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ORGANIC CONDUCTORS BASED ON POLY(P-ANISIDINE)

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ABSTRACT:

Polyansidine organic conductor, was chemically synthesized, via the chemical oxidation of ansidine by persulfate anion in aqueous solution . The prepared polymer was characterized by different methods of analysis such as: thermogravimetric analysis, electric conductivity, infrared and UV-visible absorption spectroscopy. Polyansidine showed good yield and intermediate electrical conductivity ($\sigma = 5$ S/cm). This conductivity assigns it as a semiconductor material. The present work investigates the method of preparation and characterization.

KEY WORDS

Anisidine, organic conductor, electric conductivity, chemical oxidation, aromatic, amines, and polymerization.

INTRODUCTION

Over the last decade or so there has been widespread interest in a new class of compounds known as conducting polymers. These polymers produce materials that combine the important electronic and optical properties of semiconductors and metals with specific mechanical properties. The organic polymeric conductors have attracted much scientific and technological interest in recent years. This is due to the large variety of recent and advanced applications in the electronic, photonic based devices and computer systems. The electrical conductivity of these polymers is considered to be intermediate between semiconductors and metals. It ranges between 1-1000 s/cm [1]. These properties make them ideal candidates for use in : electronic, capacitors which are used in all almost electronic equipment [2]. Exploitation

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of organic materials for electrochromic displays (ECDs) was done by several researches. More recently, the use of electroactive organic polymer has been tested widely. Polythiophene and polypyrrole and their analogues have been tested for ECDs use [3]. Currently commercial available capacitors are made of metalized polymer film using metal oxide e.g., M_nO_2 as Cathodes. They have many disadvantages. They are subjected to severe thermal shock owing to high temperature typically 400-600^o c required for the decomposition of manganese nitrate (III) during manufacture of the capacitor, also the capacitance is not constant beyond 10 kHz, and relatively low conductivity which limits the operation of the capacitor above 10 kHz. This enhances the failure rate of such capacitor in equipment assembly stage [4]. But using the conductive polymers solves these problems. Recently, conducting polymers have become one of the foci in material science research. This is due to their widespread technological applications. Also : active electrode materials in energy storage [5], opto-electronic devices [6], display devices were extensively searched to be from conducting polymers. These also may be used as chemically modified electrodes [7], and polymer temperature sensors [8]. In addition to the above applications, research and development are continuing in several areas in antistatic applications, sensors, radar blocking applications. , and recently as actuators that do work similar to mechanical-electrical micro machines (MEMs) [9]. In the present work, polyanisidine was selected to be chemically prepared via its oxidation by ammonium Persulfate in an acid medium. The prepared polymer was analyzed and investigated to explore the effect of methoxy-group substituent (p-position in aniline monomer), and consequently discover its useful applications.

EXPERIMENTAL

Chemicals :

P-anisidine (Colinbrook), Ammonium persulfate (Aldrich), Ferrous sulphate (BDH), Hydrochloric Acid (El-Naser), acetone(Prolabo), Formamide (Aldrich), Dimethyl fomamide DMF(Aldrich), benzene(adwic), ethanol (El-Naser), methanol (adwic).

Chemical Polymerization

P-Anisidine was chemically polymerized by the standard method of chemical oxidation with ammonium persulphate in the presence of hydrochloric acid as follows : Ammonium Persulfate (25 g) was dissolved in hydrochloric acid 300ml, 1M) and the solution was cooled to 0^o C using ice bath. Anisidine (25 g) was dissolved in hydrochloric acid (600ml 1M). The mixture was stirred for 15 minutes to insure complete solubility and was also cooled to 0^o C. Few

drops of ferrous sulfate aqueous solution (2.5%) were added to the anisidine solution. The ammonium Persulfate solution was gradually added to the anisidine solution all over a period of 15 minutes while cooling. After one hour of vigorous stirring of the cold mixture, it was transferred to a freezer for about two hours, a dark brown precipitate was formed, filtered, washed and dried in an oven at 50 °C for 5 days.

