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Plasma induced aniline polymerization

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This paper presents a study on the synthesis of conductive polymer thin films deposited on glass or quartz plates using radio-frequency plasma (13.56 MHz) polymerization of aniline. The resulting plasma polymerization aniline (PPAn) layer (chemical structure, conductivity) has been investigated in detail. The color, solubility and spectral characteristics (FT – IR) suggest that the conjugation in the main chain is interrupted by saturated linkages and the presence of aliphatic groups, resulted from fragmentation and hydrogenation of aromatic rings, during plasma discharge.

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1. Introduction

Conductive π conjugated polymers are promising materials for technological applications [1]. In particular, polyaniline (PAn) has been extensively investigated because of its high electric conductivity, excellent environmental stability, and ease of preparation. It possesses a nitrogen atom between phenyl rings, which allows the existence of different oxidation states that can affect its physical properties-doped state. In its undoped state, PAn can exist as three different bases: emeraldine, leucoemeraldine, and pernigraniline [2, 3]. The doping process, achieved through the addition of an acid, associates protons to nitrogen atoms and results in a displacement of π electrons [4, 5] These electrons are responsible for the high optical nonlinearities observed in organic materials because the relatively weak π -binding allows the necessary electronic mobility for the nonlinear response [6].

Polyaniline can be synthesized by chemical, electrochemical, or plasma methods [7], and in each case, the composition, morphology, and physical properties of the resulting polymer are strongly dependent on the detailed reaction conditions. PAn is the most highly conductive of all known polymers and has notably complex structure – property behavior involving four different oxidation states; the conducting form is stable in both air and water [8].

Certain gases in plasma may undergo polymerization, usually via a free radical initiation process. When a gas polymerizes and adheres to dissimilar materials sharing its plasma environment, the process is called plasma deposition. Plasma polymerization creates new and unusual polymer properties that have only begun to be explored in semiconductor science, biomedical and space technology applications. Polymerization, or deposition, processes may include reactions using a wide variety of gases, including some of the organic or organo-metallic compounds, which deposit nonvolatile polymer films. In many instances these reactant gases may be toxic, corrosive, or otherwise hazardous and require special handling such as heated gas transfer plumbing and measurement instrumentation, reactor exhaust scrubbing, and trapping of reaction byproducts.

The main reason for applying plasma polymerization is that thin, stable and pinhole-free films are obtained, which show good adherence to many substrates. A disadvantage is the poor predictability of the chemical structure of the resulting plasma polymerized layers.

Aniline and aniline derivatives were plasma polymerized by several authors [9 – 13]. Based on FT – IR and other measurements (conductivity, UV, etc.) it was concluded that the aromatic monomer structure was retained to some extent in the plasma polymerized aniline layer [9, 11, 12].

2. Experimental

2.1. Materials

Aniline (Merck, for synthesis grade) was freshly distilled before use. Iodine, tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) were also Merck reactive grade, and chloroform Chemical Company, Romania, reactive grade.

2.2. Plasma polymerization

The resulting plasma polymerization aniline (PPAn) layer was prepared in a plasma glass reactor (Fig. 1), specially designed to carry out R.F. plasma polymerizations.

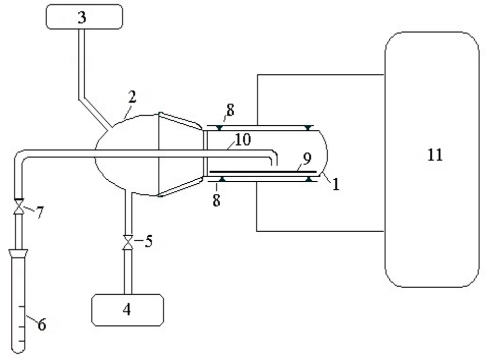


Fig. 1. Cold plasma installation for the polyaniline polymerization: 1 - the cylindrical shaped vacuum plasma reactor (neutral Pyrex glass, L = 30 cm, ∅ = 4 cm); 2 – close glass vacuum system; 3 – vacuum gauge Penning Pirani; 4 – vacuum pump; 5 and 7 – glass valves; 6 – monomer flask; 8 – semi cylindrical external silver coated electrodes; 9 – glass plate (15 X 100 mm); 10 – central monomer's admission glass tube; 11 – R. F. generator (250 W, 13.56 MHz).

