

Mechanochemical Synthesis and Characterization of Poly(2,5-dimethoxy aniline) Salts

Subramanian Palaniappan,¹ Yu-Tsern Chang,² Chung-Ming Liu,³ Paramasivam Manisankar¹

¹Department of Industrial Chemistry, School of Chemistry, Alagappa University, Karaikudi 630003, Tamil Nadu, India

²Department of Chemical and Material Engineering, Nanya Institute of Technology, Jhongli 32091, Taiwan

³Department of Chemical and Material Engineering, LungHwa University of Science and Technology, Taoyuan, Taiwan

Received 1 November 2010; accepted 2 August 2011

DOI 10.1002/app.35416

Published online 29 November 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The interfacial interaction and orientation of molecules during the polymerization process plays a vital role in the enhancement of the surface properties of conducting polymers. In this perspective, a solid-phase mechanochemical route is employed to prepare poly(2,5-dimethoxy aniline) (PDMA) and its salts with superior properties. Various studies performed on the as-prepared polymer highlights the formation of polymeric particles with excellent physicochemical properties. Elemental analysis showed the presence of dopants anion in the polymeric backbone. Spectroscopic profile of PDMA revealed the formation of emeraldine form of PDMA. Moreover, these studies indicate the formation of

PDMA-HCl in a highly doped state. The surface morphological pictures of PDMA revealed the formation of aggregated microstructured to nanostructured particulates. X-ray diffraction, cyclic voltammetry were used to evaluate the physicochemical properties of PDMA. PDMA salts exhibited crystalline behavior and good electrochemical activity. TG/DTA analysis showed that all the PDMA were thermally stable up to 240°C. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4281–4288, 2012

Key words: conducting polymers; polyaniline; solid-state polymerization

INTRODUCTION

The growing demand to prepare conducting polymers with distinct physicochemical properties for applications in various emerging technological areas^{1–5} motivates the researchers across the globe to develop alternate but attractive, easy-to-adopt and efficient synthetic routes. In this process, several synthetic methodologies have been developed for preparing conducting polymers, in particular polyaniline⁶ (PANI). The methodologies adopted for synthesizing PANI, that has good physicochemical properties does not always suit for the preparation of its derivatives.⁷ When we analyzed the earlier literature, we found several reports on the electrochemical or chemical homopolymerization of aniline derivatives⁸ and copolymerization of aniline with ring or N-substituted aniline derivatives.⁹ The most studied compounds are alkyl¹⁰ and alkoxy^{11,12} anilines, with the substituent groups in the ortho or meta position, phenyl ring,¹³ or N-position.¹⁴ Eventhough various substituted polyanilines with better solubility have been prepared in the past, it was observed that the

substituent groups present either in the phenyl ring or in the N-position of the polymer chain causes a decrease in the conductivity. However, polymerization of aniline substituted with two methoxy groups, 2,5-dimethoxy aniline (DMA), has been reported to produce soluble polymer, poly(2,5-dimethoxy aniline) (PDMA) with a conductivity similar to polyaniline.^{15,16} Moreover, PDMA is an important organic solvent soluble polyaniline derivative that has been used for variety of applications.¹⁷

Mechanochemical polymerization is a facile, easy-to-adopt and greener synthetic route for preparing conducting polymers with good properties. Taking into account the simplicity, easiness and sustainability of this route, we have attempted to prepare different PDMA salts through this solid-state polymerization method. In this work, we have performed the mechanochemical polymerization of DMA in presence of different doping agents. We have also elaborately presented the influence of three different inorganic acids on various physicochemical properties of the as prepared PDMA salts.

MATERIALS AND METHODS

Synthesis of doped/undoped PDMA

Solid DMA (1.53 g; Sigma Aldrich, 98%) was taken in a glass mortar and was hand-ground for 5 min

Correspondence to: P. Manisankar (ss: pms11@rediffmail.com).

TABLE I
Elemental Composition, Conductivity, and Yield of PDMA and Its Salts

Polymer	C (%)	H (%)	N (%)	O (%)	Cl (%)	S (%)	P (%)	Cl/N or S/N or P/N ratio	Yield (%)	Conductivity (S cm ⁻¹)
PDMA	55.09	5.09	7.61	31.82	–	0.39	–	0.05	69	0.04
PDMA-HCl	55.46	5.12	7.82	29.34	2.26	–	–	0.29	80	1.80
PDMA-H ₂ SO ₄	55.42	5.11	7.80	29.71	–	1.96	–	0.25	76	1.02
PDMA-H ₃ PO ₄	55.44	5.12	7.83	29.9	–	–	1.71	0.21	72	0.42

using a pestle. To this, finely ground DMA, 2.2 g of solid ammonium persulfate (APS) (Merck, AR Grade) was added. After the addition of the oxidant, the solid phase mixture was further hand-ground for 20 min until the color of the product turned dark green. The formed polymeric product was washed thoroughly with water, methanol, and diethyl ether. After repetitive washings, the polymer was dried in vacuum oven at 40°C for 12 h. The purified dry PDMA powder was used for further characterization.

