

Available online at www.sciencedirect.com



Sensors and Actuators B 99 (2004) 451-458



www.elsevier.com/locate/snb

# Influence of volume phase transition phenomena on the behavior of hydrogel-based valves

Andreas Richter<sup>a,b,\*</sup>, Steffen Howitz<sup>c</sup>, Dirk Kuckling<sup>d</sup>, Karl-Friedrich Arndt<sup>b</sup>

<sup>a</sup> Institute for Electromechanical and Electronic Design, Dresden University of Technology, D-01062 Dresden, Germany

<sup>b</sup> Institute for Physical Chemistry and Electrochemistry, Dresden University of Technology, D-01062 Dresden, Germany

<sup>c</sup> GeSiM mbH Großerkmannsdorf, Bautzner Landstraße 45, D-01454 Großerkmannsdorf, Germany

<sup>d</sup> Institute for Macromolecular Chemistry and Textile Chemistry, Dresden University of Technology, D-01062 Dresden, Germany

Received 24 September 2003; received in revised form 3 December 2003; accepted 15 December 2003

# Abstract

Smart hydrogels show phase transition behavior. This property can be used to operate sensors and actuators in a reversible and reproducible mode. Ignoring phenomena occurring at volume phase transition can result in a malfunction or even failure of the system. In this paper, the influence of volume phase transition phenomena on the behavior of hydrogel-based valves are discussed. Furthermore, the operation mode of such valves in dependence of various design parameters and hydrogel properties are described. © 2004 Elsevier B.V. All rights reserved.

Keywords: Smart hydrogel; Valve; Microvalve; Operation mode; Phenomena of volume phase transition

# 1. Introduction

Since 1978, as T. Tanaka [1] described the first synthesis of a hydrogel with discontinuous volume phase transition behavior, hydrogels sensitive towards e.g. temperature, pH, light, concentration of material, and ion has been developed. Their sensitivity is based on the reversible and reproducible volume change by more than one order of magnitude triggered by even small alterations of the environmental parameters. Therefore, an enormous impact of these so-called stimuli-responsive or smart hydrogels on many technological applications has been expected [2]. However, only a few special applications, particularly drug delivery systems were presented so far. Recently, the development of hydrogel-based valves and microvalves was published for the first time offering a more versatile use in the technological area. An automatic valve for process engineering applications sensitive to temperature, pH, and contents of organic cosolvents was presented [3,4]. In [5], the practical suitability of hydrogel actuators for the development of microvalves is shown. This microvalve possesses an automatic function to control the flow in dependence of pH. Other hydrogel-based microvalves can regulate the flow as a function of glucose

fax: +49-351-46339055.

concentration [6], and temperature [7]. A microvalve, which can be electronically controlled by a thermal–electronic interface, is also known [8]. However, a detailed description of both the influence of design parameters on the operation mechanism of hydrogel-based valves and phenomena occurring at volume phase transition of hydrogel actuators have not been given yet. Their knowledge is absolutely essential for the development of well working systems. In this paper we describe the design and the operation mode of an automatic macrovalve and an electronically controllable microvalve based on poly(*N*-isopropylacrylamide) (PNIPAAm), which is a temperature-sensitive hydrogel with lower critical solution temperature (LCST) characteristic. Furthermore, this hydrogel exhibits sensitivity towards organic solvents e.g. alcohols, present as aqueous mixture.

## 2. Experimental

# 2.1. Synthesis

The actuator material poly(*N*-isopropylacrylamide) (PNI-PAAm) was prepared with N,N'-methylenebisacrylamide (BIS) as cross-linking agent. The initiator and accelerator for the polymerization reaction were potassium peroxidisulfate (KPS) and N,N,N',N'-tetramethyl-ethylenediamine (TEMED) (both from Aldrich Chemical Co.). NIPAAm

<sup>\*</sup> Corresponding author. Tel.: +49-351-46332025;

E-mail address: andreas.richter@chemie.tu-dresden.de (A. Richter).

and various amounts of BIS (1–10 mol%, BIS4 indicates 4 mol%) were dissolved in deionized water. The total monomer concentration was 0.53 mol/l. To initiate the polymerization reaction 0.3 mol% of KPS and TEMED were added to the oxygen-free (bubbled with nitrogen) solution. After polymerization (ca. 12 h at room temperature) the PNIPAAm gel was stored in deionized water for about 1 week to wash out non-reacted reagents. After drying the PNIPAAm gel, particles were obtained by milling and subsequent fractionating into different particle sizes using test sieves. The particles exhibit an irregular shape.

