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Poly(*N*-isopropylacrylamide) Prepared by Free-Radical Polymerization in Aqueous Solutions and in Nanocomposite Hydrogels

*Kazutoshi Haraguchi,**[1] *Yingjia Xu,*[1,2] *Guang Li*[2]

Summary: The molecular characteristics of poly(*N*-isopropylacrylamide) (PNIPA) synthesized in aqueous solution were studied with respect to its polymer yield, molecular weight (MW), the polydispersity (the ratio of weight- to number-average molecular weight: M_w/M_n), and intrinsic viscosity ([η]). Gel permeation chromatography (GPC) measurements were performed on unfractionated and fractionated PNIPA by selecting appropriate conditions and solvents, e.g., DMF/10 mM LiBr. It was observed that the MW, M_w/M_n and [η] of PNIPA change significantly depending on the monomer concentration ([NIPA]) in the reaction solution. Linear relationships were observed for the variations of log [NIPA] and M_w/M_n with log M_w. Also, the Mark-Houwink-Sakurada equation and the molecular weight exponent α were determined for PNIPA in DMF/10 mM LiBr solution (GPC measurements) and in methanol (light scattering measurements). Also, PNIPA chains were separated from nanocomposite hydrogels with different clay concentrations by decomposing the clay using an aqueous HF solution. The resulting PNIPA showed good correlation between M_w and [η] consistent with that for PNIPA synthesized in aqueous solution. The effects of fractionation and solvents on α and chain conformations, as well as the relationship between α and [η] are discussed.

Keywords: free-radical polymerization; mark-houwink-sakurada equation; molecular weight; nanocomposite gel; poly(*N*-isopropylacrylamide)

Introduction

Poly(*N*-isopropylacrylamide) (PNIPA) is one of the most well-known thermosensitive polymers because it exhibits a clear coil-to-globule transition in aqueous media at a lower critical solution temperature (LCST ≈ 32 °C).[1] The sensitivities of an aqueous solution of PNIPA and of PNIPA hydrogel to various external stimuli such as temperature, salt concentration, pressure, and solvents and the origin of this sensitivity have been studied extensively.[2] Consequently, PNIPA has been used as a key component of functional devices in many advanced research fields, such as thermo-modulated displays,[3] microfluidic systems[4], drug delivery systems,[5] artificial glucose-responsive insulin systems,[6] protein absorption microspheres,[7] tissue and cell-cultivation engineering,[8] photoregulated devices,[9] and selective separation systems.[10] Recently, the synthesis of a new type of PNIPA hydrogel, i.e., nanocomposite hydrogel (NC gel) consisting of PNIPA and inorganic clay nanoparticles, has solved serious problems associated with conventional chemically cross-linked PNIPA hydrogels, such as structural heterogeneity and mechanical fragility.[11] These gels have a number of new functions[12] as well as extraordinary optical, mechanical, and swelling/deswelling properties due to their

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[1] Material Chemistry Laboratory, Kawamura Institute of Chemical Research, 631 Sakado, Sakura, Chiba 285-0078, Japan
Fax: (+81) 43-498-2182; E-mail: hara@kicr.or.jp
[2] College of Material Science & Engineering, Donghua University, Shanghai 200051, China

unique organic (PNIPA)/inorganic (clay) network structure. Thus, PNIPA (and its hydrogels) have attracted considerable interest and have been widely studied from both academic and technological points of view.

Although a number of papers and reviews on PNIPA have been published,[13–27] the molecular characteristics of PNIPA, such as changes in molecular weight (MW), the relationship between MW and intrinsic viscosity ($[\eta]$) (i.e., Mark-Houwink-Sakurada (M-H-S) equation), and the effect of fractionation, have still not been completely elucidated, particularly in the case of PNIPA synthesized in water. MW and the polydispersity (the ratio of weight- to number-average molecular weight: M_w/M_n) of PNIPA synthesized and characterized under various conditions in previous studies are summarized in Table 1. In these studies, PNIPA was normally synthesized in organic solvents such as methanol, benzene, t-butyl alcohol, dioxane, or their mixtures, as shown in Table 1(a), and only in a few studies (Table 1(b)) was PNIPA synthesized in aqueous media considered. MW of PNIPA was measured by gel permeation chromatography (GPC) and/or light scattering (LS) under various conditions, which are also listed in Table 1. For PNIPA synthesized in organic solvents, MW varied over a wide range (weight-average molecular weight $M_w = 10^4$–$10^7\,g \cdot mol^{-1}$) depending on the conditions for its synthesis, while

Table 1.

Molecular weight of PNIPA synthesized in (a) organic solvent and (b) water by free radical polymerization.

(a)

Polymerization condition			Molecular weight[a] (10^5 g mol^{-1})	Fractionation (M_w/M_n)	Characterization methods	Ref.
Solvent	Temperature (°C)	Time (hours)				
methanol	70	25	0.178-4.75	Yes. (1.32-2.55)	LS[c](MeOH, M_w) GPC(THF, PS[d], M_w/M_n)	14[g]
tert-butyl alcohol	55	8	0.494-1.01	Yes. (1.21-1.23)	LS(THF, 25 °C, M_w) GPC(PS) (M_w/M_n)	15
benzene	49	22	4.4 (1.6)	No.(2.8)	GPC(THF, DMF, PS, M_w, M_n, M_w/M_n, Mp)	16
dioxane	60	2	0.31 (0.19)	No.(1.63)	GPC(THF, PS) (M_w, M_n, M_w/M_n) [n][e] (THF, 27 °C)	17
benzene/acetone mixture	60	–[b]	1.38–91 (0.98–31)	Yes. (1.2–1.4)	LS(H_2O, 20 °C) (M_w) [n][f] (H_2O, 20 °C) (M_n)	18

[a] Weight-average molecular weight (M_w)was in column 4 and number-average molecular weight (M_n) was in bracket. [b] Not be mentioned. [c] Static light scattering. [d] Polystyrene as standards. [e] $[n] = 9.59 \times 10^{-3}\,M_n^{065}\,cm^3/g$. [f] $[n] = 0.145 M_n^{0.50}\,cm^3/g$. [g] In ref. 14 (LS, GPC), ref. 15 (GPC), ref. 16 (GPC), ref. 17 (GPC), authors did not mention the temperature during.

(b)

Polymerization condition			Molecular weight [a] (10^5 g mol^{-1})	Fractionation (M_w/M_n)	Characterization methods	Ref.
Solvent	Temperature (°C)	Time (hours)				
H_2O(PB)[b]	R.T.[c]	15	1.60 (0.49) 0.76 (0.11)	Yes. (3.2, 6.9)	GPC[d](THF, PS[e]) (M_w, M_n, M_w/M_n)	19, 20
H_2O (deionized)	27	10	(70 ± 5)	Yes. (1.31 ± 0.06)	LS[f] (H_2O, 25 °C)	21
H_2O	0	–[g]	23	No (6.7)	GPC (POE[h]) (M_w, M_w/M_n)	22
H_2O	0	–[g]	23 (2.9)	No.	Not be mentioned	23

[a]Weight-average molecular weight (M_w) was in column 4 and number-average molecular weight (M_n) was in bracket. [b]15 mM phosphate buffer in normal saline. [c]Room temperature. [d]In ref. 19, 20 (GPC), authors did not mention the temperature during measurement. [e]Polystyrene as standards. [f]Static light scattering. [g]Not be mentioned.[h]Poly(oxy ethylene) as standards.

