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Kinetic and degradation reactions of poly (sodium 4-styrene sulfonate) grafting “from” ozonized poly (ϵ - caprolactone) surfaces

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Abstract

The covalent grafting of poly (sodium 4- styrene sulfonate) on poly (ϵ - caprolactone) was proved to enhance the bioactivity of this polymer. The aim of this article was to perform kinetic studies of the activation and grafting processes and illustrate the influence of several parameters on the grafting rate and on the degradation of the polymer substrate. Results showed that the active groups created on poly (ϵ - caprolactone) surface by ozonation reach a maximum concentration after a short exposure time. Moreover, a kinetic study of poly (sodium 4- styrene sulfonate) grafting on poly (ϵ - caprolactone) substrate showed that the activation energy of this process was low and the influence of conditions such as pH, monomer concentration, time reaction and grafting temperature was deeply significant for the outcome of the treatment. Besides, ozone oxidation and thermal grafting lead to surface degradation, under certain conditions, for example in the presence of Mohr’s salt used as a catalyst to enhance grafting rate. The whole study illustrates that ozone-induced grafting is a strong instrument for surface functionalization, although its parameters should be wisely studied and carefully selected. Poly (sodium 4- styrene sulfonate) functionalization improves bioactivity of poly (ϵ - caprolactone) while decreasing the slowness of its biodegradation.

Key words: Degradation; Grafting; Kinetic; Poly (ϵ -caprolactone); Poly (sodium 4-styrene sulfonate)

1. INTRODUCTION

Biodegradable polymers are widely used in biological applications such as tissue engineering, medical devices (sutures, screws), and drug-delivery systems [1]. Amongst them poly (ϵ -caprolactone) (PCL) is a slowly biodegradable polymer that was early synthesized in the 1930s. This hydrophobic polyester is and known to provide sutures, patches for therapeutic agents delivery and more recently tissue engineering 3D scaffolds ; it is the object of studies to extend its use to other applications such as the reconstruction of injured anterior crucial ligament (ACL) [1] [2] [3]. PCL shows an extensive list of advantages when compared to other polyesters including long-term degradation preventing inflammatory degradation products, biocompatibility (FDA approved), easily manufacture.

Previous studies illustrated that immobilizing functional groups on PCL could change surface wettability and induce selective proteins adsorption and bioactivity. In order to enhance cell adhesion, proliferation and differentiation, polymeric surfaces can be functionalized in several ways, for example, surface treatment by oxidation (photo- irradiation, electron-beam [4], plasma [5], and ozone-induced [6]) or grafting of specific functional groups. This last technique is especially interesting for improving selective interactions between surfaces and target biological species such as cells and proteins but also organic compounds.

Sodium styrene sulfonate (NaSS) is one of the candidates selected to this grafting process due to its demonstrated ability to modulate cell attachment via proteins/material interaction [7]. Migonney *et al.* successfully enhanced *in vitro* spreading and activity of fibroblast cells on NaSS grafted poly(ethylene terephthalate) and PCL films [7] [8] [9].

To accomplish polymer or copolymer covalent grafting, it is often necessary to realize a surface activation treatment, which will generate active groups from which the grafting or polymerization will occur. Ikada *et al.* showed that ozone-induced, UV irradiation, and plasma treatment generated peroxides on polyurethane and polypropylene [6] [10] and Deopura *et al* successfully grafted acrylic acid on PCL using oxygen plasma-induced [5] activation. Similarly, type I collagen was grafted by Hyon *et al.* [11] onto ozonized polyurethane films for fibroblast attachment and proliferation enhancement. The ozonation procedure is a simple method for treating complex polymeric objects such as 3D printing scaffold, woven or non-woven fabric, and

fiber bundle of ligament prosthesis. This technique uses the gas/liquid ozone-induced mechanism to treat the surface of a polymer film, generating peroxide groups, which will introduce radicals and, indirectly, produce other activated groups such as carbonyl and carboxyl through thermal decomposition. However, such procedure can produce undesirable side effects to further bio-applications of PCL [6] [10], a biodegradable polyester which hydrolyzing in aqueous medium, especially in an oxidative environment.

In this study, PCL substrates were activated by ozonation and thermal grafted by radical polymerization, kinetic of the ozonation and polymerization reactions were carried out under several conditions. Previous studies of the poly (sodium 4- styrene sulfonate) (pNaSS) radical grafting on PCL were conducted, yet the connection between grafting parameters and degradation was not established [1] [3] [12].

Specifically, this study highlights (1) the influence of the following parameters time, temperature, pH, presence of catalyst, monomer concentration, on the grafting rate of pNaSS exhibiting bioactive functional groups on a biodegradable polymer such as PCL and (2) the influence of the functionalization steps - activation and polymerization - on the degradation of PCL.

This detailed study should allow a better understanding of the determining parameters to consider when functionalizing biodegradable polyester for biomedical applications such as ligaments prosthesis, in order to prevent uncontrolled degradation.

2. MATERIALS AND METHODS

2.1. Materials preparation

PCL pellets ($60,000 \text{ g}\cdot\text{mol}^{-1}$) (Sigma Aldrich) were dissolved in dichloromethane (DCM). The PCL solution (60% m/v) was spin-coated (1500 rpm for 30 seconds) and dried at room temperature. PCL films were punched to get 14 mm diameter disks samples. NaSS monomer (Sigma Aldrich) was purified by recrystallization to eliminate polymerization inhibitors [8]. 90 g of NaSS dissolved in 1.6 L ethanol and 178 mL distilled water (9:1, v/v) overnight. The solution was filtered and the NaSS monomer was let to recrystallize at 4°C for 24 hrs. Purified NaSS product was dried under vacuum for 6 hours at 30°C and stored at 4°C protected from light.

2.2. Polymer surface functionalization

The polymer surface functionalization is carried out in two steps:

- a) Ozonation: Ozone flow produced by an ozone generator (BMT 802 N) ($0.6 - 0.7 \text{ bar}$, $0.6 \text{ L}\cdot\text{min}^{-1}$) was introduced in a reactor containing 6 PCL disks and 100 mL of water at 30°C : (i) for 10 min - usual conditions, (ii) for times varying from 5 to 35 min - kinetics study, (iii) for 10 minutes at pH varying from (1 to 12) – pH influence study.
- b) Polymerization: 6 ozonized PCL disks were rapidly transferred into reaction flask containing 60 mL of argon degassed NaSS water solution at a determined temperature to start the thermal polymerization “grafting from the surface” process. Conditions were as following: (i) $[0.7\text{M}]$ NaSS solution at 45°C for 1 h in the absence of catalyst (usual conditions) [8] or in the presence of a catalyst Mohr salt, (ii) $[0.7\text{M}]$ NaSS solution at 45°C for times varying from 30 min to 6 hours - kinetics study, (iii) $[0.7\text{M}]$ NaSS solution at 35, 40, 50 and 55°C for 1h – temperature influence study, (iv) $[0.2\text{M}]$ to $[1\text{M}]$ NaSS solution at 45°C for 1 hour - monomer concentration effect.

In addition, some experiences of ozonation (10 min, 30°C) and of polymerization (1h, 45°C) were carried at different pH varying from 2 to 12 to study the influence of the pH of ozonation and polymerization solution on the PNaSS GD. pH water solutions were adjusted by using $0.01 \text{ mol}\cdot\text{L}^{-1}$ hydrochloric acid or sodium hydroxide solutions.

2.3. Characterization

2.3.1. Peroxide density determination by iodine method

Iodine test is a simple method to determine peroxide concentration (PC) on activated substrates using potassium iodide (KI) [6]. The decomposition of peroxidized groups present on ozonized PCL films was performed at 45 °C in 5 mL KI (1 mol.L⁻¹) solution for 30 min. The original colourless solution turned to yellow after thermal peroxide decomposition and was analysed by UV-vis spectroscopy at 352 nm. Non-ozonized PCL film was used as a reference.

