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Poly(N-vinyl imidazole) hydrogels polymerized in molds of different materials

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ABSTRACT

Hydrogels of N-vinylimidazole are polymerized in molds of different materials (acidic glass, basic glass, silanized glass, nylon, Teflon, pvc) to study the influence of the material on the gel properties. Molds are cylinders of very narrow diameter (2–8 mm) to enhance the influence of the wall. Confocal microscopy, glass transition, and degree of swelling are used to characterize the gels. A border with more dense polymer is formed close to the wall in all the materials. The hydrogels obtained in Teflon and pvc have higher glass transition, higher degree of swelling, and higher density of cross-links than the gels obtained in glass. Also, the reaction yield is lower in Teflon and pvc than in glass. For the narrower molds, the gels swell more in the direction normal to the wall than in the direction parallel to the wall, and this departure from isotropy is more noticeable in Teflon and pvc than in glass.

1. Introduction

The copolymerization of vinyl monomers with a small percentage of divinyl comonomer is the most classical method to obtain cross-linked networks. These are the basic materials for many applications in the fields of elastomers, porous solids, gels, etc. Of special interest is the cross-linked polymerization of water soluble vinyl monomers, which yield water swellable gels (hydrogels). The hydrogels thus obtained can consist of electrically neutral chains, or can be polyelectrolytes having charges along the chains, which are neutralized by counter-ions. Hydrogels of both classes are very much used in medicine, pharmacy, agriculture, cosmetics, food industry, etc.

The copolymerization is most often carried out by radical mechanism in solution. Cross-linking produces gelation and the resulting gel is an elastic swollen body that has the shape of the vessel or mold where the initial solution was contained. The initiator, monomer and cross-linker concentrations are the main factors which determine the structure and properties of the gel obtained, although other substances in the solution may interfere and act as inhibitors or chain transfer agents. The vessel or mold containing the solution is for the most supposed to be inert and not to affect the gel. We question here such assumption, and look at the possible influence of the mold on the properties of the gel obtained by polymerization. Since the mold wall is in contact with the reacting mixture, it is conceivable that interactions at the wall/mixture interface can affect the crosslinking process and modify the structure of the resulting gel, at least in the vicinity of the wall. This may not affect the bulk properties of regular-sized gels, but it can modify their surface properties. So, the study of the influence that the mold material exerts on the properties of gels is important for applications where control of their surface friction, adherence, deformability, and surface elasticity are needed. Besides, the role played by the surface layer of the gel should become increasingly relevant as the bulk size of the gel gets smaller. Smallness is needed for many applications, especially

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in the realm of thermo-sensitive and pH-sensitive hydrogels, where fast responses (swelling/deswelling) to external stimuli are desirable. Thus, the study of how the mold material influences the bulk properties of small hydrogels is of relevance for the development of smart devices based on them.

The influence of the mold walls on the polymerization is expected to be short-ranged and affect only the outer-most layer of the gel, where the gelling solution is in direct contact with the wall. But this surface layer created by the mold is not always very thin. It has been shown that, under certain circumstances, the surface layer extends over unexpected long distances of several millimeters from the wall [1–5]. So, the mold material can have influence over a sizable portion of the gel.

That the mold can have some influence on cross-linking polymerization has been documented before for a number of monomers, with certain materials of the mold. We are aware of the following monomers thus far studied: acrylamide [1,2,6]; 2-acrylamido-2-methyl-1-propanesulfonic acid (and its sodium salt) [7–13]; acrylic acid (homopolymer [14] and copolymer with styrene and with 2,2,2-trifluoroethyl acrylate [8,13]); N,N-dimethylacrylamide [8,15,16]; 2-(N,N-dimethylamino)ethyl methacrylate [17]; N-isopropylacrylamide (homopolymer [6,14,18–22] and copolymers with acrylic acid [3,4,14,18] and with 2-acrylamido-2-methyl-1-propanesulfonic acid) [3,5]; methacrylic acid [23]; styrene sulfonate (sodium salt) [13]; and vinyl alcohol [13]. These monomers are all, either non-ionic, or ionic with acid ionization. We extend those results here, by studying N-vinylimidazole, a monomer with a basic ionization.

