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High yield polypyrrole: A novel approach to synthesis and characterization

Vineet V. Karambelkar · J. D. Ekhe ·
S. N. Paul

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Abstract An improved synthetic route to polypyrrole salt was accomplished using methanesulfonic acid as a novel dopant along with potassium persulfate as the oxidant employing inverted emulsion polymerization technique. Polypyrrole salt was obtained in high-weight percent yield (83.77%) with respect to the amount of monomer used and the reaction time was drastically reduced (1 h 10 min.) as compared to the previously reported synthesis methods. Characterization of the salt yielded satisfactory results. Inverted emulsion polymerization technique has several unique and distinct advantages over conventional techniques which facilitate the synthesis of fused five membered heterocyclic rings which are otherwise difficult to synthesize, and hence sparsely reported in the literature.

Introduction

Fused five membered heterocyclic rings have been of great interest since their discovery (Shirakawa et al. [2]). These natural terthienyl compounds have excellent potential as organic semiconductors and inherent property of photodynamically destroying tumor cells [1]. Several five membered fused heterocyclic rings display the ability to conduct electricity and they tend to behave as organic semiconductors when doped [2]. Polypyrrole (Fig. 1a) and substituted polythiophenes (Fig. 1b) have been the most thoroughly investigated conductive polymers owing to their unique properties (air stability, tractability and having a low band gap) [3]. Their stability results because of the presence of lone-pair electrons on the sulfur and nitrogen atoms which stabilizes the positive charge of the polymer by removing electrons from the π-system of the polymer conjugate backbone (*p*-type doping)[4] (Scheme 1a, b). Owing to this unique blend of properties, these heterocycles find myriad applications as electrical conductors, nonlinear optical devices, photoresists, solar cells, and transistors [5].

Owing to the inherent difficulty in synthesizing 5, 5′ fused ring systems, these compounds are sparsely reported in the literature. Of all the previously reported synthetic routes, Dieckmannn's eight-step route [6] leading to a substituted thiapentalene is well-known (Scheme 2). However, this route suffered from many drawbacks including lengthy steps, low yields (65%) and high concentration of impurities. A modified Dieckmann's route was reported in which a fused 5.5′ ring system was synthesized in just one step using a dihalide and Meldrum's acid (Lue et al.) [7] (Scheme 3), in moderate yield (78%). A precursor intermediate to substituted polythiophenes, 5-carbomethoxy-5-phenylsulfonyl-1,3-dimethyl-5,6-dihydro-4H-cyclopenta[c]thiophene, a sulfone ester, was successfully synthesized in just two steps[8], with high purity but with a very low yield (5 mg) (Scheme 4).

In spite of these successes, substituted polythiophenes are difficult to make into thin films, owing to their solubility in different organic solvents, since the pendant groups of the solvents act as counter ions, to produce a self-doped conducting polymer. Their conductivity is still limited due to the entropic effects of the alkyl substituents

V. V. Karambelkar · S. N. Paul (✉)
Department of Metallurgical and Materials Engineering, Visvesvaraya National Institute of Technology, South Ambazari Road, Nagpur 440 010, Maharashtra, India
e-mail: snpaul@mme.vnit.ac.in

J. D. Ekhe
Department of Applied Chemistry, Visvesvaraya National Institute of Technology, South Ambazari Road, Nagpur 440 010, Maharashtra, India

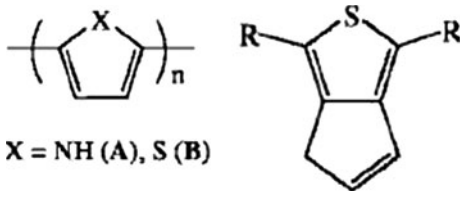
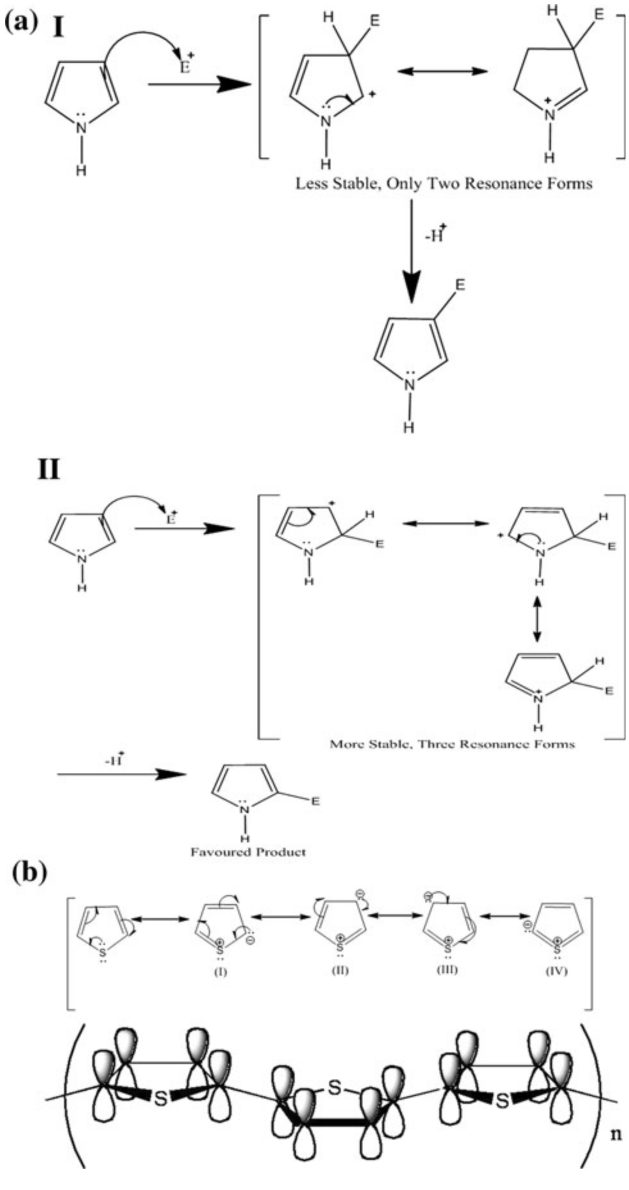


