

Factors Affecting Electro-Actuation Rate in Partially Neutralized Polyelectrolytes Gels

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ABSTRACT

Polyelectrolyte networks composed of poly(acrylic acid) (PAAc) cross-linked with poly(ethylene glycol dimethacrylate) (PEGDA) are sensitive to electrical stimuli, allowing potential use as soft actuators. In our studies, PAAc was prepared via radical polymerization using UV irradiation from pregel solutions with independent variation of the crosslinking density, the extent of neutralization, as well as the water content after polymerization. The networks thus formed underwent a swelling process that consists of, first, a soaking in deionized water to allow for the removal of the unreacted species, followed by several soakings in deionized water to reach swelling and pH equilibrium. The bending behavior of these swollen PAAc hydrogels was studied under the influence of a DC electric field when applied either in deionized water, or in solutions of varying pH. We find that the curvature observed for these hydrogels depends strongly on all of the chosen variables. However, an unexpected phenomenon is also observed: the bending behavior seems to be composed of three stages that are active over differing time-scales. The earliest stage consists of a curvature toward the anode, followed by an intermediate stage that reverses the bending direction to be toward the cathode. Finally, the last stage features hydrogel rod shrinkage in all the directions. Depending on the conditions of our electromechanical analyses, the earlier and intermediate stages are more or less improved in terms of fast response and/or higher curvature attained. Rheological measurements have also been performed and further correlated to the electroactive response observed. We find that for high modulus specimens, the compliance and electromechanical characteristics are strongly related to each other.

INTRODUCTION

Chemomechanical systems capable of responding to an external stimulus have been increasingly studied for the past two decades. Such a stimulus can be either changes in ionic forces[1], changes in temperature, or application of an electric field.[2] Soft actuators have been postulated as novel solutions for biomedical engineering applications; namely, artificial muscles, chemical valves, and drug delivery systems.[3-5] Their salient advantages over hard actuators include a close matching of stiffness with biological tissue coupled with large recoverable deformations in excess of 100%. Although a great deal has been done for applications in the medical area, such actuators are not only limited to that field. Indeed, we envision their incorporation in such diverse applications as Braille display or deformable mirror devices in telescopes, for example. Despite these attractive features of soft actuators, in general, and hydrogel actuators, in particular, there is still a need for a quantitative physico-chemical model that describes and predicts their response to specific external stimuli. The lack of such a model is a

reflection of the present incomplete understanding of the mechanism(s) underlying the actuation process.

Our present efforts focus on the response that an electrical stimulus, consisting of a DC electric field, causes when applied perpendicularly to gel slabs made of partially ionized polyelectrolyte. Our system is a non-contacting system, meaning that the gel slabs and the electrodes are apart from each other in the experimental cell. Indeed, another setup is available, the contacting system. The resultant electroactive response depends on the type of system utilized as well as the nature of the solutions in which the gels are analyzed.[6] For both cases (contacting and non-contacting), the electromechanical responses observed are explained by various phenomena that are more or less accepted. In the case of contacting systems, the coupled effect of electro-osmosis of water and electrophoresis of ions that yield changes in pH, and therefore in conformation, are thought to be the major sources for the observed bending.[3,4,7] In the case of non-contacting systems, hypotheses on potential changes in conformation of the chains within the network due to changes in the chemistry/pH as well as depletion polarization effect [8] have been discussed; however, the osmotic pressure difference effect between the anode and cathode sides of the gels is now the most accepted hypothesis to explain actuation.[9] Despite the numerous hypotheses that exist concerning the mechanisms involved in electro-actuation, the phenomenon is yet neither well understood, nor well modeled.

This report focuses on the study of poly(acrylic acid) gels and their actuation when a DC electric field is applied to them in a non-contacting system. Our primary interest was to investigate the influence of the chemical structure of the gels and the composition of the testing baths upon electro-actuation. Rheological properties have been measured and further correlated to the response of our system.

EXPERIMENTAL

Pre-gel solutions preparation

All the reagents were purchased from Aldrich and were used without further treatment. Pre-gel solutions were made by mixing together: 2,2-dimethoxy-2-phenyl acetophenone (DMPA) as UV initiator, poly(ethylene glycol-400) dimethacrylate (PEGDA) as cross-linking agent, the acrylic acid monomer, deionized water, and lithium hydroxide (LiOH) as a neutralizer for the acrylic acid, in that order. Since we later discuss the influences of the extent of neutralization, of the cross-linking density, and of the water content, the values for these parameters will be specified for each of the results presented.

Polymerization process

Pre-gel solutions were inserted between two glass slides separated by a rubber gasket. The free radical polymerization was realized under UV light for 15 minutes at a fixed wavelength of 365nm using a Spectroline, model SB-100P from Spectronic Corporation. From each pre-gel solution, four gels were polymerized and were further tested to assure reproducibility of the results throughout the overall experimental process, from the polymerization step to the final electroactuation test.

