Self-Oscillating pH-Responsive Cryogels as Possible Candidates of Soft Materials for Generating Mechanical Energy

Cigdem Bilici, Sehri Karayel, Tuba T. Demir, Oguz Okay

Istanbul Technical University, Maslak 34469, Istanbul, Turkey

ABSTRACT: This research highlights the use of poly(acrylic acid) (PAAc) cryogels as a pH oscillator in oscillatory bromate–sulfite–ferrocyanide reactions. The cryogels were prepared from frozen aqueous solutions of acrylic acid monomer and N,N'-methylenebis(acrylamide) crosslinker at $-18°C$. Fast responsive macroporous PAAc cryogels were obtained at or below 4 w/v % initial monomer concentration. SEM images of PAAc cryogel networks exhibited a heterogeneous morphology consisting of pores of sizes 10^1 μm, typical for macroporous networks formed by the cryogelation technique. PAAc cryogels coupled with the bromate oscillator oscillate between swollen and collapsed states, during which a cyclic three-fold change in the gel volume was observed. The results show that, due to the fast response rate of cryogels, macroscopic gel samples can be used as a pH oscillator which would provide generation of significant amount of mechanical energy. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2981–2988, 2010
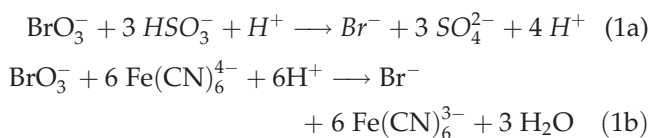
Key words: self-oscillating hydrogels; cryogelation; pH responsive gels; swelling

INTRODUCTION

Responsive hydrogels are soft and smart materials, capable of changing volume and/or shape in response to specific external stimuli, such as the temperature, solvent quality, pH, electric field, etc.[1,2] These properties of responsive hydrogels received considerable attention in the last three decades and, a large number of hydrogel based devices have been proposed, including artificial organs, actuators, and on–off switches.[3] Conventional responsive hydrogels make only a single action in response to the external variables, that is, conventional hydrogels either swell or deswell in contact with the external stimulus. In contrast, however, so-called self-oscillating hydrogels exhibit swelling–deswelling cycles in contact with a solution.[4] Thus, self-oscillating hydrogels create dynamic rhythms and may open new application areas including self-walking microactuators or micropumps with peristaltic motion, pacemakers, timers, and oscillatory drug release systems.[4]

Self-oscillating hydrogel systems can be designed by coupling a responsive hydrogel sample with the oscillating chemical reactions. For example, the Belousov-Zhabotinsky (BZ) reaction is a well known oscillating system and the overall process of the reaction is the oxidation of a substrate, such as malonic acid under coexistence of oxidizing agent (bromate) and metal catalyst in an acidic solution.[5,6] Yoshida et al.[4,7] used poly(N-isopropyl acrylamide) gel in a BZ reaction to produce self-oscillating gel system.[4,7] Crook et al.[8] used poly(methacrylic acid) (PMAAc) gel in a Landolt oscillating reaction system consisting of bromate, sulfite and ferrocyanide ions.[9] Although the actual mechanism of this bromate oscillation system is complicated, the overall reaction consists of two main steps: (i) the oxidation of sulfite by bromate and (ii) the oxidation of ferrocyanide by bromate, i.e.,[8]

$$BrO_3^- + 3\,HSO_3^- + H^+ \longrightarrow Br^- + 3\,SO_4^{2-} + 4\,H^+ \quad (1a)$$

$$BrO_3^- + 6\,Fe(CN)_6^{4-} + 6H^+ \longrightarrow Br^- \\ + 6\,Fe(CN)_6^{3-} + 3\,H_2O \quad (1b)$$

Thus, the first reaction produces H^+ ions so that pH of the reaction solution decreases whereas the second reaction consumes H^+ ions so that the pH again increases. In response to the oscillatory pH changes in the solution, a weak polyelectrolyte gel such as PMAAc oscillates between swollen and collapsed states.

All of the self-oscillating gels prepared so far are limited in their size to microscopic dimensions. This is due to the fact that the response rate of gels against the external stimuli is not as fast as required.

