



J. Chem. Pharm. Res., 2010, 2(3):647-655

ISSN No: 0975-7384
CODEN(USA): JCPRC5

Conducting polymer of aniline blended by polymethylmethacrylate metal containing polymer: *insitu* blending and characterizations

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ABSTRACT

Electrically conducting polymers describe as a new class of synthetic metals. In this study conducting polymers prepared by insitu blending technique. Aniline was blended by polymethylmetacryalte and metal alloy poly(ba acrylate). We were examined all prepared polymer films physical properties like appearance, polymerization yield, absorption quality. The conductivity levels of the blended polymers were examined by the four point probe technique. Molar magnetic susceptibility of polymer was found to be -28.8 BM so we can says the blended polymer was diamagnetic and shows bipolaron conduction mechanism. New blended polymer was highly conductive in nature . UV visible, FTIR and NMR spectra were taken in order to analyze the structural properties of the resulting copolymer. The molecular wt. of polymer was determined by GPC technique. Surface micrographs were taken by SEM.

Key words : Polyaniline, Conducting polymers, Polymers blending, Polymer alloys.

INTRODUCTION

Polymers are known as insulators. But some of the conjugated polymers show unique electronic properties derived from the presence of π -electrons which are delocalized over the long portion of the polymer chain. The essential properties of delocalized π -electron system, which differentiate a typical conjugated polymer from conventional polymers.

The unique electronic properties of the conjugated polymers are derived from the presence of π -electrons, the wave functions of which are delocalized over long portion of polymeric chain, when the molecular structure of backbone is planar. It is therefore necessary that there are no large torsion angles at the bonds, which could decrease the delocalization of the pi electron system [1,2].

Electrically conducting polymers have been the subject of considerable amount of research because of their interesting and useful electronic, optical and redox properties. One of the main characteristics required for electrical and optical activities to occurs in a polymers is a conjugated backbone which can be subject to oxidation or reduction by e- acceptors or donor, due to delocalization of the e-s in conjugated polymers.

Properties such as tensile strength, high impact strength, thermal resistance and chemical resistance; easy processing and dimensional stability etc. will be enhanced by blending the polymer. There are various types of blending the conducting polymer with other polymers. These are; dry blending, solution blending and *insitu* blending.

The conducting polymers with thermoplastic polymers *Stanke et al* [3] comparatively studied to synthetic way to synthesized copolymers of methylmethacrylatre with (N-pyrrole) and ethyl methacrylate with pyrrole.

Park et al [4] prepared a new conducting graft copolymers of poly(acryloylchloride) (PAC) and polypyrrole (PPy), PAC-g ppy by (PAP). Which is processability and has desirable mechanical,properties. The investigation of electroactive and characterization for the new conducting graft copolymers are also preformed.Among these polymers polyaniline has emerged as a promising candidate with great potential for practical uses such as in light emitting diodes, transparent electrodes, electromagnetic radiation shielding, corrosion protection of metals, gas and humidity sensing battery. Electrically conducting (conductivity $\sigma = 10^{-2} - 10$ s/cm), due to the presence of cation radical radicals in its structure.

EXPERIMENTAL SECTION

Aniline (E- Merck) used after double distillation. Polymethylmethacrylate and acrylic acid were procured from Alfa Aesar, and used after purification by standard method. Barium hydroxide procured from E.Merk. All solvents used after purification.

Synthesis of Metal Containing Polymer: Poly (Ba acrylate)

Firstly we prepared metal containing monomer (Barium acrylate). Barium acrylate was prepared by the reaction of acrylic acid (5-10 % stiochimetric excess) with basic barium hydroxide in toluene suspension at 40-50 °C. This reaction was carried out for 5 hours, with gradual addition of the reactant and with constant stirring. The evaporated toluene lost from the reaction vessel was constantly replaced water formed in the reaction vessel was removed as an azeotropic mixture with toluene. Barium acrylate after a preliminary drying was washed with acetone and finally vacuum dried. Barium acrylate was polymerized in DMSO solution at 80 °C Benzoyl Per Oxide (BPO) was used as an initiator. After 5 hours, solution was precipitated by methanol and dried on water bath.

