# Effect of Varying Preparing-Concentration on the Swelling Behavior of Poly(N-isopropylacrylamide) Gels

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The preparing concentration dependence of the swelling behavior of neutral poly(N-isopropylacrylamide) gels has been studied. A series of gel samples were prepared varying the preparing concentration systematically with the same ratio of the concentration of monomer to that of crosslinker. It was found that the temperature dependences of equilibrium swelling ratio of these gels were different and there were the two types of gels; some change their volumes discontinuously and the others continuously around the transition temperature. The graph of the preparing concentration vs. the swelling ratio of the gels corresponds qualitatively to that of the pressure vs. the volume of the van der Waals gas. By using the theory of van der Waals gels the experimental results were analyzed.
Key words: volume phase transition, Flory-Huggins theory, LCST system, van der Waals networks

## 1. INTRODUCTION

The volume phase transition of poly(N-isopropylacrylamide) (PNIPA) gels has been studied very extensively[1]. However there are many unsolved problems. One of them, the shrinking behavior in high temperature, is interesting. It is known that the fitting analysis of *Flory-Huggins* type theory is not applied well for the high temperature phase separation in LCST system. Hence the analysis of gel shrinking with F-H theory is essentially difficult and has not been clarified. In the present study, in order to elucidate such a problem, the effect of varying preparing-concentration of PNIPA gels on the volume phase transition. By varying the preparing concentrations of monomer and crosslinker in pre-gel solutions, the different network structures of chemically crosslinked polymer gels are prepared by usual radical copolymerization. The swelling behavior around the volume phase transition may depend on the kind of network structure of the gels as well as the chemistry of polymer. However such a effect of the network structure has been hardly elucidated. Further, by using a recent progress of the elastic theory of *van der Waals* networks[2], the standard F-H type theory is modified to analyze the high-order interaction among network chain and solvent molecules.

## 2. EXPERIMENTAL

### 2.1 Preperation of PNIPA gels

Sample PNIPA gels were prepared by radical copolymerization of N-isopropylacrylamide (NIPA) monomer and N,N'-methylenebisacrylamide (BIS) crosslinker (Wako Chemicals Co.) in aqueous solution. To vary the prepared concentration of pre-gel solution, $\phi_0$, systematically, two mother solutions of the concentrations close to saturation were previously made. The compositions of mother solutions are shown in Table 1. Here $N_p$ is the apparent polymerization index calculated from the ratio of the total monomer to the crosslinker concentration at preparation as

Table 1: Compositions of mother solutions

| Code | NIPA (mg/ml) | BIS (mg/ml) | $\phi_0$ | $N_p$ |
|---|---|---|---|---|
| PNIPA40 | 79.2 | 6.63 | 0.170 | 40.7 |
| PNIPA200 | 79.2 | 0.265 | 0.166 | 204 |

Table 2: Preparing concentrations of L-series

| Code | $\phi_0$ | Code | $\phi_0$ |
|---|---|---|---|
| L01 | 0.0178 | L14 | 0.0583 |
| L02 | 0.0195 | L15 | 0.0639 |
| L03 | 0.0214 | L16 | 0.0700 |
| L04 | 0.0234 | L17 | 0.0767 |
| L05 | 0.0257 | L18 | 0.0840 |
| L06 | 0.0281 | L19 | 0.0920 |
| L07 | 0.0308 | L20 | 0.101 |
| L08 | 0.0338 | L21 | 0.110 |
| L09 | 0.0370 | L22 | 0.121 |
| L10 | 0.0405 | L23 | 0.133 |
| L11 | 0.0444 | L24 | 0.145 |
| L12 | 0.0486 | L25 | 0.159 |
| L13 | 0.0533 | | |

$N_p = (C_{NIPA} + C_{BIS})/(2C_{BIS})$, where $C_{NIPA}$ and $C_{BIS}$ are the molar concentrations of NIPA and BIS of pre-gel solution, respectively. Each mother solution was diluted with water to prepare the pre-gel solution with the same $N_p$.

In the present study, we prepared two series of PNIPA gels. One of them, L-series, was made from PNIPA40 mother solution of $N_p \cong 40$. Such a $N_p$ is the same of the standard PNIPA gels that have been studied. The other, K-series, was made from PNIPA200 mother solution of $N_p \cong 200$. The volume fractions at preparation of both L- and K- series are shown in Tables 2 and 3.