Fig. 1 **a** Polypyrrole. **b** Substituted polythiophene



Scheme 1 **a** Part (I) reactivity of pyrrole, two resonance forms. **a** Part (II) reactivity of pyrrole, three resonance forms. **b** Reactivity of thiophene

and also they have a tendency to twist upon themselves, thereby further reducing their conductivity [9].

In order to counteract these difficulties, an innovative polymerization technique called inverted emulsion polymerization is employed in the research presented herein, whereby polypyrrole salt is successfully synthesized in high yields, drastically reducing the reaction time thereby avoiding lengthy steps.

Polymerization procedure: Preparation of polypyrrole salt using methanesulfonic acid as a novel dopant.

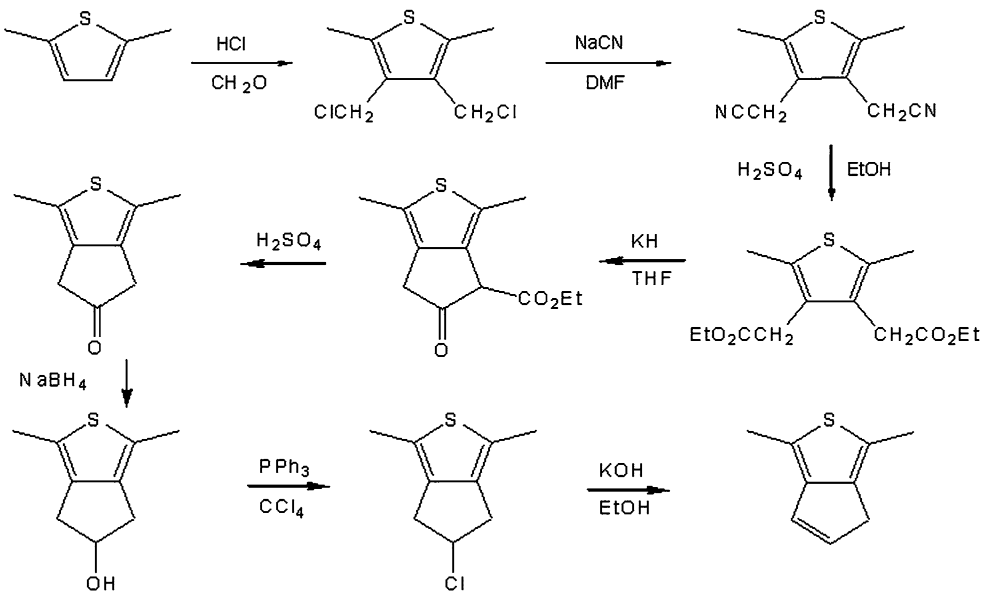
To a 250 ml Erlenmeyer flask was charged a mixture of methanesulfonic acid dopant (4 mL, 5.92 g, 61.5 mmol) and water (20 ml). Pyrrole monomer (1.2 mL, 1.16 g, 17.2 mmol) dispersed in water (30 mL) was added to the above mixture and constantly stirred at 20 °C. Sodium lauryl sulfate surfactant (1.0 g, 3.46 mmol) dispersed in water (20 mL) and Potassium persulfate initiator (3.0 g, 11.0 mmol) dispersed in Chloroform (30 mL) were added drop wise to the stirring reaction mixture. The reaction mixture was allowed to stir constantly for 1 h duration, after which it was poured in acetone to precipitate the black colored polymer. The polymer was washed with water, dried in an oven at 100 °C, and weighed until a constant weight was maintained.

