

# Cloud Points in Aqueous Poly(*N*-isopropylacrylamide) Solutions

By Tomoaki KAWAGUCHI, Yosuke KOJIMA, Masashi OSA,\* and Takenao YOSHIZAKI

The cloud point was determined for aqueous solutions of four kinds of poly(*N*-isopropylacrylamide) samples synthesized by radical polymerization in methanol, *tert*-butanol, benzene, and 1,4-dioxane by the use of azobis(isobutyronitrile) as an initiator, in the range of the weight fraction of the sample from 0.5 to 10%. It has then been found that the cloud points so determined for the samples synthesized in benzene and 1,4-dioxane are definitely lower than those for the samples synthesized in methanol and *tert*-butanol, although all the samples have almost the same stereochemical composition and the same end group. The observed deviation may be regarded as arising from the difference in the primary structure between the samples.

KEY WORDS: Poly(*N*-isopropylacrylamide) / Aqueous Solution / Cloud Point / Phase Behavior / LCST /

Poly(*N*-isopropylacrylamide) (PNIPA) has long been drawing the interest of polymer chemists because its aqueous solution shows lower-critical-solution-temperature (LCST) miscibility behavior near the human body temperature,<sup>1</sup> and not a few experimental studies have been made of behavior of its cloud-point curve, which is usually regarded as the binodal.<sup>2–10</sup> The LCST behavior may be understood as a consequence of the “hydrophobic interaction” between polymers enhanced by breakdown of hydrogen bonds between polymers and surrounding water molecules, as in the case of aqueous polyoxyethylene (POE) solutions.<sup>11,12</sup> The aqueous PNIPA solutions have then been shown to have some salient and unusual features: the cloud point is rather insensitive to its concentration,<sup>2–10</sup> and at constant concentration it decreases with decreasing the molecular weight.<sup>6,7</sup> Unfortunately, however, the literature data<sup>2–10</sup> for the cloud point are rather dispersed and differ from each other, the difference being beyond experimental error. It is therefore necessary to ascertain the cause of the dispersion of the data prior to inquiring the reasons of such characteristic features.

Recently, Ray *et al.*<sup>13</sup> pointed out that the cloud point for the aqueous PNIPA solution appreciably depends on the stereochemical composition of the sample used. In addition, it seems to be sensitive to the hydrophobic and also electrostatic interactions between the end groups of the sample used, especially in aqueous solutions. All the PNIPA samples used in the previous studies<sup>2–10</sup> of the cloud point had been synthesized by aqueous redox polymerization by the use of a redox catalyst consisting of ammonium persulfate as an oxidative part and of sodium bisulfite,<sup>2</sup> tetramethylethylenediamine,<sup>4</sup> or sodium metabisulfite<sup>9</sup> as a reductive part, or by conventional radical polymerization in a mixture of benzene and acetone,<sup>3</sup> in benzene,<sup>4,5</sup> in *tert*-butanol,<sup>6,7</sup> in tetrahydrofuran,<sup>8</sup> or in methanol,<sup>10</sup> by the use of azobis(isobutyronitrile) (AIBN) as an initiator. The fraction  $f_r$  of racemo diads, specifying the stereochemical composition, of the samples so synthesized are considered to be almost independent of the solvent condition

and the initiator used for the polymerization, so that the difference in the literature data for the cloud point may not be caused by the difference in  $f_r$ . The end groups of the samples synthesized by the use of the redox catalyst and that of AIBN are different from each other, the former end group being ionic. The difference in the cloud point, however, exists not only between the samples having the different end groups but also between those having the same end group. Under these circumstances, the cause of the difference in the cloud point between the literature data is not clear.