2.3.2. Grafting rate determination by toluidine blue colorimetric assay (TB)

Toluidine blue (TB) colorimetric method used in this study was described by Migonney *et al* [9]. TB solution (5 × 10⁻⁴ mol.L⁻¹) was prepared and its pH adjusted to 10. Grafted and non-grafted PCL films (control group) were dyed in 5 mL of TB at 30 °C protected from light. After 6 hours, the samples were washed in 5 mL NaOH (1 × 10⁻³ mol.L⁻¹) 3 times and the colorant de-complexed in aqueous acetic acid solution (50 %, v/v) for 24 hours. The de-complexed solution was analysed by UV-vis spectroscopy at 633 nm. The grafting degree (GD) of PNaSS on PCL film was calculated using the following equation:

$$GD = \frac{D \times V}{\epsilon \times A \times L} \text{ (mol.g}^{-1}\text{)}$$

Where D is absorbance intensity, V is the volume of acetic acid using de-complexion (mL), A is the area of the sample (cm²), L is the width of the spectroscopy cuvette (1 cm) and ϵ the angular coefficient from calibration curve (47000 to 50000 L.mol⁻¹cm⁻¹)

2.3.3. Contact angle (CA):

The sessile drop technique was used with a DSA10 contact angle measuring system from KRUSS GmbH with 2 solvents: water (polar), and diiodomethane (unpolar) (2 μL, 25 °C, 8s). The surface tension of polymer (γ_s) was calculated to follow Young-Dupre and Fowker's equation.

2.3.4. X-ray photoelectron spectroscopy (XPS):

XPS equipment (Omicron Nanotechnology) with a high power monochromated Al K α X-ray source was used for the analysis of surface chemical components. The scanning area was 200 μm \times 200 μm , 3 different zones of each PCL film samples were investigated. CasaXPS software was used to measure the atomic percentage.

2.3.5. *Fourier-transform infrared spectroscopy (FTIR):*

Fourier-transformed infrared (FTIR) spectra were acquired using a Perkin Elmer Spectrum Two spectrometer. Samples were uniformly pressed against the ATR crystal (128 scans, 4000 to 400 cm^{-1} , and resolution of 2 cm^{-1}).

2.3.6. *Surface morphology*

PCL surface morphology was observed using a Hitachi TM3000 SEM system and a MultiMode 8 Atomic force microscopy (AFM) (Bruker, Billerica, USA).

The AFM images were taken in ScanAsyst mode (25 $^{\circ}\text{C}$, in the air) using a triangular silicon nitrile cantilever (k 0.4 N/m, f 70 Hz). The scanning size on PCL was 1.5 μm x 1.5 μm . Mean roughness was calculated by the following equation:

$$\text{Ra} = \frac{1}{l_r} \int_0^{l_r} |Z(x)| dx \text{ (Ra is arithmetic average, nm).}$$

The images were analyzed using Gwyddion software.

2.3.7. *Size Exclusion Chromatography (SEC)*

The average molecular weights of the PCL films samples were determined using a Shimadzu Prominence instrument LC20AD pump equipped with a SIL-20A autosampler and Shimadzu RID-10A differential refractive index detector (Shimadzu Europa GmbH, Duisburg, Germany). The PCL films were dissolved in tetrahydrofuran (5mg.mL $^{-1}$) and their average molecular weight were measured using a calibration curve plotted using poly(methyl methacrylate) standards.

3. RESULTS

3.1. Kinetic and reaction study of the poly (sodium 4-styrenesulfonate) grafting on poly (ϵ -caprolactone) surface

3.1.1. Kinetics of ozonation and poly (sodium 4-styrenesulfonate) (PNaSS) grafting on poly (ϵ -caprolactone)(PCL)

- a) *Effect of the ozone exposure on the PNaSS grafting degree (GD) of PCL.* Results presented in Figure 1A showed the effect of the ozonation reaction time on the peroxide concentration generated during the ozonation step and on the PNaSS PCL GD. Results showed that : (i) the peroxide concentration (PO) increased until 10 minutes of ozone exposure after which it reached a plateau value of around $3.2 \mu\text{mol.cm}^{-2}$ showing that 10 min of ozonation reaction appears as the optimal time value to get the higher concentration of active species, (ii) the PNaSS GD increased with the time of ozonation in two phases a fast growth during the first 10 minutes (GD varying from 7.5 to $30 \mu\text{mol.cm}^{-2}$) then a continuous and less fast growth fact until 30 minutes of treatment to reach GD value of $45 \mu\text{mol.cm}^{-2}$ – this continuous increase of GD while the PO concentration is stable after 10 minutes.
- b) *Effect of the thermal grafting reaction time (kinetics) and of grafting temperature on the PNaSS grafting degree of PCL.* Figure 1B presented the evolution of the PNaSS GD with the time of polymerization and with the temperature of the reaction. Results showed that the variation of the GD with the grafting time reaction can be divided in two phases (until 1h and after 1h) the evolution of which depends on the temperature (i) Between 30 minutes and 1 hour of thermal grafting (first phase) the PNaSS GD increased strongly. During this phase it is worthy to note that the higher the temperature the higher the GD – $\text{GD}_{55^\circ\text{C},1\text{h}}$ was the highest GD value equalling $56 \mu\text{mol.cm}^{-2}$, $\text{GD}_{50^\circ\text{C},1\text{h}}$ and $\text{GD}_{45^\circ\text{C},1\text{h}}$ were quite similar around $35 \mu\text{mol.cm}^{-2}$ and the lowest GD value was $\text{GD}_{35^\circ\text{C},1\text{h}}$ equalled $20 \mu\text{mol.cm}^{-2}$, (ii) During the second phase of the kinetics, two groups of GD evolution were observed: one where the GD reached a

plateau value close to the GD value observed at 1h - this is the case for the two lowest temperatures of grafting 35 and 45°C, the other with GD values decreasing from 1h to 6h. The higher the temperature the higher the GD decrease – $GD_{55^{\circ}\text{C},6\text{h}}$ and $GD_{50^{\circ}\text{C},6\text{h}}$ were around 20 to 25 $\mu\text{mol}\cdot\text{cm}^{-2}$.

3.1.2. Influence of the NaSS monomer concentration and of the pH on poly (sodium4-styrenesulfonate) grafting on poly (ϵ -caprolactone)

Influence of the NaSS monomer concentration. The influence of the NaSS monomer concentration was studied from 0.2 to 1 $\text{mol}\cdot\text{L}^{-1}$ for 1 hour of thermal grafting at 45 °C (Figure 1C). The results showed that the PNaSS GD increased strongly when the NaSS concentration varied from 0.2 to 0.3 $\text{mol}\cdot\text{L}^{-1}$, and then regardless to the NaSS concentration after 0.3 $\text{mol}\cdot\text{L}^{-1}$, the GD decreased reaching a plateau value around 20 $\mu\text{mol}\cdot\text{cm}^{-2}$. The optimal value of the monomer concentration for the thermal polymerization grafting of PNaSS on PCL was around 0.3 $\text{mol}\cdot\text{L}^{-1}$.

Effect of pH: The influence of the pH of the water solutions during the two steps of the grafting process on the PNaSS GD was studied. Results presented in Figure 1D showed two tendencies depending on the grafting process step (i) ozonation step: the variation of the pH of the ozonation water solution induced a variation of the final GD which increased to from 22 to 27 $\mu\text{mol}\cdot\text{cm}^{-2}$ when pH increased from 2 to 4 then decreased to 18 and 8 $\mu\text{mol}\cdot\text{cm}^{-2}$ for pH values of 10 and 12 respectively. The maximum value of GD was observed for pH around 4 to 6. (ii) Polymerization step: the PNaSS GD decreased with the increase of the pH value of the NaSS solution – the lower the pH the higher the GD. The highest GD around 40 $\mu\text{mol}\cdot\text{cm}^{-2}$ was observed for pH 2 and the lowest GD around 26 $\mu\text{mol}\cdot\text{cm}^{-2}$ was observed at pH 6.6.

