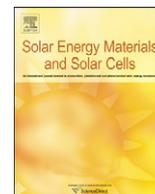




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Growth of N-substituted polypyrrole layers in ionic liquids: Synthesis and its electrochromic properties

Shahzada Ahmad^{a,*}, Songul Sen Gursoy^b, Samrana Kazim^c, Aysegul Uygun^d

^a Electronic Materials Division, National Physical Laboratory, Dr. K.S. Krishnan Road, New Delhi-110012, India

^b Mehmet Akif Ersoy University, Faculty of Arts and Science, Department of Chemistry, Burdur 15100, Turkey

^c Institute of Macromolecular Chemistry, ASCR, v.v.i, Heyrovsky Square 2, 16206 Prague 6, Czech Republic

^d Suleyman Demirel University, Faculty of Arts and Science, Department of Chemistry, Isparta 32260, Turkey

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ABSTRACT

A new series of pyrrole family, N-substituted phenyl attached alkyl at the ortho, meta and para position were synthesized by a straight forward method and were exploited as an innovative monomer for electroactive polymers. Ionic liquids were employed as a medium for electro-polymerization of these monomers to obtain N-(methyl)phenyl polypyrroles. N-substituted polypyrroles show different morphologies and conductivity according to position of methyl group on the benzene ring and synthesis medium. The electrical conductivity value varies with the position of methyl group and was $> 10^{-5}$ S/cm, higher than the sample obtained from conventional media. The resulting polymer films were characterized by FT-IR and UV-Vis spectroscopy, contact angle measurements, cyclic voltammetry and scanning probe microscopic technique along with their electrochromic behavior.

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1. Introduction

Among the various heterocycle-based conjugated polymers, such as azulenes, furans, pyrroles, thiophenes and others, polypyrrole (PPy) is one of the most studied conducting polymer and has received attention due to unusual electrical, optical and electrochemical properties [1]. Owing to its environmental stability, high electrical conductivity, ease of synthesis by chemical as well as electrochemical route, film forming ability and biocompatibility, PPy has been used in chemical sensors, photo-voltaics, actuators, electrochemical cells [2–4], biological applications [5,6] and electrochromic devices [7,8]. In spite of the many advantages of PPy, insolubility, brittleness and non-processability are some of the drawbacks of PPy, which can be easily addressed by appending a variety of substituent or fused rings into the main chain [9–13]. This structural control leads to the optimization of properties such as solution processability, better electronic conductivity and stability of polymer under environmental condition. Hence, to protect N-position in PPy by the appropriate substituent is a facile approach, which will introduce novel synergistic properties i.e. structural changes with enhanced solubility and processability.

Due to the ease of formation of relatively stable radical cations (polarons), N-substituted pyrrole readily polymerizes by oxidative polymerization chemically or electrochemically [9,14]. As a consequence, solubility and functionality of resulting polymers can be further improved. However, thin films obtained at liquid or solid interface by chemical oxidation were found with inferior quality [15,16] and to prepare adherent and uniform thin polymer films of controlled thickness directly at the electrode surface, electrodeposition is found to be cost effective and is a one step process. As a matter of fact, electrodeposition process mainly employs classical salt-solvent based electrolytes, which induces unknown changes in the microstructure by the hydrophobicity and high vapor pressure of the solvent. This results in less electrochemical stability, poor adherence with the substrate and less environmental benignity [17].

Room temperature ionic liquids, are known to be environmentally benign media and ready to use hydrophobic electrolytes, can be exploited for the growth of PPy films [3,4,17–21] due to their non-volatility and excellent electrochemical stability. Ionic liquids owing to their outstanding range of properties are known to show considerable enhancement in reaction kinetics and selectivity for processing in comparison to its counterparts derived from conventional liquid electrolyte. They provide an advantageous alternative to aqueous media, as their large potential window facilitate the deposition of polymers and metals that are otherwise inaccessible in aqueous or organic solvents. The synthesis of π -conjugated polymers in ionic liquids has demonstrated improved stability and increased lifetime. The inherent

* Corresponding author. Current address: Max Planck Institute for Polymer Research, Ackermannweg 10 D-55128 Mainz, Germany. Tel.: +496131 379115; fax: +496131 379310.

E-mail addresses: shahzada80@gmail.com, ahmad@mmp-mainz.mpg.de (S. Ahmad).

properties of ionic liquids such as high conductivity, wide potential window and air/moisture stability make them easy alternatives as chemically mild, stable electrolytes in the development of electrochemical and electrochromic (EC) devices [22]. With the use of acetonitrile, the deposition efficiency decreases as the film grows and the rate of electrodeposition is significantly faster in the ionic liquid than conventional non-polar solvents.

