



Polyelectrolyte and antipolyelectrolyte effects in swelling of polyampholyte and polyzwitterionic charge balanced and charge offset hydrogels



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ABSTRACT

The swelling properties of polyampholytic hydrogels with different charge stoichiometric ratio were characterized by continuous monitoring changes in optical length of 60 μm sized hydrogels with 2 nm resolution using an interferometric readout platform. The hydrogels were synthesized by copolymerizing acrylamide, crosslinker Bis and charged monomers. Anionic–cationic polyampholyte gels consisted of different molar ratio between anionic monomer 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) and cationic monomer (3-acrylamidopropyl) trimethylammonium chloride (APTAC). The polyzwitterionic hydrogels consisted of zwitterionic monomer [2-(methacryloyloxy)ethyl] dimethyl-(3-sulfopropyl) ammonium hydroxide (SBA) with a certain molar of AMPSA or APTAC in addition to the AAM. The observed swelling properties versus the ionic strength in the aqueous immersion solution revealed apparent anti-electrolyte signatures for both types of polyampholytic hydrogels. The swelling kinetics was not affected by charge imbalance within the polyampholyte or polyzwitterionic hydrogels. Polyampholyte hydrogels with balanced charge ratio slightly shrank and then swelled with the increase of ionic strength, which is at variance with the anionic AMPSA offset hydrogels displaying shrinking in low ionic strength and relatively small swelling at high ionic strength. The swelling properties of imbalanced polyampholyte hydrogels were not equal to simply linear overlap of those of polyampholyte hydrogels with balanced charges, and corresponding polyelectrolyte hydrogels.

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1. Introduction

One of the important challenges in biomedical fields is to prevent the non-specific attachments of microorganisms or biomacromolecules which could deteriorate the performance of biomedical devices and generate adverse effects on the scaffold implanting and tissue repairing [1]. Therefore, materials with good anti-fouling and anti-microbial abilities are highly desirable and many strategies has al-

ready targeted for these [1–3]. Among them, polyampholyte hydrogels are pursued as candidates of anti-fouling and anti-microbial materials to be applied in biomedical technology due to their high biocompatibility and low toxicity [4–6]. The structural similarity of the polyampholyte and the hydrophilic parts of the phospholipids of cell membranes is suggested to be mechanistic in this [7,8].

Polyampholyte hydrogels are 3D crosslinked polymer networks containing both positively and negatively charged groups. They can be divided into two categories by ampholyte types inside the hydrogel network. These are obtained by copolymerizing a monomer with anionic

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functional groups and a monomer with cationic functional groups forming anionic–cationic charges in different polymer repeat units [9–11], or polymerizing a zwitterionic monomer leading to the formation of anionic–cationic charges in the same polymer repeat units [7,12]. Recent studies indicated that the anti-fouling and anti-microbial abilities of polyampholyte hydrogels were due to hydration layers suggested to be induced by an electrostatic driven mechanism [13–15]. Thus the overall charge density and its distribution become more important in designing the hydrogels with anti-fouling and anti-microbial abilities. Simultaneously, hydrogel swelling property is always closely connected to molecular properties of hydrogel. Determination of swelling properties of polyampholyte hydrogels can thus provide information possibly aiding the understanding and control of anti-fouling and anti-microbial functionalities of such materials.

Several studies about the swelling properties of polyampholyte hydrogels have been reported and discussed [9,16–19]. However, up to our knowledge, the comparative studies of ionic strength dependent swelling properties of anionic–cationic polyampholyte hydrogels and mixed polyelectrolyte–polyzwitterion hydrogels are still lacking. In this paper we use high resolution interferometry as a hydrogel swelling readout technique to fill up this gap.

Interferometric technique has proved its potential in high resolution monitoring of the equilibrium swelling change and swelling kinetic of responsive hydrogels deposited at the end of optical fiber [20–26]. In this work, the readout platform supports determination of swelling properties of polyampholyte hydrogels at various ionic strengths at high resolution of optical length changes. The hydrogels were prepared with constant degree of crosslinking and with anionic–cationic monomers mixed and electrolyte–zwitterionic monomer mixed polyampholyte character with balanced charge and anionic or cationic charge offset. The swelling changes of anionic or cationic offset hydrogels were compared, as a first approximation, as the linear overlapping those of polyelectrolyte hydrogel, and the corresponding polyampholyte hydrogels with balanced charges.