Table 2.
M-H-S equation of PNIPA obtained in previous studies and present study.

K	α[a]	Viscosity	Molecular weight[b]	Fractionation	Polymerization:	Ref.
($\times 10^3$)		Measurement:	($\times 10^5$ g mol^{-1})	(M_w/M_n)	Solvent & Temperature	
110	0.51		1.38–91	Yes (1.2–1.4)	benzene/acetone, 60 °C	18
145	0.50	H_2O, 20 °C	(0.92–31)	Yes (-[c])	benzene/acetone, 60 °C	24
0.458	0.93		0.66–12.5	No	Methanol, 50–70 °C	25
0.226	0.97	H_2O, 25 °C	0.66–12.5	No	Methanol, 50–70 °C	25
29.9	0.64	CH_3OH, 25 °C	0.723–12.5	No	Methanol, 50–70 °C	25
9.59	0.65	THF, 27 °C	(0.92–31)	Yes. (-)	benzene/acetone, 60 °C	24
5.75	0.78		(0.196–2.94)	No.(1.18–1.61)	RAFT[d]	26
3.89	0.75	DMF + 10 mM LiBr, 40 °C	0.61–42.85	No.(1.52–4.69)	H_2O, 20 °C	this work
5.20	0.74		3.74–52.74	Yes.(1.35–1.75)	H_2O, 20 °C	

[a] $[\eta] = K(MW)^a$ ($[\eta]$: cm^3/g). [b] Weight-average molecular weight (M_w) was in column 4 and number-average molecular weight (M_n) was in bracket. [c] Not be mentioned. [d] RAFT: reversible addition-fragmentation chain transfer.

MW of PNIPA synthesized in water is limited to a relatively narrow range ($M_w = 10^5$–10^6 g·mol^{-1}). Several M-H-S equations for viscosity molecular weight relationship and their relevance to chain conformations have been reported for PNIPA synthesized in organic solvents in various papers cited in Table 2; however, there are conflicts between the exponents α used in these equations, as described later.

The present study focuses on PNIPA synthesized in aqueous systems, which is widely used but less studied. Firstly, PNIPA samples with a wide range of MW were prepared in aqueous solutions by altering the monomer concentration and were characterized in terms of polymer yield, MW, M_w/M_n, and $[\eta]$ by means of GPC, viscometry, and light scattering measurements. Also, the M-H-S equation was determined for the PNIPA synthesized and the effects of fractionation and solvent are discussed. Further, the results for PNIPA synthesized in aqueous solution were compared with those of PNIPA in NC gels and obtained by eliminating clay from the PNIPA/clay networks.

Experimental Part

Raw Materials

N-isopropylacrylamide (NIPA) monomer, provided by Kohjin Co., Ltd., Japan, was purified by recrystallization from a toluene/*n*-hexane mixture and dried under vacuum at 40 °C. Other reagents such as potassium peroxodisulfate (KPS), *N,N,N',N'*-tetramethylethylenediamine (TEMED), hydrofluoric acid (HF, assay of 46.0–48.0 wt%), *N,N*-dimethylformamide, and lithium bromide (anhydrous, 99.9%) were purchased from Wako Pure Chemical Industries, Japan, and used without further purification. The synthetic hectorite "Laponite XLG" (Rockwood Ltd.; $[Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4]Na_{0.66}$; layer size = φ30 nm × 1 nm) was used as the inorganic clay after washing and freeze-drying. Ultrapure water, purified by using a Puric-Mx system (Organo Co., Japan), was used for *in-situ* polymerization. For the preparation of reaction solutions, nitrogen gas was bubbled through the ultrapure water for more than 3 hr prior to use.

Synthesis of PNIPA

PNIPA was prepared by free-radical polymerization using aqueous reaction mixtures consisting of a monomer (NIPA), a solvent (water), an initiator (KPS), and an accelerator (TEMED). The initial reaction solutions, consisting of water (95 ml), the initiator (3.70×10^{-1} mmol in 5 ml H_2O), the accelerator (5.34×10^{-1} mmol), and different amounts of monomer, used for the preparation of PNIPA were prepared at ice-water temperature. Then, free-radical polymerization was allowed to proceed in a water bath at 20 °C for 20 h. The monomer concentration, [NIPA], was varied over a wide range from 0.005 to 1.0 $\text{mol} \cdot \text{l}^{-1}$. In all cases, the solutions were washed several times in an excess of pure water at 50 °C (>LCST) after polymerization to eliminate remaining monomer and additives. The solutions were then dried in an oven at 80 °C to constant weight. The resulting PNIPA is represented as PN*m* where *m* is [NIPA] in units of $\text{mol} \cdot \text{l}^{-1}$. The polymerization yield was obtained from the ratio of weights of PN*m* obtained and NIPA used. Fractionation of PN*m* was performed using mixed solvents (acetone/hexane) with different ratios in the range of 100/0 – 43/57.

Synthesis of NC Gels

NC gels were prepared in a similar manner to PNIPA, except for the presence of inorganic clay (Laponite XLG), with [NIPA] = 1 M or $m = 1$, unless otherwise noted. The NC gels prepared are referred to as NC*n* gels, where the value of *n* depends on the clay concentration ($C_{clay} = n \times 10^{-2}\,\text{mol} \cdot \text{l}^{-1}$).

Separation of PNIPA from NC Gel by Degrading the Clay

The procedure for removing clay from NC gels was the same as that described in a previous paper.[28] In brief, an NC gel was cut into small pieces (approximately 5 × 5 × 3 mm), and the pieces placed in excess aqueous hydrofluoric acid (HF) while stirring. The amount of aqueous HF solution used, e.g. 30 ml (HF = 0.2 wt%) per 1 g of the NC3 gel, was sufficient to decompose the clay. After 24 h, PNIPA was recovered from the HF solution by increasing the solution temperature to 50 °C (higher than the LCST of PNIPA) and purified by alternating the temperature between 20 and 50 °C and exchanging water at 50 °C. The inorganic precipitate formed was removed by filtering the solution at 20 °C (pore size of the filter: 3 μm). It was confirmed by thermogravimetric analyses that no PNIPA was trapped on the filter. The PNIPA obtained from an NC*n* gel is denoted as PNIPA(NC*n*$^{\text{-clay}}$).

Measurements

GPC

GPC measurements were performed using a Shodex GPC System-21 chromatograph with a Shodex RI-71S monitor and a UV/VIS detector to determine the molecular weight of PNIPA and PNIPA(NC*n*$^{\text{-clay}}$). A KD-G (guard column) and three KF-807L separation columns, each fitted with a 2 μm pore-size filter, were used. A mixed solvent (DMF + 10 mM LiBr) was mainly used as the solvent for GPC measurements because of the reasons described in the first section of the results. The concentration of PNIPA in the solution was 1 mg/1 ml, unless otherwise specified. The solution was passed through a 5 μm filter prior to GPC measurements. In some cases, a filter with a pore size of 1 or 0.45 μm was used. The calibration curve was obtained on the basis of 7 different polystyrene standards from Shodex ($M_w = 4.89 \times 10^4 - 5.80 \times 10^6$, $M_w/M_n = 1.03 - 1.05$) and fitted by a third-order polynomial. The working temperature was 40 °C (±0.1 °C) and the flow rate was 1.0 ml/min. The working temperature was higher than room temperature to enhance control in the instrument equipped only with a heater.

