formation and oscillatory electropolymerization of thiophene

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Thiophene has been electrochemically polymerized using organic and inorganic oxidizing agents, 4-toluene sulphonic acid silver salt and perchloric acid, in the absence and presence of ZnSO4. Electropolymerized aggregates have been characterized by morphological studies, growth kinetics, powder X-ray diffraction, differential scanning calorimetry, thermogravimetry and direct analysis in real time mass spectroscopy measurements. It is found that physical characteristics and morphology of polythiophene depend on the nature and concentration of the anion and field intensity. Morphologies of polymer aggregates using the silver salt of 4-toluene sulphonic acid and HClO4 are fibrillar and compact respectively. Transitions in morphology have also been observed when doped with ZnSO4. Growth kinetics during electropolymerization of thiophene has also been studied at different thiophene concentrations, field intensity, and concentrations of oxidizing agents as well as in the presence of ZnSO4. Growth rate is found to be higher with HClO4 than with 4-toluene sulphonic acid silver salt. Polymer obtained by using the silver salt is thermally more stable and of low molecular weight (416) than that obtained with HClO4 (689). During electropolymerization, change in anode potential is observed and has been monitored as a function of time. Correlation between morphology and oscillatory behaviour has been studied.

Interest in conducting polymeric materials is growing rapidly1,2. Conducting polymers are at present intensively studied in view of their multiple potential technological applications3,4. Conducting polymers have recently acquired notable importance in nanoscale science and technology5. Nanoscale conducting polymers can be used for biosensors6, electrochemical devices, single electron transistors7, nanotips in field emission displays8 and chemical sensors9,10 etc. Among the numerous conducting polymers, polythiophene has become the subject of considerable interest. Although, polythiophenes are prepared by means of two routes i.e., the chemical and electrochemical syntheses, the electrochemical preparation of conjugated organic polymers has been shown to be a useful method for obtaining high conducting good quality polymers11. The polymerization reaction is an electrophilic substitution reaction which retains the aromatic structure and proceeds via a radical cation intermediate. A review on the synthesis, mechanism, structure and properties of the polythiophene has also been published9. Although, the occurrence of oscillations and pattern formation in chemical12-17 and electrochemical systems18-22 have been known for a long time, such phenomena during electropolymerization is rarely known.

Herein, we report results of studies on the electropolymerization of thiophene using different oxidizing agents. Growth morphologies, growth kinetics at different experimental conditions and influence of ZnSO4 have been studied during the process of electropolymerization. Oscillation in potential during electropolymerization of thiophene has also been reported. Polymer aggregates have been characterized by XRD, thermal studies and DART mass spectrometry.

Materials and Methods

Thiophene (Spectrochem), perchloric acid 70% (SD Fine Chem. Ltd., AR), 4-toluene sulphonic acid silver salt (Dr. Theodor Schuchardt and Co.), zinc sulphate (Qualigens LR), acetonitrile (SD Fine Chem. Ltd., LR) were used as such.

Electrochemical synthesis and growth kinetics

The electrochemical synthesis of polythiophene was carried out at room temperature using an experimental setup consisting of a petridish containing a solution of monomer, acetonitrile and the oxidizing agent, in a total of 10 ml of the solution. A cleaned platinum vertical cathode was immersed into the solution while the other platinum vertical anode was put at air/liquid interface, 2.5 cm apart. These
electrodes were attached to a potentiostat (Scientific, India) to supply constant potential. Polymers were synthesized using 4-TSS and HClO\textsubscript{4} oxidizing agents in the absence and presence of ZnSO\textsubscript{4} (0.0008 M). Polymerization started at the anode as soon as the potential was applied across the electrodes. Microphotographs of aggregates were taken with a Kodak digital camera (Fig. 1). Microphotographs of polythiophene using HClO\textsubscript{4} in the absence and presence of ZnSO\textsubscript{4} at different time of polymerization were taken (Fig. 2). Thiophene concentration was also varied in the range 0.5-2.0 M while concentration of 4-TSS or HClO\textsubscript{4} was in the range 0.025-0.125 M. Field intensity was varied in the range 1.6-8.0 V/cm. The growth kinetics was studied by weighing the washed and dried aggregates as a function of time of polymerization, field intensity and [Thiophene]. Results are shown in Figs 2 and 3.

Table 1 — Intense lines in the XRD patterns of (a) polythiophene polymerized using 4-TSS (b) polythiophene polymerized in presence of 4-TSS and ZnSO\textsubscript{4} (c) polythiophene polymerized using HClO\textsubscript{4} and (d) polythiophene polymerized in presence of HClO\textsubscript{4} and ZnSO\textsubscript{4}. [Conditions: [Thiophene] = 1.5 M, [4-TSS] = [HClO\textsubscript{4}] = 0.05 M, [ZnSO\textsubscript{4}] = 0.0008 M, field intensity = 4.8 V/cm, separation between electrodes = 2.5 cm]

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<th>Polymer aggregates obtained from</th>
<th>4-TSS</th>
<th>4-TSS+ZnSO\textsubscript{4}</th>
<th>HClO\textsubscript{4}</th>
<th>HClO\textsubscript{4}+ZnSO\textsubscript{4}</th>
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Fig. 1 — Microphotographs of polythiophene aggregates obtained in (a) 4-TSS and acetonitrile, (b) 4-TSS, ZnSO\textsubscript{4} and acetonitrile, (c) HClO\textsubscript{4} and acetonitrile and (d) HClO\textsubscript{4}, ZnSO\textsubscript{4} and acetonitrile systems. Conditions: [Thiophene] = 1.5 M, [4-TSS] = [HClO\textsubscript{4}] = 0.05 M, [ZnSO\textsubscript{4}] = 0.0008 M, field intensity = 4.8 V/cm, separation between two vertical electrodes = 2.5 cm.

