Equilibrium swelling, conductivity and electroactive characteristics of polyacrylamide hydrogels

Rahna K Shamsudeen, Shiny Nair & V G Jayakumari*

Naval Physical and Oceanographic Laboratory, Ministry of Defence, Thrikkakkara, Cochin 682 021, India

Polyelectrolyte hydrogels are currently being studied extensively towards the realization of soft actuators. The conductivity, swelling behaviour and electroactive characteristics of partially hydrolysed polyacrylamide hydrogels, crosslinked to various extents are investigated. Conductivity studies have been made by means of dielectric relaxation spectroscopy both for hydrogels and dry gel powders over a wide range of frequency. The water dependent a.c. conductivity has been found to attain a plateau at higher frequencies whereas the a.c. conductivity of gel powders continued to increase as the frequency increases. The magnitude of the conductivity values is dependent on the extent of swelling for the hydrogels whereas it is dependent on the network structure for the gel powders. The electrical responses of hydrolysed polyacrylamide gels are also investigated and its correlation with hydration properties is also made. The on-off stimulation has been monitored by measuring the angular displacement of the hydrogels. A systematic analysis of the obtained results indicates that the electrical response and the water dependent conductivities of the gels have a direct correlation with the hydration properties.

IPC Code: C08F 120/00

Smart polymer hydrogels have been increasingly studied for the past two decades as actuators and artificial muscles for several applications like fluid pumps, valves, drug delivery devices, robotics and biomimetic transducing devices[1-5] owing to the reversible shape and volume changes in response to external stimuli such as pH, temperature, ionic concentration and electric field[6-11]. The response of the hydrogels is diffusion limited and controlled by the mobility of the ions in the surrounding solution and the counterions associated with the polymer chains. From the application point of view, the best stimulus is an electric field since it can be controlled easily. There have been a number of reports of electrically induced phenomena in charged polyelectrolyte hydrogels[12-14] and various mechanisms have also been discussed frequently[15-17], but is still controversial.

Polyacrylamide gels have been the subject of interest to several investigators[18,19]. It is easily tailorable with chemical modifications and apart from the fundamental interest, the studies on these materials are important from the practical point of view because of the biocompatibility and ease of introducing tailor-made properties by suitable

structural modifications[18,19]. Studies relating the electroactive responses and a.c. conductivities are few in the literature. In the present work, polyacrylamide gels crosslinked to various extents have been synthesized and the electroactive response is investigated. The objective of this study was the detailed investigation of the swelling behaviour, conductivity and electroactive properties of partially hydrolysed and non-hydrolysed polyacrylamide hydrogels with respect to the extent of crosslinking, aiming at an increased understanding of the structure property relationship in this class of materials, a necessary condition for optimizing the design of new materials for specific technological applications.

Experimental Procedure
Synthesis of partially hydrolysed polyacrylamide gels

Crosslinked polyacrylamide gels were synthesized by radical polymerisation. In a typical procedure, acrylamide (7.1 g) (Merck) was dissolved in distilled water (100 mL) and the required mol percentage (1, 3, 7 and 20%) of the crosslinking agent, *N,N′* methylenebisacrylamide (BIS), was dissolved along with the initiator, ammonium persulphate (Merck) (0.1 g). The reaction mixture was heated at 80°C for 2 h followed by keeping at room temperature for a further period of 6 h. Unreacted monomers and low

___
*For correspondence (E-mail: tsonpol@vsnl.com)

molecular weight polymers were washed off with deionised water. The gels were collected by filtration and were dried to constant weight. A portion of each of the dried polyacrylamide gel was suspended in 20% aqueous NaOH for 2 days at room temperature, whereby some of the amide groups were converted to COO⁻ Na⁺ by hydrolysis[20]. These were then washed free of NaOH with deionised water. The gels are represented as NHX and HX, where X denotes the percentage of crosslinking agent added and NH and H denote non-hydrolysed and hydrolysed gels respectively. The extent of hydrolysis of each gel is determined by backtitration of NaOH used for hydrolysis[21].

FTIR spectra of representative samples were taken by KBr pellet method with dry powdered polymers using Bruker Equinox model FTIR Spectrophotometer in the range 400-4000 cm^{-1}.

