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Application of Sensitive Hydrogels in Flow Control

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ABSTRACT

For any polymer gel, the amount of solvent uptake is dependent upon the chemical nature of the gel and the nature of its environment – solvent composition, temperature, pH, and so on. We discuss the use of different hydrogels based on crosslinked poly(N-isopropylacrylamide) and copolymers with basic or acidic groups as materials for flow control. The design of a chemo-mechanical valve is described. The liquid flows directly through a gel actuator, which consists of a cylinder filled with small particles of the sensitive crosslinked polymer. The flow rate as well as the pressure drop is measured in dependence on the solvent properties. The sensitivity of the gels as well as the time behavior of the valve-function is correlated with the dependence of the degree of swelling on the environment and the swelling and shrinking kinetics of the gels. The stimulus must permeate the gel itself before a gel can respond to the stimulus. By NMR-imaging it is possible to follow the transport processes inside the gel in real-time.

With the presented experimental arrangement we could show that sensitive polymers can be used for controlling the flow in dependence on temperature, pH and content of organic solvents in water. Furthermore, the synthesis of a photo-crosslinkable sensitive polymer is described, synthesized and suggestions for an application of thin layers of this polymer in micro-system techniques are made. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: temperature-sensitive polymer; mixed solvents; thin layer; valve; NMR-imaging

INTRODUCTION

A conventional system for regulating a flow of a liquid in dependence on their properties needs a sensor system and an acting system with a source of energy. Stimuli-responsive hydrogels change their volume and elasticity in response to a change in the properties of the liquid phase such as temperature, pH, solvent composition and ionic strength. The volume change occurs either continuously or discontinuously depending on the chemical compositions of gels and liquids and on experimental conditions. These polymers have promising potential to achieve smart chemo-mechanical valves because they may be utilized for the automatic regulation of a flow. The "smart polymers" connect an actuator, which can generate mechanical work, with a function of sensing. Applications of these polymers as membranes and for drug-delivery systems are well known from the literature. One of the first applications of a sensitive polymer gel as a temperature dependent valve is given in ref.1 The swelling process of a poly(acrylamide) gel in a closed swelling chamber

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was used as the driving force for a special mechanical construction. A thermo-responsive automatic separation valve system with a gel (poly(vinyl methyl ether)) directly in the liquid stream is suggested in ref.2. A gel ball swells or deswells in dependence on the temperature of flowing water. The flow-through properties of rigid polymer monoliths, a material that is characterized by a unique bimodal pore distribution consisting of large micrometer-sized convective pores and much smaller 10 nm-sized diffusive pores, can be imparted by grafting a temperature-sensitive polymer to their internal surface. A thermal gate (full opening and closing of the micrometer-sized pores) and controlled flow of water as a function of temperature (thermal valve) could be observed [3]. Great fields of application in flow control are hydrogel membranes, e.g. with temperature-controlled permeability for molecules of different size [4] and polarity [5]. 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 [6]. The structural change of PAA chains with variations in pH, ionic strength and ion type caused a change in its water permeability.

Poly(*N*-isopropylacrylamide) (PNIPAAm) is perhaps the best known of a class of temperature-sensitive polymers. The polymer exhibits a well-defined lower critical solution temperature in water. It has been known that the lower critical soluble temperature (LCST) depends on solvent composition in mixed aqueous solutions of PNIPAAm [7–10] and that the PNIPAAm gels undergo analogous volume transitions in aqueous solvents [11, 12]. This effect is observable in mixtures of solvents that show the phenomenon of cononsolvency [13].

The characteristic time for the swelling/deswelling process depends on the cooperative diffusion coefficient (mass transport of the polymeric chain) and is a function of the gel-dimension [14, 15]. In order to establish systems with a minimum response time, thin layers, small spherical particle and porous gels are used [16].

The conventional method for investigating swelling and shrinking is to measure the mass uptake of the polymer. However, since such measurements perform observations at a macroscopic level, little information has been obtained related to the nature of the solvent inside the polymer matrix and to the processes that control its diffusion. These processes can be influenced by inhomogeneities such as surface layers [17], polymer cracks, which allows a fast solvent uptake in relation to the matrix [18], or a change of the type of diffusion in some regions of the sample [19]. The penetration of solvents into solid systems in real-time was observed by nuclear magnetic resonance (NMR)-imaging. The method provides a one-, two- or three-dimensional image of the density or/and the mobility of the solvent in a material. Furthermore, an indirect observation of the diffusion is possible by observing the changes of the mobility of the polymer matrix using a non-detectable solvent (D_2O, CCl_4 in the case of ^{1}H-NMR [17]).

Our goal of our work is the design of a chemo-mechanical valve with a technical relevance and the investigation of its application-relevant properties in dependence on the gel properties and experimental conditions. As a drastic change of the gel properties is given in dependence on temperature and composition of alcoholic solutions we focused our work on these cases. If a polymer contains acid groups, pH influences the degree of swelling and a pH-sensitive valve should be possible. Furthermore, we make some suggestions for the application of photo-crosslinkable polymers in flow control.