Fig. 2 — Plots showing amount of electropolymerized aggregates as a function of time in presence and absence of ZnSO\textsubscript{4} additive. [(●) thiophene-4-TSS-acetonitrile, (▲) thiophene-4-TSS- ZnSO\textsubscript{4}-acetonitrile, (○) thiophene-HClO\textsubscript{4}-acetonitrile, (△) thiophene-HClO\textsubscript{4}, ZnSO\textsubscript{4}-acetonitrile Conditions: [Thiophene] = 1.5 M, [4-TSS] = [HClO\textsubscript{4}] = 0.05 M, [ZnSO\textsubscript{4}] = 0.0008 M, field intensity = 4.8 V/cm, separation between two vertical electrodes = 2.5 cm].

Fig. 3 — Dependence of amount of electropolymerized aggregates on field intensity in (a) thiophene-4-TSS-acetonitrile and (b) thiophene-HClO\textsubscript{4}-acetonitrile systems. [Conditions: [Thiophene] = 1.5 M, [4-TSS] = [HClO\textsubscript{4}] = 0.05 M, field intensity = 1.6, 3.2, 4.8, 6.4 and 8.0 V/cm, separation between two vertical electrodes = 2.5 cm].
Oscillation in anode potential with time during electropolymerization

The same experimental setup as employed earlier was used to monitor the potential changes at the anode during the electropolymerization of thiophene using oxidizing agents 4-TSS (0.05 M) or HClO₄ (0.05 M) at an air/liquid interface. Calomel reference electrode was used. Influence of ZnSO₄ (0.0008 M) on oscillatory behaviour was also studied. Results are shown in Figs 4 (a, d) and 5 (a, c).

Characterisation

Powder X-ray diffraction patterns of polythiophene aggregates obtained using 4-TSS and HClO₄ as oxidizing agents in the absence and presence of Zinc sulphate were taken in the 2θ range 0-100°. Results are recorded in Table 1.

Thermal characteristics of polymer aggregates were studied by DSC and TG up to 500°C using Mettler Toledo differential scanning calorimeter (model DSC 821).

Direct analysis in real time (DART) mass spectra of polymer samples were taken using Jeol-Accu TOF JMS-T100LC mass spectrometer.

Results and Discussion

Polythiophene aggregates were synthesized electrochemically using (i) 4-toluene sulphonate silver salt and (ii) perchloric acid oxidizing agents in the absence and presence of ZnSO₄. Acetonitrile was used as solvent. Corresponding morphologies are shown in Fig. 1. Fibrillar (Fig. 1a) and compact (Fig. 1c) morphologies were obtained for organic sulphonate and inorganic perchlorate ions respectively. The anion has a substantial effect on the structure, growth rate and the degree of anisotropy of the resulting polymer. Influence of ZnSO₄ on the morphology of polymer aggregates was also studied and results are shown in Fig. 1 (b, d). In the case of 4-TSS, addition of ZnSO₄ showed a morphological transition from fibrillar to compact while in case of HClO₄, a transition from compact to branched was observed. In the latter case, the dependence of morphology on time of polymerization was also studied in the absence and in presence of ZnSO₄.

Growth kinetics of polymerization was studied by measuring the weight of polymerized aggregates as a function of time in (a) thiophene – 4-TSS – acetonitrile system and (c) thiophene – HClO₄ – acetonitrile systems (Fig. 2). These results show that weight of the polymerized aggregate depends on the time of polymerization. In systems (a) and (c) the system follows an empirical equation, \( w^2 = mt + c \), where \( w \) is the weight of polymer aggregate at time \( t \), \( m \) and \( c \) are slope and intercept respectively. It is also observed that the growth rate of polymerization was higher when HClO₄ was used than that observed with 4-TSS. This
may be due to the difference in anion-polymer interaction. Perchloric acid is more rapidly ionized in acetonitrile than 4-TSS and thus forces the polymer backbone to release more and more electrons to the cathode. In the case of oxidation with 4-TSS, incorporation of ZnSO₄ in the medium reduced the growth while in the case of HClO₄, the growth was increased. In all these cases the empirical equation \( w = c t^m \) was followed as evident by linear plots between \( \log w \) vs \( \log t \). Growth also depends on the field intensity and [Thiophene] (Fig. 3).