The results showed that the presence of H^+ influenced positively the polymerization, and then the GD, by increasing the dissociation of sulfonate groups – less effect of sodium ions – but had no influence on the generation of peroxide. However, a basic environment during the ozonation step reduced significantly the GD by 80 %.

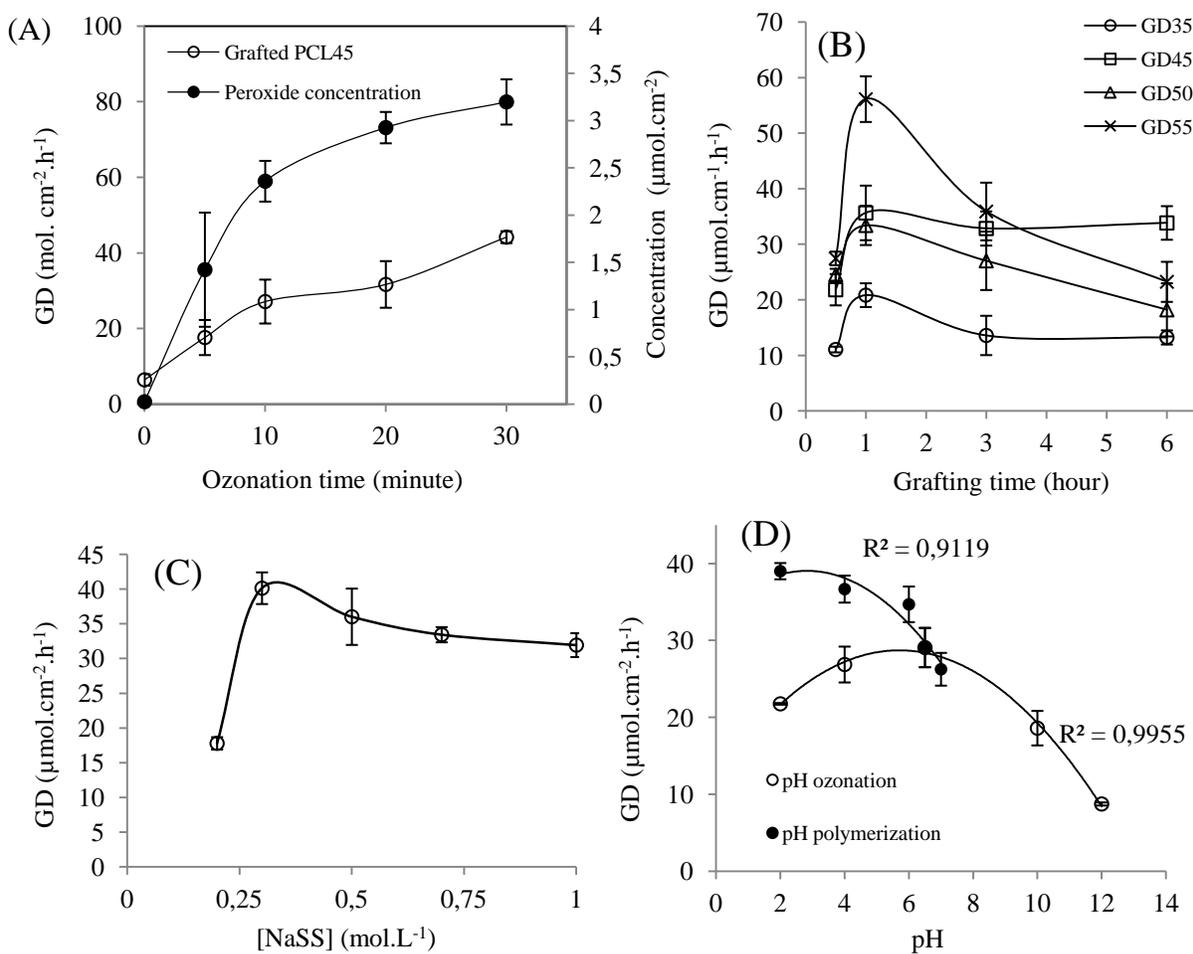


Figure 1. Modulation of the PNaSS grafting degree on PCL – Influence of various parameters (A) ozone activation time on peroxide generation and on PNaSS grafting (polymerization 1 h, 45 °C, [NaSS] = 0.7 mol.L⁻¹) (B) polymerization time and temperature (ozonation 10 min, 30 °C, [NaSS] = 0.7 mol.L⁻¹) (C) NaSS monomer concentration (ozonation 10 min, 30 °C and polymerization 1 h, 45 °C) (D) pH variation of ozonation and polymerization grafting (ozonation 10 min, 30 °C and polymerization: 1 h, 45 °C, [NaSS] = 0.7 mol.L⁻¹).

3.1.3. Effect of Mohr's salt as a catalyst:

Mohr's salt ((NH₄)₂Fe(SO₄)₂·6H₂O) (MS) is well known as an effective catalyst for grafting process [13] [14]. In addition, it has been demonstrated to depress the homopolymerization of anionic monomers such as acrylic acid and even of NaSS [8] [14].

The influence of the MS salt catalyst was studied following the variation of the PNaSS GD against MS concentration. Results presented in Figure 2 showed the very significant effect of the presence of MS: at low concentration (0 to 0.1M), GD increased from 32 $\mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ to 300 $\mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ (Figure 2). Nonetheless, for MS concentrations higher than 0.1 % w/w, a plateau value of the GD around 270 $\mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ was observed. This phenomenon can be attributed to a higher incidence of the oxidation reaction of iron (II) to iron (III) during this procedure.

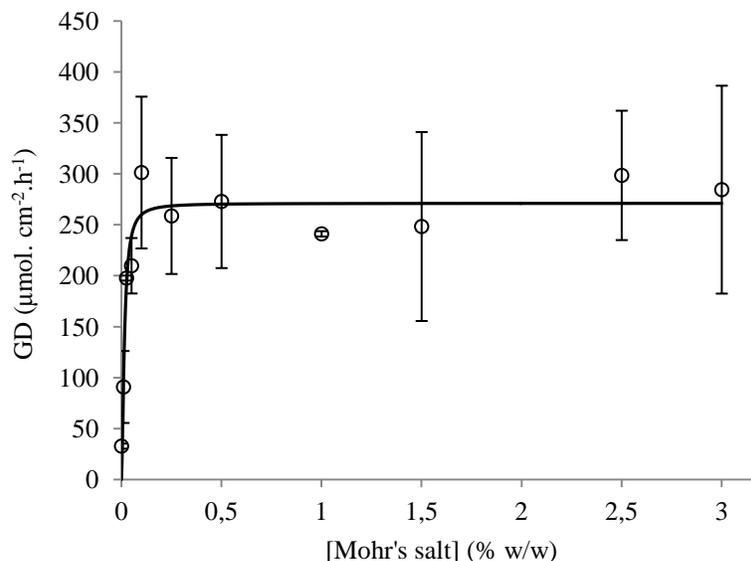


Figure 2. Effect of Mohr's salt concentration on the grafting yield (ozonation 10 min 30 °C and polymerization 1 h at 45 °C, $[\text{NaSS}] = 0.7 \text{ mol}\cdot\text{L}^{-1}$)

3.2. Activation energy determination

The activation energy (AE) of the PNaSS thermal grafting onto PCL has been determined in order to evaluate the reactivity of the generated radicals by the ozonation activation of PCL surface ((hydro) peroxide generation) followed by the thermal lysis of peroxides (radical generation) . This AE was calculated by using the Arrhenius equation (see Figure 3) and was found to equal 16.5 KJ/mol. It is noteworthy that this activation energy is comparable to the AE value observed for NaSS/acrylic acid (AA) grafting onto HDPE (22.2 KJ/mol) [15] and NaSS grafting onto PVDF (11.36 KJ/mol) [16]. Nevertheless, this value is lower than the AE of

poly(styrene) (PS) grafting on PCL which was found to equal 140 to 207 KJ/mol [17]; these differences can be explained by the anionic (NaSS, AA) versus neutral (styrene) nature of the monomer. The low AE observed when NaSS was involved can be correlated to the fast saturation (within 1 h) of the grafting process despite a temperature increase (Fig 1B) which illustrate a fast termination reaction of the growing PNaSS chains leading to low grafting degree.