The preparation of doped PDMA involves the addition of 0.5 mL of doping agent (37 wt % HCl/96 wt % H₂SO₄/87 wt % H₃PO₄ (Merck, AR grade)) to 1.53 g of solid DMA in a glass mortar. This monomer-doping agent reactant mixture was thoroughly hand-ground for 30 min to achieve homogeneity. The rest of the polymerization procedure was followed as given above. The purified PDMA salts were used for performing further studies. Herein, undoped PDMA is termed as PDMA, PDMA doped with HCl as PDMA-HCl, PDMA doped with H₂SO₄ as PDMA-H₂SO₄ and PDMA doped with H₃PO₄ as PDMA-H₃PO₄.

Characterization of PDMA and its salts

C, H, N, S, and Cl content were determined using Elementar make vario MICRO cube analytical system. The percentage composition of element "P" was evaluated by EDX data obtained using the elemental analysis option provided in the FESEM instrument. FTIR spectra of all the PDMA samples pelletized with KBr were recorded using Perkin Elmer 783 FTIR spectrophotometer in the 4000–400 cm⁻¹ region. The UV–vis spectra were recorded in dimethyl formamide (DMF) using Shimadzu UV 2401PC double beam spectrophotometer. The powder X-ray diffraction (XRD) patterns of the polymer samples were recorded on a XPERT PRO PANalytical model X-ray diffractometer using Cu K α radiation whose wavelength was 1.54 Å. The morphology of the PDMA samples was examined by field emission scanning electron microscopy (JSM 35 CF JEOL FESEM operating at 15 KV using normal incidence). Electrochemical experiments were carried out using a CHI-760C

electrochemical workstation employing a three-electrode cell assembly comprising PDMA or its salts modified glassy carbon electrode (GCE) as working electrodes, Ag/AgCl as reference electrode and platinum wire as counter electrode. For electrochemical measurements, the working electrode was fabricated as follows. One milligram of PDMA and its salts were dissolved in 1 ml of DMF and shaken for few minutes to give a homogeneous PDMA/PDMA salt solution. GCE surface was coated with 5 μ L of the resulting PDMA/PDMA salt solution and allowed to evaporate in an oven at 50°C. The as prepared PDMA/PDMA salts coated GCE was found to have same thickness in all the cases since the same quantitative procedure was adopted for fabricating PDMA salts/GCE. Electrochemical experiments were performed in 0.5M H₂SO₄ electrolyte solution with or without PDMA/PDMA salt coatings by sweeping the potential between –0.2 and +1 V versus Ag/AgCl at a scan rate of 100 mV s⁻¹. The conductivity of PDMA samples pressed into pellets was measured by employing KEITHLEY make four-probe conductivity meter and the average of four pair of readings obtained from different places in the pellet is furnished in this report. Thermal analysis of the polymer samples were performed at a heating rate of 10°C/min under air atmosphere using Perkin Elmer make simultaneous TG/DTA thermal analyzer.

RESULTS AND DISCUSSION

Elemental analysis, yield, and processability

Table I displays the elemental composition of as-prepared PDMA and its salts. The percentage composition of C, H, and N indicate that the repeating unit consists of DMA skeleton. This observation is in accordance with the earlier report on PDMA.¹⁸ The presence of Cl, S, and P in PDMA-HCl, PDMA-H₂SO₄, and PDMA-H₃PO₄, respectively, in all the polymers suggest the presence of corresponding anionic dopants in the polymeric backbone. It could be noticed from Table I that PDMA prepared without using any doping acid has trace amount sulfur, which may be either due to self-doping or due to presence of residual oxidant in the polymeric product. The

