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Semi-Interpenetrating Polymer Networks Based on *N*-isopropylacrylamide and 2-acrylamido-2-methylpropane Sulfonic Acid for Intramolecular Force-Compensated Sensors

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Stimulus-responsive hydrogels are swellable polymers that take up a specific volume depending on a measured variable present in solution. Hydrogel-based chemical sensors make use of this ability by converting the resulting swelling pressure, which depends on the measured variable, into an electrical value. Due to the tedious swelling processes, the measuring method of intramolecular force compensation is used to suppress these swelling processes and, thus, significantly increase the sensor's response time. However, intramolecular force compensation requires a bisensitive hydrogel. In addition to the sensitivity of the measured variable the gel has to provide a second sensitivity for intrinsic compensation of the swelling pressure. At the same time, this hydrogel has to meet further requirements, e.g. high compressive strength. Until now, interpenetrating polymer networks (IPN) have been used for such a force-compensatory effective hydrogel, which are complex to manufacture. In order to significantly simplify the sensor design and production, a simpler synthesis of the bisensitive hydrogel is desirable. This paper presents a new bisensitive hydrogel based on semi-interpenetrating polymer networks. It is based on a copolymer network consisting of *N*-isopropylacrylamide (NiPAAm) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and long PAMPS strands that permeate it. Measurements show, that this hydrogel meets all essential requirements for intramolecular force compensation and is at the same time much easier to synthesize than previously used IPN hydrogels.

Stimulus-responsive hydrogels represent sensor elements with a high application potential for the detection of the concentration of a solved species.[1,2] In combination with a piezoresistive pressure sensor, the hydrogel's analyte-dependent swelling pressure can be transformed into an electrical output signal.[3,4] In the past, numerous sensors with sensitivities to various analytes, like e.g. urea,[5] glucose[6] and pH,[7] have been researched using this sensor principle. However, the time span until a final steady-state value of the sensor's output signal is reached is typically in the range of minutes to hours due to the excessive diffusion processes associated with the gel's volume phase transition and visco-elastic behavior.

Previous strategies for shortening the response time mostly addressed reducing the hydrogel layer's dimensions[8] or porosity,[9] which concurrently results in a reduction of sensitivity. The measurement method of force compensation using a bisensitive hydrogel represents a sensitivity-preserving approach. The concept of force compensation with a bisensitive hydrogel is to counteract the swelling of the hydrogel with a second stimulus, in this case the temperature. A closed-loop configuration is used to control the temperature with a Peltier element in a way that the hydrogel is continuously kept at a fixed swelling state (Fig. 1). The applied temperature is therefore directly correlated to the analyte concentration to be measured and, thus, represents the sensor output signal containing the measurement information.[10] By using this configuration, the time-consuming diffusion processes can be reduced significantly. In a previous work, a force-compensated sensor utilizing a bisensitive hydrogel enabled a response time reduction of up to 70%.[10]

So far, force-compensated hydrogel-based sensors used interpenetrating polymer networks (IPN) as a bisensitive hydrogel, which is sensitive both to the ion concentration c_{Na^+} of a saline solution (measurand) and to the temperature ϑ (compensation parameter). These IPN showed sufficient compressive strength for the operation under the influence of the pressure sensor membrane's restoring force. However, its sequential two-step synthesis complicates the gel

structuring process. The reason for this is that the two individual polymer networks are created one after the other and the resulting IPN must be manually extracted from the surrounding single network at the end.[10,11] This manufacturing process is not only complex but also involves significant uncertainties in the resulting dimensions of the hydrogel transducer. This complicates the precise design of the sensor on the one hand and a reproducible sensor fabrication on the other hand. With regard to enable gel synthesis, gel structuring and gel bonding within one single process step, a single-step synthesis that yields a bisensitive gel with similar compensatory and mechanical properties is desirable.

In this paper a hydrogel based on semi-interpenetrating polymer networks (semi-IPN) is presented, which fulfills these requirements. According to IUPAC it is called [*net*-P(AMPS-*co*-NiPAAm)]-*sipn*-PAMPS.[12] It consists of a single statistical copolymer network based on *N*-isopropylacrylamide (NiPAAm) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) in which long polymer strands of the sulfonic acid (PAMPS) are incorporated, thus contributing to an improvement of the mechanical properties. A second cross-linking reaction is omitted in this way. Furthermore, the measurements in this paper show that the semi-IPN hydrogel [*net*-P(AMPS-*co*-NiPAAm)]-*sipn*-PAMPS meets the requirements for compensatory hydrogel transducers, e.g. quasi-static compensation properties, dynamic swelling compensation properties and linearity of characteristic compensation curves.