EXPERIMENTAL

Materials

Poly(*N*-isopropylacrylamide) exhibits a sharp phase transition in water at 32 °C [20]. The *N*-isopropylacrylamide (NIPAAm) (Aldrich Chemical Co.) was recrystallized from n-hexane solution. The used crosslinking agent was *N,N′*-methylenebisacrylamide (BIS). The initiator and accelerator for polymerization reaction were potassium peroxodisulfate (KPS) and *N,N,N′,N′*-tetramethyl-ethylenediamine (TEMED). They were used as received from Aldrich Chemical Co. NIPAAm and BIS (BIS content: 1–10 mol%; BIS 4 = 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 of TEMED, respectively, were added to the oxygen free (bubbled with N_2) solution. The solution was then transferred into glass tubes (diameter 7 mm) to get cylindrical gels. After the crosslinking reaction (one night at room temperature) the gels were taken out of the glass tubes. They were immersed in deionized water for about 1 week to wash out non-reacted reagents. The transition temperature can be influenced by copolymerization of NIPAAm. To develop a temperature- and pH-sensitive polymer, we copolymerize NIPAAm with different amounts of acrylamide derivatives. They contain spacer groups with different chain length and a pH-sensitive head group ($-COOH$ or $-N(CH_3)_2$, Scheme 1). For details of the monomer synthesis and properties of these polymers see previous literature [21, 22]. Another pH-sensitive polymer we used was crosslinked poly(vinyl alcohol)/poly(acrylic acid) (PVA/PAA). The polymers obtained from Aldrich were dissolved separately in distilled water. The solutions were then mixed in such a way that 80 wt% were PVA and 20 wt% PAA. Repetitive freezing and thawing cycles of the mixture leads to porous gels ("cryogel") where the equilibrium degree of swelling depends on the pH-value. Another possibility to get crosslinked polymers is the heating of dry films [23].

Thin layers of sensitive polymers were prepared by photo-crosslinking of linear temperature- and pH-sensitive prepolymers. The sensitive poly-

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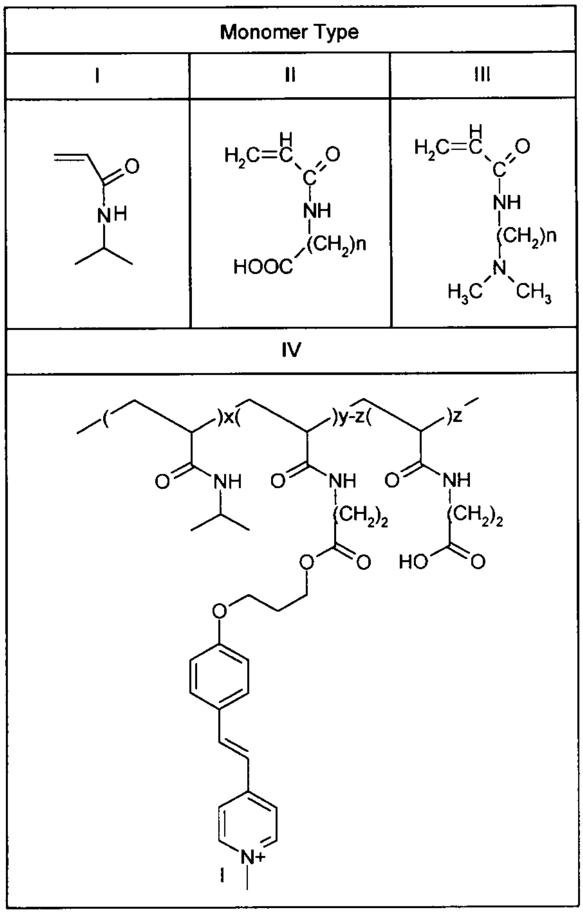

SCHEME 1. Chemical structures of NIPAAm (I), the acidic comonomer (II), the basic comonomer (III), and the photo-crosslinkable sensitive copolymer.

mer was synthesized by radical copolymerization of NIPAAm with dimethylmaleinimide (DMI) bearing acrylamide groups. The DMI-chromophore reacts via a [2 + 2]-cycloaddition under irradiation [24].

Characterization of the Gels

Measurement of the Degree of Swelling. The crosslinked samples (PNIPAAm) were cut in cylinders with about 2 mm thickness. From the extracted samples the degree of swelling as the ratio of the swollen to the dry masses of crosslinked polymer in equilibrium with the solvent ($Q_m = m_{swollen}/m_{dry}$) was determined. To measure the degree of swelling in the alcoholic mixture, the water-swollen network was put in a large amount of mixed solvent with a defined composition at constant temperature for more than 72 h. In our experiments we used methanol, ethanol, 1-propanol, 2-propanol, butanol and hexanol (all solvents of analytical grade). Butanol and hexanol are only partially mixable with water.

The degree of swelling of the thin layers was determined by measuring their thickness in dry and swollen state.

Conditions for Volume Phase Transition. The application of sensitive polymers in flow control is based on the effect of volume phase transition. For the different polymers used in this work the conditions for the volume phase transitions must be determined. These measurements gave us information about the application range of the gels.

The transition temperatures of the different polymers in pure water were determined by using a DSC 2920 (TA Instruments) at $dT/dt = 5\,°C/min$. The thermograms were obtained from 5 wt% aqueous polymer solutions. The onset of the endothermic peak (release of bonded water from the polymer chains [25]) corresponds to the temperature of the gel collapse [26]. In all other cases, we measured the equilibrium degree of swelling in dependence on the solvent properties.