Conjugated polymers exhibit a change in their optical spectra when they are exposed to a dopant. The fact that conjugated polymers can repeatedly undergo electrochemical doping/undoping processes makes them a promising class of material to be used in EC devices with wide hue of colors. These π -conjugated polymers offer support for the incorporation of ionic liquids into a variety of electrochemical materials and their reversible doping/undoping processes make them suitable for application in electrochromic devices [21–26]. In contrast, PPy has received much less attention than polyaniline and poly(3,4-ethylenedioxythiophene) and other conjugated polymers due to the poor EC properties and α , β coupling [27]. Since the oxidized state of the PPy is black, the application of the PPy for EC devices is limited. One alternative to utilize the PPy as electrochromes is the use of N-substituted PPy, to induce specific properties in polymer. Thus, functionalization offers possibility to develop materials that show behavior resulting from the combination of properties due to the conjugated backbone (electronic properties) and the functional groups.

To tune the properties of parent PPy for electroactive and EC application, we report here a series of promising monomer, which has not been reported so far, distinguished by ortho(o-), meta(m-) and para(p-) position of alkyl group and the synthesis of corresponding polymer. N-substituted PPy shows different morphologies and conductivity according to the position of methyl group on the benzene ring and synthesis medium. The obtained conductivity values of polymers are in the range of semiconductive materials, i.e. $> 10^{-5}$ S/cm. An expedient means of the preparation and electrochemical, optical along with morphological properties of a series of N-(methyl)phenyl pyrroles electropolymerized in ionic liquids is discussed.

2. Experimental

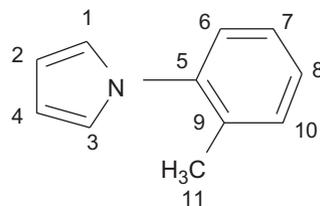
2.1. Synthesis and structural characterization of monomers

1-(2-methylphenyl)-1H-pyrrole, 1-(3-methylphenyl)-1H-pyrrole and 1-(4-methylphenyl)-1H-pyrrole: 26.5 ml glacial acetic acid and substituted toluidine (o-toluidine, m-toluidine and p-toluidine) (0.059 mol) were agitated using a magnetic stirring device and 2,5-dimethoxytetrahydrofuran (0.059 mol) was then added slowly to this mixture (10–15 min). The solution was refluxed for one hour under heating. When the color change from red to black was observed, acetic acid was removed from the solution with the aid of micro distillation setup. The residue, dark colored precipitate, was crystallized. The IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ results of monomers were given as follows:

1-(2-methylphenyl)-1H-pyrrole: (B.P: 203 °C, yield: 74%) IR ($V_{\text{max}}\text{KBr}$): 670 cm^{-1} (C–H bending), 1040 cm^{-1} (benzene), 1070–1200 cm^{-1} (aromatic C–H bending), 1325 cm^{-1} (C–H bending (alkene)), 1440–1461 cm^{-1} (CH_3 bending), 1504 cm^{-1} (aromatic), 1581 cm^{-1} (C=C stretching), 2860 cm^{-1} (aliphatic C–H stretching), 3029–3068 cm^{-1} (aromatic C–H stretching), 3129 cm^{-1} (C–H stretching (alkene)). $^1\text{H-NMR}$: $J_{\text{Ha-Hb}}$: ortho- 8.52 Hz, $J_{\text{Ha-Hc}}$: meta- 2.28 Hz, Ha: 7.39 ppm; $J_{\text{Hb-Ha}}$: ortho- 7.62 Hz, $J_{\text{Hb-Hc}}$: ortho- 7.60 Hz, $J_{\text{Hb-Hd}}$: meta- 2.30 Hz, Hb: 7.50 ppm; $J_{\text{Hc-Hb}}$: ortho- 7.42 Hz, $J_{\text{Hc-Hd}}$: ortho- 8.23 Hz, $J_{\text{Hc-Ha}}$: meta-

2.01 Hz Hc: 6.9 ppm, $J_{\text{Hd-Hc}}$: ortho- 6.72 Hz, $J_{\text{Hd-Hb}}$: meta- 2.72 Hz, Hd: 7.15 ppm; He: 2.25 ppm specific doublet peak, belongs to pyrrole H α : 6.9 ppm specific triplet peak; H β : 6.45 ppm specific triplet peak.