To determine the swelling behavior of dry networks, a network based on poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) (both from Aldrich) was used. The polymers were dissolved separately in distilled water under stirring at 80 °C (PVA 15 and PAA 7.5 wt.%). Then, the solutions were mixed to get a solution of PVA and PAA with a percent ratio of 80:20. The mixture was stirred for 1 h at 60 °C and diluted with distilled water to a total amount of dissolved polymer of 5 wt.%. The cross-linking reaction was thermally induced at 130 °C for 30 min. To remove non-cross-linked polymer an extraction step was performed.

## 2.2. Microvalve fabrication

The microvalves (see Fig. 1) are designed as three component devices consisting of a channel structure support (5), a Pyrex glass cover (not shown in Fig. 1), and a circuit card (7) for electronic control. The channel geometry (3) and the actuator chamber (4) are built by a two-side process (wet etching with 30 wt.% KOH at 80 °C; plasma etching, ASE-Bosch process). Used materials were Si wafers (4 in., orientation (100), N-type, specific resistance  $250 \Omega$  cm, thickness 500 µm, obtained from SICO Wafer GmbH Heiningen, Germany), or SiO<sub>2</sub> wafers (4 in., type Pyrex 7740, thickness 500 µm). Heating elements (6) (thickness 110 nm, resistance 50  $\Omega$ ) and temperature sensors (8) were prepared by a platinum thin film system with lift-off patterning. The heating element is located below the actuator chamber on the channel structure support, the temperature sensor is placed on the rear of the Pyrex glass cover. The microvalve can be electronically controlled using these elements. All layers were coupled by a combination of flip-chip and gluing technology. To combine the microvalve body with the actuator, hydrogel particles were manually incorporated into the actuator chamber. A detailed description of the microvalve fabrication is given in [8].

## 2.3. Macrovalve design

This valve was made from stainless steel (Fig. 2). The design consists of a double side closed wide tube forming the valve chamber (1). The valve chamber comprises two tubings and has three openings: the first nozzle is used as inlet (2), the wider tube as outlet (3), the smaller as bypass (5). All parts are connected via welding or screwing.



Fig. 1. Schematic design of a hydrogel-based microvalve: 1, inlet; 2, outlet; 3, flow channel; 4, actuator chamber filled with hydrogel particles; 5, structure layer; 6, heating meander (located at backside); 7, circuit card; 8, temperature sensor (located at topside); (a) closed state at room temperature; (b) open state (gel actuator is heated above  $T_{\rm C}$ ).



Fig. 2. Schematic design of an automatic hydrogel-based valve: 1, valve chamber; 2, inlet; 3, outlet; 4, actuator chamber filled with hydrogel particles; 5, bypass.

The wider tube contains the actuator chamber (4) filled with hydrogel particles. The actuator chamber is limited in size by two steel meshes.

# 3. Results and discussion

### 3.1. Operating principle

The direct placement of the hydrogel particle based actuator in the flow channel provides permanent contact with the process medium. The hydrogel actuator uses this medium as the swelling agent. PNIPAAm exhibits LCST behavior with a volume phase transition temperature ( $T_C$ ) of approximately 33 °C. Below  $T_C$ , e.g. at room temperature, the hydrogel is swollen, whereas above  $T_C$ , the hydrogel is de-swollen. Thus, at the usual operating temperature below  $T_C$  the valve works in the "normally closed" function. The swollen hydrogel completely blocks the flow channel (see Fig. 1a).