Experimental section

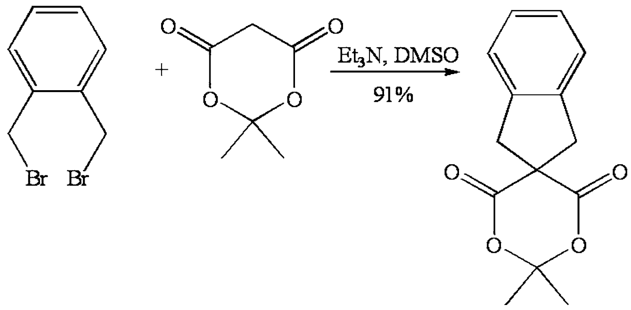
All the reactions were carried out with standard Schlenk apparatus unless otherwise noted. Pyrrole monomer (Acros) 99.9% extra pure, organic reagents like chloroform (Fischer Scientific) (99.9% extra pure), acetone (Fischer Scientific) (Analar grade, 99% pure), dopant methanesulfonic acid, and surfactant sodium lauryl sulfate (National Chemicals, India) along with oxidant potassium persulfate (Qualigens Fine Chemicals, India) were used as received. Fourier transform infra red (FTIR) spectra were recorded using a Perkin-Elmer SPECTRUM ONE system, X-ray diffraction studies were carried out using a PANalytical XPERT-PRO X-ray diffractometer with CuK$_{\alpha}$ radiation of wavelength 1.5406 Å with a continuous scan speed of 0.045^{0} min^{-1}. Thermal analysis of the polymer sample was carried out with a Mettler Toledo star system in the presence of an air atmosphere up to 1000 °C and at a heating rate of 10 °C per min. SEM micrographs of the polymer sample were taken at different magnifications using JEOL 6380 A scanning electron microscope. Particle size of the polymer sample was determined with a hot stage microscope/image analyzer PL-A662 (Carl-Zeiss, India), with a gas flow of up to 60 C/min.

Results

Polymer characterization: structural properties of the polymer:



Scheme 2 Dieckmann's eight step synthetic route to substituted thiapentalenes



Scheme 3 Modified Dieckmann's route (Lue et al. [7])

Infrared spectra The FTIR spectrum of polypyrrole (Fig. 2) shows the characteristic peaks at 3712 and 3004 cm^{-1} (N–H str), 2924 and 2851 cm^{-1} (C_{sp2}–H str), 1714 cm^{-1} (C=O), 1535 cm^{-1} (C=C), 1213 cm^{-1} (C–N), 1052 cm^{-1} (=C–H in plane vibration), 812 cm^{-1} (=C–H out of plane vibration), and 559, 582 cm^{-1} (C–Br str).

XRD studies The XRD pattern of polypyrrole (Fig. 3) shows a broad peak from $2\theta = 21^0$ with a d-spacing of 2.15 Å.

Polymer characterization: Thermal properties of the polymer.

Differential scanning calorimetry (DSC) studies: DSC curve of polypyrrole salt (Fig. 4) shows glass transition temperature (T_g) at 110 °C and no melting.

Thermogravimetric analysis (TGA) studies: TGA curve of polypyrrole salt (Figs. 5, 6) shows a two-stage decomposition pattern at 262.75 and 491.73 °C.

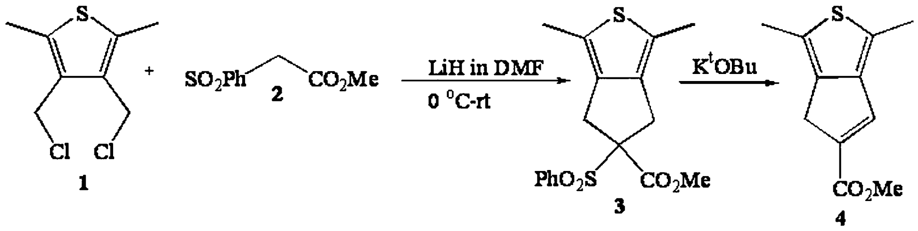
SEM studies (*Fig.* 7). SEM micrographs at 1500×, 3000×, and 8000×.

(i) *Particle size determination* (*Fig.* 8) SEM micrograph at 1500×, average particle size at 4.42 µm.

Discussion

Fused five membered heterocyclic rings are difficult to synthesize. Previously reported synthetic routes by Dieckmann [6], Lue et al. [7] and the intermediate sulfone ester synthesis [8] suffer from a few drawbacks like low yields, high concentration of impurities and lengthy steps. The resulting polymer should be stable, air tractable having a low band gap to facilitate electrical conductivity. It should remain as flat as possible, should be less reactive than poly(isothianaphthene) and should ligate with a redox active metal centre to allow for a tunable conductivity.

