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Thin films of aromatic polyazomethines

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1. Introduction

Aromatic polyazomethines, which are known also as the Schiff bases (Yang & Janekhe, 1991) belong to alternately conjugated polymers having nitrogen atoms incorporated in ordered way into the backbone. Their backbone conformation is derivative of aromatic di-amines and di-aldehydes structures, as they are prepared via condensation polymerization. Since many years this polymer family have been of interest for their good thermal stability and interesting opto-electronic properties (Yang & Janekhe, 1991; Yang & Janekhe, 1991; Kubono & Okui, 1994). Some poly(azomethines) have been prepared by solvent-based polymerization and their thin films have been deposited by spin-on technique (Yang & Janekhe, 1991; Yang & Janekhe, 1991; Kubono & Okui, 1994; Thomas & Inghes, 1998; Luzny et al., 1999; Suhl & Shim, 2000; Jung et al., 2002). However, applicability of this technique is limited only to soluble polymers and in order to prepare thin films of insoluble poly(azomethines), the thermal vacuum evaporation or chemical vapor deposition (CVD) methods based on polycondensation have been used (Kubono & Okui, 1994; Takahashi et al., 1991; Weaver & Bradley, 1996; Rohlfing & Bradley, 1998; McElvain et al., 1998). It is worth mentioning that thermally vacuum evaporated films, similarly like those prepared by CVD, are free from unintentional impurities that cannot be avoided in the case of solvent-based polymerization or spin-on coating techniques (Kubono & Okui, 1994; Takahashi et al., 1991; Weaver & Bradley, 1996; Rohlfing & Bradley, 1998; McElvain et al., 1998). The simplest representative of poly(azomethines) is 1,4-phenylene-methylidynenitrilo-1,4-phenylenenitrilomethylidyne, which hereafter will be referenced as PPI (Yang & Janekhe, 1991). PPI has the backbone consisting of alternately repeating *para*-phenylene and azomethine dimers. Being an isoelectronic counterpart of poly(*para*-phenylene vinylene) (PPV), PPI has been expected to be suitable for photovoltaic and other optoelectronic applications (Kubono & Okui, 1994; Takahashi et al., 1991; Weaver & Bradley, 1996; Rohlfing & Bradley, 1998; McElvain et al., 1998) (Kubono & Okui, 1994; Thomas & Inghes, 1998; Takahashi et al., 1991; Weaver & Bradley, 1996; Rohlfing & Bradley, 1998; McElvain et al., 1998). The aim of this work is to show how the electronic properties of PPI thin films formed by CVD based polycondensation can be tailored by technological conditions of their preparation or chain modifications. 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.

2. Polycondensation based thin film preparation

Polycondensation is polymerization process, in which polymer chain progression is running through chemical reactions between the functional groups of two bifunctional monomers with releasing low weight molecule (Flory, 1971). While preparing thin films of polyazomethines, the polycondensation process is based on chemical reaction between aldehyde and amine groups of aromatic di-aldehyde and di-amine, so that larger bi-functional species, having aldehyde and amine end groups and azomethine $-\text{CH}=\text{N}-$ linkage between phenylene rings, is formed and one water molecule being released. Such species having formed can combine with one another or with relevant monomer by means of chemical reaction between aldehyde and amine groups with forming a larger bi-functional oligomer and releasing water molecule at each stage.

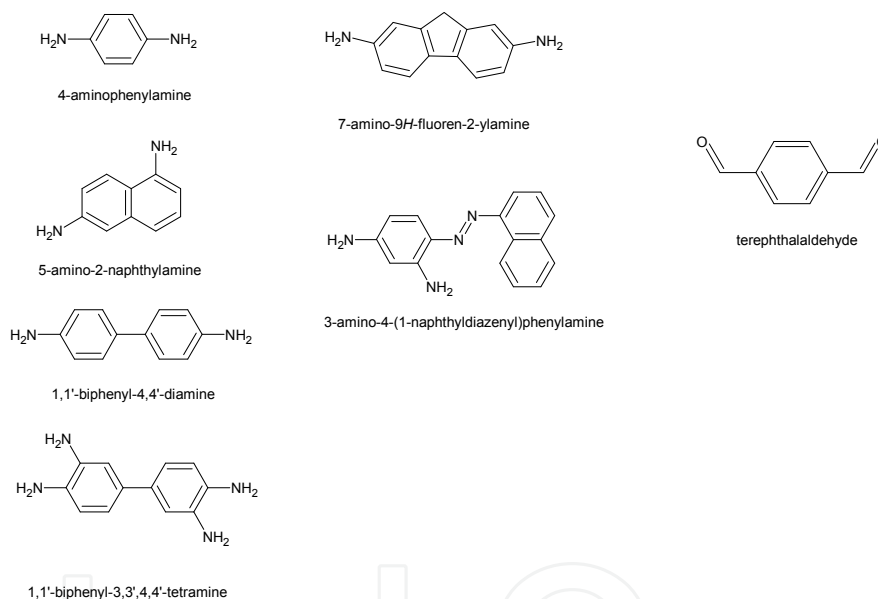


Fig. 1 Diamines and terephthal aldehyde used in polycondensation based process of polyazomethine thin film growth.

As a result many different polymer chains can progress upon the surface of the substrate and subsequently upon layers having already been formed. However, one should remember that removing this low weight molecule may be essential for polymer chain progression. While preparing poly(1,4-phenylenemethilidynenitrilo-1,4-phenylenenitrilomethilidyne) this polymerization process is illustrated in Fig. 2. According to Flory rule (Flory, 1971), which states that chemical reactivity of end groups does not depend on the length of polymer chain they are attached to, one may expect that polyazomethine thin film growth is connected closely with progressing the polyazomethine chains all over the substrate surface simultaneously. Molecules of monomers arriving at the surface can be attracted at different active points of the surface starting off polymer chains progressions, which can proceed

along many chains simultaneously. This kind of polymerization is thought to be very suitable to prepare thin films of polyazomethines with the use of such techniques as chemical vapor deposition (CVD) or thermal vacuum evaporation (TVE) from two sources. The essential and common feature of the two techniques is that thin films grown on various substrates are free from any unintentional doping and the two methods are especially very convenient for preparing thin films of polyazomethines insoluble in organic solvents.

