

High Response Smart Gels: Synthesis and Application

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Summary: Stimuli-responsive hydrogels change their volume and elasticity in dependence on the properties of the liquid phase. The amount of solvent uptake is dependent upon the chemical nature of the gel and the nature of its environment, e.g. solvent composition, temperature, pH, etc. The swelling/deswelling process is time consuming. For many applications the response time must be short. According to Tanaka's equation the rate of equilibration is inversely proportional to the square of gel size and proportional to the mutual (or cooperative) diffusion of the network and the solvent. D_{coop} is determined by the properties of the cross-linked polymer and can not be changed for a given chemical system. By decreasing the characteristic dimension of the gel, it is possible to reduce the time for equilibration. The synthesis, characterization of thin layers and small particles of T-sensitive polymers and their application in a micro-valve is described.

Introduction

Aqueous solutions of temperature-sensitive polymers like poly(*N*-isopropylacrylamide), and poly(vinyl methyl ether), show a lower critical solution temperature (LCST) at about 34 °C (PNIPAAm), or at 37 °C (PVME), respectively. Both polymers form hydrogels, which were thermo-sensitive similar to the polymer solution. They swell at temperatures below the LCST and shrink above this temperature.

Stimuli-responsive hydrogels that undergo abrupt changes in volume in response to external stimuli such as temperature, pH, concentration of organic solvent in an aqueous phase, have potential application in the creation of "smart" material systems.

Necessarily for the most conceivable applications, the response time must be short. To understand the factors, which determine the response time is a pre-condition for developing strategies for synthesizing gels with fast response. The volume phase transition is describable as a two step process. In a first step the stimuli, which induce the swelling/deswelling must penetrate the gel. We investigate the diffusion process of methanol in a gel by n.m.r.-imaging technique. From the measured time lag at a defined distance to sample surface the diffusion coefficient could be calculated. For methanol in the swollen gel (D_2O at 294 K) we get values from $1.8 \cdot 10^{-5} \text{ cm}^2/\text{s}$ up to $3.9 \cdot 10^{-5} \text{ cm}^2/\text{s}$ in dependence of methanol concentration (for D_2O in

water about $2.3 \cdot 10^{-5} \text{ cm}^2/\text{s}$). The influence of heating and cooling on the properties of the gel was detected by measurements of the mobility of the network chains (gel swollen in D_2O). From these experimental results, it was clarified, that the molecular motion of the network chains change at the volume phase transition. The rate of the first step seems to be simply dependent on the rate of heat transfer (thermal diffusivity $10^{-3} \text{ cm}^2/\text{s}$), or on the diffusion of a low molecular weight liquid phase, respectively, which occur much faster than mass transfer. The equilibrium is reached well before any significant change in the swelling degree.^[1] If conditions for the volume phase transition are met, the mechanical properties of the gel change. The reason for this is the formation of a macro-network consisting of bundles of molecules (polymer rich phase) and large pores (polymer poor phase). After formation of the bundles of molecules (isochore process) the process of deswelling starts. The mechanical properties of gels undergoing a volume phase transition were studied by S. Hirotsu^[2] (isobar gel) and M. Shibayama et al. (isochore gel).^[3]

The kinetic of volume change (second step) is determined by diffusion processes, at least by the cooperative diffusion coefficient of the polymer chains (about $10^{-7} \text{ cm}^2/\text{s}$). Since the diffusion time scales with the square of dimension, decreasing the characteristic dimension of the network will increase the swelling/deswelling rates dramatically.

The rate of response to the environmental changes may directly influence the system performance. With other words, the swelling/deswelling processes determine the characteristic time for a designed sensor-actuator system.

Different synthetic routes are described to improve the swelling rate or shrinking rate of sensitive hydrogels, i.e.

