

Structural, Electrical, and Optical Studies of Plasma-Polymerized and Iodine-Doped Poly Pyrrole

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ABSTRACT: An attempt was made to study the structural, electrical, and optical properties of plasma-polymerized pyrrole and iodine-doped pyrrole. A comparative study of the IR spectra of the monomer and polymer pyrrole gives information that the ring structure is retained during plasma polymerization. Iodine doping considerably increases the conductivity of the polymer film and decreases the optical band-gap energy. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1856–1859, 2002

Key words: plasma polymerization; doping; conductivity; band-gap energy; organic films

INTRODUCTION

Plasma polymerization is a process by which a thin layer of polymer film is deposited on any surface that is in contact with the plasma of the organic monomer. Depending on the deposition conditions, the properties of the film can be tailored to meet our requirements. Organic monomeric and polymeric materials have a number of electrical properties that are similar to those of inorganic semiconductors.¹ Besides good chemical and thermal stability, plasma polymers are highly crosslinked and are characterized by high electrical resistance.^{2–6} Much research has been devoted to enhance the conductivity of polymers by doping using suitable dopants.^{7–10} In this study we report the structure of plasma-polymerized pyrrole and the effect of iodine doping on the electrical and optical properties of the polymer.

EXPERIMENTAL

Plasma-polymerized pyrrole films were prepared using pyrrole (Aldrich Chemicals, Milwaukee, WI) by radio-frequency plasma polymerization. The experimental setup is shown in Figure 1. In this setup the polymerization section consists of a deposition cell made of a borosilicate glass tube (length, ~ 0.5 m; outer diameter, 0.035 m). The vapor container with the monomer is attached to the deposition chamber through a vacuum cock and needle valve. Power from the radio-frequency oscillator power supply is capacitively coupled to the deposition chamber by means of coiled sheathing copper wires. The monomer pyrrole was polymerized in a radio-frequency plasma under monomer vapor pressure of 0.2 Torr and at a current density of 20 mA/cm². For electrical conductivity studies, samples in the form of metal–plasma-polymerized pyrrole–metal sandwich structures (area, 0.25 cm²) were prepared. For the MIM structure, we used Al for the electrodes, which were deposited (thickness, ~ 2000 Å) by a conventional thermal evaporation technique under a pressure of 2×10^{-5} Torr on very well cleaned glass substrates. Electrical measure-

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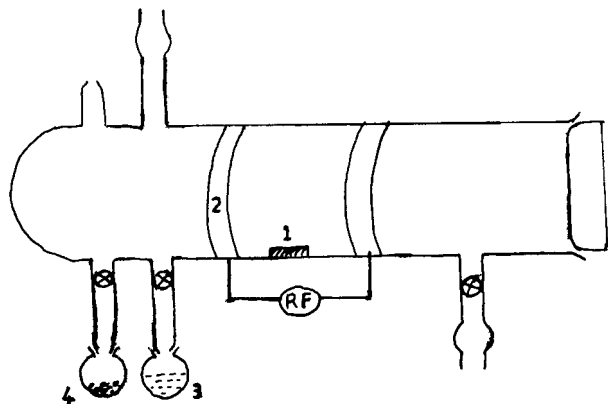


Figure 1 Plasma polymerization setup: (1) substrate; (2) copper foils; (3) monomer; (4) iodine.

ments were carried out in a metal chamber under vacuum conditions at a pressure of 1×10^{-2} Torr. The current flowing through the films was measured using an electrometer amplifier (Keithley Model 617; Keithley Metrabyte, Taunton, MA) at room temperature. Doping was done by admitting iodine vapor separately along with the monomer (shown in Fig. 1). For IR studies of the doped and undoped films, specimens were scraped from the glass substrate and pelletized after mixing with KBr; these pellets were used to record IR spectra. For recording IR spectra we used Shimadzu-IR 470 (Shimadzu, Tokyo, Japan), under identical conditions. For energy band-gap studies UV-Vis-NIR spectra of the doped and undoped films were recorded using a Hitachi 3410 spectrophotometer (Hitachi, Japan). SEM micrographs of the undoped and doped pyrrole films were obtained using SEM525M (Philips, The Netherlands).

