

ELECTRONIC PROCESSES IN POLYAZOMETHINE THIN FILMS

J. Weszka^{1,2} and J. Cisowski^{1,3}

¹*Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34, M. Curie-Skłodowskiej str., 41-819, Zabrze, Poland*

²*Institute of Engineering Materials and Biomaterials, Silesian University of Technology, 18, S. Konarskiego str., 44-1000, Gliwice, Poland*

³*Institute of Physics, Cracow University of Technology, 1, Podchorążych str., 30-084, Cracow, Poland*

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This paper is focused on thin films of various aromatic polyazomethines, undoped and doped with iodine and FeCl₃, which are expected to be promising materials for organic electronics. Polyazomethine thin films have been fabricated by thermal vacuum evaporation (TVE) and chemical vapor deposition (CVD) via the polycondensation process. The prepared films, with a typical thickness of the order of 100 nm and smooth surfaces, appear to be considerably amorphous. The measured absorption and photoluminescence (PL) spectra are discussed in terms of the electronic structure of the materials of interest. In particular, the low-energy spectra, related to transitions between the delocalized states, reveal the presence of the vibronic progression. Additionally, the influence of the polymer chain structure and its conformation on the electronic structure of polyazomethine thin films is considered. Finally, the relationship between the electronic processes occurring in polyazomethine thin films and their potential applications is discussed.

1. Introduction

In recent years, as an alternative to inorganic semiconductors, organic materials in the solid state have attracted much attention because they exhibit a variety of interesting electronic properties, suitable for potential applications. Organic materials, including polymers, have been already used in electronic and optoelectronic devices, such as sensors, solar cells, electroluminescent, display and switching devices (see, e.g., [1-3]); their role will be increasing in the future as compared to inorganic materials.

Aromatic polyazomethines (PAMs) presented in this paper and studied by our research group belong to alternately conjugated polymers with nitrogen atoms in the backbone [4, 5]. For many years this polymer family has been of interest due to their good thermal stability and possible applications in organic electronics [4-7].

Some PAMs have been prepared by solvent-based polymerization, and their thin films have been deposited by spin-on technique [4-10]. However, applicability of this technique is limited only to soluble polymers; in order to prepare thin films of insoluble PAMs, the thermal vacuum evaporation (TVE) or chemical vapor deposition (CVD) methods based on polycondensation have been used [6, 12-19]. It is worth mentioning that these methods provide films which are free from unintentional impurities that cannot be avoided in the case of solvent-based polymerization or spin-on coating techniques.

2. Experimental

A series of four aromatic polyazomethine thin films has been obtained by vapor deposition onto glass and quartz substrates, based on polycondensation reaction of terephthaldehyde (TPA) and an aromatic diamine [19]. As initial monomers, TPA and one of four different amines, i.e., paraphenylene-diamine (PDA), 7,2-diamino-fluorene, 1,1'-biphenyl-3,3',4,4'-tetramine, and 3-amino-4-(1-naphthyldiazenyl) phenylamine (fat brown RR) have been used. The use of different aromatic diamines during the polycondensation reaction has resulted in the following aromatic polyazomethines whose chemical structure is shown in Fig. 1:

- **PPI** – poly (1,4-phenylene-methylidynenitrilo-1,4-phenylenenitrilomethylene);
- **FPI** – poly (1,4-phenylene-methylidynenitrilo-2,7-9H-fluorene-nitrilomethylidyne);
- **BPI** – poly (1,4-phenylene-methylidynenitrilo-1, 1'biphenyl-3,3',4,4'-phenylene-methylidyne-imine);
- **PNAPI** – poly (1,4-phenylene-methylidynenitrilo-1,3-phenylene-(4-(1-naphthyldiazenyl)-nitrilomethylidyne).

