

# Volume-Phase Transition of Submicron-Sized *N*-Isopropylacrylamide / *N*-*tert*-Butylacrylamide Particles by Photon Correlation Spectroscopy

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**ABSTRACT:** *N*-Isopropylacrylamide (NIPA)/*N*-*tert*-butylacrylamide (NTBA) submicron-sized copolymer gel particles of various compositions were prepared by precipitation polymerization and the swelling behaviors of the gels were studied with different compositions and temperature using photon correlation spectroscopy (PCS). The experimental data showed that the volume transition temperature ( $T_v$ ) of the gels varied with the amount of monomers having different hydrophobicity added. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 2087–2092, 1998

**Key words:** volume-phase transition; submicron-sized copolymer gel; photon correlation spectroscopy

## INTRODUCTION

It is known that the volume-phase transitions of gels are induced by a continuous change in various conditions of the network, temperature, pH, electric field, light, solvent composition, concentration of salt, and type of surfactant, etc.<sup>1–3</sup> The finding of a large volume change in response to an infinitesimal alteration in the environment has opened the door to a wide variety of possible applications of gels as functional elements. For example, gels can be used as sensors, switches, or mechanochemical actuators and in drug delivery systems. In other words, the study on the swelling behavior of gel is very important in practical application.

A gel is a crosslinked polymer network im-

mersed in a fluid. The swelling behavior of a gel is induced by the interaction between the gel network and the fluid. The configuration and size of polymer chains in a solution are very sensitive to these interactions. We cannot tell of the change in these interactions by macroscopic means except for turbidity, which occurs at the so-called  $\theta$  condition. However, a gel can tell us about the change of its environment by changing its size. Thermodynamically, the swelling equilibrium of gels can be deduced from the free energy of these materials which results from the elasticity: the free energy of mixing. In the case of ionic gels, the free energy of the osmotic pressure of the counterions is added.<sup>4</sup>

Many research groups have studied the miscibility of a polymer system. Pavla et al. prepared novel pH-sensitive hydrogels by the crosslinking of polymeric precursors. The reactive polymeric precursor was synthesized by copolymerization of *N,N*-dimethylacrylamide (NTBA), acrylic acid, and *N*-methacryloylglycylglycine *p*-nitrophenyl ester. The swelling and mechanical properties of

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such hydrogels can be controlled by the modification of the polymer backbone structure and/or the crosslinking density.

In addition, there have been many reports of attempts to control the thermally induced volume-phase transition of gels, for example, through the use of mixed solvents, the addition of salt, the copolymerization of an electrolyte monomer, and the addition of surfactants.<sup>5–10</sup> Saito et al. reported that the swelling behavior of three *N*-alkylacrylamide gels was strongly dependent on the hydrophobicity of the specific *N*-alkyl group.<sup>11</sup> The transition temperature of the *N*-*n*-propylacrylamide (NNPA) gel was  $\sim 24^\circ\text{C}$ , while the *N*-cyclopropylacrylamide (NCPA) gel, which is relatively less hydrophobic than both the NIPA and NNPA gels, showed continuous swelling–deswelling behavior without undergoing a volume-phase transition.

In this study, we investigated the effect of a comonomer which has different hydrophobicity on the thermoshrinking gel. Various NIPA/NTBA copolymer gels were prepared and their swelling behavior in water were examined.

The most generally used measurement technique for the swelling behavior of the gel is to observe bulk gel, that is, in the form of a disc, sheet, or cylinder, by an optical microscope image processor or by weighing before and after swelling. However, these methods have serious problems: The gel can be contaminated and lost during measurement, due to its stickiness, and experimental errors increase due to an asymmetrical volume change. The swollen volume must be measured at a completely equilibrium state. However, it takes too much time for the gel to reach its equilibrium volume at each temperature. For example, a spherical 5% polyacrylamide gel whose diameter is about 300  $\mu\text{m}$  in water took 600 min to reach its equilibrium swollen volume at ambient temperature.<sup>12</sup> The equilibration time of swelling is proportional to the square of a linear dimension of the gel and is inversely proportional to the diffusion coefficient of the gel network, which is defined as  $D = E/f$ , where  $E$  is the longitudinal bulk modulus of the network and  $f$  is the coefficient of friction between the network and the gel fluid. Therefore, it is preferable to minimize the gel size. It is more like a real system for application.