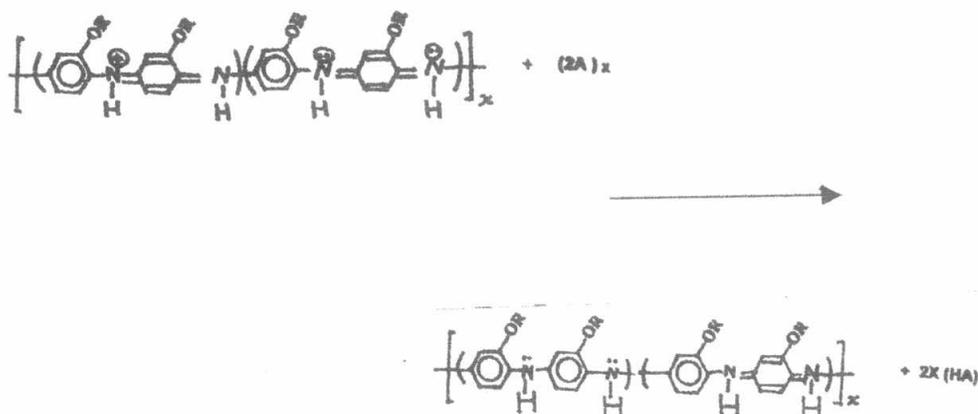
Instrumentation :

Infrared absorption spectrum was carried out by dispersing samples of the product in KBr and measured on Perkin-Elmer model 3087 Spectrophotometer, in a wave number range of 500- 4000 cm^{-1} . The visible- UV absorption spectrum of the polymer solution was determined using uv-visible Shimmedzu NIR-160 spectrophotometer (Japan). Thermogravimetric analysis (TGA) of the product was carried out with a rate of 150 °C per minute, the test was conducted in the temperature range of 0-450 °C using NETZSCH TG ZOQ instrument (west Germany). The electrical conductivity was determined using the electronic four point probe Multimeter model 120 Hewlett Packard (France). The test was carried out on a glass substrate with squared shape.

RESULTS AND DISCUSSIONS

Poly(p-anisidine) was synthesized by the standard method of chemical polymerization of aniline [10], via oxidation of anisidine by ammonium persulfate in aqueous solution of 1 M HCl. In the present polymerization, ammonium persulfate was selected as oxidant, because it was found that it gives a high yield in aniline oxidation [11]. The weight of polyanisidine product is quite high. Which agrees with our expectation. Since the presence of the electro denoting methoxy group leads to an easier oxidation compared with aniline. The proposed structure of polyansidine includes quinoid and benzenoid moities in the backbone. The ratios of these two structures depend on the oxidation state occurred. The color was also related to the nature of quinone imine in the backbone. On this base the structure may be significantly modified by doping processes. Which involve the oxidation or reduction of the polymer chain. Consequently, the electric conductivity may be enhanced the redox processes. Functionality, appropriate doping and its level, controlled synthesis and the other factors are the main parameters in these processes. As a result of these chain modification, the polymer can find unique application in advanced technologies. The proposed structure of polyanisidine as a complete reduction form 1 and a completely oxidized form 2, imine and amine and protonated forms as follows

poly(p-anisidine) compared with polyaniline can be attributed to several factors such as : chemical structure of the polymer and the extent of oxidation, the conformation of the polymer chain, its stereostructure, the chain packing pattern, the morphology of the polymer in the solid state and the presence of bulky substituents leading to the noncoplanarity of the aromatic rings. The measured conductivity lies in the semiconductor region. This classification according to Fig 1, thus this polymer may be used as a semiconductor material in electronic devices. The role of hydrochloric acid, is the protonation of poly(p-anisidine) to form the corresponding salt, this occurs preferentially at the imine nitrogen (-N=) as follows:



This protonation reaction induce a large increase in the resultant polymer conductivity, since it is known that the totally oxidized form is an insulator, this doping process leads to the formation of a positive charge localized in the polymer chain accompanied by the transformation of aromatic structure towards the quinoid form. Such conductivity can be looked as a result of both the conjugation and regularity of the polymer structure. In the same time the oxidation implies the diffusion of the oppositely charged chloride counterions from the medium to the polymer.

