Effect of Electric Field on the Swelling Behavior of Cross-linked Copolymers of Poly(ethylene oxide) Bis-macromonomers with Methacrylic Acid

Grigoriy A. Mun[1]*, Galiya Azhgozhinova[1], Erengaip M. Shaikhutdinov[1], Konstantin S. Kazanskii[2] and Marina Lagutina[2]

[1]Kazakh National University, Department of Chemical Physics & Macromolecular Chemistry, Karasai Batyra 95, 480012 Almaty, Kazakhstan

[2]N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Kosygina 4, 119991 Moscow, Russia

Abstract

The hydrogels capable to interpolymer complex formation have been synthesized by direct radical copolymerization of methacrylic acid with poly(ethylene oxide) bis-macromonomer bearing methacrylate terminal groups. The swelling behavior of these hydrogels in electric field has been studied. The hydrogels were shown to undergo contraction or additional swelling depending on solution pH. In weakly acidic region (pH 5.1) the contraction of the network was observed. In these conditions the swelling behavior of the hydrogel is affected by the complex formation between unionized carboxylic groups and oxyethylene units within the networks and the gel sample has relatively low swelling degree and network charge. In basic region (pH 9.18) the polycomplex is destroyed and the network has higher charge density and higher swelling degree. Under the action of electric field such hydrogel swells additionally. An increase in ionic strength of solution decreases the amplitude of hydrogels contraction.

Introduction

Polymeric hydrogels are promising materials for biomedical applications due to their ability to reversibly absorb considerable amounts of water and living tissue-like consistency. The special class of these polymers is so-called "intelligent" or stimuli-responsive hydrogels, which are able to change their swelling parameters in respond to external stimulation [1-3].

In recent years there has been increased interest to hydrogels, containing groups able to specific interactions through hydrogen bonding within the network [4-7]. These hydrogels can be obtained by polymerization of monomers within the swollen network of another component (interpenetrating networks) [4], cross-linking of interpolymer complexes [8], copolymerization of macromonomers containing short poly(ethylene oxyde) chains with unsaturated carboxylic acids [6,7]. Formation of complexes due to interpolymer associations in polymer networks has a significant effect on the structure and properties of these materials. A more rapid response to changes in pH was observed for complexing networks.

Earlier the same kind of gels with longer network chains were synthesized by Kazanskii *et al.* [9] using direct radical copolymerization of methacrylate bis-macromonomers of poly(ethylene oxide) (MPEO) with methacrylic acid (MAA). It was demonstrated that the swelling of these hydrogels was greatly affected by complex formation between carboxylic groups and ethylene oxide units within the network.

In the present work we have studied the swelling behavior of these hydrogels under the action of external electric stimulation.

*corresponding authors. E-mail: gamun@nursat.kz

Printed in Kazakhstan

Experimental

Materials

MPEO with molecular weight 12000 and average number of methacrylate groups per macromolecule f_n = 1.55 was synthesized and characterized by the techniques described in *ref.* [10]. Methacrylic acid was purified by double distillation under vacuum.

Synthesis of Hydrogels

Polymeric hydrogels were synthesized by radical copolymerization in the presence of $K_2S_2O_8Na_2S_2O_3 \cdot 5H_2O$ as an initiating system with the concentration 0.7 g/L of every component. The mixture of water and alcohol 2:1 by volume was used as a reaction medium for copolymerization. The pH of the reaction mixture was adjusted to pH 7 in order to avoid complex formation between components. For preparation of all solutions water was purified from oxygen by boiling in argon atmosphere. The copolymerization was carried out at 30°C for 48 hrs. After synthesis the hydrogels were purified from soluble components by free swelling in renewable distilled water for 2 weeks.

Behavior of Gels in Electric Field

The behavior of gels in electric field was studied in electrochemical cell shown in Fig. 1. Two platinum electrodes with a surface area of 0.65 cm^2 each were mounted in the cell with 4 cm separation. The gel samples had cylinder- and tablet shapes. The tablet-shape samples were with a diameter of 7-8 mm and height of 2-3 mm. The position of the gel sample was fixed in the central part of the cell by a glass needle. The experiments in electric field were conducted at the constant current I = 10 mA. The facility P-5827 (Russia) was used as a source of DC current. The change of the volume ratio of the samples, V/V_0, was monitored using cathetometer B-630 (Russia), where V and V_0 are the volumes of the gel at the moment of measurements and immediately after the synthesis, respectively. The photo-images of the hydrogels of cylinder shape were obtained using a photo-camera Zenit-E (Russia).

