

Contributions to the photochemistry of poly(4-vinylpyridine) and its ionic derivatives in the presence of water

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ABSTRACT

Films of poly(4-vinylpyridine), poly(N-carboxyethyl-4-vinylpyridine) and poly(N-allyl-4-vinylpyridine) chloride were exposed at a radiation spreading between about 250 and 270 nm, and the photochemical processes were monitored by spectroscopic methods. Reaction mechanisms considering: (i) a double role of the water molecule, to form water–pyridine ring hydrogen bonds and to accept hydrogen atoms, (ii) the scission of C–H methine bonds in units with photoexcited pyridine rings, (iii) the scission of N⁺–C bonds in betaine units, and (iv) crosslinks appearing by recombination of carbon macroradicals or by the addition of methine groups to allyl groups, were found to explain the photocrosslinking of the three polymers. Their properties of crosslinking photoresists were observed by AFM and the best ones were found for the polymer with N-allyl-pyridinium chloride units.

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1. Introduction

It is known that poly(4-vinylpyridine) (P4VPy) has got interesting photochemical properties due to the lone pair of sp² electrons on the heterocycle nitrogen atom. For example, thin films of this polymer have been crosslinked by UV irradiation to obtain microtubes by photolithographic patterning [1] or pH stimuli responsive coatings [2] or for immobilization of nanoparticles [3]. Also, some characteristics of electron beam resists have been reported [4–6]. Moreover, it has been found that the sensitivity to UV radiation and to electron beam of P4VPy increases importantly by nitrogen atom quaternization, and an explanation of such effects based on the labilization of the backbone methine C–H bond due to a strong inductive force exerted by the pyridinium cation has been advanced [4–6].

Much attention has been given to the photochemistry of pyridine [7] and P4VPy [8,9] N-oxide derivatives where it has been established that the UV irradiation generates macroradicals by N–O bond cleavage.

In the last few years, Nishiyama et al. investigated how the UV absorption and fluorescence spectra of some P4VPy derivatives are affected by exposure to 254 and 365 nm radiations [10–13].

As a momentary observation about the photocrosslinking of P4VPy and its derivatives is that the reaction mechanism based

on the cleavage of methine C–H bonds is chemically correct but its experimental support is rather poor.

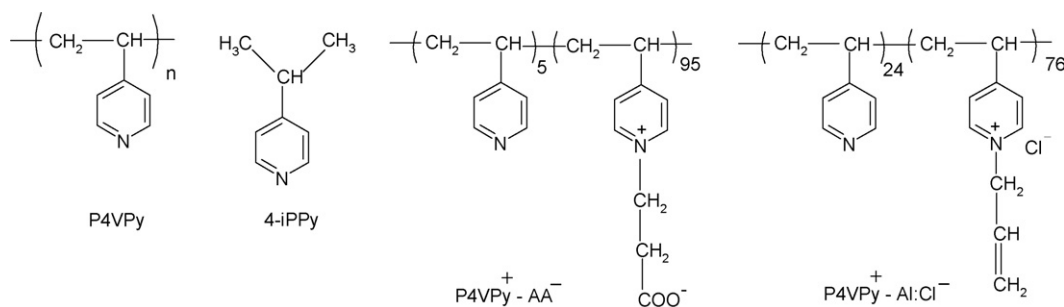
This paper presents a comparative study of the photochemical behavior of P4VPy and two of its ionic derivatives, poly(N-carboxyethyl-4-vinylpyridine) (P4VPy⁺-AA⁻) and poly(N-allyl-4-vinylpyridine) chloride (P4VPy⁺-Al:Cl⁻), under UV radiation, the aim being a better understanding of crosslinking process and a testing of photoresist properties. The identification of 4-isopropylpyridine (4-iPPy) photoproducts was used to formulate reaction mechanisms for 4-iPPy and P4VPy.

2. Experimental

2.1. Materials

4-iPPy, from Aldrich, was distilled before use. P4VPy ($\bar{M}_w = 160\,000$), also from Aldrich, was used after purification by reprecipitation from methanol in diethyl ether. P4VPy⁺-AA⁻ and P4VPy⁺-Al:Cl⁻ were prepared by reacting P4VPy with acrylic acid (AA) and allyl chloride (AC), respectively, by a procedure described elsewhere [14]. The quaternization degree was determined from ¹H NMR spectra and found 95 ± 3% for P4VPy⁺-AA⁻ and 76 ± 5% for P4VPy⁺-Al:Cl⁻. The following signals were used: the chain CH₂CH signal (1–2.8 ppm) for the total number of mers, and the signals N⁺-CH₂ (4.9 ppm) and N⁺-CH₂-CH=CH₂ (5.11, 5.48 and 6.09 ppm) for the number of modified mers of P4VPy⁺-AA⁻ and P4VPy⁺-Al:Cl⁻, respectively. The chemical structures of the studied systems are presented in Scheme 1.

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Scheme 1. Chemical structure of the studied compounds.

2.2. Characterization of reactants and products

UV-vis, IR, NMR and MS (mass spectra) were recorded with Analytik Jena Specord 200 UV-Visible, Bruker Vertex 70 FT-IR, Bruker Advance DRX 400 NMR and Agilent 6520 spectrometers, respectively. The mass spectrometer (MS) was used in ESI-QTOF (Electrospray Ionization Quadrupole-Time of Flight) mode with positive ionization by protonation.

The UV absorption spectra of the polymeric materials were obtained from thin films deposited on fused silica plates by using 5 mg/ml chloroform (for P4VPy) and methanol (for ionic polymers) solutions. The FT-IR spectra of polymers were obtained also from thin films, but coated on KRS-5 crystals. The films were finally dried in a vacuum oven at 5–8 mmHg and 80–90 °C for 3 h. The IR absorption signals of interest were resolved into individual Gaussian-Lorentzian components by using OPUS 5.5 software (Bruker Optiks GmbH). Crosslinked films were measured in ATR geometry by using a Specac Golden Gate[®] device.