2. Experimental

2.1. Materials

Acrylamide (AAM, 99%, Sigma), N,N'-Methylenebisacrylamide (Bis, 99%, Acros organics), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA, 99%, Aldrich), 1-hydroxycyclohexyl phenyl ketone (99%, Aldrich), squalane (99%, Aldrich), dimethyl sulfoxide (DMSO, 99.9%, Sigma), (3-acrylamidopropyl) trimethylammonium chloride solution (APTAC, 75 wt% in H₂O, Aldrich) and [2-(methacryloyloxy)ethyl] dimethyl-(3-sulfopropyl) ammonium hydroxide (SBA, 97%, Aldrich) were used as received for the preparation of the hydrogels. 3-(Trimethoxysilyl)propyl methacrylate (Sigma, >98%) and hydrochloric acid (37%, Merck) were used to functionalize the end of the optical fibers with methacrylate groups for covalent anchoring of the hydrogels. Deionized water (resistivity 18.2 M Ω \times cm, obtained using a Millipore setup) was used

for all aqueous solutions and sodium chloride (NaCl, 99.5%, Fluka) was used for measurements.

2.2. Polyampholytic hydrogels

Polyampholytic hydrogels, including hydrogels with zwitterionic groups, were prepared covalently attached to the end of optical fibers analogous to the procedure employed previously [20]. In detail, the appropriate amounts of AAM and Bis were dissolved in deionized water to yield 30 wt% AAM and 3 mol% Bis relative to AAM. AMPSA, APTAC and SBA, respectively, were dissolved in water (10 wt%) in separate vials. Photo initiator was dissolved in DMSO. The solutions were mixed together yielding 10 wt% of AAM, 3 mol% Bis and 0.15 mol% of initiator relative to AAM in the pre-gel solutions. The stoichiometric ratios of pre-gel solutions for the various hydrogel compositions are listed in Table 1 and structural features of various polyampholytic hydrogels are schematically illustrated in Fig. 1. Aliquots of the pre-gel solutions were deposited on the tip of the methacrylate functionalized fiber and polymerized by photoinitiation (UV light from a Dymax Bluewave 50 equipped with a light guide, for 3 min). Following the polymerization, the hydrogels were washed with deionized water for at least one day to remove possible unreacted monomers and other impurities. The resulting hydrogels attached to the end of the optical fiber were adapted a nearly hemispherical shape with a radius of about 60 μ m. The small volume of the present hydrogels (in the order of nanoL) makes it difficult to determine the final hydrogel composition, e.g. similar that reported for other polyampholytic hydrogels [27]. In the following we therefore refer to the various hydrogels composition as prepared in the pregel solution.

2.3. Interferometric determination of hydrogel swelling

The interferometric instrument for determination of hydrogel swelling has been outlined previously [20]. This consists of an optical fiber with the hydrogel bound at one end and a connector/adaptor system at the other (connector: FOC2 STD-A600, Huber + Suhner fiber optics. Adaptor: FOC2 FOC2-D001, Huber + Suhner fiber optics). An optical cable (108163/02 Suhner Fiberoptic) was attached to the detector controlled by a computer. A LabView software was used for instrument readout. The setup was used to follow the swelling response of the hydrogels to stepwise increase of the NaCl in the immersing aqueous solution at room temperature as outlined previously [20]. The changes in the optical length of the hydrogels, Δl_{opt} were determined with 2 nm resolution. Parameter Δl_{opt} values were derived from the experimentally determined changes of the phase of the interference wave and were used in the following due to its superior resolution compared to the data derived from the amplitude information [20]. The data are presented directly as either Δl_{opt} with a selected reference state, or as relative changes $\Delta l_{\text{opt}}/l_{\text{opt}}$. Parameter Δl_{opt} reflect changes in both altered refractive index, n , properties of the hydrogels as well as changes in the physical length, l , as outlined previously [26]:

$$\Delta l_{\text{opt}} = \langle n_2 \rangle l_2 - \langle n_1 \rangle l_1 \approx \langle n_1 \rangle \Delta l + l_1 \Delta n \quad (1)$$

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