A Sensor for Measuring Gel Phase-Transition Temperature, with Potential as a Metal Ion Detector

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ABSTRACT: This paper describes a sensor employing a gel formed from an interpenetrating polymer network of poly(vinyl alcohol) and a copolymer of *N*-isopropylacrylamide and acrylic acid. This gel exhibits a continuous volume-phase transition that is strongly dependent on the presence of polyvalent metal ions in the gel solvent. A sensor apparatus has been constructed that estimates, in real time, the transition temperature of a gel. When this sensor is loaded with a gel sensitive to metal ions, it could be used to detect the presence and identity of metal ions in a solution.

INTRODUCTION

A gel is a three dimensional network of polymers suspended in a solvent. Polymer gels can be fabricated to exhibit a reversible volume change in response to variations in temperature, solvent composition, pH, magnetic field, and other stimuli (Tanaka, 1981; Tanaka et al., 1982; Jackson et al., 1997; Suzuki and Tanaka, 1990). This paper examines the application of a thermally responsive gel with a continuous phase transition. Curves of the equilibrium volume versus temperature for the gel studied in this paper are strongly affected by the presence of polyvalent metal ions in the gel solvent. We have constructed a sensor that exploits this property to detect the presence and identity of metal ions in solution. Loaded with other appropriate gels, this sensor apparatus could serve as the basis for a variety of gel-based sensor and assay techniques. It could be used, for example, to detect the presence of contaminants in ground water. It could also serve as a detector for the presence or absence of critical components in electroplating baths and other industrial or commercial chemical processing operations. In addition, it may be a useful device for studying the kinetics of mass transport in gels. The sensor apparatus described in this paper illustrates how the thermal, optical, and chemical properties of responsive gels can be used in unison to create intelligent systems and sensors with this material.

Interpenetrating polymer networks (IPN) containing *N*-isopropylacrylamide (NIPA), acrylic acid, and poly(vinyl alcohol) (PVA) were formed by free-radical copolymerization. In 100 ml of degassed, deionized water at 20.0 °C, we dissolved 2 g of 115,000 molecular weight poly(vinyl alcohol) (Aldrich), 7.24 g of recrystallized NIPA (Kodak), 340 μl of acrylic acid (Aldrich), 200 mg of sodium hydroxide (Aldrich), 80 mg of *N,N'*-methylenebisacrylamide (cross-linker, Bio-Rad), and 240 μl of tetramethylethylenediamine (accelerator, Bio-Rad). To initiate the polymerization, 16 mg of ammonium persulfate (Mallinckrodt) were added. Glass capillary tubes of 1.30 mm inner diameter were inserted into this solution prior to gelation. After gelation, the cylindrical gels were removed from the capillaries and washed for two weeks in distilled, deionized water. These gels will be referred to as IPN gels throughout this paper. Three IPN gel samples were then immersed in 0.05 M baths of copper chloride ($CuCl_2$), zinc chloride ($ZnCl_2$), and manganese chloride ($MnCl_2$), respectively. These samples were washed in the metal-chloride baths for several weeks.

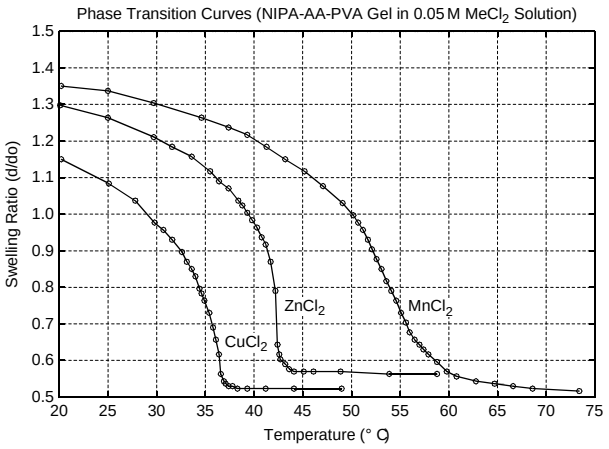

Fig. 1. Equilibrium phase transition curves.

