MECHANOCHEMICAL SYNTHESIS AND CHARACTERISATION OF POLY (2,5-DIMETHOXY ANILINE)

Poly(2,5-dimethoxy aniline) (PDMA) was mechanochemically prepared in solvent-free condition by employing two different oxidizing agents namely ammonium peroxydisulfate (APS) and ferric chloride (FC) in the presence of different doping/protonating agents namely HCl, H₂SO₄ and H₃PO₄. The influence of aforementioned oxidants and protonating/doping agents on the physicochemical properties of as prepared PDMA is discussed on a comparative basis in this chapter.

4.1. INTRODUCTION

The growing demand to prepare high quality nanostructured conducting polymers through simpler and efficient route for applications in various emerging technological areas [1-5] activates the researchers across the globe to develop alternate but attractive synthetic routes. In this process, several synthetic methodologies have been developed for preparing conducting polymers, in particular polyaniline (PANI) [6]. The methodologies adopted for synthesizing nanostructured PANI often does not suit for the preparation of its derivatives [7]. Hence many different approaches are needed to synthesize high quality polymers from aniline derivatives that are easily processable than PANI. In this perspective, a simple, sustainable and novel solid-state route has been successfully developed for preparing highly conductive and crystalline PDMA. In order to obtain materials with superior electrical properties we have selected dimethoxy aniline derivative in this investigation, which is polymerized to get more regular and processable conducting polymer. Electrochemical or chemical homopolymerization of aniline derivatives [8]
and copolymerization of aniline with ring or N-substituted aniline derivatives [9] have also been employed successfully to improve properties of PANI. The most studied ones are alkyl [10], alkoxy [11,12] anilines, with the substituent groups in the ortho or meta position. The substituent groups present in the units of polymer chain cause decrease in the stiffness of the polymer chain resulting in better solvation. Unfortunately, a decrease in conductivity has been noticed for polymers of substituted aniline with substitution in phenyl ring [13] or N-position [14]. However aniline substituted with two methoxy groups, 2,5-dimethoxy aniline (DMA), has been reported to produce soluble polymer, PDMA with a conductivity similar to polyaniline [15,16]. PDMA is an important organic solvent soluble polyaniline derivative that has been used for variety of applications [17]. All these interesting features combined with the efficiency of the polymerization methodology reported in the previous chapter have directed our focus on preparing PDMA in presence of different doping acids.

4.2. MECHANOCHEMICAL POLYMERIZATION OF DMA

4.2.1. Synthesis of doped/undoped PDMA

1.53 g of solid DMA was taken in a glass mortar and was hand-ground for 5 minutes using a pestle. To this finely grounded DMA, 2.2 g of solid APS or 2.7 g of solid FC was added. After the addition of the oxidant, the solid phase mixture was further hand-ground immediately for 20 minutes until the colour 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 prepared in the presence of APS and FC individually 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) to 1.53 g of solid DMA in a glass mortar. This monomer-doping agent reactant mixture was thoroughly hand-ground for 30 minutes in order to achieve homogeneity. The rest of the polymerization procedure was followed as given above. The purified PDMA salts obtained employing APS or FC as oxidants 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.

