

## Equilibrium Volume Change and Elastic Properties of Poly(*N*-isopropylacrylamide) Gels Containing Latex Particles

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**ABSTRACT:** The equilibrium volume change and the elastic modulus of poly(*N*-isopropylacrylamide) (PNIPA) gels containing styrene-butadiene latex were investigated. It is considered that the presence of latex particles restricts the space for polymerization and which also affects on the elastic contribution of PNIPA gels. It was found that the swelling behavior of these gels was very similar to those found in the case of dependence of cross-link density. On the other hand, tensile modulus of the gels increased drastically, although these gels seem to be swelling enough. This anomalous increment of the elasticity is assumed to depend on the way to bind two elastic components, which are the highly dense PNIPA gel phase around the latex particles and the usual PNIPA gel network. It appears that the increment of elasticity against latex concentration could be classified into two mechanisms. The first, in the low latex concentration range, the dense gel phases are dispersed apart each other, the second, in the range of high latex concentration,  $C \geq 12.0$  wt%, the elasticity of the gel obeyed parallel model because of the formation of macro network with dense gel phases overlapped whole volume of gels.

**KEY WORDS** Poly(*N*-isopropylacrylamide) (PNIPA) Gel / Volume Phase Transition / Elastic Modulus / Latex / Macro Network /

The equilibrium volume change of poly(*N*-isopropylacrylamide) (PNIPA) gel was generally explained by Flory–Rehner's theory.<sup>1–4</sup> The gist of this theory is based on the integration of thermodynamics for polymer solution and statistical mechanics for rubber elasticity. These effects act on gel to dissolve its chains into solvent, on the other hand, to tug them together, thus they are called mixing and elastic contribution, respectively. The volume of gel, *i.e.*, concentration of polymer, is determined by the equilibrium condition of mixing and elastic contribution to the osmotic pressure of gels.

As far as the application to homogeneous polymer network is concerned, the conventional theory is useful semi-quantitatively. However, it is considered that the actual gel might be formed inhomogeneous network depending on the condition of polymerization or cross-linkage.<sup>5–8</sup> Therefore, manifold experiments in different conditions of polymerization remain as an important research to be discussed further.

In this report, we would like to propose PNIPA gel containing styrene-butadiene latex as an available gel to vary only the elastic contribution. It is expected that the latex particles would not affect on the mixing contribution to PNIPA chain like as the change of solvent composition. Moreover, the presence of latex particles

restricts the space for polymerization and which also affect on the elasticity of the gels. Thus, the artificial inhomogeneity induced by latex seems to be a valid method to study the nature of inhomogeneous network of gels.

### EXPERIMENTAL

#### *Sample*

Sample gels were prepared by usual free radical copolymerization in latex-aqueous solution. Latex beads, kindly supplied by Nippon Zeon Co., Ltd., is soap free styrene-butadiene latex (NIPOL SX1105). Their known diameter and density are 0.1  $\mu\text{m}$  and 1.02 respectively. Prepared concentration range of latex-aqueous solution,  $C$ , were 0–24 wt%.

First, the NIPA monomer (0.75 g) and *N,N'*-methylenebisacrylamide (BIS: cross linker, 4.5 mg) were dissolved in each latex solution (10 mL), secondly, *N,N,N',N'*-tetramethylenediamine (TEMED; accelerators, 1.25  $\mu\text{L}$ ) and ammonium persulfate (APS: initiator, 4.5 mg) were added to the solution. After stirring a minute, these pre-gel solutions were immediately transferred into test tubes with hematocrit tubes (inner diameter,  $d_0 = 1.2$  mm). These solutions were stored at about 5°C, 24 h. After gelation was complete, the

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cylindrical gels were put out of the hematocrit tubes by utilizing the temperature-induced shrinkage. These gels were washed in large amount of distilled water for more than 3 days to remove residual chemicals and unreacted monomers. These PNIPA gels containing latex particles were opaque, same as latex solution. It should be also added that the ideal mesh size of PNIPA gels is smaller than that of the latex particles.

