

CHAPTER II

LITERATURE REVIEW

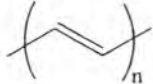
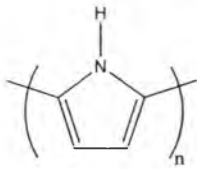
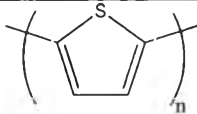

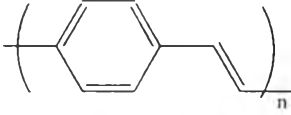
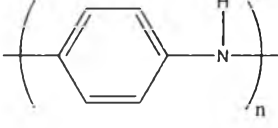
2.1 Conductive Polymer

A conductive polymer was first made in 1930 for prevention of corona discharge. The potential uses for conductively filled polymers have been multiplied due to their ease of processing, good environmental stability and wide range of electrical properties. Being a multi-phase system in nature, however, their lack of homogeneity and reproducibility has been an inherent weakness for conductively filled polymers. So, controlling the quality of dispersion to obtain homogeneous conducting polymer composites is critically important.

In 1950, CP was investigated as molecular charge transfer (CT) complexes (Akamatu *et al.*, 1954). It was developed for a superconductor with CT polymer complexes in 1980 (Jerome *et al.*, 1980) and with fullerene in 1986 (Iqbal *et al.*, 1986).

A conductive polymer can conduct electron charges by its conjugated structure. A structure with overlapped *p*-orbitals (*e.g.* N, S) can occur by alternating single and double bonds or conjugated segments coupled with atom. In a conducting polymer system, not only charge carriers but also the orbital system that provide charge carriers to move. Due to its simple conjugated molecule structure and interesting electronic properties, polyacetylene was widely investigated as a prototype for other electronically conducting polymers (Chen, 1984).

Table 2.1 Some conjugated conducting polymers (Dai, 1999)

Polymer	Structure	Band gap (eV)	Conductivity (S/cm)
Polyacetylene		1.5	10^3 - 1.7×10^5
Polypyrrole		3.1	10^2 - 7.5×10^3
Polythiophene		2.0	10 - 10^3
Poly(paraphenylene)		3.0	10^2 - 10^3
Poly(p-phenylene vinylene)		2.5	3 - 5×10^3
Polyaniline		3.2	30-200

2.2 Oxidation Polymerization

Oxidation polymerization is used to synthesize polymeric (oligomeric) products from various classes of monomers (aromatic amines, phenols, thiophenols, aromatic hydrocarbons and heterocycles) (Hideyuki *et al.*, 2004). The monomers used in the oxidative polymerization are characterized by pronounced electron donor properties and high oxidation tendency. These properties, in particular, are inherent to aromatic amines, phenols and thiophenols or sulphur- and nitrogen-containing heterocycles due to the presence of electron donor substituent in benzene or heterocyclic ring. Oxidation of monomer takes place under the action of inorganic (or organic) oxidizing agent or the applied potential. During this process, cation or

anion radical sites are generated in monomer (polymer) molecule, that initiate polymer growth. Technically, the oxidative polymerization may be considered as a formation of covalent bonds between monomer molecules at the expense of abstracting two protons. There are many types of linkage between monomer units. For example, in the case of aniline, “head-to-head”, “tail-to-tail” and “head-to-tail” configurations are possible. In addition, in the last two cases chain assembly may occur due to substitution in phenyl ring with the formation of *ortho*-, *para*- and *meta*-monomer units (Hideyuki *et al.*, 2004).

2.3 Poly *o*-anisidine Synthesis and Application

Poly *o*-anisidine (POA) or Poly (2-methoxyaniline) is a conductive polymer; a derivative of aniline, that can be synthesized by the electrochemical and chemical oxidation polymerizations (Mazrouaa *et al.*, 2012). For the chemical oxidation polymerization, the yield was higher than 90% (Stejskal *et al.*, 2002).

Polyaniline (PANI) is insoluble in common organic solvents and of low mechanical strength. To makes it soluble, PANI must increase its solubility by adding functional groups or a flexible alkyl chain to the polymer backbone (Kulkarni, 2007). POA is also soluble, it can be made to be dispersable in aqueous and organic solvents (Sivakumar, 2007).

