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Synthesis and application of electro-thermally sensitive gels

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Abstract. Stimuli-sensitive change their volume (equilibrium degree of swelling), mechanical properties (elasticity, stiffness) and molecular transport properties in response to a small change in the properties of the swelling agent, like temperature, solvent composition, pH value, ion concentration, etc. Widespread used smart gels take advantages of the volume phase transition induced by a change of temperature. The temperature of volume phase transition depends on the interaction between gel and solvent. For a gel with defined chemical structure it can be changed by the composition of the swelling agent, e.g. content of salt or organic components. For application, e.g. in MEMS, an easy and controlled stimulation of volume phase transition is required. The degree of swelling (Q) and therefore the dimension of gel structures are determined by temperature. It is possible to regulate Q to a predetermined value by heating/cooling. Thermal energy inside a gel-based device can be easily generated and regulated by incorporated heating resistors and temperature sensors. Different structures (micro-spheres, pads, patterned layers) of smart hydrogels are applied. The switching between two different states of swelling is induced by changes of temperature or by changing the environment. Using the example of gel-based microvalves, sensors, sensor arrays, pumps, and chemostats (concentration control of chemical substances) the sensor-actuator properties and advantages of this group of polymers are discussed.

Introduction

Gels are most generally understood to be polymeric networks which absorb enough solvent to cause macroscopic changes in their dimension. The material properties of stimuli-sensitive (smart) hydrogels change in response to environmental stimuli (changes of properties) of a liquid environment, e.g. temperature, pH, composition. Remarkable is the drastic change in the swollen volume which may occur discontinuously at a specific value of stimulus or gradually over a (mostly) small range of stimulus values. All of these changes are reversible. Using the properties of a large volume change, the application of gels in devices such as actuators, artificial muscles, controlled delivery systems, sensors etc. have been suggested. The practical commercial uses of gel based devices have yet to emerge.

An advantageous feature of stimuli-sensitive gels is that they combine the property of sensing with that of actuating. Smart polymeric gels thus provide an intriguing way to new sensor-actuator systems [1, 2]. The possible miniaturization of gel-based devices is a further important aspect for applications.

Widespread used smart gels take advantage of the volume phase transition induced by a change of temperature. For hydrogels based on a polymer having a lower solution temperature the heating of the swollen gel results in its deswelling, cooling in its swelling. Prominent examples for this behavior are poly(N-isopropylacrylamide) (PNIPAAm), NIPAAm-copolymers, and poly(vinyl methyl ether) (PVME). The temperature of volume phase transition depends on the interaction between gel and solvent (in pure water: PNIPAAm: 34 °C, PVME 37 °C). It can be tailored by copolymerization of monomers with different sensitivities. For a gel formed by a polymer with a specific chemical composition it can be varied by changing the composition of the swelling agent. Due to this, at a constant temperature, the degree of swelling can be influenced by the composition of the liquid phase, e.g. content of salt, organic solvents, and ionic strength. In other words, under isothermal condition, the volume phase transition is triggered by a change of the composition, e.g. content of salt, organic components etc. in the swelling agent. The concentration of the added component which is needed for a volume phase transition correlates with the working temperature.

For application, e.g. in MEMS, an easy and controlled stimulation of the volume phase transition is required. Desirable could be a direct stimulation by an electric current. This requires polymer gels containing groups which can be dissociated (charged polymers, polyelectrolytes) or swelling agents containing species which are able to undergo ionic interactions with the gel (e.g. surfactants). An electric field induces a bending motion or shrinking of polyelectrolyte gels [3].

Another useful possibility is the application of thermosensitive polymer gels and their direct or indirect heating by means of electric current or electric/magnetic field. Gels filled with ferromagnetic or ferroelectric particles generate heat in an alternating magnetic or electric field due to the hysteresis. But the effect is only remarkable at a higher content of filler, which reduces the differences in volume between swollen and shrunken state, at a high field strength (risk of electrical blow, dissociation of aqueous phase), and high frequencies [4]. The absorption of light, e.g. amplified by absorbing particles (dyes), can be used for a partial heating of a gel layer which results in a change of the layer thickness due to a release of liquid.

