

3. Structure and morphology of polyazomethine thin films

Generally, it is expected that polymer thin films are amorphous in character because they constitute entities of interpenetrating, entangled or curled polymer chains, which are not stretched ones but instead they form entity of folded back on themselves chains. However, one must remember that polymer chains do constitute ordered entities not in the sense of atom ordering in inorganic crystals, but they are ordered because their backbone makes out entity being a sequence of the same repeating units, whose conformation is resultant of interactions among atoms attached to the backbone atoms (repulsion of hydrogen atoms attached to the neighbor atoms). This polymer chain periodicity has its impact observed in their optical spectra and their optoelectronic properties, some contribution from accidentally ordered areas. Polyazomethine are aromatic polymers whose backbones are composed of sp^2 hybridized carbon and nitrogen atoms, but eventual planarity of the backbone conformation is disturbed by concurrence of steric hindrance of hydrogen atoms combined with coupling effect acting between nitrogen lone pair orbital on nitrogen atom and the nearest phenylene π system. While considering relations connecting technological conditions under which PPI thin films were deposited and their optical properties, it seems to be worth looking through all the spectra, AFM images illustrating their morphology and X-ray diffraction patterns revealing their structure. In horizontal arrangement of CVD set-up [22], all PPI thin films considered with exception of the one, which was prepared at the same source temperatures of monomers, were prepared from under such conditions that terephthal aldehyde temperature (T_{TPA}) was lower about 10K than the PPDA temperature (T_{PPDA}) and then deposited films have had nearly the same thickness of about 200 nm. At the same time, the PPI film prepared when $T_{TPA} = T_{PPDA}$ had a thickness of about 50 nm. How it is clearly seen in Figure 6 the film (a) revealed ordered structure with well defined peak at about 23.5 deg and a weaker one at about 20.95 deg. Generally all the diffraction patterns taken on those PPI thin films revealed broad amorphous background with the maximum at about 25 deg in the vicinity of the strongest peak. Morphology of the as-prepared thin films, illustrated in Figure 7 is seen to be granular with visible overlapping grains or even columns, so that something resembling ribbons or hill chains of versatile shape and twisting on running along with some random directions. The topographic image reveals nearly homogeneous film surface within 5 μm x 5 μm square with roughness heights ranging 32.23-64.45 nm.

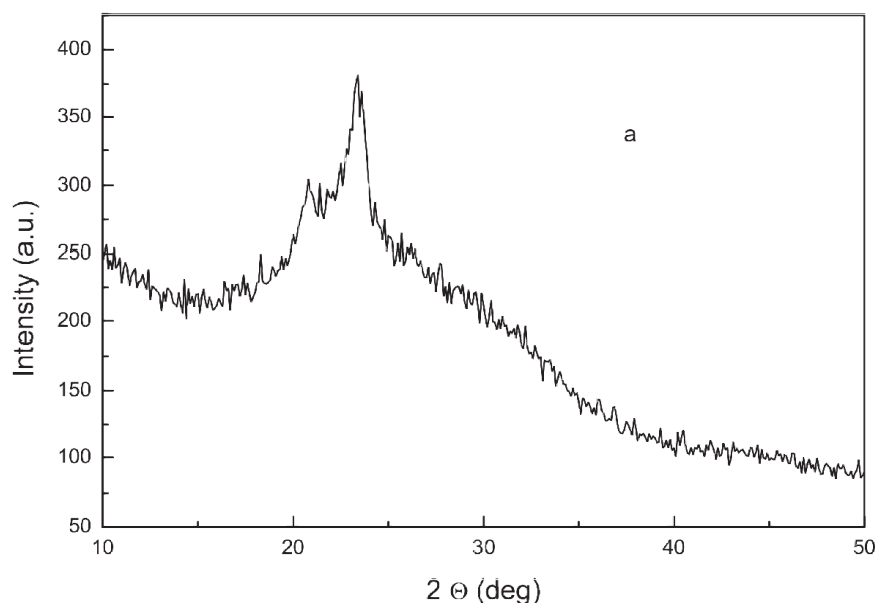


Figure 6. Diffraction pattern taken on (a) PPI thin films

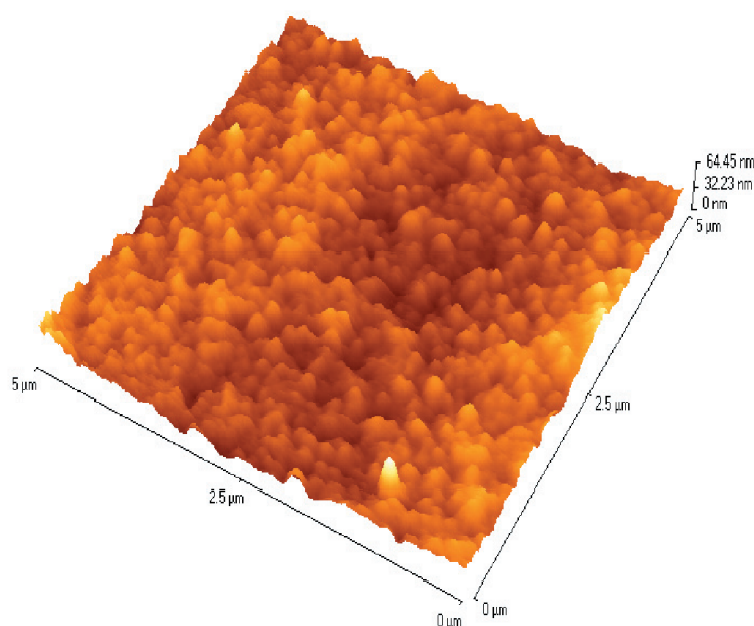


Figure 7. Topographic image of PPI thin film (a)

This surface morphology seems to correspond rather well with the absorption spectrum covering 1.5-4.5 eV UV-Vis area, which is seen to reveal “triangular shape” with distinctly visible small exciton related peak at about 2.58 eV, while the feature peaking at about 4.0 eV is observed in all the spectra at the same location, Figure 8. The peak distinctly seen at low energy part of the spectrum has been attributed to Wannier –Mott exciton, which is seen to go rather well with ordered if not to say due to some sort of crystalline character of this film.