Synthesis of Blends:

Polymethylmethacrylate and PolyBa acrylate blend was carried out by *insitu* technique. In the *insitu* synthesis, polymethylmethacrylate 2 gram dissolved in 100ml methanol and 50 mg poly (Ba acrylate) dissolve in DMF were taken in a beaker. To that, 0.51 grams of monomer aniline (0.005 M) and 5 ml of 1N HCl solution were added. About 25 ml of 0.1M initiator ammonium per sulfate was added slowly to the above reaction mixture under constant stirring. The reaction was carried out at $\pm 60^{\circ}\text{C}$ temperature for 10 hr. The blend was precipitated in distilled water, filtered, washed with distilled water several times and dried in a vacuum till moisture was removed. Film was casting by dissolving the new blended polymer in benzene.

RESULT AND DISCUSSION**Physical Measurements:****Polymerization yield**

All dried the blended polymer weighted and the percentage yields were calculate by using eq.-

$$\text{The polymerization yield} = \frac{\text{Weight of copolymer} \times 100}{\text{Percentage} (\text{Weight of } x \text{ M monomer}_1 + \text{weight of } x \text{ M monomer}_2)} \text{ was found } 43.8 \%$$

Softening Range

The blended polymer film of aniline, polymethylmethacrylate and poly (Ba acrylate) have softening range found to be from 141-146 $^{\circ}\text{C}$.

Solubility

Polymethylmethacrylate is resistant to many alkali solvents and poly aniline (emerlidine base) is water soluble. The the blended polymer of aniline, polymethylmethacrylate and poly (Ba acrylate) are soluble in many organic solvents like benzene, toluene, dioxane but insoluble in inorganic solvents like hydrochloric acid and sulfuric acid. Blended polymer was highly resistance to inorganic acids.

Electrical Conductivity:

Conductivity of prepared blended polymer film was measurement at room temperature by four-point probe method. A known current through the outer two probes (1 and 4) and voltage across the inner two probes (2 and 3) measured by voltmeter. Probes spacing about 1mm. Conductivity of copolymers films was calculated from the following equation

$$\sigma = \frac{I n_2}{(\pi R t)}$$

R is the resistance of the sample in mv and t is the thickness in cm.

The conductivity of copolymer films were highly influenced by the thickness of the blended polymer film. The new synthesis polymer showed the conductivity was $20 \times 10^{-3} \text{ Scm}^{-1}$.

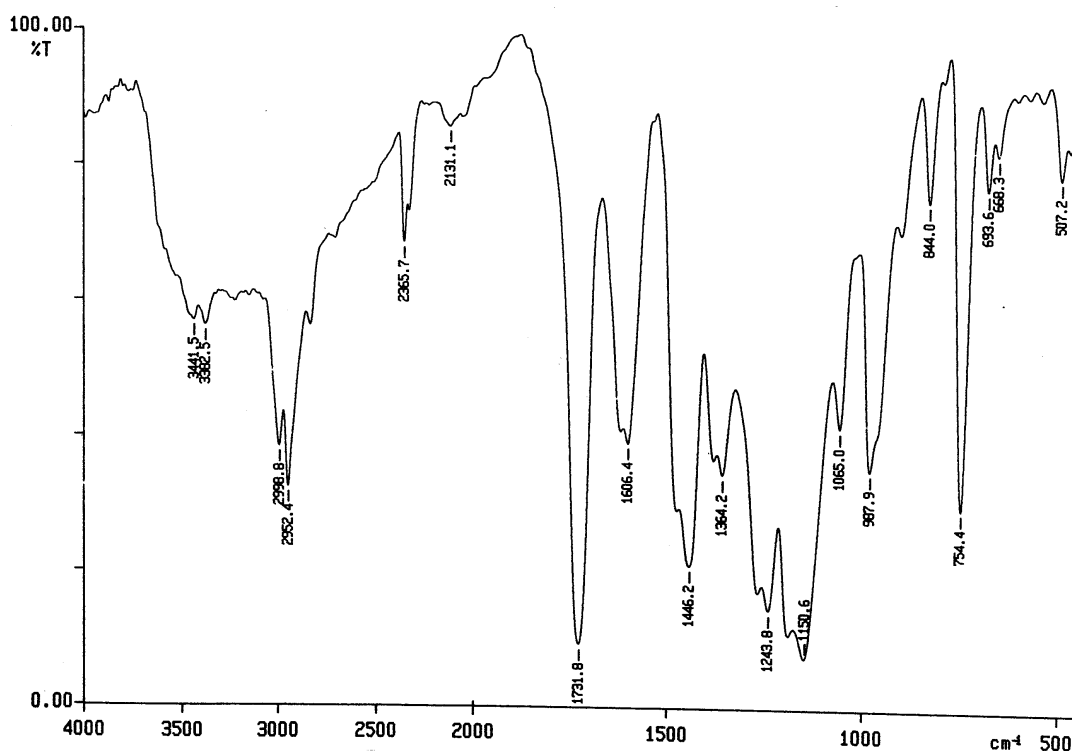
Conduction mechanism:

Conduction mechanism of copolymer film was known by Studies on Magnetic Susceptibility Measurements (Vibrating Sample Magnetometer). The molar magnetic susceptibility of copolymer of aniline and methylmethacrylate containing poly(Ba-acrylate) was found to be -28.8 BM. The negative value shows that the copolymers are diamagnetic and the conduction mechanism is bipolaron in nature.

Structural Analysis

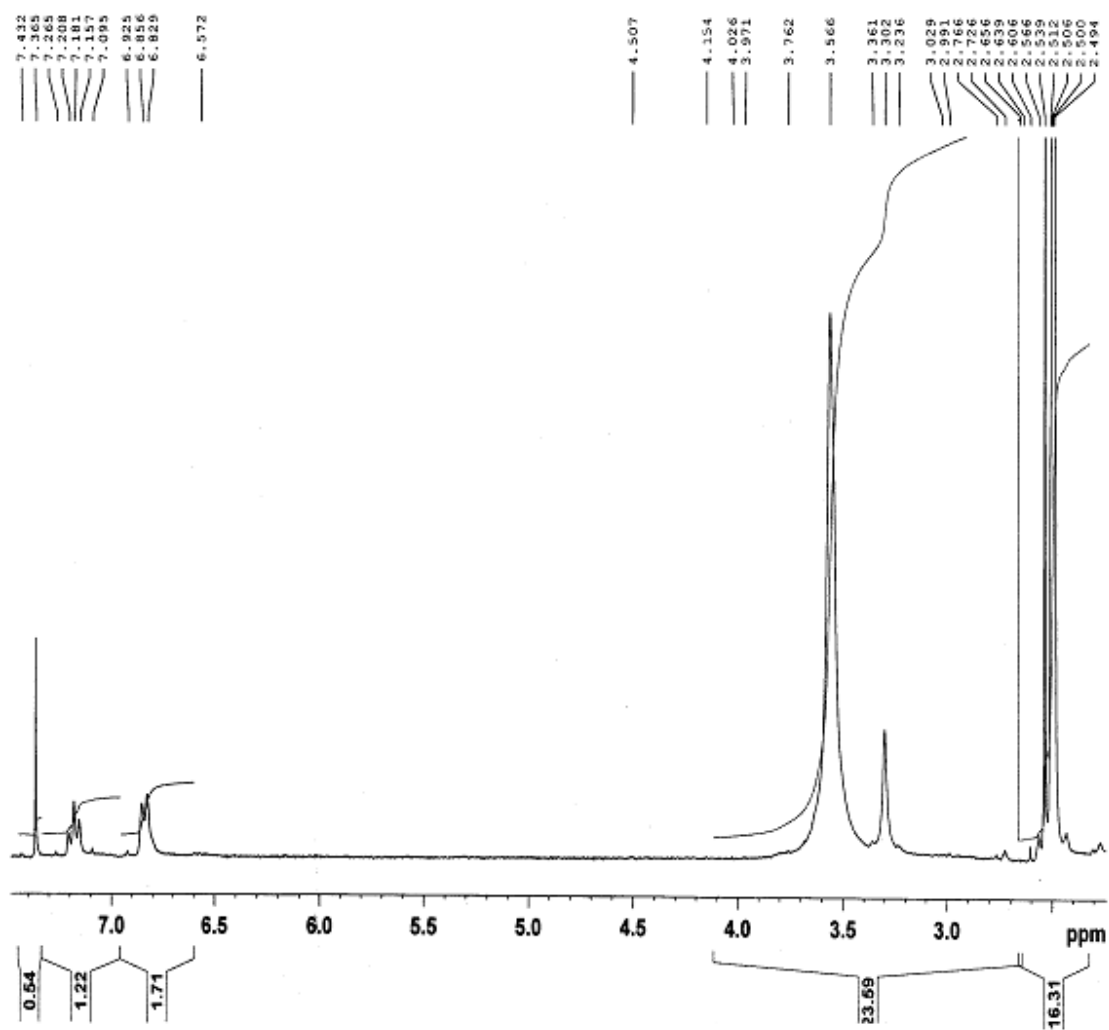
The UV-Visible spectrum for blended polymer shows absorption at 227 nm and 264 nm that correspond to π - π^* transition, this band is often called the B band and 390 nm corresponds to n - π^* transition is called the R band. A low intensity peak observed at 615 nm is assigned to conductivity band which is shown by polymer having electrical conductivity.

