

PLASMA INDUCED PYRROLE POLYMERIZATION

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This paper presents a study on the synthesis of polypyrrole thin films deposited on glass or metallic substrates by radiofrequency plasma polymerization of pyrrole. The structure of the polymer was analyzed by FT-IR, UV, GPC and its color, solubility and spectral characteristics suggest that the conjugation in the main chain is interrupted by saturated linkages resulted from fragmentation and hydrogenation of aromatic rings during plasma discharge.

INTRODUCTION

Certain gases in a 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.

Polymers are widely used in a great number of applications because of their many advantageous, general properties such as low density and cost, and processability. For applications requiring electrical conductivity, the choice of a suitable polymer is limited to polymers with a conjugated chemical structure such as polyacetylene, polypyrrole, and polythiophene.¹⁻⁶ Along the conjugated structures, charge (i.e., electricity) is

transported by charge carriers. The obtained conductivity ranges from the antistatic (10^{-11} – 10^{-6} S/cm) to the metallic ($> 10^2$ S/cm) regime. However, the stability of the conductive properties is rather low due to the high reactivity of the conjugated structure. Furthermore, the conjugated structure of conductive polymers inherently results in a non-transparent, intractable polymer that has lost some of the aforementioned advantages over the alternative conductors.

A very attractive alternative would be the plasma technique. With this method it is possible to modify the surface properties of a substrate, while retaining the transparency and bulk properties of the substrate material or to deposit thin transparent films. Furthermore, it is a solvent-free, fast and versatile process. However, plasma consists of a variety of reactive species (electrons, ions, radicals, etc.)⁷⁻¹¹ and therefore many different reactions may occur.¹²⁻¹⁵ As a consequence, the exact chemical structure of the surface after exposure to a plasma is not precisely predictable, which requires detailed investigation.¹³

The main reason for applying plasma polymerization is that thin, stable and pinhole-free films are obtained, which show good adherence to many substrates.

Because heterocyclic polymers such as polypyrrole^{2, 16-22} and polythiophene^{3, 23-26} are known for their high and relatively stable conductivity,

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many studies are reported on the plasma polymerization of these monomers. Lee *et al.* deposited polypyrrole (PPy) layers in a capacitively coupled bell jar configuration at 13.56 MHz.²⁷ After deposition, the PPy layers were heat-treated (300 °C) in a nitrogen atmosphere, which resulted in an increase of the unsaturation in the PPy layers. An increase in p-type conductivity from 10^{-9} to 10^{-5} S/cm was observed. Van Ooij *et al.* deposited PPy layers in a DC type plasma reactor.²⁸ FTIR measurements showed that no pyrrole rings were retained in the PPy layers, which indicates a total destruction of the monomer by the plasma. Without additional doping, still conductivities of 10^{-3} to 10^{-4} S/cm were determined by the Franklin test. Zhang *et al.* were able to retain the pyrrole ring (determined with FTIR and XPS) to a certain extent during plasma polymerization in a capacitively coupled coil (radio frequency) configuration, but the conductivity was not determined.²⁹

Recently, Cruz *et al.* deposited PPy layers from plasmas of pyrrole and of pyrrole and iodine.³⁰ In both cases, absorption bands characteristic for pyrrole rings were observed in the FTIR spectra of the PPy layers. The conductivity of the PPy films increased gradually from 10^{-11} to 10^{-9} S/cm with increasing (30 – 90%) relative humidity of the environment. This was explained by an increase in the mobility of the PPy chains due to the interaction with water. For the PPy/I₂ films, conductivity increases from 10^{-9} S/cm at 10^{-7} to 10^{-3} S/cm at relative humidity > 90%. The authors state that a second conductivity mechanism dominates in this latter region, which is reinforced by the presence of iodine. Another explanation would be that the sharp increase is due to water with dissolved iodine ions. At high values of the relative humidity a continuous “path” of the water phase through the layer might be obtained, resulting in a sharp increase in the conductivity.

In view of the objective to obtain conductive polymeric systems, the plasma technique can be used to obtain thin conductive polymer layers on transparent polymeric substrates or on inert surfaces (glass, platinum, etc.). The aim of this paper is to present some results on radiofrequency plasma – induced polymerization of pyrrole.

EXPERIMENTAL

Materials

Pyrrole (Merck, for synthesis grade) was freshly distilled before use. Hexane and chloroform (Merck, spectroscopy

grade) were used for UV determination and molecular weight measurements.

Plasma polymerization

Polypyrrole was prepared in a plasma glass reactor (Figure 1), specially designed to carry out R.F. plasma polymerizations.