4.2.2. Elemental analysis, yield and processability

Table 4.1 displays the elemental make-up of PDMA and its salts prepared by employing APS or FC. 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 suggested the presence of corresponding anionic dopants in the polymeric backbone. It could be noticed from table.1 that PDMA prepared without using any doping acid is negligibly doped. This might be due to the self-doping of sulphur from APS or chlorine from FC. In PDMA prepared using APS or FC, the doping level of PDMA-HCl is comparatively higher than the other PDMA salts (table 4.1). In this case, HCl is found to be more suitable for preparing highly doped PDMA through solid-phase polymerization route. The smaller ionic size, non-oxidising and less viscous nature of HCl is found to be the favourable factors assisting in the formation of PDMA-HCl with higher degree of doping. From the dopant (Cl or S or P) to N ratio (see table 4.1), the degree of doping
follows the order PDMA-HCl > PDMA-H$_2$SO$_4$ > PDMA-H$_3$PO$_4$ irrespective of the oxidants employed for polymerisation. The yield determined for all the polymers is listed in table 4.2. HCl followed by H$_2$SO$_4$ salt of PDMA is found to yield appreciable quantity of polymer rather than H$_3$PO$_4$. Under similar experimental conditions, strong non-oxidising acid is benefit for the yield of PANI while the weak acid has an opposite behaviour [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 dimethyl formamide, dimethyl sulfoxide and chloroform that suggest the processable nature of all the as prepared PDMA salts. These experimental evidences showed that the adopted synthetic route is robust and efficient in producing high quality PDMA salts.

4.2.3. FTIR spectra

Fig.4.1A (a-d) shows the FTIR spectrum recorded for PDMA salts prepared using APS. The assignments of the FTIR absorption bands for PDMA prepared using APS or FC is given in table 4.3. The broad band at ~3228-3321 cm$^{-1}$ represents the formation of N-H bonds due to the protonation of nitrogen and the bands at ~3066-3109 cm$^{-1}$ is assigned to stretching vibration of aromatic C-H bonds [20,21]. The two main peaks at ~1664-1669 and ~1595-1599 cm$^{-1}$ is attributed to the stretching vibration of quinoid and benzenoid ring respectively. The vibrational bands located in the range of 614, 569 and 492 cm$^{-1}$ is associated with (PO$_4$)$^{3-}$ and (SO$_4$)$^{2-}$ groups. 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 lesser than noticed for PDMA-HCl. The peak at ~1205-1207 cm$^{-1}$ can be assigned to C-N stretching mode.
The peak at ~1126-1150 cm\(^{-1}\) is considered as a measure of degree of delocalization of electrons in polymer chain and is often referred to as conductivity band. This particular peak is sharper in PDMA-HCl suggested the fact that more conductive PDMA is formed in the presence of HCl rather than the other salts.

FTIR spectrum of PDMA salts prepared using FC is provided in fig.4.1B (a-d). The characteristic frequencies of all the functionalities are tabulated and displayed in table.4.3. The backbone of PDMA salts prepared by using FC is almost similar to those salts prepared using APS except for a small shift in the corresponding vibrational frequencies. In this case too, PDMA-HCl is found to exhibit sharper quinoid and benzenoid bands relatively better than other doped PDMA salts. This data amply suggested that HCl acts as a more suitable protonating agent for mechanochemical polymerization of PDMA. From the above spectral data, it also inferred that coupling of monomer units has occurred predominantly in the preferred head to tail fashion.

4.2.4. UV–Vis absorption spectra

The UV-Vis spectrum of PDMA and its salts prepared by employing APS is shown in figure 4.2A (a-d). These polymer samples showed two characteristic peaks at ~301-310 and ~560-562 nm (table 4.4). The former absorption peak can be ascribed to \(\pi-\pi^*\) transition of the benzenoid rings, whereas the latter peaks can be attributed to polaron-\(\pi^*\) transition. The availability of mid-gap 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 intensity of polaron-\(\pi^*\) band roughly gives a picture of the extent of doping of PDMA and its salts. The intensity of the polaronic band is relatively higher in the case of PDMA-HCl than other salts. 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 follows the order PDMA-HCl > PDMA-H2SO4 > PDMA-H3PO4.

The UV-Vis spectrum of PDMA and its salts prepared by employing FC as oxidant are shown in figure 4.2B (a-d). As seen above, one sharper benzenoid band in the range ~306-314 nm and one broader polaronic band in the range ~567-575 nm is noticed for PDMA and its salts. The intensity of polaronic band is higher for PDMA-HCl indicating that the population of polaronic chains is more in its backbone compared to other PDMA salts. The polaronic band intensities of PDMA salts follows the same order provided in the case of PDMA prepared by employing APS as oxidizer.

