

# Design and Preparation of Temperature Responsive Gels for Polymer Actuators

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We describe the design and preparation of a novel high-performance temperature-responsive polymer gels. A temperature responsive polymer was prepared by *in situ* polymerization of N-isopropylacrylamide (NIPAAm) and methacrylic acid (MAc) monomers in a dimethyl sulfoxide (DMSO) solution of poly (vinyl alcohol). The gels were prepared by casting DMSO solution of the polymers, changing MAc content. The gels swelled at temperatures below the lower critical solution temperature (LCST) of NIPAAm and shrank above the LCST. This phenomenon was observed reversibly. The maximum strain of the gel at temperatures between 15°C and 50°C was 50%. The maximum rate in swelling and in shrinking was  $7\% \cdot s^{-1}$  and  $12\% \cdot s^{-1}$ , respectively. The mechanical strength was 1.2MPa. The gel's properties in the temperature-response and mechanical strength are enough to use for polymer actuators.

Key words: Gel, Temperature, N-isopropylacrylamide, Poly (vinyl alcohol) , Polymer actuator

## 1. INTRODUCTION

Recently, several researchers have studied the preparation of "artificial muscle" which has a high degree of mobility and dexterity as well as natural muscle, using shape-memory alloy [1-8] and ceramic [9-11]. Some of polymer gels [12-15] swell and shrink in response to external stimuli, such as temperature [12-15], pH [16-18] and electric fields [19-21]. These gels also have potentials in applications for artificial muscles because they are soft, light and move with easy mechanism. For polymer actuators, a fast response is needed. Yoshida *et al.* [10] reported that a temperature-responsive hydrogel, in which poly(N-isopropylacrylamide) [poly(NIPAAm)] chains were grafted onto crosslinked networks, collapsed in about 20 minutes, while similar gels lacking the grafted side chains took more than a month to undergo full de-swelling. However, it still is difficult to make artificial muscles having fast response and high mechanical strength from polymer gels.

The aim of this study is the design and preparation of a novel high-performance gel to apply it to polymer actuators for robots and manipulators. Thus, we synthesize a temperature-responsive polymer from NIPAAm, methacrylic acid and poly (vinyl alcohol) [PVA]. Then, we prepare a temperature-responsive gels from the polymer and examine the relationship between the preparation conditions and the swelling behavior and mechanical strength of the gels. Our strategy to prepare high-performance gel is using reversible phase separation in a temperature-responsive gel consisting of

an interpenetrating network (IPN) of PVA and temperature-responsive polymers as shown in Fig. 1.

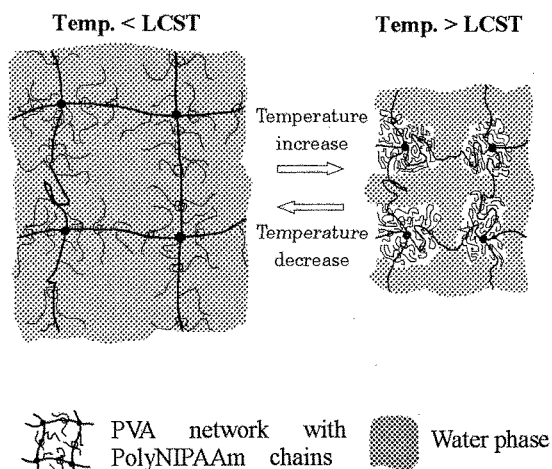


Fig.1 Schematic diagram of phase separation in interpenetrating polymer network of the temperature-responsive gel.

## 2. EXPERIMENTAL

### 2.1 Sample preparation

### 2.1.1 *In situ* polymerization

In order to obtain a temperature-responsive polymer, *in situ* polymerization of NIPAAm [N-isopropylacrylamide, Wako Pure Chemical Industries, Ltd.] and MAc [methacrylic acid, TOKYO KASEI] monomers was carried out in dimethyl sulfoxide [DMSO, Sigma Aldrich Japan] solution of PVA [poly(vinyl alcohol), Aldrich, Mw=85,000-146,000] using potassium peroxydisulfate as an initiator.

