

Electrochemical synthesis and characterization of conducting polyparaphenylene using room-temperature melt as the electrolyte

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Abstract

Freestanding polyparaphenylene films were obtained on polymerization of benzene at potential of 1.2 V versus Al wire on substrates like platinum/transparent conducting glass as an anode. The electrolyte used was chloroaluminate room-temperature melt, which was prepared by intimate mixing of a 1:2 ratio of cetyl pyridinium chloride and anhydrous aluminum chloride to yield a viscous liquid. This liquid was miscible in all proportions with benzene and other aromatic hydrocarbons in all proportions at room temperature. The polyparaphenylene films deposited on platinum anode exhibited a prominent cyclic voltammetric peak at 0.7 V versus Al wire as reference electrode in chloroaluminate medium. The impedance spectra gave low charge transfer resistance. The diffused reflectance electronic spectra of the film gave the peaks at 386 nm and 886 nm. The PPP films showed electronic conductivity around $3\text{--}4 \times 10^4$ S/cm by four probe method under nitrogen atmosphere. The polymer was also characterized by IR spectra, thermal studies, and SEM studies.

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1. Introduction

Organic-based polymers have originated possessing the remarkable ability to conduct electrical current, and are known as conducting polymers or synthetic metals, and are finding practical applications in (i) rechargeable batteries [1], (ii) electrolytic capacitors [2], (iii) bio-sensors [3], (iv) flexible light-emitting diodes [4], (v) smart windows [5], (vi) separation of gases [6], (vii) ion exchange membranes [7] and (viii) dissipation of electrostatic charge [8] etc. Researches are under process for the development of polymer magnets [9]. The envisaged applications are many, with a tremendous potential for future scientific and technological development. The excitement about these relatively new materials is high

because of the novelty of the concept that plastics, which are less corrosive, can be shaped and can perform the function of either metals or semiconductors or an insulator by modulating doping levels [10]. The basic requirement of these systems is to achieve electronic conductivity in conjugation to yield a band structure. Here, in these polymers valence electrons are completely delocalized and move almost freely along the polymer backbone to exhibit metal-like electronic conductivity.

Polyparaphenylene is a conjugated polymer with a simple molecular structure and has been widely investigated out of fundamental interest [11] and for practical applications [12]. Several reviews [13,14] and original papers have described the synthesis of polyparaphenylene (PPP) by chemical [15–21] and electrochemical methods [22–29]. Direct coupling of benzene or biphenyl using several Lewis acids and catalyst-oxidant pairs [15,16,18] also yielded PPP. The other prominent methods were to use Grignard reagents and

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aryl halides [17] and Wurtz–Fittig and Ulman reactions [19]. These methods invariably yield low molar mass polymers. The cathodic reduction of *para*-di-bromobenzene and *para*-dibromobiphenyl using Ni (II) compounds has also been discussed [26,27]; this method yields the undoped polymer and the yields are poor. The direct electrochemical oxidation of benzene and biphenyl in organic solvents like acetonitrile or propylene carbonate do yield flexible, electroactive and low conductive films [25,28] with polymerization degrees smaller than 22. The restricted metallic conductivity of poly-paraphenylene using all these methodologies is essentially either due to folding, cross-linking or involvement of a solvent molecule, due to solvated dopant.

Therefore, any improvement in conjugation length, structural order and chain alignment may dramatically improve the electrical conductivity and mechanical properties of PPP [30]. To overcome these difficulties to a certain extent, we explored a new room-temperature melt obtained by mixing freshly sublimed anhydrous aluminum chloride (67%, 2 mol) and cetyl pyridinium chloride (33%, 1 mol) to be used as the electrolyte to polymerize benzene anodically [31]. The present work involves the synthesis and detailed characterization of conducting PPP using this room-temperature melt as an electrolyte by potentiodynamic method and characterizing this polymer by cyclic voltammetry, electrochemical impedance, potential step technique, electronic and vibrational spectra, thermal studies, and scanning electron micrographs (SEM).

2. Experimental

2.1. Reagents

Anhydrous aluminum chloride, recrystallized cetyl pyridinium chloride and distilled benzene were used (Sigma–Aldrich).