In recent years, emulsion polymerization and micro-emulsion polymerization techniques have acquired significant importance in the preparation of polypyrrole [10]. These techniques offer several advantages over



Scheme 4 Intermediate sulfone ester precursor (3) to substituted polythiophenes

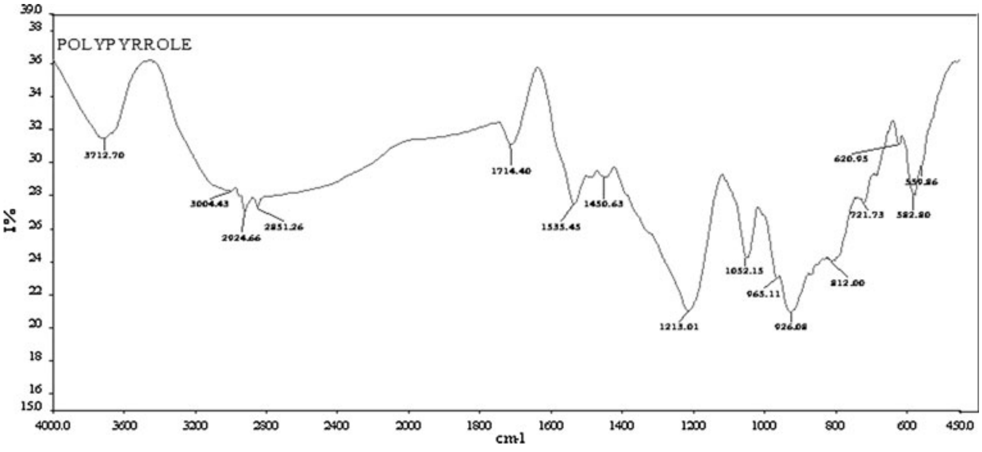


Fig. 2 FTIR spectra of as-synthesized polypyrrole salt

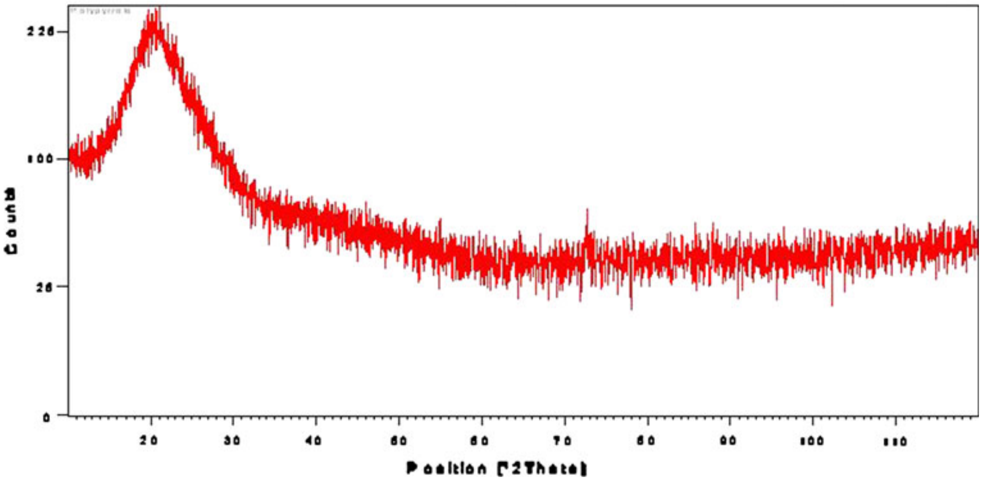


Fig. 3 XRD pattern of as-synthesized polypyrrole salt

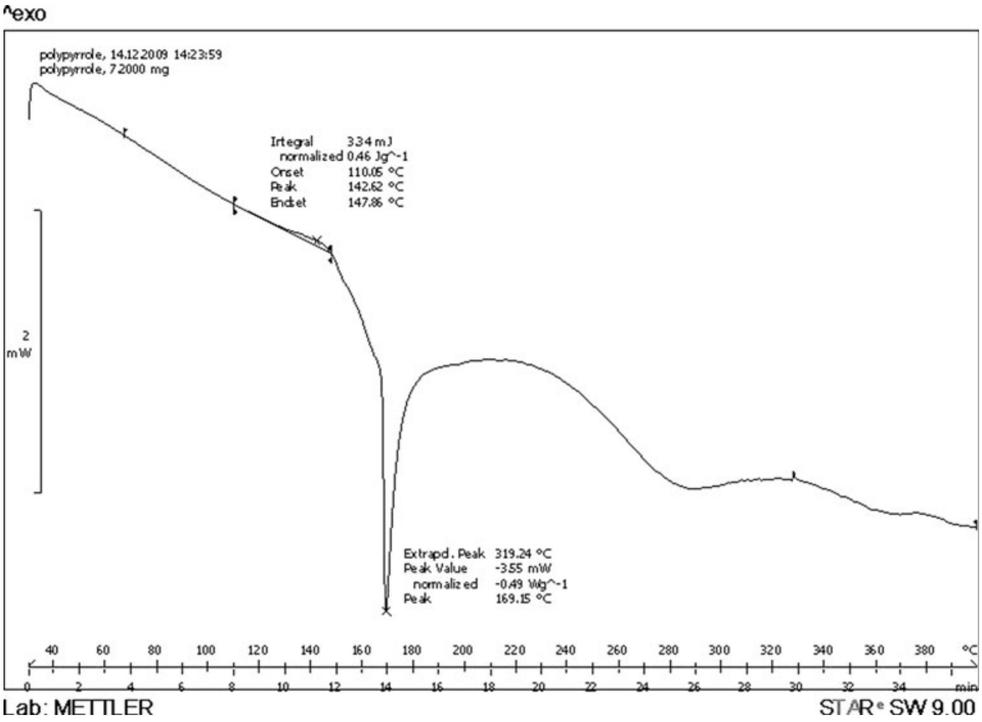


Fig. 4 DSC curve of as-synthesized polypyrrole salt

