

Tailoring electronic structure of polyazomethines thin films

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ABSTRACT

Purpose: The aim of this work is to show how electronic properties of polyazomethine thin films deposited by chemical vapor deposition method (CVD) can be tailored by manipulating technological parameters of pristine films preparation as well as modifying them while the as-prepared films put into iodine atmosphere.

Design/methodology/approach: The recent achievements in the field of designing and preparation methods to be used while preparing polymer photovoltaic solar cells or optoelectronic devices.

Findings: The method used allow for pure pristine polymer thin films to be prepared without any unintentional doping taking place during preparation methods. This is a method based on polycondensation process, where polymer chain developing is running directly due to chemical reaction between molecules of bifunctional monomers. The method applied to prepare thin films of polyazomethines takes advantage of monomer transporting by means of neutral transport agent as pure argon is.

Research limitations/implications: The main disadvantage of alternately conjugated polymers seems to be quite low mobility of charge carrier that is expected to be a consequence of their backbone being built up of sp² hybridized carbon and nitrogen atoms. Varying technological conditions towards increasing reagents mass transport to the substrate is expected to give such polyazomethine thin films organization that phenylene ring stacking can result in special π electron systems rather than linear ones as it is the case.

Originality/value: Our results supply with original possibilities which can be useful in looking for good polymer materials for optoelectronic and photovoltaic applications. These results have been gained on polyazomethine thin films but their being isoelectronic counterpart to widely used poly p-phenylene vinylene may be very convenient to develop high efficiency polymer solar cells

Keywords: Polyazomethine thin film; Chemical vapor deposition; Vacuum evaporation; Electronic structure; Polymer photovoltaics

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1. Introduction

Aromatic polyazomethines belong to alternately conjugated polymers having backbones composed of alternate phenylene rings and azomethine linkages [1-4]. The simplest one of them is poly(1,4-phenylenemethylenitrilo-1,4-phenylenitrilomethyliden), which is designated PPI [1] and this is an isoelectronic counterpart to poly(p-phenylene vinylene) (PPV), both of them having the same number of π electrons [3-6]. The UV-Vis optical spectra of PPI thin films are very similar to those of PPV ones, which means that the two polymers being quite different, their π electronic structures are very similar [3,6]. PPI thin films can be modified by means of doping with FeCl_3 during the deposition process or putting PPI thin films having grown under iodine atmosphere [7,8]. There were made modifications of the polymer backbone by incorporating into PPI chain oxygen atoms in ordered way, but these methods are beyond the scope of this paper and will not be taken into account. These efforts have been completed to understand electronic structure of thin films of aromatic polyazomethines and PPI in particular. These polymers having phenylene rings and azomethine linkages alternately distributed along with the backbone has electronic structure whose features are troublesome to describe [9-11]. The aim of this paper is to show how electronic structure of PPI thin films can be controlled by technological parameters of the deposition process used to prepare them. In the case of PPI itself this can be done by varying such technological conditions of PPI thin films depositing as the transport agent flow rate, source monomers temperatures and their difference. Our interest in PPI thin films is connected with similarities observed and reported between UV-Vis and IR spectra taken on PPI and PPV thin films [11]. Moreover, this resemblance of their optical spectra indicate that the presence of lone electron pair allocated on sp^2 orbital of each nitrogen atom along the backbone counteract against the chain planarity as steric hindrances do impose on the planarity of PPV backbone [4,11], even though one should bear in mind that quite different effects are of importance in the two cases. The purpose of our investigations on PPI thin films is connected not only with feasibility of its potential applications, but also PPI, in contrast to PPV, can be prepared in much simpler way applying technology based on polycondensation process between aromatic diamines and dialdehydes without any need to use precursor way [11]. Taking into account similarities of their electronic structures one might expect that they will be as well suitable for optoelectronic and photovoltaic applications but in contrast to PPV they can be prepared directly via polycondensation without using any precursor ways.

