

SPECTRAL AND AFM STUDIES ON UV-CROSSLINKED FILMS OF POLY(4-VINYLPYRIDINE) DERIVATIVES

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Structural changes induced by UV radiation on poly(4-vinylpyridine) and two poly(4-vinylpyridine) derivatives are presented. Poly(4-vinylpyridine), poly(N-carboxyethyl-4-vinylpyridine) (P4VPy-AA) and poly(N-allyl-4-vinylpyridine) chloride (P4VPy-CA) were exposed at 248 nm radiation. The solubility change of the exposed areas was observed and it was associated with crosslinking of the macromolecular chains. The influence of radiation on surface morphology and the quality as potential photoresist were evaluated by atomic force microscopy technique.

INTRODUCTION

Although the P4VPy derivatives are intensively studied in these days, there are few reports dealing with the crosslinking mechanism induced by UV radiation. The first report regarding the photocrosslinking of a P4VPy derivative has been made by Decout *et al.*¹ in the case of pyridine-N-oxide. Irradiation of a polymer in which the photoreactive chromophore is 4-vinylpyridine-N-oxide evidenced the cleavage of N – O bond and the photocrosslinking of polymer.

There are several groups that had reported the crosslinking of thin films of P4VPy as subjected to UV radiation for obtaining the immobilized films on substrate in view of fabricating the patterns by photolithography², as responsive coatings toward various stimuli³, or in view of immobilization of nanoparticles⁴ etc.

In this paper we present a comparative study of the photochemical behavior of poly(4-vinylpyridine) and of two poly(4-vinylpyridine) derivatives: poly(N-carboxyethyl-4-vinylpyridine) (P4VPy-AA) and poly(N-allyl-4-vinylpyridine) chloride (P4VPy-CA) under UV radiation at 248 nm. P4VPy-AA is a polycarboxybetaine, whose structure is characterized by the presence of anionic (carboxylate group) and cationic (ammonium group) moieties in the structural unit. P4VPy-CA is a quaternary salt. By extraction of

the irradiated polymer samples with solvent the insolubilization and immobilization onto substrates were observed. By this reason, a photopatterning test was made and the cross-sectional profiles of the patterns were obtained.

EXPERIMENTAL

Materials. P4VPy (Aldrich Chemical Company Inc), with $\overline{M}_w = 160000$, was used after purification by reprecipitation from methanol in diethyl ether. P4VPy-AA and P4VPy-CA were prepared by a procedure described elsewhere⁷.

Spectral measurements. The UV measurements of P4VPy, P4VPy-AA and P4VPy-CA were recorded as thin films onto quartz substrates, deposited from 5 mg/ml chloroform, and methanol solutions, respectively. Electronic absorption spectroscopy was performed by using Specord M40 and M42 spectrometers with resolution of 2 nm.

Irradiation. All samples were exposed to UV radiation, for specific time periods, at 248 nm from a 350 W Hg medium pressure lamp (LOS-2), with $I_{248} = 0.6 \text{ W/cm}^2$. Periodically, a series of UV spectra were recorded at certain moments of time during irradiation.

Photopatterning. The negative-type photopatterning method consisted of irradiation of the film through a mask which has disposed regular hexagonal openings (150 micron width). The development of the irradiated film and removal of unexposed areas were carried out in methanol. The obtained profiles were observed by atomic force microscopy.

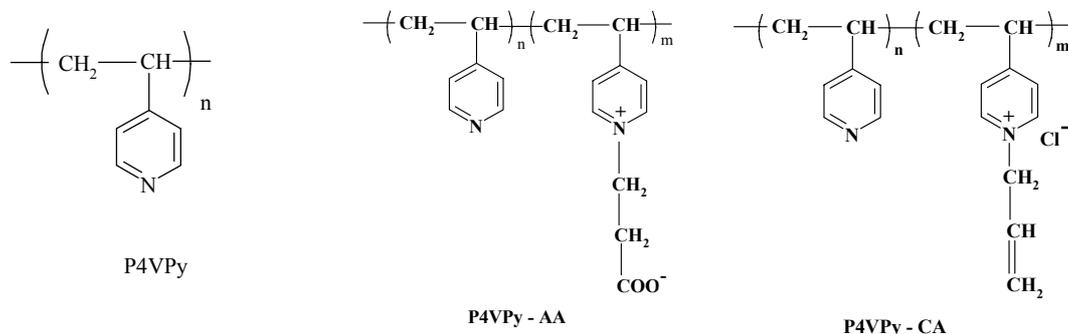
AFM Surface Analysis. A Ge surface has been employed as a substrate for surface topography analysis. The photopatterning test was performed on optical glass plates.