The experimental procedures to determine the cloud point, such as the rate of increase in temperature and/or the manner of adopting a temperature as the cloud point, are somewhat different between the investigators,<sup>2–10</sup> so that the above-mentioned difference in the cloud point between the literature data is not yet conclusive. It is therefore desirable to compare experimental data for the cloud point in aqueous PNIPA solutions determined following the same procedure in the same laboratory. In this study, we synthesize the PNIPA samples by radical polymerization in methanol, *tert*-butanol, benzene, and 1,4-dioxane by the use of AIBN as an initiator, and then determine their cloud points in aqueous solutions, in order to examine whether or not the difference in the cloud point between the samples synthesized in different solvents really exists beyond experimental error.

## EXPERIMENTAL

### Materials

Four kinds of (original) PNIPA samples were synthesized by radical polymerization in methanol, *tert*-butanol, benzene, and 1,4-dioxane by the use of AIBN as an initiator. In each case, *N*-isopropylacrylamide (*ca.* 20 g), which had been recrystallized three times from a 8/2 mixture of *n*-hexane and benzene and then dried in a vacuum for 12 h, was polymerized in the solvent (*ca.* 150 mL) with AIBN (*ca.* 1 mol %) under dry nitrogen at 60 °C for 30 h, the conversion being almost 100%. The original

Department of Polymer Chemistry, Kyoto University, Katsura, Kyoto 615-8510, Japan

\*To whom correspondence should be addressed (E-mail: omasa@molsci.polym.kyoto-u.ac.jp).

samples so synthesized were purified by reprecipitation from acetone solutions into *n*-hexane and then separated into fractions of narrow molecular weight distribution by fractional precipitation using acetone as a solvent and *n*-hexane as a precipitant, or by a column elution method with a mixture 6/4 of *n*-hexane and acetone as an eluent. The test samples so prepared were dissolved in 1,4-dioxane, then filtered through a Teflon membrane of pore size 1.0  $\mu\text{m}$ , and finally freeze-dried from their 1,4-dioxane solutions. They dried in a vacuum at *ca.* 80 °C for *ca.* 12 h just prior to use.

The solvent methanol used for light scattering (LS) measurements was purified by distillation after refluxing over calcium hydride for *ca.* 6 h. The solvent tetrahydrofuran used for analytical gel permeation chromatography (GPC) was of reagent grade with no stabilizer. The solvent deuterated dimethyl sulfoxide used for  $^1\text{H}$  NMR spectroscopy was of reagent grade. The solvent water used for the determinations of the cloud point was highly purified through a Milli-Q Labo water purification system of Millipore Co., its resistivity being 18.2 M $\Omega$ -cm.

### Light Scattering

LS measurements were carried out to determine the weight-average molecular weight  $M_w$  for all the samples, in methanol at 25.0 °C. A Fica 50 light-scattering photometer was used with vertically polarized incident light of wavelength  $\lambda_0 = 436$  nm. For a calibration of the apparatus, the intensity of light scattered from pure benzene was measured at 25.0 °C at a scattering angle of 90°, where the Rayleigh ratio  $R_{Uu}(90^\circ)$  of pure benzene was taken as  $46.5 \times 10^{-6} \text{ cm}^{-1}$ .<sup>14</sup> The depolarization ratio  $\rho_u$  of pure benzene at 25.0 °C was determined to be  $0.41 \pm 0.01$ . Scattered intensity was measured at seven or eight different concentrations and at scattering angles  $\theta$  ranging from 30.0 to 142.5°, and then converted to the excess unpolarized (Uv) components  $\Delta R_{Uv}$  of the reduced scattered intensity by the use of the scattered intensity from the solvent methanol. The data obtained were treated by using the Berry square-root plot.<sup>15</sup> For all the samples, corrections for the optical anisotropy were unnecessary since the degree of depolarization was negligibly small.