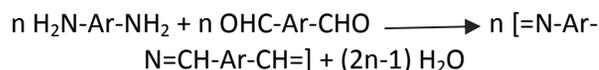
2. Experimental

Aromatic polyazomethines, sometimes called Schiff bases [1], seem to be very promising for photovoltaic or optoelectronic applications [1-8], as in many respects they resemble PPV widely used in optoelectronic applications. Thin films of PPI expected to be suitable for photovoltaic applications are prepared by chemical vapor deposition method based on polycondensation of PPDA and

TPA [12]. This technique is very convenient for preparing pure films but it can be applied only while polymerization is going through condensation as the only product that is removed from the reaction volume is a low weight molecular material. In case of polyazomethines this is one water molecule, removing of which from the reaction volume being responsible for the reaction progression. Otherwise, if such molecules were not removed the polycondensation reaction would be postponed, as increase in quantity of any reaction product results in its slowing down.

2.1. PPI thin films preparation

Thin films of PPI have been prepared by thermal high vacuum evaporation and chemical vapor deposition method (CVD) [13] based on polycondensation process between p-phenylene diamine (PPDA) and terephthal aldehyde (TPA) [6]. Pure gaseous argon as a transport agent was used in the CVD method to produce PPI thin films and its stream was forked into two or three equal streams flowing each over a boat containing one monomer and the third one flowing over a boat with doping material [6]. Then, the streams were merged into one stream transporting mixed molecules towards the substrate, following an idea outlined in the schem shown in Fig. 1 [6]. This CVD method used is thought to be the one where pure PPI thin films without any unintentional doping can be prepared, which is a consequence that no chemical reactions between transport agent and the transported monomers molecules are running. Thus, argon is used to transport monomers molecules from the source to the substrate. That technique might be used while preparing thin films of polyazomethines insoluble in organic solvents [6]. The polycondensation reaction used to produce PPI thin films is defined by:



For the chemical reaction to run towards PPI thin film formation one should have stoichiometric amounts of the two monomers and low weight molecular product, here one water molecule at each step, must be removed from the reaction chamber [6]. The technique used, it is required for monomers put into a boat to be sublimed and their vapor to be taken up by argon flowing over a boat to transport them towards the substrate, which were made of glass or fused silica plates kept at room temperature. PPDA vaporization temperature being higher than that of TPA, one should heat both boats containing monomers in such a way that PPDA temperature to be higher than that of TPA on about 10°C or more [6]. During the deposition process the system is being evacuated with the use of a rotary pump for unreacted monomers or those re-evaporated from the substrate surface to be removed out from the reaction chamber.

The same method was used to prepare thin films of other polyazomethines from TPA and larger aromatic di-amines [9,10]. It is expected that PPI thin film growth is governed the intensity of the stream of monomers impinging onto the substrate covered with growing film.

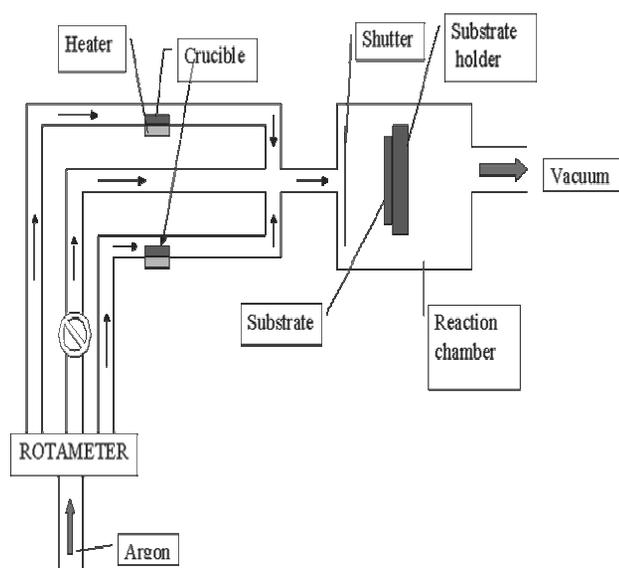


Fig. 1. The idea of the CVD deposition of PPI thin films via condensation polymerization