In a typical experiment, after several washing cycles with inert gas (nitrogen) and with the selected gaseous – phase monomer (monomer introducing and evacuating cycles), pyrrole 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 plates (9) (15 X 100 mm).

Characterization

UV spectrum of the polymer was obtained on a Varian Carry 50 UV spectrometer in hexane, and the FT-Infrared spectra were registered on a DIGILAB-FTS 2000 spectrometer (KBr pellets). SEM images were obtained on a TESLA SP 500 apparatus. Molecular weight measurements were carried out on a Beckman Instruments, with detection in UV at 254 nm, using mobile phase chloroform, flow rate 2 ml/min, column SUPELCO TSK – GEL H G1000, L=300 mm, ID=7.8 mm, particle size 5 µm, injection – polystyrene standards.

RESULTS AND DISCUSSION

Thin, well adherent yellow-brown colored polypyrrole films deposited on the internal surface of the reactor and on the glass plates were obtained during the plasma polymerization in gaseous phase of pyrrole using a cylindrical glass reactor (Figure 1).

The film thickness can be controlled using different times of glow discharge in the reactor and for short discharge times adherent films at metallic or glass support were obtained. Most of the polymer is insoluble in organic solvents, however about 20% weight from the total polymer was obtained as a soluble fraction in acetonitrile or chloroform and molecular weight measurements showed a value of 1200 daltons which corresponds to a polymerization degree of 20 (Figure 2). The insolubility of the major fraction can be associated with a higher molecular weight, and/or a cross linked structure resulted in the plasma polymerization.

The morphology of PPy films is controlled by the duration of plasma discharge and thin and compact films are constructed in the first stages of plasma discharge and than a cauliflower morphology of 0.5 µm or less diameters particles is observed (Figure 3).

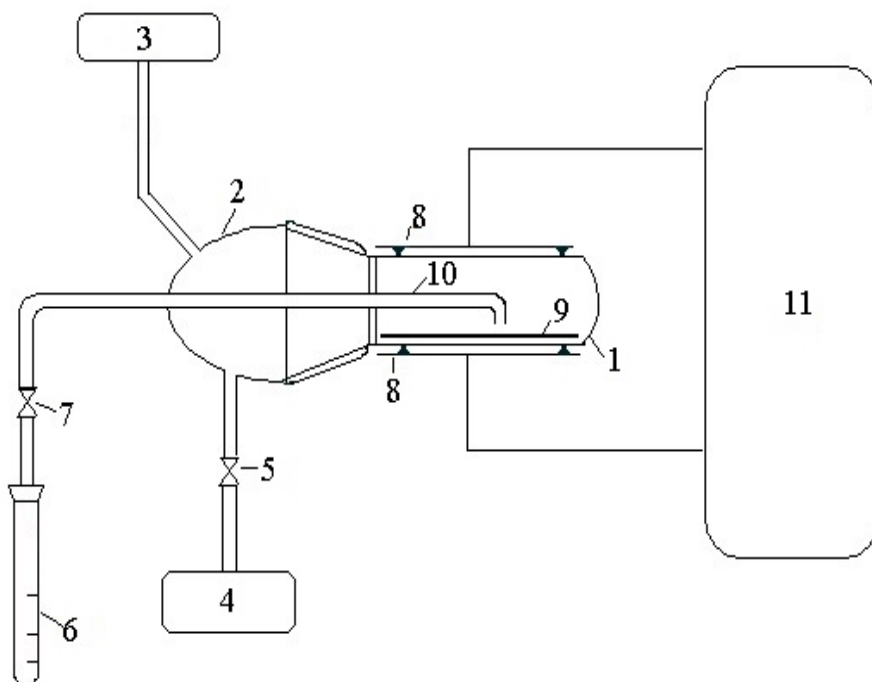


Fig. 1 – Cold plasma installation for the pyrrole polymerization: 1 - the cylindrical shaped vacuum plasma reactor (neutral Pyrex glass, $L = 30$ cm, $\varnothing = 4$ cm); 2 - close glass vacuum system; 3 - vacuum gauge Penning Pirani; 4 - vacuum pump; 5 and 7 - glass valves; 6 - monomer flask; 8 - semicylindrical external silver coated electrodes; 9 - glass plate (15 X 100 mm); 10 - central monomer's admission glass tube; 11 - R. F. generator (250 W, 13.6 Mhz).

