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Uv-Vis investigations on ion beam irradiated polycarbonate

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Abstract: UV-VIS investigations on polycarbonate irradiated with accelerated U ions are reported. The experimental data are consistent with the decrease of the energy gap due to irradiation and indicate the formation of isolated conjugated structures. The relatively weak decrease of the energy gap and the shape of the electron spin resonance lines indicate that the conjugated structures are isolated within the polymeric matrix.

Introduction

The energy deposited within polymeric targets by incident particles triggers various physical and chemical modifications [1-8]. In most cases, this process is connected to the stopping power of the target against the incident particle. The electronic stopping power dominates at shallower penetration depths whereas the nuclear stopping power reaches a maximum at the end of the ion track [1-3], where the kinetic energy of the impinging ions is small. The energy deposited within targets induces excitations and ionizations processes that finally result in scission reactions. In polymeric targets, the products of these reactions (ions, radicals and radical-ions associated to macromolecular chains, low molecular mass compounds, and volatile residues) are able - under certain conditions - to recombine. If these recombination processes are not negligible and involve dominantly fragments of macromolecular chains resulting from the previous scission step, an increase of the molecular mass is observed which is assigned to overall chemical processes defined as crosslinking reactions.

The fine balance between crosslinking and scission reactions modifies both the molecular mass distributions and the average molecular mass of the bombarded polymer, affecting its physical properties as well as its behaviour upon further bombardment.

Polycarbonate (PC) is a polymer that undergoes dominant scission reactions [9] (if the fluence and the energy of impinging ions is not too large and the irradiation is performed below the glass transition of the polymer [10]). These features have been exploited by using various polymers (including PC) as solid-state nuclear track detector [11]. The physical and chemical modifications due to the interaction between the incident ions and PC have an outstanding stability under usual storing conditions (at room temperature, in air). This is because the glass transition temperature of both pristine and bombarded PC is above room temperature [10]. Accordingly, the

macromolecular chains of polycarbonate are frozen at room temperature, as the segmental motions are not yet thermally activated. This explains the long lifetime of free radicals in irradiated PC and provides a microscopic basis for the understanding of the processes involved in nuclear track detection; the energy deposited by the incident particle within the polymer generate a track of defects and reduces locally the average molecular mass of the polymer. Consequently, the regions exposed to radiation are more easily etched revealing a track structure that contains information about impinging particles (mass, charge, energy, and fluence) [11]. The decrease in the average molecular mass expresses the local increase of free radicals due to macromolecular chain scission reactions triggered by the energy deposited by impinging particles.

Previous ESR data on the same samples (performed almost simultaneously with UV-VIS measurements) [2, 5, 12], confirmed the presence of free radicals and provided a direct connection between the energy deposited within the polymeric target by the incident beam and the concentration of free radicals. The analysis of the resonance line shape indicated that these free radicals are coupled by extreme exchange interactions [12]. The cluster-like structure of free radicals and the interaction among them stabilizes the free radicals and contributes to their very large lifetime.

Three types of radiation-induced modifications in PC have been identified [13, 14]. The first one is an intramolecular combination of phenoxy-phenyl and phenoxy-phenoxy free radicals, responsible for an UV absorption band located between 275 and 300 nm. The peak located at 275 nm did not exhibit any shift upon irradiation with Li but was shifted to longer wavelengths during the irradiation with Ni ions [14]. The second type of defects described the reaction of free radicals with oxygen (and eventually with H or H₂O), followed by the scission of macromolecular chains and the final decrease of the average molecular weight. The third group consists of intermolecular free radicals combinations.

The scission of the macromolecular chain and the gas release during the chemical processes that accompany the radiation-induced modifications in PC results in local formation of cyclic structures characterized by conjugated bonds followed by their stacking in larger structures located within the latent track and generally well dispersed within the polymer. Such structures, with highly delocalized electrons have an increased electrical conductivity. As the pristine polymer is insulator and the presence of such local structures around the particle track enhance the local electrical conductivity, the UV study is focused on the effect of the ionizing radiation on the energy (band) gap. A decrease of the band gap expresses a local transition of the polymer from an insulating material towards a semiconductor. Based on previous ESR data, the electrons are not sufficiently delocalized to behave like a gas, and hence a finite non-zero energy gap is expected in all irradiated samples. From the optical spectroscopy point of view, the irradiation of PC is increasing the density of double bonds, is increasing the conjugation length, and reduces the band gap [8]. From the electronic point of view, the decrease of the electrical resistance reflects the capability of electrons to hop over local energy barriers [8]. These electrons carry usually an uncoupled electronic spin and contribute to the ESR spectrum with a narrow, asymmetric line characterized by a g-factor of about 2,0023 [2, 5].