The aim of this work was to use centimeter-sized hydrogel samples in self-oscillating reaction systems, which would provide continuous generation of a significant amount of mechanical energy. To achieve this aim, a fast responsive hydrogel was prepared by creating an interconnected macroporous structure inside the gel network. As is well known, in macroporous gels, the absorption or desorption of solvent occurs through the pores by convection, which is much faster than the diffusion process that dominates the homogeneous gels.[10] In this work, macroporous hydrogels were prepared by use of the cryogelation technique,[11–16] which is based on the natural principle that the sea ice is less salty than sea water. As in nature, during the freezing of the monomer solution, the monomers expelled from the ice concentrate within the channels between the ice crystals, so that the polymerization reactions only take place in these unfrozen liquid channels. After polymerization and, after melting of ice, a macroporous material is produced whose microstructure is a negative replica of the ice formed.[17]

Here, macroporous poly(acrylic acid) (PAAc) cryogels were prepared by conducting the crosslinking reactions of acrylic acid monomer and N,N'-methylenebis(acrylamide) crosslinker at $-18°C$ in water. The reactions were carried out at various initial monomer concentrations to find out the optimum condition for the formation of fast responsive PAAc gels. Moreover, a pH oscillator system consisting of bromate, sulfite, and ferrocyanide ions was prepared by feeding the reactants into a continuously stirred tank reactor using a peristaltic pump while keeping the reactor volume constant. As will be seen below, PAAc cryogels immersed into the pH oscillating solution form self-oscillating gels of macroscopic sizes producing continuously mechanical energy.

EXPERIMENTAL

Materials

Acrylic acid (AAc, Fluka) was freed from its inhibitor by passing through an inhibitor removal column purchased from the Aldrich Chemical Com. N,N'-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), and sodium metabisulfite (SMS, Merck) were used as received. APS and SMS stock solutions were prepared by dissolving 0.228 g APS and 0.190 g SMS separately in 10 mL of water. BAAm stock solution was prepared by dissolving 0.222 g BAAm in 10 mL of water. The reactants of the pH oscillator, namely potassium bromate $KBrO_3$, potassium ferrocyanide $K_4Fe(CN)_6.3H_2O$, sodium sulfite Na_2SO_3, and sulfuric acid H_2SO_4, all from Merck, were also used as received.

Gelation reactions were carried out starting from partially neutralized AAc monomer at a neutralization degree of 0.75. A stock solution of the monomers AAc and sodium acrylate (NaAc) was prepared by dissolving 10 g of AAc in 8 g of distilled water and adding to this solution 12.2 mL of a 34.2% NaOH solution under cooling. 100 mL of the solution thus prepared contained 40.8 g of monomers with a mole ratio of NaAc/AAc = 3/1.

Synthesis of cryogels

PAAc cryogels were prepared by free-radical crosslinking copolymerization of the monomers AAc and NaAc using APS - SMS (both 1 mM) redox initiator system at $-18°C$. The initial concentration of the monomers varied whereas the crosslinker ratio (the mole ratio of the crosslinker BAAm to the monomers) was set to 1/80 throughout the experiments.

To illustrate the synthetic procedure, we give details for the preparation of the cryogel at an initial monomer concentration of 2 w/v %: 0.5 g of the monomer stock solution, H_2O (9.1 g), stock solutions of BAAm (0.2 mL) and SMS (0.1 mL) were first mixed and purged with nitrogen gas for 10 min. Then, APS stock solution (0.1 mL) was added and the solution was transferred to several plastic syringes of 5 mm in diameter and 1 mL in volume. The gelation reactions were carried out at in a thermostated bath at $-18°C$ for 24 h. After polymerization, the syringes were taken out of the bath and the gel rods were removed from the syringe.

Characterization of cryogels

PAAc cryogels were cut into specimens of approximately 10 mm in length and immersed in a large excess of water at $21 \pm 0.5°C$ to wash out any soluble polymers, unreacted monomers, and the initiator. To reach swelling equilibrium, the cryogels were immersed in water for at least 1 month replacing water several times. The swelling equilibrium was tested by measuring the diameter of the gel samples using an image analyzing system consisting of a microscope (XSZ single Zoom microscope), a CDD digital camera (TK 1381 EG) and a PC with the data analyzing system Image-Pro Plus. To achieve good precision, five measurements were carried out on samples of different length taken from the same gel. The interpretation of the swelling measurements in water was made on the basis of the relative volume swelling ratio V_{rel}, which was calculated as

$$V_{rel} = (D/D_o)^3 \qquad (2)$$

where D is the diameter of the equilibrium swollen gel sample in water and D_o is its diameter after

preparation. To obtain PAAc networks, swollen gel samples were taken out of water and immersed in methanol followed by drying under vacuum at room temperature.

