

Potentials in Anionic Polyelectrolyte Hydrogels

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ABSTRACT: Polyelectrolyte hydrogels perform interesting physical and chemical changes, such as motility and bend in the presence of electric fields and interaction with ionic surfactants. We think that ionizable groups of polyelectrolyte hydrogels play a vital role in these environments. In this work, we prepared three anionic polyelectrolyte hydrogels by two different routes, and micropipetts electrode was employed to determined negative potential in the gels.

Our work showed that the gels reported herein all display a high degree of swelling with hydration and have a substantial negative potential in KCl solution and a simple mechanism was also described. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1319–1321, 2003

Key words: copolymerization; hydrogels; polyelectrolytes

INTRODUCTION

Polyelectrolyte hydrogels have attracted intense attention because they exhibit interesting physical and chemical phenomena, including bend and volume changes in the presence of electric fields. Here, polyelectrolyte hydrogels refer to gels that have charge on their polymer chain. Ionic polyelectrolyte hydrogels are typically formed by a crosslinked polymer network with ionizable groups and a liquid phase. Hydrogels have been studied extensively,^{1,5–8} and interaction of ionic surfactants and polyelectrolyte hydrogels was investigated in recent years.^{2–4} We think that the radical reason is that after one polyelectrolyte hydrogel reaches water-swelling equilibrium, because the charged ions inside the gel motion that induces charge distribution in this gel, ionizable groups of polyelectrolyte hydrogel have net excesses charge, and thus this gel can efficiently interact with electric field or ionic surfactants. The result of charge distribution further induces potential between solute (the polymer) and solvent (the aqueous solution). Therefore, many interesting “intellective” deeds of the polyelectrolyte hydrogels were observed.

Gulch et al.⁹ determined the potentials of copoly acrylamide/polypotassiumacrylate and copolyacrylamide/polydiallyldimethylammoniumchloride gels, and he put forth a theoretical explanation for this potential, while unfortunately, the potential of hydrogels was investigated still much less. In this article, three anionic polyelectrolyte hydrogels were prepared

by the copolymerization of acrylamide with sodium acrylate, 4-styrenesulfonic acid sodium salt, or maleic acid disodium salt in two different methods. We used micropipetts electrode in the measurement of the potential of the three anionic polyelectrolyte hydrogels. The gels showed a substantial negative potential in KCl salt solution. These results have demonstrated anionic polyelectrolyte hydrogels could produce obvious charge redistribution after water-swelled and phase equilibrium.

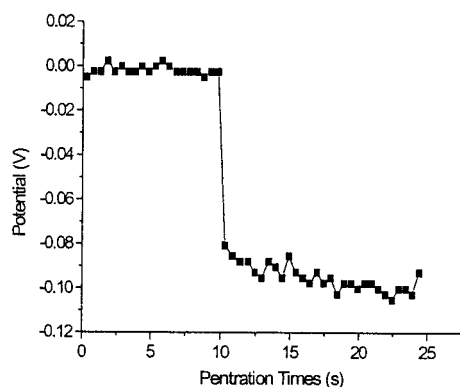
MATERIALS AND METHODS

Monomers, acrylamide sodium acrylate, 4-styrenesulfonic acid, sodium salt hydrate, and maleic acid disodium salt were purchased from Aldrich Chemical Corporation. The crosslinker, *N,N*-Methylenebisacrylamide, was a product of the above corporation. Initiators, potassium persulfate, and ammonium persulfate, were also the product of Aldrich corporation. The catalyst, *N,N,N',N'*-tetramethylethylenediamine, was from Aldrich as well.

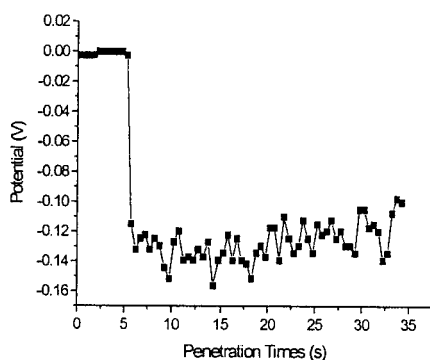
Three polyelectrolyte hydrogels were prepared by free radical polymerization. Copolymerization of acrylamide and sodium acrylate was performed in a 1 M aqueous solution of acrylamide and 1 M sodium acrylate monomer in the presence of 0.005 M of the crosslinker *N,N*-methylenebisacrylamide. After the addition of the initiator ammonium persulfate and the catalyst *N,N,N',N'*-tetramethylethylenediamine, the polymerization was carried out at 60°C for 3 h.