The microscopic changes triggered by ionizing radiation are affecting all macroscopic properties of PC. The ultimate tensile strength and the ductility of PC decreases upon irradiation [9].

Typically, pristine PC has strong absorption for wavelengths smaller than 350 nm [1, 15]. Some authors noticed a weak band localized around 400 nm [1, 15, 16] in pristine PC. Previous UV-Vis investigations on irradiated PC revealed an absorption band located at 415 nm, assigned to anionic structures with ester or ketone structure [17]. This band disappears upon thermal annealing [17]. Irradiation-induced shoulder bands located at 315 nm and 355 nm and tentatively assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the carbonyl group, respectively have been reported [18]. The intensity of these absorbance bands was changing with increasing the irradiation time, while its position was slightly shifted towards higher wavelength [18]. Absorption bands located at 320 nm and 355 nm ascribed to phenylsalicylate and dihydroxybenzophenone, respectively, have been irradiated in photodegraded PC [19]. Ion beam irradiation of PC generated also alkynes (structures with a triple bond between two carbon atoms), alkenes (structures that involve both single and double bonds for carbon atoms) [15], and aggregated or fused rings. Upon irradiation, the absorption edge of PC moves towards larger wavelengths, with an increase of the absorbance almost linearly dependent on the fluence of incoming particles [15]. Ion beam irradiation of PC results in a local amorphization of the polymer along the incident particle trajectory in the polymer [15, 20]. This competes with the drop in the average molecular mass upon irradiation and enhances the etching speed along the incident particle track [15].

The aim of this contribution is to extend the study on the nature of long-term modifications induced in polycarbonate by ion beam bombardment (as a function of penetration depth) and to elucidate the relationship between free radicals, track etchability, and energy gap. The study adds new evidences obtained by using UV-VIS spectroscopy to previous data obtained by luminescence [2] and electron spin resonance (ESR) investigations [5] on the same samples. All these experiments were done almost simultaneously (within the same week) at about one year since the irradiation was stopped

Results and discussion

This study aims to a detailed UV-VIS analysis of the radiation-induced modifications in polycarbonate (Makrofol-N polycarbonate films obtained from Bayer AG, Germany.). The repeating unit of this polymer is shown in Fig. 1. The polymer is semicrystalline and has a glass transition of about 148 °C. The chemical formula of the repeating units is shown in Fig. 1A. PC shows a decrease of the glass transition temperature, melting transition temperature, and average molecular mass when exposed to ionizing radiation [21]. ESR spectroscopy data are consistent with the formation of phenyl (Fig. 1A), phenoxy (Fig. 1B), and eventually of a small amount of the radical showed in Fig. 1C [17]. The subsequent chemical reactions triggered by impinging particles are responsible for UV-VIS characteristics. A potential conjugated structure as suggested in [18] is shown in Fig. 1 E. Fig. 1F depicts the structure of phenylsalicylate generated during the photodegradation of PC [19].

The irradiation of PC changes gradually the colour of the polymer from transparent towards brown/yellow and produces a strong increase of the absorbance in the UV-VIS range [1]. As may be noticed from Fig. 2, the UV-VIS absorbance of all polycarbonate layers presents an exponential decay as the incident wavelength is increased from 350 nm to 600 nm. The decrease of the UV-VIS absorbance, the observed red shift, and its dependence on the penetration depth is related to the energy deposited by incident ions. The intensity of the UV-VIS absorbance, at a

given constant wavelength, is larger for middle layers (for any wavelength in the UV-VIS range). The UV-VIS spectrum of the last layer was found to coincide to the UV-VIS spectrum of the pristine polymer.

