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Volume 6 (24) 2013

Jan Wieszka

**Technology and properties
of polyazomethines
thin films**



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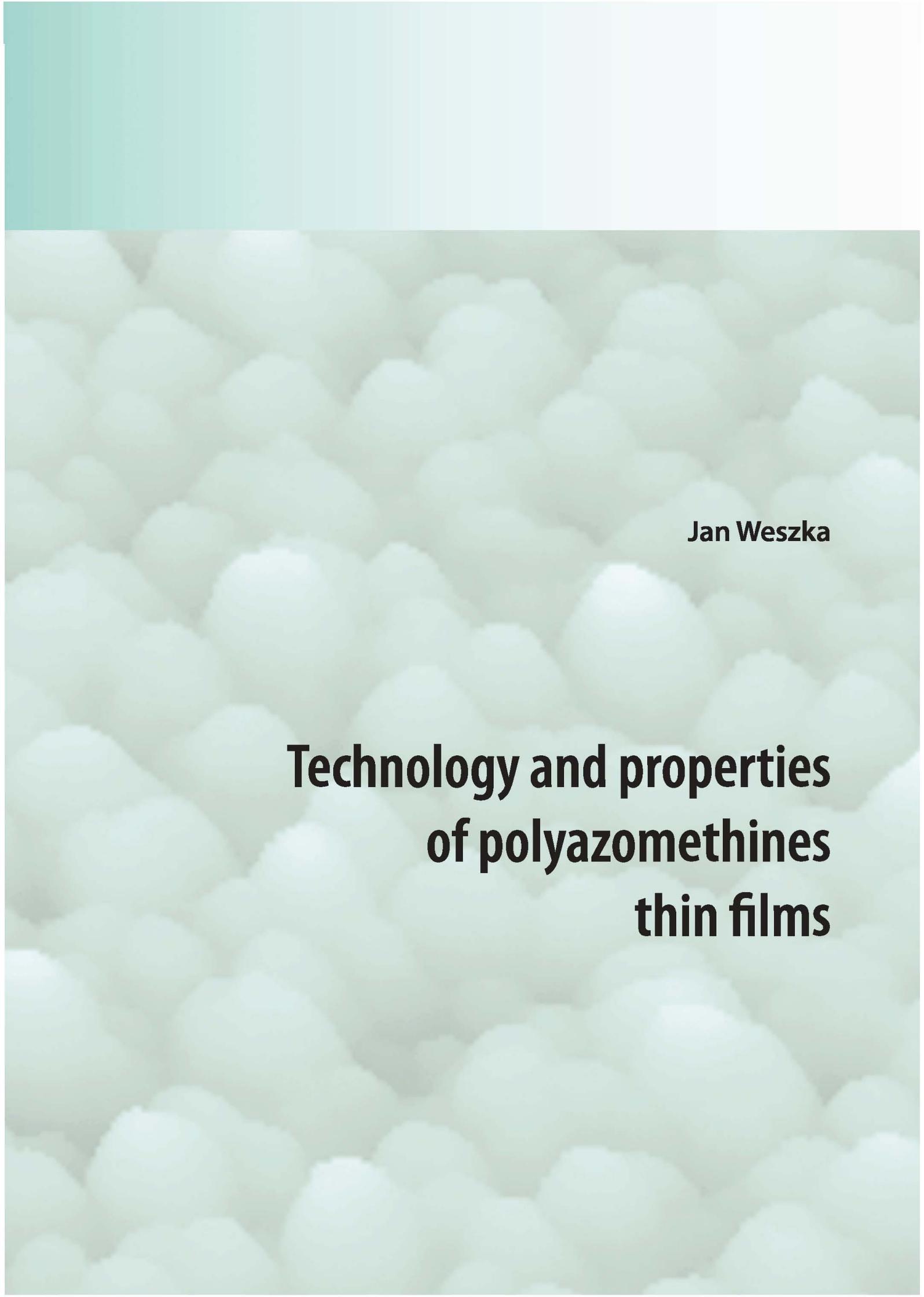
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Abstract

Purpose: *The objective of this paper is to carry out an analysis of the having so far been received results of investigating on polyazomethine thin films for their applications in photovoltaic devices and finding out any relations connecting film: morphology, structure and optical properties, as well as describing electronic structure of polyazomethines of various chain backbone and both doped and protonated polyazomethines based on the model of electronic structure of PPI thin films.*

Design/methodology/approach: *Polyazomethine thin films have been prepared using the methods of chemical vapour deposition, physical vapour deposition and spin-coating based on polycondensation of aromatic diamines and dialdehydes and thin films of polyazomethines with side chains prepared by spin-coating from solution in organic solvent. The results having so far been prepared were published, however, gaining knowledge of phenomena going on requires for the results were collected and analysed critically whether electronic and optical properties of polyazomethine thin films can be controlled by means of the film morphology.*

Findings: *It was found out that within π electron approximation one can describe the electronic structure of polyazomethine PPI, and give an account of observed variations of the optical spectra in case of soluble polyazomethine with side chains, and the spectrum variation due to doping or protonation. While using this model one can interpret optical spectra of polyazomethines having oxygen atoms or various aromatic units in the backbone.*

Research limitations/implications: *Some limitation of the used methods of preparing polymer thin films from vapour phase is technique of producing bulk p-n junction as a film with organic*

molecules homogeneously spread over throughout polymer matrix, and in case of soluble polyazomethines the limitation is the same. Other limitation seems to be aromaticity of benzene ring, its coupling with lone pair on trigonal orbital of nitrogen atom. May be some additional limitation in this sense is chain character of conjugated polymers, making them one dimensional conductor wire.

Practical implications: *It is expected the results of this paper can be used to working out technology of producing high performance organic solar cells or electroluminescent diodes.*

Originality/value: *It has been proven that the elaborated model of the electronic structure of thin films of polyazomethine PPI, whose the backbone is composed of alternately distributed phenylene rings connected at para positions (1,4) with azomethine linkages can be used successively to interpret optical effects driven by doping or protonating these layers, in case of prepared by spin-coating from solutions it explains differences observed in the shape of optical spectra taken on PPI and BOO-PPI as well as polyazomethines containing biphenyl, fluorene or naphthalene entities in the backbone.*

Keywords: *Polymer materials, Thin polymer layers, Polymeric solar cells, Optoelectronic properties of organic photovoltaic structures*

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1. Introduction

Among polymer materials there is a group of alternately conjugated polymers which have revealed interesting electronic properties resembling them to some extent to inorganic semiconductors [1-6]. Characteristic feature of conjugated polymers which distinguish them from other groups of polymers is alternation of single and double bonds along with the polymer backbone, which is possible due to sp^2 hybridization of carbon atoms constituting the backbone [4,7,8]. Aromatic polyazomethines, known also as the Schiff bases [9-11], belong also to alternately conjugated polymers having azomethine linkage in the backbone, resembling vinylene one in which one CH methine group is replaced by nitrogen atom. Polymers belonging to this family have been for many years of interest due to their good thermal stability and interesting optoelectronic properties [12-21]. There are polyazomethines with alkoxy side chains that can be prepared by solvent-based polymerization, so that their thin films can be deposited by solvent based or spin-on techniques [11-22]. However, applicability of this method concerns soluble polymers only, and that is why thin films of insoluble polyazomethines can be prepared by such methods as the thermal vacuum evaporation (TVE) or chemical vapor deposition (CVD) via polycondensation [11-22]. It should be emphasized that polyazomethine thin films while being prepared by these two methods are free from unintentional impurities, in contrast to solvent-based polymerization or spin-on coating techniques where unintentional impurities cannot be avoided [22]. The simplest representative of aromatic poly(azomethines) is poly(1,4-phenylene-methyldynenitrilo-1,4-phenylenenitrilomethyldiyne), which will be referenced as PPI [9], which has the backbone consisting of alternately repeating paraphenylene and azomethine linkage. Being an isoelectronic counterpart of poly(paraphenylene vinylene) (PPV), PPI has been expected to be suitable for photovoltaic and other optoelectronic applications [11-22]. The aim of this work is to review our achievements in studying electronic properties of PPI thin films prepared by dry methods such as CVD and VTE and wet methods concerning deposition of PPI thin films by spin-coating from solution, as well as reconsider feasibility of PPI thin films applications for photovoltaic or optoelectronic structures and their dependence on technological conditions of their preparation. Our interest in studying the CVD prepared PPI thin films is also to better understand mechanisms of condensation polymerization process running at the interface

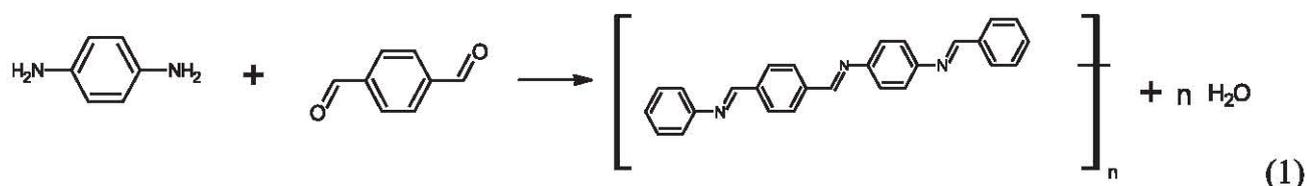
of the vapor/solid phase, structure and morphology of as-deposited films as well as the electronic structure of polymers having nitrogen atoms in the backbone [11,22,23]. These conjugated polymers have been called polymer semiconductors, but one should bear in mind that the term semiconductor means that electrical properties of this group of inorganic materials reveal conductivities small compared with metals [24,25], but much higher than this is the case in conjugated polymers[5,6,24]. Though, there have been undertaken research works to improve conductivity of these materials by means of so called doping, as this is done in case of inorganic semiconductors. However, here the term doping is used to indicate technological activities, which are thought to more resemble interstitial doping in inorganic crystals rather than substitution doping having been widely used to vary conductivities in semiconductors [23]. The backbones of the alternately conjugated polymers being built up of sp^2 hybridized carbon atoms linked together by alternate single and double bonds, electronic transitions involving π electron states are not connected with any destruction of the polymer chain. They have appeared to be of great importance, because in contrast to saturated polymers, the electrons allocated on trigonal orbitals are involved in strong enough valence σ bonds connecting two nearest neighbor carbon atoms and a hydrogen atom, while the fourth electron of each carbon atom in the chain of alternately conjugated polymer is allocated on its p_z orbital contribute to the system of delocalized electrons due to overlap of the orbitals of the nearest carbon atoms spreading out over a conjugated segment of the backbone [4-8]. Thus, one can say that alternately conjugated polymers are characterized by electron system composed of two types of electrons, the electrons involved in σ bonds and delocalized electrons from p_z orbitals, which are called π electrons. Such division of valence electrons of the constituent elements into σ and π electrons has appeared to be not only very convenient, but also it appeared to be very utile to give an account of electronic properties of the polymers under question [4,7,8]. This separation of the polymer electrons in two electron entities independent of each other makes out the core of Hückel method widely used to describe electronic properties of polymers and molecules with alternately conjugated atomic systems [7,8]. In spite of its great simplicity, this method has appeared to be very utile while interpreting electronic properties even in case of quite complex conjugated polymers [7,8]. The idea of separating σ electrons from π electrons, which is behind this model and its various modifications makes a basis for π electron approximation [7,8] and it was used in our previous paper on poly(paraphenylene azomethine) (PPI) thin films optical properties [22,26-28], with configuration interaction being

taken into account [28]. While deriving electronic structure of PPI thin films [28], its backbone was approximated with the backbone of poly(paraphenylene vinylene) (PPV) using approach resembling to some extent the one made by Brazovskii and Kirova [29-31] for PPV. Moreover, this model is thought to correspond rather well with reported similarities of both electronic structure and optical spectra of the two polymer materials [19,20,22]. Then, it is aimed in this paper to give a comprehensive description of electronic structure of polyazomethines alternately conjugated polymers with nitrogen atoms in the backbone. Taking advantage of π electron approximation it has been intended to show physics standing behind description of electronic structure of poly(paraphenylene azomethine) PPI from π electron systems of phenylene ring and azomethine linkage. This approach is thought to be suitable for discussion optical properties of not only pristine PPI thin films but also doped and protonated one, as well as PPI with alkoxy side chains and polyazomethines with larger alternately conjugated system based on phenylene, naphthylene, fluorene and biphenylene entities together with azomethine linkages [26,32,33]. On comparing alternately conjugated polymers to inorganic semiconductors one should bear in mind that in the former ones there are electrons involved in chain bonding to keep it together (σ electrons) and there are other electrons contributing to optical transitions (π electrons), while in the inorganic semiconductors the electrons involved in atom bonding contribute to optical transitions [25]. In fact, the system of atom binding in inorganic solids is the one of σ type and their structure takes on form of ordered or disordered but three dimensional networks, so that any electron excitation is not expected to destroy the network as only dangling bonds can be formed. It is thought that chain character of atom binding in thin films of alternately conjugated polymers has appeared as their drawback while considering their optoelectronic applications. It is connected also with charge density distribution in p_z orbitals, which is different from zero above and below the plane of sp^2 orbitals, in contrast to σ orbitals having charge density along the bond connecting subsequent carbon atoms [4]. This makes π electron system vulnerable on twisting of the planes of sp^2 orbitals of the carbon atoms belonging to two conjugated segments, so that it is one of the most important factors counteracting phenyl rings planarization along with the backbone and existing conjugated segments of various length that can be seen along the polymer chain. This effect is expected to be of importance in case of lamellar character of polymer crystallization, which is explained with polymer chain folding back and forth while developing during thin film growth [4]. In this monograph it is intended to put forth some ideas that can be

very utile to better understand electronic properties of thin films of alternately conjugated polymer with nitrogen in the backbone and their dependence on thin film preparation and chain conformation and structure modification. As we are concerned with polymer thin films we start from considering techniques used to prepare thin films of conjugated polymers with nitrogen and the role of polycondensation to meet these goals. Then, relations connecting morphology and structure of polyazomethine thin films with their optical properties for PPI and other more complex polyazomethines will be discussed. The next step of this paper is discussion on conformations of polyazomethines backbones. After these considerations connected with preparation of polyazomethines thin films, so called π electron approximation will be developed with its application in description of electronic structure of PPI. This method based on deriving electronic structure of polyazomethines thin films from molecular components constituting the unit cells of the polymer backbone will be used to describe electronic structure of complex polyazomethines, but also analysis of optical spectra taken on PPI thin films doped with iodine and FeCl_3 as well as protonated is thought will be some additional verification of the model of electronic structure.

2. Kinetics of PPI thin film growth via polycondensation

Polycondensation or condensation polymerization is one of many polymerization mechanisms [23], which has appeared to be very suitable and convenient to be used for preparing polymer thin films [11-22]. In this way of polymerization the elongation of a polymer chain is connected with chemical reaction between end groups of two bi-functional monomers associated with releasing low weight molecule as by-product [23]. As bi-functional monomers in the polycondensation process aromatic diamines and aromatic dialdehydes are used and the released by-product is water molecule H_2O [9-22]. This way of polymerizing monomers is of great importance especially for preparing polymer thin films by VTE and CVD methods, and what is worth emphasizing, these methods are suitable not only to preparing thin films of polymers that are insoluble in organic solvents, but above all these are the methods of preparing high purity polymer thin films without unintended impurities [22]. For the sake of this publication we are going to analyze kinetics of thin film growth of PPI, the simplest aromatic polyazomethine, with taking advantage of polycondensation process. Problem of preparation high purity polymer thin films is of particular interest for their applications in optoelectronics or photonics, and eventual impurities, if necessary, should be introduced to polymer thin films in a controllable way, as it is the case for inorganic semiconductors [5,6]. PPI thin films are prepared by CVD method via polycondensation of paraphenylene diamine (PPDA) and terephthal aldehyde (TPA) following the reaction as read below (1) [22]



One can see that this polymerization route is associated with elongation of polymer chain and simultaneous releasing one water molecule (H_2O) at each step of the reaction and removing H_2O molecules from the reaction ambience during the deposition process is of special interest. In fact, it is the case for each chemical reaction that the equilibrium conditions impose that relation of substrates and products involved in the chemical reaction are kept in quantities adequate to the equilibrium constant K [22], so that removing products molecules

from reaction volume drives the forward reaction going from the left to the right, otherwise the reaction is postponed. It is worth mentioning that chemical vapor deposition is running under conditions close to the equilibrium, because not great changes in temperature can switch reaction equilibrium between reaction postponing or going on forward. This is expressed by equation that the change in Gibbs free energy of chemical reaction is equal to the difference between the changes of Gibbs free energies of products (ΔG_{prod}) and substrates (ΔG_{subs}) (2).

$$\Delta G = \Delta G_{prod} - \Delta G_{subs} \quad (2)$$

The change in Gibbs free energy depends on the change in enthalpy (ΔH) and entropy (ΔS) (3). It is worth mentioning that entropy component is multiplied by temperature, which may have great influence on the Gibbs free energy.

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

On the other hand, the change in Gibbs free energy that is the force driving chemical reactions and structural transformations is closely connected with the chemical reaction constant K (4).

$$K = e^{-\Delta G / kT} \quad (4)$$

It is clearly seen from equ.4 that $\Delta G < 0$ is equivalent to $K > 1$ and $\Delta G > 0$, means $K < 1$. Thus, processes of polycondensation realized within vapor phase must take into account these conditions driving any chemical reaction. Mean degree of polycondensation is given by expression read below (5).

$$\bar{P}_n = \sqrt{\frac{Kc_0}{c_a}} \quad (5)$$

One can see from this equation that the mean polycondensation degree is proportional to the equilibrium constant of polycondensation reaction and starting concentration of monomers and inversely proportional to the concentration of byproducts. Thus, one may expect that the higher the concentration of the starting monomers and the lower concentration of by-product the highest degree of polycondensation process is. Then, removing by-product one pushes the equilibrium constant of the polycondensation reaction in forward direction, thus towards polymer production. To gain any insight into polycondensation process leading to formation of polyazomethine thin films our interest was connected with understanding relation among thermodynamic conditions of CVD deposition of PPI thin films and their structure, morphology and optical properties. This choice resulted from its being the simplest aromatic

polyazomethine, similitude of its optical spectra to those of poly (paraphenylene vinylene) (PPV), the most investigated polymer which was used for optoelectronic and photovoltaic applications [6,7]. This polyazomethine has been prepared by polycondensation of paraphenylene diamine (PPDA) with terephthal aldehyde (TPA). Then, studying has been undertaken on preparation of more complex polyazomethines thin films prepared also via polycondensation of diamines based on such molecules as fluorene, naphthalene, benzidine, diminebenzidine and fat Brown 15R, TPA being used as aromatic dialdehyde [27,32], all of them being illustrating in fig 1. It should be emphasized that polycondensation has appeared the most convenient way of preparing polymer thin films by CVD and TVE methods on glass or quartz substrates [33]. Beyond the diamines shown in 1, one used also complex dialdehydes to combine via polycondensation with PPDA. Polymer thin films deposition by various methods via polycondensation process included polyazomethines having prepared from several aromatic diamines with terephthal aldehyde (TPA) or more complex aldehyde like 1,4-dioksybenzaldehyde (ODBA) with PPDA [34,35]. All those monomers are illustrated in Figure 1, while polyazomethines as-produced are shown in Figure 2. Technological conditions of deposition of thin films of polyazomethines shown in Figure 2 are given in Table1.

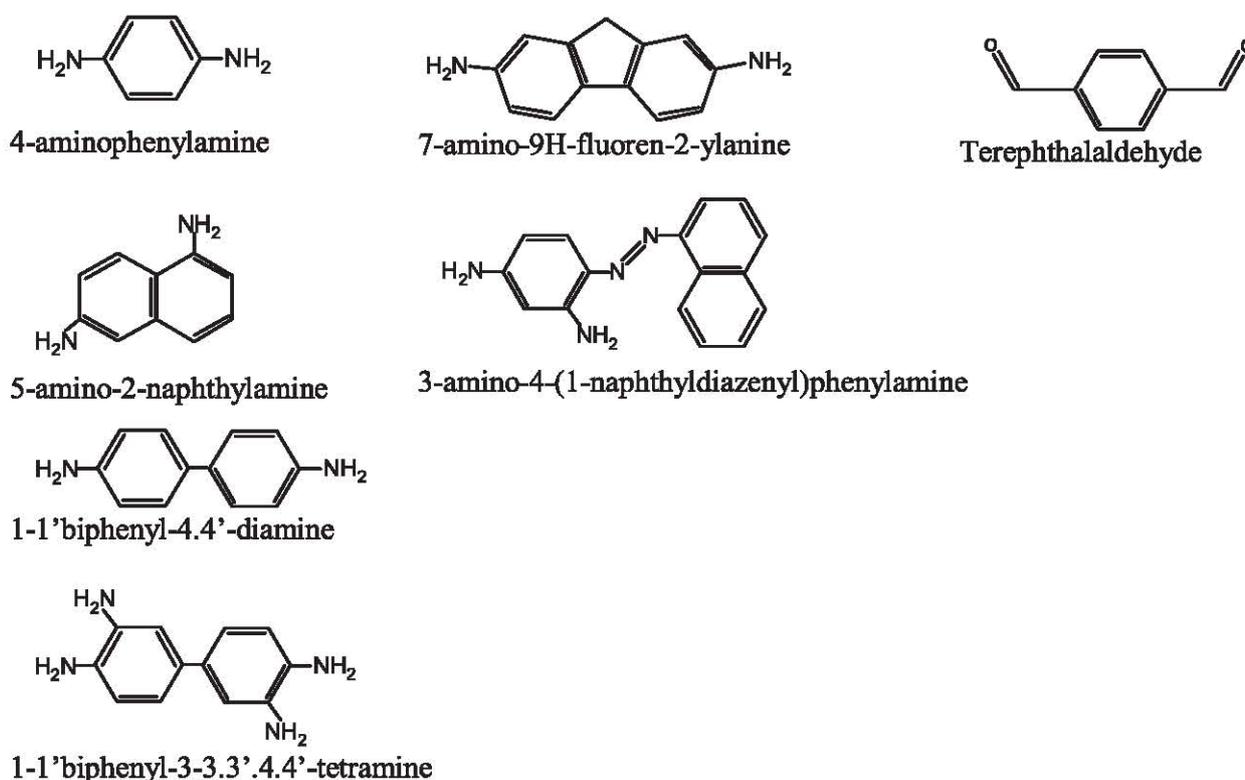
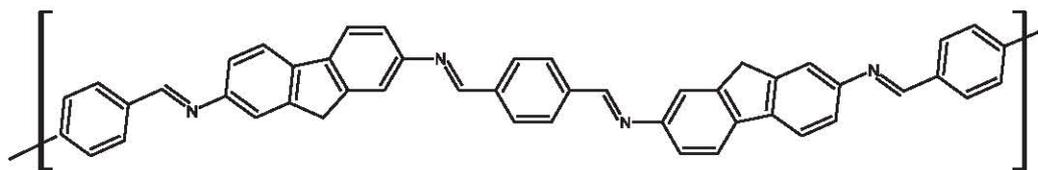
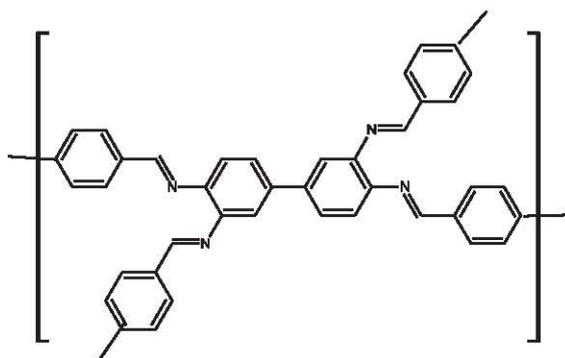


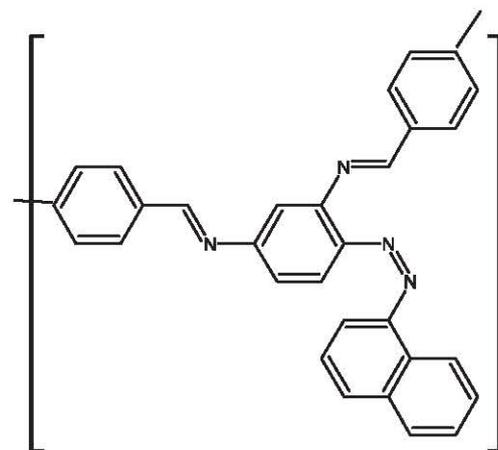
Figure 1. Aromatic diamines and terephthal aldehyde monomers for polyazomethines



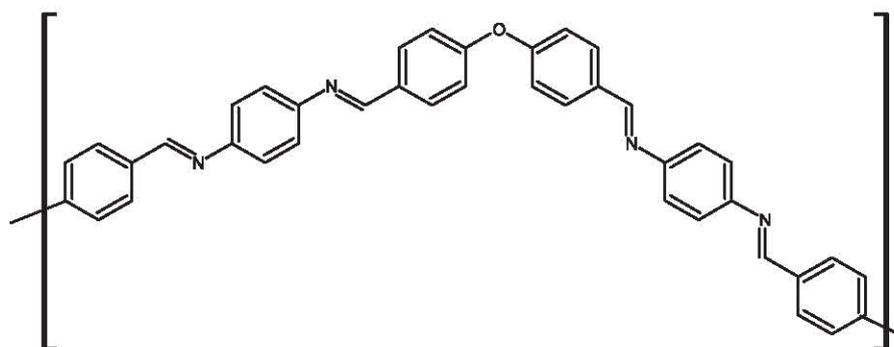
poly(2,5-fluorene-1,4-phenylene-azomethine) (FPI)



poly(tetramineboiphenylene-phenyleneazomethine) (BPI)



poly(1,3-phenylene(4-phenyleneazonaphthyl)-1,4-phenyleneazomethine) (PNAPI)



poly(p-phenyleneazomethine-oxygene) (PPI2)

Figure 2. Polymer chains of various polyazomethines

Table 1. Technological conditions of polyazomethines thin films deposition [19]

Film	Deposition time (s)	Temperature Diamine (°C)	Temperature Aldehyde (°C)	Vacuum (10 ⁻⁶ Tr)	Thickness (nm)
FPI	300	145	51	20	100
PNAPI	300	160	49	20	90
BPI	300	165	48	20	220

It seems important to indicate that TVE deposition process even though realized by means of condensation polymerization might be named also as physical vapor deposition (PVD) method to emphasis that monomers were transported from the crucible towards the substrate where within adsorption layer deposition process associated with reactions of polycondensation between end groups of the relevant monomers takes the place. The backbones of the as-prepared polyazomethines as it is seen from Figure 2, are rather complex, and their repeating units are composed of phenylene rings or biphenylene rings or fluorene or naphthyl rings and azomethine linkages connecting them with aldehyde phenylene ring, respectively.

