

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.

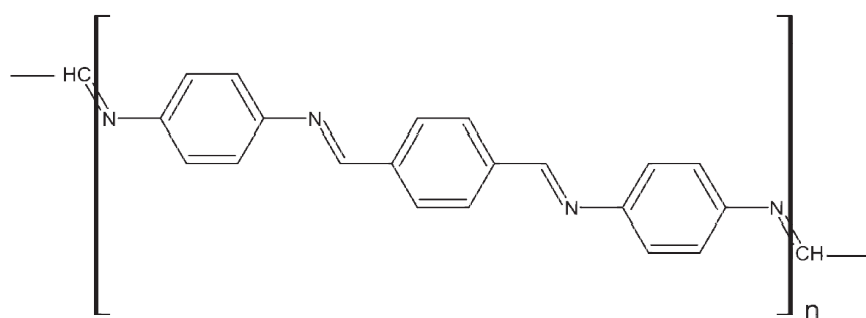


Figure 36. Fragment of PPI chain

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 latters 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

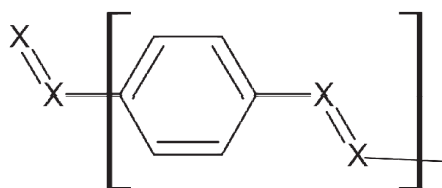


Figure 37. Unit cell of PPV-like polymer chain

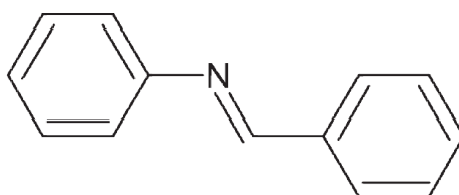


Figure 38. Benzylideneaniline

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

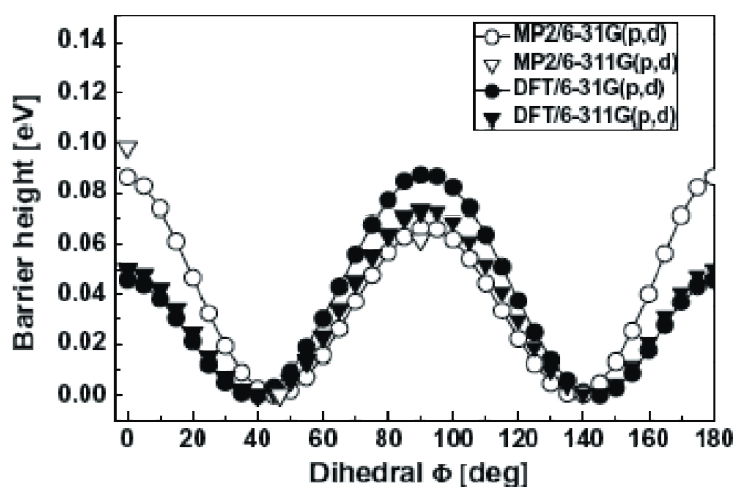


Figure 39. Energy barrier versus dihedral angle [37]

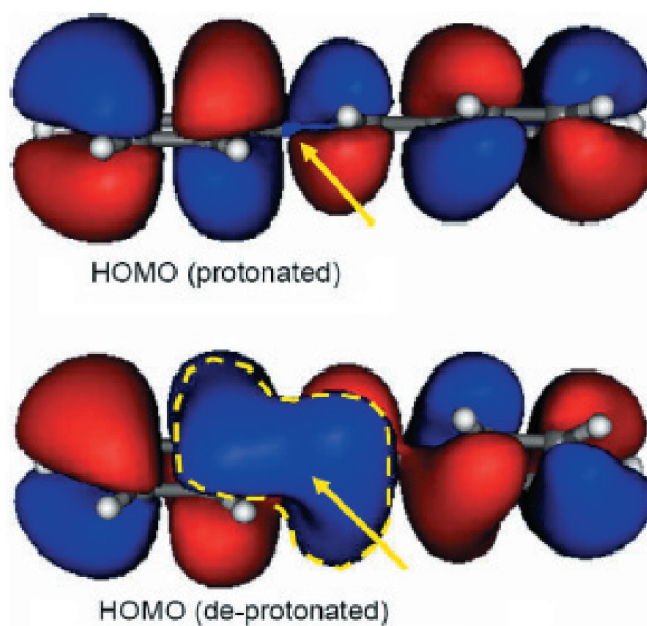


Figure 40. HOMO orbitals of protonated and de-protonated BA molecule [37]

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.