### 2.2 Measurement of swelling ratio

The gelation reaction was perform at 6°C by a common way, of which details were explained previously[3]. The equilibrium swelling-ratio of the swollen PNIPA gels was determined by cathetometer (accuracy 0.01mm). Before measurement the gels were kept at a temperature in 24 hours to wait for the swelling equilibrium.

Table 3: Preparing concentrations of K-series

| Code | $\phi_0$ | Code | $\phi_0$ |
|------|--------|------|--------|
| K01 | 0.0275 | K11 | 0.0684 |
| K02 | 0.0301 | K12 | 0.0749 |
| K03 | 0.0330 | K13 | 0.0820 |
| K04 | 0.0361 | K14 | 0.0899 |
| K05 | 0.0396 | K15 | 0.0984 |
| K06 | 0.0433 | K16 | 0.108 |
| K07 | 0.0475 | K17 | 0.118 |
| K08 | 0.0520 | K18 | 0.129 |
| K09 | 0.0570 | K19 | 0.142 |
| K10 | 0.0624 | K20 | 0.155 |

The diameters of the gels $L$ were measured. The apparent swelling ratio $\alpha$ was determined by $\alpha = (L/L_0)^3$, where $L_0$ is the inner diameter of the gel mold. The actual swelling ratio $Q$ was determined by $Q = 1/\phi = \alpha/\phi_0$, where $\phi$ is the volume fraction of swollen gels in equilibrium, and $\phi_0$ is that of as-prepared gels in preparation.

## 3. RESULTS AND DISSCUTION

### 3.1 Equilibrium swelling behavior of PNIPA gels in good solvents

The swelling behavior of the PNIPA gels in good solvent condition (25.0°C) is shown in Fig. 1. For polyacrylamide (PAA) gels, it was reported that $Q$ as a function of $\phi_0$ has a couple of regions[3]. In low $\phi_0$ region $Q$ decreases sharply as $\phi_0$ increases, while in high $\phi$ region $Q$ decreases gradually as $\phi_0$ increase. This nature is universally observed independently of the ratio of cross-linker to monomer; the swelling behavior is presented by the following experimental formula[3]:

$$Q = A\,(\phi_0 - \phi_g)^{-a}\, e^{-\phi_0/\phi_c} + \frac{B}{1 + (\phi_0/\phi_c)^b} \quad (1)$$

where $\phi_g$ and $\phi_c$ are the gelation and crossover volume fraction, $A$ and $B$ are constants. The previous results for the fittig this formula to the swelling behavior of PAA gels are also shown in Fig. 1. In comparison, the swelling behavior of the PNIPA gels is similar to that of PAA gels. In particular, PNIPA200 (K-series) directly corresponds to PAA200. On the other hand, PNIPA40 (L-series) is somewhat smaller than PAA40. We think they have the different characteristic sizes of network structure because the solubility and reaction ratio of monomers in gelation reaction are different.

### 3.2 Temperature dependences of the swelling ratio of PNIPA gels

The swelling curves of L-series gels are shown in Fig.2. The measurements of swelling ratio were made in heating process (1 plotted point/day). L-series gels undergo abrupt volume change around 33°C. For low $\phi_0$ gels, the discontinuous volume change was observed. As $\phi_0$ increases, the discontinuity of the volume change vanishes. For high $\phi_0$ gels, the volume change occurs continuously. From these
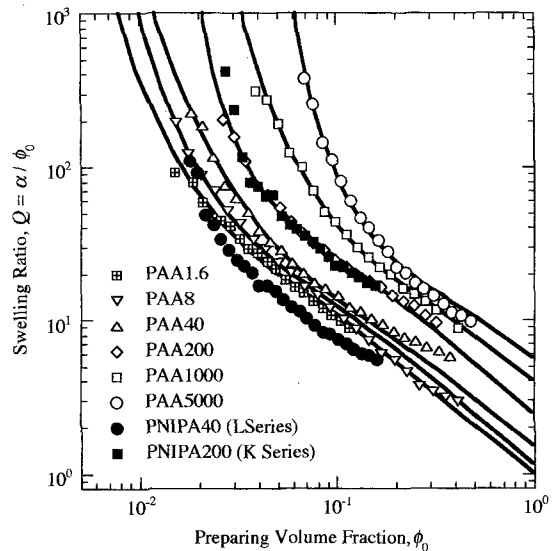