#### Measurement of Length and Diameter of Gels

The cylindrical PNIPA gels containing latex were cut into same length of 50 mm at 20°C, and put into glass tubes (inner diameter: 2.5 mm) with distilled water. These tubes were set in the temperature controlled water bath. The temperature was regulated by personal computer (NEC PC9801US) within the error of  $\pm 0.05^\circ\text{C}$ . The length of gels were measured by using of available digital camera (CASIO QV300) which takes pictures as bitmap images automatically by intercommunication with the same PC in response to temperature. On the other hand, diameters of sample gels were measured by optical microscope (OLYMPUS BH2). Each gel were cut into length of about 10 mm and sealed in a sandwich glass cell. The sealed cell was on a temperature controlled stage with an accuracy of  $\pm 0.05^\circ\text{C}$ .

#### Tensile Modulus

In order to check the elasticity of the PNIPA gels containing latex particles, the gels were elongated with uniaxial tension by following method. Both ends of gels were strapped with thin nylon thread (diameter is about 0.1 mm), and a metal weight was attached to the bottom side of thread. These gels with the weights were hung into rectangular cell, which was filled with distilled water. The neutral length of the gels, that is the length between both knots without weight, was set into just 20 mm at 20°C in the swollen state. The prepared masses of metal weight were 0.1, 0.16, 0.22, and 0.28 g. The length and diameter of these elongated gels were measured by using of the above mentioned digital camera system.

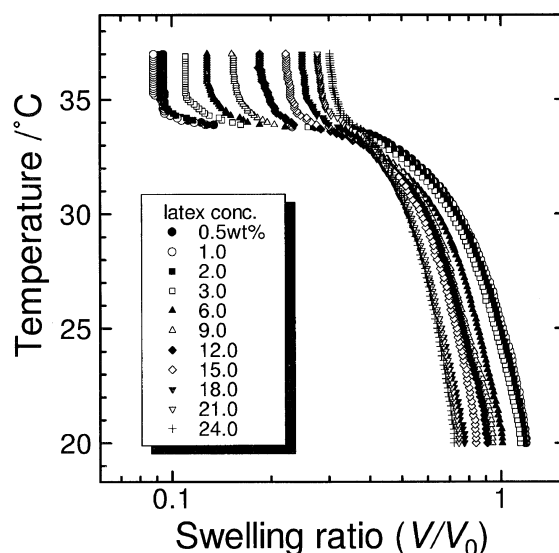
## RESULT AND DISCUSSION

#### Equilibrium Volume Change

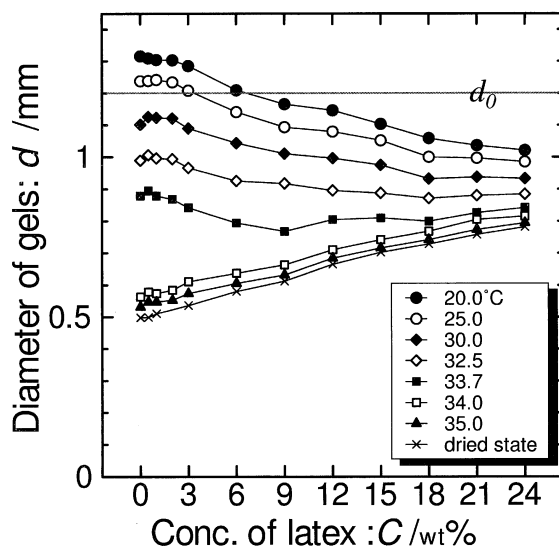
Figure 1 shows the temperature dependence of swelling ratios,  $V/V_0$ , of the PNIPA gels containing latex particles in the concentration range 0 to 24 wt%. The volume of gels,  $V$ , was calculated with a relation,  $V = \pi(d/2)^2l$ . The length,  $l$  and diameter,  $d$ , of the cylindrical gels were measured by different apparatus, as stated above. The volume of reference state,  $V_0$  was

defined as a volume of the preparation state, correspond to the inner diameter of hematocrit tube,  $d_0 = 1.2$  mm. In the swollen state, swelling ratios of gels decreased with increasing of latex concentration. Contrary, in the deswollen state, the ratios were increased, because of the volume occupied by latex particles. Therefore, total amount of volume change was reduced with increase of latex.