NMR-Imaging. The degree of swelling of a gel can only be influenced if the properties of the swelling agent (temperature, concentration of ions, composition) inside the gel are changed. That was the reason why we tried to follow these processes inside the gels in real-time. In order to get an idea about the kinetic changes in concentration of a second component in a two-component swelling agent we investigated the diffusion process of methanol in a gel by using a NMR-imaging technique. The cylindrical shaped samples were swollen in deuterated water and put in a NMR glass tube. A defined mixture of CH_3OD/D_2O was added to the swollen gel. A one-dimensional picture of the diffusion front of methanol inside the gel only takes about 1 min. Because of that it was possible to get time as well as spatially resolved pictures of the changes of the composition of the swelling agent. Furthermore we measured the self-diffusion of water inside the swollen gel. 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). The experiments were performed on a self-made NMR-microscope (Martin- Luther-University Halle, Germany) attached to a VARIAN unity 400 spectrometer. A resolution of 50 μm was achieved by using a gradient power up to 50 gauss/cm.

Design of the Chemo-Mechanical Valve

The synthesized crosslinked polymers were tested in a chemo-mechanical valve. Figure 1 shows the experimental arrangements used. The liquid flows directly through the "gel-actuator". For the preparation of this part we use a very simple method. The unswollen sensitive polymer network is milled and separated into fractions of different particle sizes with sieves, which have a defined mesh size. The particles are spherically shaped and have a broken surface. For the described experiments we used particles with a typical dimension of 0.40 ± 0.05 mm. They were put in a cylinder which consists of an o-ring (stainless steel, diameter: 5 mm; thickness: 2 mm) and on both ends of a steel

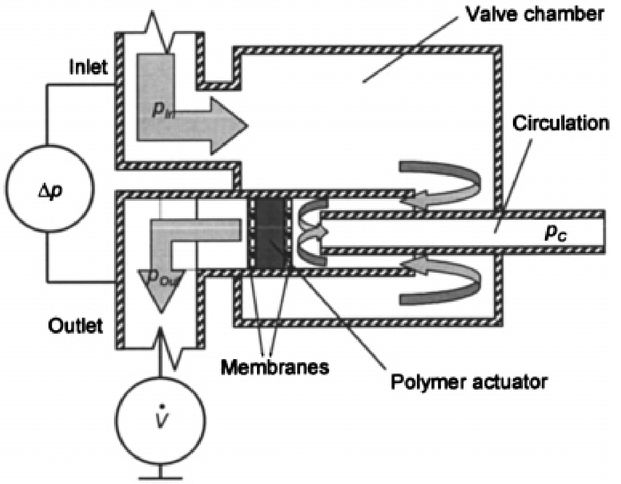

FIGURE 1. Principle of a chemo-mechanical valve with test equipment (p_{in} inlet pressure, p_{out} outlet pressure; pressure drop = $p_{\mathrm{in}} - p_{\mathrm{out}}$).

net (mesh-size 60 μm). One third of the cylinder was filled with the dry polymer.

The liquid flows through the macro-pores between the polymer particles. According to the Hagen-Poisseuille law a decrease in the tube's diameter leads to a decrease in the flow rate of a liquid through the tube at constant pressure drop, or requires a greater applied pressure to achieve the same flow rate. We can measure both the pressure drop in dependence on the properties of the flowing liquid and the flow rate. The maximum flow rate depends on the pump used, here about 300 cm^3/min. The pressure drop is given by the difference of the inlet and outlet pressure. As pressure sensor a HWSE 6910 (Bürkert) and as flow-rate sensor a 79.01 (Bürkert) are used. The pump is a model FM 30 (KNF Flodos). To get a faster change of the properties of the liquid in the valve-body, we use a circulation circuit (bypass at the inlet). We change the liquid properties in separated reservoir. The time for the flow of the liquid from this reservoir to the valve depends on the pump (in all described experiments about 20 sec). To characterize the time behavior of our valve we measure the time of the change either of the flow rate or of the pressure drop (Fig. 2).

Thin Layers of Sensitive Polymer

The swelling/deswelling process is time-consuming. This is a limitation for an application of hydrogels. The rate of swelling is inversely proportional to the square of the characteristic dimension (the thickness of the polymer layer). To improve the response time it is necessary to reduce the gel size dramatically. We synthesized thin films of sensitive polymers on Si-wafer as supporting material. The wafer was coated with a prepolymer solution. After evaporation of the solvent, the dry film was crosslinked via UV irradiation. By irradiation through a mask it was possible to design different structures on the Si-wafer and patterned networks in μm-scales were obtained. The resulting networks show temperature dependent swelling properties [27, 28].

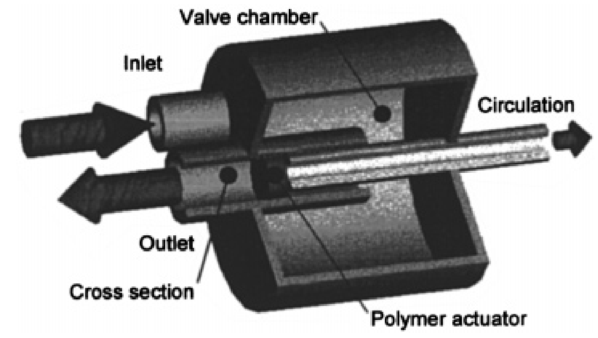

FIGURE 2. Design of the valve.

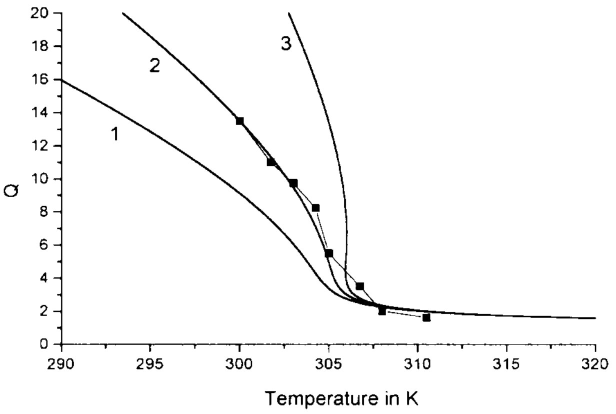

FIGURE 3. Degree of swelling of PNIPAAm as a function of temperature calculated with [eq. (1)]: (1) M_c = 8000 g/mol; (2) M_c = 18,000 g/mol; (3) M_c = 50,000 g/mol. ■, measured degree of swelling, sample BIS 4.