For the deswelling kinetics measurements, the cryogels equilibrium swollen in water at 21°C were transferred into methanol. The images of gels were monitored in real time and captured every 5 sec by the image analyzing system. With the use of the software Image-Pro Plus, the diameter of the gel samples could be determined. For the measurement of the reswelling kinetics of gels, the equilibrium collapsed gel samples in methanol were transferred into water at 21°C. The diameter changes of gels were also determined volumetrically as described above.

For the texture determination of dried cryogels, scanning electron microscopy (SEM) studies were carried out at various magnifications between 10 and 30.000 times (Jeol JSM 6335F Field Emission SEM). Before the measurements, network samples were sputter-coated with gold for 3 min using Sputter-coater S150 B Edwards instrument.

pH oscillation system

Figure 1 shows the experimental apparatus used for real-time pH and gel size measurements during the self-oscillation of PAAc cryogels. A glass beaker of 150 mL in volume having an exit opening about 20 mm above its bottom was utilized as the continuous stirred tank reactor of the oscillation reactions. The position of the exit provided a constant reaction volume of 60 mL throughout the reactions. The reactor containing a small magnetic stirring bar was placed on a magnetic stirring device and then, the whole system was situated below a XSZ zoom tube of the image analyzing system. A cylindrical cryogel sample of 5 mm in diameter and about 1 cm in length was fixed using a disposable needle and placed into the reactor. Four feed solutions, namely $KBrO_3$ (0.065 M), $K_4Fe(CN)_6.3H_2O$ (0.02 M), Na_2SO_3 (0.075 M), and H_2SO_4 (0.01 M) were pumped into the reactor through four inlet tubes by means of a Heidolph Pumpdrive PD 5201 peristaltic pump. Note that the concentration of the reactants was taken as those given before,[9] which provided satisfactory pH oscillation under certain flow rates. Readings of pH were taken using a pH electrode placed close to the gel sample and they were collected using a PC. Simultaneously, the microscope output was recorded on a digital camera from which images could be automatically captured by PC. Using the software Image-Pro Plus, the diameter of the gel sample could be determined and a plot could be constructed as pH and gel diameter against time.

Figure 1 Experimental apparatus for real-time pH and gel size measurements during the self-oscillation of PAAc cryogels. (1): Reactor. (2): Single zoom microscope. (3): CDD digital camera. (4): Peristaltic pump. (5): Feed solutions. (6): Monitor showing real-time gel images. (7): Monitor showing real-time pH versus time data. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Characteristics of PAAc cryogels

PAAc cryogels were prepared at −18°C and at a fixed crosslinker ratio but at various initial monomer concentration C_0 between 1 and 40%. The gel fraction, that is the amount of crosslinked polymer obtained from 1 g of monomer was complete at C_0 below 4%, while it rapidly decreased with increasing monomer concentration and approached to 0.05 at $C_0 = 40\%$. Moreover, the equilibrium volume swelling ratio V_{rel} of the cryogels in water increased from about 5 to 12 with increasing monomer concentration. The results thus suggest decreasing efficiency of crosslinking as the monomer concentration is increased. As our aim in this study was to utilize PAAc cryogels as an oscillating material, their response rate against the external stimuli is an important parameter. Therefore, cryogels obtained at various initial monomer concentrations were subjected to swelling and deswelling kinetics measurements. For this purpose, they were first swollen in
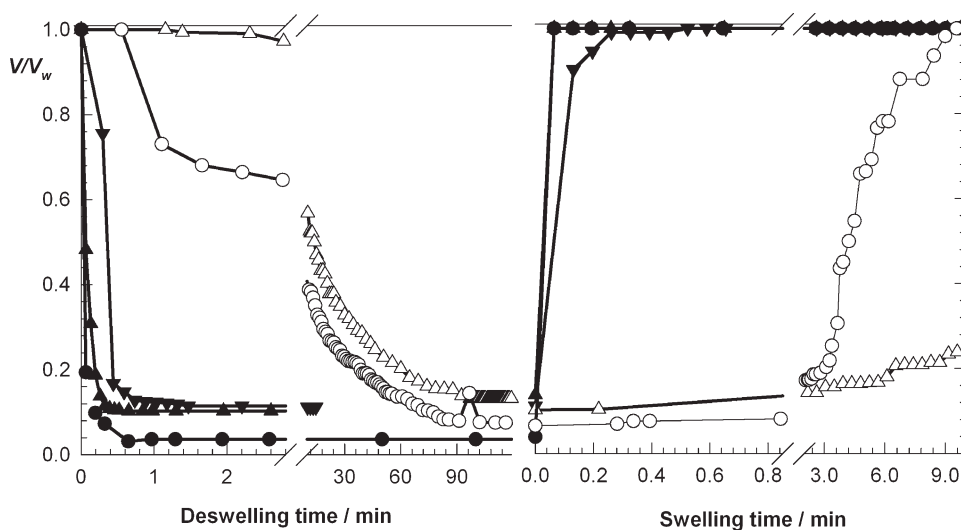
Figure 2 Deswelling–reswelling kinetics of PAAc cryogels shown as the variation of the normalized gel volume V/V_w with time. The initial monomer concentration C_0 used in the cryogel preparation = 1 (●), 2 (▲), 4 (▼), 20 (○), and 40 w/v % (△).