- formation of additional junction points in dependence of temperature

The formation of hydrophobic cluster in a comb grafted polymer gel results in additional junction points and an increase of cross-linking density.^[4]

- porous gels by synthesis at temperatures higher than $LCST$

A gel body with porous microstructure is expected to give rise to faster volume change, since the effective diffusion distance can be controlled by the average distance between neighboring pores. Porous gels swell or shrink much faster (in order of magnitude) than any other responsive gels of comparable dimension. M. Suzuki and O. Hirasa synthesized PVME gels (cross-linking by γ -irradiation)^[5] with a fine porous gel structure to obtain quick response

gels. Typical dimensions of the pores are several μm . PNIPAAm was cross-linked in the phase separated state at $T > \text{LCST}$.^[6]

- small particles (micro-spheres or nanogels)

Several papers dealing with the synthesis and potential applications of thermo-sensitive *N*-isopropylacrylamide-based micro-gels were published recently (see e.g. ref. ^[7]). Spherical hydrogel particles of NIPAAm can be formed by inverse suspension polymerization.^[8] Another method for the preparation of hydrogel beads in the submicron region ($0.2 - 1 \mu\text{m}$) is the inverse emulsion polymerization.^[9]

The goals of our work are

- Synthesis of gels with fast response in a wide range of dimensions.
For different application we need large sheets, in mm-range, of gels with fast response. We deal with gels in μm -range, for example with thin layers of different pattern of sensitive gels. Recently we start with the synthesis of thermo-sensitive gel-particles in 100 nm-range.
- Application of these gels in chemo-mechanical valves.

Experimental

Synthesis

- Thin layers

Thin layers of sensitive polymers were prepared by photo-crosslinking of linear temperature- and pH-sensitive pre-polymers on a Silicon-wafer as supporting material.^[10] By UV-irradiation through a mask it is possible to design different structures on the wafer, and patterned networks in μm -scales can be obtained. The resulting networks show temperature dependent swelling properties. In our experience gel dots of $250 \times 250 \mu\text{m}^2$ and smaller (thickness 7 - 15 μm) can be formed. If the cross-linking density is high enough, these dots are mechanical stable and can undergo a lot of swelling and shrinking processes without any destruction.

- Porous structure by irradiation cross-linking near or above the phase transition temperature

Irradiation with high-energy radiation (e-beam, γ -radiation) of a concentrated solution of the thermo-sensitive polymer poly(vinyl methyl ether) (PVME) is an interesting method to

synthesize porous materials in the mm-range.^[11] For irradiation, solutions of different concentrations were prepared by dilution of the high concentrated PVME solution with bi-distilled water. Oxygen can interfere with a free-radical polymerization. Therefore it was necessary to remove all of it by degassing the homogenized polymer solution before starting the irradiation. After degassing, the prepared solutions were poured into petri dishes (e-beam) or poly(ethylene) flasks (γ -rays) and irradiated. Purging the solution with argon and sealing with PARAFILM[®] helps to reduce the rate of oxygen uptake in the non-crosslinked polymer solution.

During e-beam irradiation the temperature of the solution increases due to the absorption of energy. The temperature of volume-phase-separation is crossed and the phase separated structure is fixed by cross-linking.

- Spherical particles by irradiation of a diluted polymer solution

The non-crosslinked PVME tends to form aggregates in water even at low temperatures and low concentrations. Heating of the diluted polymer solution induces the phase separation. The polymer particles formed by the phase transition can be cross-linked by e-beam irradiation.^[12] It is important to mention, that surfactants or any other reagents are not necessary for the synthesis.

Dynamic light scattering measurements were performed with a DLS 700 (Otsuka, Japan) at $\theta = 90^\circ$ and a concentration $c_B = 1.0$ g/l. An apparent (no extrapolation to $\theta \rightarrow 0$ and $c_B \rightarrow 0$) value of the hydrodynamic radius $R_{h,app}$ was calculated by using the Stokes-equation.

Design of valves

- Particle based actuator

Particles of “smart polymers” can be used as an actuator for autonomous flow control. Smart gels connect an actuator, which can generate mechanical work with a function of sensing.