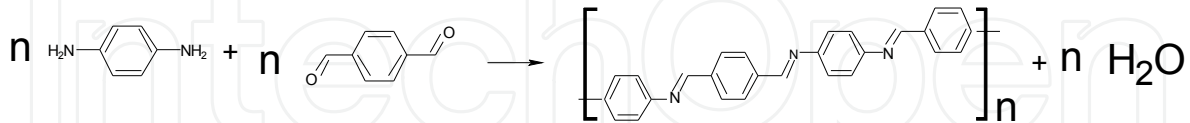


Fig. 2. Polycondensation reaction resulting in PPI polymer chain progression

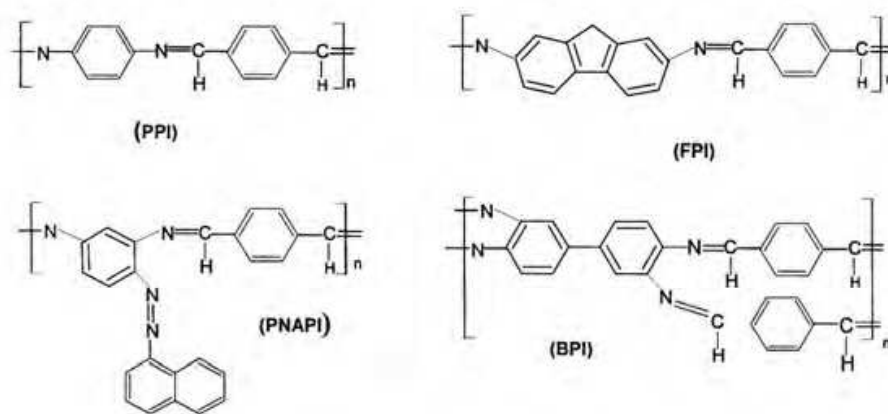


Fig. 3. Polyazomethines prepared by CVD and thermal vacuum evaporation.

2a. Chemical vapor deposition of polyazomethine thin film preparation

Chemical vapor deposition is a technique of thin film preparing, where all the reagents involved in chemical reactions driving a film growth are being transported towards the substrate wafer area with the use of carrier gas agent (Weszka et al., 2008). Here, because the process of thin film formation is based on condensation polymerization running between molecules of bifunctional aromatic diamines and dialdehydes, neutral gaseous argon is used as a carrier agent to transport reagent molecules to the reaction chamber where the substrate is mounted. The process of CVD deposition of polyazomethine thin films has been made in the technological equipment, which was built up in horizontal and vertical geometries (Weszka et al., 2008; Hajduk et al., 2009). The equipment for thin film deposition in horizontal geometry is schematically illustrated in Fig. 4, though general ideas outlined in this figure are applicable for vertical geometry of the CVD equipment illustrated in Fig. 5, too. How it can be seen in Fig. 4, argon is being dosed into the CVD system with the pressure regulator mounted on an argon reservoir while its flow rate are measured with a rotameter, similarly as it has been described for preparing PPI thin films (Weszka et al., 2008). The Ar stream, with a fixed flow rate controlled by a pressure regulator, is forked into two or three equal streams, one flowing over a boat containing PPDA and the others over a boat with TPA, while the third one, if used, it has been argon itself. The third channel has been used while preparing PPI thin films doped with ferrous three chloride (FeCl_3) in the

vertical CVD setup. It has been found out while preparing thin films of the simplest (for chemical structure) aromatic polyazomethine PPI that such technological conditions like temperatures of monomers terephthal aldehyde, T_{TPA} , and p-phenylenediamine, T_{PPDA} , their difference, ΔT , transport agent flow rate and the distance from the inlet into the reaction chamber to the substrate, d , are very important parameters determining deposition conditions. They have been found to influence the structure, surface morphology and optical properties of deposited films of polyazomethines (Weszka et al., 2008). Because thin films of polyazomethines have been prepared via condensation polymerization, one may expect that the film growth process is controlled to large extent through this polymerization process by the rate water molecules are removed into flowing out argon stream. While comparing how each of technological parameters used while preparing PPI thin films discussed influence the film thickness and the time it was deposited it seems difficult to decide which one of them has the most important impact on the PPI thin film growth. To consider these technological issues one can have a look at Tab. 1 where are collected data presented in paper (Weszka et al., 2008). It can be seen that in the processes used the TPA source temperature, T_{TPA} , has been kept fixed at about 326 K, with one exclusion when it was 313 K. The source temperature of the other monomer was about 9 to 19K higher, with one exclusion when it was as low as 315 K, so nearly coinciding with that of TPA. If one compares data for films a and b , one can see that they were prepared under the same flow rate of about 80 l/min and the same T_{PPDA} and T_{TPA} , with forking argon stream into two equal ones, the film has grown faster at the substrate placed farther from the inlet. One can see that under the same conditions three-stream prepared PPI films grew slower than two-stream ones, which could be attributed to much lower reagent concentration in the stream entering the reaction chamber diluted by the third stream used.

Film	T_{PPDA} (K)	T_{TPA} (K)	Flow rate l/min	Time (s)	Distance (cm)	Number of streams	Thickness (nm)
A	335	326	80	120	5	2	200
B	334	326	80	180	4	2	200
C	340	326	150	60	5	2	200
D	334	326	80	420	4	3	170
E	343	327	80	90	5	3	180
F	315	313	60	1500	5	3	50

Table 1. CVD technological parameters of PPI thin film preparation (according to Weszka et al., 2008)

This effect is seen to be more pronounced in case of thin films prepared when the substrate was placed 4 cm from the inlet. But most pronounced influence is seen in the case of e film prepared with slightly lower flow rate (60 l/min) and relatively low and nearly coinciding temperatures of monomers (about 313 K). Then, depending on the regimes used, two or

three relevant streams have merged into one Ar stream that transported mixed molecules of both monomers towards the inlet into the cylindrical reaction chamber of a much larger diameter, as it is schematically outlined in Fig. 4. The inlet is centered on the axis of the cylinder chamber and the substrate holder is fixed perpendicularly to the cylinder axis at a distance $d = 4$ or 5 cm from the inlet. Argon and reaction by-products or monomers that have not reacted have been removed from the reaction chamber with an exhaust rotary pump operating continuously during the deposition process.

