

Research Article

Writing in a Polyaniline Film with Laser Beam and Stability of the Record: A Raman Spectroscopy Study

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Lines were drawn on polyaniline (PANI) salt films with laser beam, and then the samples were left to age in air at room temperature. Both the irradiated and intact parts of the sample and their ageing were studied with Raman spectroscopy. It was found that the laser-written record is reasonably stable. The degradation of polyaniline by laser irradiation and ageing was compared to the changes in PANI during heating. In all cases, deprotonation and crosslinking of PANI chains proceed but the relative rates of the processes vary with degradation conditions.

1. Introduction

Conducting polymers, such as polyaniline (PANI), are widely studied due to their ease of preparation, good level of electrical conductivity, redox and ion-exchange properties, and environmental stability [1–8]. However, the understanding of the stability and the mechanism of degradation of polyaniline is of great importance for possible applications [9–13].

When PANI salt is exposed to elevated temperature, the changes at the molecular level manifest themselves by the loss of doping acid molecules and formation of phenazine-like or quinonoid segments [9]. Besides the chemical changes, conformation is changed by thermal treatment [14]. This feature is an inherent property of PANI and is not influenced by the nature of the protonating acid. Similar processes take place in PANI salt during ageing at room temperature [15, 16].

The changes in the molecular structure of PANI which occur during heating can be conveniently observed by Raman spectroscopy [17–19]. When the excitation laser line falls within the region of a permitted electronic transition of the sample, the Raman intensities associated with vibrational modes coupled with the excited electronic states can be markedly increased due to a resonance effect. The Raman features of semiquinone radical structures typical for protonated emeraldine salt are enhanced by near-infrared excitation; in

contrast, the Raman features of quinonoid units typical for the PANI base are enhanced with a red excitation line [20].

PANI strongly absorbs in the Vis-NIR region; thus, the samples can be locally heated by the irradiation. Deprotonation, degradation, and possible carbonization may occur during Raman spectrum recording [21, 22]. These degradation ways—ageing, heating, and laser irradiation—do have similar effects on PANI [9, 21, 22], but this has not been directly compared.

The possibility to locally deprotonate a PANI film with laser beam opens an interesting opportunity for organic electronics. Conducting paths of PANI salt films can be separated by lines of the deprotonated PANI base. In this work, the writing on a PANI film with laser beam and ageing of the record are studied. Raman spectra of chemically and thermally deprotonated PANI films are compared with the PANI film after laser irradiation and ageing in air.

2. Materials and Methods

2.1. Preparation of PANI Films. Polyaniline was prepared by the oxidation of 0.2 M aniline hydrochloride (Fluka, Switzerland) with 0.25 M ammonium peroxydisulfate (APS) (Lach-Ner, Czech Republic) in water [23] at room temperature. The films were deposited *in situ* on glass and gold-coated glass windows, 13 mm in diameter. A couple of films

was deprotonated with an excess of 1 M ammonium hydroxide to the PANI base. The films were then rinsed with acetone and dried in air.

2.2. Heating. PANI films were heated in ceramic oven in a nitrogen atmosphere (thermal degradation). The heating was switched on, and the temperature was increased at $22^{\circ}\text{C}\cdot\text{min}^{-1}$. After 100°C was reached, the heating was switched off and the sample was left to cool, still in the flowing nitrogen stream.

2.3. Ageing. PANI films were left in air at room temperature and analysed at selected times up to two months.

2.4. Laser Irradiation. Lines were drawn on PANI-S films with 1064 nm excitation laser of the Thermo Nicolet 6700 FTIR spectrometer with a silicon-coated calcium fluoride beam splitter and NXR FT-Raman module with a microscope accessory by simply moving the sample stage of the microscope continuously at two different speeds while simultaneously observing in white light and irradiating with the laser. Laser degradation was also induced by 514 nm and 633 nm excitation lasers of various powers by irradiation of separated spots.