water to their equilibrium state. Thereafter, the swollen gels were immersed in methanol (poor solvent) and the deswelling process was monitored by recording the diameter D of the gel sample as a function of the time of deswelling. After attaining the equilibrium collapsed state in methanol, the gels were again immersed in water and the reswelling behavior was monitored in real time until the new equilibrium state is obtained.

Typical deswelling and reswelling cycles of the cryogels formed at various C_0 are shown in Figure 2 where the gel volume normalized with respect to that in water, V/V_w, is plotted against the deswelling and swelling times, respectively. It is seen that the gel samples formed at or below 4% monomer concentration attain their equilibrium states within less than 1 min whereas those formed at higher monomer concentrations require much longer equilibration times. Thus, fast responsive PAAc cryogels were obtained at $C_0 \leq 4\%$.

Figure 2 also shows that the swelling response rate of the collapsed cryogels is much more rapid than the deswelling response rate of the same gel starting from its swollen state. For example, swollen PAAc gel formed at $C_0 = 1\%$ attains its equilibrium collapsed state within 30 s, whereas the reswelling to the same initial swollen volume requires only a few seconds. This difference may be related to the strong hydrogen bonding interactions between the carboxylic acid groups of the cryogel network and water molecules slowing down the diffusion of water out of the gel phase. In this connection, we have to mention that, although several polymerization techniques were used before successfully to increase the deswelling rate of hydrogels, the reswelling rate of collapsed hydrogels cannot be improved;

generally, such gels required tens to hundreds of minutes to attain the equilibrium swollen state in water.[18–22] This slow reswelling rate of the hydrogels reported in the literature is mainly due to the collapse of their porous structure because of the cohesional forces between the solvated polymer chains. Here, however, we show that the PAAc cryogels formed at or below 4% monomer concentration swell within seconds. This is probably due to the stable pore structure which cannot collapse during deswelling, as well as due to the large channels (pores) which enable diffusion of water in the hydrogel network.

Another point shown in Figure 2 is that the cryogels formed at $C_0 = 1\%$ exhibit the fastest response rate. However, these gels were too weak to withstand repeated swelling–deswelling cycles; during the second deswelling process in methanol, they were broken into several pieces so that further cycles cannot be conducted. In contrast, those formed at 2% monomer concentration were mechanically stable against the volume changes. This behavior is shown in Figure 3 where the diameter D of the cryogel formed at $C_0 = 2\%$ is shown as a function of time during three successive deswelling-reswelling cycles. It is seen that the gel diameter D varies between 8 and 2 mm, i.e., the gel exhibits completely reversible cycles. Thus, 64-fold change in the volume of the gel during the swelling–deswelling cycles does not induce any crack formation and, the network structure remains stable. The results suggest that these cryogel samples can be used in the oscillating reaction systems