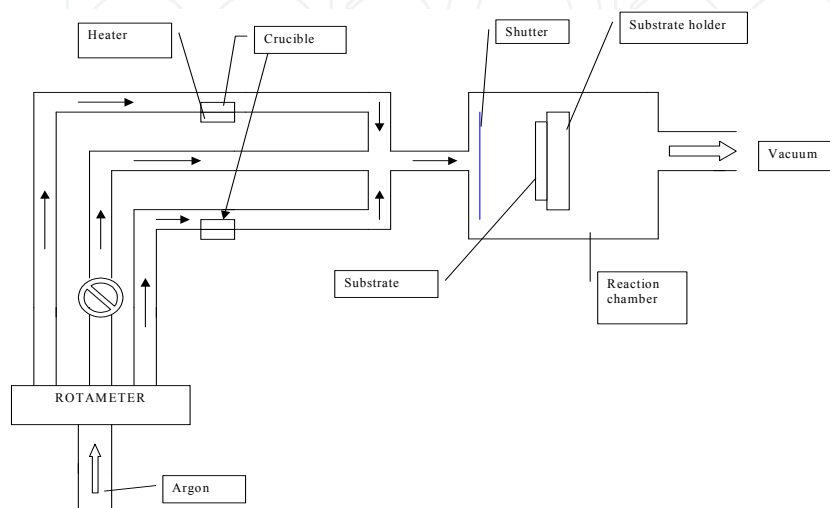


Fig. 4. Equipment for polycondensation made by chemical vapor deposition

In Fig. 5 one can see schematically drawn technological vertical setup for CVD deposition process. Essentially, this setup is similar to the precedent with the only difference that three streams were merged into one in the stream collimator, which after having passed the pupil is flowing upward towards the substrate mounted onto the rotary plate. This deposition setup allowed for five substrate to be mounted simultaneously, so that turning on the plate one can place subsequent substrate over the collimator pupile.

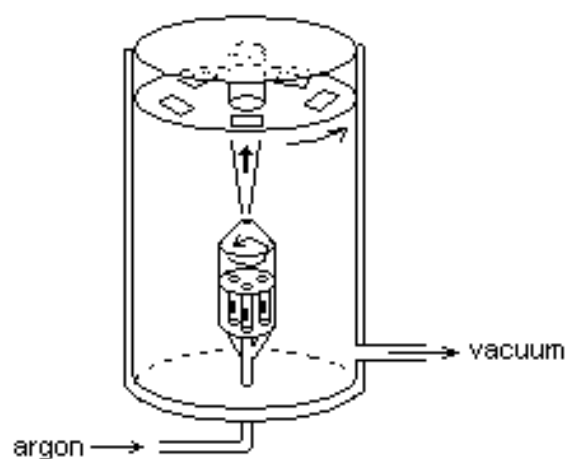


Fig. 5. Equipment for polycondensation by CVD in vertical geometry (Hajduk et.al, 2009)

Influence of technological parameters of the deposition process on PPI thin films prepared in vertical geometry has been discussed in (Hajduk et.al, 2009) and these conditions are collected in Tab. 2. Four series of PPI thin films were prepared each for five different flow rates with two minute deposition time. The series were distinguished by temperatures of terephthal aldehyde (T_{TPA}) and p-phenylene diamine (T_{PPDA}) the source materials applied (Hajduk et.al, 2009). There are also given pressures in the reaction chamber during deposition process with the relevant flow rates. These experiments have shown that there are some parallel behaviors of monomers dependently on the source temperatures as well as on their difference.

No	T_{TPA}/T_{DA}	Flow rate	Time t	Pressure
1(a,b,c,d,e)	50/50	0.05 (a)	2	$3,8 \cdot 10^{-2}$
2(a,b,c,d,e)	50/60	0.15(b)		$1,5 \cdot 10^{-1}$
3(a,b,c,d,e)	50/70	0.4 (c)		$2,5 \cdot 10^{-1}$
4(a,b,c,d,e)	50/80	1.0(d)		$3,6 \cdot 10^{-1}$
		3.0(e)		$7,6 \cdot 10^{-1}$

Table 2. Technical parameters of individual experiments (according to Hajduk et.al, 2009)

It was found that thin films, which were prepared under higher flow rates, were the thicker the higher flow rates were.

2b. Thermal vacuum evaporation

The thermal vacuum evaporation technique (Kubono & Okui,1994; Takahashi et al.,1991; Weaver & Bradley, 1996; Rohlfing & Bradley, 1998; McElvain et al., 1998) has been utilized to prepare thin films of more complex azomethines produced by polycondensation of TPA and fluorene diamine, benzidinediamine and fatt Brown 15R (Jarzabek et al.,2008). The technological conditions of the film deposition processes are collected in Tab. 3. It is seen there that they were prepared under vacuum of 2×10^{-5} Tr, while temperatures of diamines fluorine, benzidine and fatt Brown were of about 145, 160 and 165C, while TPA temperatures being 51, 59 and 48 C, respectively (Jarzabek et al.,2008). Thus, one can see that the temperature used to evaporate these complex diamines have appeared nearly twice as large as that of PPDA in CVD process (Weszka et al., 2008). Thin films of FPI, BPI and PNAPI were thermally evaporated under vacuum of 2×10^{-5} Tr onto quartz substrates. X-ray diffraction examination of as-prepared films have revealed amorphous character of polyazomethine thin films and their surface examination with atomic force microscope (AFM) indicate that the surfaces are homogenous, plane with rather small granularity, rather characteristic for polymer thin films, which is manifested by rather low value of root-mean square roughness (rms) $\sigma_{rms} \approx 3$ nm. Technological parameters of the examined polymer thin films, i.e. evaporation time, source temperatures and thicknesses of the as-prepared films are collected in Tab. 3. The as-prepared films are transparent and pale orange or pale yellow and their transmission is as high as 80 - 96%, while their reflectance is below 20% in the area of low absorption.

Layer	t (s) (± 1 s)	Amine T ($^{\circ}\text{C}$) ($\pm 2^{\circ}\text{C}$)	Aldehyde T ($^{\circ}\text{C}$) ($\pm 2^{\circ}\text{C}$)	d (nm) (± 20 nm)
FPI	300	145	51	100
PNAPI	300	160	59	90
BPI	300	165	48	220

Table 3. Technological parameters of polyazomethine thin films preparation (according to Jarzabek et al., 2008).