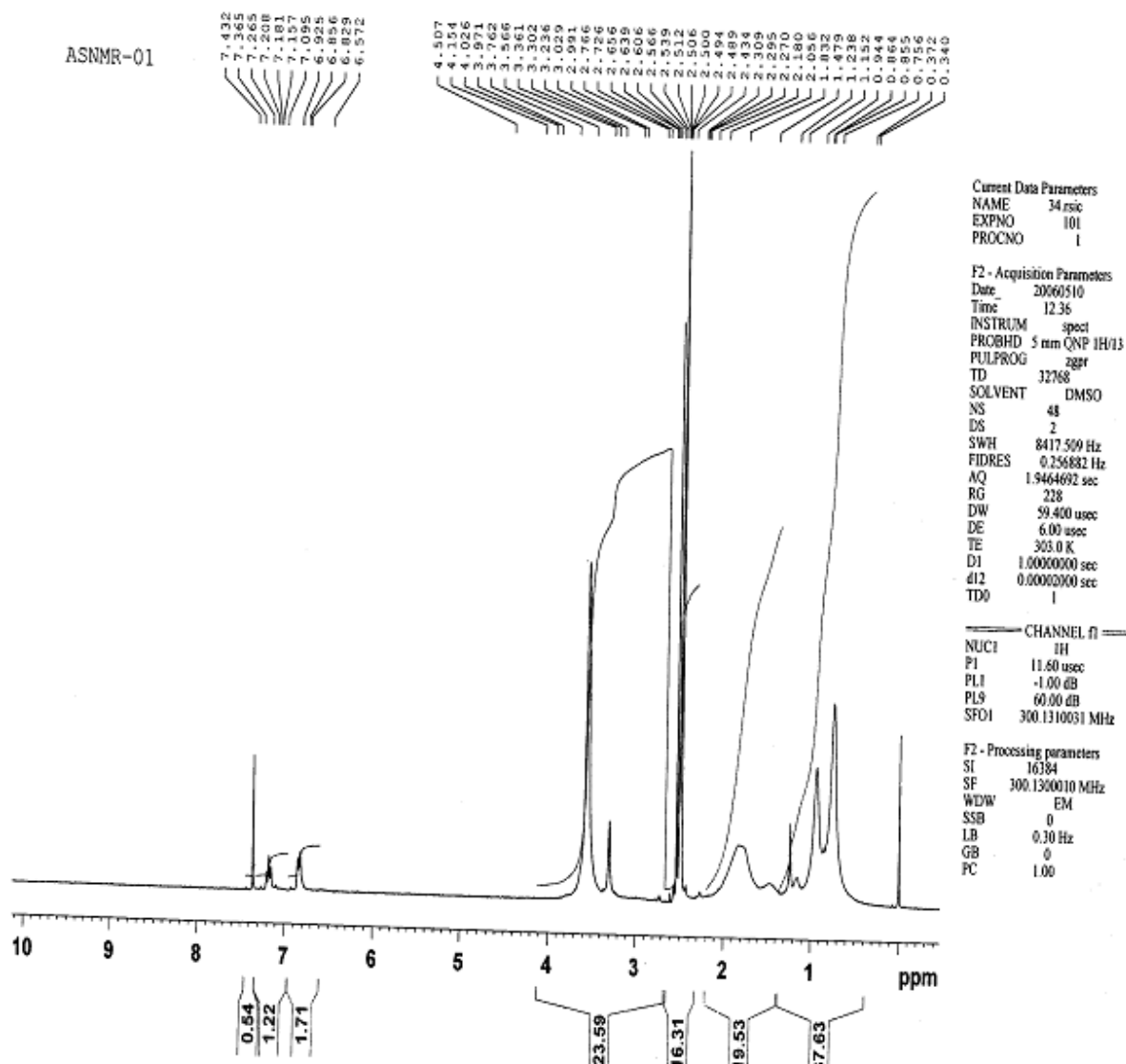
The FTIR Spectrum gives the important details of the structure. A peak obtained at 3441.5 cm^{-1} is characteristic peak of N-H stretching. This is already reported by *Kassim et al* [8]. The absorption at 2998.8 cm^{-1} and 2952 cm^{-1} arise from C-H stretching [9].



