



Influence of technological conditions on optical properties and morphology of spin-coated PPI thin films

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ABSTRACT

Purpose: The aim of this paper is to show technical and chemical parameters influence on optical properties and morphology of poly (1,4-phenylenemethylenenitrilo- 1,4-phenylenenitrilomethylene) (PPI) thin films prepared by spin-coating method

Design/methodology/approach: PPI thin films were prepared by spin-coating method with various spinning rates and molar concentrations. The monomers, terephthalaldehyde (TPA) and p-phenylenediamine (PPDA), were dissolved in tetrahydrofuran (THF) and then mixed. Optical properties of PPI thin films were examined by UV-Vis and IR spectroscopy. Surface morphology of thin films were tested by atomic force microscopy.

Findings: This paper show the influence of technical parameters of spin coating process onto properties of deposited thin films, such as thickness, optical properties and morphology.

Research limitations/implications: Optimizing spinning rates and concentrations of monomers is expected to allow for thin films to have required properties.

Practical implications: Conjugated polymers with heteroatom in the backbone like PPI are very interesting materials for their electronic properties. PPI can be used as active element in organic both solar cells and light-emitting diodes (LEDs).

Originality/value: Spin-coating method is very cheap and fast method to prepare PPI thin films as compared with CVD method. Recognizing of optimal speed rate and concentration of solution will make thin films with required properties to be prepared.

Keywords: Spin-coating; Polyazomethines; UV-Vis spectroscopy; IR spectroscopy; AFM microscopy

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MATERIALS

1. Introduction

The conjugated aromatic polyazomethine 1,4-phenylene-methylenenitrilo-1,4-phenylenetri-methylomethylene (PPI) has been synthesized and various aspects of their properties investigated for many years [1-6]. PPI thin films prepared via chemical transport method (CVD) [7-13] have been widely enough described in last several years.

PPI is isoelectronic counterpart of polyparaphenylenevinylene (PPV) [14]. The nitrogen of the PPI backbone introduces novel features and chemical flexibility in compare PPV.

The aim of this work is to find how optical properties and morphology of PPI thin films prepared by spin-coating method are affected by technological and chemical parameters. PPI has been expected to be relevant for photovoltaic and other optoelectronic applications and its investigations is very important.

Nowadays solar panels based on inorganic crystals are produced on industrial scale due to its high efficiency [15-18], however production of inorganic solar cells is quite complicated, expensive and moreover have negative effect on natural environment.

Replacing them with organic materials is expected to be justified by economic, ecological and scientific reasons [19-21].

2. Experimental

2.1. Materials and technology

Polyazomethines PPI thin films have been prepared by spin-coating method from terephthal aldehyde (TPA) and paraphenylene diamine (PPDA) via room temperature solution polycondensation (Fig. 1).

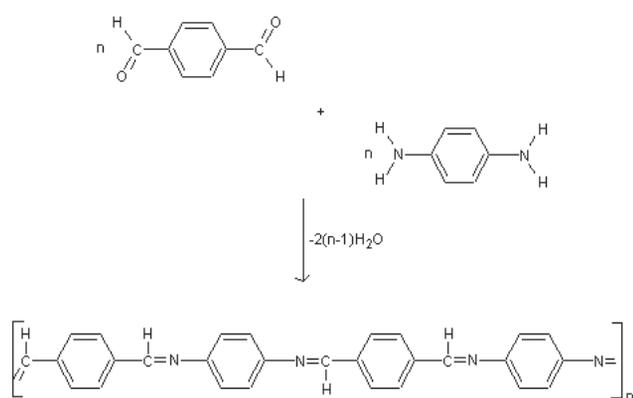


Fig. 1. Polycondensation reaction of poly(1,4-phenylene-methylenenitrilo-1,4-phenylenetri-methylomethylene)

The equimolar quantities of PPDA and TPA were dissolved each in tetrahydrofuran (THF), then put together and such mixture was stirred for about five minutes. At this time double bond -C=N- between monomers was formed and PPI chain was growing longer and longer. Number of moles, masses of monomers, volumes of solvents are given in Table 1. The monomers have been purchased from Aldrich.

Table 1. Quantity of TPA, PPDA and THF taking to experiments

N_0	n_{PPDA} [mmol]	n_{TPA} [mmol]	m_{PPDA} [g]	m_{TPA} [g]	V_{THF} [ml]
A	2	2	0.210	0.316	10
B	1.5	1.5	0.162	0.237	
C	1	1	0.108	0.158	
D	0.5	0.5	0.054	0.079	

The spin-coating process has been carried out under ambient conditions (air atmosphere, relative humidity 80-90%, room temperature). As prepared thin films have been annealed for 20 minutes at 150 °C.