2.5. Spectroscopic Characterization. Raman spectra excited in the visible range with a HeNe 633 and Ar-ion 514 nm laser were collected on the Renishaw inVia Reflex Raman spectroscope. The research-grade Leica DM LM micrometer with an objective magnification of $\times 50$ was used to focus the laser beam on the sample placed on an X-Y motorized sample stage. The scattered light was analyzed by the spectrograph with a holographic grating with 1800 or 2400 lines mm^{-1} . A Peltier-cooled CCD detector (576×384 pixels) registered the dispersed light.

3. Results and Discussion

3.1. Raman Spectra of Intact PANI-S Films. The Raman spectrum of PANI hydrochloride films was measured with 514, 633, and 785 nm excitation lines (Figure 1). It is expected that the vibrations originating from quinonoid units should be resonance enhanced with a laser excitation wavelength at 633 nm [24, 25]; however, these structures are present in the PANI-S only in a very low content and their features are not observed in the spectrum. On the other hand, the typical bands of PANI-S, mainly at 1595, 1504, 1335, and 1182 cm^{-1} , are present. Positions and assignments of all the present bands are listed in Table 1.

In the Raman spectrum of PANI hydrochloride films excited with the 514 nm laser line (Figure 1, green line), in contrast with the spectrum obtained with the 633 nm excitation line, the most intense peak in the ring stretching region is observed at 1620 cm^{-1} and in the C-H deformation region at 1194 cm^{-1} ; these bands are connected with benzenoid units [26]. This excitation line is not in resonance with any form of PANI; thus, the band intensity follows the concentration of benzenoid/quinonoid rings more reliably.

Using the 785 nm excitation line (Figure 1, black line), different semiquinone radical structures attributed to the

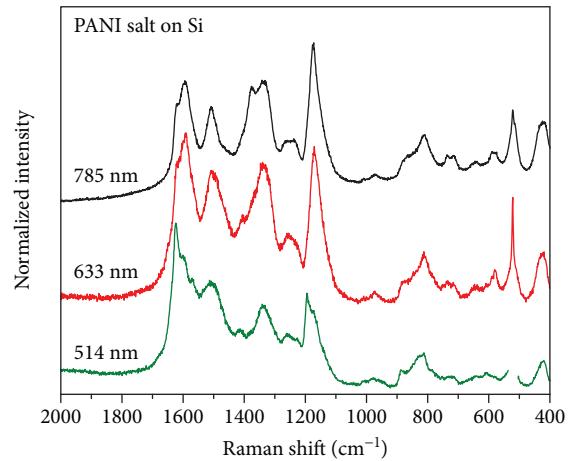


FIGURE 1: Raman spectra of intact PANI hydrochloride films on silicon support obtained with 514, 633, and 785 nm laser lines.

$\text{C}\sim\text{N}^{+\bullet}$ vibration of variously localized polaronic sites are resonantly enhanced. The spectrum is close to the spectrum excited with the 633 nm line; significant changes can be observed only in the group of bands connected with $\text{C}\sim\text{N}^{+\bullet}$ stretching vibrations, where a band at 1377 cm^{-1} connected with semiquinonoid rings with lower polaron delocalization can be observed in addition to the delocalized polaron band at 1335 cm^{-1} .

3.2. Degradation by Laser Beam. PANI is rather sensitive to irradiation and can be damaged by laser beam during measurement [16]. The excitation wavelength at 514 nm is out of resonance with both PANI emeraldine salt and base, but the photon energy is high. With this excitation line, long accumulation at low laser power is necessary to obtain acceptable quality of the spectra without any damage to the sample. The spectra change quickly with increasing laser power (Figure 2(a)).

At laser power up to 10%, the band at 1335 cm^{-1} decreased and the band at 575 cm^{-1} increased. These changes can be attributed to partial deprotonation and formation of phenazine-like structures [15, 22]. At higher intensities, the bands broadened, bands at 514, 1402, and 1620 cm^{-1} disappeared, the band at 575 cm^{-1} shifted to 560 cm^{-1} , and the band at 1335 cm^{-1} decreased significantly. Further deprotonation, random crosslinking, and bond breakage take place [15, 44].

