1. Introduction

Among polymer materials there is a group of alternately conjugated polymers which have revealed interesting electronic properties resembling them to some extent to inorganic semiconductors [1-6]. Characteristic feature of conjugated polymers which distinguish them from other groups of polymers is alternation of single and double bonds along with the polymer backbone, which is possible due to sp2 hybridization of carbon atoms constituting the backbone [4,7,8]. Aromatic polyazomethines, known also as the Schiff bases [9-11], belong also to alternately conjugated polymers having azomethine linkage in the backbone, resembling vinylene one in which one CH methine group is replaced by nitrogen atom. Polymers belonging to this family have been for many years of interest due to their good thermal stability and interesting optoelectronic properties [12-21]. There are polyazomethines with alkoxy side chains that can be prepared by solvent-based polymerization, so that their thin films can be deposited by solvent based or spin-on techniques [11-22]. However, applicability of this method concerns soluble polymers only, and that is why thin films of insoluble polyazomethines can be prepared by such methods as the thermal vacuum evaporation (TVE) or chemical vapor deposition (CVD) via polycondensation [11-22]. It should be emphasized that polyazomethine thin films while being prepared by theses two methods are free from unintentional impurities, in contrast to solvent-based polymerization or spin-on coating techniques where unintentional impurities cannot be avoided [22]. The simplest representative of aromatic poly(azomethines) is poly(1,4-phenylene-methylidynenitrilo-1,4-phenylenenitrilomethylidyne), which will be referenced as PPI [9], which has the backbone consisting of alternately repeating paraphenylene and azomethine linkage. Being an isoelectronic counterpart of poly(paraphenylene vinylene) (PPV), PPI has been expected to be suitable for photovoltaic and other optoelectronic applications [11-22]. The aim of this work is to review our achievements in studying electronic properties of PPI thin films prepared by dry methods such as CVD and VTE and wet methods concerning deposition of PPI thin films by spin-coating from solution, as well as reconsider feasibility of PPI thin films applications for photovoltaic or optoelectronic structures and their dependence on technological conditions of their preparation. Our interest in studying the CVD prepared PPI thin films is also to better understand mechanisms of condensation polymerization process running at the interface

of the vapor/solid phase, structure and morphology of as-deposited films as well as the electronic structure of polymers having nitrogen atoms in the backbone [11,22,23]. These conjugated polymers have been called polymer semiconductors, but one should bear in mind that the term semiconductor means that electrical properties of this group of inorganic materials reveal conductivities small compared with metals [24,25], but much higher than this is the case in conjugated polymers[5,6,24]. Though, there have been undertaken research works to improve conductivity of these materials by means of so called doping, as this is done in case of inorganic semiconductors. However, here the term doping is used to indicate technological activities, which are thought to more resemble interstitial doping in inorganic crystals rather than substitution doping having been widely used to vary conductivities in semiconductors [23]. The backbones of the alternately conjugated polymers being built up of sp2 hybridized carbon atoms linked together by alternate single and double bonds, electronic transitions involving π electron states are not connected with any destruction of the polymer chain. They have appeared to be of great importance, because in contrast to saturated polymers, the electrons allocated on trigonal orbitals are involved in strong enough valence σ bonds connecting two nearest neighbor carbon atoms and a hydrogen atom, while the fourth electron of each carbon atom in the chain of alternately conjugated polymer is allocated on its p_z orbital contribute to the system of delocalized electrons due to overlap of the orbitals of the nearest carbon atoms spreading out over a conjugated segment of the backbone [4-8]. Thus, one can say that alternately conjugated polymers are characterized by electron system composed of two types of electrons, the electrons involved in σ bonds and delocalized electrons from p_z orbitals, which are called π electrons. Such division of valence electrons of the constituent elements into σ and π electrons has appeared to be not only very convenient, but also it appeared to be very utile to give an account of electronic properties of the polymers under question [4,7,8]. This separation of the polymer electrons in two electron entities independent of each other makes out the core of Hückel method widely used to describe electronic properties of polymers and molecules with alternately conjugated atomic systems [7,8]. In spite of its great simplicity, this method has appeared to be very utile while interpreting electronic properties even in case of quite complex conjugated polymers [7,8]. The idea of separating σ electrons from π electrons, which is behind this model and its various modifications makes a basis for π electron approximation [7,8] and it was used in our previous paper on poly(paraphenylene azomethine) (PPI) thin films optical properties [22,26-28], with configuration interaction being

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

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