



# Synthesis and characterization of stimuli-responsive polypropylene containing *N*-vinylcaprolactam and *N*-vinylimidazole obtained by ionizing radiation



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## ABSTRACT

Polypropylene films were grafted with thermo-responsive *N*-vinylcaprolactam and pH-responsive *N*-vinylimidazole polymers by means of gamma radiation using pre-irradiation and direct methods, in order to functionalize the films with thermo- and/or pH-responsiveness. The dependence of grafting yield on parameters such as co-monomer concentration, pre-irradiation dose, temperature, and reaction time was evaluated. The samples were characterized by Fourier transform infrared and X-ray photoelectron spectroscopies, differential scanning calorimetry, thermogravimetric analysis, swelling studies in different solvents, and water contact angle. The grafted copolymers presented thermo- and pH-sensitiveness, highlighting their potential as advanced biomaterials, capable of providing adequate environment for hosting and sustained release of antimicrobial drugs bearing cationic moieties, such as groups of diclofenac, while still exhibiting good cytocompatibility.

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## 1. Introduction

The development of biomaterials to improve human life, whether for the replacement of dysfunctional or arthritic hips, atherosclerotic arteries and decaying teeth, or for the repair of injured tissues such as cartilage and skin, is ubiquitous [1]. Biomaterials can be broadly classified into three major groups: metals, polymers and ceramics [2]. With regard to polymers, polypropylene (PP) is widely used in many engineering and biomedical applications, including drug delivery [3] and biomedical devices [4,5] such as syringes [6], sutures, [3] and membranes [4]. The popularity of PP, in spite of its hydrophobic character, derives from its thermal stability and desirable mechanical properties [7]. By using appropriate surface treatments PP, which is commonly used in protein adsorption because of its hydrophobic surface [8], can be rendered more biocompatible and be provided with antimicrobial properties [4,6,9].

Radiation-induced copolymerization and crosslinking of copolymers have been increasingly used for the creation of novel biomaterials [10]. Radiation induced grafting offers many advantages over other conventional grafting methods (i.e. chemical and photochemical grafting)

such as an easier control over processing parameters, uniform grafting of monomers or other low molecular weight moieties at room temperature, flexibility and reproducibility [11–13]. Furthermore, as a result of the exposure to radiation, polymers may be simultaneously sterilized during grafting [14]. Concerning the radiation-grafting technique and depending on the chemistry of monomer-solvent-substrate system required, there are three main approaches available for grafting: mutual or simultaneous, pre-irradiation or consecutive, and oxidative methods [13,14]. In the area of biomaterials, grafting the original device with smart-, or stimuli-responsive, polymers is attractive considering that smart polymers, apart from yielding the material with new desired properties such as hydrophilicity, may also aid in physically adsorbing or chemically immobilizing drugs, enzymes, and antibodies onto the device [15]. As an example, the material may be bestowed with the ability to avoid bacterial attachment or prevent a host response.

Stimuli-responsive polymers are those that respond sharply to small changes in physical or chemical conditions with relatively large phase or property changes [16]. For instance, the term temperature-responsive refers to polymers which exhibit sharp and discontinuous changes in solubility and other physical or mechanical properties either upon heating or cooling to a lower critical solution temperature (LCST) or an upper critical solution temperature (UCST) [17]. On the other hand, pH-sensitive polymers are polyelectrolytes that contain weak acidic or basic groups in their structure, such as carboxylic groups, that either

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accept or release protons in response to changes in the pH of the environment [18].

In this work, *N*-vinylimidazole (NVIM) and *N*-vinylcaprolactam (NVCL) were grafted onto PP. NVCL and NVIM are monomers that hold thermo- [19] and pH-sensitivity [20] respectively, and to some extent, they have been widely applied for biomedical purposes [21–23]. Grafting of such monomers onto PP could broaden the applications of such materials for biomedical purposes, considering the possibility of the material response as a function of a biological change in temperature or pH, i.e. fever states, metabolic acidosis, among others [24–26]. Many polymers can be applied for biomedical applications, comprising biocompatible and degradable non-toxic components with a controllable degradation rate. The uses and applications of PP for biomedical uses have been reported by other researchers [27].

In the present work, the PP films were functionalized with NVCL and NVIM (Fig. 1) by means of direct and pre-oxidative methods using gamma radiation to investigate the influence of monomer/solvent concentrations, irradiation dose and reaction time over grafting yields, highlighting the potential of the modified PP film as a thermo- and pH-sensitive biomaterial. In order to assess the functionalization and stimuli-responsiveness, the grafts were characterized by: Fourier transform infrared and X-ray photoelectron spectroscopies (FTIR and XPS), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), swelling studies in different solvents, and water contact angle.

## 2. Experimental

### 2.1. Materials

Isotactic polypropylene films of 1 mm in thickness and 1 cm × 5 cm in size, acquired from Goodfellow (Huntingdon, UK), were washed in ethanol for 3 h and then dried under vacuum until constant weight. *N*-vinylcaprolactam and *N*-vinylimidazole were purchased from Sigma Aldrich (St. Louis, MO, USA), and distilled under reduced pressure before use. Toluene, heptane, chloroform, dichloromethane, carbon tetrachloride, hexane, and tetrahydrofuran were from J.T. Baker (Mexico) and used as received.

### 2.2. Synthesis of graft copolymers

Poly(*N*-vinylcaprolactam), PNVCL, was grafted onto PP films (PP-*g*-NVCL) using direct and pre-irradiation oxidative methods. The synthesis of PP-*g*-NVIM, (PP-*g*-NVIM)-*g*-NVCL, (PP-*g*-NVCL)-*g*-NVIM and PP-*g*-(NVCL-*co*-NVIM) copolymers was performed by the pre-irradiation oxidative method in one or two steps.

#### 2.2.1. Direct method

The PP film was weighed, placed inside an ampoule and put in contact with 5 mL of a NVIM-toluene solution, ranging from 30 to 70 vol%. Afterwards, the ampoule was degassed by repeated freeze–thaw cycles, sealed and irradiated at the desired dose within the range of 25 to 200 kGy, using a <sup>60</sup>Co source at a dose rate of 9.37 kGy/h. After grafting, the sample was washed (see Section 2.2.3).

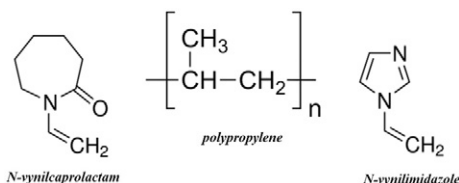


Fig. 1. Molecular structure of *N*-vinylimidazole, *N*-vinylcaprolactam and polypropylene.

#### 2.2.2. Pre-irradiation method

The PP film was weighed and placed into an ampoule to be irradiated in air at the desired dose, in the range of 25 to 250 kGy, using the above mentioned irradiation rate (see Section 2.2.1.), followed by the addition of 5 mL of the desired monomer-solvent using concentrations ranging from 20 to 100 vol%. The ampoule was then degassed by repeated freeze–thaw cycles, sealed and heated at the desired temperature, from 40 to 90 °C, and time, ranging from 10 to 90 h. After grafting, the sample was washed in toluene and heptane (see Section 2.2.3).