IR-spectrum of the polymer sample was tested and showed in Fig 2. This spectrum reveals the existence of the bands in the region of 1400-1240 cm^{-1} , which correspond to the C-N stretching characteristics of aromatic amines.

The peak at 1160 cm^{-1} corresponds to C=N in the quinone imine moiety. The aromaticity of the polymer can be shown by peaks at 745 cm^{-1} and 695 cm^{-1} . The C-O-CH₃ was shown from the peak at 3200 cm^{-1} . The strong band at about 3500 cm^{-1} region may be attributed to the N-H stretching.

UV-visible spectrometry :

It was reported that UV-visible spectra of the fully reduced form of the parent polymer, polyaniline, leucoemeraldine in N-methyl pyrrolidone NMP reveals a strong absorption band centered at 340 nm and a very weak residual absorption at 633 nm. The former band has been assigned to the $\Pi-\Pi^*$ transition corresponding to the B-band (benzenoid band). The latter band has been explained to be due to a charge-transfer excitation-like transition from the highest occupied level centered on the benzenoid rings to the lowest unoccupied energy level centered on quinoid rings. It is believed that this excitation band can be used as a measure of the oxidation state of polyaniline. As the intensity of excitation band decreases relative to $\Pi-\Pi^*$ B band, the oxidation state is probably low. The UV-visible spectrum of poly(panisidine) shown in Fig 3 shows characteristic bands at 315 nm and 350 nm. The substitution on benzen rings of methoxy group causes a hypsochromic shift of the $\Pi-\Pi^*$ transition band from 320 nm to 315 nm. This band is related to the extent of the conjugation between the adjacent rings in the polymer chain. The resonance energy is at its maximum when the rings are coplanar. So the main effect of the substituent groups of methoxy on the rings, is the destruction of that coplanarity by the steric interference leading to the formation of the stable conformation with certain angle between the planes of the rings. By this way the maximum overlap can not be achieved. The band at 620 nm in polyaniline disappears in the spectrum of the salt and new peak at 420 nm was formed. This band was to be due to the charge transfer complex formed that absorbs in the visible region. This band is also shifted to 350 nm due to the same reason mentioned before. The reported results in spite of its rarity showed that the position of excitation band is dependant on the chain length (degree of polymerization) as well as on the distribution of benzenoid and quinoid rings (extent of doping). The slight difference in absorption bands may be due to the extent of the oxidation and the used solvent.

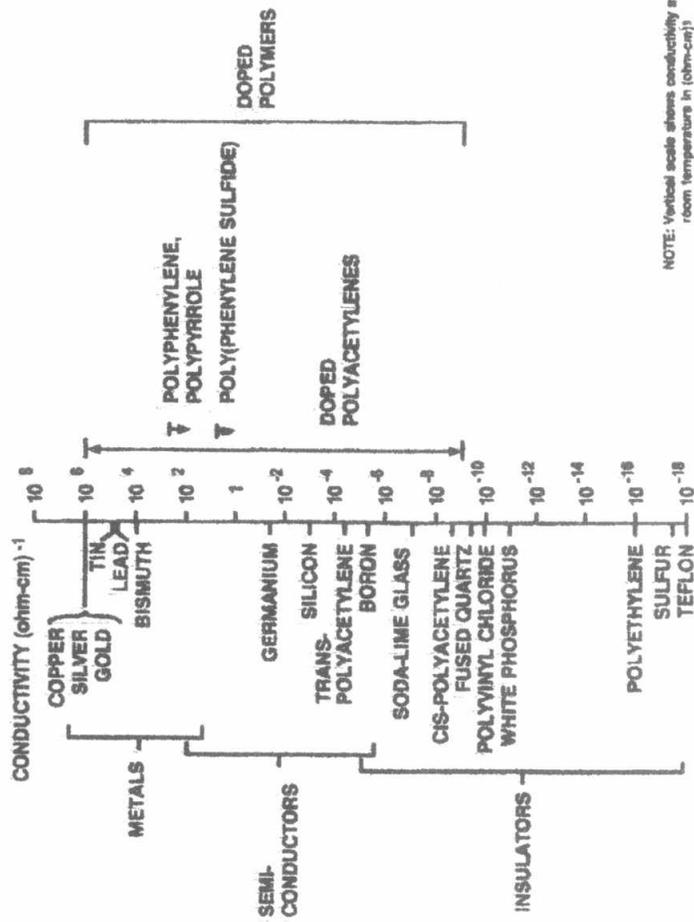
Thermogravimetric analysis (TGA) Fig 4 for the sample prepared at molar ratio 1:5 (monomer / oxidant) was tested. The polymer shows on weight loss region at 100°C with 37.8 % loss in weight. This can be attributed to the removal water. The second weight loss that was located at 295°C , can be explained by the partial decomposition of the organic polymer. This thermal analysis indicates that the sample is stable up to 290°C

