



Modulating the movement of hydrogel actuator based on catechol–iron ion coordination chemistry



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ARTICLE INFO

Article history:

Received 10 June 2014

Received in revised form

21 September 2014

Accepted 23 September 2014

Available online 2 October 2014

Keywords:

Mussel adhesive protein

Dopamine

Hydrogel actuator

Iron ion

pH responsive

ABSTRACT

Hydrogel actuators were prepared by combining ionoprinting technique with reversible metal ion coordination chemistry found in mussel adhesive proteins. Hydrogels were formulated with dopamine methacrylamide (DMA), which contains a catechol side chain that forms strong complexes with ferric (Fe^{3+}) ions. Catechol– Fe^{3+} ion complexation increased local crosslinking density, which induced hydrogel bending at the site of ionoprinting. The effect of multiple factors on the dynamic response of hydrogel actuation was tracked by following the bending curvature at the ionoprinting site. In general, the extent and rate of hydrogel actuation increased with increasing pH, deposited Fe^{3+} ion content, and DMA content but was inversely proportional to hydrogel thickness. The ability to modulate hydrogel actuation using multiple parameters is potentially useful in controlling the actuator movements. Additionally, Fe^{3+} ion-containing bulk hydrogels demonstrated significant reduction in molecular weight between crosslinks as well as elevated storage and loss modulus values based on oscillatory rheometry when compared to those of Fe^{3+} -free control. These differences in physical and viscoelastic properties contributed to the actuation of ionoprinted samples. Specifically, conditions that promoted a large crosslinking differential between the ionoprinted region and the bulk hydrogel (i.e., outside of the ionoprinted region) contributed to increased rate and extent of hydrogel folding. Faster actuation at elevated pH levels was attributed to the formation of complexes with higher catechol: Fe^{3+} ion stoichiometric ratios. Hydrogel actuation and deswelling were also observed at pH of 3.5 although to a lesser degree, potentially due to a stronger affinity between network-bound catechol and Fe^{3+} ions as compared to complexes formed in a dilute solution.

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1. Introduction

Hydrogels are three-dimensional polymer networks with water contents as high as over 99% [1,2]. The physical, chemical, and biological properties of these materials can be easily controlled by fabrication methods and chemical compositions. Hydrogels also exhibit excellent biocompatibility and structural similarity to natural extracellular matrices. As such, hydrogels have emerged as

promising biomaterials for applications ranging from scaffolds for tissue engineering and repair [3,4], drug delivery [5,6], and artificial connective tissues [7], to tissue adhesives [8–10]. Hydrogels that can change their shape and physical properties in response to various environmental stimuli (e.g., temperature, pH, humidity) are being explored as actuators for applications such as soft robotic components, biosensors, artificial muscle tissues, and controlled drug delivery [11–14].

Recently, our lab exploited the reversible metal coordination chemistry found in mussel adhesive proteins (MAPs) to create a novel pH-responsive hydrogel actuator [15]. Hydrogels were prepared with network-bound catechol through photo-initiated polymerization of dopamine methacrylamide (DMA, Fig. 1). DMA mimics the adhesive catechol moiety, 3,4-dihydroxyphenylalanine (DOPA), which accounts for as much as 25 mol% in MAPs [16]. DOPA and other catechol derivatives (e.g., dopamine, 3,4-dihydroxyhydrocinnamic acid) have demonstrated remarkable water-resistant adhesive properties to a wide range of surfaces

Abbreviations: EDTA, ethylenediaminetetraacetic acid; EWC, equilibrium water content; Fe^{3+} ion, ferric ion; DMA, dopamine methacrylamide; DMPA, 2,2-dimethoxy-2-phenylacetophenone; DOPA, 3,4-dihydroxyphenylalanine; HEA, *N*-hydroxyethyl acrylamide; MAP, mussel adhesive protein; MBAA, *N,N*-methylene-bisacrylamide; \overline{M}_c , average molecular weight between crosslinks; pHEA, poly(*N*-hydroxyethyl acrylamide); R , rate of change in the bending curvature; R_0 , initial bending curvature; R_{max} , maximum bending curvature.

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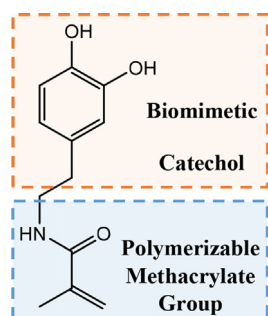


Fig. 1. Chemical structure of dopamine methacrylamide (DMA).

(e.g., mucin [17], soft tissue [18–22], bone [23], polymer [24], and metal [25–28]). Additionally, catechol is capable of forming strong complexes with metal ions (e.g., ferric ion; Fe^{3+}) with log stability constants greater than 40 (45 for Fe^{3+}) [29]. Breaking and reformation of strong, reversible catechol-metal ion-coordination bonds contributes to the wear resistance properties of the protective coatings on mussel byssus threads, which repeatedly experience large strains in the turbulent intertidal zone [30,31]. Depending on pH, catechol forms mono-, bis-, and tris-complexes with Fe^{3+} ions (Fig. 2) [32–34].