The goals of this study were as follows: We compared the conventional gel swelling behavior measurement technique (bulk gel) with the photon correlation spectroscopy (PCS) method. Submi-

**Table I Proposed Sample Composition of NIPA/NTBA Copolymer Gel**

Sample Name	Composition (NIPA : NTBA)	NIPA (g)	NTBA (g)	BIS (g)
TB0	10 : 0	0.20	0.00	0.011
TB1	9 : 1	0.18	0.02	0.011
TB2	8 : 2	0.16	0.04	0.011
TB3	7 : 3	0.14	0.06	0.011
TB4	6 : 4	0.12	0.08	0.011
TB5	5 : 5	0.10	0.10	0.011
TB6	4 : 6	0.08	0.12	0.011

cron-sized gel particles by precipitation polymerization were prepared to minimize the experimental errors mentioned previously. In an attempt to investigate the effect of the comonomer which has different hydrophobicity, we prepared NIPA/NTBA copolymer gel particles with various compositions. To observe their thermoshrinking behavior, we measured the diameters with a temperature control. To measure their diameters precisely, we used PCS.

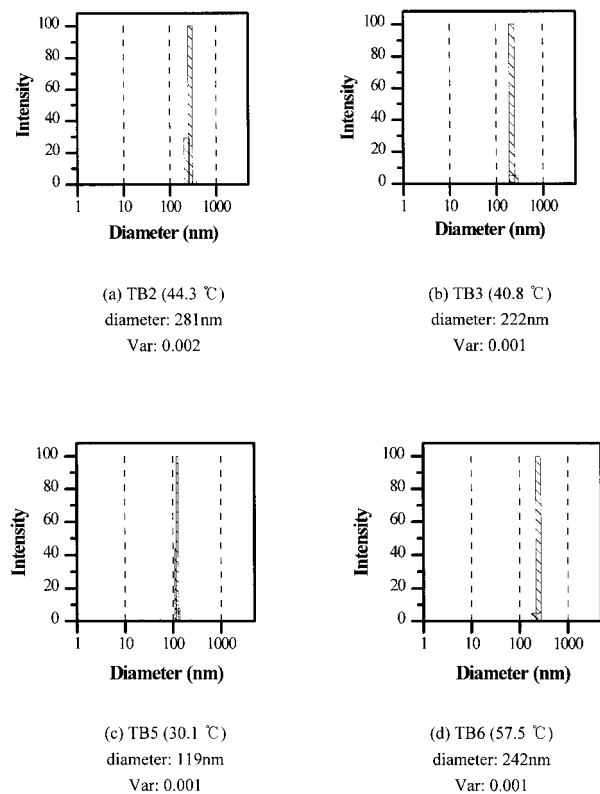
## EXPERIMENTAL

### Material

The NIPA (MW = 113.16) and NTBA (MW = 127.19), provided by TCI, were used as comonomers. NIPA and NTBA were used after recrystallization and drying in a vacuum oven for 2 days. As a crosslinking agent, *N,N'*-methylenebisacrylamide (BIS, MW = 154.17) provided by TCI was also used after recrystallization. We used 1% of an ammonium persulfate (APS) solution by weight as an initiator. We used nonionic surfactant TWEEN 20 to prevent aggregation among particles. An ionic surfactant would alter the swelling behavior.<sup>6</sup>

### Polymerization Method

The 50% (10 mL) of the total amount of distilled deionized water (DDI water) was first introduced to a round-bottom flask. Nitrogen gas was purged continuously during polymerization. At the same time, we prepared a monomer solution which was made with the remaining amount of water, NIPA, BIS, and NTBA. The ratios of the introduced comonomer were decided gravimetrically. The proposed sample compositions are listed in Table I.