4-iPPy: ¹H NMR (400 MHz, δ , ppm): in DMSO-*d*₆: 1.210 (doublet, 6H), 2.892 (septet, 1H), 7.275 (quasidoublet, 2H, aromatic), and 8.463 (quasidoublet, 2H, aromatic), and in CDCl₃: 1.255 (doublet, 6H), 2.881 (septet, 1H), 7.142 (quasidoublet, 2H) and 8.482 (quasidoublet, 2H). FT-IR (neat, cm⁻¹): 1599, 1556, 1493, 1414 (C=C/N stretching), 1220 (C–H in-plane bending), 993 (ring breathing mode), 821 (radial skeletal vibration). UV-vis (CH₂Cl₂, nm): 246 (sh), 254 ($\pi\pi^*$), 260 (sh, $n\pi^*$).

P4VPy: ¹H NMR (400 MHz, CD₃OD, δ , ppm): 1.5–2.5 (broad signals, 3H, backbone protons), 6.9 (broad signal, 2H, aromatic) and 8.3 (broad signal, 2H, aromatic). FT-IR (film, cm⁻¹): 1597, 1557, 1493, 1415 (C=C/N stretching), 1221 (C–H in-plane bending), 993 (ring breathing mode), 820 (radial skeletal vibration). UV-vis (film, nm): 257 ($\pi\pi^*$), 263 (sh, $n\pi^*$).

P4VPy⁺-AA⁻: ¹H NMR (400 MHz, CD₃OD, δ , ppm): 1.7–2.7 (broad signals, 3H, backbone protons), 3.0 (CH₂COO⁻), 4.9 (N⁺CH₂), 7.35 (2H, Py⁺) and 8.6 (2H, Py⁺). FT-IR (film, cm⁻¹): 1642 (C₅H₄N⁺), 1587 (antisym. COO⁻), 1394 (sym. COO⁻). UV-vis (film, nm): 230 (Py⁺, $\pi\pi^*$), 259 (Py, $\pi\pi^*$).

P4VPy⁺-Al:Cl⁻: ¹H NMR (400 MHz, CD₃OD, δ , ppm): 1.5–2.9 (broad signals, 3H, backbone protons), 5.11 (2H, allyl), 5.48 (s, 2H, allyl), 6.09 (1H, allyl), 6.79 (2H, Py), 7.6–7.8 (2H, Py⁺), 8.10 (2H, Py) and 8.6 (2H, Py⁺). FT-IR (film, cm⁻¹): 1645 (sh, C=C), 1638 (C₅H₄N⁺). UV-vis (film, nm): 232 (Py⁺, $\pi\pi^*$), 260 (Py, $\pi\pi^*$).

2.3. Sample irradiation

A radiation consisting of the mercury emission lines at 254 and 265 nm was used. This radiation was obtained with an intensity of about 2.5 W/m² from a 350 W medium pressure mercury lamp and an interference filter with the peak wavelength at 260 nm and band width of 20 nm, the two pieces being mounted in a LOS-2 irradiation unit (Russian Academy made). Such a radiation is rather

well matched on the absorptions near 260 nm of the four systems studied.

4-iPPy was irradiated in two situations: as pure liquid and as a miscible mixture with 4% water. A 1 mm quartz cell was used. The photoproduct was a mixture of moist crystals that was isolated by removing unreacted pyridine under vacuum at 5–8 mmHg and 80–90 °C. A quantity of about 11 mg product (3% conversion) resulted for 12 h irradiation. The 4-iPPy photoproduct was analyzed by ¹H NMR, FT-IR, HPLC and MS methods. A C-18 column with hydrophobic adsorption and water/acetonitrile eluent were used for HPLC.

For the polymer samples, the radiation effects were monitored by means of UV and/or FT-IR spectra recorded after various irradiation times. Some irradiated films were also analyzed after the soluble fraction was removed by extraction with methanol. The photooxidation was avoided by inserting the film samples in a cell with fused silica windows and nitrogen inside, but no special drying techniques were used, hence samples had various moisture contents.

2.4. Photopatterning and surface analysis

Films deposited on optical glass plates were used. The negative type photopatterning procedure consisted of the irradiation of film through a mask with regular hexagonal openings (150 μ m), followed by the removal of soluble material by proper dissolution. The substrates were cleaned before use by washing successively with piranha solution and double-distilled and deionized water. Films of about 0.5 micron thickness were obtained by spin-coating with a WS-400A-6NPP/Lite Laurell processor at 3000 rpm for 1 min, from 10 mg/ml polymer solutions in chloroform for P4VPy, and in methanol for P4VPy⁺-AA⁻ and P4VPy⁺-Al:Cl⁻. AFM measurements were performed in air at room temperature using a Solver PRO-M NT-MDT (Russian Federation) setup. NSG10/Au Silicon cantilevers with 10 nm tip radius and the semicontact mode with 243.714 kHz cantilever oscillating frequency and 11.5 N/m constant force were used.