Results and Discussion

Polyelectrolyte hydrogels inserted between a pair of planar electrodes with a DC voltage applied

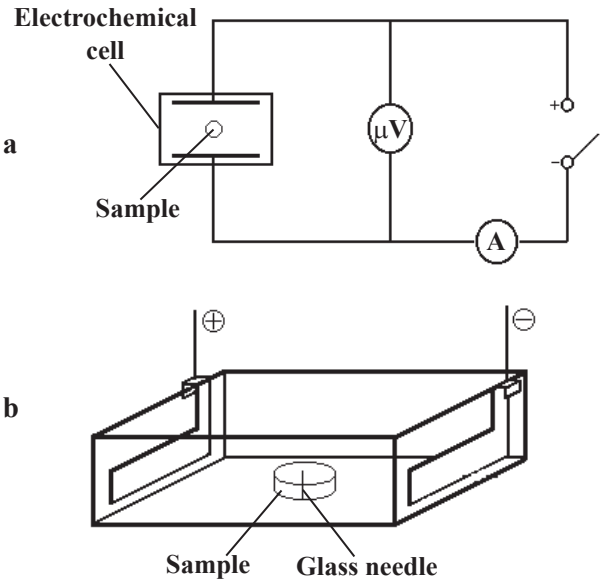

Fig. 1. Scheme of the device used in the study (a) and the electrochemical cell (b).

undergo volume and shape changes, which can be described as contraction, additional swelling or bending. The electrically induced contraction of the swollen gel is caused by the transport of hydrated ions and water in the network. The character and response speed of the gel to the electric field effect depend on many factors especially on molecular design of the gel and operating conditions. Molecular design of the gels includes ionic groups content and distribution, thickness, shape and mechanical strength of the samples. On the other hand, operating conditions include intensity and function in an applied electric field and ionic species in outer electrolyte solution (type and concentration) [11-13]. The studies of the behavior of polyelectrolyte hydrogels in the electric field are particularly interesting for the development of electrically controlled drug delivery systems [14].

The stimuli-response of hydrogels in electric field can be studied by two experimental methods involving contacting and non-contacting electrodes with gels. In the first type of experiment the current can be passed through the surrounding salt solution [15].

In the present work we have studied the behavior of MPEO-MAA hydrogels in the electric field, which was created using non-contacting electrodes. Figure 2 presents the photo-images of the volume and shape changes occurring with the samples of hydrogels under the effect of constant electric field. Before experiments the samples were of cylinder-like shape and under the action of electric field they

gain a bottle-like shape. The site of the gel, which is closer to anode, undergoes contraction and the part, which is closer to cathode, swells. The phenomenon observed may be attributed to the local pH changes by the electrode reactions.

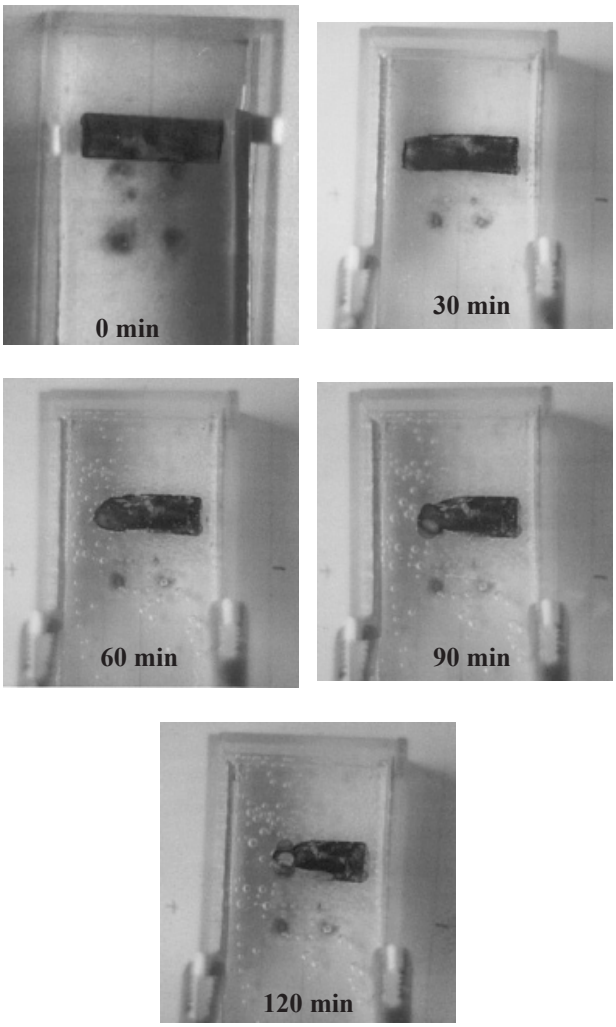

Fig. 2. Volume and shape changes of MPEO-MAA hydrogels samples in the constant electric field. I = 10 mA, $\mu = 5 \cdot 10^{-2}$.