The electronic control of the valve, shown in Fig. 1, is achieved by the heating element. To open the valve the gel actuator is heated above  $T_{\rm C}$ . The hydrogel actuator de-swells and allows the fluid to flow through the channel (see Fig. 1b). In order to obtain full control of the valve between the completely open and closed state, a temperature sensor is integrated into the setup. A detailed description of its operation mode can be found in [8].

The macrovalve illustrated in Fig. 2 is designed in such a way that the hydrogel works as the actuator in an automatic mode. Hence, a big valve chamber and a bypass to the source of the process medium is established. In the open state, the process medium is passing the actuator chamber, in the closed state, the solvent can flow back to the inlet using the bypass. This intake shunt guarantees a continuous and actual stimulus at the hydrogel actuator.

To characterize the valve performance we measure the pressure drop in dependence on the properties of the process medium or on the temperature of the actuator chamber, respectively. The pressure drop is the difference between pressure on inlet and pressure on outlet of the valve.

#### 3.2. Phenomena of swelling process

Independent of a phase transition behavior during the swelling process the polymer network can show two phenomena, which cause a transient restriction of the actuator function.

#### 3.2.1. Conditioning effect

During the first operation the hydrogel actuator often shows a bad repeat accuracy and a drift of the actuator parameters. This phenomenon is caused by changes in the microscopic structure of polymer network. It is assumed that by swelling and de-swelling too short polymer chains break, and other chains have to find their optimal arrangement.

Performing a number of conditioning cycles, the polymer network can be "warmed up". As a result, the repeating precision is significantly increased. Usually, the conditioning process is accomplished after 10–30 swelling cycles.

# 3.2.2. Softening effect

This effect is important for applications, in which the hydrogel actuator operates between dry and swollen state. Polymer networks in the dry state comprising a glass transition temperature,  $T_g$ , which is higher than the operating temperature, can cause a time delayed set-in of the swelling process (see Fig. 3). Due to the high  $T_g$  the polymer network is in the glassy state and the movement of polymer chains

Fig. 3. Softening effect of a strip actuator ( $20 \text{ mm} \times 5 \text{ mm} \times 0.15 \text{ mm}$ ) based on PVA/PAAc-hydrogel. The swelling processes were started from moist ( $\triangle$ ) and dry state ( $\bigcirc$ ).

necessary for the swelling process is disabled. The swelling agent penetrates the network by self diffusion and causes an increase of the elasticity of the polymer chains (softening effect).  $T_g$  decreases and the polymer network can swell. The softening effect can be avoided using a hydrogel with low  $T_g$ .

# 3.3. Phenomena of volume phase transition

From the functional point of view, only the kinetics of volume phase transition is interesting for the time behavior (transient response or time characteristics) of hydrogel actuators. The kinetics of the volume change of hydrogels is based on diffusion phenomena.

To initiate a volume phase transition two transport mechanisms have to be considered.

- First, the initiating stimulus such as temperature or amounts of cosolvent must be transferred into the swollen polymer network to modify the properties of the swelling agent inside the gel. Such transport occurs either energet-ically by heat transfer (described by the thermal transfer coefficient,  $D_{\rm T}$ ) or by continuous mass diffusion of the solvent into the hydrogel (described by the mass transfer coefficient,  $D_{\rm S}$ ) (Fig. 4).
- Second, the volume phase transition is accompanied by the change of the swelling degree of the gel to achieve the de-swollen state. This coupled (cooperative) diffusion is a wide-ranging process, which comprises the solvent transportation and a cooperative motion of polymer network (*D*<sub>Coop</sub>).



Fig. 4. Sketch of diffusion processes at a hydrogel.



For example, the diffusion coefficient of methanol into a water swollen PNIPAAm gel was determined by  $D_{\rm H_{2O}, MeOH} = (1.8-3.9) \times 10^{-5} \, {\rm cm}^2/{\rm s}$  [3,9], and for water into a deuterated water swollen PNIPAAm hydrogel  $D_{\rm D_{2O}, H_{2O}} = 2.3 \times 10^{-5} \, {\rm cm}^2/{\rm s}$  [10]. The thermal transfer coefficient permeating a polymer is  $D_{\rm T} = 1.6 \times 10^{-3} \, {\rm cm}^2/{\rm s}$ [11] and is by two order of magnitudes larger than the mass controlled diffusion process.