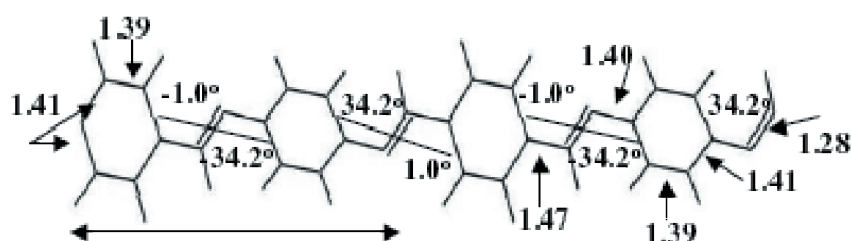


Figure 41. Optimized ground state geometry of PPI chain [28]

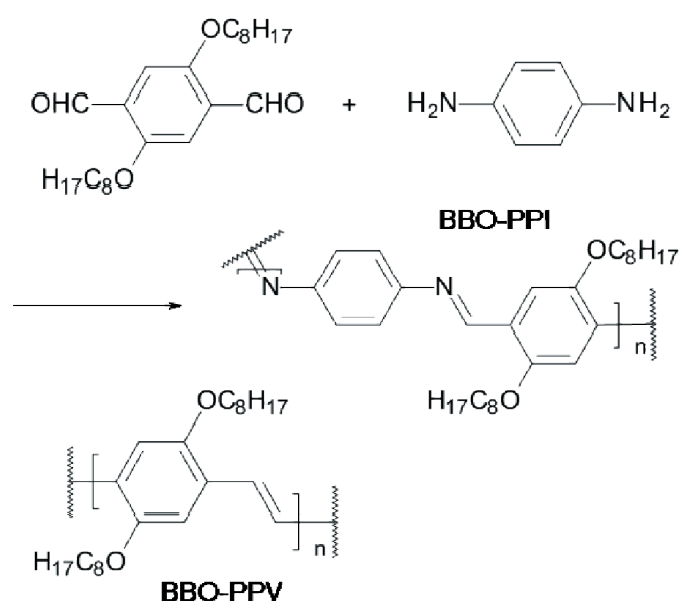


Figure 42. Polymer chain of BOO-PPI [36]

Soluble polyazomethine poly(1,4 - (2,5 - bis(octyloxy 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.

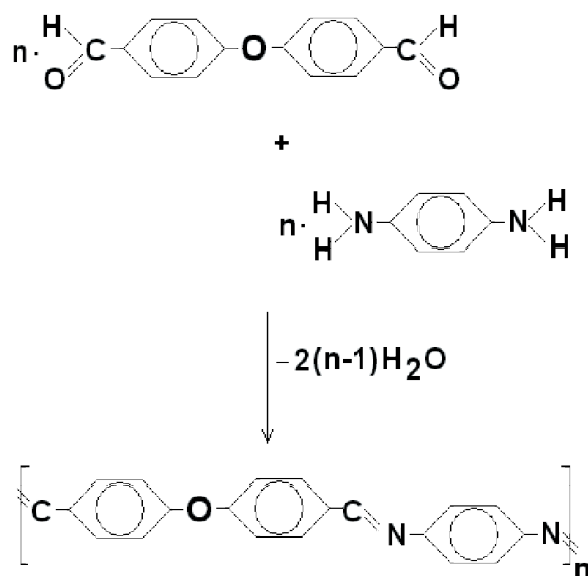


Figure 43. Polycondensation reaction of polyazomethine with oxygen in the backbone