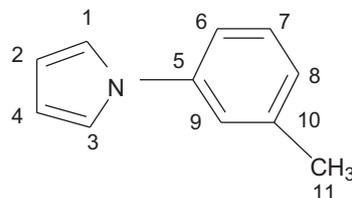
$^{13}\text{C-NMR}$: 134.05 ppm (C5), 130.79 ppm (C7), 127.82 ppm (C10), 122.67 ppm (C9), 122.32 ppm (C8), 119.11 ppm (C1–C3), 115.45 ppm (C6), 109.29 ppm (C2–C4), 17.67 ppm (C11).



1-(3-methylphenyl)-1 H-pyrrole: (B.P: 245 °C, Yield: 69%) IR ($V_{\text{max}}\text{KBr}$): 691 cm^{-1} (C–H bending), 1033 cm^{-1} (benzene), 1071–1089 cm^{-1} (aromatic C–H bending), 1322 cm^{-1} (C–H bending (alkene)), 1452 cm^{-1} (CH_3 bending), 1501 cm^{-1} (aromatic), 1592 cm^{-1} (C=C stretching), 2865 cm^{-1} (aliphatic C–H stretching), 3040 cm^{-1} (aromatic C–H stretching), 3136 cm^{-1} (C–H stretching (alkene)).

$^1\text{H-NMR}$: $J_{\text{Ha-Hb}}$: meta- 1.97 Hz, $J_{\text{Ha-Hd}}$: ortho- 7.84 Hz, Ha: 7.21 ppm; $J_{\text{Hb-Ha}}$: meta- 1.62 Hz, $J_{\text{Hb-Hc}}$: ortho- 8.42 Hz, $J_{\text{Hb-Hd}}$: meta- 1.97 Hz, Hb: 7.48 ppm; $J_{\text{Hc-Hb}}$: ortho- 6.72 Hz, $J_{\text{Hc-Hd}}$: ortho- 8.38 Hz, Hc: 7.50 ppm, $J_{\text{Hd-Hc}}$: ortho- 7.81 Hz, $J_{\text{Hd-Hb}}$: meta- 2.87 Hz, Hd: Ha meta- 1.83 Hz, Hd: 7.25 ppm; He: 2.25 ppm specific doublet peak, belongs to pyrrole H α : 7.19 ppm specific triplet peak; H β : 6.43 ppm specific triplet peak.

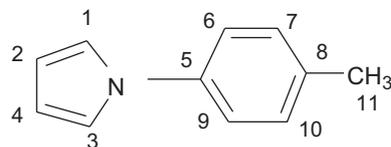
$^{13}\text{C-NMR}$: 140.92 ppm (C5), 139.67 ppm (C10), 129.54 ppm (C7), 126.57 ppm (C8), 121.40 ppm (C1–C3), 119.49 ppm (C6), 117.80 ppm (C9), 110.49 ppm (C2–C4), 21.66 ppm (C11).



1-(4-methylphenyl)-1 H-pyrrole: (Yield: 66%): IR ($V_{\text{max}}\text{KBr}$): 718 cm^{-1} (C–H bending), 1013 cm^{-1} (benzene), 1072 cm^{-1} (aromatic C–H bending), 1323 cm^{-1} (C–H bending), 1474 cm^{-1} (CH_3 bending), 1523 cm^{-1} (aromatic), 1599 cm^{-1} (C=C stretching), 2859 cm^{-1} (aliphatic C–H stretching), 3036 cm^{-1} (aromatic C–H stretching), 3141 cm^{-1} (C–H stretching (alkene)).

$^1\text{H-NMR}$: $J_{\text{Ha-Hb}}$: ortho- 7.36 Hz, Ha: 6.41 ppm, $J_{\text{Hb-Ha}}$: meta- 2.04 Hz, Hb: 7.45 ppm; He: 2.25 ppm specific doublet peak, belongs to pyrrole H α : 7.1 ppm specific triplet peak; H β : 6.35 ppm specific triplet peak.

$^{13}\text{C-NMR}$: 138.50 ppm (C5), 135.40 ppm (C8), 129.53 ppm (C7–C10), 120.56 ppm (C1–C3), 119.42 ppm (C6–C9), 110.09 ppm (C2–C4), 20.89 ppm (C11).