Because the swelling/de-swelling process is accompanied with a movement of net chains,  $D_{\text{Coop}}$  is small ( $D_{\text{Coop}} \approx 10^{-7} \text{ cm}^2/\text{s}$  [11]). A typical time constant achieving a swelling equilibrium is

$$\tau \sim \frac{d^2}{D_{\text{Coop}}},\tag{1}$$

where d is the characteristic dimension of hydrogel [12].

#### 3.3.1. Shrinkage barrier effect

The shrinkage process of hydrogels during volume phase transition is sometimes inhomogeneous. In case of a fast transition from swollen into de-swollen state a rapid formation of a collapsed outer layer can be observed, whereas the rest inside the bulk is still in the swollen state. The collapsed layer includes a thin skin at the surface and a substantial thicker de-swollen layer (see Fig. 5a), which works as a solvent barrier. This layer impedes the remaining solvent in the bulk of the hydrogel to leave the polymer network or even completely prevents its transport [13]. This phenomenon is called shrinkage barrier effect. Its is known for PNIPAAm stimulated by temperature [14,15] and alcohol [9,13]. The critical ranges for temperature stimulation are determined between 40 and 50  $^{\circ}$ C, while the critical concentrations for alcohols in water are in the range between 10 and 40 wt.% (dependent on the alcohol chain length at 20  $^{\circ}$ C).

The shrinkage barrier effect cannot be observed when only a thin film is built on the surface during the transformation process. This phenomenon is called skin effect. The skin is mostly present at volume phase transition of hydrogels (see Fig. 5b).

The shrinkage barrier effect is a time–distance problem of the different diffusion processes occurring simultaneously. The triggering stimulus is penetrating the hydrogel by a constant diffusion. As response a diffusion process starts at the surface layer of the gel, whereas the bulk is not yet effected by the stimulus. The outer region de-swells very fast and achieve a critical thickness which inhibits a transfer of the swelling agent.

Porous hydrogels show a shrinkage barrier effect by solvent and temperature stimulation. In case of homogeneous gels, this effect can be sometimes observed by temperature stimulation. However, this phenomenon is dependent on the dimensions of the hydrogel. For structures less than 200  $\mu$ m no shrinkage barrier effect is observed. The thin skin is mostly independent of the dimension, but the thick collapsed layer covers the entire gel due to the small hydrogel volume.

The random occurrence of the shrinkage barrier effect affects the reproducibility of the hydrogel actuator characteristics. Fig. 6 shows the drift of the pressure drop, which is caused by shrinkage barrier effect. The effective valve cross-section is decreased, because the gel volume increases, which is affected by the shrinkage barrier effect. This phe-



Fig. 5. Shrinkage barrier effect and skin effect for PNIPAAm by methanol (CH<sub>3</sub>OD) stimulation visualized by NMR-imaging (Fourier-slice selection), (a) (left picture): shrinkage barrier effect in highly porous PNIPAAm BIS10; (b) (right picture): skin effect at homogeneous PNIPAAm BIS4.



Fig. 6. Shift of pressure drop due to the shrinkage barrier effect observed for a macrovalve under temperature stimulation between 24 and 40 °C; particle diameter  $450 \pm 50 \,\mu\text{m}$ .

nomenon appears from time to time and cause the fluctuation of the valve parameters.

A well-thought-out choice of hydrogels respecting size and homogeneity avoids the shrinkage barrier effect.

#### 3.3.2. Two-step mechanism of volume phase transition

The volume phase transition proceeds in two steps. First, a fast phase separation of the polymer chains and the swelling agent into polymer rich and polymer poor areas occurs [16]. This effect can be observed in experiments as a prompt change of the Young's modulus of the hydrogel. The increase of stiffness induces a significant decrease of the mobility of the polymer chains, e.g. by temperature stimulation of PNIPAAm [13]. As shown in Fig. 7, the polymer chains have a very high mobility (21 °C) in the swollen state. Approaching the phase transition temperature ( $T_{C,PNIPAAm} = 33$  °C) the mobility of the network chains decreases first slightly



Fig. 7. Stimulation of volume phase transition of PNIPAAm by temperature. Visualization of the mobility of polymer chains using NMR-2D-Fourier-imaging slice selection.