#### 2.2.3. Washing process

The samples were soaked in ethanol for 10 h (changed ethanol 2 times), followed by drying under vacuum at 50 °C to constant weight, in order to extract residual monomer and homopolymer formed.

#### 2.2.4. Grafting yield (%)

The grafting yield was calculated according to Eq. (1):

$$\text{Grafting yield (\%)} = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

where  $W_g$  and  $W_o$  are the weights of the films after and before grafting, respectively.

### 2.3. Characterization

#### 2.3.1. FTIR-ATR

FTIR-ATR (attenuated total reflection) spectra of graft copolymers were recorded on a Perkin-Elmer Spectrum 100 spectrometer (Norwalk, CT, U.S.A.).

#### 2.3.2. Chemical surface composition

X-ray photoelectron spectroscopy (XPS) analyses were performed in a VG ESCALAB 3MkII instrument, using non-monochromatic Mg K $\alpha$  radiation. The analysis area was 2 mm × 3 mm. A pass energy of 100 eV and energy steps of 1 eV were used to obtain broad-scan spectra. No evidence of X-ray induced damage was ever observed. Spectra were acquired at 0° emission angles, normal to the sample surface; possible charging was corrected by referencing all peaks to the C1s peak at binding energy (BE) = 285.0 eV. The elemental chemical compositions (in atomic %, At.-%) were quantified from broad-scan spectra using CASAXPS software (Neal Fairley, UK), version 2.3.14, by integrating the areas under peaks after a Shirley-type background subtraction, and using sensitivity factors from the Wagner table.

#### 2.3.3. pH-responsiveness by swelling measurements

The pH-responsiveness of PP grafted with NVIM and binary graft copolymers was determined by measuring the sample's degree of swelling in buffer solutions of pH ranging from 2 to 11. The dried sample was exposed to each buffer solution, one at a time, for 3 h until equilibrium was attained. Afterwards, the sample's surface was gently wiped with filter paper and the swollen sample was weighed. Swelling percentage was determined gravimetrically based on the measured weights of the swollen ( $W_s$ ) and dried ( $W_d$ ) films and calculated according to Eq. (2).

$$\text{Swelling (\%)} = \frac{W_s - W_d}{W_d} \times 100. \quad (2)$$

The critical pH was defined as the inflection point of the swelling (%) vs. pH plot.

#### 2.3.4. Maximum swelling degree in different solvents

The swelling degree was measured by the immersion of dried samples in different solvents followed by constant weighing until equilibrium. The solvents used were water, methanol, ethanol, acetone, dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), chloroform, ether, acetonitrile,

Tetrahydrofuran (THF), dioxane, toluene, hexane and heptane. The swelling degree was calculated as described in Section 2.3.2.

### 2.3.5. Differential scanning calorimetry (DSC)

The thermo-responsive properties of the films were estimated by means of the lower critical solution temperature (LCST), based on the determination of thermodynamic transitions by DSC. The runs of the swollen samples (immersed in water for 24 h) were recorded under nitrogen atmosphere using a DSC 2010 calorimeter (TA Instruments, New Castle, DE USA) using a temperature range of 25 to 50 °C with a step increase of 1 °C min<sup>-1</sup>. For the thermograms of dried grafts, runs were recorded in the range of 25 to 250 °C at 10 °C min<sup>-1</sup>.

### 2.3.6. Decomposition temperature

Decomposition temperature was determined under nitrogen atmosphere using a TGA Q50 device (TA Instruments, New Castle, DE USA) from 25 to 800 °C at 10 °C min<sup>-1</sup>.

### 2.3.7. Water contact angle

Contact angle was measured using a drop shape analyzer Kruss DSA 100 apparatus (Matthews NC, USA). Small drops of distilled water were deposited onto dry films and the contact angle was measured at room temperature.

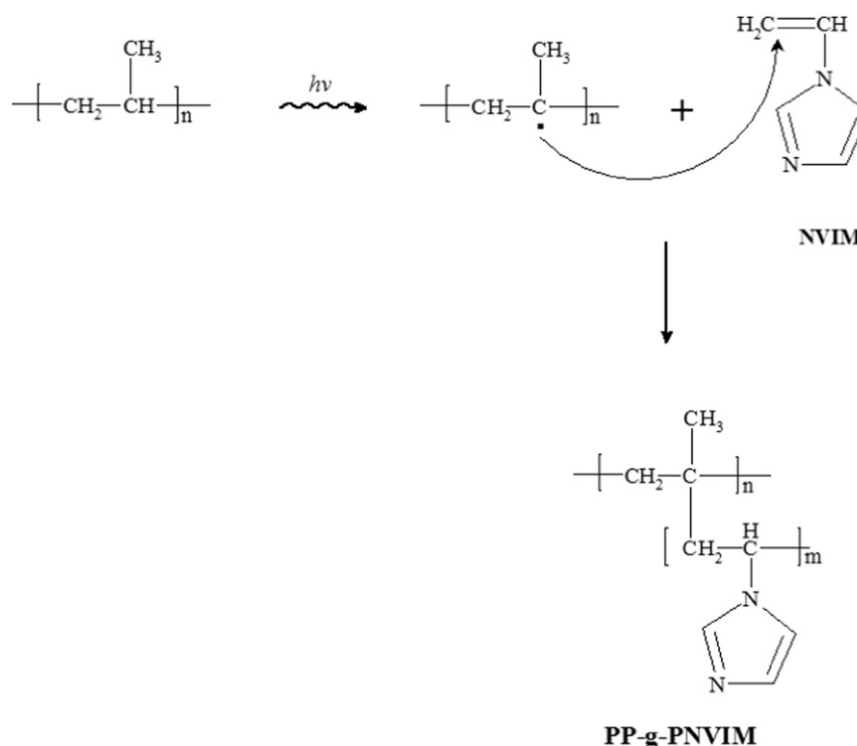
## 3. Results and discussion

Modification by gamma radiation is one of the preferred methods for surface functionalization of polymer materials, due to the uniform and rapid creation of active radical sites, rendering high values of grafting. Also, this technique is relatively simple and does not require the use of catalyst or additives to initiate the reaction. Radiation-induced polymerization reaction leading to the formation of the graft copolymer of NVIM onto PP films is given in Scheme 1 by direct method and Scheme 2 shows binary graft copolymer of NVCL and NVIM onto PP by pre-irradiation method.

