Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2012, 4(4):2081-2086

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Poly(aniline-co-*o*-anisidine): A conducting copolymer as a anion-exchange resin

Arun D Borkar

Department of Chemistry, Nabira Mahavidyalaya, Katol, Nagpur, India

---

ABSTRACT

Chemically oxidative polymerization of aniline and o-anisidine with 5 molar rations was performed using ammonium persulphate as an oxidant in HCl medium at 0-4 ^{0}C.It was observed that the copolymers were not regularly dependent on the monomer ration for yield and intrinsic viscosity.The resulting copolymers were characterized by Fourier transform IR Spectroscopy,^{1}H NMR Spectroscopy and electrical conductivity.The results showed that the actual content of the o-anisidine unit in the copolymers was much higher than the feed content of the o-anisidine unit. Given the same reaction conditions, o-anisidine showed a larger tendency toward homopolymerization rather than toward copolymerization with aniline. The electrical conductivity of the copolymers is strongly depends on the amount of aniline incorporated and it decreases with increasing the o-anisidine content in copolymer which may lowers the structural regularity of copolymer. It is suggested from the temperature dependence of electrical conductivity that the electrical conduction mechanism of copolymer is polaron hopping conduction similar to that of homopolymers. The application of copolymer as anion exchange resin and acid-base indicator are presented.

Keywords: Conducting polymers; copolymers; polyaniline; polyaniline derivatives; poly(aniline-co-o-anisidine).

INTRODUCTION

Polyanilines (PA)s have considerable significance because of their electrical and optical properties and many potential applications such as energy storage[1], electromagnetic interference shielding[2], electrochromic devices[3,4], microelectronics device[5] and sensor[6] etc. For many of these applications the solubility and processability of polyanilines are among the most important properties. The unsubstituted PA is insoluble in common organic solvents due to the stiffness of their backbone which results from its delocalized electronic structure. Consequently, their post-synthesis processability is quite difficult. Various techniques such as the modification of the monomer structure[7], utilizing functionalized acid[8], formation of blend or composite[9] and copolymerization[10] have been introduced to enhance the processability. The copolymerization is one of the simplest method for providing the processability of conducting polymer.

The conducting form of Poly(o-anisidine) PoA emeraldine salt form obtained from oxidative polymerization of o-anisidine shows good solubility in number of organic solvents. However PoA are less conducting than PA[11]. The conductivity of PoA is of the order of 10^{-4} S/cm. The steric contrains imposed by the methoxy group on PoA disrupt the coplanarity of the polymer chain as well as it increases the interchain distance. On copolymerization of aniline with o-anisidine there is a formation of material having properties intermediate to their homopolymers and more processable copolymers. In this study the homopolymers PA, PoA and series of copolymers Poly(aniline-co-o-anisidine), PA-co-PoA are prepared by chemical oxidative copolymerization method. The homopolymers and copolymers are characterized for structural information (figure 1) by IR, NMR, UV-Visible spectroscopy, solubility and the influence of copolymer composition on the properties of the copolymer is discussed.

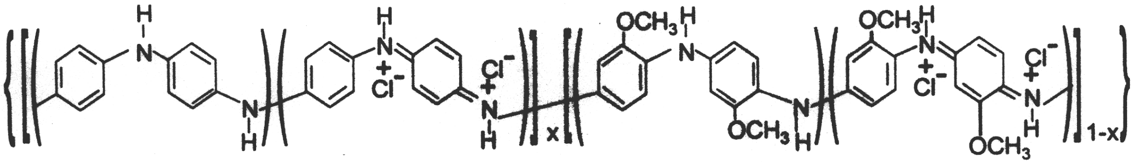


Fig. 1 Tentative structure for copolymer

EXPERIMENTAL SECTION

Reagents : Aniline and o-anisidine were purified by distillation. Ammonium peroxodisulphate and all other solvents were used as purchased.

Synthesis: Homopolymers PA, PoA and (PA-co-PoA)s were chemically synthesized using ammonium peroxodisulphate as initiator in an aqueous acid medium at 0-4^{0}C in a similar manner to that previously described[12-17]. A typical procedure for preparation of the copolymer is as follows.