Fig. 8. Switching characteristic of hydrogel (PNIPAAm BIS4 actuator)based macrovalves at ethanol stimulation (switched between 0 and 40 wt.% ethanol in aqueous solution).

(30 °C) then more rapidly (32 °C). Above  $T_{\rm C}$  (34 °C), the polymer chains are almost immobile. In a second slower step after the phase separation the de-swelling process starts. The two-step mechanism of the volume phase transition can be followed visually. The hydrogel changes immediately its color from transparent towards white. Afterwards, the volume shrinkage takes place.

The two-step mechanism of volume phase transition influences the switching behavior of hydrogel-based valves. The principal switching behavior of an automatic valve stimulated by changes of the alcohol concentration in water is shown in Fig. 8.

*3.3.2.1. Valve opening process.* Generally, two successive phenomena are characteristic for the opening process. When reaching the phase transition point (region 1, Fig. 8) a small increase in the pressure drop without any significant change in the flow rate can be detected. In region 2 (Fig. 8) the valve is switching to the open state. This region is characterized by a simultaneous occurrence of a pressure drop minimum and a flow rate maximum. This effect can be a sign of pressure decrease or is caused by an inertia of polymer chains, which leads to a short overshooting above the swelling equilibrium. The occurrence of the inverse region 4 is likely to be due to the existence of this inertia effect (see later sections).

Microvalves show an additional feature at the phase transition point. A slight change of the flow rate can be observed (Fig. 9). This effect is more pronounced the larger the gradient of the stimulus is. The reason for this behavior is the sudden increase of Young's modulus, which induced the peak of pressure drop. The very small flow rate could be an indicator of a small volume shrinkage of the hydrogel or a squeeze out of liquid which is placed between the hydrogel particles inside the actuator chamber. Stiffer particles might also not be able to seal the cross-section of the channel.

*3.3.2.2. Valve closing process.* The valve closing process exhibits a typical behavior and can also be divided into two



Fig. 9. Opening behavior of a microvalve. Hydrogel is switching from swollen to the shrunken state,  $P_{\text{heat}} = 200 \text{ mW}$ ; size of actuator chamber  $800 \text{ }\mu\text{m} \times 600 \text{ }\mu\text{m} \times 200 \text{ }\mu\text{m}$ ; actuator material PNIPAAm BIS4.

regions. In the beginning of the valve closing process (region 3, Fig. 8), a slight pressure decrease accompanied by a flow rate peak can be observed. This is the inverse behavior of region 1. The sudden change of conformation of polymer chains from the immobile state into the mobile state causes a significant decrease of Young's modulus. This "softening" of the hydrogel induces a decrease of the effective flow resistance without significant change of the hydrogel volume. Region 4 shows a pressure peak, but, in comparison with the other regions this behavior is only slightly marked.

## 3.4. Operational behavior

## 3.4.1. Switching time

3.4.1.1. Material and design parameters. The properties of the actuator material influence the switching performance of hydrogel-based valves. Since the swelling process is diffusion controlled, the switching time is mainly determined by the particle size of the actuator material rather than by the total volume of actuator. Therefore, small hydrogel particles are used as actuator material in order to obtain a fast switching time. However, only in the case of macrovalves the particle size has a strong influence on the switching time [8]. It is negligible for microvalves if the ratio of the particle size to the chamber size is between 0.075 and 0.15.