3. Kinetics of polyazomethine thin film growth

The process of PPI thin films preparation by CVD method via polycondensation of PPDA and TPA can be considered to consist of three essential stages. The first one is taking up molecules of the two monomers by argon streams flowing over boats filled with source PPDA and TPA monomers, respectively. Then, the two streams transporting monomers, and sometimes also the third of pure argon, merge together into one stream, which is associated with mixing up molecules of the complementary monomers and their transport towards the reaction chamber where the substrate is mounted. Finally, the third stage is consists of impinging the molecules onto the substrate, their adsorption at the substrate (Weszka et al., 2008). All the CVD process of the PPI film forming is thought to be due to polycondensation reactions running within the adsorption layer at the vapor/solid interface and resulting in the polymer chain progression (Kubono & Okui, 1994; Weszka et al., 2008). While monomers mixture being carried on by Ar stream towards the substrate, the polycondensation process should be postponed, which is equivalent to the positive Gibbs free energy ($\Delta G > 0$). In fact, being equal to about 50°C , the temperature of transported species has appeared sufficient for the reaction to be practically postponed as walls of the pipe transporting the reagent mixture remained clean. As switching between the reaction postponing (monomers transport) and reaction progression (film deposition) conditions is connected with the temperature decreasing from 50°C down to 25°C , one can expect rather low absolute values of ΔG at the two temperatures. Further, as the condensation polymerization runs easily the height of the reaction barrier equivalent to enthalpy of reaction (ΔH) is thought to be low. Thus, it is expected that the equilibrium constant of the polycondensation process is rather low (comparable to 1) and PPI film formation connected with the reaction progressing is maintained by removing released H_2O molecules from the reaction volume. Then, rather high rate of reaction should be attributed to high enough concentrations of PPDA and TPA molecules in the stream (Veinshtein et al., 1979; Pross, 1995), so that monomers molecules are rather near apart from one another making conditions favorable for sticking impinging molecules with complementary amine and aldehyde functional groups upon the substrate. The molecules that have not reacted and released H_2O molecules leave the substrate surface back to the vapor phase to be subsequently exhausted from the reaction chamber. It is thought that kinetics of polycondensation reaction driving PPI growth is some manifestation of the Flory rule (Flory, 1971) stating that reactivity of the end groups is independent of the chain length. Additionally, temperature T_{PPDA} being higher by 10°C or more than T_{TPA} assures nearly 1:1

ratio of the number of PPDA and TPA monomers molecules during the polycondensation process. This, together with high density of incident monomers adsorbed at the substrate surface, is expected to make reaction between aldehyde and amine end groups to run simultaneously at large number of centers. Then, a great number of oligomers being close to each other can be formed, so that interactions between fragments of PPI chain may result in stacking planarized segments of chains in the solid state. However, when the temperature difference is smaller than 10 °C or even $T_{PPDA} < T_{TPA}$, conditions become non-stoichiometric and excess monomers, escaping back to the vapor phase, perturb the polycondensation process. These results sometimes in nucleation running seemingly in the gaseous phase and such grown grains fall down onto the surface and are incorporated into a film growing on the surface. In the three-stream regime, the third Ar stream makes the reagent concentration diminish, so that unreacted excess molecules easily come back to the vapor phase without perplexing the polycondensation process. However, while the source temperature of monomer species is quite low, stacking of planarized PPI chains is expected not to be the case. It is thought that kinetics of PPI thin film growth on the substrate in the vertical setup is very similar to that in horizontal geometry. Moreover, it is expected that merging the streams in the collimator is running at the temperature sufficient to preserve film formation on the collimator wall, so that the deposition process is running on the substrate kept at room temperature just over the pupile.

4. Structure and morphology of polyazomethine thin films

Real structure of PPI thin films was examined by X-ray diffraction and X-ray diffraction patterns taken on thin films prepared under different conditions (samples *a-c* and *d-f* have been formed in the two stream- and three stream regimes, respectively) shown in Fig. 5.

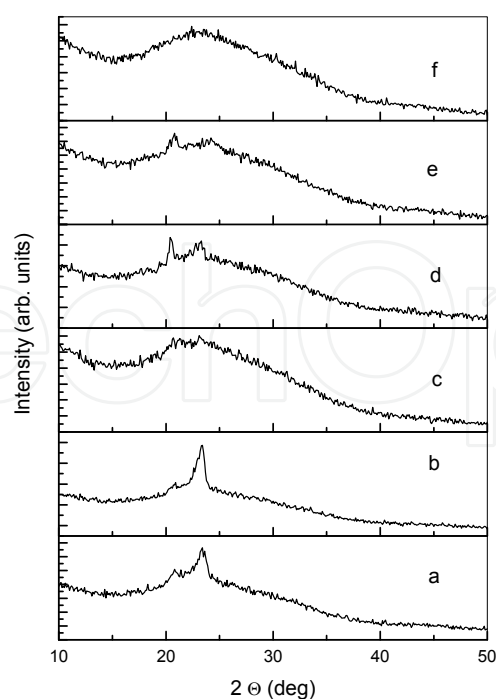


Fig. 6. X-ray diffraction patterns of PPI thin films CVD prepared in the horizontal geometry (according to Weszka et al., 2008).

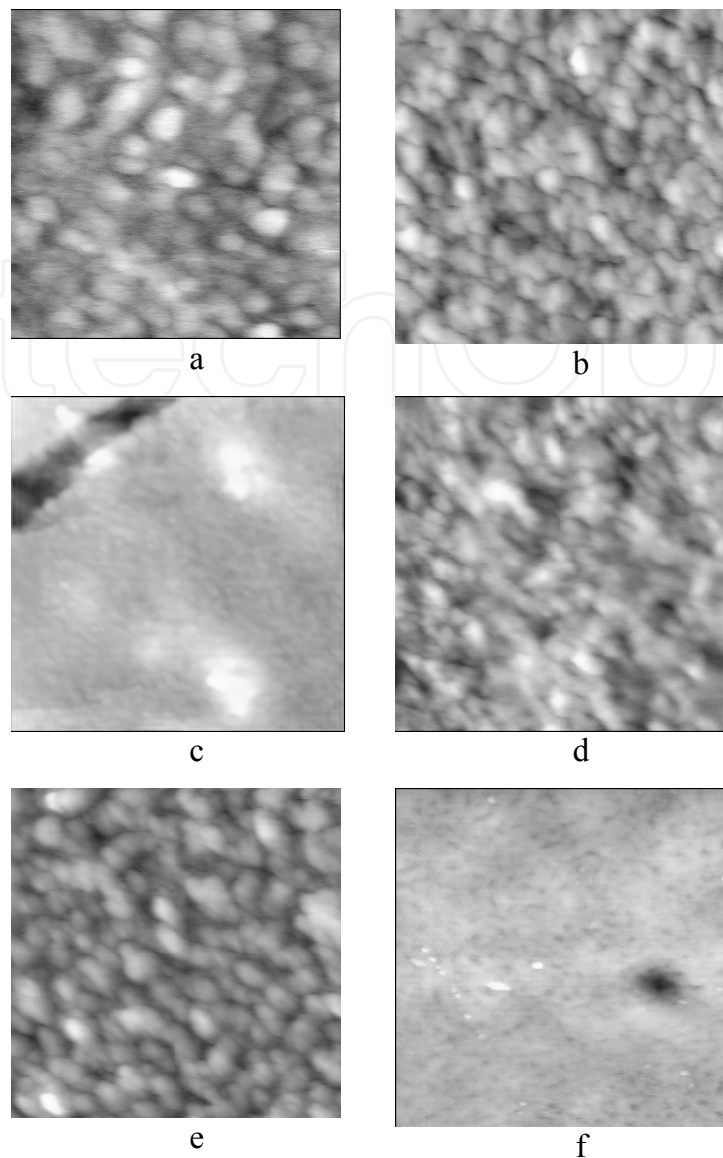


Fig. 7. Topographic AFM images of PPI thin films each in a scan area of $2.5 \mu\text{m} \times 2.5 \mu\text{m}$. The gray scales are 48, 76, 64, 64, 70 and 155 nm for (a), (b), (c), (d), (e) and (f), respectively (according to (Weszka et al., 2008))