Monomers, aniline and o-anisidine (0.4 M) were dissolved in 200 ml of 1 M HCl aqueous solution and cooled to 0-4^{0}C. The oxidant ammonium peroxodisulphate (0.4 M) was dissolved separately in 200 ml of 1 M HCl and cooled to 0-4^{O}C. Then the oxidant solution was added dropwise to the momomer solution for 1 hour with constant stirring in nitrogen atmosphere at 0-4^{0}C. After complete addition of the oxidant stirring was continued for another 7 hours to ensure the completion of the reaction. The greenish black precipitate was obtained the reaction mixture was kept overnight. Then the copolymer precipitate was filtered, washed with distilled water untill the filtrate became colourless and finally with methanol and dried in an air oven at 70^{0}C for 8 hours. Emeraldine bases were prepared by suspending a part of the virgin polymer in 1M NH_4OH solution.

Characterization

The solubility of the polymers in the base form was tested by dissolving each material in N-methyl-2-pyrrolidinone (NMP). The mixture was kept for 24 h at room temperature, afterwhich the solution was filtered through sintered glass crucible (porosity 2 micron). The room temperature solubility was determined. FTIR spectra of the polymeric samples were recorded on 550 Series II, Nicolet, using KBr pellet technique in the range 400 - 4000 cm^{-1} RSIC, Nagpur University, Nagpur. ^{1}H NMR spectra of the polymers were recorded at room temperature on a GEGN 300 MHz NMR spectrometer. DC electrical conductivity of polymer samples were measured by the two probe technique in the temperature range of 298 - 398 K. Dry powdered samples were made in to a pellet under hydraulic press IEBIG and placed between electrodes in a cell. Resistance was measured on a DC resistance bridge LCR Meter 926. The conductivity value was calculated from the measured resistance and sample dimensions.

Measurement of Viscosity

The intrinsic viscosity [η] of the base form copolymers of different comonomer composition has been measured in DMF by Tuan-Fouss viscometer at 25^{0}C. From the time of flow of solutions and solvent, the intrinsic viscosity was determined by graphical extrapolation method proposed by Huggins equation[18]

$$\eta_{sp/c} = [\eta] + k\,[\eta]^2\, c$$

for dilute solution.

Ion-Exchange Studies

The ion-exchange studies of homopolymers and copolymers salt form were carried out using column technique[12]. $NaNO_3$ (1 mol dm^{-3}) solution was passed through a glass column (20 x 1.2 cm i.d.) containing 1.0 gm of dry salt form of polymer. The elution was continued untill the eluated volume was free from Cl^- ($AgNO_3$ test). The eluate was collected at the rate of 0.5 ml/min. The eluate was then titrated with $AgNO_3$ solution (0.02 mol dm^{-3}) using K_2CrO_4 as an indicator. From the titre value and mass of polymer taken (gm) the ion-exchange capacity (millimoles g^{-1}) was calculated as

$$\text{Ion-exchange capacity} = \frac{\text{Molarity of } AgNO_3 \text{ x Equivalence point}}{\text{Mass of polymer taken}}$$