Materials and Methods

Synthesis of [*net*-P(AMPS-*co*-NiPAAm)]-*sipn*-PAMPS.—Hydrogels based on the functional monomer NiPAAm are known to have a volume phase transition temperature between 32 °C and 34 °C.[13,14] In this range the *net*-PNiPAAm hydrogel has its highest sensitivity toward temperature. This temperature range is also highly desired for the actuation via Peltier elements. This monomer is therefore particularly suitable as one component for the hydrogel transducer of the sensor. Polymers based on *N*-isopropylmethacrylamide with a volume phase transition temperature (VPTT) of 38 °C to 42 °C[15] and *N*-ethyl-*N*-methylacrylamide with a VPTT of 58 °C to 68 °C[16] are much less
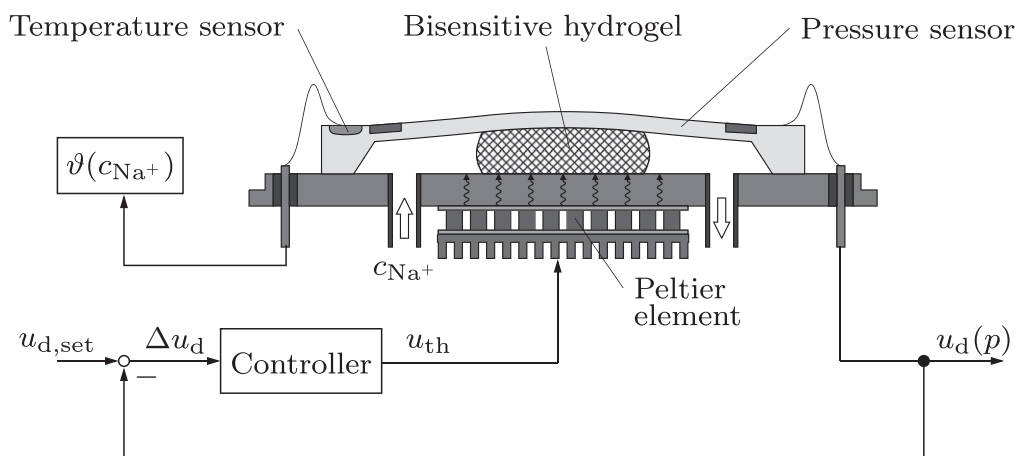
Figure 1. Piezoresistive hydrogel-based sensor embedded within a closed-loop configuration to perform measurements in force compensation mode. u_d is the pressure sensor's output voltage and is to be kept constant at a setpoint $u_{d,set}$ by controlling the Peltier element's input voltage u_{th} in a closed-loop control.

favorable regarding the operating range. Hydrogels based on AMPS are known to be sensitive to ion concentrations, e.g. sodium chloride.[17] Acrylic acid and methacrylic acid would also form NaCl-sensitive hydrogels when crosslinked, but AMPS-based hydrogels show a less pronounced cross-sensitivity to the pH value since AMPS is a strong acid.[18] Its pK_S value of 1.5 is comparatively low compared to the other two acids.[19] Hence, these two monomers were chosen to form the compensatory effective semi-IPN hydrogel. The semi-IPN synthesis steps are based on semi-IPN synthesis procedures from a previous work.[20]

For the synthesis of the bisensitive semi-IPN hydrogel NiPAAm (Acros Organics) was purified by recrystallization from n-hexane while AMPS (Sigma Aldrich), PAMPS (average molecular weight: 2,000,000 g mol^{-1}, mass fraction of the solution: 15 wt% in water, Sigma Aldrich), *N,N'*-methylenebisacrylamide (BIS, Merck) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA, Sigma Aldrich) were used without further purification. The initiator sodium peroxodisulphate (NaPS, Riedel-de Haën) was used as a 0.84 molar aqueous solution (1.00 g in 5.0 ml of water).

The semi-IPN was synthesized by redox-initiated free radical polymerization in water in an argon atmosphere. NiPAAm (1057.3 mg, 9.343 mmol), AMPS (59.9 mg, 0.289 mmol), BIS (59.4 mg, 0.385 mmol), PAMPS (363.3 mg of the solution) and NaPS (57.3 μl of the stock solution, 0.048 mmol) were dissolved in 7.9 ml deionized water. Sodium hydroxide solution NaOH (600 μl of a stock solution with concentration 1 mol l^{-1}) was added to have predominantly basic conditions. The solution was degassed and cooled in iced water for 10 min. After initiating the polymerization with TMEDA (7.3 μl, 0.048 mmol) the pregel solution with a total volume of 10 ml was filled into polymerization vials and cooled at 15 °C for 3 h. Finally, the semi-IPN hydrogel was cleaned for three days with deionized water to remove polymerization residues. This rinsing process includes a total of three changes of water after every 24 h. Finally, the hydrogels are undergoing a conditioning process based on three times swelling and deswelling in response to the temperature stimulus. The aim of gel conditioning is to break up short polymer chains that are formed between cross-linking points. Such a run-in process is necessary to achieve a high reversibility in swelling behavior.[21] The reaction scheme associated with the given synthesis is shown in Fig. 2. The material composition of the copolymer subnetwork is divided into approx. 97% NiPAAm and 3% AMPS, the weight proportion of the incorporated PAMPS chains is about 4.5% of the total polymer. Figure 3 illustrates the associated network configuration of the semi-IPN hydrogel consisting of the cross-linked copolymer permeated by the linear PAMPS polymer strands.