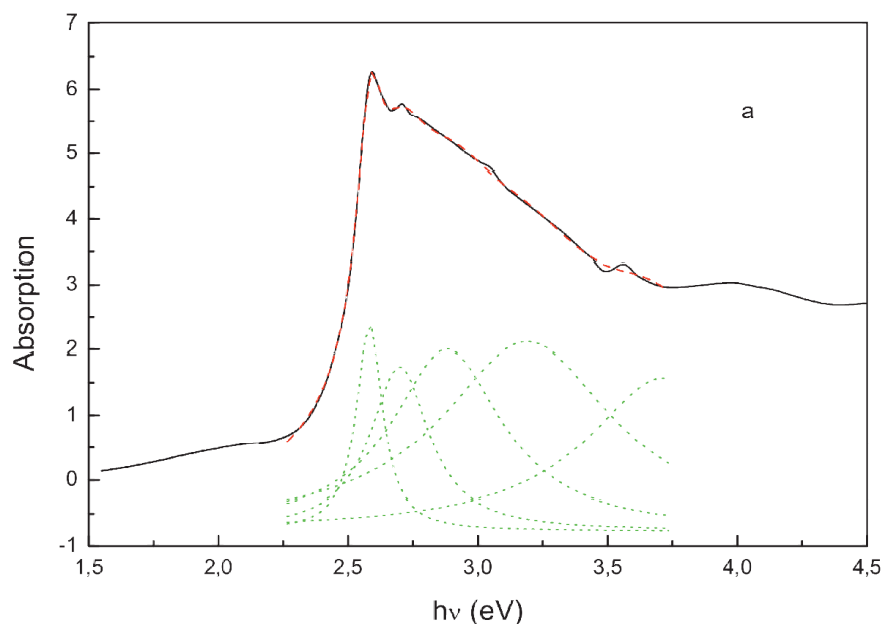


Figure 8. Absorption spectrum of (a) PPI thin film

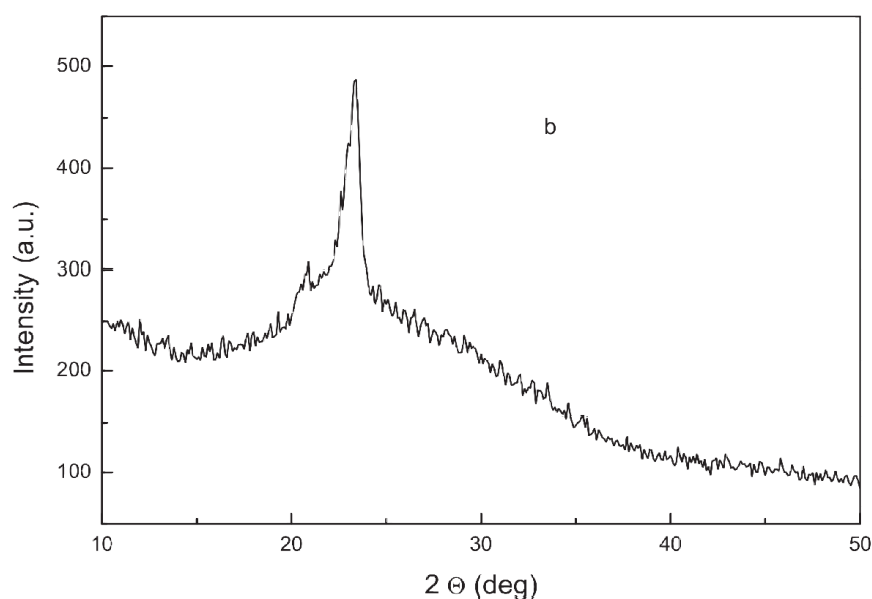


Figure 9. X-ray diffraction pattern of (b) PPI thin film

According to data given in Table 1, PPI thin film designated as (b) film was prepared under nearly the same conditions as the precedent one, but the substrate was moved 1cm nearer the stream inlet into the reaction chamber with respect to the distance while preparing (a) film. However, comparison of x-ray diffraction patterns taken on films (a) and (b), Figures. 6 and 9, is leading to conclusion that probably film designated (b) is more ordered or even more crystalline in character than film (a), because the peak at about 23.4 deg is much more intense and slightly narrower than the peak of (a) film, so that it can be expected that ordered areas

in film (b) have been larger in size than this is the case for (a) film. As it can be seen in Figure 10, at first sight morphology of (b) film seems to be nearly the same as that of (a) film, nevertheless the granules or columns are seen to overlap and form something that resemble bands or ribbons. However, absorption spectrum recorded on a film (b) (Figure 11) is seen to be slightly different from that of (a) film, missing Wannier-Mott exciton related peak in particular.

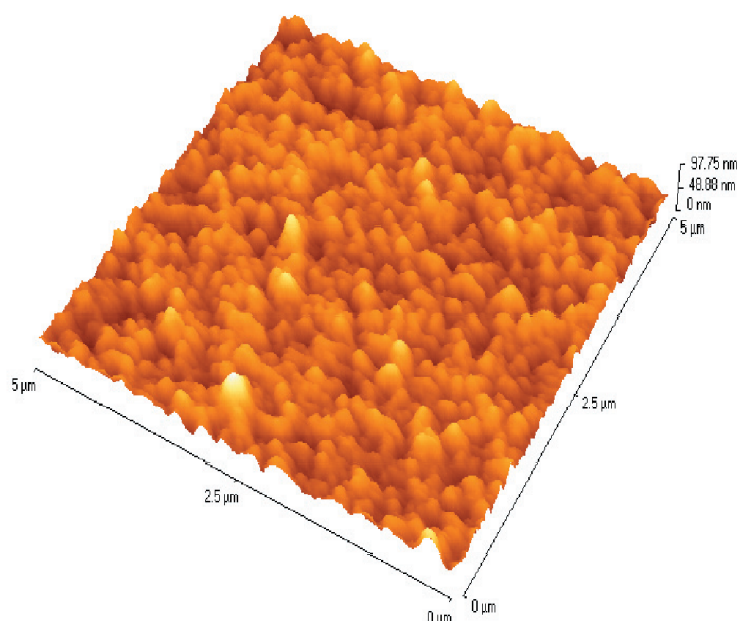


Figure 10. Topographic image of PPI thin film (b)

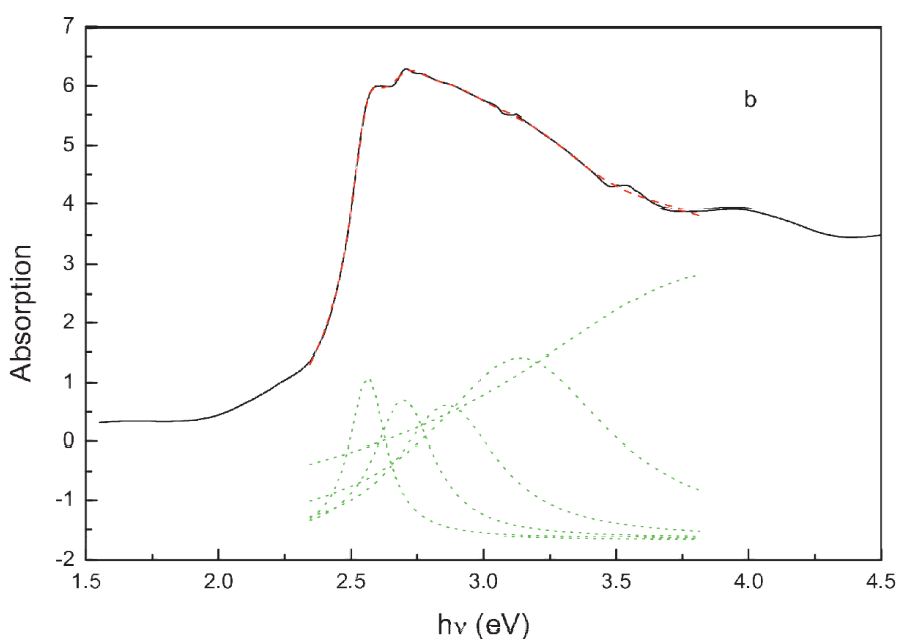


Figure 11. Absorption spectrum of (b) PPI thin film

The AFM image of the surface morphology of (c) film, shown in Figure 12, indicates the surface being more plane than the surfaces of two former films, though much higher hills are observed. One can notice that probably columnar growth is seen here as bands of overlapping columns running randomly, but the shape of its X-ray diffraction pattern, given in Figure 13, indicates towards rather amorphous character of (c) film morphology with a very fable feature at about 23,8 deg.

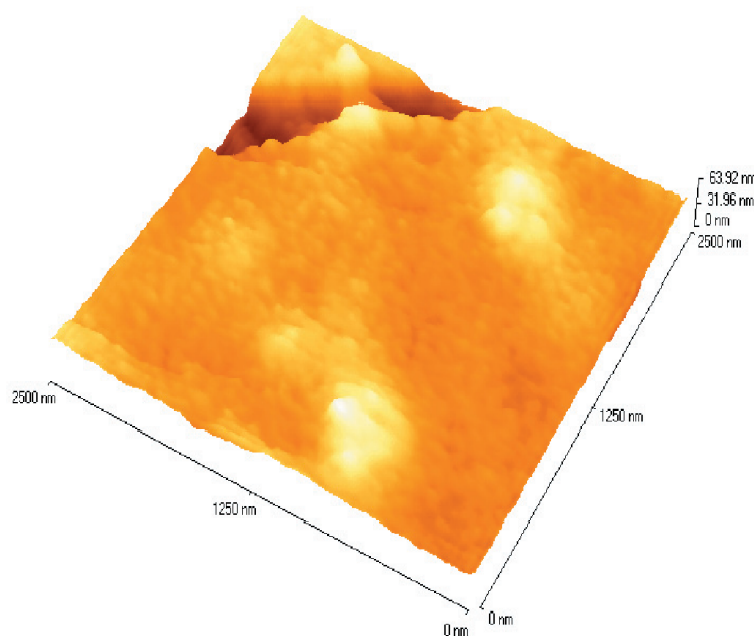


Figure 12. Topographic image of PPI thin film (c)