2.2. Deposition of the polymer films

1-ethyl-3-methylimidazolium bis(pentafluoroethylsulfonyle)imide (EMIPFSI) was synthesized according to the reported

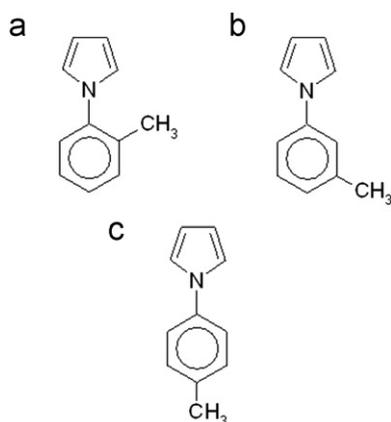


Fig. 1. Chemical structure of the ortho, meta and para N-(methyl)phenyl pyrrole (monomer) used in this study.

method [22] and was mixed with 0.1 M monomer (Fig. 1). EMIPFSI is a Bronsted acid–base ionic liquid, containing perfluorinated side chain as anion (PF₆[−]) makes them hydrophobic and has affinity toward O₂. Films were also grown galvanostatically onto conducting substrate (SnO₂:F coated glass) as anode at room temperature (25 ± 2 °C) in a glass cell including a Pt sheet as the cathode by passing current of 0.3 mA/cm² for 5 min under controlled environment. The substrates were cleaned ultrasonically prior to use, using deionized water, acetone and ethyl alcohol sequentially. In the text ortho, meta and para N-(methyl)phenyl polypyrroles will be now referred to as NoMPhPPy, NmMPhPPy and NpMPhPPy, respectively. For comparison, NoMPhPPy films were also grown in control media consisting of a 0.25 M LiCF₃SO₃ (Aldrich) in acetonitrile (Merck) with 0.1 M monomer. After the polymerization, the film was removed from growth solution, washed with isopropyl alcohol to get rid of any unreacted monomer as well as ionic liquids.

2.3. Characterization of the polymer films

FTIR spectra of the samples were recorded in the transmission mode at room temperature on a Perkin–Elmer spectrometer (HP91QA, UK) in the range of 400–4000 cm^{−1} with resolution of 4 cm^{−1}. ¹H- and ¹³C-NMR spectra were recorded on Bruker using CDCl₃ as a solvent. Conductivity measurements were carried out using a PCI-DAS6014 (Measurement Computing) as a current source, voltmeter and temperature controller following a standard four point probe method. UV–Vis absorption measurements were recorded with a Perkin Elmer, Lambda 900 spectrophotometer while the contact angle measurements were carried out by the Sessile drop method using a drop shape analyzer (DSA 100, DSA/V 1.9) from Kruss GmbH. Scanning probe microscopy (SPM) microscopy (SPM) images were recorded in intermittent contact mode (Dimension 3100, Veeco), by using Si-probes OMCL 160TS (Olympus, cantilever having a nominal spring constant 42 Nm^{−1} and a resonance frequency of 300 kHz). Electrochemical characterizations of samples were carried out in the three-electrode cell equipped with a Gamry potentiostat (Gamry Instruments). The platinum disk or conducting glass substrates were used as working electrodes, platinum wire and Ag/AgCl electrodes were used as counter and reference electrodes, respectively. Alumina polishing suspension agglomerate (0.05 μm CR) (Baikowski) was used as electrode polisher. Scanning electron microscopy images were recorded on Phillips XL-30S FEG, while transmission electron microscope (TEM) images were recorded on a Philips CM-10 instrument, and the samples were extracted onto carbon coated copper grids using N-methyl pyrrolidine and dried before use.

3. Results and discussion

3.1. Electrochemical studies

The growth of polymers was studied by cyclic voltammograms at a scan rate 50 mV/s (Supporting Info. S1). These voltammograms illustrate characteristic polymerization graphics and with the increase in the polymerization cycles the color of the polymer turned from yellow to brown-black on the electrode surface after thirty cycles (Fig. S2). The anodic oxidation peak was obtained about 1.5 V vs. Ag/AgCl for the control media (Fig. S1a), while this value was lowered by 150 mV to about 1.35 V for ionic liquids (Fig. S1b), due to the low surface potential of ionic liquids in the polymerization process [28]. After thirty scans cycle the polymer coated modified electrode was rinsed to remove the monomer and oligomer residues and dried. Fig. 2 shows the redox properties of the N-substituted polypyrroles films in monomer free EMIPFSI and the oxidation potentials shift to higher values, which indicate the polymerization of N-substituted pyrroles [29]. The polymer films shows high electroactivity in EMIPFSI. Inset of