Then, the size of the unit cell can be quite large because monomers are diamines and dialdehydes, so that like it is the case for PPI, alternate azomethine groups in the backbone of each polymer take $-\text{CH}=\text{N}-$ or $-\text{N}=\text{CH}-$ orientations. Thus, they are doubled while compared with similar conjugated polymer with vinylene linkages.

2.1. CVD PPI film deposition

Kinetics of CVD method of preparation of polyazomethine thin films has been discussed in details in our earlier paper on deposition of PPI thin films [22] and it will be outlined here, moreover the kinetics of preparation of the above mentioned polyazomethines by both CVD and VTE methods are not very different from the case of PPI thin films. In chemical vapor deposition technique with transport agent chemical reactions run under conditions close to the reaction equilibrium, so that changing temperature of the transported species can switch the chemical reaction progression between the forward and backward directions. The experimental setup for the CVD deposition of PPI thin films via polycondensation of aromatic diamines and terephthale aldehyde is outlined in Figure 3. The idea that was behind design of both horizontal and vertical arrangements was to divide the stream of gaseous argon which was the

transport agent into three equivalent streams, two of them flowing each over a boat with the relevant monomer kept at adequate temperature, and the third substream might be used to transport doping agent, so that it flows over the boat containing doping agent otherwise it was argon only stream, which effectively diluted the stream transporting monomers molecules. These streams of equal intensities transporting monomers merged into one stream in order for the monomers molecules to be mixed up before the stream as one entity was flowing into the reaction chamber where the substrate was mounted. As it was described elsewhere [22] the pipes through which stream of reagents was flowing were verified whether or not polymer film grew upon the pipe wall, but no traces of polyazomethine film on the pipe wall were found. While growing polymer films in the horizontal setup, the argon stream transporting mixed up monomers molecules entered the reaction chamber whose diameter was large compared to the inlet pipe diameter. In consequence, when entering the reaction chamber the intensity of the stream flow has undergone some drastic slow down that was accompanied with temperature decrease, because both the chamber and substrate were kept at room temperature, so that thermodynamic conditions became relevant for the polymerization process to be running forward. The CVD technique applied the polymerization is expected to run at the interface of the gaseous and solid phases within the adsorption layer formed upon the substrate by impinging molecules of reagent species. During the whole CVD processes made in both

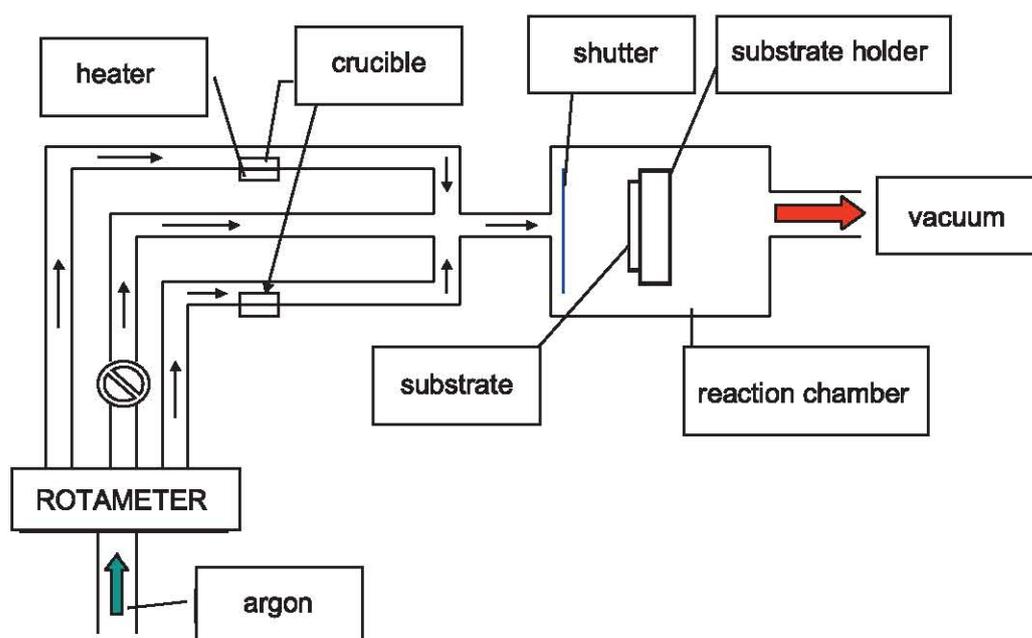


Figure 3. Set-up for CVD deposition of polyazomethines thin films, according to [22]

horizontal and vertical setups, the deposition process and the polycondensation reaction were supported with the use of the pump exhausting transport agent and byproducts from the reaction chamber. Clean pipe walls indicated that the species transported by argon essentially have not polymerized, though while sticking with one another small molecules with two distinct functional groups could eventually be formed, but this decreased number of molecules being carried on and so decreased probability for them to knock and clash to combine into oligomer with more than two repeating units. The conditions of PPI thin film deposition by CVD method and related morphology of the as-prepared films are collected in Tables 2 and 3, respectively. The reaction equilibrium constant according to (2-5) depends exponentially on Gibbs free enthalpy $\Delta G = \Delta H - T\Delta S$, where changes of free enthalpy (G), enthalpy (H) and entropy (S) concerns relevant changes of products and substrates, changing the sign of ΔG means switching the reaction between the state of reaction stoppage or reversing and the state of product formation. Thus, it is expected that $\Delta H/T$ and ΔS were not too high at room temperature, as otherwise spontaneous reaction rather than reaction reversibility conditions ($\Delta G \approx 0$) would be reached [22].

Table 2. CVD technological parameters of PPI thin film preparation

Film	T _{PPDA} (K)	T _{TPA} (K)	Flow rate l/min	Time (s)	Distance (cm)	Streams number	Thickness (nm)
A	335	326	80	120	5	2	200
B	334	326	80	180	4	2	200
C	340	326	150	60	5	2	200
D	334	326	80	420	4	3	170
E	343	327	80	90	5	3	180
F	315	313	60	1500	5	3	50

Table 3. Morphology of PPI thin films

Thin film	RMS roughness (nm)	Thickness (nm)	Growth rate (nm/s)	Grain size (μm)
<i>a</i>	5.0	200	2.5	0.4
<i>b</i>	10.3	200	2.2	0.2-0.3
<i>c</i>	7.5	200	3.1	~0.1, >1.0
<i>d</i>	9.9	170	0.4	0.2-0.3
<i>e</i>	6.3	180	1.8	~0.1
<i>f</i>	32.3	50	0.1	~0.4, ~ 1.0

On the other hand, it has been noticed that film formation process runs easily and rapidly which seems to manifest rather low energy barriers for the intermediate states and the reaction speed is attributed to rather high probability of relevant molecules sticking with one another suggesting high enough concentrations of reagents molecules in the stream. Thus, one may think that the stream impingement onto the substrate provide not only monomers molecules but also two or three molecular units which while adsorbed on the surface can combine with one another building up polymer film. It is clearly seen that reaction of polyazomethine formation run within the adlayer at the vapor phase/substrate interface between arriving jumping and knocking and clashing one against another molecules of terephthal aldehyde and paraphenylene diamine. The higher frequency of clashing events between monomers with different end groups, the higher probability their reaction, resulting in polymer chain becoming longer and longer with releasing H₂O by-products. During the process the contributing monomers are kept at relevant temperatures of about 323-350K, while the glass substrate is at temperature 300K.

Such temperatures of monomers were chosen in order for polycondensation process was running at nearly 1:1 stoichiometry of PPDA and TPA molecules being monomers, as evaporation temperature of PPDA is higher than that TPA. Then, applied temperature regime of the argon stream transporting two mixed monomers made the reaction running forward towards the film formation to be displaced towards substrate area where decreased temperature enforced reaction to be shifted towards polymer chain formation. It is thought that kinetics of polymer thin film deposition is bringing some confirmation of Flory' rule stating that the activities of end groups involved in polycondensation process are independent of the length of chain to which they are attached [23]. This seems to be in accordance with X-ray diffraction patterns nearly coinciding with those reported by Luzny et al. [13,14] for bulk PPI prepared by solution techniques. While the vertical setup was used, the transporting argon substreams flew through three pipes and in each of them the streams were flowing around the crucible filled with monomers, so that vapors of the relevant monomers molecules were undertaken mainly due to diminished static pressure in the vicinity of the crucible, as it is indicated in Figure 4. Then, the substreams flowing out of the three channels merge inside so-called collimator from which through top pupil the stream of mixed up monomers molecules is flowing towards the substrate mounted in the holder just above the collimator opening. During the deposition process the reactor volume behind the substrate is evacuated with the use of rotary pump, which seems to be element supporting reactants streams flowing throughout

the reactor [33,34]. Thin films of polyazomethines were deposited by physical vapor deposition (PVD) method in the experimental setup outlined in Figure 5.

Polyazomethine deposition process carried out by PVD method is performed by sublimating monomers placed in two separate crucibles mounted in the vacuum chamber [26]. Before deposition process started the reaction chamber with crucibles filled with the monomers is exhausted to produce high vacuum. The substrate was cut off with the shutter until the temperature of monomers in crucibles attained required temperatures and the vacuum attained the required level. Then, the shutter was opened and the deposition process started.

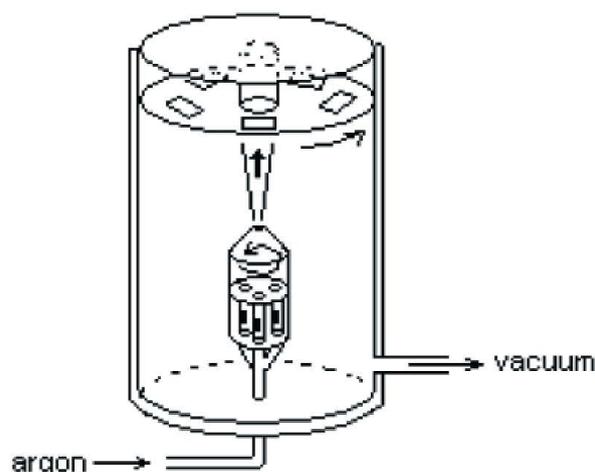


Figure 4. Set-up for double-source vacuum thermal evaporation [33]

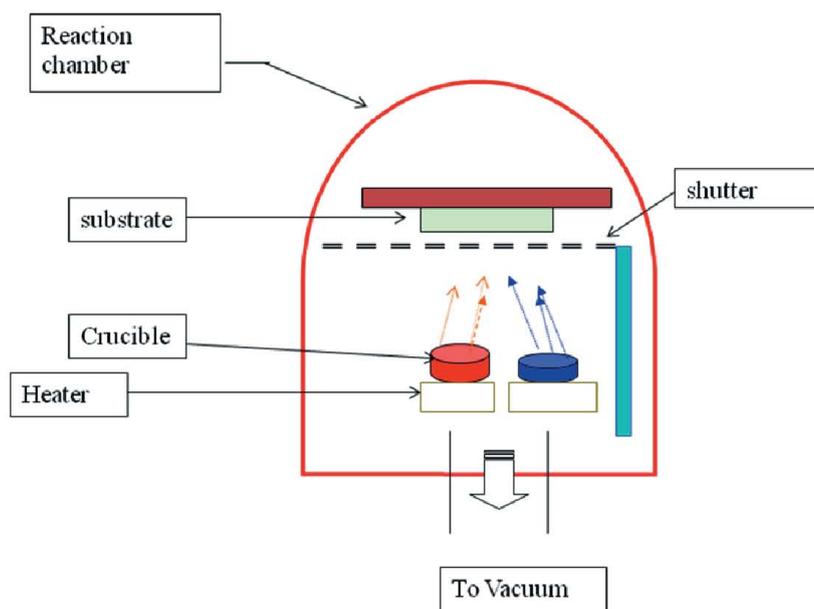


Figure 5. The technological set-up for PVD deposition form two sources

The streams of monomers transporting molecules of reactants towards the substrate, though sublimation temperatures depended on monomers used, but in case of the simplest polyazomethine they were not very different from their values applied during CVD processes. However, essentially for the same reasons, temperatures of monomers were different and their difference was of about 10-15°C in order for the film growth conditions approached polycondensation conditions with nearly 1:1 ratio of the monomers molecules impinging onto the surface of the substrate. Thin films of polyazomethines were also prepared under conditions of rather low vacuum with exhausting rotary pumping kept running during the whole deposition process. While preparing thin films of polyazomethines by condensation polymerization using much complex monomers, such as fluorene diamine, benzidine diamine or fat Brown R15 the temperatures used for subliming aromatic diamines were much higher and were within the range 145-165°C, while terephthal aldehyde temperature being at the level of 50-60°C.

3. Structure and morphology of polyazomethine thin films

Generally, it is expected that polymer thin films are amorphous in character because they constitute entities of interpenetrating, entangled or curled polymer chains, which are not stretched ones but instead they form entity of folded back on themselves chains. However, one must remember that polymer chains do constitute ordered entities not in the sense of atom ordering in inorganic crystals, but they are ordered because their backbone makes out entity being a sequence of the same repeating units, whose conformation is resultant of interactions among atoms attached to the backbone atoms (repulsion of hydrogen atoms attached to the neighbor atoms). This polymer chain periodicity has its impact observed in their optical spectra and their optoelectronic properties, some contribution from accidentally ordered areas. Polyazomethine are aromatic polymers whose backbones are composed of sp^2 hybridized carbon and nitrogen atoms, but eventual planarity of the backbone conformation is disturbed by concurrence of steric hindrance of hydrogen atoms combined with coupling effect acting between nitrogen lone pair orbital on nitrogen atom and the nearest phenylene π system. While considering relations connecting technological conditions under which PPI thin films were deposited and their optical properties, it seems to be worth looking through all the spectra, AFM images illustrating their morphology and X-ray diffraction patterns revealing their structure. In horizontal arrangement of CVD set-up [22], all PPI thin films considered with exception of the one, which was prepared at the same source temperatures of monomers, were prepared from under such conditions that terephthal aldehyde temperature (T_{TPA}) was lower about 10K than the PPDA temperature (T_{PPDA}) and then deposited films have had nearly the same thickness of about 200 nm. At the same time, the PPI film prepared when $T_{TPA} = T_{PPDA}$ had a thickness of about 50 nm. How it is clearly seen in Figure 6 the film (a) revealed ordered structure with well defined peak at about 23.5 deg and a weaker one at about 20.95 deg. Generally all the diffraction patterns taken on those PPI thin films revealed broad amorphous background with the maximum at about 25 deg in the vicinity of the strongest peak. Morphology of the as-prepared thin films, illustrated in Figure 7 is seen to be granular with visible overlapping grains or even columns, so that something resembling ribbons or hill chains of versatile shape and twisting on running along with some random directions. The topographic image reveals nearly homogeneous film surface within $5 \mu\text{m} \times 5 \mu\text{m}$ square with roughness heights ranging 32.23-64.45 nm.

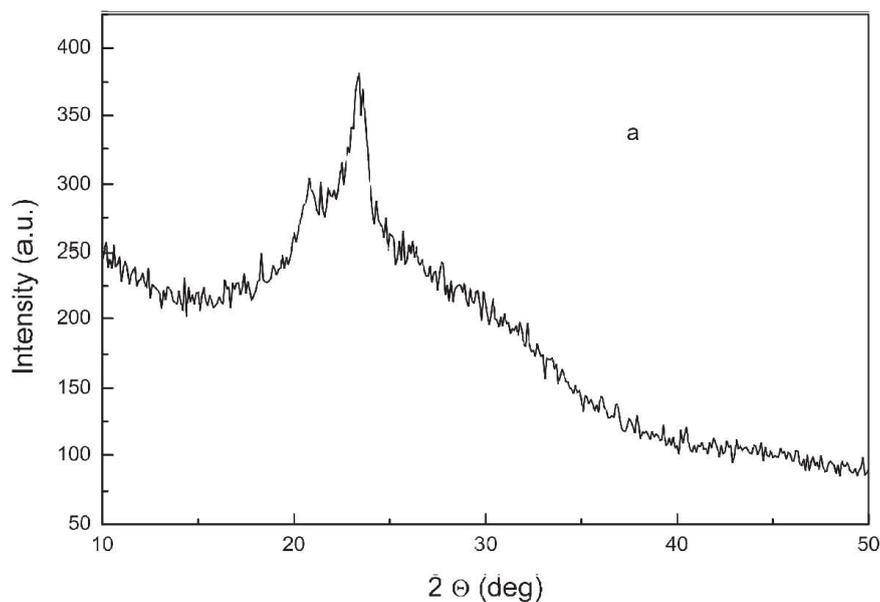


Figure 6. Diffraction pattern taken on (a) PPI thin films

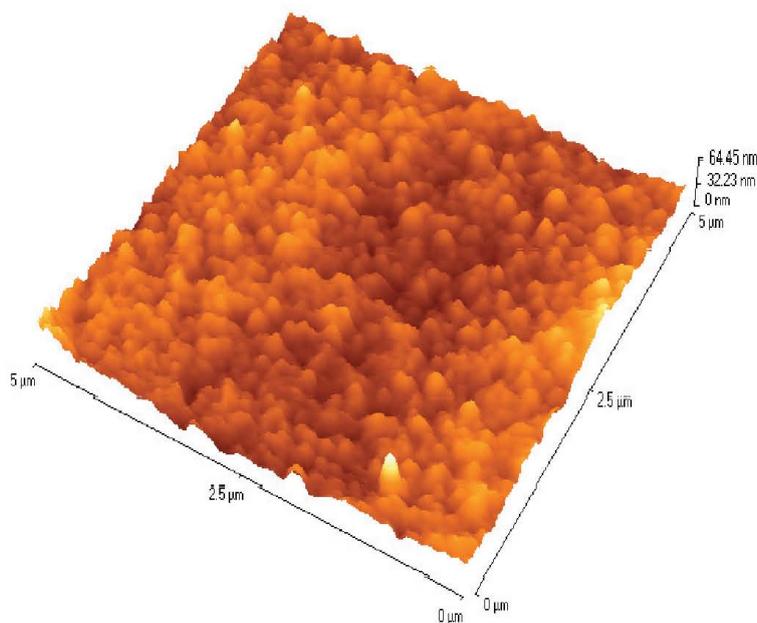


Figure 7. Topographic image of PPI thin film (a)

This surface morphology seems to correspond rather well with the absorption spectrum covering 1.5-4.5 eV UV-Vis area, which is seen to reveal “triangular shape” with distinctly visible small exciton related peak at about 2.58 eV, while the feature peaking at about 4.0 eV is observed in all the spectra at the same location, Figure 8. The peak distinctly seen at low energy part of the spectrum has been attributed to Wannier –Mott exciton, which is seen to go rather well with ordered if not to say due to some sort of crystalline character of this film.

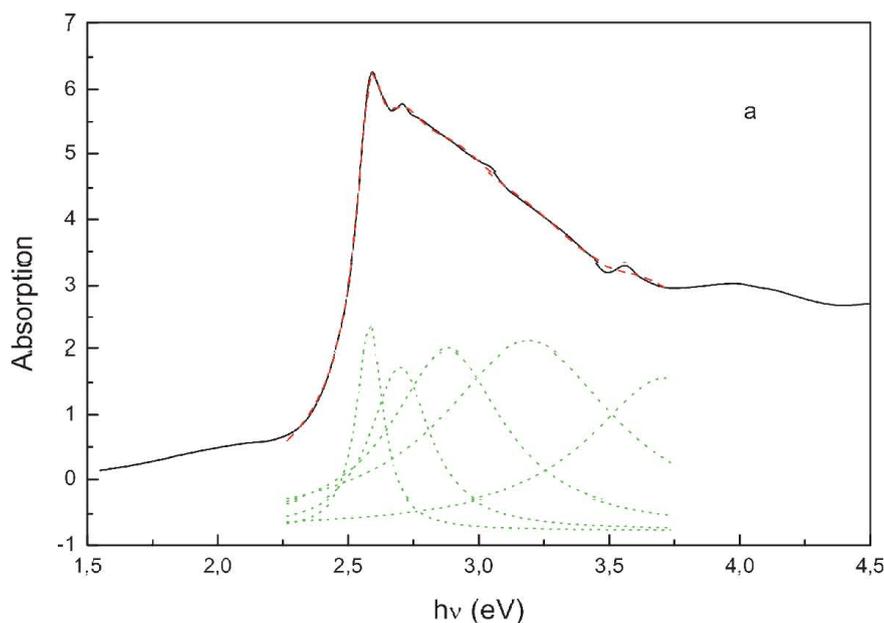


Figure 8. Absorption spectrum of (a) PPI thin film

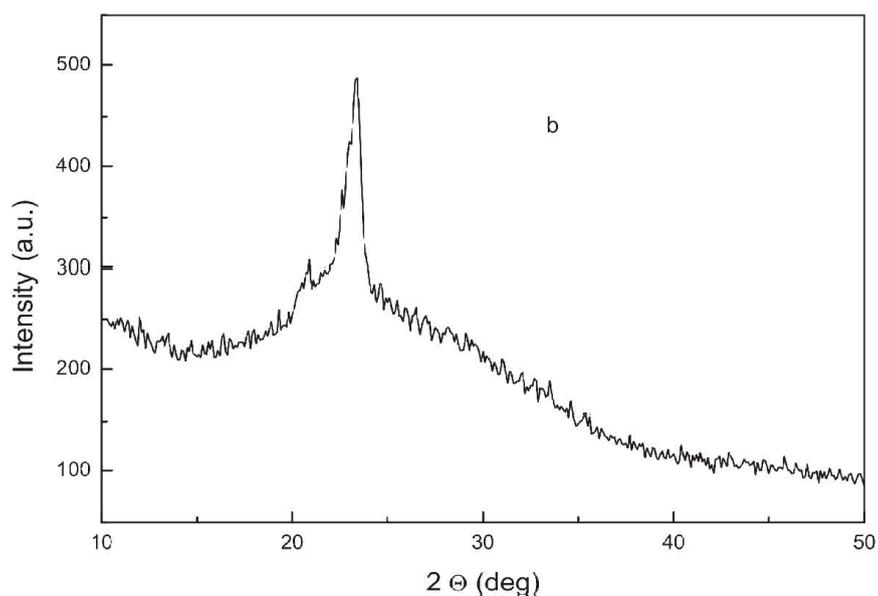


Figure 9. X-ray diffraction pattern of (b) PPI thin film

According to data given in Table 1, PPI thin film designated as (b) film was prepared under nearly the same conditions as the precedent one, but the substrate was moved 1cm nearer the stream inlet into the reaction chamber with respect to the distance while preparing (a) film. However, comparison of x-ray diffraction patterns taken on films (a) and (b), Figures. 6 and 9, is leading to conclusion that probably film designated (b) is more ordered or even more crystalline in character than film (a), because the peak at about 23.4 deg is much more intense and slightly narrower than the peak of (a) film, so that it can be expected that ordered areas

in film (b) have been larger in size than this is the case for (a) film. As it can be seen in Figure 10, at first sight morphology of (b) film seems to be nearly the same as that of (a) film, nevertheless the granules or columns are seen to overlap and form something that resemble bands or ribbons. However, absorption spectrum recorded on a film (b) (Figure 11) is seen to be slightly different from that of (a) film, missing Wannier-Mott exciton related peak in particular.