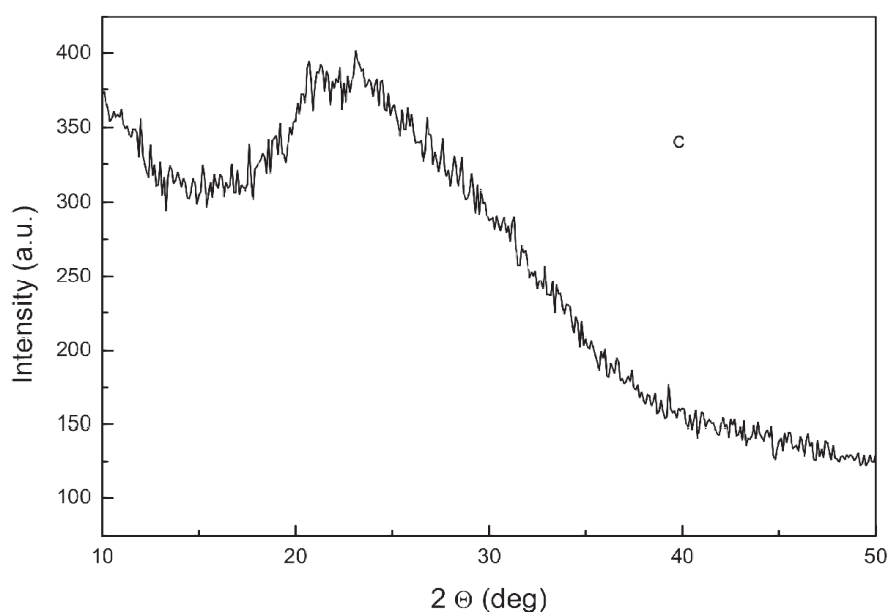


Figure 13. Diffraction pattern of (c) film

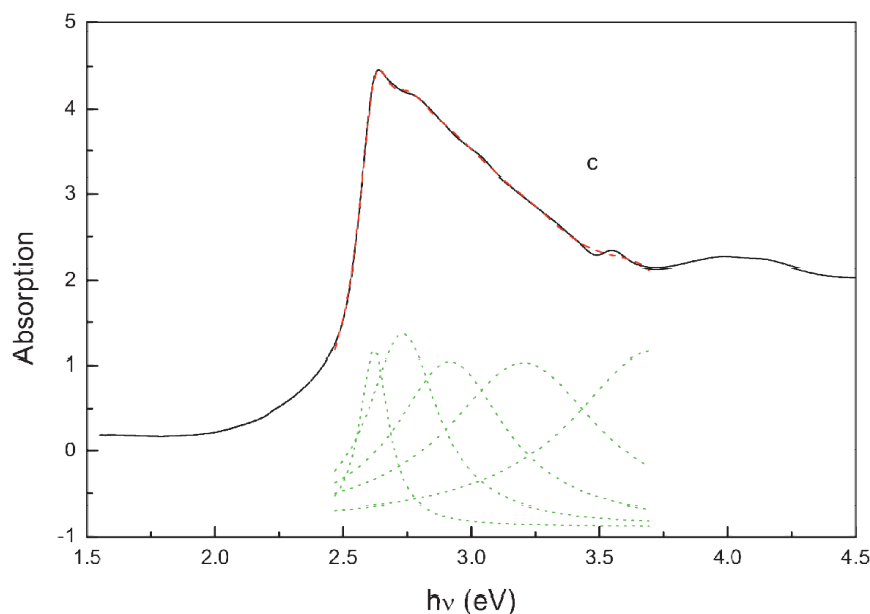


Figure 14. Absorption spectrum of (b) PPI thin film, Accord. [22]

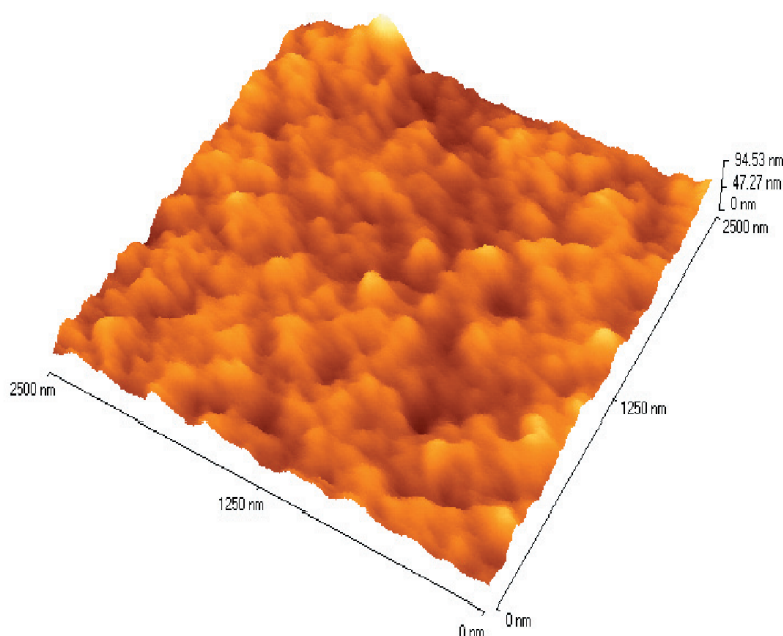


Figure 15. Topographic image of PPI thin film (d). Accord. [22]

It is worth mentioning that under nearly the same conditions of a film deposition, an increase in the distance of the substrate from the stream inlet into the reaction chamber certain structural ordering is the case, though not so well visible in the absorption spectrum (Figure 14). On the other hand, comparing films (a) and (c) one can see that nearly double increase in the stream intensity resulted in more disordered film (c) than it was the case for (a) film. While comparing films (a) and (d) which were deposited under the same conditions (temperature, stream intensity, substrate distance

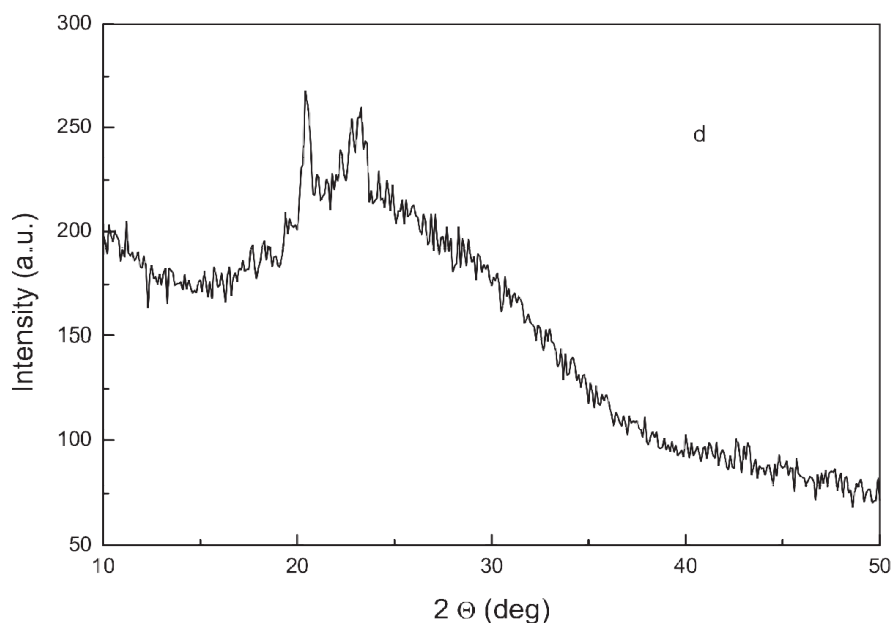


Figure 16. Diffraction pattern of (d) film. Accord. [22]