Viscosity

Viscosity measurements were carried out using an Ubbelohde capillary viscometer. Two solvents, DMF + 10 mM LiBr (at 40 ± 0.1 °C) and water (at 20 ± 0.1 °C), were used for the measurements. The viscosities of the PNIPA solutions, η_{soln}, were measured as a function of the PNIPA concentration, C_{PNIPA}. Then, the specific viscosities η_{sp} and intrinsic viscosities $[\eta]$ of the solutions were obtained according to the equations $\eta_{sp} = (\eta_{soln} - \eta_0)/\eta_0$ and $[\eta] = \lim_{(C \to 0)}\ \eta_{sp}/C_{PNIPA}$, respectively. Here, η_0 denotes the viscosity of the solvent used. For the measurement of η_{soln}–η_0, flow times were of the order of a hundred seconds and were highly reproducible with an error less than ±0.2 s. The relative error in the measurement was estimated to be approximately 0.1%.

Light Scattering

Light scattering (LS) measurements were carried out to determine M_w and A_2 (the second virial coefficient) in methanol at 25 °C using an Ar laser (wavelength $\lambda_0 = 488$ nm; DLS-7000, Otsuka Electronics Co., Ltd.). Measurements were made at scattering angles θ ranging from 30° to 150°. The data obtained were treated using Berry's square-root plot. The refractive index increment $\partial n/\partial c$ was 0.185 cm^3/g and the refractive index n_0 of methanol at 25 °C at a wavelength of 488 nm was 1.3337.[27]

Results

GPC Measurements of PNIPA

So far, various solvents such as THF,[14–17,19,20,26,29] water,[31–33] methanol,[31,34] chloroform[35] and DMF[36] have been used as the mobile phase for GPC measurement of PNIPA. However, there have been controversies regarding the validity of GPC measurement of PNIPA due to problems associated with filtration,[30] solvent effects,[31] and irreversible chain aggregation.[26] Consequently, GPC measurements were successfully conducted only for PNIPA with fairly low MW ($M_w < 5 \times 10^5$ g · mol^{-1}). In the present study, DMF/10 mM LiBr was used as solvent for PNIPA, since GPC profiles acquired using this solvent are more reliable than those using THF and water, particularly in the case of PNIPA with high M. To characterize PNm with as high MW as possible, we selected the following configuration for GPC measurements: filter pore size = (5 μm + 2 μm), solvent = DMF/10 mM LiBr, working temperature = 40 °C, and PNIPA concentration = 1 mg/ml.[37]

The results (GPC profiles) for PNm are shown in Figure 1. It was concluded that PNm ($m \leq 0.2$) can be reliably characterized under the current experimental conditions for GPC, while for PNm ($0.3 \leq m \leq 0.5$) true values will not be obtained because small amounts of very-high-molecular-weight (probably, cross-linked) PNIPA chains are excluded by trapping during GPC measurements. It was expected that trapping of some PNIPA chains by filters with small pore sizes would decrease on dilution if the problem arose from simple physical entanglements. However, the shapes of the chromatograms for PN0.3 and PN0.5 are virtually identical for PNIPA concentrations of 1 and 0.3 mg/ml, as shown in Figure 2. On the other hand, for PNm with $m > 0.5$, performing GPC measurements was impossible because PNIPA does not dissolve completely, even in DMF/10 mM LiBr. In fact, even diluted PN0.6 solution with a concentration as low as 0.1 wt% was visually inhomogeneous. This is attributed to gel formation in PNm ($m \geq 0.6$), as described in the preceding paper.

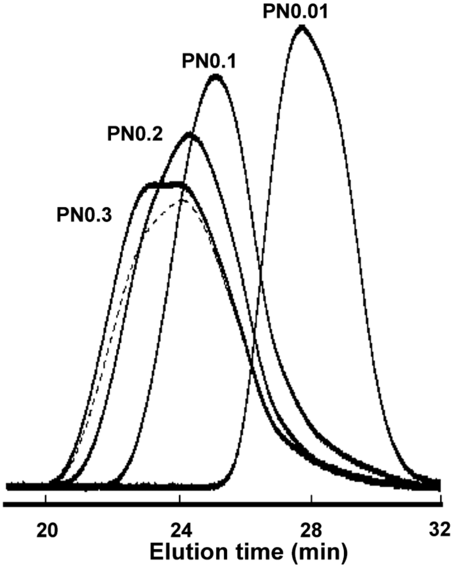

Figure 1.
GPC chromatograms for PNm samples. Solvent is DMF/10 mM LiBr (40 °C), filter pore size (prior to GPC measurement) = 5 μm (solid lines) and 1 μm (dashed lines). For PNm ($m \leq 0.2$), solid and dashed lines overlap.

Molecular Characteristics of PNIPA Synthesized in Aqueous Solution

In the present study, PNIPA was prepared by free-radical polymerization in aqueous solution at 20 °C with different [NIPA] in the range 0.005 to 1.0 mol · l^{-1}. The as-prepared PNIPA solutions were all uniform

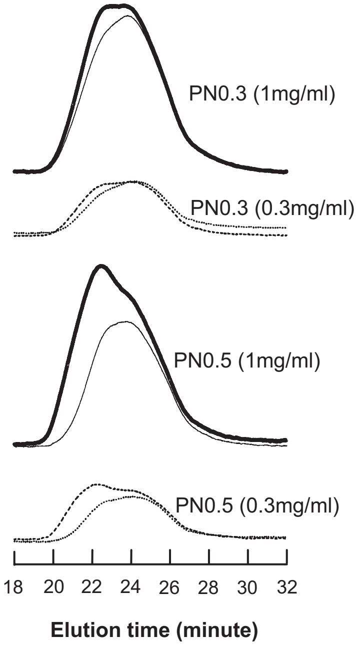

Figure 2.
Influence of polymer concentration on GPC chromatogram of PNIPA of high molecular weight (PN0.3 and PN0.5). PNIPA concentration = 1 mg/ml (solid line), 0.3 mg/ml (broken line). Flow rate = 1 ml/min. Filter pore size (prior to GPC measurement) = 5 μm (thick lines) and 1 μm (thin lines).

and transparent regardless of [NIPA], although they were very viscous and somewhat adhesive when [NIPA] was higher than $0.5\,\mathrm{mol \cdot l^{-1}}$. All PNIPA solutions produced transparent solids, PN*m*, on purification and drying. The resulting polymers were ground to powders and dissolved in a suitable solvent for characterization. Characteristics of PN*m*, such as polymer yield (conversion) by weight, MW and the polydispersity (M_w/M_n) determined by GPC, and intrinsic viscosity $[\eta]$ determined by viscometry are listed in Table 3(a). The observations are as follows:

(1) In general, the polymer yields (conversion of NIPA) were very high, more than 99.5 wt%, for PN*m* ($m \geq 0.2$). However, the polymer yields decreased steeply as [NIPA] decreased. For example, the yields were 97 wt% and 34 wt% for [NIPA] = 0.1 and $0.005\,\mathrm{mol \cdot l^{-1}}$, respectively.