Swelling studies and conductivity measurements

The swelling degree of all the gel systems was measured by the conventional method[2]. Pre-weighed dry samples were immersed in solutions of different pH and solutions of different concentrations of NaCl until they were swollen to equilibrium at room temperature. It was observed that equilibrium swelling was achieved for the hydrolysed samples within 24 h and that for non-hydrolysed gels, within 48 h. After excessive water was removed from the surface of the gels by filter paper, the swollen samples were weighed. Swelling degree was taken as the ratio of the equilibrium swollen weight to the dry weight.

Conductivities of the polymeric samples were determined with a high precision LCR meter (Agilent model – 4284A) in 20 Hz-100 kHz range. Completely dried gels (both non-hydrolysed and hydrolysed) were powdered and made into discs of dimension 10 mm × 2 mm. The conductivity was measured using the principle of capacitance. The same method is employed for hydrogel samples also. The samples were cut from equilibrium swollen hydrogels into discs of 10 mm diameter.

Electroactive response: Bending angle measurements under an electric stimulus

0.01 M Solution of NaOH is taken in a simple home-made device which is equipped with two parallel carbon electrodes of dimension (21 × 7 × 4 mm) which are 20 mm apart. Gel slabs of equal dimension (25 × 2 × 2 mm) were cut and clamped at the top of the device exactly at the middle of the pair

of electrodes. A definite voltage was applied across the solution between the electrodes by means of a d.c. power supply (APLAB L1285). The bending angle of the strip was calculated by the degree of the movement at the free end by monitoring the bending angle from an angular plot placed behind the actuator. The bending-recovery measurements were also performed by alternatively switching on and off the field at least for five times.

Results and Discussion

Infrared spectroscopy

The IR spectrum of representative samples of hydrolysed and non-hydrolysed polyacrylamide gels (H7 and NH7) is shown in Fig. 1. The IR spectrum of non-hydrolysed polyacrylamide gel shows a sharp peak at 1670 cm^{-1} which is due to the C=O of the amide group. But the IR spectrum of hydrolysed sample shows two more peaks other than the one near 1670 cm^{-1}. These peaks are at 1560 and at 1405 cm^{-1} which are due to the presence of carboxylate anion (COO⁻) group. The two identical C⎯⎯⎯O entities of the carboxylate ion give antisymmetric and symmetric stretching absorptions and the corresponding peaks appear at 1560 and 1405 cm^{-1} respectively. This result confirms the conversion of some of the amide groups to carboxylate anions, COO⁻Na⁺ while hydrolysed with NaOH. Quantitative determination by backtitration of the hydrolysing solution indicated that the carboxyl contents of H1, H3, H7 and H20 are 10, 4.75, 2.5 and 1.25 mmol/g of the sample respectively.

Swelling studies
At different pH

Fig. 2 presents the results of swelling studies of the non-hydrolysed and hydrolysed polyacrylamide gels in solutions of different pH. The swelling ratios of the hydrolysed gels are exceptionally higher at all pH
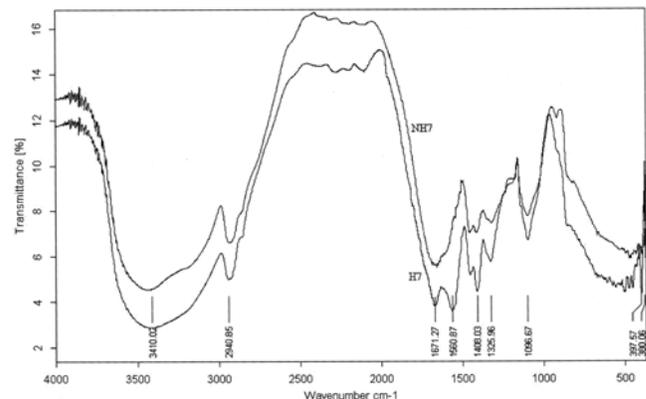

Fig. 1—IR spectra of NH7 and H7

values, when compared to the non-hydrolysed systems. For the non-hydrolysed systems, there is a gradual increase of swelling ratio in the acidic pH range whereas a more rapid increase of swelling ratio is observed in the alkaline region. Hydrolysis of the amide groups to carboxyl group can take place in the acid region as well as in the alkaline region. However, carboxyl groups (COOH) will be much less dissociated and the osmotic pressure will be low in the acid region. In the alkaline region the dissociation of the carboxyl group will be high. This results in an increase in the positive ion pressure inside the gel, just like a gas pressure, which in turn increases the osmotic pressure. This eventually results in an enhanced swelling of the gel system in the alkaline region. A higher degree of hydrolysis at higher concentrations of NaOH might be reflected in the increase in swelling ratio with increase in pH in the alkaline region for the non-hydrolysed ones.