**Figure 1** Polydispersity of prepared NIPA/NTBA copolymer gel particles with various compositions (measured by PCS).

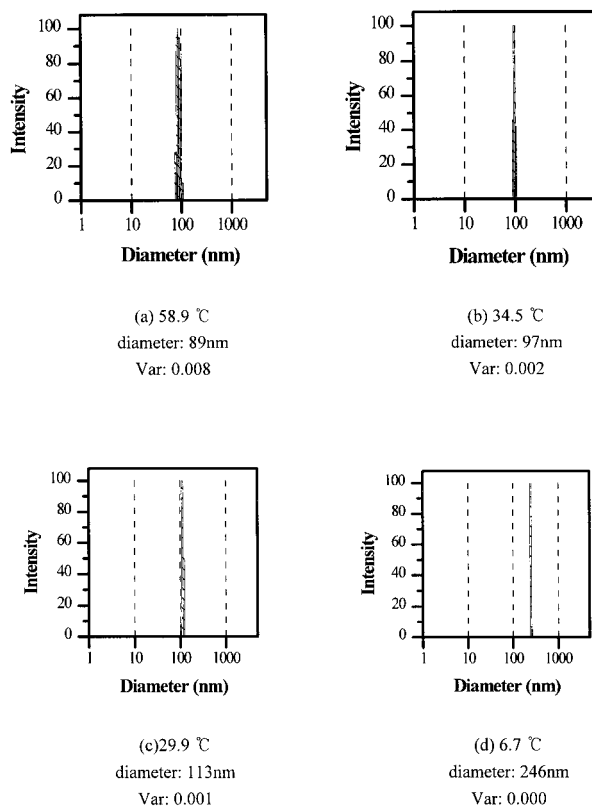
The amount of BIS was fixed at 5% of the total weight of the monomer and comonomer. After these reagents were completely dissolved, the surfactant solution and the initiator were introduced to the flask, and then the monomer solution was added. The reaction progressed with mild mixing at 70°C for 4 h after initiation.

The results of the PCS measurement of the gel particles are shown in Figure 1. For the various compositions, their variances were below 0.01. This confirms that our prepared particles are monodisperse. To observe the thermosensitive swelling behavior, the stability of the particles at various temperatures is required. Figure 2 shows the polydispersity of TB1. Its variances at each temperature did not exceed 0.01, indicating that the particles were very stable.

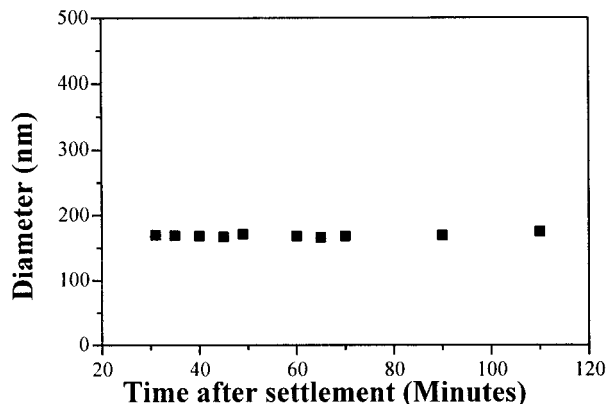
### Photon Correlation Spectroscopy

The hydrodynamic radii of the submicron gel particles were measured using PCS. The solution containing the gel particles was diluted with DDI

water filtered through a syringe filter of a 0.45- $\mu\text{m}$  (Whatman) pore size to get an appropriate concentration for PCS and then poured into a commercial glass cell (12-mm outer diameter). The cell was set inside a sample holder made of copper. The temperature was maintained at a desired temperature, about 0–70°C, using an external circulation bath. The source of the incident light was an argon ion laser (Lexel Laser Inc. Model 95-2) operated at 514.5 nm and with an intensity around 100 mW. The light scattered by the submicron gel particles was detected with a photomultiplier (Brookhaven Instrumental Co. EMI9863) at a scattering angle of 90°. The intensity of the scattered light fluctuates due to the Brownian motion of the submicron gel particles. The signal from the photomultiplier was digitized via an amplifier–discriminator and was fed into a correlator (Brookhaven Instrumental Co. BI-9000AT). The digital photon correlator accumulated the time correlation function of the intensity of the scattered light. The time correlation function was fitted using the method of CONTIN.<sup>13,14</sup> From the fits, we obtained the average diffusion coefficient



**Figure 2** Polydispersity of TB1 at various temperatures.



**Figure 3** Swelling behavior of TB1 with time at 47.6°C. The gel particles reach an equilibrium state in less than 30 min.

and, using the Stokes–Einstein relation, the hydrodynamic radius  $R_h$ .