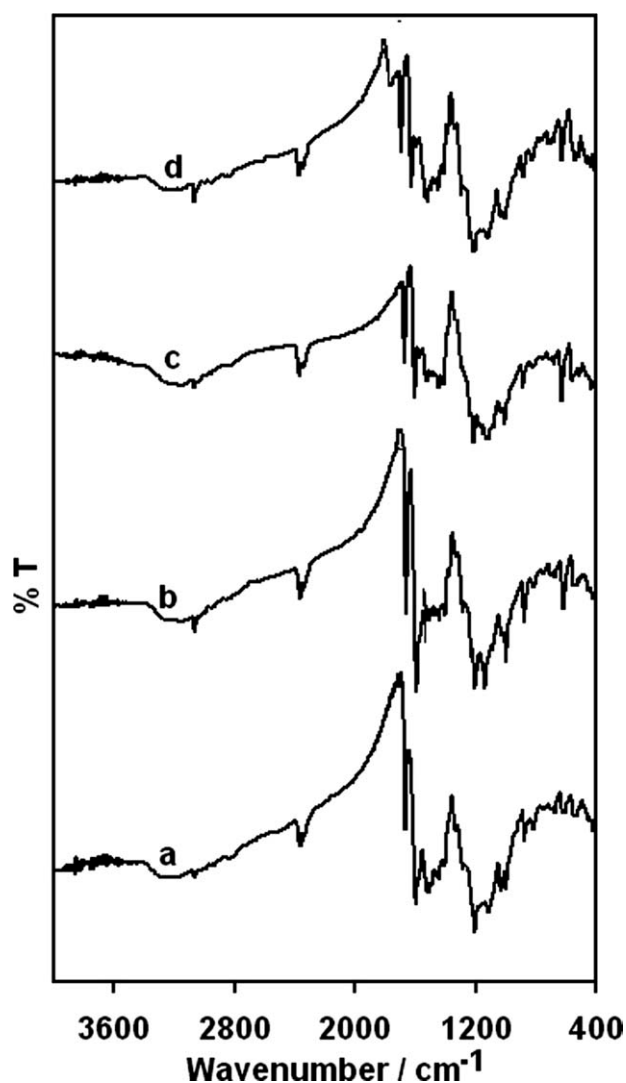


Figure 1 Background corrected FTIR spectra of PDMA and its salts using KBr pellets: (a) PDMA, (b) PDMA-HCl, (c) PDMA-H₂SO₄, and (d) PDMA-H₃PO₄.

percentage of O is higher in the case of PDMA than the corresponding PDMA-H₂SO₄/PDMA-H₃PO₄, which may also have resulted from the oxygen present in residual oxidant in the case of former polymer. The doping level of PDMA-HCl is comparatively higher than the other PDMA salts (Table I). HCl is found to be more suitable doping agent for preparing highly doped PDMA through solid-phase polymerization route. The smaller ionic size, nonoxidizing and less viscous nature of HCl is found to be the favorable factors assisting in the formation of PDMA-HCl with higher degree of doping. From the dopant (Cl or S or P) to N ratio, the degree of doping follows the order PDMA-HCl > PDMA-H₂SO₄ > PDMA-H₃PO₄ (Table I). The yield determined for all the polymers is listed in Table I. HCl followed by H₂SO₄ salt of PDMA is found to be produced in good quantity rather than H₃PO₄ salt. Under similar experimental conditions,

strong nonoxidizing acid is benefit for the yield of PANI while the weak acid has an opposite behavior.¹⁹ In line with this literature report, HCl is found to aid in the formation of more quantity of polymeric powder. All PDMA salts produced from this simple greener route are dispersible in common solvents like water, acetone, and ethanol. They are also highly soluble in DMF, dimethyl sulfoxide, and chloroform showing the processable nature of all the as prepared PDMA salts. These experimental evidences show that the adopted synthetic route is robust and efficient in producing PDMA salts.

FTIR spectra

Figure 1(a–d) shows the FTIR spectrum recorded for PDMA salts prepared using APS. The band assignments of the FTIR absorption peaks for PDMA are given in Table II. The broad band at $\sim 3228\text{--}3221\text{ cm}^{-1}$ represents the formation of N–H bonds due to the protonation of nitrogen and the bands at $\sim 3066\text{--}3109\text{ cm}^{-1}$ is assigned to stretching vibration of aromatic C–H bonds.^{20,21} The two main peaks at $\sim 1664\text{--}1669$ and $\sim 1595\text{--}1599\text{ cm}^{-1}$ are attributed to the stretching vibration of quinoid and benzenoid ring, respectively. The shift in the quinoid and benzenoid bands may be due to the difference in the protonation level and oxidation level or to the change in stability of the conjugated system.²² The two methoxy groups attached to the benzene ring might have contributed to the shift in the vibrational frequencies of the corresponding quinoid and benzenoid structures in comparison with the unsubstituted polyaniline structures. Interestingly, it could be observed that the intensity ratio of quinoid to benzenoid peak is closer to 0.8 in the case of PDMA-HCl suggesting the formation of emeraldine salt. This ratio varies in other PDMA salts and is found to be lower than the one noticed for PDMA-HCl. The peak at $\sim 1205\text{--}1207\text{ cm}^{-1}$ can be assigned to the methoxy groups present in the polymeric structure.²³ The peak at $\sim 1126\text{--}1150\text{ cm}^{-1}$ is considered as a measure of degree of delocalization of electrons in polymer chain and is often referred to as conductivity band.²⁴ This particular peak is sharper in

TABLE II
Assignment of Bands Found in FTIR Spectra of PDMA and Its Salts

Polymer	(N–H) _s	(C–H) _s	(C=C) _s	(C=C) _s	(C–N) _s
	in cm ⁻¹	in cm ⁻¹	(B) in cm ⁻¹	(Q) in cm ⁻¹	in cm ⁻¹
PDMA	3321	3109	1664	1597	1207
PDMA-HCl	3228	3066	1664	1595	1205
PDMA- H ₂ SO ₄	3261	3119	1669	1597	1207
PDMA-H ₃ PO ₄	3296	3068	1664	1599	1207