RESULTS AND DISCUSSION

Temperature Dependence of the Degree of Swelling

The Flory-Rehner equation correlates the equilibrium degree of swelling Q of a polymer with the crosslinking density and the interaction between the polymer and the swelling agent, given by the Huggins interaction parameter χ. For PNIPAAm the concentration as well as the temperature dependence of the χ value is well known [29].

$$\chi = \chi_1 + \Phi_B \chi_2; \quad \chi_1 = \frac{\Delta h - T\Delta s}{k_B T} \qquad (1)$$

where $\chi_2 = 0.518$; $\Delta h = -12.46 \times 10^{-21}$ J; $\Delta s = -4.717 \times 10^{-23}$ J/K; k_B = Boltzmann constant. By applying the Flory-Rehner equation to PNIPAAm gels, we calculated the $Q = f(T)$ curves for different crosslinking densities and compared this with experimental data for one gel (Fig. 3). The crosslinking density influences the shape of the curves. The higher the molecular weight of the network chains, the sharper the volume phase transition. For a thermal gate function (close–open)

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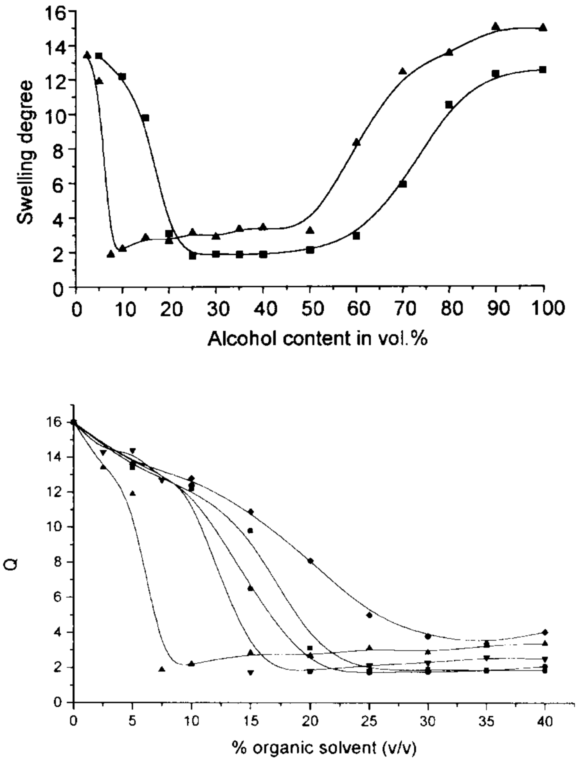

FIGURE 4. Swelling degree of PNIPAAm (BIS 4) in aqueous mixtures at $T = 298$ K. (a) ■, methanol; ▲, 1-propanol; (b) ■, methanol; ●, ethanol; ▲, 1-propanol; ▼, 2-propanol; ◆, acetone.

a sharp transition is needed, however, for a regulating system (controlled flow in dependence on temperature) a higher crosslinked polymer is useful. The crosslinking density does not only influence the characteristic swelling curve, but also the mechanical properties of a gel as well as the swell kinetics.

Degree of Swelling in Mixed Solvents

PNIPAAm is not only soluble in cold water, but also in organic solvents. In contrast to water, the degree of swelling in different types of alcohol are independent of temperature. By using solvent mixtures with various compositions, the interaction between polymer and solvent molecules can be changed in a continuous manner. In water–methanol mixtures the volume phase transition temperature depends on the methanol content [11]. As the methanol content increase, the transition temperature shifts to lower temperature and the discontinuity at the transition becomes more pronounced (at small amounts of alcohol). At a higher methanol content the transition is not observable. The behavior in mixtures of water and another alcohol is similar to that for water–methanol [11, 12]. The temperature shift and the discontinuity at the transition are stronger as the carbon number of alcohol increases. Schild *et al.* [8] applied the Flory-Huggins ternary solution theory to this phenomenon. They suggest, that the phenomenon may in fact not result from polymer induced perturbation of the water–methanol interaction parameter, but more likely from changes in local contacts between the polymer and the solvents.