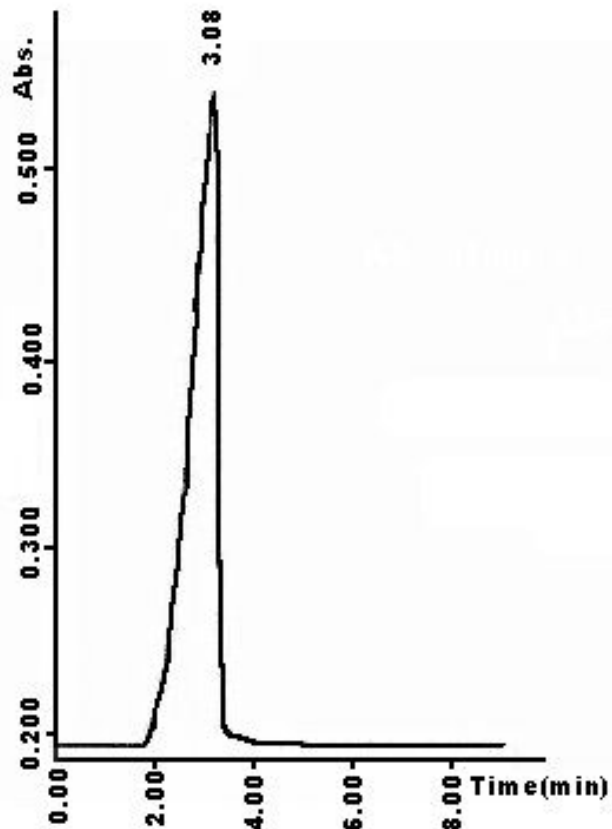


Fig. 2 – Gel permeation chromatogram of soluble product obtained in plasma.

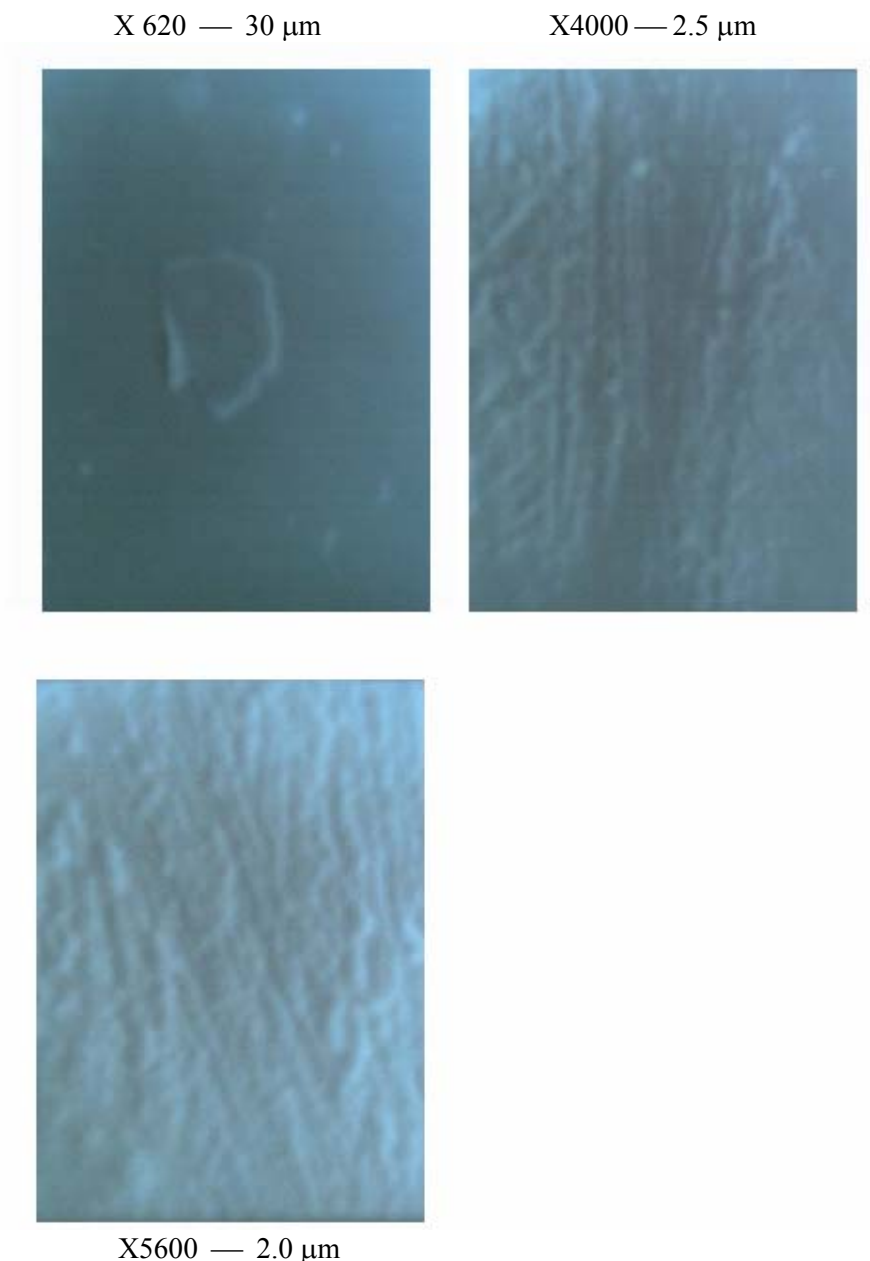


Fig. 3 – SEM micrographs plasma deposited films.