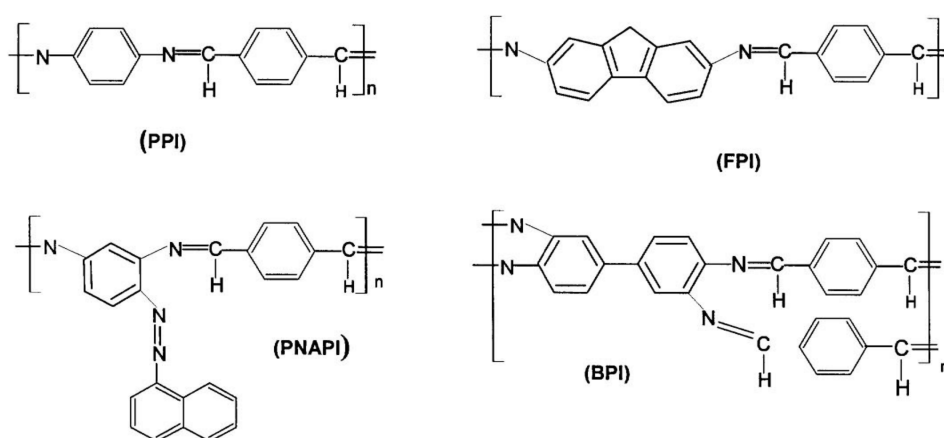
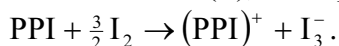


Fig. 1. Chemical structure of four aromatic polyazomethines.

Thin films of FPI, BPI and PNAPI have been prepared by TVE, while PPI films have been obtained by CVD with pure argon as a transport agent.

The structure of as-deposited PAMs films, with a typical thickness of 100 – 200 nm, is significantly amorphous as follows from X-ray diffraction investigations. The atomic force microscopy (AFM) studies demonstrate that the film surfaces are quite smooth, with the root-mean square (rms) roughness below 5 nm.

There have been also prepared PPI thin films doped with iodine and with FeCl₃ [20, 21]. In the first case, a PPI film has been inserted in the iodine vapor during the period of several hours or even several days. The process of doping of conjugated polymers is connected with removing an electron from the highest unoccupied molecular orbital (HOMO) level and transferring the electron to the doping agent, so that the backbone of polymer acquires positive charge, while doping agent becomes negative. In case of iodine molecule (I₂), the doping reaction can be read as



PPI thin films doped with FeCl₃ have been prepared during the CVD process with the third source containing dried FeCl₃ powder, so that argon flows have transported mixed molecules of relevant diamine, TPA monomers and FeCl₃ [21]. Here, the reaction of doping is connected with polymer chain oxidation and iron ion Fe⁺³ reduction into Fe⁺² that can be read as



3. Optical transitions

The absorption spectra (the absorption coefficient α versus photon energy E) taken on PAM thin films deposited on quartz substrates covering the energy range 0.5–6.2 eV are presented in Fig. 2.

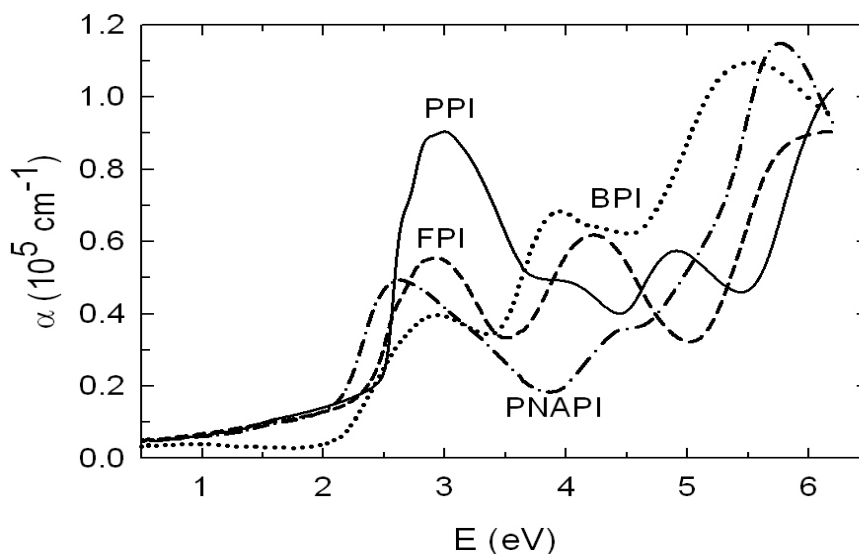


Fig. 2. Absorption spectra of four aromatic polyazomethines [19].