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The films were spin-coated (WS-400A-6NPP/Lite, Laurell Techn. Corp.) from a solution of 10 mg/mL in methanol (for P4VPy-AA or P4VPy-CA) and chloroform (for P4VPy), at 3000 rpm for 1 min. AFM measurements were performed in

air at room temperature, in tapping mode by using Solver PRO-M (NT-MDT, Russian Federation).

The studied compounds have the following structures:



RESULTS

Effects of UV radiation (248 nm) on P4VPy

Electronic absorption spectrum of P4VPy exhibits a broad absorption band ($\lambda_{\text{max}} \approx 257$ nm) which presents a vibronic structure. This band was assigned to pyridine ring absorption, and its

structured feature is explained by both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions which are located in the same spectral region. The $S_2(\pi\pi^*) \leftarrow S_0$ transition produces the major peak at 257 nm, while its shoulder at about 263 nm is attributed to $S_1(n\pi^*) \leftarrow S_0$ transition^{5,6}.

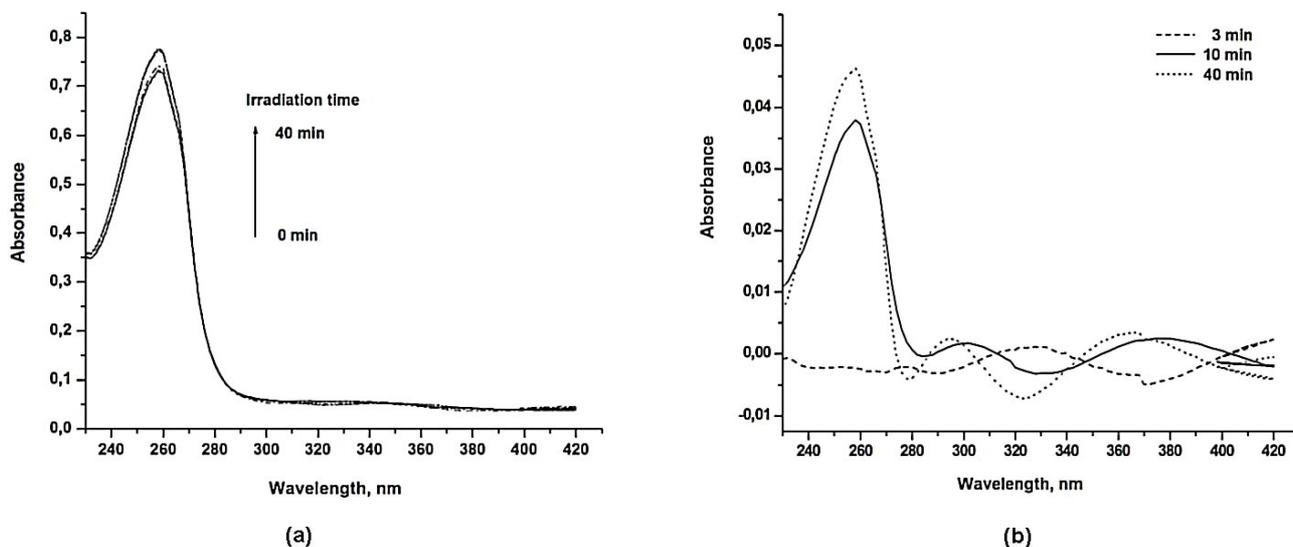


Fig. 1 – (a) UV absorption spectra of a P4VPy thin film during irradiation with 248 nm at irradiation times of 0, 3, 6, 10, 15, 20, 30 and 40 min. (b) Difference electronic spectra for 3, 10 and 40 min of irradiation.