The chemical composition of the polymer, determined by elemental analysis, shows a lower content in carbon and nitrogen and higher content in hydrogen, compared with theoretical values: anal. Calcd for $(-C_4H_3N-)_n$: C, 73.85; H, 4.61 and N, 21.54 Found: C, 78.30, H, 7.23 and N, 14.47.

FT-IR spectrum of a thin film deposited on glass plate directly in plasma reactor (Figure 4) shows absorptions compatible with the structure of PPy synthesized by chemical or electrochemical methods; strong absorptions between $3400-3500\text{ cm}^{-1}$ and 1637 cm^{-1} associated with N-H stretching and deformation bands and moderate absorptions at 1400 and 1618 cm^{-1} (ring vibrations), 1100 cm^{-1}

(the aromatic C-H in plane bending) and 800 cm^{-1} (the C-H out of plane bending mode). Therefore, the pyrrole rings remain as an important part of the plasma-synthesized polymer. However, the existence of aliphatic C-H stretching absorptions ($2800-3000\text{ cm}^{-1}$), $-C=N$ (2216 cm^{-1}) indicates that some of the pyrrole rings in the polymer are fragmented.

UV spectrum of soluble polymer is shown in Figure 5 and shows an absorption in UV region (250 nm) characteristic to $\pi-\pi^*$ transition in pyrrole ring while slight absorptions in $350-400\text{ nm}$ can be assigned to $\pi-\pi^*$ in short conjugated polymer chains.

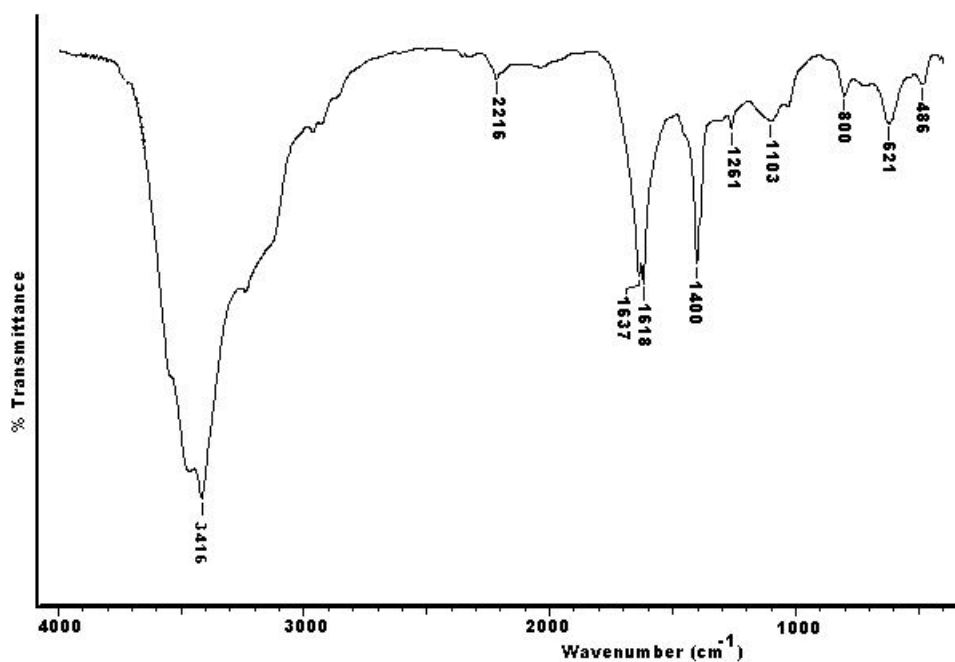


Fig. 4 – FTIR spectrum (KBr pellets) of product obtained in plasma.