### 2.1.2 Preparation of temperature-responsive gels

Type I gels were prepared by casting DMSO solution of the polymer obtained. Type I(a) and type I(b) gels contain 9wt% and 16.7wt% of PVA, respectively. Type II gels were prepared by casting DMSO solution of mixed PVA and the polymer obtained. Type II(a) and type II(b) gels contain 16.7wt% and 23.1wt% of PVA, respectively. The gels were annealed at 160°C for 20min in order to crosslink physically. The MAc content,  $C_{MAc}$ , was changed to control the water content of the gels.

### 2.2 Measurement of the water content

The water content was measured as follows: the gels, weighted in the dry state, were immersed in an ion-exchanged water at several temperatures. The gels were removed from the water, tapped with filter paper to remove excess water on the gel surface, then the gels were weighted in the wet state. The water content,  $H$ , was calculated in term of

$$H \equiv \frac{(W_w - W_d)/1.0}{(W_w - W_d)/1.0 + W_d/1.3} \quad (1)$$

where  $W_d$  and  $W_w$  are the dry weight and wet weight, respectively, and 1.0 and 1.3 are the densities of water and the polymer.

### 2.3 Measurement of the gel's strain at different temperatures

The length of the gel,  $L_0$ , was measured in an equilibrium state in an ion-exchanged solution at 50°C. Then the gel was immersed into ion-exchanged waters at temperatures between 15°C and 50°C, and the length of the gel,  $L$ , under the conditions was measured. The strain of the gel is given from the following equation;

$$\text{Strain} \equiv \left( \frac{L}{L_0} - 1 \right) \times 100 \quad (2)$$

### 2.4 Measurement of the mechanical strength of the gels

The mechanical strength of the gels was determined with a table model testing machine (SHIMADZU, EZ-Test500N). In the static stress-strain curves, specimens with a nominal 20-mm-gauge length and 0.2-mm thickness were deformed in tension at a constant strain rate of 10mm/min at 25°C, and stress-strain data were determined to failure.

## 3. RESULTS AND DISCUSSION

Fig.2 shows the water content,  $H$ , of the gel as a function of temperature. The water content decreased from 0.84 at 10°C to 0.20 at 65°C with increasing the temperature. When the temperature is lower than the

LCST, the gels have high water content because the polyNIPAAm is hydrophilic. PolyNIPAAm become hydrophobic at the temperatures above the LCST so that the gels have low water content.

Fig.3 shows the water content at 25°C and 50°C as a function of the content of MAc,  $C_{MAc}$ . The water content 25°C increased with increasing  $C_{MAc}$  and had a maximum value when the  $C_{MAc}$  was 4.5wt%. The reasons why the water content has the maximum value are that the osmotic pressure of the gel increases with increasing  $C_{MAc}$  while the hydrogen bond between the amide groups of NIPAAm and the carboxyl groups of MAc also increases with increasing  $C_{MAc}$ . The water content at 50°C slightly increased with  $C_{MAc}$ .

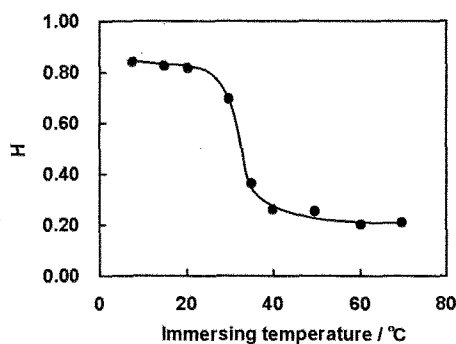


Fig.2 The water content of type I(a) gel,  $H$ , as a function of the temperature.

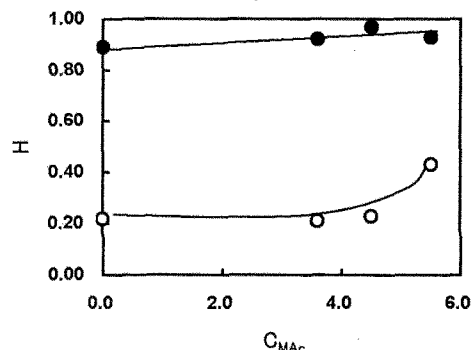


Fig.3 The water content of type I(a) gel,  $H$ , as a function of the MAc content,  $C_{MAc}$ . Temperature; ●: 25°C ○: 50°C

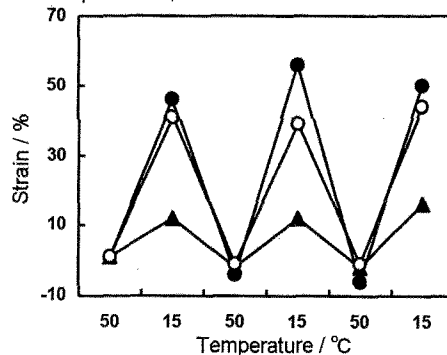


Fig.4 The strain of the type I(a) in response to the temperature changes.