Fig.1: The equilibrium swelling behavior of the PNIPA and PAA gels. The closed symbols indecate the PNIPA gels prepared in the present study. The open circle symbols indicate the PAA gels in the previous study[3]. The solid curves are fitted to the experimental formula described in the text.
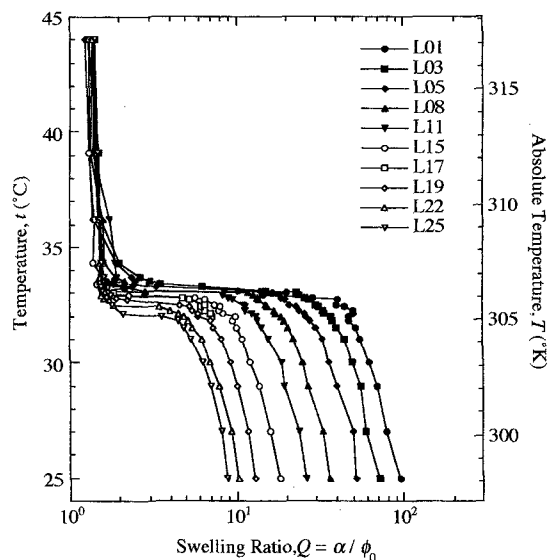


Fig.2: Temperature dependences of the swellling ratio of L-series PNIPA gels.

swelling curves, it is suggested that there are a critical point between discontinuous and continuous volume changes.

Hence we tried to plot the swelling behavior like as the $P$-$V$ graph of van der Waals gas (Fig. 3). By using such a plot, we can find a coexistent region of the discontinuous volume change and determine the position of critical point. From this results, the critical gels may be prepared at $\phi_0 \cong 0.12$ and this gel will reach near the critical point at $32.4 \sim 32.5$°C.

The swelling curves of K-series gels are shown in Fig.4. All K-series gels undergo the discontinuous volume change around 33°C. As $\phi_0$ increases, the discontinuity of the volume change
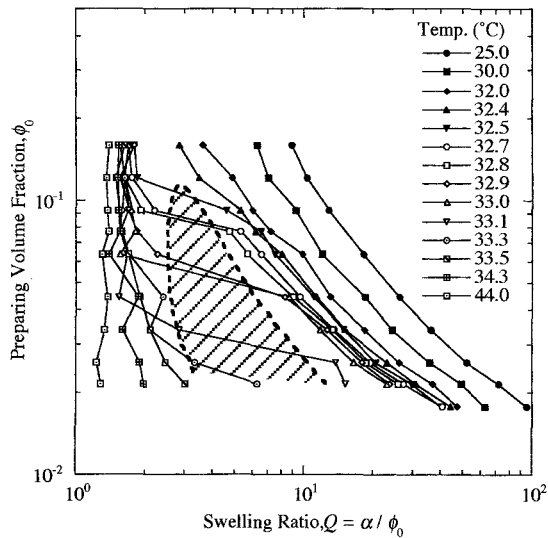
Fig.3: A trial plot of $\phi_0$ v.s. $Q$ for L-series gels. The shadowed area indicates coexistence region.



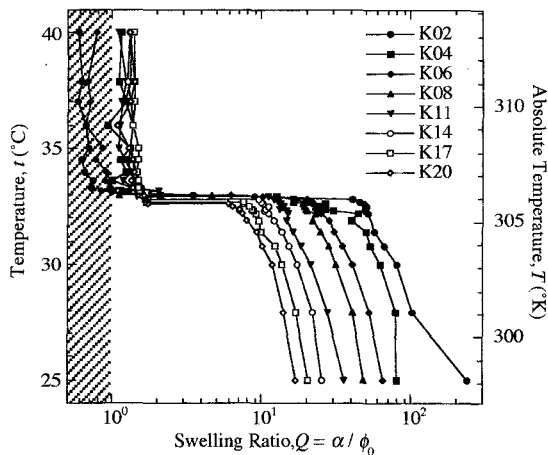Fig.4: Temperature dependences of the swelling ratio of K-series PNIPA gels.

tends to vanish. If one would make K-series gels at very high $\phi_0$, the volume change may occur continuously. However such a gel cannot be prepared because of the low solubility of BIS crosslinker. It is noted that for low $\phi_0$ gels, $Q$ becomes lower than 1 in their shrunken states. It seems to be an impossible situation. In actual, the gelation reaction may not go completely, then actual $\phi_0$ tends to decrease and the calculated $\phi_0$ becomes larger so that $Q$ is calculated to be smaller.