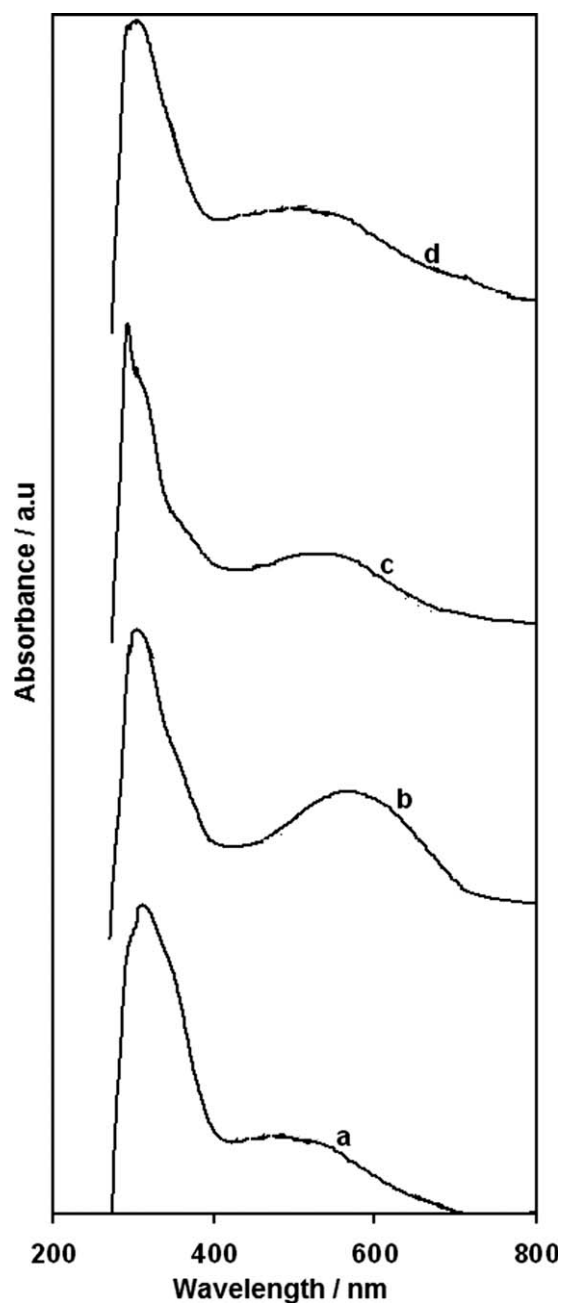


Figure 2 UV-vis spectra of PDMA and its salts in DMF recorded from 200 to 800 nm: (a) PDMA, (b) PDMA-HCl, (c) PDMA-H₂SO₄, and (d) PDMA-H₃PO₄.

PDMA-HCl suggesting the fact that highly conductive PDMA is formed in the presence of HCl rather than the other doping acids.

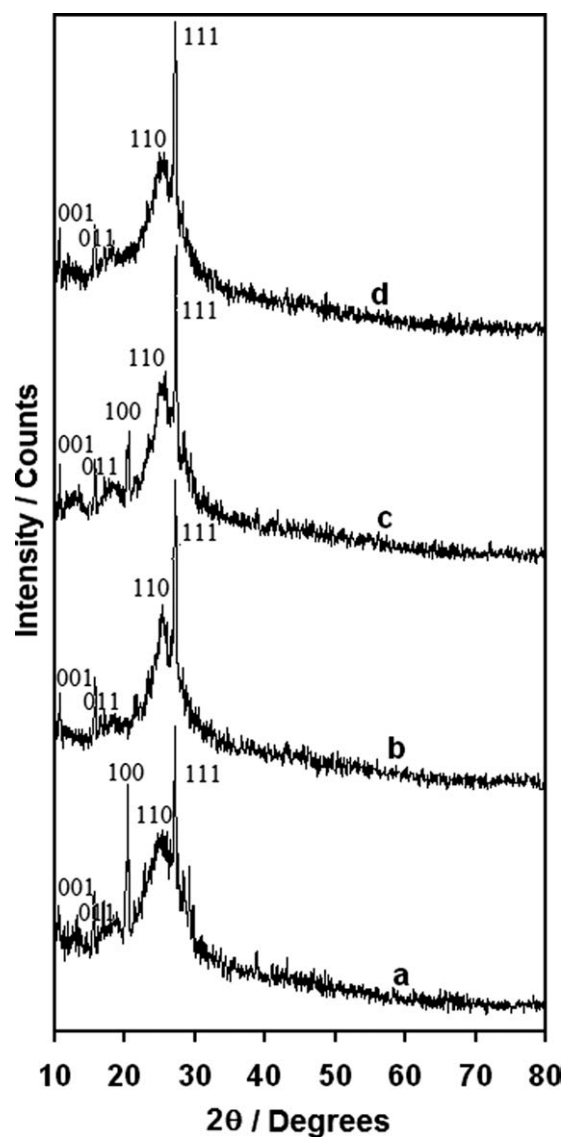


Figure 3 XRD patterns of PDMA and its salts recorded from 10 to 80°: (a) PDMA, (b) PDMA-HCl, (c) PDMA-H₂SO₄, and (d) PDMA-H₃PO₄.