Unlike the non-hydrolysed systems, for the partially hydrolysed gels, the degree of swelling increases, reaches a maximum and then decreases as the pH is increased from 2 to 14. The effect of pH in volume transition is much more prominent in the hydrolysed systems than in the non-hydrolysed gels. There is a drastic decrease (from 310 to 1.22 for H1) in the swelling degree when the immersing solution is changed from distilled water to 10^{-2} M HCl. This is a result of conformational change of the crosslinked polymer chains from an expanded state to a compact one due to the pH change. Here, the role of positive ion pressure and polymer-polymer affinity may be extremely important. The decrease of pH in the gel leads to a change of polyion, -COO⁻Na⁺ to –COOH and
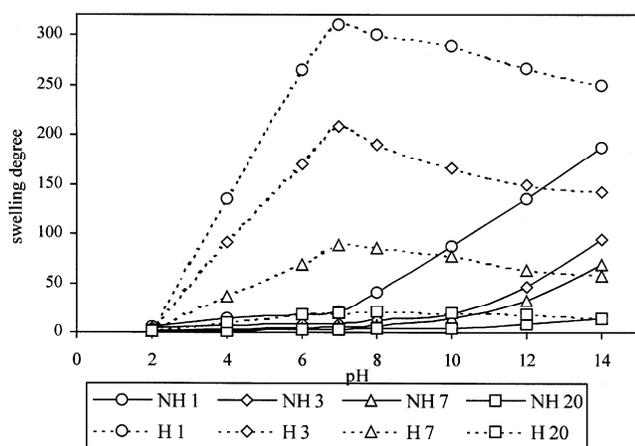
thus the strong polyelectrolyte nature of the gel is transformed into a weak polyelectrolyte nature[22]. This reduces the positive ion pressure very much. In neutral medium, the counterion in the carboxyl group is Na⁺ and here, due to complete dissociation, the ion pressure contribution towards the osmotic pressure is very high. Apart from the lower ion pressure, the affinity among the polymer chains in acidic solution may be greater than that in neutral solution due to the decrease of electro repulsive interactions between the polyions and the possibility of hydrogen bonding between the –COOH groups of different polymer chains. However, at higher concentrations of NaOH (higher pH), the swelling degree decreases. In general, the swelling ratio of the polyelectrolyte gels depends on the association state of ionic groups within the polymer and on the affinity of hydrogels for water[23]. An additional effect also can be proposed here based on the Donnan equilibrium theory[24]. According to the Donnan osmotic pressure equilibrium, an increase of movable counterions in solution leads to a decrease of osmotic pressure within the gel and causes a shrinkage of the gel.

As reflected in the swelling ratio, the effect of pH was not prominent at higher degrees of crosslinking compared to lower ones; this may be due to lesser extent of hydrolysis for highly crosslinked systems.

At different concentrations of NaCl

Fig. 3 depicts the effect of salt concentration on the swelling behaviour of the gels. As the concentration increases, the swelling ratio decreases continuously for the hydrolysed gels, especially for H1 and H3. This may be due to a similar reason as explained for

Fig. 2—Effect of pH on the swelling degree of non-hydrolysed and hydrolysed polyacrylamides
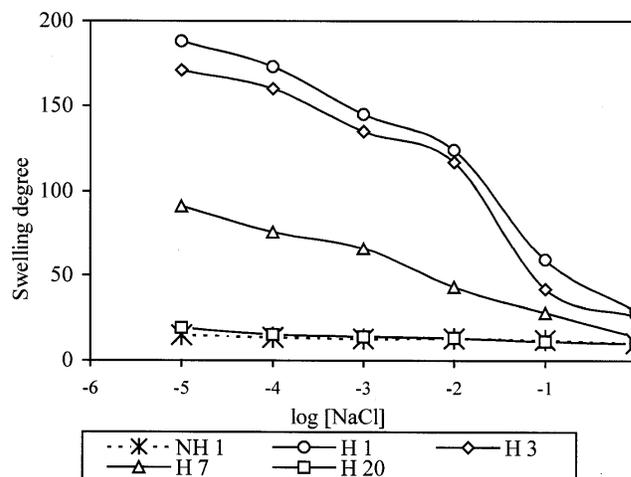