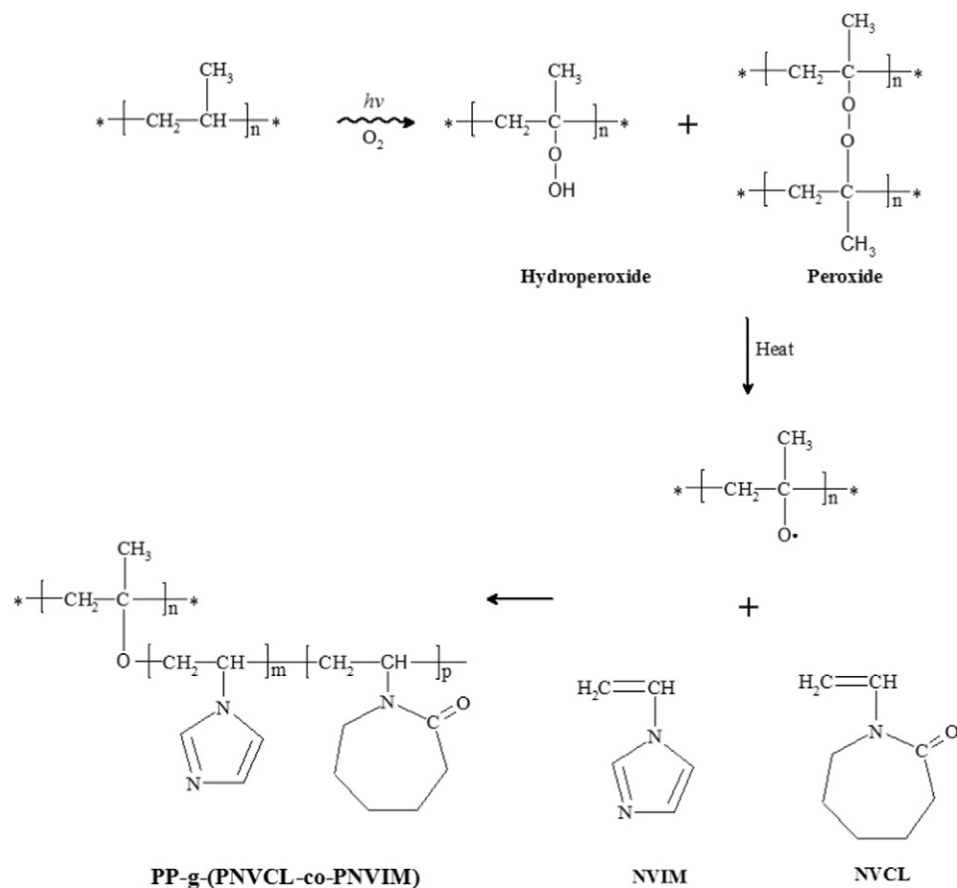
Grafting of poly(*N*-vinylimidazole), PNVIM, onto PP films was performed by direct and pre-irradiation oxidative methods (Figs. 2 and 3, respectively). Fig. 2a shows the grafting percentage of PP-g-PNVIM as a function of NVIM/toluene concentration at an irradiation dose of 200 kGy, showing a maximum at 50 vol%. At a constant monomer/solvent ratio of 50 vol%, the grafting percentage (5–15%) increased with irradiation dose (Fig. 2b). In Fig. 3, the grafting percentage (0 to 25%) was influenced by: a) NVIM/toluene concentration (maximum percent at 100 vol%), b) temperature of reaction (similar values between 80 and 90 °C), c) irradiation dose (maximum percent at 250 kGy) and d) reaction time (similar values between 40 and 60 h). Grafting yields increased as the values of the four variables (a–d) increased.

Comparing the grafting efficiency of the direct and pre-irradiation methods, it is well known that higher grafting percentages are reached with the former method. For example, a ≈ 15% graft of PP-g-PVIM was reached by the direct method using 200 kGy and a 50% VIM concentration; while using the pre-irradiation method, with the same irradiation dose and monomer concentration but a reaction time of 40 h (which implies a longer preparation time), a PP-g-PVIM graft of ≈ 13% was obtained. However, with the latter method, when a 100% monomer concentration was used, which is a concentration that did not show the best results with the direct method, alongside an irradiation dose of 200 kGy and a reaction time of 40 h, grafts of ≈ 13% were also reached. The differences in grafting yields can be explained by two aspects. The first aspect is related to the intrinsic properties of each technique, as radiation is known to create active sites in the polymeric matrix, which leads to several radiation-chemical processes involving the macromolecules that drive the grafting process. In other words, the differences arise from the distinct availability of active sites suitable for grafting formed during each irradiation method. When it comes to the pre-irradiation method, propagation time can be longer than in the direct method, meaning that the pre-irradiation method requires the generation of radicals with a long lifetime in order to reach high grafting yields, while the direct method is less time consuming.

Because in the direct method the likelihood of homopolymerization is high at monomer concentrations as low as 60 vol%, the use of pure



Scheme 1. Grafting of NVIM onto PP film by means of gamma radiation, using direct method.



**Scheme 2.** Grafting of NVCL and NVIM onto PP film by means of gamma radiation, using pre-irradiation method.

monomers in graft polymerization is limited by their undesirable homopolymerization, which is initiated by the irradiation of the polymer–monomer system in the direct method. The formation of homopolymer turns the reaction medium more viscous and limits the mobility of unreacted monomer molecules towards polymer radicals, which makes the grafting reaction unfavourable. In addition, homopolymer removal becomes more complicated as the medium becomes more viscous. This explains why the obtained maximum grafting yield of PP as a function of monomer concentration was of 15% graft at 50 vol% monomer concentration for the direct method, and of 25% graft at 100 vol% monomer concentration for the pre-irradiation methods, respectively. The contribution of homopolymerization is less, or negligible, with decreasing monomer concentration.

It is known that the yield of grafting by the pre-irradiation method depends directly on the efficiency of radical trapping. Therefore, it follows that this method is particularly favoured if the polymer is irradiated in the glassy state, or if the polymer is crystalline at the irradiation temperature. Much higher radical yields are indeed found if irradiation is carried out in the absence of oxygen, and the yield of formation of trapped radicals can be increased by irradiating the polymer surface in the presence of active free radicals, formed under pre-irradiation, leading to higher graft efficiency. On the other hand, grafting yields by the pre-irradiation method also depend on the concentration of radicals formed in the irradiated film and the monomer concentration in the reaction vessel, as stated previously. An increase in temperature results in the decomposition of peroxides and hydroperoxides, which were formed in the PP while it was irradiated, and in an increase of monomer diffusion in the film, allowing for the grafting percentage to increase with temperature and reaction time.