The most concentrated solution of each sample was prepared gravimetrically and made homogeneous by continuous stirring at room temperature for 1 d. It was optically purified by filtration through a Teflon membrane of pore size 0.10  $\mu\text{m}$ . The solutions of lower concentrations were obtained by successive dilution. The weight fractions of the test solutions were converted to the polymer mass concentrations  $c$  by the use of the densities of the respective solutions calculated with the partial specific volumes  $v_2$  of the samples and with the density  $\rho_0$  of the solvent methanol. The values of  $v_2$  in methanol at 25.0 °C were determined to be 0.903  $\text{cm}^3/\text{g}$  irrespective of the kind of test sample, by the use of a pycnometer of the Lipkin–Davison type having a volume of 10  $\text{cm}^3$ . For the value of  $\rho_0$  of methanol at 25.0 °C, we used the literature value 0.7866  $\text{g}/\text{cm}^3$ .<sup>16</sup>

The refractive index increment  $\partial n/\partial c$  was measured at the wavelength of 436 nm by the use of a Shimadzu differential

refractometer DR-1. For the refractive index of methanol at 25.0 °C at the wavelength of 436 nm, we used the literature value 1.3337.<sup>16</sup>

### Analytical Gel Permeation Chromatography

The ratio of  $M_w$  to the number-average molecular weight  $M_n$  for all the PNIPA samples were evaluated by analytical GPC with five serially connected columns (Tosoh GMH<sub>xl</sub> + G5000H<sub>xl</sub> + G5000H<sub>xl</sub> + G4000H<sub>xl</sub> + G4000H<sub>xl</sub>) connected to a HPLC pump (Jasco PU-980) and a UV detector (Tosoh UV-8000) using tetrahydrofuran as an eluent and 12 standard polystyrene (PS) samples (Tosoh,  $M_w = 2.8 \times 10^3 - 8.4 \times 10^6$ ,  $M_w/M_n = 1.02 - 1.17$ ) as reference standards.

### $^1\text{H}$ NMR

$^1\text{H}$  NMR spectra for all the PNIPA samples in deuterated dimethyl sulfoxide at 170 °C were recorded on a JEOL JNM-A500 spectrometer at 500.2 MHz by the use of an rf pulse angle of 45° with a pulse repetition time of 8 s, where tetramethylsilane was added to each test solution as an internal standard.

### Transmittance of Light

The intensity of light passing through the aqueous solution of each PNIPA sample at a given weight fraction  $w$  of the sample was monitored in order to determine its cloud point. All the measurements were carried out by the use of a self-made apparatus with incident light of wavelength 650 nm from a laser diode module, as described below. A cylindrical cell of outer diameter 10 mm containing a given test solution was immersed in a water bath, the test solution in the cell being stirred continuously. The temperature of the water bath was controlled to increase at the rate of *ca.* 1.5 °C/h. During continuous increase in temperature from 28 to 34 °C, the intensity of light passing through the cell was monitored by a photodiode. The output of the photodiode along with the solution temperature measured simultaneously by the use of a platinum resistance thermometer combined with a programmable digital multimeter (Yokokawa 7555) was recorded on a personal computer at intervals of 10 s.

The measurements were carried out at 8 different concentrations in the range of  $0.5 \lesssim w \lesssim 10\%$  for each sample. The most concentrated solution of each sample was prepared gravimetrically and made homogeneous by continuous stirring for 1 d at *ca.* 20 °C. The solutions of lower concentrations were obtained by successive dilution.

## RESULTS AND DISCUSSION

### Characterization

The values of  $M_w$  determined by LS measurements in methanol at 25.0 °C and  $M_w/M_n$  by analytical GPC using the standard PS samples as reference standards for all the PNIPA samples used in this work are given in the second and third columns of Table I, respectively, the first letters M, T, B, and D in the sample codes in the first column indicating the solvents used for radical polymerization, *i.e.*, methanol, *tert*-butanol,