Figure 4 show SEM images of the gel networks formed at various initial monomer concentrations C_0. Except samples formed at C_0 above 4%, all network samples consist of macropores of 10^1 μm in diameter typical for macropores networks formed by
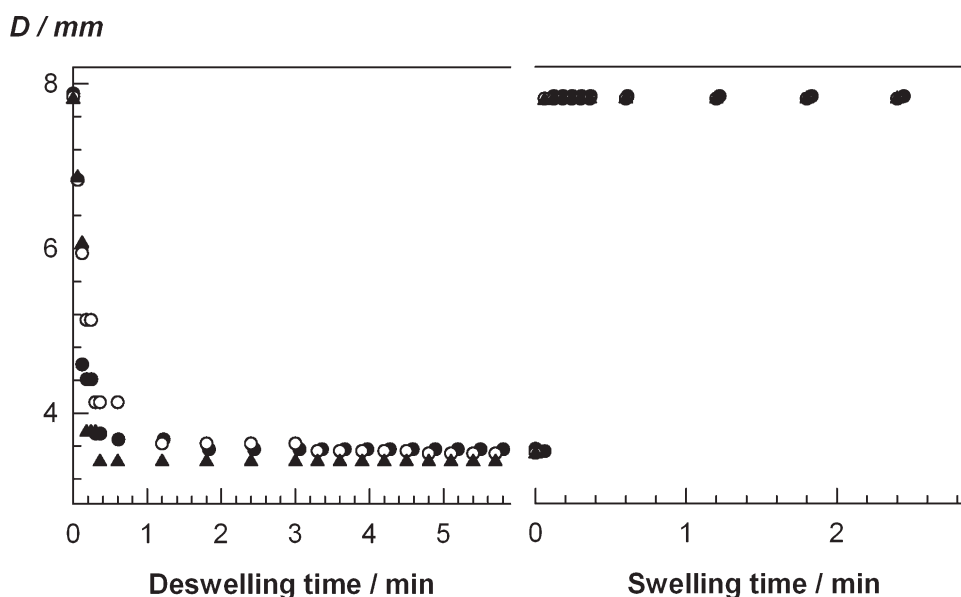
Figure 3 Deswelling–reswelling kinetics of PAAc cryogels formed at 2% initial monomer concentration shown as the variation of the gel diameter D with time. The data points are results of the measurements during the first (●), second (○), and third deswelling-reswelling cycles (▲).

the cryogelation technique.[17] We have to mention that the SEM images of the samples were taken after collapsing the cryogels in methanol and after drying. Therefore, the pore size of the initial swollen cryo-gels may significantly differ from the pore size reported above. SEM images in Figure 4 also indi-cate that the morphology of the gel network formed at $C_0 = 4\%$ is relatively regular while the regularity
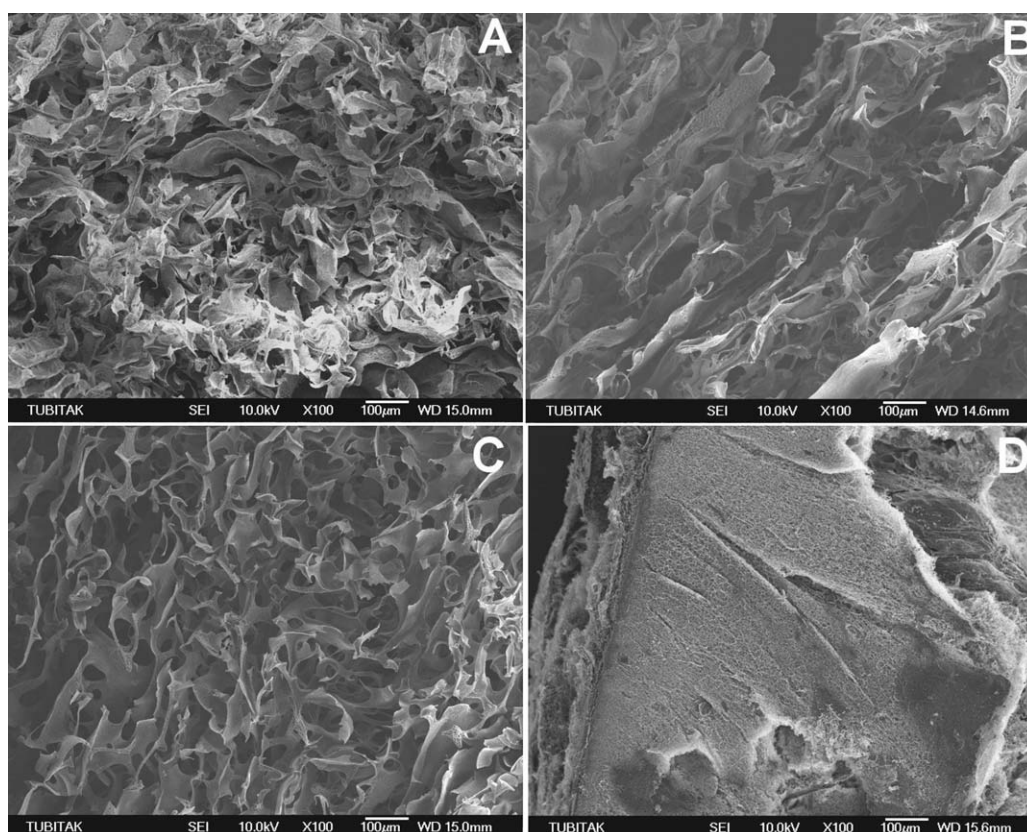