Characterization of the hydrogel properties.—A bisensitive hydrogel to be used in the intramolecular force-compensated sensor must meet the following requirements (Fig. 4):

1. The gel must be sensitive to the measured variable, i.e. the concentration of an analyte in solution. In this work, for the sake of convenience, an aqueous sodium chloride solution (NaCl) was used as the measured variable. Accordingly, the bisensitive gel should have a pronounced sensitivity to the ion concentration c_{Na^+}.
2. The gel must also have an additional sensitivity to the temperature. An operation close to room temperature of approx. 25 °C up to a maximum of 45 °C is considered appropriate when using Peltier elements.
3. A quasi-static compensation of the gel volume must be possible, i.e., there must be value pairs of ϑ and c_{Na^+} which excite to the same degree of swelling Q. This degree of swelling corresponds to a specific swelling degree Q_0 at the setpoint, which must be kept constant in case of compensation.
4. The relationship between the concentration c_{Na^+} and the compensation temperature ϑ at a specific reference swelling degree Q_0 should be linear in order to obtain a preferably linear sensor characteristic curve later on in the sensor's compensation mode.
5. The time-dependent volume change of the gel in response to the compensation stimulus ϑ should ideally occur much faster than the time-dependent volume change due to the ion concentration c_{Na^+}. In this way, a change of the gel volume can be counteracted sufficiently fast during the compensation mode so that an almost isochoric transition to the gel's new equilibrium state is possible (see exemplary trajectory in Fig. 4).
6. For the operation of the gel in the piezoresistive pressure sensor, the mechanical properties of the gel must be suitable. It must have sufficient strength to withstand the restoring force of the bending plate.

To examine whether the hydrogel [*net*-P(AMPS-*co*-NiPAAm)]-*sipn*-PAMPS fulfills these properties, samples of it were used to characterize its *static swelling behavior*, *dynamic swelling behavior* and *mechanical properties*. Experiments were conducted as follows:

Static swelling behavior.—The relationship between swelling degree, temperature and ion concentration is determined by measuring the static swelling behavior. The bisensitive free-swelling characteristics were measured by investigating the mass-based swelling degree Q_m as a function of c_{Na^+} and ϑ.[22]

For the preparation of the hydrogel samples, glass NMR tubes with an inner diameter of 3 mm were used as polymerization vessels.

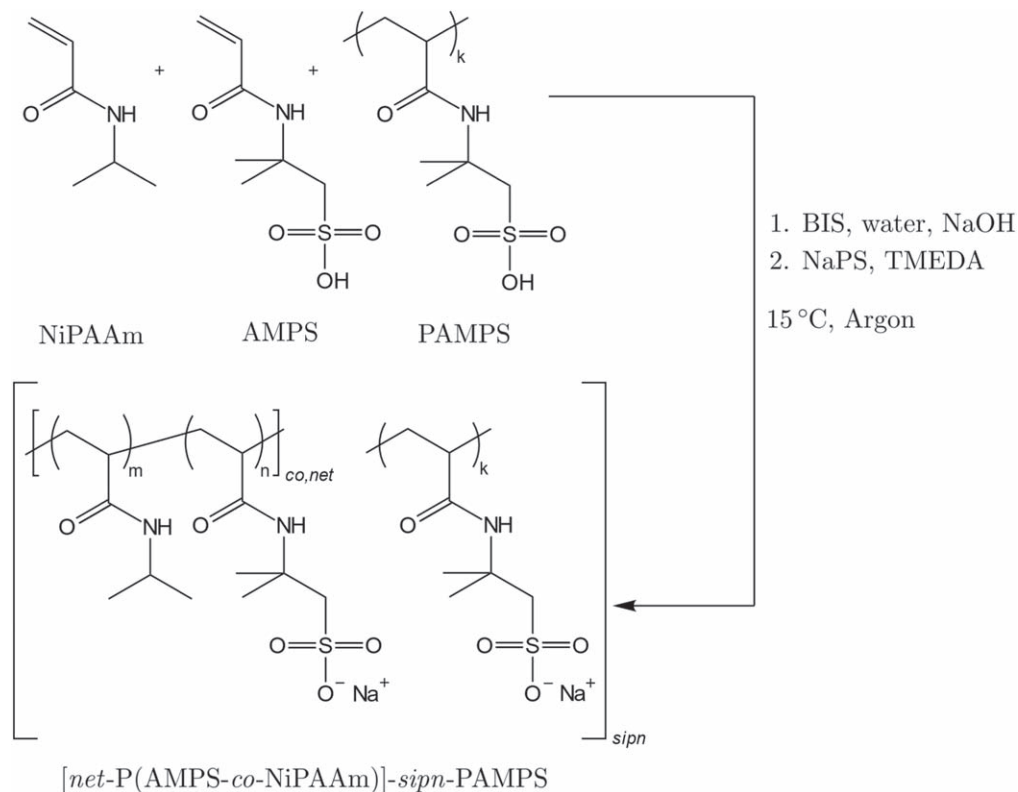**Figure 2.** Synthesis of the bisensitive semi-IPN hydrogel [*net*-P(AMPS-*co*-NiPAAm)]-*sipn*-PAMPS.