2.2. Preparation of electrolyte

Cetyl pyridinium chloride (67%) and aluminum chloride (33%) were mixed together thoroughly inside a dry box to get a highly viscous liquid (melt). The proportion of aluminum chloride is always maintained to be higher than cetyl pyridinium chloride to get the acidic melt. This viscous melt is dissolved in benzene (monomer) to reduce the viscosity.

2.3. Electrochemical polymerization

The electro polymerization of benzene was carried out by potentiodynamic technique at room temperature. A three-compartment sealed glass electrochemical cell was used with platinum sheet as the working electrode and platinum wire was used as the counter electrode. A high purity aluminum wire was used as the reference electrode. The electro deposition of PPP was carried out by sweeping potential at 50 mV/s

in the potential range of 0 to 1.7 V versus Al wire from the 0.1 M electrolyte prepared by adding the room-temperature melt in benzene.

2.4. Characterization

The characterization of PPP film was carried out under anhydrous conditions by electrochemical techniques, spectroscopic methods, conductivity measurements, thermal analysis and scanning electron micrograph.

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–0.1 Hz with an excitation signal of 10 mV.

The electronic conductivity measurements were carried out by four probe method using Keithley Model 2400 series source meter and Keithley Model 2182 nano voltmeter equipment under nitrogen atmosphere.

The electronic spectra of the electrode surface were recorded on Cary 500 scan UV-visible Near IR spectrophotometer using high alumina pellet as reference in the range 200–1500 nm. FTIR spectra were registered using Perkin-Elmer Paragon-500 FTIR spectrophotometer using KBr pellets in the region between 400 cm^{−1} and 4000 cm^{−1}.

The thermal studies were carried out in the air at the heating rate of 10°/min using Simultaneous Thermal Analyzer (Model No. STA 1500, PL Thermal Sciences, UK).

Scanning electron micrographs were recorded at various magnifications using Hitachi-S-3000H SEM machine.

3. Results and discussions

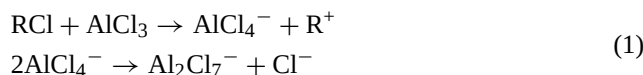
3.1. Film appearance

The color of the PPP film depends on the thickness and varies from red to dark brown in doped state on the platinum substrate. In an undoped state, PPP film is dark yellow and becomes dark red upon doping. The film turned to pale brown in the undoped state, which was obtained by washing with aqueous ammonia and final washings with water for 4 h.

3.2. Innovation of the melt

Interest in room-temperature melt in the study of conducting polymers is due to the fact that electrolyte is free from solvent, thus one can prevent a side reaction of a solvent molecule with moderately stable radical cation generated during electrochemical synthesis near the vicinity of an anode. Thus, the electrolyte, devoid of solvent, can yield a better-

oriented polymer with better conjugation and electronic conductivity. However, these melts in the synthesis of conducting polymers were elusive because of the cathodic deposition of aluminum, thereby, non-availability of $\text{AlCl}_4^-/\text{Al}_2\text{Cl}_7^-$ to initiate the polymerization reaction in an electrochemical version of Friedel–Craft reaction and also to act as a dopant. Trivedi [31] carried out extensive work on this aspect and found that when bulky cetyl pyridinium chloride is used to prepare a room-temperature melt, the cathodic deposition of aluminum is completely inhibited due to preferential absorption of bulky cetyl groups on the cathode. The other chloroaluminate melts are vogue to study the generation of organic cations due to its wide electrochemical window, which is extended up to 4.4 V.



This melt has been found to be useful as an electrolyte in battery systems using conducting polymers. Acidic ionic liquids with chloroaluminate ions proved to be effective Friedel–Craft catalysts [32].

3.3. CV studies—Electrochemical polymerization of benzene by cyclic voltammetry

The electrochemical polymerization of benzene to free-standing polyparaphenylene (PPP) film in room-temperature melt is shown in Fig. 1. The growth is reflected by the increase in peak current. The color of the film was reddish brown.