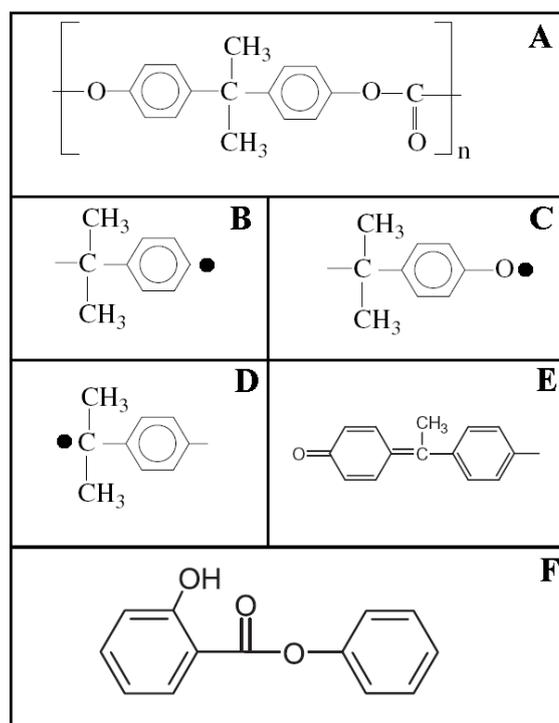


Fig. 1. The scheme depicting radiation-induced modifications in polycarbonate.

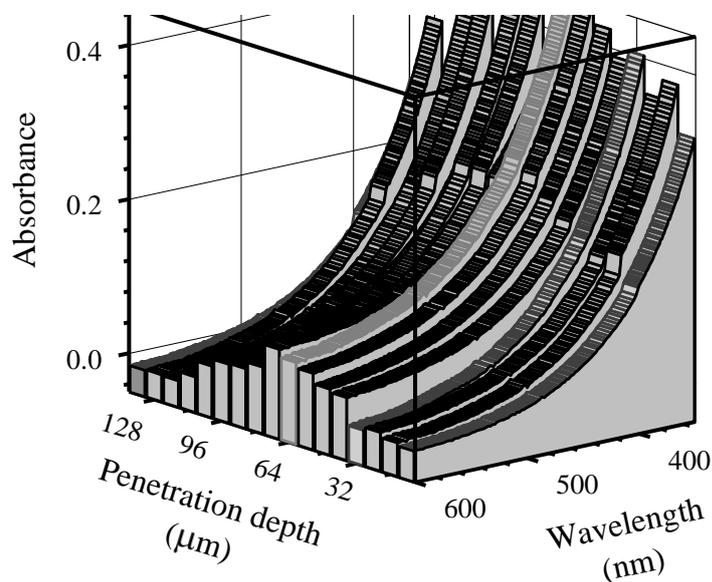


Fig. 2. UV-Vis analysis of ion beam irradiated polycarbonate. This reflects that the energy deposited by the incident particle in the last layer is extremely small, as estimated by TRIMM calculations.

For wavelengths ranging from 350 nm to 600 nm, the dependence of the UV-VIS absorbance at a given wavelength λ , in the i^{th} layer has been satisfactorily fitted by:

$$A^{(i)}(\lambda) = A_0^{(i)} + B^{(i)} \exp - K^{(i)} \lambda \quad (1)$$

where $A_0^{(i)}$ defines the background of the UV-VIS spectrum, $B^{(i)}$ is a fitting parameter, $K^{(i)}$ is a rate constant related to the generation of the chemical entities responsible for the UV-VIS absorption. Each layer has the same thickness (8 μm). In the general case, it is expected that $K^{(i)}$ is a function of the ions' fluence and electronic and nuclear energy loss.

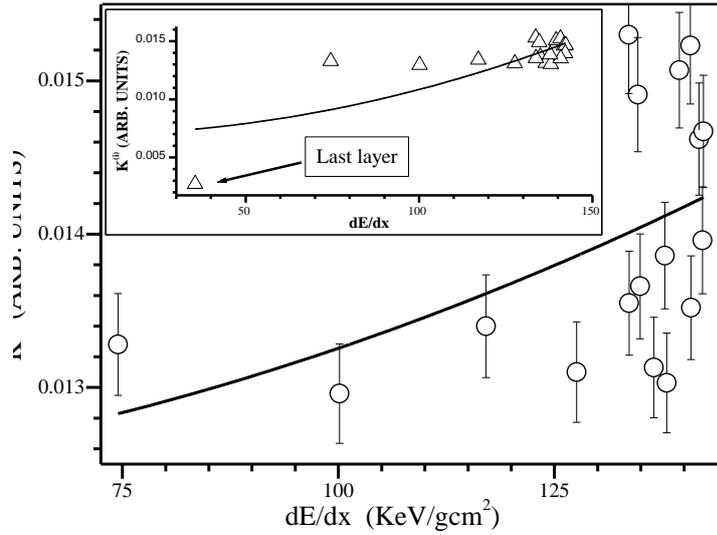


Fig. 3. The dependence of rate constant $K^{(i)}$ versus the electronic energy loss.