Figure 4 SEM of PAAc networks formed at various C_0. The scaling bars are 100 μm. Magnification = x100. $C_0 = 1$ (A), 2 (B), 4 (C), and 20% (D).
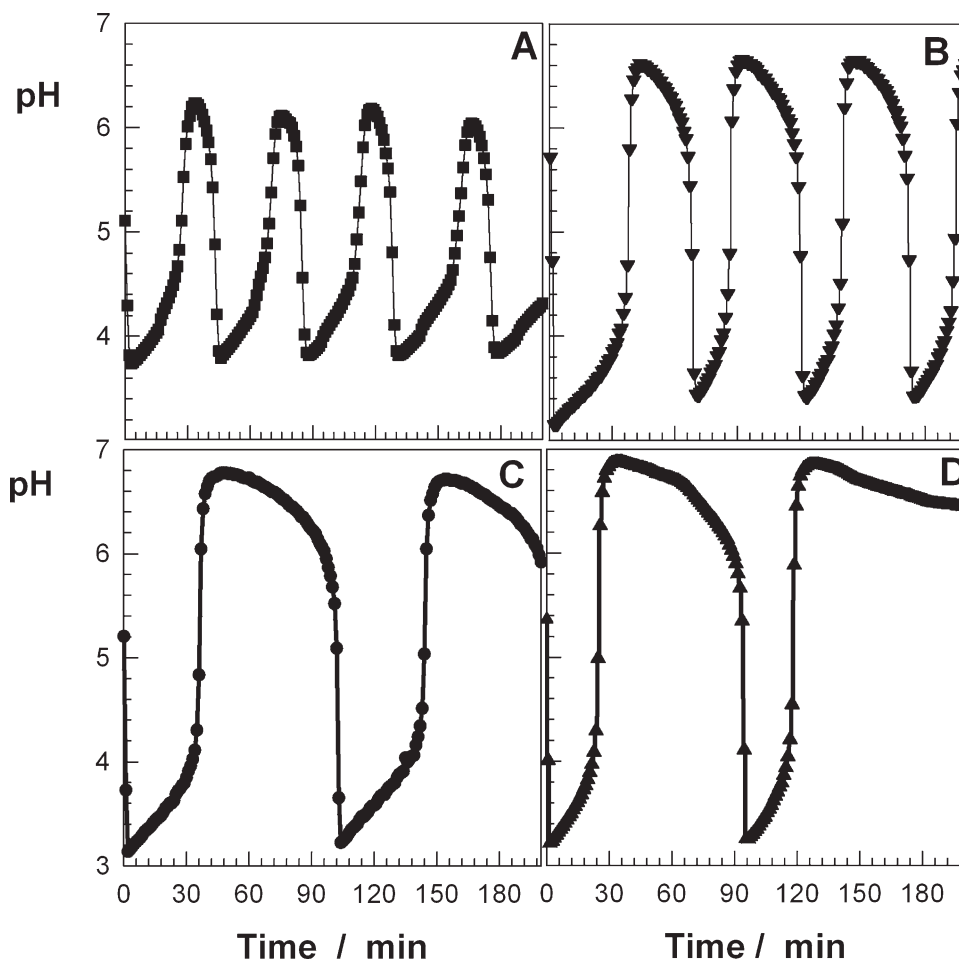
Figure 5 pH of the reaction solution shown as a function of time. $10^4 k = 1$ (A), 2 (B), 3.5 (C), and 10 (D).

of the porous structure is largely destroyed as C_0 is decreased. This is probably due to the collapse of the pores in weak network structures formed at a low monomer concentration.