The spectral changes in the absorption spectrum of P4VPy with irradiation at 248 nm are presented in Fig. 1 (a). At first glance, it can be noted that the intensity of the monomer band at 257 nm was enhanced. By digital subtraction of the initial spectrum from the 3 min irradiated one (Fig. 1, (b)), a single new band at 326 nm band is noted. In

the difference spectrum at 10 min two bands, at 301 nm and 376, are revealed. Subsequent exposure up to 40 min leads to the blue-shifting of the two bands at 294 and 366 nm, respectively. The major peak, at 257 nm, did not change its position, only its intensity increases. The P4VPy film remains colorless after exposure.

UV-VIS study of UV irradiated P4VPy-AA and P4VPy-CA

In the UV-VIS absorption spectrum of P4VPy-AA and P4VPy-CA, the main absorption at 232 nm is assigned to the pyridinium moieties due to the $\pi \rightarrow \pi^*$ transition. In the P4VPy-AA case, upon UV exposure the intensity of the 232 nm band was decreased with increasing the irradiation

time (Fig. 2) and scission of the $N^+ - CH_2$ bond accounts for this strong absorption reduction. In the same time, the long-wave absorption of pyridine ring absorption remains essentially unchanged. The slightly diminishing of its intensity is only apparent because of the overlapping of the stronger pyridinium cation absorption band.

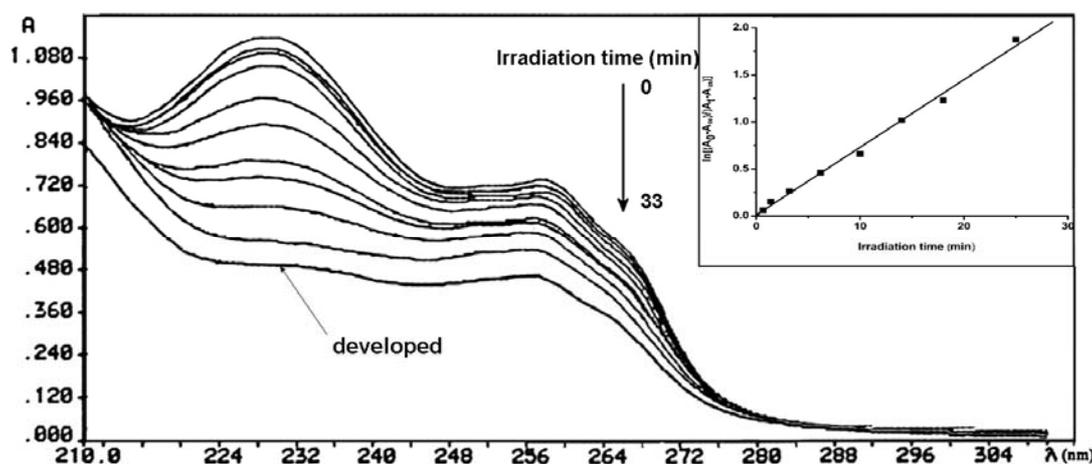


Fig. 2 – UV-VIS spectral variation of the P4VPy-AA film as a function of irradiation time and absorption spectrum of developed film (thick line); inset: kinetics of photodecomposition following the decreasing of the 232 nm absorption band.

The absorbance decay of the pyridinium salt absorption at 232 nm can be expressed by a first-order rate equation, $\ln((A_0 - A_\infty)/(A_t - A_\infty)) = k \cdot t$, where A_0 , A_t and A_∞ are absorbance values before irradiation, momentarily and at infinity (end of irradiation) respectively; k is the constant rate. The rate of decrease dropped and after cca. 30 min the photodecomposition seems to reach a stationary state. From the plot presented in Fig. 2, inset, the rate constant of photodecomposition was estimated $k = 1.199 \times 10^{-3} \text{ s}^{-1}$. The linearity proves the photoscission being the only photoreaction that took place in the system. The general feature of the electronic spectra of developed film is similar with that of just irradiated one.

The spectral changes of P4VPy-CA during irradiation were minor. As shown in Fig. 3, the peak intensity at 232 nm underwent a very slightly decreasing and no other modification is evidenced. The spectrum of extracted film is similar with that of the initial one, except a broadening of the bands. It appears that the peak intensity at 232 nm decreased and an enhancement of the shoulder attributed to the $n \rightarrow \pi^*$ transition of pyridine ring

(263 nm) could be observed. After exposure, the films become insoluble, whereas they are soluble before irradiation. Due to the reactive vinyl group, P4VPy-CA could photocrosslink easier than other quaternary salts. The minimal information obtained from electronic absorption spectra showed that there is no cleavage of $N^+ - CH_2$ bond between the pyridinium ring and pendant group or it is produced in a small extent. The crosslinking is thought to involve the $-CH=CH_2$ bond rather than coupling of two macroradicals formed both at the tertiary carbon from the backbone.

