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Physical properties of polyazomethine thin films doped with iodine

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Materials

ABSTRACT

Purpose: The aim of this paper is to show influence of doping 1,4-phenylene-methylenenitrilo-1,4-phenylenenitrilomethylene (PPI) with iodine and to propose doping mechanism and its impact on electronic structure of doped PPI thin films.

Design/methodology/approach: Influence of iodine doping on electronic structure of polyazomethine thin films was investigated. Optical absorption spectra, XRD spectra and AFM images of doped PPI thin films were recorded.

Findings: Doping mechanism relys on removing one electron from PPI π-system by I2 molecules and forming counterions I3-. Formation of positive polaron means that doping of polyazomethine PPI is p – type.

Research limitations/implications: Influence of iodine doping on electrical properties (with increasing of tempearture) of PPI thin layers will be checking with Kethley appliance. We plan these measurements to be done in the foreseeable future.

Practical implications: Iodine doping of thin PPI films process could results in better electrical conductivity of PPI, so doped polyazomethine films could find some applications for photonic and optoelectronic devices.

Originality/value: Conjugated PPI is rarely enough reported but it is very interesting material as it has nitrogen atom in the backbone and it is isoelectronic counterpart of polyparaphenylenevinylene (PPV). This paper show that doping influences on surface morphology, cristallinity and optical properties of polymer. Furthermore, doping mechanism and changes of polymer electronic structure have been proposed in this paper.

Keywords: Engineering polymer; Polyazomethine PPI; UV-Vis absorption spectroscopy; Electronic structure

1. Introduction

1,4-phenylenemethylenenitrilo-1,4-phenylenenitrilomethylene (PPI) is conjugated, semiconducting polymer. PPI is isoelectronic counterpart of polyparaphenylenevinylene (PPV) [1-3]. Having its backbone similar to that of PPV, PPI absorption spectra have revealed distinct similarity to PPV spectra [4]. Similarly to PPV, PPI can be very useful for optoelectronics devices [5]. Then, it seemed interesting to prepare PPI thin films doped with iodine and study an influence of doping on electronic properties of this polymer, having nitrogen atoms in the polymer backbone. It is possibility to see whether lone pair on nitrogen atom sp^2 orbital has any impact on electronic structure. The aim of this paper is to show influence of iodine doping on PPI physical properties, to better understand mechanism of doping in conjugated polymers having atoms with lone pair in the backbone.

2. Materials and technology

2.1. PPI polycondensation process and doping with iodine

PPI thin films have been prepared by CVD method [6, 7] with the use of argon gas as carrier agent via polycondensation of TPA (99%) and PPDA (99%). Both monomers, TPA and PPDA were purchased from ALDRICH, while iodine [I_2] was purchased from POCH. Monomers were put into separate crucibles and argon stream forked into three equal streams flow around crucibles containing two monomers. While preparing undoped PPI thin films two sources only were used. Then, streams enter the colimator where they merge into one argon stream transporting mixed molecules towards the substrate.

The substrates were placed over an oppening of the stream colimator. The temperatures of source monomers were about 60˚C for TPA and 70˚C for PPDA. PPI thin films were deposited onto glass substrates. Monomers molecules impinging onto the substrate kept at room temperature enter the polycondensation reaction resulting in polymer chain formation (Fig. 1). The most important here is reaction of functional groups [5, 8], which generate double bond –N=CH-.

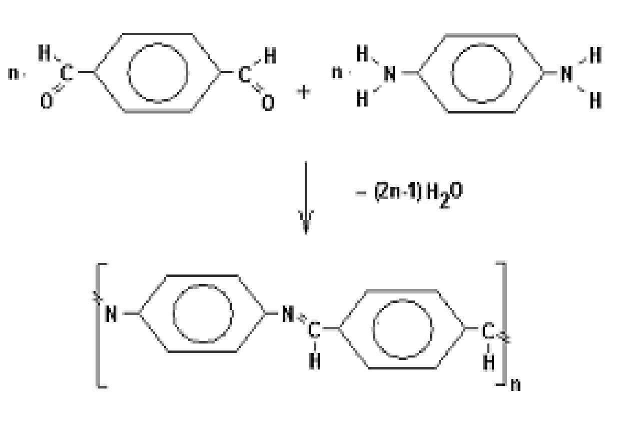

Fig. 1. The polycondensation process of terephthaldehyde and phenylenedemine

The thickness of thin films was about 100 – 300 nm, depending on time of deposition. To prepare polyazomethine layers doped with iodine, PPI thin films deposited onto glass substrates were placed in iodine atmosphere for several days. After this time the samples were uncovered and stayed in air for time long enough to remove iodine from the surfaces of samples. The doped layers were annealed at 250˚C to remove eventually I_2 adsorbed onto the film surface.Optical spectra of PPI thin films were recorded with JASCO spectrophotometer within 200 – 2500 nm wavelenght interval.AFM images were recorded on films with Atomic Forces Microscope Thopometrics Explorer, working in contact mode. Diffraction spectra were taken on X-Ray Diffractometer TUR M-62. All measurements were preformed at room temperaure.