The changes of the tablet-shape gels volume under effect of electric field are presented in Fig. 3. It is seen that the samples reduce their volume and the higher the ionic strength of environmental solution the lower the amplitude of volume-phase transition. Such a behavior is in good agreement with a capillary model proposed to describe the contraction process [11], which states that the contraction efficiency is inversely proportional to the charge density of the network and increases with an increase of its swelling degree.

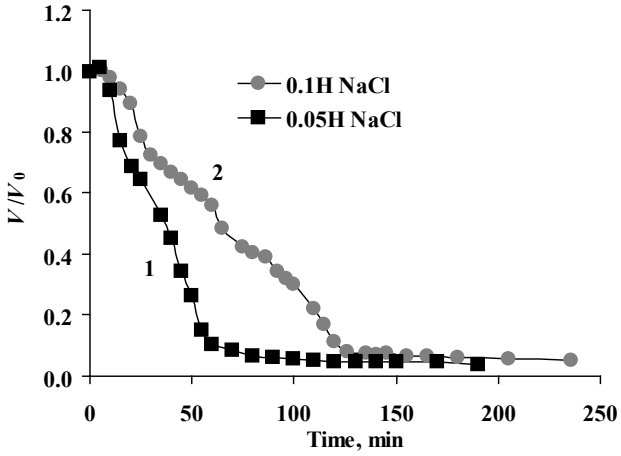

Fig. 3. Kinetics of MPEO-MAA hydrogel volume change in the electric field.

Environmental pH greatly affects the behavior of the hydrogels in the electric field (Fig. 4). The behavior of hydrogels in electric field at different pH was studied in buffer solutions with ionic strength equal 0.1 M. By this reason the hydrogels are characterized by lower swelling degree in comparison with samples studied in previous experiment. It is seen that depending on pH the hydrogels can swell additionally or shrink in response to electric field. In weakly acidic region (pH 5.1) the contraction of the network is observed. In these conditions the swelling behavior of the hydrogel is affected by the complex formation between unionized carboxylic groups and oxyethylene units within the networks and the gel sample has relatively low swelling degree and network charge. In basic region (pH 9.18) the polycomplex is destroyed and the network has higher charge density and higher swelling degree. Under the action of electric field such hydrogel swells additionally.

Contraction of MAA-MPEG hydrogel samples under different voltage electric field is presented in Fig. 5. It can be seen from the results that increasing of voltage from 3 to 7 V decreases the amplitude of hydrogel contraction.

Recently we reported [16] about the collapse of poly(methacrylic acid) (PMAA) hydrogels in response to simultaneous stimulation by an electric field and complex formation. It was found that the contraction process of these hydrogels in electric field can be accelerated considerably by the simultaneous complexation of the network with poly(ethyleneglycol) (PEG) via hydrogen bonding. In the present work we conducted experiment at the same pH-conditions and observed that amplitude of contraction of the network based on copolymers

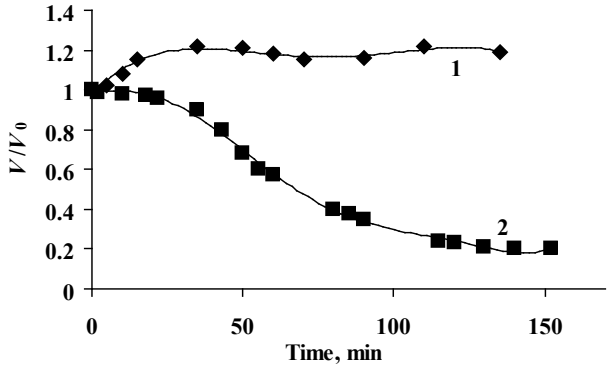

Fig. 4. Kinetics of MPEO-MAA hydrogel volume change in the electric field. pH: 9.18 (1), 5.03 (2).