▲:  $C_{MAc}=0.0\text{wt}\%$ , ●:  $C_{MAc}=4.5\text{wt}\%$ , ○:  $C_{MAc}=9.1\text{wt}\%$ .

Fig.4 shows the strain of type I(a) gels when the gels were immersed into an ion-exchange water at 15°C and 50°C for 3min. The gel swelled at 15°C and shrank at 50°C reversibly. The value of the strain depends on  $C_{MAc}$  and has a maximum value when  $C_{MAc}=4.5wt\%$ . At this MAc content, the difference of the water content between at 25°C and at 50°C has a maximum value as shown in Fig. 3.

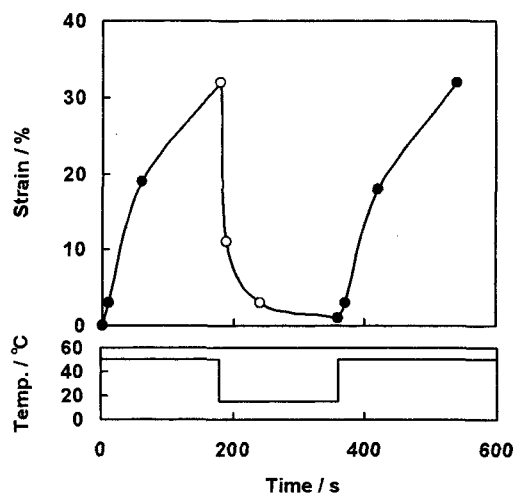


Fig.5 Time-strain curve of type I(a) gel in response to stepwise changes in the temperature between 15 °C and 50 °C. (PVA:9.1wt%, NIPAAm 86.4wt%, MAc:4.5wt%)

Fig.5 shows time-strain curve of type I(a) gel whose  $C_{MAc}$  is 4.5wt%. The initial rate of the gel in swelling and in shrinking,  $V_s$  was calculated from the strain-time curve in terms of,

$$V_s = \frac{\Delta Strain}{\Delta t} \quad (3)$$

From the time-strain curve, the maximum rate of the gel in swelling and in shrinking were  $7\% \cdot s^{-1}$  and  $12\% \cdot s^{-1}$ , respectively. This indicates that the gels have higher temperature-response both in swelling and in deswelling than the conventional temperature-responsive gels [10].

The stress-strain curve of the gel, whose data are not shown here, indicates that the mechanical strength of the gel was 0.02MPa. The value is not enough for polymer actuators. Therefore, we made temperature-responsive gels in various preparation conditions: type I and type II in order to make the gel having a higher mechanical strength and a higher temperature-responsive in volume change.

Fig.6 shows the stress-strain curves of type II gels changing PVA content. The maximum mechanical strength increased with increasing the PVA content because the degree of physical crosslinking increases with increasing PVA content. The maximum strength was more than 0.6 MPa even when the PVA content

was 16.7wt%.

Fig.7 shows the strain of type II gels in response to the temperature changes. This figure shows that the strain decreased with increasing PVA contents while the maximum strength of the gel increased with increasing PVA contents.

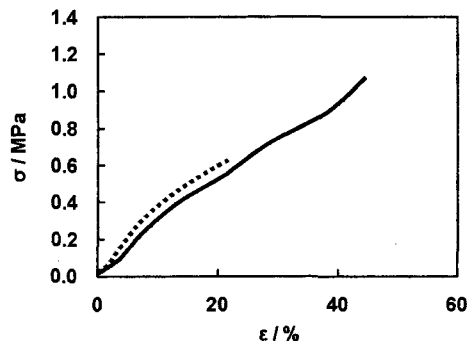


Fig.6 The stress-strain curves of type II gels changing PVA contents. PVA content; ... : 16.7wt%, — : 23.1wt%.