Gels consisting purely of NIPA and a non-ionic cross-linker are well known to exhibit a nearly discontinuous volume-phase transition in response to changes in temperature (Hirotsu, 1987). IPN gels exhibit a similar, albeit more continuous, volume-phase transition. Figure 1 shows the equilibrium diameter of the three IPN gel samples versus temperature. Diameter measurements for each gel were collected sequentially from low to high temperature, allowing sufficient time at each temperature for the gel diameter to equilibrate. The interpolating lines in Figure 1 serve as a guide for the eye. In each case, the gels shrank

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continuously over the entire temperature range. However, the largest effects generally occurred in a single, relatively steep transition region, which is centered around a "transition temperature." The presence of acrylic acid in the gel causes the transition temperature to vary with the presence of metal ions as shown by Figure 1. We have observed similar results with metal-chloride bath concentrations as low as 10 μM.

Gels formed strictly from a NIPA/acrylic acid copolymer, with no PVA, also exhibit temperature induced phase transitions that are strongly affected by the presence of polyvalent metal ions. We have observed that the equilibrium phase-transition curves for these non-IPN gels may be discontinuous, depending on the specific metal ion introduced into the gel solvent. (See Figure 8 in the Discussion section.) However, gels formed without PVA were found to be too brittle for use in our preliminary experimentation. Hence, PVA was added to substantially increase the tensile strength of the gel and thereby ease sensor construction. The addition of PVA during the gelation process generally yields more continuous phase-transition curves, as illustrated in Figure 1.

ION-SENSITIVE GELS

The essence of designing a gel that responds to metal ions is the creation of a polymer consisting of two groups of monomers, each with a different role. One group of monomers is responsible for forming a complex with the metal ions, and the other allows the gel to reversibly stretch and shrink in response to temperature changes. The behavior of this system is similar to that of proteins with absorption sites, which consist of multiple molecular groups. Sites develop an affinity to target molecules when the molecules are in close proximity. When separated, the affinity diminishes.

The carboxyl groups of two acrylic acid monomers (CH_2=CHCOOH) in the NIPA/acrylic acid copolymer gel can form a complex with one divalent ion. In this gel system, proximity can be controlled through the reversible phase transition of the gel. At a fixed temperature, the copolymer gel collapses when the metal ion concentration exceeds a certain threshold. The absorption site can be destroyed when the gel is forced to expand through a temperature induced volume-phase transition. When the groups come closer, the absorption site is restored and can capture divalent metal ions. This process is illustrated in Figure 2.

EXPERIMENTAL SETUP

To detect the presence or introduction of metal ions in the gel solvent, it is sufficient to measure the phase-transition temperature of the IPN gel. A system was devised to measure, in real time, this phase-transition temperature. We exploit the fact that when the gel is cooled below its transition temperature, it swells and becomes optically clear. When the gel is heated above its transition temperature, it shrinks and becomes opaque. Figure 3 illustrates the experimental setup used for our prototype gel sensor. It is important to note two key components of the system: the peltier junction plates and the optical photosensor. A stacked pair of peltier junctions provides a mechanism to heat and cool the gel sample, and a photosensor provides feedback of the gel state by measuring the opacity change that accompanies the phase transition. The basic operating principle behind the sensor follows.

Control electronics provide feedback from the photosensor output to the peltier junction plates. If the gel is swollen and optically clear, feedback causes the peltier plates to heat the gel, inducing a phase transition from the swollen to the shrunken state. On the other hand, if the gel is shrunken and optically opaque, the peltier plates cool the gel, inducing a phase change in the opposite direction. This feedback arrangement leads to a continuous oscillation of the gel sample between the swollen and shrunken states. The average temperature experienced by the gel during this oscillation corresponds closely to the temperature of the "steep region" in the equilibrium phase-transition curve of the gel. Strictly speaking, the gel sensor performs its measurement through a decidedly non-equilibrium process of cyclic oscillations around a setpoint in the optical clarity of the IPN gel. We have, however, observed a good correspondence between the optical clarity and the physical diameter, or swelling ratio, of IPN gels throughout their phase-transition curve. Therefore, measuring the average gel temperature during this oscillation provides a direct estimate of the gel transition temperature.