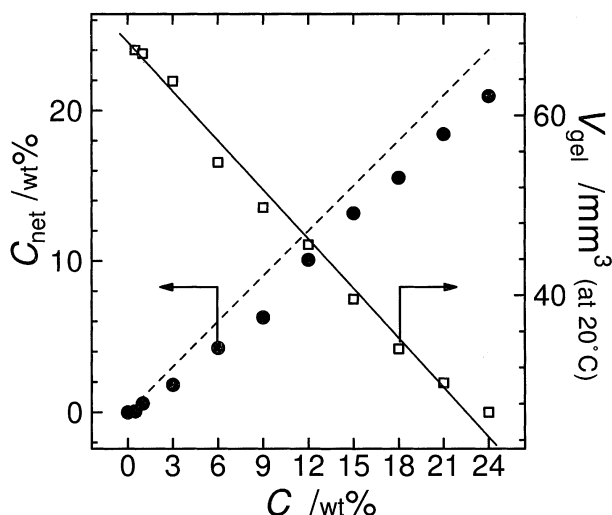
Figure 2 shows the diameter of the gels depending on latex concentration at several temperatures and in dried state. Here, we can make comparison between presence and absence of latex. There are little differences in swelling behavior of the gels, in the case of low concentration of latex (0–1.0 wt%). The volume of dried gel was just slightly smaller than the volume in the deswollen state.



**Figure 1.** Equilibrium volume ratio of PNIPA gels containing latex of various concentration.



**Figure 2.** The change in the diameter of PNIPA gels containing latex particles due to latex concentration.



**Figure 3.** The net concentration of latex contained in PNIPA gels and net volume of PNIPA gel in whole volume of gels (at 20°C) against concentration of latex at the preparation state.

It is seen from Figure 2 more clearly than Figure 1 that the volume of swollen gels decreased, and the volume of deswelling gels increased with an increase in the concentration of latex. It is considered that the former result caused by entanglement of PNIPA chain due to the decrement of the space for polymerization and adsorption of PNIPA chain onto the surface of latex particles. It might be inferred from the assumption of adsorption that PNIPA network aggregates to surface of latex particle as a high-dense phase,<sup>9,10</sup> and consequently, the partial dense phase of juxta-latex makes total volume of sample less than that of the normal swollen phase of PNIPA gel. On the other hand, the latter result indicates deswelling limit due to the volume of contained latex in the sample gels. So, it is supposed that the volume of samples in dried state is simply comparable to the sum of the volume of latex and PNIPA chains. Namely, the dried volume of PNIPA gel in the absence of latex (at  $C = 0$ ) is assumed to equal the volume of PNIPA in the gel.

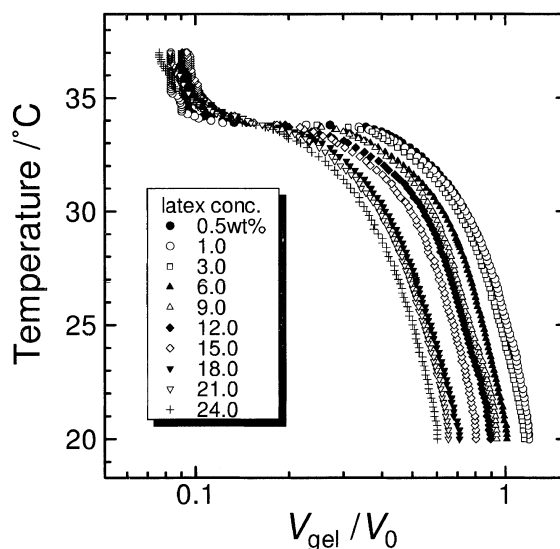
Now, we will separate net volume of PNIPA gels and volume of latex particles as follows. The net volume fraction of latex particles contained in the PNIPA network at the polymerization,  $\phi_{\text{latex}}$  may be defined as,

$$\phi_{\text{latex}} = (d_D(C)^3 - d_D(0)^3)/d_0^3 \quad (1)$$

where,  $d_D(C)$  denotes the diameter of dried gels as a function of latex concentration. This fraction can be rewritten as net weight percent of latex,  $C_{\text{net}}$  wt%, by use of density of latex,  $\rho = 1.02$ .

