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Mechanoelectrical transduction in the hydrogel-based biomimetic sensors

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ABSTRACT

The study addresses the phenomenon of mechanoelectrical transduction in polyelectrolyte hydrogels and, in particular, the search of the driving force for the change of the electrical potential of a gel under the applied mechanical stretch. Polyelectrolyte gels of calcium and magnesium salts of polymethacrylic acid were synthesized by the radical polymerization in water solution. Their electrical potential measured by microcapillary electrodes was negative and fall within 100–140 mV range depending on the nature of a counterion and the networking density of a gel. The rectangular samples (~10 mm in length and 2 × 2 mm in cross-section) of gel-based sensors underwent the dynamic axial deformation, and the simultaneous monitoring of their geometrical dimensions and the electrical potential was performed. Sensor elongation resulted in the overall increase of gel volume, and it was always accompanied by the gel potential change toward the depolarization (diminishing of the negative values). Theoretical model based on the assumption of the total electrical charge conservation in the course of the dynamic deformation of a filament was proposed to describe the dependence of the electrical potential of a gel on its volume. Good agreement between the predictions of the model and the experimental trend was shown. The proposed mechanism of mechanoelectrical transduction based on the stretch-dependant volume changes in polyelectrolyte hydrogels might be useful to understand the nature of mechanical sensing in much more complex biological gels like the cell cytoskeleton.

1. Introduction

Synthetic polymeric hydrogels are widely introduced as biomimetic materials for the biomedical applications. From the general viewpoint of physical chemistry, the cell, especially its cytoskeleton, structurally resembles a polyelectrolyte hydrogel. Such gel is a 3D cross-linked polymeric network with the electric charges localized on the macromolecular filaments, and with free counterions dispersed in the liquid phase inside the network [1]. The physical basis of the volume contraction and the expansion of polyelectrolyte hydrogels lies in the balance between interaction of polymeric filaments with the medium, the entropic flexibility of filaments, the positive osmotic pressure of counterions, and the balance of attraction and repulsion forces between the electrical charges [2].

Of course, the chemical structure and the mechanisms of molecular interactions in protein network structures in a living cell are much complex than that in synthetic hydrogels. Meanwhile, the close similarity between these two physical systems concerning their structural properties and their response to some basic external stimuli had been demonstrated in numerous studies [3–5] including some performed by us [6–8] earlier.

In particular, both cells and anionic gels are negatively charged in respect to their surroundings, and they both keep electrical potential close to −100 mV. The negative electrical potential of anionic polyelectrolyte gel is a direct result of Donnan equilibrium established on the gel/supernatant boundary [5,6,9,10]. According to IUPAC nomenclature [11], Donnan equilibrium takes place if one

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or more ionic species for some particular reason cannot cross the phase boundary while other ionic species can freely move across it.

One of the most striking and important phenomena in the cell is the mechanoelectrical transduction (MET). In general, it combines the influence of the mechanical deformation of living cells on their electrical potential [12,13]. The most clear manifestation of MET is the functioning of the excitable cells, especially the muscle cells. In particular, in the cardiomyocytes, where cyclic deformation takes place, MET plays extremely important role in the maintenance of the heart rate pattern [14].

Meanwhile, recently we have demonstrated the existence of MET in synthetic polyelectrolyte gels of calcium and magnesium salts of polyacrylic acid [15,16]. We have shown that the deformation of a gel filament in an axial direction results in the decrease of the negative electrical potential of a gel. We suppose that one of the most reasonable physical mechanisms, which can explain this phenomenon, is the possibility of gel volume changes during the deformation. As the gel is immersed in water, the condition of its constant volume is not applicable as water molecules can enter and exit the interior of gel. Consequently, the gel network extra swelling or contraction may result in the counterions concentration changes of polymer matrix, that may affect the gel electrical potential. Indirectly, the results of theoretical [17,18] and experimental [7] studies that demonstrated the effects of polyelectrolyte hydrogel free swelling on its electrical potential may support the proposed hypothesis.

The objective of the present study was to reveal the correlation between the stretching deformation, the volume changes, and the electrical potential of gel-based sensors. The experimental setup included application of the dynamic axial deformations to the sensors with simultaneous monitoring of their linear dimensions, volume and the electrical potential. Based on the experimental data obtained, we intended to develop a theoretical model for the MET phenomenon in the synthetic hydrogel filament in the ionic solution, which hopefully might be applicable to the wide range of gel systems.