Since direct, non-intrusive measurement of the gel temperature is difficult, a thermocouple temperature sensor was placed on the surface of the peltier junctions, in close proximity to the gel sample. The temperature at the peltier surface drives the oscillating gel phase transition, and its profile closely matches the temperature profile of the gel sample. A running average of the thermocouple temperature is used as the gel-sensor output. Thus, the output closely matches the average gel temperature, and it provides a good estimate of the gel transition temperature. Possible sources of error are presented in the Discussion section. Because the sample is kept in an oscillating

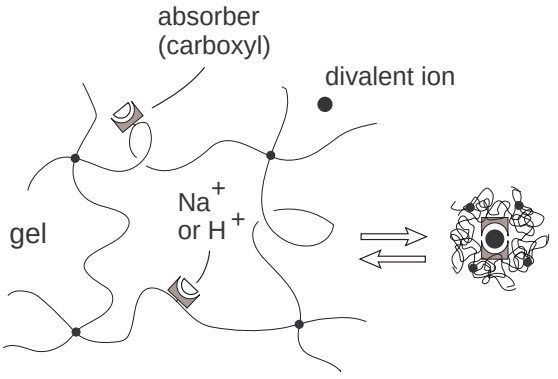

Fig. 2. Chelation of divalent metal ions.

state, the sensor outputs a continuous, real-time temperature estimate. This provides not only an estimate of the equilibrium phase-transition temperature, but also allows dynamic changes in the transition temperature to be observed.

Control of the gel sensor was accomplished using analog electronic circuitry. A block diagram of the system appears in Figure 4. The electronic system contains two control loops. An outer control loop uses a voltage comparator to test the photosensor output against a fixed reference voltage V_{ref}. The comparator output is amplified and used to drive current into or out of the peltier junctions, respectively increasing or decreasing their gel-side surface temperature. The temperature change induces a gel phase transition, and the accompanying optical change in the gel is detected by the photosensor. The closed loop is astable and leads to cyclic oscillations through the gel phase transition. A second, inner loop, acts to constrain the power through the peltier junctions, thereby safely limiting the maximum and minimum plate temperature.

Figure 5 shows sample experimental waveforms measured from the prototype system. The data was recorded while the system was in steady-state operation with a gel sample soaked in 0.05 M $CuCl_2$ solvent. Figure 5 (a) is the voltage applied across the peltier junctions. A positive voltage indicates heating, while a negative voltage indicates cooling. Figure 5 (c) is the resulting temperature as measured from the thermocouple mounted on the surface of the peltier junctions. Figure 5 (b) is the photosensor output subtracted from the reference voltage V_{ref}. Thus, positive and negative values of the voltage V_{err} indicate opaque and clear conditions, respectively. Lastly, Figure 5 (d) is the averaged, or low-pass filtered, peltier junction temperature T_{avg}. The figure indicates a steady transition

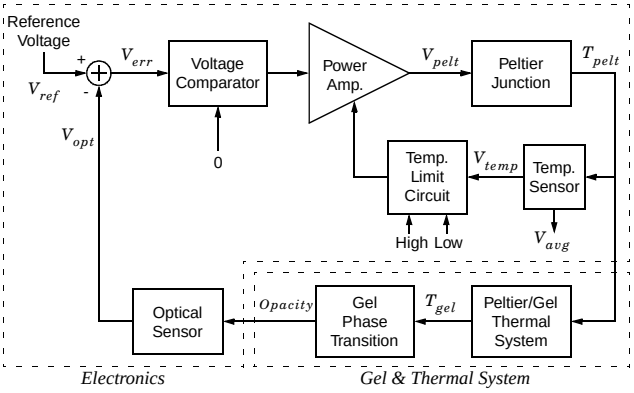

Fig. 4. Gel-sensor block diagram.