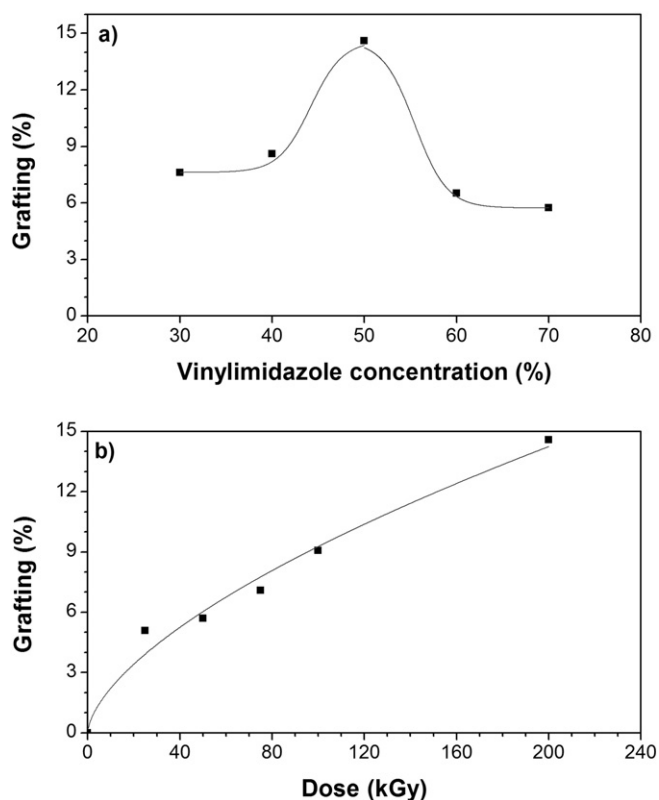
Fig. 4 shows the grafting degree of PP-g-PNVCL (pre-irradiation oxidative method) as a function of: a) PNVCL/heptane concentration

(maximum percent at 50 vol%), b) reaction temperature (similar values between 50 and 90 °C), c) irradiation dose (maximum percent at 250 kGy), and d) reaction time (maximum value at 60 h). A previous work by Ferraz et al. reported grafting percentages of PNVCL and poly(-acrylic acid) (PAAc) copolymers onto PP or SR between 3 and 25% [18]. In this work, grafting yields were improved, attaining PNVCL grafting percentages of up to 27%. The effect of monomer concentration on the grafting yield, after a 40 h reaction time at 80 °C, was examined as a first parameter. The data plotted in Fig. 4a shows that a broad range of graft content may be achieved, with graft efficiency values close to 11% for a 50 vol% NVCL concentration.

Fig. 4b shows that grafting efficiency increased to approx. 22% at 50 °C, but it decreased to 18% as the temperature was increased to 90 °C. This also highlights the relevance of temperature when it comes to controlling the grafting process.

The effect of the pre-irradiation dose on the grafting yields was examined by performing graft polymerizations between the dose range of 25 and 250 kGy, as the number of latent initiator sites is expected to increase with increasing radiation dose, although not necessarily in a proportional manner (Fig. 4c). Reaction time was also evaluated and as expected, the grafting efficacy increased as the reaction time increased from 10 to 60 h (Fig. 4d).

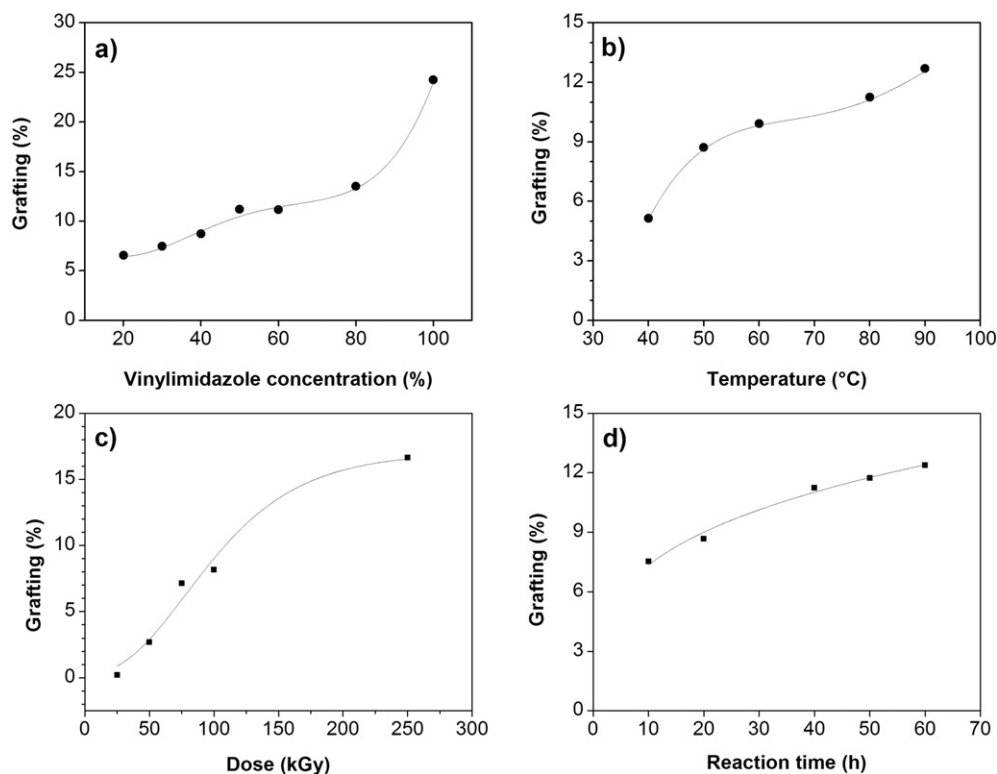
Fig. 5 shows the maximum swelling percentages reached for (a) PP and (b) PP-g-NVCL in different solvents (water, methanol, ethanol, acetone, CH<sub>2</sub>Cl<sub>2</sub>, chloroform, ether, acetonitrile, THF, dioxane, toluene, hexane and heptane). PP did not swell in water, but it did in the rest of the solvents (1–7% in 15–180 min), with the maximum swelling obtained using chloroform, followed by CH<sub>2</sub>Cl<sub>2</sub> and ether. After PP modification with PNVCL (16%), the film swelled in water (6% in 45 min); however, chloroform remained the solvent where the film reached maximum swelling (23% in 90 min). The swelling of PP-g-NVCL in different