Fig. 3—Effect of salt concentration on the swelling behaviour of non-hydrolysed and hydrolysed polyacrylamides

the swelling behaviour of the polyelectrolyte gel at increased NaOH concentration. According to Flory[25], the equilibrium volume V of a gel is determined by the following condition.

$$\pi_{\text{network}} V + RT \sum_i C_{\text{ig}} - C_{\text{is}} = 0$$

where $\pi_{\text{network}} V$ is the osmotic pressure of a neutral gel in which ionic groups of the gel are not dissociated at all, R the gas constant and T is the absolute temperature. C_{is} and C_{ig} denote the ionic concentration of species i in the outer solution and in the gel respectively. If the gel has electric charges, the concentration of free ions inside the gel is not equal to that of the ions outside the gel and this imbalance in concentration creates an additional contribution to the osmotic pressure and swells/shrinks the gel. This effect is included in the second term and $\Delta\pi \equiv RT \sum_i C_{\text{ig}} - C_{\text{is}}$. As the concentration of ions in the surrounding solution increases, $\Delta\pi$ decreases and this causes the shrinkage of the gel. However, for all the non-hydrolysed gels (the swelling ratio of only NH1 is shown in the graph), which cannot be termed as polyelectrolyte gels, the swelling ratio remained almost constant.

Conductivity studies

Dielectric relaxation spectroscopy has proved very powerful in investigating the electrical conductivity and found to be valuable in giving additional information on the conduction mechanism that d.c. conductivity measurement alone does not provide[26]. In polymeric materials, the dipoles arise predominantly from asymmetry in the monomeric structure. The dielectric studies of all the gels were performed on the high precision LCR meter at different frequencies to measure ε' (real part, dielectric constant) and ε'' (imaginary part, dielectric loss factor) and the frequency dependent a.c. conductivity, $\sigma(\omega)$ is obtained from the equation, $\sigma(\omega) = \varepsilon_0\, \varepsilon''\, \omega$, where ε_0 is the free space permittivity (8.854×10^{-12} F/m) and $\omega = 2\pi f$, f is the measuring frequency. Fig. 4 shows the conductivities of non-hydrolysed gel powders and that of hydrolysed gels. For the non-hydrolysed gels, the conductivities are in the order NH20 > NH7> NH3 $\approx$ NH1. As the degree of crosslinking was increased, the number of polar groups (amide groups) increased per unit volume (or in other words, the asymmetry in the monomeric structure increases) and this resulted in the concomitant increase of conductivity. But this was not

so prominent in the case of lower degrees of crosslinking. However, for the hydrolysed gels, no regular pattern is observed. The maximum conductivity is for H1. Among the other three hydrolysed gels, the order is H20 > H7 > H3. The conductivity of hydrolysed gels is much higher than the respective non-hydrolysed gels. This is due to the presence of carboxylate anion groups in the hydrolysed gels. In hydrolysed gels, as the crosslinking increases, two different factors are affecting the conductivity namely, the effect of carboxyl groups and the increase of polar amide groups. For H1, the carboxylate ion groups may be playing the major role imparting high conductivity to the system. But for the other three, the effect of crosslinking (increase of polar amide groups per unit volume) may be overriding the effect of increase of carboxyl groups. This in turn may be a result of the progressive lowering of the extent of hydrolysis as the degree of crosslinking increases. Fig. 5 shows the a.c. conductivities of the hydrolysed and non-hydrolysed hydrogels which were previously swollen to equilibrium in deionised water. Quite different from dry gel powders, both series exhibited similar trends. It
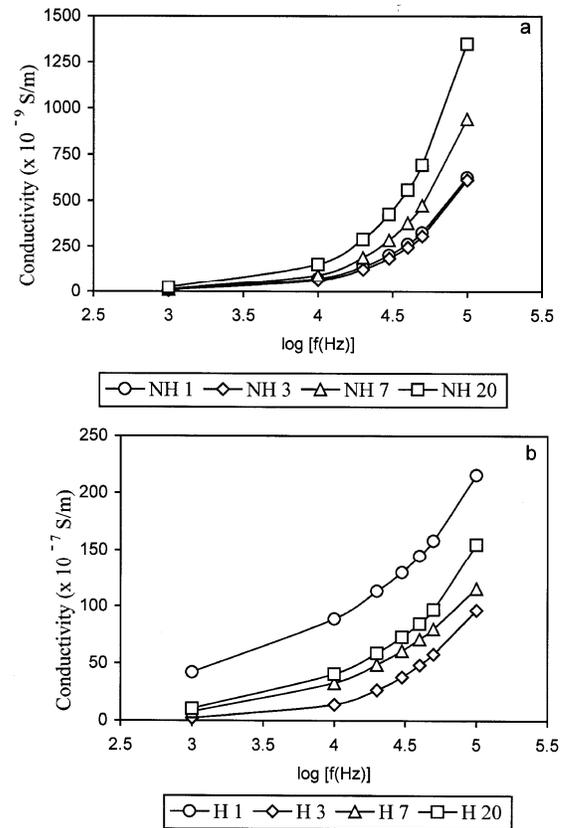