Materials and Methods

In the past, we have worked on photochemical patterning of thin layers of sensitive polymers on a support (Si-wafer, glass). A disadvantage of photo cross-linking techniques is the necessity of modification of the polymer with photo reactive groups, which influences the hydrophilic-hydrophobic balance of the system and therefore the volume transition temperature. Another technique is based on simultaneous polymerization and cross-linking initiated by a photo initiator. A patterning is possible, if the mixture of monomer, cross-linker, and photo initiator is irradiated through a mask. The resolution of photo patterning is within the µm-range which seems to be sufficient for the majority of the applications. Nevertheless, we look for possibilities to generate patterned layers with a higher resolution.

A route to cross-link polymers dissolved in water is the high-energy irradiation (γ-ray, electron beam) of the polymer. An advantage of radiochemical cross-linking is that it does not need any modification of the polymer. Radiation of a solution at low concentration gives the possibility to synthesize stimuli-sensitive micro- or nanogel particles. These particles could be filled with ferroelectric or ferromagnetic materials. A further aim of our work is the patterning in different length scales of polymer films on different supports by radiochemical methods. The experiments were done with temperature sensitive polymers, PVME and hydroxypropylcellulose (HPC). As example of a polymer which is often applied in medicine and pharmaceutics, poly(vinyl pyrrolidone) (PVP) was cross-linked by electron irradiation.

In the dry state the polymers PVME [5], PVP [6], and HPC [7] could be cross-linked with a good yield. Spin coating gives us the possibility to generate a film of defined thickness d (10^2 nm to 10^1µm). Different techniques were used for patterning of spin-coated films:

- Irradiation through a mask leads to structures with a lateral dimension in µm-range [8].
- For lateral structures in sub-µm range we used the electron beam lithography. By irradiation with a focused electron beam the lateral pattern size could be varied in the range of several µm to 100 nm.
- Combining different radiation techniques makes it possible to form layers with a gradient of cross-linking density.
- The cross-linking and patterning of a layer with inorganic filler is possible.

Different techniques were used for synthesis of the actuator material:

- PNIPAAm was prepared with *N,N´*-methylenebisacrylamide as cross-linker. Potassium peroxidisulfate and TEMED were used as initiator and accelerator for the polymerization reaction . After polymerization and cross-linking the gel was immersed in deionised water to wash out non-reacted reagents. After drying PNIPAAm gel particles of irregular shape were obtained by milling and subsequent fractionating into different particles sizes using test sieves. The particles were applied in the particle-based microvalve.
- The photo patterning was applied to a light induced polymerization and cross-linking of NIPAAm. Actuator dots were prepared from PNIPAAm containing 4.5 mol-% of a UV-sensitive chromophore based on dimethyl maleimide. By a subsequent irradiation of a dry film through a photo-mask we were able to synthesize actuator dots with a smallest lateral resolution of 2 µm spacing and 4 µm structure widths at layer thickness within the µm-range in different channel geometries (microvalve).
- A synthesis of sensitive microgels with a defined dimension is possible by means of inverse-suspension polymerization. The monomer (NIPAAm), cross-linker (N,N-methylene-bis-acrylamide), and initiator (ammonium peroxidisulfate) were dissolved in water. The aqueous solution dipersed in n-heptane containing Span80 and Tween80 is forming microscopic droplets. The polymerization inside the microscopic aqueous droplets was initiated by adding a catalyst (TEMED). This technique allows the synthesis of particles with a regular shape, and variation of the microgel diameter (from 100 nm to 100 µm). The cross-linked particles were applied in the chemostat [9].

Hydrogel actuators – control and realization in applications

The parameters to which a smart hydrogel is sensitive, such as pH, salt- or organic concentrations and temperature can be called *phase transition conditions* (PTC). The *smart hydrogel actuator* (SHA) aspires to a state of equilibrium resulting in a volume change. For application a significant and reproducible volume change in the narrow region of the control variable is important which is correlating to a high sensitivity, e.g. to temperature. A quick response as a volume change assures the required dynamics. Therefore it is the second basic precondition for the advantageous application. On the example of a NIPAAm based valve a complete switch on-switch off can be realized within only 6 K temperature difference in a time period of only 500 ms. Due to the PTC the swelling degree of the SHA can be precisely adjusted and therefore its spatial volume can be changed in a defined way. The further appropriate device characteristics are then tailored by the geometrical engineering design parameters, such as the actuator chamber size and geometrical form.

Gels with a fast response. Different techniques are described in literature to synthesize gels with a fast response. Usually, they are based on a reduction of the characteristic dimension of the gel, e.g. particles or layer in µm- or 10^2 nm-ranges. For different applications, micro-reactors, micro-fluidic devices, sensors, cell adhesion/detachment devices, displays, etc., a patterning of the gel layer is useful.