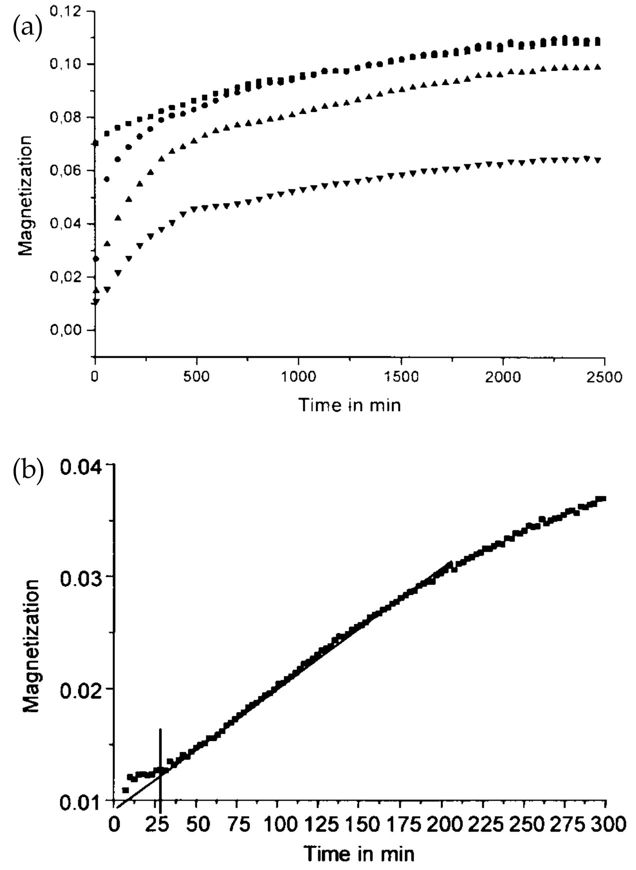

FIGURE 5. Diffusion of deuterated methanol (60 vol% CH_3OD in the swelling agent) into a swollen (D_2O) BIS 4 gel (the magnetization, in arbitrary units, is proportional to the CH_3OD concentration). (a) Time dependence of the magnetization inside the sample at different positions on the surface ■, 0.46 mm; ●, 1.38 mm; ▲, 2.76 mm; ▼, 4.6 mm ●; (b) time lag at $l = 4.6$ mm on the sample surface.

We investigated the dependence of the degree of swelling on solvent composition at constant temperature. Comparing the swelling curves shown in Fig. 4 a systematic trend becomes clear. The larger the carbon number of alcohol to be added the larger the decrease of the degree of swelling at the same concentration of the organic solvent. In mixtures of water with butanol and hexanol, both are only partially miscible with water, the drastic change of the degree of swelling is observed in the one-phase region of the mixture.

The changes of the degree of swelling in dependence on the concentration of the organic solvent can be used in a composition sensitive valve.

Diffusion and Chain Mobility

The rate of response to the environmental changes may directly influence the system performance. In

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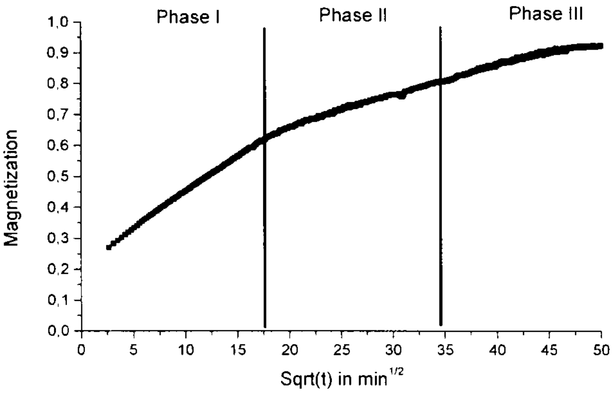

FIGURE 6. Time dependence of the magnetization. Three different diffusion regimes are observable: phase I: the concentration depends on the square root of time; phase II: the diffusion process is hindered by limited volume effect and occurrence of macro-network bundles; phase III: the diffusion process is dominated by the deswelling process (volume ratio swollen gel/solution due to the NMR sample geometry).

other words, the swelling/deswelling processes determine the characteristic time for a valve function (time to open the valve or to stop the flow). At first we tried to identify the relative rates of the different kinetic phenomena. We suggested a two step mechanism, in the first step the stimulus must permeate the gel itself. The second step is the volume change of the gel.

The time resolved as well as spatially resolved observation of the methanol concentration (Fig. 5a) inside the D_2O swollen gel gives hints for a non-Fickian diffusion process, which can be explained by a non-constant diffusion coefficient [$D = D(c)$; multicomponent diffusion process, Fig. 6] due to the interaction with the polymer matrix. Nevertheless, at the beginning of the diffusion process the concentration of methanol follows a $(\text{time})^{1/2}$ law. From the measured time lag Θ at a distance l to sample surface (here $l = 4.6$ mm) the diffusion coefficient can be calculated [eq.(2), Fig. 5b].

$$D = \frac{l^2}{6\Theta} \tag{2}$$

For methanol in the swollen gel (D_2O at 294 K) we get values from 1.8×10^{-5} cm^2/sec up to 3.9×10^{-5} cm^2/sec in dependence on the methanol concentration (for D_2O in water about 2.3×10^{-5} cm^2/sec). Typical values of the diffusion coefficients of alcohol in water are in the same range [30]. With the help of eq. (2) we can estimate the required time for the transport of methanol to the center of our gel particle at about 3 sec.

Figure 7 shows the temperature dependence of the mobility of the network chain in the swollen gel. If the transition temperature is crossed, the signals diminish abruptly. From these experimental results it was clarified that the molecular motion of the network chains change at the volume phase transition. The rate of this process seems to be simply dependent on the rate of heat transfer, which occurs much faster than mass transfer. The thermal equilibrium is reached well before any significant change in the degree of swelling (thermal diffusivity about 10^{-3} cm^2/sec [31]). In aqueous solution of PNIPAAm evidence for reversible network formation via the physical association of hydrophobic side-groups during phase separation [32] has been found. The increase of the dynamic storage modulus G' was instantaneous at the phase transition temperature and was not a progressive process. According to Shibayama *et al.* [33] a macro network is formed at the volume phase transition temperature and the Young's modulus of the network increases abruptly proportional to the ratio of the equilibrium degrees of swelling in both states. The macro network consists of bundles of polymer chains (polymer rich domain) surrounded by a polymer poor matrix. After the formation of the macro network the deswelling process starts. The volume change is governed by the mutual (or cooperative) diffusion of the network and the solvent. The rate of equilibration is inversely proportional to the square of gel size and proportional to the cooperative diffusion coefficient (D_{coop} of PNIPAAm/water: $(2.3\text{–}3.6) \times 10^{-7}$ cm^2/sec [31]). However, this will be the rate-limited process in the normal case.