(Weszka et al., 2008) reveal predominant amorphous structure with some manifestation of ordered areas, most pronounced in films *a* and *b*. Strength of the features related to ordered areas is seen to be higher while $d = 4 \text{ cm}$, independently on whether the two-stream- or three-stream regime is used. It is worth mentioning that the films prepared in the two-stream regime reveals essentially one dominant feature peaking at about 24° . In contrast, the films prepared in the three-stream regime revealed two features at about 21° and 24° , the former being more visible. The above mentioned variations of the recorded X-ray diffraction pattern may be related to the technological conditions given in Table 1. The peak locations correspond rather well to those at 20.56° and 23.86° observed for bulk PPI prepared from solution without, however, the third peak at 29.2° (Luzny et al., 1999), which is absent in the presented X-ray patterns. These angles are equivalent to the interplane distances between

consecutive atomic planes being equal to 0.434, 0.372 and 0.305 nm, respectively. 3D topographic images of surfaces of PPI samples *a-f* are shown in Fig. 7 and the data deduced from these images are presented in Table 2. It is clearly seen that essentially all the presented images reveal granular morphology with grains sizing 0.1 – 0.4 μm . However, the images taken on films *c* and *f* reveal larger grains randomly distributed on the film surface, larger even than 1 μm , with rms roughness attaining 32.5 nm. Some variations of the data given in Table 1 may be attributed to varying technological conditions. However, the large grains seen for films *c* and *f* are suggested to be amorphous rather than ordered ones in accordance with amorphous character of their X-ray diffraction patterns. Thus, there is a correspondence between the diffraction patterns of examined films shown in Fig. 6 and their AFM images from Fig. 7. The images shown in Fig. 8 were taken on PPI thin films prepared in the vertical setup under various stream flow rates in the vertical geometry shown in Fig. 4. These topographic AFM images reveal granular surface morphology, but in case of films deposited for $\Delta T=0^\circ\text{C}$ and 20°C one can see surface covered uniformly with grains of nearly the same size, while for $\Delta T=10^\circ\text{C}$ one can see larger grains distributed uniformly on the surface, while for $\Delta T=30^\circ\text{C}$ there rarely and randomly distributed large grains upon uniform film surface.

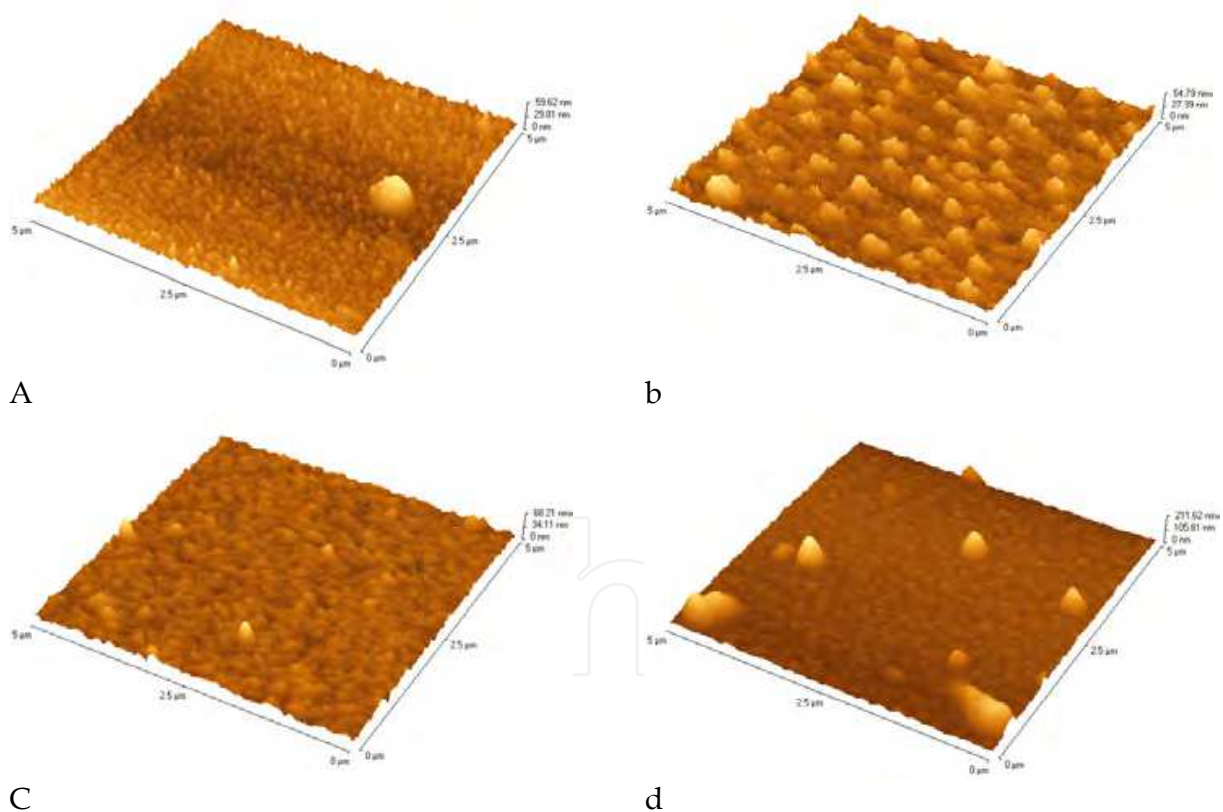


Fig. 8. AFM topographic images *a*, *b*, *c* and *d* taken on PPI thin films CVD deposited in vertical geometry with 3 Tr*1/s stream for ΔT equal to 0, 10, 20 and 30C, respectively (according to Hajduk et al., 2009).