(2) It was found that both M_w and number-average molecular weight (M_n) increased significantly with increasing [NIPA], as shown in Table 3(a). Based on polystyrene standards, both M_w and M_n were found to vary from 6.1×10^4 to $4.3 \times 10^6\,\mathrm{g \cdot mol^{-1}}$ and from 4.9×10^4 to $1.0 \times 10^6\,\mathrm{g \cdot mol^{-1}}$, respectively, as [NIPA] increased from 0.005 to $0.5\,\mathrm{mol \cdot l^{-1}}$. The relationships between log M_w and logM_n with log [NIPA] are shown in Figure 3. It was found that MW and [NIPA] ($\mathrm{mmol \cdot l^{-1}}$) correlate well with the empirical equations 1 for M_w and 2 for M_n. In both cases, linear relationships were observed over a wide range of [NIPA] values from 5 to 200 mM.

$$M_w = 1.128 \times 10^4\,[\mathrm{NIPA}]^{0.98} \qquad (1)$$

$$M_n = 1.379 \times 10^4[\mathrm{NIPA}]^{0.69} \qquad (2)$$

M_w and M_n for PN*m* prepared at high *m* ($\geq$0.6), which could not be measured due to the incomplete dissolution of PNIPA in the solvent, can be estimated from equations 1 and 2. For example, for $m = 1$, which is normally used for the preparation of conventional PNIPA hydrogels and NC gels, M_w and M_n were estimated to be $9.82 \times 10^6\ \mathrm{g \cdot mol^{-1}}$ and $1.62 \times 10^6\ \mathrm{g \cdot mol^{-1}}$, respectively.

(3) The polydispersity, represented by M_w/M_n increased rapidly with increasing *m* at low [NIPA] and reached a plateau at high [NIPA] (Table 3(a)). In detail, M_w/M_n was quite small (<2) at very low [NIPA] ($\leq 0.02\ \mathrm{mol \cdot l^{-1}}$) and reached 4.7 when [NIPA] = 0.3 $\mathrm{mol \cdot l^{-1}}$. It was also found for PN*m* ($m = 0.005$–0.2) that M_w/M_n changed almost linearly with log M_w, as expressed by Equation 3.

$$M_w/M_n = -7.67 + 1.83\,\log M_w \qquad (3)$$

(4) The incomplete dissolution of PN*m* ($m \geq 0.6$) can be attributed to gel formation from chemically cross-linked PNIPA. The spontaneous formation

Table 3.
Molecular characteristics (polymer yield, [η], M_w, and M_w/M_n) of (a) unfractionated PNIPA and (b) fractionated PNIPA polymerized in aqueous solution with different [NIPA].

(a)

samples	Conversion (%)	[η]B$_{DMF/LiBrB}$ (cm^{2}P/g)^a	M_w^b (10^{6}P g mol^{-1})	M_n (10^{6}P g mol^{-1})	M_w/M_n
PN0.005	34.4	15.66	0.061	0.049	1.26
PN0.01	60.8	24.97	0.105	0.069	1.52
PN0.02	67.6	33.22	0.192	0.098	1.95
PN0.03	80.1	51.54	0.301	0.135	2.23
PN0.04	90.0	55.67	0.381	0.151	2.51
PN0.05	90.3	82.70	0.560	0.220	2.54
PN0.06	96.1	93.85	0.645	0.216	2.99
PN0.1	97.3	135.4	1.162	0.334	3.48
PN0.2	>99.5^d	226.8	2.374	0.576	4.12
PN0.3	>99.5	311.2	3.407	0.726	4.69
PN0.5	>99.5	408.4	4.285	1.042	4.11
PN0.6^c	>99.5	–	–	–	–

(b)

samples	[η]B$_{DMF/LiBrB}$ (cm Pfg)^a	M_w^b (10^6 g mol^{-1})	M_n (10^6 g mol^{-1})	M_w/M_n
PN0.04 4th	61.87	0.374	0.258	1.45
PN0.04 3rd	81.77	0.519	0.350	1.48
PN0.1 3rd	116.4	0.781	0.579	1.35
PN0.1 2nd	191.8	1.526	1.032	1.48
PN0.3 2nd	230.2	2.054	1.385	1.48
PN0.3 1st	478.7	5.274	3.014	1.75

^{a}[η]$_{DMF/LiBr}$B is intrinsic viscosity measured in DMF + 10 mM LiBr at 40 °C. ^{b}GPC measurement: Solvent is DMF + 10 mM LiBr. Polystyrene is the standard polymer. Temperature is 40 °C, flow rate 1 ml/min. ^{c}PN0.6 cannot be fully dissolved in DMF/LiBr even when the weight ratio $W_{PNIPA}/WBDM_F/_Li_{Br}$Bis below 0.1 wt%. ^{d}PNIPA samples were dried at 80 °C in an oven until to constant weight after purification.

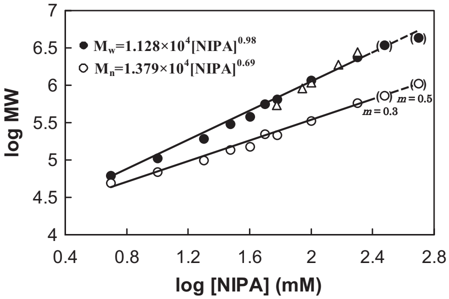

Figure 3.
Relationship between initial [NIPA] (mmol · l^{-1}) in reaction solutions and M_w or M_n of PNIPA measured by GPC. [NIPA] was varied from 5 mmol · l^{-1} to 500 mmol · l^{-1}. Data indicated by the open triangles were M_w obtained from ref. 48.

of PNIPA gel, the change in gel fraction due to [NIPA] and the polymerization temperature, and the mechanism for forming self-cross-linked PNIPA networks during the free-radical polymerization were reported in detail in the preceding paper.[37]

(5) [η] also increased with increasing [NIPA]. Further, similarly to GPC, viscosity measurements could not be performed on a diluted solution of PN*m* ($m \geq 0.6$), because the PNIPA did not dissolve completely in the solvent.

M-H-S Equation for PNIPA

The M-H-S equation (4) represents the relationship between MW and [η] of a polymer, and the molecular weight exponent α gives information on the chain conformation in solution.[38]

$$[\eta] = K(MW)^{\alpha} \qquad (4)$$

On the basis of Flory's theory,[39] this equation must be corrected for molecularly heterogeneous polymers, as follows:

$$[\eta] = KM_{\eta}^{\alpha} \qquad (5)$$

Here, M_η denotes the viscosity-average molecular weight. Since the value of M_η will always be considerably closer to M_w than to M_n for any distribution,[39] in the present study, we replace M_η with M_w in equation 5. Several methods, such as end-group titration (M_n), osmometry (M_n), light scattering (M_w), and GPC (M_w and M_n) can be used to determine M_w and M_n.[38]

In previous studies of the M-H-S equation for PNIPA, MW was obtained by light scattering[27,34] for mainly fractionated PNIPA samples. However, in the present study, first, as-prepared, unfractionated PNIPA samples were used since they are commonly employed and are useful in many practical applications. In this study, the breadth of the M_w/M_n varied widely (Table 3(a)). Since light scattering data on unfractionated PNIPA with broad polydispersity are not reliable, as described later, M_w was measured by GPC using DMF/10 mM LiBr as solvent. Actually, M-H-S equations for other polymers, such as polyacrylonitrile, poly(vinylpyrrolidone),[40] poly(vinyl acetate),[41] and poly(N-vinyl carbazole),[42] have been reported on the basis of M_w measured by GPC.

