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Phase transition of submicron sized *N*-alkylacrylamide-derivative copolymer particles: applicability of photon correlation spectroscopy

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N-isopropylacrylamide (NIPA)/*N*-*tert*-butylacrylamide (NTBA) and NIPA/*N*,*N*-dimethylacrylamide (NDMA) submicron-sized copolymer gel particles of various compositions were prepared by precipitation polymerization and their swelling behaviours were studied with different compositions and temperature using photon correlation spectroscopy. The experimental data showed that the volume transition temperature (T_V) of NIPA/NTBA copolymer gel decreased with increasing mole ratio of NTBA, while T_V of NIPA/NDMA copolymer gel increased with the mole ratio of NDMA. © 1997 Elsevier Science Ltd.

INTRODUCTION

The volume phase transition of hydrogels has been attracting much attention because of its technological and scientific importance. A gel can change in volume discontinuously as much as 100-fold when surrounding conditions such as solvent composition, salt concentration, pH, and temperature, vary continuously[1–6]. Three types of phase transitions have been reported due to temperature dependence. The first is the thermoswelling type, or expansion with temperature[1]; the second is the thermoshrinking type, or collapse with temperature[3]; and the third is the convexo type, a mixture of the two types described above[4].

It has been reported that the type of transition depends largely on the affinity of the monomers for water[7]. Therefore, it would be important to consider the molecular structure of monomer units in a gel. Thermoswelling hydrogels mostly contain hydrophilic monomers such as acrylamide, acrylic acid, and methacrylic acid, and their transition can be explained by Tanaka's thermal mixing model[1,3,4]. On the other hand, the main examples of thermoshrinking hydrogels are composed of monomers like *N*-methylacrylamide, NDMA, and NIPA, whose hydrophobic substituents make them less hydrophilic. Transition in their cases cannot be precisely depicted by the Tanaka model. Accordingly, both hydrophilicity and hydrophobicity should be borne in mind when volume phase transition, especially the thermoshrinking type, is considered.

When hydrophobic solutes are introduced into water, two phenomena are simultaneously observed[8–13]. One is hydrophobic hydration, in which the water molecules form cagelike structures around the hydrophobic solutes. As a result of this hydration, nonpolar molecules become soluble in water. The other is hydrophobic interaction, or the association of hydrophobic solutes. In general, an increase in temperature results in a reduction of the total number of water molecules structured around the hydrophobic solutes, which promotes hydrophobic interaction. Consequently, a rise in temperature strengthens the hydrophobic interaction. This is quite contrary to other interaction such as dipole–dipole, van der Waals, and electrostatic forces.

Recently Hirotsu investigated the phase behaviour of NIPA gel/water/alcohol systems and explained thermoshrinking by the destruction of hydrogen bonds between water molecules and NH or C=O of NIPA[14]. However, our above discussion seems to suggest that the hydrophobic interaction contributes to the volume phase transition of thermoshrinking polymers. Ulbrich and Kopecek also pointed out the importance of hydrophobic interactions in their studies on the mechanical properties of *N*-substituted acrylamide gels at room temperature[15].

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[16–21]. Peppas *et al.* synthesized random copolymer hydrogels of methacrylic acid (MAA) and NIPA by free-radical polymerization in the presence of a crosslinking agent[22]. The gels were characterized for their temperature- and pH-responsive behaviour by equilibrium swelling experiments, d.s.c., and t.m.a. Their results showed that the polymer composition not only determined the swelling characteristics of the gels due to pH