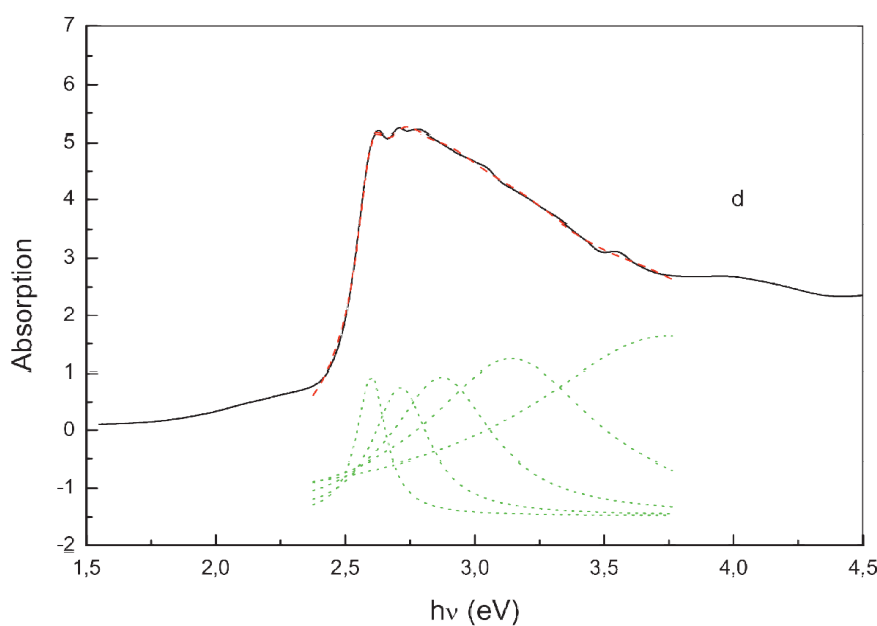


Figure 17. Absorption spectrum of (d) film. Accord. [22]

from the gas inlet), but the latter was prepared with the use of three stream and it is easily visible that its ordering is a little worse than in (a) film, but simultaneously it is slightly different than in a film (a), (b) and (c), because more defined peak is the one at 20.95 deg. One can see in Figure 15 that AFM image taken from the surface of (d) film shows off that overlapped columns form chain band or ribbons, which may be attributed to some representation of structural order in this film.

At the same time, while looking at AFM image taken on (e) film (Figure 18), it is clearly seen that columns or grains do not overlap with one another to form bands running randomly throughout the surface. This seems to find some supporting confirmation from diffraction pattern and absorption spectrum taken at film (d) and (e), as it is seen in Figures. 16 and 17 and Figures. 19 and 20, respectively. The absorption spectrum of film (e) shown in Figure 20 reveal vibronic character of low energy band related to optical interband transitions linking

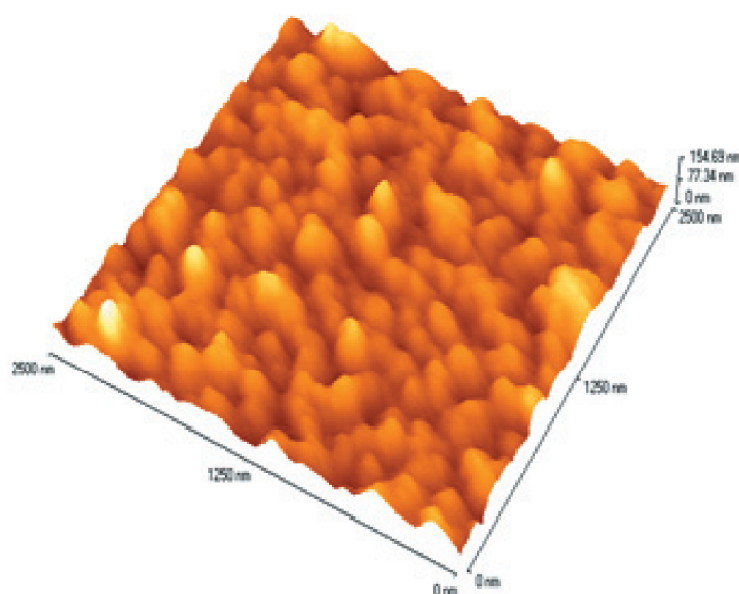


Figure 18. Topographic image of PPI thin film (e)

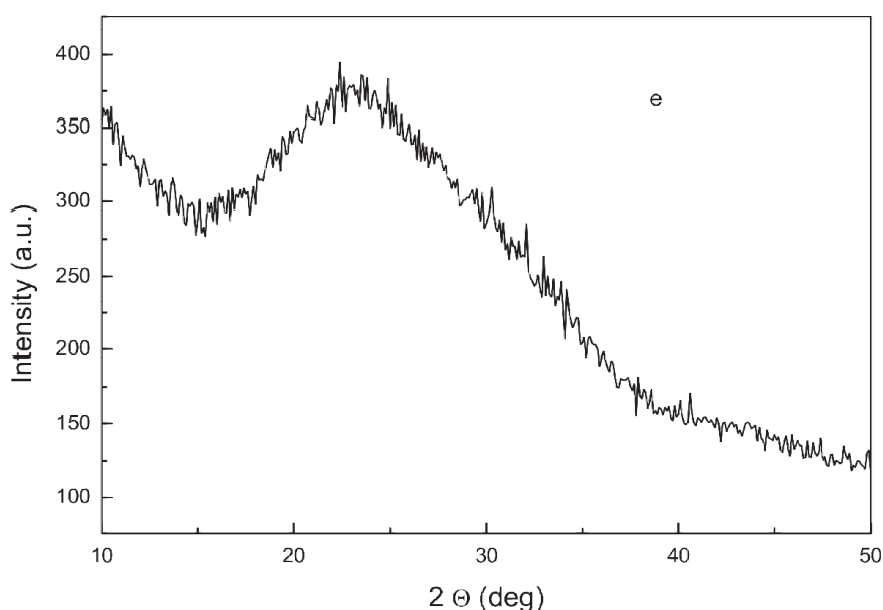


Figure 19. Diffraction pattern of (e) film

delocalized states [22]. The shape of this band is thought to point out towards conclusion that this film is constituted by PPI chains loosely connected together by means of weak van der Waals forces, so that there is quite distinct discard in potential energy minima of the electronic ground and excited states. In contrast, film (f) being the thinnest one of all the as-prepared films under that study reveals rather ordered character of its structure, which can be supported by AFM image given in Figure 21 as well as by X-ray diffraction pattern, shown in Figure 22,