It can be seen that the PAM spectra reveal considerably similar features, though some redistribution of intensity and location of absorption bands undoubtedly affected by their structure and chain conformation is distinctly pronounced. For photon energy above 2.5 eV, all samples exhibit a high absorption level (reaching 10^5 cm^{-1}), typical for amorphous polymer films.

The absorption edge of PAM films coincides significantly with low-energy wing of the first band attributed to interband transitions connecting delocalized states and one can see that their shape resembles to some extent the shape of the absorption edge observed for typical amorphous semiconductors which allows for determining the energy gap E_g from the Tauc relation $(\alpha E)^{1/2} \propto (E - E_g)$ [17–19]. The obtained values of E_g are 2.35, 2.03, 1.87, and 1.80 eV for PPI, FPI, BPI, and PNAPI, respectively. However, it seems that there is some arbitrariness in determining the width of the forbidden gap, if one treats polymer chain like one-dimensional crystal because of ordering of molecules along the chain; in particular, no atomic disorder is expected because of nature of polycondensation reaction. The only disorder effects are expected to result from chain twisting due to steric hindrance or lone pair allocated on nitrogen atom coupling to π -system of the nearest neighbor benzene ring and some distribution of chain lengths and, as a consequence, conjugation length of a given polymer.

Features observed in optical spectra of conjugated polymers can be attributed, on going on from the lowest energy to the highest one, as being due to optical transitions connecting delocalized states, delocalized and localized ones or vice versa and those due to transitions between localized states. When comparing polymers shown in Fig. 1, PPI is seen to be the simplest one as composed of alternate benzene rings and azomethine linkages, while the other PAMs reveal larger units with grouping fluorene, biphenyl, or naphthalene units. These units are made up of more developed conjugated fragments as constituted by greater number of π electrons which make that their effect on the optical spectra becomes concurrent with the effect arising from conjugation length; the latter ceases to be a crucial factor determining position of the energy edge.

The spectrum of PPI reveals the strongest low-energy band whose shape as well as the shape of the whole spectrum resembles the spectrum of poly(*p*-phenylene-vinylene) (PPV) [14, 15], so that one can expect some similarity of their π electron systems. This is consistent with similarity of their polymer chains, whose backbones are composed of alternate phenylene rings and vinylene (-CH=CH-) or azomethine (-N=CH-) linkages in PPV and PPI, respectively. Two linkages provide two π electrons each, and it seems that they can be approximated by ethylene π electron system, as it has been done for PPV within the linear combination of atomic orbitals – molecular orbitals (LCAO-MO) approximation [22, 23]. Such an approach to interpret the recorded spectra of PPI is thought to be reasonable, because PPI has been prepared by polycondensation of TPA and PPDA, so that the order of CH and N in subsequent azomethine linkage is changing alternately. This means that each benzene ring has at its para positions $\frac{1}{2}(\text{CH}+\text{N})$ unit on the average; one can approximate PPI chain with PPV-like one, where instead of vinylene unit, there is a vinylene-like hypothetical unit $\frac{1}{2}(\text{CH}+\text{N})$.

To interpret the recorded spectra of PPI, a model deriving its electronic structure from molecular orbitals of benzene and ethylene molecules is expected to be useful. Molecular orbitals of benzene are given in Fig. 3 and those of ethylene are shown in Fig. 4.

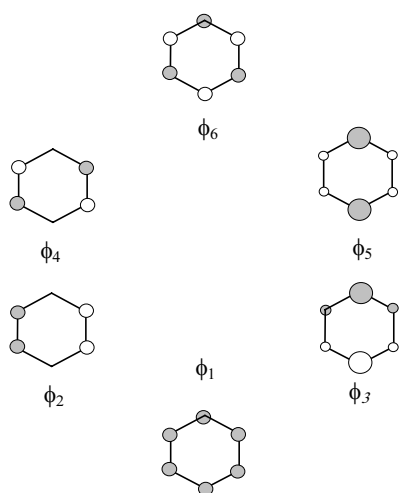


Fig. 3. Molecular orbitals of benzene molecule.