A double logarithmic plot of $[\eta]$ and M_w for unfractionated PNIPA (PN*m*) is shown in Figure 4 (indicated by closed circles). It was found that log $[\eta]$ and log M_w show a good, linear relationship, consistent with equation 6.

$$[\eta] = 3.89 \times 10^{-3}\ M_w^{0.75} \qquad (6)$$

Here, M_w is in the range of 6.1×10^4–4.29×10^6 g·mol^{-1}. The results are listed in Table 2 along with those reported previously. It should be noted that all PNIPA samples used in previous studies were obtained by polymerization in organic solvents.

In general, the value of α reflects the conformation of polymer chains in solution. For example, $\alpha = 0.5$ indicates that polymer chains are randomly coiled and the solvent is a Θ solvent. $\alpha = 0.5$–0.8 indicates that polymer chains are in a good solvent, and the increased interaction between the polymer and the solvent expands the long chains. In the case $\alpha > 0.8$, polymer chains are worm like or rod like with rigid conformations. Thus, for a flexible polymer chain, α is generally in the range of 0.5–0.8 in dilute solution.[39] In the present study, $\alpha = 0.75$, which indicates that PNIPA is flexible and randomly coiled, and the mixed solvent (DMF/10 mM LiBr) at 40 °C is a good solvent for PNIPA.

Effect of Fractionation on M-H-S Equation

The effects of fractionating PNIPA on α and the constant K in the M-H-S equation were investigated. Fractionation

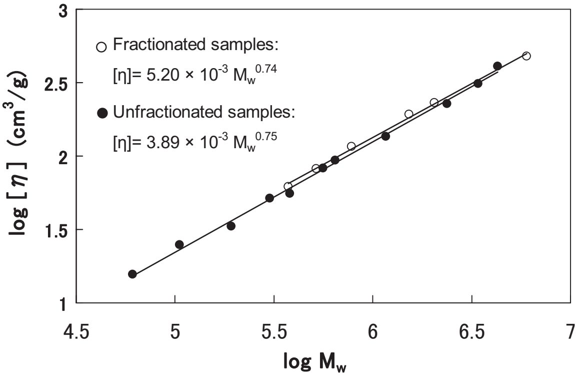

Figure 4.
Double logarithmic plot of $[\eta]$ vs. M_w of PNIPA. M_w was measured by GPC. The solvent used in $[\eta]$ and M_w measurements was DMF/10 mM LiBr.

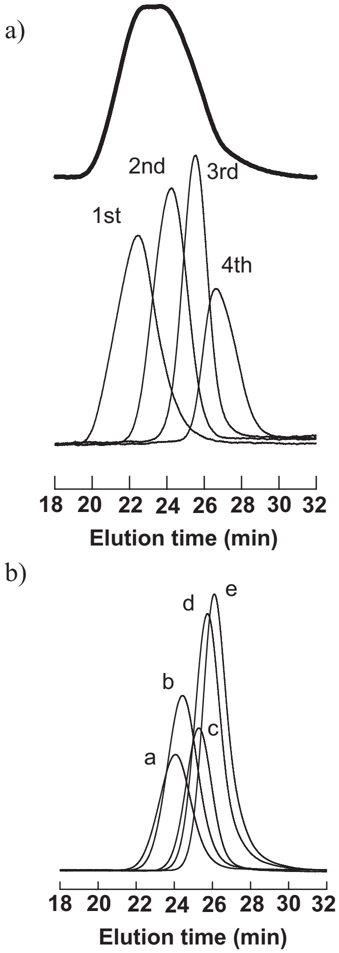

Figure 5.
(a) GPC chromatograms of unfractionated PNIPA (PN0.3) and fractionated PNIPA; (b) GPC chromatograms of fractionated PNIPA listed in 3(b); a: PN0.3 2nd, b: PN0.1 2nd, c: PN0.1 3rd, d: PN0.04 3rd, e: PN0.04 4th.

of PN*m* was performed by using an acetone/hexane mixed solvent system. Typical GPC profiles of unfractionated PN0.3 and its fractions are shown in Figure 5(a). The original PN0.3 had a broad polydispersity ($M_w/M_n = 4.69$), but was fractionated to produce fractions with narrow M_w/M_n ($=1.25 - 1.75$). GPC profiles and data (M_w and M_w/M_n) of typical fractions of PN*m* are shown in Figure 5(b) and Table 3(b), along with $[\eta]$ for each fraction. The M-H-S equation for fractionated PNIPA (equation 7) was obtained from the plots shown in Figure 4 (open circles) as follows:

$$[\eta] = 5.20 \times 10^{-3} M_w^{0.74} \tag{7}$$

Comparing this equation with equation 6, it was found that α hardly changed on fractionation ($\Delta\alpha = 0.01$). This is reasonable from the experimental and theoretical considerations[43,44] and indicates that α was the same irrespective of the M_w/M_n. On the other hand, K increased slightly ($3.89 \times 10^{-3} \rightarrow 5.20 \times 10^{-3}$) on fractionation, which is consistent with the results for poly(vinylpyrrolidone) (a water-soluble polymer),[43] but not for polystyrene, where K decreased slightly on fractionation.[44]

Light Scattering of PNIPA

Light scattering, as well as $[\eta]$, measurements on fractionated PNIPA in methanol were performed at 25 °C. The results (M_w, second virial coefficient A_2, and $[\eta]$) are shown in Table 4. From the plots shown in

Table 4.
Results of light scattering of PNIPA obtained in previous studies and present study.

Samples	Measurement condition of SLS	Mw (10P^6 g mol^{-1})	A_2 (cm^3 mol/g^2) ($\times 10^4$)	$<S^2>$ (Å^2) ($\times 10^{-4}$)	$[\eta]B_{MeOH}$ (cm P^{3P}/g)	M_w/M_n	Ref.
PN0.3 1st	MeOH, 25 °C	2.71	2.08	66.5	527.1	1.75	this work
PN0.04 2nd		0.346	4.98	29.2	129.4	1.66	
PN0.04 5th		0.135	7.35	11.8	59.74	1.43	
PN0.01		0.043	8.26	6.5	25.40	1.52	
T220		2.20	2.39	45.5	433	1.12	27
T38		0.376	3.58	6.1	127	1.20	27
Unfractionated1	THF, 20 °C	2.45	−1	106.1	/[a]	7.54	45
Unfractionated2	Water, 20 °C	2.40	−1	106.1	/	6.75	45

[a] $[\eta]$ in THF and water were not reported.

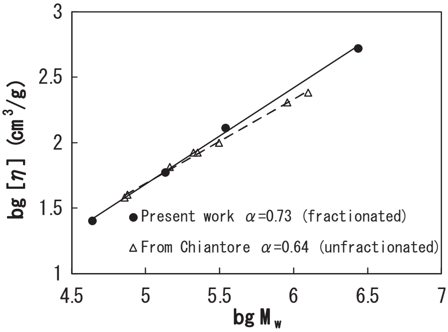

Figure 6.
Double logarithmic plot of [η] vs. M_w for fractionated PNIPA. M_w was measured by light scattering. The data indicated by triangles were obtained from ref.25. The solvent used in [η] and M_w measurements was methanol and the working temperature was 25 °C in all cases.