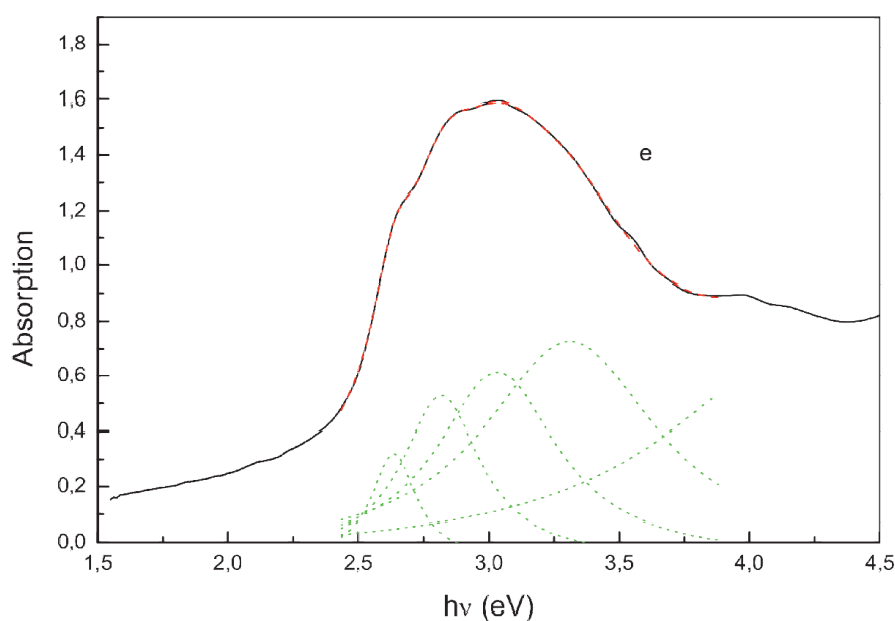


Figure 20. Absorption spectrum of (e) film

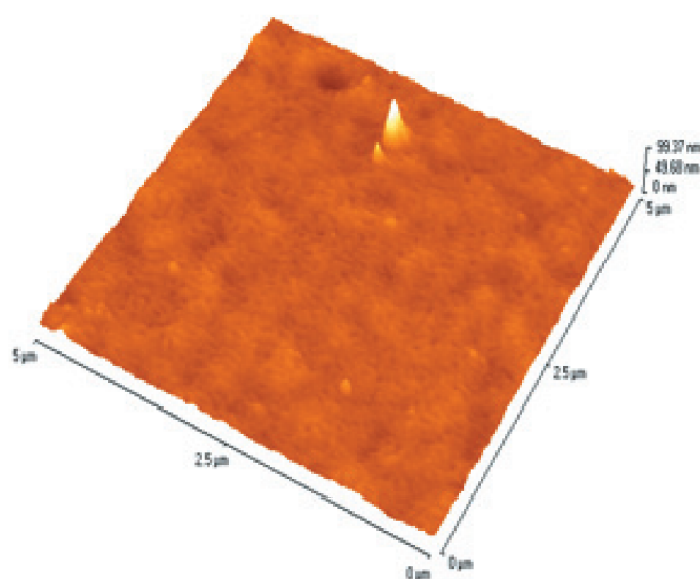


Figure 21. Topographic image of PPI thin film (f)

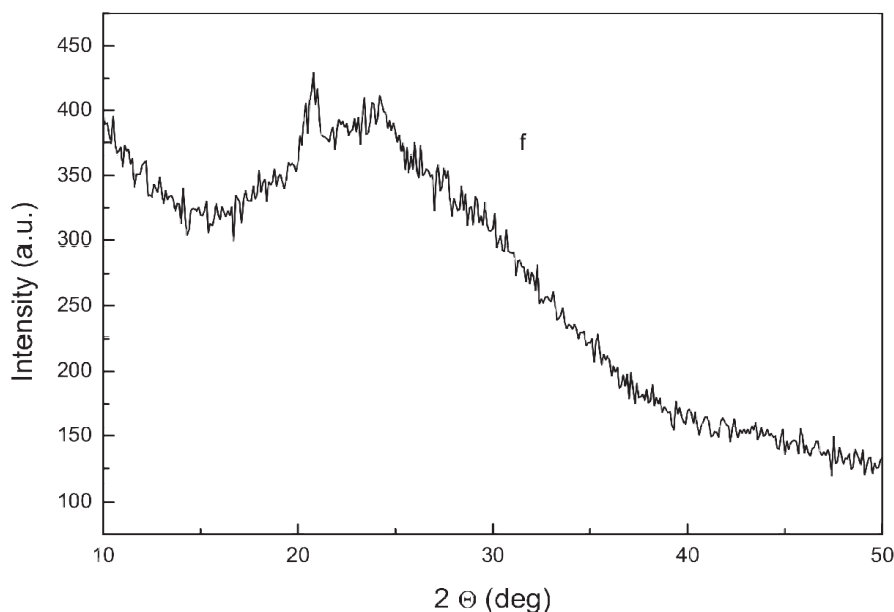


Figure 22. Diffraction pattern of (f) film

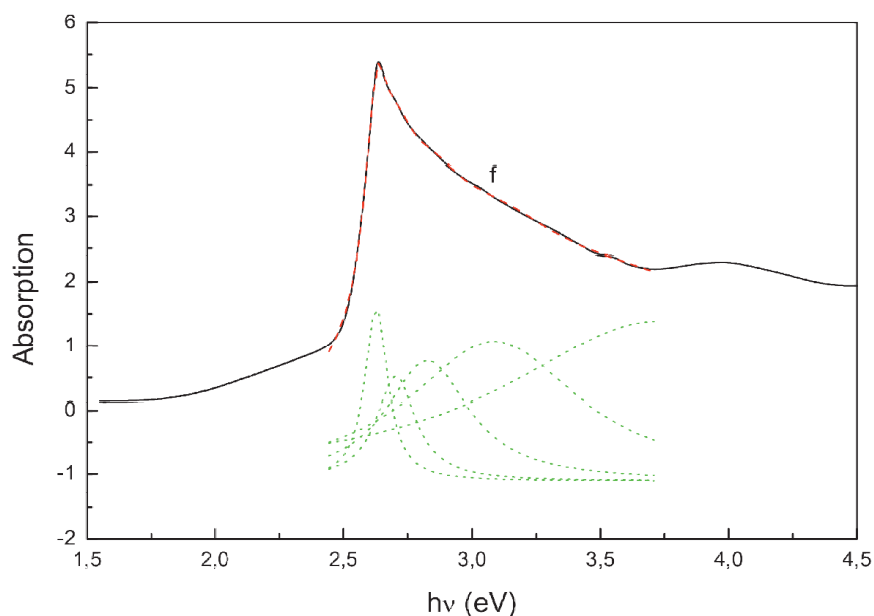


Figure 23. Absorption spectrum of (f) film

and absorption spectrum (Figure 23) in particular. AFM image reveals rather plane and smooth surface of this film, with visible bands of overlapping growth columns running throughout the film surface, while X-ray diffraction pattern reveals distinct feature superpose onto amorphous background but peaking at about 20.93 deg. It is worth mentioning that diffraction patterns of these film reveal broad amorphous background whose maximum is situated in each case more or less at the same diffraction angle. However, the absorption spectrum recorded on this film

Table 4. Results of the fitting procedure for film e

Energy (eV)	Half width (eV)	Area
2.640 ± 0.001	0.200 ± 0.002	0.120 ± 0.004
2.820 ± 0.002	0.370 ± 0.017	0.34 ± 0.05
3.030 ± 0.006	0.56 ± 0.06	0.6 ± 0.2
3.31 ± 0.02	0.81 ± 0.08	1.0 ± 0.3
4.2 ± 0.2	1.3 ± 0.5	1.5 ± 1.1

reveal the best pronounced peak attributed to Wannier-Mott exciton, rather than to vibronic feature. The two features are due to different effects, as Wannier-Mott exciton comes from interaction of excited electron and hole created behind in delocalized valence band, while vibronic features are results of electronic transition borrowing its intensity from vibrational modes [24,25,28].

3.1. PPI thin films deposited in the vertical set-up

Thin films of polyazomethines which were deposited by CVD method with argon gaseous being transport agent with the use of vertical setup have appeared to reveal similar relation between their morphology and optical spectra. How it is seen in these spectra films prepared under the highest intensities of transport agent streams have revealed surface with columnar growth where overlapping of columns or granules are observed and such bands are running along with the surface in random directions. However, such films revealed absorption spectra with visible signs of exciton formation, so that one may expect that such bands means there is order and some sort of stacking in those lamellae. Surface morphology of a PPI film prepared under lowest stream for $\Delta T = 30\text{K}$, shown in Figure 24, is seen to be nearly homogenous with several randomly distributed grains with higher height and the other of comparable height and essentially visible as separate though densely distributed. At the same time, the surface morphology of the film prepared under the highest intensity of the stream, illustrated in Figure 25, reveals as rather plane with several randomly distributed larger grains, but it is seen less rough than the film prepared under the smallest intensity of the stream. Being the more plane with roughness nearly two times smaller than the former, grains are seen to overlap giving quite plane surface. One can see that there is some correspondence between film surface morphology and optical spectra in UV-Vis range. It is clearly seen in these spectra that film

deposited with the lowest intensity of the stream (Figure 26) with slightly visible indications of vibronic character of interband transitions with maximum at about 3.0 eV, while in case of the other film (Figure 27) the band is displaced towards lower energies with rather fable peak attributed to Wannier-Mott exciton and maximum of the band at about 2.8 eV.

