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# Temperature-responsive copolymeric hydrogel systems synthesized by ionizing radiation

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## ABSTRACT

Eight different systems of hydrogel copolymers with diverse temperature responsiveness were prepared to elaborate membranes for their biomedical application. The hydrogels were synthesized using poly(N-isopropylacrylamide) (PNIPAAm) and poly(N-vinylcaprolactam) (PNVCL), which have a low critical solution temperature (LCST) close to that of the human body temperature. The networks were synthesized using gamma radiation at a dose rate of  $11.2 \text{ kGy h}^{-1}$ , and dose of 50 kGy. The LCST of each system was measured by differential scanning calorimetry (DSC). The effect of using hydrophilic monomers of acrylic acid (AAc), methacrylic acid (MAAc), dimethyl acrylamide (DMAAm), and hydroxyethyl methacrylate (HEMA) for the copolymerization on the critical point was evaluated. Five viable systems were obtained, with the best hydrogel being that of poly(NIPAAm-co-DMAAm), which an LCST at 39.8 °C. All the samples were characterized by FTIR-ATR, DSC, TGA, X-Ray Diffraction, and SEM. The proportion of monomers during the formation of the copolymers was decisive in the displacement of the LCST.

## 1. Introduction

Since the pioneering work by Toyochi Tanaka in the 1970's and 1980's (Tanaka, 1978), stimuli-responsive polymer networks that undergo volume phase transitions in response to changes in variables during their operational ranges have attracted much attention. Materials with specific properties that can respond to temperature, pH, light, and electrical or magnetical fields, among other stimuli, have found applications in the aerospace, chemical, metallurgical, automotive, and biomedical industries (Hoffman, 2013; Lorenzo et al., 2015). These sorts of materials are named "smart materials" and, in comparison with other materials like metals or ceramics, they are made up of low-cost and easily adjustable polymers. The stimulus generates a change in the material, showing a modification of structure, solubility, volume, surface composition or topography (Biazar et al., 2010; Shi et al., 2006).

In the biomedical field, stimuli-responsive hydrogels are being tested for a variety of applications including diagnosis (sensors), treatment (controlled drug biodistribution and delivery), and tissue regeneration (regulating cell attachment and proliferation) (Alvarez-Lorenzo and Concheiro, 2014; Contreras-García et al., 2011). Hydrogels are polymeric matrices with a three-dimensional structure that contains hydrophilic polymers, and thus they can absorb a high

quantity of water, or other biological fluids, without their dissolution (Peppas and Leobandung, 2004). Such structure enables the diffusion of oxygen and nutrients through them, and endows them with viscoelastic properties, making them suitable biomaterials (Rosiak et al., 1995). Both N-isopropylacrylamide (NIPAAm) and N-vinylcaprolactam (NVCL) have been identified as monomers that can endow hydrogels with a temperature-responsive behaviour. Homopolymers of NIPAAm or NVCL exhibit a low critical solution temperature (LCST) close to 32 °C (Beija et al., 2011; Zdražil and Štěpánek, 2010), which is slightly below the physiological temperature of the human body (37 °C). Moreover, the hydrophilic to hydrophobic phase transition temperature can be readily tuned by means of copolymerization (Feil et al., 1993; Liu et al., 2009; Yin et al., 2006).

One of the advantages of using gamma radiation to trigger polymerization, in comparison with chemical methods, is the high and controllable concentration of active sites that are created on the entire volume of the sample. Moreover, the method is quite versatile in terms of solvents and temperature, and it does not require additional initiators or cross-linking agents, thus avoiding the risk of remnant toxic substances in the hydrogel (Rosiak et al., 1995). Also, gamma radiation can sterilize the hydrogels for biomedical tests (Kabanov et al., 2009).

The present work reports the copolymerization of different types of

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monomers to obtain materials with tuneable temperature responsiveness. The monomers tested included NIPAAm and NVCL, which are temperature-responsive monomers; and acrylic acid (AAc), dimethyl acrylamide (DMAAm), methacrylic acid (MAAc), and hydroxyethyl methacrylate (HEMA), which are hydrophilic monomers. The networks were characterized in terms of their cross-linking (FTIR), amorphous structure (XRD), morphology (SEM), transition thermodynamics (DSC), and thermal stability (TGA). Changes in the relative proportions of temperature-responsive and non-responsive monomers caused notable shifts in the LCST, with some hydrogels showing an LCST close to the physiological temperature (37 °C).

## 2. Materials and methods

### 2.1. Materials

N-isopropylacrylamide and N-vinylcaprolactam were supplied by Sigma-Aldrich Co. (USA). NIPAAm was purified (recrystallization) with toluene and hexane (analytical grade) (50:50 vol%), and both solvents were provided by Baker (Mexico). NVCL was purified under reduced pressure. Acrylic acid, methacrylic acid, N-N dimethyl acrylamide, and 2-hydroxyethyl methacrylate were acquired by Sigma-Aldrich Co. (USA), and purified by vacuum distillation. Distilled water was used as the solvent in the polymerization synthesis.