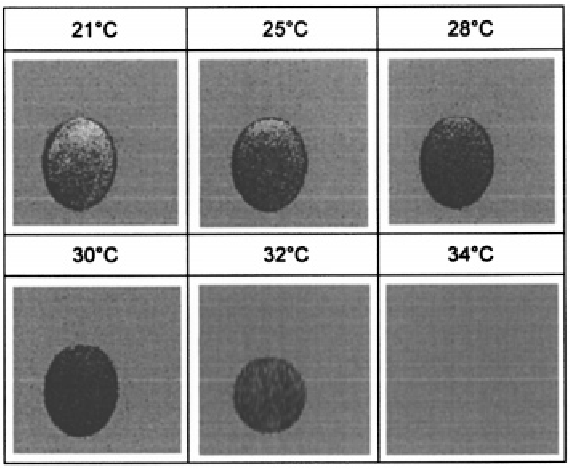

FIGURE 7. Temperature dependence of the network chain mobility (BIS 4 swollen in D_2O). The contrast is proportional to the T_2-weighted spin density of ^1H. At a temperature higher than the volume phase transition temperature no signal can be observed. The chain mobility changes drastically.

The flow-rate can be influenced by small changes in the network volume (The liquid flows through the volume between the gel-particles if the valve is open. Only this part of volume must be filled by the swelling process.) With the values of the cooperative diffusion coefficient given above, the time can be estimated which is needed for an increase of the diameter of the gel particles. A spherically gel particle swells from $d = 0.4$ mm (dry state) to $d = 1.0$ mm (equilibrium degree of swelling, $Q = 16$) in about 30 min (experimental determined). The volume between the particles in our gel actuator is filled at a degree of swelling $Q = 3$.

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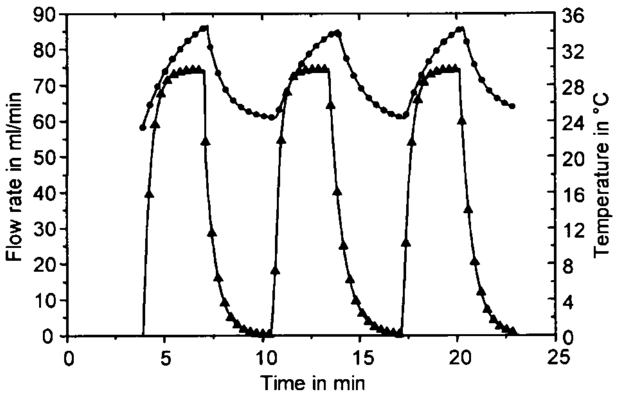

FIGURE 8. Flow rate (▲) in dependence on thermal stimulation [temperature (●)].

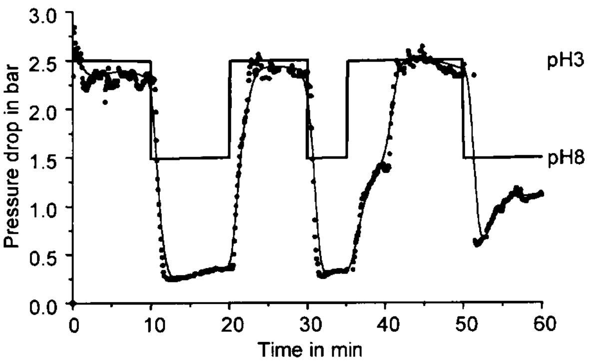

FIGURE 9. The pressure drop (●) as function of pH for a copolymer of NIPAAm and comonomer III (10 wt%, *n* = 2).

Under conditions of free swelling a spherically gel needs about 10 min to reach this degree of swelling [34].

Temperature Sensitive Valve

The degree of swelling of the PNIPAAm depends on the temperature. In our first experiments we used these gels for a temperature sensitive chemomechanical valve. Figure 8 shows the dependence of the flow rate on the temperature of the liquid (water). The temperature alters from 24.5 to 35 °C and vice versa with a non-linear temperature gradient (about 5 K/min). The temperature gradient (dT/dt) in the liquid influences the time characteristic of the valve. The higher the gradient, the faster the swelling/deswelling process. The fastest times were determined for the open process at about 25 sec and for the close process at about 40 sec. Table 1 shows the typical time constants of the sample BIS 4 at different heating rates. The change of the flow rate in dependence on the time cannot be described by a simple e-function. Therefore, the values of time constants are calculated at 90% of the end value.

Gels composed of a porous structure swell or shrink very fast compared with non-porous gels of the same size. The sample BIS 10 was synthesized with a high ratio crosslinker/monomer. The equilibrium degree of swelling ($Q_v = 1/\phi_B$) is lower than the polymer concentration in the reaction bath. Crosslinking under this condition leads to a porous, but high crosslinked sample. The influence on the characteristic time of both effects is opposite.

pH-Dependence Swelling and Pressure Drop

The used copolymers of NIPAAm are pH-sensitive. The copolymer with an acid group swells at high pH, the copolymer with a basic group, swells at low pH. Figure 9 shows the pressure drop in dependence on the pH of the flowing liquid for a copolymer with the comonomer (III). The different pH-values were realized with a borate-succimic buffer (pH = 3; according to Kolthoff) and a borate buffer (pH = 9; according to Sörensen and Clark). Typical values of the time needed to stop the flow or to open the valve are 70 and 130 sec, respectively. The time depends on the chemical composition of the copolymer. The lower the content of the monomer (III) the higher is the time. The copolymer with the comonomer (II) and the PVA/PAA cryogels show the inverse flow characteristic. The PVA/PAA samples crosslinked by heating of a film cannot be used successfully in the gel actuator. A reason for this were difficulties in obtaining spherical particles.