In addition, we used $^1\text{H-NMR}$ spectroscopy as a further proof and for a deeper insight into mechanism of reaction.

As shown in Fig. 4, the proton signal of $CH=$ in $-CH=CH_2$ units appeared at $\delta=6.22$ ppm, and $=CH_2$ appeared at $\delta=5.614$ ppm. The resonances at $\delta=7.60$ and $\delta=8.71$ ppm are assigned to quaternized pyridine ring. The peak at $\delta=5.242$ ppm is associated with CH_2 groups positioned between pyridinium ring and $CH=$ groups. After UV exposure, in the spectrum of the gelified polymer a new peak at $\delta=4.616$ ppm evolves. In addition, the intensity in the $\delta=2.3 - 1.9$ ppm domain increases.

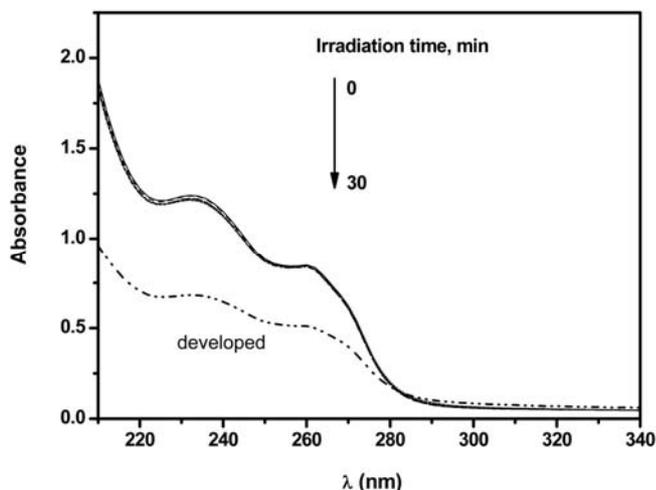


Fig. 3 – Electronic absorption evolution of P4VPy-CA while exposing at 248 nm and electronic spectra of extracted film (dashed line).

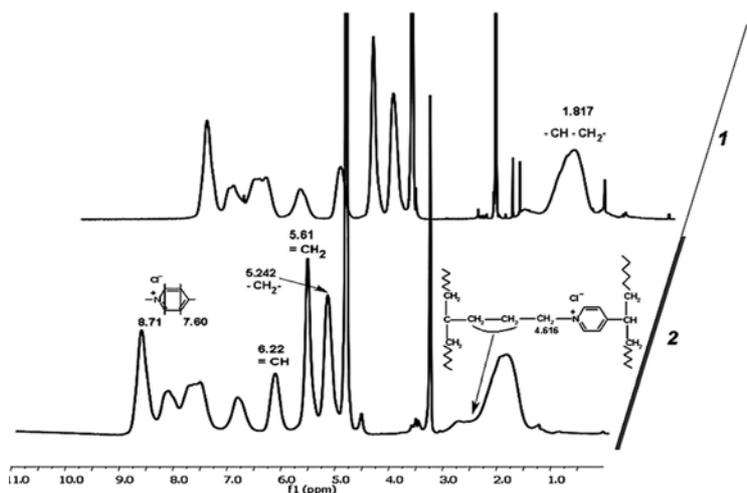


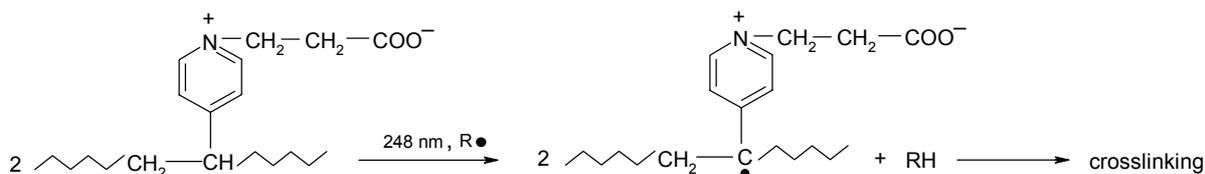
Fig. 4 – $^1\text{H-NMR}$ spectra of P4VPy-CA: (1) before irradiation; (2) light photocrosslinked.