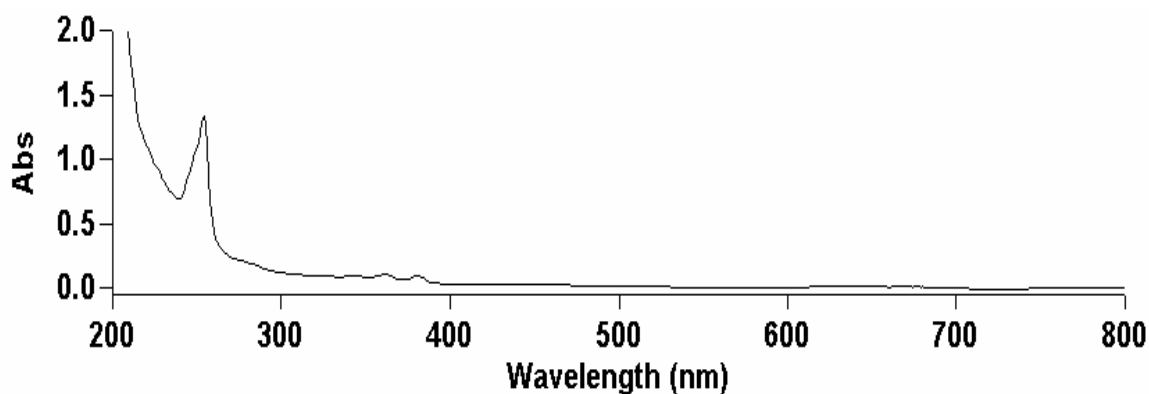
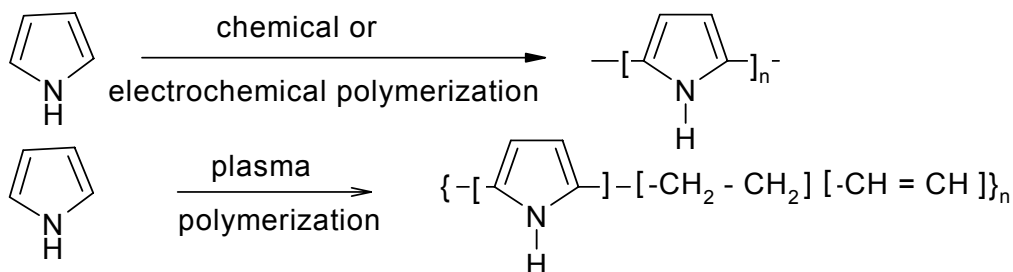


Fig. 5 – UV spectrum of product obtained in plasma (solvent - hexane, 1 cm quartz cell).

Now, the well accepted structure of polypyrrole, synthesized by chemical or electrochemical oxidation

of pyrrole, consists of 2,5-disubstituted pyrrole rings (Scheme 1):



Scheme 1 – Structure of polypyrrole.

Due its conjugated and rigid structure of the main chain, chemically and electrochemically-synthesized polypyrrole is obtained as a black colored and insoluble in most organic solvents

powder. In the case of plasma –synthesized polypyrrole, its color, solubility and spectral characteristics suggests that the conjugation in the main chain is interrupted by saturated linkages

resulted from fragmentation and hydrogenation of aromatic rings.

The electrical conductivity of undoped plasma-PPy disc-shaped pellets performed by the four-probe method at room temperature is $5 \cdot 10^{-8}$ S/cm, a lower value than the usual electrical conductivity of chemical or electrochemical undoped PPy ($\sim 10^{-2} - 10^{-3}$ S/cm) and it brings proofs for presence of unsaturations in the main polymer chain.

Although plasma polymerizations have been observed and studied for a long time, the mechanism of deposition is not clear at all.^{8, 31-33} Obviously, the mechanism depends on the species present during deposition, of which the type (e.g., radicals, ions) and amount are influenced by the process parameters. Mechanisms involving ions^{34, 35} and radicals have been described to explain the experimental data.³¹ At the present time, many investigators believe that the polymerization mechanism as proposed by Yasuda *et al.*^{33, 36-38} is the most reasonable concept. In this stepwise initiation – recombination sequence, radicals are formed upon generation of the discharge (most probably by electron impact). These primary radicals recombine to a species that again is radical initiated and so on. Polymer formation may occur at the surface and/or in the plasma phase,³⁹ both of which can be explained by this mechanism. Because of the multiple species present in a plasma, many reactions may result in the formation of radicals. For instance, in the DC plasma polymerization of pyrrole no effect of the sign of the charge on the electrode was found, showing that a radical growth mechanism should apply.⁴⁰ It has postulated that the growth is initiated by radicals present in the film surface, which are generated by impinging H^+ ions on the cathode and by electrons on the anode.

In summary, thin films of polypyrrole can be deposited on glass or metallic substrates by plasma polymerization process but structure of the synthesized polymer is complex and results from linking of pyrrole rings by 2,5 positions accompanied by fragmentation of heterocycle and hydrogenation.

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