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ABSTRACTS

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## Synthesis and Characterization of pH-Sensitive Acrylamide/Acrylic Acid Hydrogels

Virgínia Pinto<sup>a</sup>, Miguel Gonçalves<sup>a</sup>, Rolando Dias<sup>a,\*</sup> and Mário Rui Costa<sup>b,\*\*</sup>

<sup>a</sup>LSRE - Polytechnic Institute of Bragança, Campus de Santa Apolónia, Apartado 1134, 5301-857 Bragança, Portugal, [rdias@ipb.pt](mailto:rdias@ipb.pt)

<sup>b</sup>LSRE – Fac. Eng. University of Porto, Dep. Eng. Química, R. Roberto Frias, 4200-465 Porto, Portugal, [mrcosta@fe.up.pt](mailto:mrcosta@fe.up.pt)

### Introduction:

Polymers responding to changes in parameters such as temperature, pH, electric or magnetic fields are often designated as “stimuli-responsive” polymers or “smart” polymers. Smart hydrogels are water compatible polymer networks undergoing fast and reversible changes in their hydrophilic/hydrophobic microstructure. Changes at microscopic level become macroscopically apparent and include a huge shrinking/swelling of the network. These reversible transitions are driven by neutralization of charged groups due to pH shift, changes in efficiency of hydrogen bonding or in ionic strength.<sup>[1]</sup> Owing to these unique features, hydrogels have found many applications as biomaterials for drug and protein delivery, tissue engineering, nanotechnology and microfabrication techniques. pH-sensitive hydrogels are polyelectrolytes containing ionisable groups (pendant acidic or basic groups) which are able to release or accept protons. These mechanisms can be stimulated by changes in the environmental pH where the polymer network is located. Hydrogels containing weakly acid groups swell when the pH is increased and, conversely, those containing weakly basic groups collapse by increasing the pH. These phase transitions (swelling/deswelling) can be explored to synthesize useful materials for (e.g.) drug delivery systems.<sup>[2]</sup> Nevertheless, the performance of these smart hydrogels (e.g. swelling kinetics) is strongly dependent on the molecular architecture of the networks (e.g. composition or crosslinking density) and on the synthesis conditions used in their production. Temperature of preparation, polymerization medium (e.g. solution, suspension or emulsion) or the presence of a porogen leading to porous hydrogels are some parameters with influence in the end-use properties of such advanced materials.<sup>[3]</sup> The size and shape of the synthesized gel particles, conditioning the water diffusion process, also have a strong impact on the response time of pH-sensitive hydrogels.

The present work reports the synthesis and characterization of acrylamide (AAM) - acrylic acid (AA) based pH-responsive hydrogels. The polymer networks were synthesized using the inverse-suspension technique and methylene bisacrylamide (MBAM) as crosslinker. The dynamics of the formation in batch reactor of soluble and non-soluble polymer structures was experimentally measured. Final products were characterized in terms of their equilibrium swelling ratio in buffer solutions of different pH values. The dynamic swelling ratio of these hydrogels was also measured by transferring the polymer networks to alternating aqueous solutions at pH=1.2 and 7.5, in order to reproduce the gastrointestinal environment. Experiments are also used in modeling studies based on a general kinetic approach<sup>[4]</sup> aiming at the development of a computational tool allowing the design of hydrogels with tailored properties.

### Experimental Part:

Hydrogels were synthesized at 20 °C in a 2.5 L reactor which has been described in detail elsewhere.<sup>[5]</sup> Different inverse-suspension polymerization runs were performed using ciclohexane as the organic media and sorbitan monooleate (Span 80) as the suspension agent. Aqueous phase crosslinking polymerization between the three monomers (AAM/AA/MBAM) was promoted using the redox initiation system ammonium persulfate (APS)/tetramethylethylenediamine (TEMED). Sodium hydroxide was used to neutralize the AA monomer. The experimental program has explored the change of the following synthesis parameters:

- Degree of neutralization of AA monomer (50 to 90%).
- Initial mole proportion between AAM/AA monomers (1/1.6 to 1/5.2).
- Initial mole fraction of crosslinker (MBAM) in monomer mixture (1 to 2%).