As may be inferred from Fig. 3, the rate constant $K^{(i)}$ depends on the electronic energy loss, where E is the specific energy transferred to the polymer (expressed as the energy deposited by the incident particle divided by the density of the target). The rapid drop in the rate constant associated with the last layer may be explained by the fact that in the last layers the ions' fluence is no more constant due to the lateral straggling of incident ions. This effect is amplified in the last layer by the statistical significance of the particle range in a solid due to the trapping of some incident ions within the polymeric sample (near the end of the projected range).

Wang and coll. [1] investigated the changes in the UV-VIS absorbance at 380, 450 and 500 nm, in polycarbonate bombarded with Ar ions. The relative change in the UV-VIS absorbance (i.e. the difference between the absorbance of the irradiated polymer and pristine polymer, at a given UV-VIS wavelength λ), depends on the number of chromophores $n_{\lambda}^{(i)}$ (created per each incident ion and unit area) generated within the target layer "i" [1, 4]. For the PC stack this change in the absorbance occurring within the i^{th} layer, at a wavelength λ , has been fitted by:

$$A^{(i)} = A^{(0)} [1 - \exp(\lambda k_{\lambda}^{(i)} n_{\lambda}^{(i)} \sigma^{(i)} \phi^{(i)})] \quad (2)$$

where $A^{(0)}$ is the absorbance of the pristine target, $A^{(i)}$ is the absorbance of the i^{th} layer. In (2), $k_{\lambda}^{(i)}$ is the absorption cross section of the chromophores induced in the i^{th} layer at the wavelength λ , $\sigma^{(i)}$ is the production cross-section of these

chromophores in the i^{th} layer, and $\phi^{(i)}$ is the ion fluence in the i^{th} layer. As long as $(\lambda k_{\lambda}^{(i)} n_{\lambda}^{(i)} \sigma^{(i)} \phi^{(i)}) \ll 1$, the expression (2) may be developed in power series. In the linear approximation, is obtained:

$$A^{(i)} - A^{(18)} \cong \lambda k_{\lambda}^{(i)} n_{\lambda}^{(i)} \sigma^{(i)} \phi^{(i)} \quad (3)$$

The expression (3) is easily reduced to the well-known expression of the radiation-induced modifications in the UV spectra of polymers based on the Beer-Lambert equation [1, 4]. The first order approximation is valid if the overlap of latent track is negligible [4]. This proves the consistency of the relation [2], and provides a simple mathematical framework for the analysis of UV-VIS data. The number of radiation-induced chromophores, $n_{\lambda}^{(i)}$ has a power law dependence on the electronic stopping power [1,4];

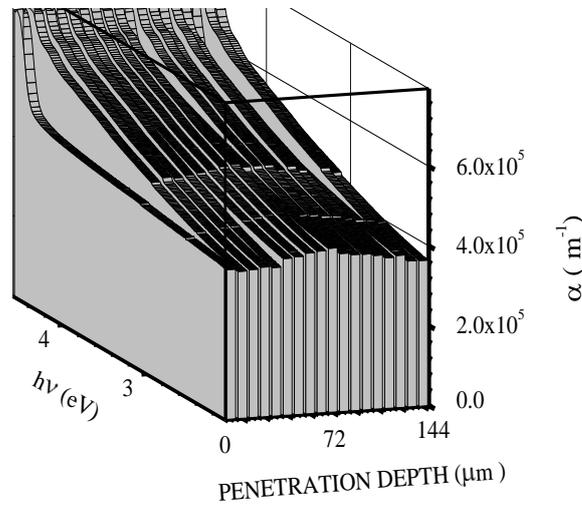


Fig. 4. The dependence of the absorption coefficient on the energy of the UV-VIS photon.