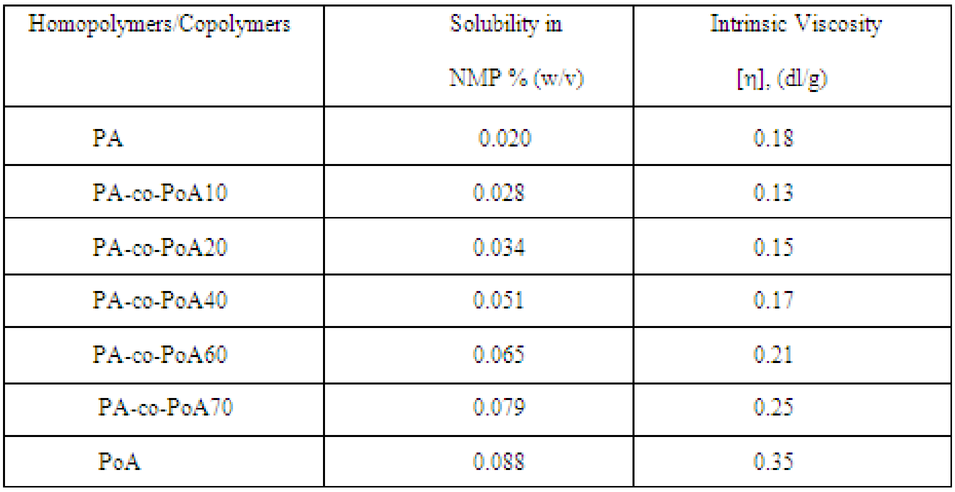
Acid-Base Indicator

20 mg of each salt form of copolymer samples were transfered in 50 ml DMF and stirred for 1 hour. The solution was filtered and filtrate solution was use as an acid/base indicator. 10 ml of 0.1 N HCl, H_2SO_4 and HNO_3 were individually transfered to 100 ml conical flask, 2-3 drops of the above copolymer solution were added to each conical flask, redish-brown colour was obtained and individually the mixture was titrated with 0.1 N NaOH until a sharp yellow colour appeared. The titre values are in full agreement with potentiometric end points.

RESULTS AND DISCUSSION

PA, PoA and its copolymers were obtained as finely powdered materials. The viscosity data (Table 1) qualitatively suggests that the viscosity of copolymer (PA-co-PoA 40, $[\eta] = 0.17$ dl/g, at 25 ^{0}C) is low as compared to PoA ($[\eta] = 0.35$ dl/g, at 25 ^{0}C). The intrinsic viscosity of PoA ($[\eta] = 0.35$ dl/g, at 25 ^{0}C) is about two times higher than PA ($[\eta] = 0.18$ dl/g, at 25 ^{0}C).

Table 1 Solubility and Intrinsic Viscosity of Homopolymers and Copolymers



Homopolymers/Copolymers	Solubility in NMP % (w/v)	Intrinsic Viscosity [η], (dl/g)
PA	0.020	0.18
PA-co-PoA10	0.028	0.13
PA-co-PoA20	0.034	0.15
PA-co-PoA40	0.051	0.17
PA-co-PoA60	0.065	0.21
PA-co-PoA70	0.079	0.25
PoA	0.088	0.35

The higher viscosity of PoA is may be due to the presence of the o-anisidine unit in the copolymer chain which might be in the coiled form showing higher viscosity on dissolution. On increasing the o-anisidine unit in copolymer the solution viscosity of copolymers increases. Fig. 2 shows IR absorption band of PA-co-PoA 40.