3. Results and discussions

3.1. Radiation effects in P4VPy films

P4VPy shows a complex UV absorption band, composed of a peak at 257 nm assigned to the S₂($\pi\pi^*$) ← S₀ transition and a shoulder at about 263 nm, attributed to S₁($n\pi^*$) ← S₀ transition, the two types of transitions originating in the pyridine ring electronic energies [15,16]. The radiation used excites well the two transitions. Its effects are illustrated in Fig. 1 by the difference UV spectra obtained after some irradiation times. One observes a small absorbance increase of the band at 257 nm as well as the rising of two very weak absorption bands whose positions blue-shift with the irradiation time. These effects are slightly different from those observed by

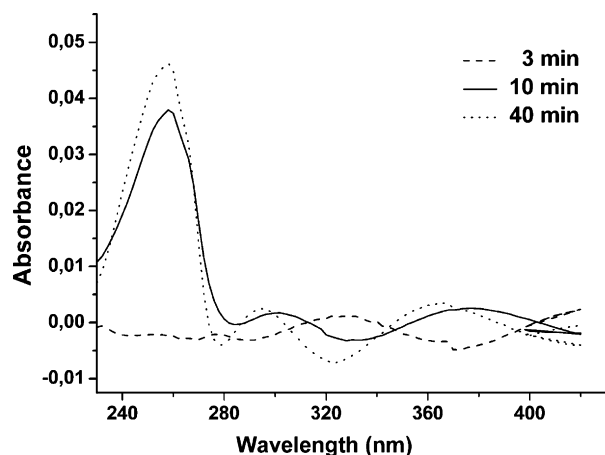


Fig. 1. Difference UV spectra ($A_t - A_0$) of a P4VPy film for three irradiation times.

Nishiyama et al. [13,17], namely no changes for the band at 257 nm and the appearance of new absorptions at 300 and 390 nm. An explanation that the effects observed by us are stronger is that we used higher irradiation doses. However, the absorbance enhancement at 257 nm has been reported in the literature [18–20] for pyridine and dialkyl pyridines and was assigned to the pyridine ring protonation.

By comparing the FT-IR spectra of irradiated and non-irradiated films (Fig. 2A), one observed that, except the rising of broad bands at 3400 and 1680 cm^{-1} , the irradiation does not produce significant changes. However, the spectrum of the insoluble fraction (Fig. 2B), where the concentration of chemical structures induced by irradiation is obviously higher than in the unextracted film, shows clear changes for the C–H stretching bands (2800–3100 cm^{-1}) in addition of the two new absorptions, especially for those belonging to the pyridine ring. It is worth mentioning that the film samples are hygroscopic regardless if they are or not irradiated. It is to be mentioned at this point that Rozenberg et al. [21] have also evidenced the new absorption at 3400 cm^{-1} , but their difference spectra do not show visible changes in the range from 2800 to 3100 cm^{-1} . The only difference between our and their experiments is that they used highly dried P4VPy films while our sample shows a weak absorption at 3400 cm^{-1} even before irradiation (Fig. 2A). This absorption intensifies in both our and their experiments, perhaps due to the humidity absorbed before and after irradiation.

3.2. Photolysis of 4-iPPy and reaction mechanism proposed for P4VPy photocrosslinking

A first observation of interest was that the quantum yield for the relatively dry reactant is much lower than that for a 4-iPPy + 4% H_2O miscible mixture. The quantity of 10–12 mg product obtained in the second case was rather sufficient to try identification of the main components. The experiment with moistened 4-iPPy was inspired by the fact that the “dry” P4VPy still contains about 6% water (NMR determined). Also, the films obtained from this polymer show a weak absorption at 3400 cm^{-1} , and this absorption was found increased during and/or after irradiation (Fig. 2). The reaction mixture remaining after the evaporation of unreacted 4-iPPy was completely soluble in DMSO and partially soluble in water and chloroform. Its ^1H NMR spectrum in DMSO shows mainly four singlet signals for the methyl group, at 1.25, 1.42, 1.47 and 1.51 ppm and with the relative intensities 9:32:54:4, as well as pairs of quasi-doublets for the pyridine ring protons associated to the methyl signals, at 7.07/8.41, 7.44/8.48, 7.41/8.52 and 4.41–7.44/8.56 ppm. The spectrum contains also two OH signals, one at 11.3 ppm and the other at 5.3 ppm, which are distinct from the water trace signal

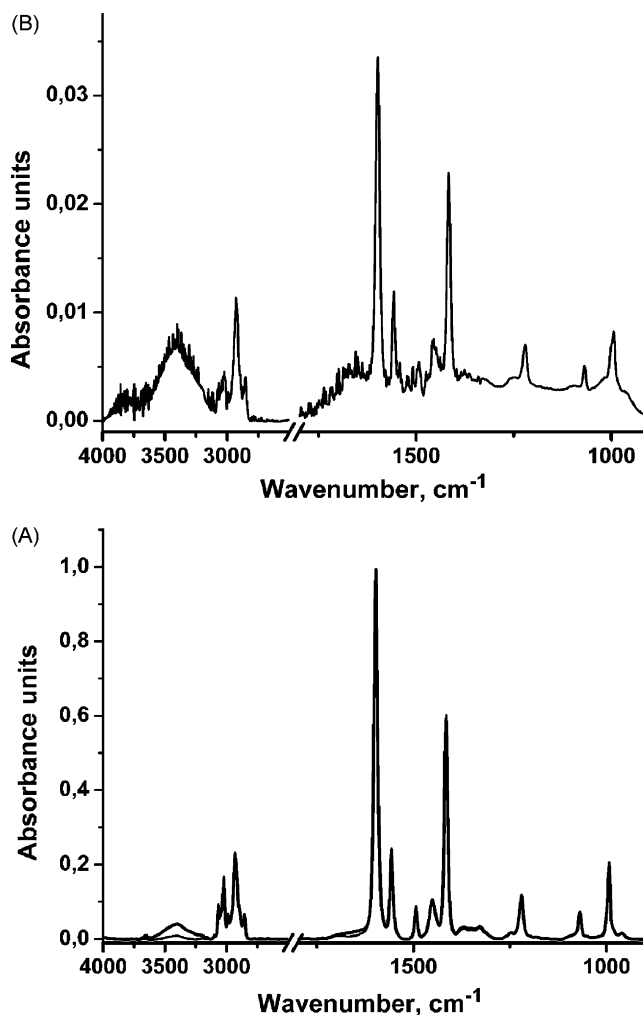


Fig. 2. FT-IR spectra of P4VPy film in the following situations: A—before (thin line) and after 200 min irradiation in nitrogen (thick line) and B—after irradiation and extraction of the chloroform soluble fraction.