Figure 6, the correlation between log M_w and log [η] is represented by equation (8). The resulting value of α (0.73) is almost the same as that (0.74) obtained using M_w from GPC (in DMF/10 mM LiBr: 40 °C) for the same fractionated PNIPA.

$$[\eta] = 1.05 \times 10^{-2}\ M_w^{0.73} \tag{8}$$

Further, as shown in Table 4, A_2 for fractionated PN*m* is comparable to that reported by Osa[27] for PNIPA with similar M_w. The values of α and A_2 also indicate that PNIPA chains have flexible random-coil conformations in methanol at 25 °C.

As shown in Figure 6, the value of α obtained in the present study is rather different to that found by Chiantore ($\alpha = 0.64$), although the same conditions for measurements were used in both studies, except for the fractionation of PNIPA. We used fractionated PNIPA ($M_w/M_n = 1.3 - 1.75$), while Chiantore used unfractionated PNIPA (M_w/M_n is unknown). In previous studies, it has been reported that light scattering data on unfractionated polymers are unreliable, for example, an abnormal negative value of A_2 or a surprisingly high MW has been observed for unfractionated PNIPA[45] or poly(n-docosyl methacrylate)[46] and isotactic polystyrene[47]. Similarly, in the present study, a negative A_2 value was obtained for unfractionated PN*m*. Therefore, it is assumed that the value of α (=0.73) obtained in the present study for fractionated PNIPA is reliable.

Molecular Characteristics of PNIPA Separated from NC Gels

In order to reveal the molecular characteristics of PNIPA in NC gels, PNIPA should be separated from its NC gel by decomposing the clay (hectorite) using hydrofluoric acid (HF).[28] The proposed reaction of HF with hectorite is expressed by Equation 9. Here, most products, such as

$$\begin{aligned}&[\mathrm{Mg}_{5.34}\,\mathrm{Li}_{0.66}\,\mathrm{Si}_8\mathrm{O}_{20}(\mathrm{OH})_4]\mathrm{Na}_{0.66}\\&\quad + 58.68\,\mathrm{HF} \rightarrow 5.34\mathrm{MgF}_2 \downarrow + 8\mathrm{SiF}_6^-\\&\quad + \mathrm{Li}^+ + \mathrm{Na}^+ + \mathrm{H_2O}\end{aligned} \tag{9}$$

SiF_6^-, Li^+, Na^+, are water soluble. MgF_2 is the only insoluble product. From FTIR spectra for original hectorite (Laponite XLG) and the white precipitate left after HF treatment, which is consistent with that of MgF_2, it was confirmed that Laponite XLG is decomposed in HF aqueous solution according to equation 9. When the clay in NC gel networks is subjected to decomposition, it is necessary to select a suitable HF concentration (C_{HF}), so as to achieve complete decomposition of inorganic clay without damaging the organic PNIPA. Consequently, it was found that very low C_{HF} (e.g., 0.2 wt%) is suitable for decomposing the clay, as shown in Table 5.

Table 5.
The phenomena of linear PNIPA and N-NC gel encountered HF aqueous solution.

	0h[a]	24 h[b]	0 h	24 h	0 h	24 h	0 h	24 h
PN1.0	○[c]	□[d]	○	□	●[e]	●	●	●
NCn gel [h]	○	Δ[g]	○	√[f]	●	●	●	●
HF wt%	2.0	0.02			20			0.2

[a]The change observed immediately after putting the gel (1 g) into HF aq (40 g). [b]The change observed after immersing the gel (1 g) into HF aq (40 g) for 24 hours [c]Symbol ○ No change. [d]Symbol □ Gels swelled a lot. [e]Symbol ● Gels shrank and turned to be white. [f]Symbol √ Gels were dissolved. [g]Symbol △ Gels were partially dissolved. [h]n = 1 ~ 7: all NC gels used, i.e. NC1, NC5, NC7, NC15, NC25 gels, shows the same phenomena.

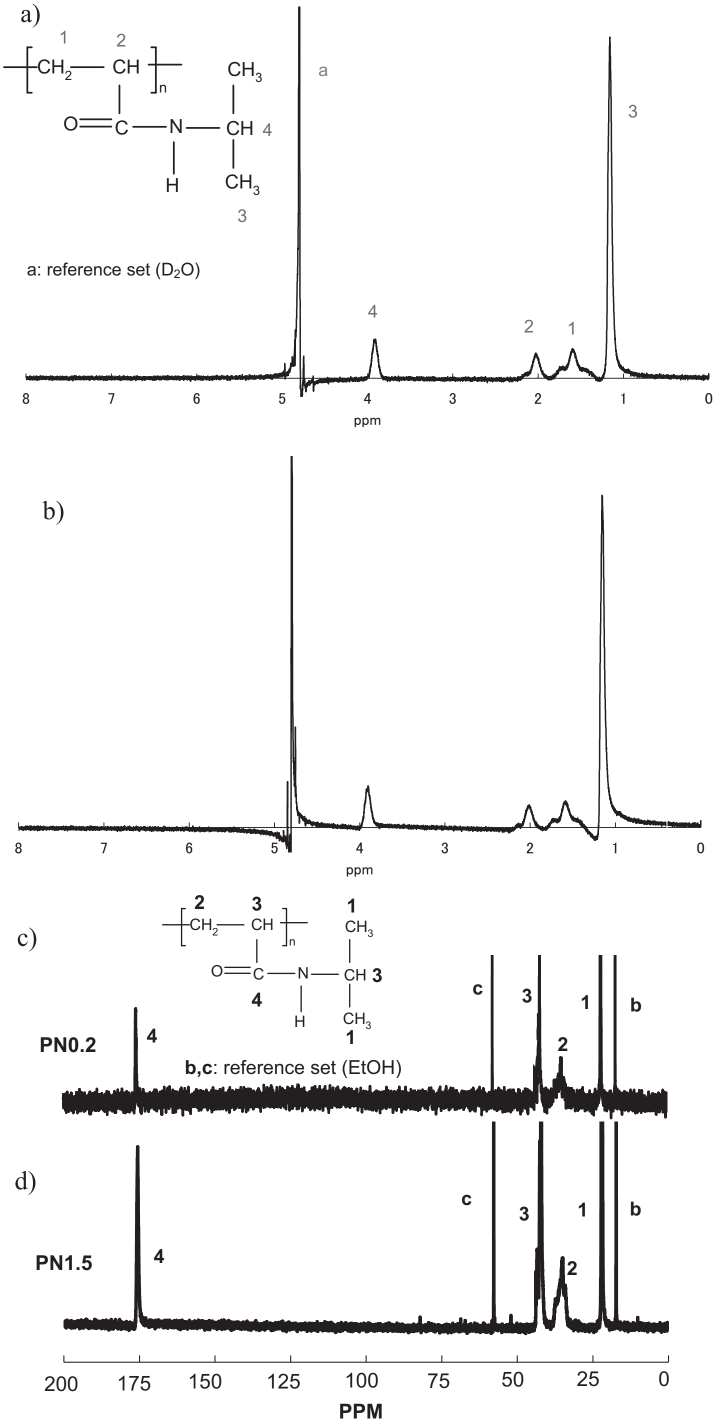

Figure 7.

NMR studies of PN1.0 and PNIPA(NC5^{-clay}).[28] (a) ^{1}H NMR spectra of PN1.0 (polymerized in D_2O). (b) ^{1}H NMR spectra of PNIPA(NC5^{-clay}). (c) ^{13}C NMR spectra of PN1.0 (polymerized in D_2O, scanning times: 16000). (d) ^{13}C NMR spectra of N-NC5-M1(-clay) (polymerized in D_2O, scanning times: 16000).

