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ORGANIC SYNTHESIS AND CHARACTERIZATION OF ELECTRICALLY CONDUCTING POLY (o-TOLUIDINE) DOPED WITH ORGANIC ACID

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Abstract. Poly(*o*-toluidine) doped with acrylic acid and without it was synthesized by using chemical oxidative polymerization technique. With the help of this method the polymer, poly(*o*-toluidine) was synthesized in the form of emeraldine salt. The oxidizing agent used for this method is the ammonium persulphate .The polymer products were characterized by UV-Visible and FTIR spectroscopy. The polymer, poly(*o*-toluidine) doped with acrylic acid was highly soluble in common organic solvents like *m*-cresol, NMP, DMF *etc*. The FTIR studies demonstrate that the acrylic acid doped poly(*o*-toluidine) shows broad and intense band at 3250–3000 cm^{-1} and 1160–1100 cm^{-1} account for the higher degree of doping. These results are well supported by conductivity measurements.

Keywords: poly(*o*-toluidine), acrylic acid, conductivity, solubility, dopant.

1. Introduction

Over last few decades polyaniline and its derivatives like poly(*o*-toluidine) have become the polymer of great scientific and industrial importance as a result of their remarkable properties. These materials have the good environmental stability, high thermal stability, and they are relatively easy in preparation. Their conductivity can be reversibly controlled either electrochemically or chemically [1-4]. Recently the excitement in the conducting polymer research has been a rich opportunity for using structural modification to change their properties for large varieties of technological application.

Obtaining a material which combines the ease of processability from the solution or melt with electrical properties of the metals is the aim of the work on conducting polymers. However, like many other conducting polymers, poly(*o*-toluidine) is insoluble in the common organic solvents. Consequently post synthesis processability is quite difficult. Much work has been done to improve its processability and conductivity. Among various methods of achieving good solubility, the preparation of the polymer from the monomer functionalized with suitable side-chain, *e. g.* alkyl anilines, gives soluble high molar mass polymers; however their conductivities are rather low. A series of substituted polyanilines has been chemically polymerized in this laboratory [5] to obtain a soluble and conductive polymer.

2. Experimental

The polymerization of *o*-toluidine monomer (Qualigen, A.R. grade) was carried out by the oxidative polymerization method [6-8]. All the chemicals used were AR grade and purified by distillation before use. The oxidizing agent used was the ammonium persulphate (Qualigen) and the acid used was tartaric acid (Qualigen).

The oxidizing agent was added drop wise in an acidified solution of the monomer under constant stirring at low temperature between 273–278 K. The acrylic acid doped polymer was synthesized by the addition of 0.2 ml of acrylic acid to the reaction mixture containing *o*-toluidine and tartaric acid prior to the addition of the oxidizing agent. After complete addition of the oxidizing agent the reaction mixture is kept under constant stirring for 24 h. The dark green color precipitate of the polymer was washed with distilled water and isolated by drying in the oven ~ 343–353 K for 48 h.

The UV-Vis spectra of the polymer solution in *m*-cresol and NMP were recorded by using λ-20 double beam spectrophotometer in the range of 300–900 nm.

The IR spectra of the polymer were taken on a Perkins Elmer 1600A FT-IR spectrophotometer between the ranges of 400–4000 cm^{-1}. For recording IR spectra, KBr pellets of the polymer were prepared in the ratio of 150:1 mg. Finally the conductivity of the sample (pellet) was measured with the help of two-probe method.

3. Results and Discussion

3.1. UV-Vis Spectra

The optical properties of conducting polymers are important for the development and understanding of the basic structures of the material. The conjugation in the polymers is implied by their electronic spectra, thus spectroscopy is a powerful probe for characterization of the electronic transitions that occurs in the conducting polymers.

