



## Behavior of thermo-sensitive gel in polymer solution



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### ABSTRACT

Particles of a thermo-sensitive gel were observed in a polymer solution. Gels of *N*-isopropylacrylamide (NIPA), which generally have a volumetric transition temperature of around 32 °C in pure water, were synthesized as porous media. The swelling ratio, mass ratio of a gel in the swollen state to that in the dry state, was measured in water as well as in an aqueous polymer solution of polyacrylamide at various temperatures. The observation in the polymer solution, where temperatures varied vertically between 10 °C and 40 °C from bottom to top, showed that gel particles repeatedly moved up and down.

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### 1. Introduction

Inverse natural convection [1] occurs in fluids with negative thermal expansion characteristics, that is, the fluid's density increases when heated and decreases when cooled. Heated fluid flows downward unlike conventional natural convection. The fluid is composed of a conventional fluid such as water and the functional particles, or fluidics, which have negative thermal expansion characteristics. If the density of the particles differs from that of the surrounding fluid, the particles move, generating flow. Kataoka and Yoshida [1] developed a particle using a piston and a cylinder filled with a compressible gas. The displacement of the piston could be changed by a shape memory alloy spring that alters its own shape owing to temperature changes. Consequently, the particle changes its volume while maintaining its weight. They found that the particles enhanced heat transfer between hot (85 °C) and cold (8 °C) water layers, which were initially stratified, in the experimental vessel. Yamaguchi and Takanashi [2] developed a different type of particle. They encapsulated air and a phase-change material separately in bellows-shaped vessels whose diameters differed from each other. These two vessels were connected end-to-end, whereby changes in the pressure inside the vessels caused them to exert force against each other and thus shift the position of the interface between them until reaching an equilibrium. When heated, the phase-change material in the smaller bellows expands more than the counter air, increasing the length of the shorter-diameter bellows. Thus, the entire volume of the two bellows decreases. We attempted to use a thermo-sensitive gel, which can be made in various forms or sizes with a simple mechanism, as the functional particle, absorbing and

releasing its surrounding fluid. The gel particles can be abundantly dispersed if needed; they move fluently through a complex flow field. Thermo-sensitive gels that change their characteristics, such as volume, have been widely studied as a drug delivery system [3,4] and as a separation mechanism [5,6]; in addition, they have been studied as functional materials in microfluidics [7,8]. One of the most popular gels is *N*-isopropylacrylamide, which has a volumetric transition temperature of approximately 32 °C [9].

When cooled and swollen, the gel has less density than that of the surrounding fluid. The gel particle rises to a warmer layer. The gel particle is then heated in the warm upper layer, and begins deswelling, thereby increasing the gel density. If the density increases beyond that of the surrounding fluid, the gel will move downward. The periodic movement is expected to continue as long as the system is heated from the top and cooled at the bottom. The density of the surrounding fluid has to be between that of a swollen gel and collapsed gel, which is higher than that of pure water. In the present study, we used an aqueous solution of polyacrylamide with an adequate concentration to help provide this required density. We detailed the preparation of the gel and obtained the swelling ratios (SR), mass ratio of gel between swollen and dried state, in a water and polymer solution. We reported observations of the gel particle's behavior in the polymer solution in a top-heated, small vessel where the temperature varied between 10 °C and 40 °C from bottom to top.

### 2. Experimental setup

#### 2.1. Preparation of gel and polymer solution

*N*-isopropylacrylamide (NIPA), the main component of the gel, shows a drastic volume transition at around 32 °C in water. NIPA gel becomes hydrophilic and swells under the lower critical solution temperature (LCST), and becomes hydrophobic and deswells above the

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LCST. The speed of volume change can be increased by preparing the gel particles as a porous structure [10–13]. We used dodecyl dimethyl benzyl ammonium bromide (DDBAB) as an initiator and ammonium persulfate (APS) to achieve a fast temperature response as shown by Zhao et al. [12,13]. The product of the reaction of DDBAB and APS, i.e., DDBAPS, is hydrophobic, and agglomerated during the reaction. In previous studies [12,13], the polymerization is assumed to occur only in the vicinity of DDBAPS agglomerations allowing the formation of macropores up to approximately 50  $\mu\text{m}$ .

The procedure for synthesizing the gel was similar to the procedure employed by Zhao et al. [12,13]. *N*-isopropylacrylamide (NIPA, Wako Chemical, Tokyo, Japan), *N,N'*-methylenebisacrylamide (BIS, Nacalai Tesque, Inc., Kyoto, Japan), *N,N,N',N'*-tetramethylethylenediamine (TEMED, Wako), APS (Nacalai Tesque), and DDBAB (Wako) were used as received. NIPA monomer, BIS, and DDBAB were dissolved in 1.5 mL deionized water. APS aqueous solution and TEMED were then added to the solution. The solution was injected into 1 mm and 6 mm i.d. silicone tubes, followed by polymerization in a refrigerator at around  $-18\text{ }^\circ\text{C}$  for a day to synthesize gels of different sizes. After polymerization, the synthesized gel was rinsed in deionized water to remove any unreacted monomer and other chemicals. As a polymer solution, the polyacrylamide (PAA) aqueous solution (molecular weight  $\sim 1500$ , 50 wt%; Sigma-Aldrich) was diluted with deionized water to 18 wt%, which was determined empirically, so that the gel particles float and sink at  $10\text{ }^\circ\text{C}$  and  $40\text{ }^\circ\text{C}$ . The density of the polymer solution was  $1.06 \times 10^3\text{ kg/m}^3$  at  $20\text{ }^\circ\text{C}$ .