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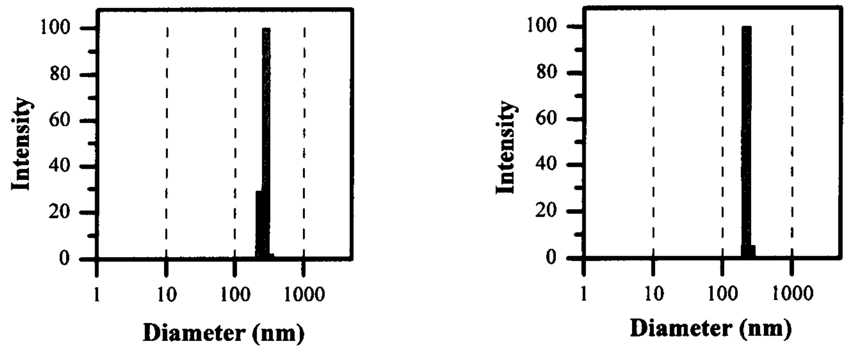
or temperature but also influenced the LCST of the hydrogel. As the MAA content of the hydrogel samples was increased, the LCST increased compared with the LCST of pure NIPA gel because the hydrogel was able to maintain its hydrated state at higher temperatures with the addition of the hydrophilic group. However, as the amount of the NIPA in the hydrogel was decreased to 75% and lower, the LCST dropped below the value for pure NIPA gel (32°C) and the sharp transition in swelling behaviour disappeared.

In addition, many research groups have studied the miscibility of polymer systems. Kopecekova *et al.* prepared novel pH-sensitive hydrogels by the crosslinking of polymeric precursors[23]. 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 hydrogels can be controlled by the modification of polymer backbone structure and/or the crosslinking density.

Table 1 Proposed sample composition of NIPA/NTBA and NIPA/NDMA copolymer gel

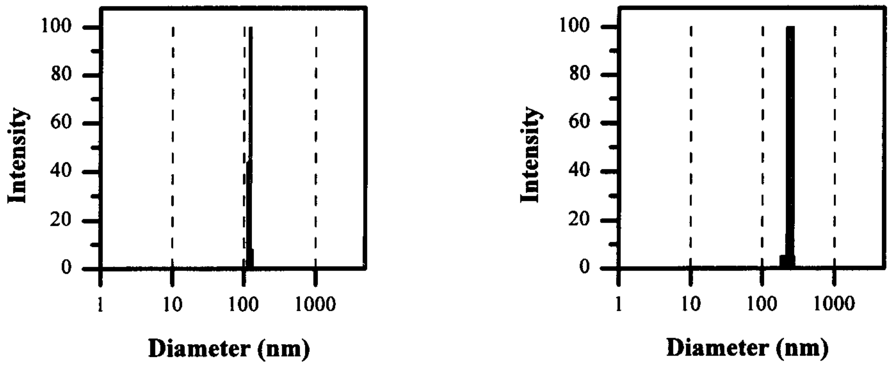
Sample name	Composition (NIPA/NTBA)	NIPA (g)	NTBA (g)	BIS (g)
NIPA/NTBA copolymer gel				
TB0	10/0	0.20	0.00	0.011
TB1	9/1	0.18	0.02	0.011
TB2	8/2	0.16	0.04	0.011
TB3	7/3	0.14	0.06	0.011
TB4	6/4	0.12	0.08	0.011
TB5	5/5	0.10	0.10	0.011
TB6	4/6	0.08	0.12	0.011

Sample name	Composition (NIPA/NDMA)	NIPA (g)	NTBA (g)	BIS (g)
NIPA/NDMA copolymer gel				
DM0	10/0	0.20	0.00	0.011
DM1	9/1	0.18	0.02	0.011
DM2	8/2	0.16	0.04	0.011



(a) TB2 (44.3 ℃)
diameter: 281nm
Var: 0.002

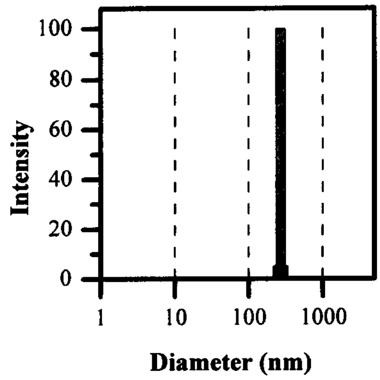
(b) TB3 (40.8 ℃)
diameter: 222nm
Var: 0.001



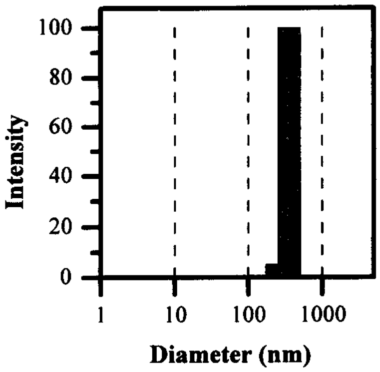
(c) TB5 (30.1 ℃)
diameter: 119nm
Var: 0.001