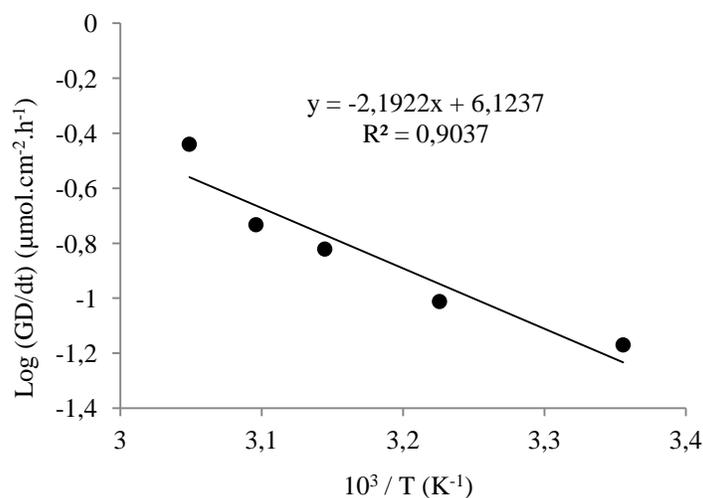


Figure 3. Estimation of the activation energy of pNaSS grafting on PCL surface from Arrhenius plot

3.3. Surface characterization:

XPS and FTIR analyses. The surface chemical compositions of NaSS grafted and virgin PCL surfaces were analysed by XPS and FTIR. The results of the XPS analysis are summarized in Table 1. The presence of NaSS units on PCL was demonstrated by the increase S percentage due to the presence from sulfonate groups: the atomic concentration of S2p attributed to the NaSS units was around 0.5 % whereas it was not present on virgin PCL. In the same time, the oxygen O percentage increased (sulfonate groups) whereas C decreased (PNaSS chains) (details are presented in Appendices Fig A.1.). This effect on S, O and C was yet observed by Migonney *and al.* on PET and PCL [7] [8]. The presence of PNaSS was also identified by FTIR spectrometry (see Appendices Fig A.2.): the presence of a shoulder at 1008 cm^{-1} is the signature of sulfonate

groups which is better detected in the case of PNaSS grafted PCL film in the presence than in the absence of SM catalyst.

Table 1. XPS analysis: atomic percentage measurement for C1s, O1s, S2p of virgin PCL and pNaSS grafted PCL film without catalyst

Atomic %	C _{1s}	O _{1s}	S _{2p}	Na _{1s}
Virgin PCL	79.55	20.45	0	0
Grafted PCL	76.90	22.60	0.50	0

Contact angle. The hydrophilicity of PNaSS grafted PCL after different ozonation times and of virgin PCL was investigated by contact angle measurements. The water contact angle (CA_{H_2O}) is correlated to the surface energy: the higher the CA the lower the surface energy. The evolution of the water drop spreading out with the ozonation time is presented Figure 4A: CA decreased from 87° to 68° when the ozone time exposure was increased from 0 to 30 min while the surface energy increased linearly (Figure 4B).

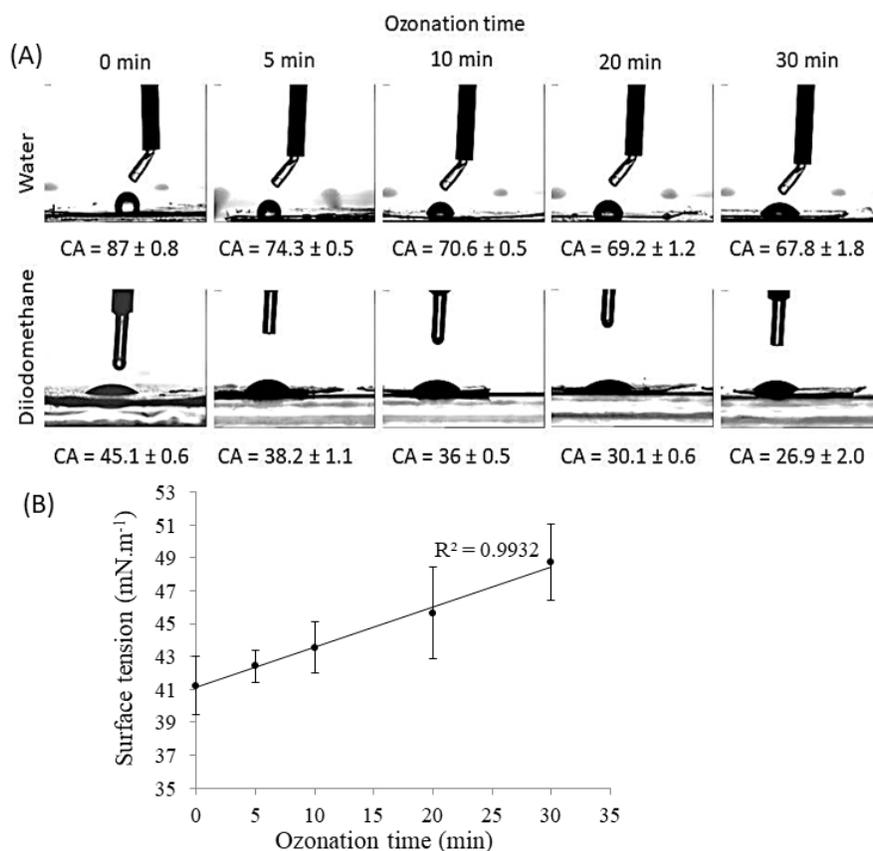


Figure 4. Evolution of hydrophilicity (A) and surface tension (B) of PNaSS grafted PCL film against the ozonation time (grafting conditions: 1 h/ 45 °C, [NaSS] = 0.7 mol.L⁻¹). The sessile drop contact angle method was used (solvents: water and diiodomethane), at 25 °C

3.4. Surface degradation:

SEM and AFM were used to detect the presence of defects (cracks, holes) on PNaSS grafted film which are due to the ozonation reaction and SEC was used to measure the degradation effect of ozonation on the length of the PCL macromolecular chains through the number average molecular weight (M_n) of PCL. Results presented in Figure 5 for SEM, Figure 6 for AFM and Figure 7 for SEC showed that:

(i) SEM. No defect was found on PNaSS grafted film for ozonation time of 10 min followed by 1 hour for grafting when compared to virgin PCL. Degradation effects such as holes on PCL films

at the frontier between spherulites started to be observed after 10 min of ozonation and 6 hours of grafting; this phenomenon was amplified when the ozonation time was increased to 30 min and grafting polymerization to 16 hours. The effect of the catalyst during the grafting process was shown to generate cracks along the fibril of the spherulites whatever the concentration of MS: even at low MS concentration 0.01%, the cracks are visible.

