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 trigonaly 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.
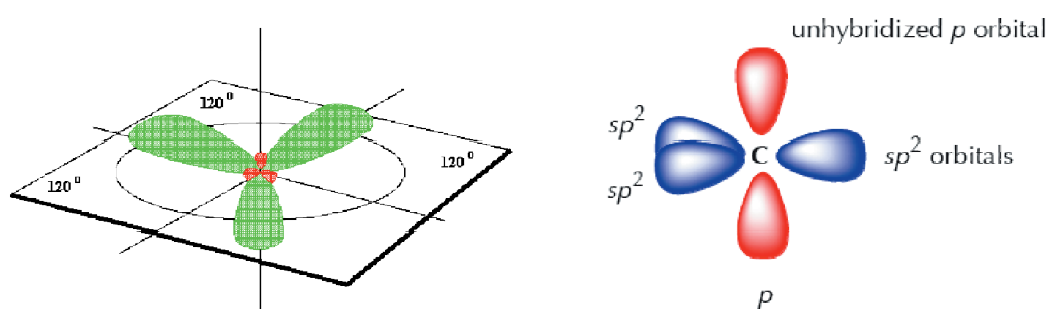

Figure 50. Electron charge distribution in the trigonal orbital

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].
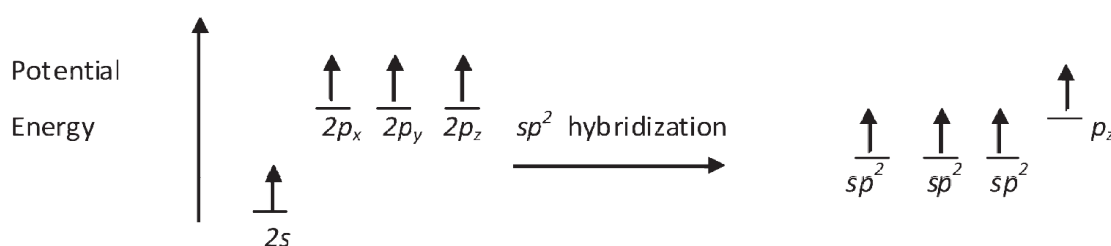

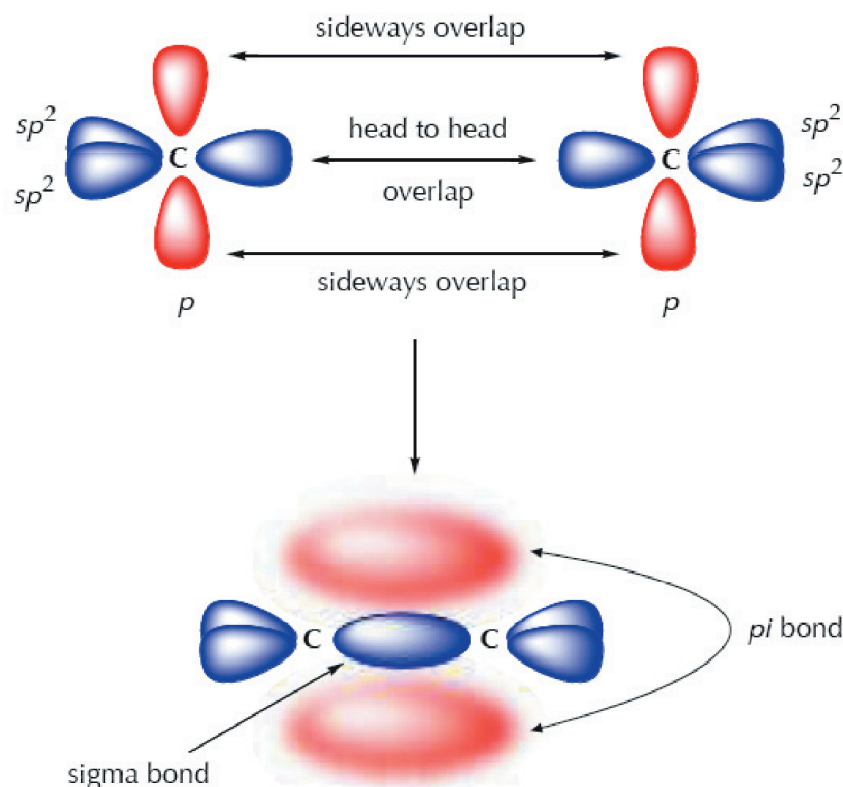Figure 51. sp^2 hybridization in carbon atoms