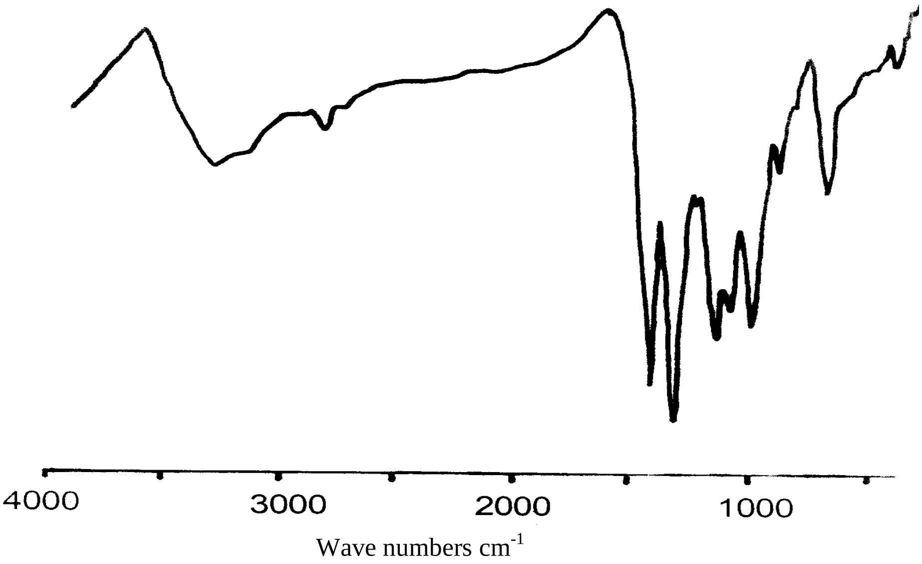


Figure 2 FTIR spectra of PA-co-PoA 40

The broad absorption band between 3500 to 3100 cm^{-1} is attributed to N-H stretching. The bands at 1587 and 1499 are assigned to imine nitrogen and benzoid ring stretching. In the spectra of copolymer fraction, there appears an absorption band at 1260 cm^{-1} and 1120 cm^{-1}, indicating the existence of methoxy group on benzene ring. The copolymer fraction, also shows new absorption band that appears at 1024 cm^{-1}, which increases in intensity with the increase of o-anisidine in the copolymer. This indicates the coexistence of o-anisidine and aniline unit in the copolymer Fig. 3 shows ^{1}H NMR spectra of PA-co-PoA 40.

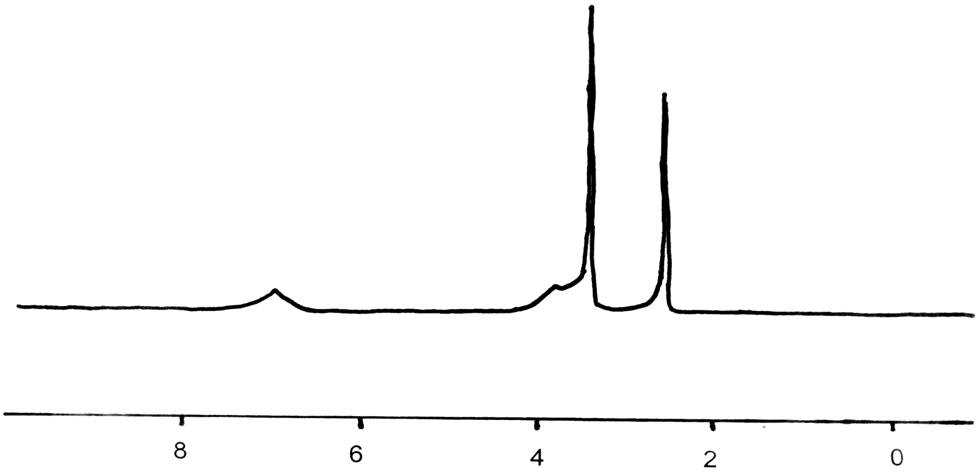
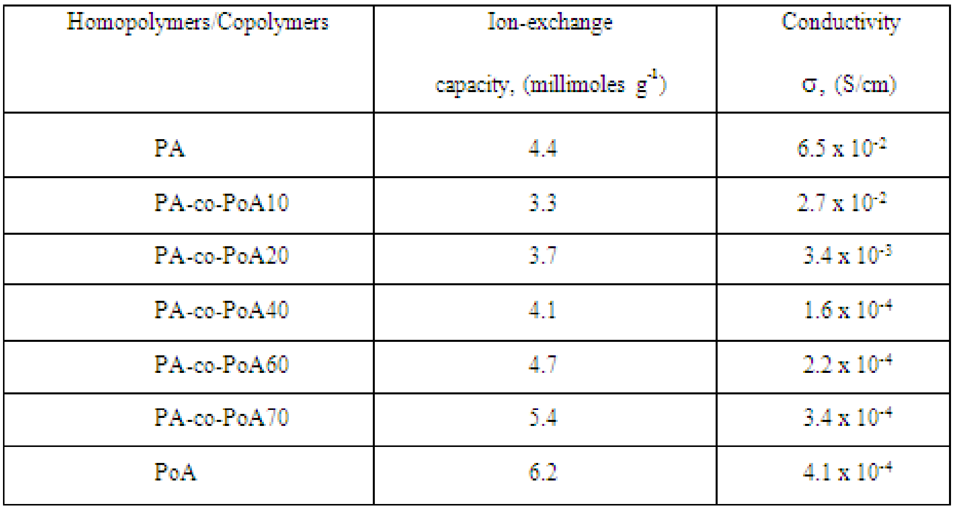


Figure 3 ^{1}H NMR spectra of PA-co-PoA 40

The electrical conductivity of the copolymer salts are measured and compared to that of homopolymer PA and PoA, the results are summarized in Table 2.