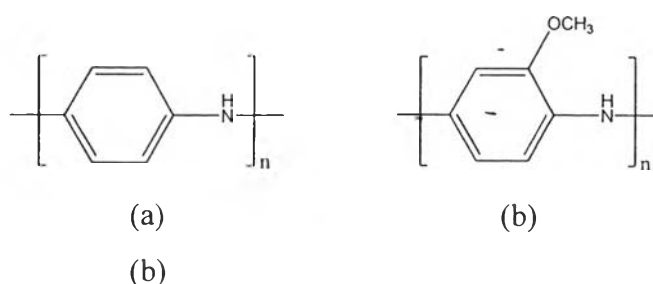


Figure 2.1 Chemical structure of (a) Polyaniline and (b) Poly (*o*-anisidine).

Poly *o*-anisidine nanoparticles can be synthesized by the emulsion polymerization via a cationic surfactant (Mazrouaa *et al.*, 2012).

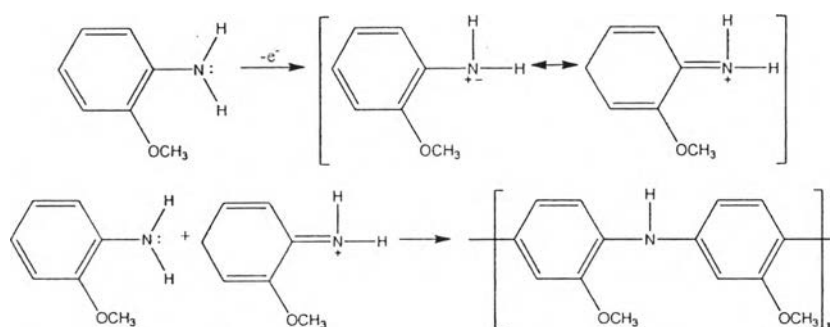


Figure 2.2 Scheme of homopolymerization of poly *o*-anisidine.

PANI and POA were mainly used for coating to improve the corrosion resistance for oxidizable metals (Jadhav, 2010). They have been considered for several other applications such as biosensors, rechargeable batteries, electrochromic displays, gas separation, and etc. Recently, it was shown that PANI and POA can act against *Escherichia coli* and Gram-positive *Staphylococcus aureus* in wound dressing application (Mazroua, 2012).

Ram *et al.* (1997) studied the effect of pH on Langmuir monolayer behavior of POA. They varied pH from 1 to pH 6.4. They found that POA films exhibited electrical conductivity values between 0.1 and 10^{-9} S/cm. The pH 1 condition was the best condition because its chain was oriented and was simultaneously doped due to the presence of a protonic acid. HCl-doped POA film did not show any time degradation on the electrical characteristics, but H_2SO_4 and HClO_4 showed large decreases in the current magnitude.

Wankhede *et al.* (2002) coated POA on low carbon steel (LSC) by electrochemical polymerization in aqueous solution of oxalic acid. It was found that POA coating occurred after the passivation of its surface via the formation of polycrystalline iron oxalate interphase. From this reaction, the induction time decreased with the applied current density and the suitable medium for the electrochemical polymerization of POA is oxalic acid because POA formed emeraldine salt as confirmed by UV-vis and FT-IR.

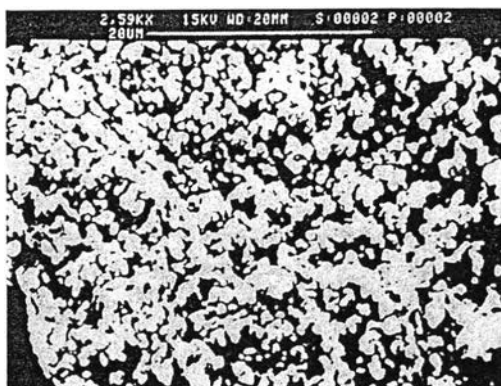


Figure 2.3 Scanning electron micrograph of POA coating synthesized on LCS substrate.