Before deposition process, all substrates were subsequently cleaned in chromic acid and cleaning mixture, bathed in deionised water, put into ultrasonic washer with acetone for five minutes, bathed in deionised water, bathed in methanol and dried.

Deposition of spinning rates were set 1000, 2000, 3000 and 4000 rpm and deposition time on 20 seconds (Table 2).

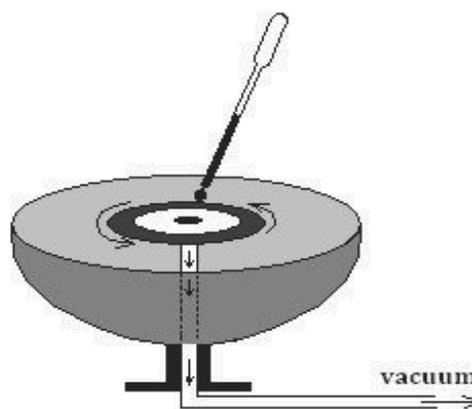


Fig. 2. Spin-coater scheme

Spin-coating process (Fig. 2) [22] of PPI thin films preparing consist of several essential stages: the first, fixing glass substrate onto rotary disc by sucking it with vacuum pump, few drops lets of

prepared PPI solution dropped onto rotating substrate while thin film deposited onto surface of glass substrate. Thin films formation is rather complex process, where simultaneously the solvent is sprawled upon the substrate surface, 90% is thrown off, out of the wafer, solvent evaporates and viscosity of a film is growing. Then, the as-deposited thin film is heated for some minutes.

Table 2. Technological parameters of spin-coating method

N_0	V [rpm]	t [s]
A	1000	20
	2000	
	3000	
	4000	
B	1000	20
	2000	
	3000	
	4000	
C	1000	20
	2000	
	3000	
	4000	
D	1000	20
	2000	
	3000	
	4000	

2.2. Experimental methods

The UV-VIS spectra were taken on the as-prepared PPI thin films on glass with the use of a Spectrophotometer Ocean Optics HR 4000 within 200-1000 nm wavelength interval. Morphology of thin films surfaces have been examined with Atomic Force Microscope (AFM). IR spectra have been recorded with IR spectrophotometer SPECORD M80 within 250-4000 cm^{-1} wave number range. Diffraction patterns were taken on X-Ray Diffractometer TUR M-62.

Thickness measurements revealed that thicknesses of thin films fell into interval 40-1500 nm, dependently on the spinning rates and molar concentrations.

All measurements were performed at room temperature.

3. Results and discussion

3.1. X-ray measurements

X-ray diffraction patterns taken on spin-coated PPI thin films prepared under different condition revealed similar features. Thus, a representative x-ray diffraction pattern is shown in Fig. 3.

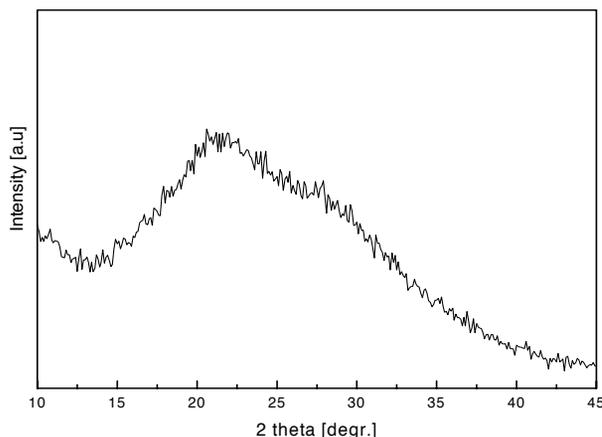


Fig. 3. X-ray diffraction pattern of PPI thin film

PPI thin films have appeared to be amorphous character of their structure, which is confirmed by X-ray diffraction pattern revealing amorphous like wide band.

3.2. AFM measurements

AFM topographic images of 5x5 μm recorded in contact mode are illustrated in Figs. 4-11. There are seen representative topographic images recorded for two series of PPI thin films prepared with various spinning rates.