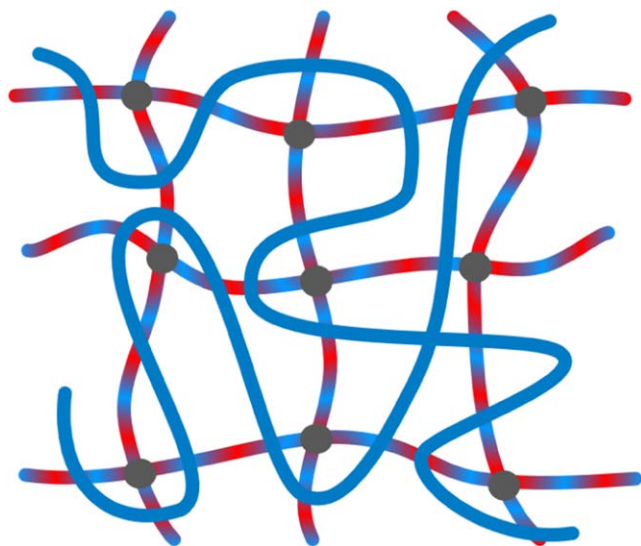**Figure 3.** Illustrative presentation of the network configuration of the bisensitive semi-IPN hydrogel [*net*-P(AMPS-*co*-NiPAAm)]-*sipn*-PAMPS.

The resulting long hydrogel cylinders were cut into pieces of 1.5 cm length. These hydrogel samples were air-dried and then each was placed in a screw-cap glass with sodium chloride solutions of different sodium ion concentrations. The concentrations used for the experiment were graded logarithmically equidistant within the range $c_{Na^+} = (0...1)$ mol l^{-1}. The second stimulus, the temperature, was applied in an oven (BR6000, Heraeus GmbH, uncertainty: ±1 K), in which the glasses with the gels in their respective solutions were stored. The temperature was varied in steps of 5 K over a temperature range from 55 °C down to 20 °C. For temperatures below room temperature, a thermostat (FBC 610, Thermo Fisher Scientific Inc., uncertainty: ±0.1 K) was used. Each tempering step

was followed by a 24-hour waiting period to ensure that the new degree of swelling was fully reached. The hydrogel samples were weighed with a laboratory balance (Sartorius CP224S, uncertainty: ±0.1 mg). Masses of the swollen hydrogel pieces m_g were determined as a function of the various ion concentrations across all temperature levels. This measuring procedure was followed by a three-fold rinsing process of the gels in deionized water. The hydrogel samples were thus freed from the ion stimulus, freeze-dried afterwards and then weighed to determine the dry mass m_p of the pure polymer. From the previously measured hydrogel masses m_g at the different swelling states and the dry mass m_p, the mass-based swelling degrees Q_m for each stimulus value pair of temperature and ion concentration were determined via the relationship

$$Q_m = \frac{m_g - m_p}{m_p}. \qquad [1]$$

Dynamic swelling behavior.—In order to assess the dynamic swelling properties, time-dependent changes of the swelling state due to abrupt temperature and concentration excitations were investigated. Qualitative statements about the swelling dynamics could be obtained from these experiments. For time-resolved measurements an optical measuring method using a light microscope and a camera was appropriate so the sample always remains in the solution and was continuously exposed to the stimulus.

For the time-dependent swelling tests, cylindrical hydrogel samples as described before were used. The diffusion-relevant characteristic length of the cylinder pieces corresponded to half the diameter of the cylinder. Hence, in this experiment the cylinder diameter was used as a measure of the change in the swelling state. The relative change in diameter was sufficient for evaluating the swelling kinetics.

