Electrochemical synthesis and characterization of conducting polymers using room temperature melt as an electrolyte

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Abstract

Aromatic monomers can be polymerised using the chloroaluminate room temperature melt obtained by mixing 1:2 ratio of cetyl pyridinium chloride and anhydrous aluminium chloride miscible in all proportions with organic solvents as an electrolyte. The chloroaluminate ($AlCl_4{}^-$) anion generated in this melt having a tetrahedral symmetry with equal bond lengths and bond angles is the dopant to stabilize macrocation generated near the vicinity of anode to yield better conducting and better ordered electronically conducting free standing polymer film. In this communication, we discuss the polymers derived from benzene and pyrrole and their characterization by various techniques.
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1. Introduction

It is well known that there exists a strong correlation between the extent of order in conjugated polymers and the maximum attainable conductivity [1]. Therefore, any improvement in orderliness would yield a conducting polymer having a better electronic conductivity. Interest in room temperature melt in the study of conducting polymers is due to the fact that electrolyte is free from solvent, thus preventing a side reaction of a solvent molecule with moderately stable radical cation generated during electrochemical synthesis near the vicinity of an anode. Trivedi [2–4] worked out a room temperature melt wherein deposition of aluminium on cathode is prevented to make available tetrahedral $AlCl_4{}^-$ ion for a doping reaction. The methodology is simple and replaces tetraalkyl salt normally used along with anhydrous aluminium chloride by Osteryoung et al. [5] by bulky cetyl pyridinium chloride which preferentially gets discharged at cathode to prevent alumininum deposit on cathode thereby $AlCl_4{}^-$ is available to stabilise macrocation by way of a doping reaction. In this presentation, we have used this melt to synthesize conducting polyparaphenylene and polypyrrole.

2. Experimental

Electro deposition of PPP and PPy were carried out by sweeping potential at 50 mV/s between 0 to 1.7 and −0.2 to 1 V versus Al wire, respectively, from the electrolyte containing 0.1 M of monomer.

Anhydrous aluminium chloride, recrystallized cetyl pyridinium chloride and distilled monomers were used (Sigma–Aldrich). Cetyl pyridinium chloride (33%) and aluminium chloride (67%) were mixed together thoroughly under a dry condition in a glove box to get a highly viscous liquid (melt).

2.1. Optical measurements

The electronic spectra of the electrodeposited conducting polymer film were recorded on Cary 500 scan UV–vis–NIR spectrophotometer using high alumina as reference in the range 200–1500 nm in a diffused reflectance mode. FTIR spectra were recorded on Perkin-Elmer Paragon −500 FTIR spectrophotometer in KBr medium in the region 400–4000 cm^{-1} (Table 1).

2.2. Conductivity and morphological studies

The electronic conductivity measurements were carried out by four probe method using Keithley Model 2400 series Source

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Table 1
IR bands in conducting polyparaphenylene and polypyrrole

PPP (cm^{-1})	Assignments	PPy (cm^{-1})	Assignments
650, 750	H in the end phenyl rings	1010; no band at 3400	C—H def; N—H absorption
805	Para substitution	1290	C—H, N—H def
1000	Aromatic in-plane H bending vibration	1529	C=C str
515, 689	Dopant peaks	510, 690	Dopant peaks

meter and Keithley Model 2182 Nano voltmeter equipment under nitrogen atmosphere. Scanning electron micrographs were recorded at various magnifications using Hitachi-S-3000H SEM machine.

2.3. Electrochemical characterization

The electrochemical characterization was carried out by cyclic voltammetric experiments at various sweep rates and electrochemical growth by step potential techniques using EG&G PARC Model 175 universal programmer and Tacussel bi-pad type potentiostat with BBC-GOERZ METRAWATT SE790 model recorder at room temperature. The impedance studies were carried out using EG&G impedance analyzer (Princeton Applied Research, USA Model no. 6310) under open circuit potential in the ac frequency range 100 kHz to 0.1 Hz with an excitation signal of 10 mV.