$$n_{\lambda}^{(i)} = \left[\left(\frac{dE}{dx} \right)^{(i)} \right]^{\gamma} \quad (4)$$

where $(dE/dx)^{(i)}$ is the electronic stopping power in the i^{th} layer estimated by using TRIMM II. For ion beam irradiated poly(para)phenylene sulfide, the estimated value of γ was found to be close to 2 [1]. In Fig. 3, the relationship (3) was tested assuming that $\gamma=2$ [1, 4]. It was reported that at low stopping powers $\gamma>2$ [4]. As may be observed from the inset of Fig. 3, the deviations from such dependence are large. However, most of the points that deviate significant from this dependence are from the last part of the ion trajectory within the polymer. Neglecting the results due to the last two foils, an acceptable power like dependence with $\gamma \cong 2.00$ is obtained (see the bold line in Fig. 3). The deviation from $\gamma=2$ in the last part of the ion trajectory within the polymer is explained by the decrease in the fluence of the ions due to lateral straggling. ESR data on the same samples were accurately fitted by assuming that the concentration of free radicals versus the deposited energy scales as a power law

with an exponential close to 2 [1, 2, 5]. The results were modelled by taking into account both the contribution of the defects confined in the track volume and in the track halo volume [22].

The absorption curves were calculated by measuring the transmittance of the specimen relative to the pristine film, of the same thickness. The absorption coefficient α was calculated by using the relation [6]:

$$\ln T = -x\alpha \quad (5)$$

where T is the measured transmission and x is the thickness of the film (8 microns in this case). The dependence of the absorption coefficient on the energy of the UV-VIS photon is represented in Fig. 4.

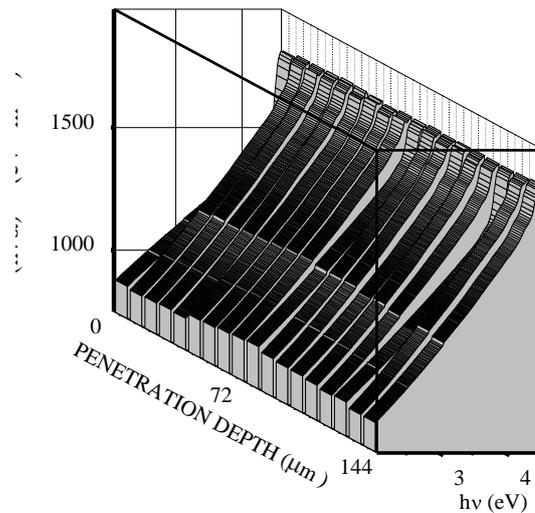


Fig. 5. The dependence of $(\alpha h\nu)^{1/2}$ on the photon energy.

In Fig. 5 it is shown the dependence of $(\alpha h\nu)^{1/2}$ on the photon energy. This dependence is expected to be linear, with a slope that defines the constant B and an ordinate equal to the optical gap [6]:

$$\sqrt{h\nu\alpha} = B(h\nu + E_{Gap}) \quad (6)$$

where h is the Planck constant and v the frequency of the UV-VIS photon.

The dependence of the gap energy and B constant on the penetration depth is given in Fig. 6. The energy gap reflects the fact that the pristine polycarbonate is a semiconductor and that even after a long storage time the changes in the value of the forbidden gap are beyond experimental errors but not spectacular. According to the thermal spikes description, local temperatures of the order of 1000 K are expected. Such huge temperatures, in air, would lead to severe evaporative processes and may produce conjugate structures (graphite like). Hence, pyrolyzed structures characterized by a zero or very small gaps are predicted by the thermal spike approach.

The UV spectroscopy was not able to provide compelling evidence for a very small energy gap. However, a decrease of the energy gap due to the ion beam bombardment was noticed. The result is in good agreement with ESR data, which failed to support for extended islands with high conductivity (no Dysonian like resonance lines were recorded in these irradiated samples).