**Table I.** Values of  $M_w$ ,  $M_w/M_n$ , and  $f_r$  for Poly(*N*-isopropylacrylamide)

sample	$M_w$	$M_w/M_n^a$	$f_r$
synthesized in methanol			
M6	$6.45 \times 10^4$	1.19	0.51
M9	$9.44 \times 10^4$	1.17	0.52
synthesized in <i>tert</i> -butanol			
T5	$5.17 \times 10^4$	1.14	0.52
T13	$1.31 \times 10^5$	1.23	0.52
synthesized in benzene			
B5	$4.65 \times 10^4$	1.17	0.52
B14	$1.44 \times 10^5$	1.14	0.51
synthesized in 1,4-dioxane			
D5	$5.18 \times 10^4$	1.28	0.52
D13	$1.27 \times 10^5$	1.18	0.52

<sup>a</sup>The values of  $M_w/M_n$  were determined by analytical GPC using standard PS samples as reference standards.

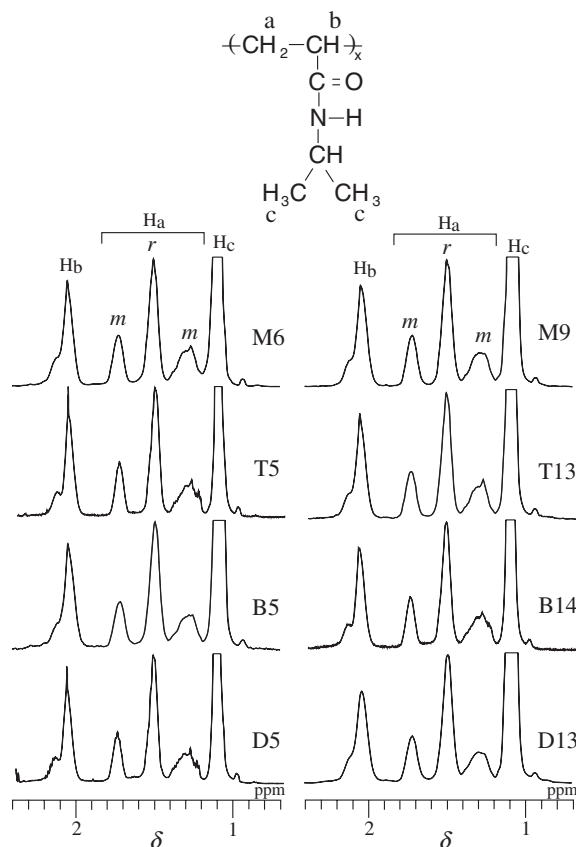
benzene, and 1,4-dioxane, respectively. We note that the values of  $\partial n/\partial c$  in methanol at 25.0 °C, which are necessary for the evaluation of  $M_w$  from the LS data, were determined to be 0.184<sub>9</sub>, 0.185<sub>7</sub>, 0.184<sub>4</sub>, 0.183<sub>7</sub>, 0.182<sub>2</sub>, 0.185<sub>7</sub>, 0.184<sub>5</sub>, and 0.185<sub>6</sub> cm<sup>3</sup>/g for the samples M6, M9, T5, T13, B5, B14, D5, and D13, respectively.

Figure 1 shows the <sup>1</sup>H NMR spectra for all the 8 samples in the range of the chemical shift  $\delta$  from 0.7 to 2.4 ppm, where the signals from the methylene (a) and methine (b) protons in the main chain and the methyl protons (c) in the side group are included. According to Isobe *et al.*,<sup>17</sup> the signals in the ranges of  $1.0 \lesssim \delta \lesssim 1.2$ ,  $1.2 \lesssim \delta \lesssim 1.8$ , and  $1.9 \lesssim \delta \lesssim 2.2$  (in units of ppm) may be assigned to the c, a, and b protons, respectively. The three signals from the a protons in the range of  $1.2 \lesssim \delta \lesssim 1.8$  may be further assigned to those in the meso (*m*), racemo (*r*), and *m* diads, respectively, from the right to the left, as explicitly shown in the spectra for the samples M6 and M9. In the last column of Table I are given the values of  $f_r$  determined from the intensities of those three signals from the a protons. All the PNIPA samples have almost the same value (0.51–0.52) of  $f_r$ , as has been expected.