3. Results and discussions

The present study is an electrochemical version of Friedel Craft's reaction where the dopant $AlCl_4^-$ ion influences the polymer structure. The polymerisation takes place at comparatively lower potentials indicating that there is a remote possibility for side reactions to yield an ordered polymer. In this medium, benzene polymerisation occurs around 1.2 V and pyrrole around 0.58 V versus Al wire comparatively less than that in acetonitrile for benzene at 2.0 V and for pyrrole at 0.8 V [6]. The electrochemical polymerisation by cyclic voltammetry of benzene to freestanding polyparaphenylene (PPP) film and pyrrole to polypyrrole film in room temperature melt is shown in Fig. 1. The first cycle is attributed for the formation of radical cation. In the subsequent cycles, appearing of new peaks indicates that these radical cations undergo further coupling and the peak current increases continuously with successive potential
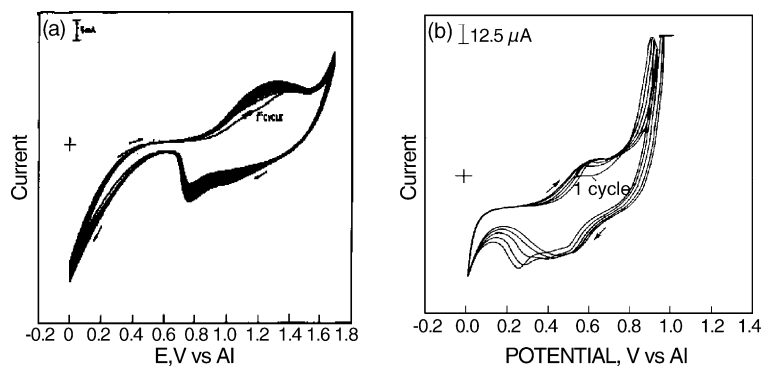

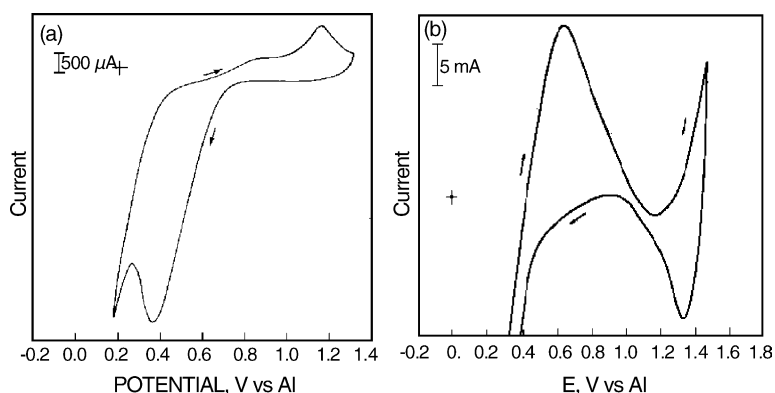Fig. 1. Cyclic voltametric growth pattern of PPP (a) and PPy (b).

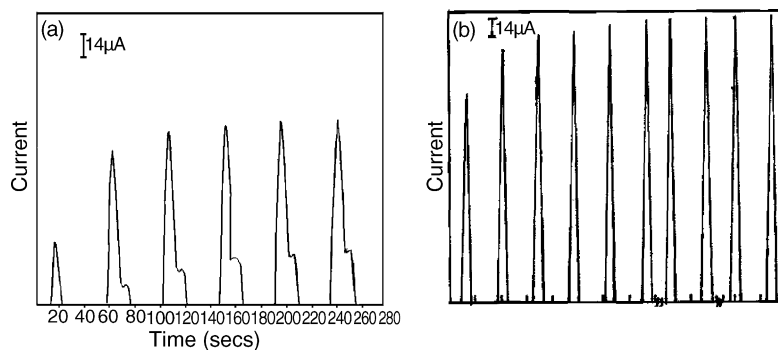Fig. 2. CV characterization of PPy (a) and PPP (b).