5. Influence of technological conditions on optical spectra of polyazomethine thin films

PPI thin films

It is interesting to have a look at and to compare optical spectra taken on PPI thin films prepared via polycondensation in both horizontal and vertical geometry (Weszka et al., 2008; Hajduk et al., 2009) under various conditions. It has been mentioned in (Weszka et al., 2008)

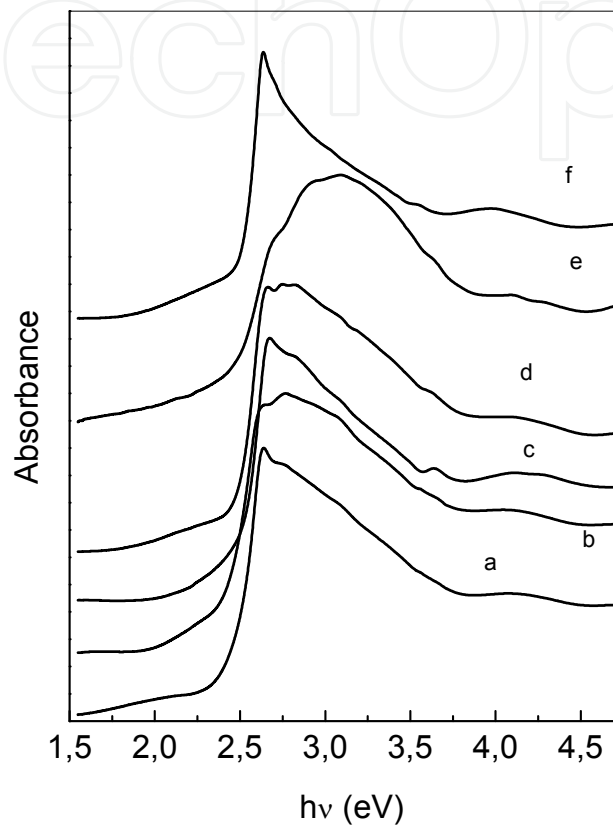


Fig. 9. Absorption spectra taken on PPI thin films prepared in horizontal geometry. Designation of the spectra coincide with film designation in Tab. 1 and Fig.6. (according to the data given in Weszka et al., 2008)

that source temperatures and the carrier agent flow rates have rather important impact on the shape of the spectra. In the case of the PPI thin films prepared in the horizontal geometry one could see that high flow rates resulted in films whose spectra reveal sharp feature superimposed onto low energy wing of the lowest energy vibronic band, which can be attributed to exciton of rather low binding energy, Wannier-Mott exciton. In case of PPI thin films prepared in the vertical geometry one can see that their thickness is growing with an increase in the flow rate of the transport agent and thin films prepared under the lowest flow rates are revealing shapes more round with less visible vibronic progressions. The latter one appears to be more pronounced in case of thin films deposited under larger flow rates. It is worth mentioning that temperature of the monomers and their difference have rather important impact on the shape of the recorded spectra UV-Vis. When temperature difference was as large as 30°C, an excitonic peak has appeared on low energy wing of the low energy band in the spectrum of PPI thin film prepared with the highest flow rate.

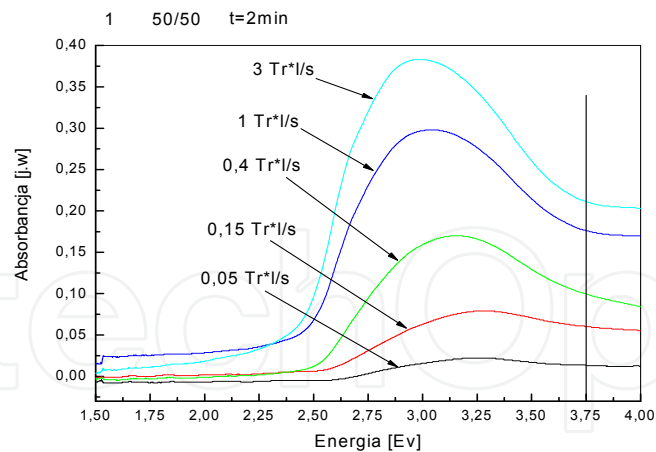


Fig. 10. Absorption spectra of PPI thin films prepared in the vertical geometry for T_{TPA}/T_{PPDA} 50°C/50°C with various flow rates (according to Hajduk et al.,2009)

Additionally, one can see that the strongest low energy band attributed to interband transitions linking delocalized states is observed at higher energy for films prepared at low flow rates in contrast to films prepared under higher temperature, which are distinctly moved towards lower energies. UV-Vis absorption spectra taken PPI thin films making part of the series prepared under conditions given in Tab.2. When comparing influence of carrier gas flow rates on optical spectra of PPI thin films, it seems that this influence has been more pronounced in the case of thin films deposited in horizontal geometry. It is thought that these effects should be linked with the rate of film growth rather than with flow rates only.

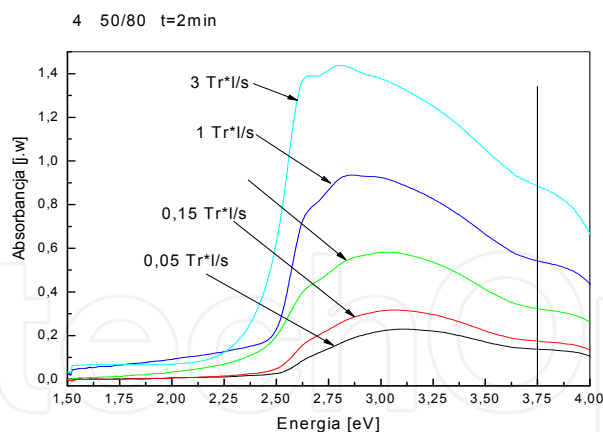


Fig. 11. Absorption spectra spectra of PPI thin films prepared in the vertical geometry for T_{TPA}/T_{PPDA} 50°C/80°C with various flow rates(according to Hajduk et al.,2009)

Polyazomethines prepared from different diamines

Absorption spectra of polyazomethines shown in Fig. 3, i.e. poly(1,4-phenylene-methylidynenitrilo-2,7,9H-fluorenenitrilomethylidyne) (FPI), poly(1,4-phenylene-methylidynenitrilo-1,1'-biphenylene-3,3',4'-phenylenemethylidyneimine) (BPI), and poly(1,4-phenylenemethylidynenitrilo-1,3-phenylene-(4-(1-naphtylenediazenneol-yl)-nitrilomethylidyne) (PNAPI), are illustrated in Fig. 12 (Jarzabek et al., 2008).

