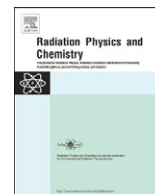




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# Synthesis and characterization of thermosensitive interpenetrating polymer networks based on N-isopropylacrylamide/N-acryloxysuccinimide, crosslinked with polylysine, grafted onto polypropylene

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## ABSTRACT

Interpenetrating polymer networks (IPNs) based on poly (N-isopropylacrylamide), (PNIPAAm) and poly (N-acryloxysuccinimide) (PNAS), grafted onto polypropylene (PP), were synthesized in three consecutive steps using ionizing radiation in the first and second steps and chemical reaction in third one. In the first step a thermosensitive graft copolymer of NIPAAm onto PP film was obtained by gamma radiation with a  $^{60}\text{Co}$  source. The grafted side chains of PNIPAAm were then crosslinked with gamma radiation to give *net*-[PP-g-NIPAAm]. The secondary network was obtained *in situ* by chemical crosslinking between PNAS and polylysine (pLys). The PP-g-IPNs exhibited the lower critical solution temperature (LCST) at around 32 °C. Based on its thermoreversible behavior, this system could be used for immobilization of biomolecules. The phase transition temperature (LCST) and network properties of the IPNs were measured by swelling behavior. Additional characterization by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and infrared (FTIR-ATR) determinations are reported.

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## 1. Introduction

In the recent years, considerable research attention has been focused on stimuli-responsive polymers which exhibit changes in shape and volume in response to small external changes in environmental conditions, such as temperature, pH, ionic strength, etc. They have been developed into a variety of functional forms to meet industrial and scientific applications (Ashok et al., 2007; Hoffman, 1995; Kabanov, 1998; Kabanov, 2000; Gil and Hudson, 2004).

One of the most studied materials is poly (N-isopropylacrylamide) (PNIPAAm), a thermosensitive hydrogel which exhibits a reversible volume phase transition at its lower critical solution temperature, LCST (32–35 °C) (Dong and Hoffman, 1986; Huang et al., 2003). Below LCST, the hydrophilic PNIPAAm chains interact with water. However, above LCST, the hydrophobic PNIPAAm chains collapse and such interactions no longer occur (Eickman et al., 2004). Therefore, it can be applied in biochemical systems as a good candidate for drug delivery systems, protein concentration and separation, and immobilization of enzymes and lipids (Candan et al., 2004). However, during some applications, an

obvious limitation of the normal PNIPAAm hydrogel is its poor mechanical properties in a highly swollen state when used as a drug delivery device (Xian-Zheng et al., 2004). In addition, PNIPAAm hydrogel has another serious limitation; it lacks sustained release capability (Gutowska et al., 1997; Alvarez-Lorenzo and Concheiro, 2002; Zhang et al., 2002). Hydrogels based on acrylamides and acryloxysuccinimide crosslinked with polylysine were studied by Percot et al. (2000) and Pollak et al. (1980) as immobilization systems. Poly (N-acryloxysuccinimide) (PNAS) provides a functional group which is readily displaced by the amino groups of polylysine (pLys); these amino groups are the anchoring elements of vesicles, and also act as a crosslinking agent of PNAS. Ortega et al. (2008) synthesized an IPN of PNIPAAm/PNAS with better apparent mechanic properties in a highly swollen state, than polymer and copolymer hydrogels, with an equilibrium swelling time of 100 min, lower than for the PNIPAAm hydrogel that requires 200 min. García-Uriostegui et al. (2010) obtained a polymeric system of NAS/NIPAAm grafted onto PP by a one step method. In this binary grafted method, the synthesis needed higher radiation doses (80–120 kGy) than the IPN (40–60 kGy). At radiation doses about 100 kGy in the presence of air, the PP films are easily broken because of degradation oxidation of the polypropylene backbone.

This paper suggests a new alternative to improve release rate and apparent mechanical properties consisting of easy handling

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without breaking when in their maximum swelling state, and thereby overcome the aforementioned property deficiencies observed, in the interpenetrating polymer network with grafting in PP, and in the binary graft system of NAS/NIPAAm grafted onto polypropylene. The new system consists of an IPN of NAS/NIPAAm grafted onto polypropylene synthesized with a new strategy in three steps: grafting of NIPAAm onto PP (PP-g-NIPAAm); crosslinking of PP-g-NIPAAm; and diffusion of PNAS and crosslinking by reaction with polylysine in the crosslinking system of PP-g-NIPAAm.

The swelling behavior and thermosensitivity of the films were characterized, and the thermal and morphological properties of the films were investigated by differential scanning calorimetry (DSC).

## 2. Experimental

All reagents were obtained from Aldrich Chemical USA. NIPAAm was purified by recrystallization in toluene/hexane (50/50). Morpholinoethanol sulfonic acid (MES), N-hydroxysuccinimide (NHS) and polylysine (Mw 400–2000) were used as received.

Isotactic polypropylene (PP) films (PEMEX, México), with a 71% of crystallinity and 60  $\mu\text{m}$  thickness, were cut in 1.2 cm  $\times$  4 cm pieces, washed with methanol for 2 h and vacuum dried at room temperature.