The excitation at 633 nm is in resonance with quinonoid structures, so partial deprotonation of PANI-S is detected easily (Figure 2(b)). Raman spectra can be safely obtained without damage to the sample at higher power, than with that of the green line. The Raman spectra of PANI-S measured with the 633 nm line of HeNe laser were obtained in acceptable quality without any damage to the sample. At higher laser power, the band at 430 cm^{-1} shifted to 419 cm^{-1} ; peaks at 577 cm^{-1} , 607 cm^{-1} , 730 cm^{-1} , 1230 cm^{-1} , 1400 cm^{-1} , and 1600 cm^{-1} increased; and bands at 1566 cm^{-1} and 1638 cm^{-1} appeared. The band at 1170 cm^{-1} and shoulder at 1470 cm^{-1} decreased. These changes are connected with deprotonation of the sample [45].

TABLE 1: Assignment of the Raman bands of PANI.

Band position (cm ⁻¹)	Assignment	References
1640	Phenazine-like crosslinking	[22]
1620	C~C stretching vibrations of the phenylene ring	[24, 27–31]
1595	C~C stretching vibrations of the semiquinonoid ring	[27, 29, 32–36]
1563–1558	C=C stretching vibrations of the quinonoid ring	[27, 29, 32–36]
1504	N-H deformation in the semiquinonoid structures	[30, 33, 34, 37–39]
1480–1468	C=N stretching vibrations in quinonoid units	[25, 32]
1415	C-N stretching in highly localized polaronic structures	[27, 32, 40]
1377	C~N ⁺ * stretching vibrations in highly localized polarons	[32]
1335	C~N ⁺ * stretching vibrations of the semiquinone cation radicals in delocalized polaronic structures	[31, 37, 41]
1257	C-N stretching in quinonoid structures	[24, 31, 42]
1221	C-N stretching in benzenoid units	[24, 31, 42]
1194	C-H deformation vibration of a benzenoid ring	[32, 35, 36, 39, 43]
1182	C-H deformation vibration of a semiquinonoid ring	[32, 35, 36, 39, 43]
1164	C-H deformation vibration of a quinonoid ring	[32, 35, 36, 39, 43]
887	C~C ring deformation vibration (out-of-plane) of the polaronic form	[29]
834	C~C ring deformation vibration (out-of-plane) in the quinonoid ring	[32]
812	The benzene ring deformation in the emeraldine salt	[29]
780	Ring deformation in the emeraldine base	[27, 32]
751	Ring deformation in the emeraldine base	[27, 32]
608	Phenylene ring torsion	[22, 29, 32]
575	Phenazine-like crosslinking	[22]
533	Out-of-plane ring deformations in the emeraldine base	[21]
417	Out-of-plane ring deformations in the emeraldine base	[21, 29]

The 1064 nm excitation is in resonance with π -polaron transition of PANI-S, and it is highly absorbed. In addition, the Raman cross-section is significantly lower at longer excitation wavelengths so higher power had to be used. As a result, it is practically impossible to obtain a Raman spectrum of nondamaged PANI-S with this excitation line. For this reason, the lines were first drawn on the PANI-S sample with the 1064 nm excitation line and then analyzed with the low-power 633 nm excitation line, which is, on the other hand, the gentlest way of PANI film measurement (Figure 2(c) and 2(d)). The fact that our FT-Raman setup allows easy and controlled movement of the sample against the laser beam is an advantage for deliberate damage—drawing on the PANI-S film. The treated area changes its color and is visible even by the naked eye (fig Foto).

There are significant changes in the spectra when irradiated with the 1064 nm laser line. The irradiation with power up to 1 W with high-speed movement of the laser beam on the sample causes partial deprotonation and formation of phenazine-like crosslinks, as manifested by appearance of the bands at 1563, 1463, 1390, and 606 cm⁻¹. The irradiation with 0.2 W at low speed deprotonates the sample completely. Higher power causes transformation to amorphous carbon analogue [9, 46].

