



# STUDIES ON PROCESSABLE POLY(ANILINE-CO-ALKOXYANILINE) COPOLYMER

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## Abstract

Aniline has been copolymerized in the presence of substituted aniline as comonomer to prepared conducting copolymer of poly(aniline-co-o-methoxyaniline) type via the chemical oxidation polymerization route. The copolymer, thermal stability and conductivity are slightly less than pure polyaniline but processability has been improved significantly. Conduction mechanism has been found to be 3D-VRH in case of pure HCl-doped polyaniline and 1D-VRH for copolymer. The room temperature conductivities of doped polyaniline and poly(aniline-co-o-methoxyaniline) are found to be  $6.55 \times 10^{-2}$  and  $2.23 \times 10^{-4}$  S  $\text{Cm}^{-1}$  respectively.

**Keywords:** Polyaniline, Copolymer, Conductivity, TGA, SEM.

## 1. Introduction

In the recent years, conductive polymers have received considerable attention worldwide due to their novel electronic and electrical properties. These polymers have diverse applications ranging from energy storage, sensors, anticorrosive materials, electromagnetic interference shielding, electrostatics charge dissipation, organic light emitting diodes, plastic solar cells[1] and supporting material for catalysis[2]. However, among other conducting polymers, polyaniline (PANI) has been extensively studied not only because its electronics conductivity can easily be tuned by adjusting the oxidation state and degree of doping of the backbone as but also due to its environmental stability as well as economic feasibility. Polyaniline is a promising material for various techno-commercial applications and hence the electrical properties, thermal and environmental stability of PANI is

highly dependent on the nature and the size of its dopant.

The basic chain structure in PANI exists in three insulating states, Leucomeraldine base (LB) Emeraldine base (EB) and Pernigraniline base. The general formula of PANI is  $[(-\text{B}-\text{NH}-\text{B}-\text{NH}-)_Y (\text{B}-\text{N}=\text{Q}=\text{N})_{1-Y}]_X$  in which B and Q denote the  $\text{C}_6\text{H}_4$  rings in the benzenoid and quinoid form respectively. The main issue with PANI is the processing difficulties due to its infusibility and relative insolubility in common solvent. It can be made processable/soluble either by polymerizing functionalised anilines[3] or by copolymerizing aniline with substituted monomers[4-5].

In the present study, the copolymerization of aniline in presence of o-methoxyaniline as comonomer to prepare conducting copolymer of poly(aniline-co-o-methoxyaniline) type via the chemical oxidative polymerization route has been reported. The copolymer was characterized by the various techniques like TGA, UV-Visible spectroscopy and FTIR and their electronic conductivity has been measured by two-probe technique, where resistivity and conductivity varies with temperature.

## 2. Polymerization

The doped polyaniline substituted polyaniline and their processable copolymer was chemically prepared by free radical oxidative polymerization route. The concentration of both of aniline and substituted aniline was 0.1M and that of HCl was 1.0 M for the copolymer, aniline and substituted aniline were mixed in the mole ratio 90 : 10 polymerization was initiated by the drop wise addition of ammonium peroxodisulphate 0.1M ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in 100 ml  $\text{H}_2\text{O}$ ). The polymerization was carried out at a temperature of 0-4<sup>0</sup>C and

over a period of 4-6 hrs. Then the doped polymer powder was obtained by the process of precipitation, filtration, rinsing and drying, successively. The above synthesized powder was treated with 0.1M aqueous ammonia and stirred for 2 hrs to obtain their base (undoped) forms.

### 3. Measurements

FTIR spectra were recorded on Shimadzu FTIR-8101A spectrophotometer. UV-Visible spectra were recorded on Shimadzu UV-1601. Temperature dependent DC conductivity measurements were carried out with the samples in the temperature range from 30 to 140°C. The resistance was measured on DC resistance bridge LCR meter 923. The conductivity value was calculated from the measured resistance and sample dimensions. TGA was recorded on TGA/SDTA851 Mettler Toledo in the inert atmosphere of nitrogen with heating rate of 15°C/min. Micromorphology was observed using SEM (S250MKIII, Cambridge Stareoscan).

## 4. Results and Discussion

### Polymerization mechanism

The Polymerization of aniline and copolymer proceeds via a typical free radical oxidative polymerization route. The main steps are involved in the process are :

#### Initiation

Initiation was effected by  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (APS), which generates the free radicals. These under the proper pH conditions react with aniline monomer to form radical cations. However, the radical cations are resonance stabilized and can be represented by various canonical forms[6].