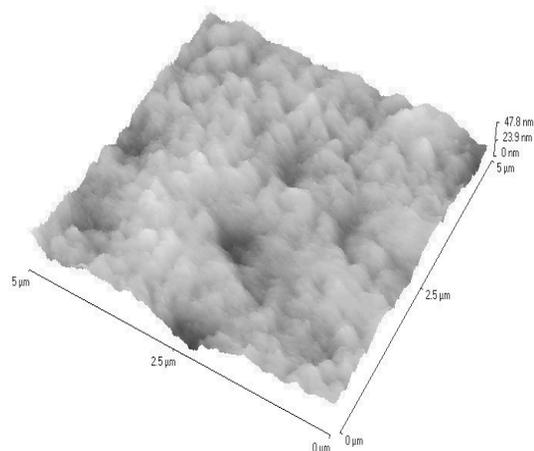


Fig. 4. Topographic image of series A, prepared with spinning rate 1000 rpm

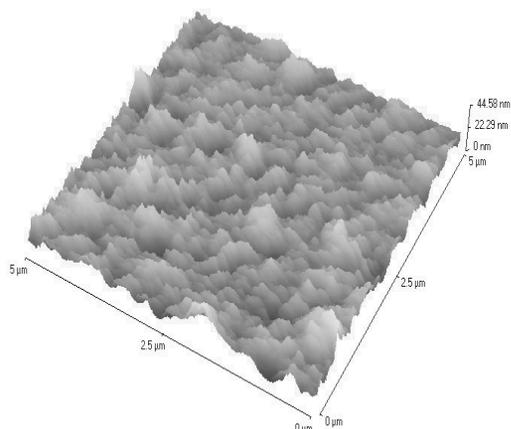


Fig. 5. Topographic image of series A, prepared with spinning rate 2000 rpm

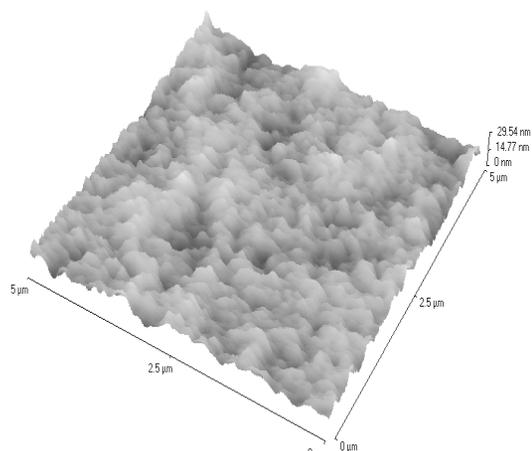


Fig. 8. Topographic image of series B, prepared with spinning rate 1000 rpm

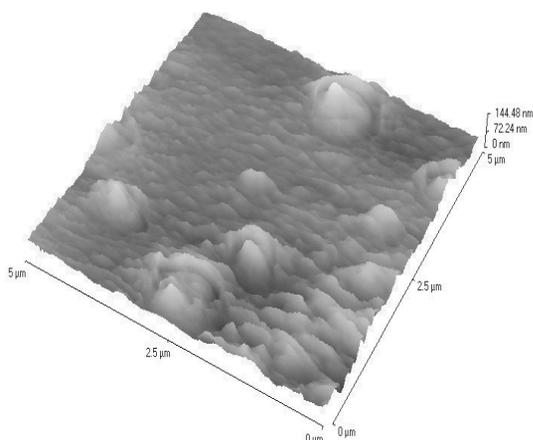


Fig. 6. Topographic image of series A, prepared with spinning rate 3000 rpm

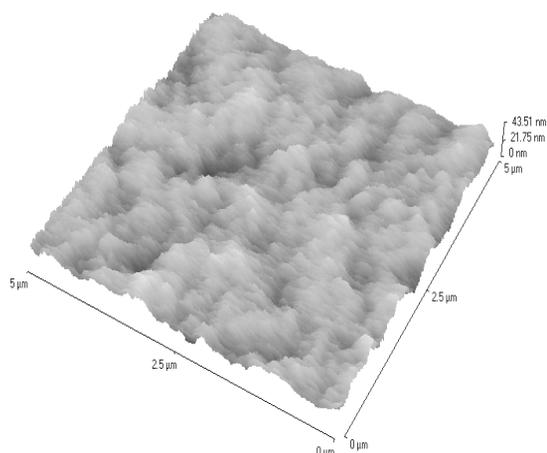


Fig. 9. Topographic image of series B, prepared with spinning rate 2000 rpm

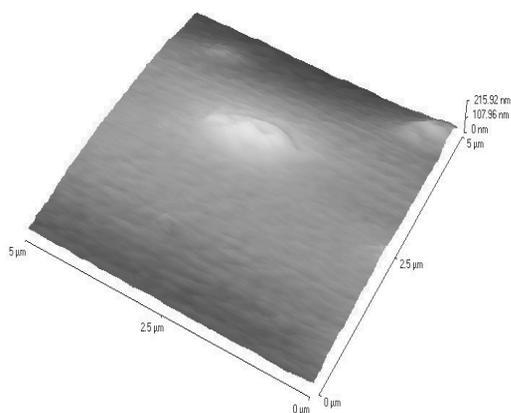


Fig. 7. Topographic image of series A, prepared with spinning rate 4000 rpm

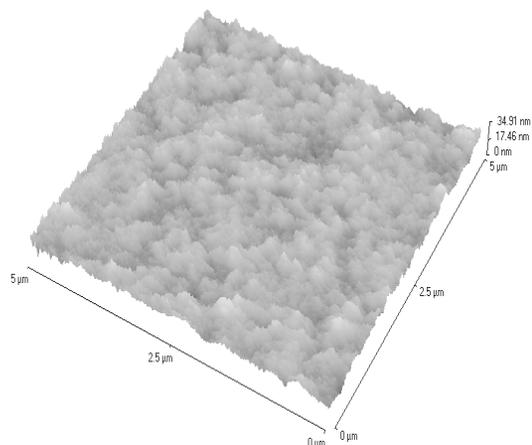


Fig. 10. Topographic image of series B, prepared with spinning rate 3000 rpm

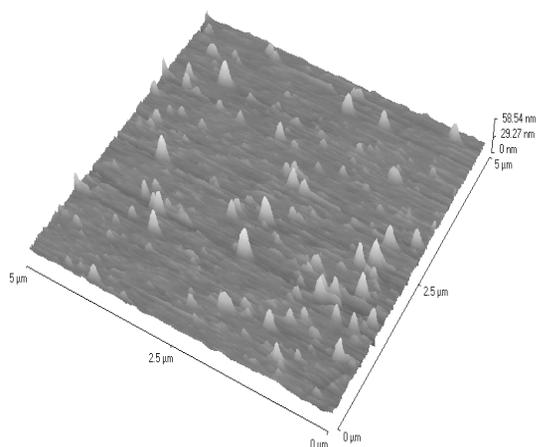


Fig. 11. Topographic image of series B, prepared with various spinning rate 4000 rpm

Morphology of all the spin-coated PPI thin films are granular with grain sizes of about 100 nm in diameter. According to data in Table 3, the roughness of thin films belonging to series B is small and nearly independent of spinning rate.

In case of series, RMS [23] of surface for 1000 and 2000 rpm are small and those for 3000 and 4000 rpm spinning rates larger.

Table 3.
Values of RMS coefficients

N_0	Spinning rates [rpm]	Spinning rates [rpm]	Spinning rates [rpm]	Spinning rates [rpm]
	1000	2000	3000	4000
A	5.97	5.06	14.78	12.99
B	3.38	5.11	3.21	3.33

While comparing topographic images one can notice that series A surface morphology is more homogeneous than in case of series B. However, one can notice hole which might be attributed to dewetting effect for a film deposition with 1000 rpm.

Generally, it is thought the height spinning rate generate the more plain surface of thin film. For films series B prepared with 4000 rpm one can see plane surface with randomly dewetting grains of simile shape.

3.3. FT-IR measurements

Since IR spectra taken on various PPI thin films were really similar, so a representative spectrum of PPI thin films which

deposited onto KBr wafers is shown in Fig. 12. The overall intensity of recorded spectra depends on the film thickness.