The hydrogels of poly(N-vinylimidazole)(PVI) studied here are pH-sensitive: in acidic media, they suffer protonation of the tertiary amine group in the imidazole ring [24–26]. This ring plays a major role in biomacromolecules such as proteins (amino acid histidine), nucleic acids (purine ring of adenine and guanine), hormones (histamine), and certain vitamins. The polymer PVI has a dual character: a hydrophobic backbone with hydrophilic pendant groups. PVI forms molecular complexes with numerous organic and inorganic substances and this accounts for its applications in industrial processes, printing, ion removal [27,28], etc. The hydrogels of PVI neutralize slightly acidic solutions and act as insoluble buffers that can be removed/renewed after application [29–31]. Also, recent publications focus on a unique class of amphiphilic PVI containing hydrogels [32–35].

Our way of probing the influence of the mold on the polymerization of PVI is by reducing the size of the reactor, thus increasing the surface/volume ratio, and by using materials of different nature: hydrophilic and hydrophobic. Similar strategy has been used before. A brief survey of the cases thus far reported is as follows.

Hirotsu, using narrow glass tubes, found that gels of ionic N-isopropylacrylamide-co-acrylic acid had different swelling depending on the radius of the tube used as mold, and attributed this effect to the ions contained in the gel and not to the material of the mold, since a similar study with neutral N-isopropylacrylamide gels gave no influence of tube radius [18,19]. Also in gels of isopropylacrylamide-co-acrylic acid, Huglin et al. found different gel behavior depending on the size and shape of the mold used, which they attributed to an easier dissipation of heat from the molds that had a thinner cross-section [14]. The school of Osada and col. have studied extensively the effect caused by hydrophobic walls, notably Teflon. With 2-acrylamido-2-methyl-1-propanesulfonic acid, they found that gelation was suppressed at the Teflon wall [7,11]. This suppressed gelation was found also in the polymerization of acrylic acid [8] and N,N-dimethylacrylamide [8,15], not only on Teflon, but also on other hydrophobic substrates, such as polypropylene, polyethylene, polyvinyl chloride, and polystyrene [8,15]. This suppressed gelation was first associated with the high interfacial tension between the hydrophobic substrate and the aqueous polymerizing solution [8,9], but later it was attributed to the presence of residual oxygen entrapped at the rough hydrophobic surfaces [12]. Teflon wall also perturbed the gelation of acrylamide, as reported by Candau et al. [1,2]. With N-isopropylacrylamide, Kato et al. found that the gels obtained in molds of glass were different from those obtained on molds of Teflon or silicone [20]. In copolymers of N-isopropylacrylamide with 2-acrylamido-2-methyl-1-propanesulfonic acid obtained between plates of glass and Teflon, Tokuyama et al. found that the contents of the acid in the copolymer gradually decreased toward the Teflon wall [3], which they attributed to repulsion of the acid monomer toward the hydrophobic Teflon interface [5]. Using silanized glass as hydrophobic mold to obtain gels of N,N-dimethylacrylamide, Tran et al. detected the existence of a less cross-linked layer at the surface in contact with the substrate [16].

In our study we also use silanized glass and Teflon as hydrophobic molds, as well as polyvinyl chloride and nylon. We compare the gels obtained in molds of these hydrophobic materials with those obtained using hydrophilic glass (acid or base soaked). The molds are narrow cylindrical vials of different diameters, such that the distance between opposite walls varies within the range where the influence of the substrate has been detected in previous studies with other monomers. The concentrations of initiator, monomer, crosslinker, and time of polymerization, are all kept constant, so the only variables in the reaction are the material of which the mold is made and its diameter. The effects of varying concentrations and time of polymerization with constant mold have been studied already in glass molds of regular diameter by Piérola and col. [24–26,36–38]. By reducing the diameter and changing to other materials, we add now the influence of the surface. For comparison purposes, we obtain also some linear polymers in the same molds.

2. Experimental section

2.1. Materials

Reactants: 1-vinylimidazole from Aldrich, distilled under reduced pressure; N,N′-methylene-bis-acrylamide 99.5% from Fluka; 2,2′-azo-bis-isobutyronitrile from Fluka, recrystallized in methanol; water distilled and deionized in a Milli-Q from Millipore (water type I); fluorescein methacrylate from Aldrich, maximum absorption at 490 nm.