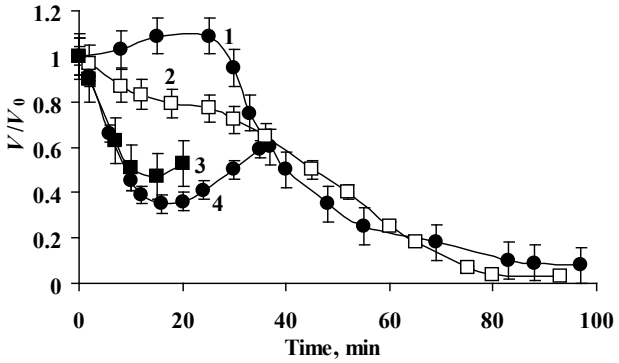

Fig. 5. Contraction of MPEO-MAA hydrogel in electric field of different voltage: 3 V (1), 5 V (2), 7 V (3) and 10 V (4).

of methacrylic acid and poly(ethyleneoxide) macromonomers is greater then that for PMAA hydrogel in PEG solution (Fig. 6). Probably such acceleration of contraction of the gels observed in the present work in comparison with PMAA hydrogels in the presence of PEG is caused by the fact that the complexation occurs already within the network and is not limited by diffusion penetration of linear macromolecules to the gel.

Conclusion

The swelling behavior of anionic hydrogels based on copolymers of methacrylic acid and poly(ethyleneoxide) macromonomers has been studied in non-contact electric field. It was found that the hydrogels undergo swelling or contraction depending on pH of solution. An increase in ionic strength decreases the contraction amplitude of the samples.

Acknowledgement

The authors would like to thank Dr. Vitaliy Khutoryanskiy for his help in preparation of this manuscript.

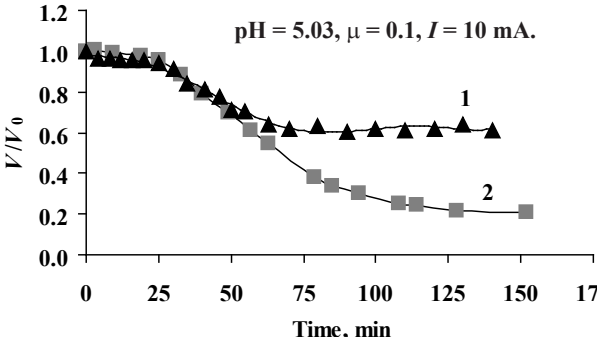

Fig. 6. Contraction of PMAA hydrogels in PEG solution (1) and of MPEO-MAA hydrogels (2) in the electric field.

References

1. Hoffman, A. "Smart" biomaterials; MRS Bulletin, 1991, 42.
2. Dusek K. (Ed.), in Responsive gels: Volume Transitions I, Adv. Polym. Sci., 1993, Vol.109.
3. Park K., Park H. Smart hydrogels, in The Polymeric Materials Encyclopedia: Synthesis, Properties and Applications, Salamone J.C. (Ed.), CRC Press: Boca Raton, Florida, 1996, 200-206.
4. Nishi, S.; Kotaka, T. Macromol. 1985, 18, 1519.
5. Nishi, S.; Kotaka, T. Polym. J. 1989, 21, 393.
6. Katono, H.; Sanui, K.; Ogata, N.; Okano, T.; Sakurai, Y. Polym. J. 1991, 23, 1179.
7. Lowman, A.M.; Peppas, N.A. Macromolecules 1997, 30, 4959.
8. Nurkeeva, Z.S.; Mun, G.A.; Khutoryanskiy, V.V. Polymer Science, Ser. B., 2001, 43, 925.
9. Lagutina, M.A.; Rakova, G.V.; Yarygina, N.V.; Dubrovskii, S.A.; Kazanskii, K.S. Polymer Science, Ser. A 2002, 44, 811.
10. Kazanskii, K.S.; Skuridin, S.G.; Kuznetsova, V.I.; Evdokimov, Yu.M. Polymer Science, Ser. A 1996, 38, 570.
11. Osada, Y.; Gong, J.-P. Adv. Mater. 1998, 10, 827.
12. Hirai, T.; Nemoto, H.; Hirai, M.; Hayashi, S. J. Appl. Polym. Sci. 1994, 53, 79.
13. Homma, M.; Seida, Y.; Nakano, Y. J. Appl. Polym. Sci. 2000, 75, 111.
14. Kim, S.Y.; Lee, Y.M. J. Appl. Polym. Sci. 1999, 74, 1752.
15. Yang, Y.; Engberts, J.B.F.N., Colloids & Surfaces A, 2000, 169, 85.
16. Mun, G.A.; Nurkeeva, Z.S.; Khutoryanskiy, V.V.; Azhgozhinova, G.S.; Shaikhutdinov, E.M.; Park, K. Macromol. Rapid Commun. 2002, 23, 965.

Received 10 October 2007