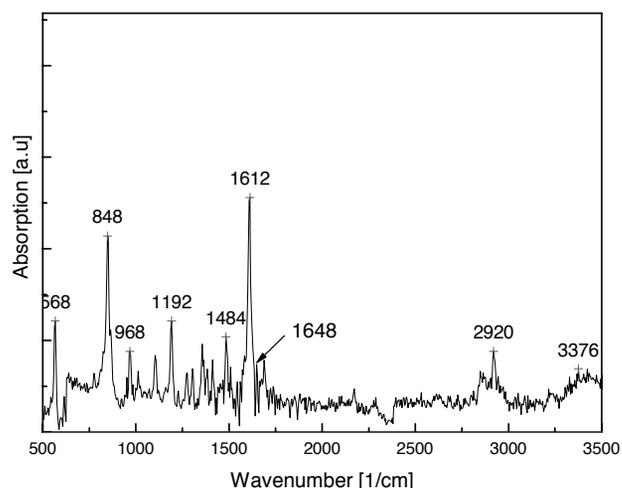


Fig. 12. IR absorption spectrum of PPI thin film deposited onto KBr wafers

Important features in IR spectra are seen within 800-1700 cm^{-1} wave number interval.

The strongest peaks in PPI spectrum are seen at 1612 cm^{-1} and 848 cm^{-1} .

Weaker peaks are observed at 1400, 1648 cm^{-1} and very wide peaks at 2880 and 3344 cm^{-1} .

The strongest peak seen in IR spectrum in Fig. 12 at about 1612 cm^{-1} is attributed to $-\text{C}=\text{N}-$ stretching vibration. Very small peak at 1648 cm^{-1} is attributed to aldehyde carboxylic group, while a very wide one at about 3344 cm^{-1} is attributed to N-H bond stretching vibrations of the amine end group, can be supported by the peak at about 1400 cm^{-1} , which is attributed to N-H-N bond bending vibrations. Another characteristic peak at 848 cm^{-1} is attributed to $-\text{C}-\text{H}$ bond out-of-plane vibrations, while that at about 2880 cm^{-1} is attributed to C-H hydrogen vibrations. Low intensities of these two peaks indicate that quantities of aldehyde and amine end groups are rather small ones, so that one can suppose the chains of PPI polyazomethine to be sufficiently long.

UV-Vis spectra correspond rather well with considered IR spectra and results of AFM measurements. Absorption measurements were performed at room temperature.

3.4. UV-VIS measurements

The UV-VIS optical absorption spectra recorded on PPI thin films series are shown in Figs.13-16. For each series, there are spectra taken on thin films deposited with various spinning rates, which are seen in subsequent figures, respectively. From series A to D concentrations of the solution used was changed with an increment 0.5 mmol.

While preparing thin films of each series, the ambient conditions, time and spinning rates used were the same.

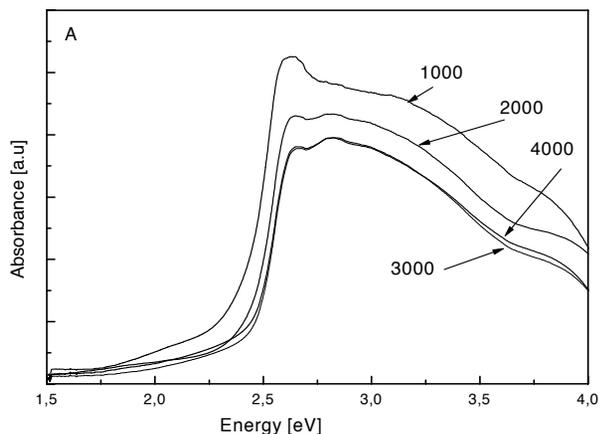


Fig. 13. UV-VIS absorption spectra of series A PPI thin films prepared with various spinning rates

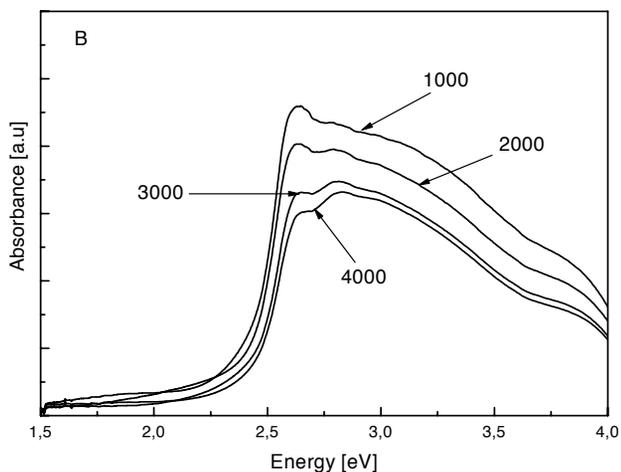


Fig. 14. UV-VIS absorption spectra of series B PPI thin films prepared with various spinning rates