Though the hydrogel actuator is swelling and shrinking the complete volume consisting of SHA and swelling agent is constant. The volume phase transition of a smart hydrogel is a two-step process. The first step is a fast phase transition. For a short time a phase separation can be observed which is coupled with an increase of stiffness, opacity and an apparent temporary increase of volume or pressure. Following, in the second step starts the time-consuming process of swelling. Comparing the time characteristic of both processes it becomes obvious, that only the process of swelling determines the swelling kinetics of a gel.

The process of switching a SHA passes two stages [18]. At first, the stimulus of the volume phase transition must permeate the hydrogel. If the condition of the volume phase transition is fulfilled, the above discussed two-step process starts. The reaction time of such an actuator defining the dynamics of operation is depending on the sum of both response times. At first the changes in the PTC spread within the volume of the SHA. This can be e.g. a pH-value difference or temperature variation. Following the SHA is swelling or deswelling, changing its volume by diffusion processes. Swelling agent is transported and the polymer chains are moved (cooperative diffusion). The time for response is determined by the square dimension of the SHA and the reciprocal value of the cooperative diffusion coefficient (10^{-7} cm²/s).

The discussed phenomena of the volume phase transition and of the relation between degree of swelling and properties of the environment are used in sensor applications, see ref. [10].

Actuators with small dimensions within the µm scale can have a response time of few ms whereas a size in the mm range results in a reaction time of several seconds, minutes or hours. A defined swelling time period of several hours is used in a further application field for low dynamic automated pumping as it can be seen in [11].

Direct actuator stimulation. By alterations of the PTC of the swelling agent supply the SHA is directly stimulated. Alterations of the composition of the swelling agent or the temperature or both of them can control the operation of the device. Interaction with the SHA without interference with the swelling agent can be realized by a global heating and cooling e.g. by a tempered agent surrounding or rinsing the actuator chamber. A slower tempering process is typical.

Electrothermic interface. For electronic control the interface transforms electrical power into heat by a resistive element. Voltage or current driven the temperature can be adjusted as precisely as necessary for the application.

The probably simplest realization, which is suitable for switching of valves, is an open loop heater increasing the temperature above the *Phase Transition Temperature* (PTT). For a faster response a heating power profile can be used. A short peak to overpower the thermal capacity is appropriate followed by a lower plateau which is compensating heat conduction and cooling phenomena as it can be seen in Fig. 2. With this strategy the upper switching temperature is reached faster and the exceeding is kept in a small range for a faster response. After switching off the power supply the actuator chamber is cooling down following an exponential time-function. If the surrounding temperature is below the PTT, a switching time in the range of few seconds can be reached with a passive cooling e.g. (1-2) s. An additional active cooling can reduce the response time of the device to the upper ms range e.g. 500 ms. A more precise thermal control can be implemented in a closed loop. Therefore several temperature sensors can be incorporated or the heating resistance itself can be used as a sensor by simultaneously monitoring of current and voltage. A precise temperature control achieving a defined swelling degree can be realized, which is necessary e.g. for chemostat valves.

Resistive structures and sensors can be produced by common well established techniques e.g. a platinum-thin-film system (110nm thickness, resistance 50 Ω, plated by GeSiM mbH with MSBA-400SP, from Malz and Schmidt) with lift-off patterning on Pyrex glass cover or on Si-wafers [17]. As it can be seen on Fig. 1 and Fig. 3 the heating meander is directly placed under the actuator of the micro valve.

Compared to the following processes the transport of heat within the SHA is usually quick and negligible. The operating dynamics of the system are therefore determined by the time necessary for tempering and SHA response. In the case of a big difference the slow process is dominating. Since the reaction time of a SHA is restricted by its geometrical dimensions and by the chemical composition most likely, this is the limiting component. The tempering process can be designed to be within the same dimension of time by the applied heating power and by the heat transfer coefficient between SHA and the tempering agent (or environment) which makes a faster cooling possible. While a low thermal reaction time can be obtained for a power-saving concept a fast tempering process is linked to a high energy demand.

Microvalves

A basic element which can be realized using the presented techniques is a valve. The swelling of the hydrogel actuator can either close a channel directly or perform mechanical work by bending a distortable diaphragm to indirectly open or close the channel.