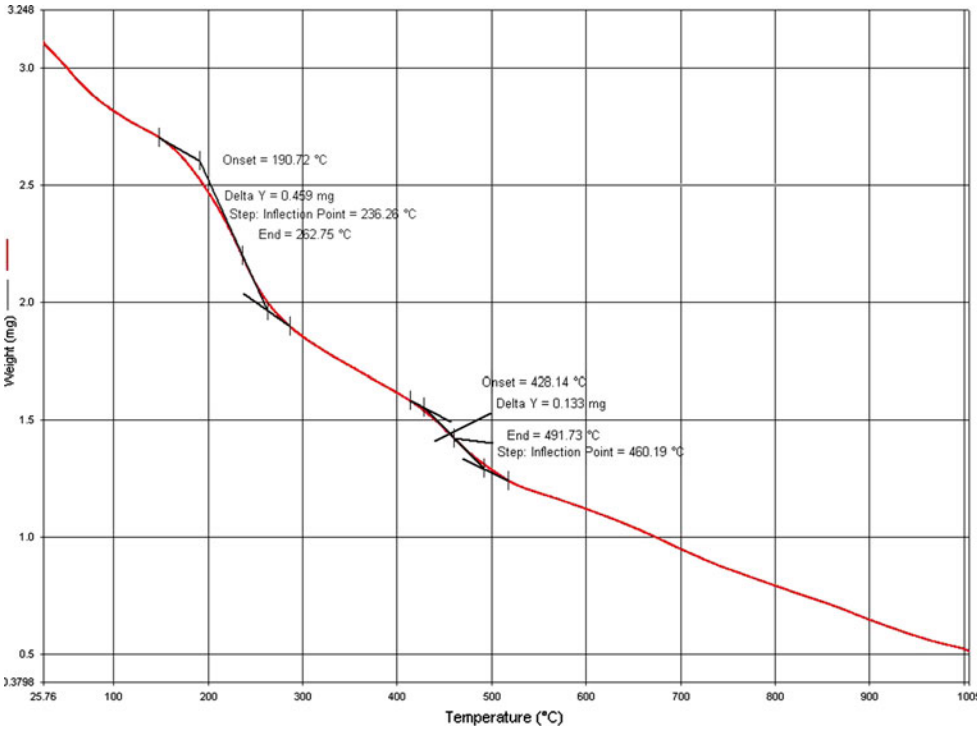


Fig. 5 TGA curve of as-synthesized polypyrrole salt

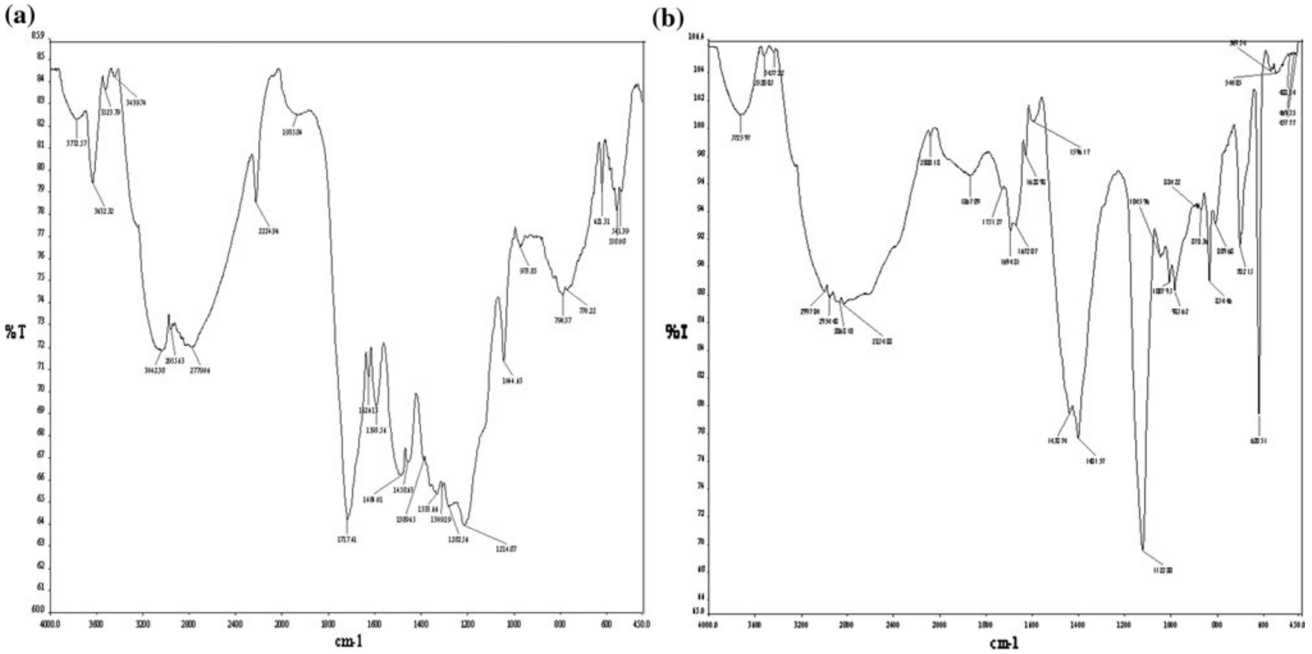


Fig. 6 **a** Decomposition pattern of as-synthesized polypyrrole salt (270 °C). **b** Decomposition pattern of as-synthesized polypyrrole salt (500 °C)

conventional synthetic methods. For example, the polymerization process is easy to control because of physical state of the emulsion system, thermal, and viscosity problems are less significant, high-reaction rate can be achieved and the product obtained can be utilized without further purification.