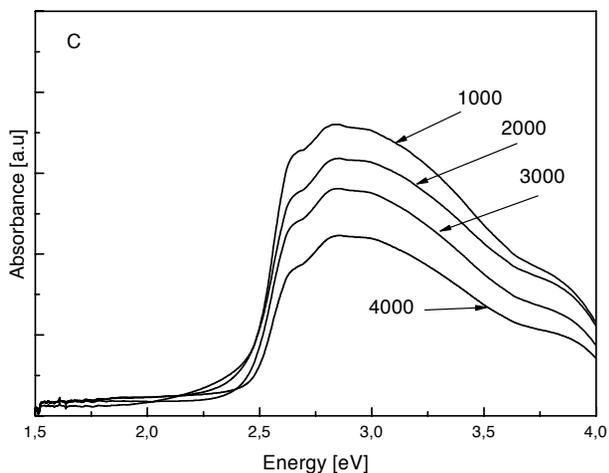


Fig. 15. UV-VIS absorption spectra of series C PPI thin films prepared with various spinning rates

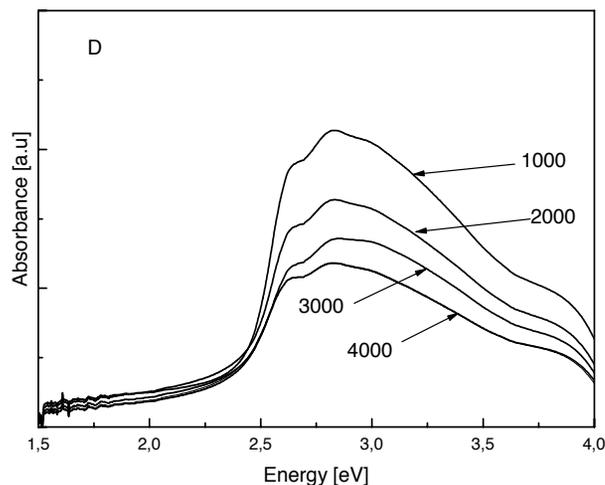


Fig. 16. UV-VIS absorption spectra of series D PPI thin films prepared with various spinning rates (1000-4000 rpm)

Absorption spectra reveal the strongest feature that is attributed to $\pi-\pi^*$ interband transitions connecting HOMO and LUMO delocalised states of PPI polymer. The exciton-like peak which is phenomena characteristic for inorganic crystalline semiconductors like Ge and Si, is visible in PPI UV-Vis absorption spectra. The exciton-like peak at about 2.6 eV, best visible in case of very slow spinning rates (1000 rpm) and high molar concentrations (series A and B), indicates that these films have higher conjugation length than the others.

The absorption spectra of PPI thin films all series are normalised at energy 3.75 eV, to eliminate influence of film thicknesses on spectra and shown in Figs. 17-20 respectively. One can see in Fig. 17, Fig. 18, and Fig. 20 that shape of absorption band is no changed as compared with Fig. 19 where shape of absorption band is changed.

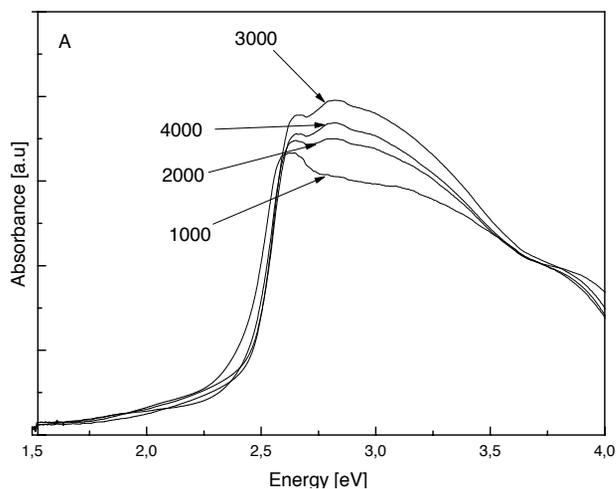


Fig. 17. Normalised spectra of PPI thin films, series A prepared with various spinning rates (1000-4000 rpm)