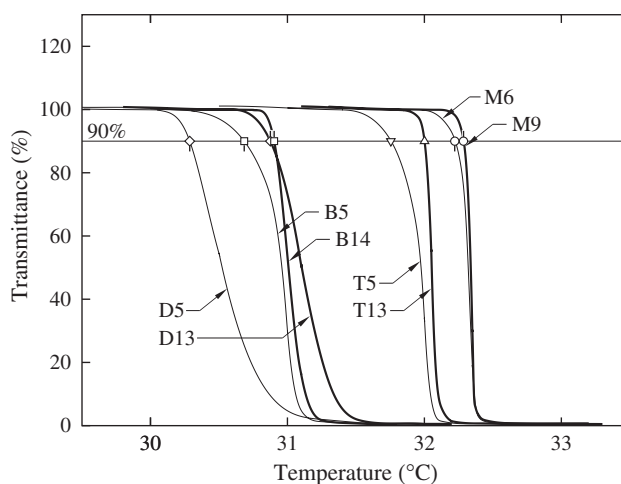
### Cloud Point

The (relative) transmittance of light through the aqueous solutions of the PNIPA samples M6, M9, T5, T13, B5, B14, D5, and D13, at the weight fraction  $w = 5.04, 4.93, 5.04, 5.07, 4.96, 5.09, 4.94,$  and  $5.02\%$ , respectively, in heating process are plotted against temperature in Figure 2. Here, the (relative) transmittance is defined as the ratio of the intensity of light passing through a test solution at a temperature to that at a lower temperature at which the test solution may be regarded as transparent. The light curves represent the values of M6, T5, B5, and D5 and the heavy ones represent those of M9, T13, B14, and D13, as indicated.

The transmittance as a function of temperature is expected to decrease steeply with increasing temperature at a threshold temperature, *i.e.*, the cloud point where the macroscopic phase separation takes place if the solution under consideration really



**Figure 1.** <sup>1</sup>H NMR spectra of the methylene (a) and methine (b) protons in the main chain and the methyl protons (c) in the side group for all the PNIPA samples.



**Figure 2.** Temperature dependence of the transmittance of light passing through aqueous solutions of the PNIPA samples M6, M9, T5, T13, B5, B14, D5, and D13, at  $w = 5.04, 4.93, 5.04, 5.07, 4.96, 5.09, 4.94,$  and  $5.02\%$ , respectively, the symbols  $\circ, \triangle, \square, \diamond,$  and  $\diamond$  representing the respective cloud points (see the text).

shows the LCST miscibility behavior. From Figure 2, however, it is seen that the shape of the transmittance curve depends on the kind of sample and also on  $M_w$  and its decrease is rather

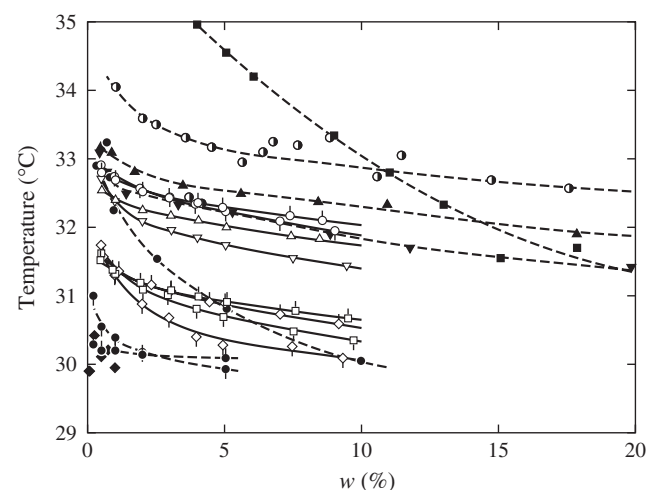
**Table II.** Cloud Points in Aqueous Poly(*N*-isopropylacrylamide) Solutions