4. Degradation by Ageing in Air

The samples with the burned record were left to age in air. The lines on the films faded, as could be seen in Figure 3. The changes of the PANI film at the line drawn with 0.2 W laser power at low speed (Figure 4) and out of the line (Figure 5) are well illustrated by the Raman spectra. The PANI-S film partially deprotonates by ageing, following the increase of intensity of Raman bands at 1470 cm⁻¹ and 1223 cm⁻¹ and the decrease of intensity of the bands at 1338 and 1257 cm⁻¹. In addition, bands at 1376, 780, 750, and 730 cm⁻¹ appear and the band at 587 cm⁻¹ shifts to 577 cm⁻¹. This is connected with the formation of phenazine-like crosslinks [15]. However, the level of protonation is still high after two months.

The Raman spectra of the line burnt with the 1064 nm excitation wavelength do not change much during time. The shoulder at 1610 cm⁻¹ increased, the band at 1470 cm⁻¹ shifted to 1480 cm⁻¹, and a small band appeared at 810 cm⁻¹. The band at 1335 cm⁻¹ increased slightly. All changes were already observed after two days and can be understood as stabilization of the thermally deprotonated sample. First, the volatile chloride anions are removed but the conformation and electron distribution are not yet changed accordingly, as suggested by the position of the C=N

