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CHEMICAL POLYMERIZATION OF SUBSTITUTED DERIVATIVES OF ANILINE IN OXALIC ACID MEDIUM

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ABSTRACT

The Chemical synthesis of substituted derivatives of polyaniline in oxalic acid media in which an H of the aromatic ring has been replaced by an methyl and methoxy group is reported. The synthesis of substituted derivative of polaniline (PANI) such as poly (o-methoxyaniline) (POMA), poly (2,5dimethoxyaniline) (PDMA), poly (o-methylaniline) (PMLA) and poly (2,5dimethylaniline) (PDMLA) were obtained from an aqueous oxalic acid solution under chemical oxidation using ammonium per sulphate as an oxidizing agent. The resulted powder of substituted derivatives of polyaniline were characterized by UV-visible absorption spectroscopy and Fourier Transform Infra Red (FTIR) spectroscopy. It is observed that the oxidation state of polyaniline can vary depending on the group substituted in which H of the aromatic ring. The FTIR Spectrum reveals the stretching and bending vibration which clearly confirm the formation of substituted derivative of aniline.

Key words: Polyaniline, Substituted derivatives.

INTRODUCTION

The field of conducting polymers has been flourishing rapidly day by day and these materials are becoming indispensable for this century. The interest has led to proving their potentialities a large number of applications. Polyaniline, one of the most promising conducting polymers, is inherently brittle and poor in processibility due to its insolubility in common organic solvents. This problem has been overcome to some extent by using substituted derivatives of anilines[1-3]. The polymers of the substituted aniline exhibit greater solubility but the conductivity is found to be slightly lower. However, efforts have been made to improve the processibility of these polymers. In recent years, by using a functionalized protonic acid, which makes polyaniline conducting as well as renders the resulting polyaniline complex soluble in organic solvents[4]. A large number of papers are available reporting the studies on substituted derivatives of polyaniline[1-3]. This paper describes a novel polymerization process for the direct synthesis of the EB phase of the polyaniline and its substituted derivatives without the need of post doping treatment. In the present work, we report the synthesis and characterization of oxalic acid doped polyaniline and their derivatives. The results are explained on comparative basis. Effect of methyl and methoxy substituent present at ortho position in polyaniline on the polymer properties has been discussed in detail. The resulted polymer powder was characterized by Uv-visible absorbance spectroscopy and Fourier Transform Infra red spectroscopy.

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The disubstituted derivatives of conjugated polymers are also potential candidates in many technological applications. Considerable research efforts are currently being devoted to chemical studies on conducting polymers. Among conducting polymers family, polyaniline and its substituted derivative have received great attention owing to its easy of synthesis.

EXPERIMENTAL

Chemical synthesis of polyaniline and its substituted derivatives

In this work, the polyaniline powder were synthesized by chemical polymerization method. The chemical polymerization synthesis set up is developed in the laboratory. The aqueous solution of oxalic acid was used as a protonic acid medium and monomer aniline with ammonium per sulphate was used as an oxidizing agent.

Freshly distilled aniline monomer is used for synthesis of polyaniline. For the chemical synthesis of polyaniline two solutions were prepared with appropriate volume concentration. In first solution, 0.3 M oxalic acid and 0.1 M aniline are dissolved in distilled water and second one is, the aqueous solution of 0.1 M ammonium persulphate. The monomer solution is cooled down in an ice bath upto 0 to 5°C under constant stirring and this was maintained for 2 hours. As the temperature reaches 5°C slowly add the oxidant solution to the monomer solution. Then this polymerization process was carried out upto 20 hrs. This powder was dried under dynamic vacuum for constant weight.

The same procedure was used for the synthesis of POMA, PDMA, PMLA and PDMLA. And these resulted polymer powder was characterized by UV- visible absorbance and FTIR spectroscopy.

RESULTS AND DISCUSSION

The PANI, POMA, PDMA, PMLA and PDMLA were synthesized by chemical oxidative polymerization method. These resulted polymer powder was characterized by UV- visible absorbance and FTIR spectroscopy

The optical absorption spectrum recorded for the PANI and substituted derivative containing methoxy group such as POMA and PDMA synthesized from oxalic acid by using ammonium per sulphate as an oxidizing agents is shown in Fig. 1.