$$C_{\text{net}} \approx 100\rho\phi_{\text{latex}} \quad (2)$$

The net latex concentration  $C_{\text{net}}$  became less than initial concentration  $C$  as shown in Figure 3 (filled circle). Residual latex particles might flow out from PNIPA



**Figure 4.** The swelling ratio of net PNIPA gel in the whole volume,  $V_{\text{gel}}/V_0$ , as a function of temperature. network in progress of polymerization. Having known the net volume of latex, we now consider the net volume change of PNIPA network without volume of latex. The volume of net PNIPA network,  $V_{\text{gel}}$  is given by

$$V_{\text{gel}} = V - \phi_{\text{latex}}V_0 \quad (3)$$

The values of net volume of PNIPA network,  $V_{\text{gel}}$  against concentration of latex at 20°C were also plotted in Figure 3.  $V_{\text{gel}}$  was linearly decreased with increment of latex concentration. This linearity was kept over the range of swollen state. The solid line shows a calculated result by least squares method ( $V_{\text{gel}} = 68.2 - 1.83C$ ).

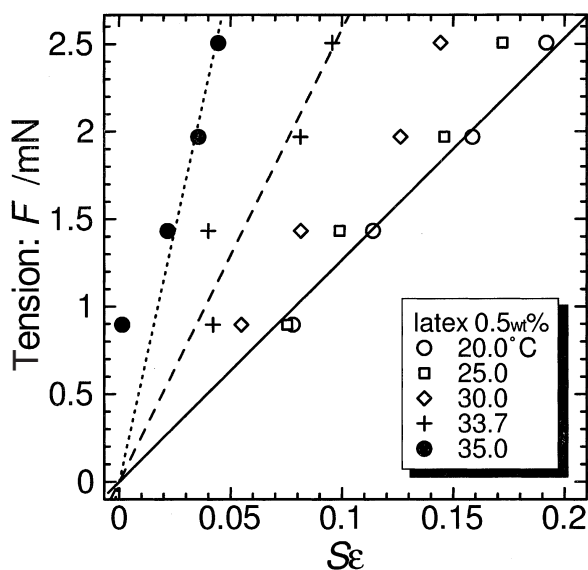
The temperature dependence of  $V_{\text{gel}}$  was shown as swelling ratio,  $V_{\text{gel}}/V_0$  in Figure 4. The swelling curves became more continuous with increase of latex concentration. Moreover, all lines cross at transition temperature,  $T_t = 33.8^\circ\text{C}$ , in spite of increment of latex particles. These results are similar to those found in the case of dependence of cross-link density.<sup>8,14</sup>

#### Elastic Modulus

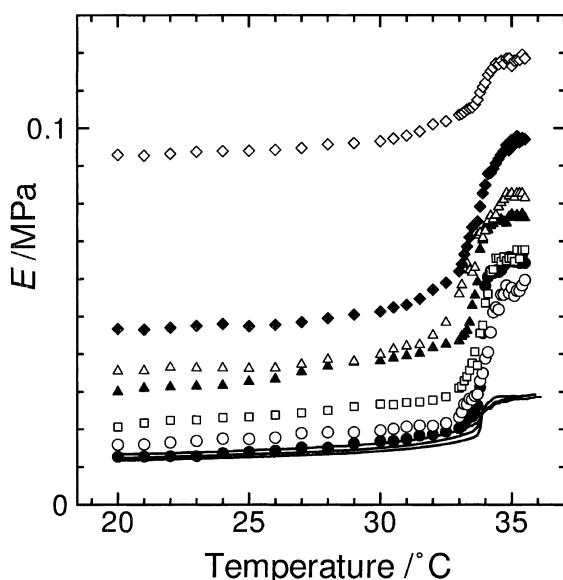
The tensile modulus was calculated with data of tensile strain,  $\epsilon = (l - l_0)/l_0$  and cross section of stretched gel,  $S = \pi(0.5d)^2$ , on the assumption of Hooke's law at each temperature,<sup>11</sup> where  $l_0$  denotes the contour length of gel without tension. The diameter of gels decreased in the similar way to the length, during heating process. Using of above data, the tensile modulus was calculated as follows,

$$E = \frac{F}{S}\epsilon^{-1} \quad (4)$$

We will give an example to show that our gels obeyed Hooke's law at this range of weight in Figure 5. The tension,  $F$ , was plotted against products of  $S$  and  $\epsilon$  of the gel containing 0.5 wt% of latex. Solid, dashed, and



**Figure 5.** A plot of tension against product of tensile strain,  $\epsilon$  and cross section of gel,  $S$ , for the sample containing 0.5 wt% latex. The straight lines were drawn by linear least squares method.