2.2. PPI thin films examination

The as-prepared PPI thin films have been investigated with the use of UV-Vis spectrophotometer, while their structure was examined by X-ray diffraction technique and morphology with atomic force microscope (AFM). To have any additional mean to confirm that these are really polyazomethine thin films FTIR spectra were taken on PPI thin films as-deposited onto plates of pressed KBr [6-8]. Methodology of PPI thin film preparation was discussed in detail elsewhere [6]. But here we would like to direct our attention to the question how variations of CVD conditions influence electronic structure of these films. Our earlier works proved that UV-Vis absorption measurements supply with quite correct data on electronic structure of PPI.

3. Results and discussion

The results of investigations made on the CVD prepared thin films of PPI are discussed below. Structure and surface morphology as well as their optical properties are presented and discussed in terms of how technological parameters of thin films preparing can be used to tailor their electronic structure.

3.1. Structure and morphology of PPI thin films

The structure of PPI thin films deposited by CVD method has been deduced from X-ray diffraction patterns illustrated in Fig. 2 for pristine and FeCl_3 doped PPI thin films. One can see that both

diffraction patterns reveal broad amorphous background with superimposed peaks indicating on the presence of ordered areas in either film. Amorphous character is pronounced by a broad maximum peaking at about 25 deg, which have appeared in both patterns to nearly coincide. On these two backgrounds one can see superimposed peaks at about 21 and 24 deg, which in case of pristine PPI are rather weak and broad ones, the latter being the strongest. In contrast, the peaks revealed by FeCl_3 doped PPI thin film have appeared to be much stronger ones and pushed slightly towards larger angles, but the intensity increase is seen to be much stronger for 24 deg peak. This effect is attributed to some decrease in atomic plane separation as a consequence of PPI chain planarization caused by transformation of some fragments of conjugated segments from benzenoid into quinoid form due to electron removing from HOMO states and polaron states formation. Such planarization could result in stronger attraction due to van der Waals forces resembling chain segments stacking. Similar effects were reported on PPI thin films iodine dope [8]. PPI thin films, independently of technological conditions under which they were prepared, have revealed granular morphology. Some changes in morphology were connected with increasing the flow rate of the transport agent stream and monomers temperatures. The latter are thought to be more important factors than the flow rate only. AFM images, sensor and three dimensional ones are shown in Fig. 3 a and b, respectively, for PPI thin films prepared under $T_{\text{TPA}}=60^\circ\text{C}$ and $\Delta T=20^\circ\text{C}$ with flow rate of about $0.07 \text{ hPadm}^3\text{s}^{-1}$. For comparison, in Fig. 4 AFM sensor (a) and three dimensional (b) images of PPI thin film prepared at the same temperature regime used but with flow rate equal to about $1.33 \text{ hPadm}^3\text{s}^{-1}$.

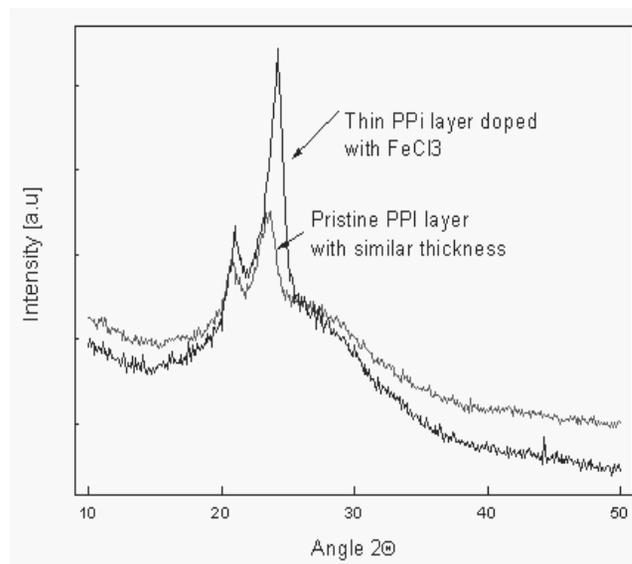


Fig. 2. Diffraction pattern of FeCl_3 doped and pristine PPI thin films

One can see that the surface morphology is granular and rather homogeneous while lower flow rate of argon stream was used.