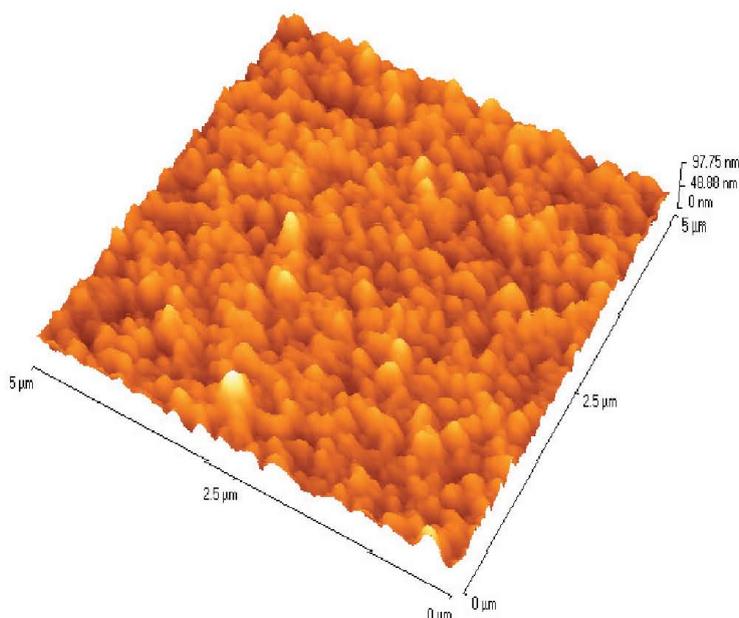


Figure 10. Topographic image of PPI thin film (b)

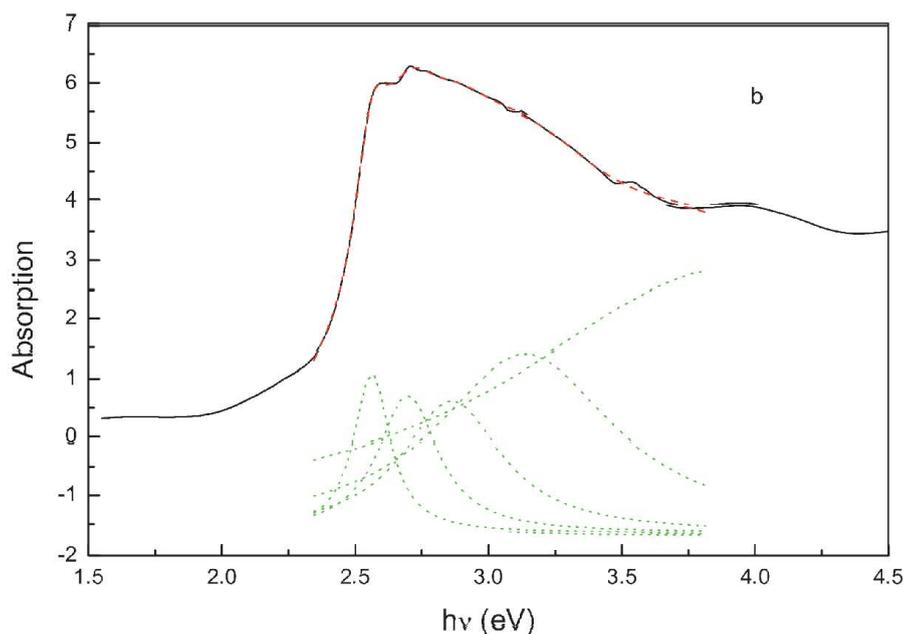


Figure 11. Absorption spectrum of (b) PPI thin film

The AFM image of the surface morphology of (c) film, shown in Figure 12, indicates the surface being more plane than the surfaces of two former films, though much higher hills are observed. One can notice that probably columnar growth is seen here as bands of overlapping columns running randomly, but the shape of its X-ray diffraction pattern, given in Figure 13, indicates towards rather amorphous character of (c) film morphology with a very fable feature at about 23,8 deg.

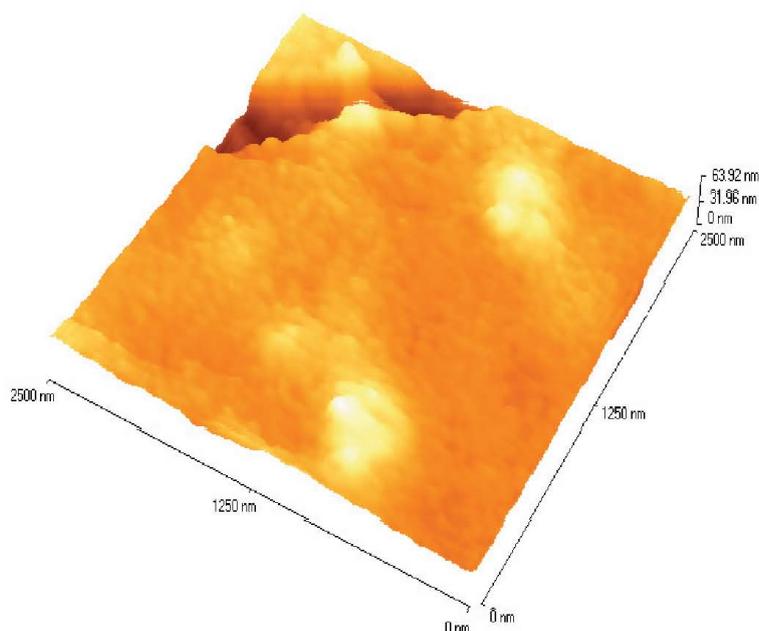


Figure 12. Topographic image of PPI thin film (c)

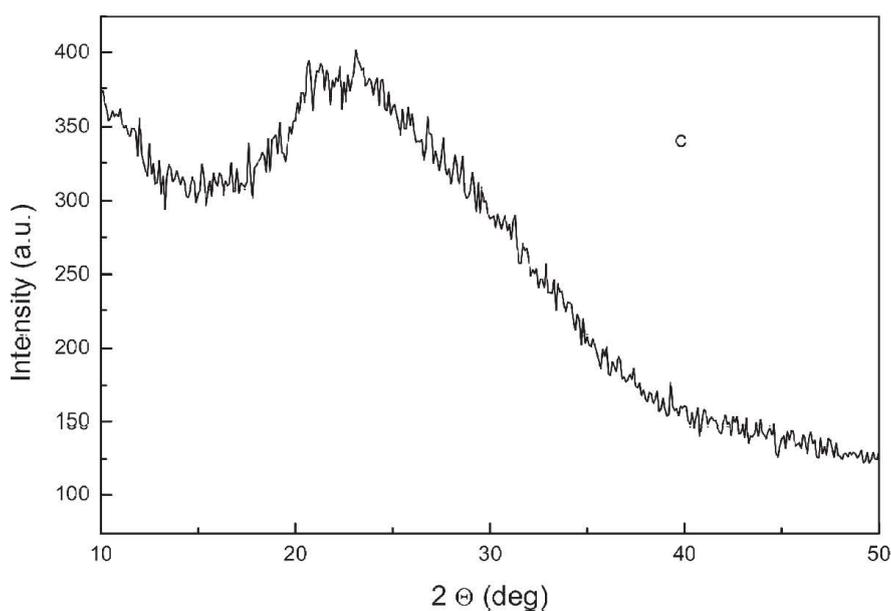


Figure 13. Diffraction pattern of (c) film

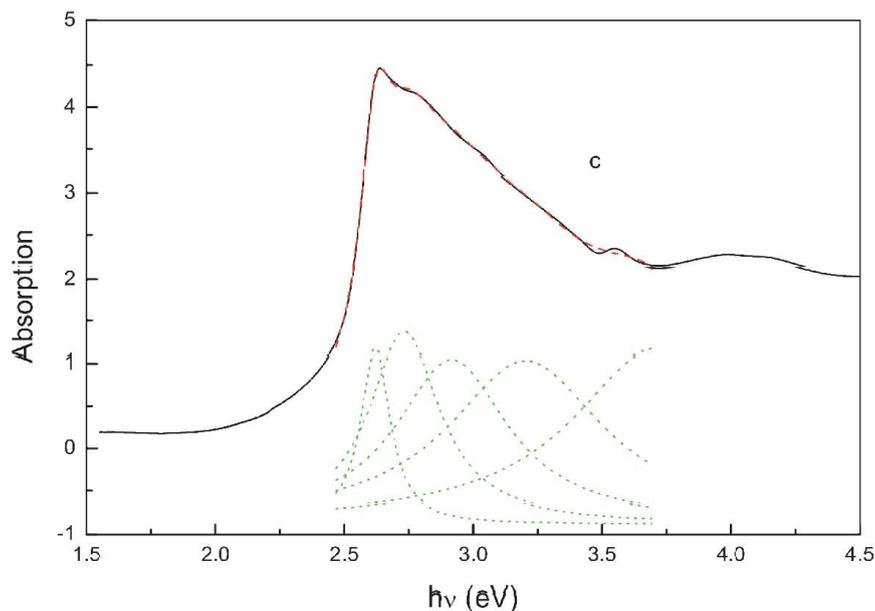


Figure 14. Absorption spectrum of (b) PPI thin film, Accord, [22]

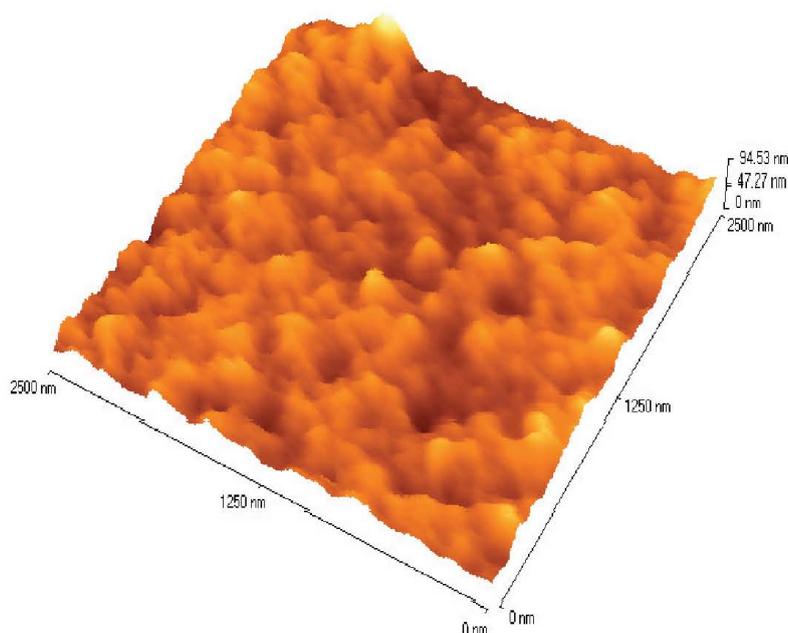


Figure 15. Topographic image of PPI thin film (d). Accord, [22]

It is worth mentioning that under nearly the same conditions of a film deposition, an increase in the distance of the substrate from the stream inlet into the reaction chamber certain structural ordering is the case, though not so well visible in the absorption spectrum (Figure 14). On the other hand, comparing films (a) and (c) one can see that nearly double increase in the stream intensity resulted in more disordered film (c) than it was the case for (a) film. While comparing films (a) and (d) which were deposited under the same conditions (temperature, stream intensity, substrate distance

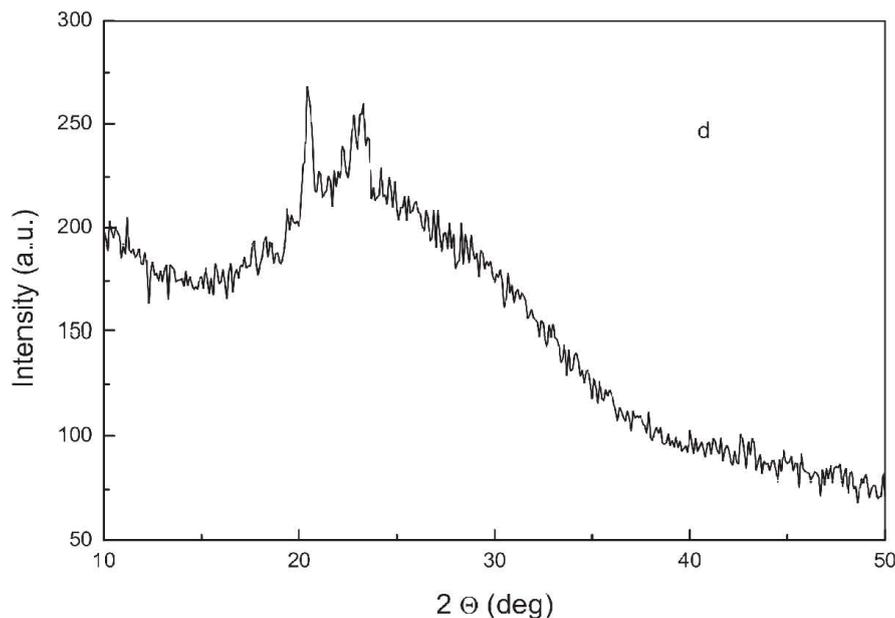


Figure 16. Diffraction pattern of (d) film. Accord. [22]

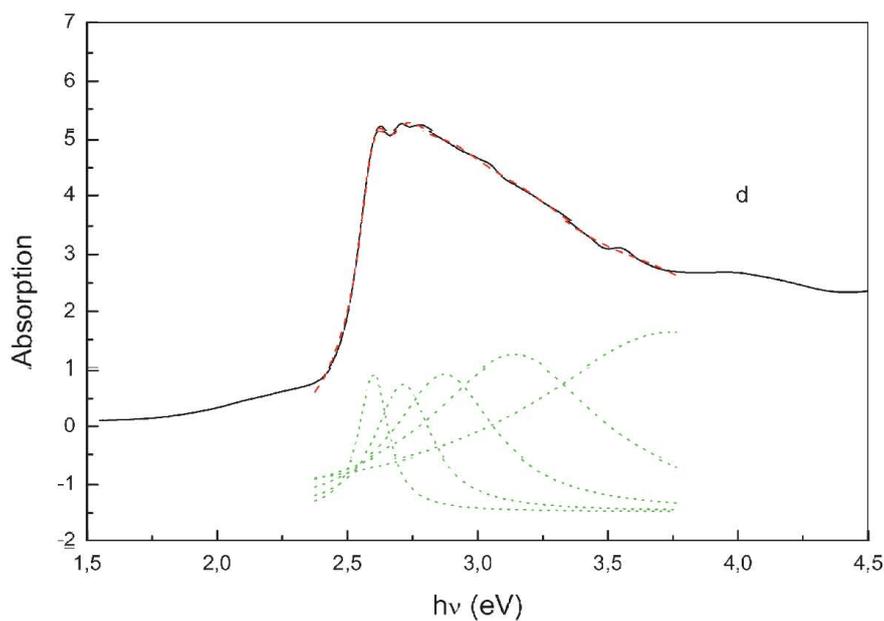


Figure 17. Absorption spectrum of (d) film. Accord. [22]

from the gas inlet), but the latter was prepared with the use of three stream and it is easily visible that its ordering is a little worse than in (a) film, but simultaneously it is slightly different than in a film (a), (b) and (c), because more defined peak is the one at 20.95 deg. One can see in Figure 15 that AFM image taken from the surface of (d) film shows off that overlapped columns form chain band or ribbons, which may be attributed to some representation of structural order in this film.

At the same time, while looking at AFM image taken on (e) film (Figure 18), it is clearly seen that columns or grains do not overlap with one another to form bands running randomly throughout the surface. This seems to find some supporting confirmation from diffraction pattern and absorption spectrum taken at film (d) and (e), as it is seen in Figures. 16 and 17 and Figures. 19 and 20, respectively. The absorption spectrum of film (e) shown in Figure 20 reveal vibronic character of low energy band related to optical interband transitions linking

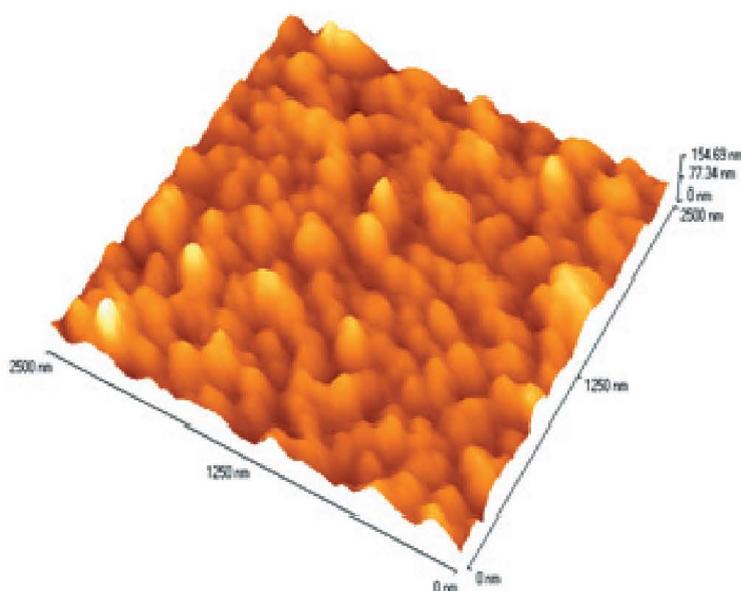


Figure 18. Topographic image of PPI thin film (e)

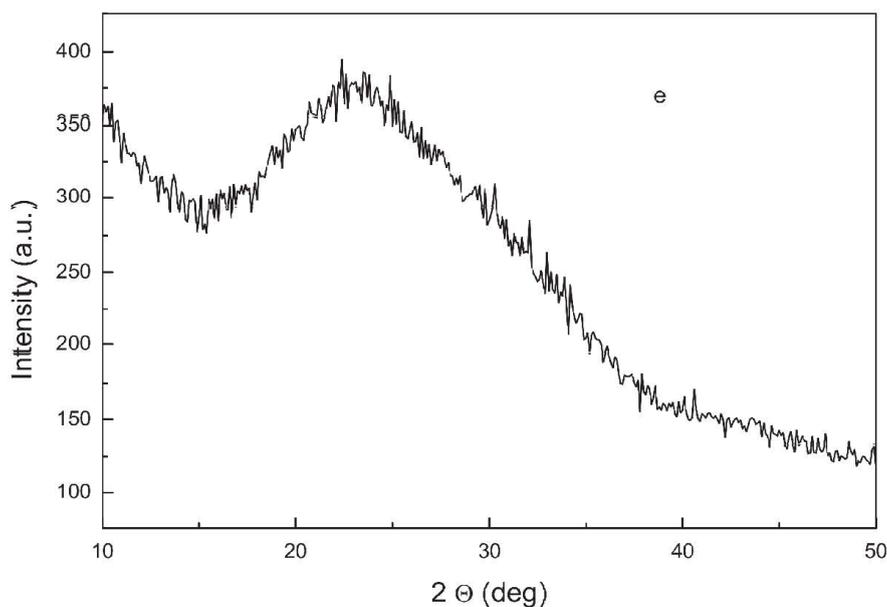


Figure 19. Diffraction pattern of (e) film

delocalized states [22]. The shape of this band is thought to point out towards conclusion that this film is constituted by PPI chains loosely connected together by means of weak van der Waals forces, so that there is quite distinct discard in potential energy minima of the electronic ground and excited states. In contrast, film (f) being the thinnest one of all the as-prepared films under that study reveals rather ordered character of its structure, which can be supported by AFM image given in Figure 21 as well as by X-ray diffraction pattern, shown in Figure 22,

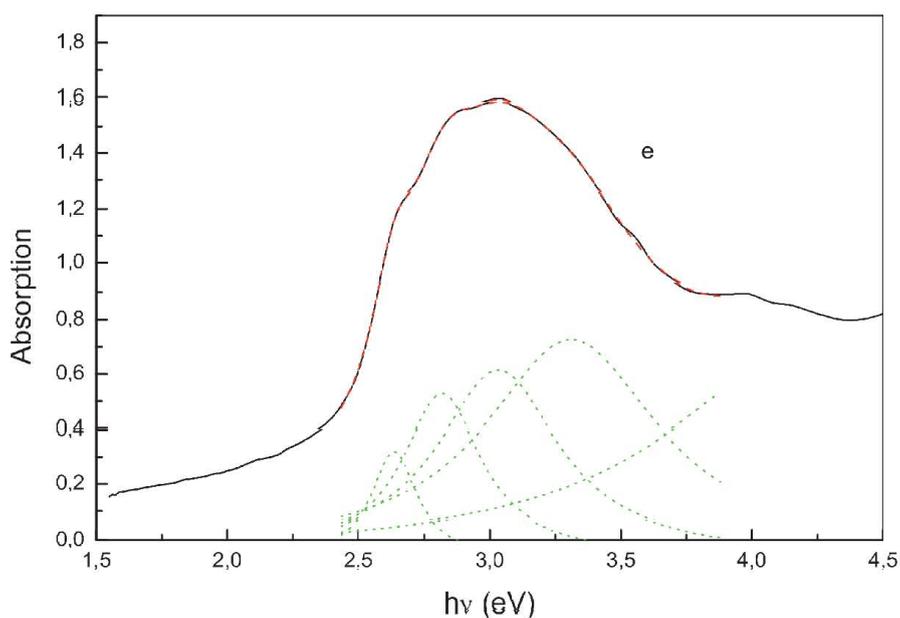


Figure 20. Absorption spectrum of (e) film

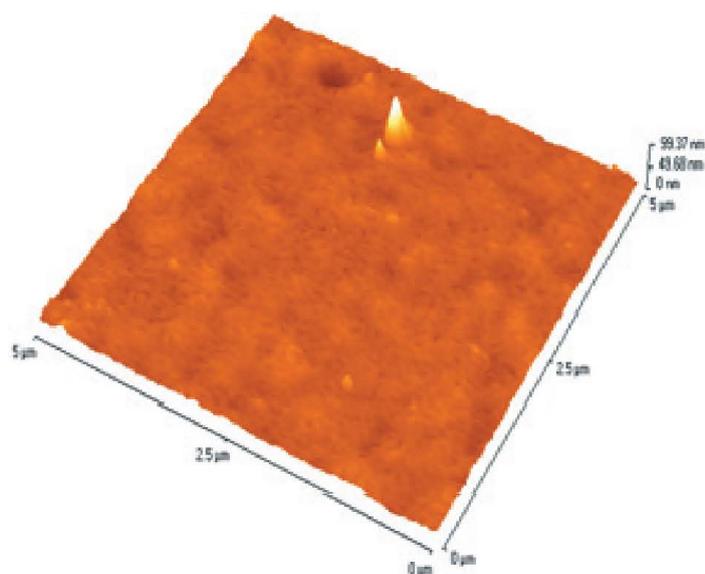


Figure 21. Topographic image of PPI thin film (f)

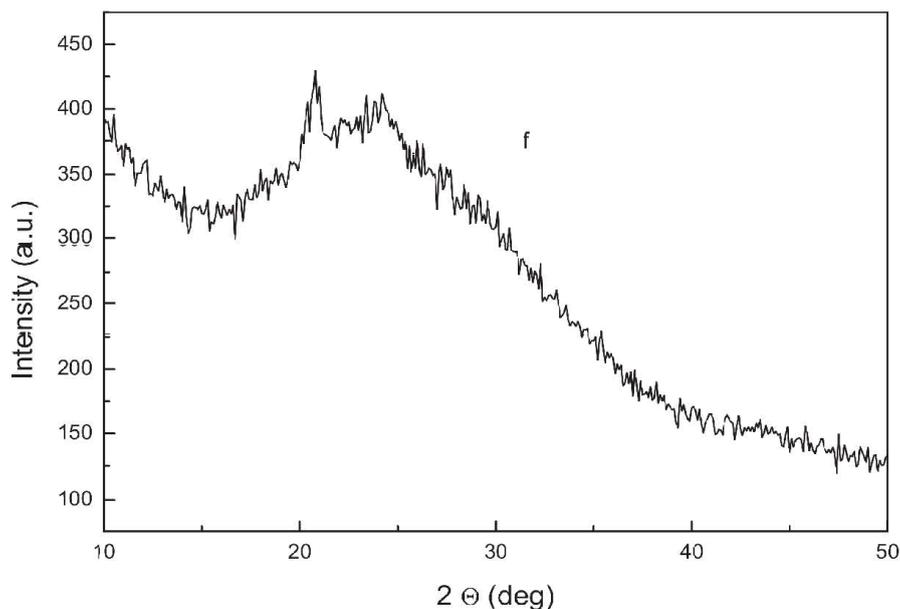


Figure 22. Diffraction pattern of (f) film

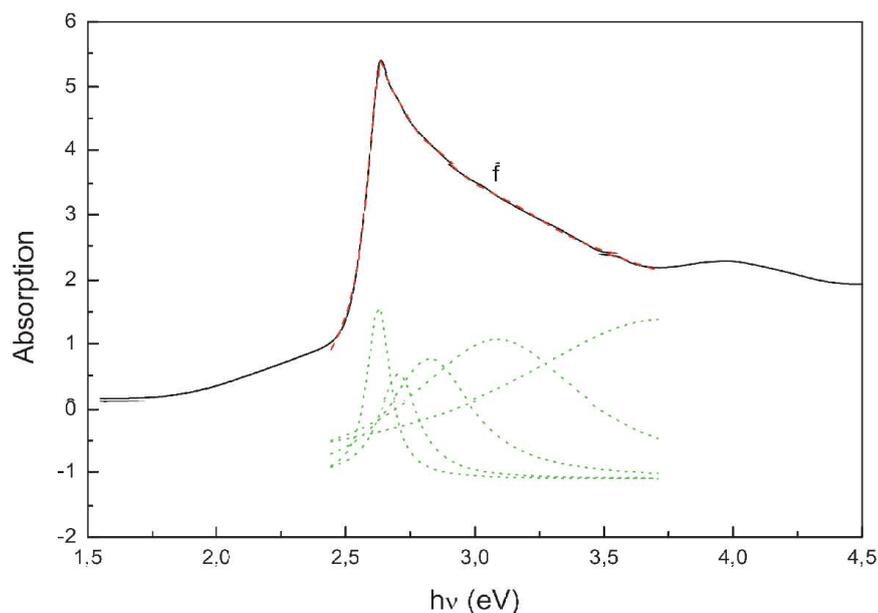


Figure 23. Absorption spectrum of (f) film

and absorption spectrum (Figure 23) in particular. AFM image reveals rather plane and smooth surface of this film, with visible bands of overlapping growth columns running throughout the film surface, while X-ray diffraction pattern reveals distinct feature superpose onto amorphous background but peaking at about 20.93 deg. It is worth mentioning that diffraction patterns of these film reveal broad amorphous background whose maximum is situated in each case more or less at the same diffraction angle. However, the absorption spectrum recorded on this film

Table 4. Results of the fitting procedure for film e

Energy (eV)	Half width (eV)	Area
2.640 ± 0.001	0.200 ± 0.002	0.120 ± 0.004
2.820 ± 0.002	0.370 ± 0.017	0.34 ± 0.05
3.030 ± 0.006	0.56 ± 0.06	0.6 ± 0.2
3.31 ± 0.02	0.81 ± 0.08	1.0 ± 0.3
4.2 ± 0.2	1.3 ± 0.5	1.5 ± 1.1

reveal the best pronounced peak attributed to Wannier-Mott exciton, rather than to vibronic feature. The two features are due to different effects, as Wannier-Mott exciton comes from interaction of excited electron and hole created behind in delocalized valence band, while vibronic features are results of electronic transition borrowing its intensity from vibrational modes [24,25,28].