#### Propagation

Propagation step involves the addition of radical cations to oligomeric species to form polymeric chains. Each radical cation has two active sites that may be attributed to the increased electron density at ortho and para positions of benzene ring. However, coupling of radicals depends upon several factors including reaction medium, temperature, pH and presence of bulky substituents. Therefore, due to the steric hindrance offered by the  $-\text{NH}_2$  group, ortho coupling has almost been excluded leading to the formation of para product. However some ortho coupling[7] also occurs leading to the formation of corrupted polymer.

Chain growth continued till it is arrested either by chain transfer or by coupling of radicals. Low temperature favours the formation of long chains (high molecular weights) due to the retardation of the rate of termination and chain transfer reactions.

### Termination

Termination occurs due to the exclusion of radicals either due to coupling or by disproportionation reaction.

The copolymerization is a powerful method to improve processability of conducting polymers. In general solubility of substituted polyanilines in organic solvents is significantly higher than pure polyaniline. However, their thermal stability and electronic conductivities are substantially lower than doped polyaniline. In order to maintain balance between conductivity, stability and processability copolymerization has been done. However, the relative proportions of aniline and substituted aniline in the copolymers determine exact properties.

### FTIR Spectra

The FTIR spectra of copolymer was obtained. The vibrational peak at  $1587\text{ cm}^{-1}$  assigned to the stretch of the quinoid ring and a peak at  $1499\text{ cm}^{-1}$  assigned to the stretch of the benzenoid ring. The stretching peak of N-H appeared in the range  $3500\text{--}3100\text{ cm}^{-1}$ . In the spectra of the salt form copolymer, absorption peak at  $1120\text{ cm}^{-1}$  and  $1260\text{ cm}^{-1}$ , indicates the existence of the methoxy group on the benzene ring.

### UV- Visible absorption spectra

The absorption band of copolymer was recorded in NMP DMF and DMSO solvents. There are two peaks in the UV –Visible range one around 328 nm is due to  $\pi\text{--}\pi^*$  transition (band gap) and is directly related to the extent of conjugation. The other peak 616 nm is due to the molecular excitation associated with the quinone-diimine structure[8], i.e transition between HOMO orbitals of benzenoid rings and LUMO orbitals of the quinoid rings. The UV- visible data reveals that  $\pi\text{--}\pi^*$  band in copolymer shifts to the lower wavelength ( hypsochromic shift) which can be attributed to the addition of more side groups which alters the torsional angle and leads to the lower conjugation lengths. The degree of hypsochromic shift is directly related to the size of the substituent.

**Conductivity**

The temperature dependence of electrical conductivity of copolymer was estimated in the range of applicability of Arrhenius type equation. The measured valued was plotted semilogarithmically as a function of reciprocal of temperature (Fig.1).The conductivity increases exponentially with temperature.Also tried to fit the appropriate model for the variation of conductivity of material with temperature. For the above model considered that sample follow the VRH model. In the VRH regime, temperature dependence of conductivity ( $\sigma$ ) follow the generalized relation.

$$\sigma = \sigma_0 [\exp^{-(T_0/T)^{1/r}}]$$

Where  $T_0$  is the Mott characteristics temperature and is a measure of the hopping barrier. The  $\sigma_0$  is the conductivity at infinite temperature. Their values are determined by density of states, localization length and average hopping distance. The value of  $r$  is related to the dimensionality ( $d$ ) of the system

as  $r = (d+1)$ . For the one, two and three-dimensional systems, $d$  is equal to the 1,2 and 3 respectively and corresponding values of  $r$  are 2,3 and 4 respectively.The temperature dependence of electrical conductivity (Fig. (b) )for copolymer, which suggests that the charge conduction is 1D-VRH between nearest neighbouring chains[9].In case of HCl doped polyaniline $Cl^{-1}$  ions are small and the interchain separation is small,resulting in appreciable coupling interaction between the chains. Thus, charge carriers could easily hop from one chain to other to give of 3D-VRH conduction[10].However in the case of copolymer although the charge carriers hop between granular particles as 3D-VRH but interchain hopping has been strongly inhibited leading to 1D-VRH.

The conductivity of copolymer increased with increase in temperature. The conductivity, activation energy, band gap and slope of PANI, PoMANI and PANI-co-PoMANI are reported in Table 1.