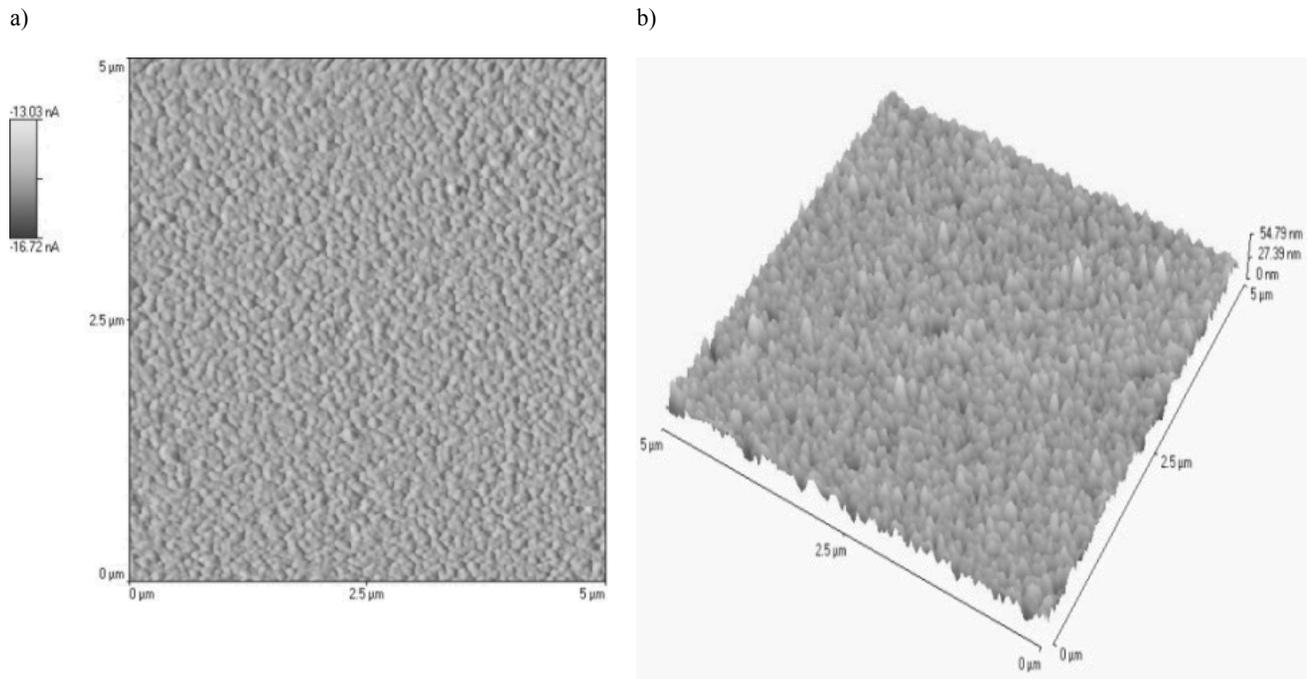


Fig. 3. AFM images of PPI thin film prepared with T_{TPA} 60C and ΔT 20C with the lowest flow rate $6.5 \text{ Padm}^3\text{s}^{-1}$