Mazur *et al.* (2003) synthesized nanosizes of PANI and POA by a polycarbonate (PC) template. They found that PANI chains were formed in a polymerization solution which included monomer, oxidant, and polycarbonate substrate. PANI can be precipitated on a membrane. Sizes of PANI were an average value of pore sizes in the PC membrane, which was about 100 nm. But in the case of POA, the oxidized POA absorbed on the PC membrane, and then, as a consequence of their accumulation, oligomers recombined to form the POA polymer by an organic solvent.

Patil *et al.* (2003) coated POA on copper plate (Cu) by the electrochemical polymerization (ECP) and studied the corrosion protection performance in a 3% NaCl solution. They found that the porosity of the polymer after synthesizing was very low (0.23%). Morphology after potentiodynamic polarization measurements in a NaCl solution was of a uniform coverage and the overall texture was ‘pumice-like’. The corrosion rate of POA coated Cu was found to be on average 100 times lower than bare Cu. This meant that POA can protect Cu against corrosion and dissolution.

Valentini *et al.* (2004) prepared sensors for inorganic vapor detection based on carbonnanotubes (CNT) and POA nanocomposite material. POA was synthesized by chemical oxidation polymerization by using APS. POA deposition onto the CNTs device was shown to impart higher sensitivity to the sensor. Upon exposure to HCl the variation of the CNTs sensitivity was less than 4%, while POA-coted CNTs devices offered a higher sensitivity (28%).

Wang *et al.* (2005) synthesized a poly (aniline-co-o-anisidine)-intercalated graphite oxide composite by the delamination/reassembling method in N-methyl-2-pyrrolidone (NMP). The thermal analysis showed that no de-intercalation of the polymer composite from graphite oxide occurred during heating. Its electrical conductivity was 1.9×10^{-2} S/cm, which was 3 times higher than graphite oxide.

Kondawar *et al.* (2006) studied the chemically synthesized doped POA and POA-co-PANI. Polymer and copolymer were synthesized by chemical oxidation polymerization by using ASP as oxidizing agent and sulfuric acid as dopant. At room temperature, the electrical conductivity of copolymer POA-co-PANI (7.88×10^{-4} S/cm) was higher than POA (2.86×10^{-4} S/cm). Temperature dependent conductivity measurements showed the characteristic thermal activation behavior that increased the electrical conductivity by increasing temperature.

Sivakumar (2006) studied dispersion of platinum nanoparticles (Pt) in POA nanofibrillar matrix, Pt in POA, and cast film. It was found that the POA film had a very high porosity when synthesized by the step wise electro-oxidation polymerization. When Pt nanoparticles were loaded into the POA nanofibrillar matrix by two-step: at first, PtCl_6^{2-} ions were sorbed into the pores of polymatrix; and then, loaded Pt nanoparticles ($10\text{-}200 \mu\text{g}/\text{cm}^2$) onto POA. Pt particles sizes were in range of 10-20 nm. POA film of this method had a high surface area than bulk Pt by 17 times and containing less methanol by 8.6 times.

Kulkarni *et al.* (2006) studied synthesized POA doped with polymeric acids by an in-situ chemical polymerization. This method used ammonium persulphate as an oxidizing agent. A thermal analysis showed that POA doped with poly(acrylic acid) had a three step decomposition pattern like polyaniline, but POA doped with poly(styrene sulphonic acid) and poly(vinyl sulphonic acid) had a four-step decomposition pattern. At room temperature, conductivity of POA was less than PANI. This was because bulky methoxy at the orthoposition has high steric hindrance.

Ismail *et al.* (2007) studied the fabrication of a PANI microfiber by wet spinning a chitosan solution, followed by the in-situ chemical polymerization. They found that fibers had an electrical conductivity value of 2.856×10^{-2} S/cm. at room temperature and the strain during the chemical actuation of 6.73%. Strain during

electrochemical actuation showed a higher value when pH was decreased. SEM images of fibers showed an agglomerated granular morphology of PANI particles coated on the surface of chitosan fibers.

Patil *et al.* (2007) prepared a humidity sensor from POA/tungsten trioxide (WO_3) composites by varying the WO_3 weight percentage. POA/ WO_3 composites showed better properties than pure POA. For the composite with 30 wt% of WO_3 , it showed the maximum response factor (S_f) about 353 at 85 % relative humidity (RH), narrow hysteresis (about 6%), and excellent repeatability of the response. Moreover, this composite was stable for more than 30 days.