IR Spectra of blended polymer of aniline, polymethylmethacrylate and polyBa acrylate

ASNMR-01





NMR spectra of blended polymer of aniline, polymethylmethacrylate and polyBa acrylate

The peak 2998 cm^{-1} is due to asymmetrical stretching and band at 2952.4 cm^{-1} is due to symmetrical stretching of CH_2 group. It is known that the positions of C-H stretching vibrations are among the most stable in the spectrum, which can be achieved with the help of fluoride prism or a grating instrument. The frequencies of methylene stretching is increased because the methylene group is in the strained position.

The bending vibrations of the C-H bonds in the methylene group obtained at 1446.2 cm^{-1} , 754.4 cm^{-1} and 1150.6 cm^{-1} . The band is obtained at 1446.2 cm^{-1} , the band at 754.4 cm^{-1} resulting from the methylene rocking vibration, in which all of the methylene groups rock in phase and the absorption at 1364.2 cm^{-1} arise due to the methylene twisting and wagging vibrations. The most prominent band in the spectrum seen at region between $900\text{--}675\text{ cm}^{-1}$. These strong absorption of out of plane bending of the ring C-H bonds.

The C=O absorption in Ba acrylate is overlapped and it can be seen at 1731.8 cm^{-1} [10]. The lowering of the frequency of C=O band indicates the conjugation of C=O bond results in delocalization with the neighboring π electrons of unsaturated groups. Delocalization of the π electrons of the C=O groups reduces the double bond character of the C to O bond, causing absorption at lower wave number.

The carboxylate anions obtained has two strongly coupled carbon to oxygen bonds with bond strength intermediate between C=O and C-O. The carboxylate ion give rise to 2 band : a strong asymmetrical stretching bond near 1596.5 cm^{-1} and a weak, symmetrical stretching band near 1400 cm^{-1} .