CONCLUSION

Polyaniline was synthesized successfully by the chemical polymerization of aniline, via its oxidation by ammonium persulfate in aqueous solution, by employing ferrous sulfate as a catalyst. The characterization of the prepared polymer was done by UV-IR-spectroscopy, thermalgravimetric analysis, solubility and electrical conductivity. The resultant electrical conductivity was in the range 0.54-1.65 s/cm, making it very useful as a semiconductor material. From TG analysis. It's clear that the polymer sample is stable up to 290^o C. Due to this thermal stability and its solubility at room temperature (which give an ease processing), it may be find suitable applications in semiconductor devices.

REFERENCES

- [1] M.Goosey, Speciality polymers, 1st ed. Chapman and Hall, New York, 1987, pag.85.
- [2] S.P.Sitaram, J.O.Stoffer, and T.J.O.KEEFE, J.of Coating Technology, 69, no 688, 1997, p 65.
- [3] A.Kitani, Junyano and Kazuosaki, J.of Electroanal.Chem. 1996, 209, 227
- [4] S.Sathiyarayanan et al, Synthetic Metals, 74, 1995, 165-170
- [5] T.A.Snothrem (ed). Handbook of Conducting Polymers, volumes 1 and 2. Marcel Decker. New York (1986).
- [6] Chao and M.S Wrighton, J.am.Chem.Soc, 109, 6627 (1987).
- [7] J.Josheph and D.C Trievedt. Bull.Electrochem, 4, 469 (1988).
- [8] J.Chem.Phys 1990, 92(4), 2187-88.
- [9] Genies.E.M, Boyle.A, Lapkowski.M and T Sintavis.C, Synthetic Metals, 36, 139- 82, 1980.
- [10] S.Sathiyarayanan et al, Corrosion Science, volume 33(12), page 1831-44, 1992.
- [11] J.Aber.Science, 246, 1989, page 208.
- [12] S.M.Fayed, M.A. Radwan, S.R.Gouda, M.A.Borham, 8th interenational conference on aerospace science and aviation technology, 4-6 may Egypt, 1999.