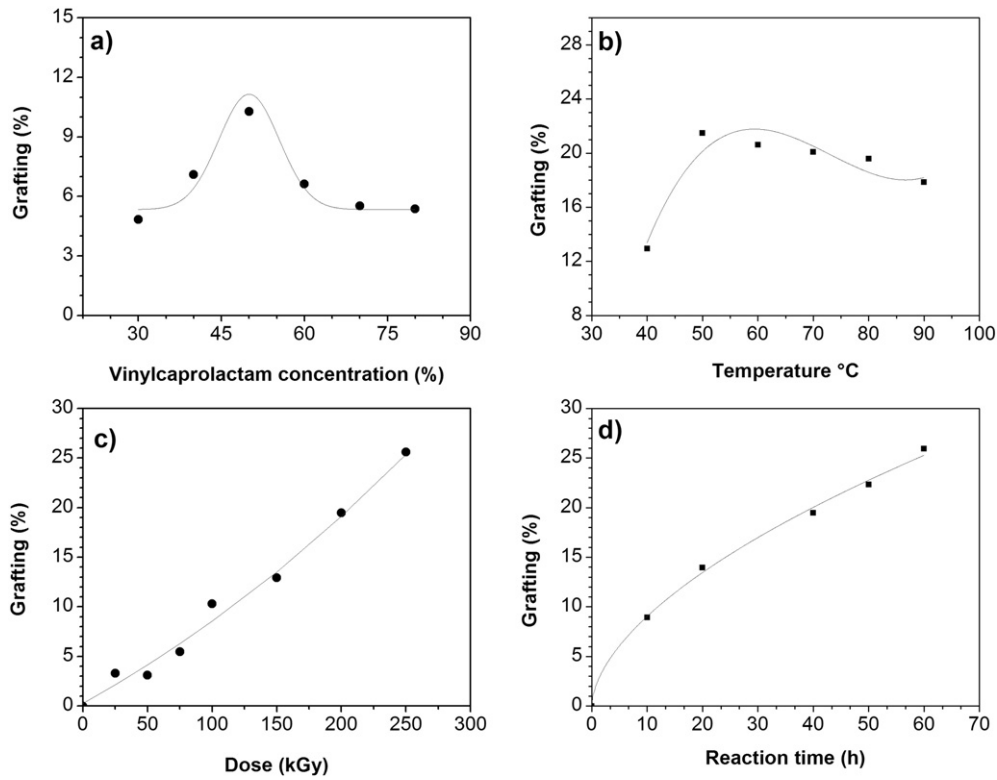
**Fig. 2.** Grafting of vinylimidazole onto polypropylene (PP-g-NVIM) as a function of: a) monomer concentration at an irradiation dose of 200 kGy, and b) irradiation dose (monomer concentration of 50 vol%). The solvent used was toluene. All samples were irradiated by the direct method using a  $^{60}\text{Co}$  source at a dose rate of 9.37 kGy/h.

solvents contributed to the understanding of the effect of solvents during grafting polymerization, providing a guide towards determining which solvent would be most ideal in the diffusion of the monomer in the polymer matrix. Chloroform reaches higher swelling values than the other solvents, which indicates that it is the best option for monomer diffusion during grafting, however, in practice, better results (higher values of swelling) are obtained employing heptane (results not presented), showing that monomer-solvent-polymer interactions affect propagation step during grafting.

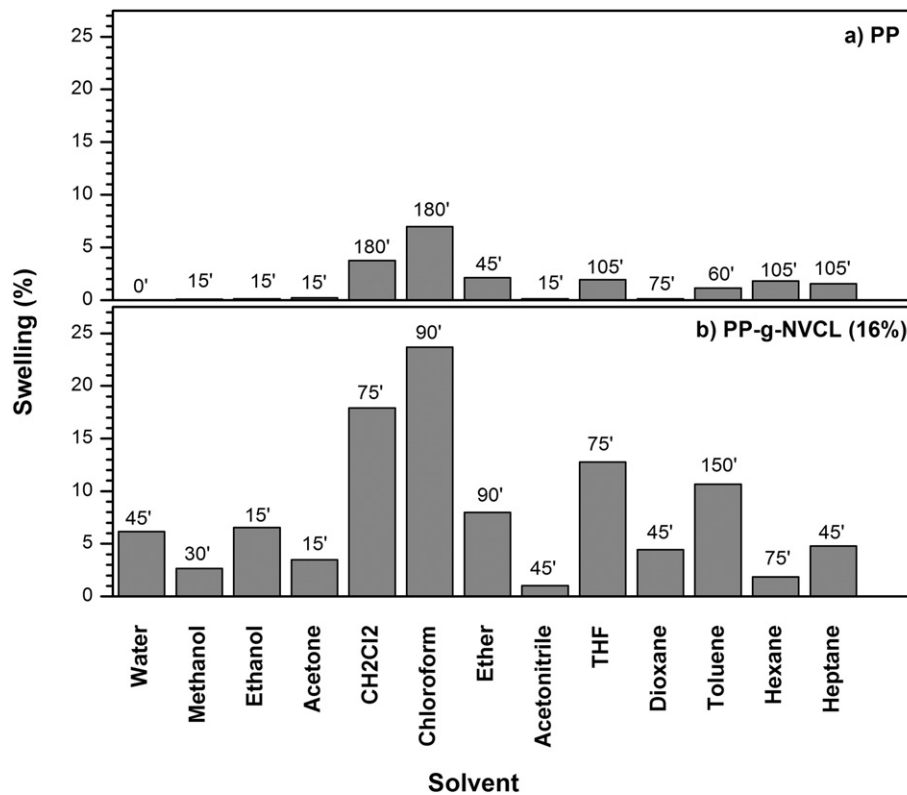
The confirmation of chemical modification of PP with PNVIM and PNCL for different grafts is presented in Fig. 6 through infrared characterization. The FTIR-ATR spectrum of PP (Fig. 6a) showed PP's characteristic bands at  $\sim 840$  and  $\sim 1160\text{ cm}^{-1}$  due to  $-\text{CH}(\text{CH}_3)-\text{C}-$  and at the region of  $\sim 2950\text{--}2840\text{ cm}^{-1}$ , caused by  $\text{CH}_3$ ,  $\text{CH}_2$  and  $\text{CH}$  stretching; and at  $1457\text{--}1375\text{ cm}^{-1}$  due to the  $\text{CH}_3$  out of plane bending vibrations and the symmetric bending vibration of  $\text{CH}_2$ . For PNVCL, the characteristic bands appeared at  $2923$  and  $2854\text{ cm}^{-1}$  (C-H), at  $1364\text{ cm}^{-1}$  ( $\text{CH}_3$ ), at  $1620\text{ cm}^{-1}$  (C=O stretch), and at  $1420\text{--}1475\text{ cm}^{-1}$  (lactam ring). Ferraz et al. found similar results [18]. The PP-g-NVCL spectrum with 23% grafting (Fig. 6c) presented both PP and PNVCL bands, thus confirming functionalization. The PNVIM spectrum (Fig. 6d) showed signals at  $3015\text{ cm}^{-1}$  (C-H stretch from imidazole ring), at  $1642\text{ cm}^{-1}$  (aromatic C=C stretch), at  $1493$  and  $1412\text{ cm}^{-1}$  (aromatic C=N and C-N stretching bonds), and at  $1226\text{ cm}^{-1}$  (N-C-N) [26]. For PP-g-NVIM with 22% graft (Fig. 6e), bands related to the incorporation of PNVCL within PP films were identified. The infrared spectra for graft copolymers synthesized in one or two steps by pre-irradiation oxidative method containing both smart polymers is presented in Fig. 6f-h. The characteristic signals of PNVIM and PNVCL were present in each spectrum, hence assuring easy monitoring of the modifications induced by both polymers upon evaluation of the two bands located within the range of  $1600\text{--}1700\text{ cm}^{-1}$ .