It was assumed that the cross-linking density of hydrogels is also an important material parameter for the operation of the microvalves. It can be changed for PNIPAAm by variation of the amount of BIS during synthesis. However, a significant influence of this hydrogel property on the switching time was not observed. The most important parameter is the filling degree of the actuator chamber with dry hydrogel particles (see Fig. 11). A low filling degree allows short opening times, but the closing time is long. Up to a filling degree of 50% the opening time is nearly constant. A further increase of the filling degree induces a short shut-off time, while the opening time increases. Depending



Fig. 10. Opening time in dependence on the heating power for microvalves with different sizes of actuator chamber filled with PNIPAAm BIS4 particles.

on the priority of opening and shut-off time this parameter has to be optimized.

Another important design parameter is the size of the actuator chamber. The bigger the actuator chamber the longer the switching time of the valve (see Fig. 10). Fig. 10 also illustrates the effect of the heat capacity of the valve body, which is important for temperature stimulation. An increase of the heat capacity (e.g. microvalves with the actuator chamber size 500  $\mu$ m × 500  $\mu$ m × 200  $\mu$ m and 800  $\mu$ m × 800  $\mu$ m × 200  $\mu$ m, respectively) increases the heating power that is necessary to obtain short opening times.

*3.4.1.2. Operational parameter.* For electronically controllable microvalves, which are controlled via a thermal electronic interface, the temperature gradient across the valve chamber is an important operational parameter. The opening time depends strongly on the applied heating power (see Fig. 10). Above a certain power value, which depends on the heat capacity of valve body, a further increase of heating power results only in a slight decrease of the opening time.

#### 3.4.2. Pressure resistance and leakage flow

Due to the softness of hydrogels the actuator chamber can be filled completely with swollen hydrogel and the valve cannot show any leakage flow. In fact, two cases must be distinguished.

First, if the actuator chamber is slightly filled with the hydrogel, the leakage flow is a function of applied pressure drop. Usually, hydrogel valves with a low filling level always show a leakage flow. They act as a passive proportional valve in that pressure range.

Second, by increase of the filling level of the actuator chamber, the pressure resistance characteristic changes significantly. The hydrogel valve shows no leakage flow up to a critical pressure drop that usually destroys the valve because the hydrogel particles are so strongly deformed that they can flush out of the chamber. The maximum pressure drop, up to which no leakage flow can be measured, is a strong function of the filling degree of the actuator chamber (see Fig. 11).



Fig. 11. Maximal pressure drop without leakage flow and switching times in dependence on the filling degree. The actuator chamber ( $800 \,\mu\text{m} \times 800 \,\mu\text{m} \times 200 \,\mu\text{m}$ ) of a microvalve was filled with dry PNIPAAm BIS 4 particles; particle size  $82.5 \pm 7.5 \,\mu\text{m}$ .

As shown in Fig. 12 the hydrogel-based microvalve shows no leakage flow up to a pressure drop of 8.4 bar. On the other side the opening time depends on the filling degree as well. Thus, a compromise between short switching time and high pressure resistance of the microvalve has to be found.

## 3.4.3. Particle tolerance

Due to the softness of the hydrogel actuator, a pronounced particle tolerance is expected. To check the particle tolerance of a microvalve with a chamber size of  $800 \,\mu\text{m} \times 800 \,\mu\text{m} \times 200 \,\mu\text{m}$  splinters from polystyrene (irregular shaped particles with diameter less than  $60 \,\mu\text{m}$ ) were added to the process medium. The shut-off function is not influenced and a leakage flow is not observed. However, single splinters can remain in the actuator chamber. A flushing step has to be executed to remove such particles.

#### 3.4.4. Reproducibility and long-term stability

At constant environmental and process conditions the behavior of hydrogel-based valves is reproducible and shows a



Fig. 12. Leakage flow of a microvalve in dependence on the applied pressure drop. Actuator chamber ( $800 \ \mu m \times 800 \ \mu m \times 200 \ \mu m$ ) was filled with dry PNIPAAm BIS4; particle size ( $82.5 \pm 7.5 \ \mu m$ ), filling degree near 90%.

maximum error in reproducibility of less than 1%. Usually, such stable conditions are not given in reality. For neutral gels, which include most of the temperature-sensitive hydrogels such as PNIPAAm, a lot of cross-sensitivities are known. In particular, adding of salt and pH changes of the process medium can shift the volume phase transition temperature of hydrogel actuators. Also cross-sensitivities to the addition of a number of organic solvents are known. This might cause serious malfunction if the composition of the process medium is not properly chosen. It is necessary to choose an appropriate hydrogel for a specific fluid.