The growth of PPP was characterized by well-defined cyclic voltammogram peaks. The electro-active PPP is obtained only when the melt is acidic, i.e. the proportion of aluminum chloride in the melt is more, giving rise to AlCl_4^- anion that is the dopant responsible for the oxidation of ben-

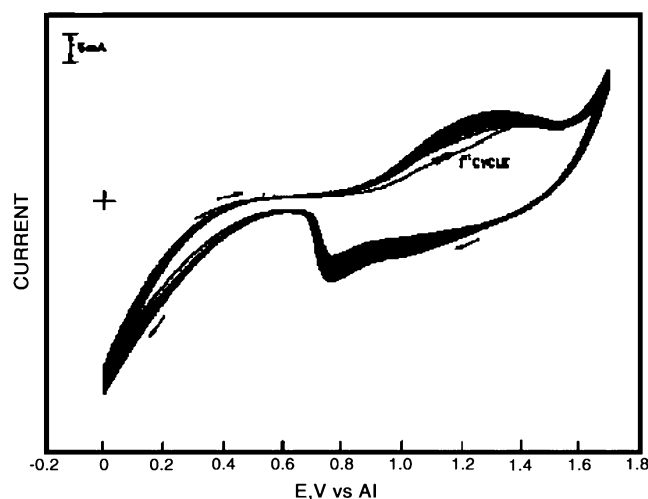


Fig. 1. Electrochemical growth pattern of polyparaphenylene in the presence of chloroaluminate room-temperature melt as the electrolyte, potential range -0.2 to 1.8 V vs. Al at sweep rate of 50 mV/s.

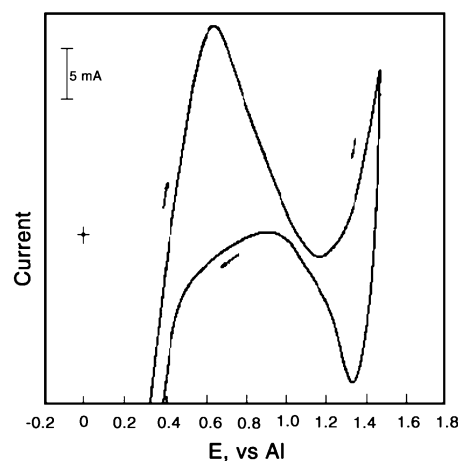


Fig. 2. Cyclic voltammogram of polyparaphenylene in the absence of monomer, potential range 0 – 1.5 V vs. Al at a sweep rate of 50 mV/s.

zene. The electro-polymerization does not occur in the neutral or basic melts.

The peak appearing at 1.4 V versus Al wire in the very first cycle is ascribed to the oxidation of benzene to benzelium 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 scans indicating the build-up of electro-active PPP on the electrode surface. In the forward cycle, during growth a well-defined peak was observed at 1.2 V versus Al, which is shifted to 1.25 V with the increase in the scan numbers; and similarly in the reverse cycle, the peak at 0.76 V versus Al was observed which is shifted slightly to 0.72 V in the negative side.

Fig. 2 shows the cyclic voltammogram for PPP on Pt electrode surface (0.25 cm²) in 1 M chloroaluminate room-temperature melt electrolyte diluted in diethyl ether (without the monomer) at the scan rate of 50 mV/s. It shows a significant redox peak at 0.7 V in the forward scan and at 1.3 V versus Al in the reverse scan. In order to explain the electrochemical behavior of PPP, the radical cations are formed in the forward cycle. It also indicates that the reaction is purely reversible redox system and can be used preferentially for rechargeable batteries.

The decrease in polymerization potential in a solvent-free medium is probably due to the fact that all nucleophilic secondary reactions are inhibited. The adhesion of the polymer film to the electrode surface was also observed, which is in good agreement with the Fowkes theory [33]. The adsorption of the polymer from the organic solvents onto inorganic surfaces is a process involving acid–base interactions between polymer and solvent and between solid and solid, “a triangular competition”.