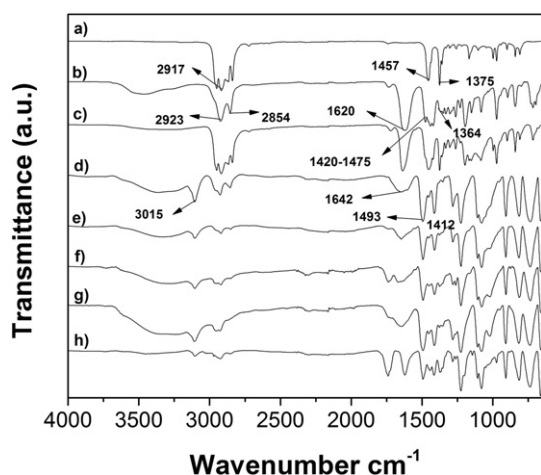
**Fig. 3.** Grafting of vinylimidazole onto polypropylene (PP-g-NVIM) obtained by the pre-irradiation oxidative method as a function of: a) monomer concentration (200 kGy,  $t = 40$ ); b) reaction temperature (200 kGy, 50 vol% NVIM/toluene,  $t = 40$  h); c) irradiation dose (50 vol% of NVIM/toluene,  $t = 40$  h); and d) reaction time (200 kGy, 50 vol% of NVIM/toluene,  $T = 80\text{ }^{\circ}\text{C}$ ).



**Fig. 4.** Grafting of vinylcaprolactam onto polypropylene (PP-g-NVCL) obtained by the pre-irradiation oxidative method as a function of a) monomer concentration ( $T = 80\text{ }^{\circ}\text{C}$ ,  $t =$  reaction time of 40 h, and 200 kGy); b) reaction temperature (200 kGy, monomer concentration of 50 vol%,  $t = 40\text{ h}$ ); c) irradiation dose (monomer concentration of 50 vol%,  $t = 40\text{ h}$ ); and d) reaction time (200 kGy, monomer concentration of 50 vol% in heptane,  $T = 80\text{ }^{\circ}\text{C}$ ).



**Fig. 5.** Maximum swelling degree of (a) PP and (b) PP-g-NVCL with 16% grafting in different solvents. The corresponding equilibrium swelling time (in minutes) is indicated above the corresponding bars.

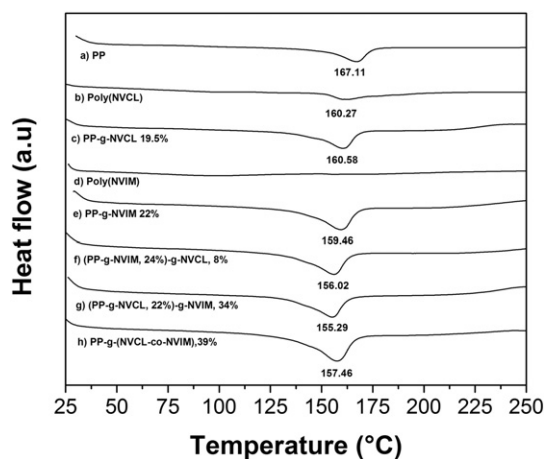


**Fig. 6.** FTIR-ATR spectra of (a) PP, (b) PNVL, (c) PP-g-NVCL (23.6%), (d) PNVIM, (e) PP-g-NVIM (22.1%), (f) (PP-g-NVIM)-g-NVCL (24% and 8%, respectively), (g) (PP-g-NVCL)-g-NVIM (22% and 24%, respectively), and (h) PP-g-(NVCL-co-NVIM) (39%).

The thermal transitions for the different systems obtained by DSC are shown in Fig. 7. The melting point ( $T_m$ ) of pristine PP is at 167 °C, whereas PNVL exhibited a glass transition temperature ( $T_g$ ) at 160 °C. No transitions were observed for PNVIM in the assayed temperature range. Graft copolymers of NVCL and/or NVIM onto PP films (c, e–h) presented a transition between 155 and 160 °C due to melting point ( $T_m$ ) of PP and as a consequence, the  $T_g$  was difficult to observe due to its close proximity to the  $T_m$ . These results confirmed that PNVIM and PNVL were grafted onto PP films with thermal stability at around 155 °C.

Thermal stability was measured by TGA at 10 °C min<sup>-1</sup> from room temperature to 800 °C and the results are presented in Table 1 and Fig. 8. This table contains the thermal decomposition temperatures (10 wt% loss) and char yield (%) of the graft copolymers and polymers (PP, PNVL and PNVIM). The graft copolymers exhibited decreased stability (compared with PP pristine) in N<sub>2</sub> (10 wt% loss at temperatures from 377 to 411 °C) as measured by TGA. It is relevant to observe that in several cases, the TGA data were similar (a difference of only 34 °C), which could be related either to the thermo-oxidative stability of these polymers or to the thermal weak linkage of NVCL and NVIM moieties to PP films.

The water uptake of the grafted PP as a function of time is shown in Fig. 9. The swelling levels of selected samples at different absorbing times in distilled water were measured, indicating that the initial



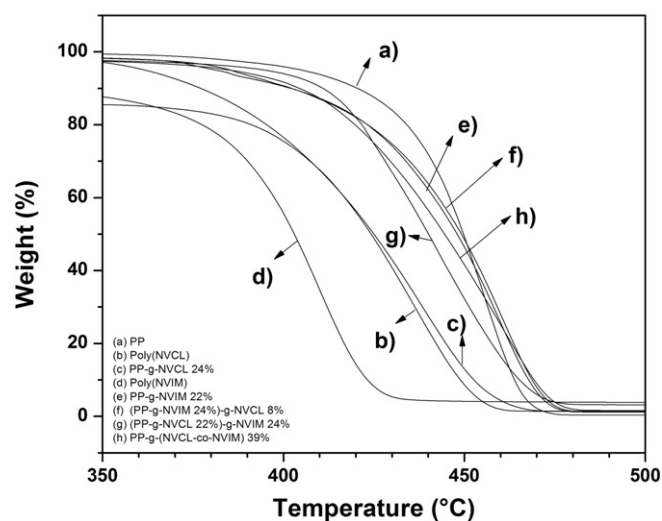
**Fig. 7.** DSC curves for the systems containing NVCL and NVIM grafted onto PP with the respective melting points (°C). The thermograms for PP, PNVL, and PNVIM are also shown.