### 3.3   Theoretical analysis of swelling curves

The temperature dependence of swelling behavior has been usually analyzed with Flory-Huggins type theory. There is, however, a well-known problem of F-H theory, which can not be directly applied for LCST systems. In the present study, F-H type theory is modified on the analogy of a new elastic theory of van der Waals (VW) networks[2]. Here we start from

usual F-H theory. The elastic energy of gel network in F-H theory is presented by[4]

$$\Delta F_{el} = \frac{3\nu_c V_0 k_B T}{2} \left[ \left( \frac{\phi_0}{\phi} \right)^{\frac{2}{3}} - 1 - \frac{1}{2} \ln \left( \frac{\phi_0}{\phi} \right)^{\frac{2}{3}} \right]$$

$$(2)$$

where $\nu_c$ is the concentration of sub-chains of gel networks, $V_0$ is the preparing volume, $\phi_0$ is the preparing volume fraction, and $\phi$ is the volume fraction of equilibrium swollen gel. On the analogy of VW networks, the swelling ratio $(\phi_0/\phi)^{2/3}$ is modified as

$$\left( \frac{\phi_0}{\phi} \right)^{\frac{2}{3}} \rightarrow \frac{\beta \left( \frac{\phi_0}{\phi} \right)^{\frac{2}{3}} + (1 - \beta) \left( \frac{\phi_0}{\phi} \right)^{\frac{4}{3}}}{\beta \left( \frac{\phi_0}{\phi_m} \right)^{\frac{2}{3}} + (1 - \beta) \left( \frac{\phi_0}{\phi_m} \right)^{\frac{4}{3}}}$$

$$(3)$$

where $\beta$ is the ratio of the usual swelling ratio to the next-high order one and $\phi_m$ is the maximum of $\phi$.

On the other hand, the mixing energy of gel network in F-H theory is presented by[4]

$$\Delta F_{mix} = \frac{k_B T V}{v_0} \left[ \frac{\phi}{N} \ln \phi \right. $$
$$\left. + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right]$$

$$(4)$$

wher $V$ is the equilibrium volume of gel, $v_0$ is the segment volume of network chains, $N$ is the polymerization index of sub-chains of gel network, and $\chi$ is the interaction parameter. On the analogy of VW networks, $\chi$ is modified as

$$\chi \rightarrow \sum_{i=1}^{n} \chi_i \phi^{(i-1)}$$

$$(5)$$

where $n$ is the number of expansion.

To analyze the temperature dependence of the swelling behavior, we introduced the temperature dependence of $\chi$-parameter in the simplest way:

$$\chi_1 = \frac{\Delta h - T \Delta s}{k_B T}$$

$$(6)$$

where $\Delta h$ and $\Delta s$ are the microscopic enthalpy and entropy variations of the interaction between the network chain segment and solvent.

By using such a modification of F-H theory, we analyzed the temperature dependence of the swelling behavior of the PNIPA gels. Figures 5-7 show the analyzed results of L-series gels. In these figure, the numbers 1~4 means the expansion index of $\chi$-parameter, $n$. For low and intermediate $\phi_0$ gels, as shown in Figs. 5 and 6, the fitting goes well at $n = 1$. As $n$ increases, the fitting becomes better. However, the fitting tends to fail as $\phi_0$ increases. For high $\phi_0$ gels, as shown in Fig. 7, the fitting does not go well at all in small $n$. When we set $n = 4$, the fitting becomes somewhat good. From these results, as the preparing concentration of PNIPA gels,
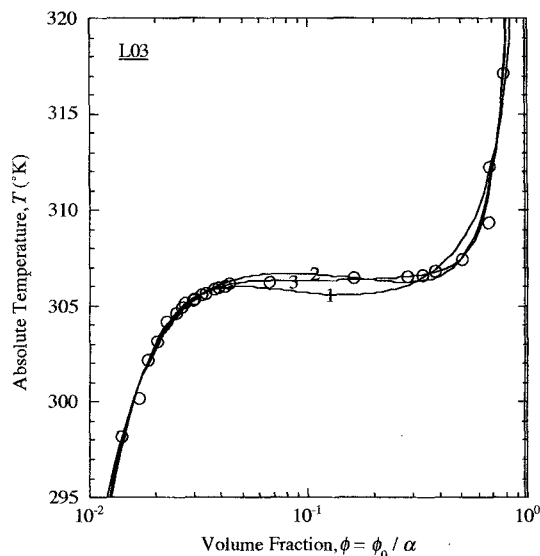
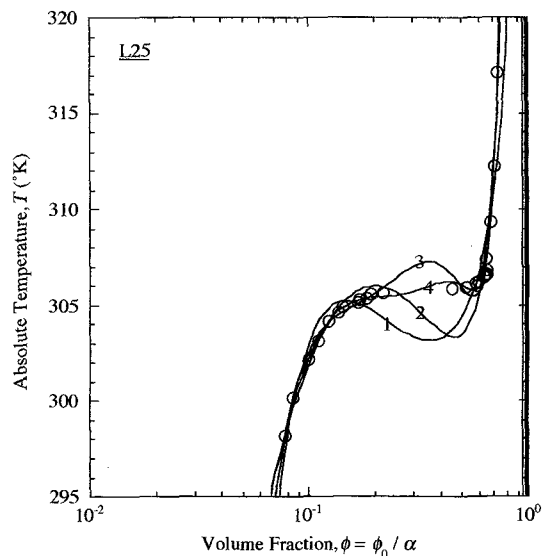Fig.5: Fitting of the experimental formulae to the swelling curve of L03.