4.2.5. XRD pattern

The X-ray diffraction patterns for the PDMA powders obtained through mechanochemical route by using APS are shown in 4.3A (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. This diffraction patterns showed all the prepared PDMA and its salts are more crystalline than those reported elsewhere [2,18]. The peaks at lowest angle are considered to be 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.4.3A (a)) rather than its salts indicating the presence of very few dopant anions. However this peak is 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 latter peak is stronger than that of former peak in all PDMA
powders in general and PDMA-HCl in particular, similar to that of highly doped emeraldine salt [22,23].

The X-ray diffraction patterns for the PDMA powders obtained by using FC as oxidant are shown in 4.3B (a-d). The Bragg’s peak at $2\theta = ~10.78^\circ$ is more visible only for PDMA-HCl [fig.4.3B (b)] suggesting the clear presence of dopants in between the PDMA stacks. In addition, highly intense peak at $~32.58^\circ$ could be noticed only for PDMA-HCl and this is absent in PDMA and its other salts. These observations indicate that PDMA-HCl is in more crystalline state. The intense peaks at around $~25^\circ$ and $~27^\circ$ is present in all the PDMA salts as found in PDMA salts prepared by using APS revealing the presence of high degree of periodicity in the respective polymer backbone. These preliminary results suggested that PDMA may be prepared in different emeraldine forms and it indicated that the steric effects introduced by two methoxy substitutents in the polymer chains does not hinder polymer crystallization. It should be probably concluded that increase in PDMA crystallinity irrespective of the oxidants used for polymerization 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 $\pi-\pi$ interaction between aromatic rings of the macromolecules thereby promoting increase in conductivity of the whole material [24].

4.2.6. Morphology

Fig 4.4A (a-d) shows the FESEM pictures of PDMA and its salts prepared with the help of APS as oxidant. PDMA-HCl is found to have 200 nm sized flakes [fig. 4.4A (a)] along with some bigger agglomerated structures. PDMA-H$_2$SO$_4$
[Fig. 4.4A (b)] comprises of irregularly shaped aggregated particulates in the nanoscale size. Fused flake like structure is found in the surface of PDMA-H$_3$PO$_4$ along with some bigger sized polymeric fractions [Fig. 4.4A (c)] whereas the undoped counterpart of PDMA has greater degree of aggregation and hence the particle appears as microstructures [Fig. 4.4A (d)].

Fig 4.4B (a-d) shows the FESEM pictures of PDMA and its salts prepared by making use of FC as oxidizing agent. The surface morphology of PDMA-HCl prepared through solid-state route indicates the formation of shorter nanobelts with size ranging from 50-60 nm [Fig. 4.4B (a)]. In some areas of the FESEM image one could notice stacked structures which may be due to the aggregation of polymeric particles. Since the mechanochemical reaction route induces the reactants only on the surface, it is quite difficult to control the morphology of PDMA-HCl. Fig 4.4B (b) displaying the image of PDMA-H$_2$SO$_4$ show clusters of small polymeric particles whereas the morphology of PDMA-H$_3$PO$_4$ [Fig. 4.4B (c)] showed large number of finer granular structures with the size ranging from 70-100 nm. FESEM image of PDMA [Fig. 4.4B (d)] indicates the formation of larger polymeric particle. This may be due to more agglomeration as a result of the absence of doping agent in the reactant mixture. We suppose that the presence of doping agent induces the formation of nanostructure. 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 [25].