3.1. PPI thin films deposited in the vertical set-up

Thin films of polyazomethines which were deposited by CVD method with argon gaseous being transport agent with the use of vertical setup have appeared to reveal similar relation between their morphology and optical spectra. How it is seen in these spectra films prepared under the highest intensities of transport agent streams have revealed surface with columnar growth where overlapping of columns or granules are observed and such bands are running along with the surface in random directions. However, such films revealed absorption spectra with visible signs of exciton formation, so that one may expect that such bands means there is order and some sort of stacking in those lamellae. Surface morphology of a PPI film prepared under lowest stream for $\Delta T = 30K$, shown in Figure 24, is seen to be nearly homogenous with several randomly distributed grains with higher height and the other of comparable height and essentially visible as separate though densely distributed. At the same time, the surface morphology of the film prepared under the highest intensity of the stream, illustrated in Figure 25, reveals as rather plane with several randomly distributed larger grains, but it is seen less rough than the film prepared under the smallest intensity of the stream. Being the more plane with roughness nearly two times smaller than the former, grains are seen to overlap giving quite plane surface. One can see that there is some correspondence between film surface morphology and optical spectra in UV-Vis range. It is clearly seen in these spectra that film

deposited with the lowest intensity of the stream (Figure 26) with slightly visible indications of vibronic character of interband transitions with maximum at about 3.0 eV, while in case of the other film (Figure 27) the band is displaced towards lower energies with rather fable peak attributed to Wannier-Mott exciton and maximum of the band at about 2.8 eV.

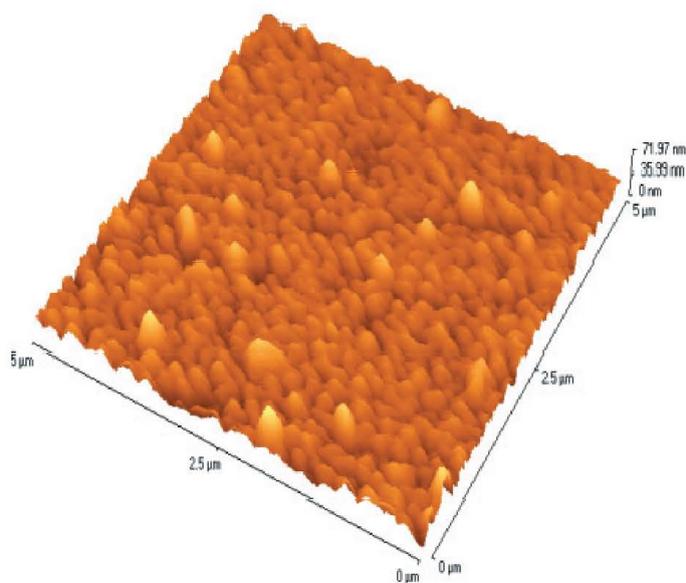


Figure 24. Topographic image of PPI thin film deposited with stream intensity $I=19.99 \text{ Pa dm}^3/\text{s}$
 $T_{TPA} = 333.15 \text{ K}$, $T_{PPDA} = 363.15 \text{ K}$

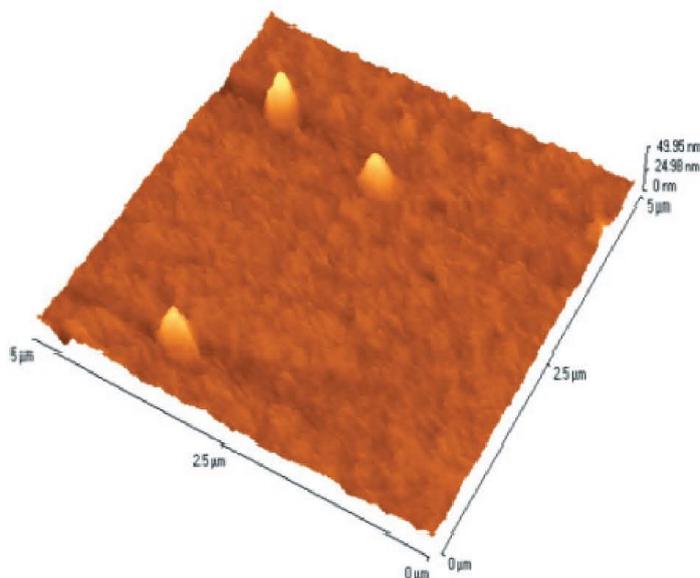


Figure 25. Topographic image of PPI thin film deposited with stream intensity $I=399.97 \text{ Pa dm}^3/\text{s}$
 $T_{TPA} = 333.15 \text{ K}$, $T_{PPDA} = 363.15 \text{ K}$

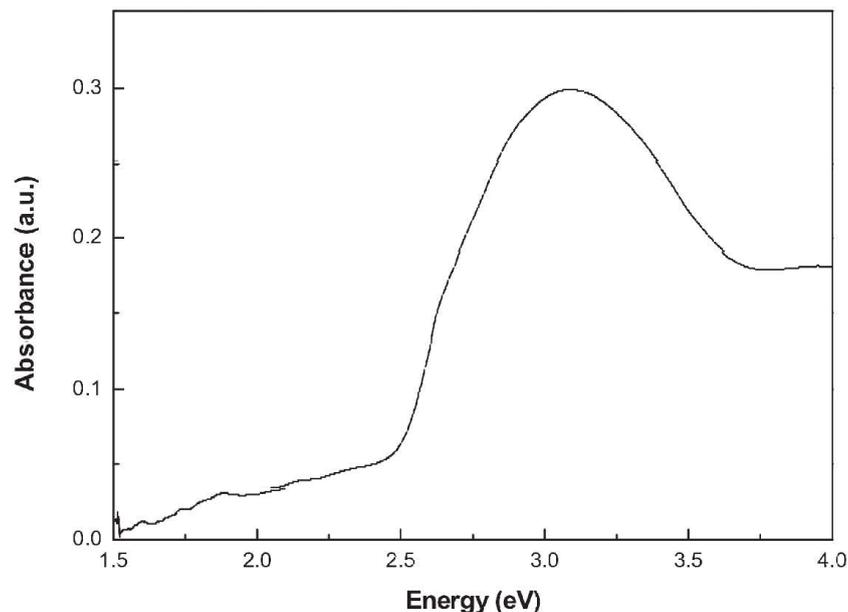


Figure 26. Stream intensity 6.66 ($\text{Pa dm}^3/\text{s}$), temperatures: $T_{TPA} = 333.15 \text{ K}$, $T_{PPDA} = 363.15 \text{ K}$

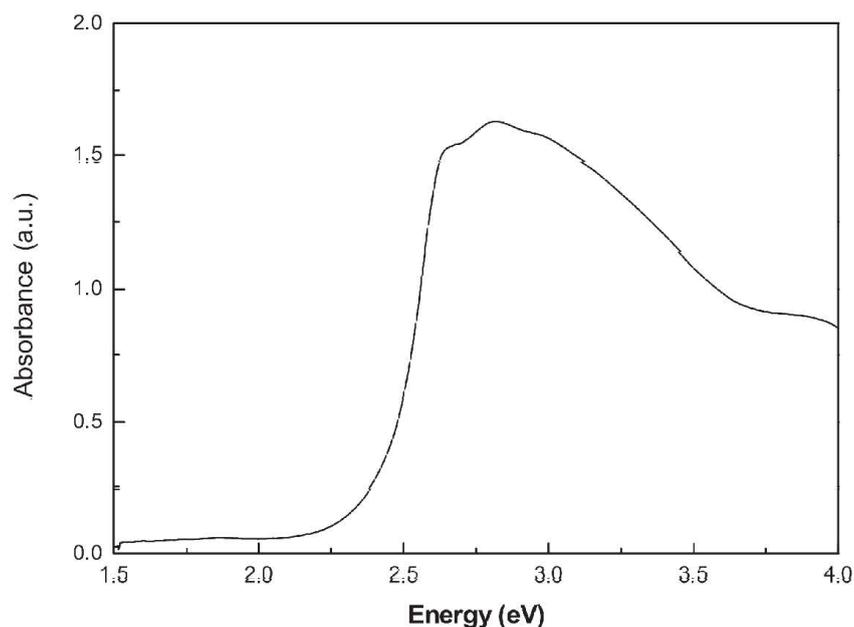


Figure 27. Stream intensity 399.97 ($\text{Pa dm}^3/\text{s}$), temperatures: $T_{TPA} = 333.15 \text{ K}$,
 $T_{PPDA} = 363.15 \text{ K}$

This difference in maxima position is indication of variations of positions of potential energy minima of electronic ground and excited states. In Figure 28 there is shown topographic image of morphology of CVD prepared PPI thin film which reveal rather rough surface with visible grains of about 200 nm in size, while in Figure 29 one can see topographic image of this film after doping with iodine vapors. This iodine doped film reveals smoother surface with quite

distinctly observed overlap of grains in form of ribbons of random length and randomly oriented. This picture is thought to rather well correspond with X-ray diffraction patterns taken on PPI thin films pristine and doped where one can see that doped film became more ordered one, with quite distinct increase in intensity of 25 deg peak (Figure 30). Then, one may expect that doping PPI thin film with iodine leads to ordering this film in such a way that feature at about 24.5deg became stronger, so that ordered areas related with this orientation became larger after doping.

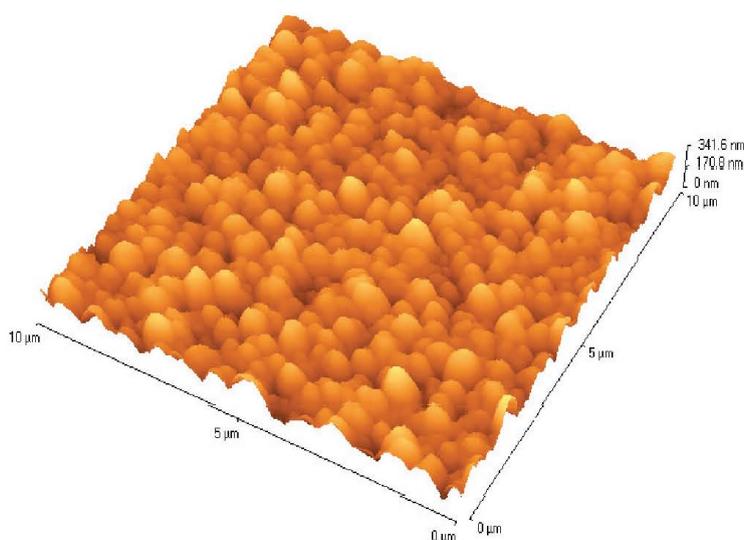


Figure 28. Topographic image of surface of CVD prepared PPI thin film

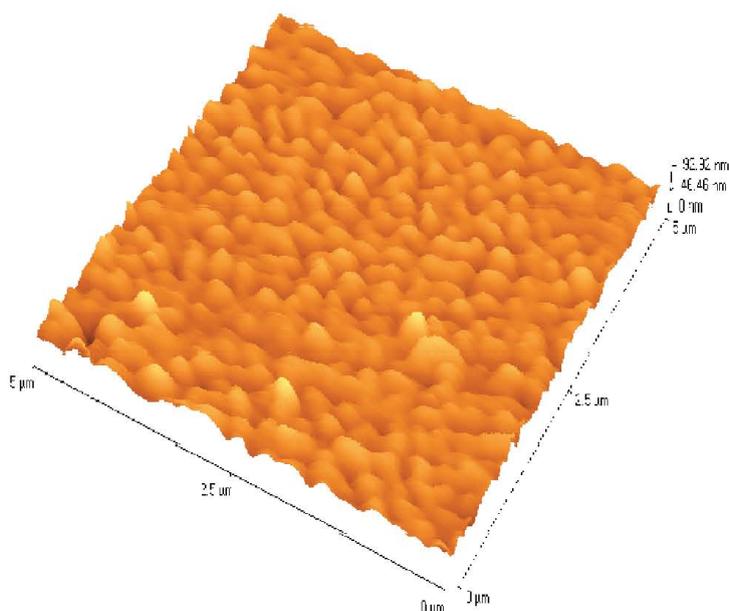


Figure 29. Topographic image of surface of CVD prepared iodine doped PPI thin film

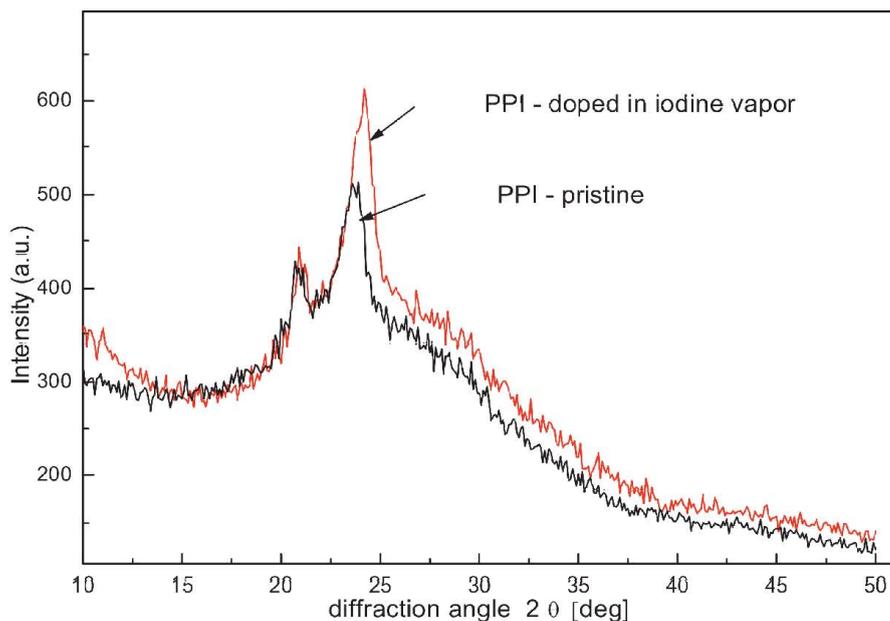


Figure 30. X-ray diffraction patterns taken on pristine and doped PPI thin films, according to [33,34]

If one assumes that iodine doping enforces chain planarization due to switching from benzenoid into quinoid form of some phenylene rings, this may be some indication that the peak at about 24.5 deg is related with ordering between phenylene rings, which is thought to correspond with eventual stacking. In Figures 31 and 32 one can see morphology of PPI2 films, pristine and iodine doped, respectively. It is clearly seen from this figures that after doping the film of PPI2 became much smoother and plane than pristine film. However, one can see in Figure 33 that X-ray diffraction patterns of PPI2 thin films pristine and doped have not shown any distinct difference, in contrast to the case of PPI pristine and dope counterparts. This discrepancy in behavior of PPI and PPI2 thin films against iodine doping seems to confirm our supposition concerning doping mechanism in the former, because the presence of oxygen atoms sp^3 hybridized can be seen as a factor acting against phenylene ring stacking. Analysis of the presented results, which include AFM images, X-ray diffraction patterns and UV-Vis absorption spectra suggest that there is quite distinct correlation for polyazomethine thin films linking their morphology and structure with technological conditions of their preparation. Thin films, whose surface morphology reveal granular character with granules essentially well separated or having contact points like osculating or touching circles, are thought to represent columnar growth with none or rather limited connection among them and in consequence among polymer chain or lamellae. Structure of such films reveal more

disordered or even amorphous structure, in contrast to films which revealing also granular morphology but with granules or columns overlapping, so that something like entities resembling ribbons or mountains of overlapping hills chains are formed. These so-called ribbons are not straight ones but they are revealing random wavy character, sometimes resembling chains of mountains are giving rise to films whose X-ray diffraction patterns show off better or less distinct peaks superimposed onto broad amorphous background. When regarding UV-Vis absorption spectra one can see that generally the structure of a film should be built up of nearly crystalline grains or at least grains or areas in which planar phenyl rings can even stack one over the another. Such supposition arise from observation, that absorption spectra taken on such films reveal at low energy side more or less pronounced feature at about 2.58 eV, which can be attributed to Wannier-Mott excitons, while the rest of the spectrum has “triangular” shape as it is well seen in Figures 8, 14 and 23, while slightly less pronounced in Figures 11, 17 and 20. The latter spectrum reveal vibronic progressions with missing indications of delocalized exciton formation. These observations can find some confirmation in morphology character of CVD prepared PPI thin films prepared pristine and doped. Generally, the pristine films are thought to reveal morphology and structure resulting from technical conditions of their preparation, however after doping these films are seen to reveal smooth surface, much smoother than the pristine ones. In the next section we try to describe electronic structure of PPI thin films starting from the simplest PPI and then we are going to prove that the proposed approach made in the frame of π -approximation is reasonable and can successfully describe electronic structure and optical spectra of other polyazomethines with more complex structure. Here it is worth mention that surface morphology of polyazomethine thin films has been taken by AFM working in so called contact mode, then with a sharp tip of about 20 nm dimension, the as-recorded images of surface roughness reveal granular features sizing some 100 and 200 nm, sometimes the features are smoothed out and wavy surface is observed. However, it is seen that films prepared under rather intense streams reveal more ordered morphology than those prepared under lower intensities of the stream of transport agent with mixed up molecules of monomers. It has been remarked in our earlier papers on PPI thin films prepared in both the horizontal and vertical setups. On the other hand the morphology of thin films prepared under strong intensity reagent streams coincide with more pronounced peaks in the X-ray diffraction patterns, but these peaks are always seen as superimposed on amorphous

background. There are reports on ordering in thin films of alternately conjugated polymers, where they are presented as long chains folded back and forth, so that one can observe lamellae. Areas composed of such ordered lamellae can be linked by entangled or curled fragments of chains, Figure 34. Crystalline areas consisting of stacks of polymer chains folded back on themselves are illustrated in Figure 35.

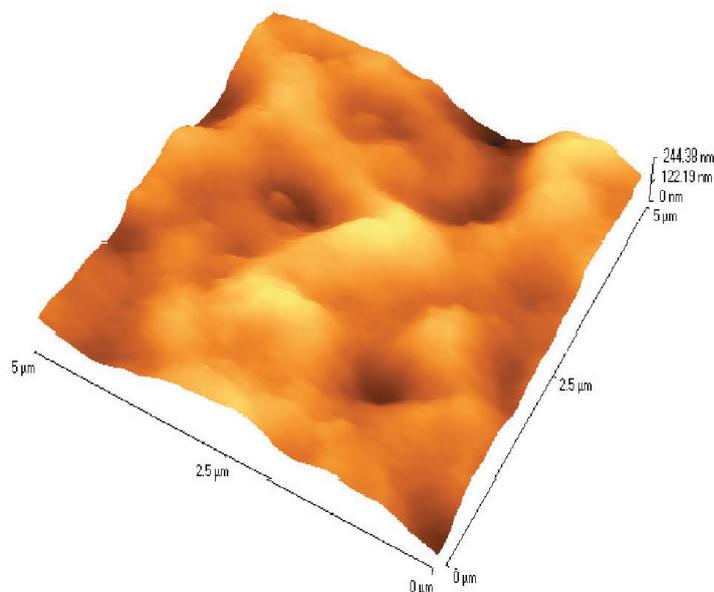


Figure 31. Topographic image of pristine PPI2 film [33,34]

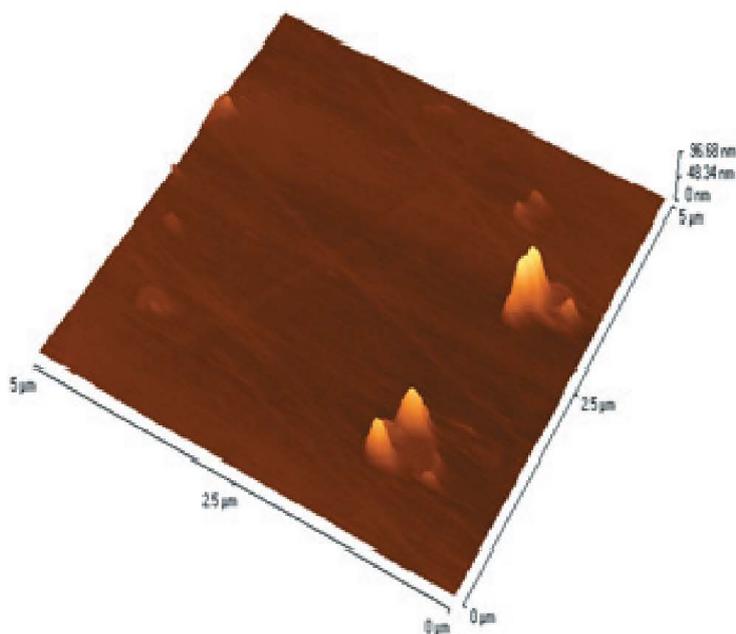


Figure 32. Topographic image of iodine doped PPI2 film [33,34]

It is thought that such lamellae are usually variously ordered in case of different polymers, but generally one may expect that such folding back of the chain seems to arise directly from the character of intratomic bonding in alternately conjugated polymers, though this is not always due to really stacking chains. In fact, alternately conjugated polymers whose chains are built up of sp^2 hybridized atoms in the backbone comprise cyclic molecules like benzene rings or thiophene rings and it seems to be quite natural that phenyl ring could accept planar conformation, but this depends on such factors like the stream intensity and when it is not too high one may expect that these folded back chain segments can be composed of a sequence of planar segments, called conjugated segments, whose lengths constitute set of randomly

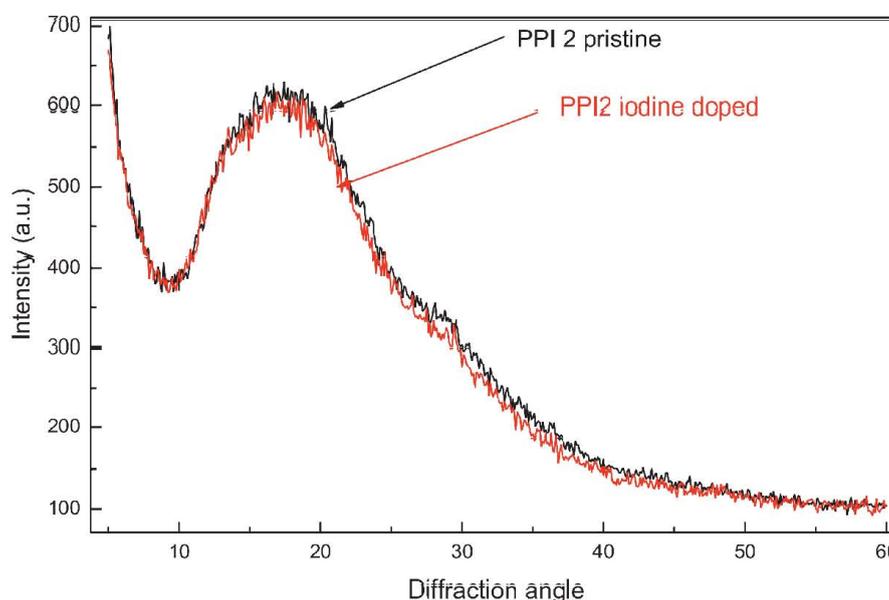


Figure 33. X-ray diffraction patterns of PPI2 pristine and iodine doped films [33,34]

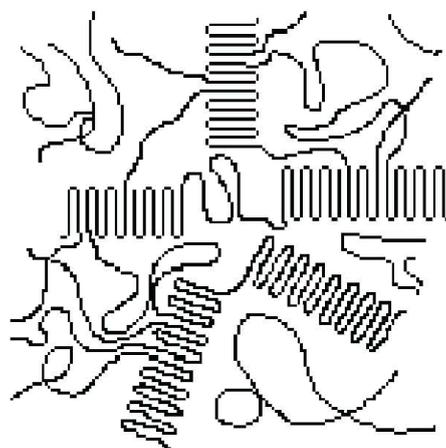
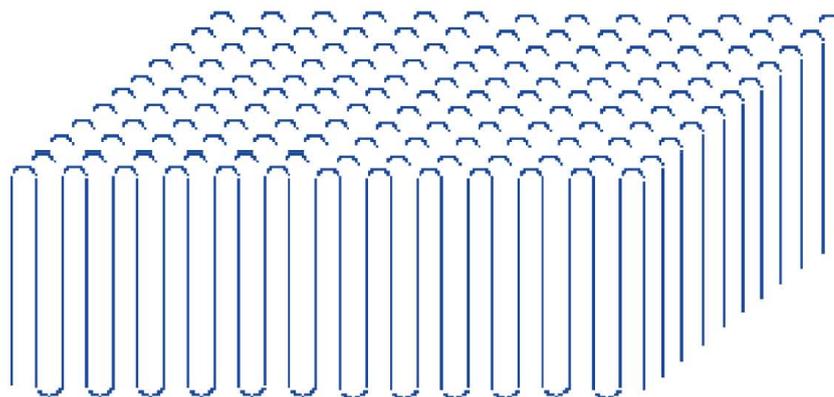


Figure 34. Structure of polymer thin films



They can fold, and they can stack. A stack of polymer chains folded back of themselves like this is called *lamella*

Figure 35. Crystalline areas of polymer thin film

distributed values. In contrast, high intensity of the stream bring about that these folded back and forth fragments are forced to strongly interact and couple when they are folded back on themselves they can form areas of polymer chains with cyclic aromatic units (phenylene or thiophene rings) stacked one over the next and in such conditions one may expect that these ordered areas are not limited to individual chains but they spread over some space volume, so that even one can speak about special kind of conjugation. These relations connecting morphology and structure with technological conditions cover also optical spectra, which reveal quite distinct dependence on preparation conditions as well as they can be linked with morphology and structures. Then, while knowing morphology and structure of a film one may expect that the shape of the optical spectra is known and determined, too.