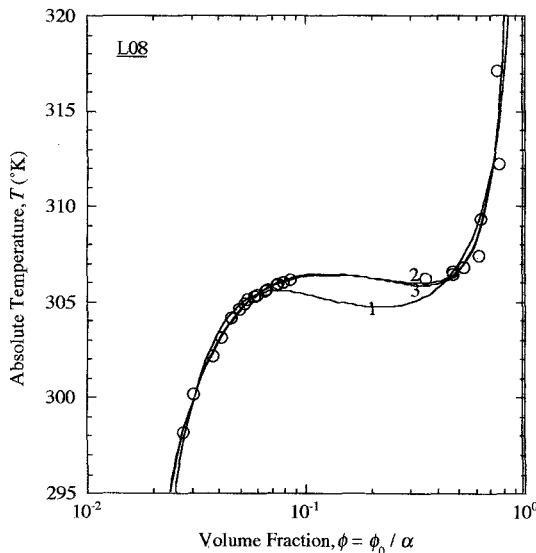Fig.7: Fitting of the experimental formulae to the swelling curve of L25.



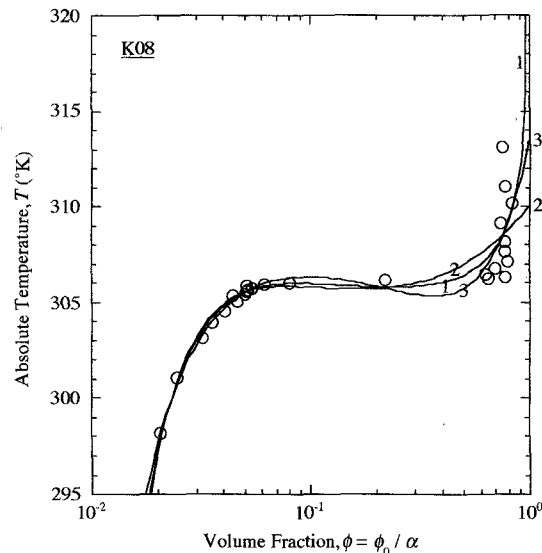Fig.6: Fitting of the experimental formulae to the swelling curve of L08.



Fig.8: Fitting of the experimental formulae to the swelling curve of K08.

*i.e.* $\phi_0$, increases, the higher order interaction among network and solvent molecules must be consider.

Figure 8 shows an example of the analyzed results of K-series gels. In this case, we found that the fitting does not go well in shrunken states. For K-series gels, as mentioned above, the calculated swelling ratio tends to be small so that $\phi$ at high temperatures becomes very close to 1. Thus it is impossible to fit the experimental formulae used in the present study to the experimental data. As this impossibility is theoretically interesting, we would like to consider it in the future studies.

## 4. CONCLUSION

The effect of varying preparing-concentration on the swelling behavior of PNIPA gels was

studied. In $N_p = 40$, the discontinuity of the volume phase transition can be controlled by the preparing concentration, $\phi_0$. For high $\phi_0$ gels, the volume change near $33°C$ become continuous. From the results of theoretical analysis, the high order interaction among network chain and solvent molecules is essentially important for high $\phi_0$ gels.

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