A specially designed thermostatic bath was used as measuring stand, which was arranged under a light microscope (Bresser GmbH) with a camera (MikroCam Pro, Bresser GmbH). The measuring
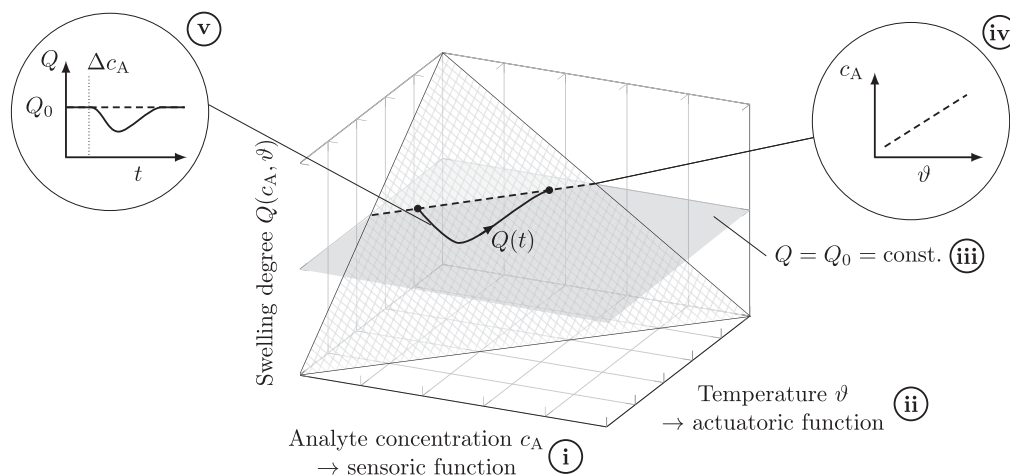
Figure 4. Illustration of the requirements on the swelling behavior of a force-compensatory effective hydrogel.

stand uses a Peltier element (BAT-PE-40-01, Belektronig GmbH), with which the sample tub was tempered. Pt1000 sensors were used as temperature sensors (BAT-TS-S200 and BAT-TS-K260, Belektronig GmbH). The driver of the Peltier element was a laboratory controller including control software (BTC-LAB-A200 and BTC Soft, Belektronig GmbH).

To record the step response, the hydrogel sample was first placed in an incubation oven (BD56, Binder GmbH) in an ion concentration bath for 24 h and pre-swollen at the desired initial values of the two stimuli temperature and ion concentration. Shortly before the measurement, the desired target concentration and target temperature of the solution was set in the sample tub of the measurement setup. The hydrogel sample was taken from the solution bath in the oven and exposed to the new pair of stimuli in the sample tub. The camera software (MikroCamLab, Bresser GmbH) took pictures of the hydrogel sample at defined intervals. After a duration of approx. 4 h the new equilibrium swelling degree was reached and the measurement was finished. From the individual images, the time-dependent change of the diameter $\Delta d(t)$ compared to the initial diameter d_0 was determined via the relationship

$$\Delta d(t) = \frac{d(t) - d_0}{d_0}. \quad [2]$$

Mechanical properties.—Compressive strength is used as a parameter to compare the mechanical load capacity of hydrogels.[23] It corresponds to the maximum compressive stress that a specimen can bear during a compression test.[24]

Cylindrical samples with diameters of more than 3 mm are typically preferred for the determination of the compression properties. The surfaces should be as smooth, flat and parallel as possible.[24] Hydrogel samples were therefore prepared with a cylindrical spacer made of Teflon with a thickness of 3 mm, which was placed between two cover glasses. Clamps fixed the cover glasses and the Teflon mould. The monomer solution was filled into the cylindrical cavity through a small opening so that hydrogels of defined layer thickness were formed. Finally, the desired hydrogel cylinders were obtained with a 15 mm diameter tissue punch. Before the compression measurement, the samples were excited with the stimuli. For the sake of simplicity these were a temperature stimulus of 23 °C (room temperature) and an ion stimulus of 0 mol l⁻¹ (deionized water).

The compression measurements were performed with a rheometer in plate-plate configuration (Anton Paar Physica MCR 301, force uncertainty: ±0.03 N). At a test speed of 0.6 mm min⁻¹ the hydrogel sample was compressed until it broke at a specific force F_B. The ISO 604 guideline for the determination of compressive properties recommends that for isotropic materials at least five specimens of each material specimen should be tested.[24] Therefore,

the measurement was repeated with seven different samples of the hydrogel.