that is located at 3.25 ppm. The singlet form of the methyl signals shows that the methine hydrogen atom of isopropyl groups is substituted, therefore the molecules resulting by the irradiation of 4-iPPy in the presence of water are built up with $\text{PyC}(\text{CH}_3)_2$ fragments. The FT-IR–ATR spectrum of the total photoproduct (Fig. 3) is also much different from that of 4-iPPy. Hydrogen bonding of the type $\text{O}-\text{H} \cdots \text{N}$ produces shifting of the $\text{C}=\text{C}/\text{C}=\text{N}$ stretching vibration, ν_{8a} , from 1599 to 1604 cm^{-1} , as well as the appearance of the intense broad band centered at 2766 cm^{-1} , with several maxima. In addition, the ring breathing mode shifts from 993 cm^{-1} (for neutral pyridine ring) to 1003 cm^{-1} . The characteristic vibrations of CH group from isopropyl moiety, positioned at 2892 cm^{-1} (stretching) and 1310 cm^{-1} (bending), are absent in the FT-IR spectrum of the photoproduct, and a very intense band attributed to dimethyl quaternary carbon skeletal vibration could be seen as a double peak at 1173 and 1163 cm^{-1} .

Other useful information was obtained from HPLC and MS analyses. The chromatogram in a 1:1 water: acetonitrile mixture showed a high peak from the most hydrophilic components and some weak peaks from the less hydrophilic ones (Fig. 4). More, the strong peak is split into two peaks in a 7:3 water: acetonitrile mixture. Taking into account the NMR and HPLC data, as well as the MS information, the compounds **A** (2,3-dimethyl-2,3-di(4-pyridyl)butane), **B** (2-(4-pyridyl)-2-propanol) and **C** (4,4'-(2,2'-dioxybis(propane-2,2-

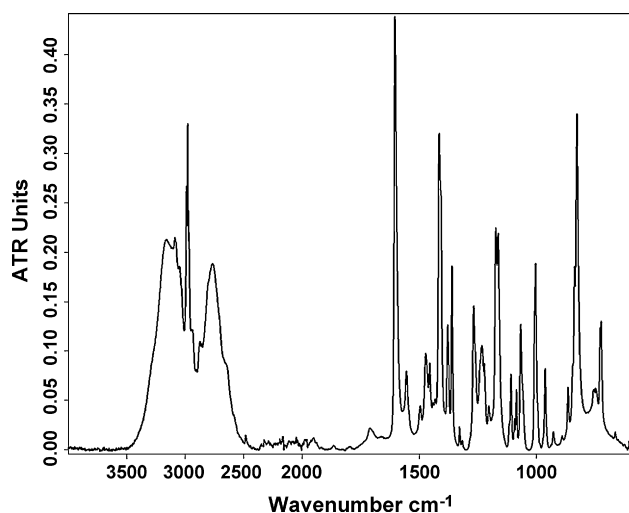


Fig. 3. FT-IR spectrum of the total 4-iPPy photoproduct.

diyl)dipyridine) in Scheme 2 would be the main three components of the global product. The alcoholic and etheric components may be considered more hydrophilic than **A**, and the methyl chemical shifts would be assigned as follows: 1.25 ppm for **A**, 1.42 ppm for **C**, and 1.47 ppm for **B**, but an inverse assignment may be also valid between **B** and **C**. A zwitterionic structure, $-\text{C}(\text{CH}_3)_2-\text{C}_5\text{H}_5\text{N}^+$, as Rozenberg et al. [21] suggested for P4VPy irradiated in absence of water, is mainly infirmed here by the methyl chemical shift, which must have been smaller than that of 4-iPPy (1.21 ppm).

The MS peaks (Fig. 5) supporting the chemical structures in Scheme 2 are the following: $m/z = 257$ for monoprotonated **C** ether, $m/z = 241$ for monoprotonated **A** dimer, $m/z = 138$ for monopro-

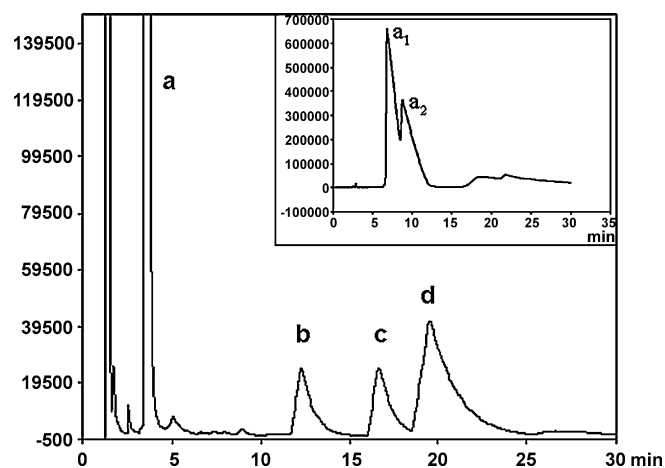
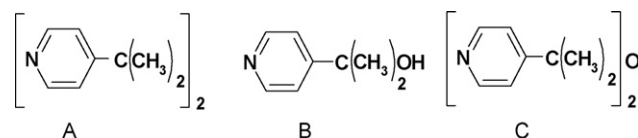


Fig. 4. HPLC chromatogram of the total 4-iPPy photoproduct with 1/1 water/acetonitrile eluent. Inset: the peak "a" for 7/3 water/acetonitrile eluent. Peak area ratios: $a_1:a_2:b:c:d = 44:32:4:5:15$.