Swelling/washing steps

The gels formed were allowed to swell for 24 hours in a 140-fold excess of deionized water, permitting the swelling equilibrium to be reached. pH values were

measured at swelling equilibrium. The swelling baths for each gel were then refreshed every 24 hours until the pH measured after each washing step leveled off to a value that was believed to reveal that of the pH equilibrium. Changing the washing bath consists of carefully taking the gel disks out of the washing bath, gently wiping the gels disks with an absorbent towel, and weighing them before finally introducing them into a new clean bath of deionized water. In the case of the gels containing much water, the gels were not wiped and not taken out of the bath between renewals, because of their great weakness. Moreover, this gel weakness made it impossible to assess the true swelling degree for those few samples.

Testing under a DC electric field and data analysis

The gels, after swelling, were cut into 40 mm long slabs with a 1 mm² square cross section. The gel slabs were further placed in a 63.5 × 63.5 mm square cell, where they were held by their center, leaving both of their ends free of any constraint. A 60 Volt DC electric field was then applied perpendicularly to the gel slabs through stainless steel electrodes (50mm×60mm). Once the electric field was turned on, pictures were taken at regular intervals of time and stored for further computational treatments. From the pictures, and using ImageTool™ software, we were able to create data points characterizing the curvature adopted by the gels at given times. These latter data sets were then fitted with a circle equation using SigmaPlot™ software. The radii obtained were simply inverted to give the curvature data that were used in our studies that define the rates of curvature. The rates of curvature are given by the first derivative of the curvature values with respect to time.

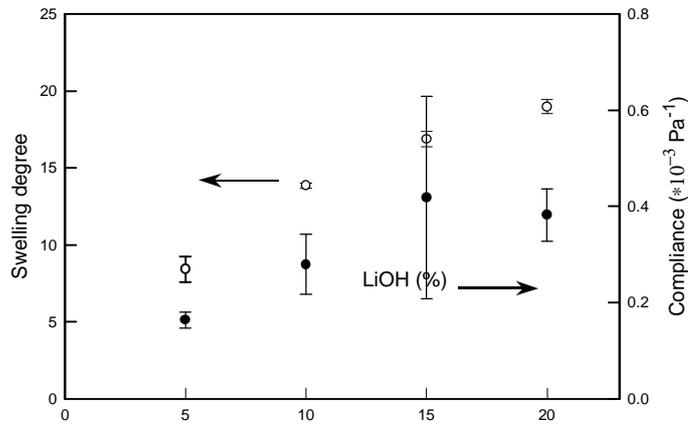
Rheological measurements

The apparatus used to monitor the changes in the rheological properties of our gels is an Advanced Rheometric Expansion System (ARES) from Rheometric Scientific Inc.. The geometries that have been used were either parallel plates with a 50mm diameter or serrated parallel plates with a 25mm diameter. The larger diameter was used for high water-containing gels (10%, 15%, 20% of LiOH and about 9.30 moles of water per cross-link point) to avoid extensive dehydration and, thus, to allow for better measurements. Dynamic Frequency Sweep Tests (Strain control) were run and the compliance data obtained as $[1/G'(\omega)]$ at 10 rad/s for every of the parameters investigated are represented in Figure 1.

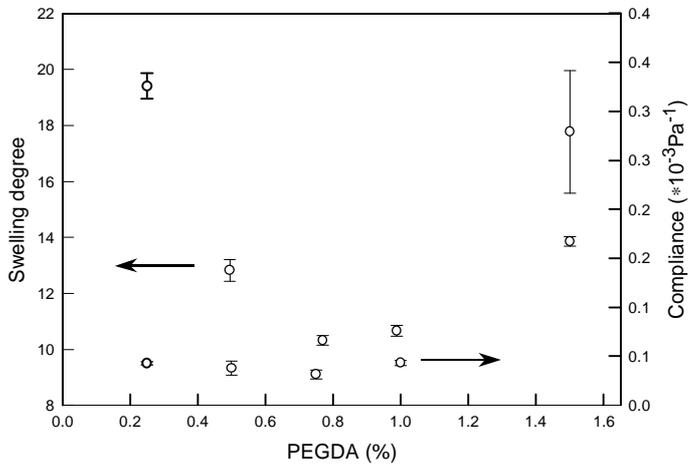
RESULTS

Figure 1 shows the swelling degree of the gels when both swelling equilibrium and pH equilibrium were reached as well as the mechanical compliance data for the three internal parameters under investigations. In Figure 1(a), which reports the ionization degree effect on both the swelling degree and the compliance data, one can see that ionization and compliance are convolved due to changes in equilibrium swelling as ionization varies. Figures 1(b) and (c) show the influence of the crosslinker agent and the water concentrations, respectively. Variations of both of these latter parameters yield changes of pore sizes within the network. Indeed, before swelling, gels exhibiting bigger pores will undergo larger water uptake during the swelling process for swelling equilibrium to be reached, thus diminishing the intrinsic stiffness of the gels, and vice versa.