The copolymerization of acrylamide and 4-styrenesulfonic acid, sodium salt hydrate, or maleic acid disodium salt were prepared with potassium persulfate as the initiator and the gelation was carried out at 60°C for 5 h under a nitrogen atmosphere without a cata-

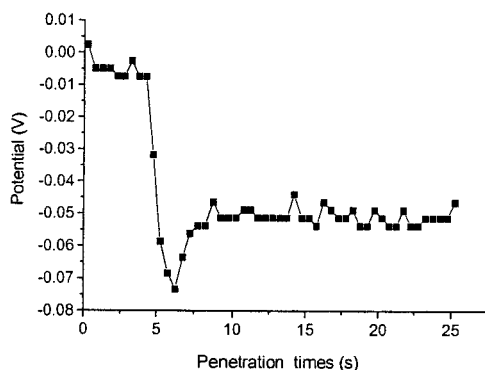
This work was finished at Prof. Pollack's lab.
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a



b



c

Figure 1 Microelectrode advances into polyelectrolyte hydrogels in 0.8 M KCl: (a) acrylamide/sodium acrylate gel; (b) acrylamide/4-styrenesulfonic acid sodium hydrate; (c) acrylamide/maleic acid disodium salt.

lyst. After the gelation was completed, the gels were thoroughly washed and swelled in distilled water, and they were in phase equilibrium before potential measurement.

RESULTS AND DISCUSSION

The measuring electrodes employed herein were micropipettes (tip diameter $<1 \mu\text{m}$) pulled from single-barreled borosilicate capillary tubes using a horizontal automatic micropipette puller. The measuring electrodes were filled with 3 M KCl and connected to a high input impedance electrometer through Ag/AgCl microelectrode holder. The reference electrodes were filled with 3 M KCl and connected directly to the electrometer. The output signals from the electrometer were acquired, displayed, and processed using Labview software. The microelectrode holder was affixed to a DC motor-driven micromanipulator, affording adjustable penetration speed, and depth (a speed of 0.27 mm/s was used for all experiments reported in this article). Before every measurement of potential of polyelectrolyte hydrogels, we tested the error of this system in KCl solution, and it was proven: $\pm 1 \text{ mV}$.

Potential in 0.8 M KCl solution

Given the net excess negative charge within the polyelectrolyte hydrogels, the microelectrode is expected to register a negative potential relative to the solution outside of the gels, and that is what is seen. Figure 1(a)–(c) gives such result for these gels in 0.8 mM KCl solution.

It can be seen from Figure 1 that as soon as the microelectrode penetrates into the polyelectrolyte hydrogel, the potential decreases sharply with depth, then reaches a constant value in a short period, consistent with a Donnan mechanism. The beginning flat line showed that microelectrode has not reached the surface of gels. While, as it touched and went into the gels, the potential changed dramatically, it even can reach about -120 mV .

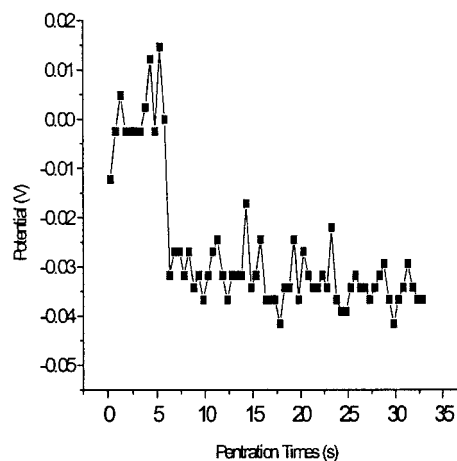


Figure 2 Microelectrode advances into copoly-acrylamide/sodium acrylate in 5.0 M KCl.