Samples of PNIPA(NC$n^{\text{-clay}}$), obtained by decomposing the clay in NCn gels and subsequent purification, were analyzed by TGA, FTIR, NMR and GPC. It was confirmed that the clay was completely decomposed and removed from NCn gels by comparing the FTIR spectra and thermal degradation (TGA) data for PNIPA(NC$n^{\text{-clay}}$) with that of PN1.0. Also, both PNIPA samples showed the same $^{[1]}$H NMR (Figure 7(a), (b)) and $^{[13]}$C NMR (Figure 7(c), (d)) spectra. Furthermore, the effect of HF treatment on the molecular weight of PNIPA was examined (Figure 8(a)). By comparing samples of PNIPA (PN0.01 and PN0.5) with different M_w (1.1×10^5 and 4.3×10^6, respectively) before and after HF treament, it was observed that values of M_w and M_w/M_n were hardly changed by the HF treatment, regardless of the original MW, as shown in 8(b), (c). Thus, it was concluded that the principal constituent, PNIPA, can be successfully separated from NC gels, by decomposing the clay in the PNIPA/clay network using HF aqueous solution (C_{HF} 0.2 wt%) treatment for 24 hrs, without chemical modification or degradation of their PNIPA chains.

As described in a preceding section, PNm prepared using [NIPA] greater than the critical concentration ($m \geq 0.6$) contains some self-cross-linked gel formed during free-radical polymerization in aqueous solution. Thus, PN1.0, prepared using the same [NIPA] as that for NCn gels, contained a gel fraction of 61 wt%. However, it was observed that all PNIPA(NC$n^{\text{-clay}}$) samples, separated from NCn gels (n = 1–25) by decomposing the clay, were completely soluble. For example, M_w and M_w/M_n of PNIPA(NC$3^{-\text{clay}}$) were 5.54×10^6 and 3.69, respectively. The effect of C_{clay} ($= n \times 10^{-2}\ \text{mol} \cdot \text{l}^{-1}$) on M_w of PNIPA(NC$n^{-\text{clay}}$) at constant [NIPA] ($= 1\ \text{mol} \cdot \text{l}^{-1}$) is shown in Figure 9. It was found that PNIPA(NC$n^{\text{-clay}}$) samples for $n \geq 0.5$ are soluble in the solvent, and that they have an almost constant M_w (approximately $5.5 \times 10^6\ \text{g} \cdot \text{mol}^{-1}$) and M_w/M_n (approximately 3.5) over a wide range of n (0.5 – 25). Therefore, the excellent mechanical and swelling/deswelling properties may be attributed to the unique PNIPA/clay network, where the concentration of clay is variable over a wide range while PNIPA has constant very high MW.

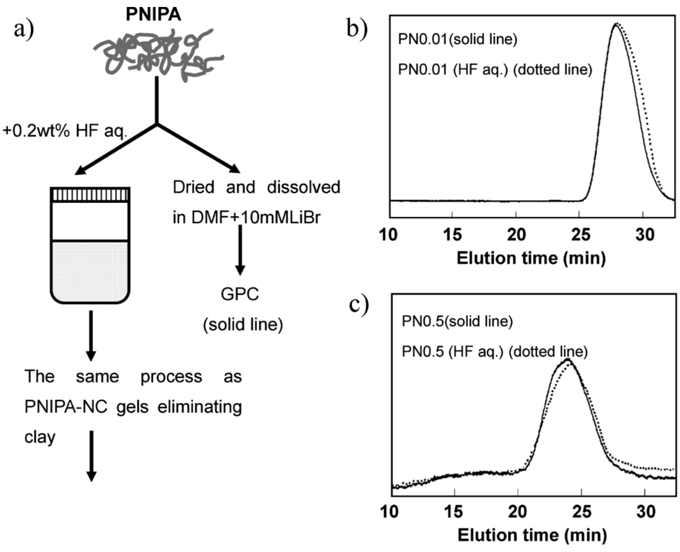

Figure 8.
GPC profiles of PN0.01 and PN0.5 before and after HF aq. treatment.

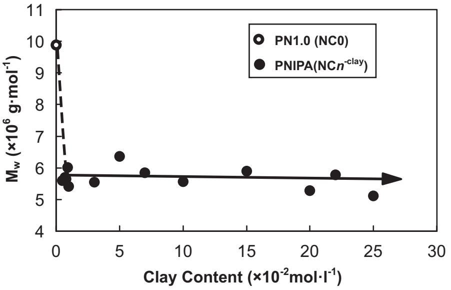

Figure 9.
Effect of C_{clay} on M_w(GPC) of PNIPA(NC$n^{\text{-clay}}$) ($n =$ 0 to 25).

M-H-S Equation on PNIPA in NC Gel

The correlation between M_w and $[\eta]$ for PNIPA(NC$n^{\text{-clay}}$) from NCn gels with different C_{clay} was evaluated. The result is shown in Figure 10 together with a plot of M-H-S equation (6) obtained for linear, unfractionated PNIPA (PNm) with different M_w. It was found that the M_w-$[\eta]$ relationship for PNIPA(NC$n^{\text{-clay}}$) is consistent with equation 6 for PNm, and that the M_w/M_n ($\approx$ 3.6) of PNIPA(NC$n^{\text{-clay}}$) is comparable to that of PNm. These data indicate that the molecular characteristics of PNIPA in NC gels are quite similar to those of PNm prepared in aqueous solution.

Discussion

Correlation between MW and [NIPA]

Shibayama et al.[48] previously reported that the dependence of M_w for PNIPA synthesized in aqueous solution with [NIPA] is given by equation 10. Figure 3 includes Shibayama's data re-plotted using

$$M_w = 1.97 \times 10^3 [\text{NIPA}]^{1.37} \qquad (10)$$

triangles as symbol. They did not measure MW directly, but estimated values from $[\eta]$ (in H_2O at 20 °C) using the M-H-S equation reported by Fujishige et al. (in H_2O at 20 °C), although Fujishige's equation is not totally reliable as pointed by Chi et al.[45]

M-H-S Equation of PNIPA

So far, different M-H-S equations with different values of the exponent α have been reported for PNIPA, depending on the solvent and conditions for PNIPA synthesis, as listed in Table 2. However, there is some conflict between them. For example, Chiantore et al.[25] reported quite different values of α for PNIPA depending on the solvent; they reported that $\alpha = 0.97$ for PNIPA in H_2O at 25 °C and $\alpha = 0.64$ for PNIPA in CH_3OH at 25 °C, which indicates that water is a considerably better solvent than methanol for PNIPA. However, for the same sample, they also reported that A_2

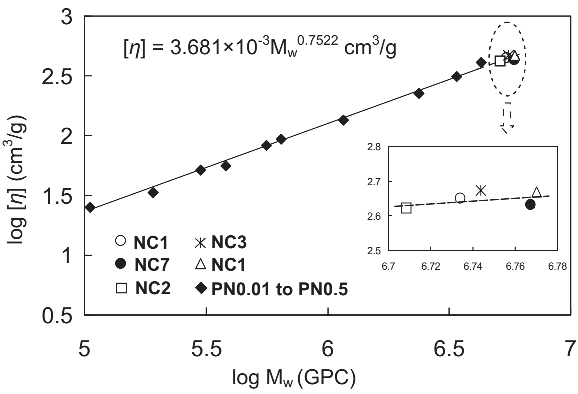

Figure 10.
Double logarithmic plot of $[\eta]$ vs. M_w(GPC) for PNm ($m = 0.01 \sim 0.5$) and PNIPA(NC$n^{\text{-clay}}$) ($n = 1 \sim 25$). GPC (DMF+10 mM LiBr, 40 °C).

measured in methanol (25 °C) is higher than that in water, which indicates that methanol is a better solvent than water. Fujishige et al.[18] reported a low value for α (=0.51 in H_2O at 20 °C) compared with Chiantore's result ($\alpha = 0.93$ in H_2O at 20 °C). Fujishige's result indicates that water is a θ solvent at 20 °C. However, according to their A_2 values, the theta temperature should be 30.59 °C, as pointed out by Chi et al.[45] Chiantore used unfractionated PNIPA samples in his study, while Fujishige's group used fractionated PNIPA. So, one possible reason for the difference in α value ($\alpha = 0.51$ and 0.93) is the error in the measurement of MW of unfractionated PNIPA by light scattering (Chiantore), as explained in the results section above.

