



Low-voltage electrically driven homeostatic hydrogel-based actuators for underwater soft robotics



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ABSTRACT

We present the synthesis, fabrication and electro-mechanical characterization of a novel electro-responsive hydrogel based on Na-4-vinylbenzenesulfonate (Na-4-VBS) that can operate as a fast response bending actuator in a low voltage regime (0.2–5 V), in NaCl aqueous solutions. The bending speed can reach values up to 22°/s at 3 V and of 2.7°/s at 1 V. The responsive behavior of the benders was observed in physiological environments as well, such as phosphate buffer solution (PBS) and Dulbecco's Modified Eagle's Medium (DMEM) and exhibited similar performance. The material is a co-polymer comprising also hydroxyethyl methacrylate (HEMA) and acrylonitrile (AN), to confer high hydrophilicity to the structure and to enhance its elastic properties. According to the swelling and electro-mechanical testing results, the electrically driven deformation of the hydrogels was interpreted as a dynamic osmotic equilibrium effect taking place at the interface between the polymer and the surrounding medium, induced by the free ionic species migration throughout the polymer. This material constitutes a promising solution for the design and production of highly performing soft underwater actuators and biomimetic smart systems that can be controllably operated at the macro and mesoscale in fluids of biological interest, with minimal power consumption and below the standard potential of water electrolysis.

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1. Introduction

Synthetic ionic hydrogels able to change their shape in response to an applied electrical stimulus in aqueous environments are of strategic importance for the development of remotely controlled soft underwater actuators and robots [1–3]. These materials have the ability to absorb and retain large water amounts, still maintaining their solid state, and they present ionic groups covalently bonded to the main backbone, to which a mobile counter-ion specie is stably coordinated [4]. The embedded intelligence of this family of polymers dwells in their capability to undergo controllable swelling–shrinking cycles in the presence of an electric field, eventually leading to a bending deformation of the hydrogel, as a result of the mobile ions migration across the polymer [5–8].

This actuation mechanism strongly depends on the inter-play between a variety of factors, such as the material inner chemical and physical structure (e.g., monomers type and cross-linking degree), the ionic concentration difference between the polymeric matrix and the outside environment and the field intensity [9–11]. More specifically, the choice of the ambient solution ionic specie, the electrode geometry and configuration, as well as the actuator distance from the same, are all key elements to enable a fine control over the electro-mechanical performance of this class of responsive polymers [12]. Furthermore, having fixed both the material properties and working conditions, the electrically induced deformation and actuation speed of the components scale according to their dimensions i.e., faster response time (up to the order of few hundred of milliseconds) and larger bending angles (above 90°) are favored at the micro-scale, as demonstrated by the production of artificial micro-swimmers and miniaturized aquabots [13,14]. Although the protocols and setups employed for the electro-mechanical characterization of hydrogel-based materials are extremely broad [2,7,12], it is possible to identify several common features related to the actuation properties of this class of polymers and to highlight their main limitations.

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Despite the low electrochemical window of water (1.23 V) [15], the actuation of electro-responsive hydrogels shaped as macroscopic bending cantilevers or freestanding cylinders in saline aqueous solutions is restricted to the use of relatively high voltages as the triggering stimulus (3–30 V) [16–19]. At this working condition, water electrolysis and perturbation phenomena connected to the generation of gases, such as bubbling at the electrodes, inevitably take place in the ambient solution, therefore limiting the life time and application area of the actuators [20–22]. Moreover the characteristic bending speed observed for the most performing electro-active hydrogels, such as polyacrylic acid, polyvinyl alcohol or polystyrene sulfonate based polymers, has showed to reach values up to 5°/s [23–26]. However, a dynamic bending behavior that could resemble the angular speed exhibited by micro-cantilevers (from 10 to 20°/s [27]) at larger spatial length scales would be highly relevant for a variety of applications, such as the production of propulsive biomimetic subaqueous soft robots and for the integration of smart stirring systems in bioreactors [28–32].

Examples of electro-active hydrogels working at the sub-Volt regime have only been reported for micro and mesoscale sized hydrogel strips, which could be operated as bending micro-actuators or smart valves and mixing pumps in microfluidic devices [33–35]. To our knowledge, no evidence of electro-responsive hydrogel-based materials that can function at the macroscale level as high-performance bending actuators at working voltages below 1 V has been reported so far.

Here we report the synthesis, fabrication and characterization of a novel electro-responsive hydrogel based on Na-4-vinylbenzenesulfonate (Na-4-VBS), which operates as a fast response soft actuator in the voltage range between 0.2 V and 5 V in NaCl aqueous solutions, with concentration going from the milli-molar to the molar range. The produced polymer showed similar performance in environments of biological interest, such as phosphate buffer solution (PBS) and Dulbecco's Modified Eagle's Medium (DMEM). The manufactured polymeric actuators are UV photo-polymerized freestanding layers, having macroscopic dimensions in their length and width and variable thickness of 0.1 and 0.3 mm. The results obtained in terms of electro-mechanical actuation are correlated to the swelling properties of the materials in the different aqueous environments, which are experimentally determined with the blot and weigh method [36].