Common microvalves use the second principle, i.e. couple a diaphragm with conventional actuators which can be e.g. piezoelectric [12], electromagnetic [13], electrostatic [14], thermo-pneumatic [15] or shape memory alloy [16]. Each of these systems has restrictions limiting the miniaturization of valves due to the big operating volume, complicated set-up or difficulties to scale the forces to the micro scale. Therefore by these techniques leakage free and particle permissive valves with dimensions smaller than 1 mm^3 can hardly be obtained.

Our microvalves [17, 18] deal with these requirements by direct placement of hydrogel in the channel. Thus the diaphragm is not necessary at all, which avoids the associated problems. As hydrogel is very soft and has excellent sealing properties, the microvalves can handle very high pressures and are tolerant to particles.

The presented microvalves consist of three layers: a channel structure support, a Pyrex glass cover and a heating structure also providing the electrical interface. The channel structures are fabricated by wet etching of Si or SiO_2 wafers. The channels have a width of 100 µm to 800 µm and a height of 50 µm to 200 µm, the actuator chambers a width of 100 µm to 800 µm and a height of 50 µm to 300 µm. The heating structure is fabricated by a platinum thin film technology like described above. The three components were coupled by flip chip and gluing technology. All valves have been fabricated by GeSiM mbH Großerkmannsdorf, Germany.

Microgel actuator. For the microvalve with an actuator chamber (Fig. 1) microgels were filled manually into the chamber. The chamber has to keep the microgels inside while allowing the process medium to flow in the open state. Thus the inlet and outlet have to be smaller than the gel particles in the shrunken state.

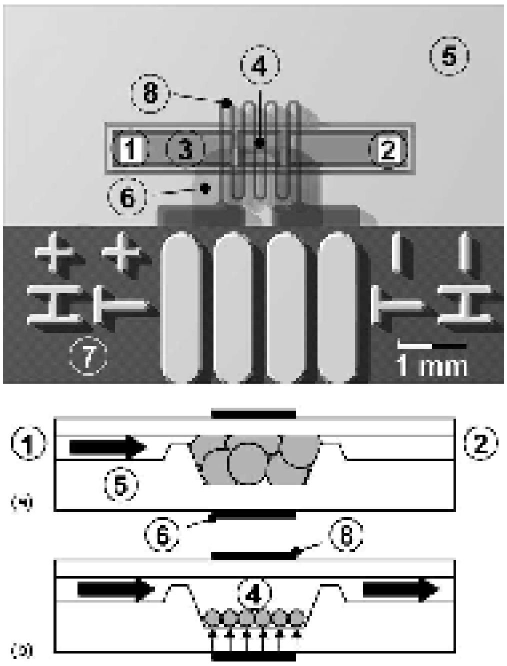

Figure 1: Schematic design of a microgel-based microvalve.

1 inlet; 2 outlet; 3 flow channel; 4 actuator chamber filled with hydrogel particles; 5 structure layer; 6 heating meander (located at back-side); 7 circuit card; 8 temperature sensor (located at topside);

(a) closed state at room temperature; (b) open state (gel actuator is heated above PTT).
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For the placement of hydrogel two different techniques were used, microgels placed in an actuator chamber and photo-patterned hydrogel within the channel. In both cases the hydrogel actuator remains in contact with the process medium, which also acts as swelling agent for the hydrogel. This means no swelling agent (e.g. H_2O) has to be provided separately and the set-up remains simple.

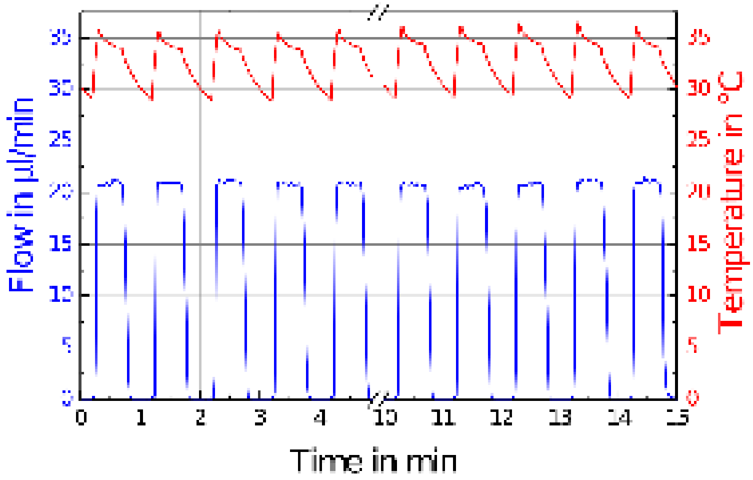

Figure 2: Performance of a micro-valve with PNIPAAm - BIS 4 micro-gel particles.

