

Thermo-responsive sandwiched-like membranes of IPN-PNIPAAm/PAAm hydrogels

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Abstract

The synthesis of sandwiched-like IPN hydrogels having cross-linked PNIPAAm interpenetrated into PAAm networks was carried out by UV-induced polymerization using potassium periodate as a sensitizer. NIPAAm monomers and MBAAm cross-linker were co-polymerized inside previously synthesized cross-linked PAAm. Through SEM images, we observed that the hydrogel membranes were formed by three layers; the internal layer was fully involved by the two others. Significant morphological difference between the internal and external layers was also observed. Thus, sandwiched-like interpenetrating polymer networks were obtained. The internal layer shrank significantly after warming the swollen hydrogel above LCST of PNIPAAm in water, 30–35 °C while the external layers remained swollen and highly porous due to the hydrophilicity of PAAm. The experiments performed at 40 °C revealed that the hydrogels shrank considerably. Collapsed PNIPAAm chains induced a substantial contraction of the internal hydrogel layer. The hydrogel contraction was accompanied by an increase in gel strength and elasticity modulus. The presence of the PNIPAAm network in the internal layer reinforced the hydrogel and this effect was more pronounced above LCST. The permeability of sandwich-like membrane significantly rather decreases as the temperature increases. There was a decrease in the permeability of 52% as the temperature was increased from 25 to 40 °C. It was suggested that the structural changes in the sandwich membrane induce to significant flux control.

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1. Introduction

Over recent years, applications of thermo-responsive hydrogels as drug delivery devices, drug permeation membranes and cell growth and detachment scaffolding [1–6] have been widely investigated. Moreover, there is an increased interest in developing polymer matrixes that present this property in common with soft biological materials [7–9]. For these reasons, particular attention has been directed to polymers that undergo phase transition under thermal stimuli in an attempt to adjust them to near human body temperature operation [2,4]. Poly(*N*-isopropylacrylamide) (PNIPAAm) is among the polymers that

respond to changes in temperature and therefore has been widely applied as a biomaterial [4,9,10]. Since the discovery of PNIPAAm by Tanaka in 1970s [11], a large number of publications on hydrogels based on PNIPAAm has already been reported in the literature. In an aqueous environment, PNIPAAm shows reversible phase transition at low critical solution temperature (LCST) with resulting dramatic shrinkage [4,12,13]. Experimentally, it occurs at temperatures between ca. 30 and ca. 35 °C [4]. However, the low mechanical strength of swollen PNIPAAm hydrogel limits its use in many applications [14,15]. In the collapsed state, PNIPAAm hydrogels have an elasticity modulus ca. 17-fold higher than that in the swollen state [16]. Interpenetrating polymer networks (IPNs) have been used to improve the mechanical properties of hydrogel [17,18]. IPNs are composed of two or more chemically distinct networks linked solely by their permanent entanglements [19–21]. On the

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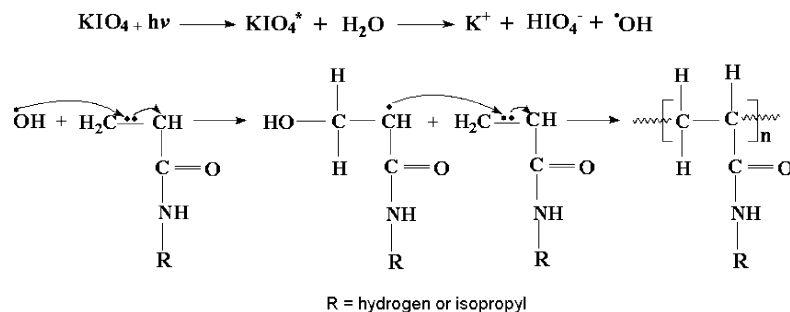


Fig. 1. Mechanism of UV-induced polymerization in aqueous environment using potassium periodate as a sensitizer.