Tan *et al.* (2007) synthesized single-phase hollow POA colloids via hydrothermal polymerization without using template by $\text{Cu}(\text{Ac})_2$ and $\text{Cu}_2(\text{OH})_3\text{Br}$; weak oxidant; as initiator. The morphology of POA displayed regular spherical particles with diameters between 240-400 nm and hollow particles with a diameter of 305 nm.

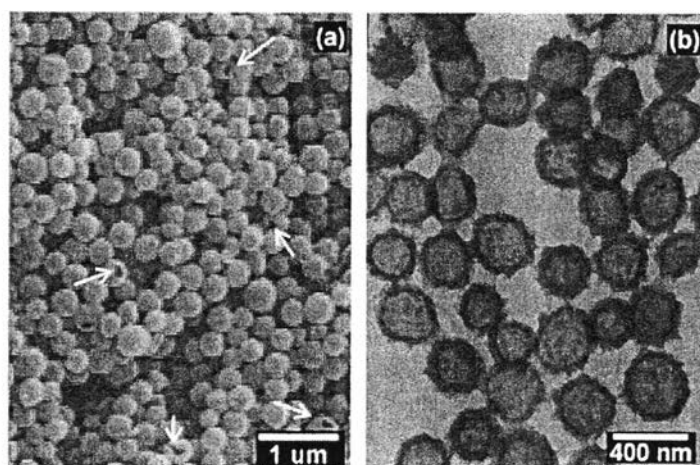


Figure 2.4 SEM (a) and TEM (b) images of poly(*o*-anisidine) synthesized by a hydrothermal reaction.

Patil *et al.* (2010) synthesized a POA-tin oxide (SnO_2) nanocomposite for humidity sensing application by the in-situ chemical polymerization. Size of SnO_2 was 25-40 nm. For the composition of 50% SnO_2 , it exhibited better humidity sensing properties than pure POA with 4% hysteresis, 87s response time, and 13s recovery time.

Jadhav *et al.* (2010) synthesized nanoparticles of PANI and POA by the emulsion polymerization with sodium dodecylsulfate (SDS) in HCl solution. These materials were dispersed in a solution of alkyd in xylene with 0.5, 1.0, and 1.5 wt%. The dispersion of a small amount of PANI and POA enhanced the scratch hardness and the impact resistance performance. Dispersion of PANI/alkyd coating showed better corrosion resistivity of mild steel in comparison with POA/alkyd coating in all corrosive media such as 5% HCl, 5% NaOH, and 3.5% NaCl. This work proved that PANI nanoparticles were better corrosion inhibitors in alkyd paint formation to protect against the mild steel corrosion.

Ozyilmaz *et al.*, (2010) prepared POA and PANI film in sulphamic acid solution for anticorrosion application. POA and PANI were synthesized by electrochemical polymerization by using sulphamic acid as electrolyte solution. PANI and POA were coated on a Pt surface. It was found that sulphamic acid led to the formation of a well-passivated layer that increased the amount of homopolymer coating with increasing rate of electropolymerization. The corrosion performance of PANI and POA depended on the formation oxide layer on surface. POA film exhibited an effective anticorrosive property than PANI film.

Ojani *et al.* (2010) prepared POA/SDS/Ni modified carbon paste electrode by using cyclic voltammetry, chronoamperometry, and chronocoulometry methods for novel sensor for cephalosporins application. First, POA was formed by cyclic voltammetry in monomer solution containing SDS, on carbon paste electrode surface. Then, Ni(II) ions were incorporated to electrode by immersion of the polymeric modified electrode having amine group in Ni(II) ion solution. It was found that cephalosporins were successfully oxidized on the surface of this electrode. This electrode was applied to determine cephalosporins in pharmaceutical preparations.

Khan *et al.* (2012) compared thermal and electrical properties of POA and poly(o-toluidine) Sn(IV) tungstate composites. They were synthesized by a modified sol-gel technique. Composites were measured by a 4-in-line-probe for DC electrical conductivity. The conductivity was found to be in range 10^{-4} - 10^{-2} S/cm.