Composition Sensitive Valve

Gel actuators based on PNIPAAm gels are qualified for the use as a flow control valve in dependence on alcohol content in water. Figure 10(a) shows the pressure drop in dependence on

TABLE 1. Time Constant in Dependence on the Heating Rate for BIS 4 in Water

Heating rate (K/min)	*Particle size (mm)*	*Time (sec)*	
		Open	*Close*
0.9		1100	1100
5	0.4	56	65
	0.6	55	50
7.5		95	45

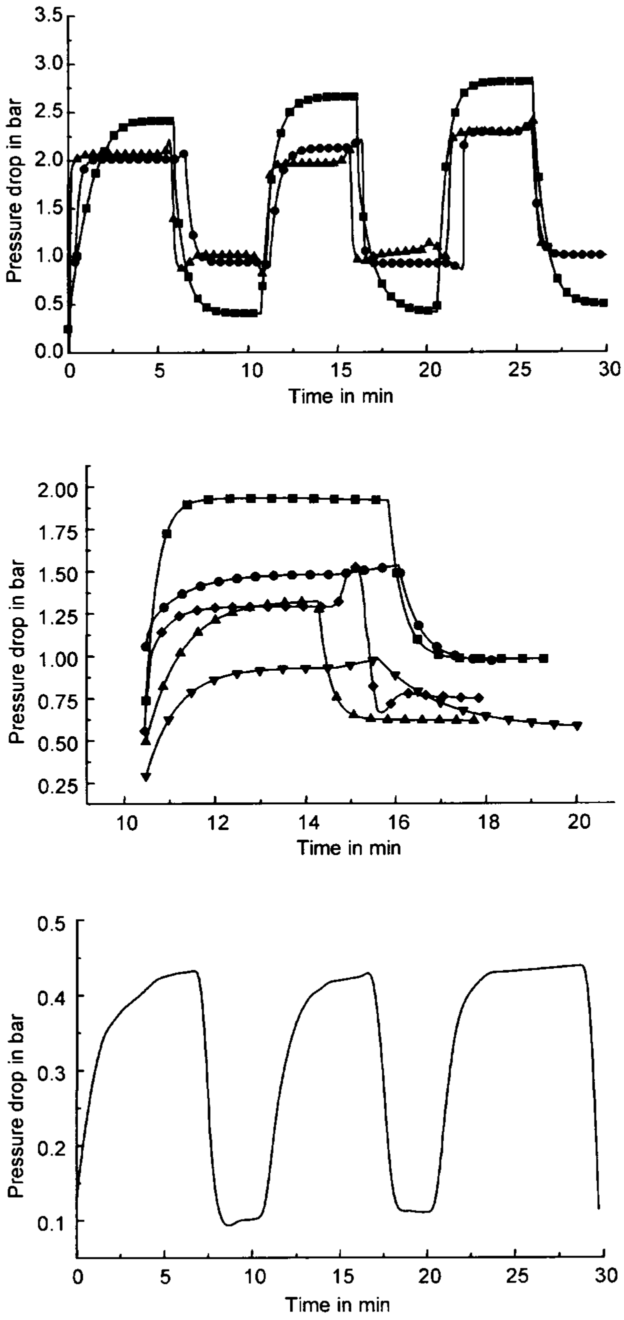

FIGURE 10. The dependence of the time behavior on the type of alcohol (BIS 4): (a) change of composition between pure water and 40 vol% of methanol, ■; ethanol, ●; 1-propanol, ▲; (b) change of composition (ethanol in water) between: ●, 0–10 vol%; ▼, 10–20 vol%; ▲, 20–30 vol%; ◆, 30–40 vol%; ■, 0–40 vol%; (c) change of composition between pure water and 0.3 vol% hexanol.

time by a change of solvent composition from pure water to a mixture with 40 vol% of organic solvent. From the experimental results follow:

(1) The higher the ΔQ (Q pure water $-Q$ mixture) the faster the valve and the higher the pressure drop.
(2) The higher the content of organic solvent the less the packaging density in the gel actuator.

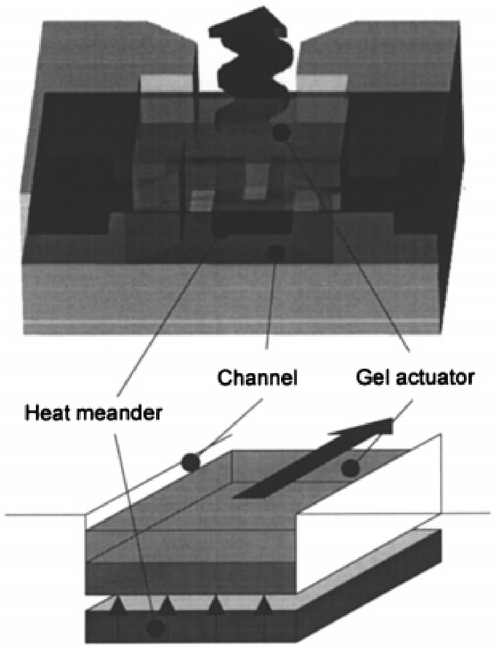

FIGURE 11. Controllable chemo-mechanical micro-valve made from a thermosensitive polymer gel.