RESULTS AND DISCUSSION

IR and SEM Studies

In the IR spectrum of the monomer of pyrrole (Fig. 2) the previously reported absorption peaks were obtained.^{11,12} The NH stretch and NH band modes were present at 3400 and 1140 cm^{-1} ; the bands were also present in the spectrum of polypyrrole at 3400 and 1120 cm^{-1} . This is a clear indication of the presence of the NH band in the polymer. Relatively strong bands at 1420 , 1460 , 1520 , and 1580 cm^{-1} represent ring frequencies in the monomer.¹³ In the polymer spectrum a strong broad band was present at 1620 cm^{-1} , representing ring frequency. In addition, the

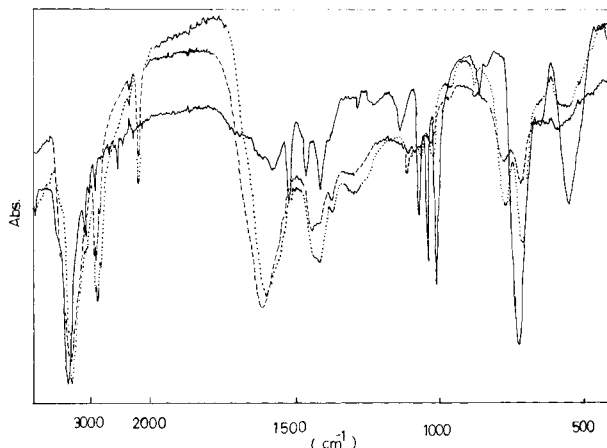


Figure 2 IR spectra: monomer pyrrole (—); polymer pyrrole (---); iodine-doped (···).

presence of bands at 1450 and 1420 cm^{-1} in the polymer spectrum indicates that the ring structure is not affected by polymerization process, which was also previously reported.¹² The strong band, characteristic of a five-membered aromatic ring occurring between 700 and 800 cm^{-1} , was present in the spectra of both monomer and polymer. Again, this strongly suggests that the ring is not opened up in the polymerization process.

An interesting observation of a new absorption peak at 2200 cm^{-1} indicates that some of the NH bond was replaced by $\text{C}\equiv\text{N}$ bonds. Another striking observation is that the bands at 1000 – 1100 cm^{-1} , representing the CH band, became relatively weak in the polymer compared to that in the monomer. This reduction of intensity in these bands seems to indicate a corresponding reduction in the number of CH oscillators in the polymer. The slight variation in the exact position of

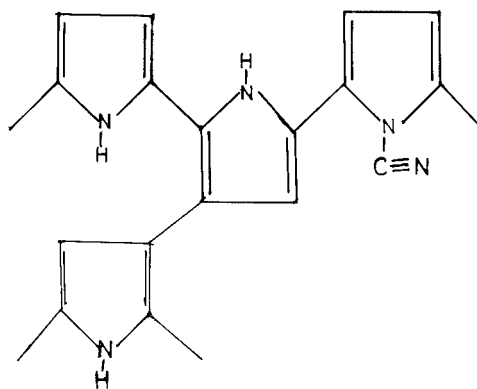


Figure 3 Proposed structure of plasma-polymerized pyrrole.



Figure 4 SEM micrograph of polymer pyrrole.

these peaks may be attributed to the change of state of the monomer (liquid) and polymer (solid). From the comparative study of IR spectra, it is reasonable to conclude that polymerization took place through hydrogen abstraction of hydrogen from the CH band, the conceivable structure of which is given in Figure 3. When we compared the IR spectra of polymer and iodine-doped pyrrole (Fig. 2), it was noticed that almost the same bands are obtained in the case of iodine-doped pyrrole, which means that during doping, iodine did not get into the polymer chain of pyrrole. The SEM micrographs of the polymer and iodine-doped polymer films (Figs. 4 and 5) give some idea of the surface morphology of these films. With the help of SEM micrographs we can observe that the iodine fills up the voids in the polymer, thus smoothing the surface of the polymer. During the iodine doping a continuous fibrillar-like structure