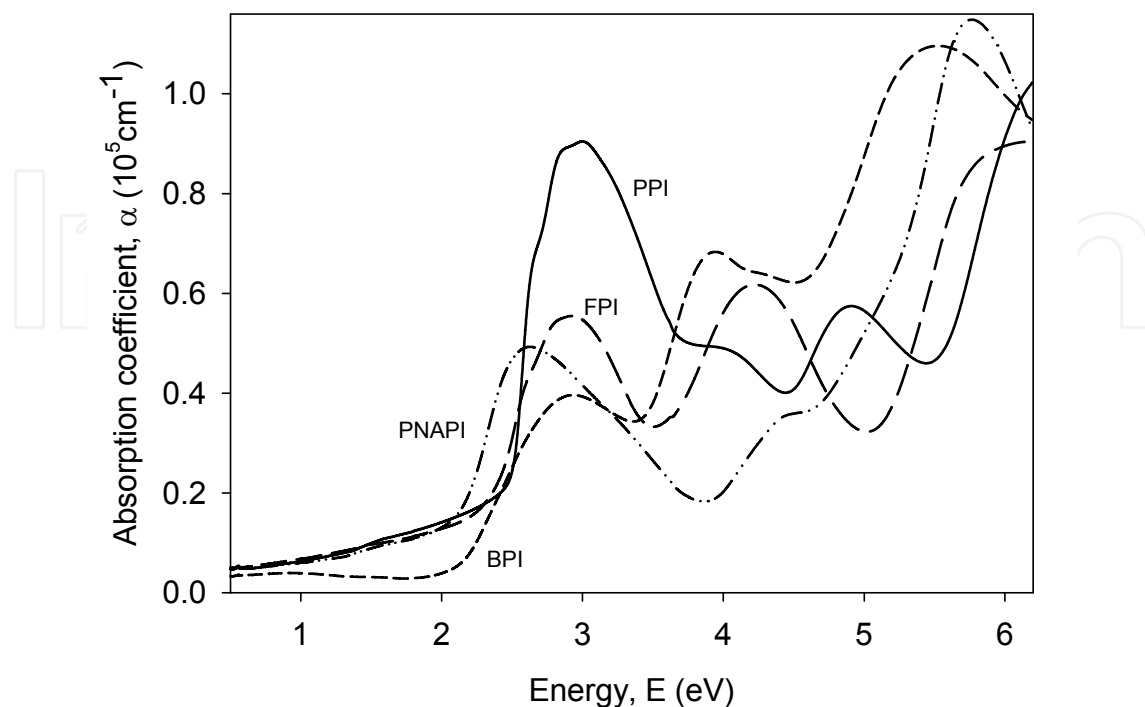


Fig. 12. Absorption in FPI, PNAPI and BPI referred to PPI thin films (according to Jarzabek et al., 2008)

How it is seen in this figure all the spectra essentially reveal similar structure like of PPI but absorption strength distribution appear to be different. The spectra taken on BPI and FPI thin films reveal features at energies close to those where bands are observed in PPI spectrum. The spectrum taken on polyazomethine PNAPI seems to be similar but its absorption distribution is thought to much different from that in the case of the two precedent films. These similarities and variations are seen to correspond rather well with conformations of their polymer chains. FPI and BPI have backbones built up of biphenylenes and phenylene ring in contrast to PPI whose backbone is built up of phenylene rings only. However, in the case of FPI biphenylene part is expected to be planar due to presence of bridging aliphatic carbon 9, while in benzidine such bridge is absent and additionally, BPI has additional two azomethine links due to benzidine diamine being one of monomers. PNAPI has quite large conjugated system because there are naphthalene rings and azomethine units are in meta position rather than para asd it is the case for all the three polyazomethiones. Taking into account large conjugated systems one can see that only in the case of PPI planarity is the largest, which is supported by high intensity of this band relatively to nearest bands in its spectrum. To some extent PNAPI show off something similar to PPI character, in contrast to the other two, whose band due to transitions between delocalized states has smaller absorption strength than the feature that can be attributed to Frenkel localize excitons connected to the gap linking delocalized and localized states and vice verse.

6. Doping PPI with iodine and FeCl₃

PPI thin films were doped with iodine and FeCl₃ in rather different ways. The iodine doping was realized by placing PPI thin films deposited within iodine atmosphere during various periods, several days included. After removing them from the iodine atmosphere they were left for some time to remove eventual I₂ molecules covering the film surface (Hajduk et al., 2007). Then, they were annealed at 250C. However, it was found that the absorption of doped film did not change very much whether the spectrum was taken on a film uncovered or annealed (Fig. 10). FeCl₃ doping was being carried out during deposition process in the vertical CVD equipment, when the third stream flew around a crucible with dried FeCl₃.

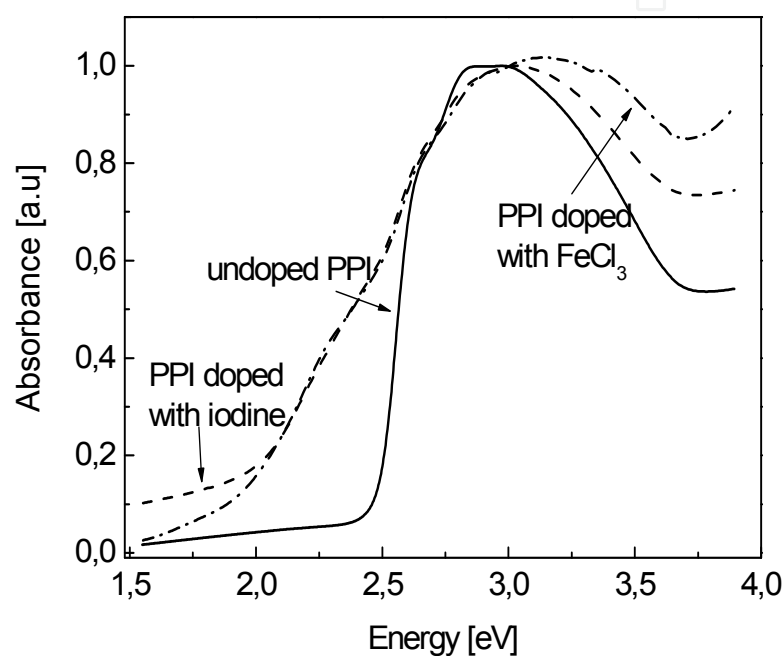
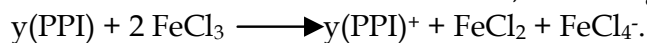


Fig. 13. Absorption spectra taken on thin films doped with iodine and FeCl₃ (according to the data in Hajduk et al., 2007a, and Hajduk et al., 2007b)