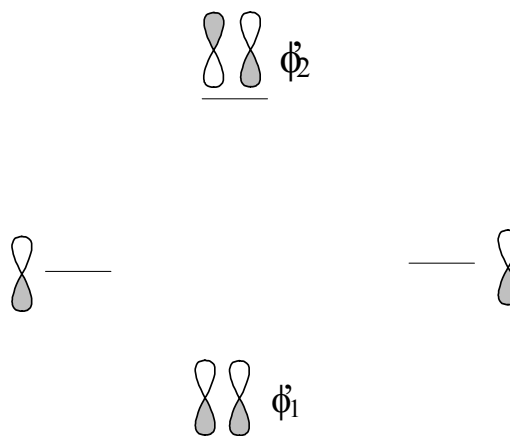


Fig. 4. Ethylene molecular orbitals.

This approximation allows for the PPI electronic structure to be treated in the manner applied to PPV, bearing in mind that, additionally, each linkage is associated with one sp^2 lone pair. Then, while applying molecular orbital picture to PPV-like polymer, one can expect that benzene ϕ_3 and ϕ_4 orbitals overlap rather strongly with ethylene ϕ_1' and ϕ_2' orbitals, respectively. It is important to underline that the benzene highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), while calculated by the Hückel method [23], are degenerate (symmetry of benzene molecule is of D_{6h} point group), so that each HOMO and LUMO is associated with a pair of molecular orbitals (ϕ_2, ϕ_3) and (ϕ_4, ϕ_5), respectively. Moreover, the Hückel method gives two HOMO and two LUMO levels of benzene having the same energy as their ethylene counterparts.

The resulting scheme of electronic states shown in Fig. 5 reflects interactions of benzene and ethylene molecular orbitals. Bands D_1 and D_1^* are a result of strong resonance between above mentioned pair of benzene and ethylene orbitals which are HOMO and LUMO levels of PPI. The latter is expected to have energy below that of nitrogen p_z orbital which

results in its interaction with PPI HOMO level (D_1 molecular orbital). Bands D_2 and D_2^* are second counterparts of this resonance benzene-ethylene picture. Bands L and L^* , and D_3 and D_3^* are, respectively, localized and delocalized bands with predominant benzene contribution.

Optical transitions corresponding to the recorded PPI spectrum can be described as follows. The strongest, broad, low-energy absorption band at about 3 eV, exhibiting the vibronic progression, is attributed to interband transitions between delocalized D_1 and D_1^* states (A1 in Fig. 5). Absorption bands at about 4.9 eV are attributed to interband transitions connecting localized and delocalized bands (L to D_1^*) and vice versa (i.e. D_1 to L^*), while the highest absorption bands at about 6.2 eV are due to transitions between localized states (L to L^*) of the phenyl ring. There are also shown Wannier-Mott and Frenkel excitons, designated as Ex1 and Ex2, respectively, and the lone electron pair (LP).

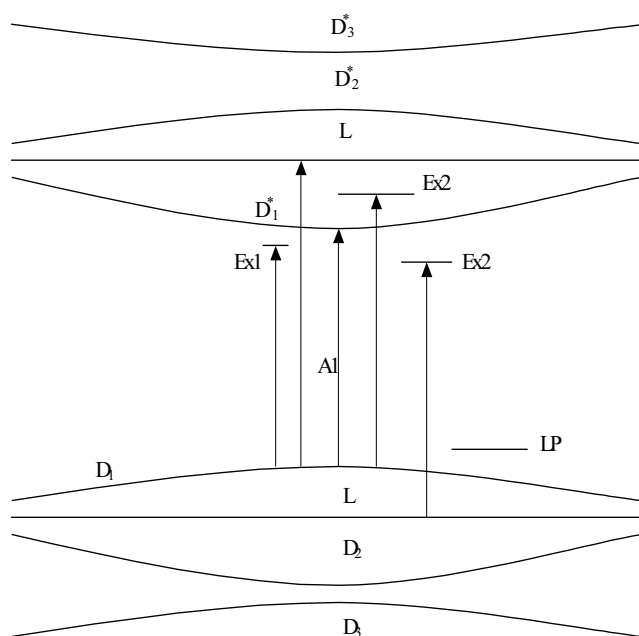


Fig. 5. Electronic structure of PPI.