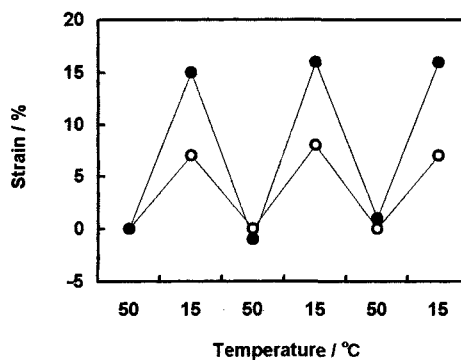


Fig.7 The strain of type II gels in response to the temperature changes. PVA content; ●:16.7wt%, ○: 23.1wt%.

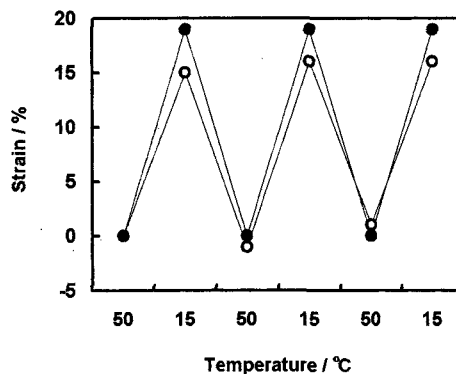


Fig.8 The strain of type I and type II gels in response to the temperature changes. ●: the data for type I gel, ○: for type II gel. (PVA:16.7wt%, NIPAAm:79.2wt%, MAc: 4.2wt%)

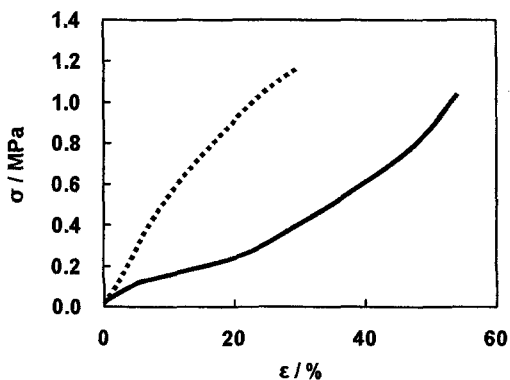


Fig.9 Stress-strain curves of type I and type II gels; ... type I gel, — type II gel.  
(PVA:16.7wt%, NIPAAm79.2wt%, MAc:4.2wt%)

Fig.8 shows the strain of type I and type II gels in response to the temperature changes. The strain of the type II gel was 15% while that of the type I gel was 20%. This indicates that the temperature-response of type I gel is larger than that of type II gel even though the two gels have the same PVA content. Fig.9 shows the stress-strain curves of type I and type II gels. The two type gels have almost the same mechanical strength of 1.1MPa while the Young's modulus of type I gel is larger than that of type II gel. These results show that the type I gel have higher temperature-response and higher Young's modulus than type II gel even though the two type gels contain the same PVA content each other. Type I gels are made from a 100% *in situ* polymer consisting of PVA and poly(NIPAAm) while type II gels are made from polymer blend of the *in situ* polymer and PVA. Hence, poly(NIPAAm) chains in the type I gel are located in the gel more homogeneously than in type II gels. This homogeneous location of the temperature-responsive chains will give the gels higher temperature-response in the swelling behavior.

#### 4. CONCLUSION

We prepared a temperature-responsive gels by *in situ* polymerization of NIPAAm and MAc monomers in a dimethyl sulfoxide solution of PVA and by casting dimethyl sulfoxide solution of the polymer obtained. The mechanical strength increased with increasing PVA content, while the strain decreasing with increasing of the PVA content. Type I gels which are made from 100% *in situ* polymer of PVA and poly(NIPAAm) have higher temperature-response and higher Young's modulus than type II gels which are made from polymer blend of the *in situ* polymer and PVA, even though the two type gels contain the same PVA content each other.

The maximum strain of the gels at temperatures between 15 °C and 50°C was 50%. The maximum rate

of the gel in swelling and in shrinking were  $7\% \cdot s^{-1}$  and  $12\% \cdot s^{-1}$ , respectively. These results indicate that the temperature-responsive gels in this study have higher performance for polymer actuators than the conventional temperature-responsive gels.

#### 5. ACKNOWLEDGMENT

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