Scheme 2. Predominant photolysis products of 4-iPPy with traces of water.

nated **B** alcohol, $m/z = 129$ for diprotonated **C** ether and $m/z = 121$ for diprotonated **A** dimer.

The hydrophilicity is not only due to the hydroxyl and ether groups but also to the pyridine ring. The affinity of pyridine to water

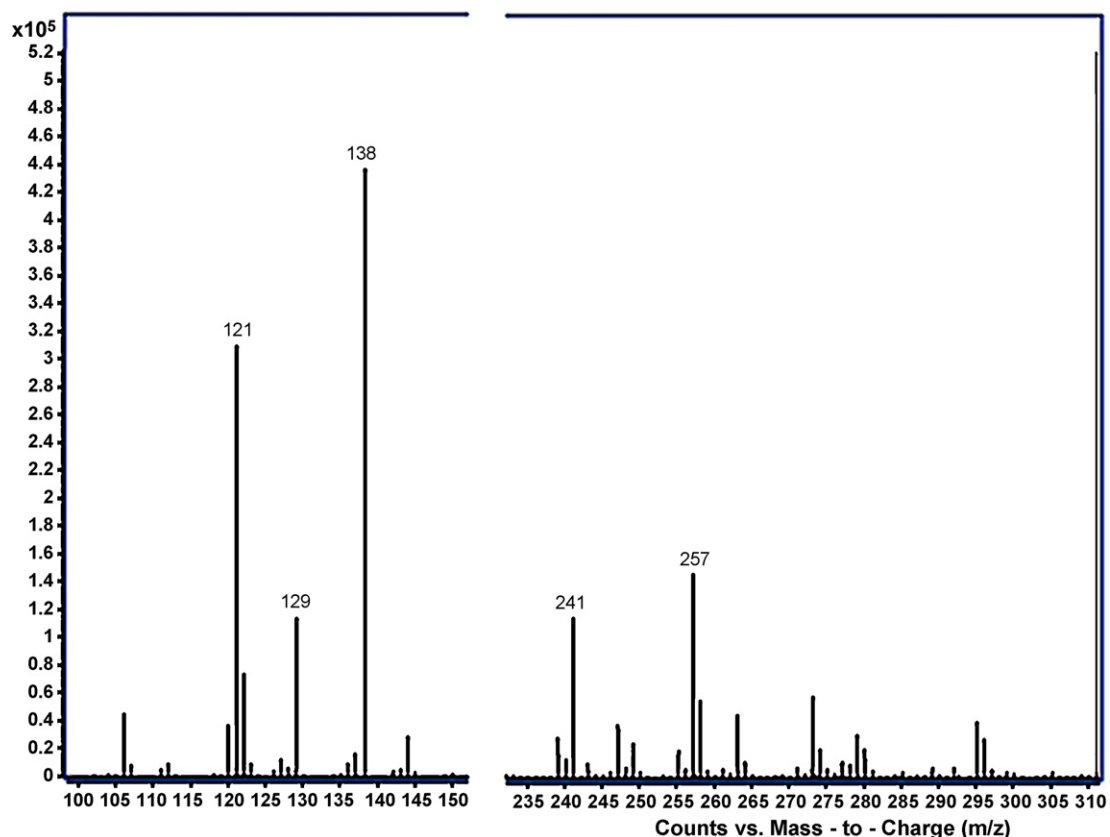
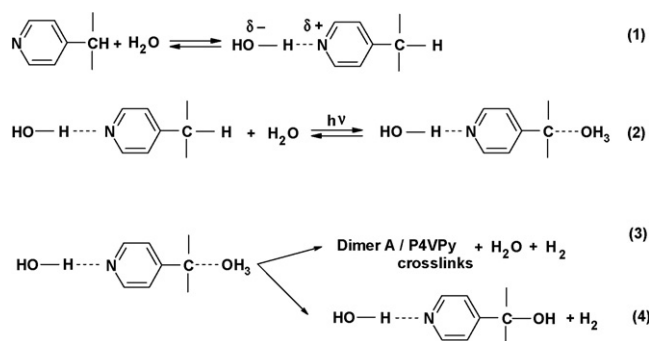


Fig. 5. ESI-QTOF mass spectrum of the total 4-iPPy photoproduct.



Scheme 3. Reaction mechanism proposed for 4-iPPy photodimerization and P4VPy photocrosslinking, as well as for formation of alcoholic products.

has been frequently mentioned in the literature either by reactions of photoexcited pyridines (Dewar form) with water [22], where the products are stable only at low temperature, or by theoretical deductions about hydrogen bonding pyridine–water complexes [23] and excited pyridine–water clusters [24]. Also, the intramolecular hydrogen atom abstraction by the nitrogen atom has been evidenced [25].

The water promoted reactions which would lead to the products **A** and **B**, for 4-iPPy, and to branching and crosslinks for P4VPy, are given in Scheme 3. As seen, we propose a weak positive charging of the pyridine ring due to the hydrogen bonding with a water molecule (Eq. (1)). On the other hand, it is considered in the literature that the basicity of the photoexcited pyridine ring is higher than that corresponding to the ground state [26,27] and that the positive charging of pyridine ring loosens the α -methine C–H bond [4–6,28]. The homoscission of this bond would take place in the photoexcited state of the pyridine ring and due to a second water molecule as hydrogen atom acceptor, the appearing hydronium and isopropyl pyridine radicals are building a cluster (Eq. (2)). The reaction between such clusters explains the formation of **A** dimers, for 4-iPPy, and of crosslinks for P4VPy (Eq. (3)). This photocrosslinking mechanism is inspired from that for polystyrene, which has been confirmed by the identification of hydrogen as the only gaseous product [29] and proved that it is not significantly affected by oxidation [30]. The appearance of the alcohol structure could be explained by reaction 4, where the hydronium radical $\cdot\text{OH}_3$ [31] changes to a hydroxyl radical by eliminating one hydrogen molecule.