Polyelectrolyte hydrogels, e.g. for automatic control of pH value or ion concentrations, exhibit a more complicated volume phase transition behavior than nonionic gels. Usually, their swelling–pH characteristic shows a hysteresis behavior, which makes it difficult to obtain a reproducible sensoractuator function. We will discuss this in a separate paper.

Generally, hydrogel actuators show a good chemical and long-term stability. Only concentrated acids and bases affect the hydrogel stability.

# 4. Conclusion and outlook

The presented results show that hydrogel actuators need a special start-up procedure, which has to include a conditioning step. In the case of polymer networks with a high glass temperature, a moisturizer step to soften the actuator material is necessary as well. Considering this, the actuator behavior is highly reproducible.

The switching behavior can substantially be influenced by the shrinkage barrier effect, which accompanies the volume phase transition. It can be avoided by the correct choice of the actuator material as well as the use of hydrogels comprising small dimensions. The two-step mechanism of volume phase transition induce a typical characteristic of the switching behavior of hydrogel actuators, but does not influence the function of the valve.

The switching behavior of the hydrogel actuators is a diffusion controlled process. The use of hydrogel particles as actuator material can decrease the switching time of hydrogel-based microvalves to 300 ms for opening and 2 s for shut-off. The most important design parameter of hydrogel particle-based valves is the filling degree of the actuator chamber with dry hydrogel particles influencing both opening and shut-off behavior in an opposite way. Hence, switching frequencies higher than 10 Hz are hardly to realize. Thus, hydrogel-based valves and microvalves cannot be used in highly dynamic applications.

Hydrogels are soft materials and show a large volume change in dependence of various environmental parameters. Therefore, hydrogel-based valves have four main advantages compared to common valves. Highly miniaturized valves can be realized showing a distinctive pressure resistance without a leakage flow. The valves are very tolerant towards particles being a part of the process medium. Due to the manifold sensitivities of hydrogels a number of automatic sensor-actuator functions can be realized. However, such functions can only be successfully realized, if cross-sensitivities caused by the composition of the process media or environmental parameters are considered. We believe that hydrogel-based actuators can lead to manifold developments in microfluidics, biotechnology, chemical, and medical engineering.

## Acknowledgements

Financial support has been provided by the Deutsche Forschungsgemeinschaft (SFB 287 "Reactive Polymers"). The authors would like to thank T. Gehring (GeSiM GmbH) for his assistance in the experimental setup.

### References

- T. Tanaka, Collapse of gels and the critical endpoint, Phys. Rev. Lett. 40 (1978) 820–823.
- [2] A.E. English, E.R. Edelman, T. Tanaka, in: T. Tanaka (Ed.), Experimental Methods in Polymer Science: Modern Methods in Polymer Research & Technology, Academic Press, New York, 2000, pp. 547–589.
- [3] K.-F. Arndt, D. Kuckling, A. Richter, Application of sensitive hydrogels in flow control, Polym. Adv. Technol. 11 (2000) 8–12, 496–505.
- [4] D. Kuckling, A. Richter, K.-F. Arndt, Temperature and pH dependent swelling behavior of poly(*N*-isopropylacrylamide)-copolymer hydrogels and their use in flow control, Macromol. Mater. Eng. 288 (2003) 2, 144–151.
- [5] D.J. Beebe, J.S. Moore, J.M. Bauer, Q. Yu, R.H. Liu, C. Devadoss, B.-H. Jo, Functional hydrogel structures for autonomous flow control inside microfluidic channels, Nature 404 (2000) 588–590.
- [6] A. Baldi, Y. Gu, P.E. Loftness, R.A. Siegel, B. Ziaie, A hydrogelactuated smart microvalve with a porous diffusion barrier back-plate for active flow control, in: Proceedings of the 15th International IEEE Conference on Microelectromechanical Systems 2002, Las Vegas, NV, 2002, pp. 105–108.
- [7] S. Mutlu, C. Yu, F. Svec, C.H. Mastrangelo, J.M.J. Frechet, Y.B. Gianchandani, A thermally responsive polymer microvalve without mechanical parts photo-patterned in a parylene channel, Transducers 1 (2003) 802–805.
- [8] A. Richter, D. Kuckling, K.-F. Arndt, T. Gehring, S. Howitz, Electronically controllable microvalves based on smart hydrogels: magnitudes and potential applications, J. Microelectromech. Syst. 12 (2003) 5, 748–753.
- [9] M. Knörgen, K.-F. Arndt, S. Richter, D. Kuckling, H. Schneider, Investigation of swelling and diffusion in polymers by 1H-nmr imaging: lcp-networks and hydrogels, J. Mol. Struct. 554 (2000) 69– 79.