DISCUSSION

On the basis of UV-VIS spectral analysis it seems that the photocleavage of the $\text{N}^+\text{-CH}_2\text{-}$ bond between the pyridine ring and the pendant group represents the first step from a series of photoinduced processes, leading to the formation of $^+\text{CH}_2\text{-CH}_2\text{-COO}^-$ and neutral pyridine ring. The $^+\text{CH}_2\text{-CH}_2\text{-COO}^-$ species are not stable and would reverse to the acrylic acid form.

The insolubility of the developed film in a good solvent for both P4VPy and P4VPy-AA is due to the crosslinking of the chains. In addition, the lability of the hydrogen methyne group is well-known and the

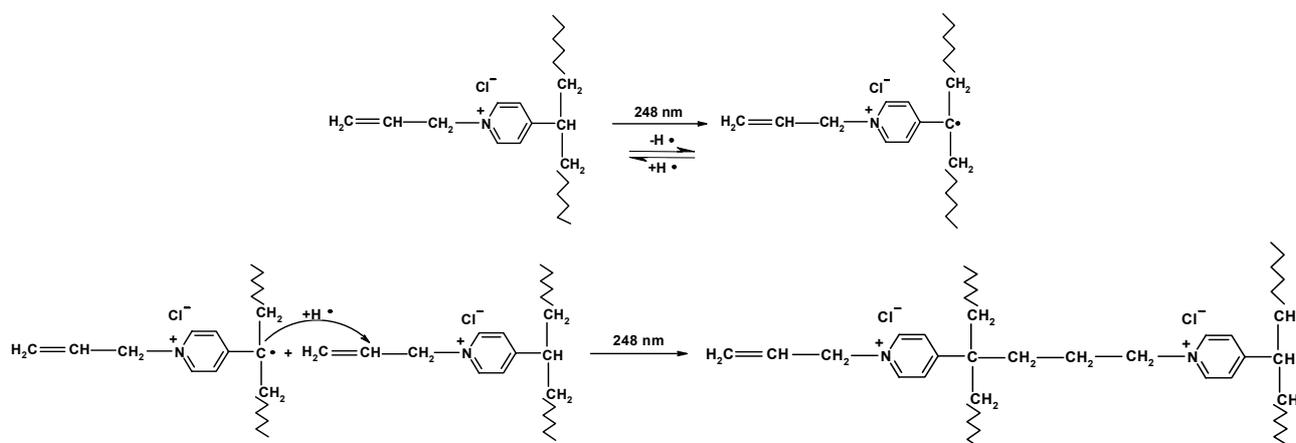
pyridine ring exerts an inductive force on this group. Quaternization results in a redistribution of the electron density in pyridine ring, and the much stronger inductive force exerted on the α hydrogen atom facilitates its removal, much easier than in P4VPy case. Terminal radicals resulting from main chain photocleavage may abstract the tertiary H atom, as we concluded in the case of P4VPy crosslinking and the insoluble network would be formed by recombination of such macroradicals. But even for longer irradiation, some of the betaine units remained unchanged. Scheme 1 shows a proposed mechanism of crosslinking.



Scheme 1 – Photocrosslinking of P4VPy-AA through zwitterions units and chain scissions.

The mechanism of two chains crosslinking of P4VPy-CA is completely different as compared with that of P4VPy-AA. It seems that the presence of the Cl^- ions in the pyridinium ring neighborhood strengthened the $>\text{N}^+ - \text{C}$ bond, preventing its scission. On the other side, P4VPy-CA contains a photocrosslinkable group, $-\text{CH}=\text{CH}_2$, which is able to participate itself in the crosslinking process. In the $^1\text{H-NMR}$ spectrum (Fig. 4), upfield shift of the signal attributed to $-\text{CH}_2-$ groups (next to pyridyl ring) with 0.6 ppm, from $\delta=5.242$ ppm to $\delta=4.616$ ppm, might be

caused by saturation of the $-\text{CH}=\text{C}$ group from vinyl. The increasing in the 2.3 – 1.9 ppm region could be due to a hidden signal of one or both CH_2 groups involved in crosslinks of $-\text{CH}_2 - \text{CH}_2 -$ type. The removal of an H atom from methyne groups from the polymer skeleton is facilitated by the same inductive force exerted by the pyridinium cation. The consumption of $\text{C}=\text{C}$ groups is evidenced in the FT-IR spectra (data not shown), but in a low extent. In conclusion, the proposed mechanism for the crosslinking is presented in Scheme 2:



Scheme 2 – The crosslinking mechanism of P4VPy-CA.