To form a pH-responsive hydrogel actuator, DMA-containing hydrogels were locally imprinted with Fe^{3+} ions through electrochemical oxidation of iron electrode in contact with the hydrogel surface [15]. When the hydrogels were submerged in a basic medium (pH 9.5), formation of the catechol- Fe^{3+} ion tris-complex increased local crosslinking density at the site of ionoprinting and resulted in hydrogel bending. When the hydrogel was submerged in an acidic medium (100 mM HCl), the catechol forms a mono-complex with reduced crosslinking density and the hydrogel returned to its original shape. Hydrogels can be programmed to adopt multiple three-dimensional shape depending on the pattern of ionoprinting. Finally, the reversibly bound metal ions can be removed by ethylenediaminetetraacetic acid (EDTA) and reintroduced in a different pattern, so that the hydrogel can be reprogrammed to transform into a different three-dimensional shape [15].

In this follow up work, we seek to understand the effect of various factors such as pH, hydrogel thickness, applied voltage, and DMA-content on the rate and the extent of hydrogel actuation. We also seek to test the hypothesis that the crosslinking density differential between the ionoprinted region and the bulk of the hydrogel (e.g., outside of the ionoprinted region) serve as the driving force for hydrogel movement. To this end, the swelling behavior, molecular weight between crosslinks, and rheological properties of DMA-containing hydrogels were determined to compare the difference in the network crosslinking density in the presence and absence of Fe^{3+} ion. Additionally, catechol forms complexes with Fe^{3+} ion with different stoichiometric ratios at different pH and the effect of pH on the crosslinking density of the hydrogels were evaluated. The

physical and viscoelastic properties of the hydrogel were used to corroborate the effect of various factors that affect the movement of the ionoprinted hydrogel actuator.

2. Materials and methods

2.1. Materials

N,N'-methylene-bisacrylamide (MBAA) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were obtained from Acros Organics (Geel, Belgium), while *N*-hydroxyethyl acrylamide (HEA) and EDTA were purchased from Sigma Aldrich (St. Louis, MO). Ferric chloride (FeCl_3), sodium borate, sodium hydroxide, dimethyl sulfoxide (DMSO) and 12 M hydrochloric acid were purchased from Fisher Scientific (Pittsburgh, PA). 7.6-mm diameter iron rods were purchased from Alfa Aesar (Ward Hill, MA). DMA was synthesized using previously published protocol [25]. Unless otherwise specified, 0.1 M NaCl solutions were buffered to the desired pH with the addition of either 12 M HCl or 6 M NaOH solutions.

2.2. Preparation of hydrogel

Previously published protocol was used to prepare DMA-containing hydrogels [15]. Briefly, precursor solutions containing 2.5 M of HEA, 4–12 mol% DMA, 0.5 mol% MBAA, and 0.04 mol% DMPA were dissolved in a DMSO and deionized water mixture (33% v/v DMSO). The precursor solution was degassed, back-filled with nitrogen three times, and then added to a mold consisting of two pieces of glass separated by a spacer. Photoirradiation was performed on both sides of the mold for a total of 20 min using a UV crosslinking chamber (XL-1000, Spectronics Corporation, Westbury, NY) located in a N_2 -filled glove box. Hydrogels were soaked in 6 mM HCl while frequently changing the dialysate for 3 days to remove unreacted monomers before testing. Hydrogels prepared using 0.5-, 1-, and 2.5-mm thick spacers resulted in equilibrium thicknesses of 0.7, 1.3, and 3.4 mm, respectively, after purification.

2.3. Ionoprinting and actuation

Hydrogels were incubated in 0.1 M sodium borate solution containing 0.1 M NaCl and 50 mM NaOH for at least 30 min. Borate acts as a temporary protecting group for catechol and can be easily removed at an acidic pH [35,36]. The presence of borate competes for binding sites with Fe^{3+} ions and concentrates the metal ions near the ionoprinting site, which is necessary for hydrogel actuation [15]. Ferric ions were patterned into the hydrogel network by placing it in contact with an iron (anode) and aluminum (cathode) electrode and applying the desired electrical potential (2.5–10 V) using a DC regulated power supply (CSI3003X, Circuit Specialists, Inc., Mesa, AZ) for 10 s. To initiate actuation, hydrogel was submerged in pH 3.5 0.1 M NaCl solution for 2 min to remove borate and then transferred to a 0.1 M NaCl solution buffered to a desired

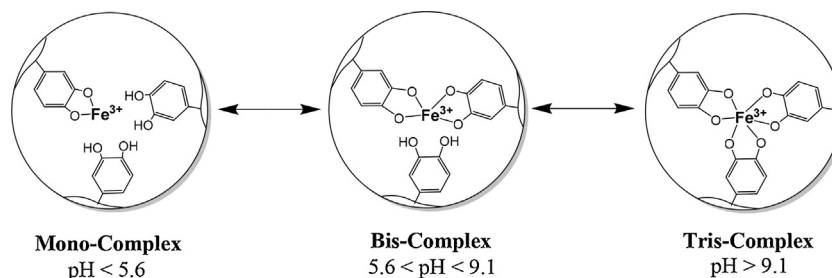


Fig. 2. Schematic representation of catechol- Fe^{3+} ion complexes at different pH levels.

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