NOTE: Vertical scale shows conductivity at room temperature in (ohm-cm)⁻¹

Fig 1. The conductivity of the different types of materials

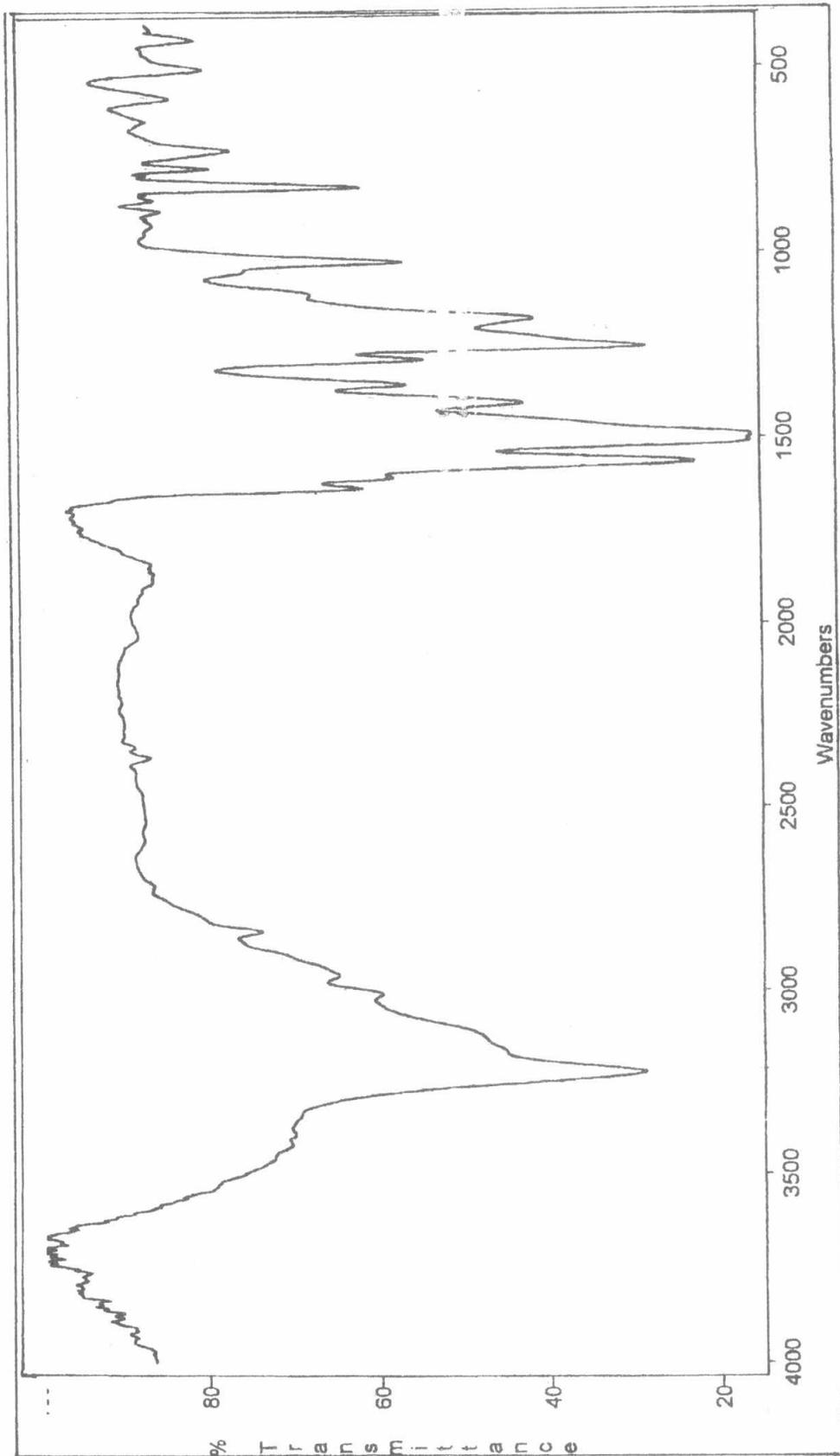


Fig 2 Infrared Spectrum of poly(p-anisidine) dispersed in KBr
Prepared at molar ratio 1:3 (anisidine/ persulfate).

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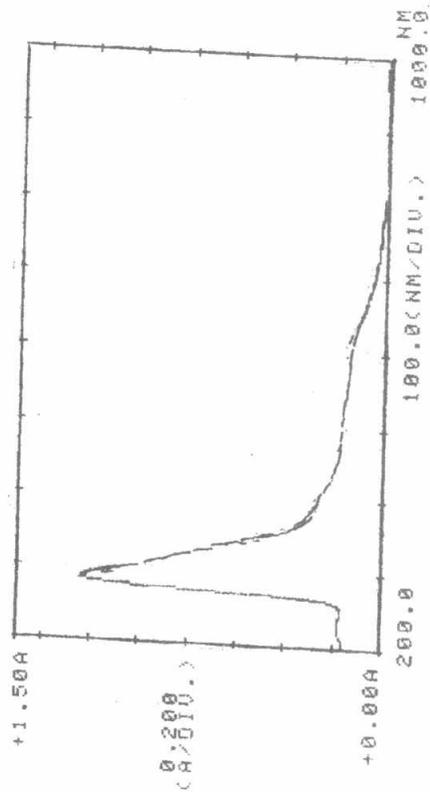


Fig 3 UV-visible absorption of poly(p-anisidine) dissolved in DMF.