Fig. 4—Conductivity of various (a) non-hydrolysed and (b) hydrolysed dry gel powders as a function of frequency

is also worthnoticing that the conductivity becomes frequency independent at high frequencies, as clear from the plateau regions. Both the frequency dependent and frequency independent conductivities increase as the crosslinking decreases. The equilibrium water

Fig. 5—Conductivity of various (a) non-hydrolysed and (b) hydrolysed hydrogels as a function of frequency

contents in the lower crosslinked hydrogels are very high as clear from their high swelling degrees. At higher frequencies, the presence of water augments the dipolar losses and a large conductivity is observed. The very large conductivity values of the hydrogels of the order of 10^{-1}-10^{-2} S/m as indicated from the plateau regions of Fig. 5 point out the influence of water content in the hydrogels towards their conductivity. Increase of water results in an overall increase of ε' and ε'' (and hence σ) due to both dipolar and "free" charge contributions. Indeed, in the high frequency region the dipolar relaxation mechanism may be becoming faster and increasing in magnitude giving rise to frequency independent conductivity values and thus a plateau region. Also the large values of the ε'' and thereby σ reflect the enhancement of the mobility of free charges with increasing water content. Apart from these effects, the plasticising effect of increasing water content at constant temperature leads to increased segmental mobility of the polymeric chains. These large frequency independent conductivity values of the hydrogels also suggest that these materials could be useful as basic materials for protonic conductors and biosensors.
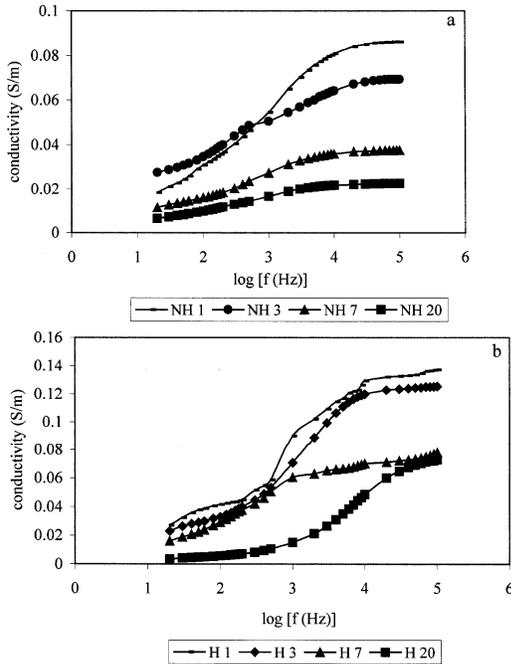
Electroactive characteristics