In a typical experiment, after several washing cycles with inert gas (nitrogen) and with the selected gaseous – phase monomer (monomer introducing and evacuating cycles), aniline was continuously distilled, from the monomer flask (6), into the cylindrical shaped vacuum plasma reactor (1); the working pressure of the monomer was established (0.3 mm Hg) and then the R.F. power was transferred to the reactor through the semi cylindrical, external, silver-coated electrodes (8). The R.F. power was dissipated to the electrodes from a R.F. generator (11) with the possibility of generating 250 W. The polymer was deposited on glass and quartz plates (9) (15 X 100 mm).

2.3. Characterization

The FT-Infrared spectra were registered on a DIGILAB-FTS 2000 spectrometer (KBr pellets). SEM images were obtained on a TESLA SP 500 apparatus. Elemental analysis was carried out on Perkin Elmer 2400 Series II CHNS/O System. DSC measurements were registered on a Mettler DSC IE apparatus.

3. Results and discussion

Thin, well adherent yellow-brown colored polyaniline films deposited on the internal surface of the reactor and on the glass or quartz plates were obtained during the plasma polymerization in gaseous phase of aniline using a cylindrical glass reactor (Fig. 1). The film thickness can be controlled using different times of glow discharge in the reactor and for short discharge times (30 min) adherent films at quartz or glass support were obtained. The polymer is insoluble in organic solvents. The insolubility of the film in THF, DMSO, can be associated with a higher molecular weight, and/or a cross linked structure resulted in the plasma polymerization. With chloroform the film swelled and was separated from the surface of the plates.

IR spectrum (Fig. 2) shows peaks at 3392 and 1633 cm^{-1} due to –N-H vibration and deformation, a peak located at 2930 cm^{-1} belonging to the –C-H aliphatic vibration, two peaks at 1310 and 1173 cm^{-1} due to the C=C and C-C interactions. There are absorptions at 802 cm^{-1} (benzene ring with disubstituition 1,4) and 753 and 696 cm^{-1} due to the C-N bond of the biphenyl amine group.

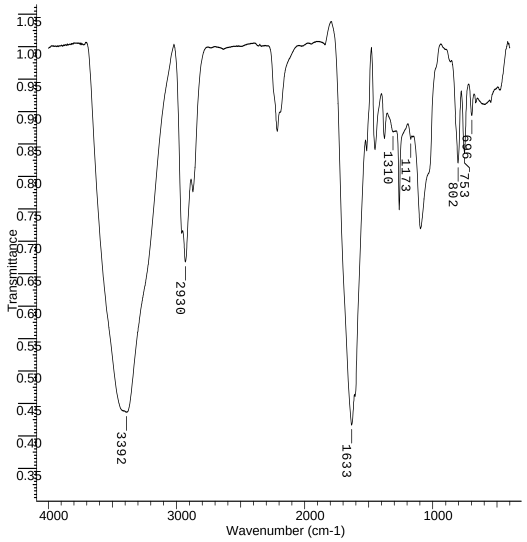
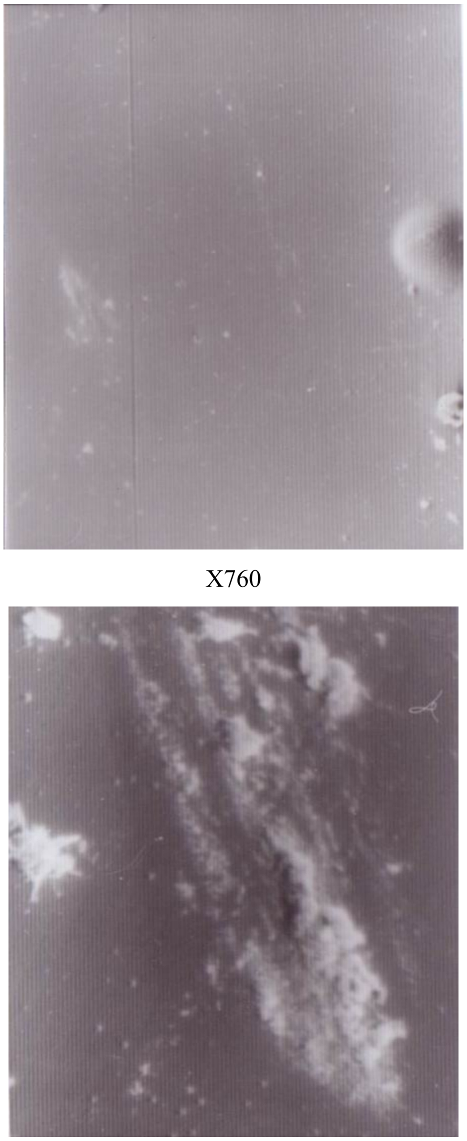