It is thought that the optical spectra of other polymers from Fig. 2 reflect their electronic structures and interactions of molecular orbitals of their structural units. As can be seen in Fig. 1, the polymer chain of FPI is built up of subsequent fluorene, azomethine, and benzene rings ordered along the backbone. Then, one can expect that the conjugated area within the FPI unit cell (repeating unit along polymer chain) is larger than that of PPI as there are three benzene rings and azomethine linkage. It is expected that fluorene unit is rather planar due to presence of CH_2 group; additional linking occurs between two benzene rings, connected with one another at para positions. Therefore, a low energy band of FPI is related to interband transitions connecting delocalized states originating from overlaps between molecular orbitals of subsequent units involving similar orbitals, like those responsible for the strongest band in PPI. However, its intensity being rather low, can be attributed to twisting of conjugated fragments along the chain, i.e., on fluorene-azomethine and azomethine-benzene ring bonds. Essentially, similar comments can be made concerning quite large unit cells of PNAPI and BPI as their conformation is explicable with the same benzene and ethylene molecular orbitals.

The recorded spectra seem to indicate that as-prepared FPI, PNAPI, and BPI films are polymers with short conjugation lengths due to rather large molecules of diamines which can

bring obstacles, while polymer chain is growing longer and longer. Observed changes in the energy gaps of PAMs can be connected with differences in polymer chain structure and, in particular, with differences of the conjugated part length.

3.1. Application of the Lorentz oscillator model (LOM) and vibronic progression

Knowledge of the optical spectrum of an organic material in a wide range of photon energy makes it possible to model the spectrum in order to determine the optical constants. Following Ref. [24], we have used the Lorentz oscillator model to describe the absorption spectrum of the basic polyazomethine, i.e., PPI for which the vibronic progression, revealing the electron-phonon interaction connected with the benzene ring stretching mode, is clearly visible (see Fig. 2).

In the Lorentz oscillator model (LOM), the real and imaginary parts of the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ are given by (see, e.g., [24])

$$\varepsilon_1 = \varepsilon_\infty + \sum_{j=1}^l \frac{F_j(E_j^2 - E^2)}{(E^2 - E_j^2)^2 + (E\Gamma_j)^2}, \quad \varepsilon_2 = \sum_{j=1}^l \frac{F_j E \Gamma_j}{(E^2 - E_j^2)^2 + (E\Gamma_j)^2},$$

where l is the number of oscillators, each with energy E_j , broadening parameter Γ_j and F_j determining the oscillator strength; ε_∞ is the dielectric constant arising from higher-lying transitions. The optical constants, i.e., the refraction coefficient n and extinction coefficient k , are connected with the dielectric function components via the relations

$$\varepsilon_1 = n^2 - k^2, \quad \varepsilon_2 = 2nk.$$

Finally, the absorption coefficient α , which can be determined from optical measurements, is $\alpha = 4\pi k/\lambda$, where λ is the wavelength.

An example of description of the experimentally determined absorption spectrum of a 100-nm thin film of PPI with LOM is shown in Fig. 6.