UV-vis absorption spectra

The UV-vis spectra were recorded for a solution of 50 mg of the polymer samples in 10 mL of DMF and the spectra are shown in Figure 2(a-d). The polymer samples show two characteristic peaks at ~301–310 and ~560–562 nm (Table III). The former absorption peak can be ascribed to π - π^* transition of the

TABLE III
Wavelength of Maximum Absorption (λ_{max}) and Maximum Molar Absorptivity (ϵ_{max}) of PDMA and Its Salts for Bipolaron-Polar Transitions

Parameter	PDMA	PDMA-HCl	PDMA-H ₂ SO ₄	PDMA-H ₃ PO ₄
π - π^* band (nm)	310	306	301	306
Polaron- π^* band (nm)	560	569	561	560
ϵ_{max} for polaron- π^* transition ($\times 10^3$ L mol ⁻¹ cm ⁻¹)	1.26	1.46	1.42	1.36

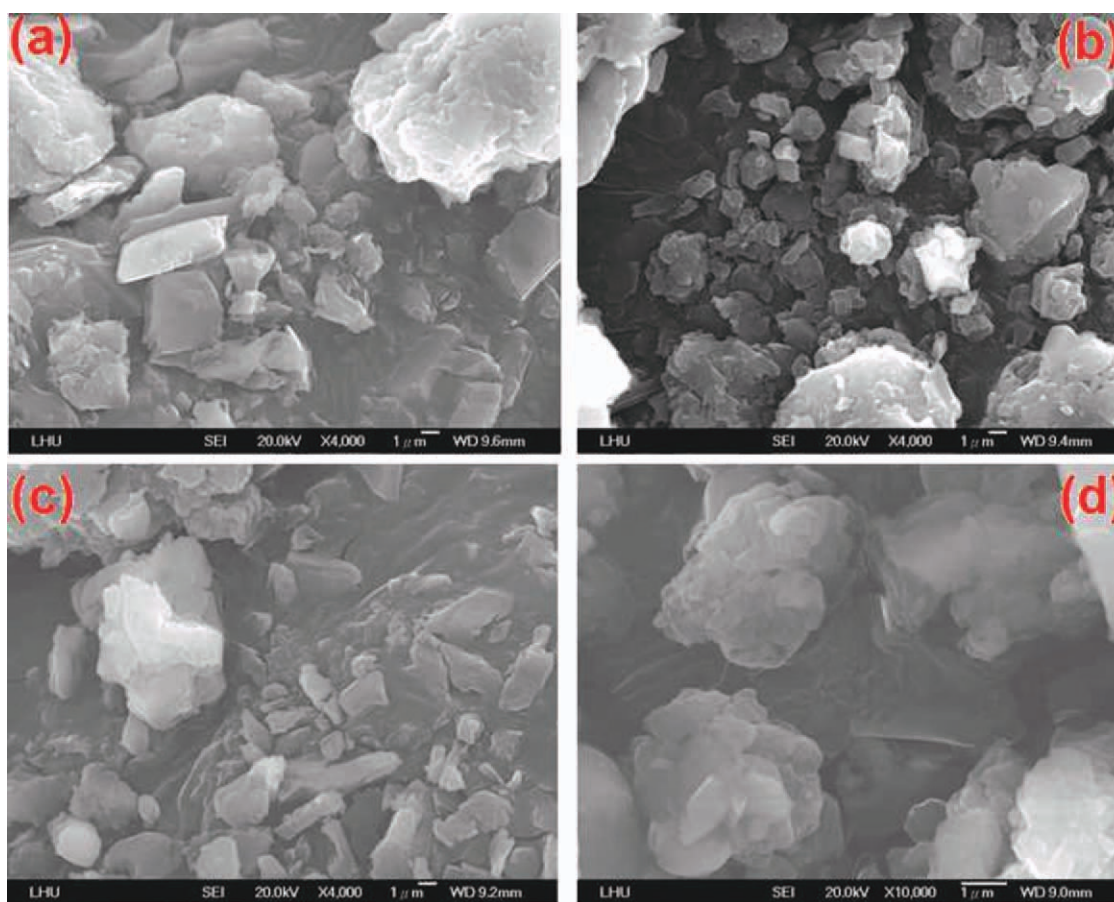


Figure 4 FESEM images of PDMA and its salts: (a) PDMA-HCl, (b) PDMA-H₂SO₄, (c) PDMA-H₃PO₄, and (d) PDMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

benzenoid rings, whereas the latter peaks can be attributed to polaron- π^* transition.²⁵ The availability of midgap state due to charge transfer in a conducting polymer can be studied through the intensity of UV-vis absorption bands of the polymeric solutions. The maximum molar absorptivity (ϵ_{\max}) of polaron- π^* band roughly gives a picture of the extent of doping of PDMA and its salts. The ϵ_{\max} value is relatively higher in the case of PDMA-HCl when compared with other PDMA salts (Table III). If the size of the doping acid is large, the diffusion of doping acid into the polymer matrix will be hindered due to steric factor. In line with this observation the doping degree among PDMA salts followed the order PDMA-HCl > PDMA-H₂SO₄ > PDMA-H₃PO₄.