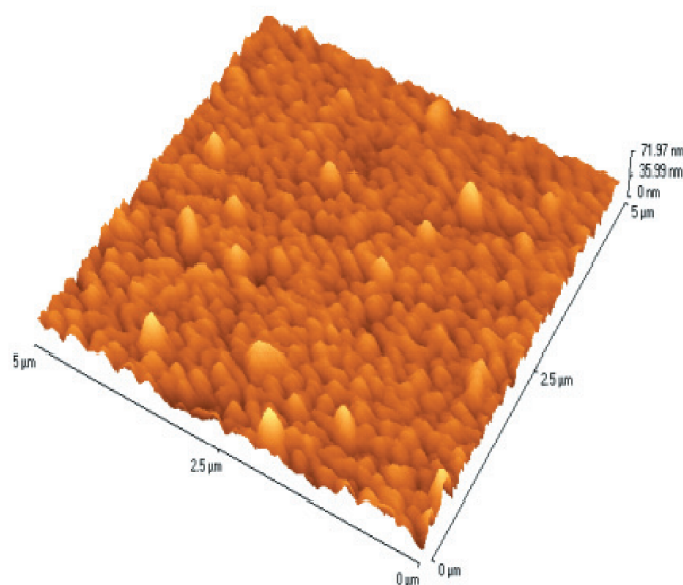


Figure 24. Topographic image of PPI thin film deposited with stream intensity $I=19.99 \text{ Pa dm}^3/\text{s}$
 $T_{TPA} = 333.15 \text{ K}$, $T_{PPDA} = 363.15 \text{ K}$

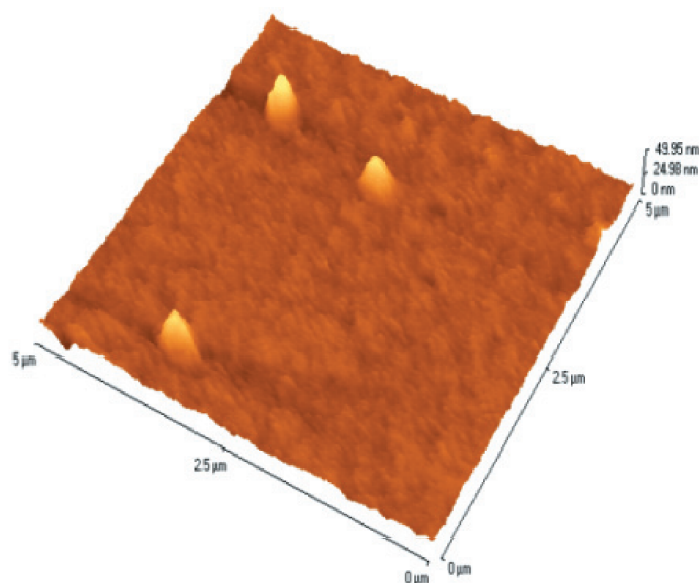


Figure 25. Topographic image of PPI thin film deposited with stream intensity $I=399.97 \text{ Pa dm}^3/\text{s}$
 $T_{TPA} = 333.15 \text{ K}$, $T_{PPDA} = 363.15 \text{ K}$

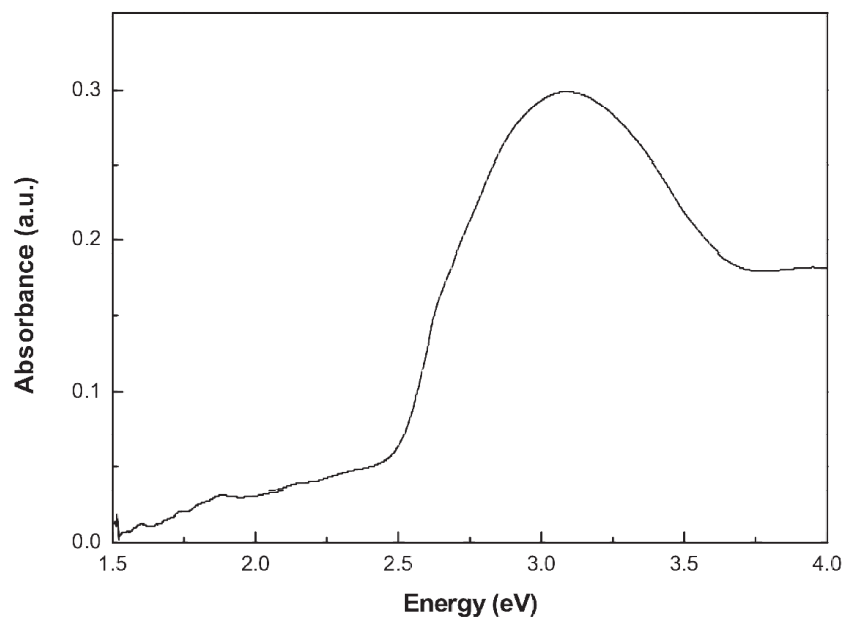


Figure 26. Stream intensity 6.66 ($\text{Pa dm}^3/\text{s}$), temperatures: $T_{TPA} = 333.15 \text{ K}$, $T_{PPDA} = 363.15 \text{ K}$

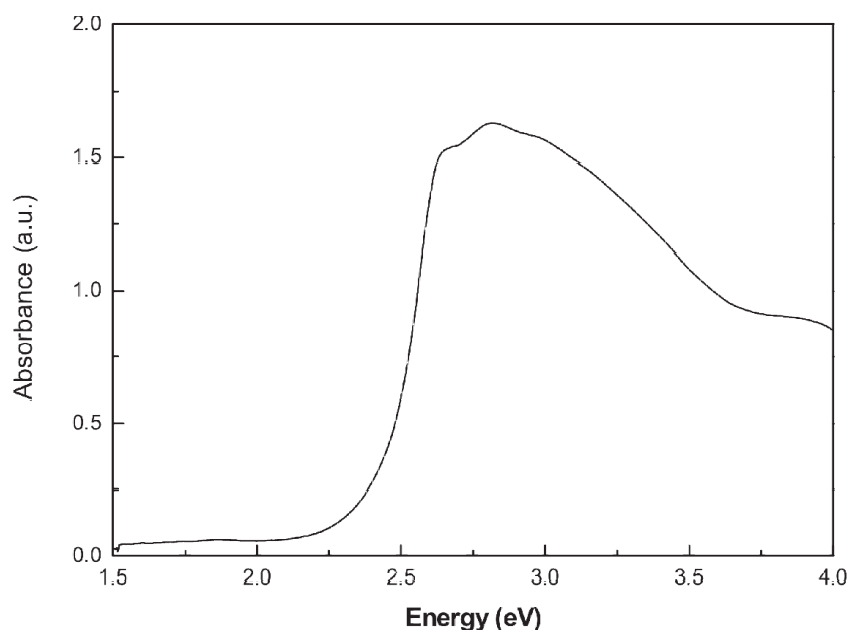


Figure 27. Stream intensity 399.97 ($\text{Pa dm}^3/\text{s}$), temperatures: $T_{TPA} = 333.15 \text{ K}$, $T_{PPDA} = 363.15 \text{ K}$

This difference in maxima position is indication of variations of positions of potential energy minima of electronic ground and excited states. In Figure 28 there is shown topographic image of morphology of CVD prepared PPI thin film which reveal rather rough surface with visible grains of about 200 nm in size, while in Figure 29 one can see topographic image of this film after doping with iodine vapors. This iodine doped film reveals smoother surface with quite

distinctly observed overlap of grains in form of ribbons of random length and randomly oriented. This picture is thought to rather well correspond with X-ray diffraction patterns taken on PPI thin films pristine and doped where one can see that doped film became more ordered one, with quite distinct increase in intensity of 25 deg peak (Figure 30). Then, one may expect that doping PPI thin film with iodine leads to ordering this film in such a way that feature at about 24.5deg became stronger, so that ordered areas related with this orientation became larger after doping.