Results show that the growth of polymerization depends on the concentration of oxidizing agent Non-linear plots obeying the empirical equation \( w^2 = m[\text{oxidizing agent}] + c \) for systems (a) and (b) were obtained. The growth of polymerization also depends on the field intensity and [Thiophene]. The sigmoidal shaped curve was obtained when 4-TSS was used while with HClO₄ growth depends on field intensity and [thiophene] with no induction time obeying the equations \( w^2 = mV + c \) and \( w = c[\text{Thiophene}]^m \) respectively. Figure 4 shows anode potential changes with time during electropolymerization and the corresponding morphologies when 4-TSS and HClO₄ oxidizing agents were used. Oscillations were observed in each case. Small portion of traces after 5 minutes of polymerization are shown in Fig. 4 (a, c). Amplitude of oscillation was more in the case of thiophene-4-TSS-acetonitrile system than in the thiophene-HClO₄ – acetonitrile system. It is generally believed that the morphology of crystals strongly depend on the distance from the thermodynamic equilibrium. Under these conditions, pattern formation is accompanied by oscillations in potential. Weight of polymer aggregates (\( w \)) was plotted as a function of [Thiophene]. In the case of oxidation with 4-TSS, \( w \) versus [Thiophene] plot is sigmoidal with an induction period and the morphology is fibrillar (Fig. 4b) while in the case of HClO₄, there is no induction period and the morphology is compact. Sigmoid and morphology (fibrillar) both support instability. When ZnSO₄ was doped, the amplitude of oscillations was increased in both the systems (Fig. 5) and a transition from compact to branch was observed. Such a transition in morphology may be explained in terms of the surface instability. Diffusion limited aggregation is a process where in successive particles moving in space undergo a random walk until they interact with a growing fractal.

Polymer aggregates were characterized by XRD, DSC, TG and DART mass spectroscopy. XRD patterns of the polymer aggregates, obtained by using 4-TSS and HClO₄ were compared (Table 1). Results indicate that the aggregates are different. On incorporation of ZnSO₄, the product is changed in both the cases (Table 1). The broadening is related with the particle size using Scherrer formula for spherical particles:

\[
D = \frac{4}{3} \times \frac{0.9\lambda}{3B\cos\theta}
\]

where \( D \) the diameter of the spherical particles, is related to the full width at half maximum B of the peak centered at \( \theta \) recorded with X-rays of wavelength \( \lambda \). This relation explains that with change in \( B \), the particle size will also change.

Simultaneous DSC and TG thermograms of polymer aggregates (systems a and c) were taken upto 500°C. Polymer aggregates obtained by using 4-TSS and HClO₄ show different thermal properties. When 4-TSS was used, the aggregate shows two endotherms at 83.4° and 300°C with corresponding weight losses of 3.19% and 29.12% respectively, while with HClO₄ these endotherms were obtained at 100.1° and 280.5 °C with the corresponding weight losses of 14.94% and 30.4% respectively. Thus, polythiophene with 4-TSS is found to be thermally more stable than that with HClO₄. Polythiophenes synthesized with 4-TSS and HClO₄ have different molecular weights and thus length of conjugation as evident by their DART mass spectra.

The mechanism of electropolymerization of thiophene starting from the monomer can be schematically represented as shown in steps (i)-(v):

(i) In presence of electric field, the oxidation of thiophene monomer to the radical cation is the first step (Scheme 1).

(ii) The electron thus released is associated with the Ag⁺ from 4-TSS or H⁺ from HClO₄ (Scheme 2).

(iii) Formation of a dimer: There are two possibilities for the formation of a dimer

(a) Radical cation-monomer coupling (Scheme 3).

(b) Radical cation-radical cation coupling (Scheme 4).

(iv) Chain propagation via oxidation of the extending polymer (Scheme 5).
Scheme 1

$$\text{Scheme 1}$$

Scheme 2

$$\text{Scheme 2}$$

Scheme 3

$$\text{Scheme 3}$$

Scheme 4

$$\text{Scheme 4}$$

Scheme 5

$$\text{Scheme 5}$$
Conclusions
Polythiophenes with fibrillar and compact morphologies have been synthesized by electrochemical polymerization method in the presence of oxidizing agents, 4-toluene sulphonic acid silver salt and perchloric acid respectively. On addition of ZnSO$_4$, the morphology of polymer aggregates changed from fibrillar to compact and from compact to branch, respectively when 4-TSS and HClO$_4$ were used. Growth kinetics of polymerization depends on experimental conditions, viz., [monomer], [oxidizing agent], field intensity, time of polymerization and presence of ZnSO$_4$ in the electrolytic medium. XRD, DSC and TG studies clearly indicate that the polymer aggregates synthesized with 4-TSS were different from polymer aggregates synthesized with HClO$_4$.

The polymer aggregate obtained by using 4-TSS is thermally more stable than HClO$_4$. Anode potential oscillates with time during electropolymerization. Amplitude of oscillation was more and of less frequency in thiophene-4-TSS-acetonitrile system than that when HClO$_4$ was used. In the former case, $w$ vs [Thiophene] plot was sigmoidal with induction period and morphology was fibrillar while with HClO$_4$ there was no induction period and the morphology was compact. Morphological transitions may be explained on the basis of surface instability.

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References