XRD pattern

The XRD pattern for the PDMA powders obtained through this mechanochemical route is shown in Figure 3(a–d). The peaks at ~ 10.5 – 10.7° , ~ 15.5 – 15.7° , ~ 25.3 – 26.03° , and ~ 27.08 – 27.28° are seen in the diffractograms. The peaks are indexed to the corresponding crystal planes in accordance with the literature.²³ These diffraction patterns show all the

prepared PDMA and its salts are crystalline. The peaks at lowest angle are considered the distance between two in the polymer chain with dopant ions situated between the two stacks. In view of this fact, one could notice very weak peak at $2\theta = 10.5^\circ$ for PDMA [Fig. 3(a)] rather than its salts indicating the presence of fewer or no dopant anions. However this peak is comparatively stronger for all the PDMA salts. The peaks at ~ 25.3 – 26.03° can be attributed to the periodicity parallel to the polymer chain and the peak at ~ 27.08 – 27.28° may have originated from the periodicity perpendicular to the polymer chain. The full width at half maximum (FWHM) value of most intense crystal peak for PDMA, PDMA-HCl, PDM-H₂SO₄, and PDMA-H₃PO₄ are 0.3626, 0.3846, 0.3801, and 0.3781, respectively. These values indicate that PDMA-HCl has characteristics similar to that of highly doped emeraldine salt.^{26,27} The peak at $2\theta = 21^\circ$ noticed only in the undoped PDMA may have originated due to some crystal defect in the polymer. The values of d spacing for the most intense peak at $2\theta = 27.08$ – 27.28° corresponding to d_{111} crystal plane are 3.42, 3.50, 3.46, and 3.44 Å for PDMA, PDMA-HCl, PDM-H₂SO₄, and PDMA-H₃PO₄, respectively. The degree of

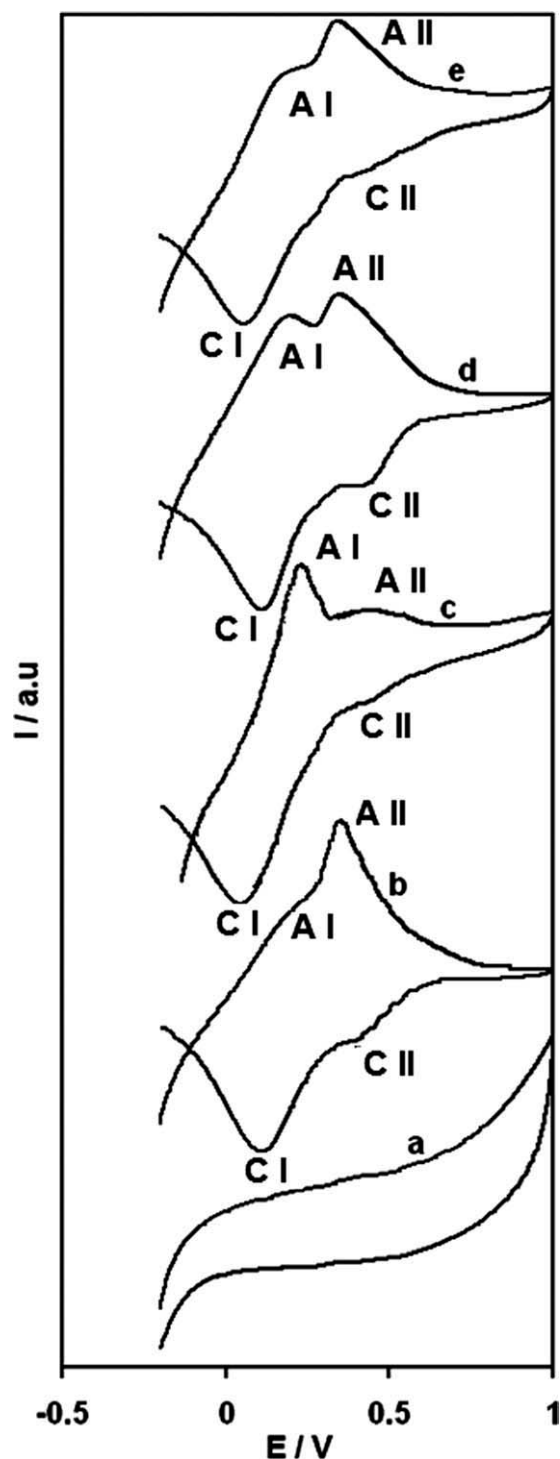


Figure 5 Cyclic voltammograms of PDMA and its salts in 0.5M H₂SO₄ at a scan rate of 100 mV s⁻¹: (a) Plain GCE, (b) PDMA/GCE, (c) PDMA-HCl/GCE, (d) PDMA-H₂SO₄/GCE, and (e) PDMA-H₃PO₄/GCE.

crystallinity calculated for the most intense crystal peak gives a value of 36.5, 37.8, 37.4, and 37.2% for PDMA, PDMA-HCl, PDM-H₂SO₄, and PDMA-H₃PO₄, respectively. These values are in close agreement with the recent report on solid-state synthesized polyaniline doped with HCl.²⁸ These results suggest

that PDMA may be formed in different emeraldine forms and it also indicates that the steric effect introduced by two methoxy substituents in the polymer chains does not hinder polymer crystallization. It should be probably concluded that increase in PDMA crystallinity is the consequence of the effect of mechanical forces, in particular, shear stress generated during treatment of the reactants in the mortar. The influence of these forces leads to ordering of the polymer chain packing due to the increase of interchain π - π interaction between aromatic rings of the macromolecules thereby promoting increase in conductivity of the whole material.²⁹