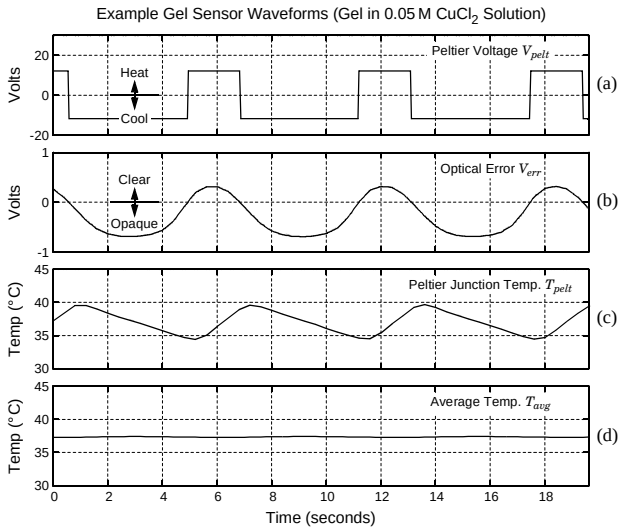

Fig. 5. Experimental gel-sensor waveforms.

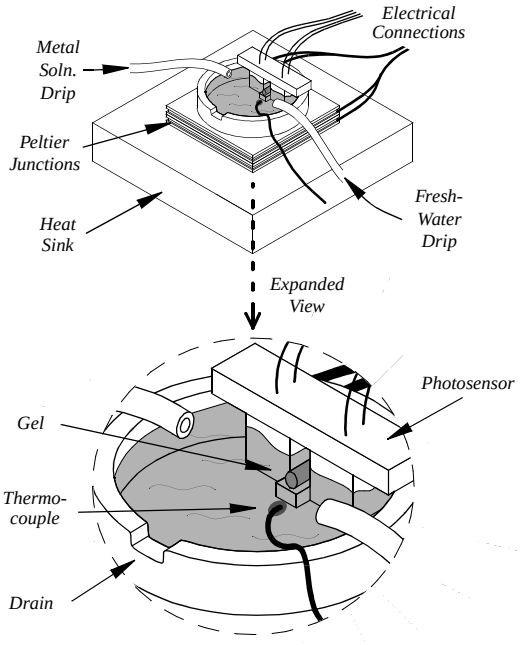

Fig. 3. Experimental gel-sensor.

temperature of about 37.3 °C.

Since the sensor outputs a continuous estimate of the gel transition temperature, it can be used to monitor dynamic changes in the phase-transition temperature of a gel. These changes could result, for example, from a change in the gel solvent composition. The results in the next section demonstrate that it is possible to detect the sudden introduction of polyvalent metal ions into the gel-sensor solvent bath.

RESULTS

The sensor described in the previous section was reloaded with an IPN gel that had been washed in deionized water, but never exposed to metal ions. Two drip lines, shown in Figure 3, are used to introduce fluids into the solvent bath, which surrounds the gel sample. The first line was used to provide a continuous drip of deionized water into the pool at a rate of approximately 0.35 ml per minute. A second drip line was used when needed to introduce a contaminating 0.05 M metal-chloride solution at a rate of approximately 0.14 ml per minute into the bath. Excess

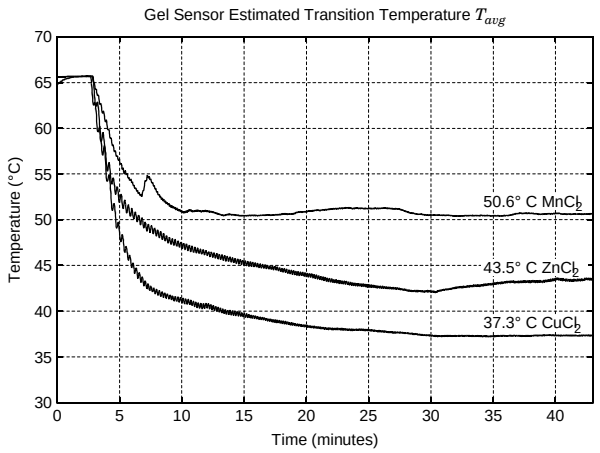

Fig. 6. Experimental dynamic gel-sensor output.