In the tested particle-based valve the “gel-actuator” is placed directly in the liquid flow. Spherically particles with a typical dimension of (0.40 ± 0.05) mm were put into a cylinder, which consists of an O-ring (stainless steel, diameter: 5 mm; thickness: 2 mm), and on both ends of a steel net (mesh-size 60 μ m). The liquid flows through the space between the polymer particles. A decrease in a diameter leads to an increase in the flow rate at constant pressure, or requires a greater applied pressure to achieve the same flow rate. For a faster change of the properties of the liquid in the valve-body, a circulation circuit (bypass at the inlet) is used (Figure 1). In our first experiments we use these gels for a temperature sensitive

chemo-mechanical valve. The temperature alters from 24.5 °C to 35°C and vice versa with a non-linear temperature gradient (Figure 2). The fastest times were determined for the open process at about 25 s and for the close process at about 40 s.

The gel actuator can be filled with gel particles of different sensitivity. The regulation of the flow is possible even in dependence on pH-value and concentration of organic component in water.

For further details see ref. ^[13].

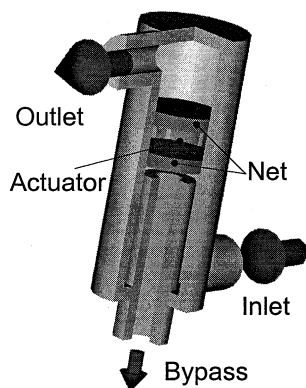


Figure 1. Chemo-mechanical valve.

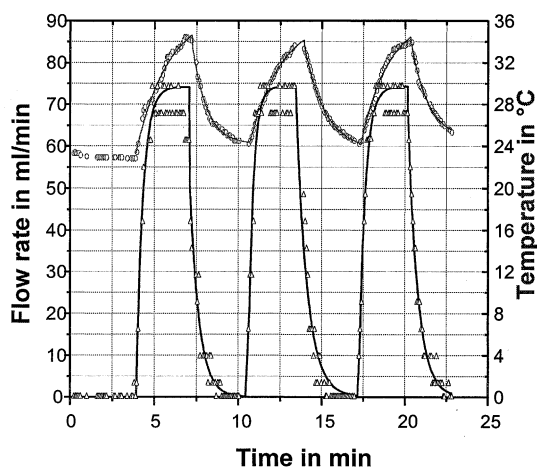


Figure 2. Flow-rate vs. time, upper curve: temperature gradient.

- Micro-valve, general remarks

The miniaturization of a chemical analysis system is supposed to yield a number of technological and economical benefits, which evolve from a drastic reduced sample and reagent consumption and reduction of analysis time. Conventional micro-valves mostly contains a flexible membrane, which can be deformed to block the flow in an adjacent channel. The actuators used to switch the membrane are based on, e.g., electromagnetic, electrostatic, piezoelectric, thermo-pneumatic, bimetallic effects, or on shape memory alloys. Disadvantages of membrane valves as well as of other conventional valves are an unavoidable leakage flow and an intolerance against small particles in the fluid. A possibility to overcome these disadvantages could be the design of gel-based micro-valves.

Some principles for regulating small flow rates based on environmental sensitive polymers are described in literature:

- A chemical valve effect in thin films with densely hexagonal packed nano-channels (diameter 17 nm) which were partially filled with poly(acrylic acid) (PAA) is reported in ref.^[14]. The structural change of PAA chains with variations in pH, ionic strength, and ion type caused a change in the water permeability of the membrane.
- A flow sorter and a shut off valve (actuator size of approximately $1000 \times 700 \times 250 \mu\text{m}^3$) with a response time of less than 10 seconds is described in ref.^[15]. A layer of a pH-dependent hydrogel based on acrylic acid was synthesized via direct photo-patterning around prefabricated posts. The posts are inside of a micro-channel (500 to 2,000 μm wide, and 50 to 180 μm deep). Changing the pH of the liquid stimulates the swelling/deswelling of the gel layer.