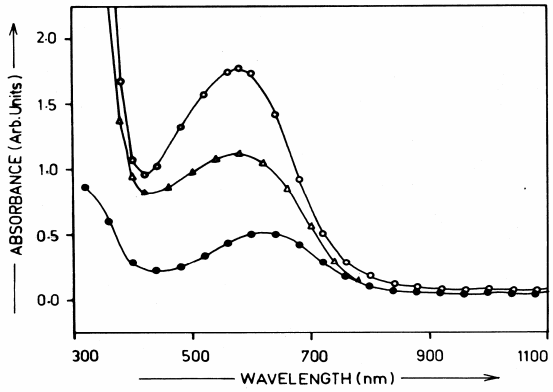

Fig. 1: The optical absorption spectrum recorded for the (a) polyaniline (b) poly (o-methoxyaniline) and (c) poly (2,5-dimethoxyaniline) powder in DMSO solution

The spectrum clearly observed a broad peak at ~ 600 nm for polyaniline. This peak is attributed to the formation of emeraldine base (EB) form of polyaniline. The EB is the fully oxidized form of polyaniline and is insulating in nature. However, in case of POMA and PDMA shows a broad peak at ~ 540 nm. This peak is attributed to the formation of pernigraniline base (PB) form of POMA and PDMA, and is also insulating in nature.

From the Fig 1, it is clearly observed that the methoxy group is substituted at benzene ring, favours the formation of PB form of polymer.

The Fig. 2 shows the optical absorption spectrum recorded for the PANI and the substituted derivative containing methyl group such as PMLA and PDMLA synthesized from oxalic acid by using ammonium per sulphate as an oxidizing agents. The spectrum clearly shows a broad peak at ~ 600 nm for all PANI, PMLA and PDMLA powder. This peak is attributed to the exclusively formation of emeraldine base (EB) form of polymer and is insulating in nature.

From the Fig 2, it is clearly observed that the methyl group is substituted at benzene ring, favors the formation of EB form of polymer.

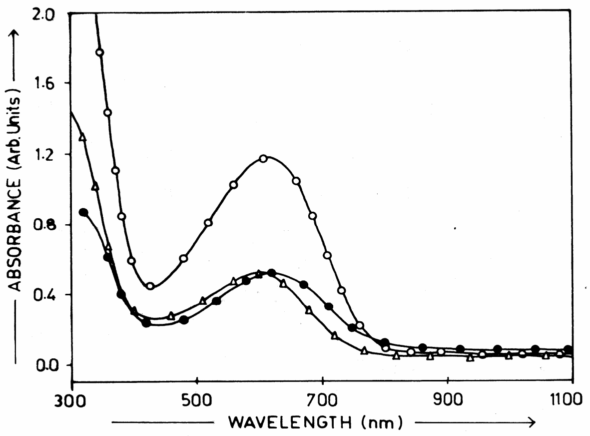

Fig. 2: The optical absorption spectrum recorded for the (a) polyaniline (b) poly (o-methylaniline) and (c) poly(2,5 dimethylaniline) powder in DMSO solution

When the chemical synthesis of POMA was carried out in oxalic acid medium, the FTIR spectrum is shown in Fig. 3. It shows the presence of strong IR bands, These bands are attributed to the formation of POMA powder. This spectrum exhibits the following spectral features[8,9]- (i) The region between 3500-3100 cm^{-1} is known as the region of N-H stretching vibrations. (ii) The band at ~ 1587 cm^{-1} is an indicative of stretching vibrations in quinoid (Q) rings (iii) The band ~ 1498 cm^{-1} represents the stretching vibrations of the benzoid (B) rings. The general features of this spectrum is similar to the spectrum of PB for POA as reported by Mattoso et al.[5] (iv) The bands at 1257 and 1655 cm^{-1} are attributed to the presence of carboxyl groups of oxalic acid in the POA. (v) The bands at 1119, 1022 and 798 cm^{-1} are attributed to the 1-4 substitution on the benzene ring. (vi) The band at ~ 1392 cm^{-1} is due to the stretching of N-N bands. (vii) In ES samples, the band at ~ 1205 cm^{-1} is considered as a measure of the degree of delocalization of electrons on POA. It is referred to as the electronic like band and thus, it is characteristic peak of POA conductivity. The absence of this band suggests the ES phase of POA in the powder is absent along with the PB.