Upper curve: temperature versus time, lower curve: flow rate versus time. The operating pressure was about 1.5 bar.

Photopatterned gel actuator. The second technique uses photopatterned hydrogel structures (Fig. 3). These are directly polymerized inside the channel. Sufficient adhesion is achieved by the use of an adhesion promoter to keep the actuator in place. The actuator chamber can be therefore omitted. This technique is more suitable for continuous manufacturing as a manual filling of hydrogel can be avoided.

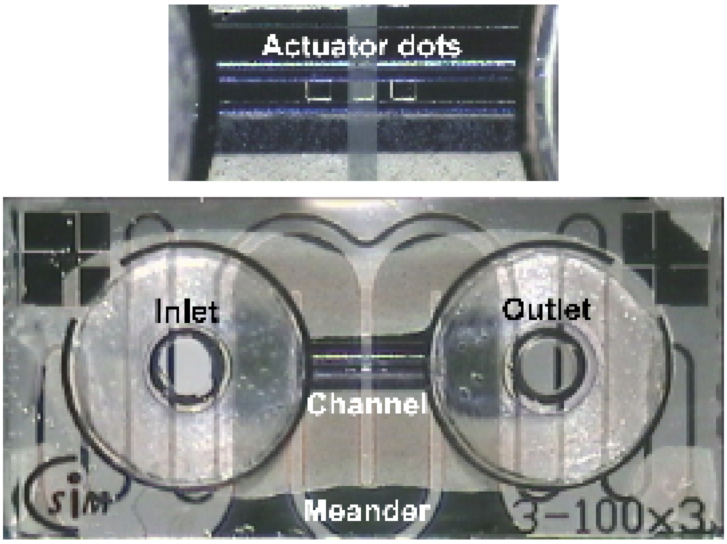

Figure 3: Microvalve with photopatterned hydrogel actuator dots.

The upper picture shows three gel dots within the channel. The meander structures in the background act as temperature sensor (thin) and heating element (thick).

The valves have a "normally closed" characteristic. As long as the temperature is below the PTT and the process medium is present the hydrogel stays in a swollen state and thus closes the channel. For opening the valve the temperature is increased above PTT. The hydrogel shrinks while releasing the absorbed medium. Since the overall volume does not change, no extra flow is generated by the valve. The increase of temperature is performed by a heating structure (Fig. 1, item 6) which is driven by a defined electrical current flow.

To close the valve again, the temperature has to drop below the PTT. This is simply achieved by shutting off or reducing the current. The time period needed to close the valve can be further reduced by an active cooling.

The characteristics of the valves are shown in Fig. 2 and 4, respectively. Important properties are e.g. the pressure resistance and the closing as well as the opening time. In particular they depend on the size of the microgels and the filling rate. An optimum has to be obtained.

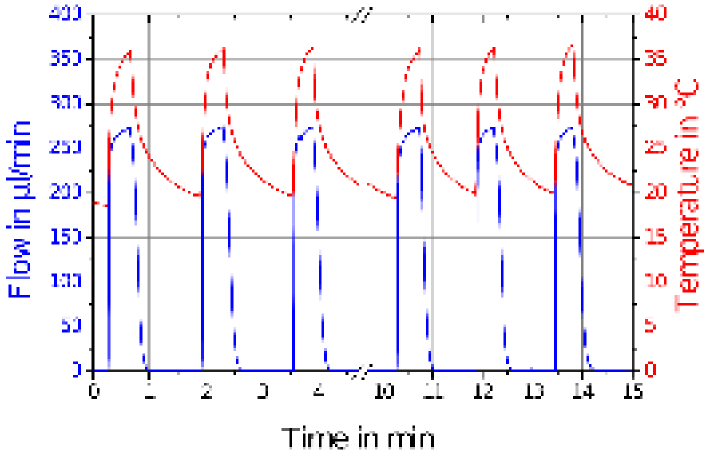

Figure 4: Performance of valve with photopatterned hydrogel actuator.

Upper curve: temperature versus time, lower curve: flow rate versus time.

The microgel valve showed no leakage flow in the closed state up to the maximum possible pressure of 1.8 bar. Water diffusion through the gel actuator could not be observed either.