M6		M9		T5		T13		B5		B14		D5		D13	
<i>w</i> (%)	Temp. (°C)	<i>w</i> (%)	Temp. (°C)	<i>w</i> (%)	Temp. (°C)	<i>w</i> (%)	Temp. (°C)	<i>w</i> (%)	Temp. (°C)	<i>w</i> (%)	Temp. (°C)	<i>w</i> (%)	Temp. (°C)	<i>w</i> (%)	Temp. (°C)
0.49	32.9 <sub>1</sub>	0.51	32.8 <sub>0</sub>	0.50	32.7 <sub>1</sub>	0.52	32.5 <sub>4</sub>	0.50	31.6 <sub>2</sub>	0.47	31.5 <sub>2</sub>	0.49	31.7 <sub>4</sub>	0.58	31.5 <sub>7</sub>
0.98	32.7 <sub>4</sub>	1.02	32.6 <sub>9</sub>	0.99	32.3 <sub>8</sub>	1.02	32.4 <sub>0</sub>	1.01	31.3 <sub>2</sub>	0.91	31.3 <sub>8</sub>	0.99	31.3 <sub>0</sub>	1.14	31.3 <sub>6</sub>
1.91	32.5 <sub>7</sub>	2.01	32.5 <sub>2</sub>	2.00	32.0 <sub>9</sub>	2.01	32.2 <sub>5</sub>	2.02	31.0 <sub>9</sub>	1.93	31.1 <sub>9</sub>	1.99	30.8 <sub>8</sub>	2.33	31.1 <sub>6</sub>
3.00	32.4 <sub>4</sub>	2.98	32.4 <sub>3</sub>	3.06	31.9 <sub>6</sub>	3.04	32.1 <sub>7</sub>	2.93	31.0 <sub>1</sub>	3.05	31.0 <sub>8</sub>	2.97	30.6 <sub>8</sub>	3.04	31.0 <sub>7</sub>
3.93	32.3 <sub>4</sub>	4.03	32.3 <sub>6</sub>	4.01	31.8 <sub>5</sub>	4.05	32.1 <sub>0</sub>	3.98	30.8 <sub>1</sub>	4.05	30.9 <sub>9</sub>	3.97	30.4 <sub>0</sub>	4.45	30.9 <sub>1</sub>
5.04	32.2 <sub>3</sub>	4.93	32.2 <sub>9</sub>	5.04	31.7 <sub>4</sub>	5.07	32.0 <sub>0</sub>	4.96	30.6 <sub>9</sub>	5.09	30.9 <sub>1</sub>	4.94	30.2 <sub>8</sub>	5.02	30.8 <sub>9</sub>
7.02	32.0 <sub>9</sub>	7.39	32.1 <sub>7</sub>	7.50	31.5 <sub>5</sub>	7.43	31.8 <sub>7</sub>	7.52	30.4 <sub>8</sub>	7.59	30.7 <sub>8</sub>	7.47	30.2 <sub>6</sub>	7.03	30.7 <sub>3</sub>
9.03	31.9 <sub>5</sub>	8.57	32.1 <sub>0</sub>	9.46	31.4 <sub>4</sub>	8.47	31.8 <sub>3</sub>	9.71	30.3 <sub>5</sub>	9.51	30.6 <sub>7</sub>	9.32	30.0 <sub>9</sub>	9.17	30.5 <sub>9</sub>

gentle except for the samples M9 and T13. Such results arouse us some doubt if the decrease in the transmittance really corresponds to the macroscopic phase separation in all cases. We note that the shape of transmittance curve is independent of the rate of increase in temperature if it is slower than 1.5 °C/h.