Table 1. Conductivity, activation energy, band gap and slope for PANI, PoMANI and PANI-co-PoMANI

Polymer/Copolymer	Conductivity	Activation energy	Band gap	Slope
PANI	$6.55 \times 10^{-2}$	0.047	0.1017	0.2562
PoMANI	$4.10 \times 10^{-4}$	0.120	0.2073	0.5218
PANI-co-PoMANI	$2.23 \times 10^{-2}$	0.130	0.2185	0.5500

Conductivity data clearly shows that the copolymer is less conducting relative to the polyaniline. The conductivity decreases both due to decrease in conjugation length as well as less doping level achieved.

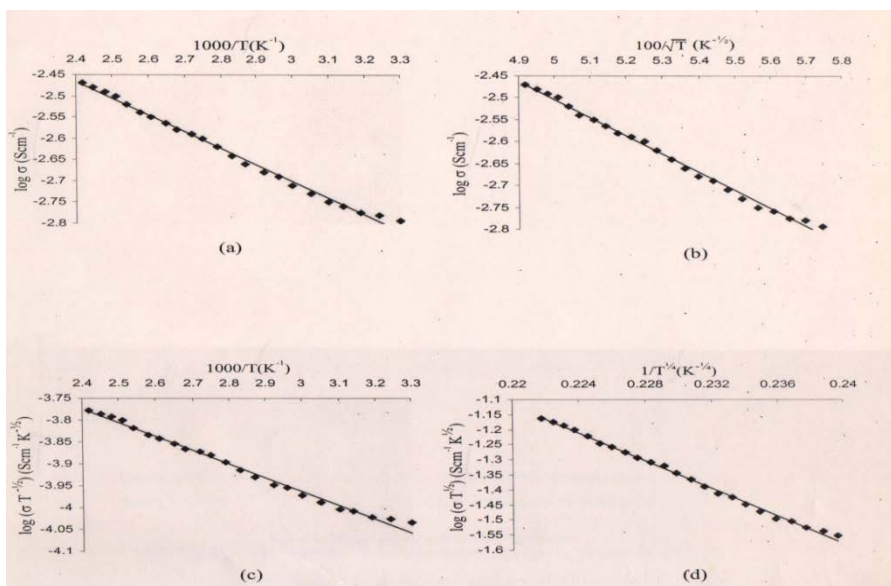


Fig.1 Electrical conductivity plots of poly(aniline-co-o-methoxyaniline)

### Thermogravimetric analysis

Figure 2 shows the thermogravimetric analysis (TGA) of copolymer. Thermogram clearly suggest that the thermal stability of copolymer is slightly less than pure polyaniline. This may be attributed to the decreased chain length due to presence of bulky alkoxyaniline moieties in the backbone. The thermal stability of copolymer depends upon the actual amount of alkoxyaniline incorporated into the polymeric backbone, which in turn governed by

the competition between reactivity and steric-hindrance.

The thermogram of copolymer represents weight loss process in three stages. In first stage, weight loss is due to the loss of moisture (absorbed water), the second stage of weight loss is due to loss of some low molecular mass and third stage of weight loss may be due to the degradation of the polymeric backbone.