Morphology

Figure 4(a–d) shows the FESEM pictures of as made PDMA and its salts. PDMA-HCl is found to have 200 nm sized flakes [Fig. 4(a)] along with some bigger agglomerated structures. PDMA-H₂SO₄ [Fig. 4(b)] comprises of irregularly shaped aggregated particulates in the nanoscale size. Fused flake like structure is found in the surface of PDMA-H₃PO₄ along with some bigger sized polymeric fractions [Fig. 4(c)] whereas the undoped counterpart of PDMA has greater degree of aggregation and hence the particle appears as microstructures [Fig. 4(d)]. Our supposition is evidenced by the well established fact that the structure of the products depends on the rate of nucleation and growth of products in the solid-state reaction.³⁰

Electrochemical activity

Figure 5(a–e) shows the cyclic voltammograms of the PDMA film on GCE in 0.5M H₂SO₄. Two redox couples are noticed for PDMA and its salts. The anodic and cathodic peak potential values are listed in Table IV. The redox peak at 0.17–0.20 V in all the PDMA is related to the conversion of leucoemeraldine base to the protonated emeraldine form.^{31,32} The second redox couple between 0.35 and 0.37 V may be associated to the incorporation of linear or cyclic dimer or to degradation products of the polymer.³³ In PDMA and its H₃PO₄ salt [Fig. 5(b,e)] the redox peaks at 0.35–0.37 V appear sharper than the

TABLE IV
Redox Potentials of PDMA and Its Salts

Polymer	First redox peak		Second redox peak	
	E_{pa}/V	E_{pc}/V	E_{pa}/V	E_{pc}/V
PDMA	0.17	0.09	0.37	0.41
PDMA-HCl	0.20	0.04	0.36	0.42
PDMA- H ₂ SO ₄	0.20	0.09	0.36	0.40
PDMA-H ₃ PO ₄	0.17	0.03	0.35	0.42

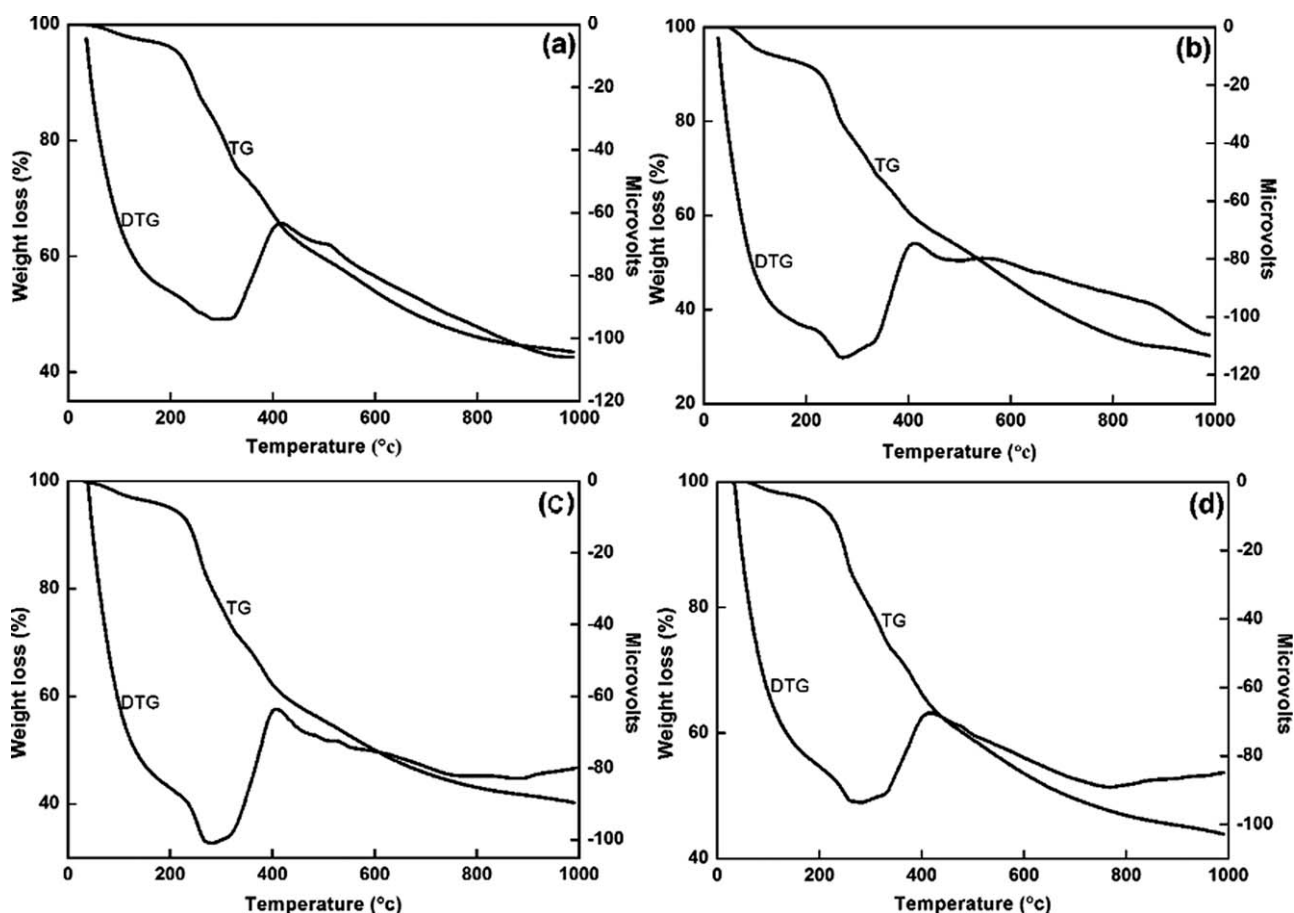


Figure 6 TG/DTA curves of PDMA and its salts: (a) PDMA, (b) PDMA-HCl, (c) PDMA-H₂SO₄, and (d) PDMA-H₃PO₄.