Polypyrrole is usually prepared employing electrochemical and chemical-oxidative polymerization techniques using water soluble oxidizing agents. However, inverted emulsion polymerization technique which employs oil soluble oxidizing agents, offers several distinct advantages like high yield of the polymer with respect to the

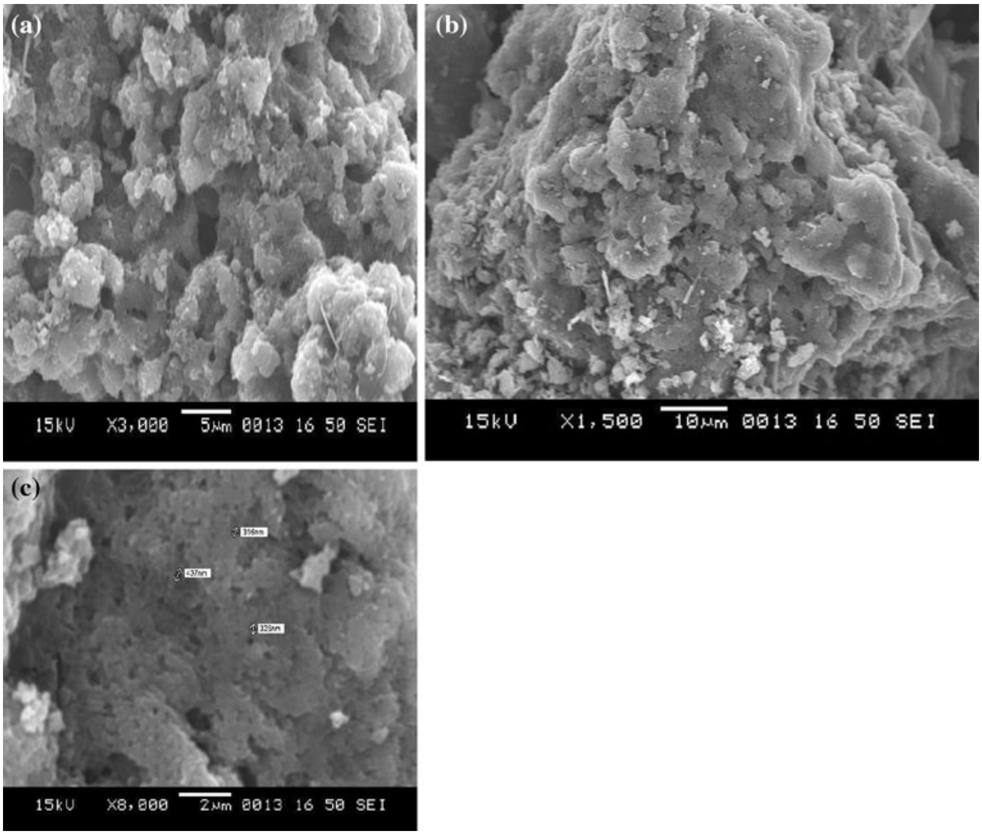


Fig. 7 **a** SEM micrograph of as synthesized polypyrrole salt at ×3000. **b** SEM micrograph of as synthesized polypyrrole salt at ×1500. **c** SEM micrograph of as synthesized polypyrrole salt at ×8000