Mazrouaa *et al.* (2012) synthesized POA nanoparticles by the electrochemical polymerization via a cationic surfactant and studied the effect of composite on sulfate reducing bacteria. POA was composited with 1.0 wt% metal oxide (Ag_2O , ZnO , CuO , TiO_2) and characterized. From all composites, the POA/ Ag_2O nanocomposite microsphere had a good effect on the sulfate reducing bacteria than POA nanoparticle. The electrical conductivity of POA nanoparticle was improved by adding metal oxides from 10^{-16} S/cm to 10^{-11} S/cm in case of POA/ Ag_2O and 10^{-12} S/cm in case of POA/ ZnO . The conductivity was increased by increasing temperature.

2.4 Synthesis of Poly *o*-anisidine Nanoparticles

Pud *et al.* (2009) studied formation and properties of nano- and micro-structured conducting polymer host-guest composites. In this work, they synthesized PANI and POA and coated on the surfaces of SiC nanoparticles, CdS nanoparticles, poly (vinylidene fluoride), polycarbonate, and polyamides-11, 12. micro-sized particles by chemical oxidation polymerization. It was found that the morphology of polymer blends were of a core-shell structure. The formation of core-shell consisted of PANI shell and a core of other components with diameter 20 nm to 100 nm. The conductivity of PANI (3-4 wt%) core-shell powder with common polymers was 0.1-0.4 S/cm.

Khan *et al.* (2009) synthesized a POA composite with Sn(IV) phosphase via chemical oxidation polymerization by using APS as an oxidizing agent. The particle size of composite was 23 to 33 nm. The electrical conductivity was found within the range of 1.65×10^{-3} to 5.4×10^{-2} S/cm. the electrical conductivity depended on the percolation behavior of the conducting phase. It was found that the slight increase in electrical conductivity of the composites was followed at a certain aniline concentration by a sudden jump, which was again followed by a moderate increase.

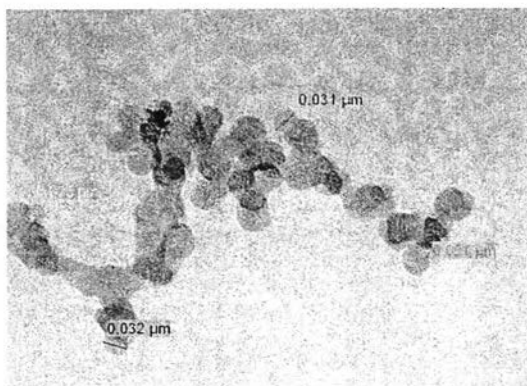


Figure 2.5 Transmission electron microphotograph (TEM) of poly-o-anisidine Sn(IV)phosphate composite.

Valtar *et al.* (2001) prepared POA fabricated on multiwall carbon nanotube (MWNTs) by oxidative polymerization in aqueous phase solution. Carbon nanotubes were forming composites with POA, resulting in doping, as observed from conductivity and optical measurement. The electrochemical degradation of POA films was investigated by cyclic voltammetry. It was found that the rate of degradation was strongly dependent on the applied potential, whereas a POA composite was formed and susceptible to higher potential. Because of the highly electrochemical resistive nature of POA-MWNTs nanocomposites

Wang *et al.* (2008) synthesized copolymer of POA, PANI and poly(sodium 4-styrenesulfonate) (PSS) and assembled on carboxylic acid-functionalized MWNT with layer-by-layer method to core-shell structure. The composite showed higher conductivity increase, 4.2 S/cm, compared to that of neat copolymer, 0.004 S/cm.

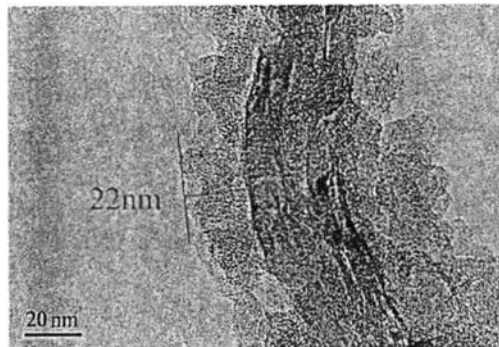


Figure 2.6 TEM images of P(An-co-o-As)/PSS/MWNTs. The red line indicates the thickness of the polymer shells assembled on MWNTs.