The cloud point is experimentally determined to be the temperature at which a given test solution just begins to be turbid, *i.e.*, its transmittance just starts to decrease from 100%, in the heating process. Because of the situation mentioned above, it is difficult to determine such a temperature unambiguously, so that we adopt the temperature at which the transmittance becomes 90% as the cloud point, for convenience. The symbols ◐, ◑, ▽, △, ◒, ◓, ◔, and ◕ in Figure 2 represent the cloud points so determined for the samples M6, M9, T5, T13, B5, B14, D5, and D13, respectively. Although there still remain some issues concerning the experimental determination of the cloud point, it is clearly seen that the cloud points for the samples M6, M9, T5, and T13 are definitely higher than those for the samples B5, B14, D5, and D13 in spite of the fact that all the samples have the same  $f_i$  and the same end group and that all the test solutions in Figure 2 are at almost the same concentration. Although the cloud point in general depends on  $M_w$  of the sample used, the above-mentioned difference in the cloud point is larger than that between the two samples of each kind (M, T, B, and D) having different  $M_w$ .

In Table II are given the cloud points so determined for aqueous solutions of all the eight PNIPA samples at various  $w$ . Figure 3 shows plots of the cloud point against  $w$  for the aqueous PNIPA solutions. The unfilled symbols represent the present data for the PNIPA samples M6 (◐), M9 (◑), T5 (▽), T13 (△), B5 (◒), B14 (◓), D5 (◔), and D13 (◕), each solid curve connecting smoothly the data points for the same sample. The filled symbols represent the literature data for PNIPA samples synthesized by radical polymerization by the use of AIBN as an initiator in various solvent conditions, *i.e.*, the data by Fujishige *et al.*<sup>3</sup> for the sample with the molecular weight  $M = 8.40 \times 10^6$  synthesized in a benzene/acetone mixture at 60 °C (◆), which have been evaluated from their transmittance data in the manner mentioned above, those by Boutris *et al.*<sup>5</sup> for the sample with  $M_n = 9.0 \times 10^3$  synthesized in benzene at 50 °C (■), those by Tong *et al.*<sup>6,7</sup> for the samples with  $M_w = 4.94 \times 10^4$  (▼) and  $1.01 \times 10^5$  (▲) synthesized in *tert*-butanol



**Figure 3.** Cloud-point curves for aqueous solutions of PNIPA. The unfilled symbols represent the present data for the samples M6 (◐), M9 (◑), T5 (▽), T13 (△), B5 (◒), B14 (◓), D5 (◔), and D13 (◕) and the filled and half-filled symbols the literature data by Fujishige *et al.*<sup>3</sup> for the sample with  $M = 8.40 \times 10^6$  (◆), by Boutris *et al.*<sup>5</sup> for the sample with  $M_n = 9.0 \times 10^3$  (■), by Tong *et al.*<sup>6,7</sup> for the samples with  $M_w = 4.94 \times 10^4$  (▼) and  $1.01 \times 10^5$  (▲), by Afroze *et al.*<sup>8</sup> for the sample with  $M_w = 1.0 \times 10^4$  (●), by de Azevedo *et al.*<sup>9</sup> for the sample with  $M_w = 6.15 \times 10^5$  (◐), and by Furyk *et al.*<sup>10</sup> for the samples with  $M_w = 5.58 \times 10^4$  (◑) and  $4.75 \times 10^5$  (◒). The solid and dashed curves connect smoothly the present and literature data points, respectively.

at 55 °C, those by Afroze *et al.*<sup>8</sup> for the sample with  $M_w = 1.0 \times 10^4$  synthesized in tetrahydrofuran at 50 °C (●), and those by Furyk *et al.*<sup>10</sup> for the samples with  $M_w = 5.58 \times 10^4$  (◑) and  $4.75 \times 10^5$  (◒) synthesized in methanol. The symbol ◐ represents the literature data for the PNIPA samples with  $M_w = 6.15 \times 10^5$  synthesized by aqueous redox polymerization at 25 °C by de Azevedo *et al.*<sup>9</sup> Each dashed curve connects smoothly the literature data points for the same sample.