3.4. Impedance Studies

The impedance spectra of conducting polymer matrix deposited using constant polarization mode may be considered

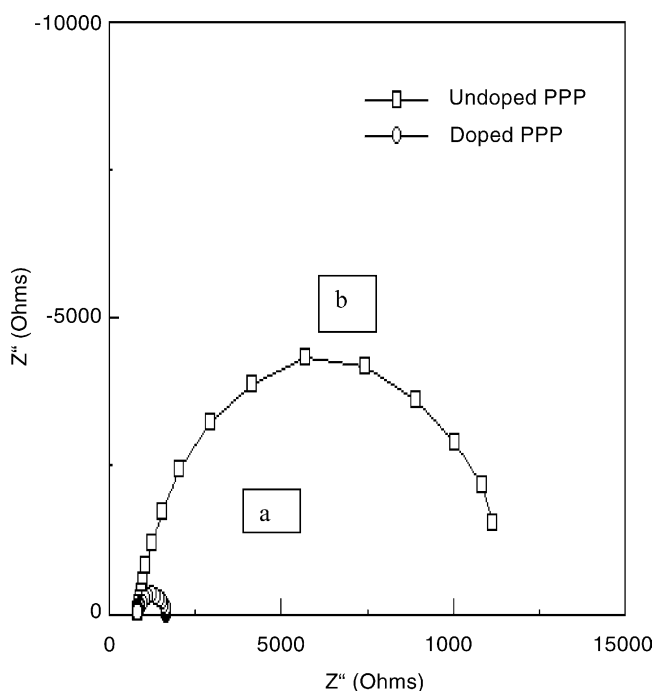


Fig. 3. Impedance spectra of (a) doped and (b) virgin PPP films in the presence of the room-temperature melt dissolved in ether after deposition by constant potential method (2 V) for 1 h under open-circuit potential in the ac frequency range 100 kHz–0.1 Hz with an excitation signal of 10 mV.

to study the characteristics of film structures and the charge transfer resistance and ion transport in the metal/polymer interface and polymer film/electrolyte interface. After preparation of PPP film by constant polarization mode, the film was subjected to an ac frequency under open-circuit potential in the frequency range 100 kHz–0.1 Hz with an excitation signal of 10 mV.

Fig. 3 gives the impedance spectra of doped (a) and virgin PPP (b) films in the room-temperature melt.

Among the two semicircles (a) is that of doped and (b) is undoped form of PPP film. The diameter of semicircle (a) is very much less than that of (b). In other words, PPP film in the doped form exhibits a very low charge transfer resistance (Rct) than the undoped form. Therefore, the doped PPP film is attributed to have a higher electronic conductivity, i.e. low impedance, and vice versa.

Table 1 gives the Rs, Rct and C values of doped and undoped PPP film synthesized using room-temperature melt.

It was found that the charge transfer resistance (Rct) increases to the three-fold greater values for undoped PPP. The solution resistance (Rs) remains almost the same for both

Table 1

Rs, Rct and C values of doped and undoped PPP film from complex plane impedance spectra (Fig. 3)

Nature of polymer film	Rs (Ω)	Rct (Ω)	C (F)
Doped PPP	570	530	1.8617×10^{-6}
Undoped PPP	877	2.1739×10^5	0.71417×10^{-7}

Rs: solution resistance, Rct: charge transfer resistance, C: capacitance.

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.

3.5. Potential step technique—nucleation studies

The potential step technique has been used to investigate nucleation and growth of PPP. In this experiment, a sudden higher potential is applied to the working electrode and the current and time transients are recorded. The shape of the transient indicates how the nucleation for the growth of polymer takes place. The nucleation gets influenced by following factors:

- (i) nature of anion present;
- (ii) concentration of the monomer;
- (iii) preparation of the electrode surface.

After each experiment the electrode surface has to be cleaned and reconditioned. The polymer growth was studied by fixing potential and time scale. The experimental setup was the same as that for CV studies. The growth of the conducting polymer can be compared with the electro-deposition of metals, the difference being that the former is an anodic reaction. In 1981, the diffusion limited aggregation (DLA) model was introduced by Witten and Sanders [34]. In this model, particles are added one at a time, to a cluster or aggregate of particles via random walk trajectories. According to this model, there is competing growth of polymer chains from a surface that leads to the formation of independent clusters. Meakin [35] modified the DLA model, in which the growth process is in a direction perpendicular to the surfaces of growth sites. Initially, each site at the electrode surface is active. Random walkers (radicals) are launched one at a time and eventually either move a long distance from the growing deposit and are terminated or find an active site. If an active site is found, this site becomes inactive and the site occupied by the random walker, before it enters the active sites, becomes the new active site. That is how the surface of an electrode becomes covered progressively. Electro-deposition of conducting polymers is a polynucleation process and transients are triggered by single potential step. Nucleation is independent of the size and shape of the electrode and polynucleation starts in synchronism with the potential step and is illustrated in Fig. 4. The current–time transient can be replotted using various equations as given by Li and Alberly [36]. Fig. 4 shows the potential step growth of PPP at 1.25 V versus Al wire, as per CV curve Fig. 1 the growth of the polymer occurs at 1.2 V, and at 1.25 V the CV curve has the maximum current. To observe proper growth transients, time scale was fixed at 20 seconds per cm with a total growth time of 560 s. There is rise in the current from 166 μ A to 229 μ A in steps. The steps in the growth curve indicate the formation of a layered structure that is uncommon in conducting polymers.