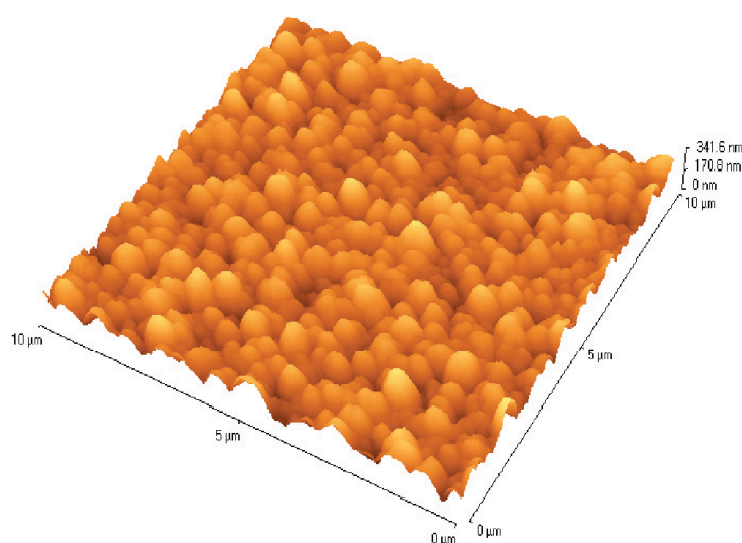


Figure 28. Topographic image of surface of CVD prepared PPI thin film

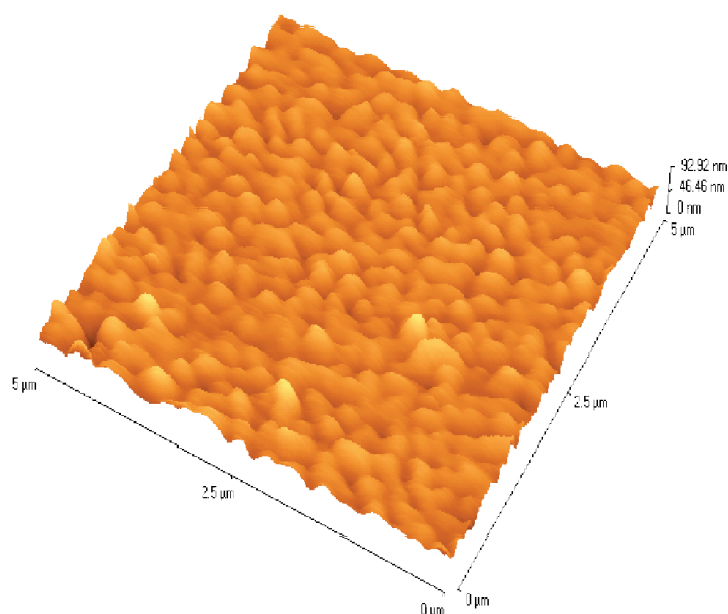


Figure 29. Topographic image of surface of CVD prepared iodine doped PPI thin film

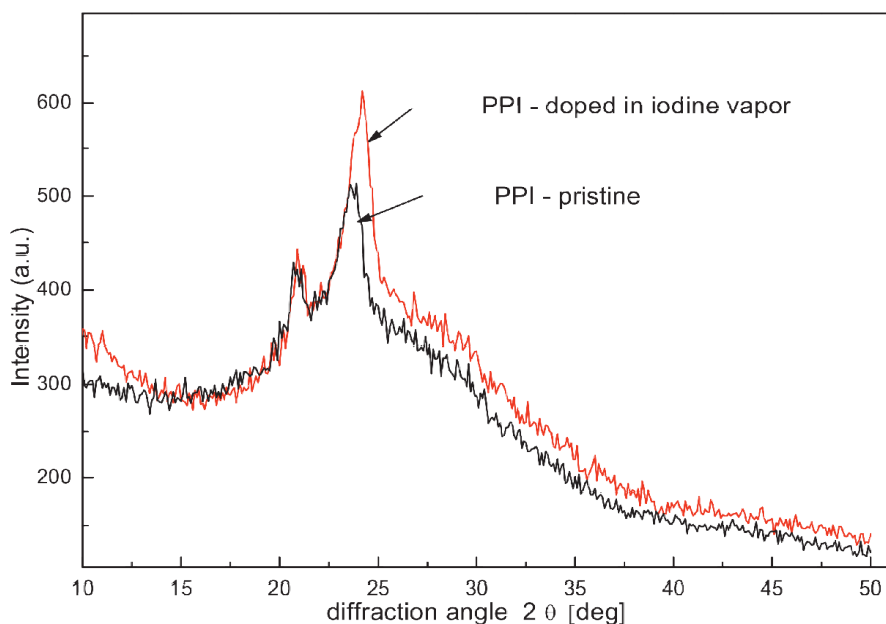


Figure 30. X-ray diffraction patterns taken on pristine and doped PPI thin films, according to [33,34]

If one assumes that iodine doping enforces chain planarization due to switching from benzenoid into quinoid form of some phenylene rings, this may be some indication that the peak at about 24.5 deg is related with ordering between phenylene rings, which is thought to correspond with eventual stacking. In Figures 31 and 32 one can see morphology of PPI2 films, pristine and iodine doped, respectively. It is clearly seen from this figures that after doping the film of PPI2 became much smoother and plane than pristine film. However, one can see in Figure 33 that X-ray diffraction patterns of PPI2 thin films pristine and doped have not shown any distinct difference, in contrast to the case of PPI pristine and dope counterparts. This discrepancy in behavior of PPI and PPI2 thin films against iodine doping seems to confirm our supposition concerning doping mechanism in the former, because the presence of oxygen atoms sp^3 hybridized can be seen as a factor acting against phenylene ring stacking. Analysis of the presented results, which include AFM images, X-ray diffraction patterns and UV-Vis absorption spectra suggest that there is quite distinct correlation for polyazomethine thin films linking their morphology and structure with technological conditions of their preparation. Thin films, whose surface morphology reveal granular character with granules essentially well separated or having contact points like osculating or touching circles, are thought to represent columnar growth with none or rather limited connection among them and in consequence among polymer chain or lamellae. Structure of such films reveal more

disordered or even amorphous structure, in contrast to films which revealing also granular morphology but with granules or columns overlapping, so that something like entities resembling ribbons or mountains of overlapping hills chains are formed. These so-called ribbons are not straight ones but they are revealing random wavy character, sometimes resembling chains of mountains are giving rise to films whose X-ray diffraction patterns show off better or less distinct peaks superimposed onto broad amorphous background. When regarding UV-Vis absorption spectra one can see that generally the structure of a film should be built up of nearly crystalline grains or at least grains or areas in which planar phenyl rings can even stack one over the another. Such supposition arise from observation, that absorption spectra taken on such films reveal at low energy side more or less pronounced feature at about 2.58 eV, which can be attributed to Wannier-Mott excitons, while the rest of the spectrum has “triangular” shape as it is well seen in Figures 8, 14 and 23, while slightly less pronounced in Figures 11, 17 and 20. The latter spectrum reveal vibronic progressions with missing indications of delocalized exciton formation. These observations can find some confirmation in morphology character of CVD prepared PPI thin films prepared pristine and doped. Generally, the pristine films are thought to reveal morphology and structure resulting from technical conditions of their preparation, however after doping these films are seen to reveal smooth surface, much smoother than the pristine ones. In the next section we try to describe electronic structure of PPI thin films starting from the simplest PPI and then we are going to prove that the proposed approach made in the frame of π -approximation is reasonable and can successfully describe electronic structure and optical spectra of other polyazomethines with more complex structure. Here it is worth mention that surface morphology of polyazomethine thin films has been taken by AFM working in so called contact mode, then with a sharp tip of about 20 nm dimension, the as-recorded images of surface roughness reveal granular features sizing some 100 and 200 nm, sometimes the features are smoothed out and wavy surface is observed. However, it is seen that films prepared under rather intense streams reveal more ordered morphology than those prepared under lower intensities of the stream of transport agent with mixed up molecules of monomers. It has been remarked in our earlier papers on PPI thin films prepared in both the horizontal and vertical setups. On the other hand the morphology of thin films prepared under strong intensity reagent streams coincide with more pronounced peaks in the X-ray diffraction patterns, but these peaks are always seen as superimposed on amorphous

background. There are reports on ordering in thin films of alternately conjugated polymers, where they are presented as long chains folded back and forth, so that one can observe lamellae. Areas composed of such ordered lamellae can be linked by entangled or curled fragments of chains, Figure 34. Crystalline areas consisting of stacks of polymer chains folded back on themselves are illustrated in Figure 35.