- Design of micro-valve

In principal, the swelling of sensitive polymers can be stimulated by changing the properties of the fluid itself, or a separate source of energy. The change of temperature of the gel and therefore its swelling/shrinking is controllable by heat flow due to an applied electrical current.

The presented micro-valve consists of components with different functions (Figure 3):

- Flow channels and actuator chamber in different design were generated on a Silicon-wafer by a photo-lithographic process. The actuator chamber, or the actuator channel, contains the sensitive polymer.
- A heater and a temperature sensor are integrated in the cover. The cover close up the flow structure and protect them.

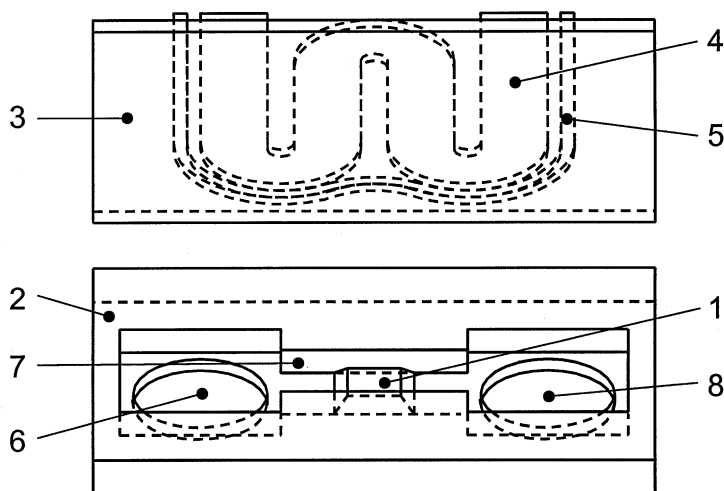


Figure 3. Design of micro-valves

1 – actuator chamber; 2 – flow structure; 3 – cover; 4 – heat meander; 5 – temperature sensor; 6 – inlet; 7 – flow channel; 8 – outlet.

Two different working principles were tested:

- particle-based actuator (Figure 4a),

The valve chamber is filled with spherical particles of PNIPAAm-network with a mean value of diameter of $(82 \pm 8) \mu\text{m}$ in the dry state.

- dots of photo-patterned sensitive polymer (Figure 4b),

The flow channel contains a certain number (mostly three) of sensitive dots.

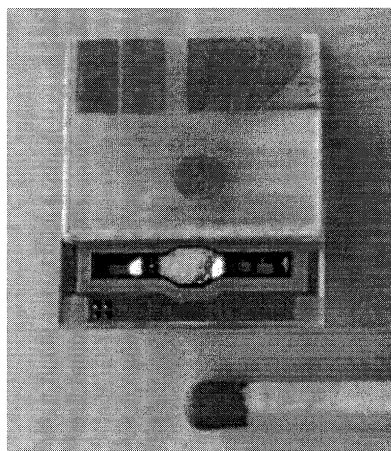


Figure 4a. Particle-based actuator.

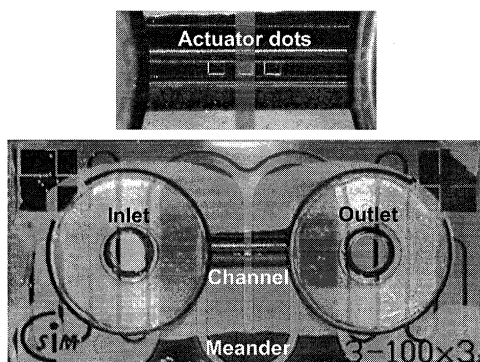


Figure 4b. Actuator based on photo-patterned dots of smart gel.

Results and discussion

- Synthesis of gels with fast response

Figure 5 shows different pattern of thermo-sensitive polymeric gel. The thickness of a mechanical stable gel increases in 5 s from 10 μm (dry state) to 30 μm (swollen state).