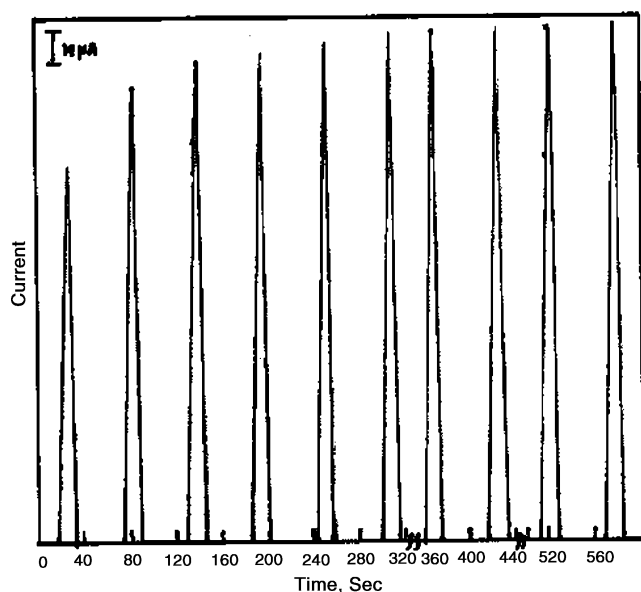


Fig. 4. Current vs. time response of a polyparaphenylene growth in the presence of room-temperature melt at 1.25 V vs. Al wire for 20 s.

The growth processes depend upon the following factors:

- (i) monomer concentrations;
- (ii) oligomerizations;
- (iii) diffusion of monomer into polymer film;
- (iv) formation of critical cluster and nucleus.

In CV curve, the random adsorption of monomer on a bare electrode surface is seen more clearly in a deposition curve where relatively a broad peak appears at potentials significantly less positive than required for bulk oxidation of monomer and is followed by sharp peaks resulting from nucleation and monolayer spreading. The sharp rising edge

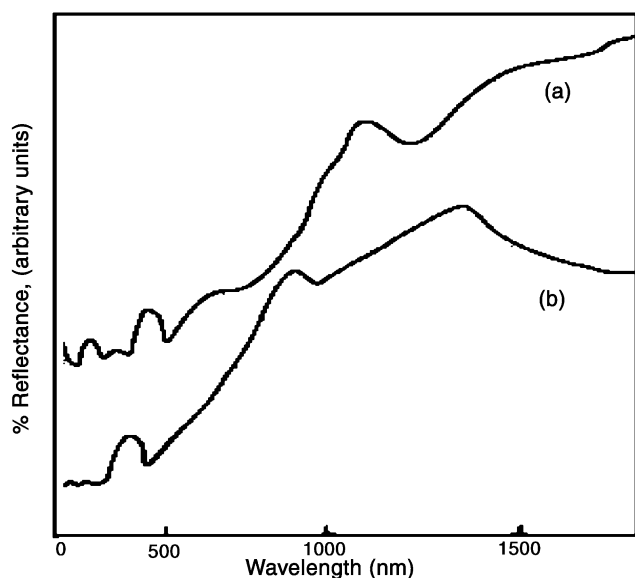


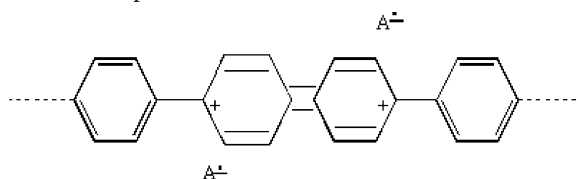
Fig. 5. The diffused reflectance UV spectra of (a) doped and (b) undoped PPP using high alumina as reference in the range 200–1500 nm.

of these peaks is linear with time, which suggests that two-dimensional patch has been expanding in a shape-preserving way. The close similarity of the peaks' shape suggests that nucleation has occurred repeatedly on the same site.