Jiang *et al.* (2010) fabricated POA composite with CoFe_2O_4 nanoparticles (20 nm) by oxidation polymerization. The SEM result showed that POA layers were wrapped on the surface of CoFe_2O_4 nanoparticles appearing as small aggregated globules (80 nm). The composite exhibited ferromagnetic behavior under applied magnetic field at room temperature. The saturation magnetization of composite nanoparticles was lower than that of the pure CoFe_2O_4 nanoparticles due to the contribution of non-magnetic POA layer.

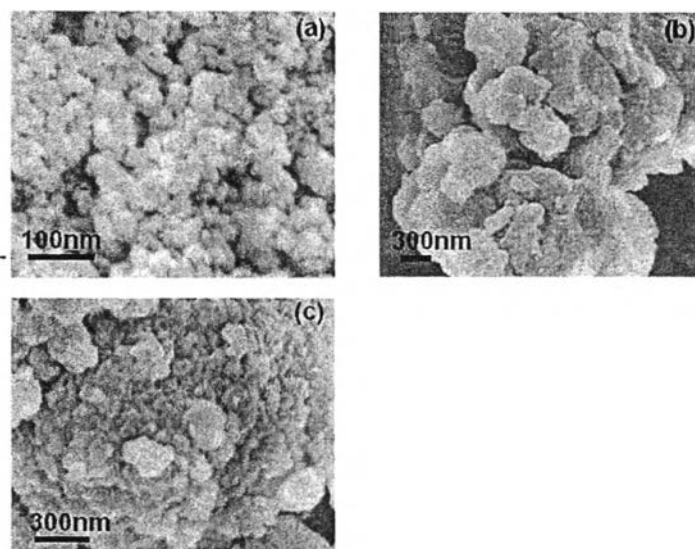


Figure 2.7 SEM micrographs of CoFe_2O_4 (a), POA (b) and POA/ CoFe_2O_4 nanocomposite (c).

Lou *et al.* (2011) synthesized POA and its derivatives by the chemical oxidation polymerization in the presence of 10-camphorsulfonic acid (CSA). The oxidation of aniline produced nanotube (250 nm), while the oxidation of most aniline derivatives produced hollow microspheres (790-2500 nm) under the same conditions. The main factors to control the polymer morphology were stability of droplets of aniline and its derivative formed in aqueous solution and the rate of exothermal reaction. The fast exothermal reaction benefited the formation of uniform microspheres, the hole on the surface of microsphere formed at the initial oxidation stage which was maintained by the flux of water and water-soluble components in the course of polymerization.

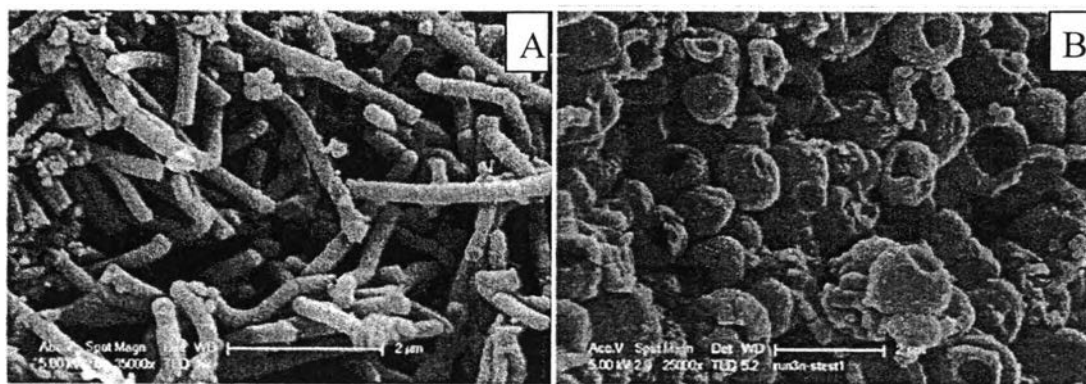


Figure 2.8 SEM images of the polymers synthesized in the presence of CSA: (A) PANI; (B) POA.