other hand, the use of semi-interpenetrating polymer networks (semi-IPNs) with hydrogels have also been subject of many investigations [15,22–24]. A system is semi-IPN if one of the assembly components is cross-linked and leaves the other in its linear form [25,26]. Semi-IPN hydrogels formed by cross-linked polyacrylamide having entangled PNIPAAm have already been reported in the literature [14,27,28]. These hydrogels have good mechanical properties at temperatures below and above LCST although PNIPAAm chains are not chemically linked to PAAm polymer chains [15]. In this work, NIPAAm monomers were reacted inside cross-linked PAAm in the presence of a cross-linker to form an interpenetrating polymer network that resulted in a sandwiched-like hydrogel. The mechanical stability of these hydrogels was studied by compressive load measurements in dependence of temperature. UV irradiation-induced photo-polymerization using potassium periodate as a sensitizer has been found to be a feasible route to cross-link PNIPAAm inside previously cross-linked PAAm. UV-induced polymerization using a periodate salt as a sensitizer has been described in the literature [29–31]. Fig. 1 shows the mechanism for radical formation through UV irradiation and the subsequent polymerization reaction. The methodology developed in this work to obtain sandwiched-like IPN hydrogel membranes has been described in a Brazilian Patent [32] recently.

2. Experimental

2.1. Synthesis of PAAm hydrogels

PAAm hydrogels were prepared from aqueous solution of acrylamide (AAm) (Aldrich, 14,866-0) with methylene-bis-acrylamide (MBAAm) (Plusone, 17-1304-02) as a cross-linker and periodate potassium (KIO_4) (Cod 700, Vetec, Brazil) as a sensitizer. After homogenization, the solution was inserted between two transparent glass plates with 0.12 m in size and separated by a rubber gasket spacer 1.5 mm thick. The solution was exposed to the light of a low-pressure Hg lamp ($\lambda = 254\text{--}580\text{ nm}$, 215 W) for 40 min. Thereafter, all hydrogels were cut in square pieces of 200 mm^2 area and completely dried in vacuum.

2.2. Synthesis of PNIPAAm inside PAAm hydrogel

In this stage, the dried PAAm hydrogels were kept in 50 ml of an aqueous solution prepared by adding the desired amount of *N*-

isopropylacrylamide (NIPAAm) (Aldrich, 41,532-4), MBAAm and KIO_4 at 25°C to swell. After 48 h, the PAAm hydrogel reached swelling equilibrium and the swollen hydrogel was placed between two transparent glass plates and then exposed to the light of the low-pressure Hg lamp for 40 min. Thereafter, co-polymerization of PNIPAAm occurred as the gel became completely opalescent. The hydrogel was dipped into distilled water for 1 week to remove non-reactants and water was renewed everyday. The swollen hydrogel was stored in distilled water at room temperature. Different NIPAAm concentrations were used in the feed aqueous solutions. The IPN hydrogels were labeled as (AAm–P) to indicate the compositions of PAAm and PNIPAAm. In this sense, the first term expresses the molar concentration of AAm (fixed at 2.5), while the second, P, represents the concentrations of the NIPAAm monomer used in the feed solution to swell the PAAm hydrogel. The cross-linker concentration was fixed at 1 mol% relative to the amounts of AAm and NIPAAm. The compositions of all reagents used to prepare the hydrogels are summarized in Table 1.

2.3. Morphological analysis of hydrogels by SEM

Hydrogel morphology was analyzed by scanning electron microscopy (SEM) (Shimadzu, model SS 550) operating at 12 keV. The hydrogels were immersed into distilled water at either 25 or 40°C until swelling equilibrium was reached. After that, the samples were removed and immediately frozen by immersion in liquid nitrogen. Thereafter, the frozen hydrogels were fractured and lyophilized by a freeze-dryer (Christ gefriertrocknungsanlagen) at -60°C for 24 h. Before observation by SEM, the dried-lyophilized hydrogels were gold-coated by sputtering.

Table 1
Amounts of AAm, NIPAAm and MBAAm used in hydrogels synthesis, in $\mu\text{mol ml}^{-1}$

Hydrogel	AAm ^a	MBAAm ^a	NIPAAm ^b	MBAAm ^b
2.5–0	2500	25	0	0
2.5–1.3	2500	25	111	1.1
2.5–2.5	2500	25	221	2.2
2.5–5	2500	25	442	4.4

^a Amount used in feed solution in the synthesis of PAAm.

^b Amount used to swell dried PAAm hydrogels.

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