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].

$$\psi_{\delta 1} = \hat{A}\psi_{\sigma}\psi_{\pi,1} \tag{6}$$

where: $\hat{A}$ - 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]

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

where: $\hat{T}_i$ – 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 $U_{\delta f}(P)$. 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. (ϕ_3 - ϕ_4) and (ϕ_2 - ϕ_5) or (ϕ_3 - ϕ_5) and (ϕ_2 - ϕ_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 naphtylene 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.

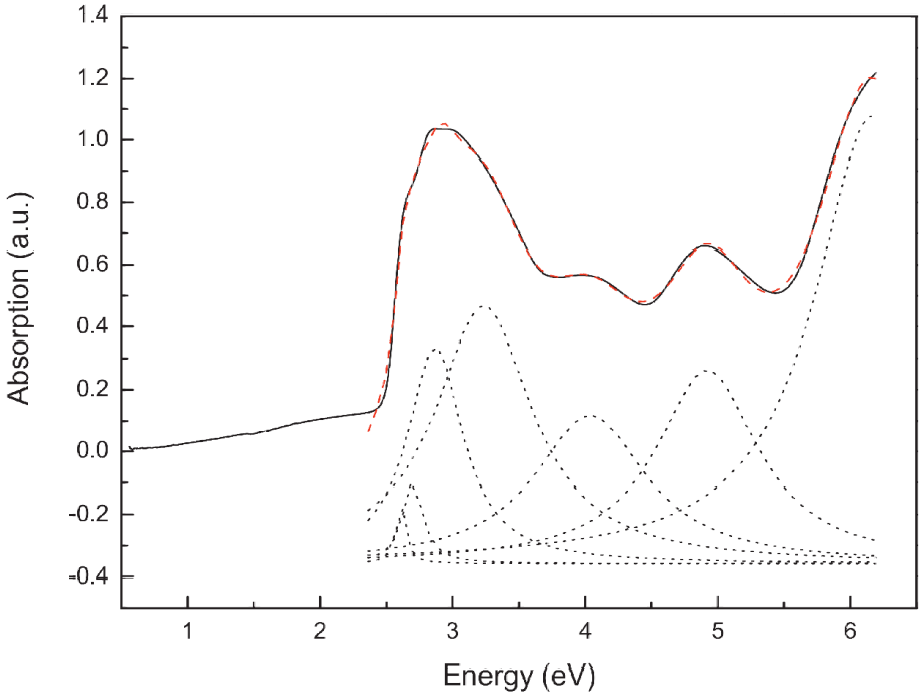

Figure 56. *Absorption coefficient of PPI thin films*

Table 5. *Fitting parameters for Marquardt-Levensberg procedure*

Peak No	Maximum (eV)	Full width half hight (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 $\Psi_0 = \left|\phi_1^+ \phi_1^- \phi_2^+ \phi_2^- \phi_3^+ \phi_3^-\right|$. 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).

$$\chi_{3\to4} = \left(\left|\phi_1^+ \phi_1^- \phi_2^+ \phi_2^- \phi_3^+ \phi_4^-\right| + \left|\phi_1^+ \phi_1^- \phi_2^- \phi_2^- \phi_4^+ \phi_3^-\right|\right)/\sqrt{2},$$

$$\chi_{3\to5} = \left(\left|\phi_1^+ \phi_1^- \phi_2^+ \phi_2^- \phi_3^+ \phi_5^-\right| + \left|\phi_1^+ \phi_1^- \phi_2^+ \phi_2^- \phi_5^+ \phi_3^-\right|\right)/\sqrt{2}, \tag{8}$$

$$\chi_{2\to4} = \left(\left|\phi_1^+ \phi_1^- \phi_2^- \phi_4^- \phi_3^+ \phi_3^-\right| + \left|\phi_1^+ \phi_1^- \phi_4^- \phi_2^- \phi_3^+ \phi_3^-\right|\right)/\sqrt{2},$$

$$\chi_{2\to5} = \left(\left|\phi_1^+ \phi_1^- \phi_2^+ \phi_5^- \phi_3^+ \phi_3^-\right| + \left|\phi_1^+ \phi_1^- \phi_5^+ \phi_2^- \phi_4^+ \phi_3^-\right|\right)/\sqrt{2}.$$