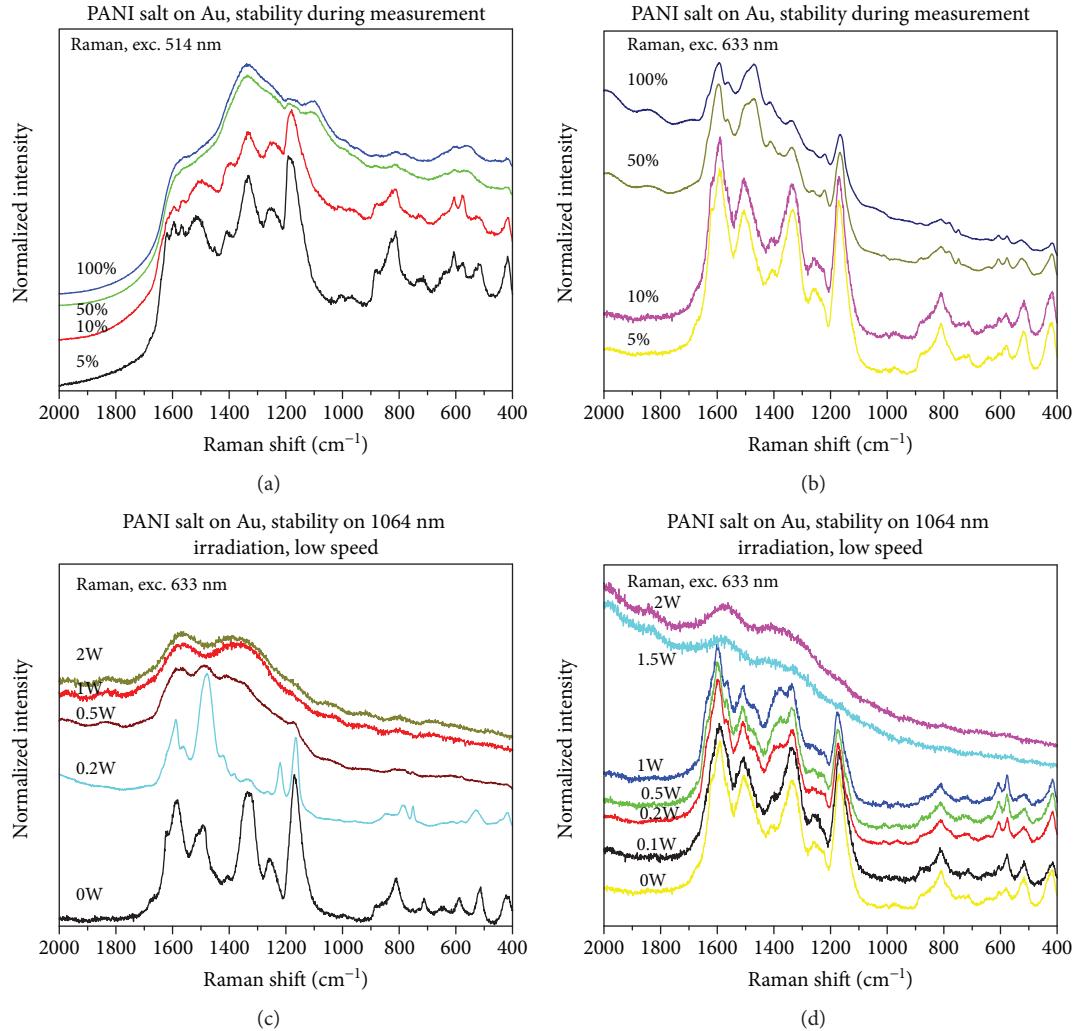


FIGURE 2: Raman spectra of a PANI film on gold support burned with various powers of 514, 633, and 1064 nm radiation (for burning with the 1064 nm line, the spectra were measured subsequently with the low-power 633 nm line).

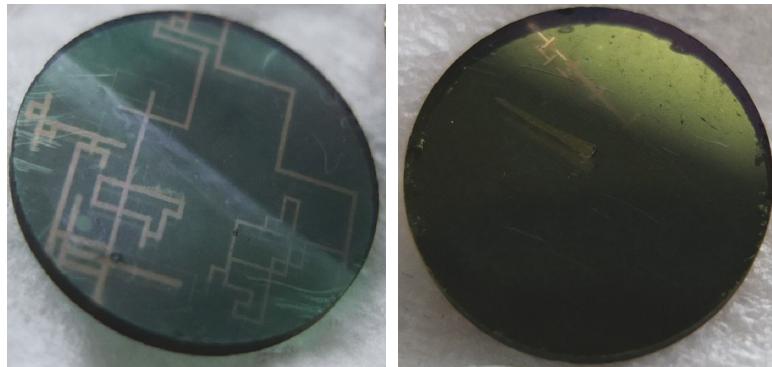


FIGURE 3: PANI-S on glass and gold with structures drawn with 1064 excitation laser. Line thickness varies from 40 to 100 μm depending on the laser power (from 0.1 to 2 W).

stretching band at 1478 cm⁻¹ typical for short pernigraniline-like or phenazine-like oligomers [27, 32, 40] (C=C stretching in emeraldine salt is also present near this Raman shift [29, 47]) and the strong dominance of the C=C stretching band of quinonoid rings at 1560 cm⁻¹ in the ring stretching

region. Later, the band of benzenoid ring stretching at 1605 cm⁻¹ appears and the C=N stretching band shifts to the standard position for the PANI emeraldine base at 1468 cm⁻¹ [25, 32]. These changes can be connected with conformational relaxation in the new deprotonated state.

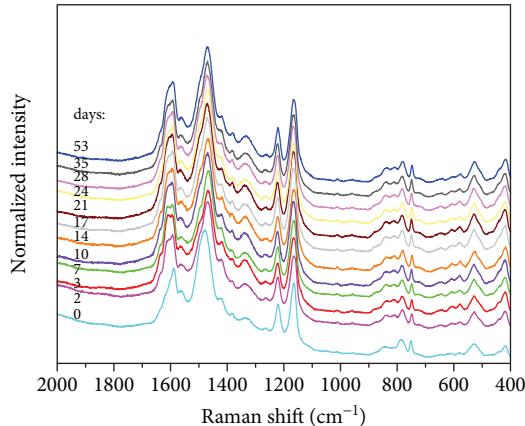


FIGURE 4: Raman spectra of a line burnt to the PANI-S film on gold with a 0.2 W 1064 nm laser line at low speed, obtained with the 633 nm excitation line at a marked time after burning. The samples were stored at room temperature in air.