If it is not a simple assumption, the presence of etheric component in the 4-iPPy photoproduct would suggest another crosslinking reaction. However, the appearance of such species cannot be explained by observations made up to now.

3.3. Behavior of P4VPy⁺-AA⁻ under UV radiation and reaction mechanism of photocrosslinking

Like its parent polymer, the polycarboxybetaine P4VPy⁺-AA⁻ was studied as thin solid films. The following findings were made on the effects of UV irradiation: (i) an important insoluble fraction resulted when the irradiation time was longer than about 30 min and (ii) the FT-IR and UV spectra show a relatively rapid transformation of 4VPy⁺-AA⁻ zwitterionic units to 4VPy units.

FT-IR spectra of P4VPy⁺-AA⁻ recorded before and after 50 min irradiation are presented for comparison in Fig. 6. One observes that the disappearance of the pyridinium cation band at 1642 cm⁻¹ is accompanied by the appearance of the characteristic absorptions of neutral P4VPy, those at 1597, 1557, 1493, 1221 and 993 being easily visible (see the P4VPy spectrum in Fig. 2A). These significant changes can be explained only by the photocission of N⁺-CH₂ bonds. It is to be mentioned that the FT-IR spectra of the

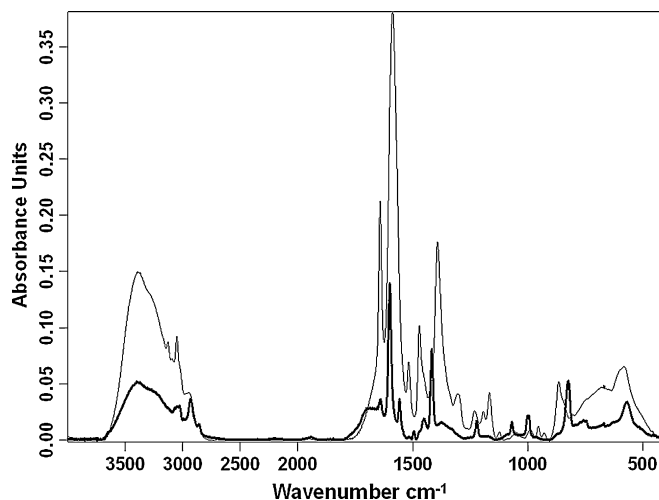


Fig. 6. FT-IR spectra of P4VPy⁺-AA⁻ recorded before (thin line) and after 50 min irradiation time (thick line).

50 min irradiated film and of its methanol insoluble fraction are practically identical. The absence of significant absorptions from COO⁻ and/or COOH carbonyl bands might be unexpected. A plausible explanation may be the fact that the molecules of acrylic acid leave the irradiated film when they appear because the interactions pyridine–acid are too weak to hold them inside. Nevertheless, the broad band that appeared in the region 1800–1600 cm⁻¹ may arise from both traces of carboxyl products and water.

An estimation of the degree of N-dealkylation can be made with the equation:

$$\gamma = \frac{A_{1597}}{A_{1597} + \varepsilon' \cdot A_{1642}}$$

where A_{1642} and A_{1597} are the integrated absorbances corresponding to quaternized and free pyridine rings bands, respectively, determined by curve-fitting procedure of the bands in the region 1800–1450 cm⁻¹. The ratio of molar absorption coefficients, $\varepsilon' = \varepsilon_{1597}/\varepsilon_{1642}$ has the value 0.595 [32]. The irradiation time dependence of γ for the experimental parameters used in our study is given in Fig. 7. The band at 1450 cm⁻¹ arising from a planar deformation vibration of CH₂ groups of the backbone was used for the normalization of spectra and the band fitting was performed using a Gauss–Lorentz mixed function. One observes in Fig. 7 that N-dealkylation of pyridinium rings is nearly complete after about

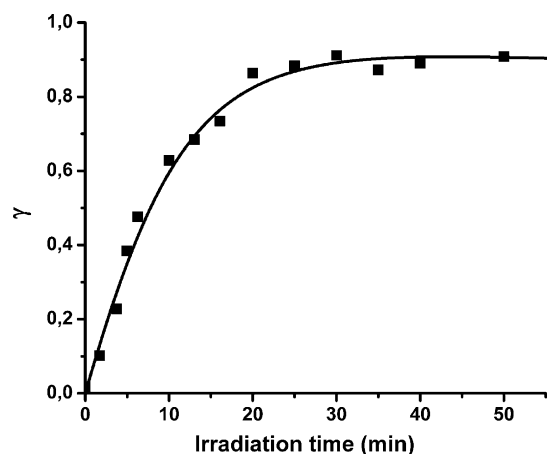


Fig. 7. Pyridinium to pyridine conversion, γ , against the exposure time for P4VPy⁺-AA⁻.