3.6. Conductivity measurements

The conductivity of freshly-deposited doped PPP film was 3.5×10^4 S/cm. Multiple experiments showed the conductivity range to be around $3\text{--}4 \times 10^4$ S/cm. When exposed to air, the conductivity slowly decreases to 0.2 S/cm. This is because after exposure to air, the dopant in doped PPP film reacts with moisture to yield aluminum oxy chloride and aluminum hydroxide, thereby, the undoping occurs; however, this PPP film can be redoped. The conductivity of undoped PPP was observed to be in 10^{-9} S/cm.

Scheme: Bipolaron structure in PPP.



3.7. UV-visible Near IR Spectroscopic Studies

The diffused reflectance UV-visible Near IR spectra of (a) doped and (b) undoped PPP are shown in Fig. 5. The absorption bands at 350 nm and 881 nm for undoped PPP (a), and at 327 nm, 386 nm, 560 nm and 1336 nm for the doped PPP (b) are observed.

The absorption peak observed between 350 nm and 390 nm is assigned to $\pi\text{--}\pi^*$ transition associated with benzenoid ring. The band, due to cation radicals, lies between 400 nm and 600 nm. The band observed near or more than 800 nm is due to the charge carriers. The tail of this band extends to the infrared region indicating that the charge carriers are bipolarons or otherwise called as trapped excitons. 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 theoretical peak position of 339 nm (3.66 eV) reported by Susuki [37] 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 [38] and 3.4–3.5 eV reported by Froyer et al. [39] for PPP films oxidized at constant voltages.

3.8. FTIR spectroscopic studies of PPP film

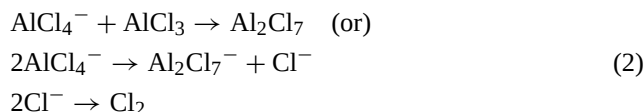
The doped polymer shows strong absorption bands in the IR region, behavior characteristic of strong free carrier absorption. The IR absorptions of virgin PPP disappear upon doping and are replaced by new absorption bands characteristic of the doped complex. The major shifts from virgin PPP are tabulated in Table 2.

Table 2

The major shifts of bands in FTIR spectra of doped PPP from virgin PPP (Fig. 6)

Virgin PPP (cm ⁻¹)	AlCl ₄ ⁻ doped PPP (cm ⁻¹)
1481	1530
1000	1080
804	810

The two absorption bands located between 650 cm⁻¹ and 750 cm⁻¹ are typical of out of plane vibrations of the five adjacent hydrogen atoms on the terminal phenyl rings and the bands around 805 cm⁻¹ are characteristic of the out-of-plane carbon–hydrogen vibrations for adjacent hydrogen atoms on *para*-substituted rings [40,41]. We can attribute the band at about 1000 cm⁻¹ to an aromatic in-plane hydrogen bending vibration, which is indicative of *para*-substitution [42]. The band located at about 1480 cm⁻¹ is due to aromatic C–C vibrations [43]. The absence of bands in the region between 860 cm⁻¹ and 900 cm⁻¹ rules out the possibility of a 2, 3 substitution pattern in the polymer chain. No cross-linking is apparent for this PPP film as shown by the absence of a band around 1600 cm⁻¹. Our results show that PPP films, obtained from chloroaluminate room-temperature melt, present a high regularity (linear chain). The dopant peaks of Al₂Cl₇⁻ appear at 517 cm⁻¹ and 689 cm⁻¹ confirmed by literature [44]. This shows that it is a super-acid electrolyte having Al₂Cl₇⁻ ion dominants following the Eq. (2).



Formation for free chlorine was not observed and therefore, we believe that Al₂Cl₇⁻ generates not by dimerization of AlCl₄⁻ but by reaction of AlCl₄⁻ with AlCl₃.