(d) TB6 (57.5 ℃)
diameter: 242nm
Var: 0.001

Figure 1 Polydispersity of NIPA/NTBA copolymer gel particles with various compositions



(a) DM1 (39.9 ℃)
diameter: 290nm
Var: 0.001



(b) DM2 (50.9 ℃)
diameter: 371nm
Var: 0.002

Figure 2 Polydispersity of NIPA/NDMA copolymer gel particles with various compositions

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

The most generally used measurement technique for the swelling behaviour of the gel is to observe the bulk gel that is in the form of disc, sheet, cylinder by optical microscope image processor or by weighing before and after swelling. However this method has serious problems. The gel can be contaminated and lost during measurement for its stickiness and experimental errors increase due to asymmetrical volume change. The swollen volume must be measured at completely equilibrium state. However it takes too much time for the gel to reach its equilibrium volume at each temperature. The equilibration time of swelling is proportional to the square of a linear dimension of the gel. Therefore, it is preferable to minimize the gel size. It is more similar to a real system for application.

The goals of this study are as follows: in an attempt to investigate the effect of comonomer with different hydrophobicity, we prepared NIPA/NTBA, NIPA/NDMA copolymer gel particles with various composition. To observe their thermoshrinking behaviour, we measured the diameter with temperature control. To measure their diameter precisely, we need photon correlation spectroscopy (p.c.s.). We also compared the conventional gel swelling behaviour measurement technique (bulk gel) with the p.c.s. method. Submicron-sized gel particles by precipitation polymerization were prepared to minimize the experimental errors, mentioned previously. We also measured the equilibration time of gel particles.

EXPERIMENTAL

Material

The NIPA ($MW = 113.16$), NTBA ($MW = 127.19$), and NDMA ($MW = 99.13$) provided by TCI were used as comonomers. NIPA and NTBA were used after recrystallization and drying them in a vacuum oven for 2 days. NDMA was used as received. As a crosslinking agent, N,N'-methylenebisacrylamide (BIS, $MW = 154.17$) provided by TCI was also used after recrystallization. NTBA, NIPA and NDMA have different hydrophobicity to each other. NTBA is most hydrophobic and NDMA is least. We used 1% of ammonium persulfate (APS) solution by weight as an initiator. Nonionic surfactant TWEEN 20 was used to prevent aggregation among particles. The ionic surfactant causes the swelling behaviour to be altered[17].

Polymerization method

We prepared submicron gel beads by precipitation polymerization at 70°C for 4 h with nitrogen blowing. Distilled deionized water (DDI) was used as a solvent. To vary the hydrophobicity, NTBA or NDMA was copolymerized with NIPA. The ratios of introduced comonomer were measured gravimetrically. The proposed sample compositions are listed in *Table 1*.

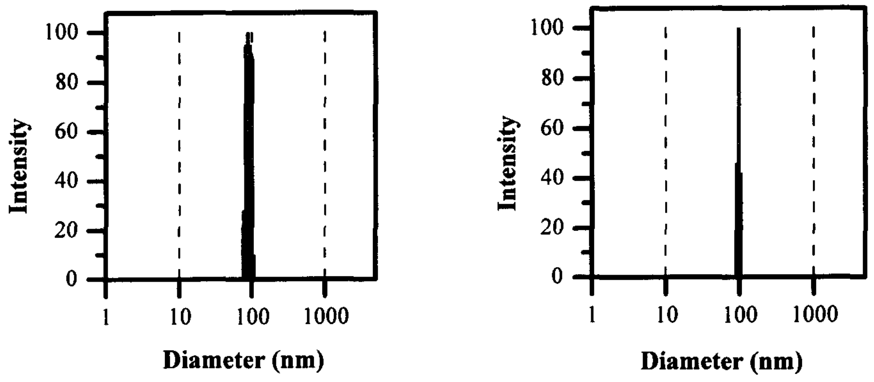
The results of p.c.s. measurement of gel particles are shown in *Figures 1* and *2*. For the various compositions, their variances were below 0.01. This confirms that our prepared particles are monodisperse. To observe thermosensitive swelling behaviour, the stability of particles at various temperature is required. *Figure 3* shows the polydispersity of TB1. Its variances at each temperature did not exceed 0.01. It confirms that the particles were very stable.