**Results:**

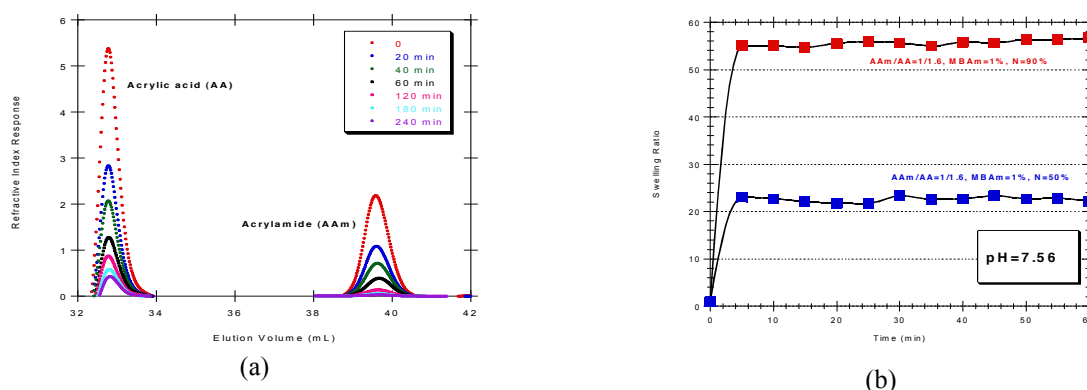


Figure 1: (a) Observed SEC traces of hydrogel samples collected at different reaction times showing the consumption of the main monomers (AAm and AA). (b) Dynamics of swelling of different samples of pH-responsive hydrogels in a buffer solution at pH=7.56.

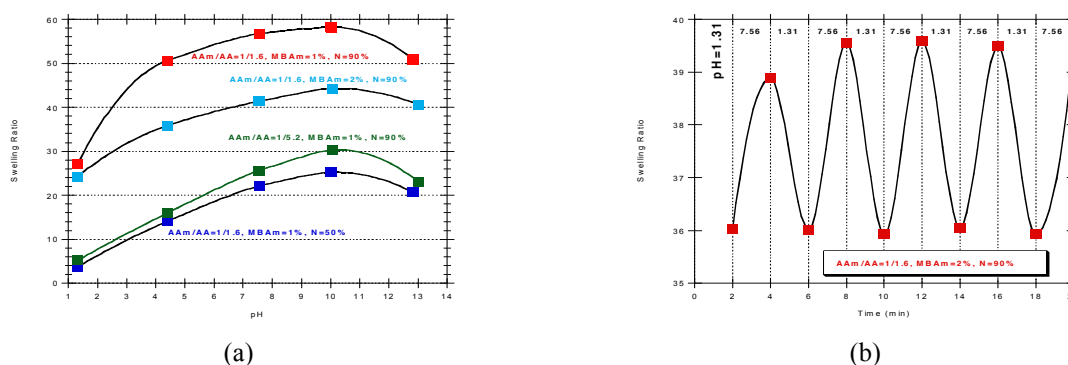


Figure 2: (a) Measured equilibrium swelling ratio of different pH-responsive hydrogels showing the influence of the synthesis conditions on end-use properties. (b) Repeated swelling and collapse of a pH-responsive hydrogel sample in alternating buffer solutions at pH=1.31 and 7.56.

**Conclusion:**

Different samples of pH – sensitive hydrogel particles were produced using inverse-suspension, leading to the identification of the influence on their end-use properties of the degree of neutralization of AA monomer and the initial composition of the terpolymerization system which are therefore the key parameters of the synthesis. These studies were also used to develop a kinetic model improving the design of production processes of tailored smart polymers.

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