Fig. 3. Current time transients by potential step technique of PPy (a) and PPP (b).

scans indicating the build up of electroactive polymer on the electrode surface. Well-defined redox peaks in the characterization curves Fig. 2 indicate the reversibility of the system. From potential step technique Fig. 3, the shape of the curve showed layered structure of the polymer. [1] The dc conductivity of freshly deposited PPP film was 3.5×10^4 S/cm and PPy was 1.3×10^2 S/cm higher than previously reported values. [7] When exposed to air the conductivity slowly decreases because after exposure to atmosphere the dopant in doped polymer films react with moisture to yield aluminum oxy chloride and aluminum hydroxide, to render the undoped state, however these films can be redoped by anodising polymer film in an electrolyte. The conductivity of undoped PPP and PPy were observed to be of the order 10^{-9} S/cm.

3.1. Impedance studies

Fig. 4 gives the impedance spectra of doped and virgin (a) PPP and (b) PPy films in the room temperature melt. PPP film in the doped form exhibits a very low charge transfer resistance (R_{ct}) than the undoped form. As can be seen in figures of doped and undoped, the doping process dramatically modifies the impedance response of the systems. The semicircle obtained from the high frequency region is ascribed to the blocking properties of a single electrode, which render extremely slow the faradic process of the ion-exchange at the polymer/electrolyte interface [8]. The doped PPP film is attributed to have a higher electronic conductivity, i.e. low impedance and vice versa. It was found that the charge transfer resistance (R_{ct}) increases to the three-fold greater values for undoped PPP because when the dopants are removed, the film becomes more stable. The solution resistance (R_s) remains almost the same for both films. From this, it is evident that the reactivity of doped PPP film is very high and hence when exposed to air it is easily attacked by moisture and a passive layer is formed which loses conductivity and reactivity and thus attains the undoped form.

The electrochemical impedance for undoped PPy shows semicircle in the entire frequency region and there is no diffusion impedance in the low frequency region. In the undoped film, mass transfer polarization will be less and activation control will take over. This will be reflected in the R_{ct} values wherein charge carrier concentration will be less, whereas the EIS of the doped PPy shows a semicircle in the high frequency region and a straight line with slope of nearly 45° in the low frequency region, Warburg diffusion impedance. The high value at the low frequency side may be due to diffusional impedance created by the charge carriers across the polymer/electrode/electrolyte interface and this is bound to be higher and this is understandable from the low capacitance value 8.8 μF. This may be due to the diffusion of $AlCl_4^-$ dopant ion across the interface and consequently to the decrease in the mobility of the dopant ions. Regarding the semicircles, both in doped (uncompleted) and in
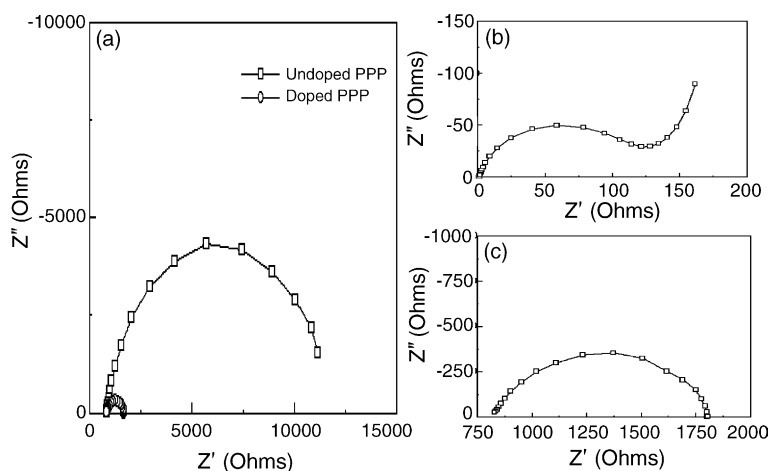