Photon correlation spectroscopy

In order to characterize the swelling behaviours of the gel particles, we determined the scattering light intensity and the autocorrelation function at an angle of 90° using p.c.s. An incident beam (514 nm) from an Ar-ion laser (Lexel Laser Inc. model 95-2) was focused to the centre of the cylindrical sample cell. The scattered light intensity and the time autocorrelation function (collected with a Brookhaven BI-9000AT correlator with CONTIN method) were determined at various temperatures.

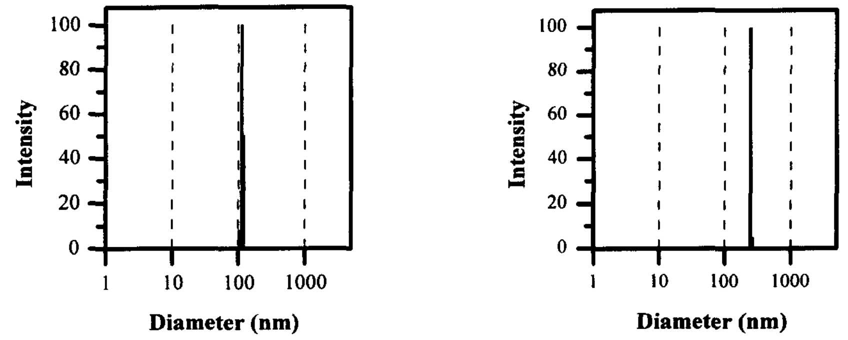
Equilibration of swelling on temperature control

When the temperature of a sample vat was set, the sizes of the gel particles varied until they reached the equilibrium volume at the set temperature. To minimize the experimental error, the measurement must be conducted at the equilibrium state. Here, we discuss



(a) 58.9 ℃
diameter: 89nm
Var: 0.008

(b) 34.5 ℃
diameter: 97nm
Var: 0.002



(c)29.9 ℃
diameter: 113nm
Var: 0.001

(d) 6.7 ℃
diameter: 246nm
Var: 0.000

Figure 3 Polydispersity of TB1 at various temperatures

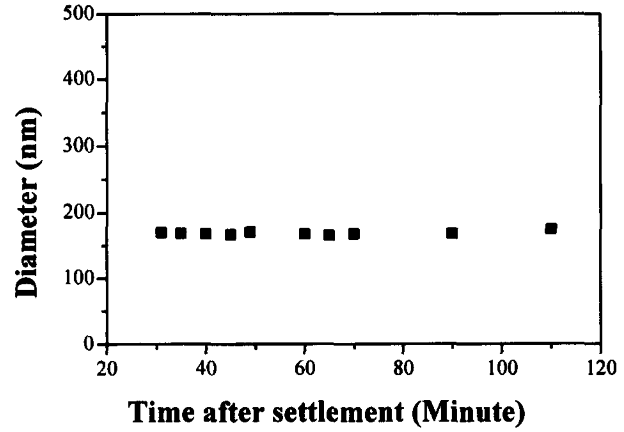


Figure 4 Swelling behaviour of TB1 with time at 47.6°C

the particle size of TB1 vs time at 47.6°C. As shown in *Figure 4*, their diameters did not change much after 30 min.

By comparing our results with those of Tanaka and Fillmore[24], we estimated the equilibration time of gel particles. The equilibration time of polyacrylamide gel particles of 300 μm in water at ambient temperature was about 600 min. In general, the equilibration time is proportional to the square of a linear dimension of the gel network. If the particle size is 1 μm, 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, our equilibration time was more than 1 h so that the sample surely reached its equilibrium state.