4. Chain conformation in chosen polyazomethine thin films

Polymer thin films are expected to be mostly built up of interpenetrating entangled or curled polymer chains and because of that X-ray diffraction patterns taken on PPI thin films reveal usually broad amorphous background with more or less pronounced peaks superimposed onto it. These diffraction patterns are some expression of degree of crystalline character of PPI thin films structures. Backbones of π -conjugated polymers are built-up of sp^2 hybridized carbon or nitrogen atoms and they can form stacks of straight line fragments folded back on themselves forming ordered entities called lamellae, not necessarily these stacked chains represent conformation with phenyl rings stacked in parallel one over the other. One might expect that these stacked chains will be rather plane, especially that overlap of p_z orbital of carbon atom with p_z orbitals on two the nearest neighbor C atoms favor such planar conformation, but hydrogen atoms attached to phenyl C atoms at ortho positions, with respect 1,4 positions on phenylene ring interact with linkage hydrogen atom at azomethine linkage (steric hindrance) and additionally sp^2 lone pair orbital on nitrogen atom couples with π electrons of the nearest phenylene ring. These two kinds of steric effects are concurrent for π electron conjugation along the chain favoring planar conformation [7,28]. Thus one may expect that depending on preparation conditions the folded chain fragments can be additionally divided into conjugated segments. Of course, one might seek for any comparisons between conjugated polymers and molecular crystals composed of π conjugated molecules. However, such look at polymer structure hurts against polymer chain character being the essential element of their structure and moreover, these chains represent ordered conformation along with chain axis. Conjugated polymers built up of sp^2 hybridized atoms, carbon or so-called hetero atoms, constituting the chain backbone, which also constitute an ordered frame, whose planarity spread relatively easy can be divided into small fragments because of various interactions called steric hindrance. Or one can say that structure of conjugated polymer is some resultant of a certain equilibrium amongst those steric hindrances and conjugative interactions between p_z electrons that reveal character towards planar orientation of the chain. One may find in the volume of thin films of conjugated polymers area where this planarity exists and reveals tendency towards chains aggregation, which here could take shape of stacking [7,8]. Above mentioned characteristic feature of π electron orbitals, their rather

easy modifying of overall phenylene rings planarization might be this force, which make conditions favorable for stacking of such planarized fragments to bring about. One can expect that polymer chain is far from being totally planarized, but instead there are conjugated segments that can be distinguished along with the polymer backbone. Moreover, π electron system can be visualized as polymer chain fragment spreading over from one carbon atom where planarization of it begins towards the atom where it is finished and then the next atom at which a new conjugated segment starts on. That means, one may expect that the chain between folding points is composed of such conjugated segments. Simultaneously, one should not exclude situation where such conjugated segments in the subsequent folded back chain fragments can be distributed vertically one over the next in such a way that their phenylene rings will be stacked, so that some sort of spatial π conjugation might be observed. Taking into account the shape of spatial charge distribution within p_z orbitals one can expect that stacking of phenylene rings making part of such fragments of the folded back and forth polymer chain is possible. Though, one may expect that eventual hydrogen bonding between lone pair orbitals on N atoms and hydrogen atoms belonging to the parallel PPI chain can support such idea, as planarization effect enforced by hydrogen bonding may be seen as driving force of stacking idea [4,7,9]. However, there have not been available data on such stacking, though exciton with low binding energy appearing on the low energy wing of the absorption band have been reported [20]. They are interpreted in terms of geminate pairs [7,8] where a hole and an electron reside on different chains, which does not exclude stacking effects to take place with spatial π electron system. Such stacking of polymer chains folded back on themselves seem to be frequently met in the world of polymers, though in case of polymer thin films this may be more complex. However, when considering alternately conjugated polymers such structure seems to be quite obvious and expected because of orthogonal relation between sp^2 hybridized orbitals and p_z orbitals, especially the charge distribution in the latter one concerned. But here, new effect enter the game, this deposition techniques of alternately conjugated thin films, which may bring obstacles for stacking developing. There are forces due to steric hindrance that try to twist phenylene rings and shorten the conjugation length of a segment. These forces result from repelling hydrogen atoms at linkages with ortho-positioned one on the phenylene ring and from coupling lone electron pair on nitrogen sp^2 orbital with π electrons of the nearest phenylene ring. It is expected that conditions of alternately conjugated polymers influence such disadvantageous effects resulting in shortening the length of conjugated segments. Of course,

this can be different in various alternately conjugated polymers, especially while prepared in precursor route, i.e. PPV thin films. The precursor film is not alternately conjugated so that special chain-chain interactions can be different from those in alternately conjugated polymers. Polyazomethine thin films are prepared in various ways, but always one has to do with final alternately conjugated polymer. In case of CVD or TVE techniques thin film is grown upon the substrate following polycondensation process where chain development is closely associated with releasing small molecule, here water molecule. Then, this is the growth rate that has decisive impact on film growth and whether or not stacking is present, though hydrogen bonds can help to attain this end. While analyzing polymer chains of polyazomethines shown in Figure 2 one expect rather important variations in their conformation and its subsequent effect on conjugation and a role of component size whether the size the unit cell embedding several phenylene rings is dominating over the conjugation length along with polymer chains.

4.1. Polyazomethine PPI

PPI is the simplest amongst aromatic polyazomethines as it is composed of phenylene rings linked at para positions by means of azomethine linkage. It is seen in Figure 36 PPI prepared via polycondensation of aromatic diamine and dialdehyde, i.e. paraphenylene diamine (PPDA) and terephthal aldehyde (TPA), subsequent phenylene rings along with its are linked alternately with two carbon atoms or two nitrogen atoms at 1,4 positions [20]. The unit cell of PPI chain comprising two phenylene rings and azomethine linkages, for alternating of CH group and N atom positions in the subsequent linkages, can be seen as being as large as doubled PPV unit cell, consisting of one phenylene ring and vinylene linkage.

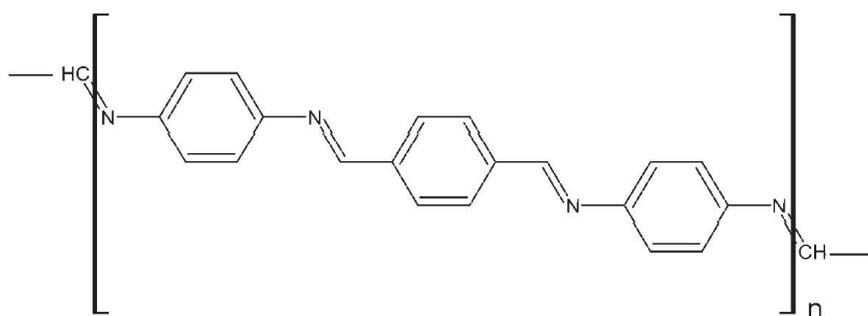


Figure 36. Fragment of PPI chain

However, while taking into account that on the average each phenylene ring has $\frac{1}{2}$ (CH+N) units substituted at para positions, as it has been discussed in our previous paper [28] and taken advantage of in order for PPI chain was approximated with PPV-like polymer chain, i.e. PPI chain being approximated with phenylene rings linked by means of vinylene-like linkages, as it is shown in Figure 37 [20]. Such approach has appeared quite successful to find confirmation for the observed similarity of UV-Vis absorption spectra of PPI and PPV [15]. Assuming more negative α ($1.5 \times \alpha_{cc}$) integral and the same resonance integral β for nitrogen like for carbon [7,8] resulted essentially in the same Hückel gap of azomethine unit like it is the case for vinylene or more precisely like the gap of ethylene molecule, though on energy scale this gap is pushed downward. However, such approach has not taken into account such shift of the gap of azomethine unit to lower energies. When considering conformation of PPI chain, ab initio quantum mechanical calculations were undertaken on molecule of the simplest aromatic Schiff base as is N-benzylideneaniline to analyze planarity for neutral and protonated molecule, that is shown in Figure 38. There have been available data revealing that B-A molecule is not plane and dihedral angle between N-phenyl ring and CH=N bond was about 45° , while dihedral angle between CH linked biphenyl ring and azomethine linkage was equal to about 10° [37]. Results on UV-Vis optical spectra carried out on BA showed that they were quite different from those taken on stilbene or azo-benzene molecules, the spectra of the two latter were reported to be similar [37]. The calculations made with the use of various basis functions proved that neutral molecule of BA is not planar and the dihedral angle was about 45° . In fact barriers for rotation from plane neutral molecules were low enough. In contrast, protonated

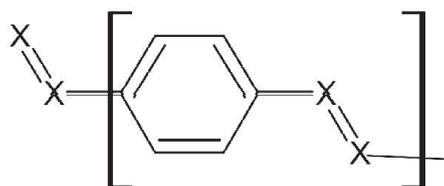


Figure 37. Unit cell of PPV-like polymer chain

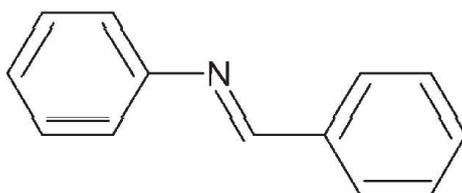


Figure 38. Benzylideneaniline

molecule was planar and barriers for rotation from planar conformation were much higher than the barrier for rotation when the dihedral angle was taken 90° . This tendency of neutral and protonated BA molecule coincide essentially with the picture of HOMO orbitals for neutral and protonated molecule. It is clearly seen in Figure 40 where HOMO orbitals of protonated and de-protonated BA are shown, that protonated molecule reveal π conjugation all over the whole molecule, while in case de-protonated BA π conjugation is disrupted by the highlighted orbital lobe. It is worth mention here, that in contrast to BA and stilbene, absorption spectra of PPI

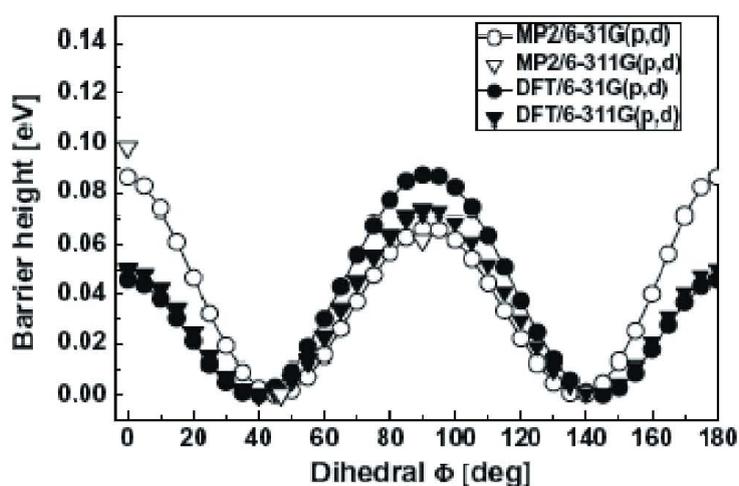


Figure 39. Energy barrier versus dihedral angle [37]

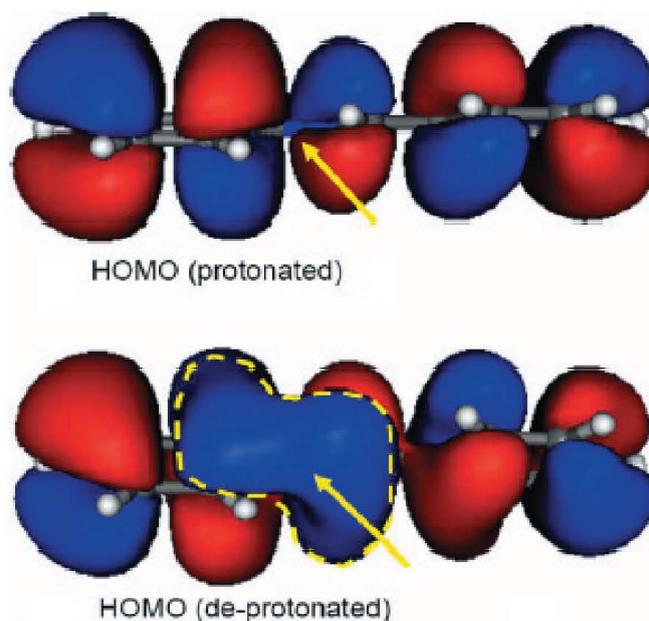


Figure 40. HOMO orbitals of protonated and de-protonated BA molecule [37]

were proved to nearly coincide with those of PPV [15]. Then, one may expect that conformation of polyazomethine PPI is not so rotated as it is the case for BA molecule. These calculations showed that BA protonation resulted in HOMO level variation as shown in Figure 39. It is clearly seen from this figure that molecule protonating brought about molecule planarising, which vanished after de-protonation process. Similar calculations were carried out on PPI thin films and they showed that equilibrium ground state geometry for neutral PPI is shown in Figure 41. As it can be shown in this figure the optimized ground state geometry reveals smaller dihedral angles than it was the case for BA molecule. Additionally, one can see that phenylene rings in the backbone of the PPI polymer chain reveal some quinoid character. It seems also that single polymer chain can have another conformation than average PPI polymer chains have in PPI thin films. While continuing these consideration one can take into account polymer chain of PPI with octyloxy side chains attached to every other phenylene ring at 2,5 positions, as it is shown in Figure 42.

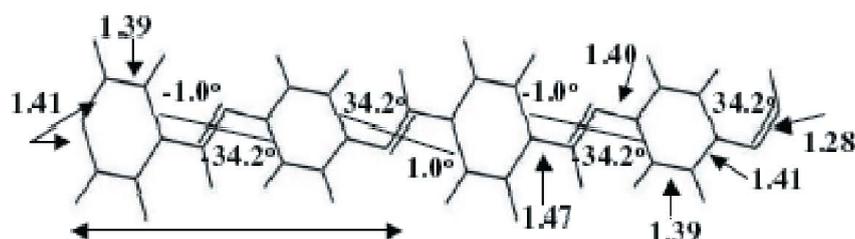


Figure 41. Optimized ground state geometry of PPI chain [28]

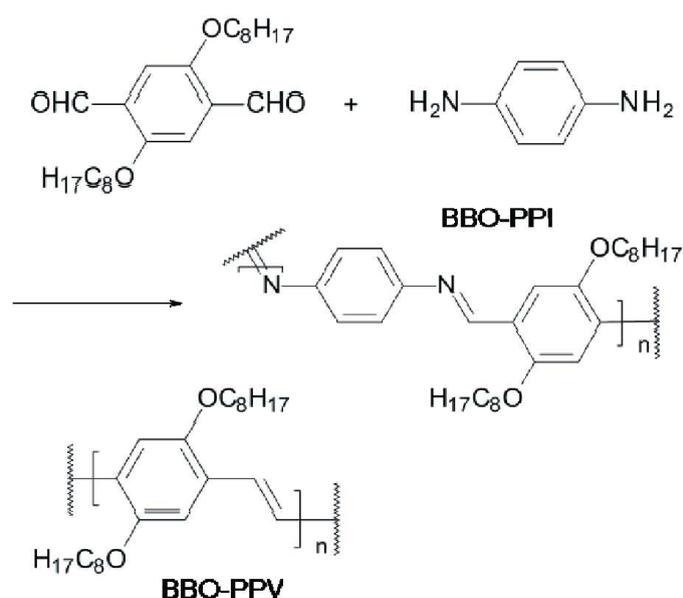


Figure 42. Polymer chain of BOO-PPI [36]

Soluble polyazomethine poly(1,4 - (2,5 - bisoctyloxy phenylenemethylidynenitrilo - 1,4 - phenylenenitrilomethylidyne) (BOO-PPI) was prepared following polycondensation polymerization of PPDA and 2,5-bis(*n*-octyloxy)terephthalaldehyde, which was described elsewhere [36]. The presence of side chains makes this form of polyazomethine soluble, so that it could be prepared in nearly “standard” polycondensation process, which means that the resulting polymer should have much longer polymer chains than those expected to be the case for CVD or VTE prepared polyazomethine. Though, while bearing in mind so close correspondence of absorption spectra of PPI and PPV, (they nearly coincide), one can expect that conjugation length of PPI chains should not be much shorter than those of PPV, which was prepared via precursor method. Our studies made on thin films of BBO-PPI and particularly those made at various temperatures indicate that spin-coated films before any thermal treatment reveal rather disordered if not amorphous structure [44]. After the first annealing at about 200°C temperature showed that the low energy absorption peak related to electronic transitions linking delocalized states revealed vibronic progression and further continued cycles of heating and cooling proved that there is tendency of crystallization of BOO-PPI thin films at about 120°C enforced by relaxed disposition of side alkiloxy chains. Generally, one can see that heat treatment only slightly influence the width of the absorption band, but it changes its shape.

4.2. Polyazomethine with oxygen in the backbone

While preparing polyazomethine via polycondensation of a complex aromatic dialdehyde [33,34] as it is the ODBA having oxygen atom in the middle of the molecule between two phenylene rings and PPDA (Figure 43), the backbone of the resulting polymer is composed of conjugated units consisting of three phenylene rings separated with two azomethine linkages placed between oxygen atoms [33,34], the resulting polymer will be designated in the text as PPI2. Oxygen atoms in the polymer chain are sp^3 hybridized with two such orbitals used to link to the nearest neighbor polyazomethine units and the two others which are two lone pair orbitals of the oxygen atom. Then, the oxygen atoms separate two neighbor conjugated segments of the same length (Figure 44). Bearing in mind that polyazomethines are prepared via polycondensation of diamine and dialdehyde aromatic, the chain of polymer can be seen as composed of periodic polyazomethine chain being multiplicity of polymer unit cell and the chain end part consisting of phenylene ring or phenylamine or benzaldehyde, which could be treated as contributing to optical spectra electronic transitions in phenyl ring or phenylamine or benzaldehyde.

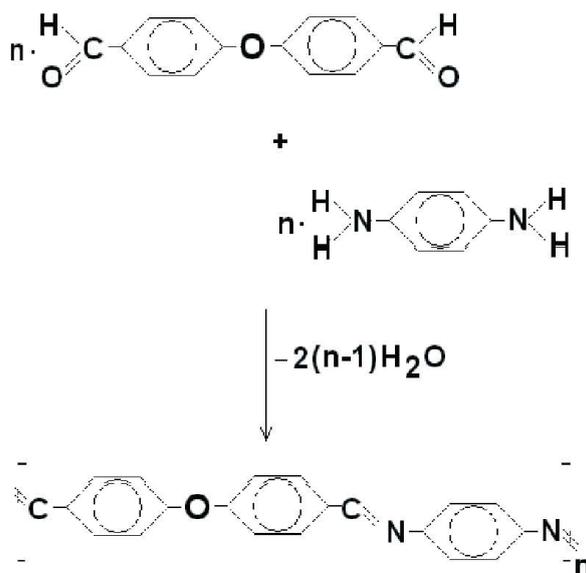


Figure 43. Polycondensation reaction of polyazomethine with oxygen in the backbone

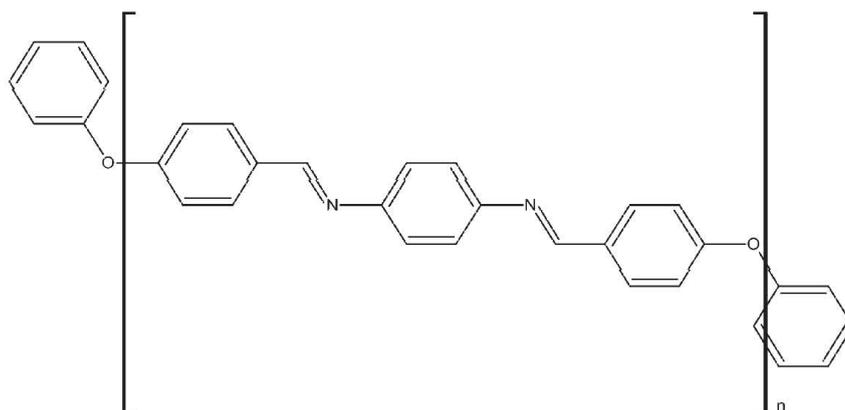


Figure 44. Polymer chain of polyazomethine with oxygen atom

In case of PPI2 chain essentially, each of them constitute double-unit molecule while the third phenylene ring may be treated as a molecule ending periodic chain, or while approximating PPI chain with PPV-like one the repeating unit consists of two PPV-like units and the third phenylene ring as additional unit attached to the short but periodic unit, similarly as it is the case for PPI chain. It is worth mentioning that such situation is ubiquitous in case of polymer chains developing following the polycondensation process, because the end elements of the chain is phenylene ring with oxygen atom. Even though PPI2 chain contains in its repeating unit only two PPV-like units, there is distinct correspondence between features observed in PPI and PPI2 UV-Vis absorption spectra, even though this time composed of only two repeating units, resembling situation while considering in linear models defect modes

associated with attachment of defect atom at the end of the line. Similarly, as it is the case of PPI, one can notice that polymer chain consists of repeating unit, i.e. polymer chain, and the end phenylene ring should be treated as if it was any defect unit attached at the end of the chain. That means, optical spectra of such polymers should be seen as some resultant of polymer (or oligomer) and this end phenylene ring, which is thought to be characteristic of polymers prepared via polycondensation process. Thus, one should expect that optical spectra of this azomethine thin film should reveal some correspondence with absorption spectra of PPI thin films, where polymer chains are finished by phenylene ring with aldehyde or amine end group. However, here those oxygen atoms incorporated into PPI backbone in an ordered sense, divide the conjugated chain into so short conjugated segments of the same length. The spectra taken on thin films of this polyazomethine can be seen as some replica of PPI but all the bands being displaced towards higher energies.

4.3. Polyazomethines based on benzidine

It can be seen in Figure 45 that polymer chain poly(benzidinephenylene azomethine) is composed of bi-phenyl rings which have at 4 and 4' positions attached nitrogen atoms, which in turn through polycondensation reaction combine with methine units coming from terephthalaldehyde, so that this polymer can be treated as if it was composed of alternate biphenylene and phenylene rings linked together by azomethine units, but always biphenylene pair is ended with two nitrogen atoms at 4,4' positions, while each singular phenylene ring has at 1,4 positions two carbon atoms (two CH groups coming from aldehyde group). Generally, it has been shown that starting bi-phenyl molecule has not undertook planar conformation, because of electrostatic interactions resulting from repulsion of π electron systems of the two phenylene rings linked together with some contribution coming from steric

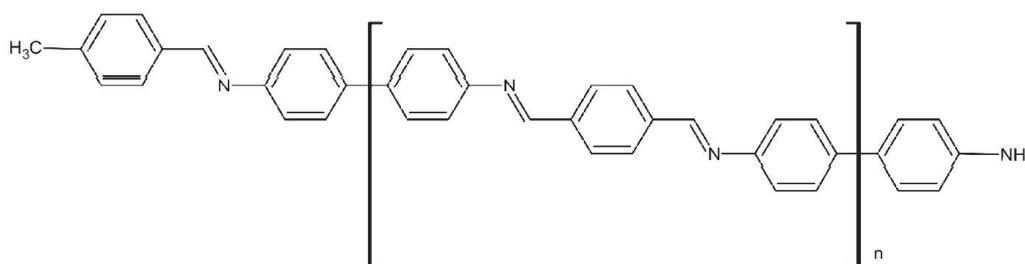


Figure 45. Polyazomethine based on benzidine monomer

hindrance of hydrogen atoms attached in the two rings at ortho- position with respect of bonds linking the phenylene rings. On the other hand, one can apply a little different approach to the conformation of the azomethine link, while considering repeating units of this chain. In fact one can notice that the unit cell or repeating unit along with the backbone can be seen as spread out over one phenylene ring of the bi-phenyl at one end to the phenylene ring of the other bi-phenyl with the phenylene ring coming from terephthalaldehyde in the middle. Moreover, one can notice that this repeating unit is composed of three phenylene rings separated with two azomethine units, similarly as it is the case for polyazomethine with oxygen atoms in the backbone (PPI2). However, because this unit cell is built up of biphenylene and phenylene ring, such unit cells interact with one another in contrast to PPI2 whose conjugated fragments are well separated from one another by oxygen atoms.