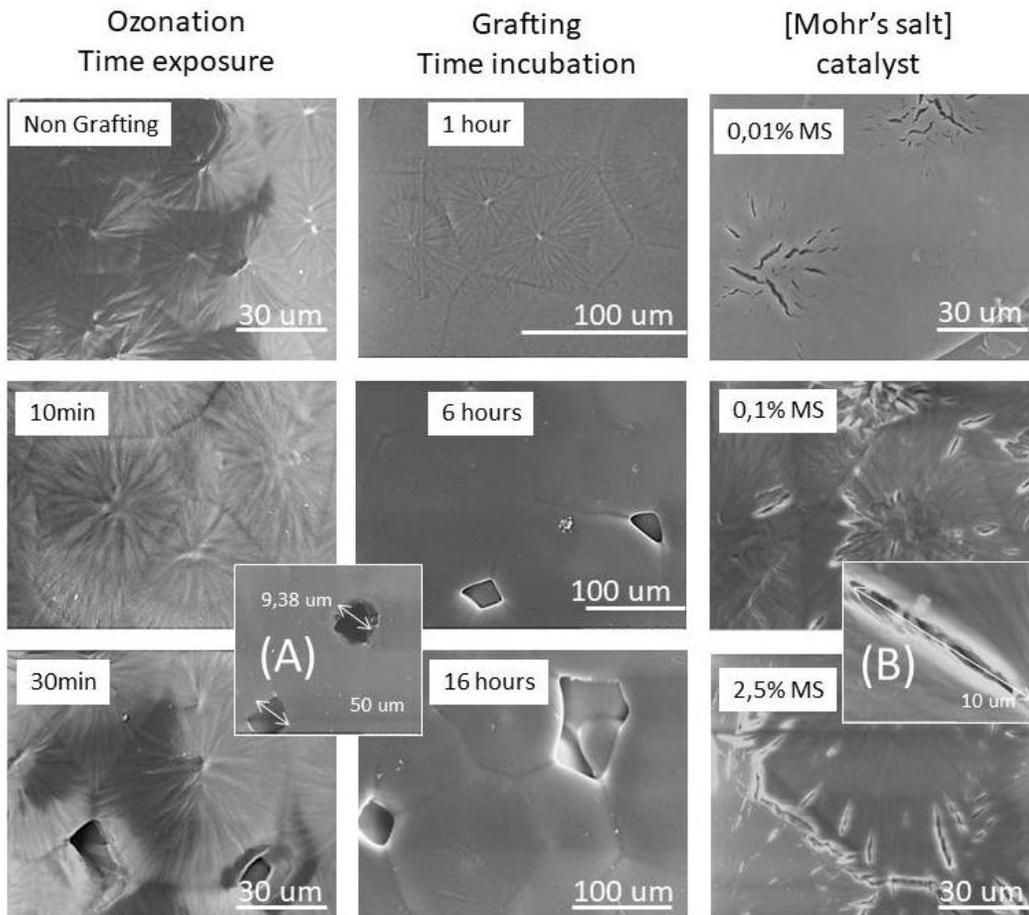


Figure 5. SEM analysis of ozonated and of PNaSS grafted PCL films: defects caused by ozonation (time ozonation 10 and 30min, 30 °C), grafting (time grafting 1, 6 and 16h, 45 °C) and Mohr's salt presence (0.01, 0.1 and 2.5 %, w/w of Mohr's salt, ozonation: 10min, 30 °C, grafting: 1h, 45 °C). (A) Defects degradation due to ozonation and grafting process; (B) defect caused by Mohr's salt

AFM. To evaluate more precisely the influence of the ozone oxidation reaction on PCL degradation, AFM scans ($0.5 \mu\text{m} \times 0.5 \mu\text{m}$) were carried out. When extending the ozonation time, surface swoll (see topography Fig 6) and the cross-section of the samples revealed an increase of the surface roughness (Ra). After 20 min of ozone treatment, the Ra value increased significantly from 2.21 to 5.47 – 5.92 nm (Figure 6).

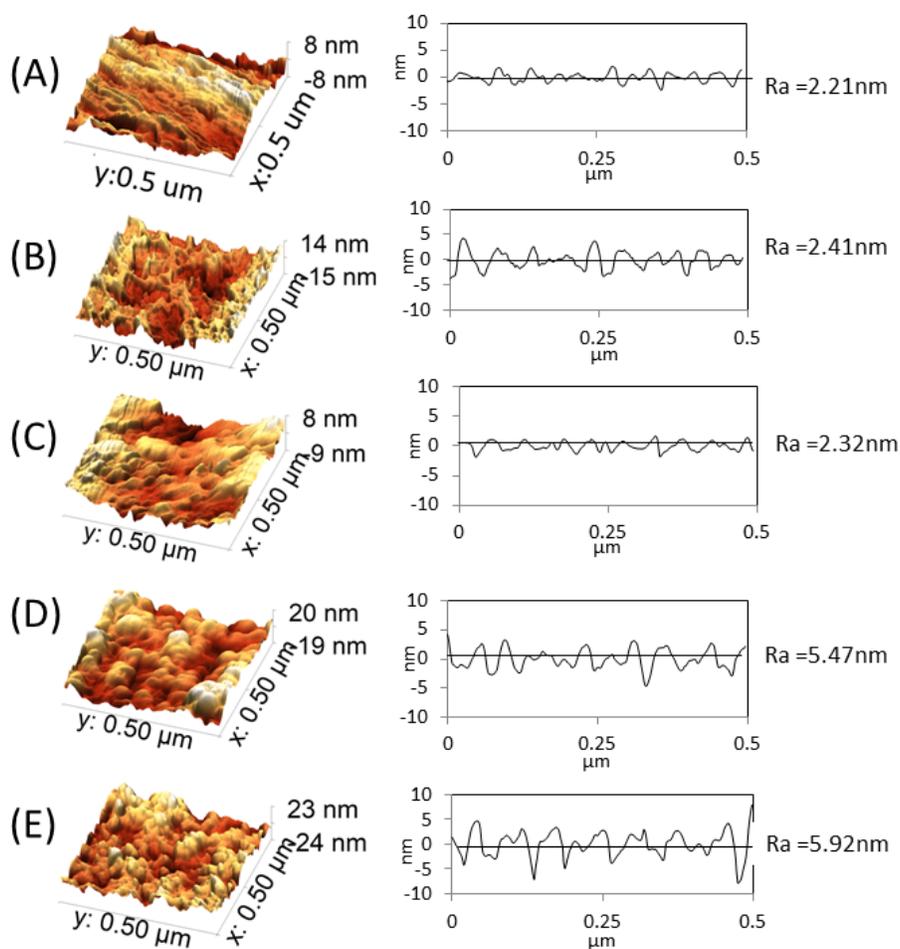


Figure 6. AFM topography images ($0.5 \mu\text{m} \times 0.5 \mu\text{m}$) and roughness cross section of: (A) virgin PCL, and grafted PCL with: (B) 5 min ozonation, (C) 10 min ozonation, (D) 20 min ozonation, (E) 30 min ozonation; Grafting for 1h at 45°C , 0.7mol.L^{-1} [NaSS]

SEC. The bulk degradation of the PCL macromolecular chains after the ozonation and PNaSS grafting was studied by using SEC through the determination of the variations of M_n and M_w after a) ozonation at different times (Figure 7A), b) followed by the PNaSS grafting for 1h to 6h at 45°C (Figure 7B) or c) 1h at 45°C in the presence of MA at different concentrations (Figure 7 C). Results showed that : The variation of M_n and M_w of PNaSS grafted PCL films a) ozonated after different times and b) PNaSS grafted during 1 to 6 h hours at 45°C were not significant except a small decrease of M_n (5 %) observed after 20 and 30 min of ozonation while M_w remained constant. At opposite, the presence of MS catalyst at 0.1 and 2.5% had a very strong effect on the M_n and M_w which collapsed. In the same time 3 PCL fractions of low molecular weight F1, F2, and F3 were detected starting from 0.1 %, w/w of MS - (M_n 57000, 4000 and 2000 $\text{g}\cdot\text{mol}^{-1}$ and M_w 75064, 4255 and 2012 $\text{g}\cdot\text{mol}^{-1}$).