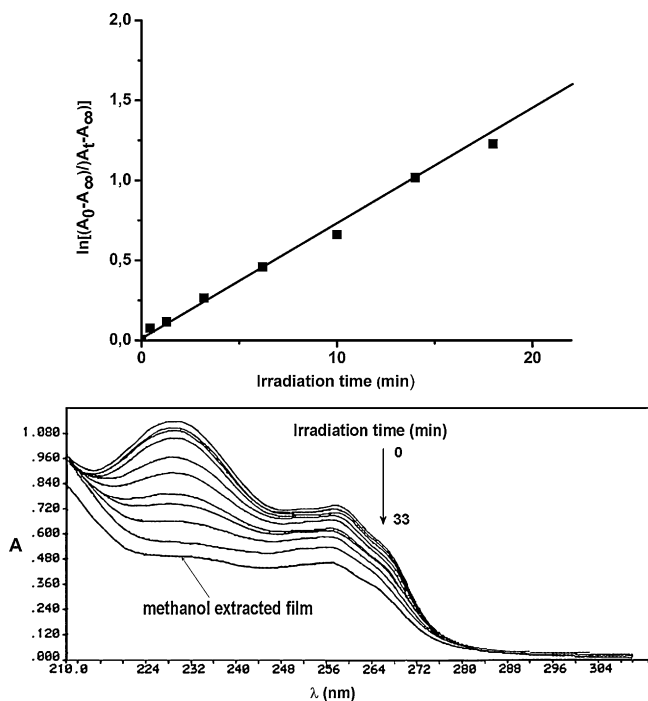


Fig. 8. UV absorption spectra of a P4VPy⁺-AA⁻ film recorded after different irradiation times. The spectrum with thick line belongs to the film irradiated for 30 min and then extracted with methanol. The upper plot is a data processing according to a first-order kinetic applied to the absorbance at 232 nm.

30 min of irradiation, the fact that the plateau is at about $\gamma = 0.9$ being due to the peak area measuring errors.

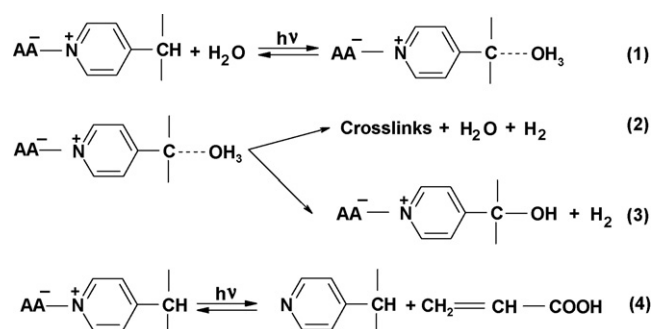
The pyridinium N-dealkylation can be also monitored qualitatively in the ring breathing mode region, between 970 and 1010 cm^{-1} , where three absorption bands can be considered: one at 993 cm^{-1} of the neutral pyridine ring [32–34], another one at 1003 cm^{-1} from pyridine rings involved in H-bonding and polar interactions [19] and the third at 982 cm^{-1} .

The evolution of the effect induced by UV irradiation on P4VPy⁺-AA⁻ can be also monitored in the electronic absorption spectra. One observes in Fig. 8 that the absorption band at 232 nm, which is assigned to $\pi \rightarrow \pi^*$ transitions of the pyridinium cation, decreases when the exposure time increases. Moreover, the first-order rate equation:

$$\ln \left(\frac{A_0 - A_\infty}{A_t - A_\infty} \right) = k \cdot t,$$

where A_0 , A_t and A_∞ are the absorbance values measured before irradiation, after an irradiation time t , and after an infinite irradiation time, respectively, is followed well up to about 30 min irradiation time. This means that although a steady state spectrum is reached after longer irradiation times, the photocleavage of N⁺-CH₂ bonds is the predominant reaction for exposure times shorter than about 20 min. The rate constant, k , was found to be equal to $1.2 \times 10^{-3} \text{ s}^{-1}$ for the experimental parameters used.

Different irradiation effects on P4VPy⁺-AA⁻ relative to P4VPy are presented in Scheme 4. An important difference is the fact that the pyridine ring is truly protonated, hence the lability of the methine C-H bond is higher. Moreover, the irradiation produces two reactions with contrary effects on the photocrosslinking: (i) a more efficient scission of the methine C-H bond (Eq. (1)) followed by parallel crosslinking reactions (Eq. (2)) and hydroxyl group formation (Eq. (3)), and (ii) the pyridinium N-dealkylation (Eq. (4)). Of course, the excitation of the appearing neutral pyridine rings would determine the reactions characteristic to P4VPy in Scheme 3.



Scheme 4. UV radiation induced reactions explaining dealkylation and insolubilization of P4VPy⁺-AA⁻.

3.4. Behavior of P4VPy⁺-Al:Cl⁻

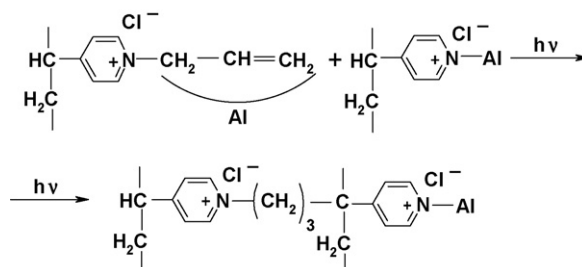
Unlike P4VPy⁺-AA⁻, the FT-IR and UV-vis spectra of P4VPy⁺-Al:Cl⁻ do not show significant changes induced by irradiation, even for irradiation times longer than 30 min. Nevertheless, the polymer became partially insoluble in methanol and water. For example, an insoluble film obtained after the extraction with methanol of a 30 min irradiated film had the absorbance at 232 nm diminished about two times. These findings lead to the idea that the cleavage of pyridinium N⁺-CH₂ bond is not a significant photoreaction and, therefore, the photocrosslinking of P4VPy⁺-Al:Cl⁻ takes place according with reactions 1–2 in Scheme 4. Thus, the crosslinking sensitivity of the three polymers would increase in the following order: P4VPy < P4VPy⁺-AA⁻ < P4VPy⁺-Al:Cl⁻.