The results shows that macroporous PAAc cryogels with a fast response rate could be prepared at $-18°C$ and at or below 4% monomer concentration. The occurrence of the polymerization and crosslinking reactions about 18°C below the freezing point of water as well as formation of a macroporous structure are due to the presence of unfrozen regions in the apparently frozen reaction system.[23–27] Thus, gelation reactions only proceed in the unfrozen microzones containing a high concentration of the monomers and the initiator, whereas the frozen zones (ice crystals) of the reaction system act as template during gelation, which is removed from the gel by thawing leading to a porous structure.[11,12]

Self-oscillating PAAc cryogels

The oscillating reactions consisting of bromate, sulfite, and ferrocyanide ions were conducted in an open continuously stirred tank reactor. Four feed solutions, namely solutions of potassium bromate, sodium sulfite, potassium ferrocyanide, and sulfuric acid were supplied continuously to the reactor during which pH of the reaction solution was monitored as a function of time (Fig. 1). Preliminary experiments showed that the flow rate of the feed solutions is an important parameter determining the extent of pH oscillations. In Figure 5, pH versus time plots are shown for four different reduced flow rates k, defined as the flow rate of feed solutions divided by the reaction volume. It is seen that the pH of the solution oscillates between 6.2–6.9 and 3.2–3.8. As the dissociation degree α of a weak electrolyte relates to pH by:

$$pH = pK_a + \log\left(\frac{\alpha}{1 - \alpha}\right) \qquad (3)$$

using $pK_a = 4.25$ reported for PAAc gels,[28] one may calculate the dissociation degree α as 0.15 and 0.99 for pH = 3.5 and 6.5, respectively. Thus, if PAAc gel is immersed into this solution, the concentration of the mobile ions (Na^+) inside the gel will seven-fold
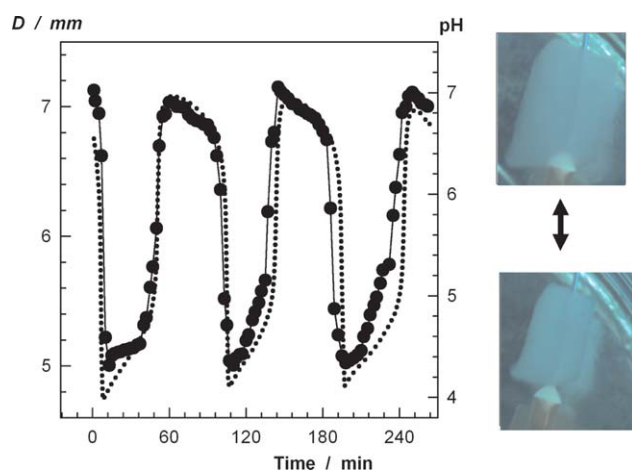
Figure 6 Variations of pH (dotted curves) and gel diameter D (symbols) as a function of time. $k = 5 \times 10^{-4}$ s^{-1}. The pictures in the right show the gel samples at high and low pH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

change during these pH oscillations. Figure 5 also shows that, as the flow rate k is increased, oscillation frequency decreases whereas the amplitude of pH oscillations increases. Further, increasing flow rate also increases the time periods at high and low pH values. For example, at $k = 1 \times 10^{-4}$ s^{-1} and 1×10^{-3} s^{-1}, pH of the solution remains above 6 for a duration of 25 and 75 min in each cycle, respectively. The results in Figure 5 also demonstrate that the oscillation proceeds monotonically with fixed values of the maximum and minimum pH.

As a next step, PAAc cryogel samples were immersed into the pH oscillating system to obtain oscillating gels. Gel samples of 5 mm in diameter and about 1 cm in length (approximately 1 cm^3) were used in the experiments; the images of the gel samples were taken every minute using the image analyzing system while pH of the solution was also monitored by PC. Figure 6 shows pH and the gel diameter D as a function of time at a flow rate $k = 5 \times 10^{-4}$ s^{-1}. The images in the figure were taken from the gel sample in swollen and collapsed states. It is seen that, depending on the pH oscillations, the diameter of the gel sample periodically varies between 7 and 5 mm, indicating three-fold change in the gel volume. At high pH, the concentration of the mobile ions inside the PAAc cryogel increases (eq. (3)) so that the difference between the mobile ion concentration inside and outside the gel rises, which creates additional osmotic pressure that expands the gel. The opposite behavior occurs at low pH, which induces the deswelling of the gel sample. We have to mention that the extent of volume change in pH oscillating reaction (three-fold) is much smaller than that observed in swelling–deswelling experiments given in Figure 3. This is due to the high salt con-

centration in oscillating reaction system, which partially screens the charge interactions within the cryogel.

The results thus show that PAAc cryogels produce periodic swelling–deswelling oscillations in the bromate oscillation system. As the response rate of cryogels does not depend on their size,[13,14] much larger cryogel samples can also be used in self-oscillating systems. This suggests that, like the back-and-forth motion of a piston of a heat engine, pH-responsive cryogel may be used as a working substance to convert random molecular energy into macroscopic mechanical energy of lower entropy.