4.2.7. Electrochemical activity

Fig 4.5A (a-e) shows the cyclic voltammograms of the PDMA (prepared by using APS) film on GCE in 0.5 mol/l H$_2$SO$_4$. Two redox couples are noticed for
PDMA and its salts. The anodic and cathodic peak potential values are listed in table 4.5. The redox peak at 0.17-0.20 V in all the PDMA based polymers is related to the conversion of leucoemeraldine base to the protonated emeraldine form [26, 27]. 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 [28]. In PDMA and its H₃PO₄ salt the redox peaks at 0.35-0.37 V appear sharper than the other polymer samples revealing the presence of some oligomers or degradation products. The CV of PDMA-H₂SO₄ [fig. 4.5A (d)] also indicates the presence of some degradation products. Interestingly in the CV of PDMA-HCl [fig. 4.5A (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 superior properties of PDMA-HCl described earlier.

Fig. 4.5B (a-e) shows the cyclic voltammograms of the PDMA (prepared by using FC) film on GCE in 0.5 mol/L H₂SO₄. The CV without characteristic peaks [fig. 4.5B (a)] shows the absence of PDMA film on GCE. Two oxidation peaks at 0.35-0.38 V along with a weak reduction peak at 0.73-0.76 V appearing in the CVs of PDMA and PDMA-H₃PO₄ [fig. 4.5B (b) & (e)] can be assigned to the conversion of leucoemeraldine base to the protonated emeraldine form and conversion of protonated emeraldine to the fully oxidized pernigraniline structure respectively. The CVs of PDMA-HCl and PDMA-H₂SO₄ [fig. 4.5B (c) & (d)] displays three oxidation peaks at 0.20-0.25 V, 0.34-0.41 V and 0.72-0.74 V together with two reduction peaks around 0.04-0.06 V and 0.53-0.57 V. The first and second redox transition is due to the conversion of leucoemeraldine to emeraldine and emeraldine to pernigraniline respectively. The intermediate oxidation peak without reduction counterpart may be
related to the presence of some negligible amount of degradation products associated
with PDMA. PDMA has first redox couple close to PANI [29,30] in all of the
prepared samples, whilst the second redox couple is facilitated by the presence of two
electron donating methoxy groups. These results suggested the formation of
electroactive PDMA salts both in the case of APS and FC.

4.2.8. Conductivity

The conductivity of PDMA salts obtained by mechanochemical
polymerization is listed in table 4.6. The conductivity of PDMA salts is 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 [32]. 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-H$_3$PO$_4$. It is reported that the conductivity of PANI and its
derivatives depends on the degree of doping, oxidation state, particle morphology,
crystallinity, inter or intra-chain interactions, molecular weight etc [33,34]. i.e., the
conductivity of PANI and its derivatives increase with increase in doping degree and
crystallinity. Based on these considerations, the differences in conductivity of these
PDMA salts can be explained by the results of FTIR spectra, UV-Vis spectra, XRD
analysis and CV studies. All these results showed 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 in turn increase the inter-chain conductivity to bring higher conductivity. The nanostructured morphology of PDMA-HCl obtained by using FC favours relatively higher conductivity that the one produced by employing APS. The higher pH value and large size of sulphate and phosphate anions may have contributed to the relatively lesser conductivity values of the corresponding PDMA salts.

4.2.9. Thermal stability

The thermal gravity analysis of the PDMA products prepared with APS and FC individually are presented fig.4.6A (a-d) and 4.6B (a-d) respectively. The DTG curve of undoped polymer samples in both cases of APS and FC shows a single weight loss above 200°C [fig. 4.6A (a) and 4.6B (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 or H₂SO₄ or H₃PO₄) and the other stage around 400°C can be attributed to the thermal decomposition of polymer molecule main chains [35,36]. All these results imply that the PDMA salts are in the doped emeraldine state.