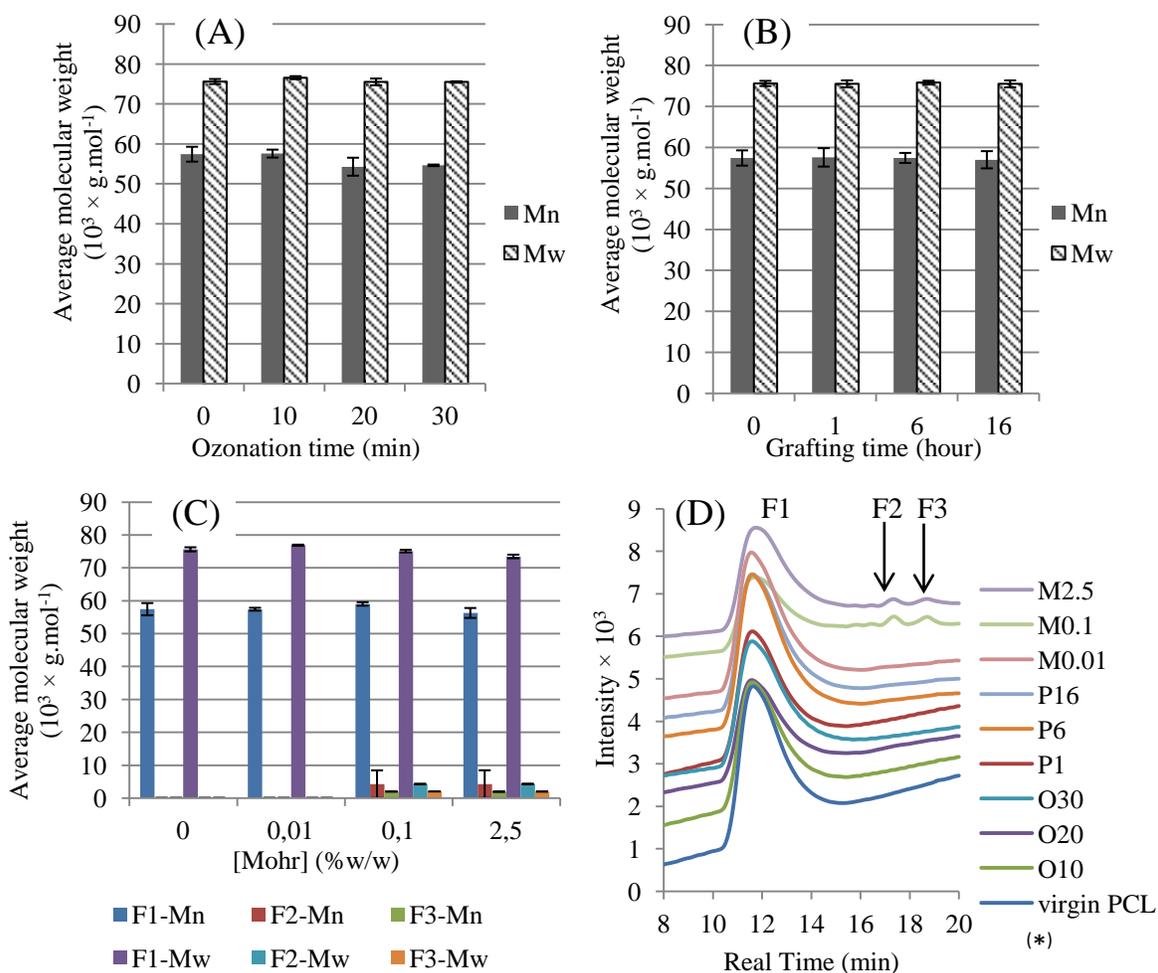


Figure 7. SEC chromatogram analysis: M_n and M_w of PNaSS functionalized PCL film after a) ozonation and b) PNaSS grafting at different times, c) grafting in the presence of Mohr's salt at different concentrations, d) SEC chromatogram of PCL films under a,b, c conditions – presence of F1, F2, F3 peaks corresponding to degraded macromolecular chains of PCL

4. DISCUSSION

4.1. Effects of the different steps of the grafting process on the grafting rate and on the PCL surfaces

4.1.1. Activation of the PCL surface

Activation energy:

Figure 1A showed that peroxide concentration was stable after 10 min ozonation whether extending the ozone exposure time, indicating that the surface is quickly saturated with peroxide groups. To explain these results we decided to analyse the activation energy involved in the grafting process. The analysis of the activation energy determined for the PNaSS grafting reaction on PCL showed low activation energies values – yet described in the literature for anionic monomers [18] [15] [16] - which could be opposed with the saturation of the PNaSS grafting degree (GD) after 10min of ozonation. That was assumed to be correlated to the rapid termination of anionic NaSS polymerization. Indeed, comparing the activation energy of PNaSS grafting to the polystyrene grafting on PCL confirm the strong effects of sulfonate groups on the termination reaction [16] [17] leading to low GD illustrated by the low S (2p) values obtained by XPS analysis.

Peroxide generation:

Peroxide generation on PCL surface was directly impacted by environmental conditions. Ozone easily decays in water to generate OH^\bullet . The pH change influences the reaction speed of ozone oxidation and acid/base equilibrium [19], impacting the activity of $\text{OH}^\bullet/\text{O}_3$ on the PCL surface.

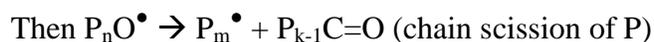
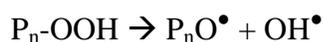
4.1.2. PNaSS grafting reaction.

In the absence of Mohr's salt (MS) catalyst, the polymerization of NaSS ended rapidly as can be seen for the low grafting rate despite increasing monomer concentration. Besides that, the presence of sulfonate was difficult to observe by FTIR. The atomic percentage of S2p was 0.5 % from XPS. Under standard conditions, NaSS grafting on PCL film reach their stables values after 1 hour at 45 – 50 °C. Grafting rate at 55°C incubation could increase by 57 % (Figure 1B), thanks to higher peroxide decomposition.

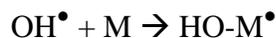
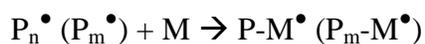
The concentration of MS drastically impacted the PNaSS grafting rate, because the presence of Fe²⁺ leads to significant peroxide decomposition acting as a catalyst. At the same time, Fe²⁺ will consume the released hydroxyl radicals (OH[•]), decreasing the competitive homopolymerization reaction in solution. The hypothesis could be simply expressed by the following scheme:

In the absence of MS catalyst (P for PCL and M for NaSS monomer)

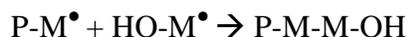
Initiation:



Propagation:



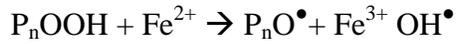
Termination:



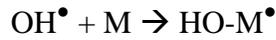
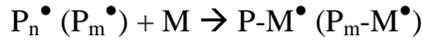
In the presence of MS catalyst:

Initiation:

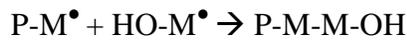
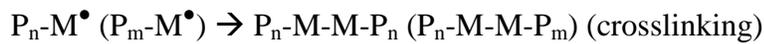




Propagation:



Termination:



[5], [6], [8], [13]

However, ferric ions which are cytotoxic and very difficult to remove completely remain on the PNaSS grafted surfaces and are not recommended for biological applications [20]

4.2. Grafting efficiency competition with degradation

Beside the PNaSS grafting reaction, chain scissions of PCL can occur by a hydrolysis process due to ozonation times over 10 min inducing degradation and creation of hydroxyl groups then more wettable PCL surfaces. This competitive hydrolysis reaction led us to analysis more deeply the TB complexation process used to determine the PNaSS GR and the observed BT results. We assume that it is necessary to take the specificity of BT molecules towards the two types of functional groups (sulfonate and hydroxyl) into account: a) specific and quantitative complexation of BT with sulfonate groups and b) unspecific adsorption/interaction of BT with hydroxyl groups. This explained BT values remained increasing for 30 min ozonation whereas the peroxide concentration was unchanged after 10 min and an the increase of O1s % and a decrease of C1s % revealing -OH and -OOH groups produced during both ozonation and grafting processes (see Figure A.1). Moreover, the observed increase of the surface tension can be related to the PCL surface degradation along ozonation time exposure.