4.4. Poly(p-fluorenephenyleneazomethine)

This polyazomethine might be seen (Figure 46) to resemble that coming from biphenylene diamine (benzidine), sp^3 hybridized carbon atom (9H) is thought to ensure the planarity of the two phenylene rings, but its π electron system constitutes two essentially separate phenylene rings. Thus, one should expect to attain situation very similar to the one meets in biphenylene, but in comparison to the latter one can see that there is planarity of the molecule, though there are reports it is contested. However, the presence of carbon atom number 9 enforces orientation of the two phenylene rings, which even though in the same plane but their axis is changed. Then, one may expect that polycondensation of 2,7-fluorene diamine will result in polymer chain with two planar phenylene rings with their 1-4 axes inclined, which may have its own impact onto π conjugation scheme of the polymer backbone. When comparing benzidine and fluorene

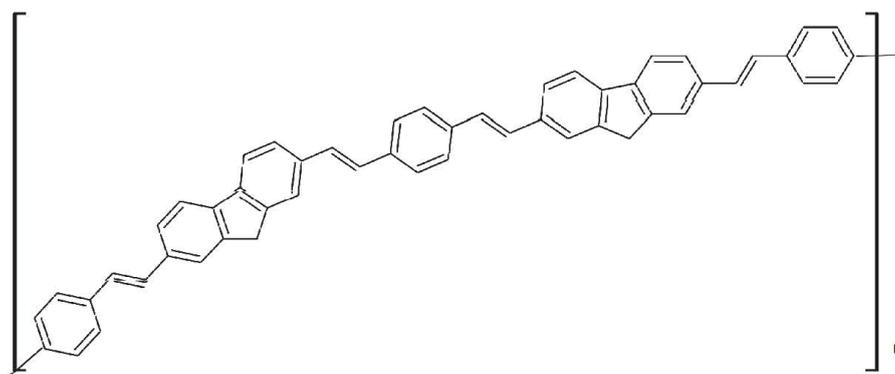


Figure 46. Poly(fluorenephenyleneazomethine)

9H one can find that the former one being built up of two phenylene rings twisted around the bond linking them seems to lose its importance because after polycondensation with terephthal aldehyde, the polymer unit cell resembles that of PPI2 rather, while the latter one has the rings planar with their axes inclined instead of being parallel.

4.5. Poly(tetraminediphenylenephenylene azomethine)

This polymer, as given in Figure 47, was prepared by polycondensation of diaminobenzidine (diphenylenetetramine) and terephthal aldehyde. Then, one may expect that as-prepared polyazomethine has large π electron system due to large tetramine part. In fact, one can imagine elongation of the polymer chain while attaching aldehyde phenylene ring, which can make entity composed of four such backbones, but one bears in mind that now each aldehyde should be linked with four-arm amine and the question arrives how will they be spread over in the space in order for not to disturb such nearly cross linked entity. However, it may be problematic whether conjugated segments are long enough. While considering thin film of tetraminebiphenylene based polyazomethine one has to do with cross-linked polymers where benzilidenephénylene azomethine chains are branched with short azomethine linkages resulting from reaction of terephthal aldehyde carbonyl groups with amine units substituted on two different benzidine based polyazomethine chains (terephthal aldehyde connect 3,3' type sites on various polymer chains).

The branched π electron system of this azomethine is resultant of overlap of HOMO and LUMO orbitals of phenylene rings with other phenylene counterparts via azomethine HOMO

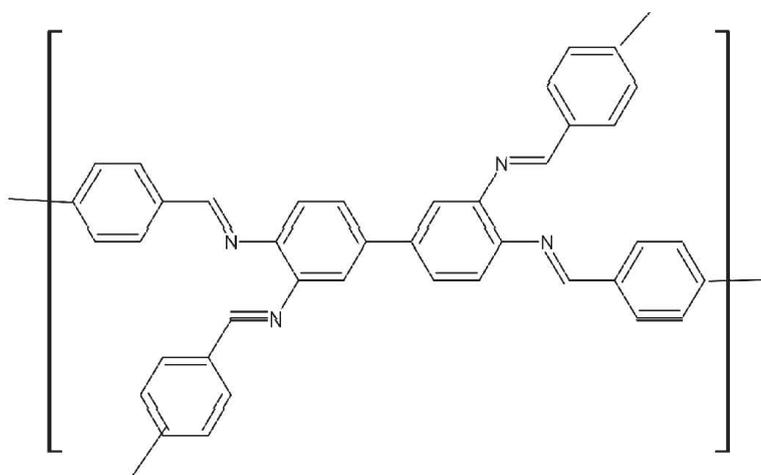


Figure 47. Poly(dibenzidinephenyleneazomethine)

and LUMO, respectively. Then, one may expect that some order is expected to develop while expecting that the branches starting from 3,3' carbon atoms on biphenylene unit, make some sort of bridges linking the above mentioned straight chains derived from benzylidene, moreover the ones expected to run nearly parallelly.

4.6. Polyazomethine derived from naphthylene diamine

This polyazomethine, illustrated in Figure 48, is prepared via polycondensation of 2,5-naphthylene diamine and terphthal aldehyde, so that there is overlap of relevant naphthalene molecular orbitals with molecular orbitals of azomethine linkage and then phenylene (from terphthal aldehyde) molecular orbitals. Thus, similarly to the above discussed polymer chains there are conjugated segments running throughout such polyazomethine backbone and some better planarity of conjugated segments are expected to be the case. Essentially, there are similarities between electronic structures of naphthalene and benzene, and also there is rather important role of configuration interactions which has rather important impact onto absorption spectra of the two aromatic molecules, but this aromaticity is stronger in benzene ring rather than in naphthalene. Moreover, it is worth mentioning that while analyzing polyazomethine chains of various length one should bear in mind that in each case there are end groups of amine or aldehyde character, and their ubiquitous presence in each polymer chains is expected to be the reason why optical transitions characteristic for benzene or naphthalene molecules are observed in the optical spectra taken on thin films prepared by CVD or VTE methods. They are some sort of prove that polymer chains of such materials are not too long, though to decide whether or not polymer chains are sufficiently long can be deduced from infrared

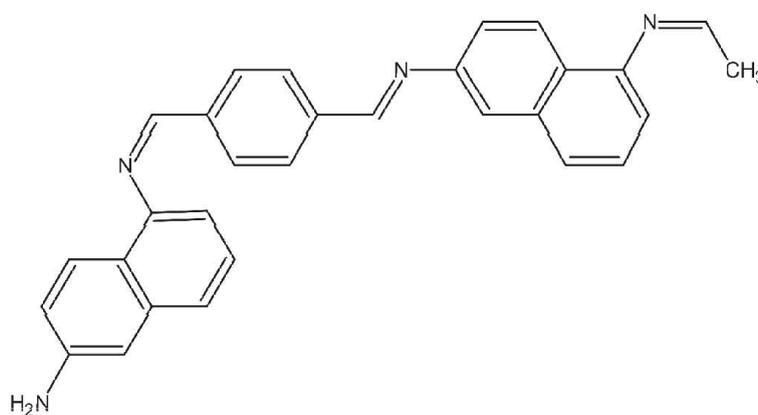


Figure 48. Fragment of the backbone of poly(naphthylene-p-phenyleneazomethine)

5. Carbon atom hybridization in alternately conjugated polymers

Carbon atoms constituting involved in the backbone of alternately conjugated polymer are sp^2 hybridized, as it is shown in Figure 50, where the electric charge of three electrons, one from s and two from p atomic orbitals are distributed in such a way that each of three trigonal orbitals has the same charge in which contribute all the atom orbitals. Thus, each orbital has one electron, so that they are involved in three valence bonds: two with the neighbor carbon atoms in the backbone and one involved in a bond with hydrogen atom [7,8]. The fourth carbon atom is allocated on p_z orbital orthogonal with all the three sp^2 orbitals. Alternately conjugated polymers with phenylene rings in the backbone have linkages connecting them at para (1,4) or meta (1,3) positions, while linkages are formed by bound carbon atoms or heteroatoms (i.e. nitrogen, sulfur) trigonally hybridized. The fourth electrons from carbon atoms or heteroatoms are involved in constituting π electron system, as it is the case for poly(p-phenylenevinylene) (PPV) [1-8]. Similarly, in the case of alternately conjugated polymers with nitrogen atoms in the backbone such as polyazomethines or Schiff bases [5,6,28], nitrogen atoms are built in linkages and they are trigonally hybridized, too [28]. Here, may be it is worth mentioning that such position of nitrogen atom is some consequence of relative easiness of polyazomethine forming through polycondensation process which is pursuing due to chemical reactions between end groups, especially when these are amine and aldehyde ones, so that the released low weight molecule is a water molecule. However, having five valence electrons, which means there are five electrons to distribute among four orbitals, so that the only reasonable solution when nitrogen atom is involved in the polymer backbone is allocating four electrons on three sp^2 orbitals, one allocating a lone electron pair, and put the fifth one onto p_z orbital.

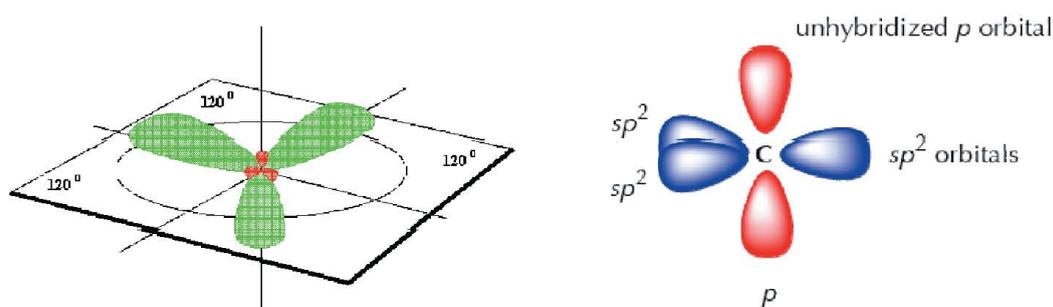


Figure 50. Electron charge distribution in the trigonal orbital

Otherwise it would not be possible for π conjugated system to be formed, because to form double bond p_z orbitals involved on carbon or nitrogen atoms can have one electron, similarly as it is the case for σ bond forming [7,8]. Thus, for nitrogen atom these four electrons can be distributed in such a way that two electrons are put individually on two trigonal orbital to make σ bonds with two nearest neighbors in the backbone, while a lone pair is allocated on the third trigonal orbital. No other possibility of valence electrons distribution is possible as p_z orbital can accept only one electron if involved in alternate conjugation. Hybridization means that charge distribution is changed in such a way that potential energy of electrons on carbon atoms is diminished. While carbon atoms are hybridized one arrives at situation that energy of three sp^2 orbitals is lower than that of p_z orbital, which means energy levels of three electrons are below the energy of the fourth one (Figure 51). Anyway, the three trigonally hybridized electrons are in position to make bonds with two similar carbon atoms and one hydrogen atom. In consequence electronic level corresponding to bonding state of electrons at sp^2 orbitals involved into σ bond are pushed down while their antibonding counterparts are pushed upward, so that there is quite large energetic gap separating so called occupied σ states from empty ones [7,8,20]. However, energies of electronic states coming from electrons allocated at p_z orbitals are situated inside this gap in such a way that the bonding states are pushed down slightly below the midgap and the antibonding ones are pushed upward to be slightly above it. This is a consequence of overlap of carbon orbitals when forming bonds with the nearest neighbors, which in the case of ethylene is illustrated in Figure 52. Nitrogen atoms in alternately conjugated polymer chains are sp^2 hybridized, but in contrast to carbon atoms they have five valence electrons, which makes that there are two ways of sp^2 hybridization of nitrogen atoms, so that there are distinguished conformations where nitrogen atoms are bonded with two atoms (as it is the case for pyridine molecule) or three atoms (as it is the case for pyrrole molecule) [7,8].

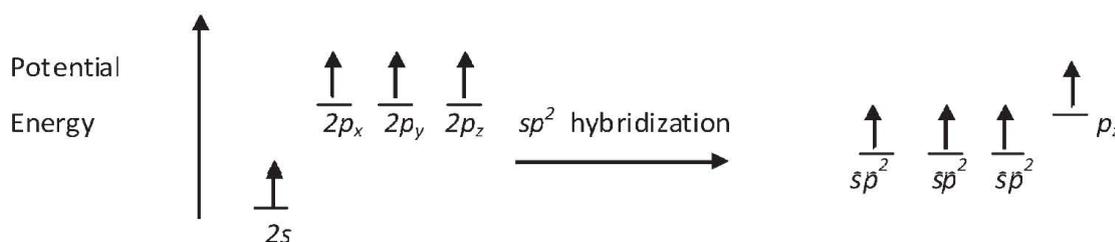


Figure 51. sp^2 hybridization in carbon atoms

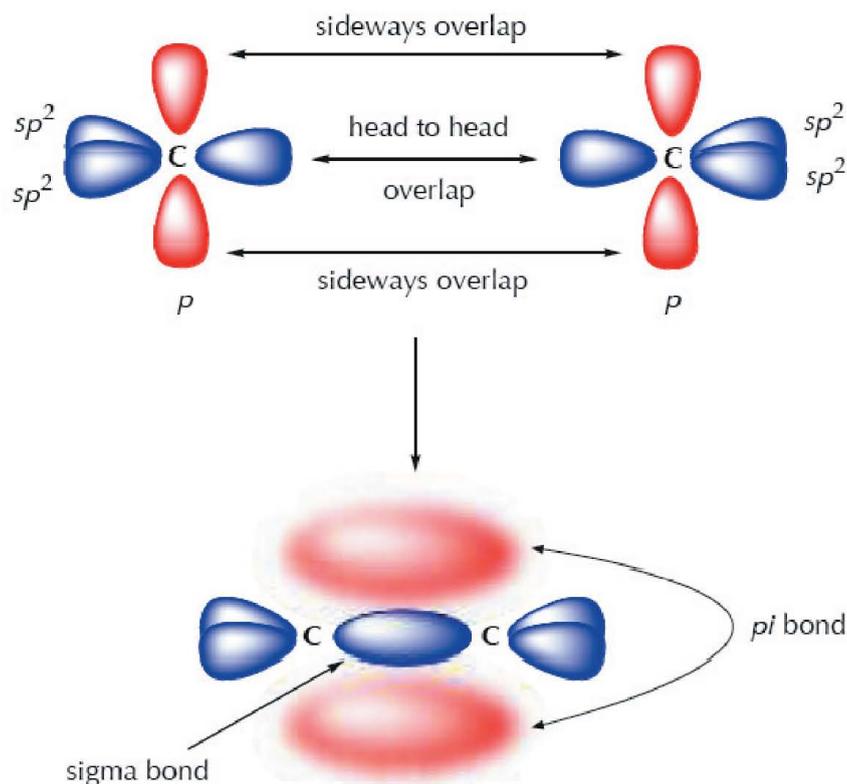


Figure 52. Formation of π electron system in ethylene the simplest conjugated molecule

The two conformations are met in polyaniline, pernigraniline in particular [1,4]. In the case of a pyridine molecule lone pair is allocated on sp^2 hybridized orbital, so that one electron is allocated on p_z orbital, while in pyrrole molecule three electrons are allocated on three sp^2 orbitals, while lone pair is at p_z orbital.

Polyazomethines are polymers having azomethine linkages with nitrogen atoms sp^2 hybridized, like this is the case of pyridine. This has its rather important impact onto polyazomethine chains conformations in general, as there is overlap of p_z orbitals on the nearest neighbor carbon or nitrogen atoms resulting from their conjugation, this overlap being the strongest the more parallel these orbitals are. However, hydrogen atom attached to carbon atom in the azomethine group repel with ortho-hydrogen atoms on the phenylene ring, so that phenylene ring is twisted around σ bond linking CH group in the linkage with phenylene ring, which can cut conjugation along the backbone, so effectively reducing conjugation length. At the same time, there are forces acting to couple lone electron pair allocated on N sp^2 orbital with π electrons of the nearest phenylene ring, so that conjugation of N p_z orbital with this phenylene ring is interrupted. Thus, electronic properties of polyazomethine chain are expected

to be some resultant of occurrence of these steric effects and N sp^2 lone pair- phenylene π electrons coupling. Thin films of alternately conjugated polymers with nitrogen atoms can be prepared by chemical vapor deposition or physical vapor deposition techniques based on condensation polymerization with polymer chain are growing all over the substrate surface following Flory rule [17]. That means that thin film of such polymer grows at various sites of the substrate independently of the length of a chain developing on the substrate to which a functional group being attached. Then, during the film growth upon the substrate folding back and forth of developing chains cannot be excluded and, moreover, it is expected to be the case. Such polymer chain growth is expected to be linked with some polymer chain ordering within the volume of the growing film, which has been confirmed by our experiments on preparing thin films of poly(paraphenylene azomethine) (PPI).

5.1. Connectivity of π electron systems in aromatic polymers

Connectivity of π electron system along with the backbone of such alternately conjugated polymers like PPI is made up through overlap of the relevant frontier molecular orbitals of constitutive units of a polymer. In case of PPI it has been shown to result from overlap of the relevant HOMO and LUMO orbitals of phenylene ring and azomethine linkage [20], similarly as it is the case for PPV thin films [29-31]. Then, in our earlier paper [20] it has been shown that like phenylene frontier orbitals can be approximated with benzene orbitals, similarly azomethine orbitals can be approximated with those of ethylene. Because, PPI chain is built up of phenylene rings and azomethine linkages, the effectiveness of this overlap can ensure one component of HOMO pair, namely the one with phase at 1,4 positions. Similarly, in case of LUMO - the one component having also phase at 1,4 positions. That means, the overlaps of components ϕ_3 and ϕ_4 of HOMO and LUMO pairs, respectively with the relevant HOMO and LUMO orbitals, respectively, of ethylene unit ensure this continuity (Figures 53 and 54). As it is shown in Figure 55, D_1 and D_2 PPI molecular orbitals are derivable from an overlap of phenylene ϕ_3 and ethylene ϕ_1' orbitals in antibonding and bonding configurations, respectively. Similarly D_1^* and D_2^* orbitals are given rise from ϕ_4 and ϕ_2' orbitals in bonding and antibonding configurations, respectively. L and D_3 are ϕ_2 and ϕ_1 phenylene orbitals, while L^* and D_3^* come from ϕ_5 and ϕ_6 phenylene orbitals. It is worth to emphasize that because

benzene is molecule of high symmetry, its HOMO and LUMO orbitals are double degenerate by symmetry, which means that these orbitals constitute pairs of orbitals of which one has nodes at para positions - ϕ_2 and ϕ_5 and others have phases at para positions - ϕ_3 and ϕ_4 , respectively (Figure 53). In case of azomethine linkage it is assumed that its molecular orbitals can be approximated with HOMO and LUMO of ethylene, ϕ'_1 and ϕ'_2 , respectively (Figure 54) [20]. Polyazomethine prepared by polycondensation of fluorene diamine and TPA and another one prepared by polycondensation of benzidine and TPA molecule should be similar, as they are built up of biphenylene units linked with azomethine linkage with phenylene unit. Two phenylene rings making part of fluorene entity are coplanar, but the presence of methylene unit (CH_2) makes axes of two phenylene ring inclined instead of their alignment as it is the case for biphenyl. In contrast, in benzidine two aligned phenylene rings are twisted around bond due to repulsion of their π electrons systems.

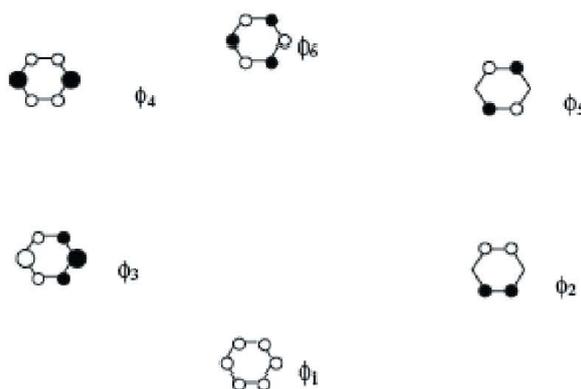


Figure 53. Benzene molecular orbitals, accordingly [20]

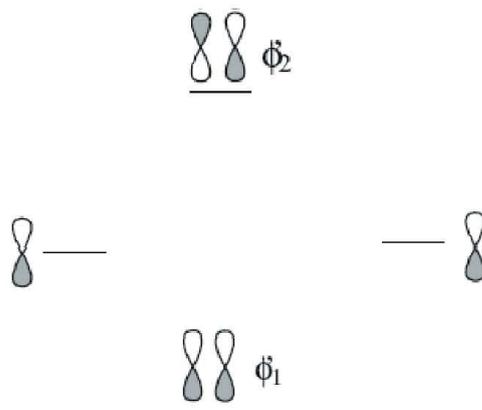


Figure 54. Molecular orbitals of vinylene unit, accordingly [20]

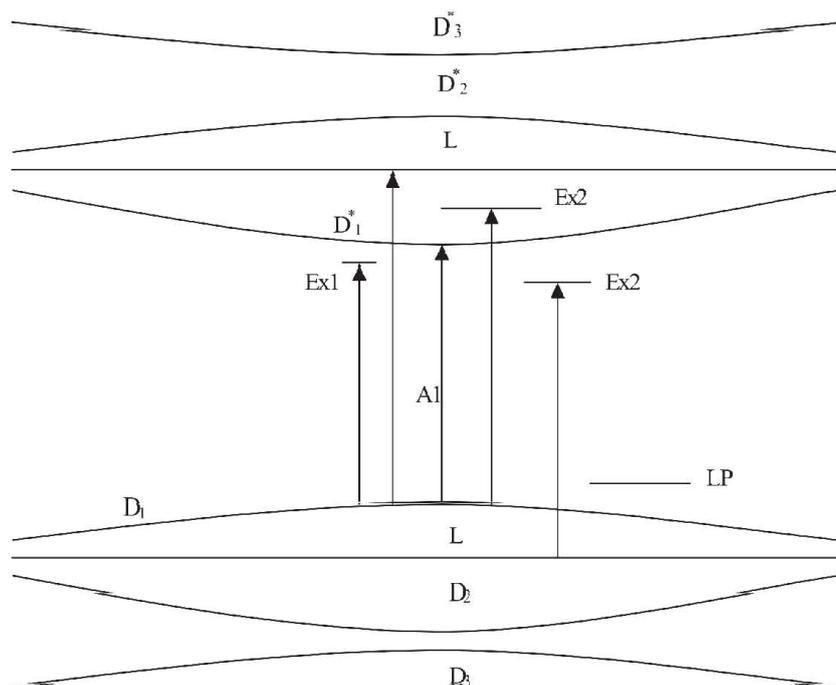


Figure 55. Electronic structure of PPI deduced from MO of benzene and ethylene acc. [20]

The system of π electrons in polyazomethine prepared from diaminebenzidine is expected to spread out over a plane due to four arms of which two are going out from each of biphenyl rings. The sites four amine groups being attached to bring about two components of the pair of phenylene frontier orbitals to be involved in proliferation of π MO across the plane. The case of fatt Brown diamine appears to be quite different, as π conjugation is running through two amine groups attached to phenylene carbon atoms in meta positions. However, π system of this monomer is additionally increased by substitution of naphthalen to phenylene ring involved in the backbone. While analyzing polymer chains of polyazomethines considered in previous sections, one should notice that polyzaomethines are products of polycondnesation, so that each polymer chain can be ended with phenylene ring and amine or aldehyde groups, and this aniline or benzaldehyde termination must be seen as attached to periodic polymer chain, being multiplicity of repeating units. While using the same approach as the one used to PPI thin films, one can approximate each repeating unit with PPV-like one. The case of PPI taken into consideration in [20] corresponds to situation with rather long PPV-like periodic chain. Then, one should expect that absorption spectrum of PPI comprises features related with periodical part of the chain and features related with azomethine benzylidene end unit. The details will be considered in further section for studied thin films of aromatic

polyazomethines. When considering thin films of polyazomethines prepared by polycondensation of diamine of fluorene and benzidine [18,19] one must first consider conjugated system of these diamines, which have biphenylene part. The shape and chemical structure of fluorene are expected to be planarized due to methylene group linked to ortho carbon atoms on two phenylene rings, while in case of diaminobenzidine one may expect the two phenylene rings being planarized due to four azomethine linkages. Thus, one may expect that components ϕ_3 and ϕ_4 are responsible for overlap, so that two molecular orbitals with energy slightly above and slightly below the two should be observed. Another components concerned, ϕ_2 and ϕ_5 ones with nodes at para positions are expected to give two nearly degenerate molecular orbitals. In case of diaminobenzidine derived polyazomethine one may expect that connectivity resembles situation like in PPI, though some twist of phenylene rings from biphenylene suppresses conjugation. While considering this monomer one should bear in mind that combining aldehyde group with amine one is nearly straightforward because TPA molecule is rather small one and having functional groups at para positions. Polyazomethine with oxygen atoms in the backbone is illustrated in Figure 44, where one can see that its chain consists of three-phenylene-two-azomethine units separated from one another by oxygen atoms. That means there are two phenylene azomethine units with attached phenylene ring. To analyze the connectivity of π -electron systems of constituent units of the polymer one should take into account benzene, naphthalene and azomethine or vinylene molecular orbitals to see how can they overlap to make conjugated system of the resultant polymer. It has been shown in our precedent paper that this π connectivity of poly(paraphenylene azomethine) (PPI) can be derived from benzene and vinylene orbitals [28], because its backbone was approximated with that PPV-like polymer. Even though such approach may seem oversimplified it is thought to explain PPI electronic structure rather well, moreover in some elements it can resemble treatment of PPV [28-31]. We try to use this approach to fluorene based polyazomethine (FPI), because one can see in Figure 1 a molecule of diamine fluorene consists of two phenylene rings which are planarized due to methylene unit at atom C9. Then, conjugation is running along with overlapping ϕ_3 and ϕ_4 orbitals which in turn overlap with azomethine molecular orbitals attached at 4 and 4' positions or from biphenylene orbitals derived from benzene components with phases at para positions. One may expect that while bringing together molecular orbitals of benzene occupied by two electrons two molecular orbitals slightly below and slightly above the starting ones will be formed. The ϕ_2 and ϕ_5 orbitals from two phenylene rings are thought to

give two pairs of nearly degenerate molecular orbitals localized each on one phenylene ring. In case BPI polyazomethine one can expect something resembling tree scheme, where one line is running essentially in the same way as in PPI or FPI. Overlaps of phenylene molecular orbitals ϕ_3 and ϕ_4 goes throughout carbon atoms at paraposition. However, an additional branch running through overlap with ϕ_2 and ϕ_5 orbitals and then through 1,4 carbon atoms on aldehyde phenylene ring. Thus, one may see several split bands, as well as those localized on aldehyde ring. If one tried to understand lateral spread of π electron system one must take into account complexity resulting from attaching tetramine molecules to aldehyde end group. Anyway, one may expect some sort of two dimensional network covering some area of the substrate. When analyzing molecule of fat Brown one can expect that polycondensation should result in some sort planar network, though not so spread over as in the precedent case. In fact, here one has two amine groups at meta position with respect to one another, while terephthalaldehyde keeping its para orientation. Thus, conjugation is amplified with respect to PPI, as connectivity is running through overlap of both types of phenylene molecular orbitals, and additionally this system is more developed through $-\text{N}=\text{N}$ -naphthylene unit attached to diamine ring at position 4. In contrast to such spread over π electron system, PPI2 can be seen as PPI backbone cut in ordered manner by oxygen atoms, which make the chain more flexible but its conjugation limited to three phenylene rings separated with two azomethine units. This is clearly visible if one compares absorption spectra of the above discussed polymers prepared in form of thin film.