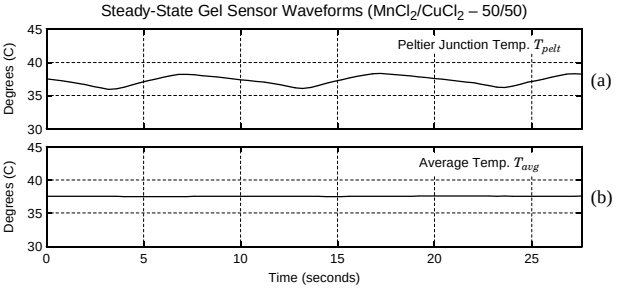

Fig. 7. Experimental gel-sensor output when exposed to a 50/50 solution of $MnCl_2$ and $CuCl_2$.

bath fluid drains from the pool through a drain port indicated in Figure 3, thus the bath volume maintains a nearly constant 2.5 ml.

Figure 6 shows the output of the gel sensor during the sudden introduction of a contaminating metal-chloride solution. The plots in Figure 6 show the averaged peltier junction temperature T_{avg} versus time for three different experiments. Each experiment was started with a fresh IPN gel in a pure, deionized water bath. Since the fresh IPN gel does not exhibit a phase transition below 66 °C, the control circuitry pins the temperature of the peltier junction at a maximum allowed temperature of 66 °C prior to the introduction of the contaminant drip.

A metal-chloride drip was initiated three minutes after the start of each experiment. Almost immediately after the drip was initiated, the outer surface of the IPN gel absorbed divalent metal ions, and, given the high initial temperature, the gel turned opaque. The sensor control circuitry responded by cooling the gel with the peltier junctions, thus initiating the astable temperature oscillation. As each experiment progressed, the gel sensor eventually reached a steady-state temperature that corresponded well with the equilibrium phase-transition temperature. The three curves shown in Figure 6 correspond, from top to bottom, to experiments with manganese chloride, zinc chloride, and copper chloride. The final steady-state sensor outputs T_{avg} for each experiment are 50.6, 43.5, and 37.3 °C, respectively.

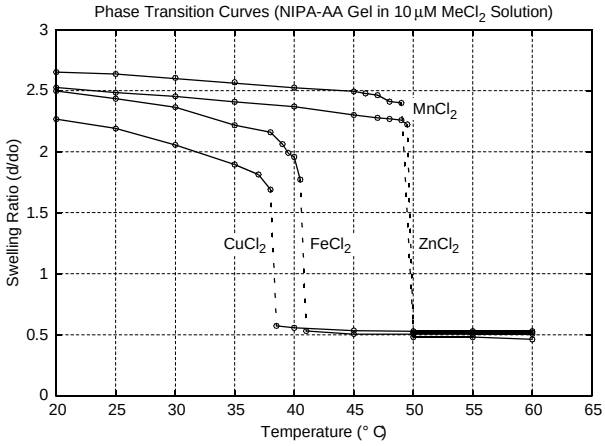

Fig. 8. Equilibrium phase transition curves.

Another experiment, shown in Figure 7, displays the steady-state response of the sensor after exposure to a mixed contaminating solution. In this experiment the contaminating solution was a 50/50 mix of 0.05 M copper chloride and manganese chloride. The steady-state output temperature T_{avg} from the sensor was 37.5 °C. The significance of this result is discussed further in the next section.