Measurement Results and Comparison

The static swelling degree Q_m of the semi-IPN hydrogel [*net*-P(AMPS-*co*-NiPAAm)]-*sipn*-PAMPS is shown in Fig. 5a as a function of the temperature ϑ and the sodium ion concentration c_{Na^+}. The bisensitive swelling behavior is present over almost the entire measured concentration and temperature range. With increasing ion concentration the swelling capacity of this anionic hydrogel decreases due to the positive mobile Na⁺ counterions in the gel.[25] In addition, the local hydrophilic properties of the NiPAAm side groups are affected by increasing temperature.[26] At the highest measured ion concentration of $c_{Na^+} = 1$ mol l⁻¹ and the highest measured temperature of 55 °C the hydrogel is almost completely deswollen.

Figure 5b shows the results for repeated changes between two swelling degrees of three hydrogel samples over a period of twelve days. The swelling degree change was excited by temperature alternation, while the ion concentration was kept constant at a value of 0.032 mol l⁻¹. In principle, semi-IPN structure could potentially cause a separation of the long PAMPS chains from the copolymer network. However, the measurement indicates that either there is no significant leakage of PAMPS chains from the network or that such leakage does not significantly influence the swelling behavior. The measurement data show a reversible swelling behavior of the semi-IPN hydrogel, which is a basic requirement for an application in the sensor.

As the isolines of the same degree of swelling in Fig. 6a show, the required quasi-static compensation capability is given. Since the hydrogel always has the same volume along one of these lines, they can also be regarded as isochores. The isochores show that an equal degree of swelling can be achieved by different value combinations of ion concentration and temperature, i.e. that the ion-induced volume of the hydrogel can be compensated quasi-statically by corresponding temperatures. Figure 6b illustrates this with photographs of flat hydrogel cylinder discs. At a low ion concentration of 0.001 mol l⁻¹ and a high temperature of 50 °C a hydrogel disc has approximately the same diameter as at a high ion concentration of 0.1 mol l⁻¹ and a low temperature of 25 °C.

The isochores also represent the characteristic curves of the eventual intramolecular force-compensated sensor. Each isochor describes a relationship between the ion concentration c_{Na^+} to be measured and the compensation temperature ϑ, which would have to be set by the closed-loop control to maintain the current swelling state. The sensor characteristic curve $\vartheta(c_{Na^+})_{Q_m=\text{const.}}$ is thus dependent on the selected degree of swelling, which must be kept constant. The semi-IPN hydrogel exhibits an almost linear relationship
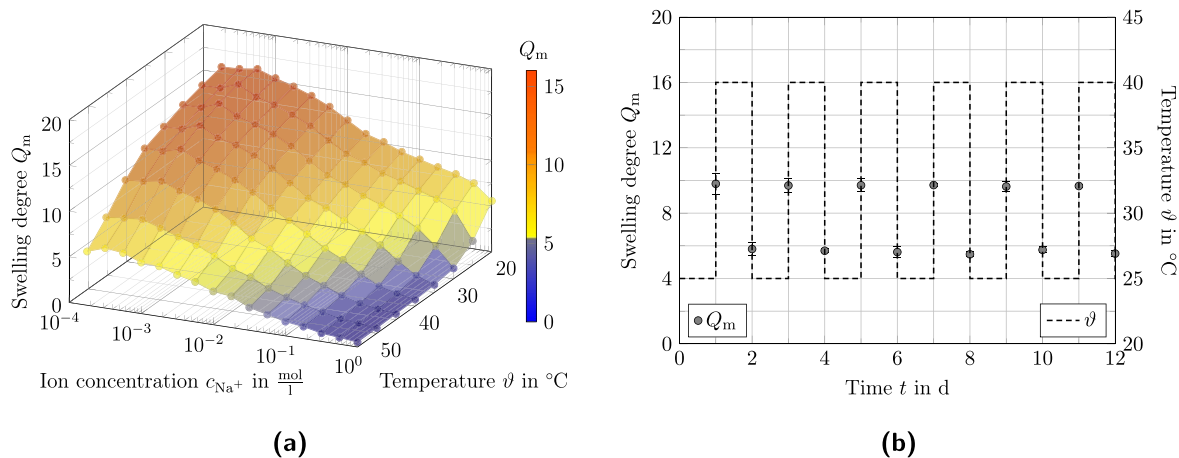
(a)

(b)

Figure 5. (a) Mass-related free swelling degree of the bisensitive semi-IPN hydrogel [*net*-P(AMPS-*co*-NiPAAm)]-*sipn*-PAMPS (relative uncertainty of the gravimetrically determined swelling degree for a 95%-level of confidence: 1.7%) as a function of ion concentration and temperature and (b) alternating between two temperature stimuli at time intervals of 24 h at a constant ion concentration of 0.032 mol l^{-1} to demonstrate reversibility ($n = 3$). For easier allocation, the individual measuring points are connected by lines.

between ion concentration (scaled logarithmically) and compensation temperature over a wide range. This is especially the case for an setpoint swelling degree which amounts to half of the highest measured swelling degree ($Q_{m,0} \approx 0.5 \cdot Q_{m,max}$). The linearity error of the characteristic curve for this setpoint swelling degree $Q_{m,0} \approx 8$ is smaller than 5 K in the range of (0.001...1) mol l^{-1}.