### 2.1. Grafting of NIPAAm onto PP films (PP-g-NIPAAm)

The pre-washed and dried PP films were irradiated in air (preirradiation peroxidation method) at room temperature with a  $^{60}\text{Co}$  Gammabeam 651-PT source at a dose rate of 9 kGy  $\text{h}^{-1}$ , and a radiation dose of 20 kGy. The irradiated samples were placed in glass ampoules containing aqueous solutions of NIPAAm (0.5 M). The ampoules were saturated with argon for 20 min, sealed and heated to 70  $^{\circ}\text{C}$  for 1–6 h. The grafted films were washed with water for 24 h to remove remaining monomers and the ungrafted homopolymer. The grafted films were dried under vacuum. The

grafting yield ( $Y_g$ ) was calculated by the equation

$$Y_g (\%) = 100[(W_g - W_o)/W_o] \quad (1)$$

where  $W_g$  and  $W_o$  are the weights of the grafted and initial films, respectively.

**Scheme 1** In order to estimate the amount of side chains grafted by the peroxy macroradicals, PP films were irradiated in air at the same irradiation dose used in the grafting of NIPAAm onto PP, and heated at 70  $^{\circ}\text{C}$  for 1 h. The peroxy macroradicals without the presence of NIPAAm decompose on heating to give oxidation products, including carbonyl compounds,  $\text{H}_2\text{O}$ , peroxides, possibly alcohols and carboxyl compounds. The carbonyl compounds are the predominant product with the highest radiochemical yield of oxidation, including both aldehydes and ketones, while alcohol appears to be intermediate products of oxidation (Woods and Pikaev, 1994). The oxygen amount due to peroxidation reaction was determined by elemental analysis (Columbia Analytics USA). If we assume that one oxygen atom in PP film forms an aldehyde (Scheme 2), then one oxygen corresponds to one  $\text{PO}^{\cdot}$  macroradical to induce the grafting reaction. This assumption is only an approximation, taking in account that the peroxy radical can abstract one hydrogen atom from PP chain, thus creating a new radical site; that new radical is transformed into an oxidized group. Then, the estimated value of initially formed radicals, are lower than the number of oxidized groups.

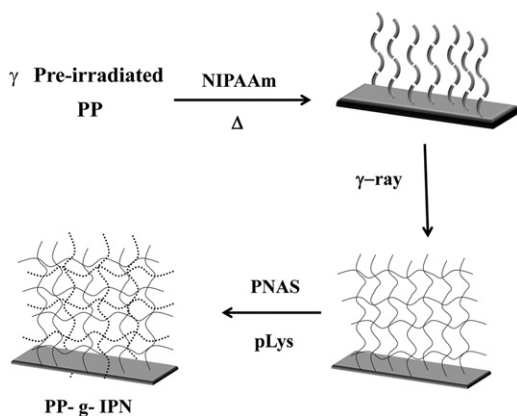
The analysis gives us the molar ratio of PP units ( $n$ ) and oxidized PP units ( $m$ ).

### 2.2. Crosslinking of the PNIPAAm Grafted onto PP

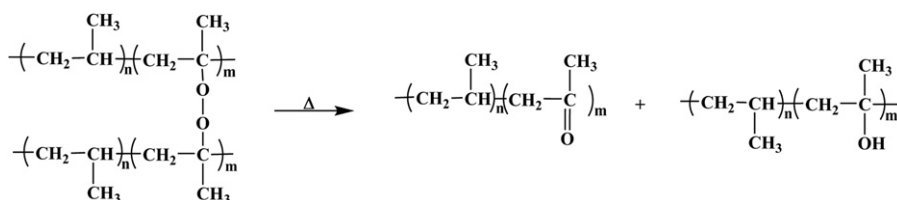
PNIPAAm grafted onto PP was crosslinked according to Ortega et al. (2008) and Ruiz et al. (2007). The PP-g-PNIPAAm films were placed in glass ampoules with distilled water (7 mL). The ampoules were saturated with argon, sealed and irradiated at a dose rate of 9 kGy  $\text{h}^{-1}$  and a total radiation dose of 20 and 40 kGy. The crosslinked films were washed with water (24 h) and then dried under vacuum. In general, the crosslinking reaction by ionizing radiation, takes place in solution or in solid state (Charlesby, 1960; Ortega et al., 2007); but if the polymeric system is in the presence of water, the OH radicals formed by water radiolysis increase the crosslinking process.

### 2.3. Polymerization of NAS

The N-acryloxysuccinimide (NAS) was synthesized by the Pollak method (Pollak et al., 1980) and polymerized with gamma radiation. Solutions of NAS in THF (0.4 M) were placed in ampoules and were degassed by repeated freeze–thaw cycles after which the ampoules were vacuum sealed. The samples were gamma irradiated at a dose rate of 4 kGy  $\text{h}^{-1}$  with a total radiation dose of 40 kGy. The non-polymerized NAS was removed by extracting the polymer with THF for 24 h. The molecular weight of linear PNAS was determined by gel permeation chromatography (GPC) using DMF as the mobile phase in a Varian 9002 with a RI-4 model (refraction index) detector. The PNAS had a number average molecular weight of 5800 and a polydispersity



**Scheme 1.** Synthesis steps of PP-g-IPN.



**Scheme 2.** Proposed structure of PP after preirradiation.

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