#### Equilibration of Swelling on Temperature Control

When the temperature of the sample cell is set, the sizes of the gel particles vary until they reach an equilibrium volume at the set temperature. To minimize the experimental error, the measurement must be conducted at the equilibrium state. Here, we discuss the particle size of TB1 versus the time at 47.6°C. As shown in Figure 3, their diameters did not change much after 30 min.

By comparing our results with that of Tanaka's,<sup>15</sup> we estimated the equilibration time of the gel particles. The equilibration time of the polyacrylamide gel particles of 300  $\mu\text{m}$  in water at ambient was about 600 min. In general, the equilibration time is proportional to the square of the linear dimension of the gel network. If the particle size is 1  $\mu\text{m}$ , and its diffusion coefficient is similar to that of Tanaka's, its equilibration time will be

$$\frac{(300 \mu\text{m})^2}{600 \text{ min}} = \frac{(1 \mu\text{m})^2}{t_c \text{ min}}$$

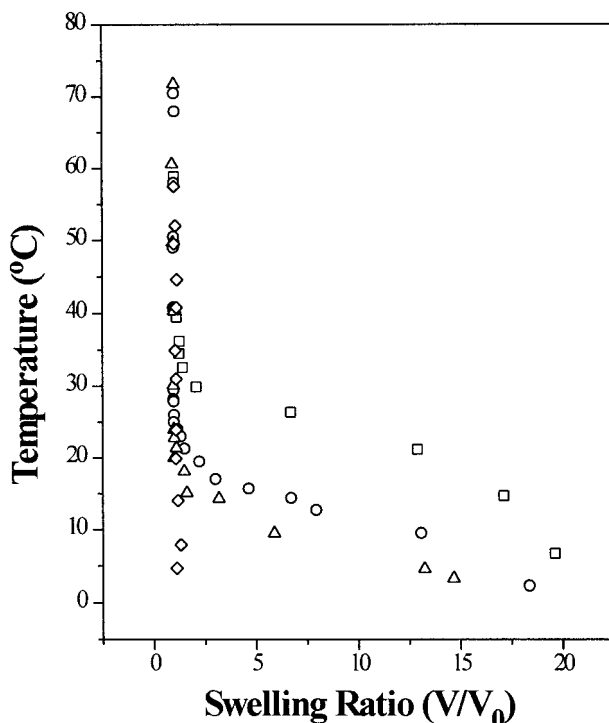
$$t_c = \frac{600}{(300)^2} = 6.667 \times 10^{-3}$$

From this result, we expected that the equilibration time for our samples would not be over 30 min. In this study, however, the equilibration time was more than 1 h, so that the sample surely reached equilibrium.

## RESULTS AND DISCUSSION

Figure 4 shows the typical swelling behavior of several NIPA/NTBA copolymer gel particles with temperature.  $T_v$  decreases with an increasing the amount of NTBA, indicating that, as the relative hydrophobicity increases with decreasing  $T_v$ ,  $T_v$  levels off at a certain composition. If the amount of NTBA is 60% by weight or more, the volume phase transition does not occur. The pure NTBA polymer gel does not show reversible properties. If the amount of NTBA was over some level, the copolymer gel loses the reversible characteristic. We assume that the hydrophobicity of NTBA was so strong that water molecules could not be mixed with the polymer gel network. In other words, the free energy of mixing is so large that the total free energy of the network swelling is increased over zero, and a spontaneous volume change could not occur. In this study, we limited the NTBA amount to less than 50% to sustain reversible properties. Figure 5 shows that  $T_v$  decreases with an increasing ratio of NIPA in the copolymer gel.