The requirements regarding the dynamic compensation properties for the semi-IPN hydrogel can be investigated by means of time-dependent swelling experiments as described above. Of special interest are the transient volume phase transitions between states of the same swelling degree as shown e.g. in Fig. 6b. For this purpose, a simultaneous, abrupt change of both concentration and temperature stimulus is applied, so that the final steady-state values of the swelling states remain the same. The hydrogel's step responses to these respective stimulus changes are shown in Fig. 7.

The measurement results lead to the following qualitative findings for the semi-IPN hydrogel used here:

- If the concentration-related swelling is compensated by temperature-related deswelling (•), the hydrogel diameter first decreases significantly after simultaneous application of both stimuli. Only after a longer period of time the degree of swelling levels off. This can be explained by the fact that a

deswelling temperature stimulus strongly dominates over the slower ion stimulus combined with a generally slower swelling process. In a preliminary test it was found that deswelling specifically for this hydrogel occurs generally faster than swelling. Therefore, the blue curve shows initially a temperature-induced deswelling, which is counterbalanced by the ion concentration stimulus after a longer period of time.

- If, on the other hand, the concentration-related deswelling is compensated by a temperature-related swelling (•), the processes balance each other in a way that the volume remains constant over the entire measurement period. This may be explained as follows: The concentration-induced deswelling process is characterized on the one hand by the slower stimulus but on the other hand by the generally faster deswelling. The temperature-induced swelling process, on the other hand, is characterized by the faster stimulus but, at the same time, the swelling that in principle occurs more slowly. As a result, both processes run at approximately the same speed, so that they equalize each other and the hydrogel volume remains constant.

The experiments show that a concentration-related swelling can be adequately compensated by a corresponding temperature input
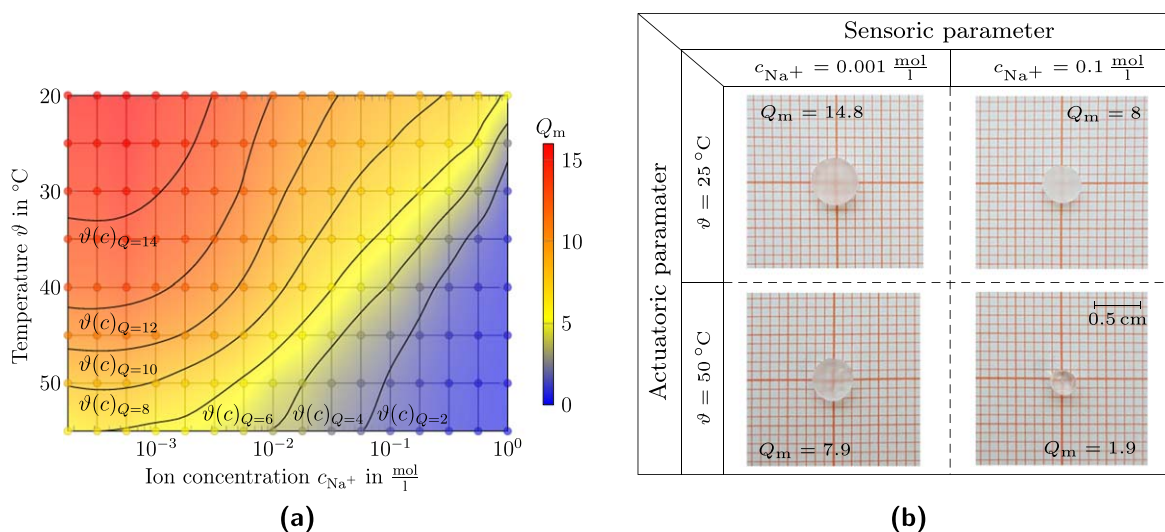

(a)

(b)