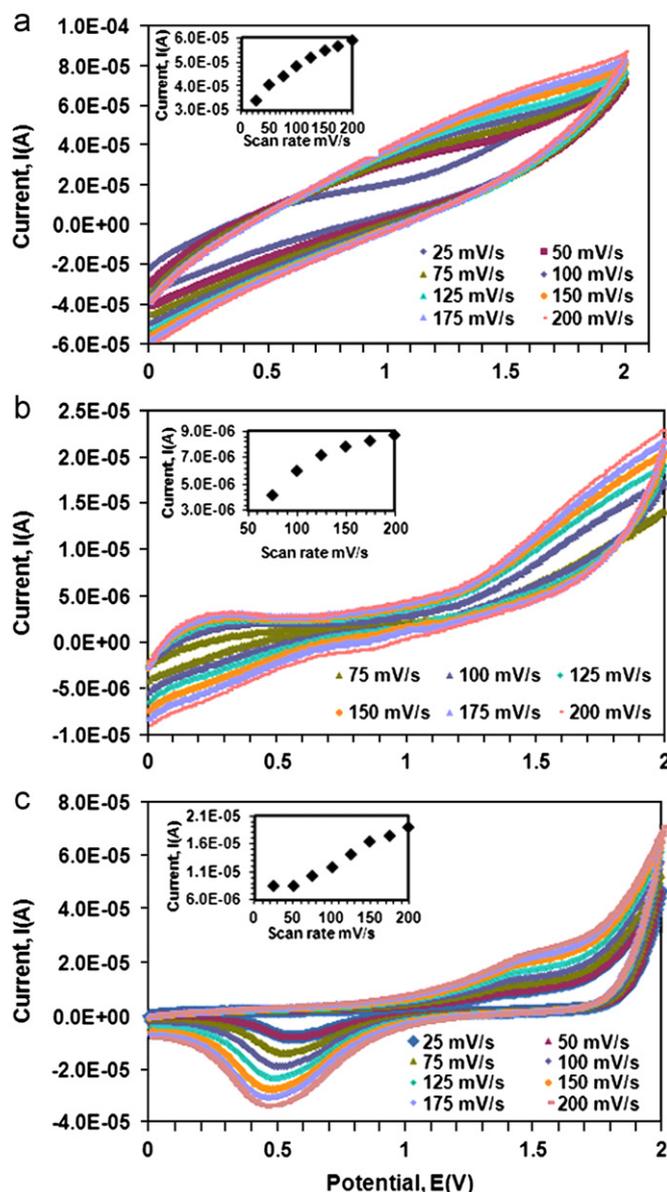


Fig. 2. Redox properties of polymer films in EMIPFSI at various scan rates (25–200 mV/s) for (a) NoMPhPPy, (b) NmMPhPPy and (c) NpMPhPPy.

Fig. 1a–c shows a linear increase in the anodic peak current density as a function of the scan rate pointing towards the redox reaction in these films is diffusion limited. The redox activity of the polymer films remains fairly constant and it follows the reversible redox couples as observed during the cycling.

3.2. FTIR of N-substituted polypyrroles

FTIR spectra of the electropolymerized NoMPhPPy synthesized in two media is distinct, the one which is prepared in ionic liquids exhibits less water uptake, are shown in Fig. 3(a–b). The observed bands from FTIR spectra of N-(methyl)phenyl pyrroles are characteristic bands for pyrrole and phenyl rings, and they are very similar to each other. The sharp peak at around 1574 cm^{-1} is one of the characteristic bands of pyrrole ring while the absorption band at 1458 cm^{-1} is attributed to the in plane =CH stretching vibrations of pyrrole and phenyl rings [30]. The peaks appeared in the range of 1223 and 1089 cm^{-1} are the signature peaks for pyrrole rings [31] while the absorption bands at 742 – 743 , 977 – 978 and 1086 – 1088 cm^{-1} correspond to C–H stretching of N-substituted pyrroles. The weak bands that appeared to be around 2980 cm^{-1} were attributed to alkyl groups for N-substituted PPy, while the appearance of band around 790 cm^{-1} was distinctive of substituted five-member heterocyclic compound indicates α -coupling of ring. The peaks at around 839 , and 643 cm^{-1} in the spectra of N-(methyl)phenyl pyrroles were assigned to the out-of-plane vibration of three adjacent carbon–hydrogen bonds in the spectrum reflect the substituted benzene ring [32]. FTIR spectra of the NoMPhPPy synthesized in two media have also indicated difference in the peak around 1033 cm^{-1} . This peak is characteristic, SO_3 stretching vibration showing the presence of LiCF_3SO_3 as doping anion [33].