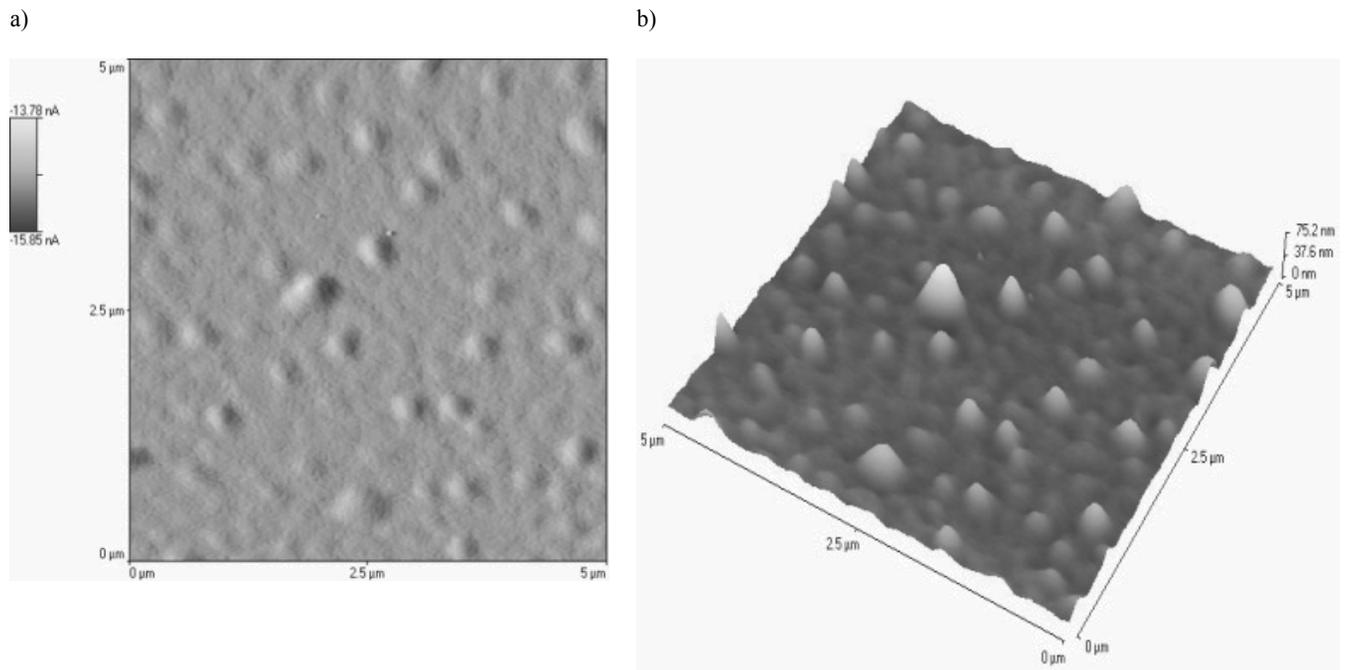


Fig. 4. AFM images of PPI thin film prepared with TTPA 60C and $\square T$ 20C with the higher flow rate $1.3 \text{ hPadm}^3\text{s}^{-1}$

Increase in flow rate brought about some fusion of nearest grains, while compared with the film deposited with lower rate, and additional larger grains randomly distributed over the film surface are observed.

The surface roughness is seen to be within 35 nm, while in case of increased flow rate it attains some 70 nm. One can also see that the increase in the stream flow rate resulted in merging neighbor granule to make the surface as it was built up of lamella.

Additionally, one can see quite numerous larger grains to grow up, which could be related with some ordering of the PPI film structure. Generally, it was found that the essential impact on the film structure and its morphology comes from variations in the intensity of the monomers stream impinging onto the substrate rather than any individual impact of temperature or their difference or flow rate individually, i.e. their combination. Some support for such conclusions come is aided by optical measurements, which have proven that this is the stream intensity having decisive impact on the recorded spectra. In fact, while the flow rate was slow enough one could see that the influence of overall heating was rather small, which was revealed by rather small variations of absorbance strengths of the UV-Vis spectra taken on the films deposited during various periods of time.

3.2. Optical spectra

Absorption spectrum of PPI thin film deposited by CVD method onto quartz substrate is illustrated in Fig. 5, where the strongest band at about 3.0 eV is due to interband transitions connecting HOMO and LUMO delocalized states, while feature at about 4.0 eV is attributed to Frenkel exciton related to interband transition peaking at about 5.0 eV with dominant contribution from benzene α band [11].