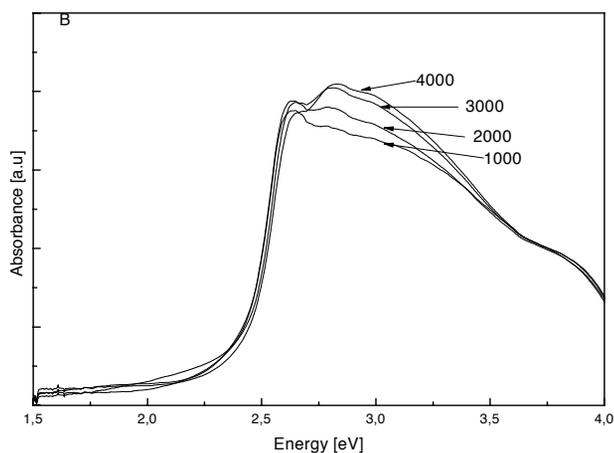


Fig. 18. Normalised spectra of PPI thin films, series B prepared with various spinning rates (1000-4000 rpm)

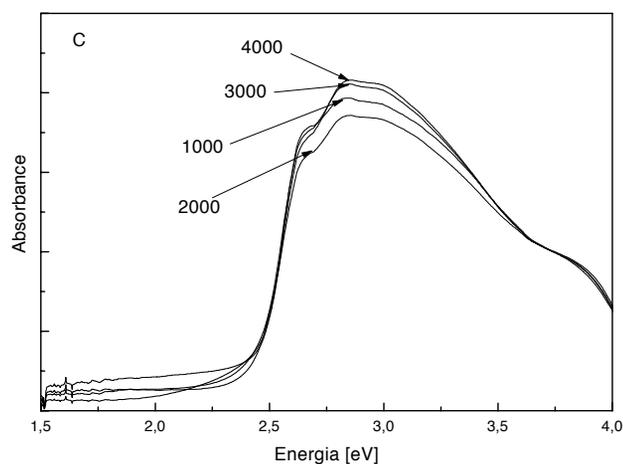


Fig. 19. Normalised spectra of PPI thin films, series C prepared with various spinning rates (1000-4000 rpm)

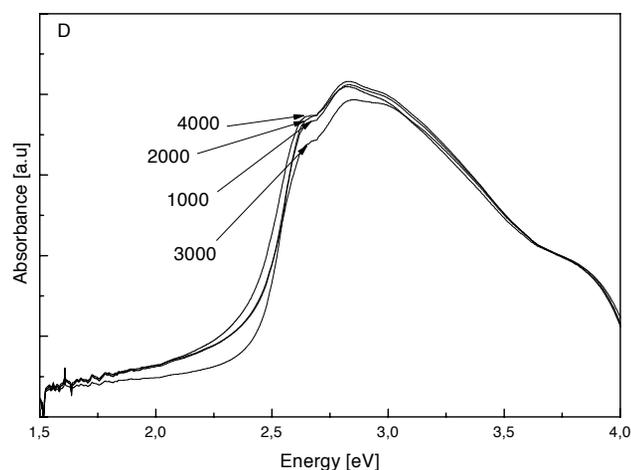


Fig. 20. Normalised spectra of PPI thin films, series D prepared with various spinning rates (1000-4000 rpm)

4. Conclusions

Poly(1,4-phenylene-methylenitrilo-1,4 phenylenitrilo-methylene) thin films were prepared by spin-coating method with various spinning rates and molar concentrations.

The presented results have shown that morphology and optical properties depend on spinning rates and molar concentration of the PPI thin films deposition. Thin surface of PPI thin films prepared with slow spinning rates is smoother, big grains are seen in topographic images samples deposited with quick spinning rates.

The UV-Vis absorption intensity of PPI films deposited with high spinning is lower than absorption intensity of PPI prepared with slow spinning rates. The absorption intensity of PPI thin films deposited with spinning rates 3000 and 4000 rpm are the same intensity in almost every series. The shape of low energy band, which is attributed to interband transition $\pi-\pi^*$ is seen to change with solution concentrations and spinning rates.

X-Ray spectra revealed predominant amorphous structure and IR spectrum revealed that polymer chains are sufficiently long.