Fig. 1 shows the gel rod polymerized in a 6 mm i.d. tube, in water and in a PAA solution. The mass of the gel in a dried state was 19.4 mg. The diameters roughly estimated with the images shown in Fig. 1 were 7.4, 6.4, 4.9, and 5.0 mm from Fig. 1(a) to (d), respectively. The SR of the gel rod in water and in a PAA solution is shown in Fig. 2. The swelling ratio was defined as the mass ratio between the swollen state and dried state. In water, the SR was 31 at  $5\text{ }^\circ\text{C}$  and gradually decreased as the temperature increased. Above  $30\text{ }^\circ\text{C}$ , the SR drastically decreased to 10.5 at  $33\text{ }^\circ\text{C}$ . At higher temperatures, it gradually decreased further. In the PAA solution, the SR was 21 at  $5\text{ }^\circ\text{C}$ , which was lower than that in water, because the PAA in the solution reduces the swelling (osmotic) pressure of the gel. In this case, the volume transition at around  $30\text{ }^\circ\text{C}$  was not observed. The SR continuously decreased and was coincident with that of the collapsed state in the water case, above  $33\text{ }^\circ\text{C}$ .

## 2.2. Experimental apparatus

Fig. 3 shows the main part of the experimental apparatus for observing particle movement. The width, depth, and height dimensions of the

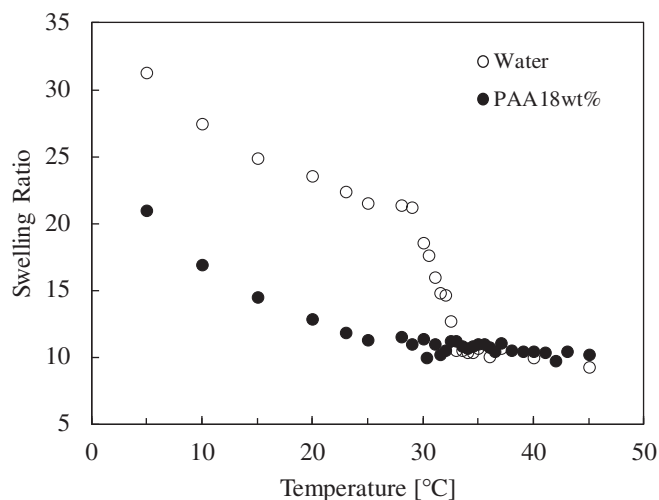


Fig. 2. Swelling ratio.

vessel, made of acrylic resin, are 16 mm, 16 mm, and 15 mm, respectively. The top and bottom walls were aluminum plates that were heated and cooled by thermostat water. During observation, the temperature of the top and bottom walls were maintained at approximately  $40\text{ }^\circ\text{C}$  and  $10\text{ }^\circ\text{C}$ . The tested gel, synthesized in a 1 mm i.d. tube, was cut in 1 mm length. Then, ten of the particles were set in the vessel with the PAA solution. The snapshots were taken at 20-s intervals.

## 3. Results and discussion

Fig. 4 shows the gel particles at 1-min intervals, commencing 145 min from the start. The bright blob on the left wall is the thermocouple covered by epoxy resin. It measured the middle point temperature at a near constant of  $25\text{ }^\circ\text{C}$ . The vertical locations referenced from the bottom of the four particles (here labeled A to D), which moved well during observation, are shown in Fig. 5. Particle A repeatedly rose and fell with a period of 10 min after the first 33 min of operation, without ever reaching the top heated wall. At 230 min, the particle adhered to the side wall and stopped moving. Particle B, which initially moved alone, attached itself to the agglomerated particles, including particle C. After the attachment, the particles kept turning in a constant location. It appeared that the particles interfered with each other's vertical movements. The movement of particle D was somewhat irregular because it

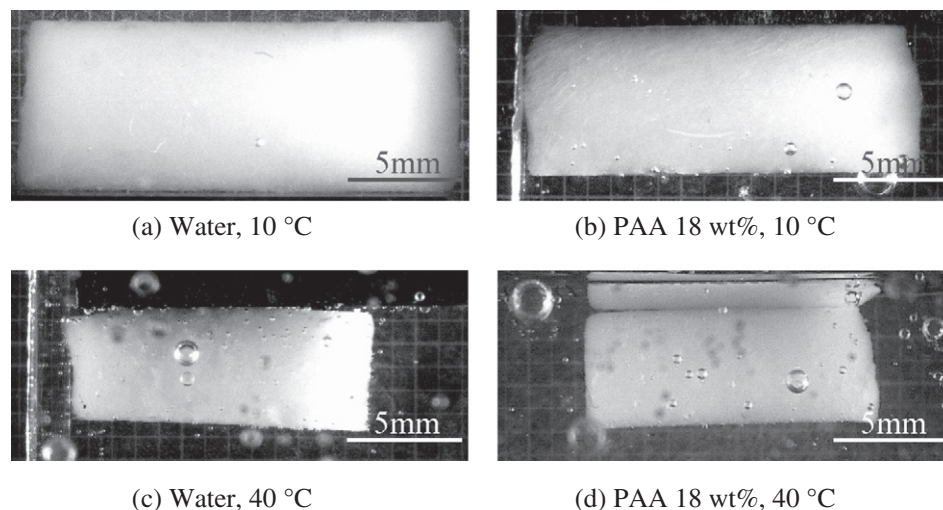


Fig. 1. Cylindrical gel in water and PAA solution.

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