UV-Vis spectra of the polymer doped in the presence of the acrylic acid and that doped with tartaric acid recorded by dissolving these polymers in *m*-cresol and NMP solvent are represented in Fig. 1. The spectral features observed in Fig. 1 reveal the enhanced solubility of the acrylic acid doped polymer which is ~ 80 % soluble, in comparison with the tartaric acid doped polymer, which is ~ 40 % soluble in each solvent. This can be attributed to the presence of a greater number of charges on the polymer chain in the acrylic acid doped polymer leading to a higher degree of solvation of the polymer due to the hydrogen bonding between the solvent and polymer chains [5-8].

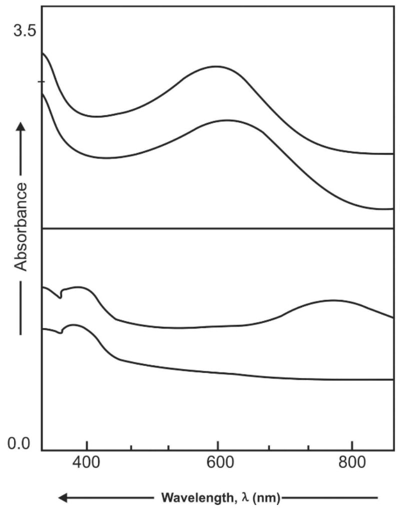

Fig.1. UV-Vis absorption spectra of DL(±) tartaric acid and acrylic acid doped polymer: tartaric acid doped poly(*o*-toluidine) in NMP (a); tartaric acid doped poly(*o*-toluidine) synthesized in acrylic acid medium in NMP (b); tartaric acid doped poly(*o*-toluidine) in *m*-cresol (c) and tartaric acid doped poly(*o*-toluidine) synthesized in acrylic acid medium in *m*-cresol (d)

The optical spectra of the polymers show appreciable changes in *m*-cresol and NMP. In *m*-cresol the polymer exhibits a shoulder peak at 408 nm with an extended free carrier tail characteristic of an extended coil conformation with the increasing absorbance 800–1100 nm. The sharp intense peak at 408 nm can be assigned to the localized polarons which are the characteristics of the protonated poly(*o*-toluidine) together with the extended tail representing the conducting forms of the polymer [5-9]. The intensity of the peak at ~ 408 nm is greater in the acrylic acid doped polymer. This implies that the doping is restored in the *m*-cresol medium apart from the solute-solvent interaction due to its polar nature, which contributes towards the expansion of the coil form of the polymer and hence the solubility. Further extended tail at higher wavelength depicts that m- cresol not only serves as a solvent, but also acts as an efficient secondary dopant [6-9].

In the presence of NMP as a solvent the extended tail at higher wavelength disappears. While a sharp peak observed at ~ 603 nm was assigned to the exciton absorption of the quinoid rings which is attributed to the intrachain or interchain charge transport representing the insulating emeraldine base form of the polymer as described in the literature [7-10]. This reflects the effect of the solvent on the polymer properties. As the NMP is a highly polar solvent, the interaction between solute solvents would be stronger than in *m*-cresol medium. The carbonyl group present in NMP molecule would try to form H– bond with the H of the –COOH group of the dopant or those present on the N atom of the polymer chain. This in turn, would bring about deprotonation of the polymer chains resulting in the formation of emeraldine base form of the polymer [6-7].

3.2. IR Spectra

The IR spectra of the tartaric acid and acrylic acid doped polymer are given in Fig. 2 and characteristic peak locations related to the corresponding chemical bonds are listed in Table 1. However a remarkable difference is observed in the IR spectra in terms of specific bands and shifts in two polymers.