How it can be seen in this figure the two spectra reveal nearly the same behaviour, which is expressed by appearance some increase in the absorbance strength below 2.4 eV, below absorption edge of PPI. Additionally one can see some decrease in intensity of the strongest low energy band due to interband transitions connecting delocalised states and some maximum shift towards higher energies, from some 2.7 eV to 3.0 eV. Then one can see some increase in absorbance level at energies above 3.5 eV. Such behavior of the absorption spectrum is similar to optical spectra of PPV doped thin films (Wohlgenant, 2005). This can be attributed to polaron formation due to removing electron from PPI chain HOMO states, which is associated changing conjugation scheme along the chain from benzenoid into quinoid one. As a consequence two polaron states are formed within the HOMO - LUMO gap, the lower energy one resulting from PPI HOMO is occupied by one electron, while other one coupled with it coming from PPI LUMO being empty. Taking into account energy value indicating on some 0.6 eV shift with respect pristine PPI HOMO-LUMO gap, which

could be attributed to transition from polaron level to empty LUMO (LUMO+1) state or from new HOMO (HOMO-1) to empty polaron level. However, it would be in contradiction with reported selection rules for transitions in doped polymers. Then, the shift of absorption band intensity on some 0.4 eV may suggest that the number of available HOMO and LUMO states is diminished due to doping and chain transformation into benzenoide modification whose size is dependent on electrostatic interactions between hole and electron residing on the extreme atom of the quionoid form. Additionally, interband transitions linking HOMO LUMO states are pushed to slightly higher energies. This is also some confirmation of rather distinct resemblance of π electron systems of PPI and PPV, moreover it indicates that doping mechanism in this polymer is connected with withdrawing electrons from the π electron system of PPI. Withdrawing π electrons is associated with electron transfer on iodine so that I_3^- counterions are formed. On the other hand, $FeCl_3$ doping mechanism is thought to be connected with Fe^{+3} reduction to Fe^{+2} , according to the chemical reaction



That means Cl^- play the role of counterion in such doping.

7. Variation of electronic structure with polyazomethine structure

In the precedent sections it has been shown how electronic structure of aromatic polyazomethines is related with monomers used in polycondensation process of thin films deposition. There were used molecules having quite large conjugated systems, so that their π electron systems have appeared to be quite developed. This is expected to give an account of their optical spectra whose structure resembles that of PPI, but the strength of absorption due to electronic states connecting their HOMO and LUMO levels is much lower compared to PPI, which might be attributed to rather bad conjugation. However, the precedent section proved that electronic structure of polyazomethine thin films can be modified by means of doping, chemical doping, while the spectra shown in Fig. 11 (Hajduk et al., 2007) were taken on thin film that could be seen as derivative of PPI, which were prepared by polycondensation of larger dialdehyde having oxygen atom to link neighbor phenylene rings.

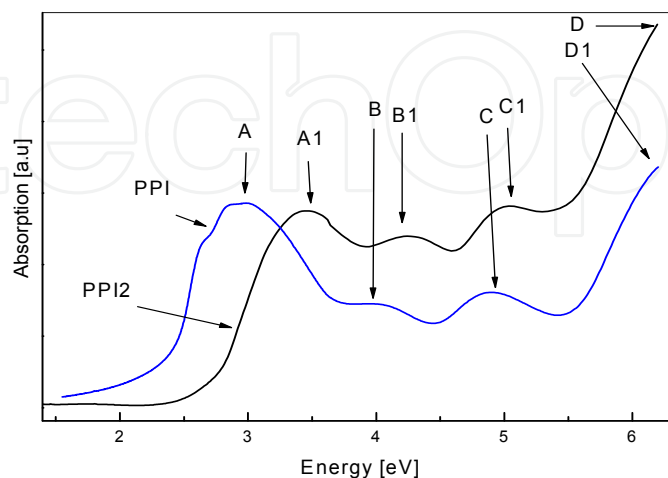


Fig. 14. Comparison of optical spectra taken on polyazomethine thin film having oxygen atoms in the backbone and that of pristine PPI

Thus, one can see that the backbone of PPI2 can be seen as modified by incorporating oxygen atoms. The spectra shown in Fig. 11.

8. Conclusions

Polyazomethine thin films can be prepared by chemical vapor deposition and thermal vacuum evaporation. It has been shown that structure, morphology and optical spectra of polyazomethine thin films are dependent on technological conditions they were deposited. Their optical spectra reveal features resembling optical spectra of polyparaphenylene vinylene. It is expected that low transport rate of monomers to the substrate independently of the setup used are favorable for small growth rates and optical spectra reveal features being resultant of distribution length of conjugated fragment in various chains within the whole thin film volume. High flow rates of transport agent have appeared favorable for excitonic feature of Wannier-Mott type to overlap low energy side of the absorption band due to transitions linking delocalized states. This could be attributed to geminate pairs or to stronger overlap of molecular orbitals of more planarized chains to form larger ordered areas where conjugation is not limited to conjugated fragments of individual chains but to some areas of thin film comprising several chains. On the other hand, one can see that polyazomethine spectra can be modified by using various more or less complex diamines aromatic with terephthal aldehyde. These spectra resemble those of PPV but one may expect that rather low intensity of low energy band due to interband transitions connecting delocalized states due to lower degree of planarity, which to some extent recompense by relatively large π -electron system within such polymer monomer. Then, doping PPI thin films have exhibited features characteristic of PPV, which support similar polaron mechanisms driving doping PPI and PPV. This has appeared to go within this picture whether PPI thin films were iodine doped by diffusion in the iodine vapor or with the use of FeCl_3 in the process of thin film deposition. Additionally, it has been proved that incorporation of oxygen atoms into PPI chain, which result in dividing its conjugated fragments into quite short ones bringing about an increase in absorption gap but other features resemble those of PPI. The scope of this chapter has not allowed for electronic structure and atom dynamics of polyazomethine thin films to be discussed in details.

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This book provides a timely overview of a current state of knowledge of the use of polymer thin film for important technological applications. Polymer thin film book covers the scientific principles and technologies that are necessary to implement the use of polymer electronic device. A wide-ranging and definitive coverage of this emerging field is provided for both academic and practicing scientists. The book is intended to enable readers with a specific background, e.g. polymer nanotechnology, to become acquainted with other specialist aspects of this multidisciplinary field. Part A of the book covers the fundamental of the key aspect related to the development and improvement of polymer thin film technology and part B covers more advanced aspects of the technology are dealt with nano-polymer layer which provide an up-to-date survey of current research directions in the area of polymer thin film and its application skills.

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