^1H NMR data for the monomer: ^1H - NMR (δ , ppm) for MMA, peak at 1.4 ppm due to CH_3 group proton at 2.0 ppm due to $-\text{OCH}_3$ group proton and at 2.3 ppm due to CH_2 group proton present in MMA monomers. For aniline, 6.6 ppm due to NH_2 group proton and 7.2 ppm due to benzenoid group proton present in aniline monomers. In the ^1H NMR spectra of the polymer viz., a wide signal in the region of 6.8 to 7.2 ppm was assigned to benzenoid hydrogen of aniline. The peak at δ 7.55- δ 7.70 ppm already, reported by *Abbasian et al* [11]. Two equal intensities peak in these region was assigned to para position of aniline is linked for the polymerization. Signal at 3.5 ppm indicate peak of $-\text{OCH}_3$ hydrogen reported by *Manirzzaman et al* [12] peak at 0.9 and 0.8 ppm is due to CH_2 and CH_3 hydrogen respectively. The shift of the CH_2 peak to highly shielded region is due to polymerization. The other signal were remained unchanged but broadened due to polymerization.

Molecular Weight Determination by Gel Permeation Chromatography): There was three separate peaks are clearly observed in chromatogram. Molecular weights of Polymethylmethacrylate varies from 90,000 to 3160,000 [13]. Whereas conducting polyanilines having an average molecular weight not higher than about 600,000 can be obtained. It is reported that in polymethylmethacrylate has $M_w = 1,63,000$ which may be due to transition of the appearance of the fracture surface. In the present study the blended polymers of aniline polymethylmethacrylate and poly (Ba acrylate) displayed a wide, molecular weight range, averaging from 60,000 to 5,000.

Morphology: Morphology of PANI film is strongly influenced by the methylmeth acrylate and poly Ba acrylate. Figure a shows SEM images of copolymer of aniline, MMA and Poly Ba acrylate in different section Morphology of PANI is also influenced by method of synthesis and also by oxidizing agent [14]. The film fibers is $10\text{ }\mu\text{m}$ in length and $1\text{ }\mu\text{m}$ in width.

The cross- section view figure 1b of copolymer flake also reveals similar compact morphology as figure 1a large number of free vacuoles is generated and more sectional view of the polymer is seen in figure 1c. Morphology of copolymers is influenced by MMA and metal containing polymers.

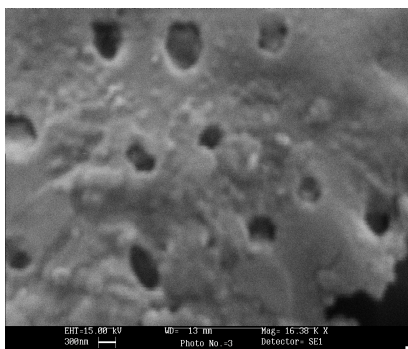


Fig : A

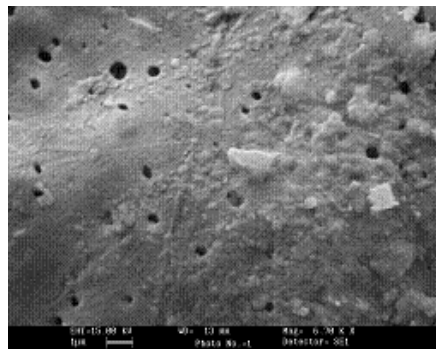


Fig : B

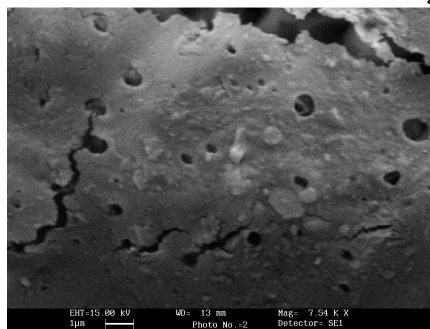


Fig : C

CONCLUSION

The blended polymer film has been successfully prepared by *insitu* blending . We improved the properties physical properties of polymer by blending. The new prepared blended polymer was found to be highly resistance to thermal and chemical. The new blended polymer was highly conducting in nature and the conduction mechanism was bipolaron in nature. GPC technique using for molecular weight the average molecular wt. of blended polymer was found between 60,000 to 5,000. SEM analysis shows the similar morphology to PMMA microgram and amorphous morphology. Morphology of polymers was affected by polymerization.

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