As compared to P4VPy-AA, photocrosslinked P4VPy-CA maintains its own ionic character.

AFM SURFACE IMAGING

The chemical changes induced by UV radiation on the studied poly(4-vinylpyridine) derivatives encouraged us to analyze the crosslinking at microscopic scale. We employed AFM as a tool in a study of surface topography and characterization of obtained profiles by photopatterning.

The surface morphology was determined prior and after irradiation, in tapping mode, with commercially available NSG10/Au Silicon cantilevers. The manufacturer's value for the probe tip radius is 10 nm, and the typical force constant is 11.5 N/m. The cantilever is oscillated at a frequency of 243.714 kHz. The roughness parameter RMS was used as a measure of the surface roughness.

The surface of non-irradiated P4VPy film is very homogenous and smooth, with $\text{RMS} = 0,89$ nm. As compared to the initial surface roughness, photocrosslinking of P4VPy produced an even

smoother surface. Root mean square roughness (RMS) decreased after exposure down to 0.52 nm.

As it can be seen in Fig. 5 A, the surface of non-irradiated P4VPy-AA is quite non-uniform, with swelling-like structures and various kinds of holes. From profile analysis, the average depth of holes is 15 - 20 nm and the RMS value is 1.09 nm. After irradiation at a fluence of 43 mJ/cm^2 , a series of small and deep holes appeared on the surface (right side of Fig.5, A) and their average depth was estimated at 80 nm. The surface roughness is increased to 2.69 nm. The surface structure is not drastically altered by crosslinking, with no cracks observed at this scale.

Unlike P4VPy-AA, the surface morphology of P4VPy-CA is smoother and very regular, with almost no particular structures. The RMS value of un-irradiated surface is 2.193 nm. 3D-AFM images of un-irradiated and irradiated P4VPy-CA films, at a fluence of 43 mJ/cm^2 are presented in Fig. 5 (B). The surface roughness is changing to 4.45 nm. On the surface new and deep holes were seen, but the surface morphology remained essentially featureless.

In the photolithography test (43 mJ/cm^2), the crosslinked area of P4VPy film is highly non-uniform, with peak-like profiles (Fig. 6, A, left

side). The edge between exposed and non-exposed areas is quite well defined.

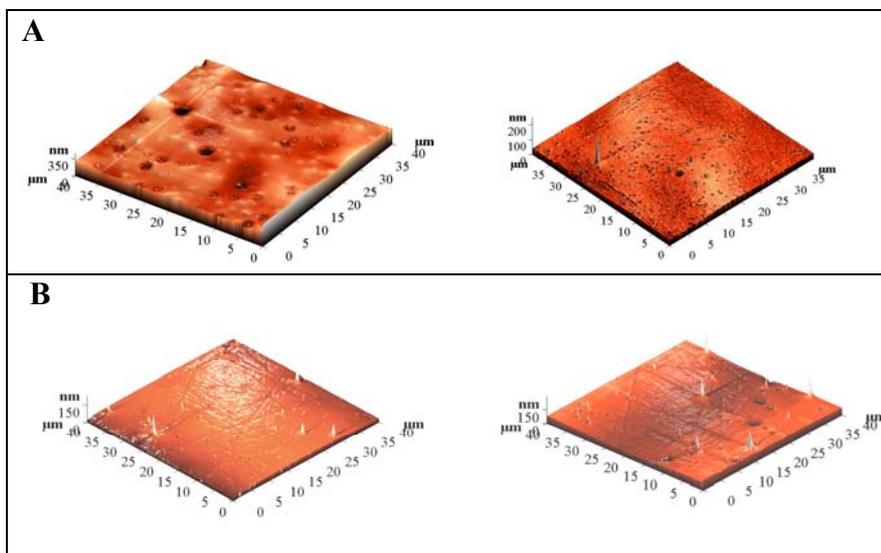


Fig. 5 – Initial (left side) and following UV irradiation (right side) AFM images of P4VPy (A) and P4VPy-AA (B) films. In all cases, the fluence was 43 mJ/cm^2 .