Fig. 2. FT – IR spectrum of polyaniline film (KBr pellet).

Elemental analysis data (C=78.30%, H=5.83%, N=15.87%) are very close to leucoemeraldine structure (C=79.10%, H=5.50%, N=15.40%).

The electrical conductivity of undoped plasma polyaniline disc-shaped pellets performed by the four-probe method at room temperature is 1.5.10^{-10} S/cm, a lower value that the electrical conductivity of iodine doped polyaniline film (~ 10^{-4} S/cm) and it brings proofs for presence of unsaturations in the main polymer chain.

Fig. 3a, shows SEM micrographs at X 760 magnification in which the surface is seen as two regions with different appearances: one is a continuously film and the other is formed from bubbles randomly distributed on the surface. The plain surface consists in the homogeneously polymer. The bubbles, with diameter range between 1 and 15 μm, can be formed from drops of aniline or oligomers trapped in the layers. Under the influence of plasma energy the monomer or oligomer bubbles can be vaporized and consequently may be the start of a large fracture. This argument is shown in Figure 3b (X 5000 magnification) in which we can observe some microstructures as a surface formed from collapsing particles of different sizes in the layer structure.


X760

X5000

Fig. 3. SEM photographs of plasma polymerized aniline films.

The DSC measurements (Fig. 4) were carried out at a heating rate of 10 °C/min and polyaniline film was found to be amorphous in the process of heating, with glass transition temperature (Tg), determined in the second heating run at 155 °C. The analysis showed that between 50 – 120 °C the adsorbed water and solvent traces are removed and a destruction process starts at 272 °C.

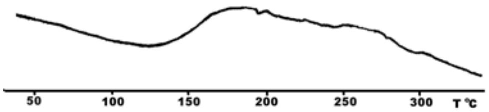
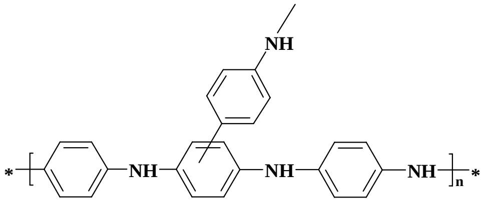


Fig. 4. DSC diagram of polyaniline film.

All the analytical data show that in cold plasma conditions aniline is transformed in films with structure close to leucoemeraldine (Scheme 1).



Scheme 1: Polyaniline structure from plasma polymerization

4. Conclusions

Thin films of polyaniline can be deposited on glass substrates by plasma polymerization processes. Analytical data show that structure presents conjugation in the main chain, and physico-chemical measurements proved that the polymer has conductivity, which increased in the case of iodine doped polyaniline film. The structure of the synthesized polymer is complex and results from linking of aniline rings in para, metha and orto positions. It is proposed a new chemical structure for the plasma polymerized aniline film, different from the idealized structure of the oxidation states.

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