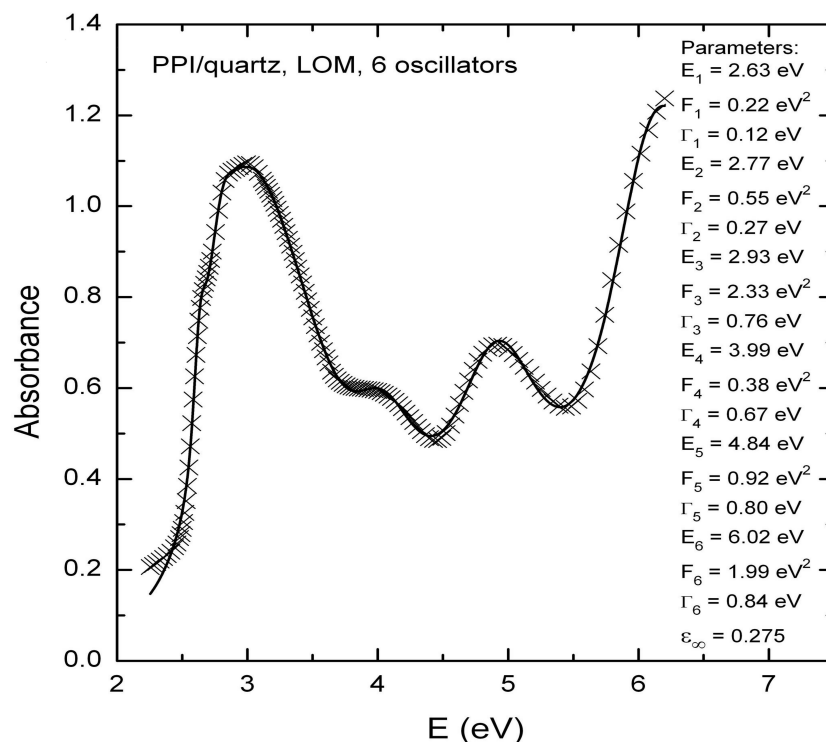


Fig. 6. Absorption spectrum of a PPI film deposited on quartz. Crosses - experimental data, solid curve – fit of the Lorentz oscillator model (LOM) with 6 oscillators.

It can be seen that LOM describes quite well the experimental data with 6 oscillators, each being characterized by 3 parameters, as inserted in Fig. 6. The first three oscillators concern the broad band peaking at about 3 eV, which is composed of three vibronic subbands separated by the energy difference of about 0.2 eV, typical for organic materials.

3.2. Doped polyazomethine thin films

The absorption spectra of PPI doped with iodine and FeCl_3 are shown in Fig. 7, while the influence of doping mechanism on the electronic structure of a polymer is outlined in Fig. 8. It can be seen that removal of one electron from the polymer HOMO level results in pushing it towards higher energies and this effect is associated with downward shift of empty LUMO level which is equivalent to creating polaron state within the HOMO-LUMO gap [25]. The lower level of polaron is occupied by single electron and the higher level is empty. This effect can be understood, if one takes into consideration that removal of one π electron means that there is a carbon atom on the phenylene ring or vinylene-like linkage that loses one electron and, in consequence, it cannot afford making double bond with a neighboring carbon atom. Thus, there is created a localized state, which is expected to contradict to nature of alternately conjugated polymers in general and, in order to avoid such situation, certain redistribution of double bonds along with the backbone is forced, and benzenoid modification transforms into quinoid one covering several polymer unit cells. However, this transformation is associated with some energy input which brings about appearance of two levels within the forbidden gap. Then, states appear which need lower energy than the HOMO-LUMO gap to complete transition from one level onto another or onto empty LUMO level; the more such centers are created, the stronger absorption band is.