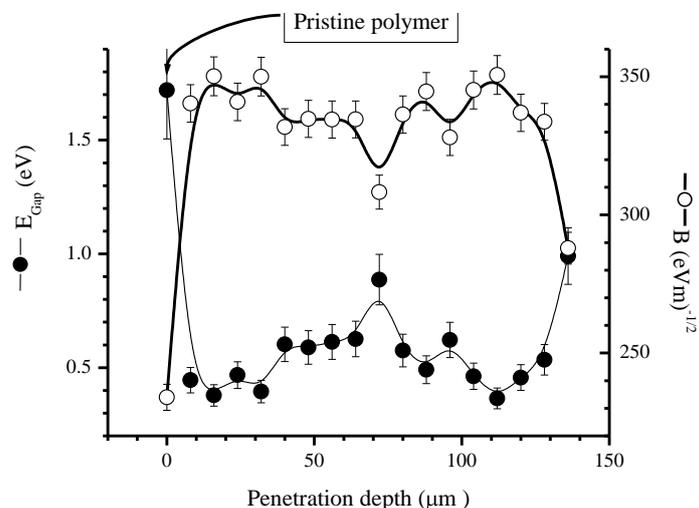


Fig. 6. The dependence of the gap energy and B constant on the penetration depth.

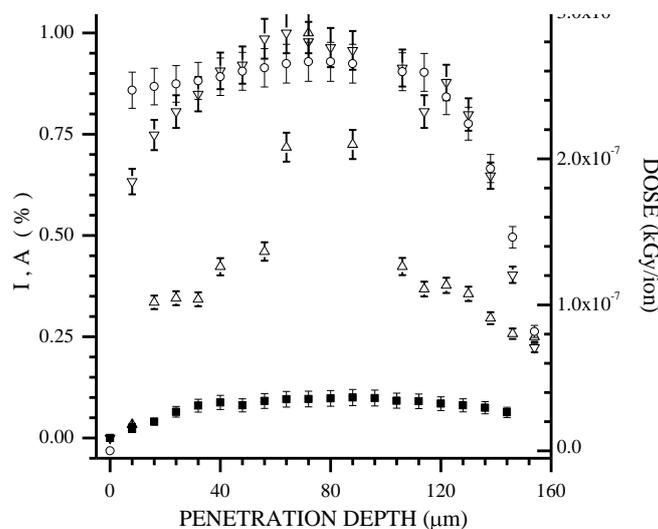


Fig. 7. The correlation between the line intensity of the ESR spectra, (down pointing triangles), luminescence data (up triangles), the normalized UV-VIS absorbance at 280 nm (filled squares), and the deposited dose (circles).

Due to sensitivity limitations of both UV-VIS and ESR spectroscopy, it is concluded that the weight of extended highly conjugated structures, in irradiated polycarbonate is negligible. The structures responsible for the electron spin resonance signal and for the observed reduction of the energy gap are confined at submicron range and dispersed (isolated) within the irradiated polymer. Earlier experimental data on irradiated polycarbonate [1-6] indicated that the chemical entities responsible for luminescence are conjugated structures. The good correlation between the

concentration of the chemical entities measured by luminescence, ESR spectroscopy and UV-VIS suggest [2, 5] that the main defects induced by ion beam bombardment of polycarbonate present a local conjugation, related with semiconducting features of irradiated polycarbonate. The experimental data concerning the effect of ion beam bombardment on polycarbonate indicate that these modifications are due to the electronic stopping power, suggesting that there is no high local overheating, as expected according to the thermal spikes description.

Previous studies on these samples [2, 5] done by ESR and luminescence are broadened to include UV-VIS investigations. The dependence of these data on the penetration length, stopping power, deposited dose, and latent track radius, was studied in detail. As may be inferred from Fig. 7, there is a noticeable correlation between the line intensity of the ESR spectra, (down pointing triangles), luminescence data (up triangles), the normalized UV-VIS absorbance at 280 nm (filled squares), and the deposited dose (circles). This indicates that while each technique aims at different defects generated within PC by ionizing radiation, all these modifications are related and governed by the energy deposited by the incident particle within the target.

Experimental part

A stack consisting of 18 polycarbonate (MAKROFOL) layers, each of 8 μm thickness, with a diameter of 5 cm, has been irradiated with Uranium ions accelerated up to about 10 MeV/nucleon, at "Gesellschaft fur Schwerionenforschung", Germany. The flux of incident ions was about 10^8 ions/cm²s and the fluency 10^{10} ions/cm². The irradiation has been performed in vacuum, at room temperature. UV-VIS spectra were recorded at room temperature, at different wavelengths ranging from 250 to 600 nm. Before measurements, the samples were stored in air, at room temperature for about 1 year. A slight change in color of the bombarded polymer (towards a light brown coloration) was observed by the naked eye.

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