RESULTS AND DISCUSSION

Figure 5 shows the typical swelling behaviour of several NIPA/NTBA copolymer gel particles with various temperatures. T_v decreases with increasing mole ratio

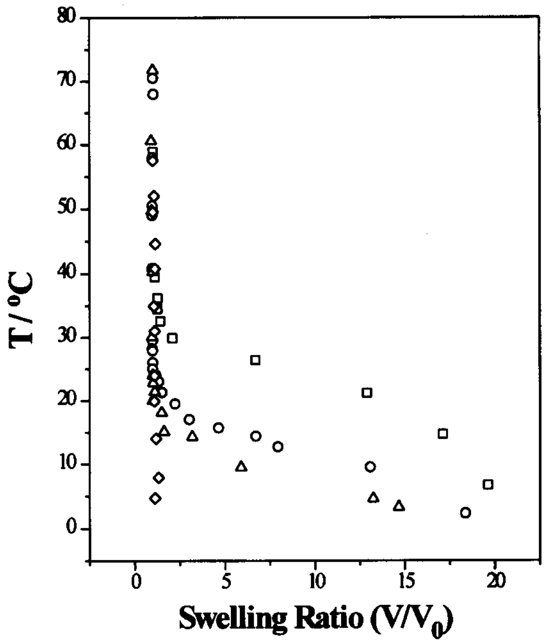


Figure 5 The swelling behaviour of several NIPA/NTBA copolymer gel particles

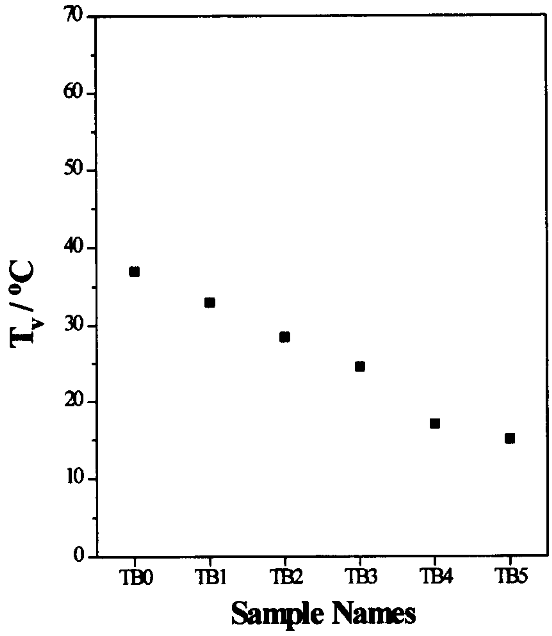


Figure 6 The composition dependence of T_v for various NIPA/NTBA copolymer gel particles

of NTBA. In other words, as the relative hydrophobicity increases, T_v decreases. T_v levels off at a certain composition. If the amount of NTBA was 60% by weight and over, the volume phase transition did not occur. The pure NTBA polymer gel does not show reversible properties. If the amount of NTBA varies to some degree, then the copolymer gels lose their reversible characteristic. We assumed that the hydrophobicity of NTBA was so strong that water molecules could not be mixed with polymer gel network. In other words, the free energy of mixing is so large that the total free energy of network swelling is increased over zero, and so spontaneous volume change could not occur. In this study, we control the NTBA amount by 50% to sustain reversible properties. *Figure 6* shows that T_v decreases with increasing mole ratio of NIPA in copolymer gel.