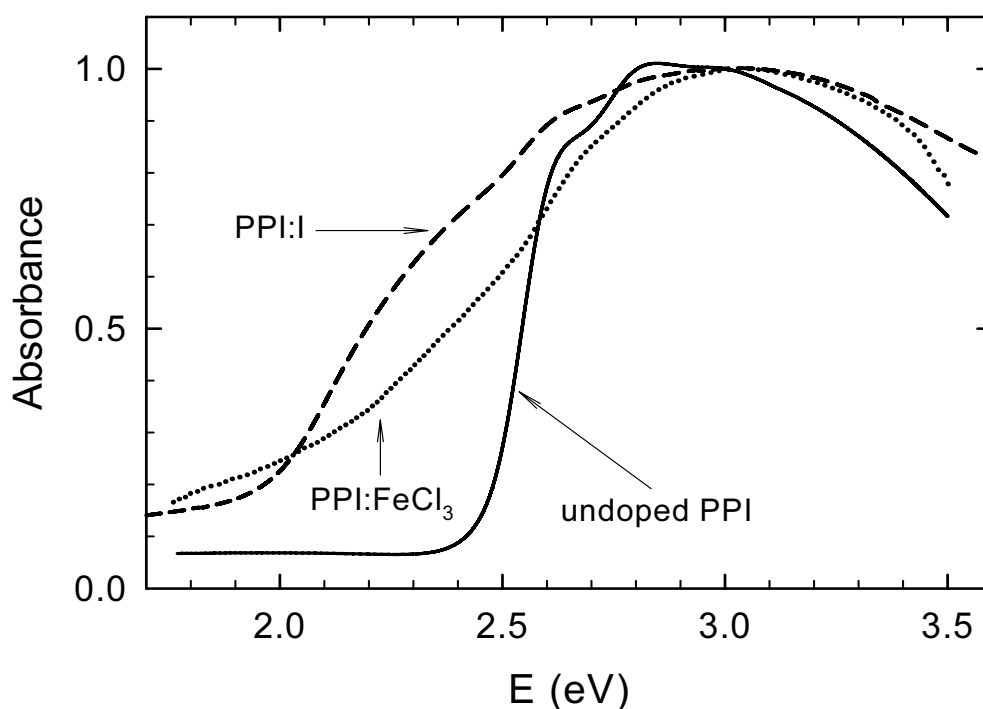


Fig. 7. Comparison of absorption spectra of undoped PPI thin film with PPI films doped with iodine and FeCl_3 [20, 21].

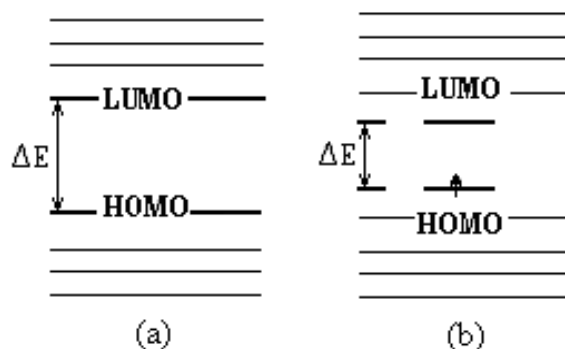


Fig. 8. Formation of the polaron state in the energy gap; (a) undoped and (b) doped PPI.

Some smearing of the absorption edge observed for both iodine- and FeCl_3 -doped PPI films (Fig. 7) is expected to be due to growing number of polaron states in the gap and diminishing number of HOMO states, and their replacing with the next pair of states taking the role of HOMO and LUMO levels.

3.3. Photoluminescence

Photoluminescence (PL) studies of organic materials provide important and complementary information on their electronic structure and give indications on possible applications in electronics as organic light-emitting diode (OLED).

Typical room-temperature PL spectra recorded for relatively thick ($0.5\text{--}1\ \mu\text{m}$) films of two PAMs, i.e., PPI and BPI, are shown in Fig. 9 [26]. Change of the excitation wavelength in the investigated range $395\text{--}425\ \text{nm}$ ($3.14\text{--}2.92\ \text{eV}$) hardly influences the shape of the observed PL spectra.