Fig. 6 shows the FTIR spectra of doped (a) and undoped PPP (b) in the region 4000–400 cm⁻¹ in the KBr medium.

The degree of polymerization may be estimated from the intensities of the bands around 800 cm⁻¹ (1, 4-disubstituted benzene ring) and 690 cm⁻¹ (monosubstituted benzene ring) following the empirical formula [45].

$$\text{DP} = 2(I_{800}/I_{690}) + 2$$

The DP was found to be 76 for doped species. This was found to be greater than usual Kovacic method [15], where the DP was just 21, and still greater than the DP that was electro-synthesized by Soubiran et al. [46]. From repetitive experiments it was found that the degree of polymerization was in the range of 60 to 70.

3.9. Thermal studies

The results of differential thermal analysis show that both the polymer films show an exothermic peak at 550 °C in air, which implies the breakdown of the polymer backbone. This inflection is in confirmation with the DTA peak observed by

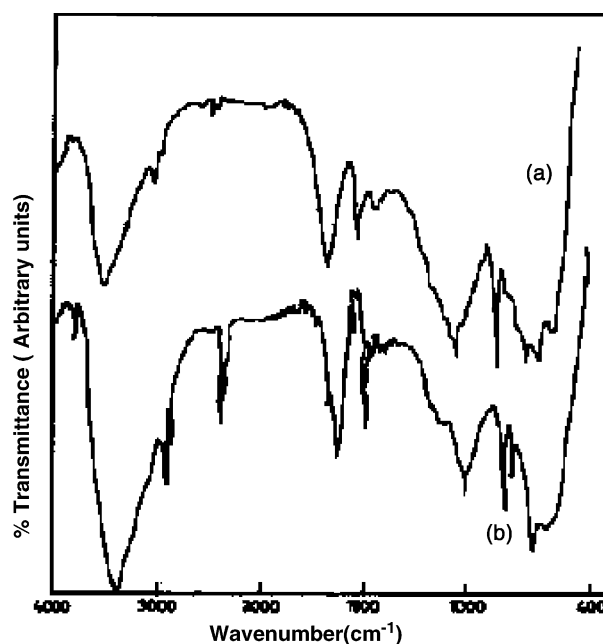


Fig. 6. FTIR spectra of (a) doped and (b) undoped PPP in the region 4000–400 cm⁻¹ in the KBr medium.

Masaharu et al. [47]. On the other hand, there is a peak at 330 °C in the doped species, which is due to the expulsion of the dopant. The thermo-gravimetric analysis (TGA) curve of doped polymer shows initial weight loss of 10% around 78 °C due to the expulsion of benzene and, thereafter, a plateau up to 290 °C. This elimination of benzene is due to the fact that the specimens are stored under benzene and given for analysis for avoiding the contact with moisture. There is a weight loss between 290 °C and 400 °C due to expulsion of dopant and, thereafter, polyparaphenylene begins to decompose. However, for undoped, there is no decomposition till 600 °C.

Figs. 7 and 8 give the TG/DTA curves for undoped and doped PPP, respectively.

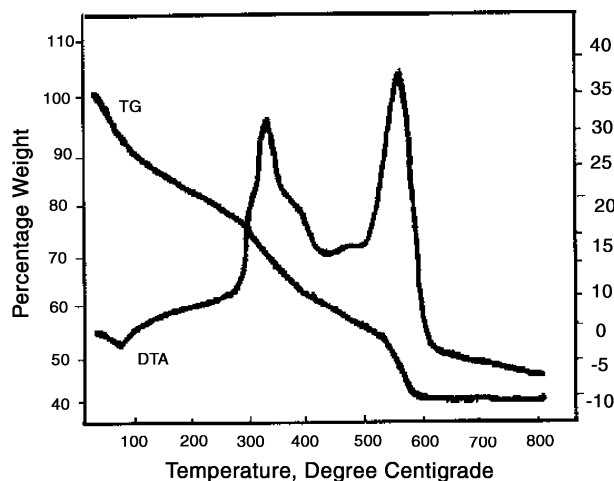


Fig. 7. TG/DTA curve for doped PPP.