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 $\chi_{3\to4}$ and $\chi_{2\to5}$ are degenerate and similarly, configurations $\chi_{2\to4}$ and $\chi_{3\to5}$ 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 $\chi_{3\to4}$ and $\chi_{2\to5}$ configurations is smaller than splitting resulting from degeneration of $\chi_{2\to4}$ and $\chi_{3\to5}$ 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 $\chi_{3\to4}$ and $\chi_{2\to5}$ 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):

$$\Psi_\alpha = \chi_{2\to4} - \chi_{3\to5}$$

$$\Psi_p = \chi_{3\to4} + \chi_{2\to5} \qquad (9)$$

$$\Psi_\beta = \chi_{3\to5} + \chi_{2\to5}\ ;\ \Psi_{\beta'} = \chi_{2\to4} - \chi_{3\to5}$$

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]

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

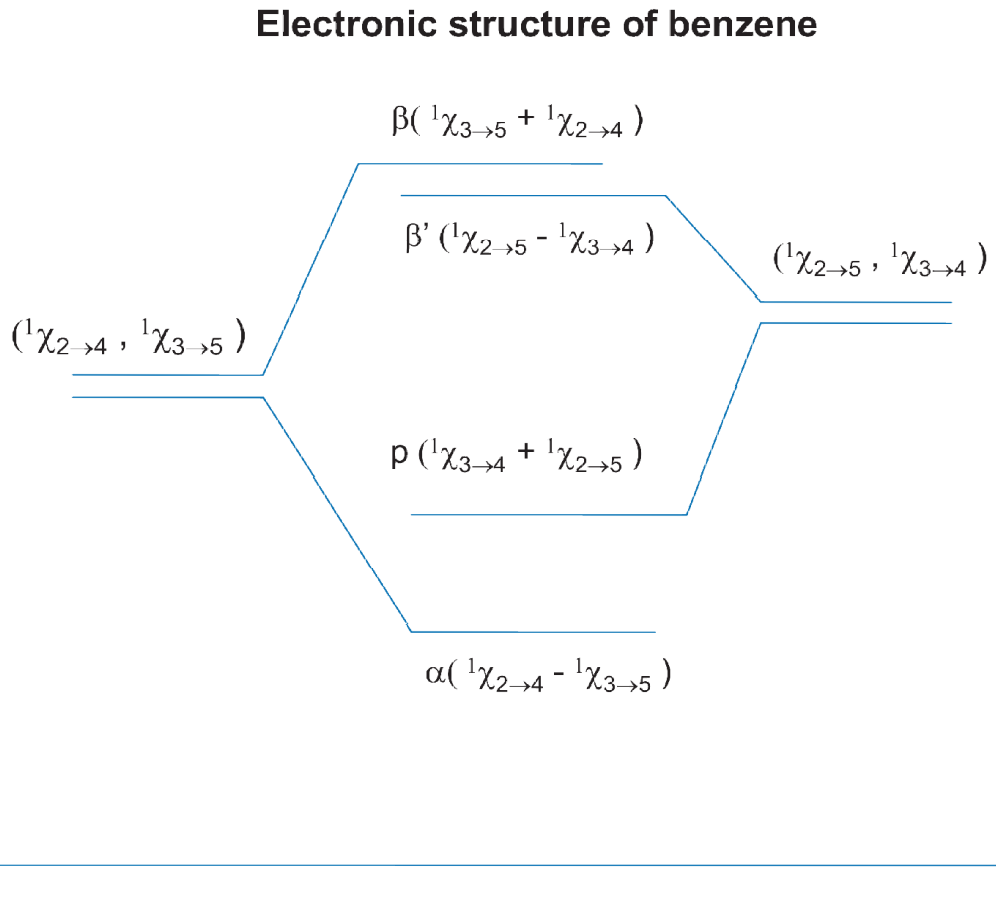

Figure 57. *Electronic excited states of benzene according to configuration interaction [8]*

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].

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

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)

$$\Psi_l(r_i,R_v)=\psi_l(r_i,R_v)\chi_v(R_v)\backslash \tag{12}$$

where: l=1 for the ground state, l=p, α, β 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)

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

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

$$\left\langle \Psi_1(r_i,Q_v)\middle|H\middle|\Psi_p(r_i,Q_v)\right\rangle' = \left\langle \chi_v(R_v)\middle\langle\psi_1(r_i,R_v)\middle|H\middle|\psi_2(r_i,R_v)\right\rangle\chi_\kappa(R_v)\right\rangle \tag{14}$$

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].