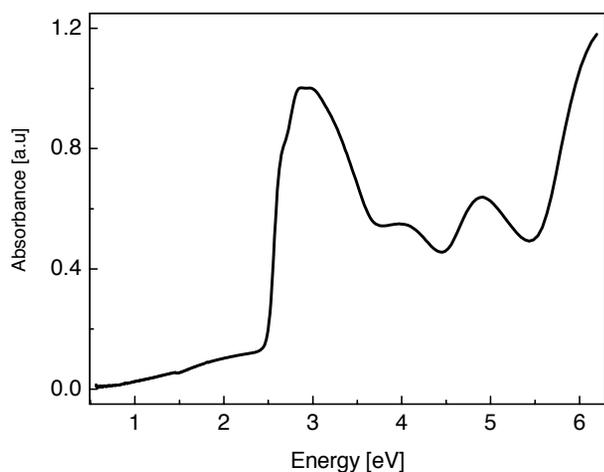


Fig. 5. Absorption spectrum recorded on PPI thin film deposited onto quartz substrate

The growing absorbance strength at energies above 6 eV due to higher energy bands with strong contribution from benzene states. As any changes in optical spectra coming from varying technological conditions are expressed by variations of the shape of the low energy band, the optical spectra recorded on PPI thin films deposited onto glass substrate under various technological conditions marked are illustrated in Fig. 6. One can see in this figure how the flow rate of the stream influences the shape of the spectrum, while temperature of terephthaldehyde was 60°C and temperature difference with respect to p-phenylene diamine was equal 20°C.

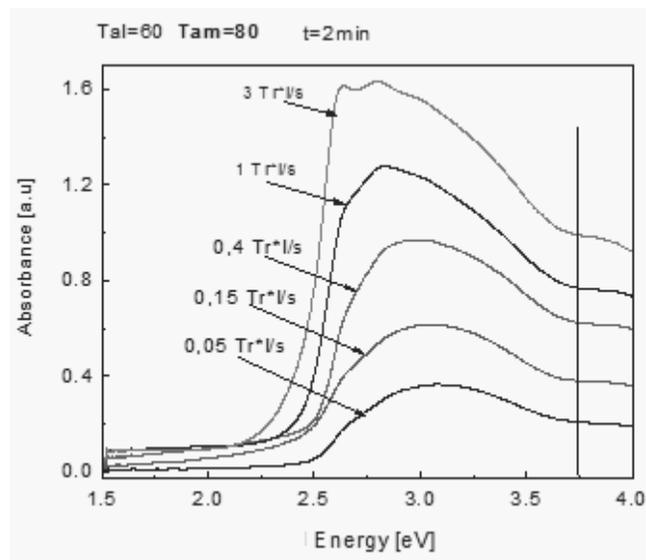


Fig. 6. Absorption spectra taken on PPI thin films prepared under conditions indicated in the figure

These spectra are limited to presentation how technological conditions influence the strongest lower energy band attributed to interband transitions connecting HOMO and LUMO delocalized states. One can see that the spectra depend in rather important way on mass transport of monomers to the substrate, which is thought to be some resultant of the source temperatures and their difference combined with flow rate of the transporting agent stream. It is indicated in this figure that the spectral area in the vicinity of 3.75 eV depends on the film thickness rather than on other effects. While comparing these spectra one can see weakly marked vibronic states associated with strong interaction of electronic transitions with chain vibrations. For low flow rates, the band maximum is pushed to higher energies, which is related to shorter lengths of conjugated segments of PPI chains. The shapes of three strongest bands indicate that some lengthening of conjugated fragments is observed in the spectra of PPI thin films prepared with higher stream intensities, while the maximum shift to lower energies may suggest that for these films the minima of potential energies of the electronic ground and excited states are less displaced than in the case of films prepared with low

flow rates of argon. The strongest spectrum taken on a film prepared with the highest flow rate one can see Wannier exciton overlapping absorption band, which is attributed to stacking planarized conjugated segment of polymer chains [6,11,14,15]. Besides of the above discussed influence of technological conditions on optical properties of PPI thin films some modifying their electronic structure can be done by placing the as-prepared thin films in the iodine atmosphere, which is frequently said doping, even though this quite different process than the one applied for inorganic semiconductors to increase their conductivity [13].