NETZSCH-Gerätebau GmbH Thermische Analyse

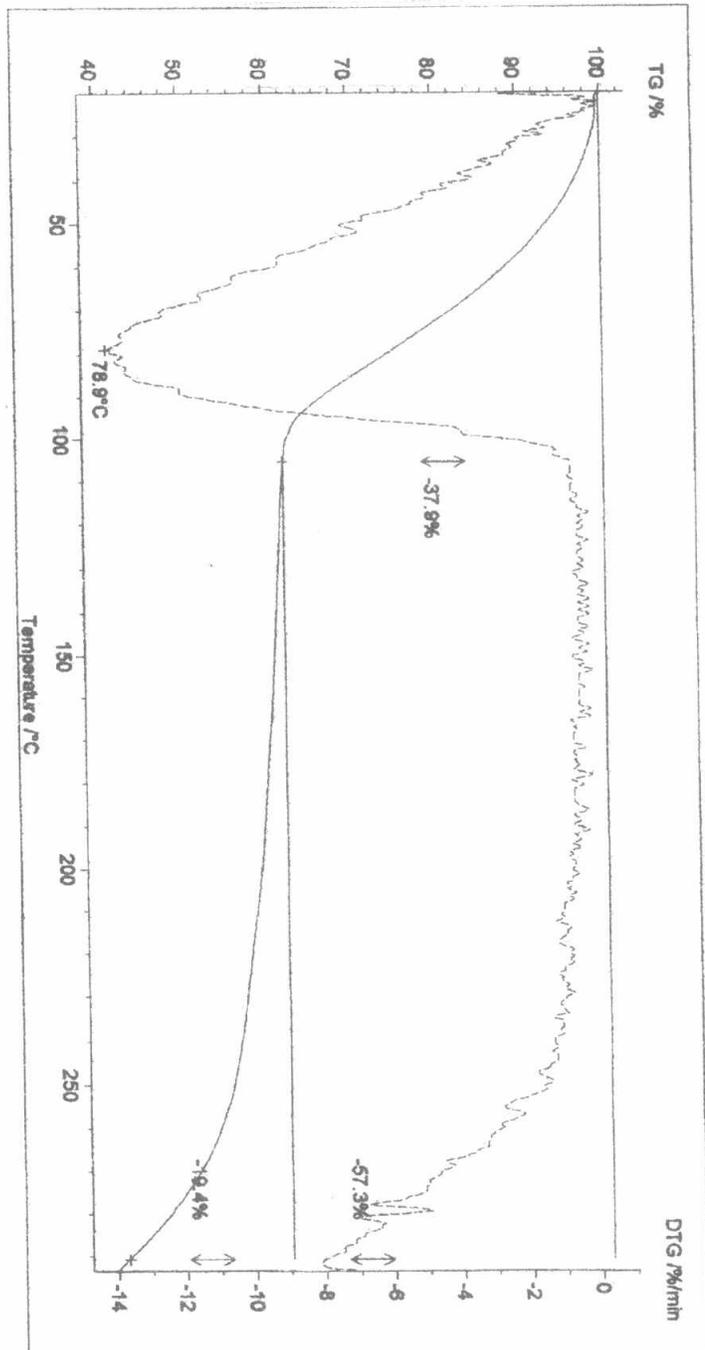


Fig 4 Thermogravimetric data for poly(p-anisidine) prepared at molar ratio 1/3 (anisidine / persulfate), in temperature range 0-300 ° C