(a)



(b)



(c)

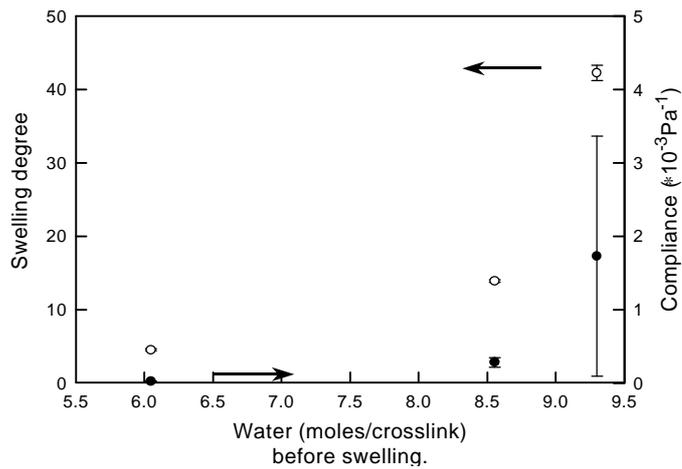


Figure 1. Swelling degree (open circles) and mechanical compliance (filled circles) values plotted against the parameters under investigations: (a) LiOH content, (b) PEGDA content and (c) synthesis water content.

As mentioned earlier, the curvature that our polyelectrolyte hydrogels undergo is composed of three distinct stages that occur over separated time scales. There is an early bending toward the anode, a large bending toward the cathode at longer times, followed by an overall shrinkage of the gel slabs in all directions at even longer times. Figure 2 shows the pictures that were taken at different times for a particular gel composition. To our knowledge, such a behavior has never been reported before when working with DC electric fields. Indeed, Shiga [6] summarized what was previously seen in contacting and non-contacting systems, and he concluded for non-contacting systems that one can either see a shrinking or swelling at the anode side of the gels depending on the external conditions of study; that is, the nature of the testing bath whether it is acid, neutral (salt solution or deionized water), or basic. However, no reference to any combination of those two phenomena has been given.

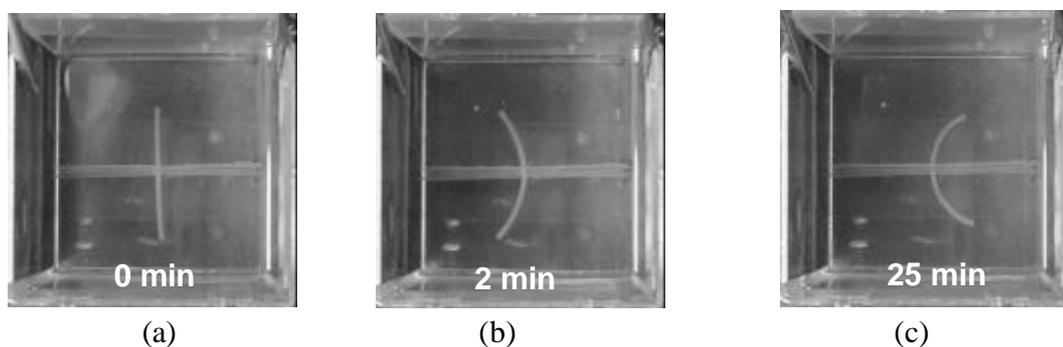


Figure 2. Pictures of the gel ((a) vertical white slab) at different times within a horizontal field of strength (V/cm) showing (b) the early bending toward the anode and (c) the late bending toward the cathode. The gel composition is 10% LiOH, 1.5% PEGDA, 8.56 mol/crosslink of water and the testing bath is an aqueous solution of LiOH at pH=9.5. The original gel slab length is 40 mm and the electrodes are spaced by 63.5 mm.