Table 2 Ion-exchange capacity and Conductivity of Homopolymers and Copolymers



Homopolymers/Copolymers	Ion-exchange capacity, (millimoles g^{-1})	Conductivity σ, (S/cm)
PA	4.4	6.5×10^{-2}
PA-co-PoA10	3.3	2.7×10^{-2}
PA-co-PoA20	3.7	3.4×10^{-3}
PA-co-PoA40	4.1	1.6×10^{-4}
PA-co-PoA60	4.7	2.2×10^{-4}
PA-co-PoA70	5.4	3.4×10^{-4}
PoA	6.2	4.1×10^{-4}

The PA hydrocloride salt shows conductivity of the order of 6.5×10^{-2} S/cm and about 4.1×10^{-4} S/cm for PoA while copolymer shows lower conductivity than PA, because of the addition of substituent (-OCH_3) group in the copolymer chain. The lower electrical conductivity of copolymer is suggested to arise from the steric effect of methoxy group that could induce additional deformation along the polymer backbone and reduce the mobility of the charge carrier along the main chain. In addition, methoxy group will increase the interchain distance which lowers the structural regularity which reduces interchain interaction and as a result lower electrical conductivity is observed in copolymers. Similar results have been reported by Chai etal[19]. The temperature dependence of electrical conductivity data was fitted to an Arrhenius equation. The conductivity is found to increase with temperature shows the semiconducting nature of the material. From temperature dependence it is suggested that the conduction mechanism in copolymers is possibly a polaron hopping conduction similar to homopolymers PA and PoA[20].

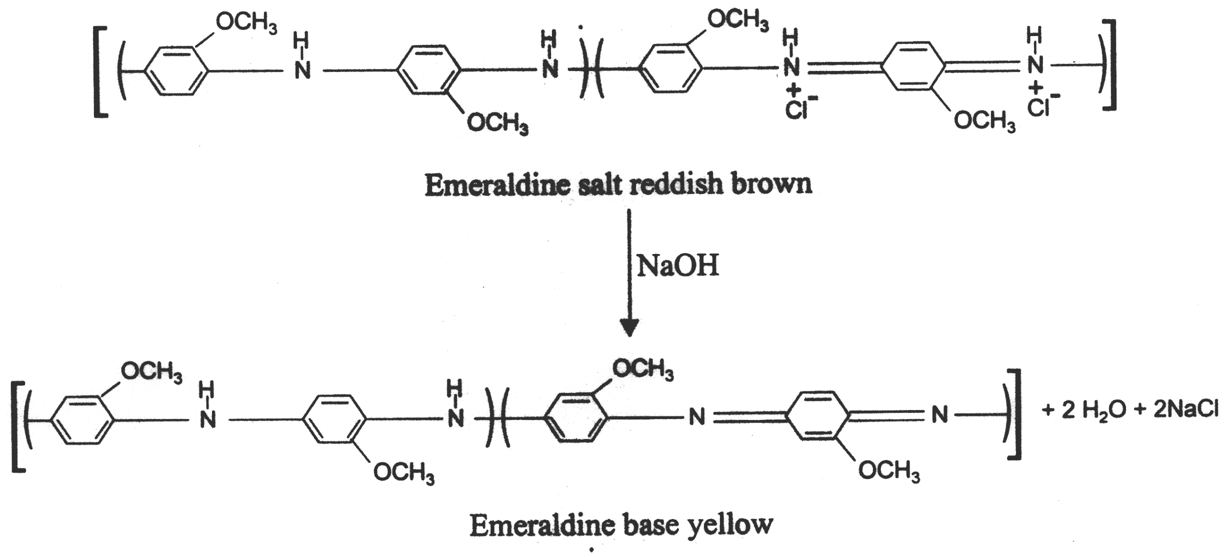


Fig. 4 Conversion of salt form to base form in acid-base titration

Applications : PoA has the highest ion-exchange capacity compared with other copolymers (Table 2). The ion-exchange capacity of copolymers increases with increase of o-anisidine in copolymer chain. The ion-exchange capacity of the copolymers are comparable with the commercial ion-exchanger[21] like Amerlite IR-4B (OH^- form)