**Figure 6.** Temperature dependence of tensile moduli of PNIPA gel containing latex. Every symbols denote the concentration of latex as same as Figures 1 and 4. The solid lines are calculated result by using of swelling ratio.

dotted lines represent calculated result by linear least squares method, at 20.0°C, 33.7°C, and 35.0°C, respectively. Here, the moduli,  $E$ , were obtained as slopes of these lines. In the state of swollen and deswollen, each data were in good agreement with Hooke's law. However, around the volume phase transition point, the tensile strain uncertainly varied due to the drastic volume change.

And then, the tensile moduli of the sample gels were calculated at each temperature, as shown in Figure 6. These moduli increased markedly with increment of latex especially in the swollen state. On the other

hand, against temperature, they show upturns beginning around  $T_t$ .

The tensile modulus,  $E$ , is related to bulk modulus,  $K$ , and shear modulus,  $G$ , by the following equation.<sup>12</sup>

$$E = \frac{9KG}{3K + G} \quad (5)$$

This equation can be rewritten by use of Poisson ratio,  $\sigma$ , which is obtained experimentally.

$$E = 2G(1 + \sigma) = 3K(1 - 2\sigma) \quad (6)$$

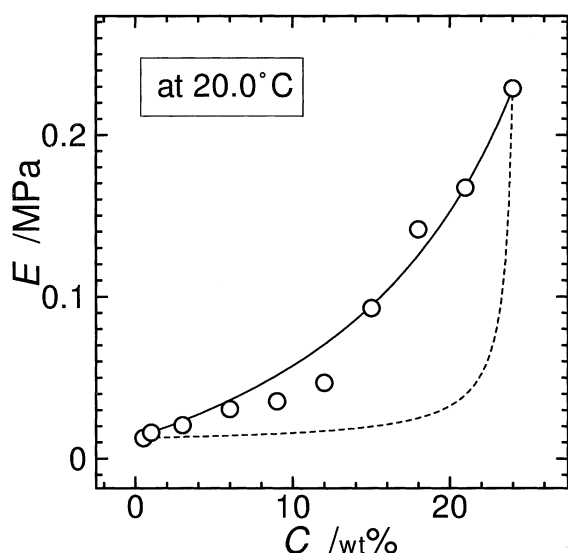
According to Flory–Rehner's theory,<sup>13</sup> the shear modulus is given by

$$G = \frac{N_c k T}{2V_0} (\phi/\phi_0)^{1/3} \quad (7)$$

On the other hand, the bulk modulus for gels are likewise given by

$$K = kT \left( \frac{N_A}{v_1} \left( \frac{\phi^2}{1 - \phi} - 2\chi\phi^2 \right) + \frac{N_c}{V_0} \left( \left( \frac{\phi}{2\phi_0} \right) - \frac{1}{3} \left( \frac{\phi}{\phi_0} \right)^{1/3} \right) \right) \quad (8)$$