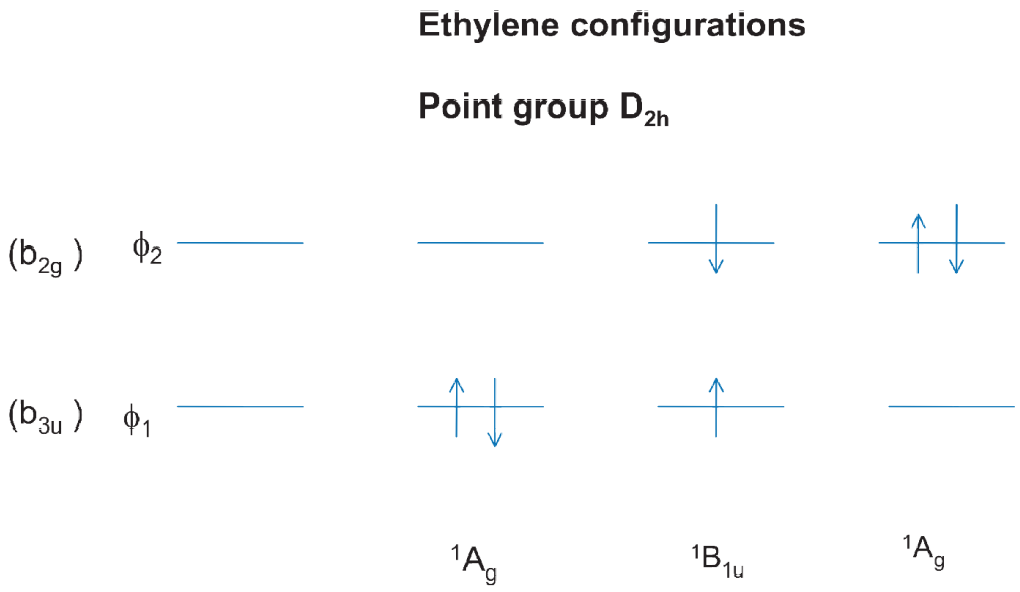

Figure 58. *Electronic configurations of ethylene [8]*

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).

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

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 o 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 verse 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.