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References

- [1] B. Jarzabek, J. Wieszka, M. Domański, J. Jurusik, J. Cisowski, Optical studies of aromatic polyazomethine thin films, *Journal of Non-Crystalline Solids* 354 (2008) 856-862.
- [2] B. Jarzabek, J. Wieszka, M. Domański, J. Cisowski, Optical properties of amorphous polyazomethine thin films, *Journal of Non-Crystalline Solids* 352 (2006) 1660-1662.
- [3] F. Rohlfing, D.D.C. Bradley, Non linear Stare effect in polyazomethine and poly (p-phenylene-vinylene): The interconnections of chemical and electronic structure, *Chemical Physics* 227 (1998) 133-151.
- [4] B. Hajduk, J. Wieszka, B. Jarzabek, J. Jurusik, M. Domański, Physical properties of polyazomethine thin films doped with iodine, *Journal of Achievements in Materials and Manufacturing Engineering* 24/1 (2007) 67-70.
- [5] W. Łużny, E. Stochmal-Pomarzańska, A. Proń, Structural properties of selected poly(azomethines), *Polymer* 40 (1999) 6611-6614.
- [6] L. Marin, V. Cozan, M. Bruma, V.C. Grigoras, Synthesis and thermal behaviour of new poly(azomethine-ether), *European Polymer Journal* 42 (2006) 1173-1182.
- [7] L.A. Dobrzański, *Engineering materials and materials design. Fundamentals of materials science and physical metallurgy*, WNT, Warsaw, 2006 (in Polish).
- [8] B. Hajduk, J. Wieszka, J. Jurusik, Influence of LCVD technological parameters on properties polyazomethine thin films, *Journal of Achievements in Materials and Manufacturing Engineering* 36/1 (2009) 41-48.

- [9] M.S. Weaver, D.D.C. Bradley, Organic elektroluminescence devices fabricated with chemical vapour deposited polyazomethine films, *Synthetic Metals* 83 (1996) 61-66.
- [10] A. Kubono, N. Okui, Polymer thin films prepared by vapour deposition, *Progress Polymer Science* 19 (1994) 389-438.
- [11] J. McElvain, S. Tatsuura, F. Wudl, A.J. Heeger, Linear and nonlinear optical spectra of polyazomethines fabricated by chemical vapour deposition, *Synthetic Metals* 95 (1998) 101-105.
- [12] W. Kwaśny, D. Pakuła, M. Woźniak, L.A. Dobrzański, Fractal and multifractal characteristics CVD coatings onto nitride tool ceramics, *Journal of Achievements in Materials and Manufacturing Engineering* 20 (2007) 371-374.
- [13] L.A. Dobrzański, D. Pakuła, Comparison of the structure and properties of the PVD and CVD coatings deposited onto nitride tool ceramics, *Proceedings of the 13th Scientific International Conference "Achievements in Mechanical and Materials Engineering" AMME'2005, Gliwice-Wisła, 2005 (CD-ROM)*.
- [14] Y. Shimoi, S. Abe, Theory on electroabsorption in poly(p-phenylene vinylene), *Synthetic Metals* 91/9 (1997) 363-365.
- [15] L.A. Dobrzański, M. Musztyfaga, A. Drygała, P. Panek, Investigation of the screen printed contacts of silicon solar cells using Transmission Line Model, *Journal of Achievements in Materials and Manufacturing Engineering* 41/1-2 (2010) 57-65.
- [16] L.A. Dobrzański, A. Drygała, P. Panek, M. Lipiński, P. Zięba, Application of laser in silicon surface processing, *Journal of Achievements in Materials and Manufacturing Engineering* 24/2 (2007) 179-182.
- [17] L.A. Dobrzański, A. Drygała, P. Panek, M. Lipiński, P. Zięba, Development of the laser method of multicrystalline silicon surface texturization, *Archives of Materials Science and Engineering* 38/1 (2009) 5-11.
- [18] L.A. Dobrzański, A. Drygała, Surface texturing of multicrystalline silicon solar cells, *Journal of Achievements in Materials and Manufacturing Engineering* 31/1 (2008) 77-82.
- [19] S.-S. Sun, N.S. Sariciftci, *Organic Photovoltaics: Mechanisms, Materials and Devices*, CRC Press, 2005.
- [20] C.W. Tang, Two-layer organic photovoltaic cell, *Applied Physics Letters* 48 (1986) 183-185.
- [21] S.H. Park, G. Huh, T. Taguchi, E. Maeder, Smart polymers with light emission ability: millennium products for intelligent displays for navigation in the transportation industry, *International Journal of Materials and Product Technology* 19/3-4 (2003) 304-313.
- [22] F. Taylor, Spin coating: An Overview, *Metal Finishing* 99/1 (2001) 16-21.
- [23] A. Borgesi, G. Tallarida, G. Amore, F. Cozzaniga, F. Queirlogo, M. Alessandri, A. Sassela, Influence of roughness and grain dimension on the optical functions of polycrystalline silicon films, *Thin Solid Films* 313-314 (1998) 243-247.