Wang *et al.* (2011) synthesized POA by chemical oxidation polymerization. APS was used as an oxidant and methane sulfonic acid (MSA), hydrochloric acid (HCl), and *p*-toluene sulfonic acid (*p*TSA) were used as dopants. *p*TSA gave the highest electrical conductivity ($8.4 \pm 0.8 \times 10^{-3}$) compared with HCl ($2.5 \pm 0.1 \times 10^{-3}$) and MSA ($1.8 \pm 0.2 \times 10^{-3}$) because the molecular structure of *p*TSA stabilized the bond between dopant and the polymer chain through the benzene ring of the dopant anion facilitating the formation of a resonance structure and electron flow over the entire polymer chain.

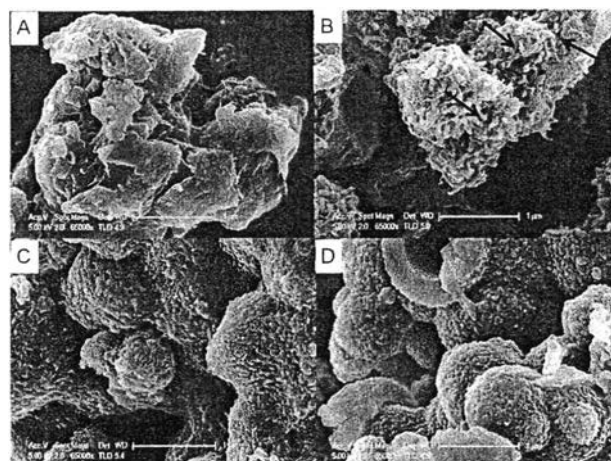


Figure 2.9 SEM micrographs of POMA doped with (A) pTSA, (B) HCl, (C) MSA, and (D) undoped POMA.

Chabukswar *et al.* (2012) synthesized poly(N-ethylaniline) (PNETA) by using tartaric acid (TA) as an organic dopant by an aqueous oxidation polymerization with APS as an oxidant and acrylic acid (AA) as a soft template. The morphology of PNETA/TA/AA consisted of coral-like granular particles with a diameter more than 100 nm and conductivity 0.36×10^{-1} S/cm. However, PNETA/TA was smooth nanoparticles with diameters between 30 nm to 50 nm and conductivity value of 0.73×10^{-2} S/cm. They were well dispersed with soft template AA but of lower conductivity because AA was induced from TA to raise the doping level on the structure of polymers.

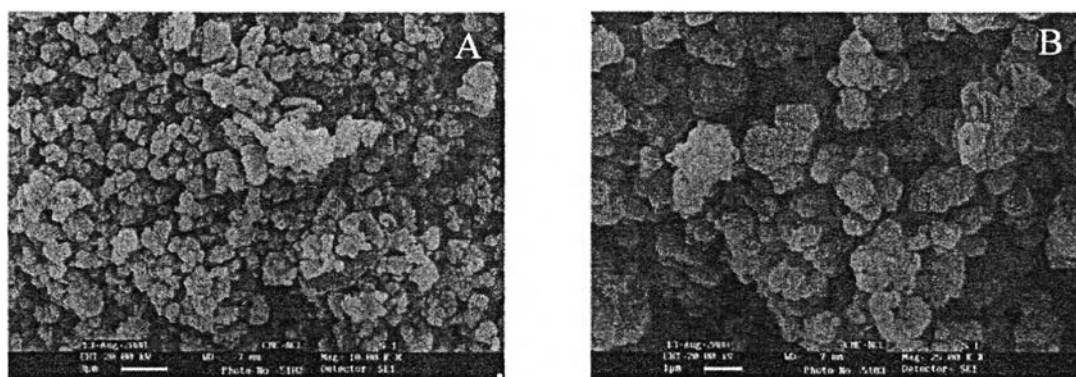


Figure 2.10 SEM images of poly(N-ethylaniline): (A) PNETA/TA; and (B) PNETA/TA/AA