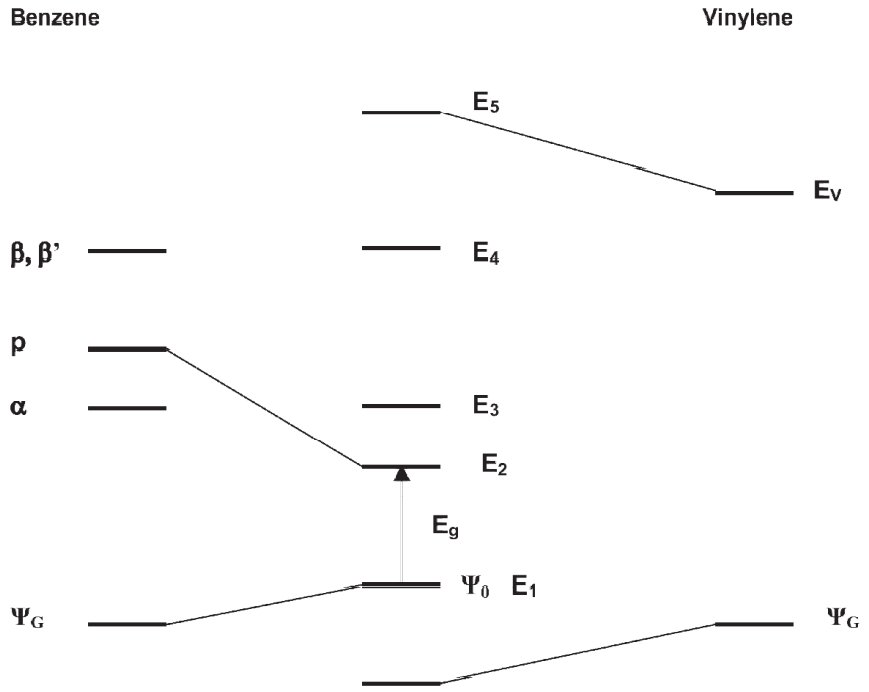

Figure 59. *Electronic levels of PPI unit cell [28]*

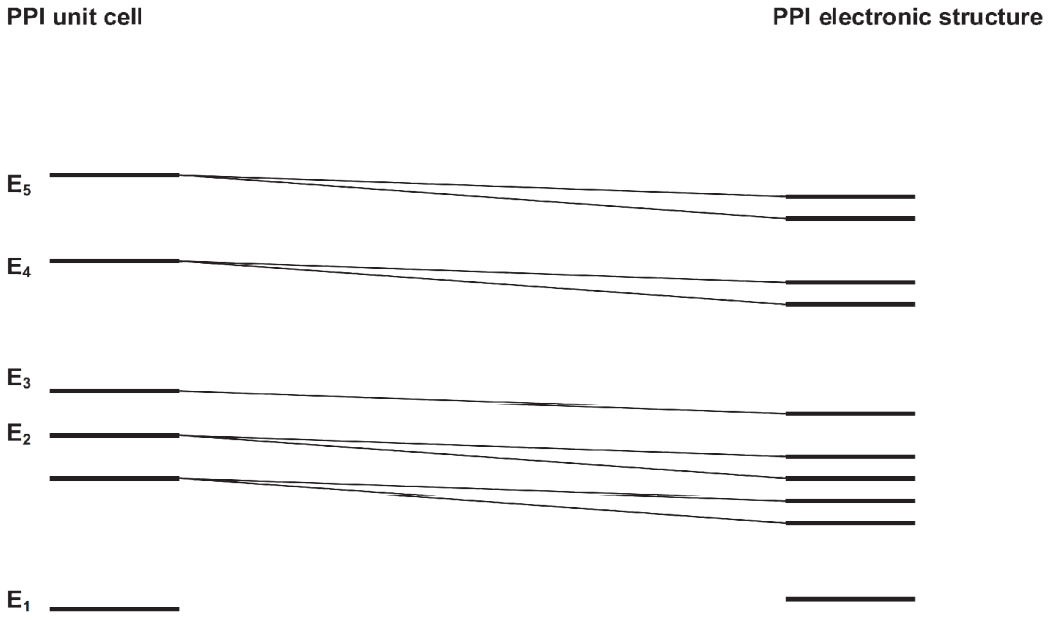

Figure 60. *Electronic states of PPI unit cell [28]*

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):

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

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.

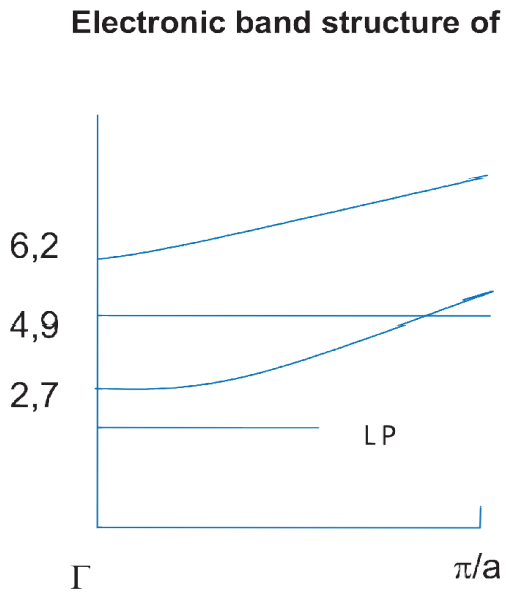

Figure 61. *Electronic structure of PPI [28]*

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 $\phi 3$ 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 theses spectra and especially to give an account of their similarity to PPI spectrum the above discussed model for PPI thin film

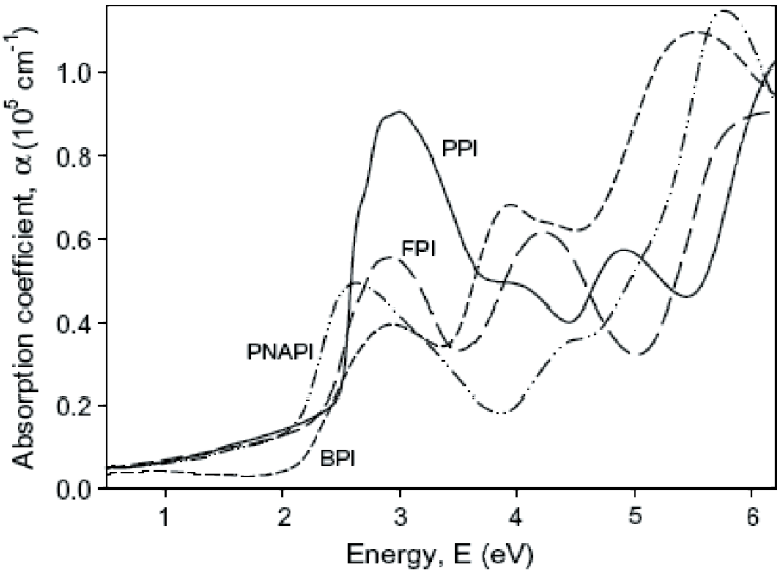

Figure 62. *Absorption spectra of various polyazomethine thin films [26]*

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 alignement. 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 abut 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 nor too long, which correspond rather well with rather large and complex unit cell of this polymer. The spectrum taken on thin films of fatt 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 phenylne 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 polizomethine 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 polzaomethine consists of three phenylene and two azomethine entities sprad 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.