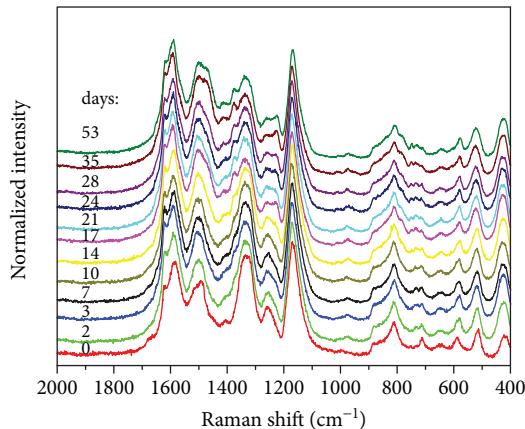


FIGURE 5: Raman spectra of the PANI-S film on gold obtained with the 633 nm excitation line at a marked time after preparation. The samples were stored at room temperature in air.

In fact, the already stabilized spectrum was observed before as the spectrum of thermally deprotonated PANI-S [46]. In this case, the spectra of the fresh record were measured within an hour after recording.

4.1. Degradation by Heating in Inert Atmosphere. Another method of PANI degradation which has been studied is heating in inert atmosphere (Figure 6). A PANI-S film on silicon support was heated to 100°C and analyzed with Raman spectroscopy [46]. The Raman spectrum obtained with the 633 nm laser displays mainly the increase of the bands connected with quinonoid structures (1595, 1558, 1468, 1415, and 1222 cm⁻¹) that are resonantly enhanced and the decrease of the intensity of benzenoid (1620, 1257 cm⁻¹) and semiquinonoid structures (1337 cm⁻¹) after heating the sample at 100°C [29]. The broad band of C=N stretching vibrations in quinonoid units at 1480 cm⁻¹ becomes the strongest band of the spectrum. The band connected with localized polarons at 1380 cm⁻¹ appeared.

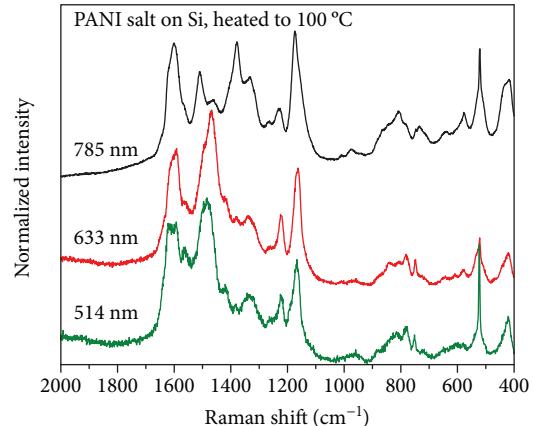


FIGURE 6: Raman spectra of the PANI film heated at 100°C in nitrogen atmosphere, excited with the 514, 633, and 785 nm laser line.

The Raman spectrum obtained with the 514 nm excitation line is very similar to the spectrum excited with the 633 nm line. This suggests that the quinonoid units are really dominant in the film and not just brought up by the resonance enhancement with the 633 nm excitation line.

With the 785 nm excitation, smaller changes of the spectrum of original PANI-S films are detected. The spectrum differs significantly from the spectra excited with visible laser lines. The semiquinonoid structures are resonantly enhanced with this excitation, so the main emeraldine salt character was preserved in the spectrum. A small band at 1465 cm⁻¹, corresponding to the C=N vibration in quinonoid units, appeared; the band at 1220 cm⁻¹ increased relatively to the band at 1257 cm⁻¹; and the intensity of the peak at 1330 cm⁻¹ decreased while the band at 1378 cm⁻¹ did not change and a small band at 1415 cm⁻¹ appeared.