2. Experimental part

2.1. Materials

Polyelectrolyte gels based on poly(methacrylic) acid (PMA) with calcium and magnesium counterions (CaPMA and MgPMA) were synthesized by free-radical polymerization in 2.7 M aqueous solution. Monomer – methacrylic acid and a cross-linker – *N,N'*-methylene-diacrylamide were purchased from (Merck, Schuchardt, Honenbrunn). Polymerization was carried out in polyethylene probe tubes, 10 mm in diameter, at 80 °C for 2 h using ammonium persulfate (APS) as initiator. Prior to polymerization, the monomeric methacrylic acid was completely neutralized by the addition of stoichiometric amount of magnesium or calcium oxides. Cross-linker concentration was set at 1:50, 1:100, 1:200, 1:400 to monomer concentration in molar ratio, which further on is named as the network density of the gel. Subsequent gels are further denoted as Ca(Mg)PMAn, where n stands for the number of monomer units per one cross-link.

After the synthesis, the gels were washed in daily renewed distilled water for two weeks to remove non-reacted monomers, salts, and linear olygomers. The actual content of ionized groups in gels was determined by means of the thermogravimetry (Netzsch STA409 thermal analyzer) by measuring the residual weight after heating of previously dried gels up to 800 °C at a heat rate 10 K/min in the air. During the heating, the gels were decomposed to water, carbon dioxide and the residue of metal oxide. The stoichiometric equation of decomposition gave metal content in the synthesized gel. The content of ionized carboxylate groups was 98% (mol) in CaPMA gels and 75% in MgPMA gels. The synthesis of polymers and their swelling behavior are described in our early publications in details [6,7]. The central part of gel cylinders was cut by a razor blade to elongated rectangular samples, 10 mm in length and approximately 2 × 2 mm in cross-section.

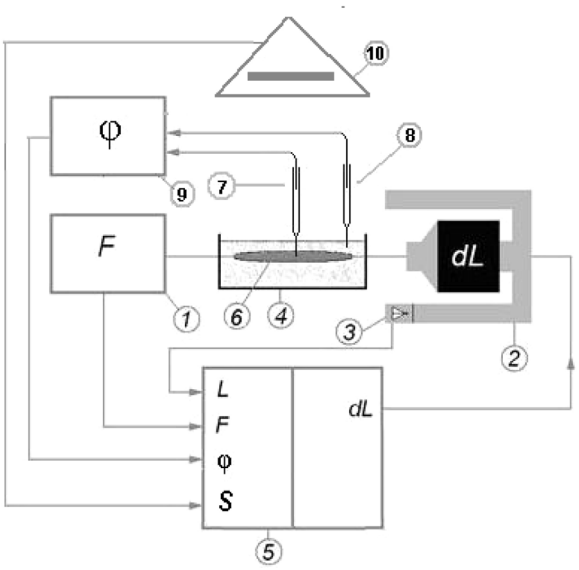

Fig. 1. Scheme of the experimental setup. 1–force transducer, 2 – electromagnetic motor, 3–length transducer, 4–experimental bath, 5–computer, 6–gel sample, 7,8 – glass-micropipette electrodes, 9 – instrumental amplifier, 10 – digital video camera.

2.2. Experimental equipment

Fig. 1 schematically displays the experimental setup of laboratory design used in this study. The equipment was built around an optical system, and contained a thermostatic bath for the gel sample, a semiconductor force transducer, an electromagnetic motor providing mechanical deformations, a semiconductor optical transducer measuring the motor's lever displacement, a personal computer equipped for controlling the experiment.

The electrical potential of a gel sensor was obtained by two identical Ag/AgCl tapered glass microelectrodes (~1 μm in tip diameter) typically used in biophysical studies for intracellular voltage measurement. The details of Donnan potential measurement in the gel were described in several studies [3,4,7]. Briefly, thin-walled, single-barrel borosilicate capillary tubes "TW150F-6" ("World Precision Instruments", USA) were single-pulled using a standard electrode puller "ME-3" ("EMIB Ltd", Russia). The pulled electrodes were immersed in a 3 M KCl solution with the tip facing upward, so that the solution climbed to the tip by capillary action.

One electrode was pinned into the gel sample, the other was placed in water outside. The potential difference between microelectrodes was measured using an instrumental amplifier on the base of an integrated circuit "INA 129" ("Burr-Brown", USA). The main amplifier parameters were: input impedance – 10^{10} Ω, frequency bandwidth – 0...107 Hz, gain – 50. To reduce the influence of electromagnetic interference on the potential difference measurement, special wire shields were provided around the unit. Typically, the peak-to-peak noise at the output of instrumental amplifier during the gel potential monitoring was no higher of 5 mV.

Computerized optical system on the base of digital video camera ("Panasonic" HX-WA2) was used for the monitoring of gel sensor