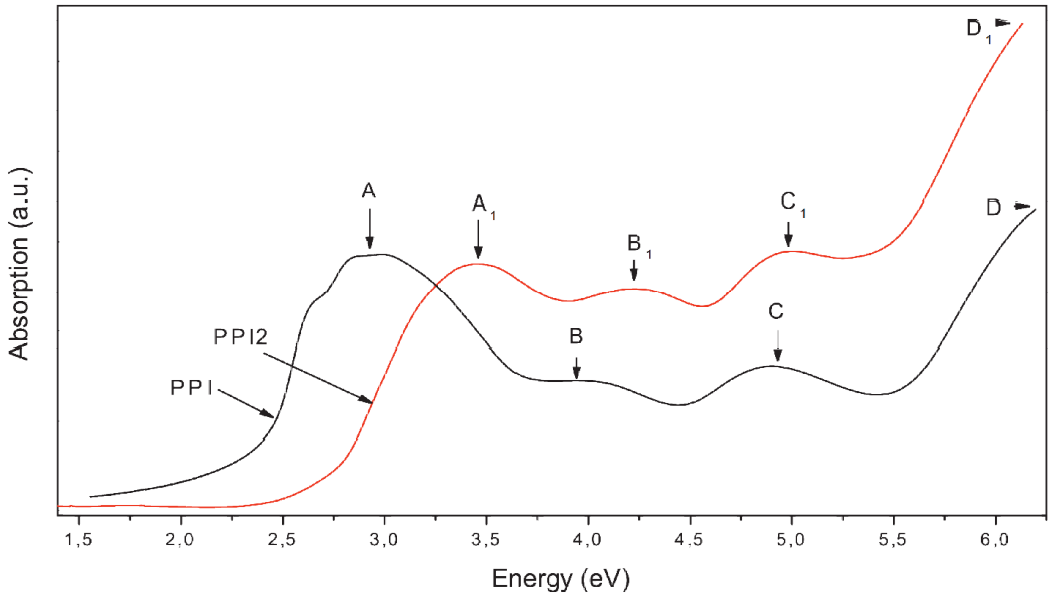

Figure 63. *Absorption spectra of polyazomethines PPI and with oxygen in the chain (PPI2) [34,35]*

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 ^{0}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].

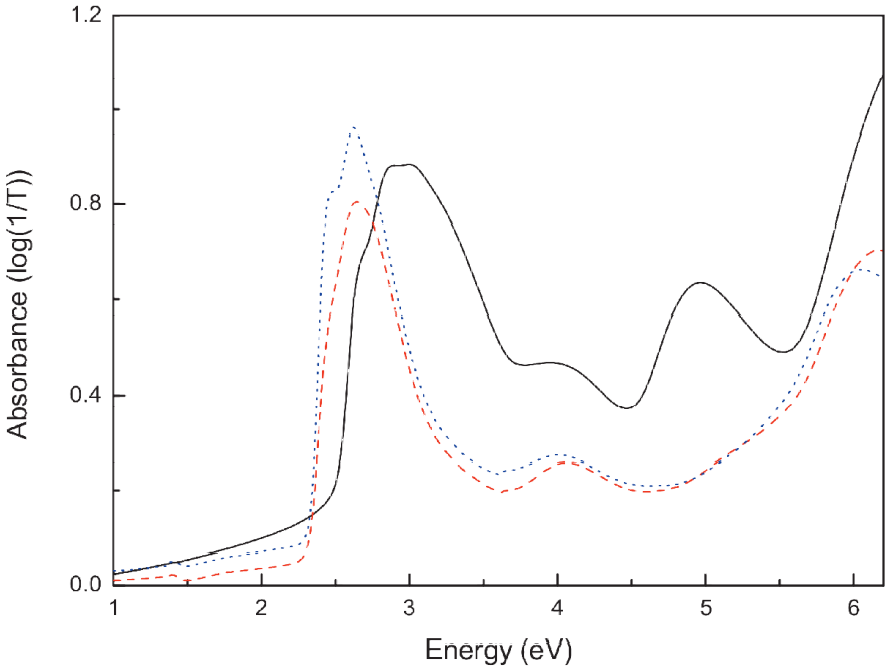

Figure 64. *Absorption spectra of PPI (solid), BOO-PPI as-deposited (dash), BOO-PPI after annealing (dot)*

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.