Where  $k$  is Boltzman constant,  $N_A$  is Avogadro's number,  $v_1$  is molar volume of solvent and  $N_c$  is number of partial chain between the cross-linked points. The volume fraction of polymer in the gel at a given state,  $\phi$ , and at the reference state,  $\phi_0$  have a relation to the swelling ratio as  $(\phi_0/\phi) \equiv (V/V_0)$ .  $\chi$  represents Flory's interaction parameter (a function of temperature). Although the value of  $\chi$  can be calculated roughly from comparison to the data of swelling ratio, it is difficult to determine the value quantitatively. The modulus of the gel is usually discussed with the bulk modulus. However, we would like to discuss with shear modulus,  $G$ , to avoid using of this uncertain  $\chi$  parameter. We tried to calculate the value of tensile modulus by former relation of eqs 6 and 7 based on Flory-type theory. The structural parameter  $N_c$  cannot be estimated from stoichiometric relation between NIPA monomer and BIS, because of the possibility of entanglement. Note that each of our gel contains NIPA and BIS in the same ratio. Here, the value of  $N_c k/V_0$  was fixed in  $1.7 \times 10^{-5}$  for agreement with the modulus data in order to estimate the dependence of swelling ratio caused concentration of latex on the tensile modulus. For the calculation, the swelling ratios,  $V_{gel}/V_0$ , were substituted into eq 7. The Poisson ratio of sample gels were almost constant value 0.25 and 0.4 for swollen ( $T < T_t$ ) and deswollen state ( $T \geq T_t$ ), respectively. Although the Poisson's ratio was reduced around the transition temperature, the negative Poisson's ratio was not observed.<sup>13</sup> The solid lines in Figure 6 show the results



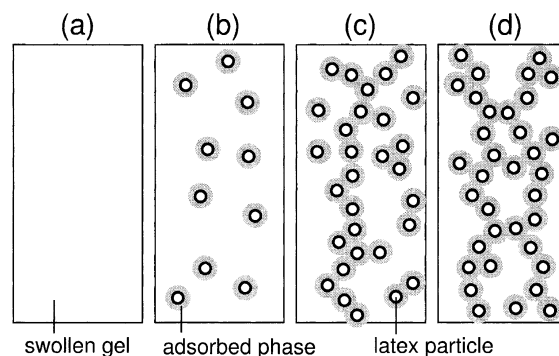
**Figure 7.** A plot of tensile modulus against concentration of latex. The solid line and dashed line represent calculated values based on the assumption of additivity of the elastic moduli as parallel model and series model, respectively.

of calculation for the case of  $C = 0.5, 6,$  and  $15$  wt%. Consequently, the calculated values were less than the experimental value. It is thought that the restriction of space for polymerization and interaction between PNIPA chain and the surface of latex particles make the network entangle in the presence of latex. Therefore, to realize the increase of tensile modulus with increment of latex, it should be assume that the number of pseudo-crosslinking points,  $N_c$ , is increased severalfold with increment of latex concentration. However, since the difference of the moduli at the swollen state and the deswollen state become less with increase of latex,  $N_c$  should not be increased evenly in the both states. Now, we thus discuss the dependence of concentration of latex on the tensile modulus on the isothermal condition.

Figure 7 shows the dependence of concentration of latex on the tensile modulus,  $E$ , of the gels. Here we try to discuss these results by use of the complex law for elastic composition. The additivity of two elastic moduli,  $E_1$  and  $E_2$ , is assumed with the following general relation.<sup>14</sup>

$$E^n = \phi_1 E_1^n + \phi_2 E_2^n \quad (9)$$

Where,  $\phi_1$  and  $\phi_2$  are volume fractions of each composition. This equation represents the so-called parallel model at  $n = 1$  and series model at  $n = -1$  for elastic composites. For simple application of this model to the experimental results, we assume that the part of the net PNIPA network in the sample gel, those volume was defined as  $V_{\text{gel}}$ , is composed of usual PNIPA gel phase and highly-dense PNIPA gel phase vicinity of latex particle.  $V_{\text{gel}}$  is linearly decreased with increment of concentration of latex,  $C$ , as shown in Figure 3. This



**Figure 8.** Schematic picture of the network structure. (a) Conventional PNIPA gel in absence of latex; (b) low concentration of latex,  $C \leq 12$  wt%; (c) the threshold,  $C = 12$  wt%; (d) high concentration of latex,  $C \geq 12$  wt%.