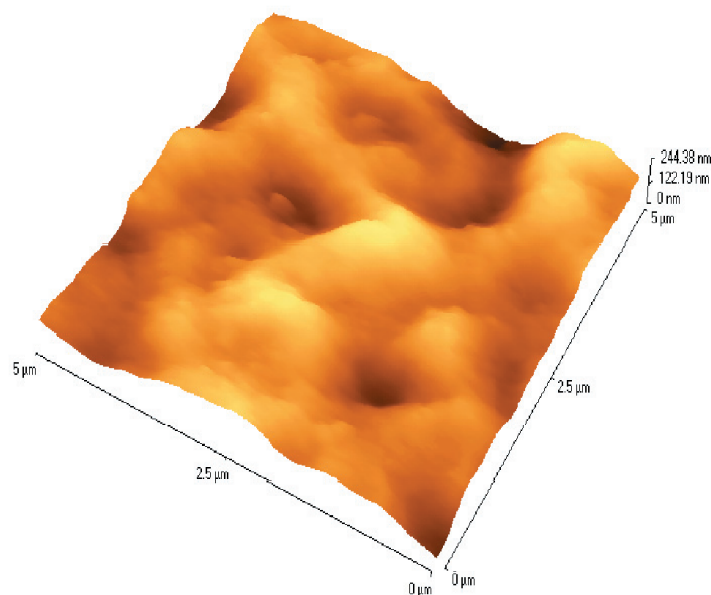


Figure 31. Topographic image of pristine PPI2 film [33,34]

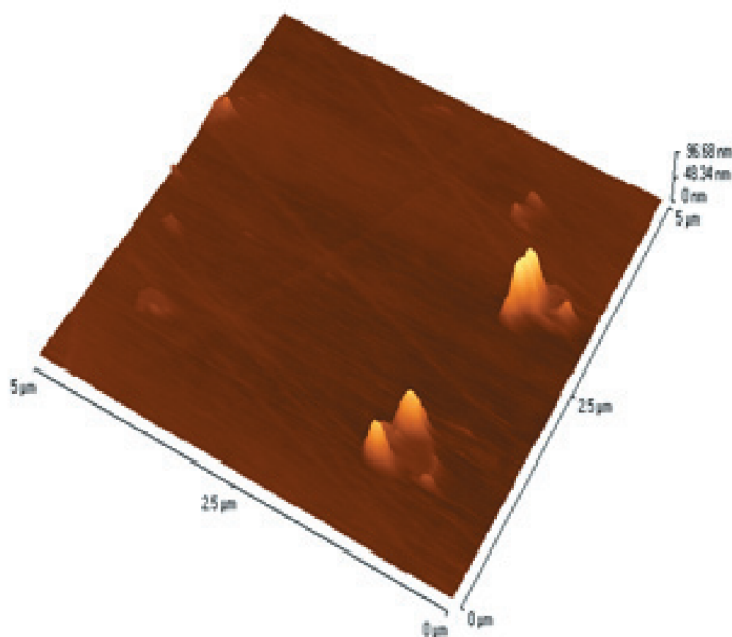


Figure 32. Topographic image of iodine doped PPI2 film [33,34]

It is thought that such lamellae are usually variously ordered in case of different polymers, but generally one may expect that such folding back of the chain seems to arise directly from the character of intramolecular bonding in alternately conjugated polymers, though this is not always due to really stacking chains. In fact, alternately conjugated polymers whose chains are built up of sp^2 hybridized atoms in the backbone comprise cyclic molecules like benzene rings or thiophene rings and it seems to be quite natural that phenyl ring could accept planar conformation, but this depends on such factors like the strain intensity and when it is not too high one may expect that these folded back chain segments can be composed of a sequence of planar segments, called conjugated segments, whose lengths constitute set of randomly

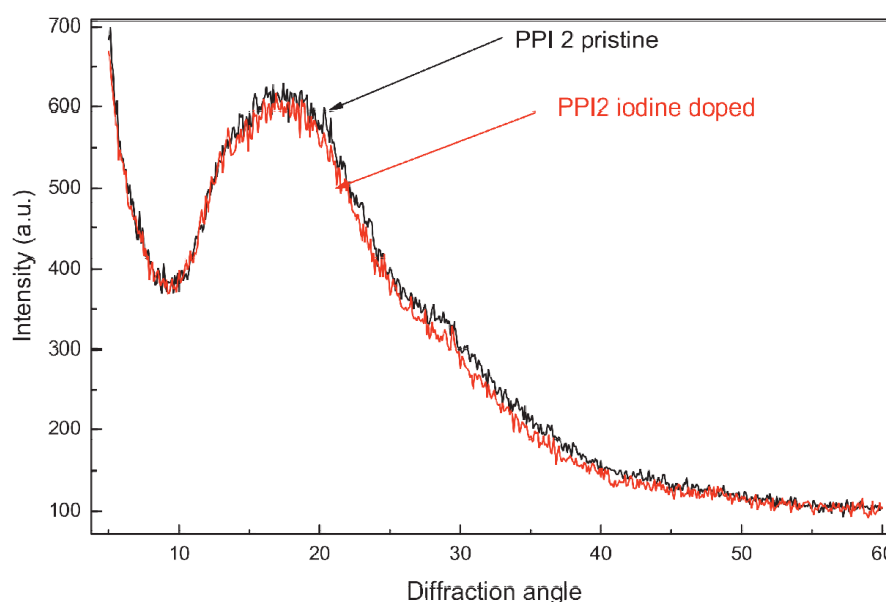


Figure 33. X-ray diffraction patterns of PPI2 pristine and iodine doped films [33,34]

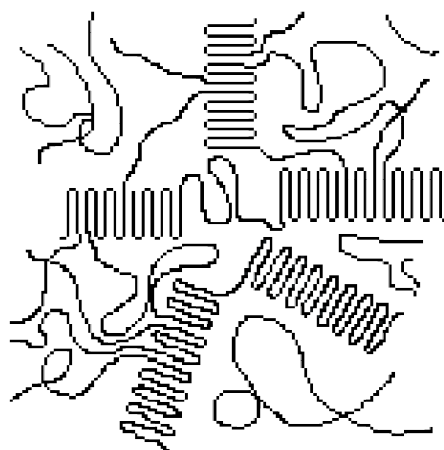
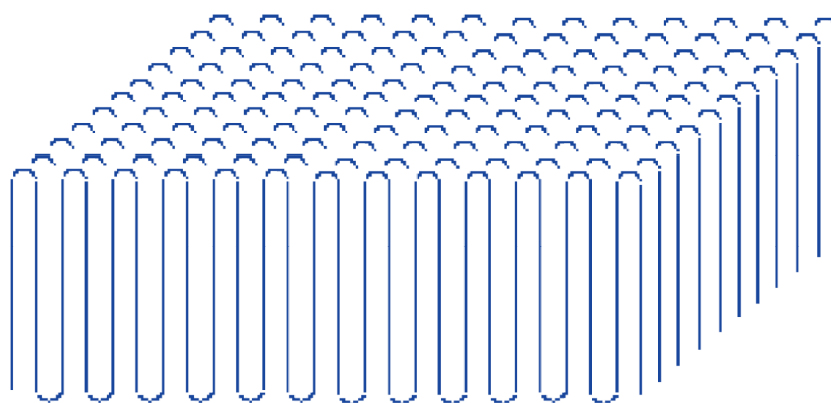


Figure 34. Structure of polymer thin films



They can fold, and they can stack. A stack of polymer chains folded back of themselves like this is called *lamella*

Figure 35. Crystalline areas of polymer thin film

distributed values. In contrast, high intensity of the stream bring about that these folded back and forth fragments are forced to strongly interact and couple when they are folded back on themselves they can form areas of polymer chains with cyclic aromatic units (phenylene or thiophene rings) stacked one over the next and in such conditions one may expect that these ordered areas are not limited to individual chains but they spread over some space volume, so that even one can speak about special kind of conjugation. These relations connecting morphology and structure with technological conditions cover also optical spectra, which reveal quite distinct dependence on preparation conditions as well as they can be linked with morphology and structures. Then, while knowing morphology and structure of a film one may expect that the shape of the optical spectra is known and determined, too.