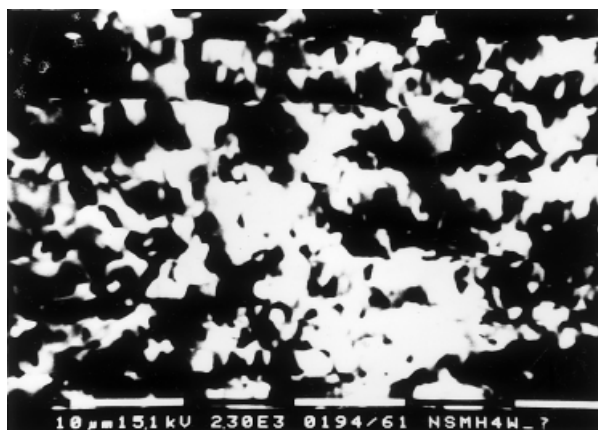


Figure 5 SEM micrograph of iodine-doped polymer pyrrole.

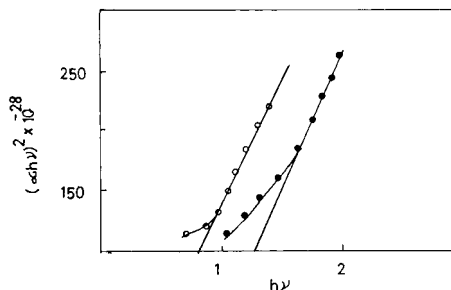


Figure 6 Plot between $(\alpha h\nu)^2$ and $h\nu$: ●, polymer pyrrole; ○, iodine-doped polymer pyrrole.

develops, giving higher connectivity and conductivity for the doped films, which may lead to an increase in the conductivity.¹⁰

Absorption in the UV-Vis Range

Figure 6 depicts a plot of $(\alpha h\nu)^2$ versus $h\nu$, where α is the absorption coefficient and $h\nu$ is the photon energy. The plot has a linear portion that, when extrapolated, cuts the energy axis. This corresponds to the threshold of optical absorption and hence optical band-gap values. From the figure we can find that optical band-gap energy values of plasma-polymerized pyrrole film and iodine-doped film are 1.3 and 0.8 eV, respectively. A similar change in the optical band-gap values, when doped with iodine, on some other materials was previously reported.¹⁴⁻¹⁶

Electrical Studies

Figure 7 shows current voltage characteristics of the undoped and iodine-doped polymer pyrrole films. It may be noted that as a result of iodine doping, the current increases and significantly similar behaviors were observed in films of differ-

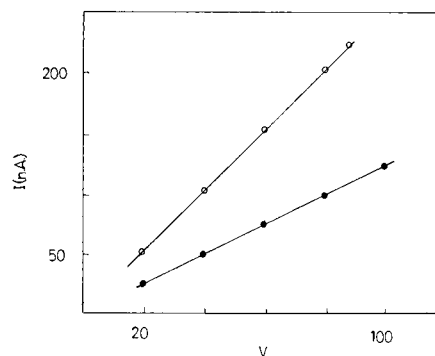


Figure 7 Plot between V and I : ●, polymer pyrrole; ○, iodine-doped polymer pyrrole.

ent thicknesses; thus, we have given values for the film of a thickness of 1600 Å.

CONCLUSIONS

The proposed structure of polymer pyrrole is in line with the proposed structure of the bipolar molecule.¹⁷ The monomer units have π -electrons, which are local to them, although upon polymerization, the spatial extent of these electrons is influenced by a significant overlap integral. In this case electrons become delocalized over the length of the polymer in the form of bands analogous to those of a semiconductor. The result is a full π band and an empty π^* band, a combination of which offers no macroscopic conductivity. In such cases a modification can be brought about by incorporation of a proper dopant that can create free electrons or holes. We investigated iodine as dopant, but IR and SEM studies revealed that iodine fills up the voids in the polymer pyrrole rather than going into the chain of the polymer pyrrole, which increases the connectivity and continuity of the polymer units; thus, we get an increase in the conductivity. This conclusion is supported by the experimental observation of a decrease in band-gap energy and an increase in electrical conductivity.

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