6. Π -electron approximation

Materials composed of π -conjugated molecules, both low weight ones and polymers, reveal properties which can be explained with π electrons. These π electron systems are built up of a sequence of alternate single and double bonds. To give an account of various phenomena in the π electron approximation means that one should assume electron wave functions which are anti-symmetric product of σ and π electron parts (6) [7,8].

$$\psi_{\delta 1} = \widehat{A} \psi_{\sigma} \psi_{\pi,1} \quad (6)$$

where: \widehat{A} - anti-symmetrizing operator, ψ_{σ} - wave function of σ electrons, $\psi_{\pi,1}$ - wave function of π electrons. What is essential for this approximation, this is interactions of σ and π electrons are neglected. As atoms constituting π electron system are sp^2 hybridized, so that it is assumed that π electrons are placed in the field of a particle skeletal, which include Coulomb interactions of nuclei with electrons from internal levels and σ electrons allocated on sp^2 hybridized orbitals. Within the frame of π electron approximation the wave function $\psi_{\pi,1}$ is determined by π electron Hamiltonian (7) [7]

$$H_{\pi} = \sum_{i=1}^n \left[\widehat{T}_i + U_{core}(P_i) \right] + \sum_{i=1}^n \sum_{j=1}^n \frac{ke^2}{r_{ij}} \quad (7)$$

where: \widehat{T}_i - kinetic energy operator of π electrons, n - number of π electrons, $U_{core}(P_i)$ - potential field of the molecule core (skeletal) in which move π electrons. This approach is the foundation of Pariser, Parr and Pople's theory, so called PPP theory. A simplified version of the π electron approximation has appeared to be Hückel methods, the basis of which is assumption that π electrons move in a field of the effective one-electron potential $U_{\mathcal{H}}(P)$.

What is most important this exceptionally simple method is capable to give an account of many properties of molecules with π electron systems. With the use of this simple method in which electron-electron interactions are neglected to a great variety of phenomena one meet in π conjugated organic molecules or polymers. Though, this method cannot explain why in the absorption spectra of benzene one observe three bands rather than one double degenerate resulting from it. This was explained by Sklar and Goeppert-Mayer [38,40] and attributed

to π electron system of this high symmetry molecule with double degenerate HOMO and LUMO levels [28]. This is Coulomb interaction among electrons on HOMO levels, so that one must always take into account that any optical transition in benzene molecule from one HOMO level is associated with second transition from another HOMO levels, and moreover these transitions linked with two different LUMO levels. In fact, each double degenerate HOMO level is associated with two molecular orbitals – one with phases at para positions and the others with nodes at para positions. That means that each transition is associated with resonance interaction of two configurations, i.e. $(\phi_3 - \phi_4)$ and $(\phi_2 - \phi_5)$ or $(\phi_3 - \phi_5)$ and $(\phi_2 - \phi_4)$. This effect results in mixing HOMO and LUMO orbitals, which in the language of the group theory results in splitting the space of two degenerate configurations into new three configurations - one double degenerate and two single degenerate ones. The procedure of taking into account Coulomb interactions among valence electrons is called configuration interactions (CI) as one can see optical transition as a result of two configurations and one can easily notice that there are two such configurations pairs which must be taken into account as considering optical transitions in materials whose molecule comprises benzene rings. As it has been discussed in previous section, thin films of polyazomethines illustrated in Figure 2 can be treated as if their chains were composed of phenylene rings and azomethine linkages in various configuration. In fact, there are phenylene rings separated by azomethine linkages and pairs of phenylene rings like in bezidine diamine or fluorine diamine and diamine benzidine, but also naphthalene rings as it is in naphthylene diamine and fat Brown. Generally, one should consider connectivity of π electron system along with the polymer backbone and then the role of aromatic ring conjugation in case of phenylene and naphthylene rings superimposed on these interactions. It will be presented here on how one can derive electronic structure of these polyazomethine starting from their frontier orbitals units following the approach developed in our earlier paper [28]. That is why it has been pointed out there that the choice of polymer unit cell is of great importance.

6.1. Poly(paraphenylene azomethine) (PPI) thin films

As a starting point of these consideration are optical spectra of polyazomethine thin films which carry on information on electronic structure of these materials. In Figure 56 one can see UV - VIS absorption spectrum taken on PPI thin film, that reveals the strongest broad band with the intensity maximum at about 3 eV and some weak peaks at about 4.0, 5.0 and 6.2 eV.

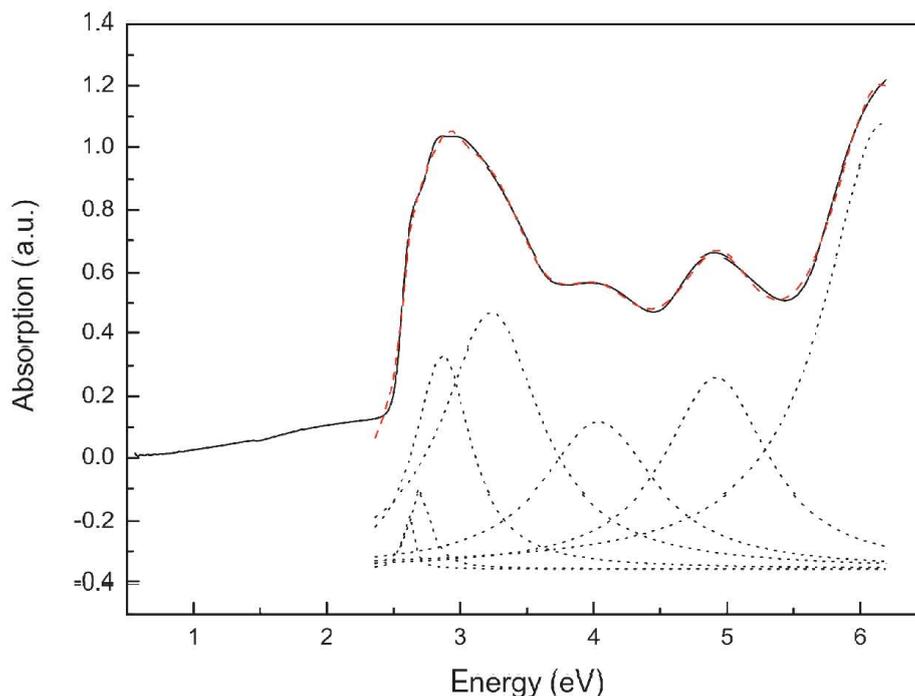


Figure 56. Absorption coefficient of PPI thin films

Table 5. Fitting parameters for Marquardt-Levensberg procedure

Peak No	Maximum (eV)	Full width half height (eV)	Area (eV)
1.	2.60684 ± 0.00478	0.08417 ± 0.02077	0.02712 ± 0.01289
2.	2.69845 ± 0.01122	0.1834 ± 0.07385	0.0759 ± 0.06194
3.	2.86855 ± 0.02116	0.50564 ± 0.09801	0.55436 ± 0.25328
4.	3.23496 ± 0.0361	0.89072 ± 0.11666	1.15652 ± 0.32463
5.	4.03812 ± 0.02076	1.01527 ± 0.11789	0.76213 ± 0.16459
6.	4.92052 ± 0.01078	0.9363 ± 0.0636	0.91364 ± 0.11204
7.	6.16973 ± 0.0157	1.0666 ± 0.05329	2.41343 ± 0.17927

All the features observed in the absorption spectrum have been fitted using the Marquardt-Levensberg least square approximation procedure [39]. The results of applying fitting procedure are shown in Figure 56 and Table 5, and the vibrational progressions visible in the absorption band are fitted with three bands peaking at 2.70, 2.87, 3.23 eV, other bands are seen to peak at 4.04, 4.92 and 6.17 eV. The difference in energy maxima of the fitted bands is of about 0.2 eV and rather well with frequency of stretching mode of benzene ring (1595 cm^{-1}).

6.2. Electronic structure of benzene molecule

The ground state configuration of a benzene molecule expressed in π electron approximation is $a_{2u}^2 e_{2g}^4$, which while expressed in Slater type [7,8,28] ground state wave function, transforming according to full symmetric A_{1g} irreducible representation, can be read

as $\Psi_0 = \left| \begin{matrix} + & - & + & - & - & - \\ \phi_1 & \phi_1 & \phi_2 & \phi_2 & \phi_3 & \phi_3 \end{matrix} \right|$. Benzene excited configuration can be written as $a_{2u}^2 e_{2g}^3 e_{2u}^1$,

but there are four electrons allocated at two degenerate benzene HOMO (BHOMO) orbitals, which means there are two electrons on ϕ_2 and two others on ϕ_3 benzene molecular orbitals (BMO). Then, one should take into consideration four configurations corresponding to four transitions connecting HOMO and LUMO orbitals. One-electron Slater type wave functions for these configurations can be read as below (8).

$$\begin{aligned} \chi_{3 \rightarrow 4} &= \left(\left| \begin{matrix} + & - & + & - & + & - \\ \phi_1 & \phi_1 & \phi_2 & \phi_2 & \phi_3 & \phi_4 \end{matrix} \right| + \left| \begin{matrix} + & - & - & - & + & - \\ \phi_1 & \phi_1 & \phi_2 & \phi_2 & \phi_4 & \phi_3 \end{matrix} \right| \right) / \sqrt{2}, \\ \chi_{3 \rightarrow 5} &= \left(\left| \begin{matrix} + & - & + & - & + & - \\ \phi_1 & \phi_1 & \phi_2 & \phi_2 & \phi_3 & \phi_5 \end{matrix} \right| + \left| \begin{matrix} + & - & + & - & - & - \\ \phi_1 & \phi_1 & \phi_2 & \phi_2 & \phi_5 & \phi_3 \end{matrix} \right| \right) / \sqrt{2}, \\ \chi_{2 \rightarrow 4} &= \left(\left| \begin{matrix} + & - & - & - & + & - \\ \phi_1 & \phi_1 & \phi_2 & \phi_4 & \phi_3 & \phi_3 \end{matrix} \right| + \left| \begin{matrix} + & - & - & - & + & - \\ \phi_1 & \phi_1 & \phi_4 & \phi_2 & \phi_3 & \phi_3 \end{matrix} \right| \right) / \sqrt{2}, \\ \chi_{2 \rightarrow 5} &= \left(\left| \begin{matrix} - & - & + & - & + & - \\ \phi_1 & \phi_1 & \phi_2 & \phi_5 & \phi_3 & \phi_3 \end{matrix} \right| + \left| \begin{matrix} + & - & + & - & + & - \\ \phi_1 & \phi_1 & \phi_5 & \phi_2 & \phi_4 & \phi_3 \end{matrix} \right| \right) / \sqrt{2}. \end{aligned} \quad (8)$$

According to Hückel method energies of ϕ_2 and ϕ_3 orbitals are equal to one another and energies of ϕ_4 and ϕ_5 orbitals are equal, too. Thus, energy gap is the same for single electron transitions from (ϕ_2, ϕ_3) to (ϕ_4, ϕ_5) BMO. That means, configurations $\chi_{3 \rightarrow 4}$ and $\chi_{2 \rightarrow 5}$ are degenerate and similarly, configurations $\chi_{2 \rightarrow 4}$ and $\chi_{3 \rightarrow 5}$ constitute another pair of degenerate configurations. Coulomb repulsion acting among electrons on benzene frontier orbitals lifts these accidental degenerations of single electron excited configurations giving rise to benzene electronic scheme shown in Figure 57 with contributions from configurations involved in each level indicated. One can see that energy splitting of degenerate $\chi_{3 \rightarrow 4}$ and $\chi_{2 \rightarrow 5}$ configurations is smaller than splitting resulting from degeneration of $\chi_{2 \rightarrow 4}$ and $\chi_{3 \rightarrow 5}$ configurations, which

seems to be reasonable enough, if one notice that the latter configurations involve transitions connecting BMO where one component has phase and the others node at para position. In case of $\chi_{3 \rightarrow 4}$ and $\chi_{2 \rightarrow 5}$ configurations there are transitions between BMO having both phase and both nodes at para positions, respectively. Then, the excited electronic states of benzene molecule connected with so called α , p and degenerate (β , β') bands are some superposition of four configurations (9):

$$\Psi_{\alpha} = \chi_{2 \rightarrow 4} - \chi_{3 \rightarrow 5}$$

$$\Psi_p = \chi_{3 \rightarrow 4} + \chi_{2 \rightarrow 5} \quad (9)$$

$$\Psi_{\beta} = \chi_{3 \rightarrow 5} + \chi_{2 \rightarrow 4} ; \Psi_{\beta'} = \chi_{2 \rightarrow 4} - \chi_{3 \rightarrow 5}$$

This is consistent with the group theory, which when applied to benzene molecule results in the following symmetry representation of its excited states (10) [28]

$$\Gamma_{exc} = A_{1g} \times e_{2g} \times e_{2u} = B_{1u} + B_{2u} + E_{1u} . \quad (10)$$

Electronic structure of benzene

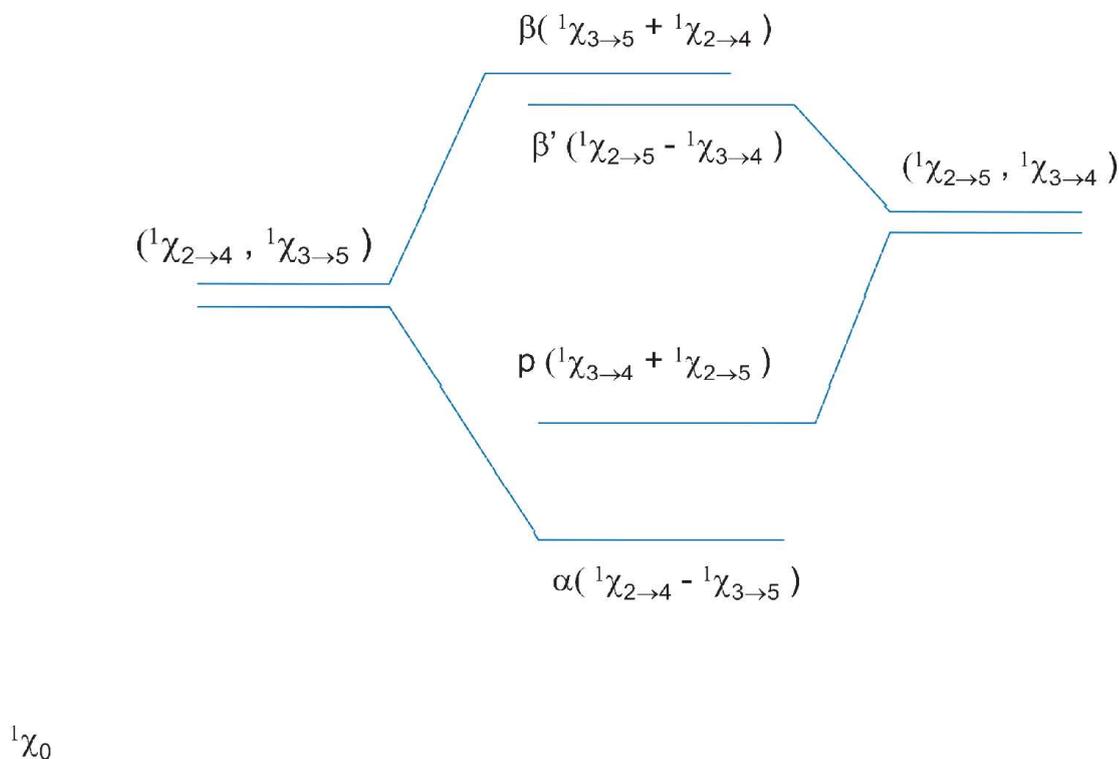


Figure 57. Electronic excited states of benzene according to configuration interaction [8]

According to the selection rules for optical dipole transitions connecting the ground state and excited states the symmetry representation of dipole moment elements is as follows (11) [27,28].

$$\Gamma_0 \cap \Gamma_{exc} = B_{1u} + B_{2u} + E_{1u} \quad (11)$$

But the only allowed transition appears to be the one connecting A_{1g} ground state with E_{1u} excited, because electronic transition dipole moment for benzene transforms according to E_{1u} irreducible representation [28,29]. However, transitions connecting A_{1g} ground state with the B_{1u} and B_{2u} excited states can become allowed through intervention of perturbation having symmetry of E_{2g} irreducible representation, i.e. the one coinciding with symmetry of benzene ring stretching modes [28,29].

Additionally, it has been proved that intensity of the two forbidden bands is due to borrowing intensity from the allowed transition to E_{1u} state, because the two excited states, B_{1u} and B_{2u} , are coupled with E_{1u} excited state by structural perturbation of E_{2g} symmetry, i.e. by benzene ring stretching mode. Such a strong coupling connecting the two excited states with E_{1u} state means that electronic states of benzene ring electronic states should be treated in terms of their vibronic states. Energy levels corresponding to electronic components of benzene vibronic states are equal to 4.7 eV for α band, 5.96 eV for p band and 6.8 eV for double degenerate allowed E_{1u} [28]. Then, it seems that vibronic wave functions for the ground and excited states can read (12)

$$\Psi_l(r_i, R_v) = \psi_l(r_i, R_v) \chi_v(R_v) \quad (12)$$

where: $l=1$ for the ground state, $l=p, \alpha, \beta$ and β' for B_{1u}, B_{2u} and E_{1u} excited states. The matrix element for electronic transition connecting A_{1g} and E_{1u} is associated with dipole moment different from zero for equilibrium geometrical configuration of benzene molecule (13)

$$\langle \Psi_1(r_i, Q_v) | H' | \Psi_\beta(r_i, Q_v) \rangle = \mu_i(R_v^{eq}) \langle \chi_1(Q_v) | \chi_\kappa(Q_v) \rangle \quad (13)$$

For electronic transitions connecting A_{1g} with B_{1u} or B_{2u} the dipole moments for equilibrium geometry are equal to zero, so that one must develop electronic dipole moment in Taylor's

$$\langle \Psi_1(r_i, Q_v) | H | \Psi_p(r_i, Q_v) \rangle' = \langle \chi_\nu(R_v) | \psi_1(r_i, R_v) | H | \psi_2(r_i, R_v) \rangle \chi_\kappa(R_v) \quad (14)$$

series with respect to normal coordinate of E_{2g} stretching mode (14) [28]. That makes that absorption band connected with this transitions will have maxima at energies corresponding to vibronic progressions [28].

6.3. Electronic states of ethylene molecule

Electronic structure of ethylene molecule in π electron MO picture is the simplest one among conjugated molecules is shown in Figure 54. However, the ethylene electronic structure arising while considering interactions between excited configurations, due to symmetry reasons [28] give rise to the electronic scheme shown in Figure 58. In case of ethylene molecule one should take into consideration interactions between single and double electron excited states of ethylene, either having A_g symmetry of D_{2h} point group. The resulting energy level scheme reveals single electron B_{1u} transition at about 7.6 eV [8].

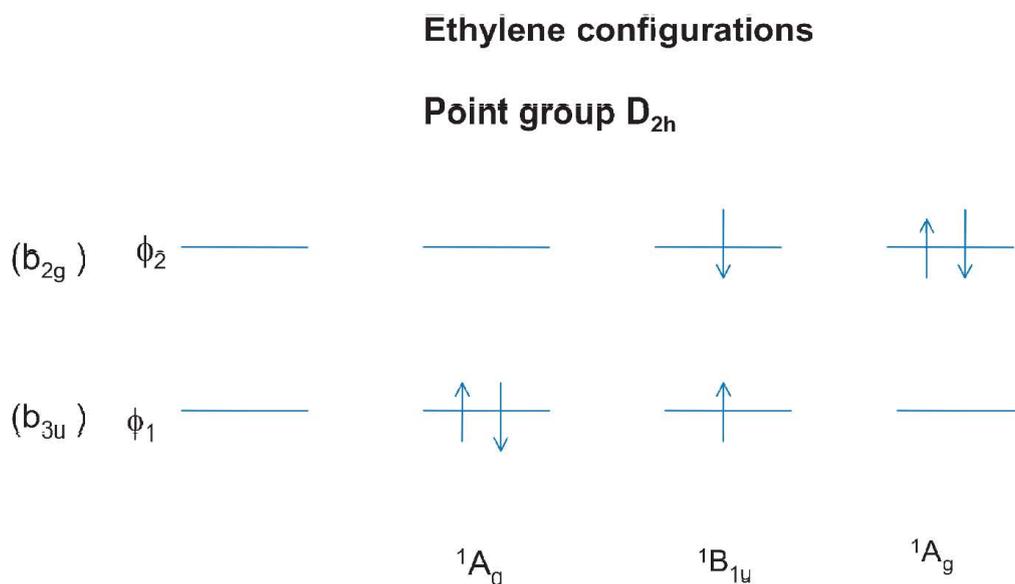


Figure 58. Electronic configurations of ethylene [8]

6.4. PPI band structure

It has been shown in sec. 4 that PPI chain can be approximated with the one of virtual PPV-like polymer, but while describing electronic structure of this virtual polymer one should go one step farther and treat it in terms of a polymer chain built up of virtual atoms of two kinds, one with benzene electronic structure and the other having ethylene electronic structure. Such approach seems to be adequate to local character revealed in optical spectra of polymer chains, in which constituent units conserve to a considerable extent their individual proper electronic structure that make analysis and building up their electronic structure simpler,

clearer and more transparent. The polymer being kept together by σ bonds π electronic states of units are linked by overlap of certain molecular orbitals of the constituting units. Taking on distribution of electronic states of the virtual atom as that shown in Figure 57 for benzene molecule and in Figure 58 for vinylene, it is assumed that lower lying states of their constituent atoms and those contributing to σ bonds are so deeply situated that their influence on π electron states can be neglected. Thus, π electronic states of benzene and ethylene provide electronic states essentially determining the electronic structure of the polymer. Then, it is expected that the band structure of PPV unit cell result from overlap between π ground states of the two virtual atoms and interaction of benzene p and β' states of benzene virtual atom with B_{1u} excited state of ethylene through overlaps of ϕ_3 with ϕ_1' and ϕ_4 with ϕ_2' molecular orbitals. Other electronic states of benzene virtual atom are assumed not too strongly interact with π -electron states of ethylene, so that they conserve their benzene character. Moreover, it seems to be justified within this approximation to treat all the electronic states of the two virtual atoms involved in terms of single electron states described with single electron wave function. Considering a chain consisting of such virtual atoms one should bear in mind that the former represents molecule with rather strong electron-phonon interactions. That means, interactions between their π systems should be treated in terms of their electronic parts while the vibrational component should be added to that atom. On considering only states originating from single electron configurations involving molecular orbitals belonging to frontier orbitals of benzene and ethylene one can construct effective Hamiltonian having at the diagonal energies of the ground and excited states of the two. Then, interactions between the two parts of PPV unit cell are taken into account in this approximated approach as off diagonal elements being equal to β_1 or β_2 for interacting states, ground states and excited states of two units, respectively (15).

$$H_{\text{eff}} = \begin{bmatrix} E_1 & 0 & 0 & 0 & 0 & \beta_1 & 0 \\ 0 & E_1 + E_4 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & E_1 + E_4 & 0 & 0 & 0 & \beta_2 \\ 0 & 0 & 0 & 0 & E_1 + E_3 & 0 & \beta_2 \\ 0 & 0 & 0 & 0 & 0 & E_1 + E_2 & 0 \\ \beta_1 & 0 & 0 & 0 & 0 & E_0 & 0 \\ 0 & 0 & \beta_2 & \beta_2 & 0 & 0 & E_0 + E_5 \end{bmatrix} \quad (15)$$

It is assumed simultaneously that interactions between closed-shell ground states of virtual benzene and ethylene atoms are rather weak. Then, one level move upward and the other downward with respect to zero level of the two ground states, as the bonding contribution of two electrons should weakly outweigh antibonding contribution of two electrons of the PPV unit ground state. It is expected that the resulting ground state of PPV have rather important contribution from benzene ground state is pushed up at about 1 eV above the benzene ground state, which seems to be reasonable if one takes on that is below the ground state of benzene. Assuming resonance integral β_2 responsible for ϕ_4 and ϕ_2 connection being equal to about 2.4 eV and energy of an excited state of ethylene to be equal to about 7.6 eV and that of benzene p state equal to 5.96 eV [8]. One can see, there is 1.66 eV difference between the two states. Then, the solution of the equation below gives $E_2 = 3.9$ eV and $E_5 = 9.7$ eV, so that one may expect that low energy state designated E_1 , is predominantly of benzene vibronic p band character, while the higher energy one, E_5 , is ethylene in character. This discussion indicates that benzene vibronic state associated with α excited state should conserve its benzene character in PPV, but one must notice that electronic configurations involved in this state are the ones where one molecular orbital has phase and the others node at benzene para position. That means, the orbitals having phases ensure delocalized character of the relevant state in PPV unit as they overlap with ethylene π orbitals and one may expect that energetic states in PPV whose energies are close to that of benzene α and β bands are connected with interband transitions of delocalized-to-localized and vice versa type. The discussion being carried out allows for one to propose electronic band structure of PPV thin film in tight binding approximation. The presented results though carried out for PPV polymer, but assuming ethylene unit is a good approximation not only for vinylene unit but also for methinimine unit [28], one may expect that the electronic structure having just derived for PPV is also adequate one for PPI electronic structure if including lone pair related level (Fig. 59). It is thought that location of the lone pair orbital level correspond rather well with the energy of nitrogen sp^2 orbital level that is expected to overlap with the PPI ground state, similarly as it has been deduced for methinimine [28].