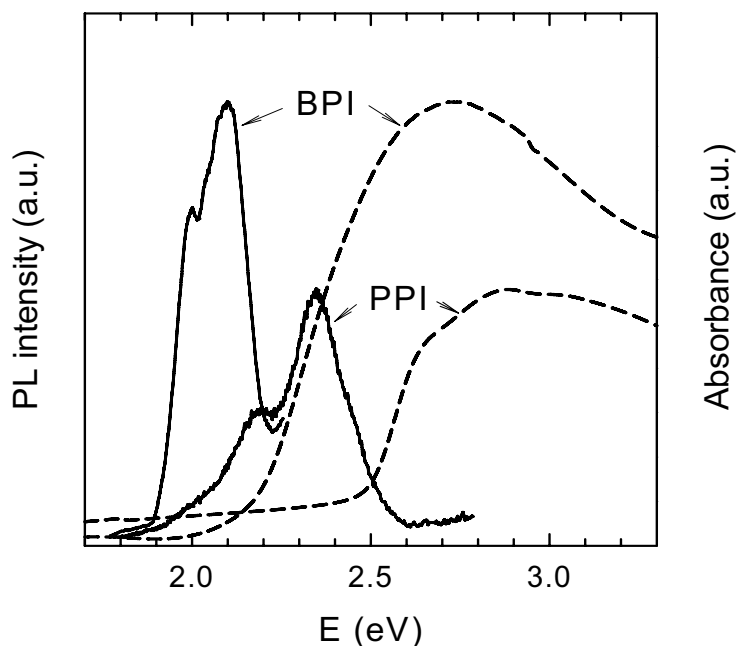


Fig. 9. PL spectra of PPI and BPI films along with the absorption spectra.

PL spectra of both PAMs have a similar shape characterized by two peaks which, however, are shifted on the energy scale. For PPI, the smaller maximum is at $E_1 = 2.2$ eV and the higher one is at $E_2 = 2.35$ eV, while for BPI $E_1 = 2$ and $E_2 = 2.1$ eV. These maxima may be connected with radiative transitions from the lowest excited vibronic state to the lowest consecutive vibronic levels of the ground state, though, in the case of the smaller maximum (shoulder), one may alternatively deal with the interchain interaction in the polymer film [27].

When comparing the PL spectra with the absorption spectra obtained for thin films, it is interesting to note that the absorption spectrum of PPI exhibits the vibronic structure of the ground state, while for BPI such a structure is not seen, probably because of higher disorder in films of BPI than in films of PPI. On the other hand, the comparison of PL spectra of PPI and BPI suggests that PPI reveals larger conjugation length than BPI, which is consistent with higher intensity of PL spectrum taken on BPI. This is in accordance with the backbone conformation of this polymer as it consists of biphenyl part that is expected to be twisted as a result of electrostatic repulsion of π electrons on the two benzene rings. In addition, there are four amine groups whose orientation makes repeating unit of this polymer rather large, so that some steric hindrances may have strong impact on the polymer conformation and its chain length.

4. Chain conformation

In the previous section, some comments on the chain conformation of polymers under discussion were given. It is easily seen from Fig. 1 that among analyzed polymers, PPI has the simplest chain as composed of alternately repeating benzene and azomethine linkages, which makes any considerations on PPI π electron system rather straightforward. Such considerations, within the linear combination of molecular orbitals, on other PAMs appear to be rather complex, even though they are significantly built up of nearly the same parts as the PPI chain. It can be expected that PPI conformation is planar enough, so that the nitrogen lone pair orbital impact on the backbone planarity is comparable to that of steric hindrance influence planarity of PPV chain. In contrast, one can expect that the process of polymer chain elongation in other PAMs, going on via polycondensation, meets spatial obstacles being not connected with linking of TPA molecule to each of amine groups of diamine monomer, but bringing large molecule with numerous amine groups to aldehyde end group. This process conserves sp^2 hybridization of carbon and nitrogen atoms constituting backbone which might appear to be troublesome for their dimensions. As a consequence, twisting constituent conjugated fragments of polymer or even its unit cell would inevitably result in low intensity of the optical band arising from interband transitions connecting delocalized bands.

5. Conclusions

In summary, we have described thin films of various polyazomethines, including doped ones, in terms of the electronic processes occurring in these materials. While discussing electronic structure of the presented polyazomethine thin films it has been emphasized that their electronic properties in many respects resemble those of PPV, which is a very promising material for applications in organic electronics. Examining various properties of PAMs, feasibility of future applications of this polymer family in the field of optoelectronics should be rather considered in view of their blending with other polymers or molecular materials to produce volume p-n junctions - basic elements of photovoltaic structures. On the other hand, their chemical and electronic structure, revealing many similarities with PPV derivatives, may be applied for preparation of layered devices based, for example, on PAM/fullerene p-n junc-

tions. In view of potential applications of various structures containing polyazomethines, further studies are desirable, involving optimization of technology, detailed knowledge of electronic structure and processes occurring at interfaces, and, finally, the design and fabrication of long-time operating devices.

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