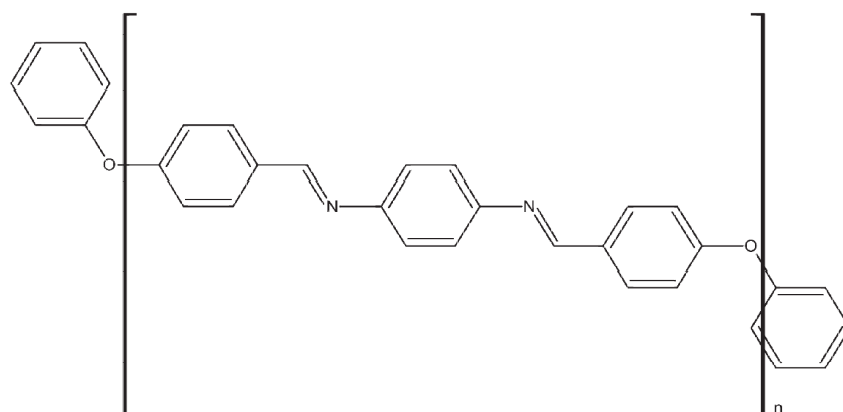


Figure 44. Polymer chain of polyazomethine with oxygen atom

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

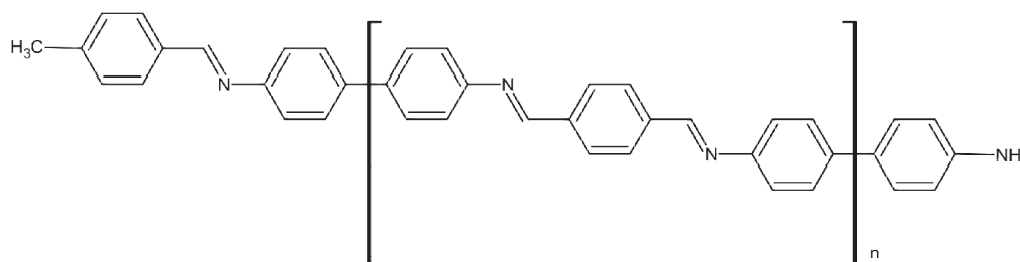


Figure 45. Polyazomethine based on benzidine monomer

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 fluorine

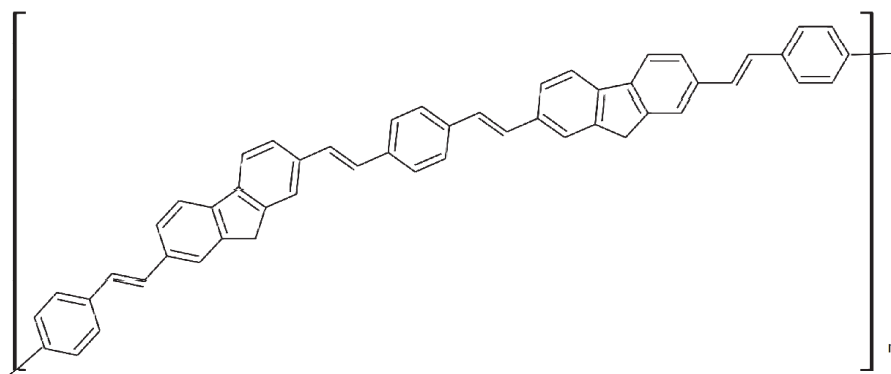


Figure 46. Poly(fluorenephenyleneazomethine)

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

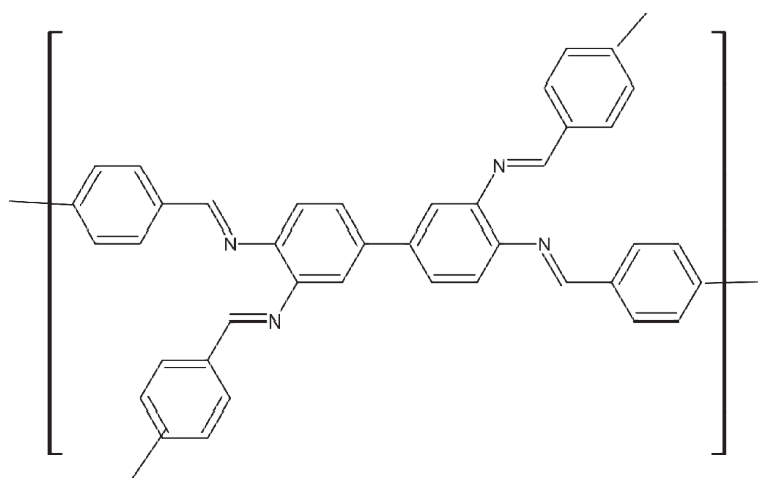


Figure 47. Poly(dibenzidinephenyleneazomethine)