MS catalyst effect.

In the presence of MS, the analysis of the GD values in the presence of MS showed that Fe^{2+} not only enhanced the PNaSS GD but also the surface degradation as illustrated by numerous cracks along the spherulite crystalline of PC (see Figure 5B). Fe^{2+} from MS was shown to decompose peroxide to radicals which participated to NaSS polymerization. However, the Fe^{3+} reduction to Fe^{2+} occurred directly decomposing peroxide groups leading to chain scission:

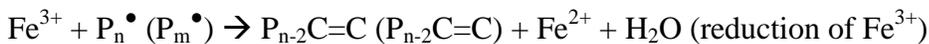
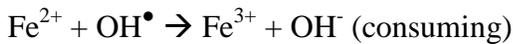
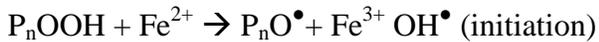


Figure 8 shows that the grafted PCL surface was smoother when PNaSS grafting was achieved in the presence of MS, indicating that a thicker PNaSS layer was grafted on the PCL substrate; this was correlated to an increase of the PNaSS GD. However, large defects (higher roughness) can also be distinguished, as seen on the texture graph in Figure 8. The defects could reach 60 nm of depth, 0.7 μm of width, and 2-10 μm of length (figure 5B and figure 8A).

In the absence of MS. Degradation caused by hydrolysis during the ozonation and grafting reactions was occurring with a different mechanism in the absence of the MS catalyst. Radicals ($\text{O}_3/\text{OH}^\bullet$) were shown attacking preferentially the boundaries areas between the spherulite regions. PNaSS grafting with longer ozonation times (over 10 min) promoted hydrolysis creating rougher surfaces (Figure 8) over the whole surface, however, amorphous structures are located at the frontier limit of the spherulites [21, 1]. Therefore, amorphous structures were strongly decomposed by chain scission into small molecules and formed holes (Figure 5A and figure 8B - size/diameter from 1 to 9.38 μm).

Moreover SEC results, demonstrated that the PCL bulk degradation – strong decrease of M_n values happened- for grafted PCL film after 20 min ozonation in the presence of MS (see Figure 7).

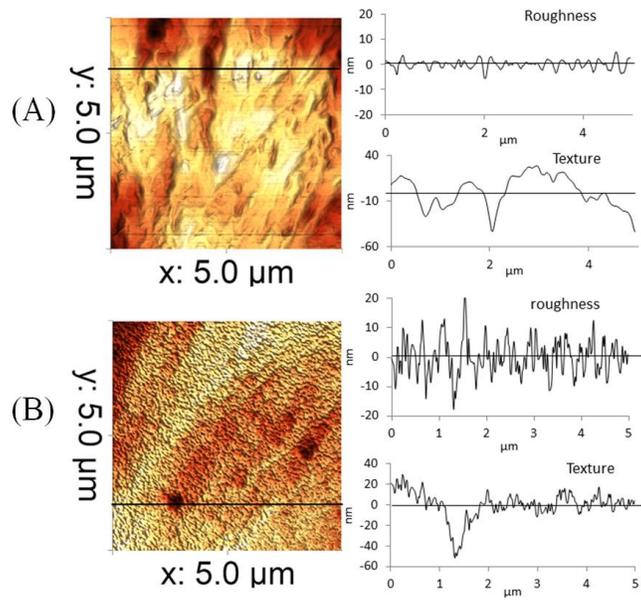


Figure 8. Topography images, roughness and texture diagram cross section of PNaSS grafted PCL film: (A) in the presence catalyst and (B) in the absence of catalyst

5. CONCLUSIONS

This study was devoted to the analysis of the effects of the different steps - a) activation by ozonation and b) thermal polymerization “from” the surface - parameters of the poly (sodium 4-styrene sulfonate) grafting process on the generation of poly(caprolactone) surface degradation. To achieve this goal, kinetics of ozonation and of poly (sodium 4-styrene sulfonate) thermal grafting were carried out on poly(caprolactone) surfaces under various conditions such as pH, monomer concentration, time and temperature, presence or absence of a catalyst.

The results showed that the activation of the grafting process leading to peroxide generation and radicals on PCL surfaces was limited after 10 minutes of ozone oxidation. This is due to the activation energy of the NaSS grafting which is fairly low (16.5 KJ/mol) and assumed to be due to the action of anionic sulfonate groups on the termination of the polymerization. In addition, the limitation of the peroxide generation on poly(caprolactone) was demonstrated despite the variation of different parameters as the extension of the reaction times of both ozonation and thermal grafting or the pH values of the reactions.

The presence of iron (II) ions was shown to increase substantially the grafting degree of the poly (sodium 4-styrene sulfonate) grafting process. However, the presence of Mohr’s salt as a catalyst generated an unexpected degradation of poly(caprolactone) as well as toxic ferric hydroxide as a by-product.

The aim was to constrain the poly(caprolactone) degradation during the functionalization process. This is a key challenge for biodegradable polymers devoted to biomedical applications. The study results demonstrated that both surface and bulk degradation could happen for long ozonation and thermal grafting times, and that the degradation effects are located in amorphous regions for regular grafting and over the whole material in the presence of Mohr’s salt.

To summarize, the kinetics and degradation study during the poly(sodium 4-styrene sulfonate) functionalization of poly(caprolactone) provided important information on the degradation of this biodegradable polymer during radical-grafting process. Optimized conditions were determined step to optimize the functionalization of polycaprolactone for further biomedical applications.