3.3. Scanning probe microscopy (SPM)

SPM measurements were performed to have an idea of root mean square (RMS) roughness and phase contrast on these different N-(methyl)phenyl polypyrrole films. Small granules like structures were observed from SPM in contrast to large granules (cauliflower) like morphology that is characteristics of PPy. These synthesized N-(methyl)phenyl substituted polypyrrole films shows nanoparticulate structure having size of $> 100\text{ nm}$, which was also observed from TEM images (Supporting info. S3). Topography of these films (Fig. 4) exhibits homogeneous morphologies and the size of grains are fairly affected from the

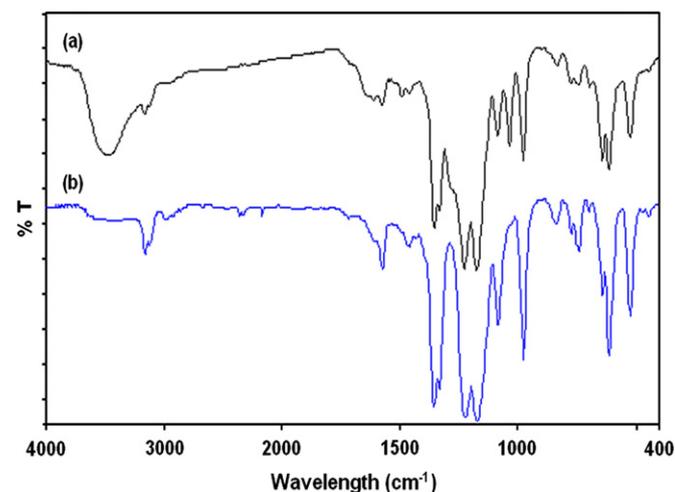


Fig. 3. FTIR spectra of (a) NoMPhPPy in control solution and (b) NoMPhPPy in ionic liquids.

position of methyl group in the polymer backbone. These granules become larger by shifting the methyl group from o- to m- to p- positions due to steric effect.

The RMS roughness value of these films was found to be of $12 \pm 0.5\text{ nm}$ estimated on an area of $1 \times 1\text{ }\mu\text{m}^2$. The phase contrast recorded at the scale of $1 \times 1\text{ }\mu\text{m}^2$ did not reveal a significant contrast (Fig. 4a') thus the substrate is covered entirely with the polymer film of uniform deformability. By varying the position of substituent, the film morphologies differ significantly. The small grain size will increase the surface area of polymer films and might facilitate ion immobilization and mass diffusion at solid/liquid interface, and thus improve the performance of the electrodes for electrocatalytic properties. The high surface area coverage and continuous film formation properties for the films deposited in ionic liquids might be potentially useful for sensor and other applications.

N-substituted PPy are known to demonstrate conductivity of many orders of magnitude lower than that of PPy. Table 1 represents the conductivity value for different substituents of alkyl group in phenyl polypyrrole. The electrical conductivity and oxidation level of the 1-alkyl-substituted polypyrroles decreases with increasing size of the alkyl substituent as substituents give rise to modifications in polymer film properties [34]. Thus, while PPy films can demonstrate a conductivity value of upto 100 S/cm , poly-1-(methyl)pyrrole has a conductivity of 10^{-3} S/cm , and here we have observed that N-(methyl)phenyl polypyrroles show conductivity in the range of $> 10^{-5}\text{ S/cm}$. Due to the large size of the substituent at the nitrogen atom, the steric interaction between the repeating units will be higher and results in lower conductivity. We speculate that the substituents alter the polymer conductivity solely via a steric effect. The substituent effects exerted by N-(p-methyl)phenyl pyrrole are much more subtle than 1-substituted pyrroles since the electronic substituent effect is first transmitted through a phenyl ring before the pyrrole structure is affected and thus has a lower conductivity among all the three substituents. Furthermore, if the phenyl ring is twisted relative to the pyrrole moieties, the substituent effect is further diluted. Thus, the substituent effect is expected to be rather modest, and this has been observed. The ionic liquids based samples show increase in the conductivity value than control one, which may be attributed due to the imidazolium cation, which also incorporate into polymer matrix when ionic liquids is used as a medium for electropolymerization.