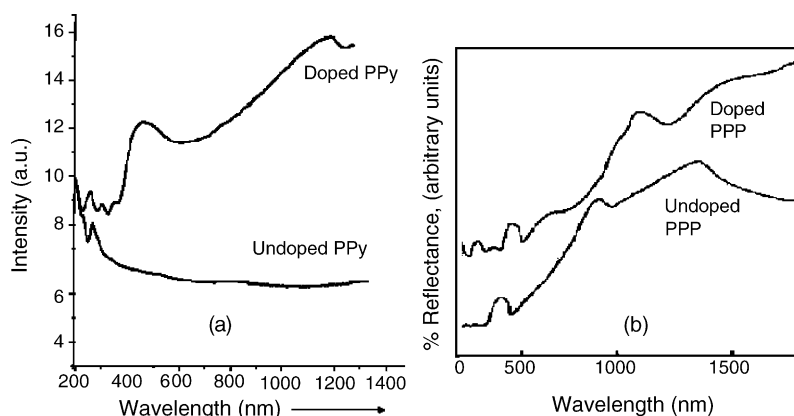Fig. 4. Impedance spectra of PPP (a) and PPy (b).

Fig. 5. Diffused reflectance UV–vis–NIR spectra of PPy (a) and PPP (b).

undoped (completed) forms are somehow compressed indicating a relaxation process. When a 'Nyquist plot contains a depressed semicircle with the center at the real axis' such behavior is characteristic for solid electrodes [9,10]. Normally, the intercept of Warburg impedance (corresponding to Z'' minimum) should lead to a value of dc conductivity. From the impedance plot, this value seems to be 132 Ω for the doped species and this value will not correspond with the measured dc conductivity. This is because the semicircle corresponds to various processes taking place at he electrode/electrolyte interface. The method of finding the dc conductivity by extrapolating the low frequency Warburg behavior will be valid only for simple cases and hence this method of getting dc conductivity value is not appropriate in the present case. However, as the dc conductivity of PPP is more than PPy and consequently the charge carrier concentration. Hence, when undoped there is a large difference in R_{ct} value in PPP than in PPy.

3.2. UV–vis–NIR spectroscopic studies for PPP

The absorption bands at 350 and 881 nm for undoped PPP and at 327, 386, 560 and 1336 nm for the doped PPP are observed.

The position of the main band at 350 nm does not significantly vary with doped and undoped species. Our λ_{max} value of 350 nm (3.4 eV) in the undoped and 386 nm in the doped PPP is in good agreement with the theoritical peak position of 339 nm (3.66 eV) reported by Susuki [11] for an infinite number of phenyl rings. It is also close to the band gap energy values of 3.4 eV obtained from diffuse reflectance experiments [12] and 3.4–3.5 eV reported by Froyer et al. [13] for PPP films oxidized at constant voltages. The band at 1336 nm is due to the bipolarons in the doped form.

The first absorption peak around 0.7 eV (1764 nm) in the doped PPy spectra can be related to a transition from the valance band to the half filled polaron bonding level while the peak around 1.4 eV (882 nm) associated with the transition between bonding and antibonding polaron levels. The peak around 2.1 eV (457 nm) corresponds to the transitions from valance band to the antibonding polaron state. The bipolaron introduces the two states in the gap, at 0.75 eV above the valance band edge and 0.79 eV below the conduction band edge. However the bonding bipolaron state is empty, the presence of bipolarons leads to only two optical transitions in the gap which explains the appearance of absorption spectra at higher oxidation levels where the two intense bands within the gap are accounted for the two wide bipolaron bands. The diffuse reflectance UV–vis–NIR spectra of PPy (a) and PPP (b) are given in Fig. 5.

3.3. FTIR studies on PPP and PPy

The FTIR bands for doped PPP and PPy are given in Table 1 and spectra in Fig. 6.