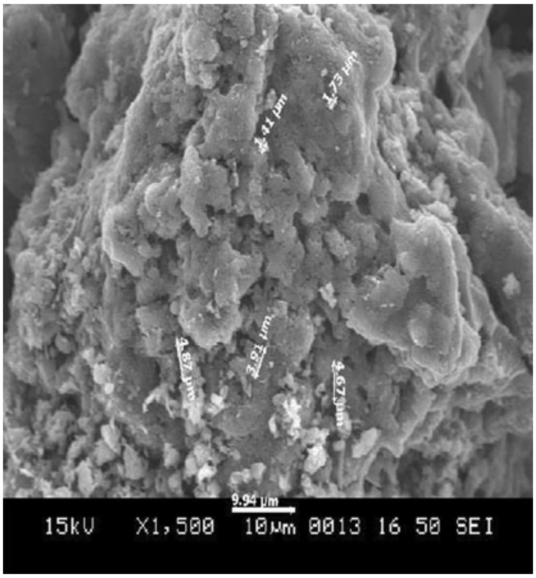


Fig. 8 Particle size determination at ×1500. Average particle size = 4.42 μm

monomer used, high-electrical conductivity and reduced reaction duration.

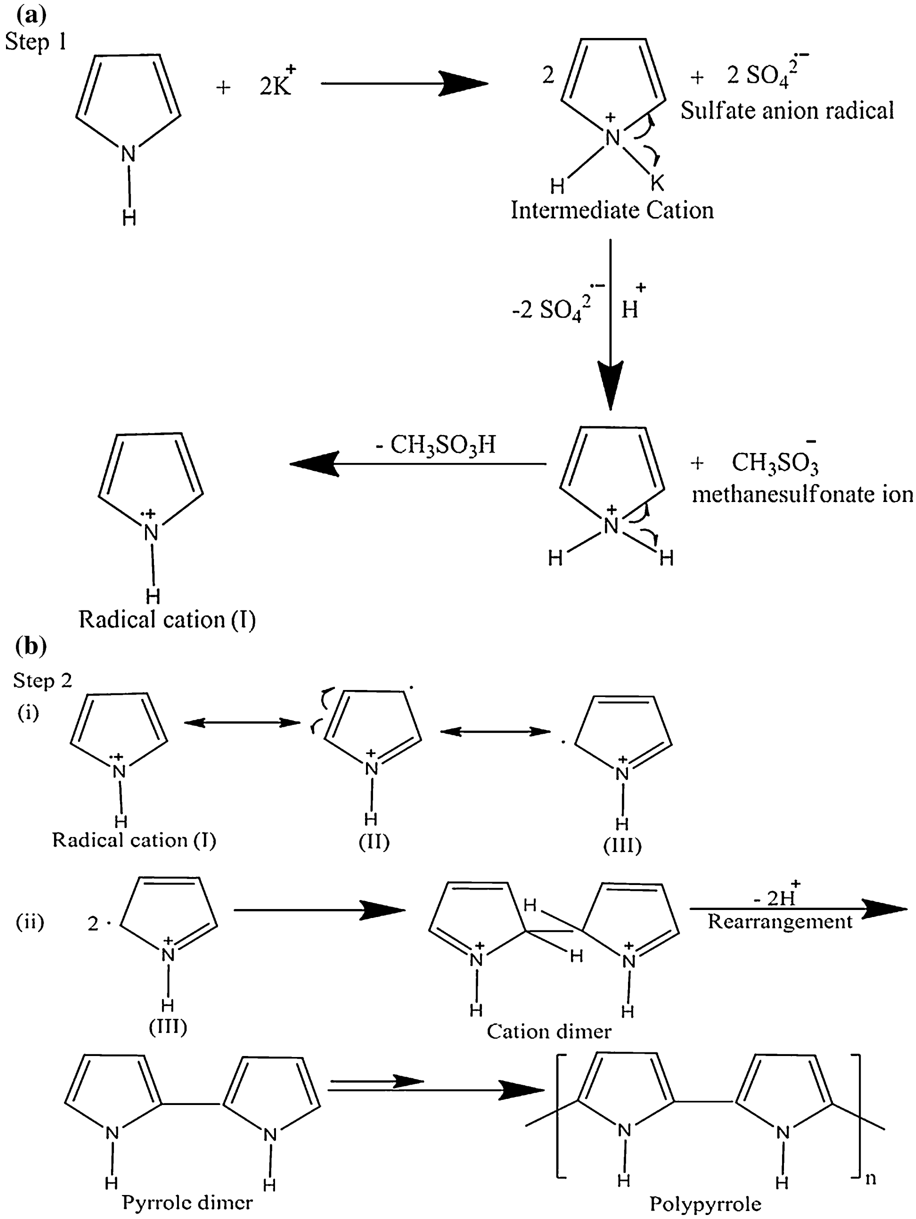
Attempts have been made to synthesize high conducting polypyrrole using benzoyl peroxide as a novel oxidizing agent [11] [12]. In the research presented herein, synthesis of polypyrrole using methanesulfonic acid as a novel-dopant employing inverted emulsion polymerization technique has been successfully accomplished with a high-percentage yield (83.77%), with respect to the monomer used and drastically reduced reaction time (1 hour 10 min) avoiding toxic and hazardous chemicals with a relatively pure polypyrrole salt.