relation is simply given by  $V_{\text{gel}} = V_{\text{gel}}^0 - AC$ , where  $V_{\text{gel}}^0$  denotes the volume of gel in absence of latex at the present temperature. The constants,  $A = 1.83$  and  $V_{\text{gel}}^0 = 68.2$  at  $20^\circ\text{C}$  were obtained, as stated above. According to our assumption,  $V_{\text{gel}}$  should be divided into the volume of usual PNIPA gel phase,  $V_u$ , and the volume of highly-dense PNIPA gel phase,  $V_d = V_{\text{gel}} - V_u$ . Moreover, we assume the linear relation between  $V_u$  and  $C$  as follows:  $V_u = V_{\text{gel}}^0 - BC$ . Where we obtain the values of  $B$ ,  $2.81$  for  $20^\circ\text{C}$  by assumption the whole of net PNIPA gel changes into dense phase completely, i.e.,  $B = V_{\text{gel}}^0/24$ . Therefore, the volume ratio of the two composites,  $\phi_u$  for the usual PNIPA gel phase and  $\phi_d$  for the highly-dense PNIPA gel phase can be represented by  $A, B,$  and  $V_{\text{gel}}^0$  as follows.

$$\phi_u = \frac{V_{\text{gel}}^0 - BC}{V_{\text{gel}}^0 - AC}, \quad \phi_d = \frac{(B - A)C}{V_{\text{gel}}^0 - AC} \quad (10)$$

The total value of the tensile moduli are obtained by substitution of  $\phi_u$  and  $\phi_d$  as  $\phi_1$  and  $\phi_2$  into eq 9. The calculated results are shown in Figure 7. The solid line represents the values of tensile modulus in the case of parallel model,  $n = 1$ , and the dashed line represents the result in the case of series model,  $n = -1$ , in eq 9. Where, we employed the experimental value of the moduli of gel containing  $0.5$  wt% latex and  $24$  wt% as the moduli of each component,  $E_1$  and  $E_2$ , at the present temperature. The increase of the modulus can be regarded as two different stages. In the range from  $C = 0$  to  $12$  wt%, the experimental values were less than those of parallel model. Over  $12$  wt%, the modulus obeyed parallel model. These results imply that the two components, the usual PNIPA gel phase and the highly-dense PNIPA gel phase vicinity of latex particles, form interpenetrated macro network in the case of the swollen gel containing over  $12$  wt% latex.

This processes may be illustrated as depictions in Figure 8. Namely, the most important point of this pro-

cess is continuity of the highly-dense PNIPA gel phase vicinity of latex particles. When the gel contains latex particles of low concentration, dense phase will be apart each other (b). In this case, elastic modulus grow in accordance with series model rather than parallel model for the components. Then, in the case that latex concentration becomes over 12 wt%, it is considered that the connected dense phase forms “macro network” (c), and this network will grow with parallel model (d).

### CONCLUDING REMARKS

The equilibrium volume change and elastic modulus of PNIPA gels containing styrene-butadiene latex were investigated. The result and discussion would be summarized as follows.

- The equilibrium swelling curves became more continuous with increase of latex concentration and all lines cross at transition temperature,  $T_t = 33.8^\circ\text{C}$  in spite of concentration of latex. This result is very similar to those found in the case of dependence of cross-link density.
- The tensile modulus of the gels increased with increment of latex, although the net PNIPA gels seem to be swelled enough. This anomalous increment of elasticity seems to be caused on the highly-dense PNIPA gel phase vicinity of latex particles.
- It was found that the increase of elasticity against latex concentration could be classified into two mechanisms especially in the swollen state. The first, in the low latex concentration range, the elastic modulus increased in accordance with series model for these elastic components simply because dense gel phases are dispersed apart each other. The second, at  $C \geq 12.0\text{ wt}\%$ , the elasticity of the gel obeyed parallel model because of the formation of macro network with high-densed gel phase overlapped whole volume of gels.

It seems that this macro network formed with dense gel phase around the latex particles would play more essential role in the dynamic process of shrinkage. It

is well known that the conventional PNIPA gel reduces its volume in long multisteps, not monotonously.<sup>15, 16</sup> However, recently, we observed the PNIPA gels containing latex around 10 wt% shrunk their volume very quickly. Some homologue of PNIPA gels has long graft chain<sup>17</sup> or macroporous<sup>18</sup> are known as specific gels exhibit fast shrinkage, but this mechanism is still unknown. So, finally we suggest that these gels and our gel have an interesting common in macro network with high density region of polymer chains.

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