**Table 1**  
Thermogravimetric analysis of the different grafts.

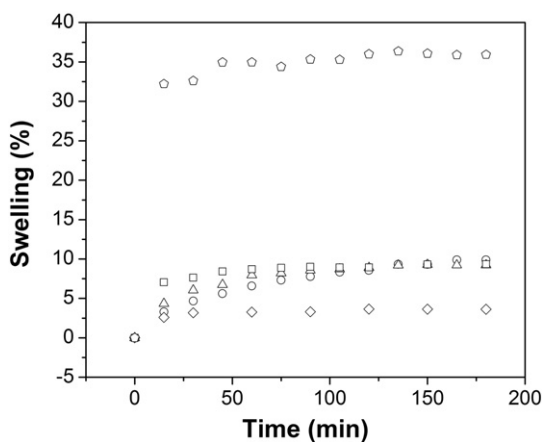
Sample	Grafting	Weight loss temperature (10 wt%, °C)	% char yield (700 °C, N <sub>2</sub> )
PP	–	420	0.9
PNVCL	–	180	1.0
PP-g-NVCL	24%	377	1.9
PNVIM	–	326	1.9
PP-g-NVIM	22%	383	2.1
(PP-g-NVIM)-g-NVCL	24 and 8%, respectively	404	1.1
(PP-g-NVCL)-g-NVIM	22 and 24%, respectively	402	0.9
PP-g-(NVCL-co-NVIM)	39%	411	0.9

swelling process occurred primarily due to the water penetrating into the copolymer film through capillarity and diffusion processes, followed by water absorption by the hydrophilic groups. Swelling was fast during the first 20 min and gradually slowed down until equilibrium was reached. The swelling rate and equilibrium time were established at around 60 min. The maximum swelling of 48% was observed for the graft copolymer obtained by the two step method when PP was modified with NVCL (first step) and NVIM (second step), indicating that grafting occurred primarily at the surface. The swelling of the other samples was much lower, between 5 and 10%, possibly due to the copolymers being grafted in bulk. In all cases, maximum swelling time occurred at 60 min.

Poly(*N*-vinylimidazole) is a water-soluble polymer possessing its backbone imidazole moieties with a value of pKa around 6. The imidazole groups become protonated and swell in acid solutions. Thus, grafting of VIm was expected to communicate pH-responsiveness to the copolymer. The critical pH point can be defined as the pH at which the polymer chains change abruptly their behavior from hydrophilic extended state) to hydrophobic (collapsed state). The pH-responsiveness of grafts containing PNVIM was confirmed by swelling studies (Fig. 10). All modified films were pH-sensitive and showed a critical pH point that was determined as the inflexion point on swelling. The average critical pH of the films was of 7.3 ± 0.4. The swelling percentages of the films grafted with PNVIM were higher than for those grafted with NVCL-co-NVIM due to the higher hydrophilicity of the NVIM component. In the binary grafting of films by the one-step and two-step methods, the critical pH point of binary PP-g-(NVCL-co-NVIM) films shifted to a higher pH



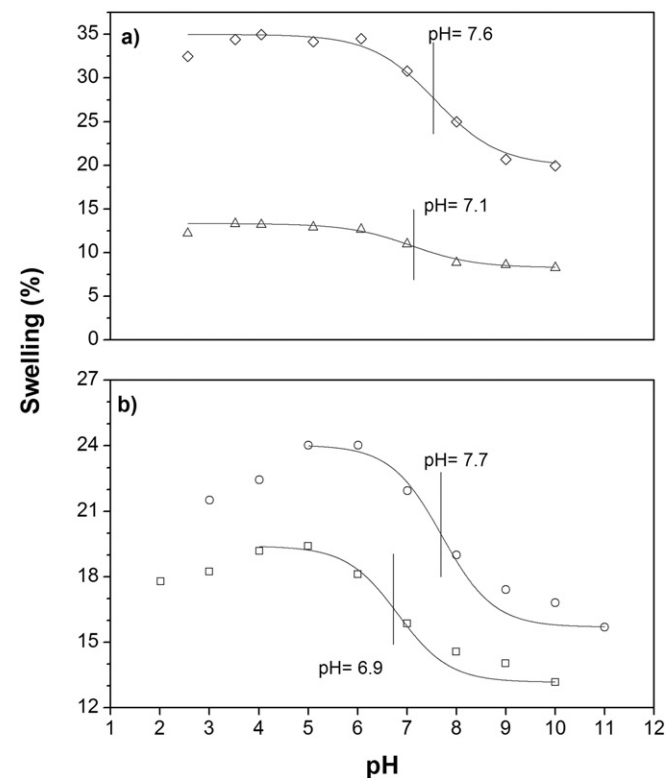
**Fig. 8.** Thermogravimetric analysis of: PP (a), poly(NVCL) (b), PP-g-NVCL 24% (c), poly(NVIM) (d), PP-g-NVIM 22% (e), (PP-g-NVIM 24%)-g-NVCL 8% (f), (PP-g-NVCL 22%)-g-NVIM 24% (g), and PP-g-(NVCL-co-NVIM) 39% (h).



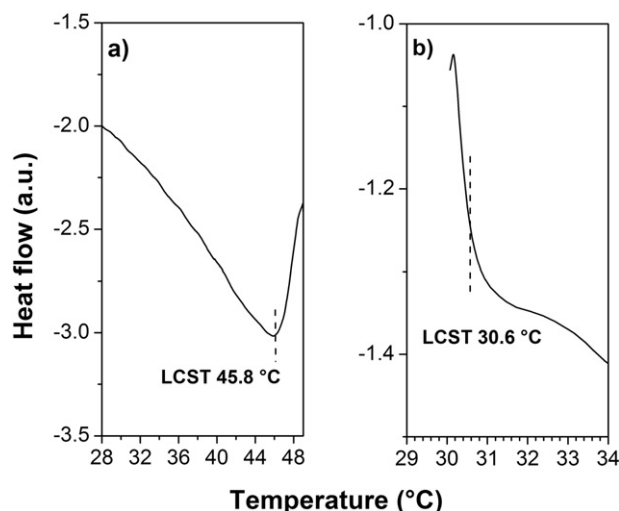
**Fig. 9.** Swelling degree of the different grafts in water (at 25 °C) as function of time: i) (PP-g-NVCL, 22%)-g-NVIM, 24% ( $\square$ ), ii) PP-g-(NVCL-co-NVIM), 39% ( $\square$ ), iii) (PP-g-NVIM, 24%)-g-NVCL, 8% ( $\circ$ ), iv) PP-g-NVCL, 19% ( $\diamond$ ), and v) PP-g-NVIM, 13% ( $\triangle$ ).

with increasing grafting percentage (Fig. 10b). Concerning the one-step method, the composition of both monomers at different grafting percentages depended on the reactivity,  $r$ , of the copolymer chains ( $r_{\text{NVIM}}$  0.35 and  $r_{\text{NVCL}}$  0.039). Therefore, the critical pH point of the one-step graft copolymer was observed at 7.7, whereas the graft copolymer synthesized by the two-step method presented a lower critical pH at around 6.9.

Temperature-responsiveness of grafts containing PNVC L was also confirmed by DSC studies in Fig. 11. Regarding LCST evaluation, thermograms of PP-g-NVCL (24%) and (PP-g-NVCL 22%)-g-NVIM 34% exhibited a LCST at 46 and 31 °C, respectively. The onset point of the endothermic peak, determined by the intersecting point of two tangent lines from the baseline and slope of the endothermic peak, was used to establish the



**Fig. 10.** Swelling degree as a function of pH for PP-g-NVIM, 19 ( $\triangle$ ) and 40% ( $\diamond$ ); (PP-g-NVIM, 24%)-g-NVCL 8% ( $\square$ ); and PP-g-(NVCL-co-NVIM), 39% ( $\circ$ ).



**Fig. 11.** DSC thermograms of water-swelled grafts. a) PP-g-NVCL (24%), and b) (PP-g-NVCL 22%)-g-NVIM, 34%. LCST values are shown.