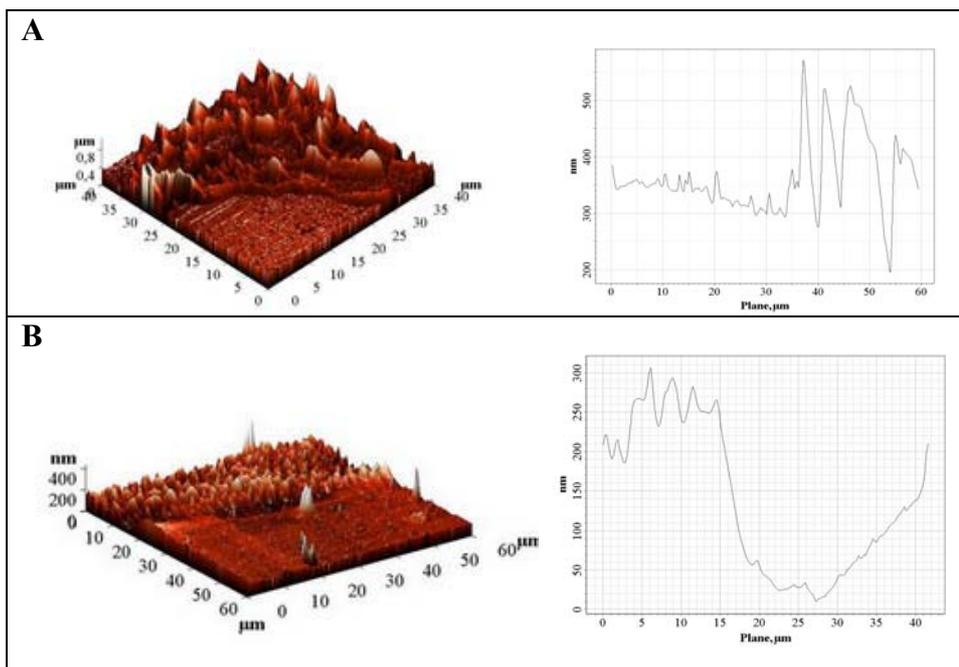


Fig. 6 – 3D AFM images (left side) and height profiles (right side) taken from the exposed/non-exposed edge for P4VPy (A) and P4VPy-AA (B) films after UV radiation and extraction of developing solvent soluble fractions.

We observed a difference regarding the developing of the two P4VPy derivatives. During extraction, P4VPy-AA remained firmly attached to the substrate (glass plate) and no significant swelling of the film could be observed. Contrary,

the film of P4VPy-CA swelled in solvent and slightly corrugated on the substrate.

Due to the limited scan size area, only the edges of the obtained patterns were observed. As Fig. 6 B shows, from cross-sectional analysis of

the scan the thickness of the remained layer of P4VPy-AA is estimated at cca. 300 nm. 2D-AFM image of a 60 × 60 micron area reveals a rather regular surface structure of crosslinked P4VPy-AA. It seems that drying of the film leads to this featured appearance as a result of shrinkage. The boundary between crosslinked and non-exposed areas is quite well delimited.

The loss of adherence to the substrate in the case of extracted P4VPy-CA made the swelled film to corrugate on it. The edges of patterns suffer a severe shrinkage when drying and we failed to put in evidence the boundary between the irradiated and covered areas due to their string-like appearance. The shrunken edges are too high to make a profile analysis.

CONCLUSIONS

Some poly(4-vinylpyridine) derivatives undergo UV-induced solubility changes. In P4VPy-AA, there are two competitive processes during irradiation: dealkylation of the pyridine ring and α H atom abstraction. These are not the major reactions in the case of quaternary salt P4VPy-

CA, where no dealkylation was observed. Quaternary salts of type $>CH-C_3H_4N^+-CH_2-R$ ($R=-CH=CH_2, -C_6H_5$) crosslink through a different mechanism, depending on the structure of the alkylation group. When comparing the photolithographic test of P4VPy with those of P4VPy-AA and P4VPy-CA, the greater crosslinking degree achieved by P4VPy derivatives is noticeable. We may conclude that UV sensitivity was significantly improved by quaternization of the pyridine ring.

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