CONCLUSIONS

PAAc cryogels were prepared from frozen aqueous solutions of acrylic acid monomer and N,N'-methylenebis(acrylamide) crosslinker at −18°C. Fast responsive pH-responsive macroporous PAAc cryogels were obtained at or below 4 w/v % initial monomer concentration. SEM images of PAAc cryogel networks exhibited a heterogeneous morphology consisting of pores of sizes 10^1 μm, typical for macroporous networks formed by the cryogelation technique. PAAc cryogels coupled with the bromate oscillator oscillate between swollen and collapsed states during which a cyclic three-fold change in the gel volume was observed. The results thus show that, due to the fast response rate of cryogels, macroscopic gel samples can be used as a pH oscillator which would provide generation of significant amount of mechanical energy.

References

1. Tanaka, T. Sci Am 1981, 244, 110.
2. Shibayama, M.; Tanaka, T. Adv Polym Sci 1993, 109, 1.
3. Gerlach, G.; Arndt, K.-F. Hydrogel Sensors and Actuators, Springer Series on Chemical Sensors and Biosensors; Springer: Berlin, 2009; Vol. 6.
4. Yoshida, R.; Takahashi, T.; Yamaguchi, T.; Ichijo, H. Adv Mater 1997, 9, 175.
5. Luo, Y.; Epstein, I. R. J Am Chem Soc 1991, 113, 1518.
6. Rabai, G.; Orban, M.; Epstein, I. R. Acc Chem Res 1990, 23, 258.
7. Yoshida, R.; Ichijo, H.; Hakuta, T.; Yamaguchi, T. Macromol Rapid Commun 1995, 16, 305.
8. Crook, C. J.; Smith, A.; Jones, R. A. L.; Ryan, A. J. Phys Chem Chem Phys 2002, 4, 1367.
9. Edblom, E. C.; Luo, Y.; Orban, M.; Kustin, K.; Epstein, I. R. J Phys Chem 1989, 93, 2722.
10. Okay, O. Prog Polym Sci 2000, 25, 711.
11. Lozinsky, V. I.; Morozova, S. A.; Vainerman, E. S.; Titova, E. F.; Shtil'man, M. I.; Belavtseva, E. M.; Rogozhin, S. V. Acta Polym 1989, 40, 8.
12. Gusev, D. G.; Lozinsky, V. I.; Bakhmutov, V. I. Eur Polym J 1993, 29, 49.
13. Lozinsky, V. I. Russ Chem Rev 2002, 71, 489.
14. Plieva, F.; Huiting, X.; Galaev, I. Yu; Bergenstahl, B.; Mattiasson, B. J Mater Sci 2006, 16, 4065.

15. Dinu, M. V.; Ozmen, M. M.; Dragan, E. S.; Okay, O. Polymer 2007, 48, 195.
16. Ozmen, M. M.; Okay, O. Polymer 2005, 46, 8119.
17. Okay, O. In Smart Polymers: Application in Biotechnology and Biomedicine; Mattiason, B., Galaev, I., Eds.; CRC Press, Taylor and Francis Group: Boca Raton, FL, 2007; pp 269–299.
18. Kabra, B. G.; Gehrke, S. H. Polym Commun 1991, 32, 322.
19. Zhang, X.-Z.; Yang, Y.-Y.; Chung, T.-S.; Ma, K.-X. Langmuir 2001, 17, 6094.
20. Dogu, Y.; Okay, O. J Appl Polym Sci 2006, 99, 37.
21. Zhang, X.-Z.; Zhuo, R.-X. Macromol Chem Phys 1999, 200, 2602.
22. Zhuo, R.-X.; Li, W. J Polym Sci Part A: Polym Chem 2003, 41, 152.
23. Butler, A. R.; Bruice, T. C. J Am Chem Soc 1964, 86, 313.
24. Bruice, T. C.; Butler, A. R. J Am Chem Soc 1964, 86, 4104.
25. Pincock, R. E.; Kiovsky, T. E. J Am Chem Soc 1965, 87, 2072.
26. Pincock, R. E. Acc Chem Res 1969, 2, 97.
27. Wolfe, J.; Bryant, G.; Koster, K. L. Cryo Letters 2002, 23, 157.
28. Ende, M. T. A.; Peppas, N. A. J Appl Polym Sci 1996, 59, 673.