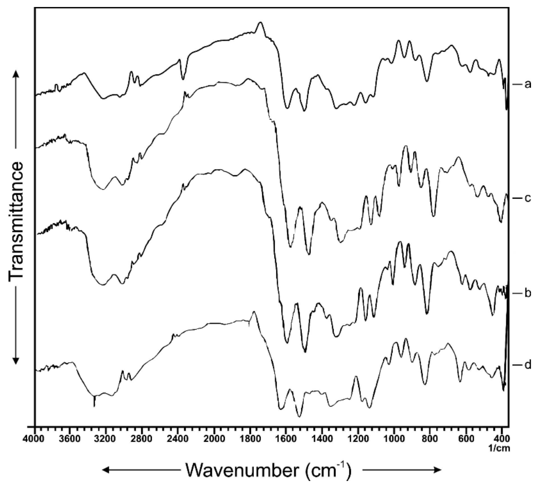

Fig. 2. FTIR absorption spectra of acrylic acid and tartaric acid doped polymer: tartaric acid doped poly(*o*-toluidine) (a); acrylic acid doped poly(*o*-toluidine) (b); tartaric acid doped poly(*o*-toluidine) exposed to ammonia (c) and acrylic acid doped poly(*o*-toluidine) exposed to ammonia (d)

The broad and intense peak at 3300–3100 cm^{-1} and 1157 cm^{-1} in the acrylic acid doped polymer accounts for the higher degree of protonation of amine and imine nitrogen but the peaks observed in tartaric acid doped poly(*o*-toluidine) polymer, is comparatively sharp and narrow, indicating to a lower degree of protonation and doping. Since both these polymers exist in the conducting polymer. This can be attributed to breaking up of a large number of interchain H– bonds that arise due to the addition of acrylic acid since it acts as a pseudo protonic acid and can coordinate with imine N atom of the polymer chain which results in disaggregation of the polymer chain and hence – its crystallinity.

The presence of the sharp peak at ~ 2883 cm^{-1} indicates to C–H stretching vibration of the acrylic acid and C–H stretching vibration of CH$_3$ group of *o*-toluidine, but the peaks obtained from the tartaric acid doped polymer is weak and broad. The strong and intense peak at 1596 cm^{-1} in the acrylic acid doped polymer is observed indicating to the quenoid ring stretching frequency, along with this peak one more peak observed at 1492 cm^{-1} indicates to the benzenoid ring stretching vibration. The band at ~ 1297–1304 cm^{-1} can be assigned to the C–N mode.

Table 1

Characteristic frequencies of acrylic acid and tartaric acid doped poly(*o*-toluidine)

Polytoluidine acrylic acid, cm^{-1}	Polytoluidine tartaric acid, cm^{-1}	Polytoluidine acrylic acid, NH$_3$ exposed, cm^{-1}	Polytoluidine tartaric acid, NH$_3$ exposed, cm^{-1}	Peak assignment
621	617	619	615	Out of plane C–H bending vibration
813	813	812	813	Disubstituted benzene ring
1117	1111	1113	1111	Vibration band of dopant anion
1157	1157	1220	1157	–
1319	1317	1325	1321	Aromatic C–N stretching band
1498	1492	1494	1492	Benzinoid ring stretching band
1587	1593	1597	1595	Quinoid ring stretching band
–	1700	1750	–	Carbonyl (C=O) stretching band
2347	2360	2312	2314	(NH$_2$)$^+$ saturated amine
2821	2833	2879	2831	Aliphatic C–H stretching freq.
3016	3043	2991	3049	C–H aromatic stretching band
3248	3250	3230	3246	N–H stretching band

The benzenoid and quinoid bands are observed at ~ 1498 cm^{-1} and 1587 cm^{-1} which are comparatively broad, weak and shifted to the lower wave number. Also the spectral intensity of these bands is comparatively typical of highly doped emeraldine salt form of the polymer. The presence of the weak peak at ~ 1700 cm^{-1} indicates to the non protonated –COOH group. The broad peak at 1319 cm^{-1} of the tartaric acid and at ~ 1321 cm^{-1} of acrylic acid doped polymer indicates to the aromatic C–N stretching frequency [7-10].

When the polymer is exposed to the ammonia vapor, it reveals differences in specific bands which are more significant in the acrylic acid doped polymer compared to the tartaric acid doped polymer. In the presence of ammonia exposure the peak at 3248 cm^{-1} is shifted to a lower frequency at 3230 cm^{-1}, which indicates that the doping level is maintained in the sample even after exposing to the ammonia vapor, but the tartaric acid doped polymer exposed to the ammonia vapor shows a slight increase in the stretching frequency.