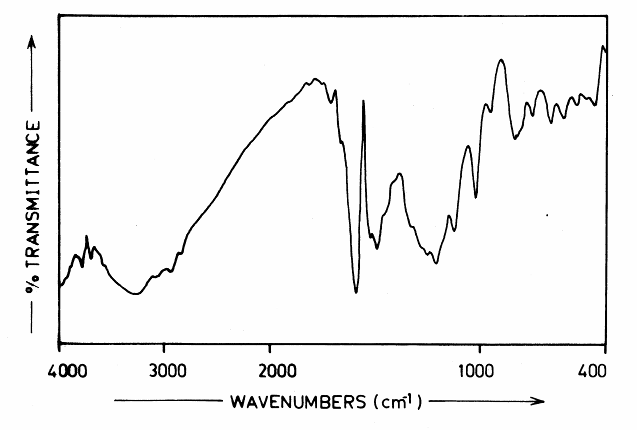

Fig. 3: FTIR spectra of the chemically synthesized of poly (o-methoxyaniline) powder from oxalic

When the chemical synthesis of PMLA was carried out in oxalic acid medium, the FTIR spectrum is shown in Fig. 4. It shows the presence of strong IR bands, This spectrum exhibits the following spectral features- (i) The broad band at ~ 3263 cm^{-1} represents the formation of NH bonds due to the protonation of nitrogen. (ii) The band at ~ 3057 cm^{-1} is associated with the C-H stretching due to methylene group. (iii) The observation of the bands at ~ 1679 and 1240 cm^{-1} suggests the presence of carboxyl groups of the oxalic acid. (iv) The band at ~ 1591 cm^{-1} is an indicative of stretching vibrations in quinoid (Q) rings (v) The band ~ 1492 cm^{-1} represents the stretching vibrations of the benzoid (B) rings (vi) The presence of the bands at 1110, 1010 and 813 cm^{-1} reveal the 1-4 substitution on the benzene ring. (vii) The observation of the bands around 943 cm^{-1} and 800-700 cm^{-1} reveals the occurrence of the 1,2- and 1,3-substitutions.

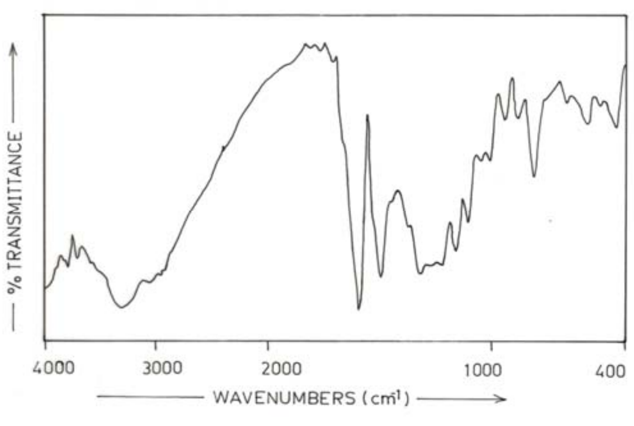

Fig. 4: FTIR spectra of the chemically synthesized of poly (o-methylaniline) powder

CONCLUSION

Successfully synthesize of POMA, PMLA, PDMA and PDMLA from oxalic acid by using ammonium per sulphate as a oxidizing agents UV-visible absorption spectroscopy study clearly observed that the methyl group favors the formation of EB form of polymer And methoxy group favours the formation of PB form of polymer. Fourier Transform Infra red spectrum clearly shows the formation of POMA and PMLA powder from the oxalic acid.

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