The non-hydrolysed polyacrylamide hydrogels were all non-responsive to the electric field under the
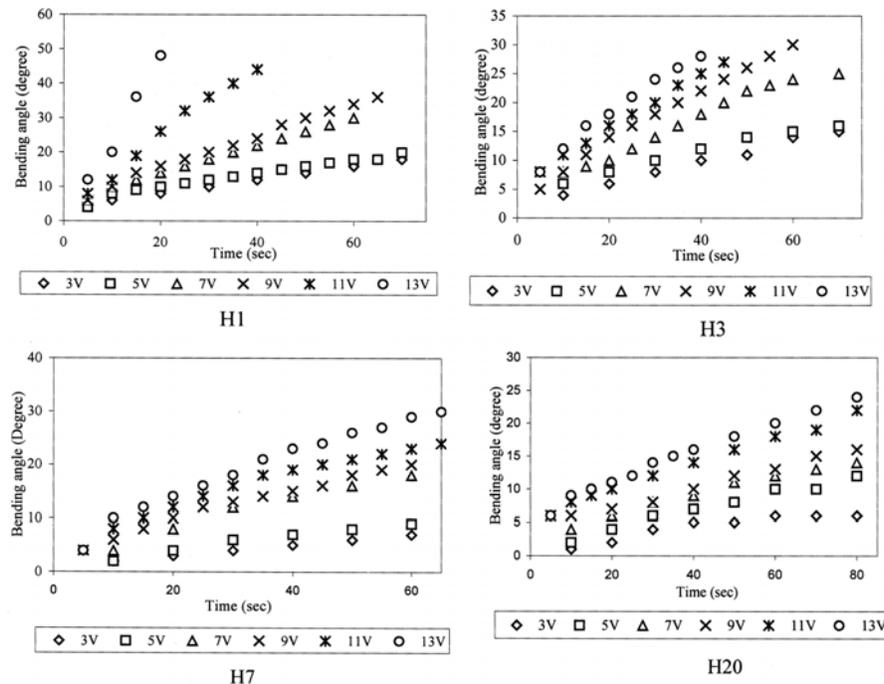

Fig. 6—Bending response of the various hydrogels at different applied potentials

experimental conditions suggesting the requirement of the presence of polyions for an electric response. All the hydrolysed polyacrylamide gels were subjected to electric field of varying potentials. All these gels showed quick bending toward the cathode in a 0.01 M NaOH solution. When the polarity of the field is reversed, the gel slabs bend to the opposite direction. Fig. 6 shows the extent of bending of the different hydrolysed gels at different applied potentials. As can be seen, as the applied potential increases, the bending angle also increases steadily. The response is much faster and higher for the lowest cross-linked hydrogel. The H1 gel bent to about 48° within 20 s at an applied potential of 13 V. The bending angle and the bending speed decreases as the crosslinking increases, which follows the same trend as that of the swelling and the hydrogel conductivity. As the swelling increases, the ionic mobility inside the gel increases, an effect similar to the effect of increasing the temperature. Indeed, the bending of polyelectrolyte hydrogels in an electric field is due to the voltage induced motion of the ions, both inside and outside the gels and the concomitant expansion of one side and contraction of the other side of the polymer gel, which in turn is due to the osmotic pressure difference. When the polyelectrolyte (in this case, it is having a polyanionic backbone) gel is subjected to electric field, the polyion remains immobile whereas the counterions inside the gel move out from the gel toward the negative electrode. At the same time the ions in the surrounding solution also move towards their counter electrodes by passing through the gel. Thus, the osmotic pressure at the positive side of the gel increases and becomes larger than that of the negative electrode side. As a result the gel swells at the positive side and bends like a bimetal towards the cathode.

Fig. 7 shows the reversible bending behaviour of all the hydrogels at an applied potential at 9 V. The d.c. electric field is alternatively switched on and off and the bending and recovery motions are monitored for at least five cycles. As soon as the stimulation is removed, the gel starts to return back to its original position by volume recovery due to the relaxation phenomenon of the gel. From the similar shape of the cycling graphs, it is understood that similar bending-recovery mechanisms may be operating for all the gels. This reversible bending behaviour in accordance with the application of electric field is important to the exploitation of these materials as muscle like contractile structures, sensors and actuators.