The contact angle value reveals the hydrophobic/hydrophilic character of the surface. The use of ionic liquids makes the polymer more hydrophobic and the position of methyl group also has a bearing on the hydrophobicity of polymer. NpMPhPPy shows higher contact angle value, which illustrates its hydrophobicity among o- and m- position alkyl group.

3.4. UV–Vis spectra

The absorption maxima in the spectra of N-methylphenyl pyrroles were shifted to the higher wavelength from monomers, shows that the conjugation is increasing when polymerization is realized. Since PPy is strongly colored in both doped–undoped states and its contrast ratio is too low for the fabrication of practical EC devices. The electrochromic properties (Fig. 5) of the N-(methyl)phenyl polypyrrole films were analyzed *ex-situ* in liquid electrolytes ($1\text{ M LiCF}_3\text{SO}_3$ in acetonitrile). The maximum absorbance in oxidized state is shown by the p-substituted followed by o-substituted (methyl)phenyl polypyrrole, which shows absorbance in photopic wavelengths at 356 and 318 nm , respectively, while the m-substituent shows up at 314 nm and the film produced in a conventional lithium triflate–acetonitrile solution shows the lowest. All the polymers film exhibit different

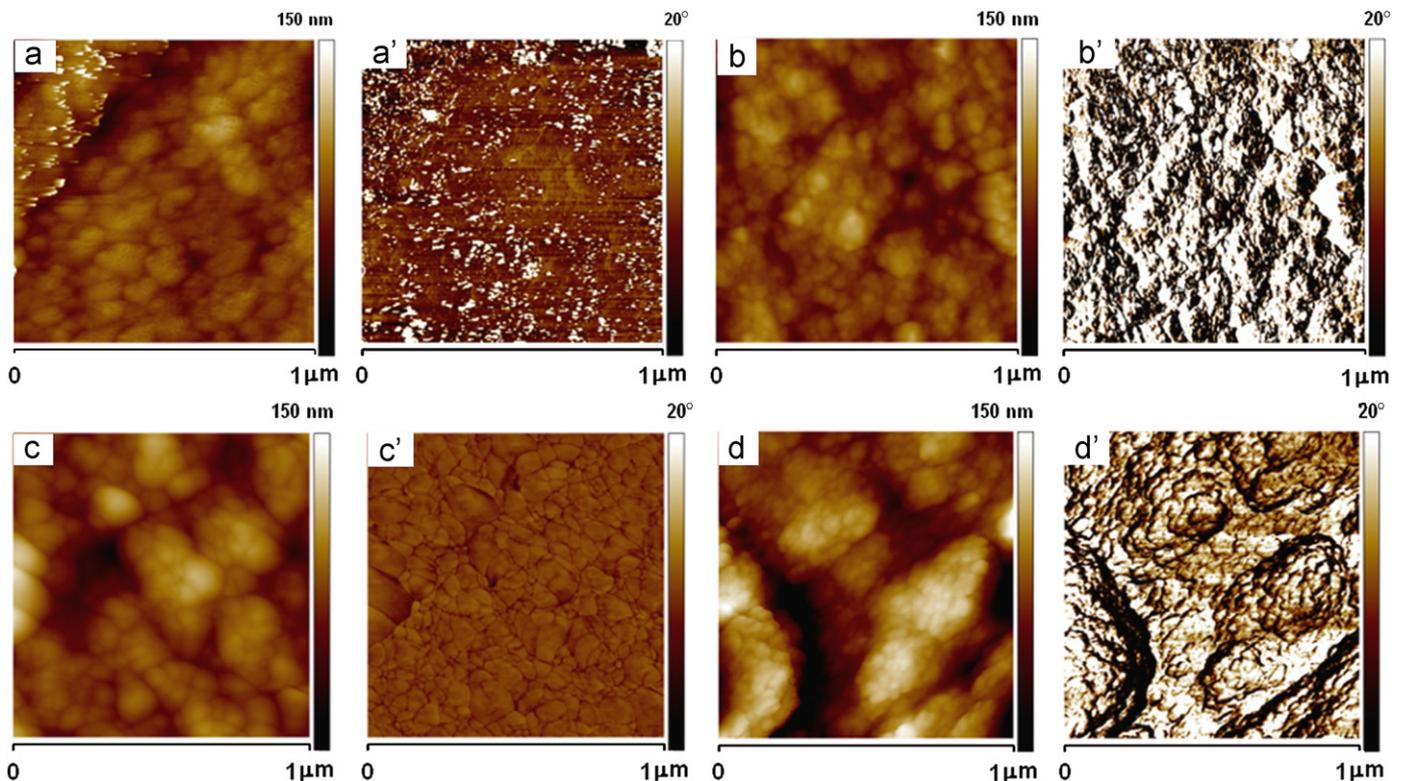


Fig. 4. Scanning probe microscopy images of (a) NoMPhPPy in control solution, (b) NoMPhPPy, (c) NmMPhPPy and (d) NpMPhPPy in ionic liquids while (a'–d') represent the corresponding phase images.