4.3. 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 two oxidants namely APS and FC individually. Elemental analysis proved the presence of corresponding dopant anions (Cl, S, P) in the polymeric backbone of PDMA prepared using APS or FC. The yield obtained from this reaction route was
found to be satisfactory. All of the prepared PDMA salts were found to be form
dispersions with common solvents like water, ethanol, acetone, 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 used in both the cases of APS and FC. FESEM picture shows the
formation of agglomerated nanostructures in the case of PDMA salts prepared using
APS as oxidant and more uniform nanostructured PDMA salts prepared using FC.
PDMA-HCl was found to be more conductive and electroactive. All the as-prepared
PDMA salts are found to be thermally stable up to 400ºC. 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 irrespective of the oxidants (APS or FC) employed for the polymerization.
These differences 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.
REFERENCES

Table 4.1. Elemental composition of PDMA and its salts

<table>
<thead>
<tr>
<th>Polymer</th>
<th>%C</th>
<th>%H</th>
<th>% N</th>
<th>% O</th>
<th>% Cl</th>
<th>% S</th>
<th>% P</th>
<th>Cl/N or S/N or P/N ratio</th>
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<tr>
<td>PDMA</td>
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<td>5.09</td>
<td>7.61</td>
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<td>0.39</td>
<td>--</td>
<td>0.05</td>
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<td>PDMA-HCl</td>
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<td>5.12</td>
<td>7.82</td>
<td>29.34</td>
<td>2.26</td>
<td>--</td>
<td>--</td>
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<tr>
<td>PDMA-H2SO4</td>
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<td>5.11</td>
<td>7.80</td>
<td>29.71</td>
<td>--</td>
<td>1.96</td>
<td>--</td>
<td>0.25</td>
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<tr>
<td>PDMA-H3PO4</td>
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<td>5.12</td>
<td>7.83</td>
<td>29.9</td>
<td>--</td>
<td>--</td>
<td>1.71</td>
<td>0.21</td>
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Table 4.2. Yield of PDMA and its salts

<table>
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<tr>
<th>Polymer</th>
<th>Yield in %</th>
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<td>PDMA-HCl</td>
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<tr>
<td>PDMA- H2SO4</td>
<td>76</td>
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<tr>
<td>PDMA-H3PO4</td>
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<tr>
<td>PDMA prepared using FC</td>
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<td>PDMA- H2SO4</td>
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<td>PDMA-H3PO4</td>
<td>73</td>
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Table 4.3. Assignment of bands found in FTIR spectra of PDMA and its salts

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(N-H) s</th>
<th>(C-H) s</th>
<th>(C=C) s (B)</th>
<th>(C=C) s (Q)</th>
<th>(C-N) s</th>
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<tr>
<td>PDMA 3261</td>
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<td>1664</td>
<td>1597</td>
<td>1207</td>
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<tr>
<td>PDMA-HCl</td>
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<td>3066</td>
<td>1664</td>
<td>1595</td>
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<td>PDMA- H2SO4</td>
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<td>3119</td>
<td>1664</td>
<td>1597</td>
<td>1207</td>
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<tr>
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### Table 4.4. Assignment of UV-Vis absorption peaks of PDMA and its salts

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<th>π–π* band (nm)</th>
<th>polaron–π* band (nm)</th>
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<tr>
<td>PDMA</td>
<td>310</td>
<td>560</td>
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<tr>
<td>PDMA-HCl</td>
<td>306</td>
<td>569</td>
</tr>
<tr>
<td>PDMA- H₂SO₄</td>
<td>301</td>
<td>561</td>
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<tr>
<td>PDMA-H₃PO₄</td>
<td>306</td>
<td>560</td>
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### Table 4.5. Redox potentials of PDMA and its salts

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<tr>
<th>Polymer</th>
<th>First redox peak</th>
<th>Second redox peak</th>
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<tbody>
<tr>
<td>PDMA</td>
<td>E_{pa}/V 0.17</td>
<td>E_{pc}/V 0.09</td>
</tr>
<tr>
<td>PDMA-HCl</td>
<td>E_{pa}/V 0.20</td>
<td>E_{pc}/V 0.04</td>
</tr>
<tr>
<td>PDMA- H₂SO₄</td>
<td>E_{pa}/V 0.20</td>
<td>E_{pc}/V 0.09</td>
</tr>
<tr>
<td>PDMA-H₃PO₄</td>
<td>E_{pa}/V 0.17</td>
<td>E_{pc}/V 0.03</td>
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### Table 4.6. Conductivity values of PDMA and its salts