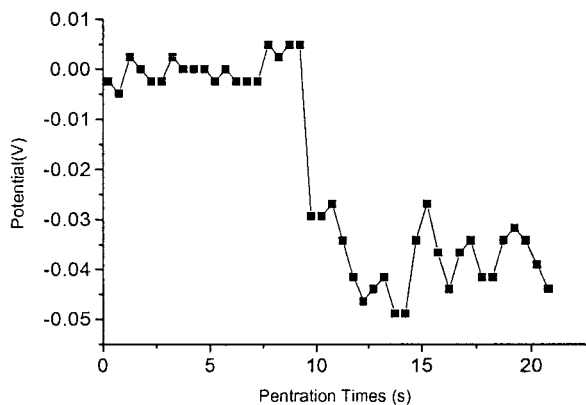


Figure 3 Microelectrode advances into acrylamide/sodium acrylate gel copolymerized at pH = 3 in 0.8 M KCl solution.

Potential in 5 M KCl solution

If negative potential arises from net excess negative charge, then charge the gel potential should go hand in hand; agents that affect matrix charge ought to affect potential in a similar way.¹⁰ Consider the effect of salt. When the KCl concentration in the bath is lowered, fewer potassium ions are available to diffuse into the gel matrix. The matrix will therefore be less neutralized. With more residual fixed charge, the potential magnitude should increase. Conversely, if the salt concentration is increased, the gel's charges will be more fully neutralized and the potential magnitude should diminish. This expectation is confirmed, and examples are shown in Figure 2. It can be seen from it that the absolute value of the potential of copolyacrylamide/sodium acrylate in high concentration salt aqueous (5 M KCl) is about half value in low salt environment (0.8 M). The same situation is to the two other polyelectrolyte hydrogels.

Effect of pH value on the potential

Hydrogen ion, as a cationic ion, should have the effect on the potential of polyelectrolyte hydrogels. In an-

other experiment, we first controlled the pH value of the reactant solution (including monomer, initiator, crosslinker, catalyst, and water) at 3.0, then the mixture was copolymerized to obtain the gel. In the same concentration salt solution, the potential's absolute value of this gel was found much smaller than that of regular gel, as shown in Figure 3 (about -40 – 80 mV). We observed the same phenomena for the other gels. It demonstrated that the most of gel's charges can be neutralized by hydrogen ion, and thus the potential diminished.

CONCLUSIONS

In conclusion, the anionic polyelectrolyte hydrogels show significant negative potential in salt aqueous solution resulting from the charged distribution within the gels.

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References

- Osada, Y.; Okuzaki, H.; Hori, H. *Nature* 1992, 355, 242.
- Narita, T.; Gong, J. P.; Osada, Y. *Macromol Rapid Commun* 1997, 18, 853.
- Chen, L.; Yu, S.; Kagami, Y.; Gong, J. P.; Osada, Y. *Macromolecules* 1998, 31, 787.
- Kim, B.; Ishizawa, M.; Gong, J. P.; Osada, Y. *J Polym Sci A Polym Chem* 1999, 37, 635.
- Matauda, A.; Sato, J.; Yasunaga, H.; Osada, Y. *Macromolecules* 1994, 27, 7695.
- Sawahata, K.; Gong, J. P.; Osada, Y. *Macromol Rapid Commun* 1995, 16, 713.
- Kim, B. S.; Chen, L.; Gong, J. P.; Osada, Y. *Macromolecules* 1999, 32, 3964.
- Kanekp, T.; Yamaoka, K.; Gong, J. P.; Osada, Y. *Macromolecules* 2000, 33, 412.
- Gulch, R. W.; Holedenried, J.; Weible, A.; Wallmersperger, T.; Kroplin, B. In *Smart Structures and Materials 2000: Electroactive Polymer Actuators and Devices*; Bar-Cohen, Y., Ed.; Proc. SPIE 2000, 3987, 193.
- Pollack, G. H. *Cells, Gels, and the Engines of Life, A New, Unifying Approach to Cell Function*; Ebner & Sons: Seattle, WA, 2000.