In Figure 3 the curvature data of a given gel composition as studied in three testing baths of various pH – that is various Li^+ contents – shows that both the early and late stage bending are influenced by the nature of the surrounding medium when an electric field is applied. Indeed, increasing the concentration of counterions in the testing bath apparently yield faster actuation for both the early and late bendings. Moreover, the maximum curvature attained during the early bending is enhanced by adding Li^+ to the surrounding medium. In Figure 4 are given the values of curvature versus time of three gels differing by their internal composition in terms of ionization degree as studied in a given testing bath composition. One can see that, even though the composition of the testing bath remains unchanged, the rates of curvature during the early stages are much faster at low ionization. Moreover, weaker ionization also maximizes the curvature attained before the late bending takes over the early bending. While, this latter figure reveals strong curvature dependence on chemical composition of the gel itself (ionization degree), similar behavior has been seen when varying either the cross-linking density or the synthesis water content. Therefore, both the early and late stage bending phenomena

are affected by both the nature of the testing bath and the chemical composition of the gel.

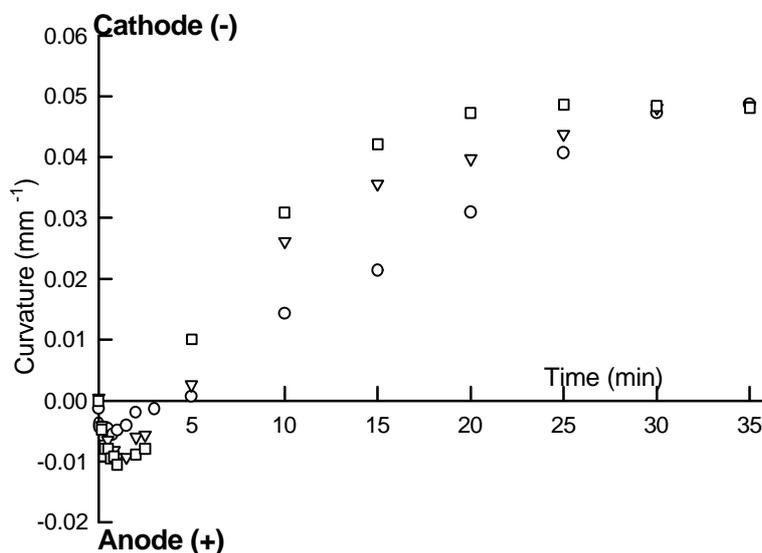


Figure 3. Curvature versus time plots for a given gel composition (15% LiOH, 1.5% PEGDA, 8.56 mol/crosslink of water) as studied in three different testing baths: in deionized water (○), in pH=8.4 (▽), in pH=9.5 (□).

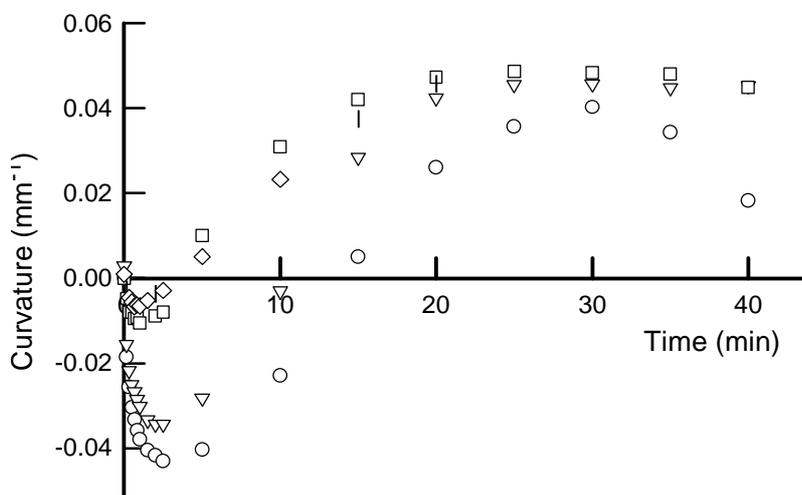


Figure 4. Curvature versus time plots for four gels of varying ionization degree (○) 5% LiOH, (▽) 10% LiOH, (◇) 15% LiOH, (□) 20% LiOH) but with fixed testing bath conditions. PEGDA concentration remains constant at 1.5% and synthesis water fixed at 8.56 mol/crosslink.

Referring back to the data in Figure 1, where the swelling data and the compliance data are summarized, the variations induced by changing the LiOH amount,

the crosslinker and the water concentrations during the synthesis of the gels strongly correlate with the swelling degree of the gels, which itself highly influences their compliance values. Therefore, it seems probable that the time scales over which the early and late stages occur (i.e., actuation rates) would be a function of the compliance arising from the changes linked to the gel composition, more than any direct effect of changing the parameters themselves.

CONCLUSIONS

Anionic poly(acrylic acid) hydrogels were successfully synthesized via radical polymerization, and their behavior under the application of an electric field studied for dependence on internal chemistry and structures of the gels and dependence on the nature of the experimental surrounding medium. Since the parameters involved in the synthesis strongly correlate with the physical properties exhibited by the gels, we expect such properties to factor prominently in a predictive model for electro-actuation response of gels with given ionization degree.

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