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<th>Polymer</th>
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<td>PDMA</td>
<td>0.04</td>
</tr>
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<td>PDMA-HCl</td>
<td>1.80</td>
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<tr>
<td>PDMA- H₂SO₄</td>
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<tr>
<td>PDMA-H₃PO₄</td>
<td>0.42</td>
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### PDMA prepared using FC

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<th>Polymer</th>
<th>Conductivity (S/cm)</th>
</tr>
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<tr>
<td>PDMA</td>
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<tr>
<td>PDMA-HCl</td>
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</tr>
<tr>
<td>PDMA- H₂SO₄</td>
<td>1.30</td>
</tr>
<tr>
<td>PDMA-H₃PO₄</td>
<td>0.51</td>
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Fig. 4.1A. FTIR spectra of PDMA and its salts prepared using APS: (a) PDMA (b) PDMA-HCl (c) PDMA-H$_2$SO$_4$ and (d) PDMA-H$_3$PO$_4$. 
Fig. 4.1B. FTIR spectra of PDMA and its salts prepared using FC: (a) PDMA (b) PDMA-HCl (c) PDMA-H$_2$SO$_4$ and (d) PDMA-H$_3$PO$_4$
Fig. 4.2A. UV-Vis spectra of PDMA and its salts prepared using APS: (a) PDMA (b) PDMA-HCl (c) PDMA-H$_2$SO$_4$ and (d) PDMA-H$_3$PO$_4$
Fig. 4.2B. UV-Vis spectra of PDMA and its salts prepared using FC: (a) PDMA (b) PDMA-HCl (c) PDMA-H₂SO₄ and (d) PDMA-H₃PO₄
Fig. 4.3A. XRD pattern of PDMA and its salts prepared using APS: (a) PDMA (b) PDMA-HCl (c) PDMA-H₂SO₄ and (d) PDMA-H₃PO₄
Fig. 4.3B. XRD pattern of PDMA and its salts prepared using FC: (a) PDMA (b) PDMA-HCl (c) PDMA-H$_2$SO$_4$ and (d) PDMA-H$_3$PO$_4$
Fig. 4.4A. FESEM image of PDMA and its salts prepared using APS: (a) PDMA-HCl (b) PDMA-H_{2}SO_{4} (c) PDMA-H_{3}PO_{4} and (d) PDMA.
Fig. 4.4B. FESEM image of PDMA and its salts prepared using FC: (a) PDMA-HCl (b) PDMA-H$_2$SO$_4$ (c) PDMA-H$_3$PO$_4$ and (d) PDMA
Fig. 4.5A. Cyclic voltammograms of PDMA and its salts prepared using APS: (a) Plain GCE (b) PDMA/GCE (c) PDMA-HCl/GCE (d) PDMA-H$_2$SO$_4$/GCE and (d) PDMA-H$_3$PO$_4$/GCE
Fig. 4.5B. Cyclic voltammograms of PDMA and its salts prepared using FC: (a) Plain GCE (b) PDMA/GCE (c) PDMA-HCl/GCE (d) PDMA-H$_2$SO$_4$/GCE and (d) PDMA-H$_3$PO$_4$/GCE
Fig. 4.6A. TG/DTA curves of PDMA and its salts prepared using APS: (a) PDMA (b) PDMA-HCl (c) PDMA-H$_2$SO$_4$ and (d) PDMA-H$_3$PO$_4$
Fig. 4.6B. TG/DTA curves of PDMA and its salts prepared using FC: (a) PDMA (b) PDMA-HCl (c) PDMA-H₂SO₄ and (d) PDMA-H₃PO₄