- [10] Z.J. Derlacki, A.J. Eastal, A.V.J. Edge, L.A. Woolf, Z. Roksandic, Diffusion coefficients of methanol and water and the mutual diffusion coefficient in methanol–water solutions at 278 and 298 K, J. Phys. Chem. 89 (1985) 5318–5322.
- [11] S.H. Gehrke, Synthesis, equilibrium swelling, kinetics permeability and applications of environmentally responsive gels, Adv. Polym. Sci. 110 (1993) 81–144.
- [12] T. Tanaka, D.J. Fillmore, Kinetics of swelling of gels, J. Chem. Phys. 70 (1979) 1214–1218.
- [13] U. Heuert, H. Schneider, M. Knörgen, K.-F. Arndt, D. Kuckling, S. Richter, Investigation of swelling and diffusion in polymers by NMR-imaging, Macromol. Symp. 145 (1999) 83–94.
- [14] N. Tanaka, S. Matsukawa, H. Kurosu, I. Ando, A study on dynamics of water in crosslinked poly(*N*-isopropylacrylamide) gel by NMR-spectroscopy, Polymer 39 (1998) 4703–4706.
- [15] M. Shibayama, K. Nagai, Shrinking kinetics of poly(*N*-isopropylacrylamide) gels T-jumped across their volume phase transition temperatures. Macromolecules, 32 (1999) 22, 7461–7468.
- [16] M. Shibayama, M. Moritomo, S. Nomura, Phase separation induced mechanical transition of poly(*N*-isopropylacrylamide)/water isochore gels, Macromolecules 27 (1994) 5060–5066.

# **Biographies**

*Andreas Richter* received the Dipl.-Ing. degree in precision/electrical engineering from Dresden University of Technology in 1996, and the PhD degree in electrical engineering from the same university in 2002. His work is focused on the development of hydrogel-based applications in chemical and biosensorics, medical engineering, micro fluidic devices, and haptic/tactile communication.

Steffen Howitz received his diploma in electrical engineering at Dresden University of Technology in 1986 and his PhD in the field of sensor technology from the same university in 1990. Since 1995, he has been the managing director of GeSiM. The main focus of his work are development and production of micro fluidic components, pipetting systems as well as microstructures with integrated microactuators for special applications in the field of molecular biology.

*Dirk Kuckling* obtained MS and PhD degrees in chemistry from Christian-Albrechts-Universität at Kiel in 1991 and 1994. After that he started a post-doctoral research work in the field of polymer networks at Dresden University of Technology, Institute of Macromolecular Chemistry and Textile Chemistry. Since 1995, he has been a research associate at that facility. His activities concern synthesis and characterization of soluble polymers and polymer networks with sensor and actuator properties.

*Karl-Fr. Arndt* studied physics at Dresden University of Technology. In 1975, he got the PhD and in 1982 the Dr.rer.nat.habil. degree at TH Merseburg. Since 1990, he works as a full professor of Physical Chemistry of Polymers at TU Dresden. His fields of interest are the characterization and synthesis of cross-linked polymers, the characterization of soluble polymers by light scattering and chromatography, as well as the application of cross-linked polymers as sensor and actuator.