Once the IPN gel sensor has been exposed to a metal-chloride solution and a steady-state output temperature has been reached, the sensor will continue to oscillate about that temperature indefinitely (over 6 hours in our experiments) even after the metal-chloride drip is removed. Apparently, the metal ions remain chelated while the gel is in an oscillating state. The sensor effectively "latches" an exposure to a pulse of metal-chloride solution. We have cleared the IPN gel of chelated metal ions by washing the *swollen* gel in a 1 mM solution of sodium chloride for 60 minutes.

DISCUSSION

The steady-state temperatures from Figure 6 are consistent with the equilibrium phase-transition curves shown in Figure 1. Since the IPN gels exhibit continuous equilibrium phase-transition curves, it is difficult to define a specific "transition temperature." The mechanical ruggedness of these IPN gels made them attractive for the preliminary experiments reported here; however, they are not optimal for comparing the oscillatory, non-equilibrium output of the sensor with equilibrium phase-transition data. Gels with discontinuous phase-transition curves have clearly defined transition temperatures. This is illustrated by the experimental curves in Figure 8. Figure 8 plots the phase-transition curves for non-IPN gels soaked in four different metal-chloride solutions. The metal-chloride concentration was 10 μM in each case. Naturally, a discontinuous phase transition would make it easier to quantitatively judge the accuracy of the sensor output. However, either type of gel might be applied effectively in a practical sensor.

The repeatability of the sensor measurements are affected by a variety of error sources. The thermocouple temperature sensor is one source. Since it is located on the surface of the peltier junction plates, its reading may differ slightly from the temperature inside the gel. This error is a function of the temperature gradient from the surface of the peltier plates to the ambient environment. Future versions of the sensor might avoid this problem by placing the thermocouple inside an inert gel. An inert gel placed in close proximity to the active gel would not interfere with the operation of the sensor, and its temperature should mimic that within the active gel.

A second source of error stems from difficulties with the optical measurement. Outgassing from the water in the gel solvent bath generates bubbles, especially at higher temperatures. These bubbles may distort the optical path, and may also cause gross motions of the gel sample. The small hump that appears approximately 7 minutes into the $MnCl_2$ data in Figure 6 is typical of the error that results from gross movement in the gel position. We are developing an automatic gain control scheme to compensate for variations in the optical transmission path. Also, we expect that gross motions of the gel can be eliminated using a mechanical fixture, which might incorporate gel-bond film (Tokita, 1991) to firmly hold the gel in place.

The mechanism used by this sensor to detect metal ions in solution can be applied more generally to sense a variety of other substances or environmental changes. Any thermally-responsive gel that exhibits an optical change during its phase transition, and whose transition characteristics are affected by an environmental parameter of interest, could be used in the sensor. For instance, work is underway to develop gels whose phase-transition characteristics are strongly affected by the presence or absence of specific target molecules.

We have observed that when exposed to solutions containing equal concentrations of two different divalent metal ions, the response of the gel sensor is strongly affected by both the total and relative ion concentrations of the constituent ion species. For example, Figure 7 shows the steady-state output from the gel sensor after exposure to a (fairly high concentration) contaminant drip of copper chloride and manganese chloride in equal parts. The sensor outputs a temperature of 37.5 °C, which is very near the expected 37.3 °C output for a solution containing copper chloride only. Therefore, the sensing scheme used here does not necessarily allow the gel sensor to identify every individual constituent in a metal ion mixture.

We suspect that it may be possible to modify this scheme and use the gel as a chromatogram to identify the components in a mixture. For example, if the constituents of a given mixture exhibit different mobilities in the gel, the gel could serve as a chromatographic or electrophoretic media for separating the mix. As the mix separates, different regions of the gel should exhibit different phase-transition temperatures, which correspond to the local concentrations of the constituents. Multiple optical sensors could be placed along the length of the gel to scan the different phase-transition temperatures in different regions of the gel, thus identifying the components of the mix.

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