3. Results and discussion

Thopographic images performed in contact mode given in Fig. 2 a) and b) show morphology of pristine and doped PPI thin films. It is very easy to see, that image of doped PPI reveals the more granular character of surface morphology. The surface of pristine PPI is more plain, which is consistent with RMS coefficients for pristine and doped PPI being 5.98 nm and 8.26 nm, respectively.

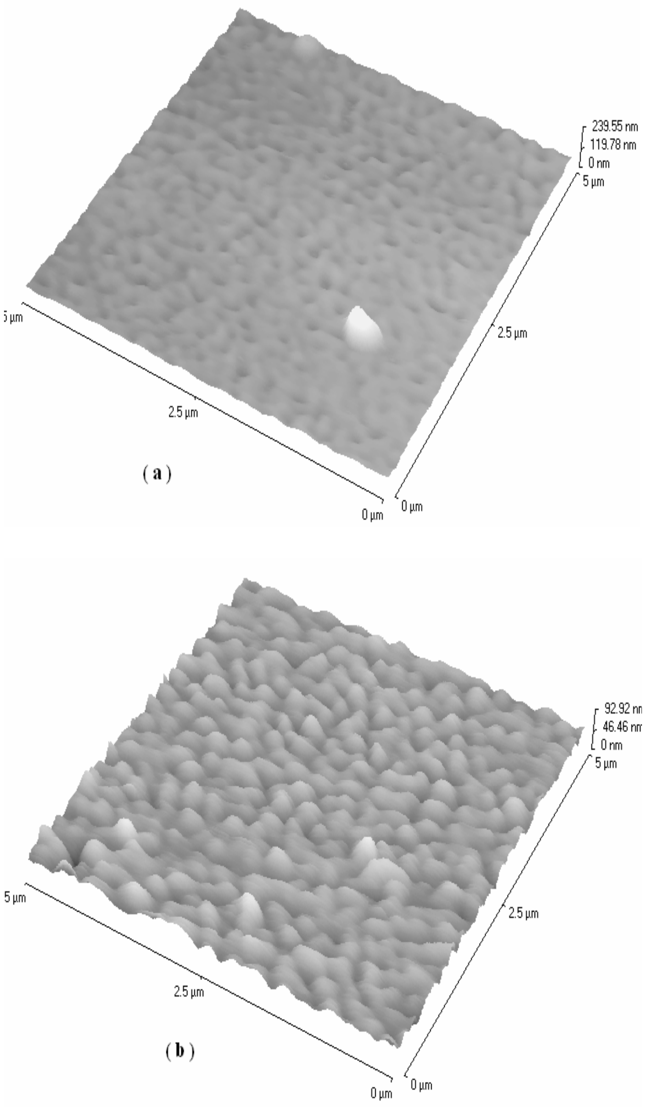

Fig. 2 a) Pristine PPI AFM (3D -) topography 5x5 µm; b) PPI doped with iodine AFM (3D -) topography 5x5 µm

Diffraction patterns of pristine and doped PPI are shown in Fig.3. It is clearly seen in Fig. 3 that there are two strong peaks at about 20.82 and 23.76 degrees, the letter one being the strongest. Location of these peaks is similar to those reported by Proń [9] for powder samples of PPI. Average size of PPI grain obtained from Scherrer's formula for pristine and doped PPI layer is similar and is about 140 Å.

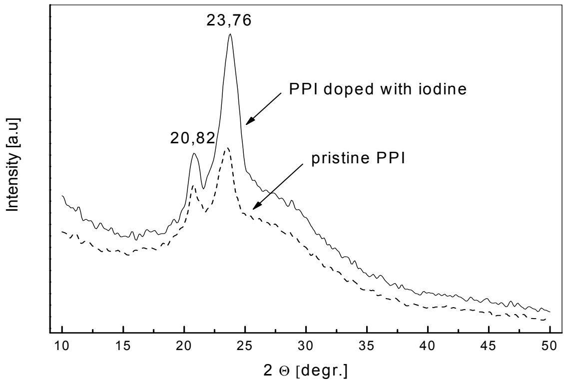

Fig. 3. XRD diffraction pattern of pristine PPI (dashed line) and PPI doped with iodine (solid line) .

The spectrum taken on PPI thin film kept under iodine vapour during 12 days and the one taken on this film after its annealing at 250 ˚C through 20 minutes are shown in Fig. 4. As reference the spectrum of pristine PPI is added. It is seen that thin film doping have resulted in smearing absorption edge and the shape of the absorption edge indicates on presence of a weak band at about 2.25 eV, absent in pristine PPI. Higher energy part of this band connected with delocalised states does not change very much. It is clearly seen that doping influences mainly HOMO and LUMO states. The absorption band at about 2,25 eV is expected to be due to dopant induced states within HOMO - LUMO gap.