Figure 6. (a) Visualization of equivalence swelling degree contours, which represent potential characteristic curves for the sensor's force compensation operation (isolines result from a biharmonic interpolation of the measuring points) and (b) photographs of hydrogel samples at different swelling states, where the swelling state of $Q_m \approx 8$ is excited by two different concentration-temperature combinations.
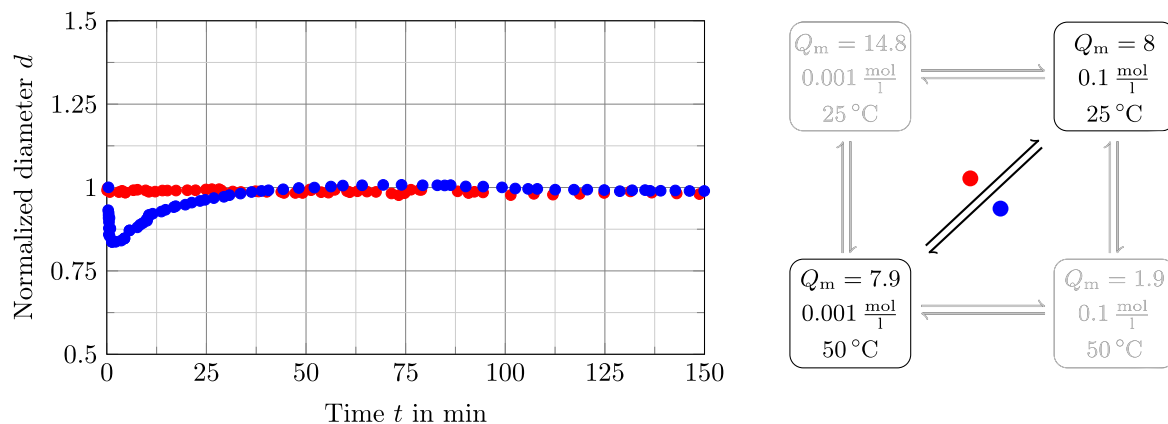
Figure 7. Time-dependent response of the normalized diameter of cylindrical hydrogel samples to a simultaneous change of the two stimuli ion concentration and temperature. The stimulus excitations are chosen so that the hydrogel volume is the same in the final steady-state values (see Fig. 6b).

without a concentration-related volume change occurring. It is always the temperature-related influence that dominates in the volume phase transition. The requirements on the dynamic swelling properties of the selected semi-IPN-hydrogel [*net*-P(AMPS-*co*-NiPAAm)]-*sipn*-PAMPS are thus fulfilled.

Table I lists further properties of the semi-IPN hydrogel and presents them in direct comparison to a hydrogel from a previous work which is also effective in force compensation.[10] The hydrogel

from the previous work is an IPN consisting of two interpenetrating copolymer networks based on AMPS and NiPAAm:

- Both hydrogels show similarly good linearity with respect to the property of a linear relationship between concentration and temperature at a defined setpoint swelling degree of $Q_{m,0} \approx 0.5 \cdot Q_{m,max}$.
- Regarding the compressive force F_B at breakage the maximum normal force of the rheometer of 40 N is achieved for all semi-IPN hydrogel samples. Thus, in terms of compressive strength, the

Table I. Properties of the semi-IPN hydrogel in comparison to a force-compensatory effective hydrogel from a previous work[10] (characteristic is strong (+), moderate (○) or hardly (−) pronounced).

Hydrogel	IPN [10]	semi-IPN
Identification	[*net*-P(AMPS-*co*-NiPAAm)]-*ipn*-[*net*-P(AMPS-*co*-NiPAAm)]	[*net*-P(AMPS-*co*-NiPAAm)]-*sipn*-PAMPS
Architecture		
Swelling behaviour		
Linear characteristic	+ Linearity error $< 5\,\mathrm{K}$	+ Linearity error $< 5\,\mathrm{K}$
Compressive strength	○ $F_B = (22.3 \pm 4.5)\,\mathrm{N}$	+ $F_B > 40\,\mathrm{N}$
Manufacturing steps	○ Two cross-linking steps	+ Single cross-linking step

mechanical properties of the semi-IPN hydrogel clearly exceed those of the IPN hydrogel. Possibly, this is due to a higher cross-linking density but also to improved elastic properties caused by the long PAMPS chains, which significantly reduce the brittleness of the hydrogel.

- In terms of manufacturing, the semi-IPN hydrogel synthesis requires considerably fewer process steps. In contrast to the sequential synthesis of the IPN, the fabrication of the semi-IPN can be performed in a one-step process. The PAMPS polymer strands are commercially available and can be simply added to the monomer solution. This simplifies the fabrication of the hydrogel transducer for the sensor drastically.

Conclusions

The measurement results show that the developed semi-IPN hydrogel fulfills the previously stated requirements for a force-compensating hydrogel: It exhibits excellent bisensitive behavior with almost linear sensor characteristics over wide concentration and temperature ranges, shows reversible swelling behavior and fulfills the targeted dynamic swelling properties. In contrast to the previously used IPN hydrogels, it has even a comparatively higher maximum compressive strength while, at the same time, offering significantly improved manufacturing properties for the sensor fabrication. Hence, the results prove the suitability of the novel hydrogel and lay the foundation for a simplified and reproducible fabrication of the hydrogel layer directly on the sensor's socket. The design and operation of intramolecular force-compensated hydrogel sensors containing this newly developed bisensitive hydrogel are subject of further research.

Acknowledgments

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