ACKNOWLEDGEMENT

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Appendices

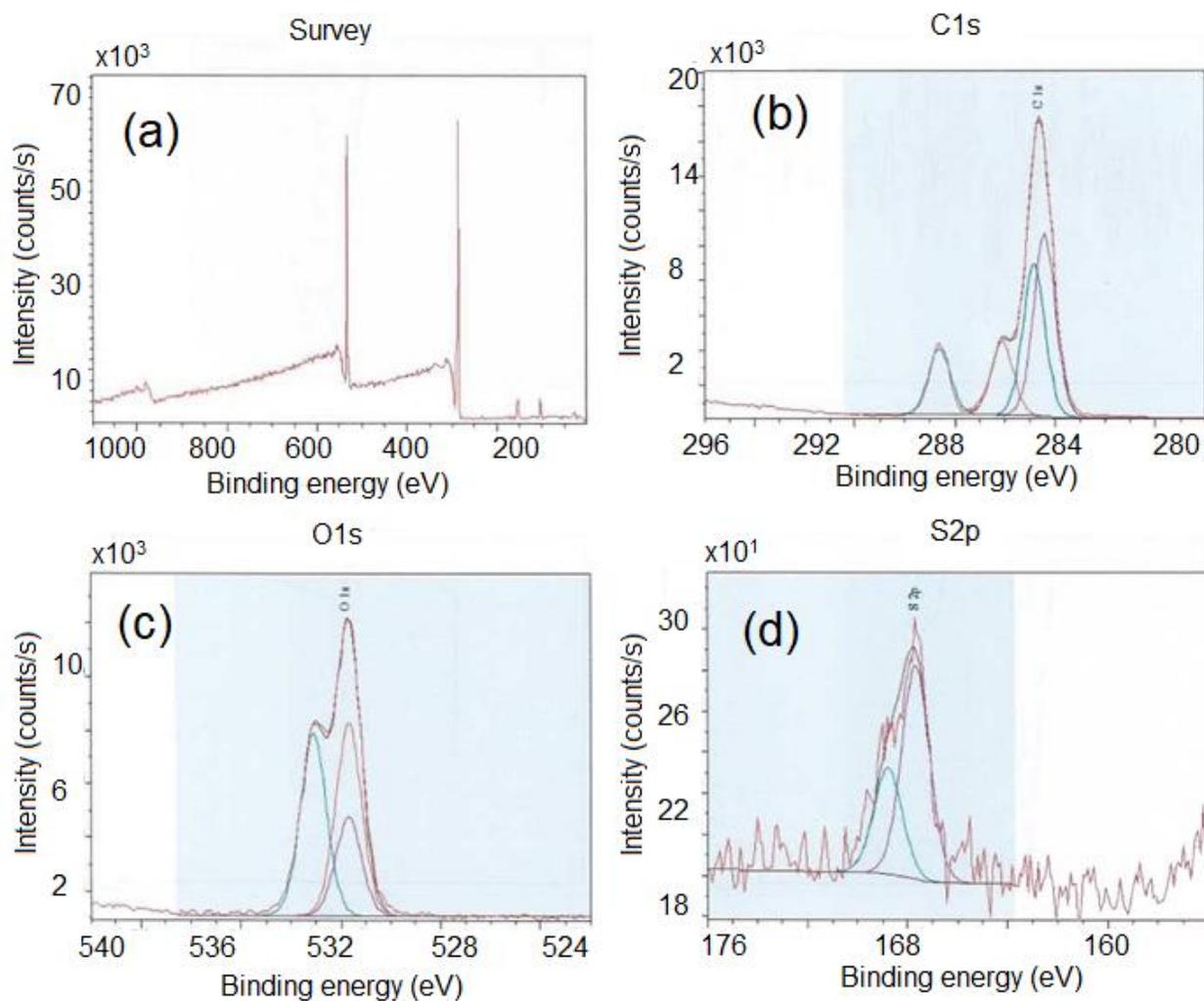


Figure A.1. The sulfonate groups were identified by XPS analysis corresponding to the S2p peak at 168 eV (0.5 %) (a) Survey, (b) C1s, (c) O1s and (d) S2p. Grafting conditions: 6 PCL disks (ϕ 14mm) ozonation for 10min at 30 °C and grafting for 1h at 45 °C in 0.7 mol.L⁻¹ of NaSS.

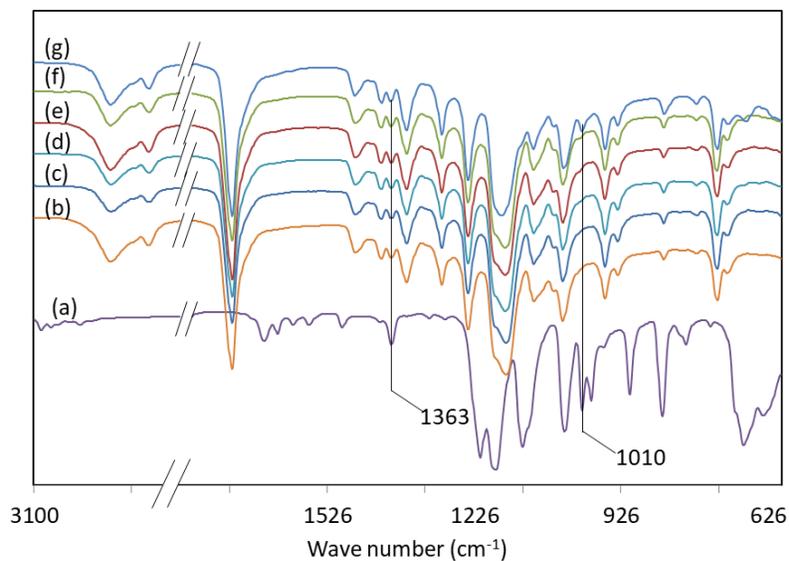


Figure A.2. FTIR spectra of: (a) PNaSS; (b) virgin PCL; and PNaSS grafted PCL with: (c) 5 min ozonation, (d) 10 min ozonation, (e) 20 min ozonation, (f) 30 min ozonation, (g) 10 min ozonation and Mohr's salt 0.1 % w/w. Grafting conditions: ozonation 30 °C, grafting: 1 h/ 45 °C, [NaSS] = 0.7 mol.L⁻¹. Styrene sulfonate groups were identified by FTIR on grafted PCL film at 1010 cm⁻¹ peak

Figure legend

Figure 1. Modulation of the PNaSS grafting degree on PCL – Influence of various parameters (A) ozone activation time on peroxide generation and on PNaSS grafting (polymerization 1 h, 45 °C, [NaSS] = 0.7 mol.L⁻¹) (B) polymerization time and temperature (ozonation 10 min, 30 °C, [NaSS] = 0.7 mol.L⁻¹) (C) NaSS monomer concentration (ozonation 10 min, 30 °C and polymerization 1 h, 45 °C) (D) pH variation of ozonation and polymerization grafting (ozonation 10 min, 30 °C and polymerization: 1 h, 45 °C, [NaSS] = 0.7 mol.L⁻¹).

Figure 2. Effect of Mohr's salt concentration on the grafting yield (ozonation 10 min 30 °C and polymerization 1 h at 45 °C, [NaSS] = 0.7 mol.L⁻¹)

Figure 3. Estimation of the activation energy of pNaSS grafting on PCL surface from Arrhenius plot

Figure 4. Evolution of hydrophilicity (A) and surface tension (B) of PNaSS grafted PCL film against the ozonation time (grafting conditions: 1 h/ 45 °C, [NaSS] = 0.7 mol.L⁻¹). The sessile drop contact angle method was used (solvents: water and diiodomethane), at 25 °C

Figure 5. SEM analysis of ozonated and of PNaSS grafted PCL films: defects caused by ozonation (time ozonation 10 and 30min, 30 °C), grafting (time grafting 1, 6 and 16h, 45 °C) and Mohr's salt presence (0.01, 0.1 and 2.5 %, w/w of Mohr's salt, ozonation: 10min, 30 °C, grafting: 1h, 45 °C). (A) Defects degradation due to ozonation and grafting process; (B) defect caused by Mohr's salt

Figure 6. AFM topography images (0.5 µm × 0.5 µm) and roughness cross section of: (A) virgin PCL, and grafted PCL with: (B) 5 min ozonation, (C) 10 min ozonation, (D) 20 min ozonation, (E) 30 min ozonation; Grafting for 1h at 45 °C, 0.7mol.L⁻¹ [NaSS]

Figure 7. SEC chromatogram analysis: M_n and M_w of PNaSS functionalized PCL film after a) ozonation and b) PNaSS grafting at different times, c) grafting in the presence of Mohr's salt at different concentrations, d) SEC chromatogram of PCL films under a,b, c conditions – presence of F1, F2, F3 peaks corresponding to degraded macromolecular chains of PCL

Figure 8. Topography images, roughness and texture diagram cross section of PNaSS grafted PCL film: (A) in the presence catalyst and (B) in the absence of catalyst