2. Materials and method

2.1. Hydrogel preparation and swelling

The material is a three-component co-polymer, comprising also hydroxyethyl methacrylate (HEMA) and polyacrylonitrile (AN). The presence of the hydroxyl side groups characteristic of the HEMA monomer confers high hydrophilicity to the hydrogel and also offers potential to its further functionalization (e.g., with bioactive molecules coating), while AN provides mechanical toughness and elasticity to the structure.

We synthesized samples using three different formulations of the material, by varying the amount and the relative ratio of the co-monomers Na-4-VBS/HEMA/AN as follows: 0.5/6.5/3.0 mmol (PSS5%), 1.0/6.5/2.5 mmol (PSS10%), 2.0/6.0/2.0 mmol (PSS20%). This approach was chosen to investigate on the effect that the amount of Na-4-VBS has on the electro-active properties of the hydrogel. The HEMA quantity was always kept at least at 60% of the total co-monomers amount to ensure a high degree of hydrophilicity to the polymers, while the AN percentage was varied accordingly. The synthesis and manufacturing procedure of the polymeric layers can be described as reported below. The UV initiator solution was prepared

using 2,2-dimethoxy-2-phenylacetophenone (DMPA), 0.7 M, in dimethyl sulfoxide (DMSO). The three monomers, Na-4-VBS, HEMA and AN, were sequentially dissolved in 1.3 mL of pure water (Milli Q type) in a glass test tube. The cross-linker, ethylene glycol diacrylate (EGDA), 0.053 mmol, and the catalyst, *N,N,N,N*-tetramethylethylenediamine (TEMED), 0.15 mmol, were then added to the mixture. Finally, 30 μ L of the initiator solution were injected and the preparation tube was vigorously stirred for 1 min. The resulting low viscosity liquid was a completely transparent solution. A three-components mold was used to shape the hydrogel layers. This comprised a square silicon spacer (80 \times 80 \times 0.3 mm³ or 80 \times 80 \times 0.1 mm³), having a 40 \times 40 mm² wide hollow region for the injection of the polymerizing solution, which was positioned on a 2 mm thick glass slide. After injection of the liquid, the mold was sealed by a second identical glass component and the system was appropriately clamped. The molding apparatus was then exposed to UV radiation (λ = 365 nm) for one hour, to ensure homogeneous and full cross-linking of the hydrogel. The equipment used was a UVLS-24 EL series (UVP) lamp, endowed with a 4 W light bulb; this relatively low power does not produce any significant heating of the samples during the irradiation process. This simple yet effective fabrication protocol enabled to achieve PSS-co-PHEMA-co-PAN co-polymer based freestanding layers. The chemical structure and synthesis scheme of the co-polymer are represented in Fig. 1. As firstly evaluated on a qualitatively level, the resulting product was a transparent, elastic and dull film. After removing the hydrogel from the mold, the material was immediately soaked in pure water, in order to wash out the unreacted compounds. During this process, which lasted 24 h, hydrogels underwent a volumetric increase due to water absorption. After hydration, each sample was cut in four pieces and then immersed for 24 h in three NaCl aqueous solutions with different concentration (0.005 M, 0.05 M, 0.5 M) and in PBS whose Na⁺ concentration was 0.137 M. To have quantitative information on the swelling phenomenon, we used the blot and weigh method and calculated the swelling ratio (S_r) as the ratio between the samples weight after and before immersion in the aqueous solutions.

2.2. Electro-mechanical characterization

Once the samples PSS5%, PSS10% and PSS20% have reached the swelling equilibrium in solution A (NaCl 0.005 M), B (NaCl 0.05 M) and C (PBS, Na⁺ 0.137 M), electro-mechanical actuation tests were carried out in the same environments. Solutions A and B were chosen because their concentration was significantly inferior to the expected Na⁺ concentration inside the gel, while PBS constitutes a solution of biological interest. For the latter reason, DMEM (high glucose type) cell medium was also used in the actuation tests (Na⁺ concentration is about 0.154 M). Bending characterization took place in a 10 cm diameter Petri dish positioned above a millimeter grid. Each swollen sample was cut as a cantilever (15 \times 2 \times 0.3 mm³ and 15 \times 2 \times 0.1 mm³), having a larger square basis to be fastened (5 \times 5 mm²). The electrodes employed were two Platinum wires (0.25 mm diameter), each of them positioned 10 mm apart from the free end of the hydrogel. Both samples and electrodes were clamped and then fixed in a custom-designed Teflon apparatus (Fig. 2). In each test, a potential difference (ΔV) going from 0.2 to 9 V was applied between the electrodes, in order to explore both low (0.2–5 V) and high (6–9 V) voltages. The frequency response of all samples was also tested by applying a square wave of variable amplitude (1–5 V) at the electrodes, with frequency ranging from 0.5 to 2 Hz, in order to assess the materials suitability to operate as resonating soft structures in liquid (e.g., soft smart stirrers, fast response valves or propulsive motion generators). To ensure a high degree of homogeneity of the electric field along the full width of the cantilever, two gold electrodes having surface area

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