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 allover 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 antibibonding 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 emphasis 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 alignement 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.
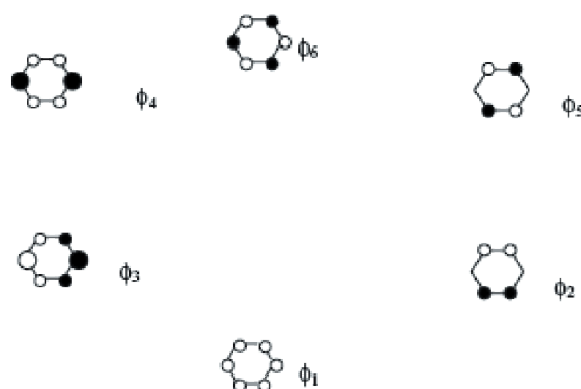

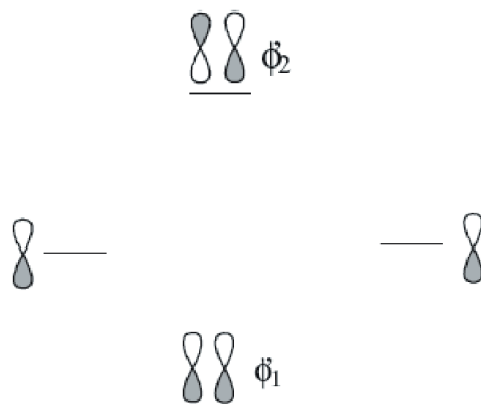**Figure 53.** *Benzene molecular orbitals, accordingly [20]*

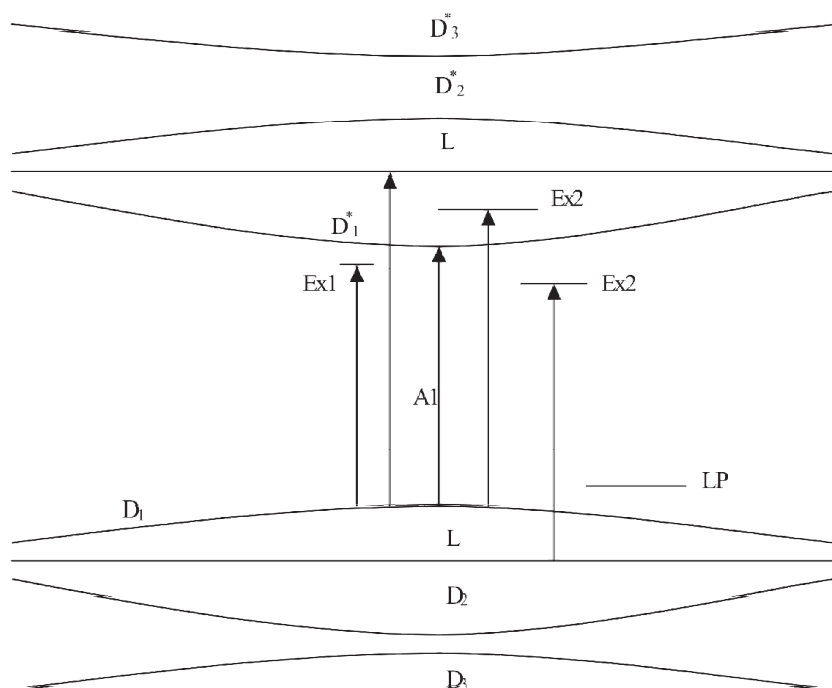**Figure 54.** *Molecular orbitals of vinylene unit, accordingly [20]*

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 poliazomethine 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 ligne 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, and 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 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 group at meta position with respect one another, while terephthale aldehehyde keeping its para orientation. Thus, conjugated 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 –N=N-naphtylene 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 clearly visible if one compare absorption spectra of the above discussed polymers prepared in form of thin film.