The degree of polymerization may be estimated for PPP from the intensities of the bands around 800 cm^{-1} (1,4-disubstituted
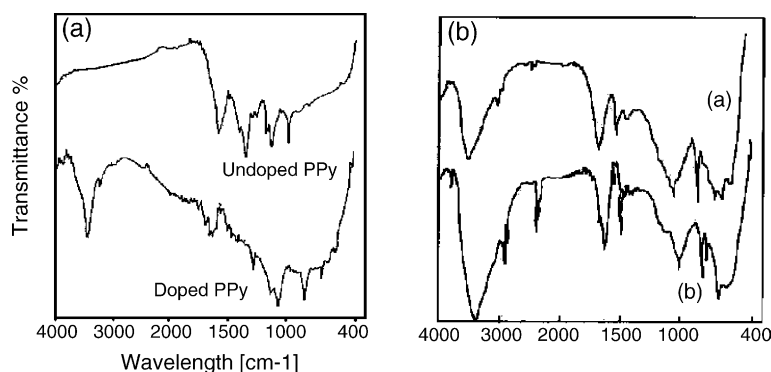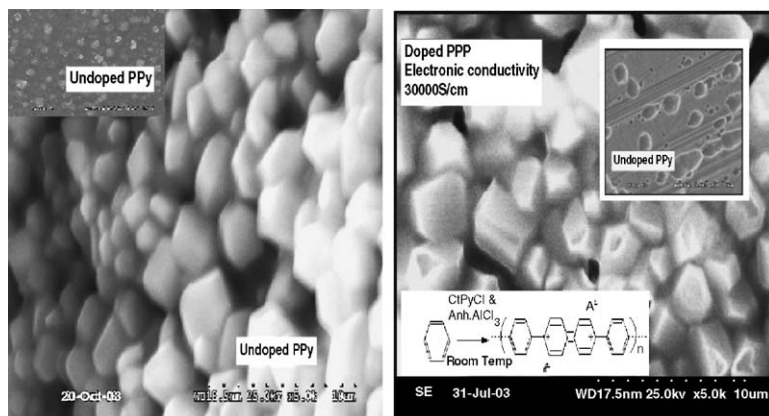

Fig. 6. FTIR spectra of PPy (a) and PPP (b).

Fig. 7. Scanning electron micrograph for PPy (a) and PPP (b).

benzene ring) and $690 \, cm^{-1}$ (monosubstituted benzene ring) following the empirical formula [14].

$DP = 2(I_{800}/I_{690}) + 2$. The DP was found to be 76 for doped species. The dopant peaks of $Al_2Cl_7^-$ appear in both spectra at 517 and $689 \, cm^{-1}$ confirmed by literature [15].

3.4. Scanning electron micrograph

Fig. 7 shows the scanning electron micrograph of doped and undoped PPy (a) and PPP (b) polymer films. Both the doped films show hexagonal morphology. A uniform bright portion in both pictures shows homogeneity of doping. The particle size in PPP film is in the range 0.8–2.8 μm and for PPy film it is between 2.5 and 3.5 μm. The undoped SEM photographs indicate dark non-conducting portions.

4. Conclusion

Benzene and pyrrole can be anodically polymerized at comparatively lower potentials in acidic room temperature melt as an electrolyte to yield uniform shining films of thickness around 100 μm which can easily be peeled off from the electrode surface. This highly conducting polymer films can be prevented from degradation due to atmospheric moisture by giving a coating of polyvinyl chloride solution. Our study also suggests that ordered dopants like $AlCl_4^-$ anion enhance the conductivity by increasing the degree of polymerisation. To find out how the dopant influences the conductivity of polymer films, we subjected electrosynthesis of polymer films in lithium perchlorate/acetonitrile medium whose conductivities were around 10 S/cm for polypyrrole and 1 S/cm for PPP. We also anodised the undoped films from our methodology using the ClO_4^- ions by sweeping the potential between -0.2 and 1.25 V versus Al wire for PPP and between -0.2 and 0.8 V versus Al wire for PPy whose conductivities were found to be around 8 S/cm for PPP and 18 S/cm for PPy. This rise in conductivity is due to the increase in degree of polymerisation due to the ordered dopant and also the electrolyte is free of any solvent reactions.

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