Besides the actuator properties the speed of the valves also depends on the time for a temperature change, thus on heating power. We obtained for the valve with photopatterned actuator opening time of about 4 s and closing time of about 10 s. The valve based on microgels in an actuator chamber worked significantly faster and opened within 300 ms and closed within 2 s without active cooling. By external fan cooling the closing time could be reduced to 1 s. We think further reduction is possible.

Microchemostat valves

Usually only one of the PTC is used for regulating or switching of a SHA. In case of double-sensitivities all further PTC are kept on a constant level and define an operating point. This is used in devices adjusting constant chemical parameters, so called chemostats.

As mentioned in the introduction, the PTT depends on the composition of the liquid phase. The concentration of the dissolved or added component determines the PTT of a sensitive hydrogel. Under isothermal condition the volume phase transition of the hydrogel can be stimulated by a defined concentration of a second component in water. Variation of this temperature shifts the concentration which is needed for obtaining the desired degree of swelling of the SHA. Due to the double sensitivity to temperature and e.g. salt- or alcohol concentration the concentration can be regulated electronically by the temperature control.

The basic set-up is identical to that of valves. The main difference to valves is the use of an appropriate hydrogel with the desired double-sensitivities. We realized a chemostat with PNIPAAm microgels as well [9]. The PTT of about 34 °C in pure water changes in the presence of certain substances like alcohol and salts. By setting the temperature corresponding to the PTT of the desired concentration, the phase transition occurs when this concentration is reached. Thereby the output concentration is automatically controlled by the SHA.

Fig. 5 shows the flow rate and thus the state of the chemostat in dependence on temperature and methanol concentrations. The degree of swelling depends on the salt concentration.

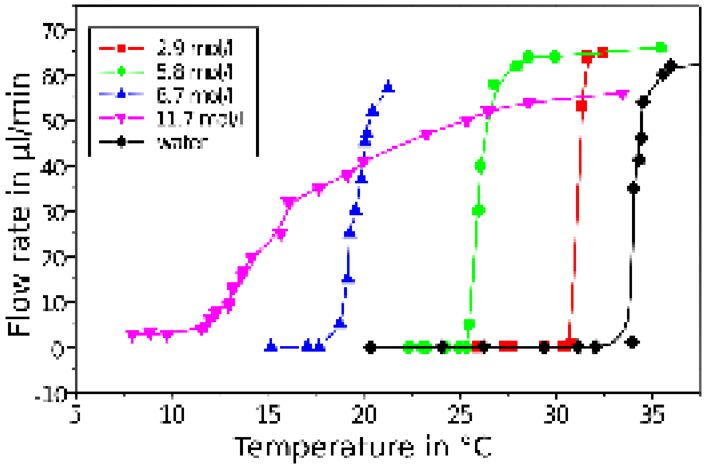

Figure 5: Behavior of chemostat.

The figure shows the flow rate of a mixture of water/methanol with different methanol concentrations dependent on temperature.

Summary and Conclusions

The macroscopic properties (elasticity, volume in swollen state) of smart stimuli-sensitive hydrogels show a strong dependence on the properties of an aqueous environment. We have demonstrated that this behavior can be used in sensors and actuators. Macromolecular chemistry offers different routes to synthesize these gels. The stimuli, which can be used to trigger a volume phase transition, depend on the chemical nature of the cross-linked polymer. A great variety of gels can be obtained by copolymerization. Hydrogels can be produced on a dimension scale between several nm to cm. Patterning of gel layers on a support is possible.

Hydrogel actuators need a liquid phase for swelling and shrinking. Therefore, devices which handle fluids seem to be the best way for these polymeric materials to find any application. A transition between two different states (degree of swelling) needs stimulation. A direct stimulation is possible, if the change of properties of the liquid phase is used. In hydrogel based sensors the change of gel properties stimulated by the fluid phase is measured. A promising approach in design of fluid handling systems is the indirect stimulation of the volume phase transition. The easiest way to do so is the stimulation by temperature. This was demonstrated on the example of a microvalve and, at first time, on example of a chemostat. The chemostat takes advantage of the fact that the conditions of the volume phase transition, e.g. temperature, depend on the composition of the liquid phase. The hydrogels show a double-sensitivity which allows an adjustment of the operation condition. The chemical challenge is to synthesize gels with tailor-made properties; the challenge for MEMS is to design elements and devices adapted for the specific properties of the hydrogels.

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