In these studies, light scattering or osmometry was normally used to determine MW; GPC (THF) was only applicable in the case of very low MW values ($M_w = 2.25 \times 10^3 - 1.45 \times 10^4$). However, in the present study, α was obtained using M_w measured by GPC (in DMF/10 mM LiBr at 40 °C), that is, $\alpha = 0.74$ and 0.75 for fractionated and unfractionated PNIPA, respectively. Here, M_w covers quite a wide range, vis: $6.1 \times 10^4 - 4.3 \times 10^6$ for unfractionated and $3.7 \times 10^5 - 5.3 \times 10^6$ for fractionated samples. In addition, almost the same value of α (=0.73) was obtained using M_w measured by light scattering (in methanol at 25 °C) for fractionated PNIPA.

Relationship between α and $[\eta]$

In order to obtain information regarding the chain conformation of PNIPA in solution, we measured $[\eta]$ for a consecutive series of PNm samples in different solvents. Figure 11 shows $[\eta]$ for PNm measured in water (20 °C) and the organic solvent, DMF/10 mM LiBr (20 and 40 °C). By comparing the $[\eta]_{\mathrm{DMF/10\ mM\ LiBr}}$ values at different temperatures (20 and 40 °C), we found that the conformation of PNIPA in DMF/10 mM LiBr is hardly affected by temperature (20 and 40 °C). On the other hand, from the $[\eta]$ values for the two solvents at the same temperature (20 °C), we found $[\eta]_{\mathrm{H2O}} > [\eta]_{\mathrm{DMF/10\ mM\ LiBr}}$, regardless of m (i.e., MW) of PNIPA.

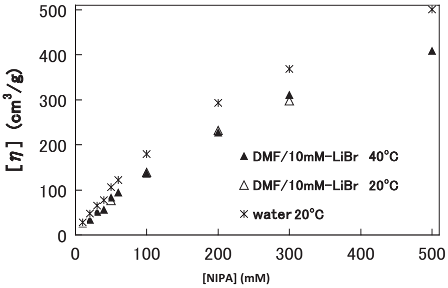

Figure 11.
Influence of solvent on the dependence of $[\eta]$ on [NIPA] for PNIPA. Solvents: DMF/10 mM LiBr (20 and 40 °C) and water (20 °C).

By comparing results from the present and previous studies, it was found that there are two different relationships between α and $[\eta]$. In the case of water-insoluble polymers, relationship 11 is observed:

$$\alpha_{\mathrm{solv.1}} > \alpha_{\mathrm{solv.2}} \text{ and } [\eta]_{\mathrm{solv.1}} > [\eta]_{\mathrm{solv.2}} \tag{11}$$

Polystyrene,[49] poly(methyl methacrylate) (PMMA),[50] poly(ε-caprolactam) (Nylon 6),[51] and poly(hexamethylene adipamide) (Nylon 66)[52] are examples of such water-insoluble polymers. Water-soluble polymers follow relationship 12:

$$\alpha_{\mathrm{solv.1}} \geq \alpha_{\mathrm{water}} \text{ and } [\eta]_{\mathrm{solv.1}} \leq [\eta]_{\mathrm{water}} \tag{12}$$

Examples of such polymers are poly(vinylpyrrolidone),[44] PNIPA[24] and cellulose acetate.[53] Current results for PNIPA are also consistent with relationship (12), i.e., $[\eta]_{\mathrm{DMF/LiBr}} < [\eta]_{\mathrm{water}}$ and $\alpha_{\mathrm{DMF/LiBr}}$ (=0.75) > α_{water} (=0.65). Here, we adopted 0.65 (±0.03) as the most reliable value of α_{water}, which is derived from $\alpha_D = 0.55$ (±0.01)[45] and the relation $\alpha_D = (1 + \alpha_\eta)/3$.[39]

It is generally considered that polymer chains in better solvents swell more extensively and adopt more-expanded conformations. This is consistent with equation 11. For example, polystyrene follows relationship 11 irrespective of the solvent pair, such as toluene & butanone, toluene & cyclohexane, and benzene & cyclohexane.[49] On the other hand, relationship 12 is specifically observed in organic solvent & aqueous systems. That is, low α and high $[\eta]$ are mostly observed in the case of water. The origin of this relationship has not been clearly elucidated, but it is probably related to the strong interaction (hydration) of water-soluble polymers with water.

Conclusion

In the present paper, we focused on PNIPA, which is one of the most well-known thermosensitive polymers and has been used as a key component of functional devices in many advanced research fields. Molecular characteristics of PNIPA synthesized by free-radical polymerization in aqueous solution with different monomer concentrations ($[\mathrm{NIPA}] = 0.005 - 1.0\,\mathrm{mol \cdot l^{-1}}$) and in NC$n$ gels with different C_{clay} ($n = 0.3$–20) were investigated in terms of the polymer yield, $[\eta]$, MW, and polydispersity (M_w/M_n) by means of GPC, viscosity, and light scattering measurements. By selecting appropriate experimental conditions and solvents, e.g., DMF/10 mM LiBr solvent (40 °C), GPC measurements were successfully performed to determine MW and M_w/M_n of PNIPA. It was found that these parameters varied significantly with [NIPA]. The correlations between [NIPA], polymer yield, MW, and M_w/M_n were clarified. In particular, linear relationships were observed between log M_w and log [NIPA] and between M_w/M_n and log M_w. Further, from the good correlation between log M_w and log $[\eta]$, the M-H-S equation and the molecular weight exponent α were obtained for both unfractionated (as-prepared) and fractionated PNIPA; the resultant α values were very close, $\alpha = 0.75$ and 0.74, respectively. An almost similar α value (0.73) was obtained for fractionated PNIPA from light scattering measurement in methanol (25 °C). In addition, PNIPA was successfully separated from NCn gels without any damage, by decomposing the clay in the PNIPA/clay network using an aqueous solution of HF. The resulting PNIPA (PNIPA(NC$n^{\text{-clay}}$)) showed a good correlation between log M_w and log $[\eta]$ which is almost consistent with M-H-S equation obtained for PNm. The effects of fractionation and solvents on α and chain conformation, as well as the relationship between α and $[\eta]$ are discussed in comparison with previous reports. All the results reported here can be used to identify molecular characteristics of PNIPA synthesized in water, which is widely used including its use in hydrogels.

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