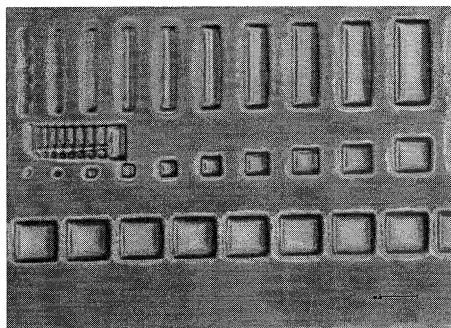


Figure 5. Patterned thin layer of PNIPAAm copolymers.

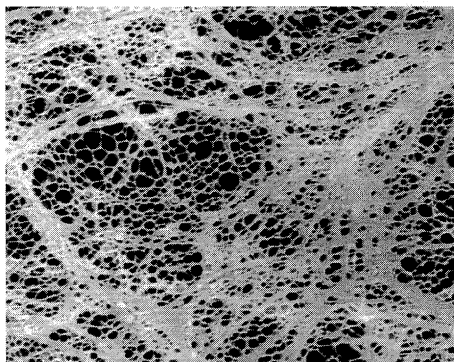


Figure 6. Bulky PVME in the high swollen state ($T = 23\text{ }^{\circ}\text{C}$).

The experiments have shown, that e-beam irradiation is a suitable procedure for the synthesis of thermo-sensitive hydrogels. A porous structure, which contains a polymer-poor phase (cavities in μm -range) and a polymer-rich phase (full of holes in nm-range) is typical. Both, the swollen state of the hydrogel at $25\text{ }^{\circ}\text{C}$ and at $40\text{ }^{\circ}\text{C}$ are characterized by three-dimensional sponge-like patterns, which consist of many small cavities ($10^2 \dots 10^3\text{ nm}$) separated permeably from each other by a thin membrane-like layer (Figure 6). This structure can be observed by images at high magnification. The layer is porous with a typical pore-size of 10 nm. After heating to $40\text{ }^{\circ}\text{C}$, the gel collapses and shrinks. The micrographs show that the collapsed gel is porous (the cavities are smaller than at $25\text{ }^{\circ}\text{C}$), but the polymer layers which separate the cavities are more compact.

The gel particles synthesized by irradiation of a diluted PVME solution were almost globular with a sponge-like structure (Figure 7). They have a mean diameter in the range of 250 – 600 nm (swollen state).

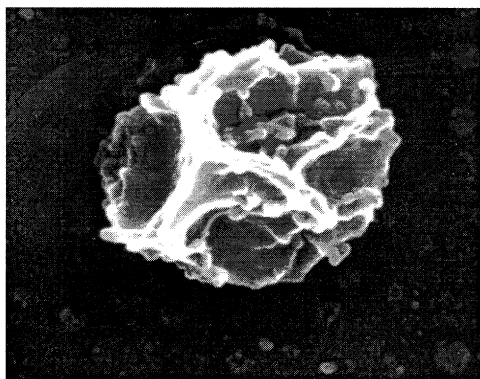


Figure 7. Thermo-sensitive PVME-particles in the swollen state.

The hydrodynamic radius depends on temperature (Figure 8). The volume phase transition is not as sharp as for the bulk gel and occurred at a higher temperature. The viscosity of solution of gel particles is temperature dependent too (two orders of magnitude for a semi-dilute solution).

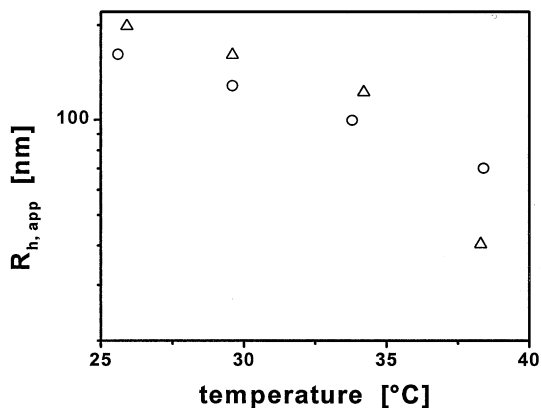


Figure 8. Temperature-dependence of apparent hydrodynamic radius.