Analysis of FTIR spectrum (Fig. 2) shows the characteristic N–H stretch at 3712 and 3004 cm^{-1}, the C=C stretch at 1535 cm^{-1} and the characteristic C–N in-plane deformation at 1213 cm^{-1} which is in accordance with the previous synthesis methods of polypyrrole salt [12], thus confirming the identity of polypyrrole.

Analysis of XRD pattern (Fig. 3) shows a characteristic broad humped peak at $2\theta = 21^0$ with a d-spacing of 2.15 Å. This value is in accordance with 2θ values ranging from 10^0–30^0 previously reported for polypyrrole [13, 16], clearly indicating amorphous nature of the salt. Also at different θ values intensity peaks were different but for all 2θ values d was found to be constant, thus confirming polypyrrole.

The DSC curve of polypyrrole salt (Fig. 4) shows the glass transition temperature (T_g) at 110 °C which is in

Scheme 5 **a** Proposed reaction mechanism of polypyrrole formation, step 1, part (I). **b** Proposed mechanism of polypyrrole formation, step 2, part (II)



accordance with the previously reported values of T_g [13, 14], of polypyrrole. No melting temperature (T_m) was observed clearly indicating that polymer chain is completely decomposed during heating. Also no crystallinity was observed further confirming the amorphous nature of polypyrrole salt.

Analysis of the TGA curve of polypyrrole salt (Fig. 5) showed a two-stage decomposition pattern at 262.75 and 491.73 °C. FTIR spectrum of the sample heated at 270 °C shows a characteristic O–H stretch at 2779 cm^{-1} confirming the complete removal of the dopant, methanesulfonic acid from the sample. Similarly, FTIR spectrum of the sample heated at 500 °C shows a characteristic N–H stretch at 3437 cm^{-1} thus confirming the complete decomposition of the polymer backbone chain.

SEM micrograph of polypyrrole salt at a magnification of 3000× (Fig. 6) clearly displays polypyrrole particles, which are resolved and distinct in their manner of formation. At a lower magnification of 1500×, aggregates of polypyrrole salt are clearly visible which would be beneficial for future conductivity studies upon the polymer as there is a decrease in the surface area of the particles. At a higher magnification of 8000× voids are clearly visible indicating lack of grains, discontinuity, and non-crystalline nature of polypyrrole salt.

Average particle size was determined on a 10 μm scale (Fig. 7) and was found to be 4.42 μm which is beneficial as smaller particle size aids in removing segregation of particles, thereby imparting a homogenous nature to them.

Solubility tests were performed on the sample as a part of physical characterization of the polypyrrole salt.

Insolubility in all the major organic solvents indicates that the salt is chemically stable. Combustion test (Spatula test) yielded only a charred residue with a lack of sooty flame indicating the complete removal of the impurities from the polypyrrole salt. However, due to the insolubility of the salt in all the major organic solvents, molecular weight determination could not be carried out.

Proposed reaction mechanism

The reaction mechanism of polypyrrole formation is based on earlier reports of polypyrrole synthesized using ferric chloride [15], benzoyl chloride [11, 12], and ammonium persulfate [16] as oxidizing agents. In this research methanesulfonic acid is used as a novel dopant along with potassium persulfate as an oxidizing agent and radical initiator.

The synthesis mechanism is essentially a two step polycondensation polymerization reaction. (Scheme 5). Step I is characterized by the formation of a pyrrole radical cation through a radical cation intermediate along with a sulfate anion radical. The sulfate anion radical itself is a powerful oxidant, and it gets oxidized by the organic solvent in which radical initiator is dissolved. When dopant is added to the reaction mixture, an ammonium pyrryl cation is generated along with a methanesulfonate ion. Ammonium pyrryl cation undergoes a homolytic fission with the subsequent removal of the dopant to yield a pyrrole radical cation (I).

Step II is characterized by the formation of three resonance forms of the pyrrole radical cation (I) (Scheme 5). Two forms of (III) (most stable form) form a radical cation dimer which on subsequent rearrangement forms a pyrrole dimer, trimer or a tetramer until polypyrrole is generated. As was discussed in the reactivity of pyrrole (Scheme 1), attack at position 2 (α position) is preferred since this position is easily deprotonated.

The mechanistic details are given in the following scheme.

Conclusions

Polypyrrole salt was successfully synthesized in high-weight percent yield (83.77%) using methanesulfonic acid as the dopant and potassium persulfate as the oxidant employing inverted emulsion polymerization technique which is eco friendly and produces high yielding polymers. Characterization of the salt yielded satisfactory results thereby confirming the salt's identity. Reaction time was drastically reduced (1 h 10 min) as compared to the previously reported synthesis methods.

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