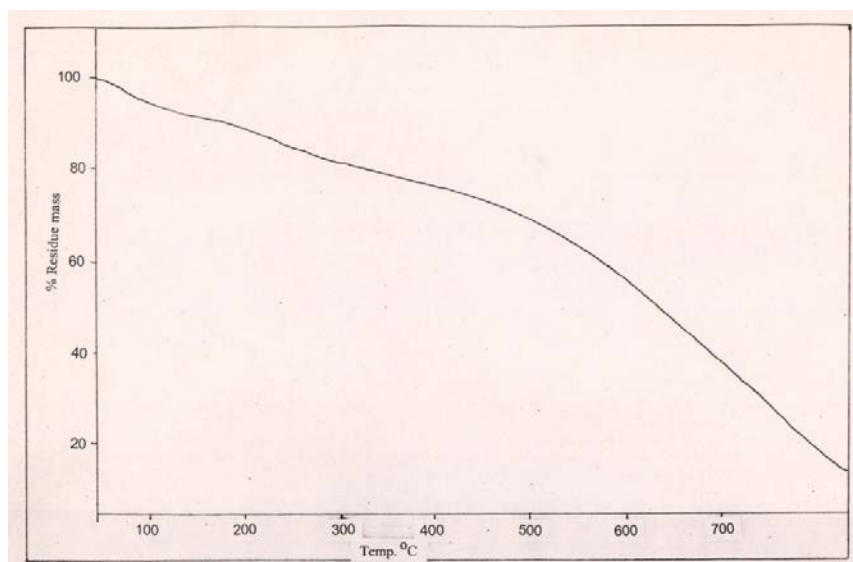
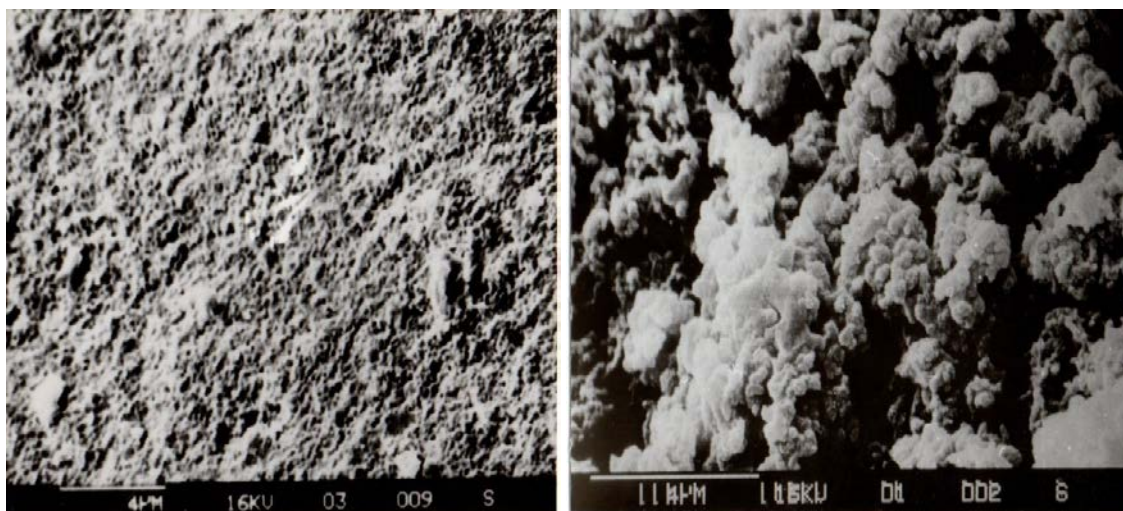


Fig.2 TGA graph of poly(aniline-co-o-methoxyaniline)

### SEM Studies

Figure 3 shows the SEM micrographs of the doped polyaniline and poly(aniline-co-o-methoxyaniline) respectively. Fig. 3 (a) micrograph exhibits continuous compact grain

like morphology. Fig. 3 (b) shows significant phase separation i.e. the micrograph demonstrates the difference between two phases.



(a)

(b)

Fig.3 SEM micrographs of (a) polyaniline (b) poly(aniline-co-o-methoxyaniline)

## 5. Conclusions

Conducting copolymer of poly(aniline-co-alkoxyaniline) type have been prepared. Their conductivity and thermal stability were found to be comparable to pure HCl-doped polyaniline. Conductivity plots suggest that 3D-VRH is proper model for HCl-doped polyaniline where as for copolymer 1D-VRH seems to be apt choice.

## References

- [1]. Fried, J. R., 2003, Polymer Science and Technology, New Delhi, Prentice Hall, 461.
- [2]. Rambu, G .A., Jackson, C.L. Scott,K., 2006, J. Optoelectron. Adv. Mater., 8, 611.
- [3]. Leclere, M. J. 1990, Electroanal Chem., 296, 93.
- [4]. Dhawan, S.K., Trivedi, D.C. 1991, Electrochemical Society Extended Abstract 682.
- [5]. Savitha, P. Rao, S.P. Sathyanarayan, D.N .2005 Polym. Int. 54, 1243.
- [6]. Genies, E.M., Boyle, A. Lapkowski,M. Tsintavis, C. 1990, Synth.Met.36, 139.
- [7]. Yu,L.T.,Borredon, M.S., Josefowicz,M., Belorgey,G. Buvet R,1987,J.Polym.Sci., 10,2931.
- [8]. Mattoso,L.H.C.,Faria,R.M., Masters,J.G., MacDiarmid,A.G.2004,Synth.Met.,1,146.
- [9].Wang,Z. Li, C.Scherr,E.M. MacDiarmid, A.G. Epstein,A.J. 1991,Phys.Rev.Lett.66,1745.
- [10].Li, J. Fang, K. Hong,Q .Li, S. W.Mao, W.2004, Synth.Met., 142,107.