other polymer samples revealing the presence of some oligomers or degradation products. The CV of PDMA-H₂SO₄ [Fig. 5(d)] also indicates the presence of some degradation products. Interestingly in the CV of PDMA-HCl [Fig. 5(c)] the peak at 0.20 V is strong and the shoulder appearing at 0.36 V is very weak. This indicates the minimum or negligible oligomeric fractions or degradation products of polymer in the selected experimental conditions for PDMA-HCl. This inference is in complete agreement with the results described earlier. PDMA has first redox couple close to PANI^{34,35} in all of the prepared samples, whilst the second redox couple is facilitated by the presence of two electron donating methoxy groups. These results suggest the formation of electroactive PDMA salts prepared through this facile route.

Conductivity

The conductivity of PDMA salts obtained by mechanochemical polymerization is listed in Table I. The conductivities of PDMA salts are lesser than those reported for PANI.³¹ Generally conducting polymers with substituent on their frameworks show lower conductivities compared with those of parent PANI.

The presence of bulky substituent in the polymer chain can induce some non-planar conformations that decrease the conjugation along the backbone.³⁶ The two methoxy-groups on the phenyl ring in the PDMA can increase the torsional angle between adjacent rings to relieve steric strain and then lead to the lower conductivities of PDMA as compared to unsubstituted PANI. To compare with others, the conductivity of PDMA synthesized by using HCl as protonating agent in both of the oxidants has resulted in higher value. The lowest value among PDMA salts is observed for PDMA-H₃PO₄. It is reported that the conductivity of PANI and its derivatives depends on the degree of doping, oxidation state, particle morphology, crystallinity, inter or intrachain interactions, molecular weight etc.,^{37,38} that is, the conductivity of PANI and its derivatives increase with increase in doping degree, crystallinity. Based on these considerations, the differences in conductivities of these PDMA salts can be explained by the results of FTIR spectra, UV-vis spectra, XRD analysis, and CV studies. All these results show that PDMA-HCl has higher doping level, crystallinity, and good electrochemical activity. The higher doping level and smaller size of chloride ions is benefit for the close-packed arrangement of chains that will

inturn increase the interchain conductivity to bring higher conductivity. The small difference in pH of acids due to the variable amount of water present in the acids and relatively large size of sulfate and phosphate anions may have contributed to the relatively lesser conductivity values for the corresponding PDMA salts.²³

Thermal stability

The thermograms of the PDMA products are presented in Figure 6(a–d). The DTG curve of undoped polymer samples shows a single weight loss above 200°C [Fig. 6(a)] indicating the absence of dopants in its backbone. Two stages of weight loss above 200°C were observed in DTG curves of PDMA salts. The stage around 240°C originates from the elimination of dopant (e.g., HCl, H₂SO₄, or H₃PO₄) and the other stage around 400°C can be attributed to the thermal decomposition of polymer molecule main chains.^{39,40} All these results imply that the PDMA salts are in the doped emeraldine state.

CONCLUSIONS

A simple solid phase reaction method for the synthesis of PDMA and its salts at room temperature was demonstrated without using any organic solvent by employing APS as an oxidant. Elemental analysis proved the presence of corresponding dopant anions (Cl, S, and P) in the polymeric backbone of PDMA. The yield obtained from this reaction route is found to be satisfactory. All of the prepared PDMA salts were found to form stable dispersions in common solvents like water, ethanol, and acetone and are completely soluble in DMF and DMSO. Spectroscopic profile of the polymeric salts highlighted the presence of quinoid and benzenoid units and formation of conducting emeraldine state in all PDMA salts. More crystalline PDMA salt was obtained by doping with HCl in comparison with other doping acids. FESEM picture shows the formation of agglomerated nanostructures of PDMA salts prepared using APS as oxidant. PDMA-HCl was found to be more conductive and electroactive. All of the as-prepared PDMA salts are found to be thermally stable up to 240°C. Among these inorganic acids used as doping agents, HCl was found to be more suitable to prepare PDMA salt with high conductivity, crystallinity, and electroactivity through this mechanochemical route. The differences in the properties of PDMA salts mainly depended on the characteristics of inorganic acids (e.g., HCl, H₂SO₄, and H₃PO₄): small amount of water in the acids; strong and weak oxidizability of the acids. All these lead to PDMA salts with different physicochemical properties. The unique structure and good processability of

the PDMA samples makes it potentially suitable for use as electrode materials in energy storage devices.

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