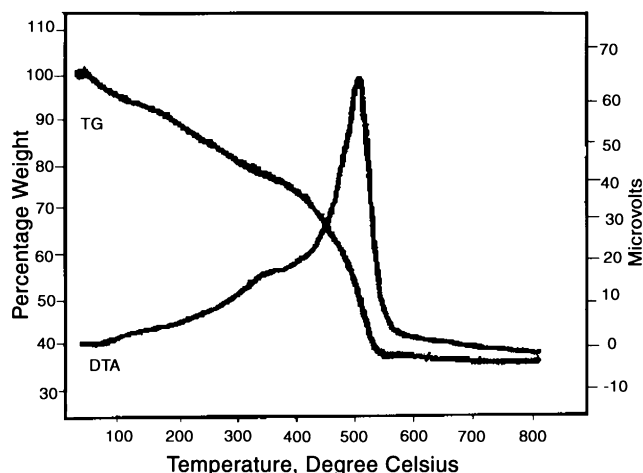


Fig. 8. TG/DTA curve for undoped PPP.

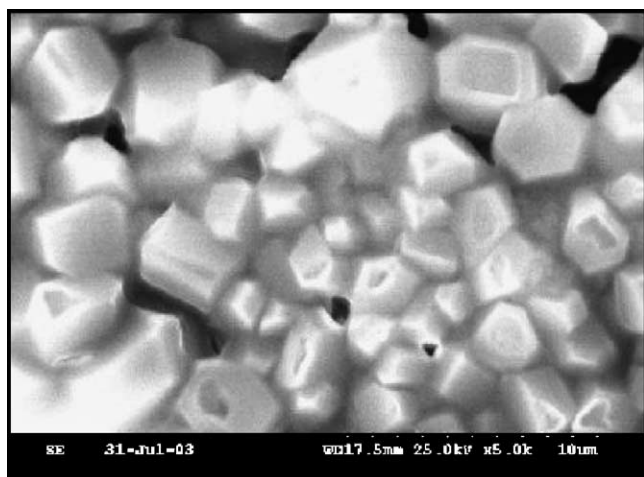


Fig. 9. Scanning electron micrograph of conducting PPP film showing crystalline structure.

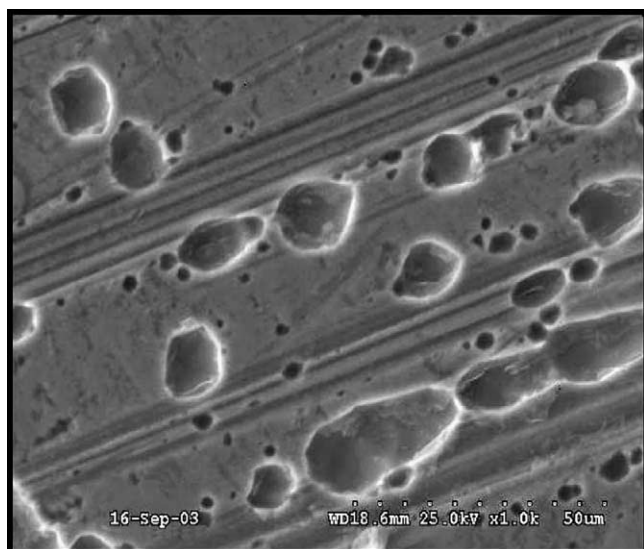


Fig. 10. Scanning electron micrograph of undoped PPP film showing non-conducting dark portions.

3.10. SEM Pictures

Figs. 9 and 10 are the scanning electron micrographs of doped and undoped PPP, respectively. Fig. 9 shows that doped polymer has a regular hexagonal geometry. The study shows that the size of the largest hexagon is $2.8\text{ }\mu\text{m}$ and that of smallest is $0.8\text{ }\mu\text{m}$ and the undoped polymer has globular structures with a size ranging from $4\text{ }\mu\text{m}$ to $15\text{ }\mu\text{m}$. The brightness of hexagon in a uniform way indicates the homogeneity of doping.

4. Conclusions

Benzene can be anodically polymerized at comparatively lower potentials in acidic room-temperature melt as an electrolyte to yield reddish brown, highly conducting freestanding PPP film. The Al_2Cl_7^- anion generated from the melt has equal bond lengths and bond angles giving rise to a layered polymer with high electronic conductivity and high crystallinity.

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