Here, iodine is used to remove electrons from HOMO level of the PPI, so that a hole is produced. At the same time negative iodine ion associates with I_2 molecule so that I_3^- counter ion is created in the vicinity of a positive hole at polymer chain. While putting PPI thin film under iodine vapor one may expect that reduction process is under way or a hole in the π system arises. For removing electrons this process resembles that of semiconductor doping but for alternate conjugation of the backbone one arrives at quite different situation, which seems to properly designate forming new material with semiclosed shell systems. PPI system is built up of units fulfilling $4n+2$ Hückel rule, which means these units form rather compact π systems even though there is distinct connectivity of their molecular orbitals extending between limits of each conjugated segment. Because of that their spectra are thought to reveal features characteristic of them. In PPI spectra of absorption one can see absorption band whose position corresponds quite well with benzene α band [11].

However, while a film is put under influence of iodine vapors, some π electrons from the system are removed and I_3^- associated counter ion appears. While considering now any conjugated segment one may expect that removing an electron is softening π system and its parts. That means, a conjugated segment with phenylene or azomethine group missing electron appears. For benzene π system it means breaking out its high symmetry and lifting degeneracy between simultaneous HOMO-LUMO transitions, which results in lifting degeneracy between (ϕ_3, ϕ_4) and (ϕ_2, ϕ_5) configurations. In effect, energy level connected with ϕ_3 molecular orbital is moved upward, while that connected with ϕ_4 molecular orbital being moved downward. At the same time, the gap between ϕ_2 and ϕ_5 molecular orbitals, having nodes at benzene para positions, related levels becomes larger. Then, one may expect that narrower gap appears, modified by their interactions with ethylene HOMO and LUMO orbitals. This effect corresponds rather well with polaron formation and gap diminishing. At the same time, one can see that configuration interaction between (ϕ_3, ϕ_5) and (ϕ_2, ϕ_4) states. Is conserved, but the gap is pushed upward. When doping level is higher, this process is very emphasized so that the number of hole being on the increase.

However, one should bear in mind that in conjugated polymers any removing or adding electron is associated with modification of π electron system of the conjugated system. Effectively it means this system is divided on three or more parts, dependently on the degree of doping. The resultant

picture that is expected to be visible in absorption spectra depends on the degree of thin film doping.

Additionally, polaron formation [7,8] results in quite visible decrease in the forbidden gap of PPI, how it is given in Fig. 7. Removing one electron from nit cell means that there missing one electron allocated on phenylene ring and some deformation is started with fully symmetric vibration and ring stretching vibrations, which split off benzene degenerate HOMO levels [11]. In consequence molecular orbital with phases at para positions displace to lower energies and the component with nodes is pushed to higher energies. Resulting spectrum is shown in Fig. 7.

While discussing optical spectra it seem reasonable to take into consideration electronic structure of elementary unit cell of PPI chain. It is shown in Fig. 8, where E'_1 represents the ground state and E'_2 is the lowest energy level from which the lowest conduction band is derived as shown in Fig. 9, corresponding to 2.8 eV, while the band observed at about 4.0 eV is due to transition to Frenkel exciton related to E'_3 . These transitions are indicated in Fig. 9 where electronic band structure of PPI is presented. The effect of doping on electronic spectra of PPI thin films is observed by decreasing the gap to E'_2 energy level, which is seen by appearance of a band at about 2.0 eV seen in Fig. 7.