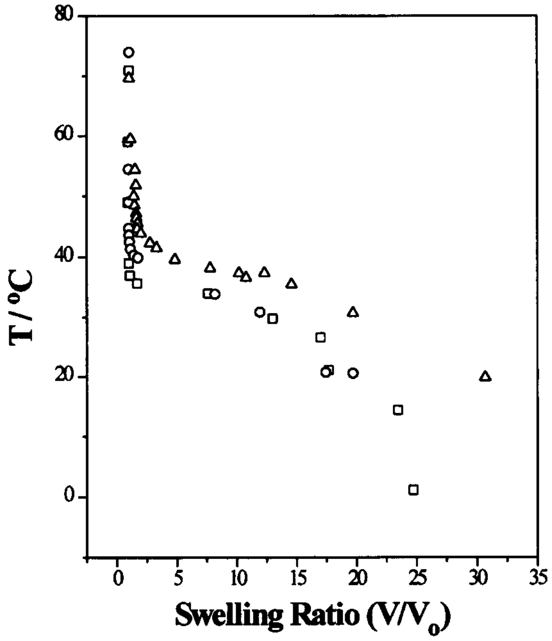


Figure 7 The swelling behaviour of several NIPA/NDMA copolymer gel particles

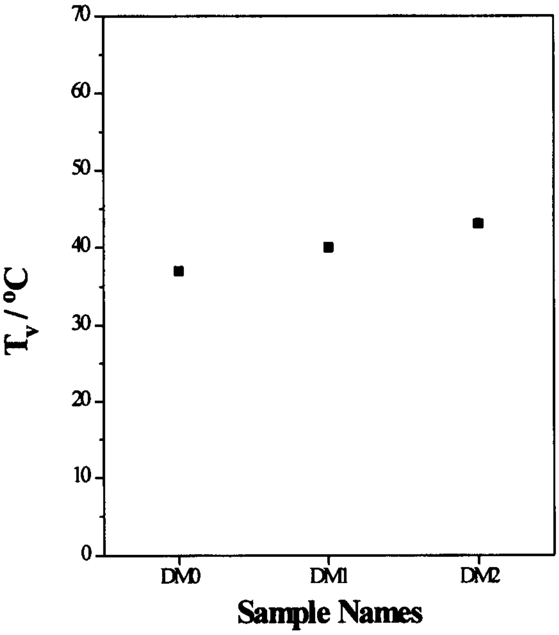


Figure 8 The composition dependence of T_v for various NIPA/NDMA copolymer gel particles

Figures 7 and *8* show the swelling behaviour of various compositions of NIPA/NDMA copolymer gel particles. Since NDMA is more hydrophilic than NIPA, contrary to NTBA, T_v increases with the mole ratio of NDMA in copolymer composition.

Our experimental results show large deviation between the bulk gel and submicron-sized gel particles. *Figure 9* shows the difference of swelling behaviour between bulk gel and submicron-sized gel particles. The data of bulk gel were obtained by Saito *et al*^{25}. T_v of pure NIPA gel particle is shown above 35°C, while that of bulk gel is 34°C. In general, T_v of bulk gel is known as 32–35°C.

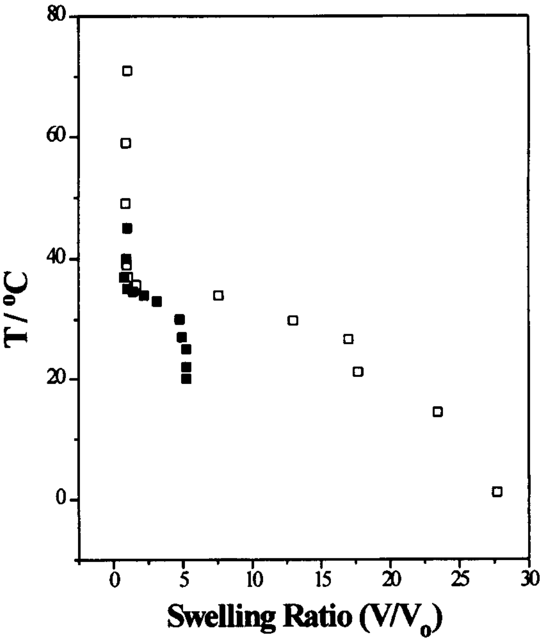


Figure 9 The difference of swelling behaviour between submicron sized gel particles and bulk gel

Our analysis for the transition temperature of gel particles 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 higher T_v than 35°C, and even if each gel particle has a discontinuous transition, the average hydrodynamic radius as measured by p.c.s. will appear smooth and continuous.

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

CONCLUSION

We have shown that T_v of *N*-alkylacrylamide-derivative copolymer gels in water with various mole ratios of two components in a copolymerization reaction. T_v of NIPA/NTBA copolymer gel decreased with increasing the mole ratio of NTBA which is more hydrophobic than NIPA. And T_v of NIPA/NDMA copolymer gel increased with increasing the mole ratio of NDMA which is less hydrophobic.

Our experimental data also showed that the submicron-sized gel particles have very short equilibration time and we were able to characterize the swelling behaviour precisely by p.c.s.

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