Considering the ambiguity in the determination of the cloud point, the present data for T5 and T13 are consistent with the corresponding literature ones by Tong *et al.*<sup>6,7</sup> but the present data for M6 and M9 and those for B5 and B14 are appreciably different from the corresponding literature ones by Furyk *et al.*<sup>10</sup> and Boutris *et al.*<sup>5</sup> respectively. The difference between the present data for M6 and M9 and those by Furyk *et al.* may be regarded as arising from the fact that the instrument used by them to determine the cloud point is a newly-designed one,<sup>18</sup>

which measures intensity of light scattered from solutions contained in rectangular capillary tubes under a temperature gradient, and completely different from those used by the others and us. The cause of the difference between the present data for B5 and B14 and those by Boutris *et al.* is not clear. As for the literature data by Fujishige *et al.*,<sup>3</sup> Afroze *et al.*,<sup>8</sup> and de Azevedo *et al.*,<sup>9</sup> we have no corresponding sample to be compared because the polymerization solvents and/or the initiators used by them are different from ours.

As first pointed out by Tong *et al.*,<sup>6</sup> the cloud point is lower for the sample with smaller  $M_w$  in the range of  $1 \lesssim w \lesssim 10\%$  for each pair of samples synthesized in the same solvent, although it is not conclusive because of the above-mentioned ambiguity in the determination of the cloud point. If such dependence of the cloud point on  $M_w$  is true, it is opposite to that of the literature data for the aqueous POE solutions,<sup>11,12</sup> the latter dependency being easy to understand on the basis of the conventional polymer solution thermodynamics.<sup>19</sup> Considering the recent results for aqueous solutions of block copolymers having hydrophobic end parts,<sup>10,20–23</sup> it may be regarded as arising from interactions between hydrophobic chain end groups.

It is more important to note that the cloud points for the samples B5, B14, D5, and D13 are definitely lower than those for the samples M6, M9, T5, and T13. Recently, Gao and Frisken<sup>24,25</sup> have carried out aqueous redox polymerization of PNIPA at various temperatures ranging from 40 to 90 °C and then found that gel particles of PNIPA have been formed by interchain self-cross-linking (or branching) through the chain transfer reaction during and after the polymerization. Their result implies that the quality (good or poor) of the solvent used for radical polymerization should probably affect the primary structure of resultant PNIPA, *i.e.*, the poorer the solvent is, the higher degree of branching the resultant PNIPA should have. The samples B5 and B14 therefore seem to have higher degree of branching than the samples M6, M9, T5, and T13, since benzene is a poor solvent for PNIPA, while methanol and *tert*-butanol are the good. The decrease in the cloud point for the samples B5 and B14 might be caused by increase in the number of the hydrophobic end groups associated with the increase in the degree of branching. As for the samples D5 and D13, we have no plausible reason for their lower cloud point.

## CONCLUDING REMARKS

The cloud point was determined for aqueous solutions of the four kinds of PNIPA samples synthesized by radical polymerization in methanol, *tert*-butanol, benzene, and 1,4-dioxane by the use of AIBN as an initiator. It has then been found that the cloud points for the samples synthesized in benzene and 1,4-dioxane are definitely lower than those for the samples synthesized in methanol and *tert*-butanol, although all the samples have almost the same stereochemical composition and the same end group. On the basis of the recent experimental results obtained by Gao and Frisken,<sup>24,25</sup> we have conjectured that the PNIPA samples synthesized in the different kinds of solvents should probably have different primary structures, *i.e.*,

the degree of branching, which might mainly be caused by the difference in the quality (good or poor) of the solvent used for radical polymerization. In order to confirm such a conjecture, it is desirable to examine the primary structure of PNIPA synthesized by radical polymerization in some solvents having different quality on the basis of, for example, its dilute solution properties.

**Acknowledgment.** This research was supported by a Grant-in-Aid for Young Scientists (B) (18750099) and in part by the global COE program “International Center for Integrated Research and Advanced Education in Materials Science,” from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Received: December 5, 2007

Accepted: February 1, 2008

Published: March 19, 2008

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