Conclusions

The polyacrylamide hydrogel systems synthesized by radical polymerization are studied for their swelling behaviour in different surroundings. The H1 system has swollen up to 310 times whereas the non-hydrolysed one has swollen up to only 21 times in distilled water. The conductivities of the hydrolysed systems are much greater than the non-hydrolysed systems. Among the non-hydrolysed systems, the number of polar groups affects the conductivity, whereas in hydrolysed ones, both carboxylate anion and the polar groups affect the conductivity. The a.c. conductivity of the hydrogel samples attains a plateau at higher frequencies. From the obtained results, it can be concluded that the magnitude of the conductivity values is dependent on the extent of hydration for the hydrogels whereas it is dependent on the network structure for the dry gel powders. The electroactive response of the gels showed that the magnitude and response times are higher and faster for the gels which are crosslinked to a minimum level, where the conductivity and swelling are maximum. Analysis of the obtained results can provide a better understanding of the structure-property relationships in this class of materials for their possible applications in novel modulation systems such as artificial muscles, switches, sensors and electric field modulated drug delivery devices.
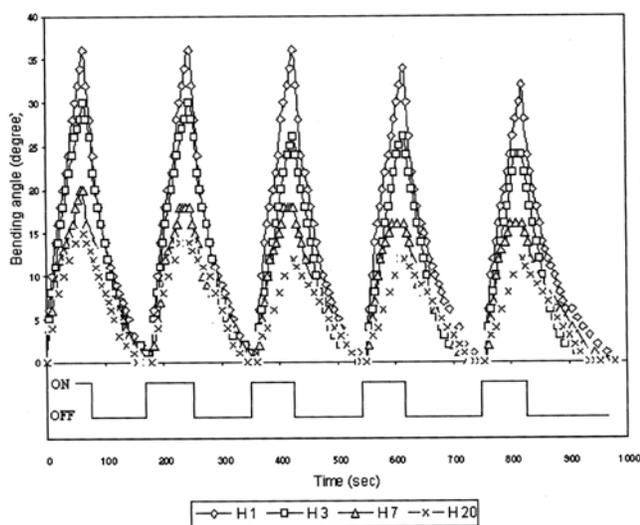

Fig. 7—Reversible bending behaviour of the hydrolysed polyacrylamide gels at 9V

References

1 Beebe D J, Moore J S, Baur J M, Yu Q, Liu R H, Devadoss C & Byung-Ho Jo, *Nature*, 404 (2000) 588
2 van der Linden H J, Herber S, Olthuis W & Bergveld P, *Analyst,* 128 (2003) 325
3 Edington D T & Beebe D J, *Adv Drug Deliv Rev,* 56 (2004) 199
4 Katoaka K, Miyozaki H, Bunya M, Kano T O & Sakurai Y, *J Am Chem Soc*, 120 (1998) 12694
5 Sutani K, Kaetsu I & Uchidu K, *Rad Phys Chem*, 61 (2001) 49
6 Kim S J, Lee C K, Lee Y M, Kim I Y & Kim S I, *React Funct Polym,* 55 (2003) 291
7 Kim S J, Lee K J, Kim S I, Lee Y M, Chung T D & Lee S H, *J Appl Polym Sci*, 89 (2003) 2301
8 Sauer M & Meier W, *Chem Commun,* (2001) 55
9 Jones C D & Lyon L A, *Macromolecules*, 33 (2000) 8301
10 Yoo M K, Sung Y K & Lee Y M, *Polymer*, 41 (2000) 5713
11 Zhang J & Peppas N A, *Macromolecules*, 33 (2000) 102
12 Kim S J, Shin S R, Kim S I, Lee J H & Lee S H, *J Appl Polym Sci*, 90 (2003) 91
13 Sun S & Mak A F T, *J Polym Sci Part B Polym Phys,* 39 (2001) 236
14 Homma M, Seida Y & Nakano Y, *J Appl Polym Sci*, 75 (2000) 111
15 Grimshaw P E, Nussabaum J H, Grodzinsky A J & Yarmush M L, *J Chem Phys* 93 (1990) 4462
16 Kwon I C, Bae Y H & Kim S W, *J Polym Sci Part B Polym Phys,* 32 (1994) 1085
17 Shiga T & Kurachi T, *J Appl Polym Sci*, 39 (1990) 2305
18 Hoffamn A S, *Adv Drug Deliv Rev*, 43 (2002) 3
19 Osada Y & Gong J P, *Adv Mater*, 10 (1998) 827
20 Tanaka T, *Sci Am*, 244 (1981) 110
21 Krause A, Lange A & Ezrin M, *Plastics analysis guide, chemical and instrumental methods,* (Hanser Publishers, NY), 1983
22 Shiga T, Hirose Y, Okada A & Kurauchi T, *J Appl Polym Sci*, 46 (1992) 635
23 Kudo S, Konno M & Saito S, *Polymer*, 34 (1993) 2370
24 Ricka J & Tanaka T, *Macromolecules*, 17 (1984) 2916
25 Flory P .J, *Principles of polymer chemistry,* (Cornell University Press, NY), 1953
26 Pissis P & A Kiritsis, *Solid State Ionics*, 97 (1997) 105