- Valve- characteristics

We investigate the behavior of the micro-valve, especially the influence of heating power on the flow rate with a test equipment. Figure 9 shows the flow rate vs. time for different values of power and different current pulses at constant parameters of the pump. The upper part of

both figures shows the temperature measured by the thermo-sensor. These curves reflect the profile of the power pulse. On Figure 9a the electrical current is given as a simple rectangular pulse (power amplitude: 120 mW).

The flow rate is reproducible only for a modified rectangular pulse and higher values of power, shown on Figure 9b. Heating the gel opens the valve in a short time (power amplitude 770 mW). After reaching the temperature for volume phase transition the power is adjusted to a lower level (180 mW). The heat losses are compensated and the gel remains in the swollen state. To stop the flow, the gel must swell, or with other words, it must cool down. The current is regulated to zero.

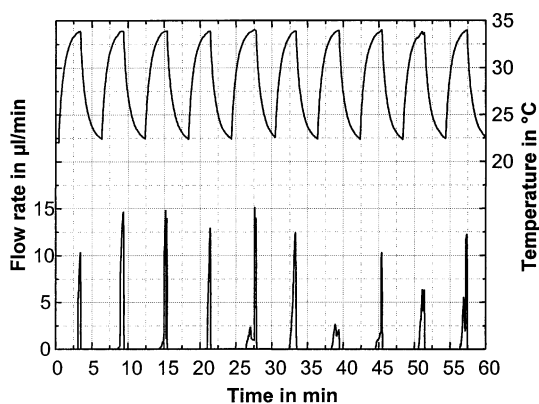


Figure 9a. Flow-rate vs. time - low power, rectangular power pulse.

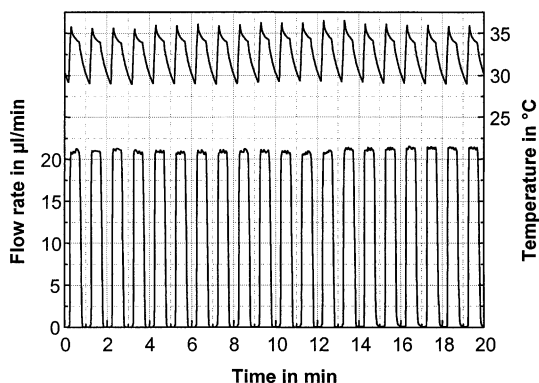


Figure 9b. Flow-rate vs. time - modified power pulse.

With the modified power pulse we were able to realize a reproducible mode of function with a short cycle time (minimum opening time 300 ms; minimum closing time: 2 s).^[16]

Furthermore we have designed a micro-valve based on dots of photo-patterned sensitive polymer. The minimum actuator size was $4 \times 4 \times 1 \mu\text{m}^3$. The cycle time was higher than for the particle-based valve.^[17]

The outcome of this part of our work is:

- it is possible to use sensitive polymer gels as materials for flow control;
- the valve behavior is reproducible, the repeat fault was less than 15 %;
- the valve was tested in a pressure range up to 5 bar.

Table 1 gives an overview on the advantages and disadvantages of conventional and gel-based valves.

Table 1. Comparison between conventional and gel-based micro-valves.

Conventional micro-valves mostly based on membrane principle	Gelbased micro-valves particles or dots of sensitive polymer
Advantages <ul style="list-style-type: none"> - universally applicable due to their electronic controllability - small cycle times, ms-range - manufacturing by established micro-technological processes 	Advantages <ul style="list-style-type: none"> - simple fabrication and set-up, integration into known layouts - high degree of miniaturization - particle tolerant - zero leakage flow - pressure independent
Disadvantages <ul style="list-style-type: none"> - pressure sensitive - particle intolerant - possess a non-avoidable leakage 	Disadvantages <ul style="list-style-type: none"> - higher cycle times - indirect mode of operation

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