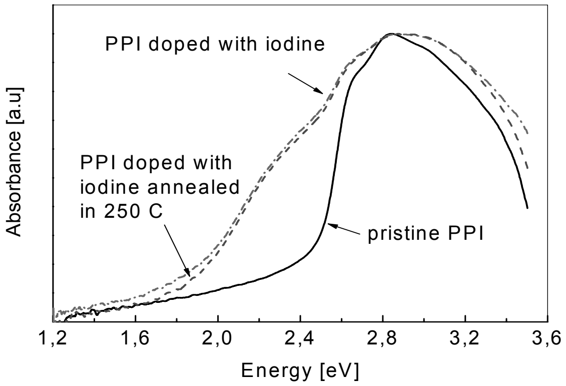

Fig. 4. UV-VIS absorption spectrum of PPI doped with iodine (dashed line) and pristine PPI (solid line)

The absorption band attributed to interband transitions between delocalised states is much broader then that of pristine PPI. It is clearly seen that spectra of PPI doped with iodine and annealed at 250 ˚C are very similar and annealing does not change location of peak maximum at 2,2 eV .

The schematic presentation of pristine PPI with marked lone pairs on nitrogen sp^2 orbitals is shown in Fig. 5:

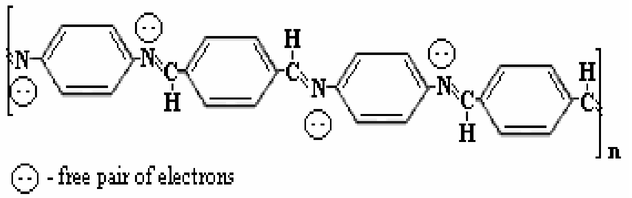

Fig. 5. Scheme of conjugated undoped polyazomethine PPI

The reaction of doping with iodine is thought to run as below [10-13]:

$$(PPI) + 3I_2 \longrightarrow 2I_3^- + (PPI)^+ \qquad (1)$$

Then, it is expected that doping mechanism is connected with removing electron from PPI HOMO level leaving positive hole behind and electron I_3^- counterions formation.

Positive polarons formation in PPI thin films is connected with tranformation of conjugated benzenoidal chain fragment into quinodal one. The scheme of PPI doped with iodine, with formed quinodal form is shown in Fig. 6 [14]:

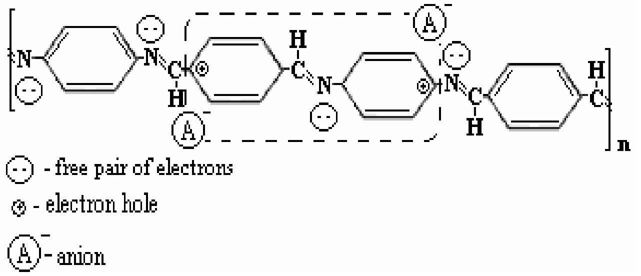

Fig. 6. Quinoidal form of polyazomethine PPI during process of dopant oxidation, A^- is dopant counterion

The forces, which are responsible for maintainig of anions near positve sites on polymer chain are Coulomb's forces. Thus, iodine doping of PPI leads to formation of polaron states inside energy gap.Polaron state consist of lower energy level with one unpaired electron and higher energy empty level, similarly as reported in [15], [16]. The scheme of polaron in doped PPI and schematic elecronic structure of pristine PPI is shown in Fig. 7.

Polaron contains one unpaired electron on HOMO[15], which is shifted into energy gap and unoccupied state which is shifted into energy gap too. So the role of LUMO takes next, nearest level in conduction band and HOMO role takes nearest level in valence band. The result of this process are additional transitions with required energy lower than HOMO – LUMO ($\pi \rightarrow \pi^*$) gap.

4. Conclusions

The doping mechanism with I_2 is p – type. Smearing of absorption edge and all the delocalised band and appearing of weak band at about 2,2 eV, which are visible in optical absorption spectra suggests formation of polarons inside PPI energy gap.

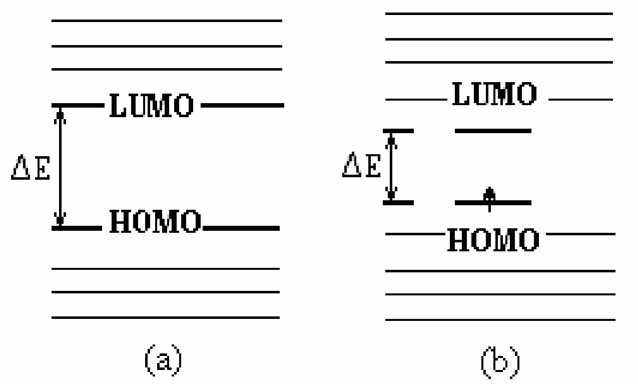

Fig. 7. Formation of polaron state in energy gap of PPI conjugated polymer, a) pristine PPI , b) doped PPI

The annealing of doped layer did not influence significantly for asbsoption spectrum. Peak maximum at about 2.2 eV did not change its location in spectra before and after annealing.

The intensity of peaks maxima at 20.82 degrees and specially at about 23.76 degrees is higher for PPI doped with iodine in XRD spectrum, also RMS coefficient of doped layer increased from 5.98 nm to 8.26 nm.

It is expected that doping process will result in better conductivity of doped PPI. The electrical measurements will be carrying out in the nearest time, and they expected to be confirmation for optical measurements.

Acknowledgement

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