The peak at ~ 3250 cm^{-1} is broadened indicating to the oxidation of nitrogen of the polymer chain. The peak at 1498 cm^{-1} is shifted slightly to the lower field, *i.e.* 1494 cm^{-1} in the acrylic acid doped polymer exposed to the ammonia vapor indicates to the increase in the quinoid form. The observed peak at ~ 1111cm^{-1}and 1157 cm^{-1} indicates that the doping is maintained by the free acrylic acid molecule.

3.3. Electrical Conductivity

These results are well supported by the conductivity data obtained for both polymers represented in Table 2. The acrylic acid doped polymer shows a higher conductivity ($0.73 \cdot 10^{-3}$ S/cm) than that doped with the tartaric acid ($0.36 \cdot 10^{-3}$ S/cm), since the acrylic acid act as a “pseudo” protonic acid dopant. It coordinates with the imine nitrogen atoms of the polymer chain. Such coordination would tend to displace the interchain hydrogen bonding which leads to desaggrigation of the polymer chain resulting in the formation of a highly protonated extended coil like conformation with the high conductivity than that observed for the tartaric acid doped polymer. It is reported that the conductivity of polyaniline depends on the degree of doping, oxidation state, particle morphology, crystallinity interior intrachain interactions, *etc.* [8-14]. These results showed that the emeraldine type structure was predominant in the acrylic acid doped polymer than the tartaric acid doped poly(*o*-toludine). It is noteworthy that the resistance of the acrylic acid doped polymer decreases with the increasing time of exposure to the ammonia vapor. These results suggest the utilization of this polymer material for preparation of the chemical sensor for the ammonia vapor [17-18].

Table 2

Conductivity values of the acrylic acid and tartaric acid doped poly(*o*-toluidine)

Sample	Conductivity before exposing to ammonia vapors, S/cm	Conductivity after exposing to ammonia vapors, S/cm
Acrylic acid doped poly(*o*-toluidine)	$0.73\cdot10^{-3}$	$0.65\cdot10^{-2}$
Tartaric acid doped poly(*o*-toluidine)	$0.36\cdot10^{-3}$	$0.72\cdot10^{-2}$

4. Conclusions

Poly(*o*-toludine) salts were synthesized by chemical oxidative method in different protonation media. During poly(*o*-toluidine) synthesis in the presence of the acrylic acid, the acrylic acid is added to the polymer chains as a dopant. In comparison with the tartaric acid doped polymer, the acrylic acid doped polymer was found to have the greater solubility in organic solvents. The conductivity of the acrylic acid doped polymer is also greater than the tartaric acid doped poly(*o*-toluidine) as observed from the UV-Visible, FTIR analysis of the polymer. Resistance of the acrylic acid doped poly(*o*-toluidine) is observed to be decreased on exposure to the ammonia vapors, which suggest the superior material as a sensor for the ammonia vapors.

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ОРГАНІЧНИЙ СИНТЕЗ ТА ХАРАКТЕРИСТИКА ЕЛЕКТРОПРОВІДНОГО ПОЛІ(*o*-ТОЛУЇДИНУ) З ДОДАТКАМИ ОРГАНІЧНОЇ КИСЛОТИ

Анотація. *Методом хімічної оксидаційної полімеризації синтезовано полі(о-толуїдин) з додатками акрилової кислоти і без неї у формі емералдіновой солі. Як окисник використано персульфат амонію. З використанням УФ- та Фур'є-спектроскопії визначено характеристики продукту. Показано, що полі(о-толуїдин) з додатками акрилової кислоти добре розчиняється у таких відомих органічних розчинниках як м-крезол, НМП, ДМФ тощо. Фур'є-спектроскопічними дослідженнями встановлено, що полі(о-толуїдин) з додатками акрилової кислоти має широку та інтенсивну смугу при 3250–3000 см*$^{-1}$ *і смугу при 1160–1100 см*$^{-1}$ *при більшій кількості додатків. Результати підтверджені вимірюванням провідності.*

Ключові слова: *полі(о-толуїдин), акрилова кислота, електропровідність, розчинність, додаток.*