Our experimental results show a large deviation between the bulk gel and submicron-sized gel particles. Figure 6 shows the difference of swell-

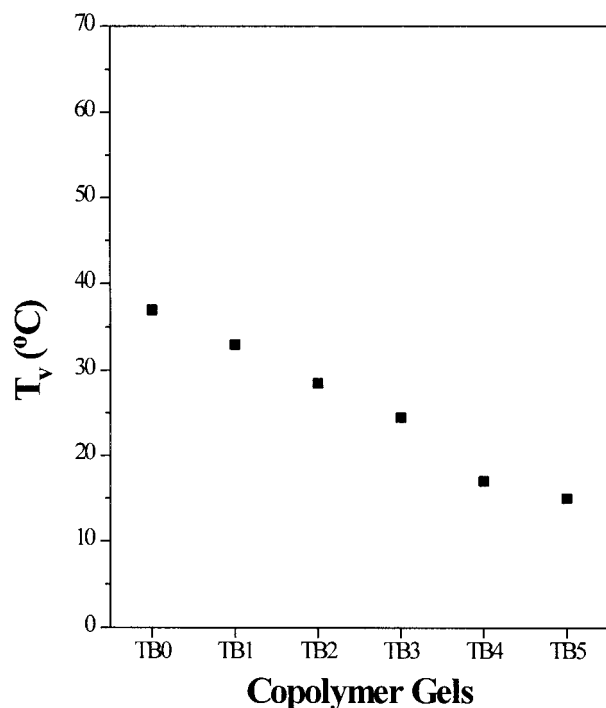


**Figure 4** The swelling behavior of several NIPA/NTBA copolymer gel particles.

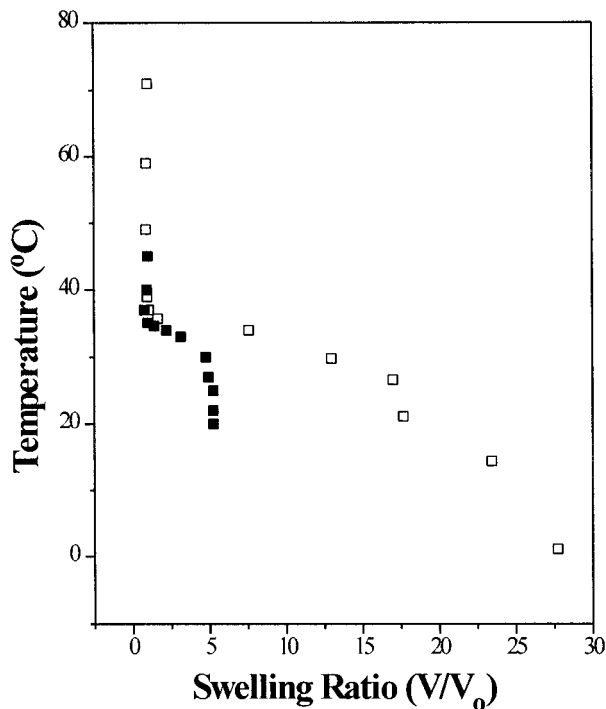
ing behavior between the bulk gel and gel particles. The data on the bulk gel were obtained by Saito et al.<sup>16</sup> The  $T_v$  of a pure NIPA gel particle is shown above 35°C, while that of the bulk gel is 34°C. In general, the  $T_v$  of the bulk gel is known as 32–35°C.

Our analysis is that each gel particle has a different transition temperature. This difference of transition temperature may result from inhomogeneities of microstructures from particle to particle. In this case, some particles have a higher  $T_v$  than 35°C, and even if each gel particle has a discontinuous transition, the average hydrodynamic radius as measured by PCS will appear smooth and continuous.

It is well known that the swelling ratio of a gel decreases with increasing the amount of the crosslinking agent. Saito et al. introduced 3.846 mol % of BIS to NIPA, and we introduced 3.881 mol % of BIS. We expected that the swelling ratio of gel particles would be similar to that of Saito et al. However, there is a big deviation in the swelling ratio. The swelling ratio obtained from the bulk gel might not be measured in the fully equilibrated state.



**Figure 5** The composition dependence of  $T_v$  for various NIPA/NTBA copolymer gel particles.



**Figure 6** The difference of swelling behavior between the particle gel and bulk gel.

## CONCLUSION

We have shown the  $T_v$  of *N*-alkylacrylamide-derivative copolymer gels in water with various compositions. The  $T_v$  of the NIPA/NTBA copolymer gel decreased with increasing the amount of NTBA, which is more hydrophobic than is NIPA. Our experimental data showed that the submicron-sized gel particles have a very short equilibration time. We were able to characterize the swelling behavior of gel particles precisely by PCS and it is a very reliable and time-saving method.

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