

Preparation and characterization of IPN composite hydrogels based on polyacrylamide and chitosan and their interaction with ionic dyes

Ecaterina Stela Dragan*, Maria Marinela Perju, Maria Valentina Dinu

"Petru Poni" Institute of Macromolecular Chemistry, Department of Functional Polymers, Grigore Ghica Voda Alley 41A, Iasi 700487, Romania

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ABSTRACT

Preparation and characterization of some interpenetrating polymer networks (IPN) composite hydrogels based on polyacrylamide (PAAm) and chitosan (CS) are presented in the paper. The reaction variables selected for the preparation of semi-IPN (s-IPN) hydrogels are the ratio of cross-linker (X), pH of the reaction mixture, and CS molar mass. The fraction of CS trapped in the s-IPN hydrogels, increased with the increase of the reaction mixture pH from 5 to 6. Full-IPN (d-IPN) hydrogels were prepared by a sequential strategy consisting of the preparation first of s-IPN, followed by the cross-linking of CS with epichlorohydrin, in 2 M NaOH. The partial hydrolysis of the amide groups in PAAm, during the generation of the second network (d-IPN) at high pH, led to the formation of d-IPN hydrogels having a cationic network based on cross-linked CS and an anionic network based on PAAm, which after hydrolysis contains carboxylate groups besides the amide groups. The swelling properties and the interaction with ionic dyes of the d-IPN hydrogels have been strongly influenced by the presence of the two oppositely charged networks. Thus, the s-IPN hydrogel, which contained only positively charged groups, sorbed a higher amount of the anionic dye (Direct Blue 1) than the d-IPN hydrogels. On the other hand, the d-IPN hydrogels sorbed a much higher amount of the cationic dye Methylene Blue than the s-IPN hydrogel.

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1. Introduction

Hydrogels are polymer networks able to absorb significant amounts of water without dissolving or losing their structural integrity (Byrne & Salian, 2008). The three-dimensional structure of a swollen hydrogel is maintained by either chemical or physical (hydrogen bonding, van der Waals interaction, hydrophobic interaction, chain entanglements, or ionic complexation) cross-links (Peppas, Hilt, Khademhosseini, & Langer, 2006; Tanaka, Gong, & Osada, 2005). Because of their high water content, hydrogels are similar to a variety of natural living tissues, having widespread applications as biomaterials. Thus, they have found large applicability in reconstructive surgery for artificial organs, tissue engineering, cartilage, muscles, immunoinsulation membranes (Berger et al., 2004; Galaev, 1995; Peppas et al., 2006), etc. Hydrogels are also recommended for controlled delivery of drugs and proteins (Hoare & Kohane, 2008; Kumbar, Soppimath, & Aminabhavi, 2003; Peppas et al., 2006; Reis et al., 2008; Satish, Satish, & Shivakumar, 2006; Muzzarelli, 2009), wastewaters remediation (Jeon, Lei, & Kim, 2008; Yilmaz, Kavakli Akkas, Şen, & Güven, 2006), or as agricultural products (Abd El-Rehim, 2006; Zohuriaan-Mehr, Omidian, Doroudiani, & Kabiri, 2010).

To enhance the biodegradability as well as the mechanical properties, and to control the diffusion of solutes in hydrogels, multicomponent networks, including biopolymers, as semi- or interpenetrating polymer networks (IPN) have been designed (Agnihotri & Aminabhavi, 2006; Dhara, Nisha, & Chatterji, 1999; Liang, Liu, Huang, & Yam, 2009; Mandal, Kapoor, & Kundu, 2009; Ramesh Babu, Hosamani, & Aminabhavi, 2008; Rodriguez, Romero-Garcia, Ramirez-Vargas, Ledezma-Perez, & Arias-Marin, 2006; Rokhade, Patil, & Aminabhavi, 2007; Varaprasad et al., 2010; Xia, Guo, Song, Zhang, & Zhang, 2005). Semi-IPNs (s-IPN) hydrogels are typically produced in a "single step" by synthesizing a hydrophilic polymer matrix around the preexisting water soluble polymer chains considered as the trapped polymer (Dinu, Perju, & Drăgan, 2011; Myung et al., 2008; Wang, Zhang, & Wang, 2011); alternatively, they are prepared by a selective cross-linking of one polymer in a blend of two polymers (Liang et al., 2009; Myung et al., 2008; Rokhade et al., 2007; Sperling, 1994). Full-IPNs represent an intimate association of two independently cross-linked polymers, at least one of which being cross-linked or synthesized in the presence of the other.

The semi-synthetic polymer chitosan (CS) (Dash, Chiellini, Ottenbrite, & Chiellini, 2011) is a hydrophilic, biocompatible, and biodegradable polymer, which provides to the composite IPN potential for various applications in biomedical, pharmaceutical, and environmental fields (Agnihotri & Aminabhavi, 2006; Berger et al., 2004; Demirel et al., 2006; Kim, Yoon, Kim, & Kim, 2004; Liang

* Corresponding author. Tel.: +40 232 217454; fax: +40 232 211299.
E-mail address: sdragan@icmpp.ro (E.S. Dragan).