(3) For the composition region 50–100 vol% the valve behavior is inverse to that of the region 0–40 vol%.

The decrease of the degree of swelling does not only depend on the chemical nature of the alcohol (the alcohol number), but also on the concentration of the alcohol (see Fig. 4). If the content of alcohol is altered in steps, the change of the pressure drop must be different for each step. Figure 10(b) shows this behavior for water–ethanol. Using butanol or hexanol as the organic component in the mixture, the degree of swelling changes drastically at low amounts of the alcohol. Figure 10(c) shows this behavior for 0.3 vol% hexanol in water. The time behavior of the valve is dependent on the type of alcohol, the higher the alcohol number the faster the gel actuator. The fastest times were determined for the open process at about 25 sec and for the close process at about 35 sec.

Swelling Properties of Thin Layer, Suggestion of a Valve for Microsystem-Techniques

A thin layer of a sensitive polymer shows very fast swelling and shrinking kinetics. We aim to use these materials in micro-systems (Fig. 11) in which gel sizes are reduced to the μm range. Thin films of sensitive polymers were synthesized on Si-wafers as supporting material. The linear polymers were crosslinked by a photoreaction and networks with well-defined structures were formed. In our experience gel dots of 250×250 μm^2 (thickness 7–15 μm) can be formed. If the crosslinking density is high enough, these dots are mechanically stable and can undergo a lot of swelling and shrinking processes without any destruction. We measured a

TABLE 2. Fundamentals of Design of a Chemo-Mechanical Valve

Requirements	*Solution*
Sensitivity	Polymer type
Selectivity	Modification by copolymerization; different sensitive polymers
Operating pressure	Mechanical strength (crosslinking density)
Flow rate and its change	Cross section; actuator size
Dynamic of actuator (time characteristic)	Characteristic dimension of the gel; gel particles, porous gels, thin layer
Insensitivity towards the environment	Isolation, volume of valve chamber
Operating function	Valve type
Operating mode (continuous, adjustable, controllable)	Polymer type; shape of the swelling curve

TABLE 3. Advantages and Disadvantages of Chemo-Mechanical Valves

Advantages	*Disadvantages*
Great effects	Swelling and shrinking influenced by different properties
Automatically function, independent on auxiliary energy sources	Volume transition is time consuming
Sensitivity against different solvent properties, chemical modification	Limited mechanical strength
	Small experiences
Patterning possible	Low acceptance
Combination of sensor and actuator properties	

time of 3 sec for the change of the thickness (proportional to $Q^{1/3}$) from 10 μm (dry state) to 30 μm (swollen state). With common techniques used in micro-electronics, structures like channels can be obtained. A heater (resistor) is located under the gel. As the thickness of a temperature sensitive layer depends on their temperature, the flow through a channel can be adjusted.

SUMMARY AND OUTLOOK

With the used experimental equipment, especially the designed valve, we are able to test the behavior of different polymers under different environmental conditions. The experiments have shown that it is possible to use sensitive polymer gels as materials for flow control. Our work was focussed on a valve that can be used without any other source of energy. Spherical particles with a non-regular surface are used as sensitive polymers. Although the swelling/shrinking processes are time consuming, the kinetic properties of our valve are good. The valve took only about 1 min to stop the flow or to open the flow. The time can be influenced by the packing density of the gel actuator and the particle size. It depends on the gradient of the change of the solvent property, respectively on the difference of the degree of swelling in both states. Comparing the discussed time constants with the measured time characteristic of the valve, the following model can be used to understand this. The time behavior of the gel actuator must be determined by the swell kinetics of a single polymer particle. To stop the flow it is not necessary that the whole volume of the gel actuator is filled with the swollen gel. In the shrunken state, the liquid flow through macro-pores formed by the gel particles (space between the particles). The change of the liquid properties near the gel particles is possible in a short time. Only a small increase of the degree of swelling stops the flow through the macro-pores. The experiments have shown that the process to stop the flow take the same or less time than the opening process. This is understandable in the case of the thermo-sensitive valve, where the heat transfer determine the change of temperature in the gel actuator, but not for the pH- or composition-sensitive valves. The flow of the liquid is hindered by the swollen gel. A transport of the liquid to the gel particles seems to be possible only by a diffusion process. However, the characteristic time of the valve cannot be determined by diffusion. An explanation of this discrepancy could be the elasticity of the gel. In the closed state a force given by the difference between the inlet and outlet pressure acts on the gel. Deswelling and deformation of the swollen gel promotes the formation of macro-pores The valve behavior is reproducible, the repeat fault (pressure drop or flow rate) was less than 15%. The valve was tested in a pressure range up to 5 bar. The application range depends on the chemical structure of the polymer.

Because of the many and diverse ways of modification of the sensitive polymers, a lot of applications are possible. The degree of swelling usually depends on different solvent properties. However, the application is restricted to changes of only one solvent property. In this case the sensitivity is quite good. Table 2 gives a survey on the demands on a valve and how they could be met.

The advantages and disadvantages of the proposed chemo-mechanical valve are listed in Table 3. Further chances for an application of sensitive polymers are the change of the degree of swelling stimulated by a separate source of energy. By this way the ability of the gels to produce mechanical forces could be used. The application of photo-crosslinkable sensitive polymers, which can be used in thin patterned layers seems promising.

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