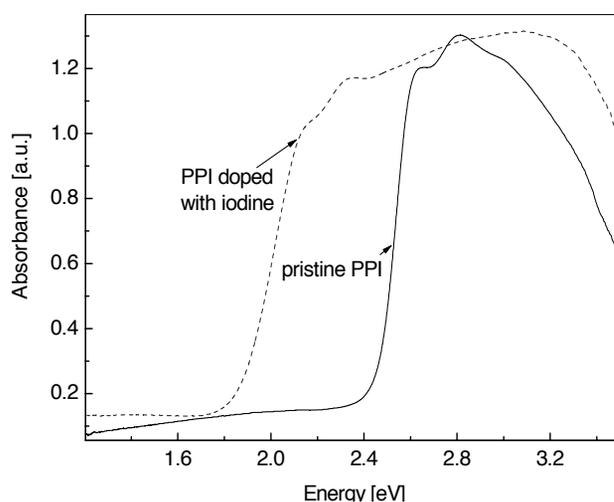


Fig. 7. Optical spectra of pristine and iodine PPI

Additionally one can see that a broad band peaking at about 3.2 eV is seen, which is attributed to shortening conjugated fragments as a result of polaron formation. This polaron formation is associated with transformation of benzenoid form of conjugated segment in the pristine PPI into quinoid one characteristic of iodine doped PPI thin film.

When analysing optical spectra shown in this paper and their relevance to PPI thin film structure one should bear in mind difference in charge density distribution deposited with very high flow rates reflect possibility of some sort of stacking

conjugated segments of neighbor chains whose π orbitals strongly interact, i.e. the segments appear to be parallel to one another.

In consequence, π electrons are not limited to σ and π orbitals. The former ones have maximum of charge distribution in the plane designated by sp^2 hybridized orbitals of chain skeletal carbon, while minimal density distributions of π orbitals are above and below this sp^2 plane.

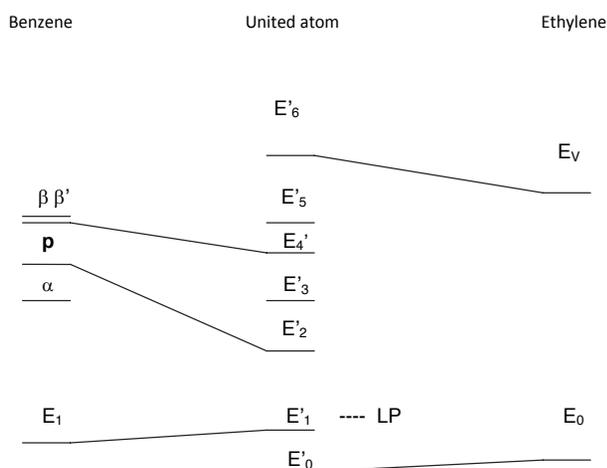


Fig. 8. Electronic levels of PPI unit cell [10]

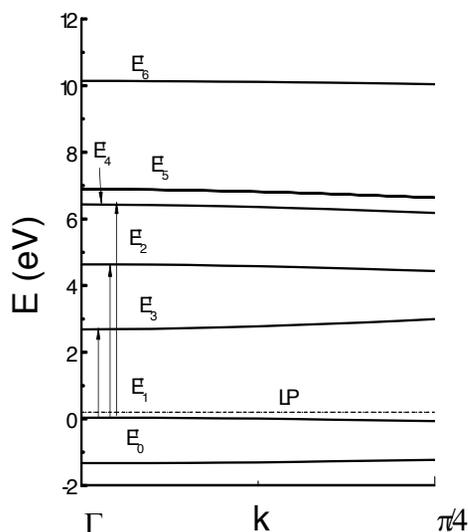


Fig. 9. PPI electronic band structure [10]

That means, small twist of a chain segment around σ bond interrupts conjugation with other segment of the polymer chain. In the spectra taken on PPI thin films deposited with low flow rates is reflected distribution of lengths of conjugated segments within

the film, on the same or other chain. In contrast, it is expected that the spectra taken on PPI thin films any individual segment but some aggregated entity resembling to some extent crystalline structure, so that Wannier exciton can be formed.

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Additional information

Selected issues related to this paper are planned to be presented at the 16th International Scientific Conference on Contemporary Achievements in Mechanics, Manufacturing and Materials Science CAM3S'2010 celebrating 65 years of the tradition of Materials Engineering in Silesia, Poland and the 13th International Symposium Materials IMSP'2010, Denizli, Turkey.

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