On the other hand, an additional photocrosslinking mechanism for P4VPy⁺-Al:Cl⁻ by the addition of methine groups of photoexcited quaternized units to allyl groups (Scheme 5) must be considered. Indication of this reaction is the presence of a small signal at 4.6 ppm in the ¹H NMR spectra of gellified samples that can be assigned to N⁺-CH₂ groups in crosslinks. Another argument for the participation of allyl groups in the photocrosslinking process is the fact that, for similar irradiation conditions, we found that the insoluble fraction resulting from films of P4VPy quaternized with benzyl chloride is much less than that of P4VPy⁺-Al:Cl⁻.

3.5. Testing characteristics of crosslinking photoresist

Films of 0.4–0.6 μm thickness deposited on optical glass plates were irradiated 30 min through mask. The soluble fractions were removed by immersion in methanol for about 30 min at room temperature. After a rinsing with water and drying at 60–70 °C under low vacuum, the layers remaining on substrates were examined by AFM method.

3D AFM images and height profiles taken at the edge between exposed and non-exposed zones are presented in Fig. 9 for the three polymers.



Scheme 5. Photocrosslinking of P4VPy⁺-Al:Cl⁻ with allyl group participation.

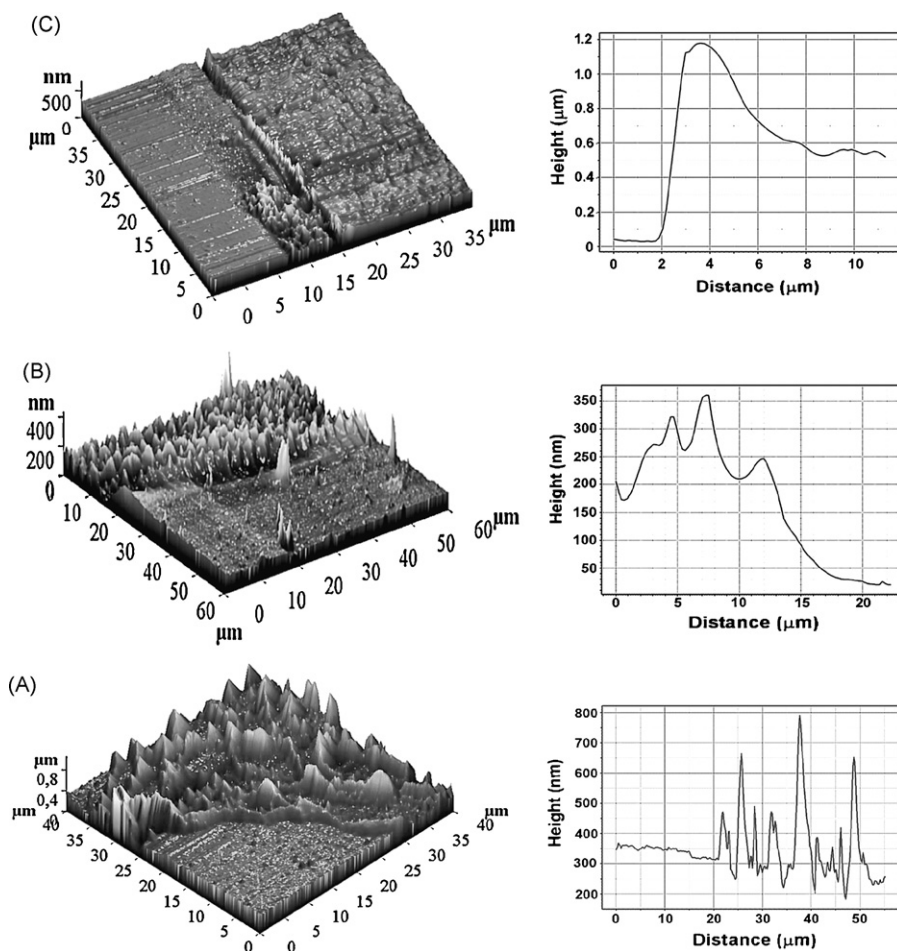


Fig. 9. 3D AFM images (left side) and height profiles (right side) taken from the exposed/no exposed edge for P4VPy (A), P4VPy⁺-AA⁻ (B) and (P4VPy⁺-Al:Cl⁻) (C) films after UV radiation and extraction of methanol soluble fractions.

One observes that the surface topography differs from one polymer to the other as follows: (i) a highly non-uniform surface, with irregular hills isolated between them by very deep and wide valleys for P4VPy, (ii) small and dense hills for P4VPy⁺-AA⁻, and (iii) a relatively smooth surface in the case of P4VPy⁺-Al:Cl⁻. We consider that the last polymer behaves the best even if some shrinkage is visible in the image (probably due to polymer–substrate adhesion).

Taken into consideration the average profile height, the ionic polymers P4VPy⁺-AA⁻ and P4VPy⁺-Al:Cl⁻ show a rather similar photosensitivity.

4. Conclusion

Macroscopically, P4VPy and its ionic derivatives, P4VPy⁺-AA⁻ and P4VPy⁺-Al:Cl⁻, behave as negative photoresists showing insolubilization when are exposed to 250–270 nm radiation, the smoothest surface being obtained from the last polymer.

The main reactions and effects induced by the photoexcitation of pyridine rings in the presence of water are the followings: (i) scission of α -methine C–H bonds, where the water molecule would be the acceptor of hydrogen atom, (ii) chain crosslinking by recombination of macroradicals resulted from C–H bond scissions, (iii) photoscission of N⁺–CH₂ bonds with high probability for P4VPy⁺-AA⁻ and with low probability for P4VPy⁺-Al:Cl⁻, (iv) an additional crosslinking of P4VPy⁺-Al:Cl⁻ due to the addition of methine group in excited units to allyl carbon-carbon double bonds, and (v) appearance of pendant hydroxyl groups.

The experiments carried out with moist 4-iPPy were useful especially for the elucidation of photoinduced P4VPy reactions.

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