The changes in the Raman spectra correspond to partial deprotonation, which is sensitively detected with the 633 nm excitation, and to the formation of quinonoid and phenazine-like defects. On the defective sites, localization of polarons takes place, resulting in the Raman band of localized (1380 cm⁻¹) and highly localized (1400–1415 cm⁻¹) polarons.

4.2. Comparison of the Different Types of Degradation. During all kinds of degradation of PANI films, similar processes like deprotonation, crosslinking, or even carbonization took place; however, their rates differ.

Deprotonation is the dominant process when moderate energy flow is delivered to the sample, either by heating or by laser irradiation. The Raman spectra of heated and irradiated PANI-S films are virtually identical with the chemically deprotonated PANI film (Figure 7); only minor differences in the intensities of the bands of both quinonoid units and residual protonated units imply varying levels of deprotonation.

By simple ageing in air or low-power irradiation, the deprotonation is accompanied by the formation of phenazine-like crosslinks. These changes are gradual. On the other hand, the deprotonated sample does not undergo crosslinking during ageing in a detectable extent. Crosslinking takes

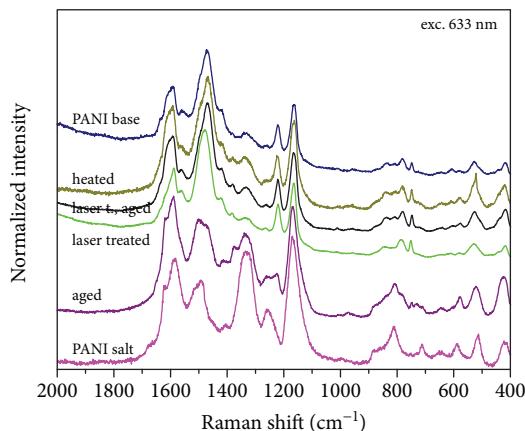


FIGURE 7: Comparison of degradation methods on a PANI-S film on gold. Raman spectra are obtained with the 633 nm excitation line.

place also during heating and irradiation, but only at a higher temperature [46].

5. Conclusions

All ways of PANI degradation, i.e., ageing in air, heating, and laser irradiation, led mainly to two effects, deprotonation and crosslinking. Strong laser irradiation or heating to temperature higher than 500°C [46] led even to carbonization of the film. The rates of these transformations varied for varying degradation conditions, but qualitatively, the processes were identical. Chemical deprotonation, however, proceeds in a different manner and has a different impact on the material stability [46–48].

Due to the different rates of degradations at different temperatures, accelerated ageing at increased temperature cannot be reliably used as a model of ageing at room temperature. At elevated temperatures, deprotonation is favored against crosslinking.

In the present paper, it is demonstrated that it is possible to write into a PANI film with a laser beam. The line thickness is large, in the order of tens of nanometers. Such low spatial resolution should be sufficient for certain applications in inexpensive electronics, such as RFID tags. The recorded pattern shows reasonable stability in air at room temperature.

Data Availability

All data (Raman spectra) used to support the findings of this study are included in the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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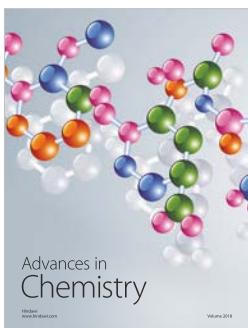
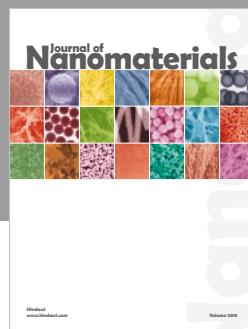
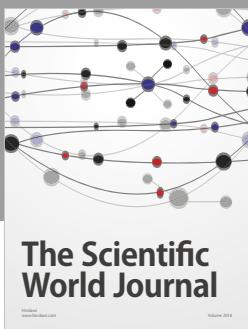
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