### 2.2. Synthesis process and hydrogels preparation

Solutions of the temperature-responsive monomer and the hydrophilic monomer were prepared under different ratios, as indicated in Table 1. First, the solid and liquid monomers were dissolved in distilled water to a concentration of 1 mol L<sup>-1</sup>. Thereafter, the solutions were placed in glass ampoules and degassed with argon for 25 min to remove oxygen from the system. In addition, all the samples were cooled to 8 °C during the degasification process to avoid their homopolymerization. The ampoules were sealed, and then irradiated by a <sup>60</sup>Co γ-rays (Gammabeam 651PT, Nordion International Inc.). The irradiation doses were 50 and 100 kGy at a fixed dose rate of 11.2 kGy h<sup>-1</sup>, with better results obtained using 50 kGy. All of the resulting hydrogels were consistent (swelling samples), with some exceptions (Table 2). To extract the hydrogels from the glass ampoules, the ampoules were soaked in methanol, and the samples on Petri dishes for their drying under a laminar flow cabinet for 24 h.

### 2.3. Measurement of water absorption

The samples were first cut into films (3×3×1 mm) and weighed (5 mg average). They were then immersed in distilled water at a mass proportion of 1:50,000 (gel:water), and at room temperature (25 °C). Thereafter, after 24 h the samples were gently wiped with filter paper to remove any water from their surface, and then weighed again. The water absorption relationship was calculated as:

$$A_w(\%) = \left[ \frac{(W_s - W_0)}{W_0} \right] * 100\% \quad (1)$$

where  $A_w$  is the water absorption,  $W_s$  is the weight of the swollen gel, and  $W_0$  is the weight of the initial gel sample before being immersed in water (Razzak et al., 2001).

### 2.4. Infrared spectra

Fourier-transform infrared (FTIR) spectra of the films were acquired in an ATR Perkin Elmer Spectrum 100 spectrometer (Perkin Elmer Cetus Instruments, USA) in the range of 550–4000 cm<sup>-1</sup>, at 16 scans. The films were dried for 24 h at 70 °C before the analysis.

**Table 1**

Relation of materials for temperature-responsive hydrogels preparation.

Thermoresponsive monomer solution A (1 mol L <sup>-1</sup> )	Hydrophilic monomer solution B (1 mol L <sup>-1</sup> )	A:B ratio <sup>a</sup> (vol%)
NIPAAm	AAc	50:50
		70:30
		80:20
		90:10
	DMAAm	50:50
		70:30
		80:20
		90:10
	MAAc	50:50
		70:30
		80:20
		90:10
HEMA	50:50	
	70:30	
	80:20	
	90:10	
NVCL	AAc	50:50
		70:30
		80:20
		90:10
	DMAAm	50:50
		70:30
		80:20
		90:10
	MAAc	50:50
		70:30
		80:20
		90:10
HEMA	50:50	
	70:30	
	80:20	
	90:10	

<sup>a</sup> Relation of monomers inside the ampoule (volume of monomer 1: volume of monomer 2) with a concentration of 1 M of each monomer. The monomers were dissolved in distilled water to obtain a 1 M solution, previously to addition in the ampoules (i.e.50:50 – total volume of 4.5 mL, 2.25 mL of NIPAAm 1 M and 2.25 mL of AAc 1 M)

### 2.5. Lower critical solution temperature (LCST)

The thermodynamic transitions were analysed using differential scanning calorimetry (DSC) in a nitrogen atmosphere (DSC 2010 calorimeter; TA Instruments, USA). The experiments were carried out with swollen samples that had been previously immersed in water for 12 h. The samples were heated from 5 to 80 °C at 1 °C min<sup>-1</sup>. The nitrogen flow purge was set at 100 mL min<sup>-1</sup> (Brazel and Peppas, 1995).

### 2.6. Thermogravimetric and calorimetric analysis

Simultaneous differential scanning calorimetry and thermo-gravimetric analysis measurements (DSC-TGA) were performed using the SDT Q600 apparatus (TA Instruments, USA), under a nitrogen atmosphere from 25 to 800 °C at 10 °C min<sup>-1</sup> (the nitrogen purge gas was set to 50 mL min<sup>-1</sup>). The average weight of the samples was 5 mg, and an open alumina pan was used. All samples were dried at 70 °C for 24 h before being tested (Jin et al., 2001).

### 2.7. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to observe and analyse the morphology of the sample's surface. The samples were processed by the electron microscope JSM-7800F (Shottky Field Emission. Jeol, USA), under vacuum conditions. The samples were cut in little films to observe the edge and the surface. The preparation

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