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

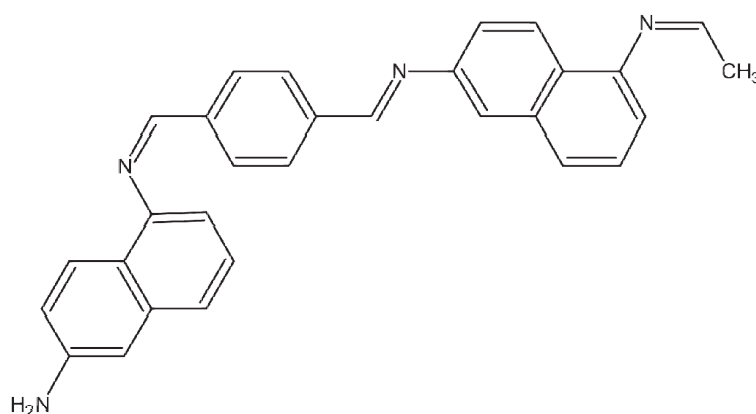


Figure 48. Fragment of the backbone of poly(naphthylene-p-phenyleneazomethine)

spectra. But always one must know that one percent of all entities in the ensemble depends on the size of the ensemble and when it is small this quantity is rather small, but when it is large it can attain quite large number. Thus, one can observe features related with end groups when they are in relevant proportion to the entities forming the ensemble.

4.7. Polyazomethine derived from fat Brown

The backbone of this polymer chain, as shown in Figure 49, is composed of alternately distributed meta- and para-substituted phenylene rings linked together by means of azomethine linkages $N=CH$.

Each phenylene ring with meta-substituted nitrogen atoms have attached azonaphthyl unit at ortho position with respect to the nitrogen atom from azomethine linkage. While considering π conjugation of fat Brown main chain one can deduce it from frontier molecular orbitals of phenylene rings both meta and para substituted as well as azomethine unit approximating it with ethylene unit. However, the system of π electrons of π -conjugated “fat Brown” based polyazomethine poly(1,3 - phenylene(4 - phenyleneazonaphthyl) - 1,4 - phenyleneazomethine) (PNAPI) is augmented by azonaphthylene units attached at each meta substituted phenylene ring. Then, those molecular orbitals which have phases at sites involved in connection $\sigma-sp^2$ binding system of the backbone, those involved in connection with side chains being included, too.

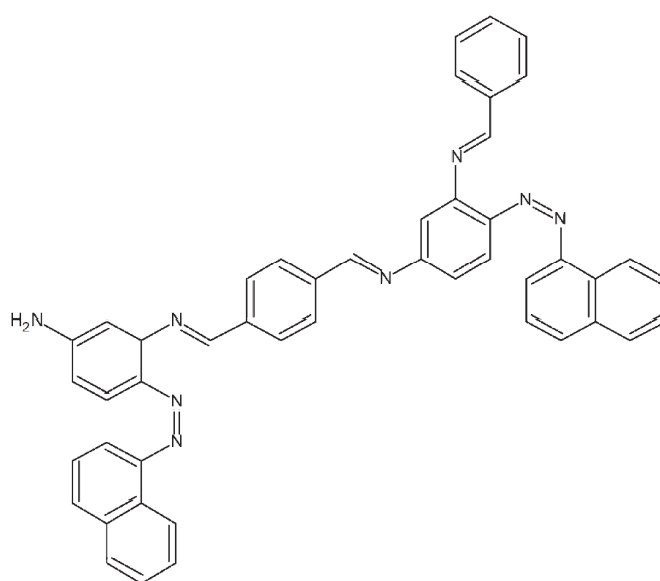


Figure 49. Fat Brown derived polyazomethine