4.2 - 9.1, De-Acidite FF (Cl^- form) 4.0, Duolite A^- 113 (Cl^- form) 4.0 millimoles per gram. Change in colour upon addition/elimination of protons is the basis for the use of homopolymers and copolymers as an acid/base indicator. At the end point emeraldine salt form of polymer is converted into emeraldine base form as shown in fig. 4

CONCLUSION

A series of poly(aniline-co-o-anisidine)s were synthesized by chemical oxidative copolymerization. Copolymers has little lower electrical conductivity and good solubility characteristics due to the existence of the methoxy side group in the main chain of the copolymers which results from the breaking of regular chain structure containing o-anisidine repeat unit. The electrical conductivity of the copolymer can be modified by varying its composition. Conduction mechanism in copolymer is of polaron type hopping conduction as in case of PA and PoA. The copolymers can be used as an anion-exchange resin and acid-base indicator which will give additional importance to the exploration of new properties of chemically synthesized copolymers.

Acknowledgements
Thanks are due to the Director RSIC, Nagpur and CDRI, Lucknow for the FTIR spectra and NMR spectra, respectively.ADB wishes to thanks the UGC, Western Region, Pune for funding a Minor Research Project F No.47-115/06.

REFERENCES

[1] F Trinidal; MC Montemayor; E Falas. *J. Electrochem. Soc.,**1991***, 138,3186.
[2] DC Trivedi; SKDhawan. *Mater. J. Chem.*, **1992**, 2, 1092.
[3] T Kobayashi; H Yoneyama ; H Tamura. *J. Electroanal. Chem.*, **1984**, 161, 419.
[4] EM Genies; M Lipkowsski; C Santier; E Viel. *Synth. Met.*, **1987**, 18, 631.
[5] EW Paul; AJ Ricco; MS Wrighton. *Phys. J. Chem.*, **1985**, 89, 1441.
[6] PN Bartlett; BMA Patricia; KLC Sin. *Sensor and Acutators* **1989**, 19, 125.
[7] M Sato; S Tanaka ; K Kaeriyama. *J. Chem. Soc. Chem. Commun.*, **1986**,873.
[8] Y Cao; P Smith;AJ Hegger. *Synth. Met.*, **1993**,55, 3514.
[9] Y Lee; D Shin; J Cho ; YH Park; Y Son; DH Baik. *J. App. Poly. Sci.,***1998**, 69, 2941.
[10] Y Siyu; NT Do; LH Dao; AK Vijh. *Synth. Met.*, **1997**,65, 88.
[11] JR Macinnes; BL Funt. *Synth. Met,.* **1988**, 25,235.
[12] AA Syed; MK Dinesan. *Ind. Analyst.*, **1992**,117, 16.
[13] MC Gupta ;SS Umare. *Macromolecules.,* **1992**, 25,135.
[14] SG Ghosh; V Kalapagam. *Synth.Met.*, **1989** 33,11.
[15] AD Borkar; MC Gupta;SS Umare. *Poly. Plast. Technol. Eng.,* **2001**, 40(2), 225.
[16] AD Borkar; SS Umare. *Int. J. Chem. Sci.,* **2010**, 8(2), 1110.
[17] AD Borkar; SS Umare; PB Heda. *Mat. Res .Innova.,* **2011**, 15(2), 135.
[18] ML Huggins. *J. Am. Chem. Soc.,* **1942** 64, 2716.
[19] HJ Chai;JW Kim; K To. *Polymer.,* **1999**,40, 2163.
[20] SS Umare; MM Huque;MC Gupta; SG Viswanath. *Macro. Report.,**1995***, 32A (supp. 3), 281.
[21] SS Dara. A Textbook of Engineering Chemistry, S Chand Publication,New Delhi, **1999,** 153.