LCST as previously described in literature [18]. These results also confirmed PNVC L grafting onto PP film.

The surface element compositions of samples (polymers and copolymers with different grafting degrees) and certain corresponding survey spectra are presented in Table 2 and in Fig. 12, respectively, obtained by XPS survey studies (experimental concentrations). Theoretical concentrations of PP, PNVC L and PNVM are also shown. For bare PP, oxygen ( $\approx 6$  At. %) is present because of oxidation and plasticizer content in the film. In the case of PNVC L, theoretical and experimental compositions ( $C \approx 80$  At. %,  $N \approx 10$  At. %, and  $O \approx 10$  At. %) were very similar and thus confirmed the synthesis of PNVC L.

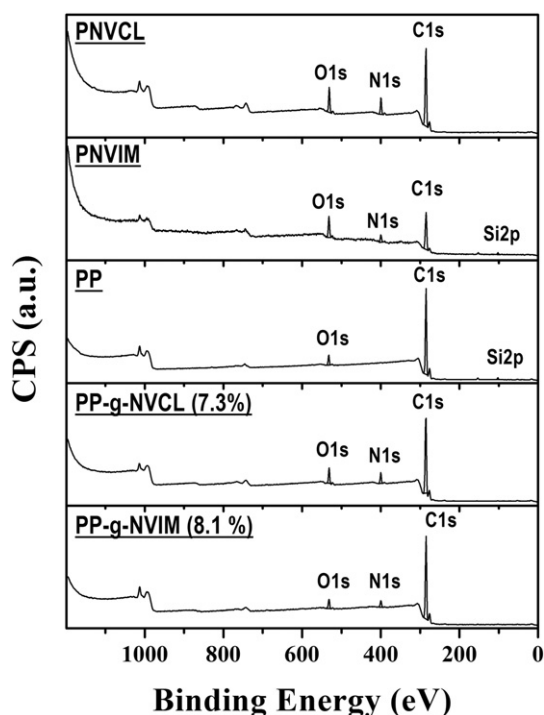
A surprising result for PNVM was obtained experimentally because a high amount of oxygen was measured (16.8 At. %), whereas theoretically no oxygen was expected; also a third of the theoretical nitrogen value (10.1 At. %) was present in the experimental result (28.6 At. %). These results suggest an oxidation process happens during polymerization due to the presence of the solvent used. For grafts synthesized in one step (PP-g-NVCL and PP-g-NVIM), the higher the grafting percentage, the more closely the copolymer composition resembled that of the homopolymer (PNVC L or PNVM). For grafts synthesized in two steps, (PP-g-NVIM)-g-NVCL and (PP-g-NVCL)-g-NVIM, nitrogen and oxygen increased as grafting percentage increased. Nitrogen concentration was higher than oxygen concentration for (PPV-NVIM)-g-NVCL,

**Table 2**

Theoretical and experimental elemental compositions of samples by XPS. Values of grafting, synthesized in one or two steps, are also indicated.

	Sample	Grafting (%)	Elemental composition (At. %)			
			C1s	N1s	O1s	Si2p
Theoretical	PP	–	100	–	–	–
	PNVCL	–	80	10	10	–
	PNVIM	–	71.4	28.6	–	–
Experimental	PP	–	91.4	–	6.2	2.4
	PNVCL	–	79.7	10.0	10.3	–
	PNVIM	–	70.7	10.1	16.8	2.5
	PP-g-NVCL	29.1	82.9	8.3	8.8	–
		7.3	85.8	6.4	7.8	–
	PP-g-NVIM	28.3	65.8	16.9	13.3	4.0
		8.1	87.9	6.1	6.1	–
	(PP-g-NVIM)-g-NVCL	16.2, 10.2	70.3	20.5	9.2	–
		6.8, 2.9	91.2	3.2	4.2	1.3
	(PP-g-NVCL)-g-NVIM	7.5, 13.6	68.0	12.2	18.2	1.6
		2.7, 5.9	77.1	10.7	12.1	–
	PP-g-NVCL-co-NVIM	26.9	68.6	17.0	13.0	1.3
	10.9	70.6	15.3	12.1	2.0	





**Fig. 12.** XPS survey spectra of: PNVCL, PNVIM, PP, PP-g-NVCL (7.3 grafting percent) and PP-g-NVIM (8.1 grafting percent).

and the opposite resulted for the latter. In the case of PNVCL and PNVIM copolymers grafted onto PP in one step, nitrogen and oxygen values were not affected by the grafting degree. The XPS results confirmed the functionalization of PP with PNVCL and PNVIM.

Table 3 shows the variation of contact angle for different NVCL and/or NVIM graft percentages and PP pristine. Contact angle for PP film without grafting was 98.7°, PP-g-NVCL 80.3° and PP-g-NVIM 85.8°; binary graft copolymer of PP-g-(NVCL)-g-NVIM, PP-g-(NVIM)-g-NVCL, and PP-g-(NVCL-co-NVIM) showed 125.5, 105.2, and 116.2° respectively. Contact angle decrease with graft percentage was due to the presence of hydrophilic polymer (NVCL or NVIM) and contact angle increase for all binary graft copolymer due to thermal (NVCL) and pH (NVIM) responsive polymers are hydrophobic at room temperature.

#### 4. Conclusions

The grafting of the copolymer was studied by varying the parameters of monomer-solvent concentration, irradiation dose, reaction time and temperature; and grafting was confirmed by the applied characterization techniques. PP-g-NVIM, PP-g-NVCL, PP-g-(NVCL-co-NVIM), (PP-g-NVIM)-g-NVCL, and (PP-g-NVCL)-g-NVIM copolymers showed sensitivity to temperature and/or pH. To obtain grafts of PP-g-NVCL over 20%, it was necessary to use high irradiation doses (200 kGy), a 50 vol% of monomer concentration (using heptane as a solvent for the pre-irradiation method), a temperature of 80 °C and reaction time higher than 40 h. The direct method was found to be more adequate for the

production of PP-g-NVIM grafts with less than 15% yield, whereas the pre-irradiation method was more suitable for the production of PP-g-NVIM grafts with yields higher than 15%.

The modified films address the need to develop novel and versatile PP based materials with improved functionality, by means of responding to biological changes, which may trigger or slow down the drug release mechanism in biological conditions. In a more specific way, our results demonstrated that the modified films had a thermal response in the range between 31 °C and 46 °C and a pH response in the range from 6.9 to 7.7.

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**Table 3**

Water contact angle for PP and modified (different grafting percentages) PP films at 25 °C.

Sample	Grafting (%)	Water contact angle (°)
PP	0	98.7
PP-g-NVCL	25	85.8
PP-g-NVIM	12	80.3
PP-g-(NVCL)-g-NVIM	56 (22 and 34, respectively)	125.5
PP-g-(NVIM)-g-NVCL	32 (24 and 8, respectively)	105.2
PP-g-(NVCL-co-NVIM)	39	116.2