

# PHOTOPOLYMERISATION OF ACRYLIC ACID AND CHITOSAN GELS (I). INFLUENCE OF PREPARATION METHOD ON THE FORMATION AND KINETIC BEHAVIOUR OF INTERPENETRATING COMPLEXES

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**Abstract--**The kinetic study of the photopolymerisation of gels of acrylic acid (AA) and chitosan (CHI) prepared by three different methods was accomplished. The kinetic parameters such as conversion and polymerisation rate were determined. The influence of the composition and the preparation method on these parameters was elucidated. The effect of the mixing order on the formation of chitosan-acrylic acid complexes (CHI<sup>+</sup>AA<sup>-</sup>) was determined by measuring the viscosity of non-polymerised gels. The presence of polyacrylic acid (PAA) grafted on to a CHI matrix after photopolymerisation and the influence of the method of preparation and feed composition on the proportion of CHI-PAA interpolymer network were demonstrated by FTIR spectroscopy. The possible mechanism of the graft copolymerisation is discussed in detail.

**Keywords—**acrylic acid, chitosan, interpolymer complexes, gels, photopolymerisation

## I. INTRODUCTION

The preparation of hydrogels based on the intimate mixture of natural or synthetic macromolecules and polymer chains formed by polymerisation reaction in the presence of the macromolecular template has received increasingly growing attention in the past few decades (Hoffman, 2002; Wang *et al.*, 1997). The macromolecular components of these hydrogels generally possess the capacity for forming between themselves the interpolymer complexes through electrostatic interactions, hydrogen bonds and Van der Waals forces, etc. Among the synthetic vinyl-like monomers the acrylates, acrylamides and acrylonitriles are the most widely used in these systems. These structures are capable of interacting with amine and hydroxyl groups of some polysaccharides to form corresponding complexes which can be polymerised by a free radical route (Gallardo *et al.*, 2005; Peniche *et al.*, 1999).

In the family of natural polymers, chitosan, CHI, is one of the most extensively employed for this purpose. It is worth mentioning that CHI itself has attracted great interest in medicine and pharmacy because of its biodegradability, biocompatibility and the wide range of positive biological responses and activities reported. It has been used in or proposed for the production of drug delivery devices, cell encapsulation (Peniche *et al.*,

2003), as a wound healing agent, in adhesive formulation for surgical applications (Gallardo *et al.*, 2005), in ophthalmology and dentistry (Xu *et al.*, 2002), etc.

It is also fungi- and bacteriostatic. In addition, this highly basic polysaccharide displays a number of ionisable primary amino groups which are readily available for chemical reaction and salt formation with acids including synthetic anionic monomers and macromolecules [interpenetrating networks (IPN), polyelectrolyte complexes, graft copolymers, blends and others]. The complex CHI-polyacrylic acid (PAA) is one of the most studied (Ahn *et al.*, 2001; Torre *et al.*, 2003a; 2003b). This type of hybrid system can be obtained by mixing polymeric aqueous solutions (Wang *et al.*, 1997) but also by the so-called template polymerisation, which involves the polymerisation of the anionic monomer (acrylic acid) in the presence of chitosan. Cross-linking of these complexes with glutaraldehyde or by thermal treatment gives rise to a complex/semi-IPN structure (Wang *et al.*, 1997) by amide formation.

There are some reports of the use of chitosan/PAA-based matrices obtained by template polymerization for mucosal delivery systems and as drug carriers (Hu *et al.*, 2002). In our laboratory we have prepared chitosan/PAA matrices by template polymerization at low temperature by taking advantage of activation of the decomposition of the initiator by chitosan (Peniche *et al.*, 1999). It was also found that during polymerization under these mild conditions some grafting of polyacrylic acid (PAA) chains on to chitosan molecules was produced, giving rise to weakly crosslinked hydrogels after neutralization. These hydrogels exhibited water uptakes as high as 560 g of water per g of dry sample.

It is important to stress, that the majority of CHI/PAA interpenetrating systems were produced by initiation of template polymerisation through thermal (Ahn *et al.*, 2001; Kurita *et al.*, 1993) or red-ox (Argüelles and Peniche, 1993; Borzacchiolo *et al.*, 2001; Kurita *et al.*, 1991) routes, there being few reports about the possibility of photochemical initiation for these systems. However, it is well known that photochemical polymerisation techniques possess an important advantage, such as the unlimited and controlled manipulation time which makes the photo-cured system very attractive for several medical applications (Davidenko *et al.*, 2003; Davidenko *et al.*, 2005; Lindén, 1993).