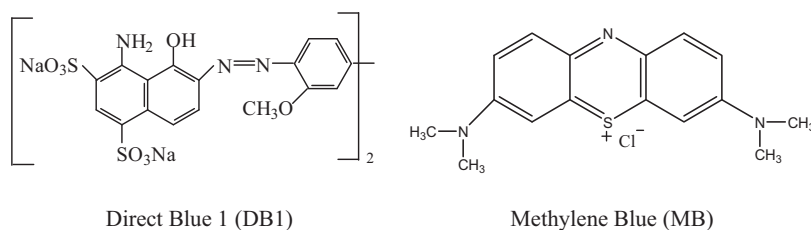


Chart 1. Direct Blue 1 (DB1) Methylene Blue (MB).

et al., 2009; Wang, Turhan, & Gunasekaran, 2004; Xia et al., 2005). In this context, the objectives of the paper were: (i) to identify the influence of the cross-linker ratio, pH of the reaction mixture, and CS molar mass on the gel fraction yield and on the fraction of CS trapped in the s-IPN hydrogels having a matrix of poly(acrylamide) (PAAm), and (ii) to prepare amphoteric full-IPN (d-IPN) hydrogels by a sequential strategy consisting of the selective cross-linking of CS trapped in the s-IPN, in alkaline conditions.

As reported in literature, ionic dyes have been used in photodynamic therapy (Hah et al., 2011), as models for drugs in preliminary tests for drug release (Kim & Shin, 2007; Thierry, Winnik, Merhi, Silver, & Tabrizian, 2003) or to test the loading/release of small molecules from multilayer thin films (Chung & Rubner, 2002). Therefore, the interaction of the IPN composite hydrogels with both anionic and cationic dyes has been investigated in the paper as a function of the gel structure to get preliminary indications on the potential applications of the gels in the drug delivery systems.

2. Materials and methods

2.1. Materials

The CS with molar mass of 235 kDa (CS1), purchased from Fluka, and CS with molar mass of 467 kDa (CS2), purchased from Sigma–Aldrich were used as received. The CS molar mass has been calculated from the intrinsic viscosity of CS dissolved in 0.3 M CH₃COOH–0.2 M CH₃COONa (1:1, v/v), at 25 ± 0.1 °C (Gamzazade et al., 1985). Degree of acetylation (DA) of CS was evaluated by infrared spectroscopy (Brugnerotto et al., 2001) by using a Vertex 70 Bruker FTIR spectrometer. Transmission spectra were recorded in KBr pellets. An average value of DA = 15%, resulted from three measurements, has been taken into account for both samples. Acrylamide (AAm, Fluka), N,N'-methylenebisacrylamide (BAAm), ammonium persulfate (APS), N,N,N',N'-tetramethylethylenediamine (TEMED), all purchased from Sigma–Aldrich, were used as received. Epichlorohydrin (ECH)

purchased from Sigma–Aldrich, has been double distilled on KOH before using. Stock solutions of APS and TEMED were prepared by dissolving 0.2 g of APS and 0.625 mL of TEMED each in 25 mL of double distilled water. Stock solutions of BAAm were prepared by dissolving BAAm calculated for a certain cross-linker ratio in 10 mL of distilled water, at 30 °C, under magnetic stirring, and used for hydrogels synthesis after 24 h. Direct Blue 1 (DB1) from Sigma–Aldrich was used after three times recrystallization from an aqueous methanol solution (methanol/water, 70/30, v/v). Methylene Blue (MB) from Sigma–Aldrich was used without purification. The structure of the dyes is presented in Chart 1.

2.2. Preparation of IPN composite hydrogels

Composite hydrogels, based on PAAm and CS, were prepared by free radical cross-linking copolymerization in aqueous medium at 22 °C. The initial concentration of monomers (AAm + BAAm), C₀, has been kept constant in all experiments (5 wt.%). The redox initiator system used consisted of APS and TEMED. The concentrations of APS and TEMED have been constant in all experiments. The cross-linker ratio X (the mole ratio of the cross-linker BAAm to the monomer AAm) varied in the range 1/80–1/20. The feed composition and the samples code of the composite gels are summarized in Table 1.

The general code of semi-IPN composite hydrogels consists of s-IPN followed by 1 or 2, for CS1 or CS2 used as trapped polymer, respectively, and a number with two figures, which represents the mole number of AAm per one mole of BAAm.

2.2.1. Preparation of s-IPN composite hydrogels

The synthesis procedure used in the preparation of s-IPN composite hydrogels is briefly presented below, taking the sample s-IPN1.80 (Table 1) as an example. Typically, 0.4868 g AAm, 6.3 g aqueous solution of CS1 (1 wt.%), obtained by dissolving the flakes in 1 vol.% acetic acid solution and moderate stirring for 48 h, 0.7 mL double distilled water, 1 mL BAAm (0.33 g/25 mL) and 1 mL TEMED

Table 1

The samples code, feed composition, gel fraction yield and percentage of CS removed from the composite gels.

Sample ^a	BAAm:AAm molar ratio	CS			
		Code	Molar mass, M _v (kDa)	GFY ^b (%)	CS removed in s-IPN (wt.%)
PAAm	1/80	–	–	95.5	–
s-IPN1.80	1/80	CS1	235	–	64.33
s-IPN1.80 ^c	1/80	CS1	235	91.1	–
s-IPN1.60	1/60	CS1	235	91.1	62.5
s-IPN2.60	1/60	CS2	467	88.8	49.7
s-IPN1.40	1/40	CS1	235	90.1	64.45
s-IPN1.40 ^c	1/40	CS1	235	90.4	54.2
s-IPN1.20	1/20	CS1	235	89.6	66.4
s-IPN1.20 ^c	1/20	CS1	235	89.4	59.1
s-IPN2.20	1/20	CS2	467	88.2	65.9
d-IPN1.60	1/60	CS1	235	–	–
d-IPN2.60	1/60	CS2	467	–	–

^a 12.6 wt.% of CS added in the reaction mixture for all composite gels.

^b Gel fraction yield.

^c pH adjusted at 6.0.

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