The energy gap $E_g = E_2 - E_1$ being equal about 2.9 eV is thought to be a good approximation to electronic structure of PPI (Fig. 60) and it is seen to correspond rather well with UVVIS spectrum shown in Figure 56. This value is expected to be rather good approximation for experimental location of the strongest band seen in Figure 56 at about 2.7 eV.

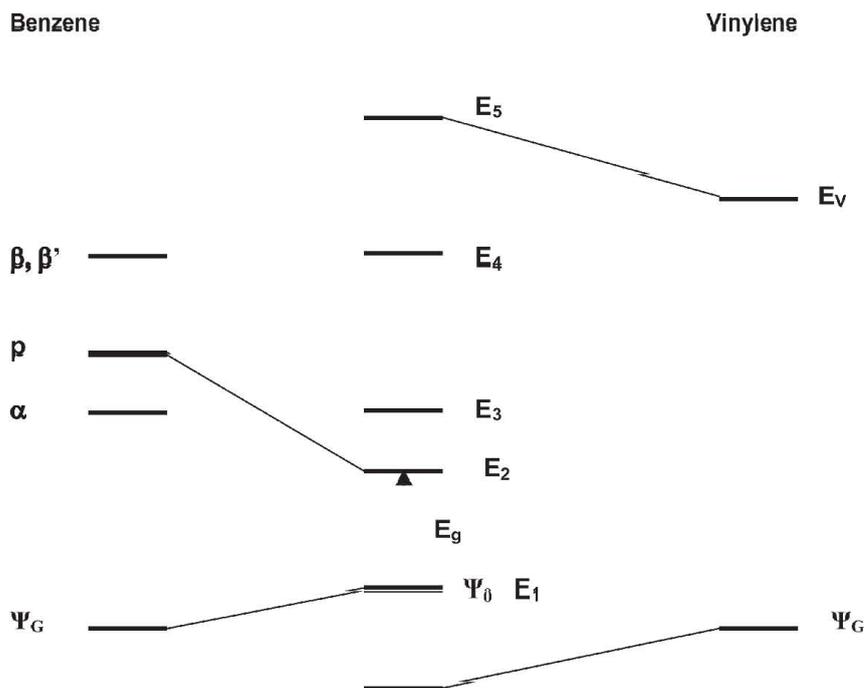


Figure 59. Electronic levels of PPI unit cell [28]

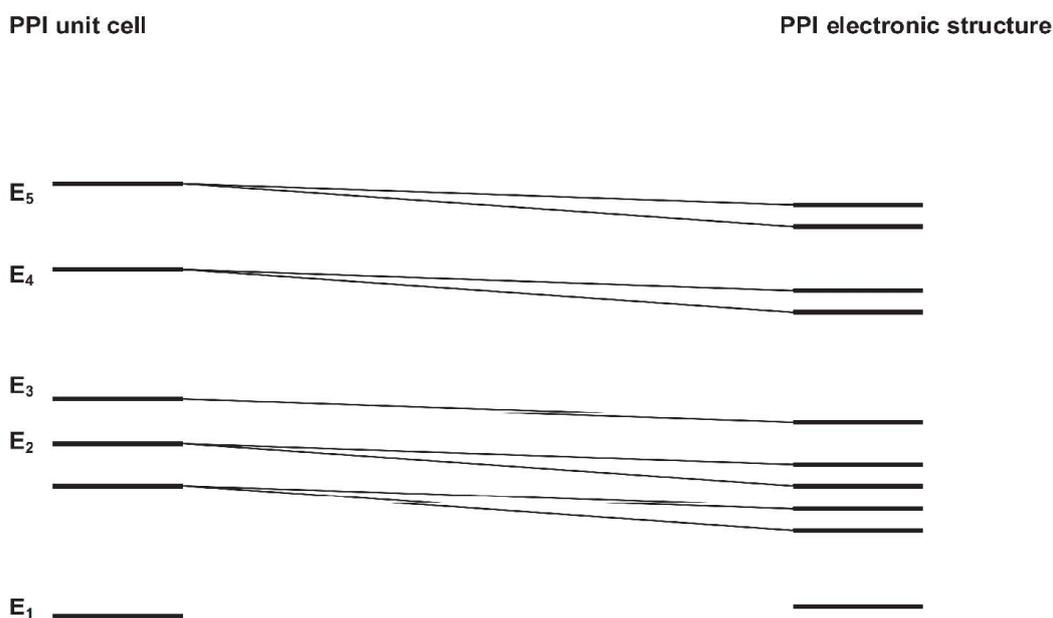


Figure 60. Electronic states of PPI unit cell [28]

The electronic band structure of PPI chain, shown in Figure 61, is developed within the tight binding approximation, as this is expected to be most adequate for peculiarities of polymer chain structure and periodicity. This is the periodicity of the polymer chain that energy levels corresponding to molecular orbitals of the unit cell split off into bands of states [12] inside the

Brillouin zone (BZ). Then, for i th energy band one write its dependence on wave vector as bellow (16):

$$E_i(\mathbf{k}) = E_{a,i} + C_i - 2\delta \cos \mathbf{k}\mathbf{a} \quad (16)$$

Intensity distribution in the absorption spectrum of PPI and its resemblance to UV-VIS spectra of PPV [5,6] correspond rather well with similitude of their π -electron systems. Then, it has been proven in the precedent section that PPI electronic structure can be derived from benzene and ethylene electronic states rather than considering one-electron molecular orbitals. Moreover, vibronic progressions observed in low energy band in the vicinity of 3 eV are thought to indicate that one should consider vibronic rather than electronic states of benzene and their nearly coincidence with 1595 cm^{-1} of benzene indicate on quite distinct contribution of benzene π system to PPI one.

On the other hand, it is thought that this model gives more straightforward interpretation of a band at about 5.0 eV, both in PPV and PPI thin film spectra conserving its delocalized-to-localized or localized-to-delocalized transition character without necessity to consider transitions $D_1 - L^* + L - D_1^*$, because they are essentially included as being connected with configurations involving transitions from orbitals with phase at para position to the one with node and vice verse. Then, it is thought that feature fitted at about 3.25 eV could be attributed to transition connecting delocalized states at phenylene ring, which can be some indication that polymer chains in PPI thin films prepared by CVD or VTE methods are not too long.

Electronic band structure of PPI

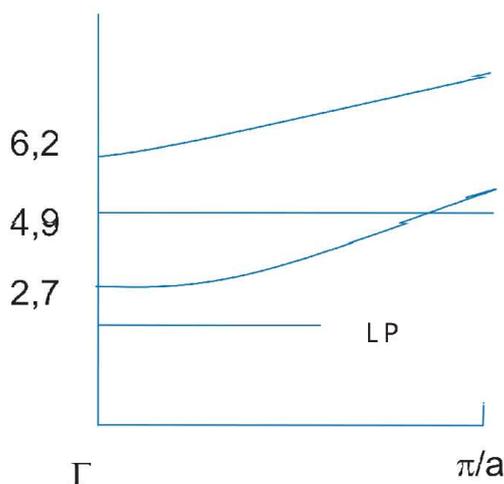


Figure 61. Electronic structure of PPI [28]

This can be in accordance with coincidence of this band with that reported for PPV. The strongest one is slightly moved to higher energies with respect to its counterpart in PPV spectrum, which can be attributed to some bonding variation and in overlap integral due to presence of nitrogen atoms. Additionally, one may expect that some effect on location of this band has location of band resulting from lone pair orbitals along the chain. One can also give an account for polarons formation as this is related to losing one π electron on carbon atom along the backbone and quinoidal modification is associated with diminishing symmetry of the ring with respect to its benzenoid form. Such change is expected to remove degeneration of HOMO level, which is connected with displacement of ϕ_3 and ϕ_4 orbitals towards the center of energy gap.

6.5. Absorption spectra of various polyazomethines

Absorption spectra of polyazomethine thin films PPI, FPI, BPI and PNAPI [59] whose structures have been discussed in previous sections are shown in Figure 62. [26], whose polymer backbones are shown in Figure 2, are seen to reveal shape and intensity distribution very similar to the absorption spectra of PPI thin films. To interpret these spectra and especially to give an account of their similarity to PPI spectrum the above discussed model for PPI thin film

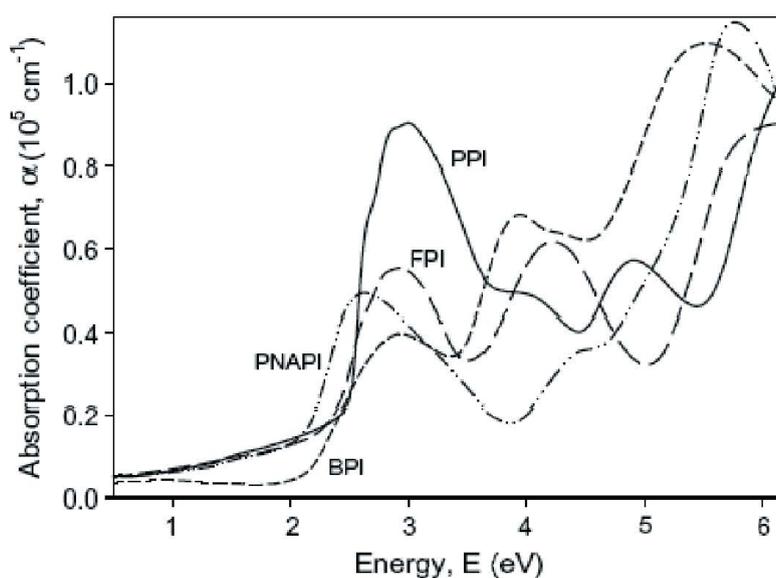


Figure 62. Absorption spectra of various polyazomethine thin films [26]

will be used. As it has been mentioned in previous sections while discussing conformations of these polyazomethine chains their unit cells or repeating units being rather complex ones can be treated in terms PPV-like approximation applied to PPI. It was mentioned that these repeating units, similarly to PPI chain, can be treated as if they composed of two parts, a fragment representing periodic structure consisting of phenylene ring and vinylene-like linkag, and phenylene molecule or phenylene with attached aldehyde or amine end groups. Simultaneously, when analyzing these polymer chains one can notice that these periodic fragments are the longest in PPI chain, while in the above mentioned polymers they are rather short. It seems important to mention here that this discussion concerns conjugated segments of polymer chains and this is important essentially for PPI only, because unit cell of other polymer are to some extent determined by complex monomers used. These repeating units are connected with one another by single bonds like 1-1' bond in bi-phenylene. The low energy bands are peaking up at about 28.-29. eV and they are attributed to interband transitions connecting delocalized states and they have dominant contribution coming from benzene p- band, similarly as it is the case of PPI thin films. They are expected to overlap with relevant contribution coming from phenylene rings, which was fitted at about 3.25 eV in PPI. Among these spectra the highest intensity reveals band due to fluorine base polyazomethine (FPI) which seems to rather well correspond with planarity of two benzene rings in fluorine due to methylene unit, though its presence enforces some deformation of two phenylene system by inclining 1-4 axes of two phenylene rings from their alignment. This effect is expected to influence overlap between frontier orbitals of two phenylene rings – diminishing it, and this is expected to be responsible for this peak intensity. Following this approach the band at about 4.0 eV is thought to be due to involvement phenylene molecular orbitals with phases and nodes at para positions, similarly to PPI peak at about 4.0 eV – configurations involved are pair orbitals where one has a node and the others –phase and vice-verse. Here in the FPI spectrum one cannot see peak at about 5.0 eV related to benzene α band, but it is seen in this spectrum that high energy band is displaced towards lower energies than this is the case for benzene molecule. But this can be explained by periodicity of this polymer chain and some overlap of molecular orbitals of unit cells along the chain. In case of the spectrum recorded on dibenzidine based BPI thin film. Similarly, the low energy band is attributed to transitions linking delocalized states with dominant contribution of benzene p band related configuration. The shape of this band toward higher energies indicate on involvement of delocalized-to-delocalized states transitions on phenylene ring,

but there is also seen some overlap of this low energy band with high enough peak at about 4.0 eV, which in turn is seen to overlap with a feature at about 4.4 eV, and again the high energy band is seen at about 5.5 eV. However, the shape of the unit cell of this polymer is rather complex and one can see that phenylene ring are aligned but there are attached chains at sites 3 and 3', which means that beyond overlap between orbitals ϕ_3 and ϕ_4 of aligned phenylene rings, the side chains, consisting of phenylene-azomethine units linked at para positions, are attached to the main chain by overlap with both HOMO and LUMO orbitals. This involvement of all frontier orbitals into π electron system has rather strong impact on the shape of the absorption spectrum of BPI. The intensity distribution in the spectrum seems to indicate that polymer chains in PBI films are not too long, which correspond rather well with rather large and complex unit cell of this polymer. The spectrum taken on thin films of *Brown* based polyazomethine PNAPI is seen to better follow similarity to the shape of PPI absorption spectrum, which can be explained by observation that the main chain of this polymer resemble PPI in the sense that there are phenylene alternately with azomethine linkages, but in contrast to PPI chain phenylene rings are linked alternately at para and meta positions. Additionally, each meta linked phenylene ring is substituted by means of azo $N=N$ group with naphthalene ring, which makes that conjugated system of this polymer at the level of unit cell is quite large, which pushes the band linking delocalized states towards lower energies. The shape of this spectrum at higher energy part is expected to have contributions from phenylene rings and naphthalene rings as well. One may expect that band at about 4.5 eV have contributions from involvement of two components of HOMO and LUMO orbitals of phenylene. Additionally, the shape of the part of this spectrum in the vicinity of 5 eV may prove on benzene α involvement.

6.6. Absorption spectrum of poliazomethine with oxygen atom in backbone

Thin films of poliazomethine with oxygen in the backbone were prepared by polycondensation of complex dialdehyde with PPDA according to reaction shown in Figure 43. The chain of this poliazomethine consists of three phenylene and two azomethine entities spread between two oxygen atoms [34,35]. Then, one can approach this polymer chain with PPV-like approach [28] with periodic part consisting of two PPV-like units and phenylene ring. Oxygen

atom being sp^3 hybridized disrupt conjugation, which means that in π electron space the chain constitute multiplicity of well separated unit cells. That means one may expect that electronic structure of this polymer thin film will be entity composed of unit cells weakly interacting with one another. When we look at Figure 63, one can easily notice rather well correspondence between relevant bands observed in two spectra, but the spectrum of PPI2 is moved towards higher energies. One can see that the low energy band in PPI due to transitions connecting delocalized states reveals vibronic progressions, which according to the discussed model are related with dominant contribution from benzene α band [8,28]. Missing vibronic progressions in the spectrum of PPI2 thin film are thought to indicate that due to presence of oxygen atoms the chains are expected to be entangled curled, so that the absorption spectrum reflects average distribution of conjugated segments and their mutual orientation. This random orientation and distribution in the film volume space of these conjugated segments of PPI2 results in smooth band without visible vibronic features. The position of this low energy peak in the spectrum of PPI2 (A_1) that delocalization is limited and because of that this band is peaking at about 3.5 eV, and its shape indicate that shift between energy minima of electronic ground state and electronic excited state is comparable to PPI. When comparing bands at about 4.0 eV one can see that the displacement of maxima in PPI and PPI2 films are smaller than this is seen for the low energy band. This effect corresponds rather well contributions to this band coming from both HOMO and LUMO orbitals, with phases and nodes at para positions.

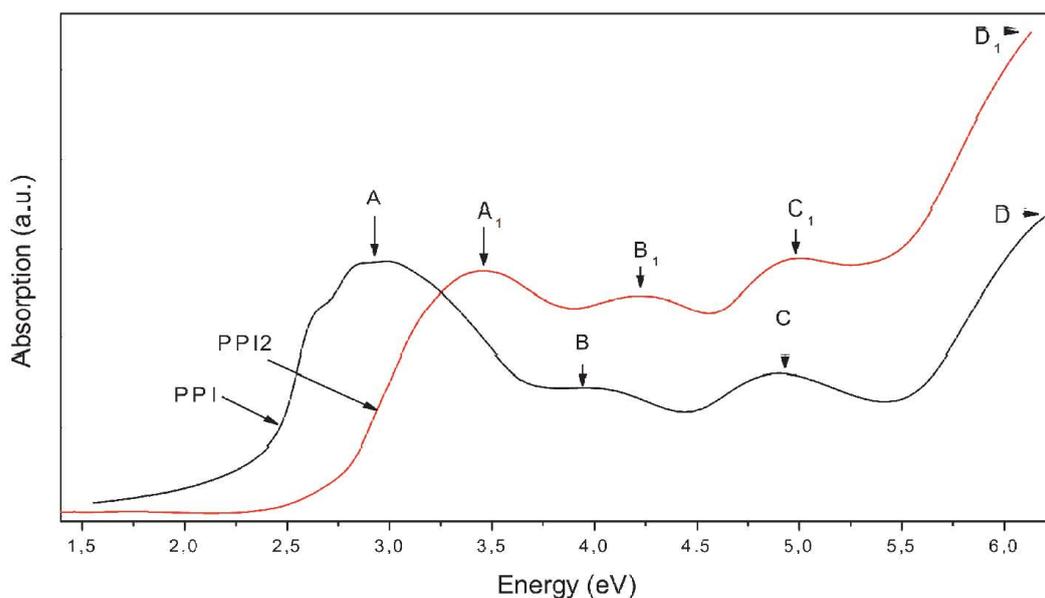


Figure 63. Absorption spectra of polyazomethines PPI and with oxygen in the chain (PPI2) [34,35]

The peaks at about 5.0 eV are attributed to benzene α band and their displacements with respect one another can be attribute to interactions of these units cells separated by oxygen atoms, this interaction being smaller than this is the case of PPI chain.

6.7. Absorption spectrum of soluble polyazomethine with octyloxy side chains

This soluble polyazomethine called BOO-PPI was prepared by polycondensation of dialdehydes with octyloxy chains substituted at 2,5 positions with PPDA in way described in [36]. Thin films of BOOO-PPI were prepared by spin-coating from solution. The absorption spectra of PPI and BOO-PPI are shown in Figure 64. When comparing absorption spectra taken on BOO-PPI with PPI prepared by CVD method, one can see that low energy band is narrower and is pushed to lower energies, while bands at about 4.0 nearly coincide. There is no band seen at about 5.0 eV in spectra of BOO-PPI. One can see that after annealing at about 250 °C [43] the shape of lo energy peak changed and vibronic progression appeared. It is thought that the observed changes in the spectra of the two poliazomethines one can give an account of them following the approach used for PPI [28].

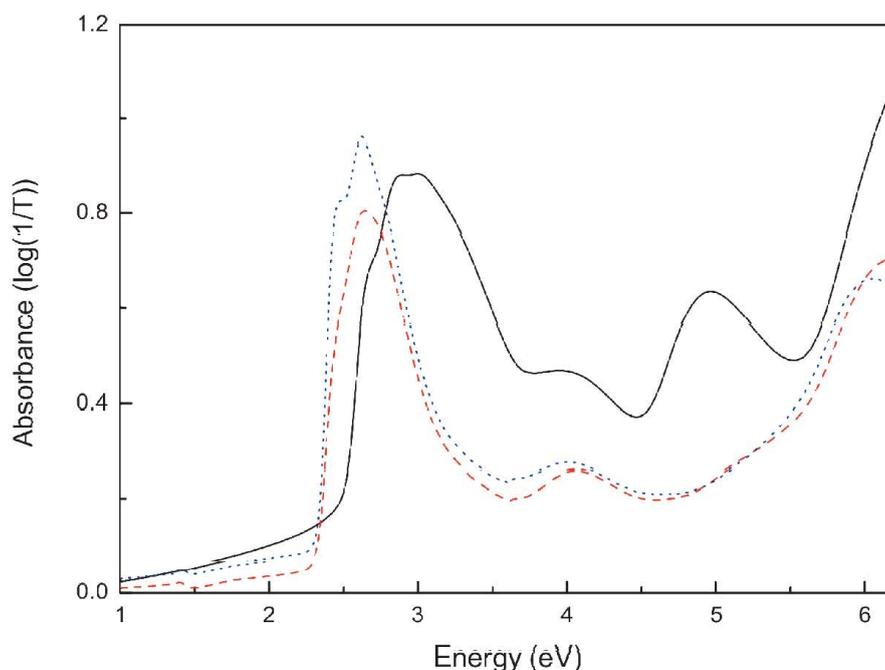


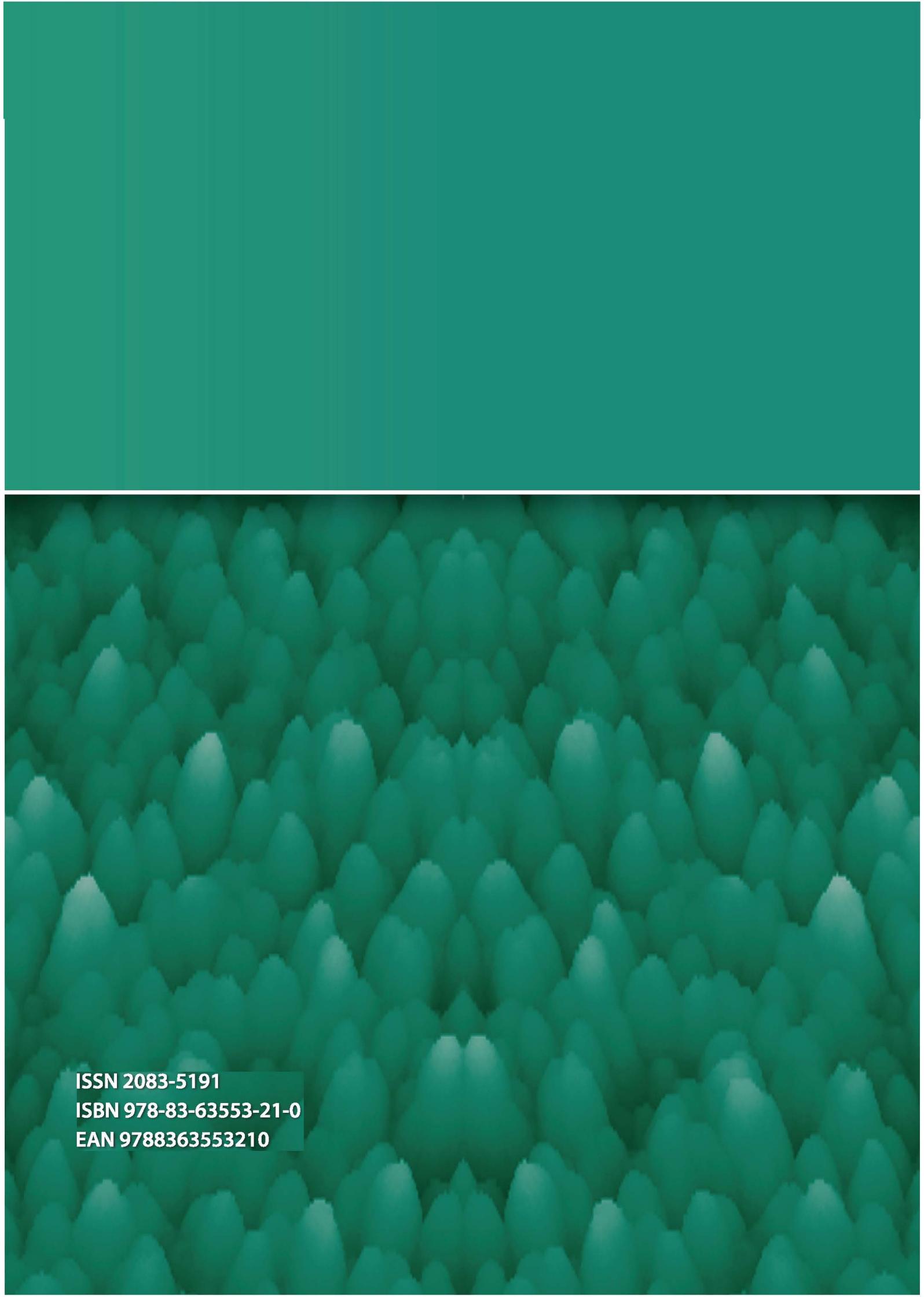
Figure 64. Absorption spectra of PPI (solid), BOO-PPI as-deposited (dash), BOO-PPI after annealing (dot)

One can expect that polymer chains of BOO-PPI produced by polycondensation in a chemical way are much longer than those prepared by CVD or VTE methods. The width of the spectra seems indicate that in case of PPI, there is some important distribution of chain lengths, and in consequence large distribution of conjugation lengths, while in case of BOO-PPI this dispersion of conjugation lengths is much narrower. That is why quantity of end phenylene rings with relevant end groups is much smaller than this is in CVD prepared PPI, so that one cannot observe distinct band related to benzene α band. In contrast, in CVD prepared PPI films proportion of phenylene rings terminating polymer chain to the number of chain is large that enough and because of that band at about 5.0eV is observed. Similarly, one could say that narrow low energy band indicates there is no trace of band at about 3.3 eV, which corresponds with missing 5.0 eV band.

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