Table 1

Conductivity and contact angle value for various substituted N-(methyl)phenyl polypyrrole.

Sample	Conductivity (S/cm)	Contact angle
NoMPhPPy (control solution)	6×10^{-5}	58.1
NoMPhPPy (ILs)	9×10^{-5}	60.4
NmMPhPPy(ILs)	5.2×10^{-5}	62
NpMPhPPy(ILs)	1.2×10^{-5}	64

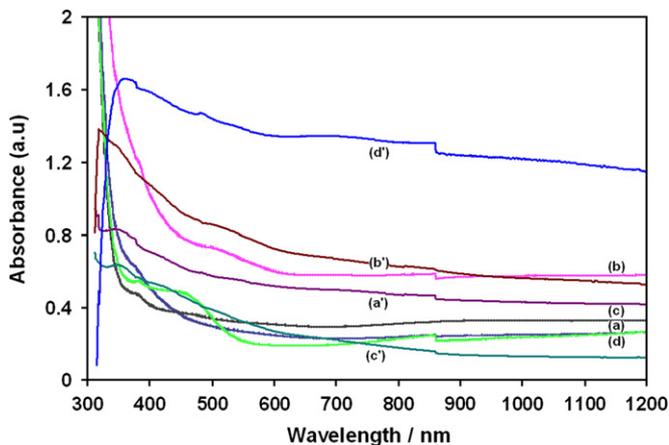


Fig. 5. Absorption spectra of (a) NoMPhPPy in control solution, (b) NoMPhPPy, (c) NmMPhPPy and (d) NpMPhPPy in ionic liquids as synthesized in colored state and (a'–d') the corresponding oxidized state obtain by passing 1.5 V for 60 sec.

$\pi-\pi^*$ transition as the λ_{\max} value is shifting with the o-, m- and p-position. The NpMPhPPy exhibits maximum change in transmission from colored to bleached state and demonstrate

relatively lower band gap as can be observed from $\pi-\pi^*$ transition in oxidized state. The UV–Vis absorption in the neutral state shows a broad peak between 400–500 nm, which corresponds to the transitions from valence band to the anti-bonding polaron state. As the extent of oxidation increases, bipolaron formation increases. The presence of bipolarons leads to only two optical transitions in the gap, which explains the appearance of absorption spectra at higher oxidation levels. All these films can be switched between the reduced (dark brown) to oxidized state. The absorption peak observed between 310 and 350 is assigned to $\pi-\pi^*$ transition associated with phenyl ring. At the neutral state due to the $\pi-\pi^*$ transitions, λ_{\max} for PPY (Fig. 5) was found to be starting at around 390 nm. N-substituents in the PPY give rise to a nano-particulate structure, where this unique geometry will facilitate ion extraction and injection along with better charge retention properties.

4. Conclusions

o-,m- and p-, (methyl)phenyl pyrrole has been synthesized by an easy synthetic approach and then electropolymerized to obtain a new series of PPY family by direct anodic oxidation in a hydrophobic ionic liquid. FTIR and UV–Visible optical results show that the spectra of the N-(methyl)phenyl polypyrroles are affected from the position of methyl group. N-(methyl)phenyl polypyrroles show different morphologies and conductivity according to the position of methyl group on the benzene ring and synthesis medium. The conductivity values of these polymers are in the range of semi conductive materials, i.e. $> 10^{-5}$ S/cm. These new series of N-(methyl)phenyl polypyrroles also exhibit switching properties, i.e. color change from golden brown to gray on an application of small dc voltage. Compact and adherent thin film was obtained, which exhibits good electrocatalytic activity

and stability. We believe that these polymers will pave way for the development of new materials with potential application.

Supporting information available

Cyclic voltammetry growth of polymers in different media, transmission and scanning electron microscope images and FTIR of polymers.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.solmat.2011.09.049.

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